Dirhenium Complexes with S_2CPR_3 Bridges Donating Four and Eight Electrons – X-ray Structures of $[Re_2(CO)_8\{\mu\text{-}\eta^1;\eta^1\text{-}S_2CPCy_3\}]$ and $[Re_2(CO)_6\{\mu\text{-}\eta^2;\eta^3\text{-}S_2CPCy_3\}]$

Bernardo Alvarez[a], **Jing Li**[a], **Daniel Miguel***[b], **M. Dolores Morales**[a], **Víctor Riera**[a], and **Santiago García-Granda**[c]

Departamento de Química Orgánica e Inorgánica/IUQOEM – Unidad Asociada del CSIC, Universidad de Oviedo[a],
E-33071 Oviedo, Spain

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid[b],
E-47071, Valladolid, Spain

Departamento de Química Física y Analítica, Universidad de Oviedo[c],
E-33071 Oviedo, Spain

Received May 26, 1997

Keywords: 1,1-Dithiolate / Rhenium / Carbonyl complexes / Bridging ligands / Bimetallic complexes

The reaction of *fac*-$[Re(CO)_3(S_2CPR_3)Br]$ with $[Re(CO)_5]^-$ affords the dinuclear octacarbonyl compounds $[Re_2(CO)_8(\mu\text{-}S_2CPR_3)]$ (**3a–b**), which have been isolated and characterized by spectroscopic methods. An X-ray crystal-structure determination of the derivative **3a** (R = Cy) shows that the S_2CPCy_3 ligand acts as an $\eta^1(S);\eta^1(S')$ bridge donating two electrons to each metal atom of a symmetrical $(CO)_4Re{-}Re(CO)_4$ unit. This unit is presumably formed through a concerted process involving carbonyl/sulfur exchange in the nonsymmetrical octacarbonyl $(CO)_3(S_2CPR_3)Re{-}Re(CO)_5$ generated after the coupling of the bromo derivative with the carbonyl anion. Complexes **3a–b** can be obtained more directly by adding S_2CPR_3 to $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}CH{=}CH\textit{n}Bu)]$, which is formed by irradiation of $Re_2(CO)_{10}$ with 1-hexene. Hydride addition to the central carbon atom of the S_2CPR_3 ligand of **3a–b** occurs with loss of PR_3, to give the anion $[Re_2(CO)_6(\mu\text{-}S_2CH)]^-$ which may be isolated as a salt with the PPN^+ cation. The octacarbonyl compounds **3a–b** can be converted into hexacarbonyl complexes $[Re_2(CO)_6(\mu\text{-}S_2CPR_3)]$ (**5a–b**) by heating in toluene or octane at reflux temperature. According to an X-ray crystal-structure determination of the derivative **5a** (R = Cy), the loss of one carbonyl ligand from each rhenium atom is accompanied by the rearrangement of the S_2CPR_3 ligand which changes its bonding mode from $\eta^1(S);\eta^1(S')$ donating four electrons to $\eta^3(S,C,S');\eta^2(S,S')$ donating eight electrons.

We have been interested in the use of trialkylphosphane/carbon disulfide adducts, S_2CPR_3, as binucleating ligands.[1][2][3][4][5] In this field, we have found that S_2CPR_3 adducts, when acting as 8e bridges in the $\eta^3(S,C,S');\eta^2(S,S')$ coordination mode,[2][3][4] are able to bind two metal-ligand fragments together very strongly, especially when there is direct metal-to-metal interaction.[2]

The first example of this coordination mode was found in the hexacarbonyldimanganese complex $[Mn_2(CO)_6(\mu\text{-}S_2CPCy_3)]$ which can be prepared by thermal reaction between decacarbonyldimanganese and the free trialkylphosphoniodithioformate adduct S_2CPR_3 in refluxing toluene.[2]

Shortly after, it was found that the heterobinuclear analogs containing manganese and rhenium may be obtained by indirect routes which involve the attack of a carbonylmetallate anion $[Mn(CO)_5]^-$ on the mononuclear bromo derivatives $[Re(CO)_3(S_2CPR_3)Br]$.[6] In these reactions it was observed for the first time that the central carbon atom of the S_2CPR_3 adduct prefers to bond to the manganese rather to the rhenium center, this being a remarkable case of regioselectivity; the extent of this effect has been explored in subsequent studies with other combinations of metals.[4][7]

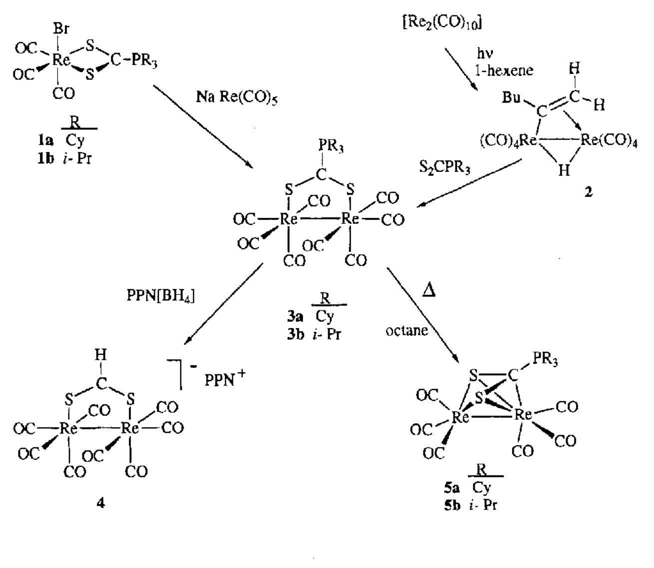
We wish to report here the preparation of a family of homonuclear dirhenium complexes containing the S_2CPR_3 adduct acting as $\eta^1(S);\eta^1(S')$ bridges, donating four electrons, and as $\eta^3(S,C,S');\eta^2(S,S')$ bridges, donating eight electrons. Part of this work has already been presented in a preliminary communication.[6]

