Ph.D. Thesis in Chemical Sciences

Synthesis and Characterization of Zwitterionic Metallates and Molecular Clusters

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To Daniela and Giorgio,
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General Introduction
Zwitterionic compounds are defined by the on-line IUPAC Compendium of Chemical Terminology\textsuperscript{[1]} as “Neutral compounds having formal unit electrical charges of opposite sign”. However, zwitterionic metal complexes need a more detailed description, which has been given by Remi Chauvin in his review concerning zwitterionic organometallates.\textsuperscript{[2]} Indeed, couples of opposite charges may be easily evidenced in the Lewis structures although it is often possible to define resonance forms in which all the atoms are neutral. In this case the molecule cannot be called zwitterion. In addition, single positive and negative charges can be delocalized over a group of atoms, as carboxylate groups in amino acids and betaines. Single, nonpolymeric, neutral molecules containing more than one charge couple\textsuperscript{[3]} may be generally called “multizwitterions,” different from polyzwitterions, which refers to polymers containing zwitterionic chain substituents.\textsuperscript{[4]} If further positive or negative charges are present, ionic molecules can be called zwitterion-cations or zwitterion-anions in order to distinguish them from ordinary ions.\textsuperscript{[5]}

As a consequence of the charge separation, a very strong molecular electric dipole moment is observed depending on the distance between the charges barycenters. This strong dipole and amphiphilicity allow these “neutral ions” to be applied in a wide range of fields. Molecular zwitterions or zwitterionic polymers are studied as stationary phases\textsuperscript{[6]} or eluents\textsuperscript{[7]} in liquid chromatography, as drugs,\textsuperscript{[8]} and as NLO chromophores.\textsuperscript{[9]} As far as zwitterionic coordination compounds are concerned, their most important and outstanding application is in metallocene catalyzed Ziegler-Natta polymerization\textsuperscript{[10]} or even as carriers for membranes.\textsuperscript{[11]}

Zwitterionic metal complexes can be prepared following different strategies, the most common being as follows: (a) by reaction of zwitterionic ligands with metal species\textsuperscript{[12]} (b) by generating the charge separation upon coordination;\textsuperscript{[13]} and (c) by association of a positive (or negative) metal center with an oppositely charged ligand maintaining the charge separation.\textsuperscript{[14]}

In addition, zwitterionic complexes can be divided in two main categories; the most common one regroups complexes in which the metal center bears the formal positive charge, while the second comprises the still uncommon “zwitterionic metallates” whose metal center is formally negative.

Since the 1870s, the reaction of PEt\textsubscript{3} with EtNCS is know as a route to obtain ethyl isocynide (Figure 1). In this reaction, the transfer of a sulfur atom from the NCS group to the phosphorus center is responsible for the formation of the corresponding phosphano-sulfide (Et\textsubscript{3}P=S) and EtNC. In fact, in the reaction PR\textsubscript{3} + RNCS = R’S + PS + RNC, a zwitterionic
intermediate is formed, which is, in turn, dissociated in R’₃PS and RNC. This process is believed to proceed by the formation of a three-membered C-P-S non-zwitterionic ring (Scheme 1).[^15]

![Scheme 1](image)

**Scheme 1.** Addition reaction of alkylphosphanes to isothiocyanates and subsequent transformation in phosphano-sulfide and isocyanide.

Similar reactions of R₃P with CS₂ give zwitterionic adducts R₃PCS₂, whose ligating properties have been reviewed.[^12]

Data reported in the literature indicates that only alkylsubstituted phosphanes, R₃P, or phosphanoamines, (R’₂N)ₐR’’₃ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ₋ₐ_-
(diphenylphosphineamine, PNP) by the planarity of the P-NH-P system.\cite{18}

Four kinds of products can be obtained in the reaction of PNP with RNCS, depending on R, the temperature, and the PNP/RNCS molar ratio (Scheme 2).

\begin{align*}
P &= \text{PNP} \\
S &= \text{RNCS} \\
A &= \text{ intermediate} \\
B &= \text{product}
\end{align*}

Reaction i represents the primary attack of PNP on RNCS giving the proposed intermediate A, via a proton migration. Intermediate A cannot be isolated because of the reactivity of its free P atom, which is able to react further with RNCS (pathway ii) or with another A molecule (pathway iii) on the electrophilic CS group. Along pathway ii, the zwitterionic compound 1 is obtained, which, in turn, can rearrange to afford quantitatively compound 2 and an isocyanide molecule. Along pathway iii, two molecules of A react with each other through the attack of the tertiary phosphorus of one molecule on the PC(S)N carbon atom of the second one. The resulting intermediate undergoes an S-atom transfer from the C-S group.
to the free P atom, probably through the formation of a C,P,N,P,S five-membered ring. After
the S-atom transfer, the C atom is formally negative and can accept the thioamidic proton
which migrates from N to C, leading to the formation of a zwitterionic N-C(S)P⁺ “arm”
(compound 3). An isocyanide molecule can be finally released by rearrangement of 3 into 4,
in the same way as the rearrangement of 1 to 2. In compound 2, the formation of the P=S
group from the PC(S)N zwitterionic arm with the release of a RNC molecule depends on the
temperature. When R = Ethyl, compound 1a (HEtSNS, Figure 2) is obtained in high yield
(100%) in EtNCS neat.

Figure 2. Ortep Plot of 1a. Thermal ellipsoids are drawn at 30% probability level. H atoms are omitted for
clarity, except for H1n.

Compound 2a can be obtained almost quantitatively (50% after recrystallization) by reacting
PNP and EtNCS (1:2 ratio) in refluxing ethanol, or by refluxing an ethanol solution of
compound 1a (Figure 3).
1. Introduction

When $R = \text{Et}$ and the ratio of PNP/EtNCS is 1:1, compound 4a can be obtained (20–30% yield, together with 1a, 2a and unreacted PNP), whereas formation of compound 3a is not observed (Figure 4).

When $R = \text{Ph}$ and the PNP/PhNCS ratio is 1:2, the transformation of 1b to 2b occurs at lower
temperatures, and only compound 2b is obtained (Yield > 85%). When the PNP/PhNCS ratio is 1:1, compounds 4b is obtained. When $R = p$-$\text{NO}_2(C_6H_4)$, only the formation of 3c is observed regardless of the temperature or the PNP/PhNCS ratio (Figure 5).

Figure 5. Ortep Plot of 4b. Thermal ellipsoids are drawn at 30% probability level. H atoms are omitted for clarity, except for H1 and H1n.

Only when $R = p$-$\text{NO}_2(C_6H_4)$ is the reaction driven towards the formation of a single zwitterionic product that is stable with respect to the subsequent P=S group and $p$-$\text{NO}_2(C_6H_4)$NC formation. Apparently, the resonance effect of the $p$-$\text{NO}_2(C_6H_4)$ group stabilizes the negative charge on the N atom.

The reactivity of RSNS ($R = \text{Me, Et}$) was studied towards M(I) salts ($M = \text{Cu, Ag and Au}$, Scheme 3).
The reaction of \([\text{Cu(MeCN)}_4]\)[PF$_6$] with HRSNS in a 1:1 molar ratio, in presence of a base t-BuOK afforded \([\text{Cu(RSNS)}]\) (R = Me, 5a; R = Et, 5b, Figure 6) in quantitative yields.

Figure 6. Ortep Plot of 5b. Thermal ellipsoids are drawn at 30% probability level. H atoms are omitted for clarity.
Complex 5b displayed a crystallographically imposed $C_2$ symmetry, the two fold axis passing through the Cu1 and N1 atoms. The PNP system maintains geometric parameters comparable to those found for the free ligand. The formal negative and positive charges are located over the copper and the two phosphorous atoms, respectively. The two fused penta-atomic Cu, S, C, P, N rings are formed by five different atoms. The [-Ph$_2$PNPPh$_2$]- cationic group can be associated with the classical [Ph$_3$PNPPh$_3$]$^+$ cation (PPN$^+$). Indeed, as evidenced by the bent geometry of the P-N-P group of PPN$^+$, the nitrogen may potentially coordinate a metal centre through the N atom lone pair, even though it has never been found coordinating. In the case of the RSNS complexes, the [-Ph$_2$PNPPh$_2$]- coordination is forced by the $S,S$ chelation that brings N1 in the good geometry.

The reaction of HRSNS with AgOTf and t-BuOK (OTf = CF$_3$SO$_3$), afforded complexes [Ag(RSNS)] (R = Me, 6a; R = Et, 6b, Figure 7) in quantitative yields.

![Figure 7. Ortep Plot of 6b. Thermal ellipsoids are drawn at 30% probability level. H atoms are omitted for clarity](image)

The ligand coordinates to the metal centres through the sulphur atoms, found one in terminal and one in bridging modality, in such a way that a four membered planar Ag$_2$S$_2$ ring is formed. The two independent molecules show remarkable structural differences. In fact, the Ag1A-Ag1A$'$ distance is longer than the Ag1B-Ag1B$'$ one [3.125(2) and 2.997(2) Å, respectively], while the Ag1A-N1A distance is shorter than the analogue Ag1B-N1B one.
Moreover, the distances between Ag1A and Ag1B from the planes defined by P1A, N1A, P2A and P1B, N1B, P2B are 1.271(1) and 1.907(1) Å, respectively. This data indicate that the more the Ag···Ag separation is short, the more the Ag···N one is long (and vice versa); therefore, in complex 6a the Ag···N interactions may exists. The sum of the bond angles of N1A and N1B (354.74(8)° and 347.49(8)°) differ significatively from that observed in compound 5b, indicating a less pronounced sp² character for the nitrogen atoms also due to the weaker coordination interaction.

The NMR data suggests that the dimer dissociates in solution at room temperature, as deduced by their 31P NMR spectra: 6a and 6b display a narrow singlet in the typical range for coordinated RSNS⁻, instead of two signals expected for the dimer. In addition, in the ¹H spectrum of 6b, the methylene groups are equivalent and resonate as doublet of quartets, being coupled also with the methyl protons.

Reaction of [(tht)AuCl] (tht = tetrahydrothiophene) with HEtSNS and t-BuOK afforded compound [Au(EtSNS)] (7), whose crystal structure is shown in Figure 8.

Complex 7 can be considered a classical 14 electrons linear AuL₂ complex. On the other hand, linear Au¹ chelates displaying a 180° bite angle are rather rare, most involving diphosphine and polysulphide ligands, and being, to the best of our knowledge, all ionic.[19] The mononuclear complexes 5a, 5b and 6a, 6b behave as metalloligands. The negative charge density on the S-M-S groups induces reactivity towards metal cations. Indeed, addition of M¹
species (M = Ag, Cu) resulted in the assembly of multinuclear cationic clusters with formation of sulphur bridges. The 3:2 reactions of complexes 5a and 5b with suitable Cu\(^{1}\) or Ag\(^{1}\) salts afforded quantitatively \([\text{Cu}_2\{\text{Cu(RSNS)}\}_3][\text{PF}_6]_2\) (R = Me, 8a; R = Et, 8b) and \([\text{Ag}_2\{\text{Cu(RSNS)}\}_3][\text{A}]_2\) (R = Et, A = OTf, 9a; R = Me, A = OTf, 9b; R = Et, A = BF\(_4\), 9c), respectively, as shown in Scheme 4. In the same way, complexes 6a and 6b reacted with suitable Ag\(^{1}\) salts yielding \([\text{Ag}_2\{\text{Ag(RSNS)}\}_3][\text{A}]_2\) (R = Me, A = PF\(_6\), 10a; R = Et, A = OTf, 10b). Reaction of complexes 6b with \([\text{Cu(MeCN)}_4]\text{PF}_6\) did not give the expected \([\text{Cu}_2\{\text{Ag(RSNS)}\}_3][\text{PF}_6]_2\) cluster.

Scheme 4.
Metalloligand cationic compounds are formed by three [M(RSNS)] units joined together by two M’ atoms (M = M’ = Cu for 8, M = Cu, M’ = Ag for 9, M = M’ = Ag for 10). The metal centres define a trigonal bipyramidal M₃M’₂ core, with the M’ atoms in the axial positions.

Looking at the formal charge distribution, they can be regarded as tri-zwitterionic, dicationic pentanuclear clusters. Views of the crystal structures of clusters 8a, 9c, 10a are depicted in Figures 9, 10 and 11.

**Figure 9.** Ortep Plot of 8a. Thermal ellipsoids are drawn at 30% probability level. H atoms and the two PF₆ are omitted for clarity.

**Figure 10.** Ortep Plot of 9c. Thermal ellipsoids are drawn at 30% probability level. H atoms, phenyl groups and the two BF₄ are omitted for clarity.
1. Introduction

For all the three structures, the ligands' sulfur atoms bridge the M–M bonds. Each nitrogen of the P-N-P groups coordinates to a M atom. All the [M(RSNS)] unities are tilted in the same direction with respect to the relative M, M, M' plane.

It is noteworthy that the core geometry of cluster 9c differs significantly from cluster 8a and 10a. A distortion of the bipyramid is observed, being the two M' axial atoms much closer. An interaction probably exists between the two Ag atoms, being the Ag···Ag distance 3.149(7) Å.

Although few examples of Cu₅[20] and Ag₅[21] clusters bearing these types of metal cores have been already reported, these are the first cases in which the cage supports positive charges. Cluster 9c represents one of the rare examples of complexes displaying an Ag-Cu bond. Surprisingly, molecules containing the Cu-Ag interaction are very rare, whereas Cu-Au and Ag-Au bonds are rather common. Only four structurally defined molecules bearing the aforementioned bond are reported in the literature[22].

The formation of pentanuclear multi-zwitterionic clusters (8, 9 and 10) suggested that any combination of M(RSNS) and M⁴ (M = Cu, Ag) could lead to the assembly of clusters with desired compositions and geometries. However, the 3:2 reaction of complex [Ag(EtSNS)] (6b) with [Cu(MeCN)₄]PF₆ did not give rise to the expected [Cu₃{Ag(EtSNS)}₃][PF₆]₂, cluster but to a mixture of species, of which [Ag₃{Cu(EtSNS)}₃]²⁺ resulted the major one, as detected
by ESI-MS analyses and confirmed by means of $^{31}$P NMR spectroscopy. The formation of the cluster with inverted metal ratio ($\text{Ag}_2\text{Cu}_3$ instead of $\text{Ag}_3\text{Cu}_2$) can be explained by the RSNS$^-$ ligand exchange:

$$[\text{Ag(RSNS)}] + \text{Cu}^+ = [\text{Cu(RSNS)}] + \text{Ag}^+$$

Several $[\text{M}_2\{\text{M}'(\text{RSNS})\}_3]^{2+}$ cations ($\text{M} = \text{Ag, Cu}; \text{M}' = \text{Ag, Cu}$) were detected in the ESI-MS spectrum of the crude product.

The reaction ratio between the complex $\text{M(RSNS)}$ and the $\text{M}^1$ ion can be different from 3:2. In fact, reaction of $[\text{Ag(EtSNS)}]$ (2b) with $\text{AgOTf}$ in a 1:1 molar ratio led quantitatively to the formation of $[\text{Ag}_2\{\text{Ag(RSNS)}\}_3(\text{OTf})_2]$ (11), a bis-zwitterion. A view of its crystal structure is shown in Figure 13.

![Figure 13. Ortep Plot of 11. Thermal ellipsoids are drawn at 30% probability level. H atoms are omitted for clarity.](image)

When complex 11 is reacted, in a 1:1 ratio, with complex 6b, cluster $[\text{Ag}_2\{\text{Ag(EtSNS)}\}_3][\text{OTf}]_2$ (10b) is quantitatively formed, as depicted in Scheme 5.
1. Introduction

Scheme 5. For clarity, only one of the three ligand molecule is completely shown for cluster 6; for the other two, only the S bridging atoms have been evidenced.

Since complex 11 is an intermediate species in the assembly of cluster 10b, it is possible to hypothesize a analogous planar Cu₄ intermediates in the formation of 8a and 8b and Cu₂Ag₂ ones for 9a, 9b, 9c. In the case of Ag¹, the coordinating OTf anion may stabilize the tetranuclear species, allowing its isolation. Cluster 10b can be thus assembled following three different strategies: a) 5:3 reaction of AgOTf with HEtSNS in the presence of a base such as t-BuOK, b) 3:2 reaction of complex 6b with AgOTf and c) 1:1 reaction of complex 10b with complex 6b.

1.1 References

1. Introduction

A study on the coordinative versatility of the zwitterionic $S,N,S$ ligand $\text{EtNHC(S)Ph}_2\text{P=NPPh}_2\text{C(S)NEt}$ in its anionic, neutral and cationic forms. Determination of absolute $pK_a$ values in $\text{CH}_2\text{Cl}_2$ of Rh$^1$ complexes.

The coordination properties of $\text{EtNHC(S)Ph}_2\text{P=NPPh}_2\text{C(S)NEt}$ towards Rh(I) species derived from $[\text{Rh(CO)}_2\text{Cl}]_2$ and $[\text{Rh(cod)}\text{Cl}]_2$ (cod = 1,5-cyclooctadiene) were studied. This ligand is an amphoteric zwitterion, which forms the $\text{H}_2\text{EtSNS}^+$ cation upon protonation and the $\text{EtSNS}^-$ dianion-cation upon deprotonation. All three forms coordinate to metal centers. Their geometrical versatility allows many coordination fashions: $S$-monodentate, $S,S$-bidentate (with a bite angle spanning from 90 to 180°), $S,N,S$-tridentate, $N,N,N$-tridentate and $S,S$-bridging, as determined by X-ray diffraction methods. The $[\text{Rh(CO)}\text{EtSNS}]$ complex is a biprotic base; its conjugated acids are $[\text{Rh(CO)}\text{HEtSNS}]^+$ and $[\text{Rh(CO)}\text{H}_2\text{EtSNS}]^{2+}$, and their $pK_a$ values were determined in dichloromethane solutions. In this triad of compounds, which are geometrically similar, the Rh(I) metal center features variable charge density as confirmed by the νCO infrared absorption frequency.
2. Determination of Absolute pKa Values of Rh(I) Complexes

2.1 Introduction

The EtSNS acts as an S,N,S-tridentate or S,S-bidentate ligand towards M(I) species (M = Rh\(^\text{[1]}\) and Cu, Ag, Au\(^\text{[2]}\)). The \([-\text{Ph}_2\text{PNPPh}_2^-]\) nitrogen atom can be coordinated as in \([\text{Rh(CO)(EtSNS)}]\) and \([\text{Cu(EtSNS)}]\) and it weakly interacts with the metal center in \([\text{Ag(EtSNS)}]\)_2, or it can be not coordinated as in the case of \([\text{Au(EtSNS)}]\). The \([-\text{Ph}_2\text{PNPPh}_2^-]\) group is reminiscent of the classical bis(triphenylphosphine)iminium cation \([\text{Ph}_3\text{PNPPh}_3^+](\text{PPN}^+)\) whose N atom, as evidenced by its bent geometry, may coordinate a metal center, although this behavior has never been observed.\(^\text{[3]}\) We became interested in studying also the coordination properties of HEtSNS and H\(_2\)EtSNS\(^+\). Their reactivity towards Rh\(^I\) species derived from \([\text{Rh(CO)}\_2\text{Cl}_2]\) and \([\text{Rh(cod)}\text{Cl}_2]\) (cod = 1,5 cyclooctadiene) is reported. Acid–base properties of complex \([\text{Rh(CO)(EtSNS)}]\) are discussed together with a general method for the determination of absolute pK\(_a\) values in dichloromethane.

2.2 Experimental

2.2.1 General procedures

All manipulations were carried out at room temperature in the air or, when necessary, under nitrogen atmosphere by standard Schlenk techniques; \(\text{tBuOK, EtNCS, [Rh(cod)}\text{Cl}_2, [\text{Rh(CO)}\_2\text{Cl}_2], \text{AgPF}_6, Ag\text{OTf (OTf} = CF_3\text{SO}_2\text{), HOTf, HPF}_6 (60\% \text{aqueous solution}) and NaH were purchased and used as received (Aldrich and Fluka). The solvents was dried and distilled by standard techniques. Ph\(_2\)PNHPPh\(_2\) (dppa),\(^\text{[4]}\) HEtSNS,\(^\text{[1]}\) (H\(_2\)EtSNS)Cl,\(^\text{[1]}\) \([\text{Rh(CO)(EtSNS)}]\),\(^\text{[1]}\) [Rh(CH\(_2\text{CN})\_2\text{CO)}\_2]\)X and \([\text{Rh(THF)}\_2\text{(CO)}\_2]\)X (X = PF\(_6\), OTf)\(^\text{[5]}\) were prepared as described elsewhere. Elemental analyses were carried out on a Carlo Erba EA1108 microanalyzer. FTIR spectra (4000-400 cm\(^{-1}\)) were recorded on a Nicolet Nexus spectrophotometer equipped with a Smart Orbit HATR accessory (diamond crystal). \(^1\text{H NMR (300.13 MHz, TMS) and }^{31}\text{P}^\{^1\text{H}\} \text{NMR (161.98 MHz, external reference 85\% H}_2\text{PO}_4\) spectra were recorded onBruker instruments (AC300 Avance and AMX400, respectively) using deuterated solvents (CDCl\(_3\), CD\(_2\)Cl\(_2\), DMSO-d\(_6\) and CD\(_3\)OD). The solid state \(^{31}\text{P}^\{^1\text{H}\} \text{NMR–MAS spectra were recorded on a Bruker Avance 300 MHz operating at a frequency of 121.57 MHz, equipped with a MAS 4 mm }^{1}\text{H–X probe. Sample rotation was set at 1010 Hz.}
2. Determination of Absolute pKa Values of Rh(I) Complexes

NH₄H₂PO₄ was used as external reference (0 ppm), and PF₆⁻ (~144 ppm) as internal secondary one. A Micromass Quattro LC triple quadrupole instrument equipped with an electrospray interface (Masslynx v. 3.4 software) was used for ESI-MS data collection and processing. The nebulizing gas (nitrogen, 99.999% purity) and the desolvation gas (nitrogen, 99.998% purity) were delivered at a flow-rate of 80 and 500 l/h, respectively. ESI-MS analyses were performed by operating the mass spectrometer in positive ion (PI) mode, acquiring mass spectra over the scan range m/z 100–2800, using a step size of 0.1 Da and a scan time of 2.7 sec. The interface operating parameters were: source temperature 70 °C, desolvation temperature 70 °C, ESI(+) capillary voltage 3.0 kV, cone voltage 15 V, rf lens 0.3 V. Absorption spectra in the range 300-600 nm were recorded with a Perkin Elmer Lambda 25 spectrophotometer using matched quartz cells of 1 cm pathlength and dichloromethane as reference.

2.2.5 Synthesis of [Na(EtSNS)]

A suspension of NaH (0.043 g, 1.79 mmol) in THF (20 mL) was added to a solution of HEtSNS (0.500 g, 0.89 mmol) in THF (20 mL) under nitrogen. The resulting suspension was stirred for 1 h. Unreacted NaH was removed via filtration. Evaporation of the solvent afforded [Na(EtSNS)] as a white powder (Yield 97%). [Na(EtSNS)] was recrystallized by slow evaporation of a CH₂Cl₂/hexane solution, yielding [Na(EtSNS)H₂O]₂. ¹H NMR (DMSO-d₆): δ = 8.0-7.2 (m, 20H, Ph), 3.42 (qd, 4H, -CH₂CH₃, ³J(H,H) = 7.2 Hz, ⁴J(H,P) = 5.0 Hz), 0.99 (t, 6H, -CH₂CH₃, ³J(H,H) = 7.2 Hz) ppm. ³¹P{¹H} NMR (DMSO-d₆): δ = 7.2 (s) ppm. C₃₀H₃₀N₃P₂NaS₂ (581.65): calcd. C 61.95; H 5.20, N 7.22; found C 62.31, H 5.31, N 7.25, S 10.87.

2.2.6 Synthesis of (H₂EtSNS)PF₆

Solid HEtSNS (0.073 g, 0.13 mmol) was dissolved in CH₂Cl₂ (10 mL) resulting in a yellow solution; a solution of HPF₆ (60% in H₂O, 0.2 mL, 2.4 mmol) was added and the reaction mixture was vigorously shaken. The aqueous phase was removed and the resulting organic phase was dried with anhydrous Na₂SO₄ and evaporated under reduced pressure to obtain (H₂EtSNS)PF₆ as a yellow powder (Yield 98%). ¹H NMR (CDCl₃): δ = 12.8 (s, 2H; N-H), 8.0-7.3 (m, 40H; Ph), 4.05 (qd, 4H, -CH₂CH₃, ³J(H,H) = 7.2 Hz, ⁴J(H,P) = 7 Hz), 1.41 (t, -
2. Determination of Absolute pKa Values of Rh(I) Complexes

\[ \text{CH}_2\text{CH}_3, ^3\text{J}(\text{H,H}) = 7.2 \text{ Hz} \text{ ppm.} \]

\[ ^{31}\text{P}\{^1\text{H}\} \text{ NMR (CDCl}_3\}: \delta = 13.3 \text{ (s) ppm. C}_{30}\text{H}_{32}\text{F}_6\text{N}_3\text{P}_2\text{S}_2 \]

(705.64): calcd. C 51.06, H 4.57, N 5.95, S 9.09; found: C 52.03, H 4.62, N 6.15, S 9.54.

2.2.7 Synthesis of \([\text{Rh(cod)}(S,S-\text{EtSNS})] \]

Solid \([\text{Rh(cod)Cl}]_2 \) (0.100 g, 0.203 mmol) and HEtSNS (0.226 g, 0.406 mmol) were dissolved in 10 mL of \(\text{CH}_2\text{Cl}_2\). A solution of \(t\)BuOK (0.046 g, 0.406 mmol) in 2 mL of MeOH was then added and the reaction mixture stirred for 30 min. The volatiles were evaporated and the resulting yellow powder was redissolved in 5 mL of \(\text{CH}_2\text{Cl}_2\). KCl was removed via filtration. Evaporation of the solvent afforded \([\text{Rh(cod)}(S,S-\text{EtSNS})] \) as yellow powder (Yield 85%). Complex 1 could be recrystallized by layering hexane onto a \(\text{CH}_2\text{Cl}_2\) solution.

\( ^1\text{H} \text{ NMR (CDCl}_3\): } \delta = 7.8-7.2 \text{ (m, 20H, Ph), 3.9-3.7 (m, 4H, -\text{CH=CH-}, cod; m, 4H, -\text{CH}_2\text{CH}_3), 1.87 (br, 4H, -\text{CH}-\text{H}, cod), 1.52 (m, 4H, -\text{CH}-\text{H}, cod), 1.18 (t, 6H, -\text{CH}_2\text{CH}_3) \text{ ppm.} \)

\( ^{31}\text{P}\{^1\text{H}\} \text{ NMR (CDCl}_3\): } \delta = 9.7 \text{ (s) ppm.} \)

\[ \text{C}_{38}\text{H}_{42}\text{N}_3\text{P}_2\text{RhS}_2 \]

(769.74): calcd. C 59.29, H 5.50, N 5.46, S 8.33; found C 59.11, H 5.64, N 5.29, S 8.16.

2.2.8 Synthesis of \([\{\text{Rh(cod)}\}_2(\mu-S,S-\text{EtSNS})]\text{OTf} \)

A solution of AgOTf (0.077 g, 0.30 mmol) in THF (10 mL) was added dropwise to a solution of \([\text{Rh(cod)Cl}]_2 \) (0.075 g, 0.15 mmol) in THF (10 mL). The resulting reaction mixture was stirred at room temperature for 10 min. Solid AgCl was removed via filtration. To the solution, complex 1 (0.115 g, 0.15 mmol) was added and the purple reaction mixture was stirred for 1 h. Evaporation of the volatiles yielded \([\{\text{Rh(cod)}\}_2(\mu-S,S-\text{EtSNS})]\text{OTf} \) as a purple powder (Yield 76%). The complex can be recrystallized by layering hexane onto a THF solution, affording violet crystals of \(2\cdot\frac{1}{2}\text{THF} \).

\( ^1\text{H} \text{ NMR (CDCl}_3\): } \delta = 7.7-7.2 \text{ (m, 20H, Ph), 4.20 (dq, 4H, -\text{CH}_2\text{CH}_3, ^3\text{J}(\text{H,H}) = 7.2 \text{ Hz, } ^4\text{J}(\text{H,P}) = 4.2 \text{ Hz), 4.23 (br, 4H, -\text{CH}-\text{CH}, cod), 3.73 (s, 4H, -\text{CH}-\text{CH}, cod), 2.40 (br, 8H, -\text{CH}-\text{H}, cod), 1.95 (m, 8H, -\text{CH}-\text{H}, cod), 1.45 (t, 6H, -\text{CH}_2\text{CH}_3, ^3\text{J}(\text{H,H}) = 7.2 \text{ Hz) ppm.} \)

\( ^{31}\text{P}\{^1\text{H}\} \text{ NMR (CDCl}_3\): } \delta = 17.9 \text{ (s) ppm.} \)

\[ \text{C}_{47}\text{H}_{54}\text{F}_3\text{N}_3\text{O}_3\text{P}_2\text{RhS}_3 \]

(1129.90): calcd. C 49.96, H 4.82, N 3.72, S 8.51; found C 50.12, H 4.83, N 3.63, S 8.74. MS (ESI\(^+\), \text{CH}_2\text{Cl}_2\): \(m/z \text{ (%) = 980.26 (100) [M]\(^+\).} \)

2.2.9 Reaction of 1 with \([\text{Rh(cod)Cl}]_2 \). Solution formation of \([\{\text{Rh(cod)}\}_2(\mu-S,S-\text{EtSNS})]\text{Cl} \)

A solution of \([\text{Rh(cod)Cl}]_2 \) (0.024 g, 0.097 mmol) in \(\text{CH}_2\text{Cl}_2 \) (10 mL) was added to a solution of 1 (0.150 g, 0.195 mmol) in \(\text{CH}_2\text{Cl}_2 \) (10 mL). The resulting orange reaction mixture
was stirred for 10 min. Methanol (40 mL) was added and the solution color turned to purple. Evaporation of the solvent yielded the starting mixture of the reagents. The same reaction was performed in CD$_3$OD in order to obtain NMR data for 3: $^1$H NMR (CD$_3$OD): $\delta = 7.5$-7.2 (m, 20H; Ph), 4.21 (m, 4H; -CH$_2$CH$_3$, m, 4H, -CH=CH-, cod), 3.7 (s, 4H; -CH=CH-, cod), 2.40 (s, 8H; -CHH-, cod), 1.95 (m, 8H; -CHH-, cod), 1.45 (t, 6H; -CH$_2$CH$_3$) ppm. $^{31}$P{$^1$H} NMR (CD$_3$OD): $\delta = 17.1$ (s) ppm. MS (ESI$^+$, CH$_2$Cl$_2$): $m/z$ (%) = 980.26 (100) [M$^+$].

2.2.10 Synthesis of [Rh(cod)(S-HEtSNS)Cl] (4)

A solution of HEtSNS (0.145 g, 0.26 mmol) in CH$_2$Cl$_2$ (20 mL) was added to a solution of [Rh(cod)Cl]$_2$ (0.064 g, 0.13 mmol) in CH$_2$Cl$_2$ (10 mL). The red reaction mixture was stirred for 10 min. Evaporation of the solvent yielded [Rh(cod)(S-HEtSNS)Cl] (4) as a yellow powder (Yield 92%) which could be recrystallized by layering hexane onto a CH$_2$Cl$_2$ solution. In solution, compound 4 was found to be in equilibrium with [Rh(cod)(S,S' -HEtSNS)]Cl (4a). 4: $^1$H NMR (CDCl$_3$): $\delta = 11.37$ (s, br, N-H), 7.7-7.2 (m, Ph), 4.15 (m, br, -CH=CH-, cod), 4.00 (m, br, -CH$_2$CH$_3$), 3.93 (m, br, -CH$_2$CH$_3$), 3.63 (m, br, -CH=CH-, cod), 2.13 (s, br, -CHH-, cod), 1.48 (m, -CHH-, cod), 1.27 (t, -CH$_2$CH$_3$, $^3$J(H,H) = 6 Hz) ppm; signals of compound 4a (except for NH group) were underimposed to signals of compound 4 thus affecting peak integration. $^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta = 11.1$ (d, $^2$J(P,P) = 15.9 Hz ), 10.5 (d $^2$J(P,P) = 15.9 Hz) ppm. C$_{38}$H$_{43}$ClN$_3$P$_2$RhS$_2$ (806.21): calcd. C 56.61, H 5.38, N 5.21, S 7.95; found C 57.46, H 5.46, N 5.37, S 8.10. 4a: $^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta = 12.4$ (s, integral ratio with respect to complex 4 = 1:10) ppm. $^1$H NMR (CDCl$_3$): $\delta = 12.82$ (s, br, N-H) ppm.

2.2.11 Reaction of [Rh(CO)$_2$Cl]$_2$ with HEtSNS

A solution of HEtSNS (0.280 g, 0.50 mmol) in CH$_2$Cl$_2$ (10 mL) was added under nitrogen to [Rh(CO)$_2$Cl]$_2$ (0.097 g, 0.25 mmol) dissolved in 15 mL of CH$_2$Cl$_2$. The solution color changed rapidly from yellow to red. Stirring was continued for 2 h and the volatiles were removed under vacuum, affording a red-orange powder. Three compounds (namely [Rh(CO)$_2$(S-EtSNS)Cl], [H$_2$EtSNS][Rh(CO)$_2$Cl]$_2$ (5) and [Rh(CO)(EtSNS)]) were spectroscopically identified as the major components of the crude product. Crystals of compound 5 were obtained by layering hexane onto a solution of the crude product. $^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta = 16.85$ (s, integration 0.75, [Rh(CO)(EtSNS)]), 13.30 (s, integration 1, compound 5), 12.90 (d, $^2$J(P,P) = 15.2 Hz, integration 0.12), 11.44 (d, $^2$J(P,P) = 15.2 Hz,
2. Determination of Absolute pKa Values of Rh(I) Complexes

integration 0.12, [Rh(CO)_2(S-EtSNS)Cl] ppm. FTIR (Diamond crystal HATR, cm^{-1}): \nu_{CO} = 2071, 1992.

2.2.12 Synthesis of [H_2EtSNS][Rh(cod)Cl_2] (6)

Solid (H_2EtSNS)Cl (0.242 g, 0.406 mmol) was added to a solution of [Rh(cod)Cl_2] (0.100 g, 0.203 mmol) in CH_2Cl_2 (20 mL). The resulting orange reaction mixture was stirred for 10 min. Evaporation of the volatiles afforded [H_2EtSNS][Rh(cod)Cl_2] (6) as an orange powder (Yield 92%). The salt can be recrystallized by layering hexane onto its CH_2Cl_2 solution.

1H NMR (CDCl_3): \delta = 12.70 (s, br, 2H, N-H); 7.6-7.1 (m, 20H, Ph); 4.18 (m, br, 8H, -CH_2CH_3 and -CH=CH-), 2.48 (m, br, 4H, -CHH-, cod), 1.73 (m, br, 4H, -CHH-, cod), 1.49 (t, 6H, -CH_2CH_3, 3J(H,H) = 7.05 Hz) ppm. 31P{1H} NMR (CDCl_3): \delta = 13.6 (s) ppm. C_{38}H_{44}Cl_2N_3P_2RhS_2 (842.67): calcd. C 54.16, H 5.26, N 4.99, S 7.61; found C 54.49, H 5.18, N 5.01, S 7.73.

2.2.13 Synthesis of [Rh(CO)(S,N,S'-H_2EtSNS)][Rh(CO)_2Cl_2]_2 (7)

A solution of (H_2EtSNS)Cl (0.100 g, 0.17 mmol) in CH_2Cl_2 (10 mL) was added under nitrogen to a solution of [Rh(CO)_2Cl_2] (0.099 g, 0.255 mmol) in CH_2Cl_2 (10 mL). Stirring was continued for 2 h and the solution color turned to dark-red. Evaporation of the volatiles afforded [Rh(CO)(S,N,S'-H_2EtSNS)][Rh(CO)_2Cl_2]_2 (7) as a red microcrystalline powder (Yield 91%). 1H NMR (DMSO-d_6): \delta = 11.08 (s, br, 2H, N-H); 7.9-7.3 (m, 20H, Ph); 4.15 (dd, 4H, -CH_2CH_3, 3J(H,H) = 6.5 Hz, 4J(H,P) = 6.3 Hz), 1.25 (t, 6H, -CH_2CH_3) ppm. 31P{1H} NMR (CDCl_3): \delta = 13.6 (s) ppm. C_{35}H_{32}Cl_4N_3P_2O_5Rh_3S_2 (1151.26): calcd. C 36.51, H 2.80, N 3.65, S 5.57; found C 36.39, H 2.86, N 3.54, S 5.71. MS (ESI^+, CH_2Cl_2): m/z (%) = 691.6 (100) [M]^+. FTIR (Diamond crystal HATR, cm^{-1}): \nu_{CO} = 2074 (s, \nu_{CO}[Cl_2Rh(CO)_2^+]), 1998 (s, \nu_{CO}[Cl_2Rh(CO)_2^+]), 2014 (m, sh, \nu_{CO}Rh–CO).

2.2.14 Synthesis of [Rh(CO)(S,N,S'-HEtSNS)]PF_6 (8)

A solution of HEtSNS (0.280 g, 0.50 mmol) in CH_2Cl_2 (10 mL) was added under nitrogen to a solution of [Rh(CH_2CN)_2(CO)_2]PF_6 (0.193 g, 0.50 mmol) in CH_2Cl_2 (10 mL). Stirring was continued for 2 h and the solution color turned to violet-red. Evaporation of the volatiles afforded [Rh(CO)(S,N,S'-HEtSNS)]PF_6 (8) as a red microcrystalline powder (Yield 89%). The complex can be recrystallized by layering pentane onto a THF solution of 8.
affording red crystals of 8 · 2THF. \(^1\)H NMR (DMSO-d\(_6\)): \(\delta = 11.0\) (s, br, 1H, N-H); 7.7-7.4 (m, 20H, Ph); 3.67 (m, 4H, -CH\(_2\)CH\(_3\)); 1.16 (t, 6H, -CH\(_2\)CH\(_3\)) ppm. \(^{31}\)P\(\{^1\)H\} NMR (CDCl\(_3\)): \(\delta = 35.0\) (s), 19.9 (s) ppm. C\(_{31}\)H\(_{32}\)F\(_6\)N\(_3\)P\(_4\)ORhS\(_2\) (835.55): calcd. C 44.56, H 3.74, N 5.03, S 7.67; found C 44.45, H 3.69, N 4.96, S 7.58.

