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Review

Coordination properties of the multifunctional *S*,*N*,*S* zwitterionic ligand $EtNHC(S)Ph_2P{=}NPPh_2C(S)NEt$

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Dedicated to our friend Fausto Calderazzo for his extraordinary scientific career on the occasion of his 80th birthday.

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ABSTRACT

The reaction of trialkylphoshanes and amino-phosphanes with isothiocyanates yields adducts containing the zwitterionic thioamidyl-phosphonium $P^+C(S)N^-$ functional group. Ligands containing this group were not previously studied, probably due to their instability towards dissociation, in the presence of metal species able to coordinate the P atom. The ligand $EtNHC(S)Ph_2P{=}NPPh_2C(S)NEt$ (HEtSNS) was obtained by reaction of $Ph_2PNHPPh_2$ with ethylisothiocyanate and proved to be very versatile: it can be protonated giving cation H_2EtSNS^+ and deprotonated forming the dianion–cation $EtSNS^-$. HEtSNS and its derivatives behave as ligands showing five possible coordination fashions, *S*,*N*,*S* tridentate and *S*,*S*-bidentate (with a bite-angle varying from 180° to 90°), *S*-monodentate, *S*,*S* bridging and *N*,*N*,*N* interaction. Here we describe the coordination chemistry of HEtSNS, in particular towards Rh, Cu, Ag and Au, and some properties of its complexes which are still the only examples containing the $P^+C(S)N^-$ zwitterionic group.

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1. Introduction

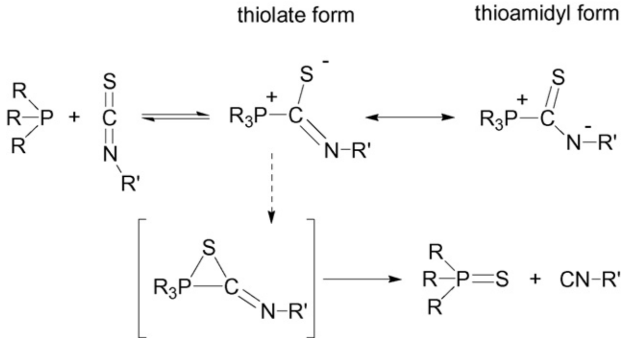
The nucleophilic addition of amines, phosphanes and aminophosphanes to heterocumulenes, such as CO_2, CS_2, COS, RNCS and RNCO (R = alkyl, aryl) allows the preparation of molecules which are extensively studied in coordination chemistry. Among the most common, substituted ureas, carbamates, thioureas, thio- and dithiocarbamates can be respectively prepared from amines and isocyanates, CO_2, isothiocyanates, COS and CS_2. When the reacting amine or phosphane contains a mobile hydrogen atom, a formally non-polar molecule is formed; when tertiary phosphanes are used, zwitterionic molecules can be obtained, as exemplified for RNCS and CS_2 in Scheme 1.

In particular, the reaction of trialkyl phosphanes with CS_2 [1] is known since the 1860s and the reaction of Et_3P with EtNCS was proposed as a route to obtain ethyl isocyanide [2]. The transfer of a sulfur atom from the NCS group to the phosphorus is responsible for the formation of the corresponding phosphano-sulfide, $Et_3P{=}S$, and EtNC. In this reaction the zwitterionic intermediate is formed, in turn decomposing in R_3PS and RNC (Scheme 2), possibly proceeding through the formation of a three-membered C–P–S non-zwitterionic ring [3], which however was never isolated in such reactions. Three-membered C–P–S rings can be found in other but scarce compounds [4].

Few examples of adducts, obtained by reacting phosphanes and isothiocyanates, can be found in the literature. This reaction is started by a nucleophilic attack of the phosphorus atom on the carbon of the heterocumulene group and reaches an equilibrium depending on R, R′, solvent and temperature. A polar solvent and an electron-withdrawing group on the isothiocyanate can shift the equilibrium completely to the right [5]. Data reported in the literature indicate that not only alkyl-substituted phosphanes but also phosphanoamines, $[(R_2N)_xR_{3-x}]P$, which contain P–N bonds, can react with isothiocyanates and form stable zwitterionic products. Dipolar compounds obtained from phoshano-amines were first characterized by Engels and Dahl [6]. The higher nucleophilic character of the P atom in these reagents is due to the N lone pair delocalization, identified for instance in the solid state structure of $Ph_2PNHPPh_2$ (dppa) by the planarity of the P–NH–P system [7]. As a consequence, triphenylphosphane does not react with EtNCS, because of its lower nucleophilicity.

2. Reaction of $Ph_2PNHPPh_2$ with RNCS

We were interested in studying the reaction of $Ph_2PNHPPh_2$ with RNCS, in order to prepare zwitterionic potential ligands. This reaction was investigated, yielding different products (compounds **1**-**4**, Scheme 6), depending on the R group, the dppa to RNCS ratio, the solvent and the temperature [8]. The first addition of dppa to RNCS, followed by a proton shift, gives intermediate A which was not observed by routine techniques (NMR, FTIR) and is not isolable (Scheme 3).



Scheme 2. Adduct formation and decomposition.

Nevertheless, intermediate A was found coordinated in its deprotonated form, originating from fragmentation of **1** (*vide infra*). Intermediate A can react with another molecule of RNCS giving **1** (Scheme 4) or with another molecule of A yielding compound **3** (Scheme 5).

When **1** and **3** are heated, compounds **2** and **4** are obtained respectively, forming a P═S group due to the loss of one molecule of RNC (Scheme 6). The proposed mechanism is illustrated in Scheme 2. For R = Ph this transformation happens at room temperature.

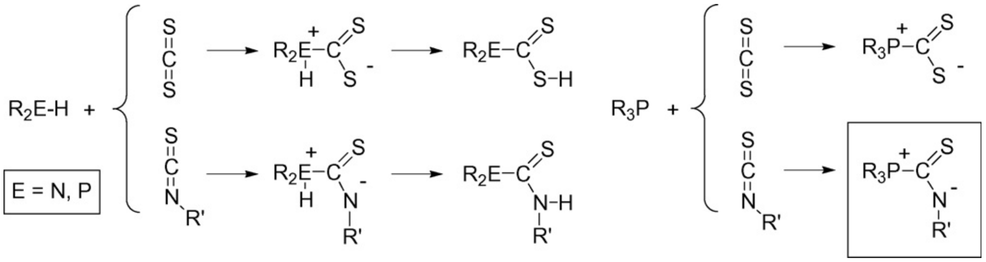
As expected, compounds **3** and **4** are obtained in higher yield when the dppa to RNCS ratio is one. Nevertheless, intermediate A can preferentially react with another molecule of A if the carbon atom of the C═S group is more electrophilic with respect to the carbon atom of the isothiocyanate. This is the case when R is electron-withdrawing as in R = *p*-$NO_2(C_6H_4)$ [8] and *p*-$Cl(C_6H_4)$ (unpublished results) as observed experimentally. With these two groups, compound **3** is formed in quantitative yield, also in the presence of a strong excess of RNCS.

When R = Ph, transformation of **1** to **2** is achieved at room temperature while, when R = Et, CH_3 or Pr, the loss of RNC is complete only at higher temperature (boiling ethanol). This different behavior is probably due to the higher stability of the thiolate form of the zwitterion, due to the conjugation of the CN double bond with the phenyl ring (Scheme 7).

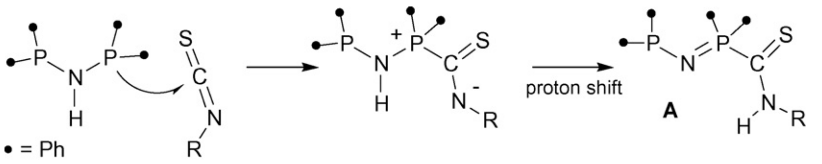
As said before, when R is electron-withdrawing, the zwitterionic compound **3** is formed and is very stable towards transformation in **4**, due to stabilization of the negative charge on the N atom (thioamidyl form), by resonance (Scheme 8) in the case of R = *p*-$NO_2(C_6H_4)$ or induction when R = *p*-$Cl(C_6H_4)$.