Results and Discussion

The mononuclear bromo complexes $[Re(CO)_3(S_2CPR_3)Br]$ (**1a–b**)[8] react with the anion pentacarbonylrhenate(–I) to afford ultimately the binuclear octacarbonyl complexes $[Re_2(CO)_8(S_2CPR_3)]$ (**3a–b**), which can be isolated as red crystals in good yields (62–78 %). Analytical and spectroscopic data (see Experimental Section) suggest the structure depicted in Scheme 1 for complexes **3a–b**.

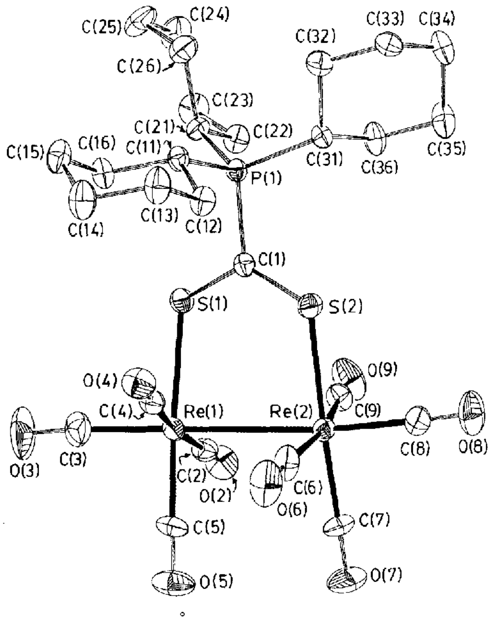
The most informative data, apart from IR spectra which were consistent with a dirhenium octacarbonyl unit, came from $^{13}C\{^1H\}$-NMR spectra in the region at $\delta \approx 200$. Both complexes exhibit the same pattern of signals corresponding to three sets of equivalent carbonyl ligands with intensities 2:4:2. Additionally, the signal attributable to the central carbon atom of S_2CPR_3 appears as a doublet at $\delta = 215.3$ [$^1J(P{-}C) = 40$ Hz] for **3a** and at $\delta = 218.7$ [$^1J(P{-}C) = 41$ Hz] for **3b**. This strongly indicates that the central carbon atom of the S_2CPR_3 unit is not involved in bonding with the metal centers since in all the cases known

Scheme 1



so far, when the central carbon atom is bonded with the metal center, the corresponding signal is shifted to the region δ = 80−100.[2][3][4][5][6][7] An X-ray crystal-structure determination was carried out with a crystal of the cyclohexyl derivative **3a** to confirm the structure and to study in detail the geometrical parameters of these octacarbonyl complexes. A perspective view of the structure is presented in Figure 1.

Figure 1. Perspective view (EUCLID Package)[20] of the structure of $[Re_2(CO)_8(S_2CPCy_3)]$ (**3a**), showing the atom numbering[a]



[a] Selected bond lengths [Å] and angles [°]: Re(1)−Re(2) 2.987(1), Re(1)−C(3) 1.935(9), Re(1)−C(5) 1.932(8), Re(1)−C(2) 1.958(8), Re(1)−C(4) 1.988(9), Re(1)−S(1) 2.464(2), Re(2)−C(8) 1.944(8), Re(2)−C(7) 1.943(11), Re(2)−C(9) 1.954(8), Re(2)−C(6) 1.978(8), Re(2)−S(2) 2.442(2), S(1)−C(1) 1.690(7), S(2)−C(1) 1.671(7), C(1)−P(1) 1.822(8); C(2)−Re(1)−C(4) 173.1(3), C(5)−Re(1)−S(1) 173.4(3), C(3)−Re(1)−Re(2) 177.2(3), C(9)−Re(2)−C(6) 167.8(3), C(7)−Re(2)−S(2) 176.7(3), C(8)−Re(2)−Re(1) 173.7(3), S(2)−C(1)−S(1) 128.6(5), S(2)−C(1)−P(1) 116.0(4), S(1)−C(1)−P(1) 115.1(4).

