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Phosphine–carbon disulfide adducts, S_2CPR_3: versatile ligands in coordination chemistry[☆]

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Contents

[☆] Dedicated to Professors Ernesto Carmona and Víctor Riera, distinguished researchers and exceptionally good people. They, with some others, are responsible for the foundations and most of the building of Organometallic Chemistry in Spain.

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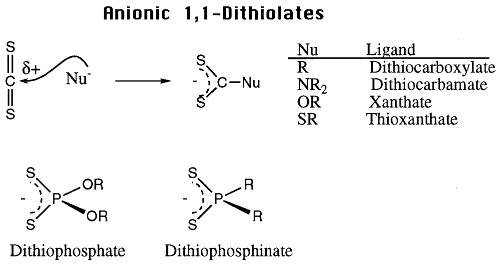
Abstract

Phosphine–carbon disulfide adducts, S_2CPR_3, are very versatile ligands that exhibit a variety of coordination modes to transition metal centers. These compounds are able to formally donate from 2 to 8e$^-$ to a metal (or metals). A resume of the synthetic methodology to prepare them, a rationalization of the structural diversity found in this type of complexes, and their main spectroscopic and chemical properties will be the scope of this review.

Keywords: Phosphine–carbon disulfide adducts; Phosphoniodithiocarboxylate; Phosphoniodithioformate; Carbon disulphide derivatives

1. Introduction

Ligands containing sulfur donor atoms have been used from the beginning of the coordination chemistry and have attracted the interest of many researchers in



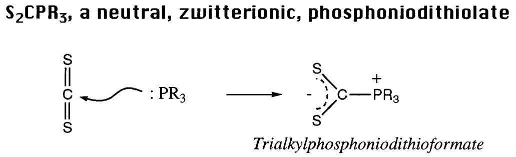
Scheme 1.

different fields [1]. Among these, 1,1-dithiolate ligands constitute a well-known class, the chemistry of which has been studied for several decades. It is well-known that CS_2 is able to undergo nucleophilic addition at the carbon atom, to produce a variety of 1,1-dithiolate anions which have been widely used as ligands in coordination chemistry. Some of them are summarized in Scheme 1, together with two related phosphorus analogues. The chemistry of these anionic ligands and their complexes have been repeatedly reviewed over the years [2].

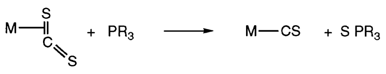
Similarly, carbon disulfide is known to react with basic, nucleophilic trialkylphosphines to give neutral adducts (Scheme 2), which can be isolated as crystalline solids. The first report, due to Hoffmann, goes back to 1880 [3].

Less basic trialkylphosphines are not able to react with free CS_2 to afford stable adducts. However, quite surprisingly, the first example of a coordinated phosphoniodithioformate was $[Ir(S_2CPPh_3)(CO)(PPh_3)_2]BF_4$, which contained the otherwise unstable triphenylphosphine–carbon disulphide adduct. The complex was prepared, eighty eight years after the preparation of the first S_2CPR_3 adducts, by Yagupsky and Wilkinson in 1968 [4], although it was incorrectly formulated as a CS_2 complex. Some years later, a crystallographic study by Boniface and Clark [5] revealed the presence of the S_2CPPh_3 ligand coordinated as S,S′-chelate which had been produced by nucleophilic attack of PPh_3 on the carbon atom of a coordinated CS_2 ligand. The earliest reports of complexes containing S_2CPR_3 ligands are always connected to the exploration of the activation of CS_2, proposed as a model to study CO_2 activation [6–9]. Not surprisingly, the interest in S_2CPR_3 complexes increased rapidly when they were considered as intermediates in the desulfurization of CS_2 promoted by phosphine [10], as shown in Scheme 3.

In those years, most complexes were prepared either by attack of phosphine to coordinated CS_2 or by insertion of CS_2 into a phosphine–metal bond (see below).



Scheme 2.



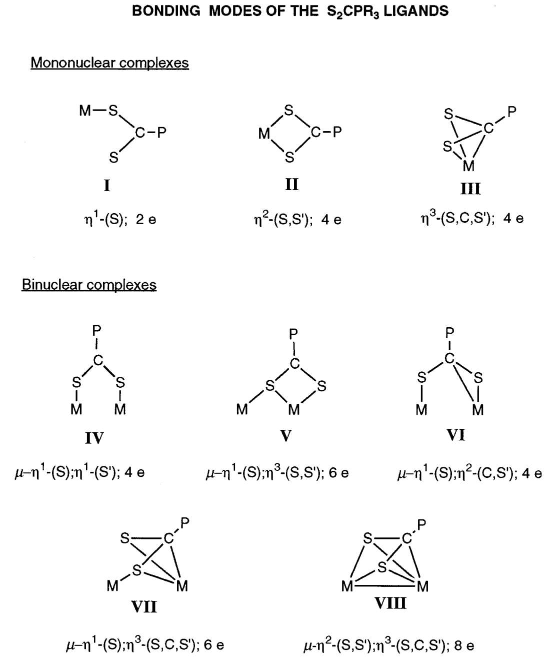
Scheme 3.

Only after 1980 pre-formed S_2CPR_3 adducts began to be used and rational methods to yield S_2CPR_3 complexes began to appear. It was soon evident that S_2CPR_3 ligands are able to coordinate metals in many differents ways and, in some cases, are able to undergo unexpected reactivity, leading to new ligands or unprecedented bonding and structural types. That made the field sometimes intriguing, sometimes fascinating, and kept us on the trail of S_2CPR_3 complexes for many years.

A detailed historical account of the developement of the field, although tempting for us, would not be useful for the general reader. Therefore, we will follow a more rational pattern, by using a classification based on the different bonding modes displayed by the S_2CPR_3 ligands.

2. Preparation of complexes containing S_2CPR_3 ligands

Phosphoniodithioformate adducts, S_2CPR_3, exhibit a variety of coordination modes to transition metal centers, being able to formally donate from 2 to 8e$^-$ to the metal(s).



Scheme 4.

Scheme 4 displays the general bonding modes found in structurally characterized compounds in which S_2CPR_3 can function as an η^1(S) (**I**), η^2(S,S′) (**II**) or η^3(S,C,S′) (**III**) ligand in mononuclear complexes, and as a μ-η^1(S),η^1(S′) (**IV**), μ-η^1(S),η^2(S,S′) (**V**), μ-η^1(S),η^2(C,S′) (**VI**), μ-η^1(S),η^3(S,C,S′) (**VII**) or μ-η^2(S,S′),η^3(S,C,S′) (**VIII**) bridging ligand. Since the preparation and reactivity are markedly different for each structural type, we will deal with them separately in the following sections.

2.1. Mononuclear complexes

*2.1.1. Coordination η^1(S), monodentate (Type **I**)*

Only a few families of complexes are known, and the structures of some of them have been determined by X-ray crystallography (see Section 3.1). These complexes are usually made by displacement, at room temperature (r.t.), of a weakly coordinated ligand by S_2CPR_3, as summarized in the following equations:

$$[\mathrm{LnM(THF)}] + \mathrm{S_2CPR_3} \rightarrow [\mathrm{LnM\{SC(S)PR_3\}}] + \mathrm{THF}$$

LnM = $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$, $CpFe(CO)_2^+$, $CpMn(CO)_2$; R = Et (Ref. [11]); LnM = $Cp'Mn(CO)_2$; R = Cy; Cp′ = C_5H_4Me (Ref. [12])

$$[\mathrm{W({\equiv}CR)(CO)_2(dppe)(NCMe)}]^+ + \mathrm{S_2CPCy_3}$$

$$\rightarrow [\mathrm{W({\equiv}CR)(CO)_2(dppe)\{SC(S)PCy_3\}}]^+ + \mathrm{NCMe}\ \text{(Ref. [13])}$$

$$[\mathrm{Au(C_6F_5)_3(tht)}] + \mathrm{S_2CPR_3} \rightarrow [\mathrm{Au(C_6F_5)_3\{SC(S)PR_3\}}] + \mathrm{tht}$$

PR_3 = PCy_3, PEt_3, PBu_3, $PPhMe_2$, $PPhEt_2$; tht = tetrahydrothiophene (Ref. [14])

$$[\mathrm{M(C_6F_5)(L)_2(OClO_3)}] + \mathrm{S_2CPR_3} \rightarrow [\mathrm{M(C_6F_5)(L)_2\{SC(S)PR_3\}}]\mathrm{ClO_4}$$

M = Pd, Pt; L = PEt_3, PPh_3, PBu_3, PEt_2Ph; $(L)_2$ = bipy; R = Et, Bu, Cy (Ref. [15])

$$[\mathrm{RuH(OClO_3)(CO)(CNCMe_3)(PPh_3)_2}] + \mathrm{S_2CPCy_3}$$

$$\rightarrow [\mathrm{RuH\{SC(S)PR_3\}(CO)(CNCMe_3)(PPh_3)_2}]\mathrm{ClO_4}\ \text{(Ref. [16])}$$

$$[\mathrm{(L)_5Mn{-}OClO_3}] + \mathrm{S_2CPR_3} \rightarrow [\mathrm{(L)_5Mn\{SC(S)PR_3\}}]\mathrm{ClO_4}$$

R = Cy; $(L)_5$ = $(CO)_5$, $(CO)_3(dppm)$, $(CO)_3(bipy)$, $(CO)_3(S_2CPR_3)$ (Ref. [17]); R = Et; $(L)_5$ = $(CO)_5$, $(CO)_4(PEt_3)$, $(CO)_3(PEt_3)_2$, $(CO)_3(dppe)$, $(CO)_3(bipy)$ (Ref. [18])

When two positions are available, the reaction proceeds further to give a η^2(S,S′) chelate. Therefore, the method is applicable to substrates in which only one labile ligand is present. However, in some cases, it is possible to introduce more than one S_2CPR_3 adduct, one of them acting as η^2 chelate, and the remaining acting as monodentate:

$$[\mathrm{Mn(CO)_3(Me_2CO)_3}]^+ + 2\mathrm{S_2CPR_3}$$

$$\rightarrow [\mathrm{Mn(CO)_3(S_2CPR_3)\{SC(S)PR_3\}}]^+ + 3\mathrm{Me_2CO}$$

R = Et, Cy (Ref. [17])

$[WI_2(CO)_3(NCMe)_2] + 3S_2CPCy_3$

$\rightarrow [W(CO)_3(S_2CPR_3)\{SC(S)PR_3\}_2]I_2 + 2NCMe$ (Ref. [19])

Some of the Pd and Pt complexes metioned above can be also prepared by insertion of CS_2 into a M–PR_3 bond [15]:

$[M(C_6F_5)(PR_3)_3]ClO_4 + CS_2 \rightarrow [M(C_6F_5)(PR_3)_2\{SC(S)PR_3\}]ClO_4$

The attack of phospine on coordinated CS_2 usually gives S_2CPR_3 ligands acting as chelates (see below), however some examples have been reported to afford a monodentate S_2CPR_3.

$[(triphos)RhCl(\eta^2\text{-}CS_2)] + PEt_3 \rightarrow [(triphos)RhCl\{SC(S)PEt_3\}]$

triphos = $MeC(CH_2PPh_2)_3$ (Ref. [20])

$[W(PR_2C_2H_4PR_2)(CO)_3(CS_2)] + PBu_3 \rightarrow [W(PR_2C_2H_4PR_2)(CO)_3\{SC(S)PBu_3\}]$

R = Me, Ph (Ref. [21])

An analogous complex containing monodentate Se_2CPEt_3 has been also prepared by the same method [22].

Finally, a few complexes containing monodentate S_2CPR_3 ligands have been made by ring-opening reactions of chelating S_2CPR_3 [12,23]. These will be discussed in Section 4.

2.1.2. Coordination η^2(S,S′), chelate (Type **II**)

Many examples were reported in the earlier literature, and some others have appeared through the years, this being the most abundant class of mononuclear complexes. The bonding mode as η^2-chelate is more stable than monodentate, and this permits the use of more forcing conditions for the preparation. On the other hand, the higher stability of complexes containing chelate S_2CPR_3 permitted a wider exploration of their reactivity.

Three general procedures have been used to prepare complexes with chelate S_2CPR_3: attack of phosphine to coordinated CS_2, insertion of CS_2 into M–PR_3 bonds, and substitution of other ligands by S_2CPR_3. These procedures are described separately in the following sections.

2.1.2.1. Addition of phosphine to a coordinated CS_2 ligand. As previously mentioned in the Introduction, this method produced the first complex containing a S_2CPR_3 ligand [4,5]. In the early stages of the studies on CS_2 activation, it was found that the reaction of a suitable substrate with PPh_3/CS_2 can afford a thiocarbonyl ligand, liberating $SPPh_3$ [6–9]. However, in some cases, the reaction results in the formation of a S_2CPR_3 ligand, coordinated as an η^2(S,S′) chelate. The method, when applicable, affords compounds containing triaryl phosphines, which are not able to form stable adducts to be employed in other synthetic methods.

$[IrCl(CO)(PPh_3)_2] + CS_2 + PPh_3 \rightarrow [Ir(S_2CPPh_3)(CO)(PPh_3)_2]BF_4$ (Refs. [4,5])

$[Fe(CO)_3(PPh_3)_2]PF_6 + CS_2 + PPh_3$

$\rightarrow [Fe(CO)_3(PPh_3)_2(S_2CPPh_3)](PF_6)_2 + [Fe(CO)_3(PPh_3)_2]$ (Ref. [24])

2.1.2.2. Insertion of CS_2 into a metal–phosphine bond. Some complexes have been prepared by reaction of metal–phosphine complexes with CS_2:

$[RuCl_2(PEtPh_2)_3] + CS_2 \rightarrow [RuCl_2(PEtPh_2)_2(S_2CPEtPh_2)]$ (Ref. [25])

$[RuClH(CO)(PCy_3)_3] + CS_2 + NaBPh_4$

$\rightarrow [RuH(CO)(PCy_3)_2(S_2CPCy_3)]BPh_4 + NaCl$ (Ref. [26])

$[RuCl_2(CO)(PPr^i_3)_2] + CS_2 \rightarrow [RuCl_2(CO)(PPr^i_3)(S_2CPPr^i_3)]$ (Ref. [27])

$[Pd(COMe)(PMe_3)_3]BPh_4 + CS_2 \rightarrow [Pd(COMe)(PMe_3)_2(S_2CPMe_3)]BPh_4$

$[PdI(COMe)(PMe_3)_2] + CS_2 \rightarrow [PdI(COMe)(PMe_3)(S_2CPMe_3)]$ (Ref. [28])

$(PEt_3)_3CuBPh_4 + CS_2 \rightarrow [(PEt_3)_2Cu(S_2CPEt_3)]^+$ (Ref. [29])

$[Mn(CO)_4(PCy_3)Br] + CS_2 \rightarrow [Mn(CO)_3(S_2CPCy_3)Br] + CO$ (Ref. [17])

These reactions can be described as an insertion of CS_2 into the metal–phosphine bond. As discussed by Bianchini et al. [29], the intimate mechanism can proceed through coordination of CS_2 and subsequent transfer of PR_3 to the carbon of coordinated CS_2 or, alternatively, through PR_3 dissociation from the complex, followed by formation of the zwitterionic S_2CPR_3 which could then react with a complex molecule or with a metal–ligand fragment. The nature of the phosphines involved can be determinant on the mechanism in each particular case. Metal complexes with basic trialkyl phosphines, capable of forming stable CS_2 adducts, may follow both mechanisms, while less basic triaryl phosphines, which are not able to form stable S_2CPR_3 adducts, would require the previous coordination of CS_2 to the metal, followed by the intramolecular attack of the phosphine to the central carbon of CS_2, whose electrophilic character is increased by coordination.