MS (ESI\(^+\), CH\(_2\)Cl\(_2\)): \(m/z\) (%) = 690.6 (100) [M\(^+\)]. FTIR (Diamond crystal HATR, cm\(^{-1}\)): \(\nu\)\(_{CO}\) = 1979.

### 2.2.15 Synthesis of \([\text{Rh}(CO)(S,N,S'-\text{H}_{2}\text{EtSNS})]\{\text{PF}_6\}_2\) (9)

A solution of \([\text{Rh}(\text{CH}_3\text{CN})_2\text{(CO)}_2]\text{PF}_6\) (0.193 g, 0.50 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added under nitrogen to a solution of \((\text{H}_{2}\text{EtSNS})\text{PF}_6\) (0.352 g, 0.50 mmol) in CH\(_2\)Cl\(_2\) (15 mL). Stirring was continued for 2 h and the solution color turned to red. Evaporation of the volatiles afforded \([\text{Rh}(CO)(S,N,S'-\text{H}_{2}\text{EtSNS})]\{\text{PF}_6\}_2\) (9) as an orange microcrystalline powder (Yield 88%). \(^1\)H NMR (DMSO-d\(_6\)): \(\delta = 11.1\) (s, br, 2H, N-H); 7.8-7.4 (m, 20H, Ph); 4.15 (m, 4H, -CH\(_2\)CH\(_3\)), 1.18 (t, 6H, -CH\(_2\)CH\(_3\)) ppm. \(^{31}\)P\(\{^1\)H\} NMR (CDCl\(_3\)): \(\delta = 38.2\) (s) ppm. C\(_{32}\)H\(_{31}\)F\(_3\)N\(_3\)O\(_4\)P\(_2\)RhS\(_3\) (981.52): calcd. C 37.93, H 3.29, N 4.28, S 6.53; found C 37.55, H 3.21, N 4.15, S 6.38. MS (ESI\(^+\), CH\(_2\)Cl\(_2\)): \(m/z\) (%) = 691.6 (100) [M\(^+\)]. FTIR (Diamond crystal HATR, cm\(^{-1}\)): \(\nu\)\(_{CO}\) = 2013.

### 2.2.16 Synthesis of \([\text{Rh}(CO)(S,N,S'-\text{HEtSNS})]\{\text{OTf}\}_2\) (10)

A solution of \([\text{Rh}(\text{CH}_3\text{CN})_2\text{(CO)}_2]\text{OTf}\) (0.200 g, 0.37 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added under nitrogen to a solution of HEtSNS (0.215 g, 0.37 mmol) in CH\(_2\)Cl\(_2\) (15 mL). Stirring was continued for 2 h and the solution color turned to red. Evaporation of the volatiles afforded compound \([\text{Rh}(CO)(S,N,S'-\text{HEtSNS})]\{\text{OTf}\}_2\) (10) as an orange microcrystalline powder (Yield 87%). \(^1\)H NMR (DMSO-d\(_6\)): \(\delta = 11.0\) (s, br, 1H, N-H); 7.7-7.4 (m, 20H, Ph); 3.67 (m, 4H, -CH\(_2\)CH\(_3\)); 1.16 (t, 6H, -CH\(_2\)CH\(_3\)) ppm. \(^{31}\)P\(\{^1\)H\} NMR (CDCl\(_3\)): \(\delta = 38.2\) (s) ppm. C\(_{32}\)H\(_{32}\)F\(_3\)N\(_3\)O\(_4\)P\(_2\)RhS\(_3\) (839.65): calcd. C 45.77, H 3.72, N 5.00, S 11.45; found C 45.62, H 3.69, N 4.97, S 11.39. MS (ESI\(^+\), CH\(_2\)Cl\(_2\)): \(m/z\) (%) = 690.6 (100) [M\(^+\)]. FTIR (Diamond crystal HATR, cm\(^{-1}\)): \(\nu\)\(_{CO}\) = 1977.

### 2.2.17 Synthesis of \([\text{Rh}(CO)(S,N,S'-\text{H}_{2}\text{EtSNS})]\{\text{OTf}\}_2\) (11)

In a Schlenk tube and under nitrogen, a solution of \([\text{Rh}(\text{CO})(\text{EtSNS})]\) (0.200 g 0.29 mmol) in 10 mL of chloroform was treated with 10 mL of a water solution of HOTf in large excess with respect to the rhodium precursor. The yellow solution turned orange-red and a
precipitate formed which was separated by decanting. The two liquid phases were separated, and the organic one dried, giving an orange red solid. The two solids were recrystallized from hot methanol affording compound [Rh(CO)(S,N,S-H2EtSNS)](OTf)2 as an orange microcrystalline powder (Yield 90%). 1H NMR (CDCl3): δ = 11.1 (s, br, 2H, N-H); 7.8–7.4 (m, 20H, Ph); 4.15 (m, 4H, -CH2CH3); 1.18 (t, 6H, -CH2CH3) ppm. 31P{1H} NMR (DMSO-d6): δ = 38.2 (s) ppm. C33H32F6N3O7P2RhS4 (989.73): calcd. C 40.04, H 3.26, N 4.24, S 12.96; found C 39.97, H 3.23, N 4.19, S 12.89. MS (ESI+, CH2Cl2): m/z (%) = 691.6 (100) [M]+. FTIR (Diamond crystal HATR, cm⁻¹): νCO = 2011.

2.2.18 UV-Visible Titration

The spectra of reference complexes [Rh(CO)(EtSNS)], [Rh(CO)(H2EtSNS)]OTf and [Rh(CO)(H2EtSNS)](OTf)2 were recorded in ca. 1x10⁻⁵ M dichloromethane solutions (Respectively, Figure S1, S2 and S3 of the Appendix 1). Purity was previously checked by 1H NMR, 31P{1H} NMR, and elemental analysis. A dichloromethane stock solution of [Rh(CO)(EtSNS)], ca. 7x10⁻³ M, was prepared by weight and diluted to ca. 1x10⁻⁴ M for the UV–Visible titration. KOH aqueous solutions (ca. 0.2 M) were prepared by diluting concentrated Merck Titrisol ampoules and standardised with the reported procedures.[6]

The titrant solution of HOTf (ca. 15x10⁻³ M) was prepared by dissolving pure triflic acid (15 μl) in 10 mL of CH2Cl2 with the addition of 150 μl of reagent grade methanol. Its titre was determined by titrating a suspension of 2 mL of a dichloromethane solution in water with the standard KOH solution, using phenolphthalein as indicator. Thirty UV–visible spectra were collected at different acid : complex ratios (range between 0 and 2.2) by the addition of 25 μL of titrant at each step (concentration of [Rh(CO)(EtSNS)] = 1x10⁻⁴ M, V0 = 50 mL). The spectroscopic data were processed to calculate the protonation constants (pKₐ) by means of the program SPECFIT 32 using the molar absorbance values of the pure protonated complexes as fixed parameters.[7] The wavelength range taken into account in the calculations was limited to 380–600 nm, where the complexes shown major variations in their absorption spectra. The distribution diagram was calculated and plotted using the program HYSS.[8]

2.2.19 X-ray Data Collection, Structure Solution, and Refinement

The intensity data of all compounds were collected at room temperature on a Bruker AXS Smart 1000[9a] single crystal diffractometer equipped with an area detector using a
graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Crystallographic and experimental details of the structures are summarized in Table 1. When necessary, an empirical correction for absorption was made. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on \( F_o^2 \)) first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms except for the amidic hydrogen atoms and those of the water molecule in [Na(EtSNS)H₂O]₂ which were localized in the 2F₀-Fc map and refined isotropically. In (H₂EtSNS)PF₆, one of the two ethyl groups and PF₆ anion was found disordered in two positions; in 2·½THF the THF molecule was found disordered around the two fold axis and in 8·2THF the PF₆ anion was found disordered in two positions.

Table 1 Crystal Data and Structure Refinement for [Na(EtSNS)H₂O]₂, (H₂EtSNS)PF₆, 1, 2·½THF, 4, 5, 6, 7 and 8·2THF

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2. Determination of Absolute pKa Values of Rh(I) Complexes

2.3 Results and Discussion

2.3.1 Acid-base properties of HEtSNS

The thioamidyl moiety of HEtSNS can be protonated with acids as HCl or HPF₆, forming the respective salts, while deprotonation of HEtSNS can be achieved with NaH (Scheme 1).

![Scheme 1. Lewis structures and formal charge distribution of HEtSNS and its deprotonated (EtSNS⁻) and protonated (H₂EtSNS⁺) forms.](image)

Single crystals of (H₂EtSNS)PF₆ (yellow) and [Na(EtSNS)H₂O]₂ (colorless) were obtained. Views of their crystal structures are reported in Figures 1. Selected bond distances
and angles are listed in Table 2 and compared to those previously reported for HEtSNS\textsuperscript{[1]} and to those of the complexes described herein.

![Figure 1](image.png)

**Figure 1.** ORTEP plots of the molecular structures of (H\textsubscript{2}EtSNS)PF\textsubscript{6} and [Na(EtSNS)H\textsubscript{2}O\textsubscript{2}]. Thermal ellipsoids are drawn at 30% probability level. H atoms are omitted for clarity. Only one of the two crystallographic independent (H\textsubscript{2}EtSNS)PF\textsubscript{6} units is depicted.

In the crystals of (H\textsubscript{2}EtSNS)PF\textsubscript{6}, two independent H\textsubscript{2}EtSNS\textsuperscript{+}/PF\textsubscript{6}\textsuperscript{−} couples are present and display similar geometrical parameters. The N1⋯N2 separation of 4.315(3) Å is larger than that of HEtSNS [2.856(8) Å]\textsuperscript{[1]} the latter featuring an intramolecular hydrogen bond (Scheme 1). Differently from HEtSNS, the P–N–P system is coplanar with the two thioamidic groups.
[maximum deviation from the mean plane defined by C1, N1, S1, C2, N2, S2, P1, N3, P2 = 0.104 Å], probably due to a bifurcated (on the donor atom) hydrogen bonding of the type N1–H···N3···H–N2 (H1···N3 and H2···N3 distances: 2.396(1) and 2.418(1)Å). The presence of an interaction with the N3 lone pair is also suggested by the P–N–P angle, which is significantly narrower than those of HEtSNS and [Na(EtSNS)H$_2$O]$_2$.

The hydrated dimeric salt [Na(EtSNS)H$_2$O]$_2$ crystallized in the air by evaporation of a CH$_2$Cl$_2$/hexane solution of [Na(EtSNS)]. Each Na$^+$ cation interacts with the three nitrogen atoms of EtSNS$^-$ (Na–N3, Na–N1, Na–N2 distances: 2.592(2), 2.478(2), 2.503(3) Å, respectively) and with the oxygen atom of a water molecule (Na–Ow separation: 2.277(3) Å). The two units are connected by S···Na interactions (Na–S1' distance is 2.893(1) Å) resulting in a distorted square pyramidal geometry around Na$^+$ ions. It is worthy to note that sulfur–bridged complexes of alkaline metals are far less common than their oxygen-containing counterparts.$^{[10]}$

Solid Na(EtSNS) is not stable towards hydrolysis. When left in the air it reacts with water vapor, transforming to HEtSNS. The presence of coordinated water in the crystals of [Na(EtSNS)H$_2$O]$_2$ seems to indicate that the dimerization results in a much lower reactivity towards hydrolysis. When a sample of Na(EtSNS) was dissolved in $d$-chloroform, spontaneous re-transformation in H(D)EtSNS was monitored by $^{31}$P{$^{1}$H} NMR over a period of ca. two hours, the 8.0 ppm signal of colorless Na(EtSNS) being replaced by that of yellow HEtSNS at 8.4 ppm.$^{[11]}$ The initial observation of a sharp singlet (regardless of the temperature) suggested that, in this solution, the salt is present in its monomeric form. On the contrary, monomeric NaEtSNS is stable in DMSO solution. Also in this case, only a sharp singlet was observed in the $^{31}$P{$^{1}$H} NMR spectrum in DMSO-$_d_6$ ($\delta = 7.2$ ppm) and even the addition of a large excess of water did not result in the formation of HEtSNS ($\delta = 13.8$ ppm). This stabilizing effect is probably stemming from the interaction of Na$^+$ with DMSO, through the oxygen atom.$^{[12]}$

In (H$_2$EtSNS)PF$_6$, [Na(EtSNS)H$_2$O]$_2$ and HEtSNS the P1–N3 and P2–N3 bond distances are rather similar while variations can be evidenced in the C–S and C–N distances. As expected, the protonation of the thioamidyl group results in the lengthening of the corresponding C–N bonds and in shorter C–S distances; the same behavior is observed in the complexes described herein.
2. Determination of Absolute pKa Values of Rh(I) Complexes

<table>
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<th>Table 2. Selected bond lengths (Å) and angles (°).</th>
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2.3.2 Coordination properties and geometrical versatility of EtSNS⁺, HEtSNS and H₂EtSNS⁺.[13]

**Reaction of HEtSNS with [Rh(cod)Cl]₂ in the presence of tBuOK.** The reaction of HEtSNS and [Rh(cod)Cl]₂ in the presence of a stoichiometric amount of tBuOK (Scheme 2) yields [Rh(cod)(S,S–EtSNS)] (I) in quantitative yields. A view of its molecular structure is depicted in Figure 3.
2. Determination of Absolute pKa Values of Rh(I) Complexes

In complex 1, EtSNS\(^{-}\) chelates the metal centre through both sulfur atoms, forming an 8-membered ring. The distorted square planar coordination is completed by a chelating cod molecule. The S1–Rh1–S2 angle of 92.90(2)\(^{\circ}\) is dramatically narrower than that observed in the S,S–chelated complex [Au(EtSNS)]\(^{2+}\) in which the coordination over the metal centre is almost linear [S1–Au1–S2 = 177.73(6)\(^{\circ}\)].

An intermediate geometry was found in dimer [Ag(EtSNS)]\(_2\) [mean value of the S–Ag–S angles = 136.6(1)\(^{\circ}\)].\(^{14}\) The structural flexibility of EtSNS\(^{-}\) allows the ligand to comply with the coordination requests of the different metal centres. In 1, the charge separation is conserved so that this complex belongs to the category of zwitterionic metallates.\(^{15}\)

**Reaction of HEtSNS with [Rh(CO)\(_2\)Cl]\(_2\) in the presence of tBuOK.** The reaction of HEtSNS and [Rh(CO)\(_2\)Cl]\(_2\) in the presence of a stoichiometric amount of tBuOK results in the quantitative formation of [Rh(CO)(EtSNS)]. This compound was previously reported as the
2. Determination of Absolute pKa Values of Rh(I) Complexes

Product of the reaction between NaEtSNS and [Rh(CO)₂Cl]₂.[¹b] In the same work, [Rh(CO)₂(S₆N–EtSNS)] was proposed as intermediate product of the reaction (evidenced by FTIR spectrophotometry). In view of the isolation of compound 1, we now propose [Rh(CO)₂(S₆S–EtSNS)] to be the actual intermediate, as shown in Scheme 3.

Complex 1 undergoes cyclooctadiene substitution by bubbling CO in dichloromethane solution, at room temperature and atmospheric pressure, transforming quantitatively to [Rh(CO)(EtSNS)].

A Rh₂ dinuclear complex. Reaction of 1 with [Rh(cod)(THF)₂]OTf results in the formation of the purple dinuclear compound [{Rh(cod)}₂(µ-S,S–EtSNS)]OTf (2). An ORTEP plot of the structure of [{Rh(cod)}₂(µ-S,S–EtSNS)]⁺ in 2⋅½THF is reported in Figure 4.
2. Determination of Absolute pK<sub>a</sub> Values of Rh(I) Complexes

Figure 4. ORTEP plot of the molecular structure of the cation of \( \textbf{2} \) in \( \textbf{2} \cdot \frac{1}{2} \text{THF} \). Thermal ellipsoids are drawn at 30% probability level. H atoms are omitted for clarity. Selected distances [Å] and angles [°]: P1–N3 1.591(4), P2–N3 1.587(4), P1–C1 1.834(5), P2–C21.829(5), C1–S1 1.786(5), C2–S2 1.790(5), C1–N1 1.244(6), C2–N2 1.250(6), S1–Rh1 2.417(1), S2–Rh1 2.400(1), S1–Rh2 2.369(1), S2–Rh2 2.407(2), Rh1–Rh2 2.942(1), P1–N3–P2 128.0(3).

Dinuclear complex \( \textbf{2} \) can be seen as an adduct between \( \textbf{1} \) and the fragment [Rh(cod)]<sup>+</sup>. Both sulfur atoms of EtSNS<sup>−</sup> bridge the metal centres forming a Rh<sub>2</sub>S<sub>2</sub> core, rather common for dithiolate complexes.\(^{[16]}\) The Rh–S bond lengths range from 2.369(1) Å for Rh2–S1 to 2.417(1) Å for S1–Rh1. The ligand geometry differs from that observed in compound \( \textbf{1} \), emphasizing its geometrical versatility. In particular, the P1, C1, S1, N1 and P2, C2, S2, N2 mean planes are almost orthogonal in \( \textbf{1} \) [88.2(1)°] while in \( \textbf{2} \) they are almost parallel [19.2(4)°].

A similar reaction, between \( \textbf{1} \) and [Rh(cod)Cl]<sub>2</sub>, carried out in chlorinated solvents, did not afford the expected dinuclear complex [{Rh(cod)}<sub>2</sub>(µ–S,S–EtSNS)]Cl (\( \textbf{3} \)), analogous to \( \textbf{2} \), as evidenced by the \( ^{31}\text{P}\{^1\text{H}\} \) NMR spectra in which only the signal of \( \textbf{1} \) (9.7 ppm, CDCl<sub>3</sub>) was visible.

On the other hand, \( \textbf{3} \) was quantitatively formed when methanol was used as solvent, as confirmed by \( ^{31}\text{P}\{^1\text{H}\} \) NMR and the ESI–MS spectrum, showing the expected (M–Cl)<sup>+</sup> peak at 980.26 m/z. The assembly of \( \textbf{3} \) was monitored using \( ^{31}\text{P}\{^1\text{H}\} \) spectroscopy by addition of known quantities of CH<sub>3</sub>OH into a stoichiometric solution of \( \textbf{1} \) and [Rh(cod)Cl]<sub>2</sub> in CD<sub>2</sub>Cl<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH = 5). Any attempt to obtain \( \textbf{3} \) in the solid state failed: re-formation of \( \textbf{1} \) and
[Rh(cod)Cl]₂ was observed upon solvent removal. Moreover, only crystals of the two precursors could be separated by any crystallization method that was tried. This equilibrium strongly depends on the dielectric properties of the solvent but also on the ionic strength of the solution, since upon addition of (Et₄N)PF₆, assembly of 3 can be achieved in CHCl₃.

**Reaction of HEtSNS with [Rh(cod)Cl]₂.** Complex [Rh(S–HEtSNS)(cod)Cl] (4), in which HEtSNS behaves as monodentate, was prepared by reacting HEtSNS with [Rh(cod)Cl]₂ (Scheme 4).

![Scheme 4](image)

In the ³¹P{¹H} NMR of 4 in d-chloroform, two sets of peaks are present. Two doublets (δ = 11.1 (d), 10.5 (d) ppm; ²J(P,P) = 15.9 Hz) can be assigned to 4 while a singlet at 12.4 ppm suggests the presence of a second species, probably isomer [Rh(S,S'–HEtSNS)(cod)]Cl (4a), which may be in slow equilibrium with 4 (integral ratio 4/4a ≈ 10, see spectrum in Figure S1 of the Appendix 1). In complex 4a, HEtSNS could behave as an S,S chelating ligand, similarly to what observed in 1.

Isomer 4a is only present in solution, since the HATR infrared spectrum of the crude powder obtained by evaporation of the reaction solvent, was found superimposable to the spectrum of a single crystal of 4. In the ¹H NMR spectra, two broad N–H signals can be observed at 11.4 and 12.8 ppm, (assigned to 4 and 4a, respectively). In the solid state structure of 4, HEtSNS is coordinated through the sulfur atom of the thioamidyl group, a chloride and a chelating cod being bound to the Rh atom. A N2H₃n···Cl interaction is present, forming a 10-membered pseudo-ring (Figure 5).
2. Determination of Absolute pKa Values of Rh(I) Complexes

Figure 5. ORTEP plot of the molecular structure of 4. Thermal ellipsoids are drawn at 30% probability level. H atoms are omitted for clarity.

As evidenced by *in situ* $^{31}$P{$^1$H} NMR, when tBuOK was added to a CDCl$_3$ solution of 4, compound 4a was first, quickly and completely consumed, slowly followed by deprotonation of compound 4. Both reactions converged to the formation of [Rh(cod)(S,S–EtSNS)] (1, singlet at 9.7 ppm). This fast reactivity is in agreement with the proposed structure of 4a whose formula can be written as 1·HCl. When methanol was added to a chloroform solution of 4 (Scheme 5), the solution color instantly changed from yellow to purple. The $^{31}$P{$^1$H} NMR suggested the formation of H$_2$EtSNS$^+$ along with the dinuclear compound 3 (13.3 and 17.9 ppm respectively).

Scheme 5. Solvent dependent equilibrium for complex 3 and 4.
This equilibrium, which implies the autoprotonation reaction:

$$2 \text{HEtSNS} \rightarrow \text{H}_2\text{EtSNS}^+ + \text{EtSNS}^-$$

is somehow similar to the formation of 3 in methanol, confirming that the cationic dinuclear entity $$\{\text{Rh(cod)}\}_2(\mu-S,S-\text{EtSNS})$$ is favored in polar solvents. Moreover, the attempt to perform a chloride abstraction from 4 using AgOTf, with the aim of obtaining a $$S,S'–\text{HEtSNS}$$ chelated complex analogous to 4a failed, resulting in the formation of $$\{\text{Rh(cod)}\}_2(\mu-S,S-\text{EtSNS})\text{OTf}$$ (2).

**Reaction of HEtSNS with [Rh(CO)$_2$Cl]$_2$.** In the reaction of HEtSNS with [Rh(CO)$_2$Cl]$_2$ in dichloromethane (Scheme 6) three products are formed, as detected by $^{31}$P{$^1$H} NMR.

![Scheme 6.](image)

The main products of the reaction correspond to the $$S,N,S$$ tridentate complex $$[\text{Rh(CO)}(\text{EtSNS})]$$ (16.6 ppm) and to $$[\text{H}_2\text{EtSNS}][\text{Rh(CO)}_2\text{Cl}_2]^-$$ (5) (13.3 ppm). Two low intensity doublets at 11.9 and 11.4 ppm ($^2J_{PP} = 15.2$ Hz) suggest the formation of monodentate complex $$[\text{Rh(CO)}_2(\text{S–HEtSNS})\text{Cl}]$$, analogous to 4, as intermediate minor product. Compound 5 was separated by crystallization and its molecular structure determined by X-ray diffraction (see Figure S2 of the Appendix 1) and it displays geometrical parameters analogous to those observed for compound 6 (*vide infra*). The cation in compound 5 stems from the protonation reaction of HEtSNS due to the scavenging of HCl liberated in the formation of $$[\text{Rh(CO)}(\text{EtSNS})]$$. The chloride was found coordinated by the Rh atom of anion $$[\text{Rh(CO)}_2\text{Cl}_2]^-$$. The reaction is probably driven by the stability of the $$S,N,S$$ tridentate complex $$[\text{Rh(CO)}(\text{EtSNS})]$$. Complex $$[\text{Rh(CO)}_2(\text{S–HEtSNS})\text{Cl}]$$ can be regarded as the first reaction product, successively yielding 5 and $$[\text{Rh(CO)}(\text{EtSNS})]$. 
Determination of Absolute $pK_a$ Values of Rh(I) Complexes

Reaction of (H$_2$EtSNS)X (X = Cl, PF$_6$) with [Rh(cod)Cl]$_2$. The reactivity of (H$_2$EtSNS)X (X = Cl, PF$_6$) depends on the coordinative properties of the anion. The reaction of (H$_2$EtSNS)Cl with [Rh(cod)Cl]$_2$ yielded [H$_2$EtSNS][Rh(cod)Cl]$_2$ (6). A view of its molecular structure, determined by X-ray diffraction methods, is reported in Figure 6.

Figure 6. ORTEP plot of the molecular structure of 6. Thermal ellipsoids are drawn at 30% probability level. H atoms are omitted for clarity.

In the crystal structure, bond lengths and angles of H$_2$EtSNS$^+$ are similar to those observed for (H$_2$EtSNS)PF$_6$, except for the P–N–P angle which is slightly bigger [6: 136.7(2)$^\circ$; (H$_2$EtSNS)PF$_6$: 132.9(1)$^\circ$, 133.9(1)$^\circ$] and the value of the C1–P1–P2–C2 torsion angle (circa 1$^\circ$ for (H$_2$EtSNS)PF$_6$ and 91$^\circ$ for 6). The cation–anion interaction features two H⋯Cl contacts as depicted in Figure 6. Being the positive charge located on the P–N–P system, this interaction is reminiscent of the anion coordination by neutral thioureas and ureas.$^{[17]}$ No reaction was observed between (H$_2$EtSNS)PF$_6$ and [Rh(cod)Cl]$_2$. The cation H$_2$EtSNS$^+$ is thus unable to open the chloride bridge of the dimeric precursor and coordinate to the Rh centre (see below for the coordination properties of H$_2$EtSNS$^+$).

Reaction of (H$_2$EtSNS)X (X = Cl, PF$_6$) with [Rh(CO)$_2$Cl]$_2$. Although 6 can be quantitatively prepared by the aforementioned reaction of (H$_2$EtSNS)Cl with $\frac{1}{2}$ [Rh(cod)Cl]$_2$, a similar reaction pathway can not be followed for the synthesis of 5.
The reaction of \((\text{H}_2\text{EtSNS})\text{Cl}\) with \([\text{Rh(CO)}_2\text{Cl}]_2\) in \(\text{CH}_2\text{Cl}_2\) afforded \([\text{Rh(CO)}(\text{S,N,S–H}_2\text{EtSNS})][\text{Rh(CO)}_2\text{Cl}]_2\) (7); two unreacted \((\text{H}_2\text{EtSNS})\text{Cl}\) were also observed, by \(^{31}\text{P}\{^1\text{H}\}\) NMR. The coordination of the \(\text{Cl}^-\) liberated in the formation of \([\text{Rh(CO)}(\text{S,N,S–H}_2\text{EtSNS})]^{2+}\) afforded the two chloro-rhodates \([\text{Rh(CO)}_2\text{Cl}]^-\) and, due to the formation of a new coordination site by the loss of a CO molecule, the cation \(\text{H}_2\text{EtSNS}^+\) could act as ligand for a \(\text{Rh(CO)}^+\) group. A more convenient preparation of 7 was achieved by reacting \((\text{H}_2\text{EtSNS})\text{Cl}\) with \([\text{Rh(CO)}_2\text{Cl}]_3\) in a 2 : 3 ratio (Scheme 7). A view of its structure, determined by X-ray diffraction methods, is reported in Figure 7.

**Figure 7.** ORTEP plot of the molecular structure of 7. Thermal ellipsoids are drawn at 30% probability level. H atoms are omitted for clarity. Symmetry transformation used to generate equivalent atoms: \(1 – x, y, \frac{1}{2} – z\).
The formation of 7 suggested that other stable protonated derivatives of [Rh(CO)(EtSNS)] could be obtained (Scheme 8). Indeed, [Rh(CO)(S,N,S′–HETNS)]PF₆ ([Rh(CO)(EtSNS)]·HPF₆, 8) was synthesized by protonation of [Rh(CO)(EtSNS)] with an equimolar amount of HPF₆ or by complexation of [Rh(CO)(MeCN)₂]PF₆ with HETNS. In a similar manner, [Rh(CO)(S,N,S–H₂EtSNS)](PF₆)₂ ([Rh(CO)(EtSNS)]·2HPF₆, 9) was prepared by protonation of [Rh(CO)(EtSNS)] with two equimolar amounts of HPF₆ or by reacting [Rh(CO)(MeCN)₂]PF₆ with (H₂EtSNS)PF₆. The latter reaction is an example of complex formation by reacting a cationic ligand and a cationic metal fragment, not frequent in coordination chemistry. The cations of 7 and 9, [Rh(CO)(S,N,S–H₂EtSNS)]⁺, are identical. Single crystals of 8-2THF were obtained. Its structure is depicted in Figure 8.

Scheme 8. Formation of complexes 8 and 9 by protonation of [Rh(CO)EtSNS] and direct complexation of [Rh(CO)]⁺ species.
2. Determination of Absolute $pK_a$ Values of Rh(I) Complexes

![Figure 8. ORTEP plot of the molecular structure of 8·THF in 8·2THF. Thermal ellipsoids are drawn at 30% probability level, H atoms are omitted for clarity. The second THF molecule was not involved in direct interactions with the complex and is omitted for clarity.](image)

It is worthy to note that in 7, 8 and [Rh(CO)(EtSNS)] the coordination geometry is almost identical. The ligands correspond to, respectively, cationic $\text{H}_2\text{EtSNS}^+$, neutral–zwitterionic HEtSNS and dianionic–cationic EtSNS$^-$. In the solid state infrared HATR spectra of the complexes [Rh(CO)(EtSNS)], 8 and 9, the CO stretching frequency increases (1951, 1979, and 1996 cm$^{-1}$ respectively in the solid state; 1968, 1994 and 2017 cm$^{-1}$ respectively in CH$_2$Cl$_2$ solution), suggesting that the protonation of [Rh(CO)(EtSNS)] results in a decreased electron density on the metal centre and thus in a weaker Rh→CO back donation.$^{[19]}$ The P–N distances in 7 and 8 are slightly shorter than those of [Rh(CO)(EtSNS)], as well as the P–C ones. Since the protonation of HEtSNS does not affect the P–N–P system (see Table 2), this small change could stem from a variation of the ligating properties of the thioamidyl/thioamidic groups. In fact, the Rh–S bond length increases in the 7, 8, [Rh(CO)(EtSNS)] series, in turn affecting the P–N–P system through the metal centre. The thioamidyl fragment, more thiolato in character, is a stronger donor than the thioamidic group of thione character. The Rh–N distance is slightly shorter in the protonated species, probably influenced by the lower electron density on the Rh atom. The $^{31}\text{P}$ chemical shift is strongly affected by the protonation: [Rh(CO)(EtSNS)] shows a sharp singlet at 16.6 ppm (CDCl$_3$) while in 9 the two equivalent P atoms resonate at 38.2 ppm. The $^{31}\text{P}^{'1\text{H}}$ NMR data recorded in $d$-chloroform for 8 shows two sharp singlets (35.0 and 19.9 ppm), assigned respectively to the P atoms bound to the thioamidic and thioamidyl coordinated functions$^{[20]}$ suggesting the
absence of fast proton exchange. The solid state $^3$P NMR of compound 8 was recorded and the two peaks (36.1 and 24.1 ppm) were observed. As a reference, in the solid state NMR spectrum of HEtSNS, two singlets are found at 8.1 (thioamidic) and 2.6 ppm (thioamidyl), showing that Rh coordination exerts a strong influence on the chemical shift of the P atoms. The formal Lewis structures depicted in Scheme 8 are in agreement with this observation and with the bond distances discussed above. The thioamidic groups can be considered neutral in 8 and 9; the formal charge on the Rh atom is negative in [Rh(CO)(EtSNS)], neutral in 8, positive in 9. The Mulliken atomic net charge for complex [Rh(CO)(EtSNS)] (-0.150, -0.157, -0.177 in gas, cyclohexane and THF respectively) was calculated by DFT methods.$^{[1a]}$ A positive charge is always shared by the two P atoms.

Protonation reaction of complex 1. The protonation behaviour of complex 1 using HCl or HOTf doesn’t parallel the one of [Rh(CO)EtSNS]; change of the ligand coordination geometry was observed, as depicted in Scheme 9. When one equivalent of HCl was used, S–monodentate HEtSNS was formed and the chloride anion substituted a sulfur atom in the coordination sphere of Rh, yielding complexes 4 and 4a. With two equivalents of HCl, cation H$_2$EtSNS$^+$ formed, the second chloride anion entered in the coordination sphere of Rh, and complex 6 was obtained. When HOTf was used the formation of 2 was observed, together with one equivalent of H$_2$EtSNS$^+$. The different reactivity is apparently due to the lower stability of the bidentate complex with respect to the tridentate [Rh(CO)EtSNS].

Scheme 9. Acid–base reactions for complex 1
2.3.3 Acid–base properties of [Rh(CO)(EtSNS)]

Protonation equilibria of [Rh(CO)(EtSNS)] were studied by means of spectroscopic UV–Visible titration in CH₂Cl₂, using a solution of HOTf in a 1.5% mixture of methanol in dichloromethane. Under these conditions it was assumed that HOTf is completely dissociated and acts as a superacid, so that the concentration of H⁺ can be considered equal to the analytical concentration of the acid added (the methanol is present to allow the triflic acid to completely dissolve and to level HOTf to CH₂OH₂⁺). These circumstances allow for the determination of the p𝐾ₐ in this solvent on an absolute scale. In the literature, protonation equilibria of ligands and complexes in CH₂Cl₂ were studied by means of proton exchange reactions using HP(Cy)₃⁺ (Cy = cyclohexyl) as weak acid, for which a p𝐾ₐ = 9.7 was established by literature convention. This p𝐾ₐ scale, however, represents a relative p𝐾ₐ ladder which should be rescaled to the real HP(Cy)₃⁺ acidity constant. The employment of triflic acid as titrant, dissolved in CH₂Cl₂ with small amounts of methanol, allows for a direct evaluation of protonation equilibria, in a similar way as studying the protonation equilibria in water by means of fully dissociated HCl.

In the titration of [Rh(CO)(EtSNS)] with triflic acid three very well defined isosbestic points were detected: one at 438 nm for acid to complex ratios from 0 to 1, and two at 509 and 385 nm for acid to complex ratios from 1 to 2 (Figure 9). These results are in agreement with the expected diprotic nature of [Rh(CO)(H₂EtSNS)]²⁺ and the presence of two distinct protonation processes involving [Rh(CO)(EtSNS)].
Two pK<sub>a</sub> values of 4.8(4) and 6.5(3) (σ = 4.11·10<sup>−2</sup>) were determined for the dissociation processes:

\[
[Rh(CO)(H_2EtSNS)]^{2+} \rightleftharpoons [Rh(CO)(HEtSNS)]^+ + H^+
\]

\[
[Rh(CO)(HEtSNS)]^+ \rightleftharpoons [Rh(CO)(EtSNS)] + H^+
\]

A representative distribution diagram for the \([Rh(CO)(H_2EtSNS)]^{2+}\) complex is shown in Figure 10 (UV-Vis spectra of pure samples of \([Rh(CO)(EtSNS)]\), \([Rh(CO)(EtSNS)] \cdot HOTf\) and \([Rh(CO)(EtSNS)] \cdot 2HOTf\) are reported in Appendix 1). Recently, a similar acid–base behavior was observed for Pd complexes of thioamidic SNS pincer ligands but protonation constants were not determined.\textsuperscript{25} Unfortunately, although the protonation equilibria of several complexes were investigated in the last decade\textsuperscript{22, 23} the dissociation constants were all referenced to the HP(Cy)<sub>3</sub>\textsuperscript{+} standard, and no direct comparison with those values is possible. Titration of HEtSNS by UV-Vis was not possible due to the absence of suitable variation in the absorption spectra. The titration was performed monitoring the protonation by \textsuperscript{31}P NMR. In these conditions, the basicity of the ligand is too high for pK determination.
2.4 Conclusions

The zwitterionic ligand HEtSNS is amphoteric and possesses ligating properties in all of its three forms: zwitterionic–neutral, zwitterionic–anionic and cationic. This work, together with previous results, evidenced its geometrical versatility which allows the following coordination fashions: \( S \)–monodentate (compound 4) eight-membered chelating \( S,S \)–bidentate with 180° bite-angle ([Au(EtSNS)]\(^2^\){}) or 90° bite-angle (compound 1), \( S,N,S \)–bischelating ([Rh(CO)EtSNS]\(^1^\){}), \( N,N,N \)–tridentate coordination in [Na(EtSNS)\( \text{H}_2 \text{O} \)]\(^2^\), in which monodentate \( S \)–coordination is also found. The S atoms are also able to bridge as in clusters described in Ref. 2, and in dinuclear complex 2. In the case of [Rh(cod)]\(^+\) precursors, the coordination geometry and complex nuclearity in solution are strongly dependent on the polarity of the solvent. Noteworthy, HEtSNS, EtSNS\(^-\) and H\(_2\)EtSNS\(^+\) show the same \( S,N,S \) coordinating properties towards the cationic metal species [Rh(CO)]\(^+\) (compounds [Rh(CO)EtSNS], 7, 8 and 9 respectively). Protonated complexes can be prepared also by reaction of acids with [Rh(CO)EtSNS], whose two pK\(_a\) have been determined in CH\(_2\)Cl\(_2\) solution. The protonation causes a change in the electron density on the Rh atom, as

![Distribution diagram for the titration of [Rh(CO)(EtSNS)] (C\(_{Rh} \) = 1x10^{-4} M).](image-url)
evidenced by the stretching vibration of the coordinated CO molecule, which could be exploited in tuning its catalytic properties, for instance in reactions involving oxidative addition on the metal centre.

