Hydride Addition to Coordinated S_2CPR_3 Ligands in Mononuclear Mn and Re Complexes: Phosphane-Dithioformate Adducts as Five-Electron Bridging Ligands

Georgina Barrado[a], Daniel Miguel*[a], Jesús A. Miguel[b], Víctor Riera[a], and Xavier Soláns[c]

Instituto Universitario de Química Organometálica "Enrique Moles" – Unidad Asociada del CSIC Universidad de Oviedo[a],
E-33071 Oviedo, Spain

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid[b],
E-47005 Valladolid, Spain

Departamento de Cristalografía, Mineralogía y Depósitos Minerales, Universidad de Barcelona[c],
Martí y Franqués s/n, E-08028 Barcelona, Spain

The cationic tetracarbonyl complex *cis*-[Mn(CO)₄-(S₂CPCy₃)]⁺ undergoes addition of hydride ion to the central carbon of the S_2CPR_3 ligand to afford, after spontaneous dimerization with loss of CO, the dimer [Mn₂(CO)₆{μ-S₂C(H)PCy₃}₂] (5a), which was characterized by analytical and spectroscopic methods as well as by X-ray diffraction. In the molecule of 5a each S₂C(H)PCy₃⁻ ligand is coordinated to one manganese in an η²-*S,S'* chelate fashion, and one sulfur of each ligand serves as a bridge to bind the other manganese atom, thus forming a distorted Mn₂S₂ square. This appears to be a very stable arrangement. Compound 5a can be more easily prepared by treating the perchlorato complex [Mn(CO)₃(S₂CPCy₃)(OClO₃)] (2a) with NaBH₄. This procedure is general and can be used for the preparation of several derivatives containing either manganese or rhenium [M₂(CO)₆{μ-S₂C(H)PR₃}₂] 5a–d. The reaction of cationic tricarbonyl complexes [M(CO)₃(S₂CPR₃)(PPh₃)]PF₆ (M = Mn, Re) with NaBH₄ produces the same dimers 5a or 5c by displacement of the PPh₃ ligand. Treatment of the dimer 5a with excess PEt₃ or P(OMe)₃ leads to the cleavage of the bridges and loss of one CO and the PR₃ group from the S₂C(H)PR₃ unit to afford ultimately the dithioformate complexes [Mn(CO)₂(S₂CH)(L)₂] [L = PEt₃, P(OMe)₃].

It is well known that the central carbon of coordinate S_2CPR_3 ligands in mononuclear complexes undergoes nucleophilic attack by hydride ion[1−10]. Depending on the combination of ligands and metal center, two types of products arise from these reactions: in some cases, the initial hydride attack produces (trialkylphosphonio)methanedithiolate, S₂C(H)PR₃⁻, which remains attached to the metal atom as a chelate[1−6], whereas in other cases the PR₃ group is lost to afford a complex with dithioformate S₂CH⁻[9,10]. Several examples of both types of behavior are known and, although both electronic and steric factors[8] have been invoked in particular cases, no regular trend for this behavior has been found so far. On the other hand, several complexes have been reported in which the ligands S₂C(H)PR₃⁻ are produced by the addition of PR₃ to a coordinated S₂CH⁻[11−15].

Our previous studies[10,16,17] of the reactivity of complexes of manganese and rhenium containing S_2CPR_3 ligands have made available a wide range of cationic carbonyl complexes with different degrees of substitution which are suitable substrates for hydride addition reactions. We report here the results of such a study, which has led to the preparation of dinuclear complexes containing the phosphane-dithioformate adducts acting as five-electron bridges in an unprecedented coordination mode. In fact, the only other example is present in the complex [Rh(TeB₁₀H₁₀)-

{S₂C(H)(PPh₃)}]₂ which was reported by Spalding et al.[15] simultaneously with a preliminary account of this work[18].

Results and Discussion

The reaction of cationic tetracarbonyl complex [Mn(CO)₄(S₂CPCy₃)]ClO₄ (3a) (see Scheme 1) with NaBH₄ produces yellow solutions from which the dinuclear complex of formula [Mn₂(CO)₆{μ-S₂C(H)PCy₃}₂] (5a) can be isolated in good yield as orange-yellow crystals. Since on the basis of the available spectroscopic data (see Table 1 and Experimental) it was not possible to establish the structure of the compound, a crystal of 5a was subjected to an X-ray determination. A perspective view of the central part of the structure is presented in Figure 1.

Table 1. IR and ³¹P{¹H}-NMR data for the new complexes

Compd.	IR (THF): ν(CO), cm⁻¹	³¹P{¹H} NMR[a]
4a	2044 vs, 1966 s, 1942 s	32.10 [d[b], S2CP], 57.3 [s (br), MnP]
4b	2040 vs, 1961 s, 1938 s	43.4 [d[b], S2CP], 23.0 [s (br), ReP]
5a	2006 s, 1984 vs, 1912 m, 1895 vs, 1887 (sh)	28.0 [s, S2CP]
5b	2006 s, 1984 vs, 1912 m, 1895 vs, 1887 (sh)	39.8 [s, S2CP]
5c	2013 s, 1995 s, 1908 m, 1885 vs	33.3 [s, S2CP]
5d	2013 s, 1995 s, 1907 m, 1886 vs	44.9 [s, S2CP]
7a	1957 s, 1884 s	181.1 [s (br),P(OMe)₃]