Each molecule of **3a** consists of two *cis*-tetracarbonylrhenium fragments held together by a tricyclohexylphosphoniodithioformate ligand which is bonded through one sulfur atom to each rhenium atom, thus acting as an $\eta^1(S);\eta^1(S')$-S_2CPR_3 bridge donating four electrons (i.e. two electrons to each rhenium atom) to the bimetallic unit. The Re(1)−Re(2) distance of 2.987(1) Å is shorter than that of 3.041(1) Å found in $[Re_2(CO)_{10}]$,[9] and is thus consistent with the existence of a direct Re−Re bond, as required by the EAN rule. Each rhenium atom is surrounded by four carbonyl groups, one sulfur atom of S_2CPR_3, and the other rhenium atom, forming a slightly distorted octahedral coordination, with interligand angles ranging from 81.5(2) to 97.0(3) °. Two features of the structure of **3a** are reminiscent of those observed in the parent $Re_2(CO)_{10}$. First, the substituents on each rhenium atom adopt a staggered disposition with respect to those of the other rhenium atom, the pertinent torsion angles ranging from 26.47(7)° for S(1)−Re(1)−Re(2)−S(2), to 34.1(4)° for C(4)−Re(1)−Re(2)−C(6). Additionally, the ligands on the *equatorial* positions of each rhenium atom move towards the other rhenium center [angles C(carbonyl)−Re−Re' or S−Re−Re' range from 81.5(2) to 88.9(3) °], with the only exception being the carbonyl ligand *trans* to S(2) [angle C(7)−Re(2)−Re(1) 94.2(3) °]. In both cases, the deviations from the more regular geometry found in the parent $[Re_2(CO)_{10}]$ can be ascribed to the constraints imposed by the formation of the Re−S−C−S−Re ring in **3a**. Nevertheless, the flexibility of the ligand when acting as an $\eta^1(S)$−$\eta^1(S')$ bridge is remarkable. In the few examples reported so far, the ligand has been found to span distances of 2.1384(8) Å, between two quadruply bonded molybdenum atoms in $[Mo_2(S_2CPEt_3)(O_2CCH_3)_3(OPEt_3)](BF_4)$,[10] or 2.452(1) Å between two singly bonded cobalt atoms in $[Co_3(CO)_7(\mu_3\text{-}CH)(\mu_2S_2CPCy_3)]$.[11]

The symmetric bis(tetracarbonylrhenium) moiety $(CO)_4Re$−$Re(CO)_4$ of **3a** is formed from the $Re(CO)_3$ fragments of **1a** and $Re(CO)_5$ fragments of the anion. Additionally, the S_2CPR_3 ligand, which was initially bonded as an $\eta^2(S,S')$ chelate towards one rhenium atom, changes its coordination mode to $\eta^1(S);\eta^1(S')$ as described above for **3a**. This means that the reaction should involve the migration of one carbonyl ligand from one rhenium atom to the other, while one of the sulfur atoms of S_2CPR_3 must migrate in the opposite direction to reach the final structure. Due to their complexity, the IR spectra recorded during the reaction are not informative about the possible intermediates. According to the mechanism proposed for the related reaction of $[Mn(CO)_3(R\text{-}DAB)(Br)]$ (R-DAB = substituted diazabutadiene) with $[Co(CO)_4]^-$,[12] the attack of the pentacarbonylrhenate anion on the bromo complexes **1a**−**b** should produce initially an asymmetric octacarbonyl complex, $[(CO)_3(S_2CPR_3)Re$−$Re(CO)_5]$. From this, the final symmetric octacarbonyl compound could be reached in a concerted step involving the simultaneous migration of the sulfur and the carbonyl ligands. The well-known ability of both CO and sulfur to act as bridges between two metal centers supports this proposal. In any case, the relatively high yield of isolated **3a**−**b** suggests that the rearrangement could not involve dissociation of CO since, due to the low solubility of free CO, a significant amount would be lost, especially in the case of **3b** which may be prepared in refluxing THF.

Once the structure of **3a** was established, we searched for a more straightforward route for the preparation of these octacarbonyl compounds. Quite surprisingly, the treatment of *eq,eq*-$[Re(CO)_8(NCMe)_2]$[13] with S_2CPR_3, in CH_2Cl_2 or THF, failed to render the desired compounds **3a**−**b**. Apparently such reactions give a mixture of compounds containing PR_3 ligands directly bonded to rhenium, even when excess CS_2 was added to avoid the dissociation of the S_2CPR_3 adduct. In contrast, complexes **3a**−**b** could be obtained by treating $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}CH{=}CH\textit{n}Bu)]$ (**2**)[14] with S_2CPR_3 in a mixture of THF and CS_2. This seems to be a convenient route since the starting complex **2** can be prepared directly from $[Re_2(CO)_{10}]$ by irradiation with 1-hexene, thus avoiding the multistep synthesis involving: (1) bromination of $Re_2(CO)_{10}$ to $[Re(CO)_5Br]$, (2) refluxing in acetonitrile to give $[Re(CO)_3(NCMe)_2Br]$, (3) reaction with S_2CPR_3 to give the tricarbonyl compounds **1a**−**b**, and (4) treatment with $[Re(CO)_5]^-$, which is in turn prepared from $[Re_2CO)_{10}]$ and Na[Hg]. It must be considered, however, that the successful preparation of the alkenylhydrido complex **2** requires careful control of the conditions of the irradiation reaction.