2.1. Properties of HEtSNS

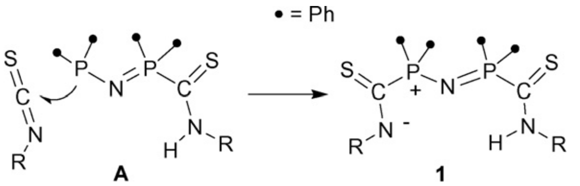
We will describe in particular the chemistry of $EtNHC(S)Ph_2P{=}NPPh_2C(S)NEt$ (HEtSNS), which is the compound easiest to obtain in the series HRSNS. Ligand HEtSNS can be prepared in quantitative yield when EtNCS is used neat, as a solvent for $Ph_2PNHPPh_2$ [9]. Opposite charges are *formally*



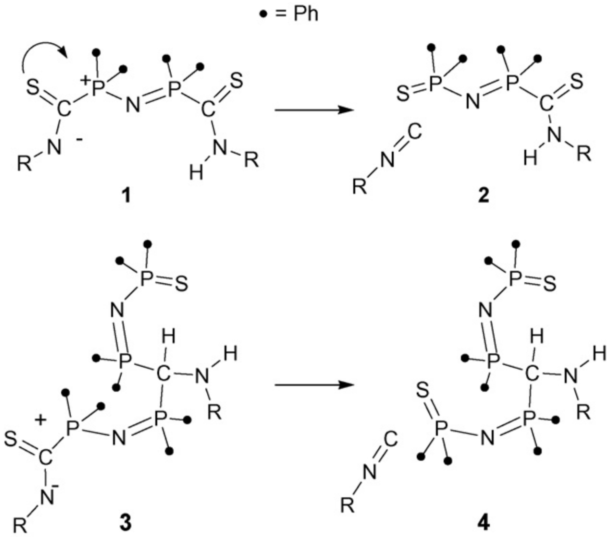
Scheme 1. General reactivity of amines and phosphanes towards CS_2 and RNCS (R = alkyl, aryl).



Scheme 3. First step of the nucleophilic addition of dppa to RNCS.



Scheme 4. Second step of the formation of compound **1**.



Scheme 6. Transformation of **1** to **2** and **3** to **4** upon loss of RNC.

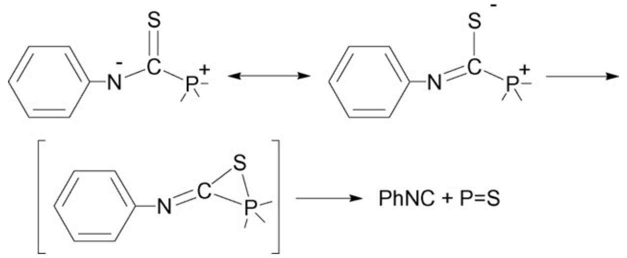
located on the zwitterionic thioamidyl-phosphonium, $N^{-}C(S)P^{+}$, functional group. In solution, a rapid proton exchange between the thioamidic–thioamidyl functions is present, facilitated by the formation of a intramolecular N–H···N hydrogen bonding, as found in the solid state structure (Fig. 1). The positive charge should be distributed by resonance in the P–N–P system and the negative one should be delocalized on the two EtNC(S) groups. No theoretical investigation of the charge distribution in HEtSNS was performed. In solution, the two P atoms have the same resonance in the ^{31}P NMR spectrum (8.4 ppm) while, in the solid state, they are not equivalent, two singlets are found at 8.1 ppm (thioamidic) and 2.6 ppm (thioamidyl), suggesting that the electronic resonance on the PNP system is due to the proton exchange.

HEtSNS can be protonated by strong HX acids (X = Cl, I, PF_6, BF_4, HSO_4, NO_3, etc.) to cationic H_2EtSNS^+, or deprotonated, using a strong base, such as NaH, yielding the dianion–cation $EtSNS^-$ (Scheme 9).

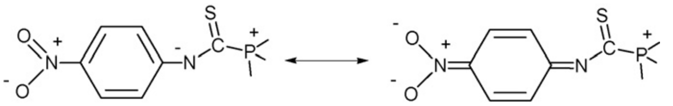
The structures of HEtSNS, $H_2EtSNS(PF_6)$ and NaEtSNS are depicted in Fig. 1. In $(H_2EtSNS)PF_6$, differently from HEtSNS, the PNP system is coplanar with the two thioamidic groups, showing a narrower P–N–P angle, due to a bifurcated hydrogen bonding involving the two NH groups and the N atom of the P–N–P system. NaEtSNS crystallized as a hydrated dimeric salt $[Na(EtSNS)H_2O]_2$ each Na^+ cation interacts with the three nitrogen atoms of $EtSNS^-$ and with the oxygen atom of a water molecule. The two NaEtSNS units are connected by S···Na interactions. Noteworthy, S-bridged complexes of alkaline metals are far less common than their oxygen-containing counterparts [10].

3. Zwitterionic complexes

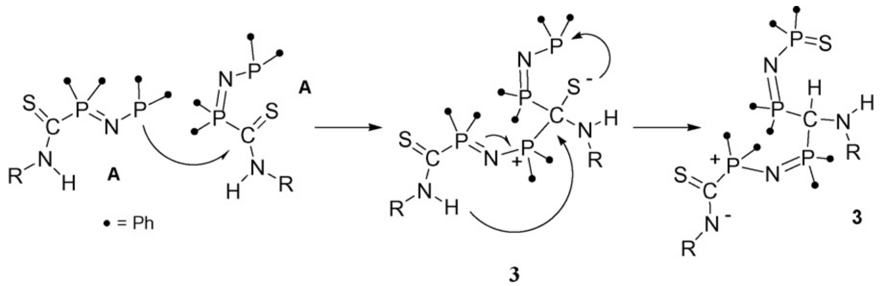
Zwitterionic metal complexes need a more detailed description than the simple IUPAC definition of zwitterion: neutral compound having formal unit electrical charges of opposite sign. They



Scheme 7. A phenyl group stabilizes by conjugation the resonance form with a C=N bond and a negative charge on the S atom, inducing the decomposition of the NC(S)P group.



Scheme 8. The para-nitro phenyl group stabilizes by resonance the negative charge on the N atom, increasing the thermal stability of the NC(S)P group.



Scheme 5. Reaction steps for the formation of compound **3**.

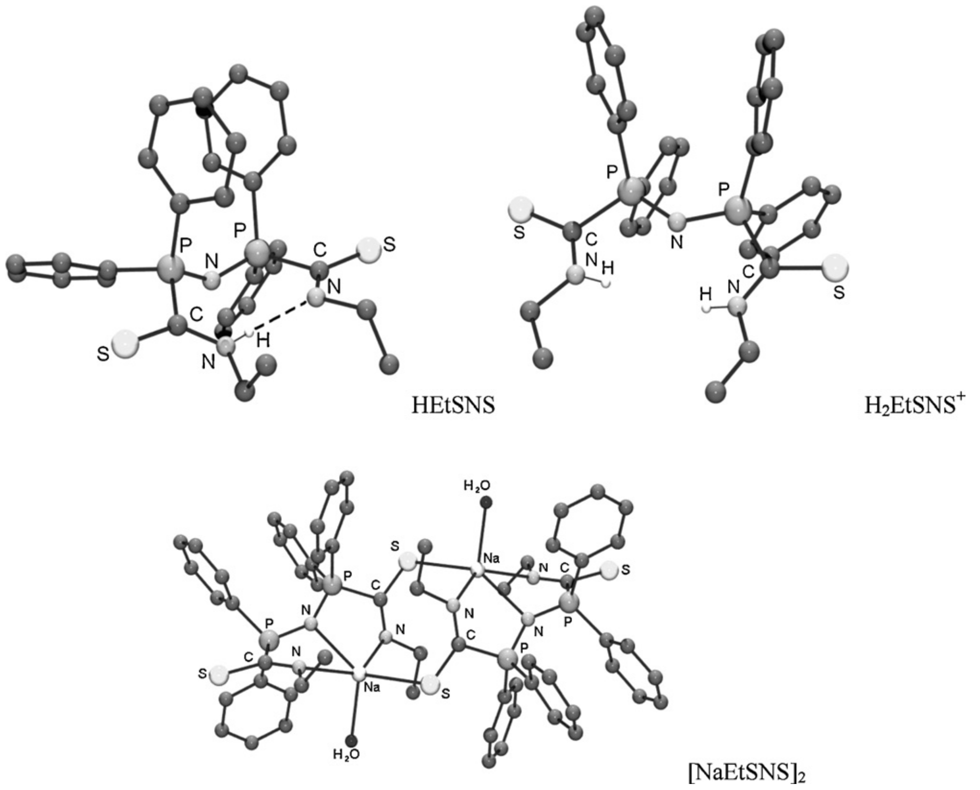
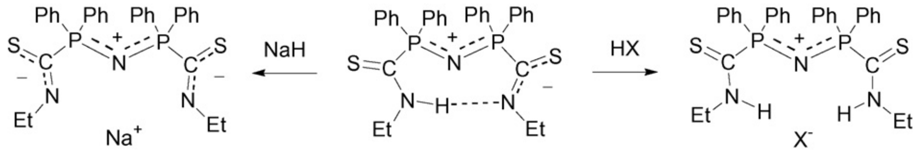


Fig. 1. Views of the crystal structures of HEtSNS, $H_2EtSNS(PF_6)$ (anion PF_6 is omitted for clarity) and $[Na(EtSNS)]_2$.