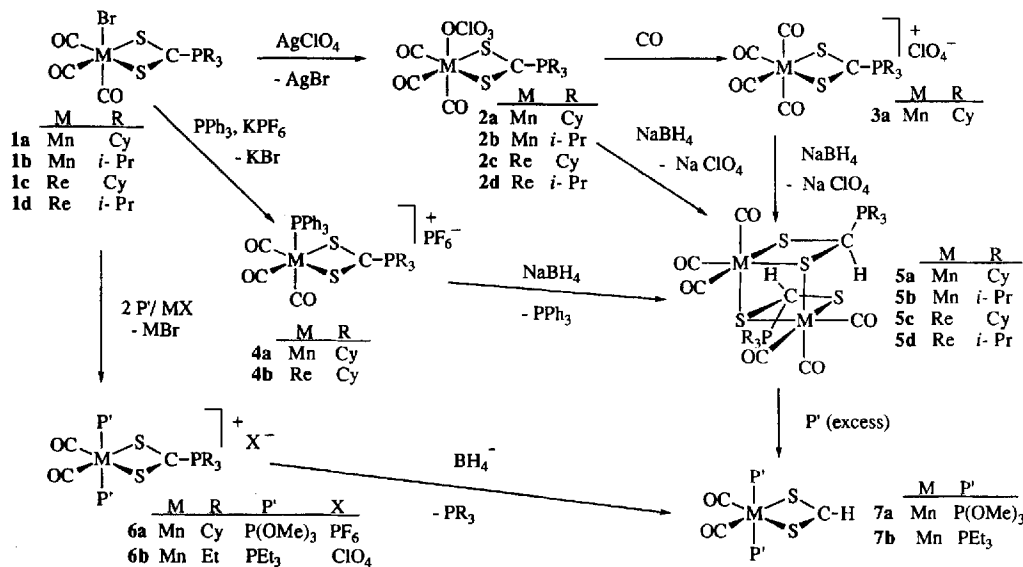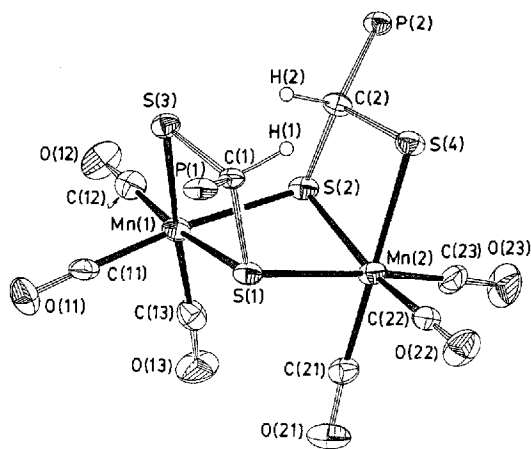[a] In solutions of CD₂Cl₂, δ from internal 85% H₃PO₄. – [b] J = 10 Hz.

Scheme 1

Figure 1. Perspective view (EUCLID Package)[31] of the structure of [Mn₂(CO)₆{S₂C(H)PCy₃}₂] (**5a**) showing the atom numbering; cyclohexyl rings have been omitted for clarity[a]

[a] Selected bond lengths [Å] and angles [°]: Mn(1)−S(1) 2.379(2), Mn(1)−S(2) 2.426(2), Mn(1)−S(3) 2.388(2), Mn(2)−S(1) 2.445(2), Mn(2)−S(2) 2.410(2), Mn(2)−S(4) 2.375(2); S(2)−Mn(1)−S(1) 83.3(1), S(3)−Mn(1)−S(1) 75.1(1), S(3)−Mn(1)−S(2) 95.0(1), C(11)−Mn(1)−S(2) 174.3(3), C(12)−Mn(1)−S(1) 172.6(3), C(13)−Mn(1)−S(3) 171.7(3), C(21)−Mn(2)−S(4) 179.2(3), C(22)−Mn(2)−S(2) 168.1(3), C(23)−Mn(2)−S(1) 169.6(3); H(1)−C(1) 1.06(5), H(2)−C(2) 1.13(5); short contacts affecting hydrogen atoms: H(1)···S(1) 2.36(2), H(2)···S(2) 2.34(2), H(1)···S(3) 2.39(2), H(2)···S(3) 2.37(2), H(1)···S(4) 2.55(2), H(2)···S(4) 2.35(2), H(1)···Mn(2) 3.29(1), H(2)···Mn(1) 3.09(1).

The molecule of **5a** is a dimer in which two Mn(CO)₃ fragments are bridged by two S₂C(H)PCy₃⁻ ligands which are coordinated as η²(S,S) chelate towards one metal atom, and as η¹(S) towards the second metal. Since the distance between the two metals is too long to permit any significant interaction, each bridge must donate five electrons to the metals to satisfy the EAN rule.

The formation of the dimanganese hexacarbonyl compound **5a** from the cationic tetracarbonyl complex **3a** can be explained by considering a nucleophilic attack by the

hydride ion on the central carbon of the S₂CPCy₃ ligand. This produces the neutral species [Mn(CO)₄{S₂C(H)PCy₃}] which spontaneously loses CO and dimerizes to give **5a**. Monitoring of the reaction by IR spectroscopy in solution showed the growth of the ν(CO) bands of the final dimer **5a** with the simultaneous decrease of the bands of the starting **3a** without any signal attributable to the neutral tetracarbonyl complex. It seems therefore that the phosphoniomethanedithiolate ligand S₂C(H)PCy₃⁻ produces a considerable *cis*-labilizing effect on the adjacent CO groups, and therefore loss of CO and subsequent dimerization are fast. The same effect was found for other reactions and will be discussed below.