It has been shown recently that some binuclear complexes containing S_2CPR_3 bridges are able to undergo hydride addition at the metal−metal bond, thus producing carbonylhydrido anions which are able to react further with nucleophiles.[3] We have explored this reactivity on the octacarbonyl complexes **3a**−**b** with limited success. Thus, the reaction of complexes **3a**−**b** with $[PPN][BH_4]$ affords the dithioformate anionic complex **4**, which was isolated as a PPN salt, and characterized by analytical and spectroscopic methods (see Experimental Section). The $^{31}P\{^1H\}$-NMR spectra only show the signal of the PPN cation at $\delta = 21.6$ and no signal for the phosphane. $^{13}C\{^1H\}$-NMR spectra display the expected pattern of CO signals (4:2:2) for the $(CO)_4Re{-}Re(CO)_4$ fragment, and the signal attributable to the central carbon atom of dithioformate at $\delta = 236.2$, which was confirmed as arising from a C−H group by a DEPT experiment. Additionally, the ^1H-NMR spectrum shows a singlet, corresponding to one hydrogen atom at $\delta = 12.36$, attributable to the hydrogen atom of the dithioformate ligand.

The production of **4** suggests that the addition of hydride goes directly to the central carbon atom of the S_2CPR_3 ligand. Therefore, the reactivity of the $\eta^1{:}\eta^1\text{-}S_2CPR_3$ bridge is similar to that observed for the ligands acting as η^2-chelate in mononuclear complexes.[1b][15]

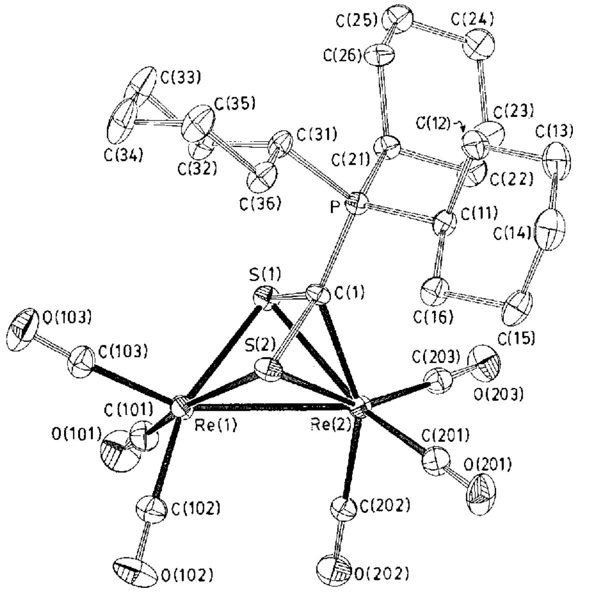
Decarbonylation of octacarbonyl compounds **3a**−**b** leads to the production of hexacarbonyl complexes $[Re_2(CO)_6(\mu\text{-}S_2CPR_3)]$ (**5a**−**b** in Scheme 1), which have been isolated and characterized by analytical and spectroscopic methods (see Experimental Section). The structure of these hexacarbonyl compounds have been confirmed by an X-ray crystal-structure determination with a crystal of the derivative **5a** (R = Cy) and will be discussed below. The conversion from octacarbonyl compounds **3a**−**b** to hexacarbonyl compounds **5a**−**b**, which can be considered as an intramolecular replacement of one CO on each rhenium atom by a sulfur atom of the S_2CPR_3 group, is somewhat difficult, and requires temperatures of boiling toluene or *n*-octane. Additionally, the reaction is not clean, and the yield is diminished by the appearance of a by-product, **6**, which resisted all our attempts at characterization. The separation of hexacarbonyl compopunds **5** from the reaction mixture is very easy due to the greater solubility of the by-product **6**, and it can be best achieved when the reaction is performed in *n*-octane, in which the desired compounds **5a**−**b** precipitate out of the solution. The IR spectra of the by-product **6** exhibit six bands in the carbonyl region, with frequencies (2041 cm^{-1} m, 2012 vs, 1950 s, 1939 s, 1914 m, 1907 m; for R = Cy; octane solution) which are between those of the starting octacarbonyl compound **3a**, and the hexacarbonyl compound **5a**. This led us to think that compound **6** could be an intermediate heptacarbonyl compound. However, **6** could not be converted into the hexacarbonyl compound **5** even after prolonged heating in toluene. Therefore, if **6** is a heptacarbonyl compound, it cannot be an intermediate in the conversion from **3** to **6**. Unfortunately, we have not been able to grow crystals of **6** suitable for an X-ray study.

As has been pointed out in the introduction, the analogous dimanganese compounds $[Mn_2(CO)_6(\mu\text{-}S_2CPR_3)]$ (R = Cy, *i*Pr) can be obtained directly from the parent decacarbonyl complex $Mn_2(CO)_{10}$ and the free ligand S_2CPR_3 by thermal reaction in refluxing toluene.[2] This contrasts sharply with the behavior of the dirhenium compounds described here, since $Re_2(CO)_{10}$ fails to react with S_2CPR_3 even after heating the mixture overnight in refluxing xylene. The use of a decarbonylating agent such as Me_3NO, at room temperature; or to promote CO replacement by irradiation, led to the formation of *ax*-$[Re_2(CO)_9(\eta^1\text{-}S_2CPR_3)]$, which was identified by comparison of its IR spectra in solution [$\tilde{\nu}(CO) = 2095\ cm^{-1}$ w, 2036 m, 1986 vs, 1954 m, 1904 m in CH_2Cl_2] with those of the dimanganese analogue.[2b] Heating this nonacarbonyl compound in toluene led to extensive decomposition within 5 h, apparently to give mononuclear *fac*-tricarbonyl complexes. Neither the octacarbonyl compound **3a**, nor the hexacarbonyl compound **5a**, were observed in the monitoring of the reaction. The difficulty of achieving the direct substitution of CO by S_2CPR_3 in $Re_2(CO)_{10}$ may reflect the greater inertness of the Re−CO bond, when compared with Mn−CO, this being a well-known feature in carbonyl substitution reactions.