Scheme 9. Protonation and deprotonation of HEtSNS.

have been classified [11] depending on where the formal charges, deduced by drawing the Lewis structure of the complex, are located and dividing them in two main categories: complexes in which the formal positive charge is on the metal centre, and the still uncommon “zwitterionic metallates” whose metal centre is formally negative.

They can be prepared following several strategies, among the most common: by reaction of zwitterionic ligands with metal species [12] (the case of some complexes presented here); by generating the charge separation upon coordination [13], by association of a positive (or negative) metal centre with an oppositely charged ligand maintaining the charge separation [14].

As above-mentioned, reactions of R_3P with CS_2 give zwitterionic adducts R_3PCS_2, whose ligating properties have been reviewed [12]. On the other hand, when we started this research, the coordination chemistry of the thiomidyl-phosphonium functional group $P^+C(S)N^-$ was not previously studied; only one fully characterized complex containing a coordinated $N^-C(S)P^+$ zwitterionic group was reported, but was obtained by insertion of an isothiocyanate in a preformed complex [15]. Probably, the reason of this lack of data can be ascribed to the dissociation of the adduct, due to the phosphorous coordination to a metal centre (Scheme 10).

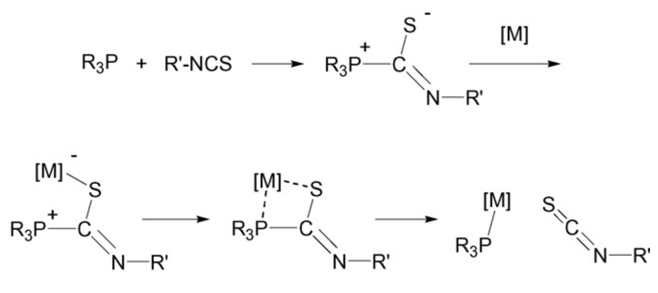
As a matter of fact, when we tried the reaction of the zwitterion $Cy_3PC(S)NPh$ (Cy = cyclohexyl, prepared in high yield from Cy_3P and PhNCS) with $[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadiene), the only complex obtained was $[Rh(cod)(PCy_3)Cl]$ (unpublished results).

4. Coordination chemistry of HEtSNS and its derivatives

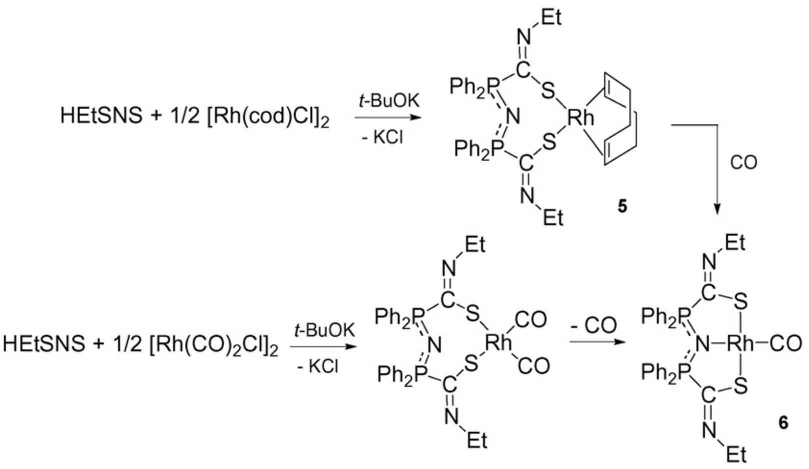
Ligand HEtSNS is a versatile multifunctional ligand having *S*,*N*,*S* donor sites and acid–basic sites. It can coordinate to metal centres in its three, differently charged, forms: neutral zwitterionic HEtSNS; dianionic–cationic $EtSNS^-$; cationic H_2EtSNS^+. Anion $EtSNS^-$ is a suitable ligand for M(I) species, forming neutral complexes.

4.1. Reactivity towards Rh(I) precursors

The coordination reactivity of $EtSNS^-$, HEtSNS and H_2EtSNS^+ has been extensively studied towards Rh(I) complexes, namely



Scheme 10. Proposed path for the dissociation of $R_3PC(S)R'$ adducts mediated by P coordination to a metal centre.



Scheme 11. Reactions of HEtSNS with $[Rh(cod)Cl]_2$ and $[Rh(CO)_2Cl]_2$ with HEtSNS in the presence of a base. Transformation of [Rh(*S,S*-EtSNS)(cod)] (**5**) to [Rh(*S,N,S*-EtSNS)(CO)] (**6**).

$[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadiene), its related carbonyl complex $[Rh(CO)_2Cl]_2$ and derived species, containing the metal moieties $[Rh(cod)]^+$ and $[Rh(CO)_2]^+$ [16]. For the [Rh(cod)] fragment, up to two coordination sites around the Rh atom are allowed, one by the opening of the Cl bridge and the other by loss of the Cl ligand; for $[Rh(CO)_2]$, up to three coordination sites are possible, upon further loss of one CO molecule.

4.1.1. Reactivity of EtSNS⁻

When $[Rh(cod)Cl]_2$ and $[Rh(CO)_2Cl]_2$ are reacted with NaEtSNS or with HEtSNS in the presence of a base (potassium *t*-butoxide or triethylamine, Scheme 11), complexes [Rh(*S,S*-EtSNS)(cod)] (**5**) and [Rh(*S,N,S*-EtSNS)(CO)] (**6**) are obtained; in the former, the ligand coordinates to the metal through the two sulfur atoms, forming an eight-membered chelation ring. In the latter, the loss of a CO molecule allows the nitrogen atom to enter the coordination sphere of Rh, forming a bis-chelate complex with two fused five-membered rings. The bond distances between the atoms of the N–C–S system suggest a thiolate configuration. Both complexes can be described as zwitterionic metallates: the formal negative charge is located on the Rh atom, the positive one still being delocalized on the P–N–P system. This group is related to the PNP group of the bis(triphenylphosphine)iminium cation $[Ph_3PNPPh_3]^+$ (PPN⁺) whose N atom, as identified by its bent geometry, may coordinate a metal centre, although this behavior has never been observed [17]. The structures of **5** and **6** are depicted in Fig. 2. Noteworthy, in the cod complex the EtSNS⁻ ligand shows a conformation that allows a S–Rh–S angle of 90° while, in the carbonyl complex, this angle is 180°. As shown below in other examples, the structural flexibility of EtSNS⁻ allows the ligand to comply with the coordination requests of the different metal centres. The cod complex **5** can be transformed in **6** by bubbling CO in dichloromethane solution.

4.1.2. Reactivity of HEtSNS

When HEtSNS is reacted with $[Rh(cod)Cl]_2$ without a base (Scheme 12), the *S*-monodentate complex [Rh(*S*-HEtSNS)(cod)Cl] (**7**) is obtained; its structure is depicted in Fig. 3. In solution, the $^{31}P\{^1H\}$ NMR suggests the presence of an equilibrium with an *S,S*-bidentate species, as shown in Scheme 12.

In the reaction of HEtSNS with $[Rh(CO)_2Cl]_2$ three species were identified at the end of the reaction in dichloromethane, as detected by $^{31}P\{^1H\}$ NMR (Scheme 13). Compound $[Rh(S\text{-HEtSNS})(CO)_2Cl]$ (**8**) was identified in solution in low quantity, showing an NMR pattern very similar to **7**. It is probably the first product of the reaction, as in the case of $[Rh(cod)Cl]_2$, and undergoes to the same equilibrium (**8a** was not observed in solution). Due to the possibility of losing a CO molecule and HCl, it then disproportionates in **6** and $[H_2EtSNS][Rh(CO)_2Cl_2]$ (**9**). The complex anion $[Rh(CO)_2Cl_2]^-$ is found as counter-ion for H_2EtSNS^+, formally obtained by Cl coordination to a $[Rh(CO)_2Cl]$ moiety and by protonation of one molecule of HEtSNS. We will see below that this does not happen when a