This kind of dimerization leading to **5a** has been observed before in carbonyl complexes of manganese, rhenium, and other metals containing 1,1-dithiolato and related ligands[19−25]. Depending on the relative position of the chelate rings, two types of structure, which we have labelled *cisoid* and *transoid* in Scheme 2, can be expected in the final products. Several examples of each type have been determined by X-ray crystallography[19−21], and others have been proposed on the grounds of the spectroscopic data, mainly based on the analysis of the pattern of the carbonyl stretching absorptions[22−25].

Scheme 2

cisoid   transoid
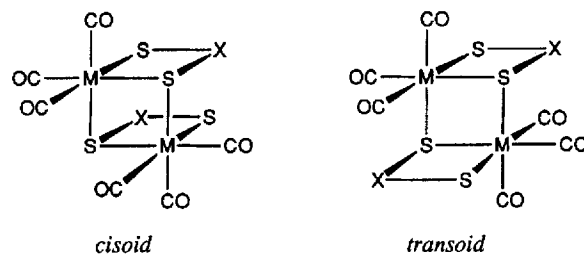
As can be seen in Figure 1, the two chelate rings in **5a** adopt a *cisoid* orientation, very similar to that found for

the dirhodium complex [Rh(TeB$_{10}$H$_{10}$){S$_2$C(H)(PPh$_3$)}]$_2$[15] which, together with **5a**, constitute the first examples containing S$_2$C(H)PR$_3^-$ bridges. Interestingly, while **5a** is produced by hydride addition to the central carbon of S$_2$CPR$_3$, the Rh complex is formed by the attack of PPh$_3$ at the central carbon of a coordinated S$_2$CH$^-$. A *cisoid* configuration is found also in the structures of [Mn$_2$(CO)$_6${μ-SC(SMe)(NMe)}$_2$], which contains bridging (methylimino)(methylthio)methanethiolato[20], and [Mo$_2$(CO)$_2$(NO)$_2$(Et$_2$NCS$_2$)] with dithiocarbamate bridges[21]. On the other hand, the dimer [Re$_2$(CO)$_6$(S$_2$PEt$_2$)$_2$], containing diethyl dithiophosphinate, presents a *cisoid* geometry[19].

Spalding et al. have described the core arrangement of the dirhodium complex mentioned above[15] as a cubane-type M$_2$S$_4$C$_2$ structure with two edges broken in opposite sides of the same face. This description can be also applied to **5a**, which also presents the same distortions from the ideal cubane geometry as found for the Rh$_2$ complex. The face formed by the two manganese atoms and the two bridging sulfurs, Mn(1)−S(1)−Mn(2)−S(2) is the one most deviated from planarity with S(1) at 0.317(2) Å from the best LS plane. In fact, this face can be viewed as formed by two triangles: Mn(1)Mn(2)S(1) and Mn(1)Mn(2)S(2), which form an angle of 151.84(8)° far from the value of 180° required for a planar arrangement. Another deviation from the ideal cubane structure comes from the small "bite" of the chelate S$_2$C(H)PCy$_3^-$ ligands, which leads to angles S(3)−Mn(1)−S(1) of 75.1(1)° and S(4)−Mn(2)−S(2) of 75.0(1)°, both very far from the ideal values of 90°. Quite remarkably, the arrangement of the chelate rings forces the hydrogen atoms attached to the central carbon of the methanedithiolate ligands to occupy positions nearly inside the cubane cage. As a result each hydrogen lies in close proximity to the two sulfurs and the metal atom of the opposite chelate ring. From the data presented in Figure 1, it can be seen that the distances are well below the value of the sum of the van der Waals radii of the atoms involved. Although such interaction may produce some effect in the chemical shift of the hydrogen atoms, as will be discussed below, it is not possible to conclude that it has any influence on the adoption of the *cisoid* geometry for the dimer. In fact, neither in [Mn$_2$(CO)$_6${μ-SC(SMe)(NMe)}$_2$][20] nor in [Mo$_2$(Et$_2$NCS$_2$)(CO)$_2$(NO)$_2$][21], both of which display a *cisoid* structure, are such hydrogen atoms found. On the other hand, since [Rh(TeB$_{10}$H$_{10}$){S$_2$C(H)(PPh$_3$)}]$_2$[15] is *cisoid*, there is to date no example of a *transoid* structure for dimers containing S$_2$C(H)PR$_3^-$ bridges.

The starting cationic tetracarbonyl compound **3a** is prepared from the bromotricarbonyl derivative **1a** by bromide abstraction with AgClO$_4$ and subsequent carbonylation of the resulting perchlorato complex **2a**. Since one CO group is lost in the dimerization process, it seemed reasonable to attempt the preparation of the dimer **5a** from the tricarbonyl compounds **1a** or **2a**. After several attempts it was found that the reaction of the bromo derivative **1a** with NaBH$_4$ does afford the dimer **5a**. However, this reaction is of no great synthetic value due to the presence, as a byproduct, of the dimanganese(0) complex [Mn$_2$(CO)$_6$(μ-

S$_2$CPR$_3$)], which had been prepared earlier in our laboratory by another procedure[26]. The separation of these mixtures requires careful chromatography, and only poor yields of **5a** could be obtained.