The result of the X-ray determination carried out on **5a** is presented in Figure 2.

The geometric parameters are close to those encountered for the analogous complexes $[Mn_2(CO)_6(\mu\text{-}S_2CPCy_3)]$[2] and $[MnRe(CO)_6(\mu\text{-}S_2CPCy_3)]$,[6] the main differences coming from the greater atomic radius of rhenium when compared to manganese. Thus, the Re−Re distance of 2.975(1) Å is consistent with the existence of a direct Re−Re bond of order 1. The Re(1)−S(1)−S(2)−C(1) ring is close to planar,

Figure 2. Perspective view (EUCLID Package)[20] of the structure of [$Re_2(CO)_6(S_2CPCy_3)$] (**5a**), showing the atom numbering[a]



[a] Selected bond lengths [Å] and angles [°]: Re(1)−C(103) 1.882(5), Re(1)−C(102) 1.918(5), Re(1)−C(101) 1.929(5), Re(1)−S(1) 2.4106(13), Re(1)−S(2) 2.4250(13), Re(1)−Re(2) 2.975(1), Re(2)−C(201) 1.914(5), Re(2)−C(203) 1.928(5), Re(2)−C(202) 1.930(5), Re(2)−C(1) 2.176(4), Re(2)−S(2) 2.494(2), Re(2)−S(1) 2.4955(13), S(1)−C(1) 1.804(4), S(2)−C(1) 1.798(4); C(103)−Re(1)−C(102) 92.7(2), C(103)−Re(1)−C(101) 87.9(2), C(102)−Re(1)−C(101) 89.4(2), C(102)−Re(1)−S(1) 160.6(2), C(101)−Re(1)−S(2) 163.1(2), S(1)−Re(1)−S(2) 71.86(4), C(103)−Re(1)−Re(2) 153.7(2), C(102)−Re(1)−Re(2) 106.6(2), C(101)−Re(1)−Re(2) 109.5(2), C(201)−Re(2)−C(203) 92.8(2), C(201)−Re(2)−C(202) 86.3(2), C(203)−Re(2)−C(202) 90.9(2), C(202)−Re(2)−C(1) 152.2(2), C(203)−Re(2)−S(2) 151.84(13), C(201)−Re(2)−S(1) 157.4(2), S(2)−Re(2)−S(1) 69.33(5), C(201)−Re(2)−Re(1) 131.79(14), C(203)−Re(2)−Re(1) 133.48(13), S(2)−Re(2)−Re(1) 51.73(4), S(2)−C(1)−S(1) 104.0(2).

the maximum deviation affecting C(1), at 0.056(4) Å from the best plane. As was observed for the dimanganese compound, the plane of the ring is nearly parallel to the plane formed by the three carbonyl ligands of Re(2) {angle between planes 3.3(1) ° [cf. 2.3 (2) ° for $Mn_2(CO)_6(\mu\text{-}S_2CPCy_3)$]}.[2b] Similarly, the whole molecule can be described as a pseudo-cymentrene derivative in which the nearly planar rhenadithiabutene ring, donating 5e, acts as a pseudo-cyclopentadienyl ligand towards a $Re(CO)_3$ fragment.

A comparison of the structure of **5a** with some related complexes reveals again, as with the $\eta^1;\eta^1$ complexes discussed above, a remarkable geometric flexibility of the S_2CPCy_3 ligand when acting as $\eta^3;\eta^2$ bridge between two directly bonded metal atoms. Thus, the intermetallic distances found range from 2.599(1) Å in [$MnCo(CO)_5(\mu\text{-}S_2CPCy_3)$], 2.737(1) Å in [$Mn_2(CO)_6(\mu\text{-}S_2CPCy_3)$], 2.830(1) Å in [$MnRe(CO)_6(\mu\text{-}S_2CPCy_3)$], to 2.975(1) Å in **5a**. Additionally, $\eta^3;\eta^2$-S_2CPR_3 bridges have been found spanning intermetallic nonbonding distances up to 3.636(2) Å in [$Mo(CO)_2(PCy_3)(\mu\text{-}Cl)(\mu\text{-}S_2CPCy_3)(BuSnCl_2)$].[4c]

We thank the *DGICYT* (Project PB 94-1332) for financial support, and the *Ministerio de Educacion* for the concession of a grant to J. L.

Experimental Section

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

[$Re_2(CO)_8(\mu\text{-}H)\{\mu\text{-}CHC(H)nBu\}$] (**2**): This was prepared as described by Nubel and Brown[14] with some modifications. [$Re_2(CO)_{10}$] (0.3 g, 0.46 mmol) was dissolved in a mixture of toluene (9 ml) and 1-hexene (3 ml). The mixture was cooled to 5°C, and irradiated, while a slow stream of dry N_2 (ca. one bubble per second) was passed through the solution. The reaction was completed after 3.5 h, when IR monitoring (toluene solution) showed the bands of **2** at 2111 cm^{-1} w, 2080 m, 2015 vs, 1970 s, and 1956 m. The color of the solution was yellow-brown. Evaporation of the solvent gave **2** as an oil which was redissolved in THF to be employed in subsequent reactions.