2.5 References

[1] a) M. Asti, R. Cammi, D. Cauzzi, C. Graiff, R. Pattacini, G. Predieri, A. Stercoli, A. Tiripicchio, Chem. Eur. J. 2005, 11 (11), 3413–3419. b) [Rh(CO)(EtSNS)]: $^1$H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): δ = 7.48–7.26 (m, 20H; Ph), 3.75 (qd, $^3$J(H,H) = 7.2, $^4$J(H,P) = 3.9 Hz, 4H; CH$_2$), 1.19 ppm (t, $^3$J(H,H) = 7.2 Hz, 6H; CH$_3$); $^{31}$P{$^1$H} NMR (400 MHz, CDCl$_3$, 25 °C): δ = 16.6 ppm (s). FTIR (Diamond crystal HATR, cm$^{-1}$): $\nu$CO = 1951.


[3] In more than one thousand structures of metal compounds, containing the PPN$^+$ cation, found in the Cambridge Crystallographic Data Base, the shortest distance is reported in: P. G. Jones, Z. Kristallogr. 1995, 210, 375.


[13] The overall reactivity towards [Rh(cod)Cl]$_2$, solvent-dependent equilibria and the reaction of complex 1 with CO are depicted in Scheme S1 and S2 of the supplementary material

[14] The mean value between 180° and 90°(respectively found in [Au(EtSNS)] and in 1) is 135° as found in [Ag(EtSNS)]$_2$.

Determination of Absolute pKₐ Values of Rh(I) Complexes


[21] During the titration, 30 additions of 25 µL of HOTf dissolved in CH₂Cl₂/CH₃OH, were made to 50 mL of solution of [Rh(CO)EtSNS] in neat dichloromethane. In this condition, the final quantity of methanol in the titrated solution is negligible (0.02%).


3. Charge-tuned Rh(I) Complexes

Oxidative Addition of Iodomethane to Charge-tuned Rh\(^{1}\) Complexes

The zwitterionic Rh\(^{1}\) monocarbonyl complex [Rh(EtSNS)(CO)] (1, EtSNS = EtNC(S)Ph=NPPh\(_{2}\)C(S)NEt\(^{-}\) ) was reacted with iodomethane in dichloromethane, yielding the stable acetyl-Rh\(^{III}\) complex [Rh(EtSNS)(COCH\(_{3}\))] (4). Complex 4 was characterized in solution and in the solid state by X-Ray diffraction analysis. The rate constant of the reaction \([5.48 (7) \times 10^{-2} \text{ M}^{-1} \text{s}^{-1} \text{ at } 25 \, ^{\circ}\text{C} \text{ CH}_2\text{Cl}_2]\) and the activation parameters \(\Delta H^\ddagger \[28(3) \text{ kJ mol}^{-1}\] \text{ and } \Delta S^\ddagger \[-173(10) \text{ J mol}^{-1} \text{ K}^{-1}\] \) were determined, confirming a nucleophilic addition mechanism. The rate constant was obtained by monitoring the acetylic product by \(^1\)H NMR, under second-order conditions ([Rh] / [CH\(_{3}\)I] = 1). Complex 1 can be mono- and bi-protonated with HX (X = PF\(_{6}\), OTf, NO\(_{3}\)), forming [Rh(HEtSNS)(CO)]X (2·X) and [Rh(H\(_{2}\)EtSNS)(CO)]X\(_{2}\) (3·X\(_{2}\)) respectively. A decrease of the calculated DFT Mulliken atomic population is observed along the series 1 > 2 > 3 in accordance with the variation of the coordinated CO stretching frequency. Compounds 2·X were also reacted with iodomethane forming complexes [Rh(HEtSNS)(COCH\(_{3}\))]X (5·X), stable in solution for a short time, that transform by deprotonation in 4 and in unidentified decomposition products. The rate constants were determined under pseudo first-order conditions due to the lower reactivity \([2\cdot\text{NO}_3 = 24.6 (6) \times 10^{-5} \text{ M}^{-1} \text{s}^{-1}; 2\cdot\text{OTf} = 12.7 (3) \times 10^{-5} \text{ M}^{-1} \text{s}^{-1}; 2\cdot\text{PF}_6 = 2.50 (6) \times 10^{-6} \text{ M}^{-1} \text{s}^{-1}]\). The activation parameters for 2·PF\(_{6}\) were also determined. The influence of the counterion could be explained assuming that the different non metal-coordinated anions form hydrogen bonding with the NH group of 2·X, that in turn causes a variation of the electron density on the Rh centre. A good correlation between the CO stretching frequencies and the rate constants was observed. The experimental rate constant for complex 1 is one order of magnitude higher than the one calculated using the linear regression function obtained for the 2·X series (experimental = 5.48 x 10\(^{-2}\) M\(^{-1}\) s\(^{-1}\); calculated = 1.29 x 10\(^{-3}\) M\(^{-1}\) s\(^{-1}\)), pointing out that the monoprotonated complexes react more slowly than expected. Both steric and electronic effects were examined and held responsible of this reduced reactivity. Complexes 3·X\(_{2}\) reacted too slowly, yielding complex 4 and unidentified decomposition products, hindering the determination of the rate constants.
3.1 Introduction

It is established, by experiment and calculation, that oxidative addition of methyl iodide to square-planar rhodium(I) carbonyl complexes proceeds via a nucleophilic mechanism, where the rate determining step shows a $S_N2$ transition state. Consequently, if the reactivity is not strongly moderated by steric effects, due to bulky substituents or ligand orientation that hinder the space above and below the Rh coordination plane, higher reaction rates are found for complexes with high electron density on the Rh center, which behaves as a nucleophile towards the carbon atom of CH$_3$I. The value of the IR stretching frequency of coordinated CO is taken as an indicative measure of the electron density on the Rh atom, and a qualitative correlation between the electronic density, the CO frequency and the reaction rate is possible (as a rule of thumb, faster kinetics are observed for complexes with a CO frequency of about 1990 cm$^{-1}$ or lower). However, Haynes et al. suggest that similar complexes with sensibly different CO stretching frequency, namely trans-[Rh(CO)(PPh$_3$)$_2$I] and [Rh(CO)(dppe)I] (dppe = 1,2-bis(diphenylphosphino)ethane; $\nu$(CO) = 1981 and 2011 cm$^{-1}$ respectively), might be expected to have similar electron density on the Rh center. In our opinion, this shows that the Rh electron density is not only dependent on the kind of donor atoms in the ligands, but also on their orientation and geometry, and that this density is indeed reflected by the CO stretching frequency. Nonetheless, in different complexes with the same donor atoms and the same coordination geometry, the CO stretching frequency can be used, with confidence, as a measure of the electronic densities.

The rhodate complex [Rh(CO)$_2$I$_2$] (the “Monsanto” catalyst) is taken as reference in comparing kinetic constant values; to now, the highest ones have been determined for carbonyl complexes containing bis(imino)carbazolide and N-heterocyclic carbene ligands. It can be assumed that for geometrically analogous complexes whose CO stretching frequency are equal, the electron density on the Rh atom is the same and the variation of the steric of ligand substituents allows the observation of steric effects alone. For Rh carbonyl complexes, the oxidative addition is often followed by the migratory CO insertion, forming an acetyl complex. This reaction seems faster when steric demand is high but slower for high electron density complexes. Apparently, rate-enhancing electronic effects in the migratory CO insertion are observed when strong $\pi$-donor ligands are used. In this chapter we report kinetic and thermodynamic studies of the oxidative addition of iodomethane to the
3. Charge-tuned Rh(I) Complexes

Zwitterionic metallate\[^{[12]}\] \([\text{Rh(EtSNS})(CO)]^{[13]}\) (1) and its protonated derivatives:\[^{[14]}\] 
\([\text{Rh(HEtSNS})(CO)]\ X \ (2\cdot X)\) and \([\text{Rh(H2EtSNS})(CO)]\ X_2 \ (3\cdot X_2)\) \(\ X = \text{PF}_6, \text{OTf}, \text{NO}_3; \) EtSNS = EtNC(S)Ph\(_2\)P=NPh\(_2\)C(S)NEt\(_\bar{2}\).\[^{[15]}\] In the case of \([\text{Rh(EtSNS)}(CO)]\), \(^1\)H NMR was useful to obtain real second-order kinetic parameters, while in most literature cases, pseudo-first order rate constants were determined.\[^{[16]}\] In the case of the mono-protonated compounds \(2\cdot X\), a quantitative correlation between their CO stretching frequency with different counterion and the kinetic constant was observed, showing a long-range electronic effect due to the different hydrogen bonding acceptor properties of the anion. The bi-protonated complexes were found, as expected, to react very slowly.

3.2 Experimental

3.2.1 General procedures

All operations were carried out under nitrogen atmosphere using standard Schlenk techniques. Methyl iodide (Aldrich) and dichloromethane were distilled from calcium hydride. \([\text{Rh(CO)}\text{EtSNS}]^{[13]}\) \([\text{Rh(CO)}(\text{HEtSNS})]X\) and \([\text{Rh(CO)}(\text{H2EtSNS})](X)\) \(\ X = \text{PF}_6, \text{OTf}\)\[^{[14]}\] and \([\text{Rh(CH3CN)}_2(\text{CO})_2\text{NO}_3]\)\[^{[17]}\] were prepared as described elsewhere. HNO\(_3\) (65%) and \([\text{Rh}(\text{CO})_2\text{Cl}]\) \(\ \) (Aldrich) were used as supplied. Elemental analyses were carried out on a Carlo Erba EA1108 microanalyzer. FTIR spectra (4000–400 cm\(^{-1}\)) were recorded on a Nicolet Nexus spectrophotometer equipped with a Smart Orbit HATR accessory (diamond crystal and ZnSe). IR cell: CaF\(_2\) windows, 0.5 mm path length. \(^1\)H NMR (300.13 MHz, TMS) spectra were recorded on Bruker 300 Avance, \(^{31}\)P\(^{\text{(1H)}}\) NMR (161.98 MHz, external reference 85% H\(_3\)PO\(_4\)) and \(^{103}\)Rh NMR (12.65 MHz, the absolute \(^{103}\)Rh frequency was determined by relating it to the reference frequency \(\Xi = 3.16 \text{ MHz}\)), spectra were recorded on Bruker AMX400, using deuterated solvents (CDCl\(_3\), CD\(_2\)Cl\(_2\) and CD\(_3\)OD). All solid-state NMR spectra were recorded on a Bruker Avance II 400 operating at 400.23 and 100.65 MHz for \(^1\)H and \(^{13}\)C, respectively. All spectra have been recorded at room temperature with a spinning speed of 12-14 kHz. Cylindrical 4 mm o.d. zirconia rotors with sample volume of 120 µL were employed. A standard ramp cross-polarization pulse sequence were used with a contact time of 5 ms, a \(^1\)H 90° pulse of 3.35 ms, recycle delays of 10 sec and a number of 264-1000 transients. A two pulse phasemodulation (TPPM) decoupling scheme was used with an rf field of 75 kHz. \(^{13}\)C chemical shifts were referenced via the resonance of solids HMB (hexa-methyl benzene,
3. Charge-tuned Rh(I) Complexes

A Micromass Quattro LC triple quadrupole instrument equipped with an electrospray interface (Masslynx v. 3.4 software) was used for ESI–MS data collection and processing. The nebulizing gas (nitrogen, 99.999% purity) and the desolvation gas (nitrogen, 99.998% purity) were delivered at a flow-rate of 80 and 500 l/h, respectively. ESI–MS analyses were performed by operating the mass spectrometer in positive ion (PI) mode, acquiring mass spectra over the scan range \( m/z \) 100-2800, using a step size of 0.1 Da and a scan time of 2.7 sec. The interface operating parameters were: source temperature 70 °C, desolvation temperature 70 °C, ESI(+) capillary voltage 3.0 kV, cone voltage 15 V, rf lens 0.3 V.

3.2.2 Preparation of \([\text{Rh(CO)}(\text{HEtSNS})]\text{NO}_3 (2\cdot\text{NO}_3)\).

A solution of \([\text{Rh(CH}_3\text{CN)}_2\text{(CO)}]_2\text{NO}_3\) (0.200 g, 0.26 mmol) in \(\text{CH}_2\text{Cl}_2\) (10 mL) was added under nitrogen to a solution of \(\text{HEtSNS}\) (0.148 g, 0.26 mmol) in \(\text{CH}_2\text{Cl}_2\) (15 mL). Stirring was continued for 2 hs and the solution color turned to red. Evaporation of the volatiles afforded compound \([\text{Rh(CO)}(\text{HEtSNS})]\text{NO}_3 (2\cdot\text{NO}_3)\) as a red microcrystalline powder (Yield 87%).

Analytical Calcd. for \(\text{C}_{31}\text{S}_2\text{H}_{31}\text{O}_4\text{N}_4\text{P}_2\text{Rh} (M = 752.59): C 49.47; H 4.15; N 7.44; S 8.52. Found: C 49.30; H 4.12; N 7.40; S 8.49.

\(^1\text{H NMR (CD}_2\text{Cl}_2): \delta = 10.5 (s, br, 1H, N-H); 7.7-7.4 (m, 20H, Ph); 3.67 (m, br, 4H, -CH}_2\text{CH}_3, \beta = 7.2 Hz), 1.16 (t, 6H, -CH}_2\text{CH}_3, \beta = 7.2 Hz) ppm. \(^{31}\text{P}\{^1\text{H}\} \text{NMR (CD}_2\text{Cl}_2): \delta = 35.2 (s), 25.1 (s) ppm.}

ESI-MS [MeOH solution: \(m/z\) (rel. int., formula): 690.6 (100%, [Rh(CO)(HEtSNS)]+). FTIR (Diamond crystal HATR, \(\text{cm}^{-1}\)): \(\nu_{\text{CO}} = 1968\text{s}; (\text{CH}_2\text{Cl}_2, \text{cm}^{-1}): \nu_{\text{CO}} = 1989\text{s.}

3.2.3 Preparation of \([\text{Rh(CO)}(\text{H}_2\text{EtSNS})](\text{NO}_3)_2[3\cdot\text{(NO}_3)_2]\).

In a Schlenk tube and under nitrogen, a solution of \([\text{Rh(EtSNS)(CO)}] (0.200 g 0.29 mmol) in 10 mL of \(\text{CH}_2\text{Cl}_2\) was treated with 10 mL of a water solution of \(\text{HNO}_3\) (5 M) in large excess with respect to the rhodium precursor and the yellow solution turned orange. The two liquid phases were separated, and the organic one dried, giving an orange red solid. The solid was recrystallized from hot methanol affording compound \([\text{Rh(CO)}(\text{H}_2\text{EtSNS})](\text{NO}_3)_2[3\cdot(\text{NO}_3)_2]\) as an orange microcrystalline powder (Yield 92%).

Analytical Calcd. for \(\text{C}_{31}\text{H}_{32}\text{N}_5\text{O}_7\text{P}_2\text{RhS}_2 (815.61): C 45.65, H 3.95, N 8.57, S 7.86. Found C 45.48, H 3.91, N 8.52, S 7.83. \(^1\text{H NMR (CD}_2\text{Cl}_2): \delta = 10.4 (s, br, 2H, N-H); 7.7-7.4 (m, 20H, Ph); 3.82 (m, 4H, -CH}_2\text{CH}_3, \beta = 7.2 Hz), 1.27 (t, 6H, -CH}_2\text{CH}_3, \beta = 7.2 Hz) ppm. \(^{31}\text{P}\{^1\text{H}\} \text{NMR (CD}_2\text{Cl}_2): \delta = 41.1 (s) ppm.}
3. Charge-tuned Rh(I) Complexes

ESI–MS [MeOH solution: m/z (rel. int., formula): 691.6 (100%, [Rh(CO)(H₂EtSNS)]²⁺).

FTIR (Diamond crystal HATR, cm⁻¹): v₁ = 1986s; (CH₂Cl₂, cm⁻¹): v₂ = 2008s.

3.2.4 Reaction of [Rh(EtSNS)(CO)] with CH₃I.

Methyl iodide (0.014 g, 0.98 mmol) was added to a solution of [Rh(EtSNS)(CO)] (0.068 g, 0.98 mmol) in CH₂Cl₂ (10 mL). The resulting red reaction mixture was stirred for 3 hs. Evaporation of the solvent afforded compound [Rh(EtSNS)(COCH₃)I] (4) as a red powder. (Yield: 91%). The complex could be recrystallized by layering hexane onto a CH₂Cl₂ solution of crude product at -20 °C affording red crystals of [Rh(EtSNS)(COCH₃)I] (4).

Anal. Calcd. for C₃₂H₃₃IN₃OP₂RhS₂ (M = 831.51): C 46.22; H 4.00; N 5.05; S 7.71. Found: C 46.12; H 3.97; N 4.99; S 7.66.

1H NMR (CDCl₃): δ = 7.60–7.30 (m, 20H, Ph); 3.79 (m, br, 4H, -CH₂CH₃), 2.80 (s, 3H, COCH₃); 1.23 (t, 6H, -CH₂CH₃, 3J_H,H = 7.1 Hz) ppm.

31P{¹H} NMR (CDCl₃): δ = 27.4 (s) ppm.

CP-MAS ¹³C NMR: δ = 210.8 (s, CO), 181.5 (d, 1J_C,P = 151 Hz, C=N), 175.9 (d, 1J_C,P = 161 Hz, C=N), 137.2–120.9 (m, Ph), 51.8 (s, -CH₂CH₃), 49.1 (s, -CH₂CH₃ + COCH₃), 12.1 (s, -CH₂CH₃) ppm. FTIR (Diamond crystal HATR, cm⁻¹): v_CO = 1709s [Rh₃⁺(C(OMe))].

3.2.5 Reaction of [Rh(CO)(HEtSNS)]X (X = PF₆, OTf, NO₃) with CH₃I.

Methyl iodide was added to a solution of [Rh(HEtSNS)(CO)]X (X = PF₆, OTf, NO₃) ([CH₃I]/[Rh] = 100) in CH₂Cl₂ (10 mL). The reactions were monitored by FTIR spectrophotometry (CaF₂ windows, 0.5 mm path-length) until the absorption of the νCO of the starting materials were completely absent. The crude solutions were chromatographed by preparative TLC silica plate (CH₂Cl₂/Hexane = 8/2), affording the monoprotonated Rh₃⁺ acetyl complexes [Rh(HEtSNS)(COCH₃)I]X (5·X, X = PF₆, OTf, NO₃), 4 and unidentified products. 5·PF₆: ³¹P{¹H} NMR (CDCl₃): δ = 44.5 (s), 23.2 (s) ppm. FTIR (CH₂Cl₂, cm⁻¹): v_CO = 1725s [Rh₃⁺(C(OMe))]. 5·OTf: ³¹P{¹H} NMR (CDCl₃): δ = 44.3 (s), 23.6(s) ppm. FTIR (CH₂Cl₂, cm⁻¹): ν_CO = 1721s [Rh₃⁺(C(OMe))]. 5·NO₃: ³¹P{¹H} NMR (CDCl₃): δ = 44.1 (s), 23.9(s) ppm. FTIR (CH₂Cl₂, cm⁻¹): ν_CO = 1717s [Rh₃⁺(C(OMe))].

3.2.6 X-ray Data Collection, Structure Solution, and Refinement.

The intensity data of compound 4 were collected at room temperature on a Bruker AXS Smart 1000[18] single crystal diffractometer equipped with an area detector using a graphite
monochromated Mo Ka radiation ($\lambda = 0.71073$ Å). Crystallographic and experimental details of the structure is summarized in Table 1. An empirical correction for absorption was made. The structure was solved by direct methods and refined by full-matrix least-squares procedures (based on $F_o^2$) first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms.

Table 1. Summary of Crystallographic Data for 4

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<td>$F(000)$</td>
<td>1656</td>
</tr>
<tr>
<td>crystal size, mm$^3$</td>
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</tr>
<tr>
<td>$\mu$, cm$^{-1}$</td>
<td>16.37</td>
</tr>
<tr>
<td>rflns collected</td>
<td>42555</td>
</tr>
<tr>
<td>rflns unique</td>
<td>8298</td>
</tr>
<tr>
<td>rflns observed [$I &gt; 2\sigma(I)$]</td>
<td>5383</td>
</tr>
<tr>
<td>parameters</td>
<td>379</td>
</tr>
<tr>
<td>R indices [$I &gt; 2\sigma(I)$]</td>
<td>$R_1 = 0.0372$ (wR2 = 0.0902)</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>$R_1 = 0.0670$ (wR2 = 0.0998)</td>
</tr>
</tbody>
</table>

$^4R_1 = \Sigma ||F_o||-|F_c||/\Sigma |F_o||$, wR2 = $[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

3.2.7 Kinetic Experiments

The kinetics of the oxidative addition of CH$_3$I to the complexes 1, 2·X (X = PF$_6$, OTf, NO$_3$) were studied by $^1$H NMR in CD$_2$Cl$_2$. For the complexes 1 and 2·PF$_6$, the reaction rates of the oxidative addition were determined at different temperatures.

Samples for the kinetic measurements of the complexes ($C_{\text{Rh}}$ 1.57-1.98 $10^{-2}$ M) were prepared by weighting an appropriate amount of the recrystallized complex and dissolving its in CD$_2$Cl$_2$ (ca. 0.6 mL) in a sealed NMR tube. Second order conditions for the neutral 1 complex ($C_{\text{Rh}} / C_{\text{CH3I}} = 1-4.3$) were obtained by adding a proper amount (20-60 µL) of a ca. 1 M CH$_3$I
solution in CD$_2$Cl$_2$ to the complex solution. Pseudo-first-order conditions for 2·X (X = PF$_6$, OTf, NO$_3$) complexes (C$_{Rh}$ / C$_{CH3I}$ = 100) were obtained by adding a proper amount (ca. 80 µL) of neat CH$_3$I to the complex solution. The precise concentration of CH$_3$I in the tube was obtained by referencing the integrals of the CH$_3$ group of CH$_3$I and the acetyl complex to the integral of the CH$_3$ groups of the complex (used as internal standard) in the first collected spectrum. Spectra were collected as single FID acquisition at intervals of 30-60 s (1) and 45-180 s (2·X) making use of a dedicated Bruker MULTIZG program. Time zero offsets (t$_{first}$ spectrum - t$_{reactants mixing}$) for any kinetic run were 90-120 s. Spectra collection lasted up to 2 h.

For each kinetic run, the NMR spectrum collected prior to CH$_3$I addition was used as reference spectrum. Measurements were performed in the temperature range 273.16-298.16 K for 1 (4 experiments), and 280.16-298.16 K for 2·PF$_6$ (3 experiments). Temperature was controlled by the dedicated Bruker TopSpin software function.

Processing of the spectra (30-50 for each kinetic run) was performed by using MestreNova, and all integrals were normalized using the TMS or solvent peaks (CH$_2$Cl$_2$ in CD$_2$Cl$_2$). Calculations of the kinetic constants were performed processing the integrals of the signals of the reactants and the products vs. time using the SPECFIT 32 software.$^{[20]}$ For 1, both the variation of the acetyl CH$_3$ signal (2.80 ppm) and the disappearance of the CH$_3$I signal (2.20 ppm) were take into account in the calculations, while for the monoprotonate complexes only the appearance of the acetyl CH$_3$ signal (2.80 ppm) was considered (C$_{Me}$ constant in pseudo-first-order conditions). Integrals were correlated to the CH$_3$I and acetyl complex concentrations considering that I$_{Me}$ or complex = I$^\prime$·[CH$_3$I or complex], where I$^\prime$ is the calculated integral for a CH$_3$ group at 1 M concentration as obtained from the spectrum collected prior to CH$_3$I addition {I$^\prime$ = I$_{2xMe}$ / (2·[Rh])}. A second-order and both a second-order and a pseudo-first-order fitting functions were used to process the spectra for 1 and 2·X (X = PF$_6$, OTf, NO$_3$) complexes, respectively.

For 1, best fit was obtained using a second-order reaction function. For the monoprotonate complex, best fit was obtained using either one second-order or one pseudo-first-order functions. For the latter complex, a good fitting was obtained only using the spectra collected within 15 min after reagents mixing. After this time, a marked deviation from the calculated fitting function was obtained, indicating the occurrence of a second subsequent reaction after this reaction time. For all complexes, the fitting for the acyl complex signal was obtained with
a single function, indicating that the migratory CO insertion is faster than the oxidative addition step.

The second-order rate constants determined for complexes 1 and 2-PF₆ as a function of the temperature were processed to obtain the activation ΔH‡ and ΔS‡ parameters by means of the Eyring function k = (κT/h)·exp(-ΔH‡/RT)·exp(ΔS‡/R), where k is the rate constant at temperature T, κ is the Boltzmann’s constant, h the Planck’s constant and R the gas constant. A non-linear least-square algorithm implemented in SPSS 14.0 software was used for the calculations.

Each kinetic run was repeated at least twice to check reproducibility, the k₂ (for 1) and k₂obs (for 2-OTf, 2-PF₆ and 2-NO₃) values given being averaged values with the component measurements deviating from each other by ≤ 5%. The error in temperature was assumed to be 1 K.

### 3.2.8 Computational details

The geometries of all minimums were optimized in the gas phase at density functional theory (DFT) level by means of hybrid B3LYP functional. The geometries were optimized in gas phase with 6-31g** basis set on H, C, N, O, P and S atoms and Lanl2DZ basis and pseudopotential on Rh developed by Hay and Wadt (BS-0). This last uses a semicore double-ζ contraction scheme for the heavy elements such as Rh. A more wide basis set has been used to evaluate the pseudopotential effects on some molecular properties, substituting the Lanl2DZ functions and potential with complete dgdzvp functions (BS-I). All the simulations were performed both in the gas phase and solution by means of Polarizable Continuum Model (PCM). The continuum were built in CH₂Cl₂ environment and standard PCM energies were computed with UA0 cavity model. Thermochemical analysis has been performed on all the minimum and no imaginary frequencies were found. Accurate energy calculation has been performed at same level with tight SCF criteria on the wavefunction. Mulliken population analysis study were performed at each calculation level. The MO rendering was performed with the cubegen utility provided in the Gaussian03 package. All the calculations has been performed with Gaussian03 and gdv package.
3.3 Results and Discussion

As previously reported,[13,14] the $S,N,S$-$\kappa^3$ complex $[\text{Rh(ETsNS)(CO)}]$ (1) can be prepared by reaction of HEtSNS with $[\text{Rh(CO)}_2\text{Cl}]_2$ in the presence of $t$-BuOK or by bubbling CO in a solution of the $S,S$-$\kappa^2$ complex $[\text{Rh(ETsNS)}(\text{cod})]$ (cod $= 1,5$-cyclooctadiene). During these reactions, the unstable $S,S$-$\kappa^2$ intermediate $[\text{Rh(ETsNS)}(\text{CO})_2]$ was observed, monitoring the solution reaction by FTIR ($v_{\text{CO}}: 2075, 2009$ cm$^{-1}$). The coordination of the nitrogen atom raises the electron density of the Rh, as inferred from the lower CO stretching frequency of 1 ($v_{\text{CO}} (\text{CH}_2\text{Cl}_2): 1967$ cm$^{-1}$). Compound 1 is a diprotic base and can be protonated affording cationic species $[\text{Rh(HEtSNS)(CO)}]^+$ (2) and $[\text{Rh(H$_2$EtSNS)(CO)}]^2+$ (3) in which protons bind to the nitrogen atoms of the thioamidyl functions ($pK_a$ in CH$_2$Cl$_2 = 6.5(3)$ and 4.8(4))$^{[14]}$ (Scheme 1). Compound 3 can be conveniently prepared by using an excess of acid, while 2 is obtained by mixing 1 and 3 in 1:1 molar ratio.

![Scheme 1](image)

Scheme 1. Formation of the mono-cationic complex 2 and the di-cationic complex 3 by protonation of the zwitterionic complex 1.

The electronic distribution varies dramatically, as evidenced by the C-S and C-N bond distances$^{[14]}$ and by the $^{31}$P{$^1$H} NMR chemical shift values (Table 1). In the case of 2·X ($X = \text{PF}_6, \text{OTf}, \text{NO}_3$), two $^{31}$P resonances are present,$^{[14]}$ suggesting that proton exchange is very slow (exchange can be fast, i.e. when $X = \text{CF}_3\text{COO}^-$; $\delta = 27.9$ ppm, unpublished results). In turn, protonation influences the electron density on the Rh(CO) system, as reflected by the infrared CO stretching frequencies (Table 2).
Table 2. νCO stretching (CH₂Cl₂ solution and HATR-ZnSe crystal) and relevant ¹H NMR, ³¹P{¹H} NMR and ¹⁰³Rh NMR chemical shifts of 1, 2·X, and 3·X₂ (X = PF₆, OTf, NO₃).

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2·NO₃</th>
<th>2·OTf</th>
<th>2·PF₆</th>
<th>3·(NO₃)₂</th>
<th>3·(OTf)₂</th>
<th>3·(PF₆)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>νCO (HATR, ZnSe, cm⁻¹)</td>
<td>1953</td>
<td>1968</td>
<td>1977</td>
<td>1979</td>
<td>2006</td>
<td>2011</td>
<td>2013</td>
</tr>
<tr>
<td>¹H NMR (NH, CD₂Cl₂, ppm)</td>
<td>-</td>
<td>10.5</td>
<td>10.8</td>
<td>11.0</td>
<td>10.4</td>
<td>10.6</td>
<td>11.1</td>
</tr>
<tr>
<td>³¹P{¹H} NMR (CD₂Cl₂, ppm)</td>
<td>16.6</td>
<td>35.2-25.1</td>
<td>36.7-22.1</td>
<td>36.7-19.9</td>
<td>41.1</td>
<td>39.3</td>
<td>38.2</td>
</tr>
<tr>
<td>¹⁰³Rh NMR (CD₂Cl₂, ppm)</td>
<td>-6886</td>
<td>-</td>
<td>-6888</td>
<td>-</td>
<td>-</td>
<td>6901¹[a]</td>
<td></td>
</tr>
</tbody>
</table>

¹[a]: in CD₂Cl₂/CD₃OD (1:1 ratio)

The Mulliken populations for the Rh atom was calculated at the BS-0 level for 1, 2 and 3 in the gas phase and varies from -0.338 a.u. to -0.263 a.u. (Table 3), showing that the protonation of one thioamidic function induces a 13% decrease in the electronic population for the mono-protonation and a 22% decrease for the bi-protonation (a decreasing of 8% and 16% respectively has been found in solution simulation). This decrease in the calculated population is in agreement with the trend found experimentally for the CO stretching frequencies.

Table 3. Mulliken populations (a.u.) for selected atoms, in the gas phase and in solution (PCM, CH₂Cl₂) for 1, 2 and 3. For compound 2, the protonation is on the N1 atom [B3LYP/BS-0//B3LYP/BS-0; BS-0=6-31g** + Lanl2DZ(Rh)].

<table>
<thead>
<tr>
<th></th>
<th>Rh</th>
<th>S1</th>
<th>S2</th>
<th>N1</th>
<th>N2</th>
<th>N3</th>
<th>C</th>
<th>O</th>
<th>P1</th>
<th>P2</th>
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<tbody>
<tr>
<td>Gas Phase</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-0.338</td>
<td>-0.055</td>
<td>-0.055</td>
<td>-0.381</td>
<td>-0.381</td>
<td>-0.820</td>
<td>0.313</td>
<td>-0.271</td>
<td>0.937</td>
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<tr>
<td>2</td>
<td>-0.294</td>
<td>0.087</td>
<td>0.0095</td>
<td>-0.409</td>
<td>-0.373</td>
<td>-0.823</td>
<td>0.315</td>
<td>-0.229</td>
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<td>0.922</td>
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<tr>
<td>3</td>
<td>-0.263</td>
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<td>0.311</td>
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<td>0.903</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
<td>3</td>
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<td>0.123</td>
<td>-0.402</td>
<td>-0.413</td>
<td>-0.827</td>
<td>0.337</td>
<td>-0.239</td>
<td>0.908</td>
<td>0.912</td>
</tr>
</tbody>
</table>

A more detailed calculation has been carried out at BS-I level, both in the gas and solution phase, to confirm the BS-0 data. The results are consistent with the abovementioned trend (see Table S1 of the Appendix 2).
The $^{103}\text{Rh}$ NMR chemical shifts are very similar for 1, 2-PF$_6$ and 3-(PF$_6$)$_2$ (Table 1). Nevertheless, $^{103}\text{Rh}$ shielding seems to be mainly dependent on the kind of coordinated atoms and on the coordination geometry, both identical in our case.$^{[25]}$

The $\nu$CO stretching in complexes 2-X, and 3-X$_2$ (X = PF$_6$, OTf, NO$_3$) is slightly different (Table 1). As shown by the value of the $^1$H NMR (CD$_2$Cl$_2$) chemical shift of the NH group, the anion interacts with the cation through hydrogen bonding (Table 1). The NH values of mono- and di-protonated complexes move, as expected, downfield along the series NO$_3$ (coordinating), OTf (less coordinating) and PF$_6$ (non coordinating) in good correlation with the variation of the CO stretching. The more coordinating anion lowers the positive charge on the Rh centre through the hydrogen bonding, causing the decreasing of the CO stretching value and suggesting that the Rh electron density can be fine-tuned by changing the anion.

### 3.3.1 Reaction of [Rh(EtSNS)(CO)] (1) with CH$_3$I.

Treatment of 1 with a stoichiometric amount of CH$_3$I in CH$_2$Cl$_2$ at 25 °C resulted in the quantitative formation of the stable Rh$^{III}$ acetyl-complex [Rh(EtSNS)(COCH$_3$)I] (4) characterized in solution and in the solid state (Scheme 2).

![Scheme 2. Reactivity of complex 1 with CH$_3$I](image)

The FTIR spectrum of the reacting solution (Figure 1) shown the decay of the intensity of the $\nu$CO stretching of 1 at 1967 cm$^{-1}$, accompanied by the formation of a new adsorption at 1712 cm$^{-1}$, assigned to the acetyl complex 4 (for ca. 30 mg of complex 1 the reaction was completed in ca. 8 minutes).
The intensity of the νCO band of the methyl-carbonyl Rh\textsuperscript{III} intermediate A (2065 cm\textsuperscript{-1}, observed as a shoulder of the CH\textsubscript{2}Cl\textsubscript{2} absorption at 2055 cm\textsuperscript{-1}) was very weak and absent at the end of the reaction. Another weak band started to form at 1736 cm\textsuperscript{-1} and then decayed after \textit{circa} 5 minutes, finally disappearing at the end of the reaction. This band can be possibly assigned to isomer B. The intermediate A and isomer B were not evidenced in the \textsuperscript{1}H NMR spectra at room temperature. The complex A could be observed by \textsuperscript{1}H NMR only by slowing the reaction at 250 K (\(\delta = 1.92\ \text{J}\text{Rh,H} = 2\) Hz, integral = 3% with respect to the integral of the CH\textsubscript{3} signal of the ligand ethyl groups). When the reaction was performed at 280 K, two sets of peaks with very close chemical shifts and different intensities were present (Figure 4, \textit{vide infra}). They were assigned to the ethyl groups of 4 and, possibly, to the acetyl isomer B [\(4 = 1.208\) (t, -CH\textsubscript{2}CH\textsubscript{3}), 3.699 (m, -CH\textsubscript{2}CH\textsubscript{3}); \(B = 1.214\) (t, -CH\textsubscript{2}CH\textsubscript{3}), 3.800 (m, -CH\textsubscript{2}CH\textsubscript{3})]. The solution was then warmed from 280 to 300 K, and only the peaks of 4 were present. At r.t. the presence of the CO absorptions of A and B in the infrared spectra, at low relative concentrations not detectable by \textsuperscript{1}H NMR, is probably due to a high infrared absorbitivity of these Rh\textsuperscript{III} complexes. The \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectrum of the reacting solution shows the
formation of only one singlet at 27.4 ppm (4), and the complete decay of the signal of 1 (16.6 ppm).

Crystals of 4 were obtained at -20 °C by layering hexane on a CH₂Cl₂ solution. The ORTEP plot of the structure of 4 is depicted in Figure 2.

**Figure 2.** ORTEP plot of the structure of 4. Thermal ellipsoids are drawn at 30% probability level. H atoms are omitted for clarity. Selected distances [Å] and angles (°): Rh1-S1 2.340(1), Rh1-S2 2.322(1), Rh1-I1 2.619(4), Rh1-N3 2.128(3), Rh1-C31 1.950(4), C31-O1 1.194(5), C31-C32 1.475(6), C1-S1 1.743(4), C2-S2 1.721(4), C1-N1 1.278(5), C2-N2 1.271(5), P1-N3 1.622(3), P2-N3 1.626(3), P1-N3-P2 133.8(1), S1-Rh1-N3 89.8(1), S1-Rh1-I1 89.7(1), S1-Rh1-C31 101.4(1), S2-Rh1-N3 91.8(1), S2-Rh1-I1 86.2(1), S2-Rh1-C31 91.5(1), S1-Rh1-S2 168.0(1), C31-Rh1-I1 98.9(1), C31-Rh1-N3 91.8(1), C32-C31-O1 122(4), I1-Rh1-N3 169.1(1).

The complex shows a slightly distorted square-pyramidal coordination geometry with the acetyl group occupying the apical position. The coordination around the metal involves the S1, N3 and S2 atoms of the ligand, in a S,N,S-κ³ coordination fashion, the carbon atom of the acetyl and the iodine atom. The Rh atom lies at 0.24(1) Å from the mean plane defined by I1-S1-S2-N3. The oxidation to Rh³⁺ causes a slight variation of the bond lengths and angles of the EtSNS ligand with respect to the Rh¹ complex 1. In particular the Rh1-N3 [2.128(3) Å], Rh1-S1 [2.340(1) Å] and Rh1-S2 [2.322(1) Å] bond distances are slightly shorter than those observed in 1.[13] The bond distances Rh1-I1 [2.619(4)Å] and Rh1-C31 [1.950(4)Å] are among the shortest found in the Cambridge Structural Database for similar fragments.[26] The acetyl group adopts a conformation that minimizes steric interactions with the close phenyl group of the EtSNS ligand, directing the methyl group between the I1 and S2 atoms (I1-Rh1-C31-C32 torsion angle 48.9°).
The $^1$H-$^1$H 2D NOESY NMR spectrum of 4 (CD$_2$Cl$_2$ at 25 °C) displays cross-peaks between the acetyllic CH$_3$ group and some of the phenylic hydrogens. This is consistent with the square-pyramidal coordination geometry with an apical acetyl ligand as found in the solid state (Figure 2).