Better results can be achieved if the perchlorato complex **2a** is used as substrate for the hydride addition. This method is of general application and can be used to prepare a family of dimers containing Mn or Re with cyclohexyl or isopropyl substituents at the phosphorus atom of the S$_2$C(H)PR$_3^-$ bridge (**5b−d**, see Scheme 1). Analytical and spectroscopic data for each of the complexes **5b−d** are fully consistent with their formulation as dimers with structures as that found for **5a**. The ^{1}H-NMR spectra (see Experimental) show the signal of the hydrogen atom of the S$_2$C(H)-PR$_3^-$ ligand in the range δ = 9.26 to 10.51. It appears as a broad singlet in the Mn complexes (at δ = 9.26 for **5a** and 9.49 for **5b**) and as a doublet with ^2J(P-H) = 3 Hz for the Re derivatives (at δ = 9.85 for **5c** and 10.51 for **5d**). This region is unusual for the resonance of a hydrogen atom bound to the central carbon atom of the S$_2$C(H)PR$_3^-$ ligand: in the mononuclear complexes characterized previously, in which this ligand acts as a chelate, the signal appears in the region δ = 5.20 to 6.25[1,2,5−8,11]. It seems that the coordination of the S$_2$C(H)PR$_3^-$ ligand as a bridge produces a considerable shift of the signal towards lower fields. This is confirmed by the data reported for the only other complexes containing phosphoniomethanethiolato bridges: for [Rh(EB$_{10}$H$_{10}$){S$_2$C(H)(PPh$_3$)}]$_2$ the signal appears at δ = 9.99 (E = Se) and at δ = 9.87 (E = Te)[15]. This marked shift of the signal may be due to the interaction of the hydrogen atom with the metal and the sulfur atoms which has been discussed above for the structure of **5a**. In view of the close structural relationship of the bridging systems of **5a** and [Rh(TeB$_{10}$H$_{10}$){S$_2$C(H)(PPh$_3$)}]$_2$[15] it is most likely that the same interactions are present in the Rh dimers.

The ^{13}C{^{1}H}-NMR data available are more scarce. In our case, only the complexes containing PCy$_3$ were sufficiently soluble to render informative spectra. The signal of the central carbon of the S$_2$C(H)PR$_3^-$ ligand appears at δ = 35.5 [d, ^1J(PC) = 28 Hz] for **5a** and at 37.2 [d, ^1J(PC) = 30 Hz] for **5c**. The only data available for comparison in the literature correspond to the mononuclear complexes [M(CO)$_2${S$_2$C(H)PMe$_3$}(PMe$_3$)$_2$] [M = Mo: δ = 64.9, ^1J(PC) = 44 Hz; M = W: δ = 67.6, ^1J(PC) = 44 Hz][7] and [Pd(PMe$_3$)$_2${S$_2$C(H)PMe$_3$}] [δ = 45.27, ^1J(PC) = 53.7 Hz][1]. In view of the paucity of data, no meaningful attempt at correlation can be made.

Following our study of the hydride addition, we used as substrates the cationic complexes *fac*-[M(CO)$_3$(S$_2$CPCy$_3$)(PPh$_3$)] PF$_6$ (M = Mn, **4a**; M = Re, **4b**; Scheme 1). The final products of the reactions of **4a**, **b** with NaBH$_4$ were the corresponding hexacarbonyldimanganese and -dirhenium dimers **5a** and **5c**, respectively. This can be rationalized by assuming that the hydride attack produces a neutral tricarbonyl complex [M(CO)$_3${S$_2$C(H)PCy$_3$}(PPh$_3$)], the PPh$_3$ ligand of which is then displaced by the sulfur atom of a second molecule to give the final dimer **5**. This is re-

markable since a displacement of PPh$_3$ is not commonly encountered in the chemistry of octahedral manganese or rhenium carbonyl complexes[27]. As has been pointed out above, it seems that the S$_2$C(H)PR$_3^-$ ligand produces a very high *cis*-labilizing effect on the other ligands bound to the metal. In fact, it has been reported that nucleophilic attack of PMe$_2$Ph on the carbon atom of the coordinated S$_2$CH$^-$ ligand in [Ru(S$_2$CH)(PMe$_2$Ph)$_3$\{P(OMe)$_3$\}]$^+$ catalyses the substitution of PMe$_2$Ph by P(OMe)$_3$ via the intermediate [Ru\{S$_2$C(H)PMe$_2$Ph\}(PMe$_2$Ph)$_2$\{P(OMe)$_3$\}][13]. Similarly, the addition of hydride to the central carbon of S$_2$CPR$_3$ in **3** or **4** would increase the electron density in the metal, thus facilitating the dissociation of one ligand by the stabilisation of the pentacoordinate intermediate. In the case of **4**, the increase of electron density reinforces selectively the metal-carbonyl bonds (by backbonding) and, to a lesser extent, the bond with the P atom of PPh$_3$, which is therefore selectively released in the dimerization process.

Additional experimental data suggest that the driving force for the dimerization process is the great thermodynamic stability of the bridging arrangement in the dimer. Thus, compounds **5a, b** are very stable in solution and can be hated for several hours at the temperature of refluxing CH$_2$Cl$_2$ without significant decomposition. The bridging system can be cleaved by treatment with phosphorus ligands only with some difficulty. Thus, no significant reaction occurs between **5a** and excess PPh$_3$ at room temperature after overnight stirring. However, when the mixture was heated in refluxing THF, extensive decomposition was observed, and no stable compound could be isolated. Treatment of **5a** at room temperature with a fourfold excess of smaller phosphorus ligands, such as PEt$_3$ or P(OMe)$_3$, resulted in cleavage of the dimer to give, ultimately, the dicarbonyls *cis,trans*-[Mn(CO)$_2$(S$_2$CH)(L)$_2$] (L = P(OMe)$_3$, **7a**; L = PEt$_3$, **7b**), which could be isolated in good yields as crystalline solids. Compound **7b** had been obtained previously by treatment of *cis,trans*-[Mn(CO)$_2$(S$_2$CPEt$_3$)(PEt$_3$)$_2$]ClO$_4$ (**6b**) with NaBH$_4$, and its structure was determined by X-ray crystallography[10]. The analytical and spectroscopic data of the bis-phosphite complex **7a** are consistent with a structure similar to that observed for **7b**. As can be seen in Scheme 1, the final product contains a dithioformate, which results from the loss of PCy$_3$ from the central carbon atom of the S$_2$C(H)PCy$_3^-$ ligand. The process can be understood in terms of the excess of incoming ligand causing cleavage of the bridges to give *fac*-[Mn(CO)$_3$\{S$_2$C(H)PCy3\}(L)], which then undergoes substitution of one CO group and the loss of PCy$_3$. Despite making several attempts, we were unable to isolate the intermediates: it appears that the excess ligand required to cleave the bridges makes it impossible to stop the reaction at the intermediate stage.