[$Re_2(CO)_8(S_2CPCy_3)$] (**3a**). − *Method A, from [$Re_2(CO)_8(\mu\text{-}H)\{\mu\text{-}CHC(H)nBu\}$]* (**2**): To a solution of **2** (ca. 0.46 mmol) in THF (20 ml) was added CS_2 (3 ml) and S_2CPCy_3 (0.164 g, 0.45 mmol), and the mixture was stirred for 8 h. After evaporation of the solvent, the dry residue was dissolved in CH_2Cl_2/hexane (1:1) and separated by chromatography through a column of Alox-III. A red band was eluted which, on slow evaporation of the solvent, gave 0.28 g of **3a** (65 %) as red microcrystals. − $C_{27}H_{33}O_8PRe_2S_2$ (953.05): calcd. C 34.03, H, 3.49; found C 33.92, H 3.56.

[$Re_2(CO)_8(S_2CPCy_3)$] (**3a**). − *Method B, from [$Re(CO)_3(S_2CPCy_3)Br$]* (**1a**): A solution of Na[$Re(CO)_5$] (ca. 0.17 mmol) was prepared from [$Re_2(CO)_{10}$] (0.11 g, 0.17 mmol) and sodium amalgam (1 % w, 10 g, excess) in THF (20 ml), and was filtered through a cannula under nitrogen, into a slurry of [$Re(CO)_3(S_2CPCy_3)Br$] (**1a**) (0.2 g, 0.283 mmol) in THF (20 ml). The mixture was stirred for 10 h at room temperature, and then filtered through kieselguhr. The solvent was evaporated in vacuo, and the dry residue was washed with hexane (3 × 15 ml) to remove some [$Re_2(CO)_{10}$] and then recrystallized from CH_2Cl_2/hexane at −20°C, to obtain 0.21 g of **3a** (78 %) as red microcrystals. − $C_{27}H_{33}O_8PRe_2S_2$ (953.05): calcd. C 34.03, H, 3.49; found C 33.80, H 3.34. − IR (THF): $\tilde{\nu}$(CO) = 2064 cm^{-1} m, 2007 s, 1969 vs, 1939 m, 1935 m, 1908 s. − ^1H NMR ($CDCl_3$): δ = 2.58 [m, 3 H, C*H* of Cy], 1.93−1.42 [m, 30 H, and C*H*$_2$ of Cy]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 43.9 − $^{13}C\{^1H\}$ NMR: δ = 215.3 [d (40), S_2CP], 207.7 [s, 4 CO], 199.8 [s, 2 CO], 193.1 [s, 2 CO], 32.3 [d (33), C^1 of Cy], 26.9 [d (11), C^3 and C^5 of Cy], 26.8 [s, C^2 and C^6 of Cy], 25.5 [s, C^4 of Cy].

Crystal-Structure Determination of [$Re_2(CO)_8(\mu\text{-}S_2CPCy_3)$][16] (**3a**): $C_{27}H_{33}O_8PRe_2S_2$, (953.02), a = 13.287(4), b = 11.401(4), c = 11.276(2) Å, α = 100.17(2), β = 74.53(2), γ = 96.78(2) °, V = 1615.9(6) Å^3, d = 1.96 g/cm^3, Z = 2, triclinic, $P\bar{1}$, crystal size 0.3 × 0.2 × 0.1 mm, μ = 77.07 cm^{-1}, scan range 1 ° ≤ θ ≤ 25 °, 4657 reflections collected, 3992 observed [$I \geq 2\sigma(I)$]. Enraf-Nonius CAD4 diffractometer, radiation (Mo-K_α), λ = 0.71073. Unit-cell parameters were determined from the least squares refinement of 25 centered reflections in the range 20 ° < θ < 24 °. Three reflections were measured every 2 h as an orientation and intensity control. Significant decay was not observed. The structure was solved with DIRDIF[17] by Patterson methods, phase expansion, and subsequent Fourier maps. A semi-empirical absorption correction was made with DIFABS.[18] Full-matrix least-squares refinement on F^2 (359 parameters) was made with SHELX93.[19] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically positioned, and they were given an overall isotropic thermal parameter which was refined. Final residues were $R = 0.032$ (for observed reflections) and $wR2 = 0.091$ (for all reflections, g.o.f. = 1.14).

$Re_2(CO)_8(S_2CPiPr_3)]$ (**3b**). – *Method A:* The procedure was as described for **3a** (Method A) above, starting from **2** (ca. 0.46 mmol), P*i*Pr$_3$ (91 µl, 0.46 mmol), and CS_2 (2 ml, excess), in THF (30 ml), to obtain 0.24 g of **3b** (62 % based on $[Re_2(CO)_{10}]$) as red microcrystals. – $C_{18}H_{21}O_8PRe_2S_2$ (832.85): calcd. C 25.96, H 2.54; found C 25.72, H 2.79.