In the solid state, 4 seems to partially transform in the methyl complex A as evidenced by FTIR-HATR. In the spectrum, a weaker νCO band at 2049 cm$^{-1}$ is present, together with the stronger one at 1709 cm$^{-1}$ assigned to the acetyl complex. When the solid is dissolved on the HATR crystal, by addition of few µL of dichloromethane, the spectrum shows only one band at 1712 cm$^{-1}$. By evaporating the solvent on the crystal, the band at 2049 cm$^{-1}$ reappears. A similar behavior was already reported in the literature, with the acetyl complex undergoing reductive elimination reforming the parent Rh$^I$ complex.$^{[2,27]}$

A CP-MAS $^{13}$C solid state NMR was collected on 4, in order to verify the presence of A. Only the peaks of 4 were present, probably due to the very low concentration (< 3%) of A in the solid (< 3%, see Figure S1 and S2 of the Appendix 2).

3.3.2 Reaction of the mono-protonated complexes [Rh(HEtSNS)(CO)]X (2·X, X = PF$_6$, OTf, NO$_3$) with CH$_3$I.

The reaction of complexes 2·X with CH$_3$I in 1:100 ratio (CH$_2$Cl$_2$ at 25 °C, Scheme 3) was monitored by FTIR, $^1$H NMR and $^{31}$P$^{[1]}$H$^{[1]}$ NMR. In the infrared spectrum of the reacting solution of 2·OTf (Figure 3, the same discussion applies for X = PF$_6$ and NO$_3$; see superimposed spectra in Figures S3 and S4 of the Appendix 2), the presence of a very weak band at 2066 cm$^{-1}$ (PF$_6$ = 2068 cm$^{-1}$, NO$_3$ = 2061 cm$^{-1}$) indicated the formation of the methyl-Rh$^{III}$ intermediate A$'$. 

![Scheme 3](image)

Scheme 3. Reactivity of 2·X (X = PF$_6$, OTf, NO$_3$) with CH$_3$I in CH$_2$Cl$_2$.
The change in the intensity of this band was in agreement with a steady state intermediate and the band disappeared at the end of the reaction (after 48 hours). The formation of the acetyl complex [Rh(HEtSNS)(COCH₃)I]OTf (5·OTf) was evidenced by the raising of a band at 1721 cm⁻¹ (PF₆ = 1725 cm⁻¹, NO₃ = 1717 cm⁻¹). After circa 50 minutes, for all the three anions, a shoulder band at 1712 cm⁻¹ was evident in the spectra and was ascribed to the deprotonated acetyl-complex 4. At the end of the reaction, only this band was present (Figure S5 of the Appendix 2 for X = OTf). During the reaction, a weak shoulder band at 2013 cm⁻¹ formed and then disappeared [2017 cm⁻¹ for 3·(PF₆)₂ and 2009 cm⁻¹ for 3·(NO₃)₂]. It could be due to the formation of the diprotonated complex 3·(OTf)₂ by protonation of 2·OTf.¹⁴ In the ¹H NMR spectrum of the CD₂Cl₂ reacting solution, the methyl group of intermediate A’ is not observable, due to the strong excess of CH₃I whose peak resonates in the same region. The -CH₂CH₃ groups of 2·X and 5·X (X = PF₆, OTf, NO₃) are broad, probably due to proton exchange, and resonate in the same range, resulting undistinguishable. Moreover, only one peak attributed to acetyl complexes is present.

In the ³¹P{¹H} NMR spectrum of the reacting solution, a similar situation was observed. The intensity of the two peaks of 2·OTf (Table 2) decreased along with the formation of two new
3. Charge-tuned Rh(I) Complexes

Absorptions at lower field (44.6, 23.7 ppm) which were attributed to complex 5·OTf. The methyl-Rh intermediate A’ was not evidenced in the spectra. After *circa* 50 minutes, a new band at 27.4 ppm was starting to form and was attributed to complex 4, obtained by deprotonation of 5·OTf (see Figure S6 of the Appendix 2). After two days, the peak of 4 was still present in the $^{31}$P{¹H} NMR spectrum. Other unidentified decomposition products, that were not observed in the carbonylic region of the FTIR spectrum, were also formed (see Figure S7 of the Appendix 2). The decomposition of the protonated complexes 5·X can be due to the strong excess of CH$_3$I present in solution or to the intrinsic incompatibility of the acid with the acetyl group.$^{[1d]}$ Compounds 5·OTf and 4 could be separated by preparative TLC (in a test reaction that was stopped before completion, using silica plates and CH$_2$Cl$_2$/Hexane 8:2 as eluent). The $^{31}$P{¹H} NMR spectra of the separated compounds confirmed the assignment. In the $¹$H NMR spectrum, the acetyl group of complexes 5·X and 4 resonates at the same chemical shift.

3.3.3 Reaction of the di-protonated complexes [Rh(H$_2$EtSNS)(CO)]X (3·X$_2$, X = PF$_6$, OTf, NO$_3$) with CH$_3$I.

The diprotonated complexes 3·X$_2$ reacted very slowly with CH$_3$I in 1:100 ratio, the band of the starting reagents disappearing from the solution FTIR spectra only after 5 days. No Rh-methyl complexes were evidenced in the FTIR spectra and only the formation of the acetyl complex 4 was observed (FTIR absorption at 1712 cm$^{-1}$ for all three complexes). This complex was separated by TLC, as in the case of the reactions of compounds 2·X, and identified by $^{31}$P{¹H} NMR. Unidentified decomposition compounds were also evidenced in the $^{31}$P{¹H} NMR spectrum of the crude product, but no further investigation was performed.

3.3.4 Kinetics of the reaction of 1 and 2·X with CH$_3$I.

At the concentrations employed for the kinetic measurements for the oxidative addition of CH$_3$I on 1 and 2·X (X = PF$_6$, OTf and NO$_3$), $¹$H NMR spectra obtained by a single FID collection were of good resolution and good signal-to-noise ratios, and prompted us in the use of this technique for the determination of the reaction rates. For the 2·X complexes, the experiments were performed in order to evaluate the effect of protonation and the role of the counterion.
In the case of 1 the reaction with CH\textsubscript{3}I is quite fast and its constant could be determined at different temperatures under second-order conditions ([CH\textsubscript{3}I] / [Rh] = 1 – 5). The calculation was performed by processing the integral of the signals of the CH\textsubscript{3} groups of CH\textsubscript{3}I and -C(O)CH\textsubscript{3} as a function of time (Figure 4), using non-linear least-squares fitting functions.

On this ground, their integrals could be related to the concentrations of the species making use of appropriate equations as reported in the experimental section. At r.t. the migratory CO insertion is a very fast reaction compared with the oxidative addition of CH\textsubscript{3}I. Only at 250 K the methyl intermediate A was detected, but its relative concentration was too low for the determination of the migratory insertion rate. Thus, it was not possible to determine the kinetic rate constants for both reaction steps, but only the reaction rate of the slowest one (oxidative addition) which was then approximated to the overall rate for the reaction: 1 + CH\textsubscript{3}I \rightarrow 4 with \( v = k \cdot [1][CH\textsubscript{3}I] \). The rate constants determined at different temperatures for this reaction are reported in Table 4. They were employed for the calculation of the activation parameters \( \Delta H^\ddagger \) [28(3) kJ mol\textsuperscript{-1}; 6.7(7) kcal mol\textsuperscript{-1}] and \( \Delta S^\ddagger \) [-173(10) J mol\textsuperscript{-1} K\textsuperscript{-1}; -41(2) cal mol\textsuperscript{-1} K\textsuperscript{-1}].

**Figure 4.** \(^1\text{H} \) NMR stack plot spectra for the reaction of 1 with CH\textsubscript{3}I (ratio 1:1) at 280 K in CD\textsubscript{2}Cl\textsubscript{2}. 
3. Charge-tuned Rh(I) Complexes

mol$^{-1}$ K$^{-1}$] by means of the non-linearized Eyring function and using the least-square procedure (see Figure S8 of the Appendix 2). As expected, the oxidative addition of CH$_3$I on the Rh$^1$ complex to reach the transition state is an endothermic process, to which corresponds a negative activation entropy, confirming an associative mechanism.$^{[16]}$

Table 4. Second-order rate constants for the reaction of 1 with CH$_3$I at different temperatures (standard deviations are given in parentheses). The corresponding least-square sample standard deviations ($\sigma$) are also reported.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>k (M$^{-1}$ s$^{-1}$)</th>
<th>$\sigma^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.16</td>
<td>1.53(3) x 10$^{-2}$</td>
<td>1.23 x 10$^{-3}$</td>
</tr>
<tr>
<td>278.16</td>
<td>2.31(3) x 10$^{-2}$</td>
<td>1.64 x 10$^{-3}$</td>
</tr>
<tr>
<td>286.16</td>
<td>3.56(7) x 10$^{-2}$</td>
<td>1.39 x 10$^{-3}$</td>
</tr>
<tr>
<td>298.16</td>
<td>5.48(7) x 10$^{-2}$</td>
<td>1.38 x 10$^{-3}$</td>
</tr>
</tbody>
</table>

$^a\sigma = [\Sigma (I_i' - I_i)^2/(n - m)]^{1/2}$, where $I_i', I_i$ are the observed and calculated integral values, $i$ is the number of the spectrum, $n$ is the number of observations and $m$ is the number of parameters refined.

For the monoprotonate complexes 2·X (X = PF$_6$, OTf and NO$_3$) the reaction is slower than for 1 and pseudo-first-order conditions were used ([CH$_3$I] / [Rh] = 100). Under these conditions, both a second-order treatment and a pseudo-first-order treatment gave the same values for the second-order rate constants. Being CH$_3$I in large excess, the decrease in its $^1$H NMR peak integral could not be observed, and only the increase of the CH$_3$ signal of the Rh acetyl complex 5·X was considered in the calculations. We decided to take into account only the integral values at $t < 15$ min. During this time, as observed in the FTIR and $^{31}$P{$^1$H} NMR spectra, A’ and 5·X are the only product observed. Taking into account a single reaction step under pseudo-first order conditions, a very good fitting of the intensity of the acetyl $^1$H NMR signal vs. time was obtained, as evidenced by the very low standard deviations of the calculated rate constants, at 298.16 K, (Table 5). This suggested that, although in steady-state, under this approximation the concentration of the methyl complex A’ is very low, as supported by the $^{31}$P{$^1$H} NMR spectrum and as also found for the reaction of complex 1.
3. Charge-tuned Rh(I) Complexes

Table 5. Second-order rate constants for the reaction 2·X (X = PF₆, OTf and NO₃) with CH₃I at 298.16 K (standard deviations are given in parentheses). The corresponding least-square sample standard deviations (σ) are also reported.

<table>
<thead>
<tr>
<th>Counterion</th>
<th>k₁ (M⁻¹ s⁻¹)</th>
<th>σ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF₆</td>
<td>2.50 (6) 10⁻⁵</td>
<td>7.66 10⁻³</td>
</tr>
<tr>
<td>OTf</td>
<td>12.7 (3) 10⁻⁵</td>
<td>2.88 10⁻²</td>
</tr>
<tr>
<td>NO₃</td>
<td>24.6 (6) 10⁻⁵</td>
<td>1.67 10⁻²</td>
</tr>
</tbody>
</table>

*σ = [Σᵢ (Iᵢ - Iᵢ')²/(n - m)]¹/², where Iᵢ, Iᵢ' are the observed and calculated integral values, i is the number of the spectrum, n is the number of observations and m is the number of parameters refined.

The ΔH‡ and ΔS‡ activation parameters were determined for the 2·PF₆ complex and resulted 45(7) kJ mol⁻¹ and -180(30) J mol⁻¹ K⁻¹, respectively (see Table S1 of the supporting information for kinetic rate constants at different temperature for 2·PF₆). The ΔH‡ value is markedly higher than that determined for 1, indicating, as expected, that the activation process for an oxidative addition of CH₃I on a positively charged complex is more endothermic. The ΔS‡ value is similar to that of the neutral complex (-175 J mol⁻¹ K⁻¹) but, due to the high standard deviation, is not possible any clear discussion on the entropic activation change during the reaction. It seems clear that the decreased reaction rate for the monoprotonate complexes might be due to enthalpic factors associated to the oxidative addition step.

A similar cationic tridentate S,N,S-κ³ Rh¹ monocarbonyl complex, namely [Rh(L)CO]PF₆ [νCO (CH₃CN) = 2015 cm⁻¹; L = 2,6-bis(benzylthiomethyl)piridine] was reported to react with CH₃I.[16h,16n] In this case, the kinetic constants of both the oxidative additon step (1.4 x 10⁻⁴ M⁻¹ s⁻¹) and the migratory CO insertion (4 x 10⁻⁵ M⁻¹ s⁻¹) were determined in CH₃CN at 31 °C. Under these conditions, the rate determining step of the reaction is apparently the migratory insertion while, in our case, is the oxidative addition. Nevertheless, the observed rate constant in CH₂Cl₂ is very close[16h] (5.9 x 10⁻⁵ M⁻¹ s⁻¹; see Table 5 for 2·X rate constants).

As expected taking into account the νCO stretching frequency of the complexes, the reactivity decreases in the order 1 >> 2·NO₃ > 2·OTf > 2·PF₆ >> 3·X₂. The effect of the protonation can be also seen in the energy of the gas phase DFT-calculated MOs. Assuming that the suitable MO for the nucleophilic attack of the Rh atom on the CH₃ group must be the one at the highest energy with a s-simmetry, the energies found for these MOs in 1, 2 and 3 were -0.167 a.u., -0.278 a.u. and -0.393 a.u. respectively.
A similar situation can be found in the literature for β-aminovinylketonato complexes of formula \{\text{Rh}[\text{R}^1\text{C(O)CHC(NH)R}^2\text{]}(\text{PPh}_3)(\text{CO})]\} where the \(\text{R}\) groups can be \text{CH}_3 or \text{CF}_3; it was observed that the presence of one or two electron-attractive fluorinated substituents in the ligand retards the oxidative addition. In this case, however, quantitative kinetic parameters were not determined.\(^{[28]}\)

A correlation between the \(\nu\text{CO}\) stretching and the global kinetic constants for \(1\) and \(2\cdot X (X = \text{PF}_6, \text{OTf}, \text{NO}_3)\) should be possible. This is only true for the \(2\cdot X\) series, as depicted in Figure 5.

![Figure 5](image)

**Figure 5.** Linear regression function of the correlation between the frequency value of the \(\text{CO}\) stretching and the rate kinetic constants of the monoprotonated complexes \(2\cdot X\).

The experimental rate constant for complex \(1\) is one order of magnitude higher than the calculated one, (using the linear regression function obtained for the \(2\cdot X\) series: experimental = 5.48 x 10^{-2} \text{ M}^{-1} \text{s}^{-1}; calculated = 1.29 x 10^{-3} \text{ M}^{-1} \text{s}^{-1})\) pointing out that the monoprotonated complexes react more slowly than expected. Two simultaneous effects could be responsible of this behavior. A steric effect can be due to the variation in the geometry of the two penta-atomic chelation rings (Rh-S-C-P-N) when complex \(1\) is protonated, causing one axial phenyl ring to move towards the Rh metal centre [the distance of the Rh atom from the phenyl carbon atoms directly bonded to the P atoms of the PNP group are 3.92 for \(1\), and 3.75 and 3.86 for \(2\cdot \text{PF}_6\)]. A superposition of the solid state structures of \(1\)\(^{[13]}\) and \(2\cdot \text{PF}_6\)\(^{[14]}\) is depicted in Figure 6 (the atoms used for superposing the structures were the Rh and the coordinated \(S, S', N\) and C).
This higher steric hindrance would lower the rate of the oxidative addition but enhance the rate of the migratory insertion. As previously reported\textsuperscript{[3,9-11]} the migratory CO insertion rate can be higher when a p-donor ligand is present, forming a molecular orbital of suitable energy in which the contribution of the methyl ligand is not negligible and is in-phase with Rh and CO(\(\pi^*\)), thus generating a continuous lobe that contains the three atoms involved in migratory CO insertion. A DFT calculation was performed to optimize the possible Rh\textsuperscript{III}-CH\textsubscript{3} intermediate for the reaction of complex 1 and complex 2 with CH\textsubscript{3}I (A and A’, respectively). An octahedral geometry for the Rh-CH\textsubscript{3} complex was adopted, with the CH\textsubscript{3} group and the I atom in \textit{trans} axial positions with respect to the S, N, S, C, Rh plane. Only in the case of the neutral complex A we found one MO spreading on the atoms involved in the migratory CO insertion, whereas no similar orbital was present in the cationic A’. This two effects, one reducing the oxidative addition rate and the other reducing the migratory CO insertion rate, could be responsible of the lower than expected reactivity of 2·X (X = PF\textsubscript{6}, OTf and NO\textsubscript{3}).

### 3.4 Conclusions

The zwitterionic Rh\textsuperscript{1} monocarbonyl complex [Rh(EtSNS)(CO)] (1) can be mono- and bi-protonated affording cationic complexes [Rh(HEtSNS)(CO)]X (2·X) and [Rh(H\textsubscript{2}EtSNS)(CO)]X\textsubscript{2} (3·X\textsubscript{2}) (X = PF\textsubscript{6}, OTf, NO\textsubscript{3}). In these compounds, the electron density
3. Charge-tuned Rh(I) Complexes

on the Rh atom varies, as pointed out by the change of the IR stretching frequency of the coordinated CO, and confirmed by the DFT-calculated Mulliken atomic populations. The effect of the protonation was studied in the reaction with iodomethane. In the case of 1 and 2-X the oxidative addition of CH$_3$I was followed by the migratory CO insertion, forming the acetyl-Rh$^{II}$ complexes [Rh(EtSNS)(COCH$_3$I)] (4) and [Rh(HEtSNS)(COCH$_3$I)]X (5), respectively. Complex 4 was characterized in solution and its solid state structure was determined by X-Ray diffraction methods. Compounds 5-X are stable in solution for a short time, undergoing deprotonation forming complex 4, and also decomposing in unidentified products. The rate constants of the reaction were determined by means of $^1$H NMR spectroscopy; in the case of complex 1, second order conditions ([CH$_3$I] / [Rh] = 1) could be employed. The reactivity decreases in the order 1 [5.48(7) x 10$^{-2}$ M$^{-1}$ s$^{-1}$] >> 2-NO$_3$ [24.6 (6) x 10$^{-5}$ M$^{-1}$ s$^{-1}$] > 2-OTf [12.7 (3) x 10$^{-5}$ M$^{-1}$ s$^{-1}$] > 2-PF$_6$ [2.50 (6) x 10$^{-5}$ M$^{-1}$ s$^{-1}$] >> 3-X$_2$ at 25 °C in CH$_2$Cl$_2$. Complexes 3-X$_2$ reacted too slowly, hindering the determination of the rate constants. The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were determined for 1 and 2-PF$_6$, confirming the nucleophilic addition mechanism. Calculations showed that the suitable MO for the nucleophilic attack of the Rh atom on the CH$_3$ group of iodomethane (that must be the one at the highest energy with a $\sigma$-simmetry), displayed a variation of its energy that paralleled to the reactivity trend of 1, 2 and 3. A good correlation was found between the rate constants, along the series 2-NO$_3$, 2-OTf and 2-PF$_6$, with the corresponding CO stretching frequency values. This correlation could be explained assuming that the different non metal-coordinated anions form a hydrogen bonding with the NH group of 2 (as evidenced by its $^1$H NMR chemical shift), that in turn causes a variation of the electron density on the Rh centre (as observed by the change in the CO stretching frequency). In conclusion, the reactivity of complex 1 towards iodomethane could be tuned by protonation and fine-tuned by changing the counterion.

3.5 References

3. Charge-tuned Rh(I) Complexes


3. Charge-tuned Rh(I) Complexes


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Reactivity of the Zwitterionic Ligand

EtNHC(S)Ph₂P=NPPh₂C(S)NEt towards [Ru₃(CO)₁₂].

Sulfur Transfer and Ligand Fragmentation Leading to the Methideylamide [-N(Et)-CH(R)-] µ₃-Bridging Moiety.

The reaction of EtNHC(S)Ph₂P=NPPh₂C(S)NEt with [Ru₃(CO)₁₂] has been carried out under two different experimental conditions: in the first case [Ru₃(CO)₁₂], previously turned into the labile intermediate [Ru₃(CO)₁₀(CH₃CN)₂], afforded, at room temperature in dichloromethane, the trinuclear clusters [Ru₃(CO)₁₁(CNEt)] (1), {Ru₃(CO)₉(µ-H)[(µ-S:κ-P)Ph₃PN=PPh₂C(S)NEt]} (2), {Ru₃(CO)₉(µ-H)[(µ-S:κ-P)Ph₃PN=P(S)Ph₂PN=P(S)Ph₂]} (3) and {Ru₃(CO)₁₀[(µ-κ²P)Ph₃PNHPPh₂]} (4). Ligand fragmentation occurs via loss of EtNC or EtNCS, without sulfur transfer to the cluster core. In the second case, [Ru₃(CO)₁₂] reacted with HEtSNS in toluene at 70 °C, giving the trinuclear clusters 4, {Ru₃(CO)₉(CNEt)(µ-κ-S)[(µ-κ-η¹-C:κ¹-P)Ph₃PN=PPh₂C(H)NEt]} (5), {Ru₃(CO)₈(µ-κ-S)[(µ-κ-η¹-C:κ¹-P)Ph₃PN=PPh₂C(H)NEt]} (6) and {Ru₃(CO)₈(µ-κ-CO)(µ-κ-S)(EtNC)(µ-κ²P)Ph₃PNHPPh₂]} (7). Cluster 5 shows an open triangle of Ru atoms capped by a µ₃-sulfide and by the unprecedented methideylamide –N(Et)CH(R)– µ₃-bridging moiety of the Ph₃PN=PPh₂C(H)NEt ligand. It formally derives from cluster 6 by substitution of ethyl isonitrile with one CO molecule.
4.1 Introduction

This chapter deals with the results of a research work matching our longstanding interest in cluster chemistry\(^1\) with our recent investigations on the coordination behaviour of the zwitterionic ligand EtNHC(S)Ph\(_2\)P=NPPh\(_2\)NEt (HEtSNS).\(^6\) It can be turned into the phosphine sulfide derivative Ph\(_2\)(S)PN=PPh\(_2\)C(S)NHEt by moderate heating\(^6\) (Scheme 1).

![Scheme 1](image)

The aim of this work was to investigate the reactivity of HEtSNS, towards the trinuclear cluster [Ru\(_3\)(CO)\(_{12}\)]. Two different experimental strategies were followed: HEtSNS was reacted with [Ru\(_3\)(CO)\(_{10}\)(CH\(_3\)CN)\(_2\)] under mild conditions and with [Ru\(_3\)(CO)\(_{12}\)] under pyrolytic conditions. These reactions led to novel ruthenium carbonyl clusters and gave insight into the fragmentation behaviour of HEtSNS. Their major products, in terms of yield, were isolated and characterized and the structure of the most significant ones are described herein.

4.2 Experimental

4.2.1 General procedures.

Crystalline [Ru\(_3\)(CO)\(_{12}\)] was a commercial product (Aldrich) and used as received. EtNHC(S)Ph\(_2\)P=NPPh\(_2\)C(S)NEt (HEtSNS)\(^6\) and [Ru\(_3\)(CO)\(_{10}\)(CH\(_3\)CN)\(_2\)]\(^9\) were prepared according to published procedures. The solvents (J.T. Baker) were dried and distilled by standard techniques. Elemental analyses (C, H, N, S) were carried out on a Carlo Erba EA1108 microanalyzer. Solution FTIR spectra (4000-400 cm\(^{-1}\), CaF\(_2\) cell) were recorded on a Nicolet Nexus spectrophotometer. \(_1^H\) (300.13 MHz, TMS) and 2D \(_1^H\)-\(_1^H\) COSY spectra in
CDCl₃ were recorded on a Bruker Avance 300; ³¹P{¹H} NMR (161.98 MHz, external reference 85% H₃PO₄) spectra in CDCl₃ were recorded on a Bruker AMX400. The ³¹P-¹H heterocorrelation NMR experiment (HETCOR) was recorded at room temperature in CDCl₃ on a Varian Inova-600 (600 MHz, ¹H; 125 MHz, ³¹P). For the two-dimensional experiment phase-sensitive detection of the directly observed frequency (³¹P) was achieved by the TPPI method. Multiplicity and coupling constants for ¹H NMR spectra of cluster 5 and 6 were simulated, in very good accordance with those observed experimentally, by using the MestReC program.¹⁰ Experimental mass measurements were made on a LTQ XL (Thermo Electron Corporation) equipped with an ESI interface operating in positive ion (PI) mode, acquiring mass spectra over the scan range m/z 200-2000, using CH₃OH as solvent. The source introductions were carried on by a pneumatically assisted syringe (5 µL/min) flowing into a continuum flow (200 µL/min) of pure methanol from an LC pump (Finnigan Surveyor-Thermo Electron Corporation). Spray voltage were set to 4.5 KV and capillary temperature was 250°C. All other instrumental parameters were automatically tuned in order to achieve best ion transmission to the analyzer.

4.2.2 Reaction of HEtSNS and [Ru₃(CO)₁₀(CH₃CN)₂].

To a solution of [Ru₃(CO)₁₀(CH₃CN)₂] (0.200 g, 0.30 mmol) in CH₂Cl₂ (40 mL) HEtSNS (0.168, 0.30 mmol) was added, resulting in an orange reaction mixture. After stirring for 2 h at room temperature, the volatiles were removed in vacuo. The residue was chromatographed by preparative TLC. Elution with CH₂Cl₂ : n-Hexane (3:2, v/v) developed four bands. The third yellow (Rf = 0.52) and the fourth orange (Rf = 0.38) bands gave the known compounds {Ru₃(CO)₉(μ-H)[(μ-S:κ-P)Ph₂PN=PPh₃S]}¹¹ ³ (3%) and {Ru₃(CO)₁₀[(μ-κ³P)Ph₂PNH₂PPH₂]}¹² ⁴ (13%) respectively. The first yellow band (Rf = 0.73) gave the new compound [Ru₃(CO)₁₀(CN)(CH₃CN)] (1) (18%) as a yellow powder. Anal. Calc. for C₁₄H₅NO₁₁Ru₃: C, 25.23; H, 0.76; N, 2.10. Found C, 25.17; H, 0.75; N, 2.08. FTIR (CH₂Cl₂, νCO, cm⁻¹): 2190w, 2094m, 2060s, 2044vs, 2008s. ¹H NMR (300 MHz, CDCl₃, 25°C): δ = 3.91(q, 2H, -CH₂-, 3J_HH = 7.7 Hz), 0.88 (t, 3H, -CH₃, 3J_HH = 7.7 Hz) ppm. The second red band (Rf = 0.62) gave the new compound [Ru₃(CO)₉(μ-H)[(m-S:κ-P)Ph₂PN=PPh₃C(NEt)S]} (2) (25%) as red crystals after recrystallization from hexane/CH₂Cl₂ at −4 °C. Anal. Calc. for C₃₆H₂₆N₂O₉P₂Ru₃S: C, 42.07; H, 2.55; N, 2.73; S, 3.12. Found C, 41.89; H, 2.51; N, 2.69; S, 3.09. FTIR (CH₂Cl₂, νCO, cm⁻¹): 2085s, 2048s,
2009s, 1958sh. \(^1\)H NMR (300 MHz, CDCl\(_3\), 25°C): \(\delta = 8.20-7.26\) (m, 20H, Ph), 4.10 (m, br, 1H, -CHH-), 3.85 (m, br, 1H, -CHH-), 1.36 (t, 3H, -CH\(_3\)), \(^3\)J\(_{\text{HH}}\) = 7.2 Hz), -14.7 (d, 1H, \(\mu\)-H, \(^2\)J\(_{\text{HP}}\) = 9.0 Hz) ppm. \(^3\)P\(^{1}\)H NMR (161.98 MHz, CDCl\(_3\), 25°C): \(\delta = 10.42\) (s), 54.09 (s) ppm.

4.2.3 *Thermal treatment at 50 °C of cluster 2; conversion in cluster 3 in a sealed tube.*

A solution of cluster 2 (0.154 g, 0.15 mmol) in toluene (20 mL) was heated at 50°C for 1 h in a sealed tube. Conversion in cluster 3 was detected by \(^1\)H NMR, \(^3\)P\(^{1}\)H NMR, FTIR (Yield 92% by NMR peak integration).

4.2.4 *Pyrolitic reaction between HEtSNS and [Ru\(_3\)(CO)\(_{12}\)].*

To a solution of [Ru\(_3\)(CO)\(_{12}\)] (0.200 g, 0.31 mmol) in CH\(_2\)Cl\(_2\) (40 mL) HEtSNS (0.175, 0.31 mmol) was added, resulting in an orange reaction mixture. After stirring for 2 h at 70°C, the solvent was removed in vacuo. The residue was chromatographed by preparative TLC (CH\(_2\)Cl\(_2\): n-Hexane = 3:2) and the four resulting bands collected.

The third yellow band (Rf = 0.56) gave the known compound 4 (9%).

The first yellow band (Rf = 0.81) gave the new compound \{Ru\(_3\)(CO)\(_3\)(CNEt)(\(\mu\)-S)[(\(\mu\)-N:\(\eta^1\)-C:\(\kappa^1\)-P)Ph\(_2\)PN=PPh\(_2\)CHNEt]\} (5) (14%) as yellow crystals after recrystallization by layering n-hexane on a dichloromethane solution of 5. Anal. Calc. for C\(_3\)H\(_{31}\)N\(_2\)O\(_2\)P\(_2\)Ru\(_4\)S: C, 43.28; H, 3.04; N, 4.09; S, 3.12. Found C, 43.21; H, 3.01; N, 4.02; S, 3.08. FTIR (CH\(_2\)Cl\(_2\), νCO, cm\(^{-1}\)): 2186s, 2054m, 2000sh, 1972sh. \(^1\)H NMR (300 MHz, CDCl\(_3\), 25°C): \(\delta = 8.02-7.14\) (m, 20H, Ph), 4.16 (d, 1H, -RuCH-, \(^2\)J\(_{\text{HP}}\) = 7.5 Hz), 3.73 (q, 2H, CH\(_2\)CH\(_2\)NCRu, \(^3\)J\(_{\text{HH}}\) = 7.2 Hz), 2.60 (observed multiplicity: m, simulated (line width 1 Hz), qdd, 2H, -CH\(_2\)-, \(^2\)J\(_{\text{HP}}\) = 6.9 Hz, \(^4\)J\(_{\text{HP}}\) = 3.20 Hz, \(^4\)J\(_{\text{HP}}\) = 3.80 Hz), 1.40 (t, 3H, CH\(_2\)CH\(_2\)NCRu, \(^3\)J\(_{\text{HH}}\) = 7.2 Hz), 0.86 (t, 3H, CH\(_2\)CH\(_2\)NCRu, \(^3\)J\(_{\text{HH}}\) = 6.9 Hz) ppm. \(^3\)P\(^{1}\)H NMR (161.98 MHz, CDCl\(_3\), 25°C): \(\delta = 77.6\) (d, \(^2\)J\(_{\text{HP}}\) = 37 Hz), 35.5 (d, \(^2\)J\(_{\text{HP}}\) = 37 Hz) ppm.

The second yellow band (Rf = 0.75) gave the new compound \{Ru\(_3\)(CO)\(_3\)(\(\mu\)-S)[(\(\mu\)-N:\(\eta^1\)-C:\(\kappa^1\)-P)Ph\(_2\)PN=PPh\(_2\)CHNEt]\} (6) (26%) as yellow powder. Anal. Calc. for C\(_3\)H\(_{24}\)N\(_2\)O\(_2\)P\(_2\)Ru\(_4\)S: C, 42.05; H, 2.62; N, 2.80; S, 3.21. Found C, 41.93; H, 2.58; N, 2.74; S, 3.18. FTIR (CH\(_2\)Cl\(_2\), νCO, cm\(^{-1}\)): 2070vs, 2034s, 2016m, 1997sh, 1981sh, 1961m. \(^1\)H NMR (300 MHz, CDCl\(_3\), 25°C): \(\delta = 8.1-7.15\) (m, 20H, Ph), 4.23 (d, 1H, -RuCH-, \(^2\)J\(_{\text{HP}}\) = 6.3 Hz), 2.59 (observed multiplicity: m, simulated (line width 1 Hz), qdd, 2H, -CH\(_2\)-, \(^3\)J\(_{\text{HH}}\) = 6.6 Hz,
$^4J_{H,P} = 3.0 \text{ Hz, } ^4J_{H,P} = 3.0 \text{ Hz}, 0.91 \text{ (t, 3H, } CH_2CH_2NRu, ^3J_{HH} = 6.6 \text{ Hz) ppm. } ^{31}P\{^{1}H\} \text{ NMR (161.98 MHz, CDCl}_3, 25^\circ C): } \delta = 68.54 \text{ (d, } ^2J_{PP} = 35 \text{ Hz), 34.80 \text{ (d, } ^2J_{PP} = 35 \text{ Hz) ppm.}

The fourth yellow band (Rf = 0.41) gave the new compound \{Ru$_3$(CO)$_6$(µ$_3$-CO)(µ$_3$-S)(EtNC)((µ-κ$^2$P)Ph$_2$PNHPPh$_2$)} (7) as yellow crystals of 7-CH$_3$OH after recrystallization by layering methanol on a dichloromethane solution (21%). Anal. Calc. for C$_{34}$H$_{26}$N$_2$O$_7$P$_2$Ru$_3$: C, 42.02; H, 2.70; N, 2.88; S, 3.30. Found C, 41.95; H, 2.67; N, 2.84; S, 3.27. FTIR (CH$_2$Cl$_2$, νCO, cm$^{-1}$): 2055m, 2037s, 2009vs, 1975s, 1652br.

$^1H$ NMR (300 MHz, CDCl$_3$, 25°C): δ = 7.62-7.22 (m, 20H, Ph), 4.02 (t, 1H, NH, $^2J_{PP} = 6 \text{ Hz}$), 3.63 (q, 2H, -CH$_2$, $^3J_{HH} = 7.5 \text{ Hz}$), 1.35 (t, 3H, -CH$_3$, $^3J_{HH} = 7.5 \text{ Hz}$) ppm. $^{31}P\{^{1}H\} \text{ NMR (161.98 MHz, CDCl}_3, 25^\circ C): } \delta = 82.1 \text{ (s) ppm.}

4.2.5 Thermal treatment at 80 °C of cluster 2; conversion in cluster 7.

A solution of cluster 2 (0.154 g, 0.15 mmol) in toluene (20 mL) was heated at 80°C for 1 h. Conversion in cluster 7 was detected by $^1H$ NMR, $^{31}P\{^{1}H\} \text{ NMR, FTIR (Yield 82% by NMR peak integration).}

4.2.6 X-Ray data collection, structure solution and refinement of 2, 5 and 7-CH$_3$OH.

The intensity data of 2, 5 and 7-CH$_3$OH were collected at room temperature with a Bruker AXS Smart 1000$^{[13]}$ single crystal diffractometer equipped with an area detector, using a graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å). Crystallographic and experimental details of the structures are summarized in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares procedures (based on $F_o^2$)$^{[14]}$ first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atoms, introduced into the geometrically calculated positions, were refined riding on the corresponding parent atoms, except for the hydride in 2, H1 in 5 and H1N in 7-CH$_3$OH that were found in the ΔF maps and refined isotropically.
4. Methideylamide [-N(Et)-CH(R)-] Ruthenium Cluster

Table 1 Crystal Data and Structure Refinement for 2, 5 and 7·CH₂OH

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>5</th>
<th>7·CH₂OH</th>
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<tr>
<td>formula</td>
<td>Ru₃SP₂N₂O₉C₃₆H₂₆</td>
<td>Ru₃SP₂N₂O₉C₃₇H₃₁</td>
<td>Ru₃SP₂N₂O₉C₃₄H₂₆·CH₃OH</td>
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<td>monoclinic</td>
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<td>C2/c</td>
<td>P₂₁/a</td>
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<td>20.304(5)</td>
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<tr>
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<td>10.518(2)</td>
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<td>7869(2)</td>
<td>3904(2)</td>
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<tr>
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<td>8</td>
<td>4</td>
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4.3 Results and Discussion

4.3.1 Reaction between Ru₁₀(CO)₁₀(MeCN)₂ and HEtSNS

In CH₂Cl₂, the 1:1 room temperature reaction between the labile [Ru₁₀(CO)₁₀(MeCN)₂] and the zwitterionic ligand HEtSNS, gives rise to four main products, as depicted in Scheme 2. Ligand fragmentation is observed, without sulfur transfer to the metal core.

![Scheme 2](image-url)
Clusters \( \{\text{Ru}_3(\text{CO})_{10}(\mu-H)((\mu-S:k-P)\text{Ph}_2\text{PN}P\text{Ph}=\text{PPh}_2\text{S})}\}^{[10]} \) (3) and \( \{\text{Ru}_3(\text{CO})_{10}(\mu-k^3\text{P})\text{Ph}_2\text{PNHPh}_2\}\}^{[11]} \) (4) were identified by comparison of their spectroscopical data with those reported in the literature. Cluster \( [\text{Ru}_3(\text{CO})_{11}(\text{CNEt})] \) (1) was identified by \(^1\text{H} \) NMR spectrum, in which only the coordinated ethyl isonitrile peaks were present, and by comparison of its FTIR spectrum with that of published \( [\text{Ru}_3(\text{CO})_{11}(\text{CNBu})].^{[15]} \) Cluster 1, 3 and 4 can be seen as the products of the reaction of \( [\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2] \) with CNEt, \( \text{PPh}_2\text{NHP(S)Ph} \) and dppa respectively, that are degradation products of HEtSNS.

The cluster \( \{\text{Ru}_3(\text{CO})_{9}(\mu-H)((\mu-S:k-P)\text{Ph}_2\text{PN}P\text{Ph}_2\text{C}((\text{NEt})\text{S})}\} \) (2) is a new compound and it has been recognized by X-ray diffraction analysis. In the crystals, two crystallographically, but very similar, independent molecules are present (A and B). An ORTEP view of molecule A is reported in Figure 1.