In an analogous manner to **7b**, the bis-phosphite complex **7a** can be alternatively obtained by hydride addition to the cationic *cis,trans*-[Mn(CO)$_2$(S$_2$CPCy$_3$)\{P(OMe)$_3$\}$_2$]PF$_6$ (**6a**). The reaction proceeds with difficulty, even by using the more soluble PPN[BH$_4$], and the yield is low due to decomposition. This is somewhat surprising since the bis-

phosphite complex cation **6a** should be less electron-rich, and hence a better electrophile, than the bis-phosphane derivative **6b**.

From the facts described above, it is apparent that the addition of hydride to cationic tetra- or tricarbonyl complexes of manganese or rhenium containing S$_2$CPR$_3$ ligands, where R = cyclohexyl or isopropyl, leads to the formation of dimetallic hexacarbonyl dimers with S$_2$C(H)-PR$_3^-$ bridges in a process which requires the loss of CO or PPh$_3$ ligands. The resulting dimers are difficult to cleave, requiring a large excess of the incoming ligand or high temperatures. This characterizes the S$_2$C(H)PR$_3^-$ anions as very good bridging ligands, a remarkable feature since preferential loss of the bulky PCy$_3$ or PiPr$_3$ groups leading to complexes with S$_2$CH$^-$ might have been expected in the light of previous work. Considering steric factors, it has been postulated that the formation of chelating S$_2$C(H)PR$_3^-$ ligands would be feasible in five-coordinated complexes, but that steric hindrance would forbid it in octahedral complexes, where loss of PR$_3$ would lead to S$_2$CH$^-$ [9]. In the complexes **5a–d** reported here, there are S$_2$C(H)PR$_3^-$ ligands with bulky R groups in an octahedral environment and, moreover, serving as bridges towards a second metal. Additionally, in **5a–d** and also in the related Rh$_2$ dimer[15] the two chelate rings addopt a *cisoid* arrangement which, in principle, would increase the steric hindrance within the core of the dimer. It is clear, therefore, that steric arguments alone cannot be used to predict whether S$_2$C(H)PR$_3^-$ or S$_2$CH$^-$ units will result from hydride addition to complexes with S$_2$CPR$_3$ ligands.

Experimental

Reactions and workup were carried out under nitrogen. – IR: Perkin-Elmer FT 1720-X. – NMR: Bruker AC-300 (300.1 MHz for ^{1}H, 121.5 MHz for ^{31}P, 75.5 MHz for ^{13}C). – Analyses: Perkin-Elmer 240B analyzer. – Literature procedures for the preparation of starting material are quoted in each case.

[Mn(CO)$_3$(S$_2$CPCy$_3$)(PPh$_3$)]PF$_6$ (**4a**): A mixture of [Mn(CO)$_3$(S$_2$CPCy$_3$)Br] (**1a**)[16] (0.4 g, 0.76 mmol), PPh$_3$ (0.2 g, 0.76 mmol), and KPF$_6$ (0.268 g, 1.45 mmol) in CH$_2$Cl$_2$ (25 ml) was stirred for 5 h at room temp. The mixture was filtered, and hexane (20 ml) was added to the filtrate. Slow evaporation in vacuo gave **4a** as red microcrystals. Yield 0.52 g (76%). – ^{1}H NMR (CDCl$_3$): δ = 7.43–7.31 (m, 15H, C$_6$H$_5$), 2.69 (m, 3H, CH of Cy), 1.86–1.37 (m, 30H, and CH$_2$ of Cy). – C$_{40}$H$_{48}$F$_6$MnO$_3$P$_3$S$_4$ (902.8): calcd. C 53.22, H 5.36; found C 52.96, H 5.13.

[Re(CO)$_3$(S$_2$CPCy$_3$)(PPh$_3$)]PF$_6$ (**4b**): A mixture of [Re-(CO)$_3$(S$_2$CPCy$_3$)Br] (**1c**)[29] (0.1 g, 0.142 mmol), PPh$_3$ (0.045 g, 0.173 mmol), and KPF$_6$ (0.055 g, 0.3 mmol) in CH$_2$Cl$_2$ (15 ml) was stirred for 12 h at room temp. The workup was a described above for **4a** and gave 0.12 g of compound **4b** (80%) as red microcrystals. – ^{1}H NMR (CDCl$_3$): δ = 7.53–7.26 (m, 15H, C$_6$H$_5$), 2.72 (m, 3H, CH of Cy), 2.18–1.31 (m, 30H, CH$_2$ of Cy). – C$_{40}$H$_{48}$F$_6$O$_3$P$_3$ReS$_2$ (1034.0): calcd. C 46.46, H 4.68; found C 46.28, H 4.53.