In any case, many of the mentioned complexes can be obtained, usually with better yields, by substitution methods, which also allow for the preparation of 'mixed' derivatives, i.e. in which the phosphine groups in the S_2CPR_3 ligand and those directly bonded to the metal are different (see the following section).

2.1.2.3. Use of S_2CPR_3 in substitution reactions. The most general procedure exploits the presence of two easily displaced ligands in *cis* positions. Since the coordination of the S_2CPR_3 group as chelate is thermally robust, sometimes the displacement of ligands such as carbonyls can be promoted by heating even in refluxing toluene. However, due to the thermal lability of the free S_2CPR_3 adduct, and the volatility of CS_2, the yields of the desired product are often reduced by the formation of metal–phosphine complexes. The yields can be improved by adding an excess of CS_2, to inhibit the dissociation of the adduct, and hence the presence of free phosphine, which would coordinate the metal to give undesired by-products.

The procedures for the preparation of complexes are summarized in the following reactions:

$$[M(H_2O)_6]^{2+} + \text{triphos} + S_2CPEt_3 \rightarrow [(\text{triphos})M(S_2CPEt_3)]^{2+} + 6H_2O$$

$M = Co, Ni$; triphos $= MeC(CH_2PPh_2)_3$ (Ref. [30])

$$[Fe(H_2O)_6]^{2+} + \text{depe} + S_2CPEt_3 \rightarrow [(\text{depe})_2Fe(S_2CPEt_3)]^{2+} + 6H_2O$$

depe $= Et_2PCH_2CH_2PEt_2$ (Ref. [31])

$$[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC{\equiv}CMe)_2]^+ + S_2CPCy_3$$
$$\rightarrow [W(CO)(S_2CNC_4H_8)(S_2CPCy_3)(\eta^2\text{-}MeC{\equiv}CMe)]^+ + MeCN$$
$$+ MeC{\equiv}CMe \text{ (Ref. [32])}$$

$$[MI_2(CO)_3(NCMe)_2] + S_2CPCy_3 \rightarrow [MI_2(CO)_3(S_2CPCy_3)] + 2MeCN$$

$$[MI_2(CO)_3(NCMe)(L)] + S_2CPCy_3 \rightarrow [MI(CO)_3(S_2CPCy_3)]I + MeCN$$

$$[MI_2(CO)_3(NCMe)_2] + 2S_2CPCy_3 \rightarrow [M(CO)_3(S_2CPCy_3)_2]I_2 + 2MeCN$$

$M = Mo, W$ (Ref. [19])

$$[M(\eta^3\text{-allyl})(CO)_2(NCR')_2Br] + S_2CPR_3$$
$$\rightarrow [M(\eta^3\text{-allyl})(CO)_2(S_2CPR_3)Br] + 2\ NCR'$$

$R = Cy, Pr^i$; $M = Mo$, $R' = Me$, $M = W$, $R' = Et$ (Ref. [33])

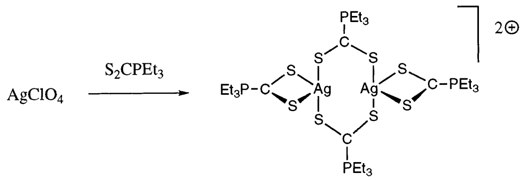
$$[M(CO)_3(NCMe)_2Br] + S_2CPR_3 \rightarrow [M(CO)_3(S_2CPR_3)Br] + 2\ NCMe$$

$M = Mn, Re$; $R = Cy, Pr^i$ (Ref. [34])

$$[Mn(CO)_5Br] + 3S_2CPEt_3 \xrightarrow[\text{toluene, reflux}]{} [Mn(CO)_2(PEt_3)_2(S_2CPEt_3)]Br + 2CO$$
$$+ 2CS_2 \text{ (Ref. [18])}$$

$$1/2[(\text{arene})RuCl_2]_2 + S_2CPR_3 + KPF_6 \xrightarrow[\text{EtOH, reflux}]{} [(\text{arene})RuCl(S_2CPR_3)]PF_6$$
$$+ KCl \text{ (Ref. [35])}$$

In one case, a dimer containing both chelate and $\eta^1(S);\eta^1(S')$ bridges is produced in the same reaction (Scheme 5) [36]:



Scheme 5.

2.1.3. Coordination η^3(S,C,S′), pseudoallyl (Type **III**)

In some cases, the central carbon of the phosphoniodithioformate is also bonded to the metal, and the ligand adopts a coordination mode reminiscent of an η^3-allyl. The involvement of the central carbon in the bonding with the metal is more frequently found in binuclear complexes (Types **VI**, **VII**, and **VIII**, in Scheme 4). Nevertheless, several examples of mononuclear complexes containing η^3-S_2CPR_3 have been reported, and they have provided structural data for the bonding analysis of this type of coordination [37], and its comparison with the bonding as η^2 chelate, which will be discussed in detail in Section 3. When acting as η^3 pseudoallyl, the ligand usually donates $4e^-$, and formally replaces two neutral $2e^-$ ligands. The situation is therefore similar to that found for η^2 chelates. The adoption of either η^2-chelate or η^3-pseudoallyl bonding modes is dictated by the electronic properties and the set of orbitals offered by the metal center, as discussed in Section 3.2. The preparation of complexes with η^3-S_2CPR_3 ligands relies in the choice of the metal–ligand fragment which, generally speaking, should be electron rich to support this kind of coordination.

The first examples were prepared by Carmona and co-workers [38], from the reaction:

$$[MoCl(NO)(PMe_3)_4] + CS_2 \rightarrow [MoCl(NO)(PMe_3)_2(\eta^3\text{-}S_2CPMe_3)] + PMe_3$$

The appearance in the ^{13}C-NMR spectra of the $S_2\mathit{C}PMe_3$ signal at δ 82.7 ppm ($^1J_{PC} = 82.5$ Hz), suggested the involvement of the central carbon in the bonding with the metal, since the same signal appears in the region δ 220–230 ppm for complexes containing monodentate or chelate S_2CPR_3 ligands. The η^3-(S,C,S′) coordination was confirmed by an X-ray determination (see Section 3.1). Another η^3-(S,C,S′) derivative was prepared by substitution of chloride and PMe_3 ligands by dithiocarbamate [38]:

$$[MoCl(NO)(PMe_3)_2(\eta^3\text{-}S_2CPMe_3)] + NaS_2CNMe_2$$

$$\rightarrow [Mo(S_2CNMe_2)(NO)(PMe_3)(\eta^3\text{-}S_2CPMe_3)] + NaCl + PMe_3$$

The compound $[Mo(S_2CPMe_3)(CO)_2(PMe_3)_2]$ was prepared by Carmona, one of us, and co-workers, in low yield, by treatment of $[Mo(C_2S_4)(C_2H_4)(PMe_3)_3]$ with CO (2 atm) and PMe_3, in a reaction which involves the cleavage of a coordinated dimer of CS_2 [39]. Soon after, a more rational synthetic approach was devised which, whilst not giving better yields of the Mo complex, permitted the high-yield preparation of the tungsten analogue [40]:

$$[MHCl(CO)_2(PMe_3)_3] + CS_2 + PMe_3$$

$$\rightarrow [M(\eta^3\text{-}S_2CPMe_3)(CO)_2(PMe_3)_2] + HCl{\cdot}PMe_3 \ (M = Mo,\ W)$$

Iron carbonyl complexes containing the η^3-(S,C,S′) coordination were prepared by Riera, some of us, and co-workers [37]:

$$[Fe(CO)_3(bda)] + S_2CPR_3 \rightarrow [Fe(CO)_3(\eta^3\text{-}S_2CPR_3)] + bda \ (R = Cy,\ Pr^i)$$

More recently, Gimeno and co-workers reported [13] that when complex $[W(\equiv CR)(CO)_2(dppe)\{SC(S)PCy_3\}]^+$, containing monodentate S_2CPCy_3 is stirred in solution for 24 h, an intramolecular replacement of CO takes place, to afford $[W(\equiv CR)(dppe)(\eta^3\text{-}S_2CPCy_3)]^+$ which, as revealed by an X-ray determination, contains S_2CPCy_3 bonded as η^3-(S,C,S′) pseudoallyl.

2.2. Binuclear complexes with S_2CPR_3 ligands as bridges

2.2.1. $\eta^1(S);\eta^1(S')$ bridges of $4e^-$ (Type **IV**)

Two main cases arise, depending on the existence of a direct bond between the metals.

2.2.1.1. $\eta^1(S);\eta^1(S')$ bridges without a metal–metal bond. These are usually prepared by ligand displacement reactions on substrates which offer only one coordination position available for substitution. Most complexes are binuclear complexes of the symmetrical type, i.e. the two sulphur atoms are bonded to identical metal–ligand fragments. This can be accomplished in one-pot reactions by adjusting the stoichiometry, as in the formation of the complex $[Ag(S_2CPR_3)_2]_2^{2+}$ which contains two chelate and two bridging S_2CPR_3 ligands [35] (see Scheme 5).

Several families of gold(I) and gold(III) neutral complexes have been prepared in this way [14]:

$$2[AuX(tht)] + S_2CPR_3 \rightarrow [XAu(\mu\text{-}S_2CPR_3)AuX] + 2tht$$

$X = Cl, C_6F_5$; $R_3 = Cy_3, Et_3, Bu_3, PhMe_2, PhEt_2$

The same procedure affords cationic binuclear Au(I) complexes which presumably contain two S_2CPR_3 bridges:

$$2[Au(tht)_2]ClO_4 + 2S_2CPR_3 \rightarrow [Au_2(S_2CPR_3)_2](ClO_4)_2 + 4tht$$

$R_3 = Et_3, Bu_3, PhMe_2$ (Ref. [14])

A tungsten carbonyl complex has also been reported [19]:

$$2[WI_2(CO)_3(PPh_3)(NCMe)] + S_2CPCy_3 \rightarrow [\{WI_2(CO)_3(PPh_3)\}_2(\mu\text{-}S_2CPCy_3)]$$

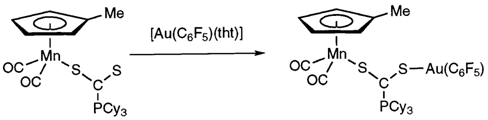
The same binuclear complexes can often be obtained in two steps, by using the uncoordinated sulfur of a complex containing a monodentate S_2CPR_3, as the entering ligand in a second molecule of substrate:

$$[Au(C_6F_5)_3\{SC(S)PR_3\}] + [Au(C_6F_5)_3(OEt_2)]$$

$$\rightarrow [(C_6F_5)_3Au(\mu\text{-}S_2CPR_3)Au(C_6F_5)_3]OEt_2$$

$R_3 = Cy_3, Et_3, Bu_3, PhMe_2, PhEt_2$ (Ref. [14])

This method is potentially more useful since it can be used to prepare unsymmetrical binuclear complexes with each sulfur bonded to a different fragment [12], as in Scheme 6.



Scheme 6.

However, only a few complexes of this type have been reported: the uncoordinated sulfur of monodentate S_2CPR_3 behaves often as a poor donor, unable to produce the displacement of the leaving ligand in the second step [12,14].

The $\eta^1(S);\eta^1(S')$ bridge is easily cleaved by donor molecules, sometimes even by diethyl ether [14]. This has precluded the exploration of the reactivity of these complexes.

2.2.1.2. $\eta^1(S);\eta^1(S')$ bridges spanning a metal–metal bond. Only three examples have been reported, and the methodology is different in each case.

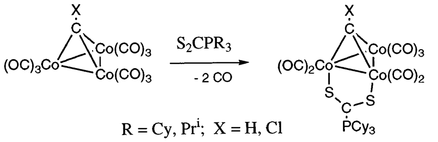
It is possible to introduce a S_2CPR_3 ligand in methylidine tricobalt clusters by direct displacement of two CO groups on adjacent Co atoms at r.t. [41] (Scheme 7).

The only example in which a S_2CPR_3 ligand bridges two multiple bonded metal atoms was obtained by proton-induced displacement of one acetato bridge of $Mo_2(O_2CMe)_4$ (Scheme 8).

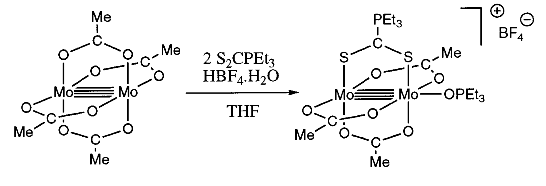
In this case, one additional mole-equivalent of S_2CPEt_3 serves as a source of triethylphosphine oxide ligand [42].

Finally, a dirhenium octacarbonyl complex can be obtained by reacting $[Re(CO)_3(S_2CPR_3)Br]$ with pentacarbonylrhenate anion [43] (Scheme 9).

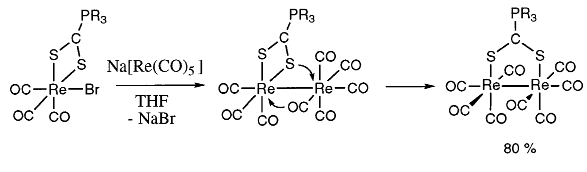
The first step is the formation of the Re–Re bond, through NaBr elimination, which would give an unsymmetrical octacarbonyl, as depicted in Scheme 9. In order to reach the final symmetrical octacarbonyl, the reaction must include the ring opening of the chelate S_2CPR_3 in the tricarbonyl moiety, and the intramolecular



Scheme 7.



Scheme 8.



Scheme 9.

displacement of one CO ligand from the pentacarbonyl fragment to afford, ultimately, two identical $Re(CO)_4$ fragments. Considering the fairly good isolated yield of the reaction, and since no external source of CO is present, it seems that the complementary migration of sulfur and CO may be effected in a concerted process, probably through an intermediate containing a bridging carbonyl. In fact, at least two examples of complexes containing semi-bridging carbonyls have been structurally characterized by some of us recently [44,45] in the studies of reactivity of complexes with S_2CPR_3 bridges.

Alternatively, the mentioned octacarbonyls $[Re_2(CO)_8(\mu\text{-}S_2CPR_3)]$ can be obtained by direct displacement of 1-hexene from $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}\eta^2\text{-}CH{=}CHBu)]$ with S_2CPR_3 [43].

2.2.2. $\eta^1(S);\eta^2(S,S')$ bridges of $6e^-$ (Type V)

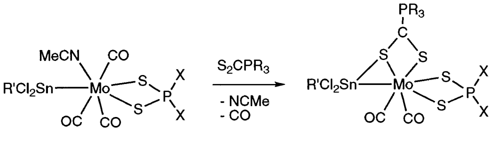
While the $\eta^1(S);\eta^2(S,S')$ bonding mode is the most frequently found for anionic 1,1-dithiolato bridges, such as dithiocarbamate or xanthate, this type of coordination is very rare for S_2CPR_3 ligands. Only two examples are known, both containing at least one main group metal.

In one case, the S_2CPR_3 ligand is bonded as $\eta^2(S,S')$ chelate towards molybdenum, and one of the sulfur atoms approaches the tin atom of a $SnPhCl_2$ group also bonded to molybdenum atom [46]. The preparation is outlined in Scheme 10.