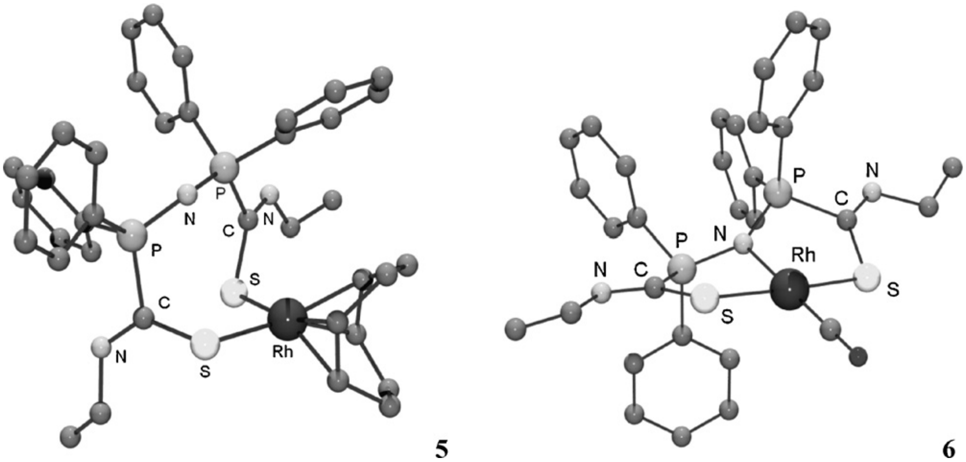
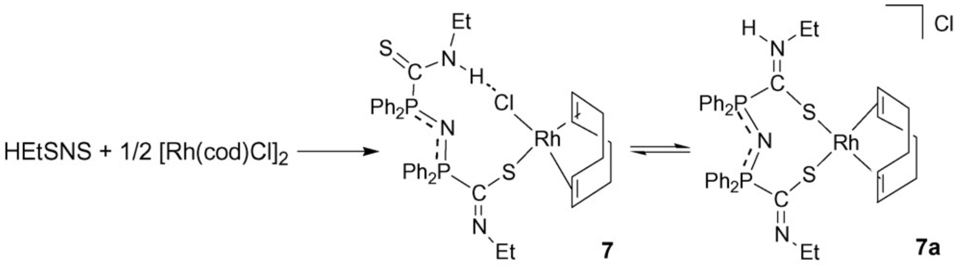
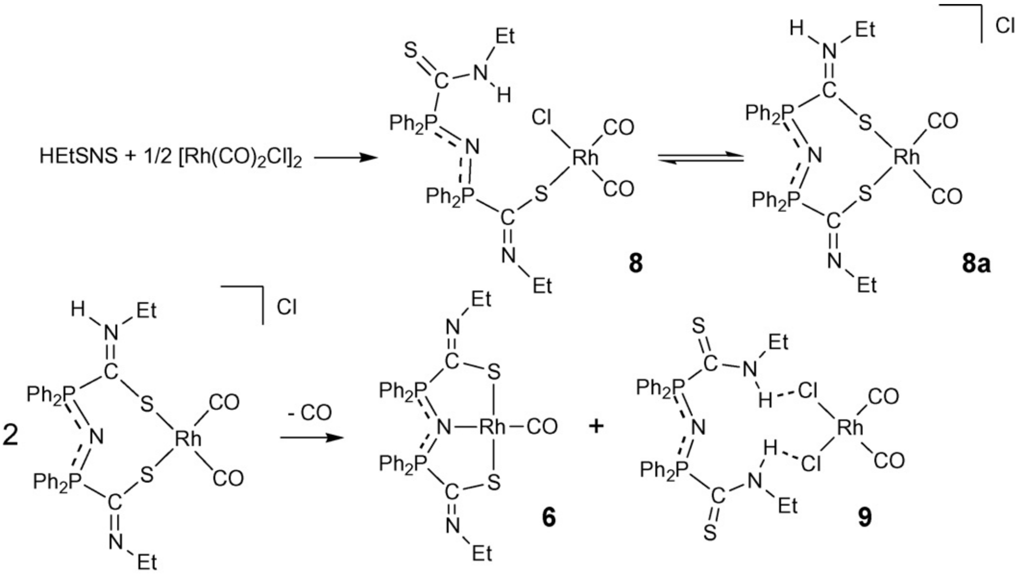


Fig. 2. Views of the solid state structures of [Rh(*S,S*-EtSNS)(cod)] (**5**) and [Rh(*S,N,S*-EtSNS)(CO)] (**6**).



Scheme 12. Reaction of HEtSNS with $[Rh(cod)Cl]_2$ and solution equilibrium.



Scheme 13. Reaction of HEtSNS with $[Rh(CO)_2Cl]_2$.

non-coordinative anion, in place of Cl^-, is present. The ionic complex **9** was isolated and characterized in the solid state (Fig. 4).

When Rh precursors $[Rh(cod)(CH_3CN)_2]OTf$ and $[Rh(CO)_2(CH_3CN)_2]PF_6$, in which low- or non-coordinating anions are present, are reacted with HEtSNS, different products are obtained; also in this case the reactivity of the carbonyl precursor differs from the one of the cod precursor due to the loss of a CO molecule, allowing the ligand to coordinate in a *S*,*N*,*S* fashion.

With $[Rh(CO)_2(CH_3CN)_2]PF_6$, complex [Rh(*S*,*N*,*S*-HEtSNS)(CO)] PF_6 (**10**) is obtained quantitatively (Scheme 14); its structure

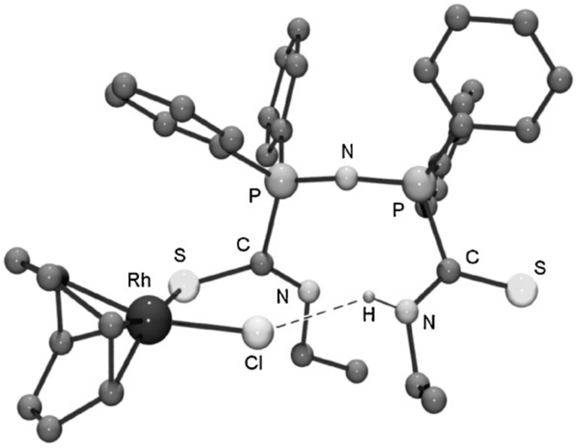


Fig. 3. View of the solid state structure of complex [Rh(*S*-HEtSNS)(cod)Cl] (**7**).

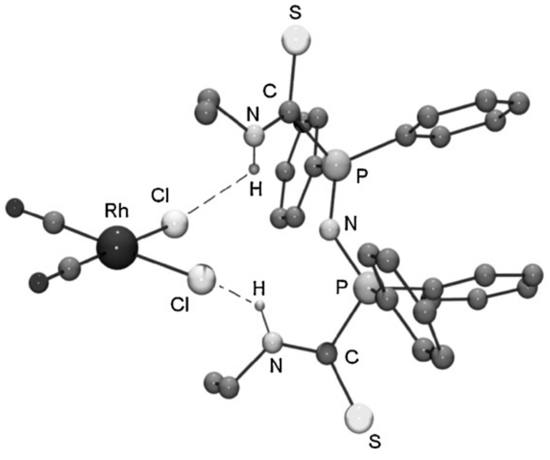
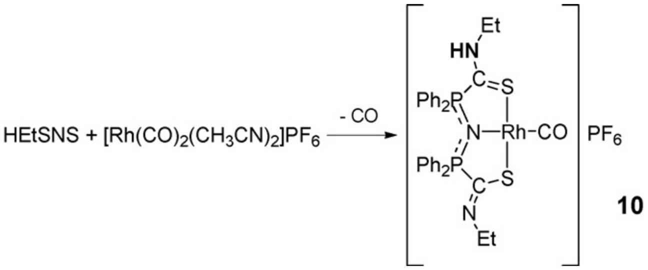


Fig. 4. View of the crystal structure of complex $[H_2EtSNS][Rh(CO)_2Cl_2]$ (**9**).



Scheme 14. Reaction of HEtSNS with $[Rh(CO)_2(CH_3CN)_2]PF_6$.

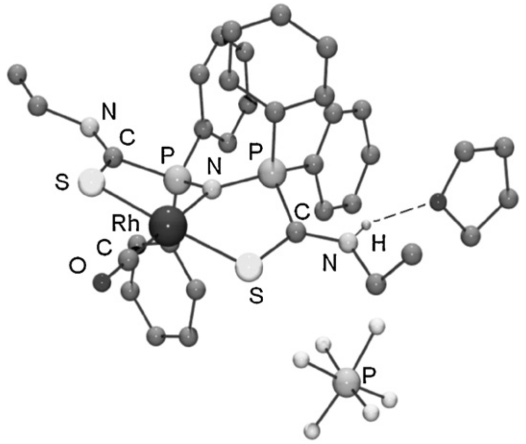


Fig. 5. View of the crystal structure of complex [Rh(*S*,*N*,*S*-HEtSNS)(CO)]PF_6 (**10**) in **10**·THF.

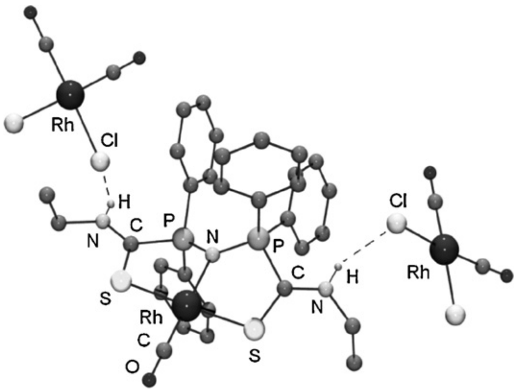


Fig. 7. View of the crystal structure of complex [Rh(*S*,*N*,*S*-H_2EtSNS)(CO)][Rh$(CO)_2Cl_2]_2$ (**13**).