[Mn$_2$(CO)$_6$\{μ-S$_2$C(H)PCy$_3$\}$_2$] (**5a**). – *Method A, from [Mn(CO)$_4$(S$_2$CPCy$_3$)]ClO$_4$* (**3a**): To a stirred solution of **3a**[16].

(0.3 g, 0.48 mmol) in CH_2Cl_2 (20 ml) a solution of $NaBH_4$ (0.09 g, 2.38 mmol) in ethanol (1 ml) was added. After stirring for 15 min, the solvents were evaporated in vacuo, the dry residue was dissolved in CH_2Cl_2/hexane (1:1, v/v), and the solution then filtered through alumina. The filtrate was concentrated in vacuo to ca. 5 ml and then stored overnight at $-20\,°C$ to yield 0.213 g of **5a** (85%) as yellow-orange crystals. $-$ $C_{44}H_{68}Mn_2O_6P_2S_4$ (993.1): calcd. C 53.22, H 6.90; found C 52.95, H 6.73.

Method B, from [Mn(CO)₃(S₂CPCy₃)Br] (**1a**): A mixture of **1a**[16] (1.0 g, 1.74 mmol) and $AgClO_4$ (0.5 g, 2.41 mmol) in CH_2Cl_2 (25 ml) was stirred in darkness for 1.5 h to obtain a solution of $[Mn(CO)_3(S_2CPCy_3)(OClO_3)]$ (**2a**) [v(CO) bands at 2039 vs, 1955 s, and 1936 s, cm^{-1}]. This was then filtered through celite to remove the AgBr precipitate. To the filtrate a solution of $NaBH_4$ (0.32 g, 8.46 mmol) in ethanol (2 ml) was added, and the mixture was stirred for 30 min. The solvents were evaporated to dryness, and the residue was treated as described in Method A to obtain 0.57 g of **5a** (66%) as yellow-orange crystals. $-$ $C_{44}H_{68}Mn_2O_6P_2S_4$ (993.1): calcd. C 53.22, H 6.90; found C 53.05, H 6.77.

Method C, from [Mn(CO)₃(S₂CPCy₃)(PPh₃)] PF₆ (**4a**): To a solution of **4a** (0.5 g, 0.55 mmol) in CH_2Cl_2 (25 ml) a solution of $NaBH_4$ (0.13 g, 3.4 mmol) in ethanol (1 ml) was added. The mixture was stirred for 30 min and then evaporated to dryness. The residue was chromatographed on alumina by using CH_2Cl_2/hexane (1:1, v/v) as eluent. A yellow band was collected, evaporation of which in vacuo gave 0.43 g of **5a** (78%) as a yellow solid, which was washed with hexane. $-$ $C_{44}H_{68}Mn_2O_6P_2S_4$ (993.1): calcd. C 53.22, H 6.90; found C 53.38, H 7.05. $-$ ^1H NMR ($CDCl_3$): δ = 9.26 [s (br), 2H, S₂C(H)PCy₃], 2.89 (m, 6H, CH of Cy), 2.27–1.37 (m, 60H, CH₂ of Cy). $-$ $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 223.9, 221.1 and 220.3 (MnCO), 35.5 [d, J = 28 Hz, S₂C(H)PCy₃], 30.4 [d, J = 39 Hz, C-1 of Cy], 28.1–27.0 (m, C-2,3,5,6 of Cy), 25.6 (s, C-4 of Cy).

Crystal Structure Analysis of [Mn₂(CO)₆{µ-S₂C(H)PCy₃}₂] (**5a**)[28]: $C_{44}H_{68}Mn_2O_6P_2S_4$ (993.09), a = 22.670(4), b = 12.694(2), c = 16.426(3) Å, β = 91.46(2)°, Z = 4, d(calcd.) = 1.39 g/cm³, monoclinic, $P2_1/a$. Crystal size $0.2 \times 0.1 \times 0.1$ mm, μ = 8.49 cm^{-1}, scan range $2° \leqslant \Theta \leqslant 25°$, 8435 reflections collected, 3272 observed $[I \geqslant 2.5\sigma(I)]$. Philips PW-1100 diffractometer, radiation (Mo-K_α), λ = 0.71069 Å. Unit cell parameters were determined from the least-squares refinement of 25 centered reflections in the range 4 < Θ < 12°. Three reflections were measured every 2 h as orientation and intensity control. A significant decay was not observed. The structure was solved by direct methods with MULTAN[29] and subsequent Fourier maps. Full-matrix least-squares refinement was performed with SHELX76[30]. All non-hydrogen atoms were refined anistropically. The positions of 60 hydrogen atoms were found from a difference synthesis, and they were refined with a given overall isotropic thermal parameter. The function minimized was $\Sigma w|$ $(|F_o|-|F_c|)$, where w = $[\sigma^2(F) + 0.0008\ F^2]^{-1}$. Final residues for all observed reflections were R = $\Sigma(||F_o|-|F_c||/\Sigma|F_o|$ = 0.045, R_w = $\{\Sigma[w(|F_o|-|F_c|)^2]/\Sigma w|F_o|^2\}^{1/2}$ = 0.046.

[Mn₂(CO)₆{µ-S₂C(H)PiPr₃}₂] (**5b**) was prepared as described above for **5a** (Method B), by using **1b**[31] (0.5 g, 1.1 mmol), $AgClO_4$ (0.35 g, 1.69 mmol), and $NaBH_4$ (0.2 g, 5.26 mmol). The intermediate complex **2b** showed v(CO) bands at 2039 vs, 1957 s, and 1937 s, cm^{-1}. Yield 0.2 g (42%), yellow crystals. $-$ ^1H NMR ($CDCl_3$): δ = 9.49 [s (br), 2H, S₂C(H)PiPr₃], 3.29 (m, 6H, CH of iPr), 1.43–1.19 (m, 36H, CH₃ of iPr). $-$ $C_{26}H_{44}Mn_2O_6P_2S_4$ (752.7): calcd. C 41.49, H 5.89; found C 41.63, H 6.02.