The other example is complex $[Pb_2(OSCPh)_4(\mu\text{-}S_2CPCy_3)_2]$ which constitutes, so far, the only case in which the S_2CPR_3 ligand is bonded exclusively to main-group metal atoms [47]. The preparation is shown in Scheme 11 and some structural data are collected in Section 3.1.

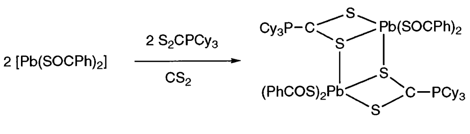
2.2.3. $\eta^1(S);\eta^2(C,S')$ bridges of $4e^-$ (Type **VI**)

The only examples of this type belong to the same family of isostructural palladium complexes containing a variety of phosphine groups bonded to the metal, and to the central carbon of CS_2. The complexes can be prepared by displacement of phosphine ligands with S_2CPR_3 [9,48] (Scheme 12) or, alternatively, by a formal insertion of CS_2 into metal–phosphine bonds (Scheme 13).

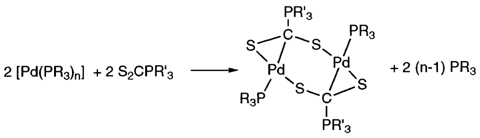


X = OEt, Ph; R = Cy, Pr^i; R' = Ph, Bu;

Scheme 10.

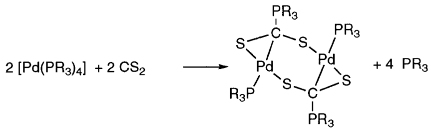


Scheme 11.



$PR_3 = PPr^i_3, PPh_3, PMePh_2, PMe_2Ph, PMe_3; PR'_3 = PMe_3$
$PR_3 = PPh_3, PMePh_2, PMe_2Ph; PR'_3 = PMe_2Ph$

Scheme 12.



$PR_3 = PMe_2Ph, PMe_3$

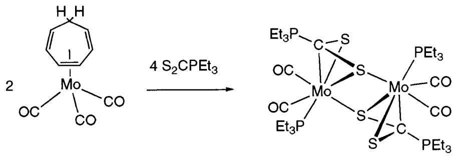
Scheme 13.

These complexes are reported to be labile in solution and the bridges can be easily cleaved by the addition of phosphine, to give mononuclear complexes with chelate S_2CPR_3 ligands $[Pd(PR_3)_2(S_2CPR'_3)]$ [9]. Analytical and spectroscopic data are in agreement with the structure proposed, which was confirmed by an X-ray determination of an isostructural analogue containing the Se_2CPR_3 ligand [49].

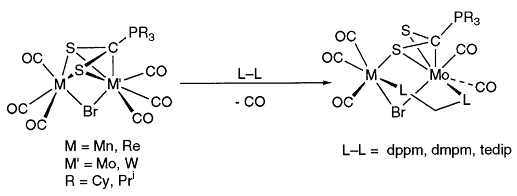
2.2.4. *$\eta^1(S);\eta^3(S,C,S')$ bridges of $6e^-$ (Type **VII**)*

There are only two families of complexes with this kind of coordination. The first example was prepared by Bianchini et al. by treatment of $[Mo(CO)_3(CHT)]$ (CHT = cycloheptatriene) with two molar equivalents of S_2CPEt_3 [11,50]. The substitution of CHT is followed by a spontaneous dimerization to give the dinuclear complex $[Mo(CO)_2(PEt_3)(S_2CPEt_3)]_2$ as it is displayed in Scheme 14. The structure was confirmed by an X-ray determination (see Section 3.1).

Some other examples of coordination $\eta^1(S);\eta^3(S,C,S')$ appeared as a consequence of substitution reactions of dinuclear derivatives containing $\eta^2(S,S');\eta^3(S,C,S')$ S_2CPR_3 and halide bridges. Thus, for example, treatment of hexacarbonyls $[MM'(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)]$ with bidentate phosphorus ligands such as dppm, dmpm, or tedip, produces initially the substitution of one carbonyl group from the metal supporting the η^3 coordination [51]. The second phosphorus atom of the diphosphine produces the cleavage of a S–M bond in the opposite metal, yielding



Scheme 14.



Scheme 15.

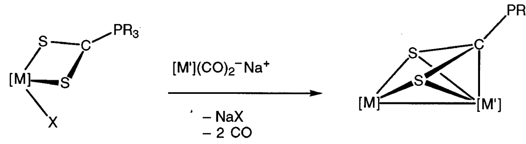
pentacarbonyls which contain three different bridges: one S_2CPR_3 adduct coordinated as $\eta^2(S);\eta^3(S,C,S')$, one bidentate phosphorus ligand, and the halogen bridge (Scheme 15). This behavior is reminiscent of the ring-opening reactions found for mononuclear complexes with chelate S_2CPR_3 which will be discussed in Section 4.

2.2.5. $\eta^2(S,S');\eta^3(S,C,S')$ bridges of $8e^-$ (Type *VIII*)

This group comprises a wide number of series of complexes which have been prepared by some of us at the University of Oviedo. Two main strategies have been devised for the rational synthesis of these complexes. Both of them use, as starting material, mononuclear complexes containing one chelate S_2CPR_3 contiguous to a halogen ligand.

2.2.5.1. Compounds with $\eta^2(S,S');\eta^3(S,C,S')$ bridges spanning a metal–metal bond. The general method involves the treatment of the halide–S_2CPR_3 complex with a carbonyl metallate anion at r.t., as summarized in Scheme 16 [52,53].

In the general case, the reaction proceeds smoothly, at r.t., with loss of two carbonyl groups, to afford complexes with $\eta^2(S,S');\eta^3(S,C,S')$ bridges. Only when the two metals are rhenium, the reaction stops in a symmetrical octacarbonyl containing a η^1-η^1 bridge, as discussed in Section 2.2.1.2. The conversion to the desired hexacarbonyl requires the heating of the octacarbonyl in refluxing octane [43].



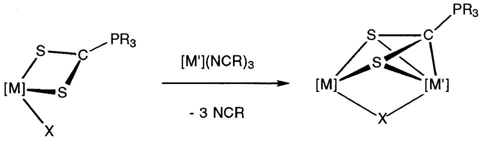
(Ref.)	[M]	[M']
[52]	$(CO)_3Mn$	$Mn(CO)_3$
	$(CO)_3Re$	$Mn(CO)_3$
[43]	$(CO)_3Re$	$Re(CO)_3$
[53]	$(CO)_3Mn$	$Co(CO)_2$
	$(CO)_3Re$	$Co(CO)_2$
	$(\eta^3\text{-allyl})(CO)_2Mo$	$Co(CO)_2$
	$(\eta^3\text{-allyl})(CO)_2W$	$Co(CO)_2$

Scheme 16.

There are other routes to prepare some of these compounds. Thus, the dimanganese complex [$Mn_2(CO)_6(\mu$-$S_2CPR_3)$], which constituted the first example of this type of coordination, was firstly prepared, in low yield, by refluxing [$MnBr(CO)_3(S_2CPR_3)$] in toluene [54,55]. This complex reaction, which occurs with loss of one equivalent of S_2CPR_3, and two bromide ions, may proceed through a disproportionation of the starting mononuclear Mn(I) species to yield the final dinuclear Mn(0) complex and Mn(II) salts [55]. Subsequent studies revealed that [$Mn_2(CO)_6(\mu$-$S_2CPR_3)$] can be prepared, in good yield, by direct thermal replacement of four carbonyl groups from $Mn_2(CO)_{10}$. This direct method can not be used, however, to prepare the dirhenium complex [43].

In the preparation of the cobalt complexes in Scheme 16, it is possible to use $Co_2(CO)_8$ instead of the anion $Co(CO)_4^-$. In this case, a disproportionation of $Co_2(CO)_8$ to give the tetracarbonyl cobaltate anion and Co(II) salts, is likely to occur [53].

2.2.5.2. Compounds with $\eta^2(S,S');\eta^3(S,C,S')$ and halide bridges, without a metal–metal bond. Mononuclear complexes containing one chelate S_2CPR_3 and one halide ligand can be also used in displacement reactions on substrates containing three labile ligands to obtain binuclear complexes in which the S_2CPR_3 ligand acts as a $\eta^2;\eta^3$ bridge (Scheme 17) [56–60].



(Ref.)	[M]	[M']
[51,56]	$(CO)_3Mn$	$Mo(CO)_3$
	$(CO)_3Mn$	$W(CO)_3$
[57]	$(CO)_3Re$	$Mo(CO)_3$
	$(CO)_3Re$	$W(CO)_3$
[58]	$\{(\eta^6$-arene$)Ru\}^+$	$Mo(CO)_3$
	$\{(\eta^6$-arene$)Ru\}^+$	$W(CO)_3$
	$Cl(CO)_2Ru$	$Mo(CO)_3$
	$Cl(CO)_2Ru$	$W(CO)_3$
[33]	$(\eta^3$-allyl$)(CO)_2Mo$	$Mo(CO)_3$
	$(\eta^3$-allyl$)(CO)_2Mo$	$W(CO)_3$
	$(\eta^3$-allyl$)(CO)_2W$	$Mo(CO)_3$
	$(\eta^3$-allyl$)(CO)_2W$	$W(CO)_3$
[59]	$(NO)(CO)_2Mo$	$Mo(CO)_3$
	$(NO)(CO)_2Mo$	$W(CO)_3$
[60]	RCl_2Sn	$Mo(CO)_2(PR_3)$

Scheme 17.

In this case, no metal–metal bond is formed and the halide ligands serves as a second bridge to hold together the binuclear unit. The entering fragment ([M′] in Scheme 17) has to be electron-rich to support the coordination η^3(S,C,S′) of the S_2CPR_3 ligand in the dinuclear complex. Additionally, it has to bear three labile ligands to be replaced in the reaction, as outlined in Scheme 17. This reduces in practice the range of substrates to be employed in this method and, in fact, we have obtained good results only with $Mo(CO)_3(NCMe)_3$ or $W(CO)_3(NCEt)_3$. The range of fragments '$M(S_2CPR_3)X$' is more extensive, and permits the preparation of neutral and also cationic binuclear complexes, such as $[(\eta^6\text{-arene})Ru(\mu\text{-}S_2CPR_3)M(CO)_3]^+$ (M = Mo, W) [58].

Compounds $[Mo(CO)_2(PR_3)(\mu\text{-}Cl)(\mu\text{-}S_2CPR_3)(SnBuCl_2)]$ can be considered as belonging to the same general type, although they are prepared in a somewhat different way [60]:

$$1/2[Mo_2(CO)_4(PR_3)_2(\mu\text{-}S_2CPR_3)_2] + SnBuCl_3$$

$$\rightarrow [Mo(CO)_2(PR_3)(\mu\text{-}Cl)(\mu\text{-}S_2CPR_3)(SnBuCl_2)] \quad (R = Et,\ n\text{-Bu},\ Cy)$$

Alternatively, the same complexes are produced by reaction of $[Mo(CO)_3(SnBuCl_2)(Cl)(NCMe)_2]$ with S_2CPR_3. A crystallographic study (R = Cy) showed that these complexes can be considered as intermediates in both the oxidative addition and reductive eliminaton of $SnBuCl_3$ at Mo(0) centers [60].

3. Structural properties and bonding capabilities: a MO rationalization

As we stated before, S_2CPR_3 adducts display, from a structural point of view, a diversity of coordination modes to transition metal centers. The S_2CPR_3 ligand is capable, depending on the structural coordination modes, to formally donate from 2 to $8e^-$ to the metal or metals (see Scheme 4). The structural preferences observed in structurally characterized complexes are discussed in the following section.

3.1. Structural preferences of S_2CPR_3 complexes

Table 1 compiles some bond lengths and angles for the free S_2CPR_3 adducts structurally characterized by X-ray crystallography. Their molecular structures show a planar S_2CP moiety, according to the approximately 360° value found for the sums of the three angles around the S_2C carbon atom. The geometry around the P atom is tetrahedral. These geometrical characteristics are roughly maintained when the adduct acts as a ligand bonded to a transition metal center. The C–S bond distances are similar and have values between those of a C–S single bond (around 1.8 Å [61]) and a C=S double bond (1.560(3) Å for CS_2 [62]). Fig. 1 shows the crystal structure of the simplest S_2CPR_3 zwitterion structurally characterized, namely S_2CPEt_3.

Other compounds containing the S_2CP fragment, and consequently connected to phosphonodithiformate adducts, are known, but not discussed here. They are, for example, the diphenylphosphinodithioformate anion, $S_2CPPh_2^-$ [63], and its transi-

Table 1
Selected structural data of S_2CPR_3 adducts

	Distances (Å)		Angles (°)		Ref.
	C–S	C–P	S–C–S	S–C–P	
S_2CPEt_3	1.68(3)	1.79(3)	128(2)	113(2)	[68]
	1.69(3)			119(2)	
$S_2CP(NMeCH_2CH_2)_3N$	1.675	1.849	126.7	115.3	[69]
	1.655			118.0	
$[S_2CPCy_2CH_2]_2C_5H_8$	1.664(6)	1.835(5)	129.5(4)	113.9(2)	[70]
	1.654(6)			116.5(4)	
	1.639(6)	1.835(6)	130.3(3)	118.0(3)	
	1.667(6)			111.7(3)	

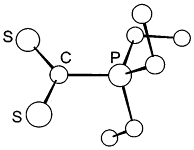


Fig. 1. Molecular structure of S_2CPEt_3.

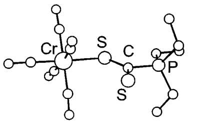


Fig. 2. Molecular structure of $Cr(CO)_5(\eta^1\text{-}S_2CPEt_3)$.

tion metal compounds, $S_2CPPh_2M(CO)_n^-$ (M = W, *n* = 5 [64]; M = Fe, *n* = 4 [65]), and other special compounds, such as $S_2CP[OCMe_2C(O)O]_2^-$ [66] and $S_2CP(NH^tBu)(\mu\text{-}N^tBu)_2P(NH^tBu)$ [67].

There are five examples of X-ray characterized complexes containing the S_2CPR_3 ligand coordinated in the η^1-fashion (**I**). Selected structural parameters are collected in Table 2. Two of them correspond to d^6 octahedral species (Cr(0) and Mn(I)), while the other are d^8 square planar derivatives (Pd(II), Pt(II) and Au(III)). Figs. 2 and 3 display one example of each geometry, respectively.

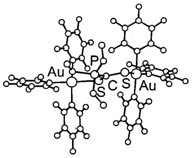
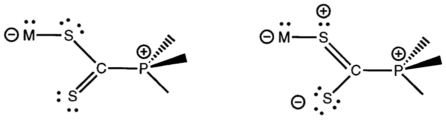


Fig. 3. Molecular structure of $Pt(C_6F_5)_2(CO)(\eta^1\text{-}S_2CPCy_3)$.