(containing one molecule of THF present in the crystallization solution) is reported in Fig. 5. Compound **10** is a cationic complex in which the HEtSNS ligand is coordinated in *S*,*N*,*S* way similar to $EtSNS^-$. The structural parameters of the EtNHC(S) group suggest a C═S double bond coordinated to the Rh atom.

Unexpectedly, when [Rh(cod)$(CH_3CN)_2$]OTf was used, the dinuclear complex [{Rh(cod)}$_2$(μ-*S*,*S*-EtSNS)]OTf (**11**) formed, together with 1 equiv. of (H_2EtSNS)OTf. Its structure is reported in Fig. 6. It can be seen, and obtained, as an adduct between **5** and the fragment $[Rh(cod)]^+$ and is also obtained by protonation of **5** with one molar equivalent of HOTf and, only in solution, when the monodentate complex **7** is dissolved in methanol, upon disproportionation of the HEtSNS ligand (see Ref. [16] for details).

4.1.3. *Reactivity of (H_2EtSNS)X (X = Cl, PF_6)*

In the reaction of $[Rh(cod)Cl]_2$ with (H_2EtSNS)Cl, the Cl anion coordinates to the Rh atom, yielding [H_2EtSNS][Rh(cod)Cl_2] (**12**) whose structure is analogous to that of complex **9**. No reaction was observed between (H_2EtSNS)PF_6 and $[Rh(cod)Cl]_2$. The cation H_2EtSNS^+ is thus unable to act as a ligand in the presence of chloride anions. When $[Rh(CO)_2Cl]_2$ is used, the unexpected complex [Rh(*S*,*N*,*S*-H_2EtSNS)(CO)][Rh$(CO)_2Cl_2]_2$ (**13**) was produced. The coordination of the Cl anion liberated in the formation of $[Rh(S,N,S\text{-}H_2EtSNS)(CO)]^{2+}$ by the loss of a CO molecule, afforded the two chloro-rhodates $[Rh(CO)_2Cl_2]^-$. The structure of **13** is reported in Fig. 7.

Complexes of the kind $[Rh(HEtSNS)(CO)]^+$ and $[Rh(H_2EtSNS)(CO)]^{2+}$ can also be respectively prepared by protonation of **6** with one molar equivalent or an excess of a strong acid, or reacting HEtSNS and H_2EtSNS^+ with Rh(I) species containing non-coordinating anions. The case of *i.e.* H_2EtSNS(PF_6) and $[Rh(CO)_2(CH_3CN)_2]PF_6$ yielding $[Rh(H_2EtSNS)(CO)](PF_6)_2$ is a rare example of a cationic ligand coordinating to a cationic metal species. A more convenient way to prepare complexes of formula $[Rh(HEtSNS)(CO)]^+$ is by the comproportionation reaction of **6** with $[Rh(H_2EtSNS)(CO)]^{2+}$ (Scheme 15) [18].

The stretching frequency value of the coordinated CO can be taken as a measure of the charge population on the Rh atom. Frequency values for complexes **6** and **8a** are 1967 and 2075–2009 (cm^{-1}, CH_2Cl_2 solution) respectively, pointing out that the N atom coordination is strongly electron donating, inducing retrodonation from the Rh atom to the CO ligand. Protonation and biprotonation, on the other hand, reduce the population with the expected shift of the CO frequencies to higher values: 1994, 2017 and 2014 cm^{-1} are the frequencies measured in CH_2Cl_2 solution for complexes **10**, $[Rh(H_2EtSNS)(CO)](PF_6)_2$ and **13** respectively. The effect of the charge change has been studied in the oxidative addition of CH_3I to some of these complexes (see below).

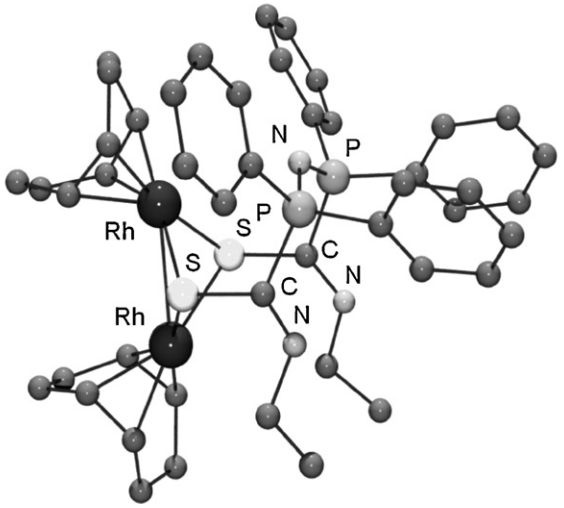
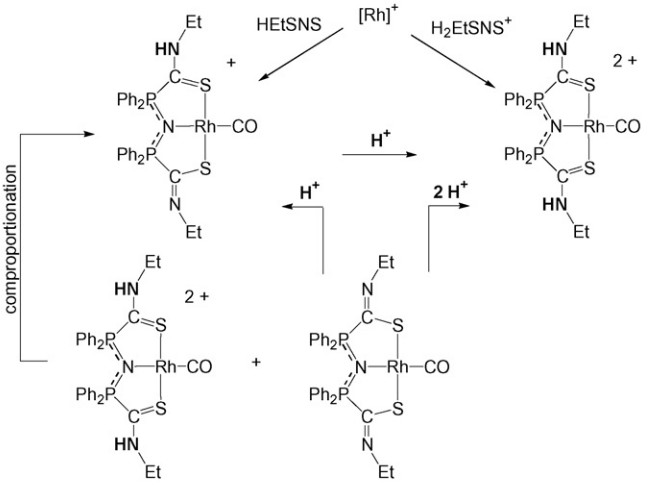


Fig. 6. View of the crystal structure of complex [{Rh(cod)}$_2$(μ-*S*,*S*-EtSNS)]OTf (**11**); the OTf anion is omitted for clarity.



Scheme 15. Reaction strategies for the preparation of complexes $[Rh(HEtSNS)(CO)]^+$ and $[Rh(H_2EtSNS)(CO)]^{2+}$.

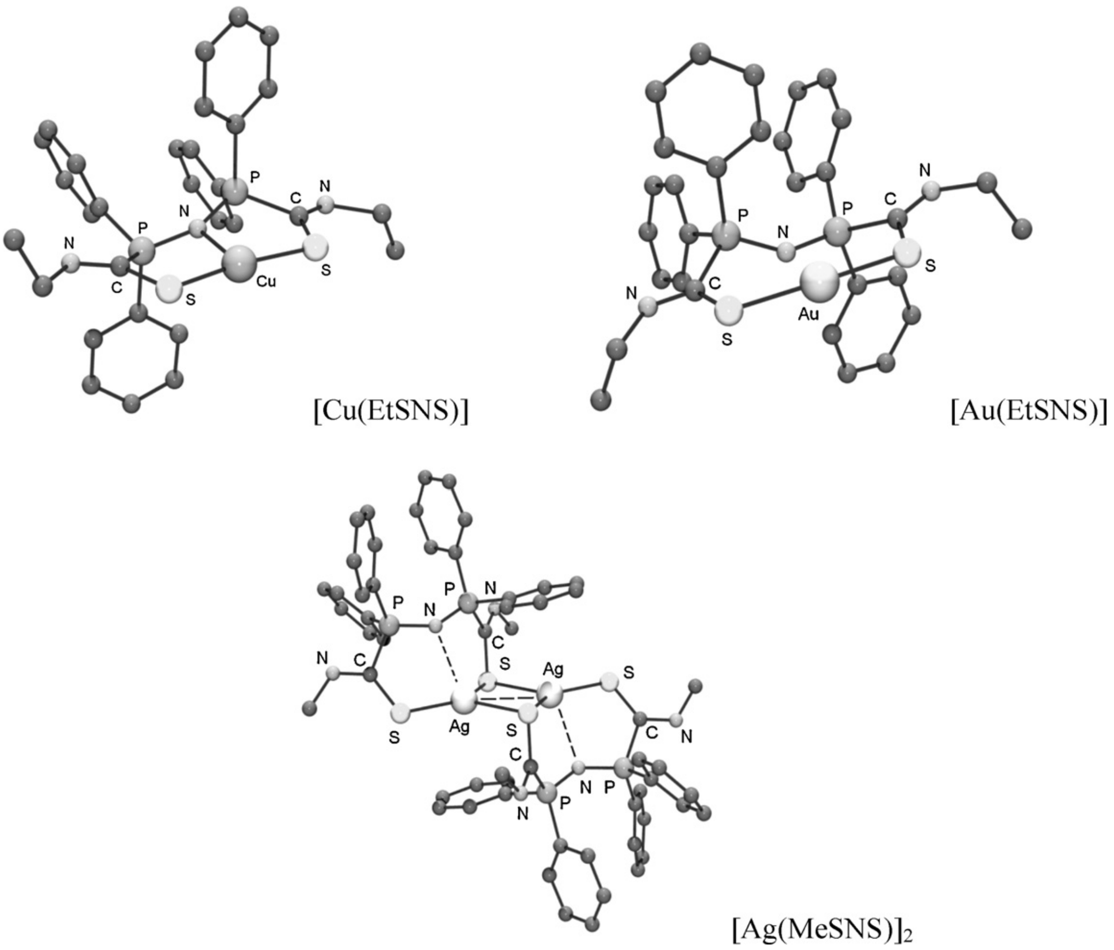
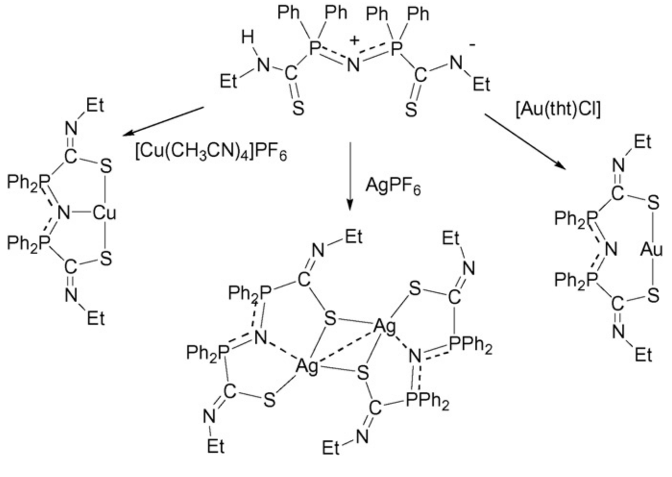