[Re₂(CO)₆{µ-S₂C(H)PCy₃}₂] (**5c**). $-$ *Method B, from [Re(CO)₃(S₂CPCy₃)Br]* (**1c**): A mixture of **1c**[29] (0.5 g, 0.71 mmol)

and $AgClO_4$ (0.2 g, 0.96 mmol) in CH_2Cl_2 (25 ml) was stirred in darkness for 2 h to obtain a solution of $[Re(CO)_3(S_2CPCy_3)$-$(OClO_3)]$ (**2a**) [v(CO) bands at 2036 vs, 1939 s, 1919 s, cm^{-1}]. This was then filtered through celite to remove the AgBr precipitate. To the filtrate a solution of $NaBH_4$ (0.12 g, 3.15 mmol) in ethanol (2 ml) was added, and the mixture was stirred for 30 min. The solvents were evaporated to dryness, and the residue was treated as described for **5a** (Method A) to obtain 0.26 g of **5c** (63%) as pale yellow crystals. $-$ $C_{44}H_{68}O_6P_2Re_2S_4$ (1255.6): calcd. C 42.09, H 5.46; found C 41.87, H 5.61.

Method C, from [Re(CO)₃(S₂CPCy₃)(PPh₃)] PF₆ (**4b**): To a solution of **4b** (0.054 g, 0.06 mmol) in CH_2Cl_2 (15 ml) a solution of $NaBH_4$ (0.1 g, 2.6 mmol) in ethanol (1 ml) was added, and the mixture was stirred for 30 min. It was then evaporated to dryness, and the residue was chromatographed on alumina by using CH_2Cl_2/hexane (4:1, v/v) as eluent. A yellow band was collected, evaporation of which in vacuo gave 0.011 g of **5b** (15%) as a pale-yellow solid. $-$ $C_{44}H_{68}O_6P_2Re_2S_4$ (1255.6): calcd. C 42.09, H 5.46; found C 41.98, H 5.28. $-$ ^1H NMR ($CDCl_3$): δ = 9.85 [d, J = 3 Hz, 2H, S₂C(H)PCy₃], 2.79 (m, 6H, CH of Cy), 2.17–1.19 (m, 60H, CH₂ of Cy). $-$ $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 198.0, 197.8, and 196.0 (ReCO), 37.2 [d, J = 30 Hz, S₂C(H)PCy₃], 30.8 (d, J = 39 Hz, C-1 of Cy), 28.3 –27.2 (m, C-2,3,5,6 of Cy), 25.9 (s, C-4 of Cy).

[Re₂(CO)₆{µ-S₂C(H)PiPr₃}₂] (**5d**) was prepared as described for **5a** (Method B) by using **1d**[29] (0.4 g, 0.68 mmol), $AgClO_4$ (0.21 g, 1.0 mmol), and $NaBH_4$ (0.13 g, 3.4 mmol). v(CO) bands for **2d** appeared at 2037 vs and 1934 s (broad) cm^{-1}. Yield 0.08 g (23%) pale yellow solid. $-$ ^1H NMR ($CDCl_3$): δ = 10.51 [d, J = 3 Hz, 2H, S₂C(H)PiPr₃], 3.27 (m, 6H, CH of iPr), 1.78–1.57 (m, 36H, CH₃ of iPr). $-$ $C_{26}H_{44}O_6P_2Re_2S_4$ (1015.2): calcd. C 30.76, H 4.37; found C 31.02, H 4.59.

[Mn(CO)₂(S₂CH){P(OMe)₃}₂] (**7a**): A mixture of **5a** (0.1 g, 0.1 mmol) and P(OMe)₃ (48 µl, 0.4 mmol) in THF (20 ml) was stirred for 3 h at room temp. and then evaporated to dryness. The residue was extracted with CH_2Cl_2/hexane (1:1, v/v) and the solution filtered through alumina. The filtrate was concentrated in vacuo and stored overnight at $-20\,°C$ to afford 0.036 g of **7a** (82%) as orange crystals. $-$ ^1H NMR ($CDCl_3$): δ = 10.73 (t, J = 9 Hz, 2H, S₂CH), 3.76 [m, 18H, P(OCH₃)₃]. $-$ $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 236.6 (t, J = 12 Hz, S₂CH), 223.5 [s (br), MnCO], 52.3 [s, P(OCH₃)₃]. $-$ $C_9H_{19}MnO_8P_2S_2$ (436.2): calcd. C 24.78, H 4.39; found C 25.10, H 4.53.

[Mn(CO)₂(S₂CH)(PEt₃)₂] (**7b**): A mixture of **5a** (0.05 g, 0.05 mmol) and PEt₃ (30 µl, 0.2 mmol) in THF (15 ml) was stirred for 4 h at room temp. and then evaporated to dryness. The workup was as described for **7a** and yielded 0.015 g of **7b** (71%) as red crystals. $-$ $C_{15}H_{31}MnO_2P_2S_2$ (424.4): calcd. C 42.45, H 7.36; found C 42.28, H 7.22. $-$ The spectroscopic data were identical to those published for the complex prepared by reaction of cis-[Mn(CO)₂(S₂CPEt₃)(PEt₃)₂]ClO₄ with NaBH₄[10].