Table 2
Selected structural data of η^1-S_2CPR_3 complexes

Complexes η^1-S_2CPR_3	Distances (Å)			Angles (°)			Ref.
	$M–S_1$	$C–S_1$ $C–S_2$	C–P	$M–S_1–C$	$S_1–C–S_2$	$S_2–C–P$ $S_1–C–P$	
$Cr(CO)_5(\eta^1$-$S_2CPEt_3)$	2.389(4)	1.68(1) 1.65(1)	1.82(1)	115.4(4)	130.8(7)	114.4(7) 114.8(7)	[11]
$[Pd(C_6F_5)(PEt_3)_2(\eta^1$-$S_2CPEt_3)]ClO_4$	2.342(3)	1.699(16) 1.632(15)	1.838(15)	109.5(5)	129.4(9)	117.1(9) 113.3(8)	[15]
$Pt(C_6F_5)_2(CO)(\eta^1$-$S_2CPCy_3)$	2.348(2)	1.682(6) 1.643(7)	1.840(6)	108.6(3)	128.8(4)	118.1(4) 113.0(4)	[23]
$Au(C_6F_5)_3(\eta^1$-$S_2CPEt_3)$	2.366(1)	1.690(4) 1.630(4)	1.829(4)	104.4(2)	131.4(3)	114.0(3) 114.5(2)	[14]
$[Mn(CO)_3(\eta^2$-$S_2CPCy_3)(\eta^1$-$S_2CPCy_3)]ClO_4$	2.349(2)	1.689(7) 1.648(9)	1.848(6)	112.4	129.5(3)	116.0(4) 114.3(5)	[17]

In all cases, the S_2CPR_3 ligand occupies one coordination position through one sulphur atom and behaves as a $2e^-$ donor ligand. No bonding interaction between the metal and the second sulphur atom is detected. The two C–S bond lengths are not markedly different being the non bonded to the metal ($C–S_2$ in Table 2) shorter than the coordinated one ($C–S_1$ in Table 2). However, the latter distance is still smaller than the 1.8 Å corresponding to a C–S single bond and this fact indicates some degree of electron delocalization as suggested in **IX**. The S–C–S angle covers the range 128.8(4)–131.4(3)°, and it is slightly higher than the ideal value of 120° expected for sp^2 hybridization.



IX

The M–S–C angle values are in agreement with sp^3 hybridization at sulphur. The bigger values (115.4°, Cr, and 112.4°, Mn compound) correspond to the octahedral species and probably this fact reflects some degree of steric congestion that does not exist in the square planar derivatives.

No significant differences are apparent when comparing the structural data of ligated η^1-S_2CPEt_3 in the Cr, Au and Mn complexes with respect to the uncoordinated ligand.

The structural diversity of compounds containing the η^2-S_2CPR_3 ligand (**II** in Scheme 4) is bigger than that observed for the η^1-S_2CPR_3 derivatives. Table 3 display some bond distances and angles for d^6 octahedral (Mn(I), Fe(II) and Ru(II)), d^8 trigonal bipyramid (Ir(I)), d^8 square planar (Pd(II)) and d^{10} tetrahedral (Cu(I)) complexes. Additionally, there is a particular Ag(I) example containing also a bridging S_2CPEt_3 ligand, displaying highly irregular geometry. Compound $[Mn(CO)_3(\eta^1\text{-}S_2CPCy_3)(\eta^2\text{-}S_2CPCy_3)]ClO_4$ is a good candidate to make comparisons between the mono and bidentate nature of the dithiocarboxylate ligand (see Fig. 4).

The four C–S distances are not significantly different, including those between the carbon and the non-bonded sulphur, and fall in the range 1.648(9)–1.689(7) Å, very close to similar C–S distances observed in Tables 1–3. The most important difference between the two coordination modes is related to the S–C–S angle. The

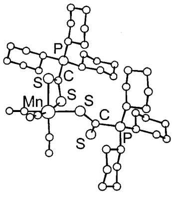


Fig. 4. Molecular structure of cation $[Mn(CO)_3(\eta^2\text{-}S_2CPCy_3)(\eta^1\text{-}S_2CPCy_3)]^+$.

Table 3
Selected structural data of η^2-S_2CPR_3 complexes

Complexes η^2-S_2CPR_3	Distances (Å)			Angles (°)			Ref.
	M–S	C–S	C–P	S–C–S	S–C–P	S–M–S	
$[Ir(CO)(PPh_3)_2(\eta^2\text{-}S_2CPPh_3)]BF_4$	2.307(5)	1.66(2)	1.79(2)	110.7(4)	119.5(4)	72.2(2)	[5]
	2.377(5)	1.70(2)			129.4(4)		
$[Fe(depe)_2(\eta^2\text{-}S_2CPEt_3)](BPh_4)_2$	2.261(3)	1.68(1)	1.78(3)	109.9(5)	123.0(6)	74.1(1)	[31]
	2.305(3)	1.68(1)			127.0(6)		
$[Cu(PPh_3)_2(\eta^2\text{-}S_2CPEt_3)]BPh_4$	2.416(3)	1.670(9)	1.822(9)	123.5(5)	116.6(5)	71.5(5)	[29]
	2.600(3)	1.660(9)			119.7(5)		
$[Ag(\mu\text{-}S_2CPEt_3)(\eta^2\text{-}S_2CPEt_3)]_2(ClO_4)_2$	2.812(2)	1.653(7)	1.819(7)	126.5(4)	119.6(4)	65.5(1)	[36]
	2.668(2)	1.671(7)			113.8(4)		
$Pd(C_6F_5)_2(\eta^2\text{-}S_2CPCy_3)$	2.368(2)	1.672(4)	1.838(5)	119.0(3)	121.3(4)	73.8(2)	[23]
	2.415(2)	1.662(6)			119.4(3)		
$[Mn(CO)_3(\eta^1\text{-}S_2CPCy_3)(\eta^2\text{-}S_2CPCy_3)]ClO_4$	2.383(2)	1.660(10)	1.815(9)	116.4(5)	121.9(4)	73.37(9)	[17]
	2.361(3)	1.673(7)			121.6(6)		
$[Mn(CO)_2(PEt_3)_2(\eta^2\text{-}S_2CPEt_3)]ClO_4$	2.375(1)	1.680(3)	1.795(3)	113.5(2)	122.4(2)	72.82(2)	[18]
	2.354(1)	1.677(3)			123.9(2)		
$Mn(CO)_3(SnCl_3)(\eta^2\text{-}S_2CPCy_3)$	2.362(2)	1.676(8)	1.817(8)	113.9	122.8	72.9(1)	[71]
	2.348(3)	1.663(7)			122.8		
$Mn(CO)_4(\eta^2\text{-}S_2CPCy_3)$	2.363(3)	1.679(6)	1.80(1)	112.8(1)	123.5(3)	72.6(1)	[72]
	2.363(3)	1.679(6)			123.5(3)		
$RuCl_2(CO)(P^iPr_3)(\eta^2\text{-}S_2CP^iPr_3)$	2.477(1)	1.670(4)	1.815(4)	115.2(2)	122.2(2)		[27]
	2.349(1)	1.667(4)			122.6(2)		

Table 4
Selected structural data of η^3-S_2CPR_3 complexes

Complexes η^3-S_2CPR_3	Distances (Å)			Angles (°)			Ref.
	M–S	C–S	M–C	C–P	S–C–S	S–C–P	
$MoCl(NO)(PMe_3)_2$ (η^3-S_2CPMe_3)	2.492(8) 2.500(11)	1.75(2) 1.76(3)	2.14(3)	1.74(3)	123(2)	117(2) 118(2)	[38]
$W(CO)_2(PMe_3)_2$ (η^3-S_2CPMe_3)	2.505(8) 2.541(7)	1.73(2) 1.77(2)	2.12(2)	1.74(2)	117(1)	120(1) 121(1)	[73]
$Fe(CO)_3$ (η^3-S_2CPCy_3) (molecule 1)	2.322(3) 2.300(3)	1.73(1) 1.76(1)	1.96(1)	1.80(1)	113.9(6)	121.0(6) 119.5(6)	[37]
(molecule 2)	2.328(3) 2.311(3)	1.77(1) 1.76(1)	1.99(1)	1.774(9)	112.5(5)	122.9(5) 120.0(6)	
[W(CR)(dppe) (η^3-S_2CPCy_3)]BF_4	2.404(4) 2.401(4)	1.75(1) 1.77(1)	2.142(10)	1.82(1)	120.8(6)	120.9(6) 117.1(6)	[13]

change from the monodentate to bidentate bonding mode represents a closure of the S–C–S angle from 129.5(3) to 116.4(5)°, respectively.

The crystal structures of only four complexes containing η^3-S_2CPR_3 ligands have been determined by X-ray methods. Table 4 show selected data. If the η^3-S_2CPR_3 ligand is considered to occupy two coordination sites, the geometries correspond to two d^6 distorted octahedral compounds (Mo and W), to one tungsten d^2 distorted square pyramidal complex and to a d^8 iron pentacoordinate derivative. The molecular structure of the latter is displayed in Fig. 5.

The central carbon atom of the S_2C fragment is well within bonding distance to the metal. These bond lengths range from 1.96(1) Å for the Fe compound to 2.14(1) Å in [W(CR)(dppe)(η^3-S_2CPCy_3)]BF_4. A salient feature of the η^3-coordination is the elongation of the S–C distances (1.73(1)–1.77(1) Å) with respect to those observed for the η^1- and η^2-derivatives.

Tables 5 and 6 collect selected data for complexes containing a bridging S_2CPR_3 ligand with coordination modes of the type represented in **IV** and **V** (see Scheme 4).

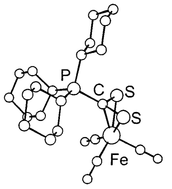
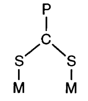


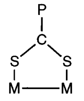
Fig. 5. Molecular structure of $Fe(CO)_3$(η^3-S_2CPCy_3).

In these cases we have considered together the complexes carrying a metal–metal bond and those without this interaction. However, it is possible to define more precisely the structurally characterized bonding modes μ-η^1(S),η^1(S′) and μ-η^1(S),η^2(S,S′) through the structures **X**–**XIV**.

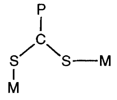
μ-$\eta^1\eta^1$



X

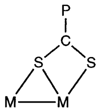


XI

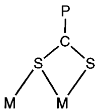


XII

μ-$\eta^1\eta^2$



XIII



XIV

X represents the complex $[Ag_2(\eta^2\text{-}S_2CPEt_3)_2(\mu\text{-}S_2CPEt_3)_2](ClO_4)_2$, **XI** depicts a metal–metal interaction that can be single (for $Re_2(CO)_8(\mu\text{-}S_2CPCy_3)$ and $Co_3(CO)_7(\mu\text{-}CH)(\mu\text{-}S_2CPCy_3)$ derivatives) or multiple (in complex $[Mo_2(OAc)_3(OPEt_3)(\mu\text{-}S_2CPEt_3)]BF_4$) and, finally, **XII** designates compound $[Au(C_6F_5)_3]_2(\mu\text{-}S_2CPEt_3)$. A general property encountered for all these examples are the planarity of the $M(\mu\text{-}S_2CPR_3)M$ fragment.

Complex $[Au(C_6F_5)_3]_2(\mu\text{-}S_2CPEt_3)$ (Fig. 6) merit some discussion because the two P–C–S–Au moieties differ apreciably, with Au–S bond lengths of 2.409(8), and 2.343(9) Å; and Au–S–C bond angles of 118.7(11), and 107.7(12)°. It seems that there is little delocalization in the S_2C group and that a suitable description of the hybridization would be sp^3 for S(1) and sp^2 for S(2). This would imply retention of

Table 5
Selected structural data of μ-$\eta^1\eta^1$-S_2CPR_3 complexes

Complexes μ-$\eta^1\eta^1$-S_2CPR_3	Distances (Å)		Angles (°)		Ref.
	M–S	C–S	C–P	S–C–S	
$[Ag(\eta^2\text{-}S_2CPEt_3)(\mu\text{-}S_2CPEt_3)]_2(ClO_4)_2$	2.468(2)	1.680(6)	1.817(6)	130.3(4)	[36]
	2.495(2)	1.661(7)			
$[Mo_2(OAc)_3(OPEt_3)(\mu\text{-}S_2CPEt_3)]BF_4$	2.380(2)	1.692(7)	1.792(7)	123.5(4)	[42]
	2.386(2)	1.673(7)			
$[Au(C_6F_5)_3]_2(\mu\text{-}S_2CPEt_3)$	2.409(8)	1.67(3)	1.87(3)	123(2)	[14]
	2.343(9)	1.66(3)			
$Re_2(CO)_8(\mu\text{-}S_2CPCy_3)$	2.462(1)	1.690(5)	1.830(6)	129.0(3)	[43]
	2.442(2)	1.666(5)			
$Co_3(CO)_7(\mu\text{-}CH)(\mu\text{-}S_2CPCy_3)$	2.253(2)	1.672(6)	128.2(4)		[41]
	2.246(2)	1.670(6)			

Table 6
Selected structural data of binuclear μ-$\eta^1\eta^2$- and μ-$\eta^1\eta^3$-S_2CPR_3 complexes

Complexes μ-$\eta^1\eta^2$-S_2CPR_3	Distances (Å)			Angles (°)			Ref.
	M–S	M′–S	C–S	C–P	S–C–S	S–C–P	
$Mo(CO)_2[S_2P(OEt)_2](SnPhCl_2)(S_2CPCy_3)$	2.488(2) 2.531(2)	2.999(2)	1.669(7) 1.684(7)	1.812(7)	114.9(4)	123.4(4) 121.7(4)	[46]
$[Pb(SOCPh)_2(S_2CPCy_3)]_2$	2.885(2) 3.639(2)	3.350(2)	1.685(7) 1.660(7)	1.826(7)	125.7(4)	114.7(4) 119.6(4)	[47]

Complexes μ-$\eta^1\eta^3$-S_2CPR_3	Distances (Å)				Angle (°)	Ref.
	M–S	M′–S	M–C	C–S	S–C–S	
$[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$	2.551(3) 2.520(3)	2.631(3)	2.14(1)	1.76(1) 1.75(1)	123.8(6)	[11]
$[MoMn(CO)_5(\mu\text{-}Br)(\mu\text{-tedip})(\mu\text{-}S_2CPCy_3)]$	2.502(8) 2.487(7)	2.383(7)	2.12(2)	1.76(2) 1.73(2)	123(1)	[51]

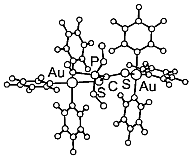


Fig. 6. Molecular structure of $[Au(C_6F_5)_3]_2(\mu\text{-}S_2CPEt_3)$.

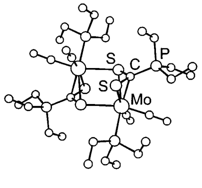


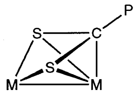
Fig. 7. Molecular structure of $[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$.

some double bond character for C–S(2), which cannot be confirmed because of the large esd values of the C–S bond lengths.

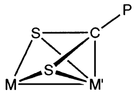
Coordination $\mu\text{-}\eta^1(S),\eta^2(S,S')$ is exemplified by complexes $Mo(CO)_2[S_2P(OEt)_2](SnPhCl_2)(S_2CPCy_3)$ and $[Pb(SOCPh)_2(S_2CPCy_3)]_2$. The former exhibits a short Sn–S intramolecular distance (2.999(2) Å), which is indicative of a bonding interaction. The latter is the first S_2CPR_3 complex of a main group element and shows a S_2CPCy_3 ligand binding the Pb center in an anisobidentate manner. The weakly bound sulphur of the S_2CPCy_3 acts as an intermolecular bridge.