Fig. 8. Views of the crystal structures of [Cu(EtSNS)] [Au(EtSNS)] and $[Ag(MeSNS)]_2$.

4.2. Complexes of Cu, Ag and Au

Cu, Ag and Au complexes of formula [M(EtSNS)] were obtained [9] by reacting HEtSNS in the presence of *t*-BuOK with $[Cu(CH_3CN)_4]PF_6$, $AgPF_6$ and [Au(tht)Cl] (tht = tetrahydrothiophene) respectively (Scheme 16).

The solid state structures of [Cu(EtSNS)], [Au(EtSNS)] and $[Ag(MeSNS)]_2$ are depicted in Fig. 8. In [Cu(EtSNS)] the ligand was found in k^3-*S*,*N*,*S* coordination fashion, as in the case of complex **6**.



Scheme 16. Preparation of complexes of formula [M(EtSNS)] M = Cu, Ag, and Au.

In the crystal structure of [Au(EtSNS)] the anion $EtSNS^-$ chelates the metal centre through the two sulfur atoms in a k^2-*S*,*S* fashion, with an S–Au–S angle of circa 180°, giving rise to an eight-membered chelation ring.

While in solution all [M(EtSNS)] (M = Cu, Ag, Au) complexes are mononuclear, in the solid state the Ag complex of $MeSNS^-$ is dimeric. The ligand coordinates to the metal centres through the sulfur atoms, one in terminal and one in bridging modality, in such a way that a four-membered planar Ag_2S_2 ring is formed. The S–Ag–S angle is about 136°, a value in between 90° (found in **5**) and 180° (as found in **6**, [Cu(EtSNS)] and [Au(EtSNS)]).

5. Properties of zwitterionic complexes of HEtSNS and derivatives

5.1. Protonation equilibria: the first determination of absolute pK_a's in dichloromethane

In the literature, protonation equilibria of ligands and complexes in CH_2Cl_2 were studied by means of proton exchange reactions using $HP(Cy)_3{}^+$ (Cy = cyclohexyl) as a weak acid; its $pK_a = 9.7$ was established by convention [19]. This relative pK_a scale, however, should be rescaled to the real $HP(Cy)_3{}^+$ acidity constant, which is unknown [20]. Protonation equilibria of [Rh(EtSNS)(CO)] were studied by means of spectroscopic UV–Visible titration in CH_2Cl_2 [16] using a solution of HOTf in a 1.5% mixture of methanol in dichloromethane; the methanol is present to allow the triflic acid to completely dissolve and to level HOTf to $CH_3OH_2{}^+$. Under these conditions it can be assumed that the concentration of H^+ is equal

Table 1
νCO stretching (CH_2Cl_2) and relevant ^{1}H NMR chemical shifts.

	[Rh(EtSNS)(CO)]	[Rh(HEtSNS)(CO)]NO_3	[Rh(HEtSNS)(CO)]OTf	[Rh(HEtSNS)(CO)]PF_6
νCO (CH_2Cl_2, cm^{-1})	1967	1989	1992	1994
^{1}H NMR (NH, CD_2Cl_2, ppm)	–	10.5	10.8	11.0
		[Rh(H_2EtSNS)(CO)]$(NO_3)_2$	[Rh(H_2EtSNS)(CO)]$(OTf)_2$	[Rh(H_2EtSNS)(CO)]$(PF_6)_2$
νCO (CH_2Cl_2, cm^{-1})		2008	2013	2017
^{1}H NMR (NH, CD_2Cl_2, ppm)		10.4	10.6	11.1

to the analytical concentration of the acid added. In this way, two well distinct protonation processes were identified and the two pK_a in CH_2Cl_2 of [Rh(H_2EtSNS)(CO)]$(OTf)_2$ were determined on an absolute scale, with values of 4.8(4) and 6.5(3) ($\sigma = 4.11 \times 10^{-2}$).

5.2. *Oxidative addition of CH_3I to charge tuned Rh(I) complexes*

The Rh^I complex [Rh(EtSNS)(CO)], was considered a good candidate for the reaction of oxidative addition of CH_3I. It was reacted with iodomethane in dichloromethane, yielding the expected acetyl-Rh^{III} complex [Rh(EtSNS)($COCH_3$)I] which was very stable and characterized in solution and in the solid state by X-ray diffraction analysis [18]. The rate constant of the reaction and the activation parameters were determined, confirming a nucleophilic addition mechanism. [$K = 5.48\ (7) \times 10^{-2}\ M^{-1}\ s^{-1}$ at 25 °C CH_2Cl_2; $\Delta H^\ddagger = 28(3)\ kJ\ mol^{-1}$ and $\Delta S^\ddagger = -173(10)\ J\ mol^{-1}\ K^{-1}$]. The rate constant was obtained by monitoring the acetylic product by ^{1}H NMR, and high enough to be determined under second-order conditions ([Rh]/[CH_3I] = 1). The mono- and di-protonated complexes [Rh(HEtSNS)(CO)]X and [Rh(H_2EtSNS)(CO)]X_2 (X = PF_6, OTf, NO_3) were also studied in the same reaction, in order to observe the effects of the ligand protonation on the Rh atom electron density, and its influence on the reactivity. Moreover, the long-range effect of the different counteranions could be observed. The Mulliken atomic population on the Rh atom was calculated by DFT methods and the expected decrease was observed along the series [Rh(EtSNS)(CO)], [Rh(HEtSNS)(CO)]X and [Rh(H_2EtSNS)(CO)]X_2, in accordance with the variation of the coordinated CO stretching frequency (Table 1). The rate constants of the addition of CH_3I to [Rh(HEtSNS)(CO)]X were also determined, under pseudo first-order conditions due to the lower reactivity [X = NO_3, 24.6(6); OTf, 12.7(3); PF_6, $2.50(6) \times 10^{-5}\ M^{-1}\ s^{-1}$]. The influence of the counter-ion could be explained assuming that the different non-metal-coordinated anions form hydrogen bonding with the NH group of the HEtSNS ligand, as pointed out by the ^{1}H NMR chemical shift, that in turn causes a variation of the electron density on the Rh centre. Using different anions can "tune" the charge on the Rh reactive centre, depending on their hydrogen bonding properties (Fig. 9).

A good correlation between the CO stretching frequencies (related to the Rh population) and the rate constants was observed (Fig. 10). Complexes [Rh(H_2EtSNS)(CO)]X_2 reacted too slowly hindering the determination of the rate constants, and confirming the effect of protonation on the nucleophilicity of the Rh atom.

6. Ligand fragmentation induced by metal species

Low-valent metal species can induce the fragmentation of HEtSNS.