![Figure 1. ORTEP plot of the structure of cluster 2 (molecule A). Thermal ellipsoids are drawn at the 30% probability level. H atoms, except the hydride, are omitted for clarity. Selected bond distance (Å) and angle (°) (Values for molecule B are given in parenthesis): Ru1A-S1A 2.433(1) [2.417(2)], Ru1A-Ru3A 2.828(1) [2.849(1)], Ru1A-Ru2A 2.850(1) [2.834(1)], Ru2A-Ru3A 2.876(1) [2.877(1)], Ru3A-P1A 2.341(1) [2.342(1)], Ru3A-S1A 2.419(1) [2.409(1)], Ru2A-Ru1A-Ru3A 60.87(2) [60.82(2)], Ru1A-Ru2A-Ru3A 59.18(1) [59.83(1)], Ru1A-Ru3A-Ru2A 59.95(2) [59.34(2)], P2A-N1A-P1A 131.1(2) [133.5(3)].](image)

In the structure of cluster 2 the metal centres form a triangle showing Ru-Ru distances consistent with metal-metal bonds [spanning from 2.828(1) to 2.876(1) Å]. The anionic ligand \( \text{Ph}_2\text{PN}=\text{PPh}_2\text{C}(\text{NEt})\text{S} \) chelates the Ru3 atom through the phosphorus and sulfur atoms, giving
rise to a six-membered chelation ring. The phosphorus is approximatively trans to the Ru3-Ru2 bond, while the sulfur further coordinates to Ru1, thus bridging a triangle edge [Ru1-S1 and Ru3-S1 distances: 2.433(1) [2.417(2)] and 2.419(1) [2.409(1)] Å, respectively]. The C-S (S1A-C10A 1.793(5) [1.788(6)]) and C-N 8 N2A-C10A 1.252(5) [1.278(6)]) distances suggest for these bonds single and double characters, respectively. The P-N-P group is asymmetric, P-N distances confirming, for P1 and P2, oxidation states III and V respectively (P1A-N1A 1.620(4) [1.638(5)], P2A-N1A 1.581(4) [1.548(5)]). The Ru1-Ru3 bond is bridged by the hydride. Nine terminal CO ligands complete the coordination over the metal centres (two for Ru3, four for Ru2 and three for Ru1). An analogous ligand arrangement was observed for a similar 2-(diphenylphosphanyl)thiophenolate derivative.[16,17]

Cluster 2 derives formally from the reaction of Ph3PNPPh3CSNHEt, formed by HEtSNS via loss of a molecule of isothiocyanate (EtNCS), with [Ru3(CO)10(MeCN)2] (Scheme 3).

![Scheme 3](image)

The fragmentation could be facilitated by the metal centre, shifting the reaction to the right side, by forming the Ru-P bond. The PC(S)NHEt moiety could then react in its thiolic form [PC(SH)NHEt] by oxidative addition of the SH group to the metal triangle with hydride transfer from the thiolic group to the cluster core, as observed in the case of thiols and thioureas.[18-20]

In the 1H NMR spectrum, the hydride resonates at δ = -14.7 (d, 2JP,H = 9.0 Hz) ppm, as typically found for bridging hydrides. In the 31P{1H} NMR spectrum two singlets are present at δ = 10.42 (s) and 54.09 (s) ppm, assigned respectively to P2 and to the P1 atoms. Noteworthy, the Ph3PNPPh3C(S)NHEt ligand is the non-isolable intermediate in the preparation reaction of HEtSNS between dppa and EtNCS.[6]

The thermal treatment at 50 °C of cluster 2 in closed vessel affords cluster 3 in a quantitative yield by elimination of EtNC, as observed by 1H and 31P{1H} NMR spectroscopy.
4.3.2 Pyrolytic reaction between Ru₃(CO)₁₂ and HEtSNS.

When [Ru₃(CO)₁₂] and HEtSNS were reacted at 70°C in toluene, several products, some of them present in trace amount, were detected. The isolated clusters are depicted in Scheme 4. The multi-component crude mixture results from the tendency of the ligand to fragment in various ways at high temperature.

![Scheme 4](image)

The product corresponding to the first yellow TLC band (Rf = 0.81) was identified as \{Ru₃(CO)₇(CNEt)(µ-S)[(µ₂-N:η₁-C:κ₁-P)Ph₂PN=PPh₂CHNEt]\} (5) by X-ray diffraction methods; an ORTEP view of its structure is shown in Figure 2.

![Figure 2](image)

**Figure 2.** ORTEP plot of the structure of cluster 5. Thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity. Selected bond distance (Å) and angle (°): Ru1-N2 2.130(4), Ru1-P2 2.286(1), Ru1-S1 2.366(1), Ru1-Ru2 2.775(1), Ru2-N2 2.170(3), Ru2-S1 2.407(1), Ru2-Ru3 2.790(1) Ru3-C11 2.176(4), Ru3-S1 2.366(1), P1-N1 1.587(4), P2-N1 1.613(3); P2-Ru1-Ru2 135.07(4), Ru1-Ru2-Ru3 88.51(2), C11-Ru3-Ru2 72.5(1), S1-Ru3-Ru2 54.92(3), Ru1-S1-Ru3 110.30(5), Ru1-S1-Ru2 71.11(4), Ru3-S1-Ru3 71.52(4), P1-N1-P2 127.7(2), Ru1-N2-Ru2 80.4(1).
The structure of cluster 5 shows an open Ru$_3$ triangle with Ru1-Ru2 and Ru2-Ru3 distances of 2.775(1) and 2.789(1) Å respectively. The cluster is capped by a triple bridging sulphide and by the -N(Et)CH(R)- moiety of the PPh$_2$NPPh$_2$C(H)NEt fragment. The carbon atom is $\eta^1$ bound to Ru3 [Ru3-C11 2.176(4) Å] while the nitrogen atom is bridging Ru1 and Ru2 [Ru1-N2 2.130(4), Ru2-N2 2.170(3) Å]. Ligand PPh$_2$NPPh$_2$CHNEt further coordinates to Ru1 atom through the tertiary P atom [Ru1-P2 2.286(1) Å], forming a six-membered chelation ring around Ru1 and adopting a chair conformation. The two P-N bond distances in the P-N-P moiety are similar being 1.587(4) (P1-N1) and 1.613(3) Å (P2-N1). The coordination around the ruthenium atoms of the cluster core is completed by seven terminal carbonyls and one ethyl isonitrile. To our knowledge the -N(Et)CH(R)- bridging moiety is unprecedented in coordination chemistry. Nevertheless, this coordination mode resembles that of an h$_2$-formimidoyl ligand (RN=CH) obtained through step by step coordination and fragmentation (sulfur transfer) of p-fluoro-phenylisothiocyanate on a tri-osmium hydrido-carbonyl cluster.[21] Another similar coordinating group is the triple bridging 1-(methylamino)-2,3-diphenylallyl fragment of a μ-N(Me)C(H)C(Ph)CPh ligand also found on a tri-osmium cluster.[22] In this case, however, the allyl PhC(Ph)CC(H) fragment is π-bonded to an Os atom.

In order to reach the 50 electrons required for an open triangular cluster, the -N(Et)CH(R)-group should donate four electrons to the metal centres, suggesting that the N atom participates to the electron count with three electrons, through one $\sigma$-bond and one coordination bond. Following the Mingos-Wade’s rules,[23-29] cluster 5 is to be considered a nido-square pyramidal cluster with five apices: three RuL$_3$ fragments (two electrons), one sulfur (four electrons) and one -N(Et)CH(R)- group (four electrons) permit to attain seven skeletal electron pairs (s.e.p.’s).

The solution spectroscopic data ($^1$H and $^{31}$P{$^1$H} NMR, FTIR) for 5 are consistent with the solid state structure. The $^{31}$P{$^1$H} NMR spectrum shows two doublets at $\delta = 77.6$ ($^2J_{PP} = 37$ Hz) and 35.5 ($^2J_{PP} = 37$ Hz) ppm, assigned, respectively, to P2 (directly coordinated to Ru atom) and P1. This was confirmed by 2D $^{31}$P-$^1$H Hetcor NMR. Besides, in the FTIR spectrum (CH$_2$Cl$_2$) the coordinated isonitrile characteristic absorption is observed at 2186 cm$^{-1}$.

The cluster generating the second yellow TLC band (Rf = 0.75) has been recognized as {Ru$_3$(CO)$_9$($\mu_3$-S)[($\mu_2$-N:η-C:κ-P)Ph$_2$PN=PPh$_2$CHNEt]} (6). The coordination around the Ru$_3$ core is the same found in cluster 5, CNEt being replaced by a CO molecule as confirmed by $^1$H NMR, FTIR and positive ion ESI-MS experiments (Figure 3).
The $^{31}$P$\{^1$H$\}$ NMR spectrum shows the relevant peak of the coordinated P2 at $\delta = 68.54$ ppm upfield with respect to the same atom signal in cluster 5. Negligible shift was observed for the P1 atom. The significant increase in chemical shift of the P2 atoms resonances, could be explained with a change in the coordination around the Ru1 atom. In fact, the P2 atom could be coordinated by the Ru1 in equatorial position. This behaviour was observed for the $[\text{Ru}_3(\text{CO})_6(\mu_3-\text{Se})_2(\mu-\kappa^2\text{P})\text{dppf}]$ (dppf = diphenylphosphine ferrocene),\cite{30,31} where a shift of $\sim17$ ppm was present between the $\text{P}_{\text{ax}}$ and $\text{P}_{\text{eq}}$. The flexibility of the ligand can allow the coordination either in axial or equatorial position. Unfortunately, we were not able to produce single crystals of 6.

Clusters 5 and 6 can be regarded to the products of sulfur migration from the thioamidic group on the cluster core, by the rupture of the C-S bond, as observed with various thioureas.\cite{32}

From the same reaction, $\{\text{Ru}_3(\text{CO})_6(\mu_3-\text{CO})(\mu_3-\text{S})(\text{EtNC})[(\mu-\kappa^2\text{P})\text{Ph}_2\text{PNHPPh}_2]\}$ (7) was also isolated and structurally characterized. An ORTEP view of its crystal structure is shown in Figure 4.
Figure 4. ORTEP plot of the structure of cluster 7 in 7·CH₃OH. Thermal ellipsoids are drawn at the 30% probability level. H atoms and MeOH are omitted for clarity. Selected bond distance (Å) and angle (°): Ru1-C7 2.176(6), Ru1-P1 2.331(2), Ru1-S1 2.364(2), Ru1-Ru2 2.809(1), Ru1-Ru3 2.815(1), Ru2-C7 2.138(6), Ru2-P2 2.289(2), Ru2-S1 2.366(2), Ru2-Ru3 2.793(1), Ru3-C7 2.165(5), Ru3-S1 2.367(2), P1-N1 1.670(5), P2-N1 1.692(5); Ru2-Ru1-Ru3 59.55(3), C7-Ru2-Ru1 49.96(15), C7-Ru2-Ru3 49.95(14), C7-Ru3-Ru2 49.12(15), Ru3-Ru2-Ru1 60.33(4), Ru2-Ru3-Ru1 60.13(4), Ru1-S1-Ru2 72.87(5), Ru1-S1-Ru3 73.02(5), Ru2-S1-Ru3 72.33(5), N1-P1-Ru1 111.13(18), N1-P2-Ru2 114.43(19), P1-N1-P2 122.6(3).

The structure of cluster 7 contains a Ru₃S nido core (6 s.e.p’s). The sulfide is bound in a μ₃ modality to the metal triangle with the sulfur atom lying at a distance of 1.724(1) Å from the Ru₃ plane. The dppa ligand coordinates through the tertiary P atoms to Ru1 and Ru2 metal [Ru1-P1 2.331(2) and Ru2-P2 2.289(2) Å]. The two P-N bond distances are similar [1.670(5) and 1.692(5) Å]. A triple-bridging carbonyl, seven terminal carbonyls and an isonitrile group complete the coordination around the ruthenium atoms of the cluster core. The isonitrile ligand is attached to the ruthenium atom not coordinated by the phosphorous. The short O7···O1S separation, 2.762(3) Å, suggests an hydrogen bond between the oxygen of μ₃-CO bridging molecule and the hydroxy group of methanol.

The spectroscopic data (FTIR, ¹H NMR, ³¹P{¹H} NMR) for 7 agree with the solid state structure. The FTIR spectrum in solution (CH₂Cl₂) shows a characteristic absorption at 1652 cm⁻¹, attributed to a μ₃-CO bridging molecule. The ³¹P{¹H} NMR spectrum contains one singlet at δ = 82.1 ppm, indicating the magnetic equivalence of the phosphorus atoms. Sulfido clusters analogue to cluster 7 are well know and can easily be prepared upon reaction of phosphano sulfides with [Ru₃(CO)₁₂].³²-³⁷
4.4 Conclusions

This chapter gave further insight into the chemistry of the zwitterionic ligand HEtSNS. In particular it enabled us to understand its fragmentation behaviour in the reaction with [Ru₃(CO)₁₂]. Under room temperature condition only fragmentation via loss of EtNC or EtNCS, without sulfur transfer to the cluster core is observed. On the other hand, under pyrolytic condition sulfur transfer on the cluster core occurs with unprecedented formation of the methideylamide -N(Et)CH(R)- µ₃-bridging ligating moiety.

4.5 References

4. Methideylamide [-N(Et)-CH(R)-] Ruthenium Cluster


5. Zwitterionic Metallates of Pd(II)

Synthesis, characterization and reactivity of zwitterionic metallates of Palladium (II)

The reaction of Ph\(_2\)PNHPPPh\(_2\) with EtNCS in 1:2 molar ratio leads to the formation of the zwitterionic ligand EtNHC(S)PPh\(_2\)NPPh\(_2\)C(S)NEt (HEtSNS). This ligand is amphoteric, forming by protonation the cation H\(_2\)EtSNS\(^+\) and, when deprotonated, dianion-cation EtSNS\(^-\). All the three forms can coordinate to metal centres. Reaction of [Pd(CH\(_3\)CN)\(_2\)Cl\(_2\)] with HEtSNS affords [Pd(HEtSNS)Cl]Cl (1). When a base is added, [Pd(EtSNS)Cl] (3) is obtained as an orange powder. The reaction of 2 with AgOTf in 1:1 molar ratio affords the trimeric complex [Pd(EtSNS)]\(_3\)(OTf)\(_3\) (5a). When 3 reacts with three eq. of K[Ag(CN)]\(_2\), a yellow powder of [Pd(EtSNS)(CN)] (6) is produced. The presence of a terminal cyano-group can afford the formation of a bridge with other metal. In fact, when 5b reacts with 3 in CH\(_2\)Cl\(_2\), in the presence of one eq. of AgPF\(_6\), a dark orange powder of [Pd(EtSNS)\(_2\)(\(\mu\)-CN)]PF\(_6\) (5) is obtained. Moreover, 6 reacts with [Rh(cod)(CH\(_3\)CN)\(_2\)]OTf to give [Rh(cod)(\(\mu\)-CN)\(_2\)PdEtSNS\(_2\)]OTf (8).
5.1 Introduction

Pincer complexes of transition metal have recently attracted much attention in catalysis and material science.\textsuperscript{[1]} In particular, N-heterocyclic carbenes (NHCs)\textsuperscript{[2]} have been used in different field as homogeneous catalysis,\textsuperscript{[3]} polymer and dendrimer chemistry\textsuperscript{[4]} and sensing application.\textsuperscript{[5]} These symmetrical pincer type structures are XCX, where X = N, P, S, O, but in last years the asymmetrical pincer complexes with mixed donor atoms or ring sizes have been studied.\textsuperscript{[6]}

In this chapter are described on the synthesis, reactivity, spectroscopic and structural characterization of the novel pincer-type complexes of Pd(II) with the zwitterionic ligand HRSNS \([\text{RNHC(S)Ph}_2\text{P=NPPh}_2\text{C(S)NR, R = Et,}^{[7]} (R)-\text{Ph(CH)}_3\text{CH}].\)

5.2 Experimental

5.2.1 General procedures.

All manipulations were carried out at room temperature under nitrogen atmosphere by standard Schlenk techniques; \(t\)-BuOK, \(\text{PdCl}_2\), \(K[\text{Ag(CN)}]_2\), \(\text{AgPF}_6\), \(\text{AgOTf} \) (OTf = \(\text{CF}_3\text{SO}_3\)), \((R)-[(\text{C}_6\text{H}_5)\text{CH}_3\text{CHNH}_2]\) and \(\text{CSCl}_2\) were purchased from Aldrich and Fluka. The solvents was dried and distilled by standard techniques. \(\text{dppa,}^{[8]} \text{HEtSNS and H}_2\text{EtSNSCl}_1^{[7a,b,c]} \) \(\text{[Pd(CH}_3\text{CN)}_2\text{Cl}_2]^{[9]} \) \(\text{[Pd(CH}_3\text{Cl}(\text{cod})]\text{[10]} \) (\(\text{cod} = \text{1,5-cyclooctadiene} \)) and \(\text{[Rh(cod)(CH}_3\text{CN)}_2\text{OTf]}^{[11]} \) and were prepared as described elsewhere. Elemental analyses were carried out on a Carlo Erba EA1108 microanalyzer. FTIR spectra (4000-400 cm\(^{-1}\)) were recorded on a Nicolet Nexus spectrophotometer equipped with a Smart Orbit HATR (diamond or \(\text{ZnSe} \) crystals). \(^1\text{H} \text{NMR (300.13 MHz, TMS) and}^{[1]} \text{\textsuperscript{31}P\{\textsuperscript{1}H\} NMR (161.98 MHz, external reference 85%-H}_3\text{PO}_4\) spectra were recorder on Bruker instruments (AC300 Avance and AMX400, respectively) using deuterated solvents (CDCl\(_3\), CD\(_2\)Cl\(_2\), dmso-d\(_6\) and MeOD-d\(_4\)).

5.2.2 Preparation of \((R)-[(\text{C}_6\text{H}_5)\text{CH}_3\text{CHNCS}]\) \(\chi\text{NCS}\)

A mixture of thiophosgene (1.4 mL, 81.1 mmol) and \(\text{CH}_2\text{Cl}_2\) (50 mL) were cooled to \(-5^\circ\text{C}\) after which a water solution of \(K_2\text{CO}_3\) (50 mL, 0.33 M) was added. A solution of (R)-
[(C₆H₅)CH₂CHNH₂] (2.13 mL, 16.5 mmol) was added dropwise over a period of 15 min with vigorous stirring and maintaining of the temperature between 0 and 5°C. After an additional 10 min a cold (0°C) 100 ml of water solution of KOH (50 mL, 0.1 M) was added in one portion with cooling below 0°C. The organic layer and three extracts (30 mL x 3) of ethyl ether were dried over MgSO₄. The solution was concentrated under reduced pressure and a yellow-orange oil of (R)-[(C₆H₅)CH₂CHNCS] was obtained (Yield 85%). E.A. % calcd. for: C₉H₉NS (M = 163.24): C 66.22; H 5.56; N 8.58. Found: C 66.10; H 5.51; N 8.53. ¹H NMR: (CDCl₃): δ = 7.33-7.15 (m, 5H, Ph); 4.90 (q, 1H, -CH₂, ³J_H,H = 6.9 Hz), 1.67 (d, 3H, -CH₃, ³J_H,H = 6.9 Hz) ppm.

5.2.3 Preparation of (R)-PhCH₂CHNHC(S)Ph₂P=NPPh₂C(S)N-(R)-CHCH₂Ph (HₓSNS)
A solution of HN(PPh₂)₂ (1.387 g, 3.86 mmol) in CH₂Cl₂ (15 mL) was added to a stirred solution of KCNCS (1.021 g, 2.6 mmol) in CH₂Cl₂ (10 mL) and left at room temperature for 4 h under stirring. The volatile was removed and the resulting rubbery yellow products was re-crystallized in EtOH (5 mL, 96%) giving (R)-PhCH₂CHNHC(S)Ph₂P=NPPh₂C(S)N-(R)-CHCH₂Ph (HₓSNS) as yellow crystals (Yield 92 %). E.A. % calcd. for: C₄₂H₃₉N₃P₂S₂ (M = 711.87): C 70.86; H 5.52; N 5.90; S 9.01. Found: C 70.53; H 5.45; N 5.82; S 8.96. ¹H NMR: (CDCl₃): δ = 13.0 (s, br, 1H, NH); 7.62-7.15 (m, 40H, Ph); 5.62 (qd, 2H, -CH₂, ³J_H,H = 6.9 Hz, ⁴J_H,P = 2.4 Hz), 1.49 (d, 6H, -CH₂CH₃, ³J_H,H = 6.9 Hz) ppm. ³¹P{¹H} NMR (CDCl₃): δ = 7.29 (s) ppm.

5.2.4 Preparation of [Pd(HEtSNS)Cl]Cl (I)
Solid [Pd(CH₂CN)₂Cl₂] (0.100 g, 0.385 mmol) was dissolved in 10 mL of CH₂Cl₂. To this, solid HEtSNS (0.215 g, 0.385 mmol) was added and the reaction mixture stirred for 30 min. Evaporation of the solvent afforded complex [Pd(HEtSNS)Cl]Cl (I) as brown powder. The complex can be recrystallized by layering hexane onto a CH₂Cl₂ solution, affording dark red crystals of I·(CH₂Cl₂)₂. E.A. % calcd. for: C₃₀H₃₁Cl₂N₄P₂S₂ (M = 736.99): C 48.89; H 4.24; N 5.70; S 9.62. Found: C 48.78; H 4.21; N 5.66; S 9.58. ¹H-NMR: (MeOD-d₄): δ = 7.84-7.57 (m, 20H, Ph); 3.80 (qd, 4H, -CH₂CH₃, ³J_H,H = 3.0 Hz, ⁴J_H,P = 7.5 Hz), 1.28 (t, 6H, -CH₂CH₃, ³J_H,H = 7.50 Hz) ppm. ³¹P{¹H} NMR (MeOD-d₄): δ = 43.5 (s) ppm.
5.2.5 Preparation of [Pd(EtSNS)Cl] (2)
Solid [Pd(CH₃CN)Cl]₂ (0.100 g, 0.385 mmol) was dissolved in 10 mL of CH₂Cl₂. To this, solid HEtSNS (0.215 g, 0.385 mmol) was added. A solution of t-BuOK (0.043 g, 0.385 mmol) in 2 mL of MeOH was then added and the reaction mixture stirred for 30 min. The volatiles were evaporated and the resulting dark yellow powder was redissolved in 5 mL of CH₂Cl₂. KCl was removed via filtration. Evaporation of the solvent afforded complex [Pd(EtSNS)Cl] (2) as orange powder. The complex can be recrystallized by layering hexane onto a CH₂Cl₂ solution, affording orange crystals of 2. E.A. % calcd. for: C₃₀H₃₀ClN₃PdP₂S₂ (M = 700.53): C 51.44; H 4.32; N 6.00; S 9.15. Found: C 51.35; H 4.29; N 5.96; S 9.11. ¹H NMR: (CDCl₃): δ = 7.64-7.38 (m, 20H, Ph), 3.67 (qd, 4H, -CH₂CH₃, ³J_H,H = 7.50 Hz, ⁴J_H,P = 3.00 Hz), 1.22 (t, 6H, -CH₂CH₃, ³J_H,H = 7.50 Hz) ppm. ³¹P{¹H} NMR (CDCl₃): δ = 25.8 (s) ppm.

5.2.6 Preparation of [Pd(HKSNS)Cl]Cl (3)
Solid [Pd(CH₃CN)Cl]₂ (0.036 g, 0.14 mmol) was dissolved in 10 mL of CH₂Cl₂. To this, solid HKSNS (0.100 g, 0.14 mmol) was added and the reaction mixture stirred for 30 min. Evaporation of the solvent afforded complex [Pd(HKSNS)Cl]Cl (3) as brown powder. E.A. % calcd. for: C₄₂H₃₉ClN₃PdP₂S₂ (M = 889.19): C 56.73; H 4.42; N 4.72; S 7.21. Found: C 56.65; H 4.41; N 4.69; S 7.19. ¹H NMR: (MeOD-d₄): δ = 8.05 (m, 10H, Phisothio), 7.75-7.06 (m, 40H, Ph), 5.36 (q, 2H, CH, ³J_H,H = 4.8 Hz), 1.51 (d, 6H, CH₃, ³J_H,H = 4.8 Hz) ppm. ³¹P{¹H} NMR (MeOD-d₄): δ = 42.8 (s) ppm.

5.2.7 Preparation of [Pd(χSNS)Cl] (4)
Solid [Pd(CH₃CN)Cl]₂ (0.036 g, 0.14 mmol) was dissolved in 10 mL of CH₂Cl₂. To this, solid HEtSNS (0.100 g, 0.14 mmol) was added. A solution of t-BuOK (0.016 g, 0.14 mmol) in 2 mL of MeOH was then added and the reaction mixture stirred for 30 min. The volatiles were evaporated and the resulting dark yellow powder was redissolved in 5 mL of CH₂Cl₂. KCl was removed via filtration. Evaporation of the solvent afforded complex [Pd(χSNS)Cl] (4) as orange powder. E.A. % calcd. for: C₄₂H₃₈ClN₃PdP₂S₂ (M = 852.74): C 59.16; H 4.49; N 4.93; S 7.52. Found: C 59.08; H 4.45; N 4.89; S 7.49. ¹H NMR: (CDCl₃): δ = 7.96 (m, 10H, Phisothio), 7.67-6.98 (m, 20H, Ph), 5.32 (q, 2H, CH, ³J_H,H = 6.6 Hz), 1.32 (d, 6H, CH₃, ³J_H,H = 6.6 Hz) ppm. ³¹P{¹H} NMR (CDCl₃): δ = 28.4 (s) ppm.
5.2.8 Preparation of $[\text{Pd(EtSNS)}]_3(X)$, $[X = \text{OTf} (5a), \text{PF}_6 (5b)]$

Complex 2 (0.200 g, 0.285 mmol) was dissolved in 10 mL of CH$_2$Cl$_2$. To this, AgX ($X = \text{OTf}$, $\text{PF}_6$, 0.285 mmol) was added and the reaction mixture stirred for 1 h. The volatile was evaporated and the resulting orange powder was redissolved in 5 mL of CH$_2$Cl$_2$. AgCl was removed via filtration. Evaporation of the solvent afforded complex $[\text{Pd(EtSNS)}]_3(\text{OTf})$ (5a) as orange powder. Suitable crystals for the X-ray analysis of complex 5a were obtained by layering hexane onto dichloromethane solutions (Yield 91%).

E.A. % calcd. for: C$_{93}$H$_{90}$F$_9$N$_9$O$_9$P$_6$Pd$_3$S$_9$ (5a, $M = 2442.45$): C 45.73; H 3.71; N 5.16; S 11.82. Found: C 45.68; H 3.69; N 5.15; S 11.78.

$^1$H NMR: (CD$_2$Cl$_2$): $\delta = 8.37$ - 6.64 (m, 60H, Ph), 4.17 - 3.53 (4 multi., 12H, -CH$_2$CH$_3$), 1.24 (2 trip., 18H, -CH$_2$CH$_3$) ppm.

$^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta = 37.5$ [d, $^2J_{p,p} = 9.7$ Hz], 35.4 [d, $^2J_{p,p} = 9.7$ Hz] ppm.

5.2.9 Preparation of $[\text{Pd(CN)}(\text{EtSNS})](6)$

(a) Complex 5 (0.110 g, 0.045 mmol) was dissolved in 10 mL of CH$_2$Cl$_2$. To this, a solution of K[Ag(CN)$_2$] (0.027 g, 0.135 mmol) in 5 mL of methanol was added and the reaction mixture stirred for 1 h. The volatiles were evaporated and the resulting yellow powder was redissolved in 5 mL of CH$_2$Cl$_2$. AgCN and KOTf were removed via filtration. Evaporation of the solvent afforded complex [PdEtSNS(CN)] (6) as lemon-yellow solid (Yield 88%).

(b) Complex 2 (0.200 g, 0.285 mmol) was dissolved in 10 mL of CH$_2$Cl$_2$. To this, a solution of K[Ag(CN)$_2$] (0.057 g, 0.285 mmol) in 5 mL of methanol was added and the reaction mixture stirred for 1 h. The volatiles were evaporated and the resulting yellow powder was redissolved in 5 mL of CH$_2$Cl$_2$. KCl and AgCN were removed via filtration. Evaporation of the solvent afforded complex [PdEtSNS(CN)] (6) as lemon-yellow solid. Suitable crystals for the X-ray analysis of complex 6 were obtained by layering hexane onto dichloromethane solution (Yield 93%).

E.A. % calcd. for: C$_{93}$H$_{90}$N$_9$O$_9$P$_2$PdS$_2$ (6, $M = 691.10$): C 53.88; H 4.38; N 8.11; S 9.28. Found: C 53.80; H 4.35; N 8.05; S 9.24. $^1$H NMR: (CDCl$_3$): $\delta = 7.58$-7.33 (m, 20H, Ph); 3.74 (qd, 4H, -CH$_2$CH$_3$), $^3J_{H,H} = 7.15$ Hz, $^4J_{H,P} = 4.2$ Hz), 1.12 (t, 6H, -CH$_2$CH$_3$), $^3J_{H,H} = 7.15$ Hz) ppm. $^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta = 24.4$ (s) ppm. FTIR (ZnSe HATR, cm$^{-1}$): $\nu_{CN} = 2131$. 

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5.2.10 Preparation of \([\text{PdEtSNS}_2(\mu\text{-CN})]X [X = \text{OTf (7a)}, \text{PF}_6 (7b)]\)

Complex 2 (0.152 g, 0.217 mmol) and 6 (0.150 g, 0.217 mmol) were dissolved in 15 mL of \(\text{CH}_2\text{Cl}_2\). To this, a solution of \(\text{AgX (X = OTf, PF}_6\)) (0.217 mmol) in 5 mL of THF was added and the reaction mixture stirred for 4 h. The volatiles were evaporated and the resulting orange powder was redissolved in 5 mL of \(\text{CH}_2\text{Cl}_2\). AgCl was removed via filtration. Evaporation of the solvent afforded complex \([\text{PdEtSNS}_2(\mu\text{-CN})]\text{PF}_6 (7b)\) as dark-orange powder (Yield 95 %). Suitable dark-orange crystals for the X-ray analysis of complex 7b were obtained by evaporation of a \(\text{CH}_2\text{Cl}_2/\text{pentane}\) solution. E.A. % calcd. for: \(\text{C}\_7\text{H}_{60}\text{F}_6\text{N}_7\text{P}_5\text{Pd}_2\text{S}_4 (7b, M = 1501.14): C 48.81; H 4.03; N 6.53; S 8.54.\) Found: C 48.75; H 3.99; N 6.47; S 8.48.

\(^1\text{H NMR: (CDCl}_3): \delta = 7.75 - 7.40 (\text{m, 40H, Ph}); 3.68 (\text{qd, 8H, CH}_2\text{CH}_3, ^3J_{\text{HH}} = 7.15 \text{ Hz, } ^4J_{\text{HP}} = 4.2 \text{ Hz}), 1.24 (\text{t, 12H, CH}_2\text{CH}_3, ^3J_{\text{HH}} = 7.15 \text{ Hz}) \text{ ppm.} \) \(^{31}\text{P}\{^1\text{H}\} \text{NMR (CDCl}_3): \delta = 32.14 (\text{s}), 27.52 (\text{s}), -145 (\text{sept, PF}_6, ^1J_{\text{FP}} = 704 \text{ Hz}) \text{ ppm.} \)

\(\text{FTIR (ZnSe ATR, cm}^{-1}): \nu\text{CN} = 2326.\)

5.2.11 Preparation of \([\text{Rh(cod)][PdEtSNS(\mu-CN)]_2] \text{OTf (8)}\)

A solution of \([\text{Rh(cod)(CH}_3\text{CN)}_2\text{OTf}_3 (0.100 g, 0.226 mmol) in CH}_3\text{CN (10 mL) was added dropwise to a solution of complex 6 (0.312 g, 0.452 mmol) in CH}_3\text{CN (10 mL). The orange reaction mixture was stirred for 1 h. Evaporation of the volatile yielded compound \([\text{Rh(cod)][PdEtSNS(\mu-CN)]_2] \text{OTf (8)}\) as a purple powder (Yield 87%).\) E.A. % calcd. for: \(\text{C}\_7\text{H}_{60}\text{F}_6\text{O}_3\text{Pd}_2\text{RhS}_3 (M = 1742.35): C 48.94; H 4.16; N 6.43; S 9.20.\) Found: C 48.89; H 4.12; N 6.39; S 9.16. \(^1\text{H NMR: (CD}_2\text{Cl}_2): \delta = 7.66 - 7.41 (\text{m, 40H, Ph}); 4.14 (\text{br, 4H, CH=CH-, cod}), 3.72 (\text{qd, 8H, -CH}_2\text{CH}_3, ^3J_{\text{HH}} = 7.2 \text{ Hz, } ^4J_{\text{HP}} = 3.9 \text{ Hz}), 2.35 (\text{br, 8H, -CHH-, cod}), 1.79 (\text{m, 8H, -CHH-, cod}), 1.27 (\text{t, 12H, -CH}_2\text{CH}_3, ^3J_{\text{HH}} = 6.6 \text{ Hz}) \text{ ppm.} \) \(^{31}\text{P}\{^1\text{H}\} \text{NMR (CD}_2\text{Cl}_2): \delta = 29.37 (\text{s}) \text{ ppm.} \) FTIR (ZnSe HATR, cm}^{-1}): 2165.

5.2.12 Preparation of \([\text{Pd(CH}_3\text{)][EtSNS]} (9)\)

To a solution of \([\text{PdCl(CH}_3\text{)(cod)]] (0.100 g, 0.377 mmol) of \text{CH}_2\text{Cl}_2 (20 mL) was added HEtSNS (0.211 g, 0.377 mmol) in \text{CH}_2\text{Cl}_2 (10 mL) and t-BuOK (0.042 g, 0.377 mmol) in MeOH (2 mL). The red mixture was left for 3h. The solvents were evaporated and a reddish powder was obtained. This was redissolved in 20 ml of \text{CH}_2\text{Cl}_2. KCl was removed via filtration. Evaporation of the solvent afforded complex \([\text{Pd(CH}_3\text{)][EtSNS]} (9)\) as light orange powder. Suitable orange crystals for the X-ray analysis of complex 9 were obtained by
layering hexane onto dichloromethane solution (Yield 93%). E.A. % calcd. for:
\[ \text{C}_{31} \text{H}_{33} \text{N}_{3} \text{P}_{2} \text{PdS}_{2} \ (M = 680.11): \ C, 54.75; \ H, 4.89; \ N, 6.18; \ S, 9.43. \] Found: \ C, 54.67; \ H, 4.85; \ N, 6.13; \ S, 8.14. \n
1H-NMR: (CDCl\(_3\)): \( \delta = 7.49-7.23 \) (m, 40H, Ph), 3.76 (qd, 4H, -CH\(_2\)-), \( ^3J_{HH} = 7.25 \) Hz, \( ^4J_{HP} = 2.2 \) Hz), 1.25 (t, 6H, -CH\(_3\)), \( ^3J_{HH} = 7.25 \) Hz), 0.54 (s, 3H, Pd-CH\(_3\)) ppm. \n
31P{\(^1\)H} NMR (CDCl\(_3\)): \( \delta = 14.1 \) (s) ppm.

5.2.13 Preparation of [Pd(COCH\(_3\))(EtSNS)] (10)

Compound 9 (g, mmol) was dissolved in THF (10 mL). CO was then bubbled through this solution for 15 minutes at 60 Atm. The solution was concentrated and n-pentane (20 mL) was added. Red powder of [Pd(COCH\(_3\))(EtSNS)] (10) was obtained (Yield 92 %). Suitable red crystals for the X-ray analysis of complex 10 were achieved by layering n-pentane onto dichloromethane solution. E.A. % calcd. for: \[ \text{C}_{32} \text{H}_{33} \text{N}_{3} \text{OP}_{2} \text{PdS}_{2} \ (M = 707.06): \ C, 54.28; \ H, 4.70; \ N, 5.93; \ S, 9.06. \] Found: \ C, 54.12; \ H, 4.67; \ N, 5.89; \ S, 9.00. 1H NMR: (CDCl\(_3\)): \( \delta = 7.64-7.23 \) (m, 40H, Ph), 3.74 (qd, , 4H, -CH\(_2\)CH\(_3\)), \( ^3J_{HH} = 6.88 \) Hz), 2.36 (s, 3H, Pd-COCH\(_3\)), 1.20 (t, 6H, -CH\(_2\)CH\(_3\)), \( ^3J_{HH} = 6.88 \) Hz) ppm. \n
31P{\(^1\)H} NMR (CDCl\(_3\)): \( \delta = 12.98 \) (s) ppm. FTIR (ZnSe ATR, cm\(^{-1}\)): \( \nu \text{COCH}_3 = 1689 \).

5.2.14 X-Ray data collection, structure solution and refinement of \( ICH_2Cl_2 \), 2, 5b, 6, 7b, 9 and 10

The intensity data of all compounds were collected at room temperature with a Bruker AXS Smart 1000\(^{[12]}\) single crystal diffractometer equipped with an area detector, using a graphite monochromated Mo-K\(_\alpha\) radiation (\( \lambda = 0.71073 \) Å). Crystallographic and experimental details of the structures are summarized in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares procedures (based on \( F_o^2 \))\(^{[13]}\) first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms, except for the amidic hydrogen atoms in 1 which was localized in the 2Fo-Fc map and refined isotropically.
Table 1 Crystal Data and Structure Refinement for 1·(CH₂Cl₂), 2, 5b, 6, 7b, 9 and 10

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5. Zwitterionic Metallates of Pd(II)
5.3 Results and discussion

The chiral isothiocyanate was obtained by reaction of the parent amine with CSCl₂ in presence of a base (Scheme 1).