The two $\mu\text{-}\eta^1(S),\eta^3(S,C,S')$ examples (structure **VII** in Scheme 4), namely $[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$ and $[MoMn(CO)_5(\mu\text{-}Br)(\mu\text{-tedip})(\mu\text{-}S_2CPCy_3)]$, contain a S_2CPR_3 ligand that bridges two metals not connected by bonding. For the molybdenum dimer (Fig. 7) two somewhat different Mo–S bonds can be envisaged: those involving the η^3-system (average 2.535(15) Å) and the η^1-Mo–S bond distance of 2.631(3) Å.

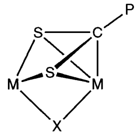
S_2CPR_3 ligand acting as a $\mu\text{-}\eta^2\eta^3$-bridge in binuclear complexes is the coordination habit more studied by diffraction methods. Riera, Miguel and co-workers have reported 16 crystal structures of homo- and hetero-bimetallic complexes, with or without metal–metal bonds (structures **XV**–**XVIII**) for which selected data are compiled in Table 7.



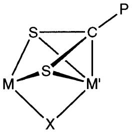
XV



XVI



XVII



XVIII

Table 7
Selected structural data of binuclear μ-$\eta^2\eta^3$-S_2CPR_3 complexes

Complexes μ-$\eta^2\eta^3$-S_2CPR_3	Distances (Å)			Angles (°)			Ref.
	M–S	M–C	M′–S	C–S	S–C–S	M–S–M	
$[Mn_2(CO)_6(\mu\text{-}S_2CPCy_3)]$	2.335(2)	2.023(7)	2.282(2)	1.773(7)	103.7(3)	72.7(1)	[55]
	2.333(2)		2.276(2)	1.785(6)		72.9(1)	
$[Mn_2(CO)_4(\mu\text{-dppm})(\mu\text{-}S_2CPCy_3)]$	2.379(1)	2.026(3)	2.232(1)	1.793(2)	102.3(1)	76.5(1)	[55]
	2.378(1)		2.309(1)	1.813(2)		75.1(1)	
$[MnRe(CO)_6(\mu\text{-}S_2CPCy_3)]$	2.351(2)	2.030(5)	2.407(1)	1.761(5)	105.6(3)		[43]
	2.343(2)		2.395(1)	1.775(5)			
$[MoMn(CO)_6(\mu\text{-Br})(\mu\text{-}S_2CP^iPr_3)]$	2.513(1)	2.138(5)	2.387(2)	1.787(5)	106.9(3)	82.6(1)	[51]
	2.506(1)		2.403(2)	1.776(5)		82.4(1)	
$[Mo(CO)_2(PCy_3)(\mu\text{-Cl})(SnCl_2Bu)(S_2CPCy_3)]$	2.496(4)	2.16(1)	2.720(4)				[60]
	2.579(4)		2.538(4)				
$[WRu(C_6Me_6)(CO)_3(\mu\text{-Cl})(\mu\text{-}S_2CPCy_3)]$	2.524(4)	2.12(1)	2.429(4)	1.81(1)	103.4(6)		[58]
	2.523(4)		2.433(4)	1.80(1)			
$[MnMo(CO)_6(SnPh_3)(\mu\text{-}S_2CP^iPr_3)]$	2.377(1)	2.029(4)	2.453(1)		105.7(2)		[74]
	2.352(1)		2.464(1)				
$[Mo_2(CO)_5(\eta^3\text{-}C_3H_5)(\mu\text{-Br})(\mu\text{-}S_2CPCy_3)]$	2.518(2)	2.132(8)	2.604(2)	1.758(8)	110.4(5)		[33]
	2.519(2)		2.568(2)	1.770(8)			
$[CoMn(CO)_5(\mu\text{-}S_2CPCy_3)]$	2.282(1)	1.966(3)	2.294(1)	1.754(3)	107.6(2)		[53]
	2.279(1)		2.313(1)	1.757(3)			
$[CoMo(CO)_4(\eta^3\text{-}C_3H_5)(\mu\text{-}S_2CPCy_3)]$	2.289(3)	1.91(1)	2.493(3)	1.70(1)	114.3(7)	69.2(1)	[53]
	2.285(4)		2.496(3)	1.75(1)		69.2(1)	
$[MoMn(CO)_6(\mu\text{-SePh})(\mu\text{-}S_2CP^iPr_3)]$	2.499(1)	2.145(5)	2.394(1)	1.793(4)	106.1(2)		[75]
	2.520(1)		2.409(1)	1.801(5)			
$[MnMo(CO)_5(\mu\text{-}PPh_2)(\mu\text{-}S_2CP^iPr_3)]$	2.274(3)	2.052(9)	2.452(3)	1.787(8)	106.6(5)		[75]
	2.367(3)		2.584(2)	1.765(9)			
$[MnMo(CO)_4(SnPh_3)(\mu\text{-tedip})(S_2CP^iPr_3)]$	2.38(1)	1.99(4)	2.45(1)	1.76(4)	103(2)		[76]
	2.34(1)		2.44(1)	1.81(4)			
$[Mo_2(CO)_4(PEt_3)(NO)(\mu\text{-Br})(\mu\text{-}S_2CPCy_3)]$	2.54(2)	2.20(4)	2.57(2)	1.87(5)	106.1(22)	82.8(5)	[77]
	2.52(2)		2.59(2)	1.83(4)	82.9(5)		

Table 7 (continued)

Complexes μ-$\eta^2\eta^3$-S_2CPR_3	Distances (Å)			Angles (°)			Ref.
	M–S	M–C	M′–S	C–S	S–C–S	M–S–M	
$[Re_2(CO)_6(\mu\text{-}S_2CPCy_3)]$	2.494(2)	2.176(4)	2.4250(13)	1.804(4)	104.0(2)		[43]
	2.4955(13)		2.4106(13)	1.798(4)			
$[MoMn(CO)_6(\mu\text{-}CCPh)(\mu\text{-}S_2CPCy_3)]$	2.503(5)	2.10(2)	2.521(5)	1.74(2)	111(1)	78.5(1)	[78]
	2.505(5)		2.506(5)	1.77(2)		78.7(1)	
$[MoMn(CO)_6(\mu\text{-}S_2CPCy_3)]_2(\mu\text{-}CC)$	2.502(6)	2.13(2)	2.377(7)	1.77(2)	107(1)	74.7(2)	[78]
	2.486(6)	2.10(2)	2.359(6)	1.78(2)	108(1)	75.3(2)	
	2.482(6)		2.367(6)			75.6(2)	
	2.496(6)		2.350(6)			75.7(2)	
$[Mo(CO)_3Re(CO)_3(SnPh_3)(\mu\text{-}S_2CPCy_3)]$	2.500(8)	2.18(3)	2.432(7)	1.70(3)	109.7(15)	72.4(2)	[44]
	2.507(9)		2.468(8)	1.80(3)		71.7(2)	
$[Mo(CO)_3(SnPh_3)Re(CO)_3(\mu\text{-}S_2CPCy_3)]$	2.533(5)	2.18(1)	2.417(4)	1.78(2)	106.2(7)	76.6(1)	[44]
	2.525(5)		2.404(6)	1.75(1)		77.0(1)	

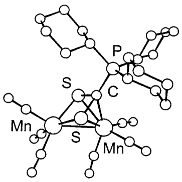


Fig. 8. Molecular structure of $[Mn_2(CO)_6(\mu\text{-}S_2CPCy_3)]$.

In all cases, a bonding connection is considered for the distance observed between the carbon atom of the S_2C group and the metal (1.91(1)–2.16(1) Å). Additionally, the largest S–C bond lengths are found in these complexes with respect to the previously discussed bonding modes.

Homonuclear derivatives containing identical coligands around the two metal centers, as for example $[Mn_2(CO)_6(\mu\text{-}S_2CPCy_3)]$ (Fig. 8) or $[Mn_2(CO)_4(\mu\text{-dppm})(\mu\text{-}S_2CPCy_3)]$, allow precise comparisons to be made between the two metal–sulphur bond types (η^2 and η^3). In both examples, the S–Mn bonds corresponding to the η^2-interaction (σ type) are shorter than the other S–Mn bonds involved in the η^3-coordination (π type).

The complexes carrying the $\mu\text{-}\eta^2(S,S'),\eta^3(S,C,S')\text{-}S_2CPR_3$ bridging ligand without a direct metal-to-metal bond always exhibit a second bridging coligand to maintain the dimetallic assembly. Fig. 9 displays complex $[MoMn(CO)_6(\mu\text{-Br})(\mu\text{-}S_2CP^iPr_3)]$, the first reported of this type.

Finally, we have surveyed the structural properties of S_2CPR_3 ligands coordinated to transition metal centers by using the Cambridge Structural Database [79] (CSD, Version 5.15, 181309 entries). We have centered our attention on S–C bond distances and the S–C–S angle and we analyzed the dispersion of both parameters. The final data files contained 57 fragments from 36 structures. The distribution of the S–C distance in this type of compounds is relatively narrow. The observed range goes from the minimun value of 1.630(4) Å for $Au(C_6F_5)_3(\eta^1\text{-}S_2CPEt_3)$ (FUCXOQ, CSD reference code) to 1.81(4) Å corresponding to $[MnMo(CO)_4(SnPh_3)(\mu\text{-tedip})(S_2CP^iPr_3)]$ (YUGZIJ). The range for S–C–S angles is wider in dispersion than the S–C length and covers from 102.3(1)° in $[Mn_2(CO)_4(\mu\text{-dppm})(\mu\text{-}S_2CPCy_3)]$ (TAGWUT) to 131.4(3)° for compound $Au(C_6F_5)_3(\eta^1\text{-}S_2CPEt_3)$ (FUCXOQ). We have analyzed the possible correlation between the

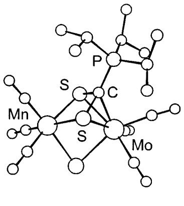


Fig. 9. Molecular structure of $[MoMn(CO)_6(\mu\text{-Br})(\mu\text{-}S_2CP^iPr_3)]$.

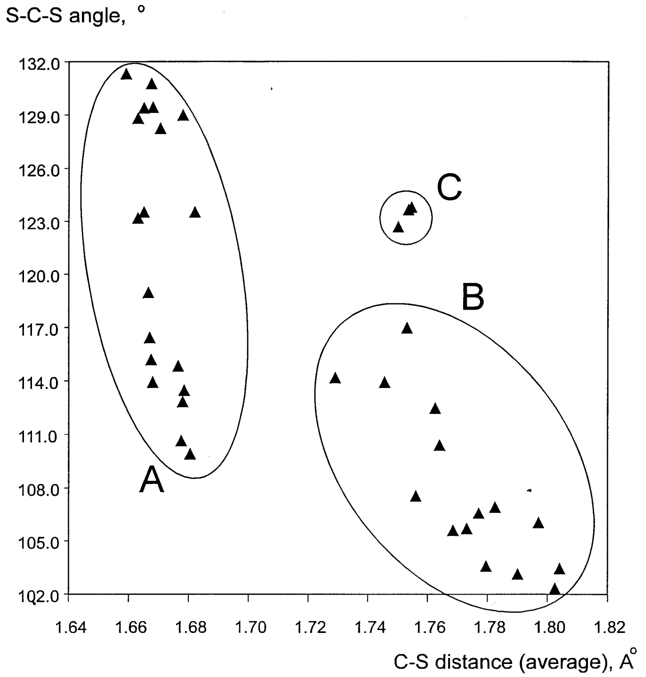
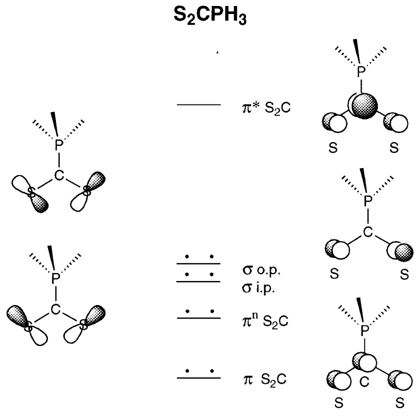


Fig. 10. Scattergram for the 36 structures under observation.

closure of the S–C–S angle with respect to a elongation of the S–C distance. This trend exists and it is clearly evidenced in the scatter representation of the S–C–S angle versus the S–C average for each complex. Fig. 10 displays the corresponding scattergram. The 36 structures are clustered in three separate regions labelled A, B and C. Interestingly, the B and C zones correspond only to mononuclear or binuclear complexes containing the η^3-coordination mode for the S_2CPR_3 ligand (includes the η^3(S,C,S′) (**III**), μ-η^1(S),η^3(S,C,S′) (**VII**) and μ-η^2(S,S′),η^3(S,C,S′) (**VIII**) modes of bonding). On the contrary, the area A involves only the other modes of connectivity in which there is no participation of the central carbon atom (it comprises the η^1(S) (**I**), η^2(S,S′) (**II**), μ-η^1(S),η^1(S′) (**IV**) and μ-η^1(S),η^2(S,S′) (**V**) modes). This bond and angles distribution can be described approximately in the following manner: long C–S distances and acute S–C–S angles are characteristic of η^3(S,C,S′) bonding form while, conversely, short C–S bonds and S–C–S angles close to 120° are indicative of the absence of such carbon–metal interaction.

3.2. Bonding analysis

The frontier FMOs of the model ligand S_2CPH_3 have been described recently [13]. They are represented in Scheme 18 and, essentially, these consist of two sets of σ (left side) and π (right side) FMOs. The former are two filled in-plane combina-



Scheme 18.

tions of sulphur lone pairs (in-phase $\sigma_{i.p.}$ and out-of-phase, $\sigma_{o.p.}$), while the latter are the π-S_2C system containing 4e$^-$. Beside the empty π^*-S_2C level, these include the π-S_2C and π^n-S_2C combinations.

The use of symmetry considerations and qualitative MO theory allows the rationalization of the bonding modes found in complexes containing these ligands.

η^1(S) bonding can be defined in terms of a 2e$^-$ σ-donation by using a combination of $\sigma_{i.p.}$ and $\sigma_{o.p.}$ FMOs (Scheme 18). Therefore, the η^1(S)-S_2CPR_3 ligand must be encountered with C_{4v} d^6-ML_5 and 16e$^-$ C_{2v} d^8-ML_3 metal fragments as effectively occurs in the examples reported in Table 2. Other examples, with a proposed η^1(S) coordination, but whitout the X-ray characterization, are known (see Section 2.1.1) for the same metal fragments.

The bridging examples in which the S_2CPR_3 acts as μ-η^1(S),η^1(S′) ligand can be also explained on the basis of the previously summarised considerations, that is the use of in plane σ-sulphur FMOs and, consequently, the donation of 4e$^-$, two for each metal.

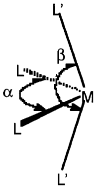
The bidentate η^2(S,S′) mode is an example of a two site-4e$^-$ σ-donation through also the $\sigma_{i.p.}$ and $\sigma_{o.p.}$ combinations. Thus, this coordination pattern fits well with C_{2v} d^6-ML_4 (complexes of Mn(I), Fe(II) and Ru(II) of Table 3), C_{3v} d^8-ML_3 (Ir(I) complex of Table 3) and 16e$^-$ C_{2v} d^8-ML_2 (Pd(II) complex of Table 3) metal fragments. Various complexes displaying bidentate S_2CPR_3 ligands, not structurally distinguished, have been reported [12,19,25,35] with identical metal ML_n entities.