$Re_2(CO)_8(S_2CPiPr_3)]$ (**3b**). – *Method B:* The procedure was as described for **3a** (Method B) above, starting from $Na[Re(CO)_5]$ (ca. 0.17 mmol), and $[Re(CO)_3(S_2CPiPr_3)Br]$ (**1b**) (0.15 g, 0.212 mmol) in THF (40 ml). The mixture was heated for 1.5 h at the reflux temperature. The workup was as described for **3a** above to obtain 0.14 g of **3b** (79 %) as red microcrystals. – $C_{18}H_{21}O_8PRe_2S_2$ (832.85): calcd. C 25.96, H 2.54; found C 25.64, H 2.39. – IR (THF): $\tilde{\nu}(CO) = 2064\ cm^{-1}$ m, 2008 s, 1969 vs, 1941 m, 1936 m, 1907 s. – ^1H NMR ($CDCl_3$): $\delta = 2.84$ [m, 3 H, C*H* of *i*Pr], 1.63–1.29 [m, 18 H, C*H*$_3$ of *i*Pr]. – $^{31}P\{^1H\}$ ($CDCl_3$): $\delta = 53.6$. – $^{13}C\{^1H\}$ NMR: $\delta = 218.7$ [d (41), S$_2$*C*P], 207.5 [s, 4 *C*O], 199.8 [s, 2 *C*O], 193.0 [s, 2 *C*O], 23.34 [d (40), *C*H of *i*Pr], 17.0 [s, *C*H of *i*Pr].

$[PPN][Re_2(CO)_8\{\mu\text{-}S_2CH\}]$ (**4**): To a stirred solution of **3a** (0.1 g, 0.105 mmol) in THF (20 ml) was added $[PPN]BH_4$ (0.056 g, 0.105 mmol). After stirring for 2 h at room temperature, the solvents were evaporated in vacuo. The dry residue was dissolved in diethyl ether and filtered through kieselguhr. The filtered solution was evaporated and the residue was recrystallized from a mixture of CH_2Cl_2/hexane at –20°C to obtain 0.06 g of **4** (45 %) as red microcrystals. – $C_{45}H_{31}NO_8P_2Re_2S_2$ (1212.21): calcd. C 44.59, H 2.58, N 1.16; found C 44.91, H 2.80, N 1.23. – IR (THF): $\tilde{\nu}(CO) = 2059\ cm^{-1}$ w, 2007 s, 1998 s, 1959 vs, 1950 s, 1926 m, 1905 m, 1888 s. – ^1H NMR ($CDCl_3$): $\delta = 12.36$ [s, 3 H, S$_2$C*H*], 7.70–7.26 [m, 20 H, C$_6$*H*$_5$ of PPN]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.6$. – $^{13}C\{^1H\}$ NMR: $\delta = 236.2$ [s, S$_2$*C*H], 209.4 [s, 4 *C*O], 199.9 [s, 2 *C*O], 193.6 [s, 2 *C*O], 133.8–127.0 [m, *C*$_6$H$_5$ of PPN].

$[Re_2(CO)_6(\mu\text{-}S_2CPCy_3)]$ (**5a**): Compound **3a** (0.2 g, 0.21 mmol) was heated in refluxing octane (25 ml) for 30 min. A yellow solid separated from the solution. The mother liquors were decanted and the yellow solid was redissolved in CH_2Cl_2 and chromatographed in alumina (activity III, 2.5 × 15 cm column). Elution with CH_2Cl_2 gave a bright-yellow band which was concentrated in vacuo to give 0.11 g of **5a** (56 %), as yellow crystals. – $C_{25}H_{33}O_6PRe_2S_2$ (897.03): calcd. C 33.48, H 3.71; found C 33.21, H 3.54. – IR (CH_2Cl_2): $\tilde{\nu}(CO) = 2028\ cm^{-1}$ s, 1999vs, 1923s, 1895m.

Crystal-Structure Determination of $[Re_2(CO)_6(\mu\text{-}S_2CPCy_3)]$[16] (**5a**): $C_{25}H_{33}O_6PRe_2S_2$ (897.03), $a = 11.154(3)$, $b = 11.434(5)$, $c = 11.679(2)$ Å, $\alpha = 84.01(4)$, $\beta = 77.90(3)$, $\gamma = 85.99(2)$ °, $V = 1446.6(9)$ Å^3, $d = 2.06$ g/cm^3, $Z = 2$, triclinic, $P\bar{1}$, crystal size 0.2 × 0.2 × 0.1 mm, $\mu = 86.0\ cm^{-1}$, $1° \le \theta \le 25°$, 5089 reflections collected, 4387 observed [$I \ge 2\sigma(I)$]. Nonius CAD4 diffractometer, radiation (Mo-K_α), $\lambda = 0.71073$. Unit-cell parameters were determined from the least squares refinement of 25 centered reflections in the range $15° < \theta < 20°$. Three reflections were measured every 2 h as orientation and intensity control. Significant decay was not observed. The structure was solved with DIRDIF[17] by Patterson methods, phase expansion, and subsequent Fourier maps. A semi-empirical absorption correction was made with DIFABS.[18] Full-matrix least-squares refinement on F^2 (326 parameters) was made with SHELX93.[19] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically positioned, and they were given an overall isotropic thermal parameter which was refined. Final residues were $R = 0.029$ (for observed reflections) and $wR2 = 0.052$ (for all reflections, g.o.f. = 1.03).