![Scheme 1](image)

The chiral isothiocyanate was reacted with Ph₃PNPh₂ in CH₂Cl₂ solution in a 2.1 : 1 ratio. Yellow crystals of \((R)-\text{PhCH}_3\text{CHNHC(S)Ph}_2\text{P=NPPh}_2\text{C(S)N-(R)-CHCH}_3\text{Ph}\) \((\text{H}_2\text{SNS})\) were obtained.

5.3.1 Synthesis and characterization of chloro complexes.

The \([\text{Pd(CH}_3\text{CN)}]_2\text{Cl}_2\) precursor was reacted with HRSNS \((R = \text{Et}, (R)-[(\text{C}_6\text{H}_5)\text{CH}_3\text{CH}], \) Scheme 2) in CH₂Cl₂, affording chloro-palladium complex \([\text{Pd(HRSNS)Cl]}\text{Cl}\) \((R = \text{Et}, 1; R = (R)-[(\text{C}_6\text{H}_5)\text{CH}_3\text{CH}], 2)\) (or \([\text{Pd(RSNS)Cl]}\cdot\text{HCl}\) as dark red solids.

![Scheme 2](image)

The $^{31}\text{P}^2^{}$ NMR spectrum (MeOD-d₄, 25 °C) of 1 exhibit a singlet at 43.5 ppm; instead in CDCl₃ solution at the same temperature, a broad band was observed (ca. 33 ppm), probably due to the lowest rate exchange of the counter anion in this solvent. This behaviour was also
observed in the zwitterionic complexes of Rh(I) with the same ligand with different counter anion (PF$_6$, OTf, NO$_3$, TFA).\[^{14}\]

Red single crystals of $1 \cdot 2$ (CH$_2$Cl$_2$) were obtained by layering hexane on a CH$_2$Cl$_2$ solution. View of the crystal structure of $1$ in $1 \cdot 2$ (CH$_2$Cl$_2$) is reported in Figure 1.

![Figure 1. ORTEP plot of the molecular structure of $1$ in $1 \cdot 2$ (CH$_2$Cl$_2$).](image)

In the solid state structure, the ligand coordinates in a $S,N,S$-$\kappa^3$ modality to the Pd atom, which is found in a slightly distorted square-planar environment. The coordination around the metal center is completed by a chlorine atom (Cl1). An N2H1n···Cl2 interaction is present, in order to neutralize the remaining positive charge of the HEtSNS ligand. Distances P1-N1 and P2-N2 have approximately equal values, as should be expected for a delocalized P-N-P system and therefore that the positive charge is distributed on the two P atoms. The P1-C1 and P2-C4 bonds are of similar lengths, while variations can be evidenced in the C-S and C-N distances. The proton on the thioamidyl group causes the lengthening of the C1-N2 bond; in turn, the C1-S1 distance decreases, resulting in an improved double bond character. Similar behaviour was observed for Pd complexes of thioamidic $S,N,S$ pincer ligands.\[^{15}\]

When $1$ and $2$ were reacted with a base ($t$-BuOK, NEt$_3$) an orange powder of [Pd(EtSNS)Cl]$_2$ (3) or [Pd(KSNS)Cl] (4) were obtained, respectively (Scheme 2). As evidenced in situ by
$^{31}$P$^{1}{\text{H}}$ NMR spectroscopy, when t-BuOK was added to a solution of 1, it was quickly and completely consumed in few minutes, and it was accompanied by formation of 3 (singlet at 25.8 ppm). This fast reactivity is in agreement with the proposed structure of 1 whose formula can be written as [Pd(EtSNS)Cl] · HCl. View of molecular structure of 3, obtained by single crystal X-ray diffraction, is reported in Figure 2.

*Figure 2. ORTEP plot of the molecular structure of 3. Thermal ellipsoid are drawn at 30% probability level. H atoms are omitted for clarity. Selected distances [Å] and angles [°]: P1-N1 1.619(3), P1-C1 1.823(6), C1-S1 1.739(7), C1-N2 1.263(9), S1-Pd1 2.323(3), Cl1-Pd1 2.296(4), N1-Pd1 2.078(8), P1-N1-P1' 134.0(5), P1-N1-Pd1 113.0(2), N1-Pd1-C11 180.000(1), N1-Pd1-S1 89.76(5), S2-Pd1-S1 179.52(9), C11-Pd1-S1 90.24(5). (symmetry transformation used to generate equivalent atoms: ' = x + 1, y, z + 1/2).*

In the solid state, the coordination geometry of 3, is almost identical to that of 1. The complex has a crystallographically imposed C$_2$ symmetry. Molecules all oriented in the same direction are disposed in layers in a head-to-tail fashion. Adjacent layers contain molecules with opposite orientations. The shortest intermolecular Pd···Pd separation, between two molecules with different orientations in two adjacent layers in the same column, is 8.883 Å. The shortest Pd···Pd separation between two equally oriented molecules in the same layer is 11.804 Å, as found in [Rh(CO)EtSNS].[7a] Deprotonation of the thioamidic group causes the decrease of C1-N1 bond, resulting in a double bond, in turn the C1-S1 increase, becoming a single bond.
5.3.2 Synthesis and characterization of trinuclear complexes.

The reaction of 3 with a stoichiometric amount of AgX (X = OTf, PF₆) in CH₂Cl₂ solution results in the quantitative formation of [Pd(EtSNS)]₃(X)₃ (X = OTf, 5a; X = PF₆, 5b). A view of the molecular structure of 5b is depicted in Figure 3.

Figure 3. ORTEP plot of the molecular structure of 5b. Thermal ellipsoid are drawn at 30% probability level. H atoms and PF₆ are omitted for clarity. Selected distances [Å] and angles [°]: C1-N1 1.255(4), C1-S1 1.756(3), C2-N2 1.242(4), C2-S2 1.808(3), N3-P2 1.637(2), N3-P1 1.591(2), N3-Pd1 2.092(2), Pd1-S1 2.293(1), Pd1-S2 2.299(1), Pd1-S2' 2.340(1), P2-N3-P1 130.10(14), N3-Pd1-S1 90.27(2), N3-Pd1-S2' 173.63(6), S1-Pd1-S2' 92.06(2), N3-Pd1-S2 90.46(6), S1-Pd1-S2 179.11(3), S2-Pd1-S2' 87.16(3), Pd1-S2-Pd1' 106.60(3).

The tri-anionic Pd(II) trimer consists of a Pd₃S₃ core in a chair configuration. This type of core has been reported previously for group 10 (Ni, Pd, Pt) complexes.[16] The trimer has a crystallographic threefold symmetry. The Pd(II) atom is coordinated by three S atoms and one N atom in a approximately square planar arrangement. Two of these three S atoms and N atoms belong to the same zwitterionic ligand and the other S atom comes from to adjacent complex, forming a six member-ring of alternating Pd-S atoms. The bridging S atoms is bonded to two Pd(II) atoms and one C atoms located at the apex of a pyramidal structure. The torsion angle of S1-Pd1-S2′-C4’ are within 12.65°. The dihedral angles between monocomplex planes (S1-Pd1-N1-S2-S2′) in the trimeric unit is 68.89(3)°. The distance between the Pd(II) centres is 3.721(6) Å forming a equilater triangle. This distance indicates that there is not bonding between the metals (the maximum reported value for weak
interaction in Pd(II)-Pd(II) is 3.539(1) Å. The angles involving bridging sulfur atoms are for Pd1-S2′-Pd1′ 106.60(3) Å and for S2-Pd1-S2′ 87.16(3) Å. The formation of a trimer changes considerably the distances with respect to 2. The Pd1-S1 and S1-C1 bond distances decrease, 2.291(1) and 1.756(3), respectively. The P1-N3 and P2-N3 bonds are 1.591(2) and 1.637(2) respectively. In $^{31}$P{¹H} NMR spectrum two doublets are present [$\delta =37.5$ (d, $^{2}J_{P,P} = 9.7$ Hz) and 35.4 (d, $^{2}J_{P,P} = 9.7$ Hz) ppm]. The resonance at low fields is attributed to the quaternary phosphorus (P2). The Pd1-S2 bond lengths are almost equal to 3 while a variations is present in C2-S2 distances. This is due to the formation of bridge between two palladium atoms. Interestingly, it is the higher decrease of C1-N1 bond distance [1.255(4)], strengthening the the character of double bond (CSD, December 2008, mean = 1.271 Å). The angle of the P-N-P system decreases [130.10(14)] with a lengthening of the Pd1-N3 bond.

The ESI-MS analysis confirms the formation of the Pd$_3$S$_3$ cluster also in methanol solution, indicating the stability of the trinuclear molecule.

5.3.3 Synthesis and characterization of cyano complexes
When 5 was reacted with 3 equivalents of K[Ag(CN)$_2$], a lemon yellow microcrystalline product of [Pd(CN)(EtSNS)] (6) was achieved. The same product was obtained reacting 3 with 1 equivalent of K[Ag(CN)$_2$]. A view of its molecular structure is depicted in Figure 4.

![Figure 4](image-url)

**Figure 4.** ORTEP plot of the molecular structure of 6. Thermal ellipsoid are drawn at 30% probability level. H atoms are omitted for clarity. Selected distances [Å] and angles [°]: P1-N1 1.6113(11), P1-C1 1.818(2), C1-S1 1.742(2), C1-N2 1.251(3), S1-Pd1 2.310(11), N1-Pd1 2.093(2), C16-Pd1 1.944(4), C16-N3 1.143(5), P1-N1-P1′ 134.70(16), P1-N1-Pd1 112.65(8), S1-Pd1-S1′ 90.001(15), S1-Pd1-C16 89.999(15), S1-Pd1-S1′ 180.00(3) (symmetry transformation used to generate equivalent atoms: $x \rightarrow x + 1$, $y, z + 1/2$).

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Complex 6 is isostructural to 3 and displays analogous geometrical parameters. The bond distances Pd1-C16 [1.944(4)] and C16-N3 [1.143(5)] are in agreement with those found in CSD. In the FTIR spectrum, a characteristic absorption at 2130 cm\(^{-1}\) was visible and it was ascribed to the CN group, coordinated to the metal centre.

The present of a terminal cyano group can afford the formation of bridge with other metal. In fact, when 6 was reacted with 3 in dichloromethane solution, in the presence of 1 equivalent of AgPF\(_6\), a dark orange powder of \([\text{Pd(EtSNS)}_2(\mu-\text{CN})]\text{PF}_6\) (7a) was obtained (Scheme 3).

View of the crystal structure of 5 is reported in Figure 5.

---

**Scheme 3**

**Figure 5.** ORTEP plot of the molecular structure of 7a. Thermal ellipsoid are drawn at 30% probability level. H atoms and PF\(_6\) are omitted for clarity. Selected distances [Å] and angles [°]: C1-N1 1.252(5), C1-S1 1.739(4), C2-N2 1.263(4), C2-S2 1.747(3), N3-P1 1.616(3), N3-P2 1.623(2), N3-Pd1 2.056(2), Pd1'-N101 1.960(2), Pd1-C101 1.97(3), Pd1-S1 2.309(1), Pd1-S2 2.317(1) C101-N101 1.147(3), P1-N3-P2 133.44(15), N101-Pd1'-N3' 174.2(3), C101-Pd1-N3 172.9(4), N101-Pd1'-S1' 83.5(3), N101-Pd1'-S2' 96.0(3), C101-Pd1-S2 83.1(4), N3-Pd1-S2 89.77(7), Pd1-C101-N101 166.7(2), Pd1'-N101-C101 179.3(3) (symmetry transformation used to generate equivalent atoms: \(x' = x + 1, y, z + 1/2\)).
In the solid state, two unit of [Pd(EtSNS)] are held together by a CN bridge. The coordination around the Pd(II) atoms is the same found in 6 and displays anologues geometrical parameters. The distance C101-N101 [1.147(3)] is in line with the reported for similar complexes. In the structure a disorder is present in the CN group, and is not possible clarify which atom is coordinate to the metal centre. Note that the Pd1-C101-N101 [166.7(2)] are not co-linear, but a slight deviation are present [166.7(2)], probably due to the steric hindrance of the two units. The coordination planes (Pd1-S1-S2-N3-N101 and Pd1’-S1’-S2’-N3’-C101) of the two unit lie in the same plane and no torsions are present.

In order to obtain novel cyano bridge with different metals, the reaction of 6 with a cationic Rh(I) precursor affords the quantitatively formation of {[Rh(cod)][PdEtSNS(µ-CN)]_2}OTf (8) (Scheme 3). Any attempt to obtain single crystals failed. In the FTIR spectrum a not negligible shift of the CN stretching frequency was observed and indicating the formation of 8 (2130 cm\(^{-1}\) for 6, 2165 cm\(^{-1}\) for 8). The \(^{31}\)P{\(^1\)H} NMR spectrum of the reacting solution shown the decay of the intensity of the chemical shift of 6 at 24.7 pppm accompanied by the formation of a new peak at 29.4 ppm assigned to the eteronuclear compound 8.

5.3.4 Synthesis and characterization of methyl and acetyl complexes

The reaction of HEtSNS with [Pd(CH\(_3\)Cl(cod)\)] in the presence of 1 equivalent of t-BuOK in dichloromethane solution afforded compound [Pd(CH\(_3\))(EtSNS)] (9) as reddish powder in good yield (Scheme 4).

In \(^1\)H NMR spectrum a characteristic signal at 0.54 ppm of methyl palladium is presented. The molecular structure of 9 was confirmed by single-crystal X-ray structure anaysis. A view of its molecular structure is depicted in Figure 6.
Figure 6. ORTEP plot of the molecular structure of 9. Thermal ellipsoid are drawn at 30% probability level. H atoms are omitted for clarity.

Selected distances [Å] and angles [°]: P1-N1 1.6039(13), P1-C1 1.825(3), C1-S1 1.731(3), C1-N2 1.266(4), S1-Pd1 2.3107(9), C16-Pd1 2.178(3), N1-Pd1 2.140(3), P1-N1-P1’ 136.4(2), P1-N1-Pd1 111.8(1), N1-Pd1-S1 89.572(19), N1-Pd1-C16 180.0(1), S1-Pd1-C16 90.428(19), S1-Pd1-S1’ 179.14(4) (symmetry transformation used to generate equivalent atoms: x+1, y, z+1/2).

In the solid state of 9, the palladium atom adopts a square-planar geometry. Ligand coordinated by means of S,N,S atoms as in the other complexes described before and methyl group completed the coordination around the palladium atom. In addition, complex 9 has a crystallographically imposed C$_2$ simmetry, that implies the magnetic equivalence of phosphorus atoms, as confirmed by the presence in $^{31}$P{$^1$H} NMR spectrum of a singlet at 14.1 ppm.

On bubbling CO for a few minutes at 60 Atm through THF solution of complex 9 no palladium black was formed and [Pd(COCH$_3$)(EtSNS)] (10) was obtained as red powder after precipitation with n-pentane (Scheme 4). Red crystals of 9 were achieved. Its structure is depicted in Figure 7.
The CO insertion is demonstrated by $^1$H NMR spectroscopy; the disappearance of the Pd-CH$_3$ signal of 9 is followed by a new singlet at 2.36 ppm. This value is typical for an acetyl group $\sigma$ bonded to Pd. The formation of acetyl complex 10 is also confirmed by $^{31}$P {$^1$H} NMR. The singlet of 9 is replaced by a singlet at 12.98 ppm. In FTIR-HATR spectrum is presented the vCO stretching frequency of the acetyl group at 1689 cm$^{-1}$.

In solid state, 9 is coordinated in $S,N,S$-$\kappa^3$ coordination fashion. The square planar coordination around the metal is completed by the acetyl group. The plane of acetyl group is tilted by ca. 83° with respect to the mean plane (Pd1-S1-N3-S2) of the complex. This value is in agreement as found in Cambridge Structural Database (from 68° to 90°).

### 5.4 Conclusions

This chapter gave further insight into the coordination chemistry of the zwitterionic ligand HRSNS, in particular with respect to the Pd(II) atom. Novel zwitterionic metallate are obtained and are fully characterized.
5.5 References


5. Zwitterionic Metallates of Pd(II)


Enchainment Cooperativity Effects in Neutrally Charged Bimetallic Nickel (II) Phenoxyiminato Polymerization Catalysts, and Enhanced Selectivity for Polar Comonomer Enchainment

The synthesis and characterization of the bimetallic 2,7-di-[2,6-diisopropylphenyl]imino]1,8-naphthalenediolato group 10 metal polymerization catalysts \{[\text{Ni}(\text{CH}_3)]_2[1,8-(\text{O})_2\text{C}_6\text{H}_4-2,7-{\text{CH}}=\text{N}(2,6-^1\text{Pr}_2\text{C}_6\text{H}_3)](\text{PMe}_3)_2\} \text{([FI}^2\text{-Ni}_2\text{-A])} \) and \{[\text{Ni}(\text{Naphthyl})]_2[1,8-(\text{O})_2\text{C}_6\text{H}_4-2,7-{\text{CH}}=\text{N}(2,6-^1\text{Pr}_2\text{C}_6\text{H}_3)](\text{PPh}_3)_2\} \text{([FI}^2\text{-Ni}_2\text{-B])}\) are presented, along with the synthesis and characterization of the mononuclear analogues \{[\text{Ni}(\text{CH}_3)][3-^3\text{Bu}-2-(\text{O})\text{C}_6\text{H}_4\text{CH}=\text{N}(2,6-^1\text{Pr}_2\text{C}_6\text{H}_3)](\text{PMe}_3)\}_2 \text{([FI}-\text{Ni}-\text{A])} \) and \{[\text{Ni}(\text{Naphthyl})][3-^3\text{Bu}-2-(\text{O})\text{C}_6\text{H}_4\text{CH}=\text{N}(2,6-^1\text{Pr}_2\text{C}_6\text{H}_3)](\text{PPh}_3)\}_2 \text{([FI}-\text{Ni}-\text{B])}\). Monometallic Ni catalysts were also prepared by functionalizing one ligation center of the bimetallic ligand with a trimethylsilyl group (TMS), yielding \{[\text{Ni}(\text{CH}_3)][1,8-(\text{O})_2\text{TMS}-\text{O})\text{C}_6\text{H}_4-2,7-{\text{CH}}=\text{N}(2,6-^1\text{Pr}_2\text{C}_6\text{H}_3)](\text{PMe}_3)\}_2 \text{([TMS-FI}^2\text{-Ni}-\text{(PMe}_3)\text{])}\). The \text{FI}^2\text{-Ni}_2\text{ catalysts exhibit significant increases in ethylene homopolymerization activity versus the monometallic analogues, as well as increased branching and methyl branch selectivity, even in the absence of a [Ni(cod)]_2 cocatalyst. Increasing ethylene concentrations significantly suppresses branching and branch morphology. \text{FI}^2\text{-Ni}_2\text{-mediated copolymerizations with ethylene + polar-functionalized norbornenes exhibit a four-fold increase in comonomer incorporation versus FI}-\text{Ni}, yielding copolymers with up to 10% norbornene copolymer incorporation. \text{FI}^2\text{-Ni}_2\text{-catalyzed copolymerizations with ethylene + methacrylate or methyl methacrylate incorporate up to 11% acrylate comonomer, while the corresponding mononuclear FI}-\text{Ni} catalysts incorporate negligible amounts. Furthermore, the \text{FI}^2\text{-Ni}_2\text{-mediated polymerizations exhibit appreciable polar solvent tolerance, turning over in the presence of ethyl ether, acetone, and even water. The mechanism by which the present cooperative effects take place is investigated, as is the nature of the copolymer microstructures produced.
6.1 Introduction

Over the past few years much research attention has focused on discovering more efficient and selective homogeneous catalytic processes made possible by cooperative effects between proximate active centers in multinuclear metal complexes.\cite{1} In some cases, these complexes mimic the capabilities of enzymes in enforcing conformational control and preorganization to promote selectivity.\cite{1} Research from this laboratory in the field of single-site\cite{2} bimetallic olefin polymerization catalysis has shown that in group 4 constrained geometry\cite{3,4} and aryloxyiminato\cite{5} catalytic systems, exhibit increased activity, branch formation and comonomer enchainment versus their mononuclear analogues (Chart 1).

Chart 1. Group 4 Mononuclear and Bimetallic Olefin Polymerization Catalysts

The origin of these effects is proposed to include non-negligible comonomer secondary binding to weakly basic groups on the olefin which modifies relative chain transfer rates and facilitates comonomer enchainment at the second, proximate metal center, as shown in A.\cite{4,5} An excellent example of this is observed in polystyrene homopolymerizations with the binuclear CGC catalysts\cite{4} (II).
Here binuclear cooperative Ti···arene interactions significantly enhance styrene homopolymerization rates, modify enchainment regioselectivity, and greatly increase comonomer enchainment selectivity (e.g., B).\textsuperscript{[4]} The group 4 studies indicate that the degree of cooperativity between the two catalytic centers in these catalysts scales roughly inversely with intermetallic distance.\textsuperscript{[6]}

Although very high olefin polymerization and copolymerization activities can be achieved with the group 4 catalysts, be it \textit{via} the CGC ligation or otherwise, the electrophilicity of these metal centers greatly depresses their activity in the presence of polar comonomers or solvents. Desirable properties arising from the incorporation of polar functionalities into polyolefins include precise control over polymer characteristics such as mechanical toughness, rheology, and surface functionalization properties,\textsuperscript{[7]} while the ability of the catalyst to withstand polar solvents allows bypassing the need for rigorous drying of polymerization solvent. In order to develop single-site catalysts capable of achieving these properties, our attention turned from the oxophilic group 4 metals towards catalyst systems with more electron-rich catalyst centers, such as the group 10 metals. The cationic and neutrally-charged group 10 systems pioneered by Brookhart, Johnson and Ittel\textsuperscript{[8,9]} (Chart 2, C and D) demonstrated that coordinative enchainment of polar monomers such as acrylates is indeed possible in highly branched polyethylenes or polypropylenes, where the enchained acrylate units cap the branch ends.

\textbf{Chart 2.} Ni(II) Mononuclear Olefin Polymerization Catalysts
Contemporaneously, Grubbs et al\(^{[10,11]}\) demonstrated that neutrally-charged Ni catalytic system E mediates ethylene copolymerization with functionalized norbornenes while producing very highly branched polymers. Controlled branching in polyolefins is desirable to depress the glass transition and melting temperatures, thus enhancing processability.\(^{[8-12]}\) Also of note is that the group 10 catalysts are active in the presence of polar solvent additives, with only minor reductions in activity,\(^{[11]}\) bypassing the need for hyperpurification of polymerization media. Although polar comonomers can be introduced into polyolefins via radical and other polymerization methods, single-site catalysts offer the attraction of greater control over polymer microstructure, polydispersity, and tunability of comonomer content.\(^{[8-13]}\) The ability to effect these polymerizations via a coordinative/insertive pathway instead of the typically used free-radical processes also circumvents the need for expensive reactors and extremely high pressures. The above Ni catalyst systems are capable of introducing over 50 branches /1000 C into the polymer chain, yielding polymers with lower melting points than those produced by their group 4 counterparts, although typically with lower molecular weight. The group 10 systems typically incorporate 2-4 mol % of functionalized and non-functionalized norbornenes, further depressing the melting point and serving as an interesting starting point for determining what comonomers can be incorporated and to what extent.

The above results raise the intriguing question of whether the advantageous characteristics of binuclear polymerization catalysts (Chart 1) might be applied to group 10 catalytic systems. Attraction includes the possibility of modifying polymerization rates and selectivities while enhancing selectivity for monomers having basic substituents, as in structures A and B, above, and tolerance to polar media, which is not possible for the group 4 catalysts. A group 10 binuclear catalyst would also allow probing the full scope of the bimetallic cooperativity effects first demonstrated with the aforementioned group 4 catalysts by providing a broader spectrum of polymerization conditions and monomers to be explored.

We recently communicated\(^{[14]}\) the synthesis of binuclear phenoxyiminato Ni(II) catalysts [FI²-Ni₂-A] and [FI²-Ni₂-B] in which the rigid ligation ensures that the metal centers are bound in close spatial proximity (Chart 3).
In initial ethylene homopolymerizations mimicking the reaction conditions of the previous monometallic group 10 work,\textsuperscript{[10,11]} the \textit{FI}_2-Ni\textsubscript{2} systems exhibited a doubling in catalytic activity for ethylene homopolymerizations and introduced significantly more alkyl branches than the mononuclear \textit{FI} catalysts, and exhibited a strong selectivity for methyl-only branch formation (>99%). Intriguing preliminary binuclear copolymerization effects were observed with norbornene, including a four-fold increase of enchainment selectivity over the monometallic catalyst. In the present contribution, we present a detailed study of \textit{FI}_2-Ni\textsubscript{2} synthetic, solid-state and solution structural, and olefin polymerization catalytic chemistry. Using the monometallic Ni analogues as controls, we show that: 1) Ethylene homopolymerizations in the presence of the \textit{FI}_2-Ni\textsubscript{2} exhibit significantly increased activity to produce different product microstructures than the mononuclear \textit{FI}-Ni catalysts. 2) This enhanced activity is maintained in the presence of polar cosolvents, while concurrently retaining the selectivity for large branch densities. 3) Substantial cooperativity effects operate in the \textit{FI}_2-Ni\textsubscript{2}-mediated copolymerizations of ethylene with functionalized norbornenes, and 4) Ethylene copolymerizations with normally unresponsive acrylate esters achieve up to 11% comonomer incorporation in reactions catalyzed by \textit{FI}_2-Ni\textsubscript{2}, versus negligible enchainment by \textit{FI}-Ni catalysts. As supported by structural, in situ NMR spectroscopic, and product polymer microstructure studies, these results are in accord with strong Ni⋯Ni mediated cooperative effects in the enchainment process.

Recent complimentary binuclear group 10 catalyst studies by Hu, \textit{et al}\textsuperscript{[15b]} (Chart 4, F) and Mecking, \textit{et al}\textsuperscript{[15c]} (Chart 4, G), report enhancements in non-cocatalyzed polymerization
activity vis-à-vis the mononuclear analogues as well as differences in polyolefin microstructure. The degree to which these observations reflect cooperative effects is not obvious, especially in view of the ligand conformational flexibility and/or the sizable metal-metal distances. [15]

Chart 4. Ni(II) Binuclear Olefin Polymerization Catalysts

6.2 Experimental

6.2.1 General procedures.

All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high-vacuum line (10^{-5} Torr), or in a nitrogen-filled Vacuum Atmospheres glove box with a high capacity recirculator (<1 ppm O_2). Argon and ethylene (Matheson, polymerization grade) were purified by passage through a supported MnO oxygen-removal column and an activated Davison 4A molecular sieve column. Ether solvents were purified by distillation from Na/K alloy/benzophenone ketyl. Hydrocarbon solvents (n-pentane and toluene) were dried using activated alumina columns according to the method described by Grubbs,[16] and were additionally vacuum-transferred from Na/K alloy immediately before vacuum line manipulations. All solvents for high-vacuum line manipulations were stored \textit{in vacuo} over Na/K alloy in Teflon-valve sealed bulbs. Deuterated solvents were obtained from Cambridge Isotope Laboratories (all ≥ 99 atom %D), were freeze pump-thaw degassed, dried over Na/K alloy and were stored in resealable flasks. Other non-halogenated solvents were dried over Na/K alloy, and halogenated solvents were distilled from CaH_2 and stored over
activated Davison 4A molecular sieves. The reagents $\text{trans-}[\text{Ni(CH}_3\text{)}\text{Cl(PMe}_3\text{)}_2]$,[17] $\text{trans-}[\text{Ni(Naphtyl)}\text{Cl(PPH}_3\text{)}_2]$ (Naphtyl = C$_{10}$H$_7$),[18] 2,7-di(2,6-diisopropylphenyl)imino-1,8-dihydroxynaphthalene,$^{[5,14]}$ salicylaldimine and salicylaldiminate sodium salt$^{[10,11]}$ were prepared according to literature procedures. $\text{[Ni(cod)}_2$] (cod = 1,5-cyclooctadiene) was purchased from Aldrich.

6.2.2 Physical and Analytical Measurements.

NMR spectra were recorded on Bruker AVANCEIII (FT, 600 MHz, $^1$H; 150 MHz $^{13}$C), Varian $^{\text{UNITY}}$Inova-500 (FT, 500 MHz, $^1$H; 125 MHz, $^{13}$C), $^{\text{UNITY}}$Inova-400 (FT, 400 MHz, $^1$H; 100 MHz, $^{13}$C) and Mercury-400 (FT 400 MHz, $^1$H; 100 MHz, $^{13}$C; 162 MHz, $^{31}$P). Chemical shifts ($\delta$) for $^{1}$H and $^{13}$C spectra were referenced using internal solvent resonances and are reported relative to tetramethylsilane. Chemical shifts ($\delta$) for $^{31}$P spectra were reported relative to an external 85% H$_3$PO$_4$ standard. NMR experiments on air-sensitive samples were conducted in Teflon valve-sealed sample tubes (J.Young). Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana. $^1$H and $^{13}$C NMR spectra of polymers were collected in either 1,1,2,2-tetrachloroethane-$d_2$ at 130°C and CDCl$_3$ at 25°C at 400 or 600 MHz, as specified in each spectrum. In ethylene polymerizations, spectral assignments were made as described in the literature,$^{[19]}$ with extra care taken to ensure that peak widths of the methyl branch signal are representative of the true branch density. In copolymerizations, the additional product resonances were assigned to the corresponding comonomer functional groups as determined by the literature.$^{[13,19]}$ In each of the copolymerizations, $^{13}$C NMR integration of the comonomer resonances versus those in the PE backbone was used to determine the density of incorporation. Signals were assigned according to the literature for the polyethylene part.$^{[19]}$ FTIR spectra were collected on a Bio-Rad FTS spectrophotometer (KBr pellet). Melting temperatures of polymers were measured by DSC (DSC 2920, TA Instruments, Inc.) from the second scan with a heating rate of 10 °C/min. GPC-RI measurements were performed on a Polymer Laboratories PL-GPC 220 instrument using 1,2,4-trichlorobenzene solvent (stabilized with 125 ppm BHT) at 150 °C. A set of three PLgel 10 µm mixed columns was used. Samples were prepared at 160 °C. GPC-UV measurements were performed on a Waters GPC 484 instrument using chloroform at 35 °C using two linear 500 X 10mm columns. Molecular weights determined by GPC used narrow polystyrene standards and are not corrected. NMR, DSC, GPC-RI and GPC-UV measurements were
performed as explained above, on both product copolymers and on control physical mixtures of the corresponding homopolymers.

6.2.3 X-Ray crystallography.
The intensity data of $[\text{FF}_2\text{Ni}-(\text{OPMe}_3)]_2(\text{OPMe}_3)$ was collected at 173 K on a Bruker AXS Smart 1000 single crystal diffractometer equipped with an area detector using a graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Crystallographic and experimental details of the structures are summarized in Table 1. An empirical absorption correction were applied to the data. The structure was solved by direct methods and refined by full-matrix least-squares procedures (based on $F_o^2$) first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms.

Table 1. Crystallographic data and structure refinement details for $[\text{FF}_2\text{Ni}-(\text{OPMe}_3)]_2(\text{OPMe}_3)$.

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6.2.4 Synthesis of 2,7-Di-[(2,6-diisopropylphenyl)imino]-1,8-naphthalenediolate disodium salt (1).

To a solution of 2,7-di(2,6-diisopropylphenyl)imino-1,8-dihydroxynaphthalene (1.0g, 1.87 mmol) in THF dry (30 mL) was added NaH (0.224, 9.35 mmol). The resulting mixture was
stirred at 25°C for 1 h, filtered, and the filtrate evaporated. The yellow residue was washed with pentane (30 mL) and dried in vacuo. This product was immediately used without further purification for the synthesis of Ni complexes. Yield, 83%. 1H NMR (CDCl₃, 25°C, 500 MHz): δ = 8.13 (s, 2H, HC=N), 7.53-6.75 (m, 10H, Ph) 3.07 (sept, 4H, 3JHH = 6.8 Hz, CHMe₂), 1.34 (s, 12H, CHMe₂) ppm.

6.2.5 Synthesis of \( \text{[Ni(CH₃)]}_2 [1,8-(O)_2C_{10}H_4] [2,7-[CH=N(2,6-iPr₂C₆H₃)](PMe₃)₂] \) (\( \text{[FF²-Ni₂-A]} \)).

A solution of 1 (0.900 g, 1.55 mmol) in Et₂O (25 mL) was added dropwise at 25°C to a stirring solution of \( \text{trans-[Ni(CH₃)Cl(PMe₃)₂]} \) (0.815 g, 3.12 mmol) in benzene (25 mL). A rapid color change from yellow to dark red was observed, and after 1 h the mixture became dark orange. After this time, the reaction mixture was filtered by cannula. The volatiles were then removed from the filtrate in vacuo and the residue was washed with pentane. A light orange powder of \( \text{[Ni(CH₃)]}_2 [1,8-(O)_2C_{10}H_4] [2,7-[CH=N(2,6-iPr₂C₆H₃)](PMe₃)₂] \) (\( \text{[FF²-Ni₂-A]} \)) was obtained. Yield, 73%. 1H NMR (C₆D₆, 25°C, 500 MHz): δ = 7.65 (d, 3JHH = 8.0 Hz, 2H, HC=N), 7.13-6.43 (m, 10H, Ph), 4.13 (sept, 2H, 3JHH = 6.5 Hz, CHMe₂), 3.73 (sept, 2H, 3JHH = 6.5 Hz, 6H, CHMe₂), 1.56 (d, 3JHH = 6.5 Hz, 6H, CHMe₂), 1.08 (d, 3JHH = 6.5 Hz, 6H, CHMe₂), 0.95 (d, 3JHH = 9.5 Hz, 18H, PMe₃), -1.15 (d, 3JHH = 7.3 Hz, 6H, NiMe) ppm. 13C NMR (C₆D₆, 25°C, 125 MHz): δ = 170.33, 163.93, 150.17, 145.26, 141.96, 133.50, 125.96, 123.91, 123.02, 115.97, 113.51, 28.47, 24.45, 14.15, -12.23 ppm. 31P NMR (C₆D₆, 25°C, 162 MHz): δ = -7.58 ppm. Anal. Found: C, 63.12; H, 7.71; N, 3.29. Calcd. for C₄₄H₆₆N₂₂O₂P₂: C, 63.49; H, 7.75; N, 3.37.

6.2.6 Synthesis of \( \text{[Ni(CH₃)]}_2 [1,8-(O)_2C_{10}H_4] [2,7-[CH=N(2,6-iPr₂C₆H₃)](PPh₃)₂] \) (\( \text{[FF²-Ni₂-B]} \)).

A solution of 1 (0.800 g, 1.38 mmol) in Et₂O (25 mL) was added dropwise at 25°C to a stirring solution of \( \text{trans-[Ni(Naph)Cl(PPh₃)₂]} \) (2.06 g, 2.76 mmol) in benzene (25 mL). A rapid color change from yellow to dark pink was observed, and after 2 h the mixture became dark purple. After this time, the reaction mixture was filtered by cannula. The volatiles were next removed in vacuo from the filtrate and the residue was washed with pentane. Compound \( \text{[Ni(CH₃)]}_2 [1,8-(O)_2C_{10}H_4] [2,7-[CH=N(2,6-iPr₂C₆H₃)](PPh₃)₂] \) (\( \text{[FF²-Ni₂-B]} \)) was isolated as a
purple powder. Yield, 74%. ^1^H-NMR (C^6^D^6^, 25°C, 500 MHz): δ = 11.07 (d, ^3^J^PH_ = 14.0 Hz, 2H, Naph-H), 10.16 (d, ^4^J^PH_ = 8.0 Hz, 2H, Naph-H), 8.90 (d, ^4^J^PH_ = 8.0 Hz, 2H, Naph-H), 7.88 (d, ^4^J^PH_ = 6.6 Hz, 2H, HC=N), 7.53-6.24 (m, 48H, Ph), 3.09 (sept, 2H, ^3^J^HH_ = 6.9 Hz, CHMe^2_2_), 1.22 (d, ^3^J^HH_ = 6.9 Hz, 6H, CHMe^2_2_). ^1^3^C NMR (C^6^D^6^, 25°C, 125 MHz): δ = 177.47, 159.34, 152.28, 144.14, 140.62, 137.41, 134.14, 130.37, 129.91, 123.86, 122.50, 118.79, 113.20, 28.08, 22.96 ppm. ^3^1^P NMR (C^6^D^6^, 25°C, 162 MHz): δ = 33.2 ppm. Anal. Found: C, 77.16; H, 6.01; N, 2.11. Calcd. for C_{92}H_{86}Ni_{10}O_{32}P_{2}: C, 77.33; H, 5.92; N, 1.96.

6.2.6 Synthesis of {Ni(Naph)[1,8-(O)(TMS-O)C_{10}H_{2}-2,7-\{CH=N(2,6-^4^Pr_{2}C_6H_3)\](PPh^3_)} ([TMS-F^2^1^Ni-(PPh^3_)]).

A solution of 1 (0.800 g, 1.38 mmol) in Et_2O (25 mL) was added dropwise at rt to a stirring solution of trans-[Ni(Naph)Cl(PPh^3_)] (1.03 g, 1.38 mmol) in benzene (25 mL). A rapid color change from yellow to dark pink was observed, and after 2 h the mixture became dark red. After this time, 1 equivalent of trimethylsilane was added to react with the second Na^+ site. The reaction mixture was then filtered by cannula. The volatiles were next removed from the filtrate in vacuo from the filtrate and the residue was washed with pentane. A red powder of {Ni(Naph)[1,8-(O)(TMS-O)C_{10}H_{2}-2,7-\{CH=N(2,6-^4^Pr_{2}C_6H_3)\](PPh^3_)} ([TMS-F^2^1^Ni-(PPh^3_)])) was obtained. Yield, 78%. ^1^H NMR (CDCl^3_, 25°C, 500 MHz): δ = 11.07 (d, ^4^J^PH_ = 14.0 Hz, 1H, Naph-H), 10.16 (d, ^5^J^PH_ = 8.0 Hz, 1H, Naph-H), 8.90 (d, ^4^J^PH_ = 8.0 Hz, 2H, Naph-H) 8.13-8.22 (d, 2H, HC=N), 7.53-6.75 (m, 30H, Ph) 3.07 (m, 4H, ^3^J^HH_ = 6.8 Hz, CHMe^2_2_), 1.34 (s, 12H, CHMe^2_2_), 0.04 (s, 9H, SiMe^3_). ppm. ^3^1^PNMR (C^6^D^6^, 25°C, 162 MHz): δ = 31.0. Anal. Found: C, 75.16; H, 5.98; N, 2.96. Calcd. for C_{92}H_{86}Ni_{10}O_{32}P_{2}Si: C, 75.16; H, 5.99; N, 2.97.