Considering the C_{2v} d^6-ML_4 case, the major interactions would be those of the empty $2a_1$ and b_2 metal FMOs [80] with the sulphur $\sigma_{i.p.}$ and $\sigma_{o.p.}$ combinations, respectively. Analogous description can be outlined for the bonding with the C_{2v} d^8-ML_2 metal fragment ($2a_1$ and b_2 metal FMOs). Specific calculations have been carried out [37,81] on the model $[Ir(CO)(PH_3)_2(\eta^2\text{-}S_2CPH_3)]^+$ that highlights the dominant interactions ($2a_1$ and $2e_s$ metal FMOs of the ideal C_{3v} d^8-ML_3) with the in plane sulphur FMOs.

The $\eta^2(S,S')$ bonding type has been recently considered in the MO study, by EH methods, for several Mn(I) model compounds [72], in order to explain the experimental electrode oxidation potentials observed for the real complexes.

The electron counting for the $\eta^3(S,S',C)$ coordination of the S_2CPR_3 ligand is also four as in the $\eta^2(S,S')$ mode (although there is one example in which donation of $6e^-$ has been proposed [13]). Consequently, the same metal fragments previously discussed for the bidentate coordination can accomodate the $\eta^3(S,S',C)$ mode. The electronic factors affecting the dichotomy between the two coordination modes in dithiocarboxy complexes have been discussed by Mealli and us [37]. The $4e^-$ donation comes from the two filled π-S_2C and π^n-S_2C levels. Most critical for the η^3-coordination is the nature of the filled metal $d\pi_\perp$ orbital suited to interact with the empty π^*-S_2C level centered on the central carbon of the S_2C fragment. MO studies [13,37] on the interaction between the ligand S_2CPR_3 and the metal fragments corresponding to all the structurally identified η^3-compounds (Table 4) pointed out the importance of the back-donation into the FMO π^*-S_2C (generally, the strongest observed in terms of overlap populations between fragment orbitals). In general, the HOMO of $M(\eta^3$-$S_2CPR_3)L_n$ complexes appears as the bonding combination between the two levels in question ($d\pi_\perp$ and π^*-S_2C).

The more hybridized and destabilized is the metal FMO, the better is the back-donation. Thus, beside the nature of the metal (the oxidation state and the charge are of importance) and that of the coligands, the effects of the deformation of the geometry seem to be crucial. For example, concerning the ML_4 fragments ($W(CO)_2(PMe_3)_2(\eta^3$-$S_2CPMe_3)$ and $MoCl(NO)(PMe_3)_2(\eta^3$-$S_2CPMe_3)$ complexes), the two angles α and β (shown in **XIX**) do in general vary from 90 to 110° and from 180 to 150°, respectively. Similar structural deformations have been observed [82] in complexes containing other π-$4e^-$ donor ligands coordinated to ML_4 fragments.



XIX

Analogously, the same effect can be observed in compound $Fe(CO)_3(\eta^3$-$S_2CPCy_3)$, where the pyramidalization of the ML_3 fragment produces the development of the $2e_s$ metal hybrid of the ideal C_{3v} d^8-ML_3 and justify the staggered disposition of the S_2CP group with respect to the three CO ligands in terms of a better overlap between fragments. The barrier of rotation of the η^3-S_2CPCy_3 pseudoallyl has been analyzed by DFT methods [83].

The fluxional behaviour of the $W(CO)_2(PMe_3)_2(\eta^3$-$S_2CPMe_3)$ complex has been studied by EHMO calculations. The dynamic NMR spectra has been explained [84] through a restricted intramolecular process where the S_2CPMe_3 fragment undergoes propeller rotation between the two W–CO bonds in a concerted Berry-pseudorotational process on the $W(CO)_2(PMe_3)_2$ fragment.

The same arguments outlined for the $\eta^3(S,C,S')$ derivatives must be considered for the bridging S_2CPR_3 complexes in which there is a carbon–metal bond, that is the coordination modes: μ-η^1(S),η^3(S,C,S′) and μ-η^2(S,S′),η^3(S,C,S′). The bonding description of these cases would be the following: the π fraction of the S_2CPR_3 ligand is responsible for the η^3(S,C,S′) coordination (4e$^-$ to one metal), while the σ component accounts for the η^1(S) or η^2(S,S′) bonding (2 or 4e$^-$ to the second metal, respectively).

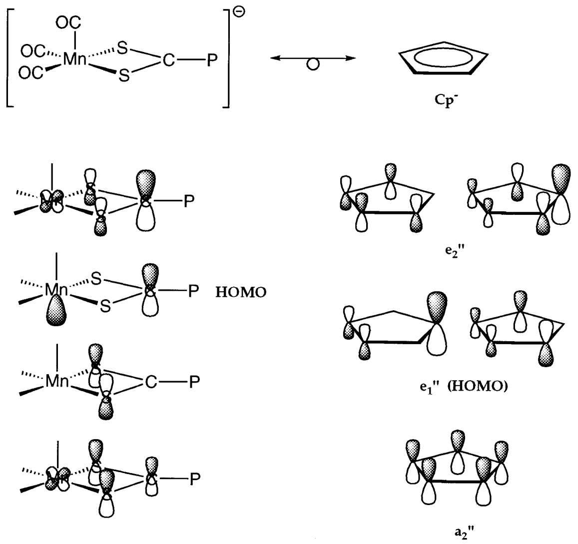
Considering the examples of Table 7 (μ-η^2(S,S′),η^3(S,C,S′)) containing a metal–metal bond (**XV** and **XVI**), there are the following possibilities of metal–metal fragments: d^7ML_3–d^7ML_3, d^7ML_3–d^9ML_2, d^5ML_4–d^7ML_3, d^5ML_4–d^9ML_2 and d^6ML_4–d^6ML_3. On the other hand, for those non containing a metal–metal bond (**XVII** and **XVIII**), there are the following metal–metal fragments: d^6ML_4,d^6ML_4 and d^4ML_5,d^6ML_4. For all the cases, 8e$^-$ would saturate the metal centers and this can be attained through the simultaneous use of the σ and π combinations. The predictable question is: what metal will accomodate the η^3(S,C,S′) interaction?

Jemmis and co-workers have communicated [85] a MO study of μ-S_2CPR_3 complexes devoted to evaluating the direction of tilting of the bridging ligands. The concept of compatibility of orbitals in overlap has been used to explain the observed preferential tilting toward the metal that provides more diffuse orbitals. In this and previous works [86], Jemmis highlights the effect of pyramidalization of one metal of the dimer, precisely that bonding the central carbon atom of the S_2CPR_3 ligand.

However, Miguel, Riera and co-workers have shown different examples in which the prediction made by Jemmis is not observed. For example, in [MnMo(CO)$_5$(μ-PPh$_2$)(μ-$S_2CP^iPr_3$)], [CoMn(CO)$_5$(μ-S_2CPCy_3)], [CoMo(CO)$_4$(η^3-C_3H_5)(μ-S_2CPCy_3)] and [MnMo(CO)$_6$(SnPh$_3$)(μ-$S_2CP^iPr_3$)] complexes. From experimental findings, the central carbon atom of the S_2CPR_3 ligand in these cases prefers to bind the metal in the lower oxidation state. The general η^3-MO description stands between two limiting situations. The first picture is consistent with the typical model of donation and back-donation. The second interpretation suggests that an oxidative addition of the metal may have occurred in going from η^2 to η^3 coordination [37]. Both representations requires invariably a low oxidation state metal.

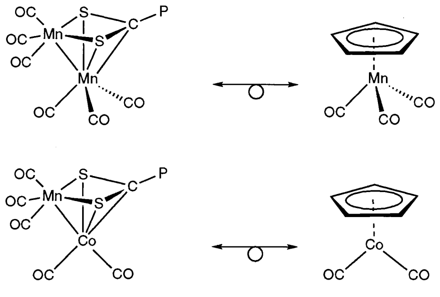
The observed preferences of the η^3-mode might be a balance between several electronic factors, including the diffuseness of the orbitals (Jemmis prediction explains satisfactorily the preferential tilting of S_2CPR_3 ligand in [MnRe(CO)$_6$(μ-S_2CPCy_3)], where the oxidation state guidelines can not be invoked) and the electron richness of the fragment involved. This balance is very subtle and the recent preparation [44] and structural characterization of the two isomers of the complex [MoRe(CO)$_6$-(SnPh$_3$)(μ-S_2CPCy_3)] confirms this assertion. Both isomers have the S_2CPCy_3 ligand η^3-coordinated to the molybdenum atom, but in the case of the isomer [(CO)$_3$Mo(μ-S_2CPCy_3)Re(CO)$_3$(SnPh$_3$)] the carbon atom bonds the metal in lower oxidation state, meanwhile for the [(CO)$_3$(SnPh$_3$)Mo(μ-S_2CPCy_3)Re(CO)$_3$] example the ligands tilts to the metal that provides more diffuse orbitals. Interestingly, both isomers interconvert reversibly at r.t. [44], through intramolecular migration of the SnPh$_3$ group, this suggesting that, in this case, the two factors (electron richness of the fragments and diffusiveness of the offered orbitals) are close enough to balance to each other.

DFT ab initio calculations and experimental charge density studies have been carried out on [M(CO)$_6$(μ-S_2CPR_3)] dimers [87].



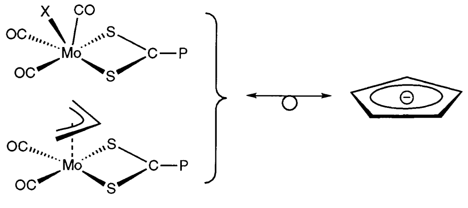
Scheme 19.

Finally, the structural results collected in Table 7 prompted us to compare some M(η^2-S_2CPR_3)L_n fragments with ligands that will bond with the remaining part of the dimetallic unit. In this context, we have correlated some of these metallic fragments to Cp^- and C_6H_6 ligands by using the isolobal analogy [88]. Scheme 19 shows a qualitative description of such isolobal connection. It displays the main high energy occupied and low energy unoccupied orbitals of the Mn(η^2-S_2CPH_3)$(CO)_3^-$ model fragment and those of cyclopentadienyl anion. The appearance and nodal properties of the four FMOs depicted for the metallic fragment are very similar with respect to those of Cp^-. Decisive for the electronic relationship to Cp^- are the π contribution of the S_2CPR_3 ligand in the M(η^2-S_2CPR_3)L_n fragment. The bonding towards another fragment involves in each case the S_2C group and the metal center, so that overlap with a second metal fragment necessarily implies a metal–metal bond and a carbon–metal bond (η^3-coordination). **XX** shows the isolobal relationship between [$Mn_2(CO)_6$(μ-S_2CPCy_3)] and [$CoMn(CO)_5$(μ-S_2CPCy_3)] complexes and the known cyclopentadienyl derivatives $CpMn(CO)_3$ and $CpCo(CO)_2$, respectively.



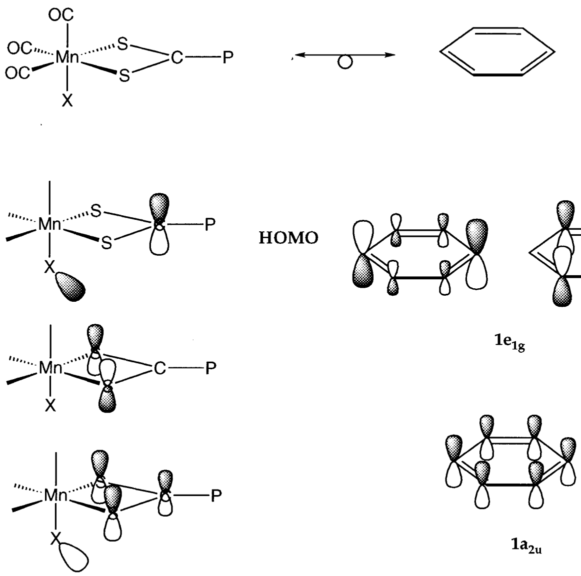
XX

Besides the d^7 $M(\eta^2\text{-}S_2CPR_3)L_3^-$ example, other metallic fragments that can be correlated with the Cp^- ligand are d^6 $M(\eta^2\text{-}S_2CPR_3)XL_3$. **XXI** displays the isolobal analogy between this type of fragments and the cyclopentadienyl ligand. Therefore, $[MnMo(CO)_6(SnPh_3)(\mu\text{-}S_2CP^iPr_3)]$ and $[CoMo(CO)_4(\eta^3\text{-}C_3H_5)(\mu\text{-}S_2CPCy_3)]$ complexes can be also compared to $CpMn(CO)_3$ and $CpCo(CO)_2$ derivatives, respectively.



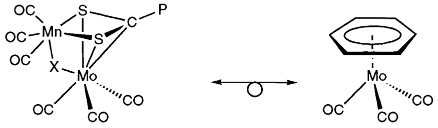
XXI

Analogously, Scheme 20 displays a qualitative drawing of selected MOs corresponding to the $Mn(\eta^2\text{-}S_2CPH_3)(X)(CO)_3$ model compound. They show comparable nodal properties to those orbitals known for the C_6H_6 ligand and both can be related through the isolobal analogy. In this case, the bonding toward the other metal fragment involves also the S_2C group and the halogen atom (or pseudohalogen group), so the overlap with a second metal fragment necessarily implies an halogen (or pseudohalogen) bridge and not a metal–metal bond. **XXII** shows the isolobal relationship between $[MoMn(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CP^iPr_3)]$ and [MoMn-



Scheme 20.

$(CO)_6(\mu\text{-SePh})(\mu\text{-}S_2CP^iPr_3)]$ complexes and the known benzene derivative $(C_6H_6)Mo(CO)_3$.



XXII

These isolobal relationships illustrate in some cases the appropriate synthetic methodology used for the preparation of several of these dimetallic complexes (see for example the Schemes 16 and 17).

4. Reactivity of complexes containing S_2CPR_3 ligands

For most types of complexes the studies of reactivity have been limited by the lability of the ligands, as it has been pointed out in the appropriate paragraphs of Section 2. The reactions reported concern mainly with the most robust coordination modes such as $\eta^2(S,S')$ chelate, $\eta^3(S,C,S')$ pseudoallyl, or $\eta^2(S,S');\eta^3(S,C,S')$ bridges. These will discussed briefly in the following sections.

4.1. Mononuclear complexes

4.1.1. η^2-(S,S) chelates

4.1.1.1. Ligand substitution, ring opening and closing, and insertion reactions. All these reactions have the common feature of producing new complexes containing S_2CPR_3 ligands.