In the case of [$Ru_3(CO)_{12}$] the following paths have been observed [21]:

(a) loss of EtNCS due to the formation of a M–P bond (Scheme 10);
(b) loss of EtNC, formation of a P=S group; EtNC can be found coordinated to a metal (Scheme 2);

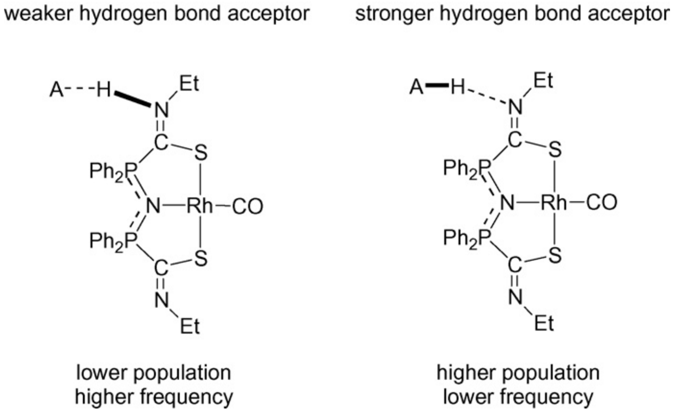


Fig. 9. Effect of the hydrogen bond of the anion (X) with the NH group of [Rh(HEtSNS)(CO)]X complexes.

(c) subsequent oxidative addition of P=S forming a M–P bond and a coordinated sulfide [22];
(d) oxidative addition in thiolic form, affording S and H bridging ligands [23];
(e) oxidative addition of C=S in thioamidic form, yielding an M–C bond and a coordinated sulfide [24].

The reaction of HEtSNS with [$Ru_3(CO)_{12}$] was carried out under two different experimental conditions: (1) [$Ru_3(CO)_{12}$], was previously turned into the labile intermediate [$Ru_3(CO)_{10}(CH_3CN)_2$] and, reacting at room temperature in dichloromethane with HEtSNS, yielded several product, separated by preparative TLC. The most significant one is the trinuclear cluster {$Ru_3(CO)_9$(μ-H)[(μ-S:κ-P)Ph_2PN=PPh_2C(NEt)S]} obtained in 25% yield (Scheme 17). (2) [$Ru_3(CO)_{12}$] was reacted with HEtSNS in toluene at 70 °C, giving related clusters: {$Ru_3(CO)_7$(CNEt)(μ_3-S)[(μ_2-

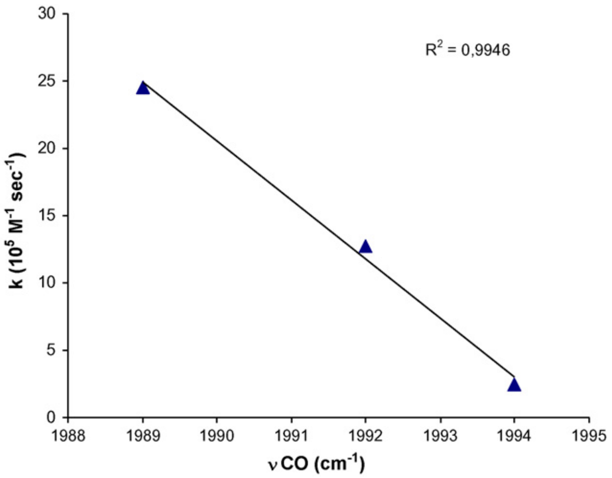
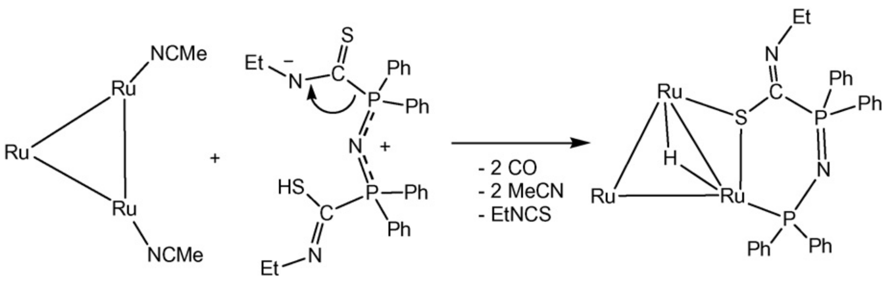
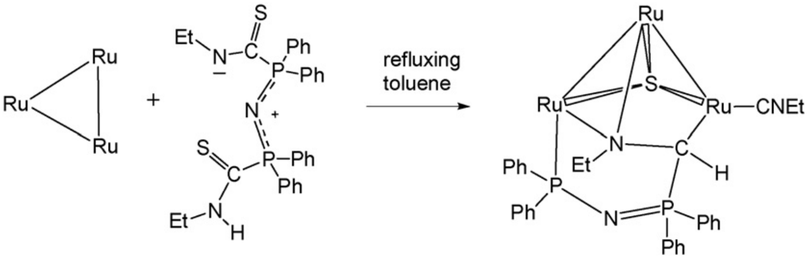


Fig. 10. Linear regression function of the correlation between the CO stretching frequencies and the rate kinetic constants of the oxidative addition of CH_3I to the monoprotonated complexes [Rh(HEtSNS)(CO)]X (X = PF_6, OTf, NO_3).



Scheme 17. Reaction of $[Ru_3(CO)_{10}(MeCN)_2]$ with HEtSNS; formation of cluster $\{Ru_3(CO)_9(\mu\text{-}H)[(\mu\text{-}S:\kappa\text{-}P)Ph_2PN{=}PPh_2C(NEt)S]\}$ (carbonyls omitted).



Scheme 18. Structure drawing of cluster $\{Ru_3(CO)_7(CNEt)(\mu_3\text{-}S)[(\mu_2\text{-}N:\eta^1\text{-}C:\kappa^1\text{-}P)Ph_2PN{=}PPh_2CHNEt]\}$ (carbonyls omitted).

$N:\eta^1\text{-}C:\kappa^1\text{-}P)Ph_2PN{=}PPh_2CHNEt]\}$ (Scheme 18) and $\{Ru_3(CO)_8(\mu_3\text{-}S)[(\mu_2\text{-}N:\eta\text{-}C:\kappa\text{-}P)Ph_2PN{=}PPh_2CHNEt]\}$ among other products.

Cluster $\{Ru_3(CO)_9(\mu\text{-}H)[(\mu\text{-}S:\kappa\text{-}P)Ph_2PN{=}PPh_2C(NEt)S]\}$ (Fig. 11) preserves the original Ru_3 triangular core in which an edge is bridged by a hydride ligand and by the sulfur atom of the $Ph_2PNPPh_2C(S)NEt$ ligand-moiety. Ligand HEtSNS fragmented by losing a EtNCS molecule and coordinating through the free P atom. The PC(S)NHEt moiety reacted in its thiolic form [PC(SH)NEt] 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 (path d).

Cluster $\{Ru_3(CO)_7(CNEt)(\mu_3\text{-}S)[(\mu_2\text{-}N:\eta^1\text{-}C:\kappa^1\text{-}P)Ph_2PN{=}PPh_2CHNEt]\}$ (Fig. 11) shows an open triangle of Ru atoms capped by a μ_3-sulfide and by the unprecedented μ_3-bridging methideylamide –N(Et)CH(R)–, moiety of the $Ph_2PN{=}PPh_2C(H)NEt$ ligand. It can be regarded to as the product of sulfur migration from the thioamidic group on the cluster core, by the rupture of the C–S bond, as observed with various thioureas (path e).

7. Zwitterionic complexes [M(EtSNS)] (M = Cu, Ag, Au) as metalloligands: rational assembly of cluster complexes

The 3:2 reactions of [Cu(RSNS)] ($R = CH_3$, Et) with suitable Cu(I) or Ag(I) salts afforded quantitatively $[Cu_2\{Cu(RSNS)\}_3](PF_6)_2$ (Cu_5) and $[Ag_2\{Cu(RSNS)\}_3](OTf)_2$ (Cu_3Ag_2) [9]. They are ionic compounds: the cation is formed by three [Cu(RSNS)] units joined together by two M'^+ ions (Scheme 19, R = Et). The metal centres define a trigonal bipyramidal $M_3M'_2$ *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. The reaction of [Ag(RSNS)] with AgOTf in a 3:2 ratio yielded cluster $[Ag_2\{Ag(RSNS)\}_3](OTf)_2$ while, in 1:1 molar ratio, led quantitatively to the formation of $[Ag_2\{Ag(EtSNS)\}_2(OTf)_2]$ (Ag_4) a bis-zwitterion cluster, in which two [Ag(EtSNS)] groups are held together by two AgOTf units, the four metal centres forming a planar Ag_4 ring. When $[Ag_2\{Ag(EtSNS)\}_2(OTf)_2]$ was reacted, in a 1:1 ratio, with [Ag(EtSNS)] cluster Ag_5 was quantitatively formed. Since Ag_4 is an intermediate species in the