6.2.7 Synthesis of {Ni(CH^3)[3-^4^Bu-2-(O)C_{6}H_{5}CH=N(2,6-^4^Pr_{2}C_{6}H_{3})](PMe)^3_)} ([FI-Ni-A]).

A solution of the appropriate salicylaldiminate sodium salt (0.400 g, 1.11 mmol) in Et_2O (30 mL) was added dropwise at 25°C to a solution of trans-[Ni(CH^3)Cl(PMe)^3_)] (0.290 g, 1.11 mmol) in Et_2O (25 mL). The orange mixture was stirred for 2 h at 25°C. After this time, the reaction mixture was filtered by cannula. The filtrate was then evaporated in vacuo and the solid residue was washed with pentane. A yellow-orange micrscristalline powder of {Ni(CH^3)[3-^4^Bu-2-(O)C_{6}H_{5}CH=N(2,6-^4^Pr_{2}C_{6}H_{3})](PMe)^3_)} ([FI-Ni-B]) was obtained. Yield, 74%. ^1^H NMR (C^6^D^6^, 25°C, 500 MHz): δ = 7.84 (d, ^4^J^PH_ = 8.8 Hz, 1H, HC=N), 7.42-6.56 (m,

6H, Ph), 3.96 (sept, 1H, J_{HH} = 6.7 Hz, CHMe), 1.51 (s, 9H, CMe), 1.32 (d, J_{HH} = 6.7 Hz, 6H, CHMe), 0.97 (d, J_{HH} = 6.7 Hz, 6H, CHMe), 0.95 (d, J_{HH} = 9.1 Hz, 9H, PMe), -1.10 (d, J_{HH} = 7 Hz, 3H, NiMe) ppm. \(^{13}\)C NMR (C\(_6\)D\(_6\), 25°C, 125 MHz): \(\delta = 166.25, 149.49, 141.45, 140.62, 133.69, 126.22, 123.45, 120.19, 34.67, 30.02, 28.45, 24.45, 21.43 ppm. \(^{31}\)P NMR (C\(_6\)D\(_6\), 25°C, 162 MHz): \(\delta = -12.57 \) ppm. Anal. Found: C, 66.53; H, 8.63; N, 2.91. Calcd. for C\(_{27}\)H\(_{42}\)NNiOP: C, 66.69; H, 8.71; N, 2.88.

6.2.8 Synthesis of \([\text{Ni(Naphtyl)][3-Bu-2-(O)C}_6\text{H}_7\text{CH}=\text{N}(2,6-\text{Pr}_2\text{C}_6\text{H}_3)\](PPh\(_3\))) \((\text{FI-Ni-B})\)

A solution of the appropriate salicylaldiminate sodium salt (0.500 g, 1.39 mmol) in benzene (30 mL) was added dropwise at 25°C to a stirring solution of trans-[Ni(Naphtyl)Cl(PPh\(_3\))] (1.037 g, 1.39 mmol) in benzene (25 mL). The orange mixture was stirred for 2 h at 25°C. After this time, the reaction mixture was filtered by cannula filtration. The filtrate was then evaporated in vacuo and the solid residue was washed with ethanol. A yellow-orange microcrystalline powder of \([\text{Ni(Naphtyl)][3-Bu-2-(O)C}_6\text{H}_7\text{CH}=\text{N}(2,6-\text{Pr}_2\text{C}_6\text{H}_3)\](PPh\(_3\))) \((\text{FI-Ni-B})\) was obtained. Yield, 75%. \(^{1}\)H NMR (C\(_6\)D\(_6\), 25°C, 500 MHz): \(\delta = 10.47 \) (d, J\(_{HH} = 8.8 \) Hz, 1H, NiC-CH\(_{\text{para}}\) )), 7.96 (d, J\(_{HH} = 8.8 \) Hz 1H, H,C=N), 7.69-6.55 (m, 24H, Ph), 5.56 (sept, 1H, J\(_{HH} = 6.5 \) Hz, CHMe), 2.98 (sept, 1H, J\(_{HH} = 6.5 \) Hz, CHMe), 1.68 (d, J\(_{HH} = 6.6 \) Hz, 3H, CHMe), 1.10 (d, J\(_{HH} = 6.6 \) Hz, 3H, CHMe), 0.90 (s, 9H, CMe), 0.85 (d, J\(_{HH} = 6.6 \) Hz, 3H, CHMe), -0.07 (d, J\(_{HH} = 6.6 \) Hz, 3H, CHMe) ppm. \(^{13}\)C NMR (C\(_6\)D\(_6\), 25°C, 125 MHz): \(\delta = 167.11, 165.13, 150.59, 141.56, 140.51, 136.42, 134.82, 133.42, 132.16, 131.73, 129.55, 127.51, 125.79, 123.71, 122.18, 121.56, 120.70, 114.20, 34.67, 30.02, 28.45, 24.45, 21.43 ppm. \(^{31}\)P NMR (C\(_6\)D\(_6\), 25°C, 162 MHz): \(\delta = 24.21 \) ppm. Anal. Found: C, 77.78; H, 6.81; N, 1.86. Calcd. for C\(_{51}\)H\(_{82}\)NNiOP: C, 78.07; H, 6.86; N, 1.79.

6.2.9 Synthesis of \([\text{Ni}(n\text{-butyl})]_2[1,8-(O)C_10H_{12}-2,7-[\text{CH}=\text{N}(2,6-\text{Pr}_2\text{C}_6\text{H}_3)]\](PPh\(_3\))] \((\text{FF-Ni}_2\text{-(n-butyl)}_2)\) and in situ NMR studies.

One equivalent of a solution of 1 in benzene (30 mL) was added dropwise at -78°C to a stirring solution of trans-[NiCl\(_2\)(PPh\(_3\))] in benzene (25 mL). After stirring for 4 h, two equivalents of n-BuLi (2.5M) was added dropwise and allowed to stir at -78°C for an additional 4 h. The resulting salt is filtered off via cannula and the thermally unstable dinickel complex is dried via evaporation at 0°C. The dinickel complex is loaded into an NMR tube along with two equivalents of [Ni(cod)] and dissolved in \(d_6\)-toluene. Due to the instability of
the complex, the NMR is cooled to -80°C beforehand. Spectra are collected on a Varian
UNITY Inova-400 (FT, 400 MHz, $^1$H; 100 MHz, $^{13}$C) at -80°C, -60°C, -40°C, and -20°C to
monitor the presence of any agostic interactions.

6.2.10 General procedure for Ethylene Polymerization by Ni complexes.
A 200 mL glass pressure vessel (dried in 120°C oven overnight prior to use) was equipped
with a large magnetic stirbar, and was heated to the required temperature by oil bath, with the
temperature monitored by thermocouple. At no time was the temperature allowed to deviate
more than 2°C. Next, 25 mL of toluene was injected via syringe into the reactor and the
reactor was pressurized with ethylene to 1.0 atm. For trias without cocatalyst, 20 µmol of
catalyst solution was then injected and the pressure brought to 7.0 atm for 2 h with rapid
stirring. For cocatalyst-activated trials, a solution of 10 µmol of catalyst in [Ni(cod)$_2$] was
injected, after which the pressure was increased to 7.0 atm and rapid stirring maintained for
40 min. After the desired run time, the reactor was vented, and the reaction mixture was
quenched with 10% HCl in ethanol. The precipitated polymer was stirred overnight, collected
by filtration, and dried under vacuum at 80°C overnight.

6.2.11 General procedure for Ethylene Polymerization by Ni complexes in Polar Solvents.
A 200 mL glass pressure vessel (dried in 120°C oven overnight prior to use) was equipped
with a large magnetic stirbar and heated to the required temperature by oil bath. Next, 25 mL
of toluene was injected into the reactor along with 1500 eq. of the desired rigorously degassed
polar solvent additive. The reactor was then pressurized with ethylene to 1.0 atm. 10 µmol of
catalyst solution was then injected and the pressure brought to 7.0 atm for 1 h with rapid
stirring. After the desired run time, the reactor was vented, and the reaction mixture was
quenched with 10% HCl in ethanol. The precipitated polymer was stirred overnight, collected
by filtration, and dried under vacuum at 80°C overnight.

6.2.12 General procedure for Ethylene Co-polymerization by Ni complexes with Acrylates or
Functionalized Norbornenes.
A 200 mL glass pressure vessel (dried in 120°C oven overnight prior to use) was equipped
with a large magnetic stirbar and heated to the required temperature by oil bath. Next, 25 mL
of toluene was injected via syringe into the reactor along with 225 eq. of the desired polar
comonomer. The reactor was then pressurized with ethylene to 1.0 atm. 20 µmol of catalyst solution was then injected and the pressure brought to 7.0 atm for 1.5 h with rapid stirring. After the desired run time, the reactor was vented, and the reaction mixture was quenched with 10% HCl in ethanol. The precipitated polymer was stirred overnight, collected by filtration, and dried under vacuum at 80°C overnight.

6.3 Results

The goal of this study was to explore the scope and mechanism of Ni center- Ni center cooperative enchainment effects in polymerizations mediated by binuclear $\text{FI}^2\text{-Ni}_2$-derived catalysts. This included defining the scope of this cooperativity in ethylene homopolymerizations and in ethylene copolymerizations with polar functionalized norbornenes and acrylates. Here rigorous copolymer microstructure analysis is carried out to differentiate copolymers from mixtures of the corresponding homopolymers. Ethylene homopolymerizations were also carried out in the presence of polar additives to assess the stability of the binuclear cooperativity effects in the presence of coordinating and protic media. Finally, the pathway by which this cooperativity takes place is explored by means of product polymer microstructure analysis, and structural characterization of the catalytic species in the solid state and in solution via in situ low temperature NMR studies.

6.3.1 Synthesis and Characterization of Bimetallic Catalysts

The sodium salt of ligand $\text{FI}^2\text{-H}_2$ was obtained by treating 2,7-di(2,6-diisopropylphenyl)imino-1,8-dihydroxy-naphthalene with NaH in THF. The bimetallic catalysts $\text{FI}^2\text{Ni}_2\text{-A}$ and $\text{FI}^2\text{Ni}_2\text{-B}$ were then prepared as shown in Scheme 1. All new compounds were characterized by standard analytical and spectroscopic techniques. The imine protons in the $\text{FI}^2\text{Ni}_2\text{-A}$ $^1\text{H}$ NMR spectrum exhibit a characteristic $J_{\text{PH}} \approx 9$ Hz, corresponding to PMe$_3$ coordination trans to the ketimine (confirmed by $^1\text{H}$ NOESY and $^1\text{H}$ COSY). Close proximity of the Ni-CH$_3$ group and the methyls of one iPr group is also detected in the NOESY spectrum. In contrast, $J_{\text{PH}} \approx 6$ Hz and the $^1\text{H}$ NOESY spectrum indicate cis-PPh$_3$ binding in $\text{FI}^2\text{Ni}_2\text{-B}$. The $^1\text{H}$-decoupled $^3\text{P}$ singlets in both complexes are consistent with the proposed $\text{FI}^2\text{Ni}_2\text{-A}$ and $\text{FI}^2\text{Ni}_2\text{-B}$ symmetries. Upon standing at elevated
temperatures (≥35 °C), the presence of free phosphine is also detected in the $^{31}$P NMR along with a dimeric phosphine-free complex (see more below). For polymerization control experiments, mononuclear complexes FI-Ni-A and FI-Ni-B were synthesized via reaction of the corresponding mono-salicylalldiminate sodium salt$^{[10,11]}$ with the aforementioned Ni(II) precursors. A monometallic control complex with one Ni site replaced by a bulky TMS group was prepared by reaction of 1.0 equiv. of the Ni(II) precursor with the disodium salt of FI$^2$-H$_2$, followed by addition of TMS-Cl in situ to yield [TMS-FI$^2$-Ni-(PPh$_3$)] (Scheme 1).

Scheme 1. Synthesis of binuclear FI$^2$-Ni$_2$-A, FI$^2$-Ni$_2$-B and mononuclear FI$^2$(TMS)-Ni catalysts.

Stepwise Ni incorporation can be monitored by integration of the now inequivalent $i$-propyl and imine $^1$H NMR resonances. This monometallic complex was designed to probe the nature and extent of Ni···Ni cooperativity effects on polymerization and to verify that the effects observed are not the result of simple steric crowding, but are due to the presence of two active metal sites.

Any attempt to obtain single crystals of FI$^2$-Ni$_2$-A/B failed. Otherwise, bischelating complex [FI$^2$-Ni-(OPMe$_3$)]$_2$(OPMe$_3$) was achieved. The ORTEP plot of the structure of [FI$^2$-Ni-(OPMe$_3$)]$_2$ in [FI$^2$-Ni-(OPMe$_3$)]$_2$(OPMe$_3$) is depicted in Figure 2. Selected bond distances (Å) and angles (°) are given in Table 2.
Figure 1. ORTEP plot of the molecular structure of $[\text{Fl}_2^2-\text{Ni}(\text{OPMe}_3)_2](\text{OPMe}_3)$. Thermal ellipsoids are drawn at the 30 % probability level. H atoms are omitted for clarity. The OPMe$_3$ molecules are not involved in interactions with the complex are omitted for clarity. Symmetry transformation used to generate equivalent atoms: $^\prime = -x, -y, -z$.

Table 2. Selected distances [Å] and angles [°] for $[\text{Fl}_2^2-\text{Ni}(\text{OPMe}_3)_2](\text{OPMe}_3)$

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</tr>
<tr>
<td>O1-Ni1-O2</td>
<td>88.5(1)</td>
<td>N1-Ni1'-O1</td>
<td>90.4(1)</td>
</tr>
<tr>
<td>O1-Ni1-O1'</td>
<td>79.5(1)</td>
<td>N1-Ni1'-O2'</td>
<td>94.9(1)</td>
</tr>
<tr>
<td>Ni1-O1-Ni1'</td>
<td>100.5(1)</td>
<td>N1-Ni1'-O3</td>
<td>97.0(1)</td>
</tr>
<tr>
<td>O1-Ni1-O3</td>
<td>98.3(1)</td>
<td>P1-O3-Ni1</td>
<td>138.1(1)</td>
</tr>
</tbody>
</table>

The resultant dimer is catalytically inactive due to the absence of a free coordination site and is of a type well documented in the literature,$^{[8d,11a,21]}$ several of which are derived from redistribution of monometallic polymerization catalysts. Each nickel is coordinated by two Fl$_2^-$ ligands in a square-planar fashion with a trans-NO$_3$ arrangement of the donor atoms. In addition, the phenol oxygen atoms (O1 and O1’) bridge both Ni metal. The double O-bridge give rise to a Ni$_2$O$_2$ metallacycle, with interatomic Ni1···Ni1’ separation of 3.092(3) and Ni1-O1-Ni1’ angle of 100.5(1). The Ni···Ni distance is shorter than the sum of the Ni(II) atomic van der Waals radii (3.3 Å) and the chemical interaction may be considered to be
There exists an inversion center at the center of the four-membered ring formed by the two Ni atoms and the two phenolic O atoms. The Ni1-O1-Ni1’ and O1-Ni1-O1’ angles are 100.5(1) and 79.5(1), respectively. The coordination sphere of the nickel centres are completed by the oxygen atom [Ni-O3 1.982(2)] of dimethyl phosphine oxide, yielding the five-coordinate species and causing an offset binding of the ligands and a deviation in planarity of the metals, each being pulled away from the ligand plane. The Ni-O bridge distances span from 2.008(3) to 2.013(2) (Ni’-O1 and Ni-O1, respectively), while the Ni1-O2’ and Ni1’-O2 distances are 1.924(2). The Ni1-N2 and Ni1’-N2’ distances are 1.924(2). The Ni-O and the Ni-N distances in \([\text{FF}_2\text{-Ni-(OPMe}_3\text{)}]_2\) are slightly longer than those found in the bis\([(N\text{-2,6-diisopropylphenyl)salicyclaldiminate}]\text{Ni(II)}\) complex,[10,11] probably due to the steric hindrance around the metals. In the crystal, other two molecules of O=PMe_3 are presented and they are not involved in interaction with the complex.

### 6.3.2 Polymerization Experiments and Polymer Characterization. General Remarks.

All olefin polymerizations were performed as described in the Experimental Section. Polymeric products were characterized by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy, gel permeation chromatography, FT-IR spectroscopy, and differential scanning calorimetry as required. To determine the density of alkyl group branching in polyethylene homo- and copolymers, integration of the \(^1\text{H}\) NMR spectra yields the relative density of methyl and other groups versus the polymer backbone resonances.\(^{[19]}\) For other copolymerizations, the comonomer incorporation density is determined by integration of the \(^{13}\text{C}\) NMR spectra using standard procedures.\(^{[19]}\) Characterization of the ethylene + acrylate copolymerization products included NMR spectroscopy (\(^1\text{H}, ^{13}\text{C},\) and \(^1\text{H}^-\text{H}\) COSY) and DSC to differentiate copolymers from simple physical mixtures. Similarly, both the copolymers and representative physical mixtures were subjected to selective solvent extraction experiments to verify that a heterogeneous polyethylene + polyacrylate physical mixture could be cleanly separated, while a random ethylene + acrylate copolymer would remain homogeneous. Furthermore, GPC with UV detection was also performed in addition to GPC with RI detection to allow more accurate detection of acrylate containing polymers.\(^{[23]}\) Utilizing both refractive index and ultraviolet GPC detection aids in differentiating mixtures of homopolymers from acrylate-containing random copolymers.
6.3.3 Ethylene Homopolymerization Experiments.

Room temperature ethylene homopolymerizations using the present catalysts were carried out in the presence of the phosphine scavenger/cocatalyst \([\text{Ni(cod)}_2]\) under conditions minimizing mass transport and exotherm effects.\(^{3,4}\) It can be seen in Table 3 that bimetallic \(\text{FI}^2\text{-Ni}_2\text{-A}\) and \(\text{FI}^2\text{-Ni}_2\text{-B}\) catalysts afford polyethylenes with molecular weights comparable to those produced by the analogous monometallic \(\text{FI}\text{-Ni}_1\text{-A}, \text{FI}\text{-Ni}_1\text{-B},\) and \([\text{TMS-}\text{FI}^2\text{-Ni}_1\text{-}(\text{PPh}_3)]\) controls, having polydispersities consistent with single-site processes.

Table 3. Ethylene Homopolymerization Data with and without Cocatalyst Using Mono and Binuclear Ni Aryloxyiminato Catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Cocatalyst</th>
<th>Yield (g)</th>
<th>(M_w)(^a)</th>
<th>(M_m/M_n)</th>
<th>Branches/1000(^b)</th>
<th>m.p °C(^c)</th>
<th>Activity(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\text{FI}^2\text{-Ni}_2\text{-A})(^e)</td>
<td>(\text{Ni(cod)}_2)</td>
<td>0.663</td>
<td>10300</td>
<td>2.6</td>
<td>80</td>
<td>68</td>
<td>7.1</td>
</tr>
<tr>
<td>2</td>
<td>(\text{FI}\text{-Ni}_1\text{-B})(^e)</td>
<td>(\text{Ni(cod)}_2)</td>
<td>0.684</td>
<td>10100</td>
<td>2.6</td>
<td>93</td>
<td>66</td>
<td>7.4</td>
</tr>
<tr>
<td>3</td>
<td>(\text{FI}^2\text{-Ni}_2\text{-B})(^e)</td>
<td>(\text{Ni(cod)}_2)</td>
<td>0.631</td>
<td>10700</td>
<td>2.6</td>
<td>92</td>
<td>68</td>
<td>6.8</td>
</tr>
<tr>
<td>4</td>
<td>(\text{FI}^2\text{-Ni}_2\text{-B})(^e)</td>
<td>(\text{Ni(cod)}_2)</td>
<td>0.566</td>
<td>10900</td>
<td>2.6</td>
<td>86</td>
<td>68</td>
<td>6.2</td>
</tr>
<tr>
<td>5</td>
<td>(\text{FI}\text{-Ni-A})(^e)</td>
<td>(\text{Ni(cod)}_2)</td>
<td>0.167</td>
<td>11700</td>
<td>2.5</td>
<td>52</td>
<td>93</td>
<td>3.6</td>
</tr>
<tr>
<td>6</td>
<td>(\text{FI}\text{-Ni-B})(^e)</td>
<td>(\text{Ni(cod)}_2)</td>
<td>0.175</td>
<td>10500</td>
<td>2.5</td>
<td>54</td>
<td>97</td>
<td>3.7</td>
</tr>
<tr>
<td>7</td>
<td>([\text{TMS-}\text{FI}^2\text{-Ni}_1\text{-}(\text{PPh}_3)])(^e)</td>
<td>(\text{Ni(cod)}_2)</td>
<td>0.141</td>
<td>11200</td>
<td>2.6</td>
<td>40</td>
<td>98</td>
<td>3.3</td>
</tr>
<tr>
<td>8</td>
<td>(\text{FI}^2\text{-Ni}_2\text{-A})(^h)</td>
<td>-</td>
<td>0.103</td>
<td>6000</td>
<td>2.7</td>
<td>102</td>
<td>60</td>
<td>0.2</td>
</tr>
<tr>
<td>9</td>
<td>(\text{FI}^2\text{-Ni}_2\text{-B})(^h)</td>
<td>-</td>
<td>0.196</td>
<td>7000</td>
<td>2.7</td>
<td>105</td>
<td>61</td>
<td>0.4</td>
</tr>
<tr>
<td>10</td>
<td>(\text{FI}\text{-Ni-A})(^i)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>(\text{FI}\text{-Ni-B})(^i)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\)Determined by GPC vs polyethylene standards, uncorrected. \(^b\)Determined by \(^1\)H NMR. \(^c\)Melting temperature determined by DSC. \(^d\)Kg polyethylene/ (mol of Ni·h·atm). \(^e\)Polymerizations carried out with 10 µmol catalyst and 2.0 equiv. cocatalyst / Ni center at 25°C for 40 min in 25 mL toluene at 7.0 atm ethylene pressure. \(^f\)Polymerizations carried out with 10 µmol catalyst and 2.0 equiv cocatalyst / Ni at 25°C for 60 min in 25 mL toluene at 7.0 atm ethylene. \(^g\)Polymerizations carried out with 10 µmol of catalyst and 2.0 equiv cocatalyst / Ni at 25°C for 90 min in 25 mL of toluene at 7.0 atm ethylene. \(^h\)Polymerizations carried out with 20 µmol of catalyst at 25°C for 2 h in 25 mL toluene at 7.0 atm ethylene. Negligible polymer obtained.

Note however that the bimetallic catalysts exhibit an approximately two-fold greater polymerization activity along with increased methyl branch density. The branch density assayed by \(^1\)H NMR\(^{19}\) is ~ 2x that achieved by the mononuclear catalysts under identical reaction conditions, with the greater branch density also supported by depressed DSC-determined melting points. Interestingly, no branches longer than methyl are detected under these reaction conditions in the \(\text{FI}^2\text{-Ni}_2\)-mediated polymerization products. The polymerizations mediated by the PMe\(_3\) and PPh\(_3\)-containing catalysts exhibit similar activities,
regardless of the phosphine, reflecting the role of the [Ni(cod)₂] cocatalyst as an effective phosphine-abstracting “sponge”. When no cocatalyst is used in the bimetallic polymerizations, modest activity is still exhibited, presumably due to nonbonded repulsions of the proximate phosphine groups, favoring dissociation and catalyst self-activation. Not surprisingly, this effect is slightly more pronounced in the PPh₃ complex than in the PMe₃ analogue (compare Table 3, entries 8 and 9). In contrast, negligible catalytic activity is observed with the monometallic catalysts in the absence of the phosphine-abstracting cocatalyst. Attempts to conduct polymerizations with the bimetallic catalysts at higher temperatures yield negligible polyolefin product and formation of coordinatively saturated [FI₂-Ni-(OPMe₃)]₂ species, as described above. This result is reminiscent of the Ni dimers reported by Grubbs et al[11,21] and Brookhart et al[8d] for other classes of mononuclear Ni catalysts. Furthermore, variable-temperature ³¹P NMR spectroscopy was performed on the present binuclear catalyst solutions to examine the phosphine dissociation characteristics of FI₂-Ni₂-A and FI₂-Ni₂-B. On warming solutions of FI₂-Ni₂-B from 25 to 35°C, a free triphenylphosphine signal is observed at δ = 4 ppm in addition to that for FI₂-Ni₂-B, the intensity of which declines as the free PPh₃ resonance grows in. No other ³¹P resonances are observed. Furthermore, cooling the solution back to room temperature does not result in recoordination of the free phosphine to the Ni centers.

6.3.4 Ethylene Homopolymerizations at Varying Ethylene Pressure

One distinctive characteristic of the FI₂-Ni₂ catalysts is the nearly exclusive formation of methyl branches under our standard reaction conditions (7.0 atm ethylene), while significant densities of longer branching are produced in the present monometallic control experiments, as well as with monometallic catalysts investigated by other groups.[10-13,15] As has been previously shown regarding branch formation in other Ni(II)-mediated polymerization processes, the degree and length of branching obtained is highly dependent on the ethylene concentration during the polymerization,[13] a consequence of so-called “chain-walking” processes[8] (Scheme 2) in which incoming monomer activation/enchainment (k_inem) competes with β-H elimination/isomerization (k_elim).
To determine whether similar processes are operative in the present bimetallic systems, polymerizations were carried out over a range of ethylene pressures. As shown in Table 4 and Figure 3, when the ethylene pressure is increased from 3.0 atm to 5.0 to 7.0 atm, $^{13}\text{C}$ signals representative of ethyl branching are suppressed. Polymerizations carried out with the present monometallic catalysts parallel previously reported trends\[^{8d}\] in polyethylene microstructure, as do the $\text{FI}^2\text{Ni}_2$ bimetallic systems, with a direct proportionality between ethylene concentration and polymerization activity, and suppression of branch formation with increasing ethylene concentration. Note in Figure 3 the relative intensities of the signals corresponding to the $\alpha$, $\beta$, and $\gamma$ carbons proximate to a methyl branch compared to the polyethylene backbone. These results are in agreement with the pressure dependence trends observed previously by Brookhart.\[^{8d}\] Long branches are the result of the competing rates of ethylene coordination/insertion versus Ni-alkyl isomerization, where long branches are formed via multiple chain-walks prior to olefin (Scheme 2). In the case of the bimetallic catalyst systems, no more than one isomerization takes place (See Discussion section for additional remarks).
Table 4. Ethylene Homopolymerization at Varying Ethylene Pressure Using Mono and Binuclear Catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>P (atm)</th>
<th>Yield (g)</th>
<th>Activity</th>
<th>Mₐ</th>
<th>Mₐ/Mₙ</th>
<th>M.p °C</th>
<th>Branches/1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FI²-Ni₂-A</td>
<td>3.0</td>
<td>0.113</td>
<td>7.5</td>
<td>8400</td>
<td>2.4</td>
<td>52</td>
<td>107</td>
</tr>
<tr>
<td>2</td>
<td>FI-Ni-A</td>
<td>3.0</td>
<td>0.027</td>
<td>3.9</td>
<td>8200</td>
<td>2.5</td>
<td>88</td>
<td>71</td>
</tr>
<tr>
<td>3</td>
<td>FI²-Ni₂-B</td>
<td>3.0</td>
<td>0.108</td>
<td>7.2</td>
<td>8200</td>
<td>2.5</td>
<td>53</td>
<td>115</td>
</tr>
<tr>
<td>4</td>
<td>FI-Ni-B</td>
<td>3.0</td>
<td>0.022</td>
<td>3.9</td>
<td>7900</td>
<td>2.5</td>
<td>82</td>
<td>68</td>
</tr>
<tr>
<td>5</td>
<td>FI²-Ni₂-A</td>
<td>5.0</td>
<td>0.292</td>
<td>19.7</td>
<td>9200</td>
<td>2.4</td>
<td>64</td>
<td>99</td>
</tr>
<tr>
<td>6</td>
<td>FI-Ni-A</td>
<td>5.0</td>
<td>0.070</td>
<td>10.5</td>
<td>9100</td>
<td>2.6</td>
<td>92</td>
<td>62</td>
</tr>
<tr>
<td>7</td>
<td>FI²-Ni₂-B</td>
<td>5.0</td>
<td>0.286</td>
<td>19.7</td>
<td>9700</td>
<td>2.4</td>
<td>66</td>
<td>101</td>
</tr>
<tr>
<td>8</td>
<td>FI-Ni-B</td>
<td>5.0</td>
<td>0.069</td>
<td>10.0</td>
<td>9600</td>
<td>2.5</td>
<td>91</td>
<td>66</td>
</tr>
<tr>
<td>9</td>
<td>FI²-Ni₂-A</td>
<td>7.0</td>
<td>0.703</td>
<td>46.9</td>
<td>10100</td>
<td>2.6</td>
<td>68</td>
<td>80</td>
</tr>
<tr>
<td>10</td>
<td>FI-Ni-A</td>
<td>7.0</td>
<td>0.167</td>
<td>25.2</td>
<td>11700</td>
<td>2.5</td>
<td>93</td>
<td>52</td>
</tr>
<tr>
<td>11</td>
<td>FI²-Ni₂-B</td>
<td>7.0</td>
<td>0.711</td>
<td>47.6</td>
<td>10000</td>
<td>2.6</td>
<td>68</td>
<td>92</td>
</tr>
<tr>
<td>12</td>
<td>FI-Ni-B</td>
<td>7.0</td>
<td>0.175</td>
<td>25.6</td>
<td>10500</td>
<td>2.5</td>
<td>97</td>
<td>54</td>
</tr>
</tbody>
</table>

Polymerizations carried out with 10 µmol catalyst and 2 equiv cocatalyst / Ni center at 25°C for 90 min in 25 mL toluene. aKg of polyethylene/ (mol of Ni·h) Not normalized for atm to illustrate the change in activity. bDetermined by GPC vs polyethylene standard, uncorrected. cMelting temperature determined by DSC. dDetermined by ¹H NMR.

Figure 3. ¹³C NMR spectra in CDCl₃ at 100MHz of PE polymer produced by (a) monometallic catalyst FI-Ni at 7.0 atm (b) bimetallic catalyst FI²-Ni₂ at 7.0 atm, (c) 5.0 atm, and (d) 3.0 atm ethylene pressure. Note the increase in relative intensity of branches compared to the polymer backbone resonance with decreasing ethylene concentration. Spectral assignments are as indicated.
6.3.5 Ethylene Homopolymerizations in Presence of Polar Additives

Previous work has shown that in the presence of polar co-solvents such as water, the Ni (II) phenoxyiminato catalysts exhibit activity, but it is severely diminished, as are branch densities.\textsuperscript{111} In view of the bimetallic vs. monometallic catalyst enchainment selectivity differences identified above, it was of interest to investigate the polymerization characteristics of the $\text{FI}_2\text{Ni}_2$ systems versus their $\text{FI-Ni}_1$ analogues in the presence of 225 eq. of various polar additives. Thus, ethylene homopolymerizations were carried out in toluene solutions containing polar additives. As shown in Figure 4 and Table 5, polymerization activities decline in the order, toluene $>$ diethyl ether $>$ acetone $>$ water.

Table 5. Ethylene Homopolymerization Data in Presence of 5% Polar Additives with Mono and Bimetallic Ni Catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Cocatalyst</th>
<th>Polar Additive</th>
<th>Yield (g)</th>
<th>$M_n$ $^a$</th>
<th>$M_w/M_n$</th>
<th>Branches/1000C$^b$</th>
<th>m.p °C $^c$</th>
<th>Activity$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{FI}_2\text{Ni}_2\text{-A}$</td>
<td>Ni(cod)$_2$</td>
<td>Et. Ether</td>
<td>0.299</td>
<td>12700</td>
<td>5.4</td>
<td>86</td>
<td>71</td>
<td>2.2</td>
</tr>
<tr>
<td>2</td>
<td>$\text{FI}_2\text{Ni}_2\text{-B}$</td>
<td>Ni(cod)$_2$</td>
<td>Et. Ether</td>
<td>0.314</td>
<td>13200</td>
<td>5.2</td>
<td>81</td>
<td>72</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>$\text{FI-Ni}_1\text{-A}$</td>
<td>Ni(cod)$_2$</td>
<td>Et. Ether</td>
<td>0.077</td>
<td>12800</td>
<td>2.4</td>
<td>18</td>
<td>98</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>$\text{FI-Ni}_1\text{-B}$</td>
<td>Ni(cod)$_2$</td>
<td>Et. Ether</td>
<td>0.060</td>
<td>12000</td>
<td>2.4</td>
<td>13</td>
<td>98</td>
<td>0.9</td>
</tr>
<tr>
<td>5</td>
<td>$\text{FI}_2\text{Ni}_2\text{-A}$</td>
<td>Ni(cod)$_2$</td>
<td>Acetone</td>
<td>0.067</td>
<td>20200</td>
<td>5.6</td>
<td>82</td>
<td>80</td>
<td>0.5</td>
</tr>
<tr>
<td>6</td>
<td>$\text{FI}_2\text{Ni}_2\text{-B}$</td>
<td>Ni(cod)$_2$</td>
<td>Acetone</td>
<td>0.074</td>
<td>21100</td>
<td>5.8</td>
<td>90</td>
<td>78</td>
<td>0.5</td>
</tr>
<tr>
<td>7</td>
<td>$\text{FI-Ni}_1\text{-A}$</td>
<td>Ni(cod)$_2$</td>
<td>Acetone</td>
<td>0.010</td>
<td>21000</td>
<td>2.9</td>
<td>h</td>
<td>122</td>
<td>0.1</td>
</tr>
<tr>
<td>8</td>
<td>$\text{FI-Ni}_1\text{-B}$</td>
<td>Ni(cod)$_2$</td>
<td>Acetone</td>
<td>0.009</td>
<td>19100</td>
<td>2.9</td>
<td>h</td>
<td>122</td>
<td>0.1</td>
</tr>
<tr>
<td>9</td>
<td>$\text{FI}_2\text{Ni}_2\text{-A}$</td>
<td>Ni(cod)$_2$</td>
<td>Water</td>
<td>e</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>$\text{FI}_2\text{Ni}_2\text{-B}$</td>
<td>Ni(cod)$_2$</td>
<td>Water</td>
<td>0.036</td>
<td>23700</td>
<td>3.9</td>
<td>39</td>
<td>103</td>
<td>0.3</td>
</tr>
<tr>
<td>11</td>
<td>$\text{FI-Ni}_1\text{-A}$</td>
<td>Ni(cod)$_2$</td>
<td>Water</td>
<td>e</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>$\text{FI-Ni}_1\text{-B}$</td>
<td>Ni(cod)$_2$</td>
<td>Water</td>
<td>0.006</td>
<td>21800</td>
<td>3.1</td>
<td>f</td>
<td>122</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Polymerizations carried out with 10 $\mu$mol catalyst and 2.0 equiv cocatalyst / Ni center at 25°C and 1500 equiv. polar additive for 40 min in 25 mL toluene at 7.0 atm ethylene pressure. $^a$Determined by GPC vs polyethylene standards, uncorrected. $^b$Determined by $^1$H NMR. $^c$Melting temperature determined by DSC. $^d$Kg of polyethylene/ (mol of Ni·h·atm). $^e$Negligible polymer obtained. $^f$Insufficient sample.

While the polar additives significantly reduce polymerization activity, it can be seen that the binuclear catalysts remain ~ 3x more active than the mononuclear analogues and achieve far greater branch densities (~6x for Table 5 entry 2 vs. 4). Note that polymer molecular weights are greatly increased as the polarity of the co-solvent is increased, both in the case of the monometallic and bimetallic catalysts.

Figure 4. Ethylene Polymerization Activity in kg PE/mol Ni⋅h⋅atm in toluene with the Indicated Cosolvents, Mediated by Mononuclear and Binuclear Ni Phenoxyliminato Catalysts.

6.3.6 Ethylene-Norbornenes Copolymerizations

As alluded to in the introduction, previous reports\textsuperscript{[11b]} indicate that norbornene incorporation in mononuclear Ni(II)-catalyzed ethylene copolymerizations is possible but at very low levels. To investigate the comonomer enchainment selectivity of the new FI\textsuperscript{2}-Ni\textsubscript{2} catalysts, ethylene + norbornene copolymerizations were investigated with the present mono and bimetallic catalysts, using a diversity of norbornenes bearing polar substituents (Figure 5).

Figure 5. Functionalized Norbornenes Used as Comonomers for Ethylene Copolymerizations.

It is found that modest comonomer enchainment levels are achieved with the present monometallic FI-Ni\textsubscript{i} catalysts (Table 6), in accord with the results reported for comparable mononuclear catalysts systems.\textsuperscript{[11b]} In marked contrast, ethylene + norbornene copolymerizations mediated by binuclear FI\textsuperscript{2}-Ni\textsubscript{2}-A and FI\textsuperscript{2}-Ni\textsubscript{2}-B proceed with 3-4 x greater activity and with 3-4 x greater selectivity for comonomer enchainment than the FI-Ni mediated processes under identical reaction conditions. Note that product molecular weights are comparable to those in the homopolymerization experiments discussed above. Despite somewhat increased polydispersities, both FI\textsuperscript{2}-Ni\textsubscript{2}-A and FI\textsuperscript{2}-Ni\textsubscript{2}-B produce polymers with microstructures and with molecular weights similar to those of the monometallic catalysts. Attempts to carry out ethylene copolymerizations in the presence of monomer NB4 yielded
negligible polymeric product. This result likely reflects the acidity of this comonomer, since \textsuperscript{1}H NMR spectra show that the ligand has been protonated at the hydroxyl functionality.