A number of derivatives have been made by substitution reactions, especially in carbonyl complexes. Several examples are:

$$[RuCl_2(S_2CPEtPh_2)(PEtPh_2)_2] + MeOH$$

$$\rightarrow [RuCl(MeOH)(S_2CPEtPh_2)(PEtPh_2)_2]^+ + Cl^- \quad \text{(Ref. [25])}$$

$$[Mn(CO)_3(S_2CPCy_3)Br] + AgClO_4 + L$$

$$\rightarrow [Mn(CO)_3(S_2CPCy_3)(L)]ClO_4 + AgBr$$

$L = P(OR)_3$, $CNBu^t$ (Ref. [12])

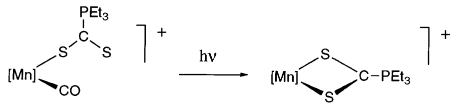
In some cases, the entering ligand produces the opening of the M–S–C–S ring, thus affording a complex with monodentate $SC(S)PR_3$:

$$[(C_6X_5)_2Pt(S_2CPCy_3)] + CO \rightarrow [(C_6X_5)_2(CO)Pt\{SC(S)PCy_3\}]$$

$X = F$, Cl (Ref. [23])

$$[Mn(CO)_3(S_2CPCy_3)(L)]ClO_4 + L \rightarrow [Mn(CO)_3(SC(S)PCy_3)(L)_2]ClO_4$$

$L = P(OR)_3$, $CNBu^t$ (Ref. [12])



[Mn] = $Mn(CO)_4$, $Mn(CO)_3(PEt_3)$, $Mn(CO)_2(PEt_3)_2$, $Mn(CO)_2\{P(OR)_3\}_2$

Scheme 21.

Complexes with monodentate $SC(S)PR_3$ ligands are prone to lose carbon disulfide upon heating, providing complexes with the PR_3 group bonded to the metal. However, in some cases it is possible to force the substitution of CO by UV irradiation, producing a complex with chelate S_2CPR_3, in a ring-closing reaction (Scheme 21) [12].

In one case, the ring-closing of S_2CPR_3 has been promoted by creating a coordination position through oxidation of the metal [89]:

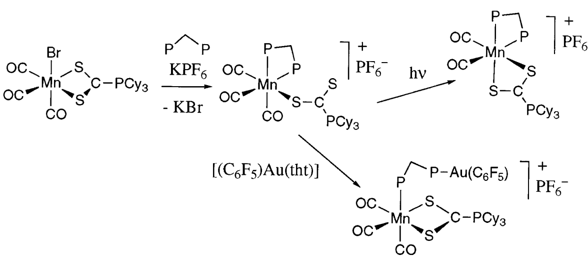
$$[(\mathrm{triphos})\mathrm{RhCl}\{\mathrm{SC(S)PEt_3}\}] + \mathrm{I_2} \rightarrow [(\mathrm{triphos})\mathrm{RhCl}(\mathrm{S_2CPEt_3})]\mathrm{I_2}$$

When $[Mn(CO)_3(S_2CPCy_3)Br]$ is treated with dppm, in the presence of KPF_6, both halide displacement and ring-opening of S_2CPR_3 are produced spontaneously (Scheme 22) to afford $[Mn(CO)_3(dppm)\{SC(S)PCy_3\}]PF_6$ in a one-pot reaction [12]. Displacement of carbonyl in this complex can be promoted by UV irradiation, to give $[Mn(CO)_2(dppm)(S_2CPCy_3)]PF_6$, in which both dppm and S_2CPCy_3 act as chelates. Quite remarkably, the reaction of $[Mn(CO)_3(dppm)\{SC(S)PCy_3\}]PF_6$ with $[(C_6F_5)Au(thf)]$, in an attemp to obtain a complex with $\eta^1(S);\eta^1(S')$-S_2CPR_3 bridge, gives instead complex $[(S_2CPCy_3)(CO)_3Mn(P–P)Au(C_6F_5)]PF_6$ (see Scheme 22), containing chelate S_2CPCy_3 and bridging dppm. The process involves the ring-opening of the dppm chelate, and the closing of the M–S–C–S ring of S_2CPR_3 [12].

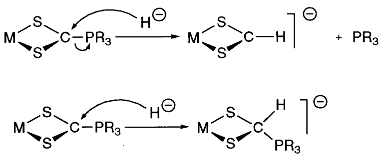
Several examples have been found of facile insertion of SnX_2 into X–M bonds, as summarized in the following reactions:

$$[(\eta^6\text{-arene})\mathrm{Ru}(\mathrm{S_2CPR_3})\mathrm{Cl}]^+ + \mathrm{SnCl_2}$$
$$\rightarrow [(\eta^6\text{-arene})\mathrm{Ru}(\mathrm{S_2CPR_3})\mathrm{SnCl_3}]^+ \text{ (Ref. [35])}$$
$$[\mathrm{M(CO)_3(S_2CPR_3)X}] + \mathrm{SnX_2} \rightarrow [\mathrm{M(CO)_3(S_2CPR_3)SnX_3}]$$

(M = Mn, Re; X = Cl, Br) (Ref. [71])



Scheme 22.



Scheme 23.

While in the case of the arene ruthenium complexes the insertion of SnX_2 was well precedented, in manganese and rhenium compounds it was found that these insertion were favored by the presence of the S_2CPR_3 chelate, and did not occur in similar complexes containing other chelating ligands such as bipy, phen, or diphosphines.

4.1.1.2. Nucleophilic addition to carbon. Apart from their use as starting materials for the preparation of binuclear compounds (see Section 2.2.5), the most important reactivity of chelate S_2CPR_3 complexes is confined to nucleophilic attack by hydride ion on the central carbon atom of the S_2CPR_3 ligand. Depending on the combination of ligands and metal center, two types of products arise from these reactions (see Scheme 23). In some cases, the initial hydride attack produces (trialkylphosphonio)metanedithiolate, $S_2C(H)PR_3^-$, which remains attached to the metal atom as a chelate, whereas in other cases the PR_3 group is lost, to afford a dithioformate (S_2CH^-) complex.

Several examples of both types of behavior are known and, although both electronic and steric factors have been invoked in particular cases [31], no regular trend for this behavior has been found so far.

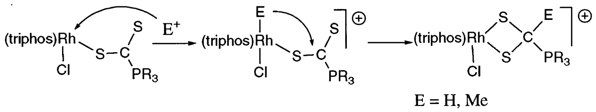
$[(depe)_2Fe(S_2CPEt_3)]^{2+} + H^- \rightarrow [(depe)_2Fe(S_2CH)]^+ + PEt_3$ (Ref. [31])

$[Mn(CO)_2(PEt_3)_2(S_2CPEt_3)]^+ + H^- \rightarrow [Mn(CO)_2(PEt_3)_2(S_2CH)]$ (Ref. [18])

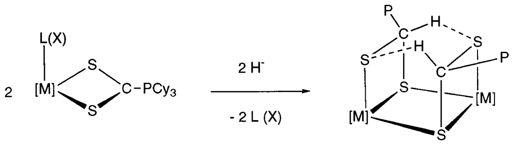
$(triphos)M(S_2CPEt_3)^{2+} + H^- \rightarrow (triphos)M\{S_2C(H)PEt_3\}^+$

M = Co [30,90], Ni [91]

The electron-rich rhodium(I) complex $[(triphos)ClRh\{SC(S)PEt_3)]$ undergoes addition of electrophiles such as H^+ or Me^+ to afford a Rh(III) complex containing a chelate $S_2C(E)PR_3^-$ (E = H, Me) ligand [89]. The electrophile is probably added to the metal atom in the first step, which would be followed by an intramolecular nucleophilic attack of hydride (or methyl) to the central carbon of S_2CPR_3, affording the final complex, as outlined in Scheme 24.



Scheme 24.



$[M] = Mn(CO)_3^+$, $Re(CO)_3^+$; L= CO
$[M] = Mo(CO)_2$, X = Br

Scheme 25.

In octahedral carbonyl complexes of Mn [92,93], Re [93] and Mo [94], the formation of the $S_2C(H)PR_3^-$ ligand is followed by spontaneous dimerization to afford binuclear complexes in which the M–S–C–S rings adopt a *cisoid* disposition (see Scheme 25), thus forming a distorted quasi-cubane cage. Crystallographic and NMR data suggest that the presence of S···H(C–P) contacts may be the driving force responsible for the formation of the cage.

The central carbon of coordinated S_2CPR_3 in $[(triphos)Co(S_2CPEt_3)]^{2+}$ can be attacked by nucleophiles other than hydride, such as OH^-, RO^-, S^{2-}, RS^-, or NR_2^-, but the addition products are not stable. However, if the resulting solutions are treated with O_2 or S_8, stable complexes containing dithiocarbonate, $[(triphos)Co(S_2CO)]$, or trithiocarbonate, $[(triphos)Co(S_2CS)]$, ligands can be isolated and characterized [90].

Some cases have been reported in which the phosphoniomethanedithiolate complex can be obtained directly by addition of S_2CPR_3 to a suitable precursor, usually a hydride complex, or a metal complex in a protic solvent:

$$[Co(H_2O)_6]^{2+} + L_3 + S_2CPEt_3 \rightarrow [(triphos)Co\{S_2C(H)PEt_3\}]^{2+}$$

$L_3 =$ triphos, $MeC(CH_2PPh_2)_3$; etriphos, $MeC(CH_2PEt_2)_3$ (Ref. [30])

$$[(PR_3)_3PdH]^+ + CS_2 \rightarrow [(PR_3)_3Pd\{S_2C(H)PR_3\}]^+ \quad (R = Me, Et; Ref. [28])$$

In one case, a mixture of the complexes with S_2CPR_3, and $S_2C(H)PR_3$ are obtained in the same reaction: treatment of $[RuClH(CO)(PPh_3)_3]$ or $[RuH(CO)(NCMe)_2(PPh_3)_2]ClO_4$ with S_2CPCy_3 gives a mixture of hexacoordinate $[RuH(CO)(PPh_3)_2(S_2CPCy_3)]^+$ and pentacoordinate $[Ru(CO)(PPh_3)_2\{S_2C(H)PCy_3\}]^+$ [16]. Interestingly, the reaction of $[RuHCl(CS)(PPh_3)_3]$ with S_2CPCy_3 gives only the η^2-S_2CPCy_3 complex $[RuH(CS)(PPh_3)_2(S_2CPCy_3)]^+$.

Alternatively, phosphoniomethane dithiolate ligands can be formed by attack of phosphine to a coordinated dithioformate:

$$[W(Cp)(CO)_2(S_2CMe)] + PMe_3 \rightarrow [W(Cp)(CO)_2\{S_2C(Me)PMe_3\}]$$

R = Me [95]

When the carbon atom is bonded to aryl groups, desulfurization takes place, to afford a phosphoniothiolate ligand coordinated through sulfur and carbon:

$$[W(Cp)(CO)_2(S_2CR)] + PMe_3 \rightarrow [W(Cp)(CO)_2\{(\eta^2\text{-}SC(R)PMe_3\}] + SPMe_3$$

$R = Ph$, C_6H_4Me [95]

In other cases, the addition of PR_3 to the carbon atom of dithiocarboxylate, xanthate, or dithioxanthate is not followed by desulfurization:

$$[W(Cp)(Ph)(NO)(S_2CPh)] + PMe_3 \rightarrow [W(Cp)(Ph)(NO)\{S_2C(Ph)PMe_3\}] \text{ [96]}$$

$$MOCl_2(PMe_3)_3 + KS_2CER \rightarrow MO\{S_2C(ER)PMe_3\}(S_2CER) + 2PMe_3 + 2KCl$$

$M = Mo, W$; $E = O$ [97], S [98]

$$[(tppme)M(S_2CSMe)]^+ + PEt_3 \rightarrow [(tppme)M\{S_2C(SMe)PEt_3\}]^+$$

$tppme = CH_3C(CH_2PPh_2)_3$; $M = Co, Ni$ [99]

Analogous species have been produced by intramolecular attack of a diphosphine or polyphosphine to the central carbon of a dithioformate ($M = Mn, Re$ [100]), or dithiocarboxylate ($M = Co$ [101], Ni [102]), as outlined in Scheme 26.

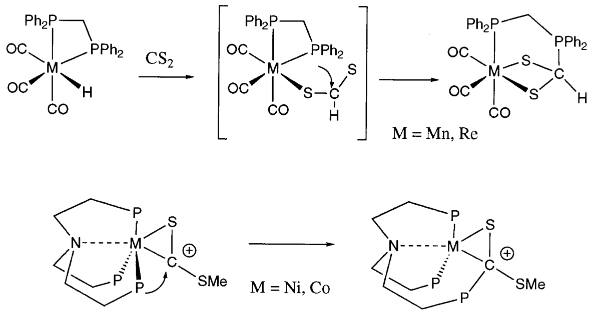
The reverse migration of the phosphine group from the central carbon of $S_2C(H)PR_3$ to the metal, leaving a dithioformate ligand, has also been reported [103,104].

$$[Ru(PMe_2Ph)_3\{S_2C(H)PMe_2Ph\}]^+ \rightarrow [Ru(PMe_2Ph)_4(S_2CH)]^+$$

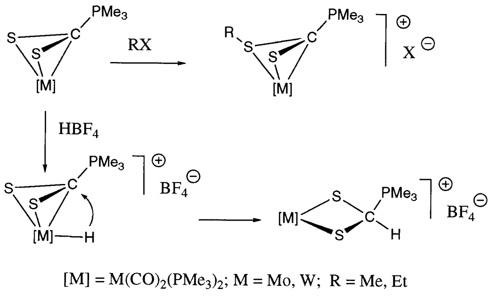
4.1.2. *η^3-(S,C,S′) pseudoallyls: electrophilic addition to sulfur*

Apart from the substitution reaction mentioned in Section 2.1.3, the main reactivity of complexes containing η^3(S,C,S′) S_2CPR_3, derives from their ability to undergo electrophilic addition at the ligand. This reactivity is modulated by the electron richness on the metal ligand fragment. Thus, $[M(CO)_2(PR_3)_2(\eta^3\text{-}S_2CPR_3)]$ ($M = Mo, W$) react with MeI or EtBr undergoing alkylation at one sulfur atom, thus yielding complexes containing trialkylphosphoniodithioesters (Scheme 27) [40].

When the same complexes are reacted with acid, the resulting products contain η^2(S,S′)-$S_2C(H)PMe_3$ chelates, i.e. the proton ends up bonded to the central carbon,



Scheme 26.



Scheme 27.

and the carbon–metal bond is cleaved in the process (Scheme 27). Since the central carbon of S_2CPR_3 usually behaves as an electrophile, it does not seem likely a direct attack of the proton to the central carbon. Instead, it is reasonable to assume a first step in which the proton is added to the metal to give a cationic hydride [40]. The final product would result then from an intramolecular attack of hydride to the central carbon, a mechanism which has been already discussed in Section 4.1.1.2 (Scheme 24) for the rhodium complex $[(triphos)Rh(Cl)\{S_2C(H)PR_3]^+$.

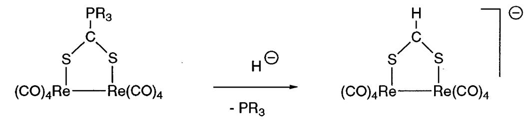
It is interesting to notice that the same phosphoniomethanedithiolate complexes are obtained by reacting the hydride $[MHCl(CO)_2(PMe_3)_3]$ with CS_2. This can be taken as support for the initial formation of a hydride complex followed by migration of hydride from the metal to the central carbon atom. Nevertheless, an alternative mechanism for this reaction, involving CS_2 insertion into the M–H bond, followed by intramolecular attack of PMe_3 to the carbon, can not be ruled out on the basis of the available data.

On the other hand, complexes $[Fe(CO)_3(\eta^3\text{-}S_2CPR_3)]$, with η^3(S,C,S′)-S_2CPR_3 ligands bonded to the electron-poorer $Fe(CO)_3$ fragment do not react with alkyl halides [37]. A stronger electrophile, such as methyl triflate, is needed to accomplish alkylation which is produced, as in the molybdenum complexes, at the sulfur atom. In contrast, complexes $[Fe(CO)_3(\eta^3\text{-}S_2CPR_3)]$ can not be protonated. This reflects again the lower electron density of the metal fragment, and can be taken as indirect support for the mechanism of the protonation at the metal.