Reaction of [Mn(CO)₂(S₂CPCy₃){P(OMe)₃}₂]PF₆ (**6a**) *with PPNBH₄*: To a solution of **6a**[17] (0.2 g, 0.23 mmol) in THF (20 ml) PPN[BH₄] (0.64 g, 1.15 mmol) was added, and the mixture was stirred at room temp. IR monitoring showed the slow formation of **7a** accompanied by extensive decomposition. After 20 h the mixture was filtered, and the filtrate was evaporated to dryness. Compound **7a** was isolated as described above. Yield 0.02 g, (20%).

---

[1] H. Werner, W. Bertleff, *Chem. Ber.* **1980**, *113*, 267–273.
[2] C. Bianchini, A. Meli, A. Orlandini, *Inorg. Chem.* **1982**, *21*, 4161–4165.

[3] C. Bianchini, A. Meli, A. Orlandini, *Inorg. Chem.* **1982**, *21*, 4166−4169.

[4] C. Bianchini, C. Mealli, A. Meli, G. Scapacci, *Organometallics* **1983**, *2*, 141−143.

[5] C. Bianchini, A. Meli, P. Daporto, A. Tofanari, P. Zanello, *Inorg. Chem.* **1987**, *26*, 3677−3682.

[6] A. Galindo, E. Gutiérrez-Puebla, A. Monge, M. A. Muñoz, A. Pastor, C. Ruiz, E. Carmona, *J. Chem. Soc., Dalton Trans.* **1992**, 2307−2308.

[7] A. Galindo, E. Gutiérrez-Puebla, A. Monge, A. Pastor, A. Pizzano, C. Ruiz, L. Sánchez, E. Carmona, *Inorg. Chem.* **1993**, *32*, 5569−5575.

[8] A. L. Hector, A. F. Hill, *J. Organomet. Chem.* **1993**, *447*, C7−C9.

[9] C. Bianchini, P. Innocenti, A. Meli, A. Orlandini, G. Scapacci, *J. Organomet. Chem.* **1982**, *233*, 233−246.

[10] D. Miguel, V. Riera, J. A. Miguel, F. Diego, C. Bois, Y. Jeannin, *J. Chem. Soc., Dalton Trans.* **1990**, 2719−2727.

[11] F. W. Einstein, E. Enwall, N. Flitcroft, J. M. Leach, *J. Inorg. Nucl. Chem.* **1972**, *34*, 885−891.

[12] T. Ashworth, E. Singleton, M. Laing, *J. Chem. Soc., Chem. Commun.* **1976**, 875−876.

[13] T. Ashworth, D. J. A. de Waal, E. Singleton, *J. Chem. Soc., Chem. Commun.* **1981**, 78−79.

[14] C. Bianchini, A. Meli, F. Nuzzi, P. Dapporto, *J. Organomet. Chem.* **1982**, *236*, 245−255.

[15] Faridoon, T. R. Spalding, G. Ferguson, J. D. Kennedy, X. L. R. Fontaine, *J. Chem. Soc., Chem. Commun.* **1989**, 906−908.

[16] D. Miguel, V. Riera, J. A. Miguel, C. Bois, M. Philoche-Levisalles, Y. Jeannin, *J. Chem. Soc., Dalton Trans.* **1987**, 2875−2880.

[17] D. Miguel, V. Riera, J. A. Miguel, *J. Organomet. Chem.* **1991**, *412*, 127−136.

[18] D. Miguel, J. A. Miguel, V. Riera, X. Soláns, *Angew. Chem.* **1989**, *101*, 1078−1079; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1014−1016.

[19] G. Thiele, G. Liehr, E. Lindner, *Chem. Ber.* **1974**, *107*, 442−447.

[20] S. R. Finnimore, R. Goddard, S. D. Killops, S. A. R. Knox, P. Woodward, *J. Chem. Soc., Chem. Commun.* **1975**, 391−392; *J. Chem. Soc., Dalton Trans.* **1978**, 1247−1255.

[21] K. B. Shiu, S. T. Lin, D. W. Fung, T. J. Chan, S. M. Peng, M. C. Cheng, J. L. Chou, *Inorg. Chem.* **1995**, *34*, 854−863.

[22] E. Lindner, H. M. Ebinger, *Z. Naturforsch., Part B*, **1973**, *28*, 113−119.

[23] E. W. Abel, M. O. Dunster, *J. Chem. Soc., Dalton Trans.* **1973**, 98−102.

[24] E. Lindner, H. M. Ebinger, *Chem. Ber.* **1974**, *107*, 135−144.

[25] K. Tanaka, Y. Miya-Uchi, T. Tanaka, *Inorg. Chem.* **1975**, *14*, 1545−1550.

[26] D. Miguel, V. Riera, J. A. Miguel, M. Gómez, X. Soláns, *Organometallics* **1991**, *10*, 1683−1692.

[27] See G. A. Carriedo, V. Riera, *J. Organomet. Chem.* **1990**, *394*, 275−283, and references therein.

[28] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405762, the names of the authors, and the journal citation.

[29] P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. Declercq, M. M. Woolfson, *MULTAN80: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data*, Universities of York and Louvain, York, U.K. and Louvain, Belgium, **1980**.

[30] G. M. Sheldrick, *SHELX76, Program for Crystal Structure Determination*, University of Cambridge, **1976**.

[31] B. Alvarez, D. Miguel, J. A. Pérez-Martínez, V. Riera, S. García-Granda, *J. Organomet. Chem.* **1992**, *427*, C33−C36.

[32] A. L. Spek, *The EUCLID Package* in *Computational Crystallography* (Ed.: E. Sayre), Clarendon Press, Oxford, UK, **1982**, p. 528.

[96137]