\textbf{Table 6.} Ethylene Copolymerization Data in the Presence of Norbornene and Functionalized Norbornenes NB1-4 Using Mono- and Bimetallic Ni Phenoxyiminato Catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Comonomer</th>
<th>Yield (g)</th>
<th>M_n</th>
<th>M_w/M_n</th>
<th>Branches/1000°C</th>
<th>m.p °C</th>
<th>Activity \textsuperscript{a}</th>
<th>% Incorporation \textsuperscript{f}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FT\textsuperscript{2}-Ni\textsubscript{2}-A\textsuperscript{a}</td>
<td>NB</td>
<td>0.558</td>
<td>66400</td>
<td>5.2</td>
<td>34</td>
<td>107</td>
<td>1.3</td>
<td>9</td>
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<tr>
<td>2</td>
<td>FT\textsuperscript{2}-Ni\textsubscript{2}-B\textsuperscript{a}</td>
<td>NB</td>
<td>0.504</td>
<td>65800</td>
<td>4.5</td>
<td>38</td>
<td>106</td>
<td>1.2</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>FT-Ni-A\textsuperscript{a}</td>
<td>NB</td>
<td>0.072</td>
<td>63200</td>
<td>2.3</td>
<td>9</td>
<td>124</td>
<td>0.3</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>FT-Ni-B\textsuperscript{a}</td>
<td>NB</td>
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<td>64000</td>
<td>2.1</td>
<td>11</td>
<td>124</td>
<td>0.3</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>FT\textsuperscript{2}-Ni\textsubscript{2}-A\textsuperscript{a}</td>
<td>NB\textsubscript{1}</td>
<td>0.488</td>
<td>62600</td>
<td>4.6</td>
<td>39</td>
<td>105</td>
<td>1.2</td>
<td>8</td>
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<td>6</td>
<td>FT\textsuperscript{2}-Ni\textsubscript{2}-B\textsuperscript{a}</td>
<td>NB\textsubscript{1}</td>
<td>0.502</td>
<td>63500</td>
<td>4.8</td>
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<td>109</td>
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<td>9</td>
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<tr>
<td>7</td>
<td>FT-Ni-A\textsuperscript{a}</td>
<td>NB\textsubscript{1}</td>
<td>0.067</td>
<td>64900</td>
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<td>9</td>
<td>122</td>
<td>0.3</td>
<td>≤2</td>
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<tr>
<td>8</td>
<td>FT-Ni-B\textsuperscript{a}</td>
<td>NB\textsubscript{1}</td>
<td>0.059</td>
<td>63800</td>
<td>2.1</td>
<td>9</td>
<td>122</td>
<td>0.3</td>
<td>3</td>
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<tr>
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<td>FT\textsuperscript{2}-Ni\textsubscript{2}-A\textsuperscript{a}</td>
<td>NB\textsubscript{2}</td>
<td>0.444</td>
<td>61800</td>
<td>5.2</td>
<td>33</td>
<td>112</td>
<td>1.1</td>
<td>8</td>
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<td>10</td>
<td>FT\textsuperscript{2}-Ni\textsubscript{2}-B\textsuperscript{a}</td>
<td>NB\textsubscript{2}</td>
<td>0.450</td>
<td>67300</td>
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<td>110</td>
<td>1.1</td>
<td>8</td>
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<tr>
<td>11</td>
<td>FT-Ni-A\textsuperscript{a}</td>
<td>NB\textsubscript{2}</td>
<td>0.054</td>
<td>65400</td>
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<td>8</td>
<td>122</td>
<td>0.2</td>
<td>≤2</td>
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<tr>
<td>12</td>
<td>FT-Ni-B\textsuperscript{a}</td>
<td>NB\textsubscript{2}</td>
<td>0.058</td>
<td>62000</td>
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<td>8</td>
<td>126</td>
<td>0.3</td>
<td>2</td>
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<td>13</td>
<td>FT\textsuperscript{2}-Ni\textsubscript{2}-A\textsuperscript{a}</td>
<td>NB\textsubscript{3}</td>
<td>0.398</td>
<td>66100</td>
<td>4.4</td>
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<td>120</td>
<td>0.9</td>
<td>7</td>
</tr>
<tr>
<td>14</td>
<td>FT\textsuperscript{2}-Ni\textsubscript{2}-B\textsuperscript{a}</td>
<td>NB\textsubscript{3}</td>
<td>0.411</td>
<td>64200</td>
<td>4.6</td>
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<td>NB\textsubscript{3}</td>
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<td>64100</td>
<td>2.2</td>
<td>8</td>
<td>122</td>
<td>0.1</td>
<td>≤2</td>
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<tr>
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<td>NB\textsubscript{3}</td>
<td>0.033</td>
<td>62900</td>
<td>2.5</td>
<td>8</td>
<td>124</td>
<td>0.1</td>
<td>≤2</td>
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</tbody>
</table>

\textsuperscript{a}Polymerizations carried out with 10 µmol catalyst and 2.0 equiv. cocatalyst / Ni center at 25°C and 225 equiv. of comonomer for 60 min in 25 mL toluene at 7.0 atm ethylene pressure. \textsuperscript{b}Determined by GPC vs polyethylene standard, uncorrected. \textsuperscript{c}Determined by \textsuperscript{1}H NMR. \textsuperscript{d}Melting temperature determined by DSC. \textsuperscript{e}Kg of polyethylene/mol of Ni-h-atm. \textsuperscript{f}Molar percentage determined by \textsuperscript{13}C NMR.

### 6.3.7 Ethylene-Acrylate Copolymerizations

Up to this point, we have focused on determining whether a second catalytic center might enhance the enchainment characteristics that make neutrally charged monometallic Ni catalytic systems distinctive. However, there are also polar comonomers of interest that are only minimally responsive to the monometallic FI-Ni systems, such as methylacrylate or methyl methacrylate. It was therefore of interest to investigate the copolymerization characteristics of the present FT\textsuperscript{2}-Ni\textsubscript{2} catalysts. Thus, ethylene + methylacrylate (MA) and methylmethacrylate (MMA) copolymerizations mediated by the FT\textsuperscript{2}-Ni\textsubscript{2} and FI-Ni\textsubscript{1} catalytic systems were studied in detail. While the present monometallic catalysts co-enchain
negligible MA or MMA, as assayed by $^1$H and $^{13}$C NMR spectroscopy, the bimetallic catalysts incorporate up to 8% methyl methacrylate and up to 11% methacrylate in the polyethylene (Table 7).

**Table 7. Ethylene Copolymerizations in the Presence of Methylacrylate (MA) and Methylmethacrylate (MMA)**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst$^a$</th>
<th>Comon.</th>
<th>Yield (g)</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
<th>Br/1000$^c$</th>
<th>m.p.$^d$</th>
<th>Activity$^e$</th>
<th>% Incorp.$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FI$^2$-Ni$_2$-A</td>
<td>MMA</td>
<td>0.700</td>
<td>8000</td>
<td>1.4</td>
<td>48</td>
<td>106</td>
<td>1.7</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>FI$^2$-Ni$_2$-B</td>
<td>MMA</td>
<td>0.690</td>
<td>7900</td>
<td>1.7</td>
<td>39</td>
<td>106</td>
<td>1.6</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>FI-Ni-A</td>
<td>MMA</td>
<td>g</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>FI-Ni-B</td>
<td>MMA</td>
<td>g</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>FI$^2$-Ni$_2$-A</td>
<td>MA</td>
<td>0.722</td>
<td>6300</td>
<td>1.6</td>
<td>36</td>
<td>108</td>
<td>1.8</td>
<td>11</td>
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<tr>
<td>6</td>
<td>FI$^2$-Ni$_2$-B</td>
<td>MA</td>
<td>0.741</td>
<td>6700</td>
<td>1.7</td>
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<td>7</td>
<td>FI-Ni-A</td>
<td>MA</td>
<td>g</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>8</td>
<td>FI-Ni-B</td>
<td>MA</td>
<td>g</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>

$^a$Polymerizations carried out with 10 µmol catalyst and 2.0 equiv. cocatalyst / Ni center at 25°C and 225 equiv. of polar additive for 60 min in 25 mL toluene at 7.0 atm ethylene pressure. $^b$Determined by GPC vs polyethylene standard, uncorrected. $^c$Determined by $^1$H NMR. $^d$Melting temperature determined by DSC. $^e$Kg of polyethylene/ (mol of Ni·h·atm). $^f$Molar percentage determined by $^{13}$C NMR. $^g$Negligible polymer obtained.

In both cases, the copolymers produced yield physical and NMR characteristics similar to random ethylene-acrylate copolymers reported in the literature$^{[24,25]}$ prepared using other transition metal catalysts and/or completely different polymerization pathways (Figure 6).

![Figure 6. $^{13}$C NMR spectra at 100 MHz in CDCl$_3$ of (top) the ethylene + MMA copolymer and (bottom) ethylene + MA copolymer produced by bimetallic catalyst FI$^2$-Ni$_2$-A.](image)
In the present copolymers, the absence of significant $^{13}$C NMR resonances at $\delta = 120$ (a) and 149 (b) ppm rule out the possibility of significant methylenoate terminated branching end groups.$^{[25]}$

Therefore, essentially all of the MMA units incorporated into the copolymer are enchained in the polymer backbone. In addition, we find that the monometallic catalyst $[\text{TMS-FF}_{2}-\text{Ni}-(\text{PPh}_{3})]$ is also incapable of mediating ethylene + acrylate copolymerizations, further supporting a bimetallic enchainment pathway. All product polymer NMR spectra were assigned according to the literature for the products of cationic, monometallic Ni catalysts competent to copolymerize acrylates + ethylene, and are in complete agreement.$^{[25]}$

Additional selective extraction, GPC, and NMR experiments were conducted to establish that the products of these $\text{FF}_{2}\text{Ni}_{2}$-mediated copolymerizations are indeed random copolymers and not simple physical mixtures of polyethylene and polymethacrylate or polymethylmethacrylate. These experiments included selective extraction of the copolymers with hot dichloromethane, which dissolves commercially available MMA homopolymers ($M_w = 120,000$) but not PE ($M_w = 21,000$; Sample of Table 5, entry 6); results are shown in Figures 7 ($^{13}$C NMR) and 8 (RI-GPC), which indicate that the physically mixed homopolymers are readily separated by extraction.

These results are obtained by selective extracting 10:1 of PE:PMMA physical mixture of two homopolymers. While the homopolymers could be completely separated, in the case of the copolymer, no separation is achieved.
Figure 8. $^{13}$C NMR of at 100MHz in CDCl$_3$ of (a) the solid highly-branched PE phase and (b) the wash commercially available PMMA extract after extracting a physical mixture of the homopolymers with hot CH$_2$Cl$_2$. Note the resulting spectra show complete separation of homopolymers, as determined by the presence or absence of carbonyl resonance at 175 ppm and the PE backbone resonance at 30 ppm.

Figure 8. GPC with RI detection of (a) the residual solid PE phase and (b) the PMMA extract after extracting a physical mixture of homopolymers with hot CH$_2$Cl$_2$.

In addition to the above evidence, the monomodal traces in the RI-detected GPC (Figure 8) for the isolated pure PE phase and the pure PMMA extract, in conjunction with the NMR spectra, demonstrate that the physical mixture can be separated. To further distinguish the copolymer from its homopolymer mixture, UV detected GPC was also performed to demonstrate that the FF-Ni$_2$-derived MMA + PE copolymer is monomodal and distinct from a PMMA homopolymer. As shown in Figure 9, ethylene + acrylate copolymer (blue) is clearly monomodal and distinguishable from the PMMA homopolymer (red). DSC was also
performed on the MMA + ethylene copolymer and the same physical mixture of homopolymers.

![Figure 9. GPC with UV detection at 210 nm from polymer samples of (red) PMMA homopolymer (Mw=120,000) and (blue) FF-Ni₂⁺-derived ethylene + MMA copolymer (Entry 1, Table 7). Note the distinct retention time of each sample.](image)

As seen in Figure 10, two distinct thermal transitions are observed in the case of the physical mixture, whereas a single transition is evident for the copolymer at 108°C, in agreement with the literature.

![Figure 10. Second scan DSC of (a) physical mixture of PMMA and PE homopolymers (b) the ethylene + PMMA copolymer (Entry 1, Table 7). Note the single T_g obtained in the copolymer as opposed to the individual T_g values observed in the polymer mixture](image)

Additional copolymer characterization was carried out by IR spectroscopy. The FT-IR spectrum, shown in Figure 11 exhibit characteristic MMA ν_C=O mode at 1738 cm⁻¹ and two PE
modes at 1480 and 718 cm\(^{-1}\), corresponding to the scissoring and rocking vibrations of the ethylene co-units.\(^{[13b,26]}\)

**Figure 11.** IR spectra of the ethylene + PMMA copolymer copolymer in a KBr pellet produced by bimetallic catalyst FF-Ni\(_2\). The band at 1738 cm\(^{-1}\) corresponds to MMA and two bands at 1480 and 718 cm\(^{-1}\) correspond to a polyethylene chain.

Finally, \(^1\text{H}-\text{H} \) COSY NMR spectroscopy was performed on both homopolymers and the result compared to that on the ethylene + MMA copolymer. The PMMA homopolymer exhibits no discernable cross-peaks as expected, and the PE spectrum exhibits a single cross-peak indicating branch proton interactions with the backbone protons, as expected. In contrast, the ethylene + MMA copolymer exhibits new cross-peaks absent in the homopolymer spectra at \(\delta = 1.4\) and 1.8 ppm (Figure 12, circled), corresponding to the proximate enchained acrylate (A-CH\(_3\)) andethylene units (PE-CH\(_2\)). This crosspeak is relatively weak compared to the PE-CH\(_3\) to PE-CH\(_2\) interaction, since the copolymer is very highly branched and contains far more methyl branches than enchained acrylate units (the acrylate content is only 8%). The results of this experiment, in conjunction with the \(^{13}\text{C} \) NMR chemical shift arguments, FT-IR, and DSC data, show definitively that this material is a true random copolymer.
6.3.8 Ethylene-Acrylate Copolymerization Mechanism

With the identity of the \( \text{FI}_2\text{-Ni}_2 \)-derived ethylene + acrylate copolymers confirmed, the next question that arises regards the pathway leading to their formation. To date, the vast majority of group 10 catalysts that produce ethylene + acrylate copolymers are either cationic Ni systems proceeding via a coordinative/insertive pathway, or Pd systems which initiate via a radical pathway.\[27\] It is therefore important to establish the pathway traversed in the present bimetallic catalysts. To explore the possibility of radical pathways, \( \text{CH}_3\text{OD} \) was employed as a radical trap.\[28\] In the case of metal complex-mediated radical polymerization, it has been shown that the weaker methanol C-H bond is abstracted by radical species, whereas for ionic polymerization systems, the more acidic methanol OD is abstracted to yield deuterated acrylate monomer.\[28\] In the present case, \( \text{CH}_3\text{OD} \) (0.02 mmol) was added to a solution of \( \text{FI}_2\text{-Ni}_2\text{-B} \) (0.01 mmol), [Ni(cod)\(_2\)] (0.02 mmol), and MMA (0.04 mmol) under an ethylene atmosphere. \(^1\text{H}\) and \(^2\text{D}\) NMR spectroscopic analysis of the reaction solution shows that the
CH₃OD remains unreacted, ruling out the possibility of either predominant cationic or radical copolymerization pathways.

To further probe the nature of the of $\text{FF}^2\text{-Ni}_2$-mediated copolymerization process, ethylene and methylmethacrylate reactivity ratios were determined for the present copolymer formation process. The analysis was performed using the Mayo-Lewis equation \[^{[29]}\text{(eq. 1)}\], and compared to published reactivity ratios \[^{[30]}\]. In eq. 1, $\vartheta_m$ is the mole fraction of monomer i incorporated into the copolymer, $M_i$ is number of moles of monomer i present in the reaction solution, and $r_i$ is the reactivity ratio.

\[
\frac{\vartheta_m_1}{\vartheta_m_2} = \frac{M_1(r_1M_1 + M_2)}{M_2(r_2M_2 + M_1)}
\] (1)

Under the present polymerization reaction conditions, the radical copolymerization of ethylene + MMA should yield $r_{\text{ethylene}} = 0.2$ and $r_{\text{mma}} = 17$.\[^{[28]}\] Calculating the same $r$ values for the $\text{FF}^2\text{-Ni}_2$-mediated copolymerizations, as determined by the NMR assay, yields $r_{\text{ethylene}} = 0.34$ and $r_{\text{mma}} = 12.2$. Likewise, under the present reaction conditions, the radical copolymerization of ethylene + MA would yield an $r_{\text{ethylene}} = 0.2$ and $r_{\text{mma}} = 11$. In contrast, the $r$ values for the present $\text{FF}^2\text{-Ni}_2$-mediated copolymerizations, as determined by the NMR assay are $r_{\text{ethylene}} = 0.33$ and $r_{\text{mma}} = 12.9$. These results argue strongly against significant radical pathway contributions to product formation.

6.3.8 Low Temperature Catalyst NMR Studies

In neutral Ni aryloximinato coordinative polymerization catalysts, an agostic interaction can be identified by $^1\text{H}$ NMR at low temperatures \[^{[6d]}\] involving the vacant Ni coordination site and a $\beta$ C-H unit on the growing polymer chain (Complex R, Scheme 3). It was therefore of interest to determine whether similar interactions take place in the present bimetallic catalysts or whether the presence of a second Ni center might offer additional possibilities. To this end, low temperature $^1\text{H}$ NMR studies were undertaken on \textit{in situ} generated $\text{FI-Ni}_1$ and $\text{FF}^2\text{-Ni}_2$ alkyl derivatives. Thus, $[\text{NiCl}_2(\text{PMe}_3)_2]$ \[^{[17]}\] was reacted with the sodium salt of ligand $\text{FF}^2\text{-H}_2$, affording $[\text{FF}^2\text{-Ni}_2\text{-Cl}_2(\text{PMe}_3)_2]$ (complex K in Scheme 3). Next, $n$-butyl Grignard was used to generate the very thermally unstable Ni-alkyl species.
Scheme 3. Synthesis and Possible Agostic Interactions in Model n-Butyl Derivatives of Catalysts FI-Ni
and FI²-Ni².

This solution was rapidly transferred to a cold NMR tube containing [Ni(cod)₂] and maintained at -20°C until spectroscopic experiments could be performed. The same procedure was then used to produce an FI-Ni₁ n-butyl derivative of the mononuclear Ni catalyst. Note that instead of the n-propyl derivative originally investigated by Brookhart in mononuclear complexes,[8d] the longer n-butyl group was chosen to provide a branch more capable of simultaneously accessing both Ni sites. This is evidenced in molecular modeling[31] where a doubly-bond n-propyl chain would have an C-H···Ni bond length of ~3.5 Å at lowest energy (Figure 13a), as opposed to a C-H···Ni bond distance of ~2.8 Å in the butyl species (Figure 13b).
Figure 12. Molecular models of (a) sec-Propyl branched model compound and (b) Butyl branched model compound.

The $^1$H NMR spectrum of the FI-Ni$_i$ alkyl complex at -20°C suggests that $n$-alkyl isomerization has already taken place, similar to that observed by Brookhart, *et al*\(^{[8d]}\) for $n$-propyl complexes, yielding here complex R (Scheme 3) and exhibiting a Ni-CH resonance as a very broad singlet at $-2.2$ ppm. Lowering the temperature to -80 °C reveals a broad signal at $-9.9$ ppm, assignable to a Ni agostic species, similar to that of a previously reported example where Brookhart, *et al*\(^{[8d]}\) installed an $n$-propyl group and observed an agostic signal at $-13.9$ ppm.
At the same low temperatures, the bimetallic FI₂-Ni₂ dibutyl complex exhibits a similar agostic resonance, as shown in Figure 14. However, solely in the binuclear case is a second resonance is observed at -4.1 ppm. The ¹H-¹H COSY NMR spectrum of [FI₂-Ni₂-(n-butyl)₂] at -80°C (Figure 15) exhibits two separate alkyl chains- one chain bond to a Ni participating in no agostic interaction, and another chain participating in two agostic interactions (Scheme 3). These two alkyl chains can readily be distinguished by the localized interactions between the agostic protons at -4.1 ppm, and -9.9 ppm with the protons on the CH₂ between them, at 1.9 ppm, as well as with other proximate protons. The non-agostic chain exhibits a separate group of alkyl proton interactions within the -1.0 ÷ 1.9 ppm region, which can only be tentatively assigned.
6.4 Discussion

6.4.1 Ethylene Homopolymerizations

Comparing the ethylene homopolymerization characteristics of the monometallic FI-Ni$_1$- and [TMS-FI$_2$-Ni$_1$]-derived catalysts with the FI$_2$-Ni$_2$-derived bimetallic systems reveals significant differences which are most plausibly attributed to cooperative effects involving both Ni centers. The FI$_2$-Ni$_2$-A/B catalyst activity and product polyethylene branch density and architecture determined by $^1$H NMR$^{[19]}$ is $\sim 2x$ that achieved by the mononuclear catalysts under identical reaction conditions, and is confirmed by depressed DSC-determined melting points. As noted above, the branching in the FI$_2$-Ni$_2$-derived polyethylenes is more methyl-rich. Moreover, [TMS-FI$_2$-Ni$_1$-(PPh$_3$)] polymerization properties show both activity and polymer microstructure similar to that of the present FI-Ni and other monometallic catalysts,$^{[8-11]}$ verifying that the increased activity and methyl-rich branch density is exclusive...
to catalysts bearing a second, adjacent catalytic Ni center. Interestingly, product molecular weights and polydispersities are essentially indistinguishable for the monometallic and bimetallic polymerization systems.

In the absence of a cocatalyst, the present mononuclear systems do not produce significant polyethylene, in agreement with previous observations for similar mononuclear catalysts,[8-11] In contrast, the present bimetallic catalysts produce essentially the same polyethylenes but with increased branch densities and concurrently depressed melting points, albeit at somewhat reduced activities versus the cocatalyzed polymerizations (Table 1, entries 8-11). This particular cocatalyst-related productivity difference between FI²-Ni₂-A, FI²-Ni₂-B, and the mononuclear analogues may reflect previously reported phosphine dissociation-related steric and electronic factors.[14] Typically, equilibria between such phosphine-coordinated and uncoordinated species heavily favor the former, however the proximate bulky phosphine ligands in FI²-Ni₂-A and FI²-Ni₂-B likely favor phosphine dissociation, as indicated by both 31P NMR and x-ray diffraction results.

The distinctive ethylene homopolymerization characteristics of the FI²-Ni₂-based catalysts doubtless reflect a complex interplay of kinetics and thermodynamics. In regard to those factors underlying the relative importance of propagation and chain walking rates versus the mononuclear analogues, it is clear that any cooperative effects such as enhanced substrate binding/preorganization (e.g. structure A) as proposed for bimetallic group 4 polymerization catalysts, do not influence the overall propagation/chain transfer rate ratios in a way that significantly alters the product polyethylene Mₜ or the polydispersity. However, significant differences in product macromolecule architecture are observed, with higher branch densities and the greater selectivity for methyl branch formation in the FI²-Ni₂-mediated homopolymerizations (Tables 3,4; Figure 3) indicating that the presence of the second Ni center enhances chain walking but suppresses ethyl branch formation versus FI-Ni-mediated processes: 1) by intercepting species such as S in Scheme 4 prior to isomerization to species such as T (k_{PropagationMe}[ethylene] >> k_{EtBranch}, 2) because the equilibrium to form T is for steric and/or electronic reasons unfavorable, or 3) because (k_{PropagationEt}[ethylene] is for steric and/or electronic reasons slower than (k_{PropagationMe})[ethylene].

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From the low temperature NMR studies of \([\text{FF}^2-\text{Ni}_{2}\text{-}(n\text{-butyl})_2]\) (Figures 14, 15) implicate binuclear agnostic interactions, it is conceivable that secondary agnostic binding as in \(U\) may influence the \(\beta\)-H elimination/-readdition kinetics of the chain walking processes, while increased propagation kinetics may reflect monomer binding to the neighboring Ni center, thereby increasing local concentrations (Scheme 5).

The predominance of methyl branch formation likely suggests that the presence of the second Ni center suppresses insertion pathway 2 versus pathway 1 (Scheme 4) via the rapid switching of the ethylene monomer from one catalyst center to the other before a second chain-walk can take place, in addition to the amount of monomer coordinated from solution. When the ethylene concentration is increased, the propagation rate is greatly increased and the competing rate of chain-walking reduced, suppressing ethyl branch formation, indicating that pathway 1 takes place faster than \(\beta\)-H/rearrangement.
In both this and our previously reported work\cite{14} the FL^2-Ni$_2$-B catalysts adhere to the same trends in activity and polydispersity as the FL^2-Ni$_2$-A analogues: polymerizations exhibit comparable activities between large and small phosphine bearing complexes in all cases, except when water is added. Note also that while significant increases in activity and branching are observed for the bimetallic catalysts, the molecular weights of the polyethylene produced by the mono and binuclear systems are similar.

6.4.2 Copolymerizations with Polar Comonomers

In copolymerizations with functionalized norbornenes (Figure 5), the present mononuclear catalysts produce copolymers with relatively small levels of polar commoner incorporation, in agreement with literature results for similar mononuclear Ni(II) catalysts.\cite{8-11} In marked contrast, the bimetallic FL^2-Ni$_2$-derived catalysts exhibit 3-4x enhanced enchainment selectivities and polymerization activities (Table 6) versus the mononuclear analogues, regardless of the polar norbornene substituent, as assayed by NMR spectroscopy. Minimal influence of NB polar substituent skeletal position is observed, similar to previous reports with other mononuclear Ni(II) catalysts.\cite{11b} FL^2-Ni$_2$-A and FL^2-Ni$_2$-B enchain significant quantities of polar-functionalized norbornene (7-9%) while simultaneously maintaining high methyl branch densities (~ 8-10 x the level of the mononuclear catalysts) in the oligoethylene blocks. This is likely due to rapid re-insertion of the growing polymer onto the second metal site after it has undergone elimination by the first.

In the case of ethylene copolymerizations with methylacrylate or methylnmethacrylate as comonomers, the present monometallic Ni(II) catalysts are incapable of significant comonomer co-enchainment. However, in the case of the bimetallic FL^2-Ni$_2$-derived systems, 8-11% incorporation is achieved as determined by NMR spectroscopic assay. As expected from the ethylene homopolymerizations, once again the [TMS-FL^2-Ni$_2$-(PPh$_3$)$_2$] exhibits reduced activity and minimal polar comonomer enchainment, similar to that of the conventional monometallic phenoxyiminate systems. To explain selectivity for co-enchainment of a previously unresponsive comonomer, we consider the insertion pathway and its potential modification when two metal centers are in close proximity. It has been proposed\cite{25} that acrylate enchainment in the mononickel polymerization systems is impeded by the formation of a relatively stable/inert six-membered resting state that occupies the
otherwise vacant Ni site used for subsequent ethylene binding/insertion (Scheme 2, Figure 16a).

![Scheme 2](image)

**Figure 16.** Proposed Resting States of Mono and Binuclear Catalysts After Acrylate Insertion

Interestingly, it was recently argued that in the case of styrene polymerizations with monometallic organotitanium CGC catalysts,[3,4] an analogous “back-biting” occurs, in which a styreneic arene group binds to the cationic metal catalytic center and effectively blocks the monomer (Structure B). However, in the case of bimetallic CGC Ti$_2$ catalytic systems, the styrene $\pi$-system is proposed to be pulled away from one Ti center by the second, proximate Ti, resulting in far greater monomer access, enhanced propagation rate and altered insertion regiochemistry.[3] We therefore suggest that an analogous process is operative in the present bimetallic group 10 systems, wherein a second catalytic site ‘peels’ the acrylate away from the insertion site and thereby facilitates macromolecule propagation subsequent to acrylate activation/enchainment (Figure 16B). The wide array of characterization techniques applied confirm that the resulting copolymer is a genuine random copolymer rather than a physical mixture of the homopolymers. The copolymer can differentiated from a physical admixture by DSC, GPC, FT-IR, and selective extraction. Furthermore, $^1$H-$^1$H COSY NMR experiments evidence distinctive spin-spin interactions within the copolymer structure, not present in the homopolymers, corresponding to neighboring enchained acrylate and ethylene units, seen in Figure 11 as cross-peaks at $\delta = 1.8$ and $1.4$ ppm. Note that polymerizations activities are reduced approximately four-fold in copolymerizations of acrylate with ethylene compared to ethylene homopolymerizations under the same reaction conditions. While the present density of acrylate incorporation is by no means the highest possible for all transition metal catalysts capable of producing PE + acrylate copolymers under all polymerization conditions,[25] it is the highest, to our knowledge, of all neutrally-charged catalytically systems.

**6.4.3 Bimetallic Influence on Olefin Polymerization Pathways**
The pathway by which the present bimetallic catalyst olefin enchainment cooperativity effects take place is the central interest in this investigation: What is the nature of the catalytic interaction between the two Ni centers? Radical trapping via CH₃OD was performed to test for radical polymerization pathways, as alternatives to a coordinative polymerization process. The deuterated methanol probe argues that no significant concentrations of radical species are present. However, since radical traps can potentially modify the catalyst under investigation influence subsequent polymerization pathways, ethylene + acrylate reactivity ratios were also analyzed for the FI²-Ni₂-mediated copolymerizations. For a radical polymerization process the ethylene + MMA reactivity ratios under the present reaction conditions should be approximately: \( r_{\text{ethylene}} = 0.2 \) and \( r_{\text{MMA}} = 17 \) whereas values for FI²-Ni₂-mediated copolymerizations are: \( r_{\text{ethylene}} = 0.34 \) and \( r_{\text{MMA}} = 12.2 \). For ethylene and MA, a radical copolymerization mechanism would give: \( r_{\text{ethylene}} = 0.2 \) and \( r_{\text{MA}} = 11 \) whereas the measured values for the present copolymerizations are: \( r_{\text{ethylene}} = 0.33 \) and \( r_{\text{MA}} = 12.9 \). In fact, solving for the incorporation ratio (\( \delta m_{\text{ethylene}} / \delta m_{\text{MMA}} \)) in the Mayo-Lewis equation for a radical process yields an ethylene/MMA incorporation ratio of 1.7 under the present conditions. Because the moles of monomer incorporated into the copolymer is known, solving for the expected MMA incorporation were this a radical process under the same reaction conditions yields a predicted MMA incorporation level of over 30 mol%, a value in large excess of that observed in the present copolymer, 9 mol%.

Low temperature \(^1\text{H}\) and 2D NMR spectroscopy of the thermally labile \([\text{FI}^2\text{-Ni}_2\text{(n-butyl)}_2]\) derivative provides evidence for an agostic species at \( \delta = -9.9 \) ppm. However, a second agostic interaction is observed in the bimetallic complex at \( \delta = -4.2 \) ppm (Figure 14). The exclusivity of this peak to the bimetallic system suggests a second agostic interaction of an alkyl coordinated to one Ni communicating with a second Ni, suggested to be H₃, the \( \gamma \)-proton of a sec-Bu ligand (Scheme 3, Figure 14). Furthermore, the methyl branch signal at \( \delta = 1.9 \) ppm remains unchanged with temperature, while the protons corresponding to those on the \( \beta \) and \( \gamma \) carbons are both shifted slightly upfield and decrease in intensity as temperature is decreased. This observation, in conjunction with the exclusivity of the second peak to the bimetallic complex, also rules out the possibility of an equilibrium between species such as V and W, as this would also be present in the mononuclear complex NMR spectrum.
Instead we confirm that the secondary agostic interaction involves a proton from the terminal carbon of the alkyl chain. Warming the NMR tube results in complete degradation of the complex by -10 °C. Furthermore, low temperature $^1$H-$^1$H COSY NMR (Figure 15) shows definitively that one Ni-alkyl group has no agostic interactions, while another has agostic protons occupying both of the open coordination sites provided by the metal centers. Thus, the agostic proton on the $\gamma$ C shows a cross peak with the protons on the $\beta$ carbon and with no other. The $\beta$ agostic proton shows two cross peaks, one with the adjacent $\alpha$ C-H at $\delta = -1.6$ ppm and the other with $\gamma$ C-H at $\delta = 1.5$ ppm. The intensity of these crosspeaks suggest that this secondary agostic interaction ($H_b$) is somewhat weaker than that of the primary agostic interaction ($H_a$), possibly because of the increased degree of rotational freedom at the end of the sec-butyl chain. These experiments provide strong evidence that the vacant coordination site provided by the second Ni center during polymerizations is structurally/mechanistically communicating with the growing polymer on the first, and that this interaction is crucial for the reported increases polymerization activity and comonomer enchainment selectivity.

6.5 Conclusion

The synthesis and characterization of two structurally rigid, neutrally charged bimetallic phenoxyiminato Ni(II) polymerization catalysts and their monometallic analogues is presented. The bimetallic catalysts evidence significant active center-active center cooperative effects in ethylene homopolymerization versus their mononuclear analogues. This cooperativity reflects that a rigid ligation environment that binds the Ni centers in close enough proximity. Evidence for the Ni⋯Ni communication includes agostic interactions which span both metal centers. Cooperative bimetallic catalytic interactions are associated with the doubling of the ethylene homopolymerization activity, as well as an increased polar
comonomer enchainment selectivity for functionalized norbornenes (4x) and for acrylates (≈10-100x). The selectivity of the bimetallic systems for incorporating higher densities of comonomer, as well as their significantly higher oligo/polyethylene branch content, affords substantially altered polymer microstructures, with lowered melting points and greater solubility. Furthermore, the bimetallic catalysts exhibit significantly higher activities than the monometallic catalysts in the presence of polar solvents, while concurrently achieving higher molecular weights and branch densities. This feature permits using less rigorously dried media for polymerization while preserving the desired product microstructure. Mechanistic studies confirm that, as in the monometallic species,\textsuperscript{[8-11]} polymerizations follow a coordinative insertion process, with enhanced monomer enchainment facilitated by the second catalytic center.

The point of greatest interest here is not the polymerization activities or levels of incorporation alone. It is instead that the cooperativity between group 10 catalytic centers, as shown with the present model complexes, affording both substantial enhancements in the catalyst/polymer properties that make the monometallic analogs of interest, while also expanding the scope of polymerizations possible.

6. 6 References


Appendix
Appendix 1

A study on the coordinative versatility of the zwitterionic $S,N,S$ ligand $\text{EtNHC(S)Ph}_2\text{P=NPPh}_2\text{C(S)NEt}$ in its anionic, neutral and cationic forms. Determination of absolute $pK_a$ values in $\text{CH}_2\text{Cl}_2$ of $\text{Rh}^1$ complexes.

Figure S1. In situ $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction $[\text{Rh(cod)}_2\text{Cl}]_2 + 2\text{HEtSNS}$ in $\text{CDCl}_3$.

Figure S2. ORTEP plot of the molecular structure of $5$. Thermal ellipsoid are drawn at 30% probability level.
Figure S3. UV-Visible spectra (300-600 nm) of [Rh(CO)(EtSNS)] (C_{Rh} = 1x10^{-3} M, \lambda_{\text{max}} = 397 nm).

Figure S4. UV-Visible spectra (300-600 nm) of [Rh(CO)(H_{2}EtSNS)]OTf (C_{Rh} = 1x10^{-3} M, \lambda_{\text{max}} = 517 nm).

Figure S5. UV-Visible spectra (300-600 nm) of [Rh(CO)(H_{2}EtSNS)](OTf)_{2} (C_{Rh} = 1x10^{-3} M, \lambda_{\text{max}} = 467 nm).
Table S1. Mulliken populations in gas phase and solution (PCM, CH₂Cl₂) for 1, 2 and 3. Only the relevant atoms are reported. For compound 2, the protonation is on the atom N1 [B3LYP/BS-I/B3LYP/BS-I; BS-I = 6-31g** + DGDZVP (Rh)]

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Figure S1. CP-MAS $^{13}$C NMR of 1.

CP-MAS $^{13}$C NMR: $\delta = 189.8$ (d, $^1J_{C,Rh} = 80.5$ Hz, CO), 178.5 (d, $^1J_{C,P} = 151$ Hz, C=N), 136.0-123.4 (m, Ph), 50.4 (s, -CH₂CH₃), 17.0 (s, -CH₂CH₃) ppm.
Figure S2. CP-MAS $^{13}$C NMR of 4.

Figure S3. Superimposed FTIR spectra in CH$_2$Cl$_2$ solution of 2-PF$_6$ + CH$_3$I. (* = possible isomer of 5-PF$_6$)
Figure S4. Superimposed FTIR spectra in CH$_2$Cl$_2$ solution of 2-NO$_3$ + CH$_3$I. (* = possible isomer of 5-NO$_3$)

Figure S5. Superimposed FTIR spectra in CH$_2$Cl$_2$ solution of 2-OTf + CH$_3$I at the beginning (1992 cm$^{-1}$) and at the end (1712 cm$^{-1}$) of the reaction.
Figure S6. $^{31}\text{P}^{1\text{H}}$ NMR spectrum of the reaction of 2-OTf + CH$_3$I in CD$_2$Cl$_2$ after 2 hours.

Figure S7. $^{31}\text{P}^{1\text{H}}$ NMR spectrum of the reaction of 2-OTf + CH$_3$I in CD$_2$Cl$_2$ after 2 days; * corresponds to unidentified decomposition products.
Figure S8. Linearized Eyring plot [log (k/T) vs. 1/T] for the reaction of 1 with CH₃I

Table S2. Second-order rate constants for the reaction 2·PF₆ + CH₃I at different temperatures (standard deviations are given in parentheses). The corresponding least-square sample standard deviations (σ) are also reported.

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*σ = [Σ (Iᵢ° - Iᵢ)²/(n - m)]¹/², where Iᵢ°, Iᵢ are the observed and calculated integral values, i is the number of the spectrum, n is the number of observations and m is the number of parameters refined.
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Vorrei prima di tutto ringraziare i miei genitori per avermi aiutato spiritualmente, ma soprattutto economicamente in questi anni. Questo lavoro è dedicato a voi.

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