$[Re_2(CO)_6(\mu\text{-}S_2CPiPr_3)]$ (**5b**): The procedure was as described for **5a** above, by refluxing **3b** (0.2 g, 0.24 mmol) in octane (25 ml). Subsequent workup gave 0.095 g of **5b** (51 %), as yellow crystals. – $C_{16}H_{21}O_6PRe_2S_2$ (776.83): calcd. C 24.74, H 2.73; found C 24.95, H 2.45. – IR (CH_2Cl_2): $\tilde{\nu}(CO) = 2029\ cm^{-1}$ s, 1999 vs, 1926 s, 1900 m. – ^1H NMR ($CDCl_3$) δ 2.80 [m, 3 H, C*H* of *i*Pr], 1.56–1.45 [m, 18 H, C*H*$_3$ of *i*Pr]. – $^{31}P\{^1H)$ ($CDCl_3$): $\delta = 45.9$. – $^{13}C\{^1H\}$ NMR: $\delta = 195.6$ [s, 3 *C*O], 192.2 [s, 3 *C*O], 73.4 [d (45),S$_2$*C*P], 24.3 [d (44), *C*H of *i*Pr], 18.5 [s, *C*H of *i*Pr].

---

[1] [1a] D. Miguel, V. Riera, J. A. Miguel, C. Bois, M. Philoche-Levisalles, Y. Jeannin, *J. Chem. Soc., Dalton Trans.* **1987**, 2875–2880. – [1b] D. Miguel, V. Riera, J. A. Miguel, F. Diego, C. Bois, Y. Jeannin, *J. Chem. Soc., Dalton Trans.* **1990**, 2719–2727.

[2] [2a]D. Miguel, V. Riera, J. A. Miguel, X. Soláns, M. Font-Altaba, *J. Chem. Soc., Chem. Commun.* **1987**, 472–474. – [2b] D. Miguel, V. Riera, J. A. Miguel, M. Gómez, X. Soláns, *Organometallics* **1991**, *10*, 1683–1692.

[3] B.Alvarez, S. García-Granda, Y. Jeannin, D. Miguel, J. A. Miguel, V. Riera, *Organometallics* **1991**, *10*, 3005–3007; B. Alvarez, S. García-Granda, J. Li, D. Miguel, V. Riera, *Organometallics* **1994**, *13*, 16–17.

[4] [4a]D. Miguel, J. A. Pérez-Martínez, V. Riera, S. García-Granda, *Organometallics* **1993**, *12*, 1394–1400. – [4b] D. Miguel, J. A. Pérez-Martínez,V. Riera, S. García-Granda, *Organometallics* **1993**, *12*, 2888–2889. – [4c] D. Miguel, J. A. Pérez-Martínez, V. Riera, S. García-Granda, *Angew. Chem.* **1992**, *104*, 81–83; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 76–77.

[5] A. Galindo, C. Mealli, J. Cuyás, D. Miguel, V. Riera, J. A. Pérez-Martínez, C. Bois, Y. Jeannin, *Organometallics* **1996**, *15*, 2735–2744.

[6] B. Alvarez, D. Miguel, V. Riera, J. A. Miguel, S. García-Granda, *Organometallics* **1991**, *10*, 384–387.

[7] J. Cuyás, D. Miguel, J. A. Pérez-Martínez, V. Riera, S. García-Granda, *Polyhedron* **1992**, *11*, 2713–2716; E. M. López, D. Miguel, J. A. Pérez-Martínez, V. Riera, *J. Organomet. Chem.* **1994**, *467*, 231–235; D. Miguel, J. A. Pérez-Martínez, V. Riera, S. García-Granda, *Organometallics* **1994**, *13*, 1336–1340.

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

[9] M. R. Churchill, K. N. Amoh, H. J. Wasserman, *Inorg. Chem.* **1981**, *20*, 1609–1611.

[10] D. M. Baird, P. E. Fanwick, T. Barwick, *Inorg. Chem.* **1985**, *24*, 3753–3758.

[11] B. Alvarez, D. Miguel, V. Riera, S. García-Granda, *J. Organomet. Chem.* **1992**, *430*, C19–C2.

[12] G. van Koten, K. Vreeze, *Adv. Organomet. Chem.* **1982**, *21*, 151–239.

[13] S. Top, M. Gunn, G. Jaouen, J. Vaissermann, J. C. Daran, M. J. McGlinchey, *Organometallics* **1992**, *11*, 1201–1209.

[14] P. O. Nubel, T. L. Brown, *J. Am. Chem. Soc.* **1984**, *106*, 644–652

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

[16] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-407235 (for **3a**) and CSD-407236 (for **5a**), the names of the authors, and the journal citation.

[17] P. T. Beurskens, G. Admiraal, W. P. Bosman, G. Beurskens, H. M. Doesburg, S. García-Granda, R. O. Gould, J. M. M. Smits, C. Smikalla, *The DIRDIF Program System*, Technical Report of the Crystallography Laboratory. University of Nijmegen, The Netherlands, **1982**.

[18] N. Walker, D. Stuart, *Acta Crystallogr.* **1983**, *A39*, 158.

[19] G. M. Sheldrick, *SHELXL-93*, Universität Göttingen, **1993**.

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

[97121]