4.2. Binuclear complexes

4.2.1. Reactivity of μ-η^1-(S); η^1-(S′) bridges

Only those complexes containing a direct metal–metal bond are stable enough to be used in reactivity studies. Since the central carbon of the ligand is not involved in the bonding to the metal atoms, the electronic properties of the ligand are similar to those found for the η^2-(S,S′) chelates and the reactivity is dominated by the electrophilic character of the central carbon. Only a few reactions of hydride addition have been made, resulting in the net replacement of the phosphine group [43] (see Scheme 28).



Scheme 28.

The extension of this chemistry to other dirhenium substrates is currently being developed.

4.2.2. Reactivity of complexes with *μ-η²-(S,S′); η³-(S,C,S′) bridges*

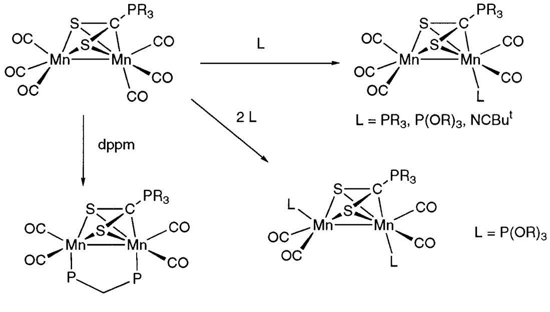
The remarkable stability of these complexes have allowed a wide study of their reactivity, which is currently offering new points of interest. Again, the type of chemical reactivity found depends greatly on the type of compounds, and we will treat them separately in the sections below.

4.2.2.1. Substrates containing a metal–metal bond

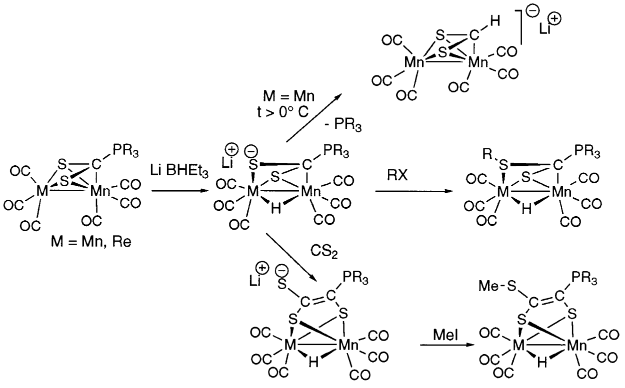
4.2.2.1.1. Carbonyl substitution. Hexacarbonyls $[Mn_2(CO)_6(\mu\text{-}S_2CPR_3)]$ react with monodentate ligands such as PEt_3, phosphites or isocyanide, under thermal conditions to afford pentacarbonyl derivatives (see Scheme 29). Further substitution to give tetracarbonyls can only be achieved by using large excess of ligand and only in the case of phosphites.

When the diphosphine dppm is used, the reaction requires the temperature of refluxing xylene (140°C) and the resulting complex is a tetracarbonyl containing dppm as bridging ligand. In all these reactions the $\eta^2;\eta^3\text{-}S_2CPR_3$ bridge of $8e^-$ is maintained in the final product [55]. This provides evidence of the stability of this type of bridge, when compared with other types described above (cf. Types **IV** and **VI**, which are labile at r.t. and can be easily cleaved by ligands or donor solvents).

4.2.2.1.2. Hydride addition to the metal–metal bond and subsequent reactivity. The reactivity is confined to complexes in which both metals belong to Group 7. Some attempts to extend the chemistry to the derivatives containing cobalt, described in Section 2.2.4, have been fruitless so far. From the point of view of the studies of functionalization of S_2CPR_3 ligands, this section is the most interesting, since the



Scheme 29.



Scheme 30.

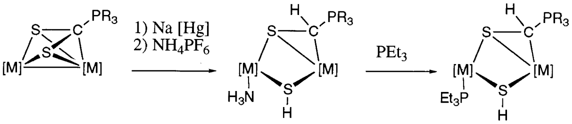
ligand itself is involved in the chemical transformation, thus giving rise to new sulfur species coordinated to the metal.

The general features of this reactivity are summarized in Scheme 30.

Complexes $[Mn_2(CO)_6(\mu\text{-}S_2CPR_3)]$ and the Mn–Re and Re–Re analogues undergo hydride addition at the metal–metal bond, to afford anionic hydridocarbonyl species $[MM'(CO)_6(\mu\text{-}H)\{\mu\text{-}\eta^2(S,S');\eta^2\text{-}(C,S)\text{-}S_2CPR_3\}]^-$ [105]. According to an X-ray analysis carried out on a crystal of the Mn–Re derivative [34], the addition of the hydride ligand produces the cleavage of the M–S bond, M being the metal bonded to the central carbon of the S_2CPR_3 ligand, which therefore changes its coordination mode from $\eta^2(S,S');\eta^3\text{-}(S,C,S)$, donating $8e^-$, to $\eta^2(S,S');\eta^2\text{-}(C,S)$, donating $6e^-$. The stability of the resulting anions depend markedly on the combination of metals. Thus, while Re–Mn or Re–Re hydridocarbonyls are stable in solution at r.t., the dimanganese analogue rearranges spontaneously, with loss of phosphine, within 30 min at r.t., to afford $[Mn_2(CO)_6(S_2CH)]^-$ where the dithioformate ligand, S_2CH^- acts as a $\eta^2;\eta^3$ bridge (see Scheme 30) [105]. The reaction involves the migration of hydride from the bridging position at the metals to the central carbon of S_2CPR_3, with simultaneous loss of phosphine. This rearrangement can be inhibited by cooling below 0°C, and the dimanganese hydridocarbonyl anions can be used in subsequent reactions. In contrast, the Mn–Re and Re–Re hydridocarbonyl analogues are stable at r.t., although they can be forced to rearrange to the corresponding dithioformate complexes by heating in refluxing THF.

Hydridocarbonyl anions $[MM'(CO)_6(\mu\text{-}H)\{\mu\text{-}\eta^2(S,S');\eta^2\text{-}(C,S)\text{-}S_2CPR_3\}]^-$ easily undergo alkylation with alkyl halides at the non-bridging sulfur (see Scheme 30), affording neutral complexes which contain formally cationic trialkylphosphoniodithioformate esters, $[R'SC(S)PR_3]^+$ as briging ligands [105].

A variety of neutral electrophiles have been assayed in the reactions with hydridocarbonyl anions. However, only the reaction with CS_2 yielded stable compounds. Addition of CS_2 to $[MMn(CO)_6(\mu\text{-}H)\{\mu\text{-}\eta^2(S,S');\eta^2\text{-}(C,S)\text{-}S_2CPR_3\}]^-$ (M = Mn, Re) resulted in the formation of the new anionic species $[MMn(CO)_6(\mu\text{-}$



Scheme 31.

H){μ-SC(S)=C(S)PR_3}]$^-$ which contain the novel trialkylphosphonioethenetrithiolate ligand $[S_2C{=}C(S)PR_3]^{2-}$ (see Scheme 30). The formation of this new ligand involves the formal desulfurization of CS_2, and the insertion of the resulting CS into a carbon–sulfur bond of the S_2CPR_3 ligand present in the starting complex [106].

4.2.2.1.3. Cleavage of C–S bonds by reduction and protonation. Complexes $[M_2(CO)_6(\mu\text{-}S_2CPR_3)]$ (M = Mn, Re) react with sodium amalgam to produce very reactive anionic species which could not be isolated. However they can be protonated with NH_4PF_6, to afford neutral compounds $[M_2(CO)_6(NH_3)(\mu\text{-}SH)\{\mu\text{-}SC(H)PR_3\}]$ [107].

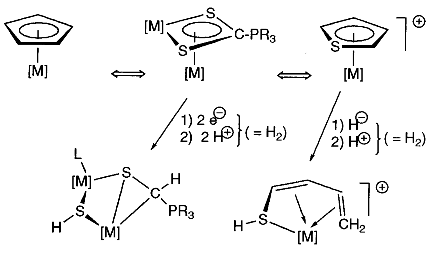
An X-ray determination (M = Re), showed that these complexes contain a bridging hydrogenosulfide, and the new ligand $R_3PC(H)S^-$, which is bonded as η^1(S);η^2(C,S′) bridging the two metals (Scheme 31). Both bridges resulting from the cleavage of a C–S bond of the starting S_2CPR_3 ligand in the reduction/protonation process. The NH_3 ligand can be easily replaced by phosphines at r.t.

The isolobal analogy between complexes $[MM'(CO)_6(\mu\text{-}S_2CPR_3)]$ and cymantrene, which has been discussed in Section 3.2 (see Scheme 19 and structure **XX**), can be extended to the cation $[Mn(CO)_3(\eta^5\text{-thiophene})]^+$. In this way, the reduction/protonation process of the bimetallic complex may serve as a model for the hydrogenolysis of a η^5-coordinated thiophene (Scheme 32) [107].

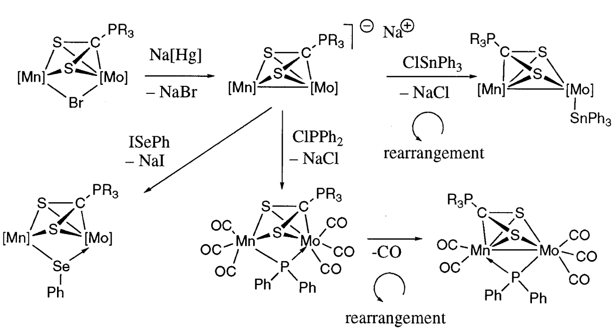
Similar reactions, starting from heterobinuclear Mn–Re complexes and using other electrophiles against the carbonyl anions resulting from the protonation, are under current investigation.

4.2.2.2. Substrates with halide bridges

4.2.2.2.1. Replacement of carbonyl. Complexes $[MMo(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)]$ (M = Mn, Re) react with phosphines undergoing substitution of one CO group coordinated to molybdenum to give pentacarbonyls [MMo(CO)$_5$(μ-Br)(μ-



Scheme 32.



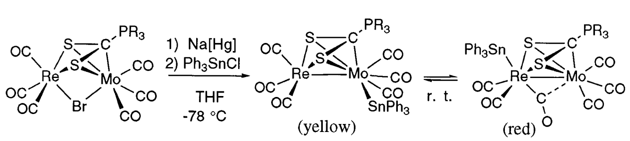
Scheme 33.

$S_2CPR_3)(PR'_3)]$ (M = Mn [51], Re [57]). On the other hand, the use of bidentate ligands (dppm, dmpm, tedip) in these reactions results in substitution of CO at Mo and the cleavage of a M–S (M = Mn, Re) bond to afford complexes containing three bridges: halide, diphosphine, and S_2CPR_3 which is now coordinated as η^1(S) toward Mn or Re, and as η^3(S,C,S′) toward Mo (Type **VII**). These reactions, which can be related to the ring-opening processes, have been described in Section 2.2.4.

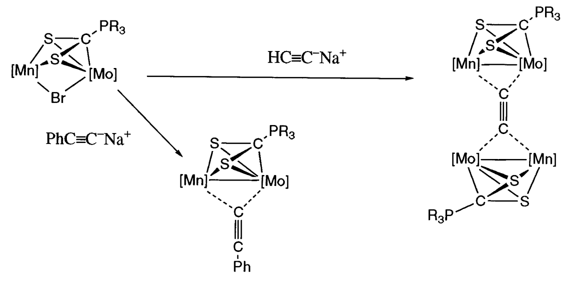
4.2.2.2.2. Reaction with sodium amalgam followed by addition of electrophiles. Reduction of $[MnMo(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)]$ with Na[Hg] in THF produces anions $[MnMo(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)]^-$ which, in turn, are able to undergo electrophilic addition at the Mo atom (Scheme 33) affording neutral complexes which contain a direct Mn–Mo bond.

Interestingly, in the final compound the S_2CPR_3 ligand is bonded as η^3(S,C,S′) to Mn, and as η^2(S,S′) to Mo, i.e. the reduction/stannylation process involves the migration of the central carbon of the S_2CPR_3 ligand from Mo to Mn. This is consistent with the tendency of the central carbon to bond the metal atom with the lowest oxidation number: Mn(+ 1), Mo(0) in the starting complex; Mn(0), Mo(+ 1) in the final compound [74]. The same trend is observed when the intermediate anion is reacted with electrophiles such as ISePh or $ClPPh_2$, as outlined in Scheme 33.

In contrast, when the starting complex contains rhenium instead of manganese, a different behavior is observed. The reduction, and subsequent addition of stannyl group at low temperature (– 80°C) does not produce the rearrangement of the S_2CPR_3 ligand, as in the manganese compound, rather affording a yellow complex which contains both the stannyl group and the central carbon bonded to molybdenum (Scheme 34) [44].



Scheme 34.



Scheme 35.

Upon warming to r.t., the yellow compound isomerizes, partially and reversibly, to give a red compound in which the stannyl group is now bonded to rhenium, while the central carbon remains attached to molybdenum. Both isomers, which are in equilibrium at r.t. (yellow:red ratio of 5:4), can be separated by crystallization, and the structures of both have been determined [44]. Remarkably, if a pure sample of any of the isomers is taken into solution, the equilibrium mixture of ratio 5:4 is regenerated. This can be regarded as the first example of migration of a stannyl group between two metal atoms, the closest precedent being the migration of silyl groups between two Ru atoms (reversible) [108], or from Fe to Pt (irreversible) [109]

4.2.2.2.3. Reactivity at the halogen bridge. The presence of the halogen bridge in complexes $[MM'(CO)_6(\mu\text{-}X)(\mu\text{-}S_2CPR_3)]$ can be exploited to introduce new functionalities at the metals by nucleophilic substitution. Thus reaction of $[MnMo(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)]$ with phenylethynylsodium (Scheme 35) introduces a μ_2-η^1-alkynyl bridge of $1e^-$. Accordingly, the resulting complex contains a M–M bond. Similar reaction with ethynylsodium results in the formation of the tetrametallic derivative $[\{MnMo(CO)_6(\mu\text{-}S_2CPR_3)\}_2(\mu_4\text{-}\eta^1;\eta^1;\eta^1;\eta^1C_2)]$ [78].

The structural data of this complex suggest that this complex can be considered as a tetrametallated acetylene, this being the first example of a ethynediyl with a bimetallic unit at each end of the C_2 fragment. The extension of this chemistry to other bimetallic fragments, and the use of other nucleophiles are now under investigation.

5. Concluding remarks

Phosphoniodithioformate compounds (S_2CPR_3) are very versatile ligands which are able to formally donate to the metal (or metals) a variable number of electrons (from two to eight). The adaptability as ligands of these compounds is also manifested by the diversity of structurally charaterized coordination modes to transition metal centers (Scheme 4). Both bonding modes and electron counting, can be rationalized in terms of simple MO considerations. The chemical properties studied are indicative of a versatile behaviour and, accordingly, different sulfur-containing ligands can be synthesized through different reactions (nucleophilic or electrophilic attack, reduction, etc.) on coordinated S_2CPR_3 complexes. The exploitation of the potentiality of this ligand on coordination and organometallic chemistry is not finished and further studies will give surely new interesting results.

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