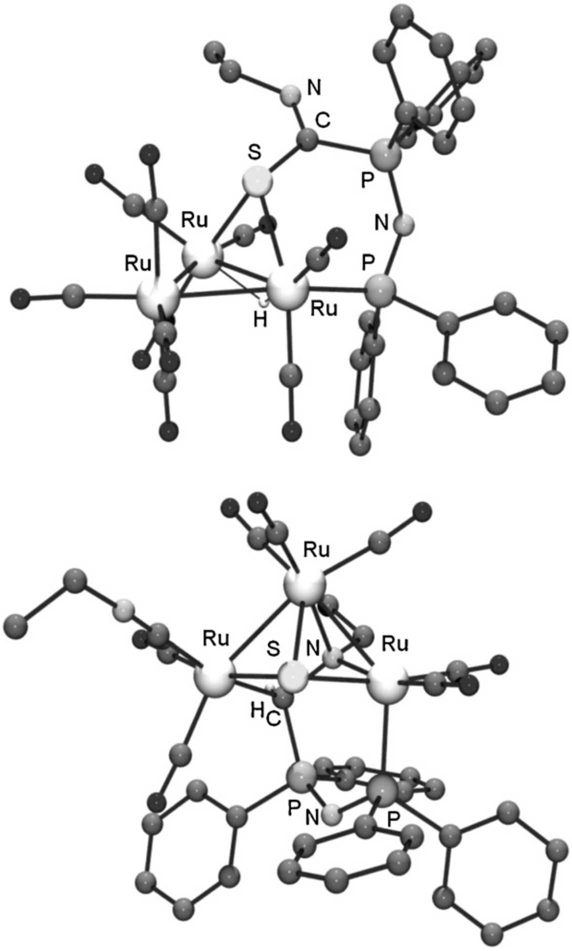


Fig. 11. Views of the crystal structures of clusters $\{Ru_3(CO)_9(\mu\text{-}H)[(\mu\text{-}S:\kappa\text{-}P)Ph_2PN{=}PPh_2C(NEt)S]\}$, top, and $\{Ru_3(CO)_7(CNEt)(\mu_3\text{-}S)[(\mu_2\text{-}N:\eta^1\text{-}C:\kappa^1\text{-}P)Ph_2PN{=}PPh_2CHNEt]\}$, bottom.

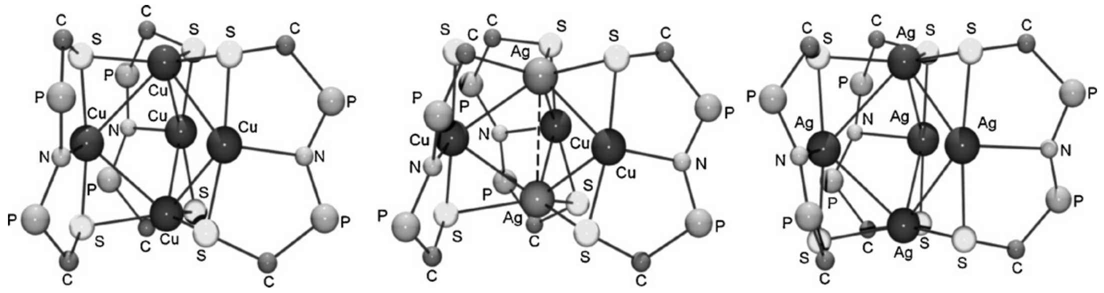
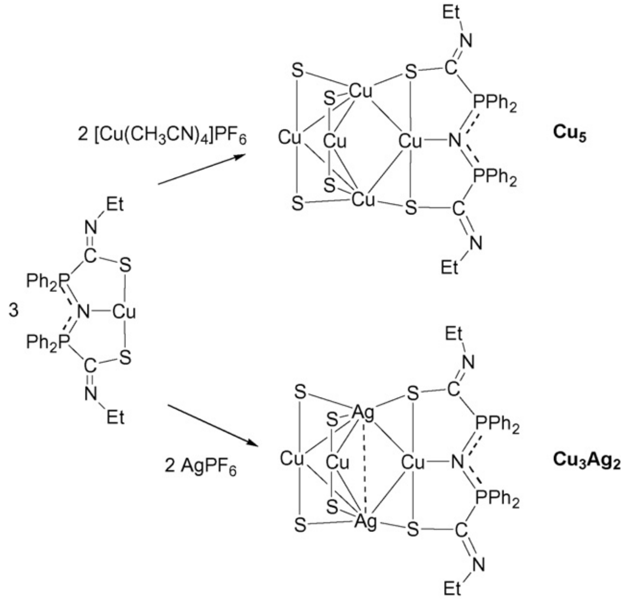
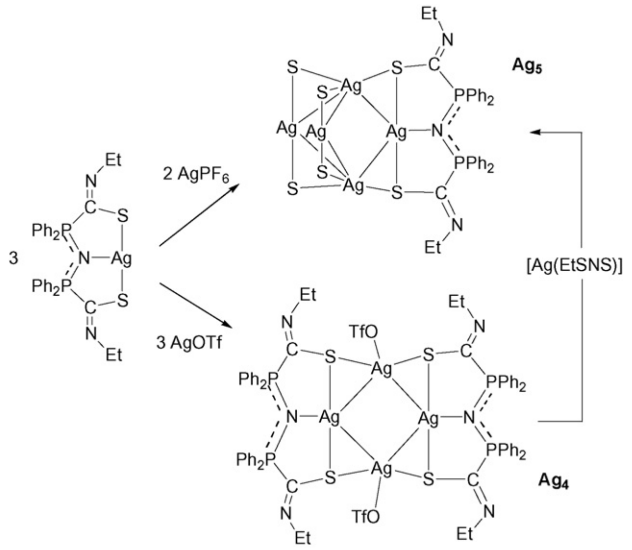


Fig. 12. Views of the structures of the metal cores of Cu$_5$ (left), Cu$_3$Ag$_2$ (centre) and Ag$_5$ (right). For clarity, Ph and Et/Me groups have been omitted.



Scheme 19. Assembly of Cu$_5$ and Cu$_3$Ag$_2$ clusters (for clarity, only one complete EtSNS$^-$ ligand is visible. For the other two, only the sulfur atoms have been identified).



Scheme 20. Assembly of Ag$_5$ and Ag$_4$ clusters (for clarity, in Ag$_5$ only one complete EtSNS$^-$ ligand is visible. For the other two, only the sulfur atoms have been identified).

assembly of cluster Ag$_5$, analogous planar intermediates can be hypothesized in the formation of the Cu$_5$ and Cu$_3$Ag$_2$ clusters (Scheme 20).

Their X-ray structures were determine, and comparing the structural parameters of the metal *cores* of the three clusters (Fig. 12), it is noteworthy that the geometry of the Cu$_3$Ag$_2$ *core* differs significantly from Cu$_5$ and Ag$_5$. A distortion of the bipyramid is observed, being the two axial Ag atoms much closer, probably due to a metallophilic interaction between the two Ag atoms.

8. Conclusions

The ligand HEtSNS contains the zwitterionic PC(S)N functional group, obtained by nucleophilic addition of an aminophoshine to a isothiocyanate. It is the first and only ligand of this kind that was studied in coordination chemistry. Zwitterionic HEtSNS is amphoteric and can be protonated to H$_2$EtSNS$^+$ (cationic) or deprotonated to EtSNS$^-$ (dianionic–cationic), possessing ligating properties in all of these three forms. The study of its coordination chemistry properties identified its geometrical versatility, which allows several coordination fashions: *S*-monodentate, as in complex **7**; eight-membered chelating *S*,*S*-bidentate with 180° bite-angle, as in complex [Au(EtSNS)], 90° bite-angle, as in complex **5** and intermediate values such as 136° in [Ag(MeSNS)]$_2$; *S*,*N*,*S*-bis-chelating (as found in **6** or [Cu(EtSNS)]) and N,N,N-tridentate coordination as in [Na(EtSNS)H$_2$O]$_2$, in which monodentate S coordination is also found. The S atoms are also able to bridge two metallic units as in the dinuclear complex **11**.

Moreover, complexes [Cu(EtSNS)] and [Ag(EtSNS)] can be used as metalloligands, forming unusual zwitterionic coordination clusters containing $M_3M'_2$ metal cores (M, M' = Cu, Ag). Some of these clusters are fluorescent and their properties are under study.

Among the EtSNS$^-$ complexes, compound **6** could be protonated using strong acids, yielding mono- and dicationic complexes of general formula [Rh(HEtSNS)(CO)]X [Rh(H$_2$EtSNS)(CO)]X$_2$. In the case of X = OTf the protonation constants were determined, obtaining for the first time absolute pK_a values in dichloromethane. Complexes in the series [Rh(EtSNS)CO] [Rh(HEtSNS)(CO)]X [Rh(H$_2$EtSNS)(CO)]X$_2$ (X = PF$_6$, OTf, NO$_3$) were studied in the oxidative addition of CH$_3$I, allowing to observe the long-range effects of different anions on the electronic population of the reactive Rh centre and, consequently, on its reactivity.

HEtSNS also showed a reactivity towards metal species in low oxidation states, as [Ru$_3$(CO)$_{12}$]. In this case, extensive fragmentation of the ligand was observed, leading to a series of products, one containing the unprecedented μ_3-bridging methideylamide –N(Et)CH(R)– fragment.

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