Reversible Isomerization via Migration of $SnPh_3$ in S_2CPCy_3-Bridged Heterobinuclear Compounds. X-ray Structures of $[(CO)_3Re(\mu\text{-}S_2CPCy_3)Mo(SnPh_3)(CO)_3]$ and $[(CO)_3(Ph_3Sn)Re(\mu\text{-}S_2CPCy_3)Mo(CO)_3]$

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The reduction of $[(CO)_3Re(\mu\text{-Br})(\mu\text{-}S_2CPCy_3)Mo(CO)_3]$ (**1**) with Na/Hg and subsequent reaction of the resulting anionic species with Ph_3SnCl yields $[(CO)_3Re(\mu\text{-}S_2CPCy_3)Mo(SnPh_3)(CO)_3]$ (**2**), which, as the temperature increases, partially isomerizes reversibly, through migration of $SnPh_3$, to $[(CO)_3(Ph_3Sn)Re(\mu\text{-}S_2CPCy_3)Mo(CO)_3]$ (**3**).

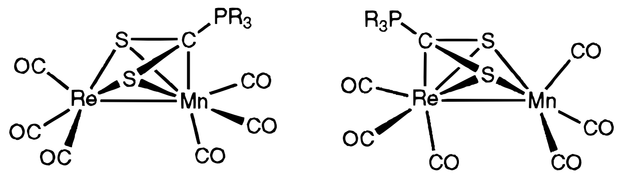
Introduction

During the last years we have developed synthetic routes to binuclear complexes with bridging $\eta^3;\eta^2$-S_2CPR_3 ligands.[1] This bridge imparts a remarkable stability to the binuclear unit and, at the same time, rearranges facilely to adapt to changes in the molecule.

The S_2CPR_3 ligand was found for the first time as a $\eta^3;\eta^2$ bridge in the symmetric template $(CO)_3Mn-Mn(CO)_3$.[1a] When it bridges two different metal fragments, M and M′, two isomers can be expected, depending on which metal is bonded to the central carbon of the ligand.

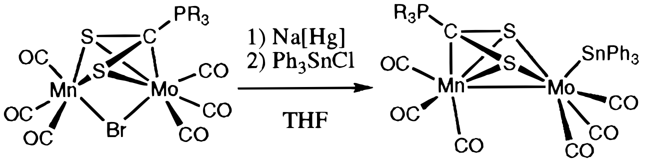
Interestingly, a definite preference for one of the isomers has been found in all the examples. For M = $Mn(CO)_3$, M′ = $Re(CO)_3$, only isomer **A** (see Scheme 1) is obtained either by reaction of $[MnBr(CO)_3(S_2CPCy_3)]$ with $Na[Re(CO)_5]$ or by reaction of $[ReBr(CO)_3(S_2CPCy_3)]$ with $Na[Mn(CO)_5]$.[1b] Therefore, with equal coordination sphere and oxidation states, the nature of the metal dictates the selective formation of the metal−carbon bond. No isomerization to **B** was detected upon prolonged heating. Hence, either there is a large kinetic barrier for the breaking of the Mn−C bond, or a large thermodynamic advantage can be attributed to the observed product.[2]

Scheme 1



A **B**

Scheme 2



C **D**

For complexes with a S_2CPCy_3 bridge between Mo and Mn, we found a sequence of reactions in which the central carbon of S_2CPCy_3 shifts from one metal to another, showing that changes in the coordination sphere overcome the nature of the metal as a factor in determining the carbon preference.[3,4] Thus, sodium amalgam reduction of $[(CO)_3Mn(\mu\text{-Br})(\mu\text{-}S_2CPCy_3)Mo(CO)_3]$ and reaction of the resulting anion with Ph_3SnCl yields $[(CO)_3(Ph_3Sn)Mo(\mu\text{-}S_2CPCy_3)Mn(CO)_3]$.[3]

The overall reaction results in the formation of the Mo−Mn and Mo−Sn bonds and the shift of the central

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(1) (a) Mn−Mn: Miguel, D.; Riera, V.; Miguel, J. A.; Gómez, M.; Soláns, X. *Organometallics* **1991**, *10*, 1683. (b) Mn−Re: Alvarez, B.; Miguel, D.; Riera, V.; Miguel, J. A.; García-Granda, S. *Organometallics* **1991**, *10*, 384. (c) Re−Re: Alvarez, B.; Li, J.; Miguel, D.; Morales, M. D.; Riera, V.; García-Granda, S. *Chem. Ber./Rec.* **1997**, *130*, 1507. (d) Mo−Sn: Miguel, D.; Pérez-Martínez, J. A.; Riera, V.; García-Granda, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 76. (e) Mo−Mn: Miguel, D.; Pérez-Martínez, J. A.; Riera, V.; García-Granda, S. *Organometallics* **1993**, *12*, 1394. (f) Mo−Re: López, E. M.; Miguel, D.; Pérez-Martínez, J. A.; Riera, V. *J. Organomet. Chem.* **1994**, *467*, 231. (g) Mo−Mo, Mo−W, W−W: Miguel, D.; Pérez-Martínez, J. A.; Riera, V.; García-Granda, S. *Organometallics* **1994**, *13*, 1336. (h) Mo−Ru, W−Ru: Cuyás, J.; Miguel, D.; Pérez-Martínez, J. A.; Riera, V.; García-Granda, S. *Polyhedron* **1992**, *11*, 2713. (i) Mo−Co, W−Co, Mn−Co, Re−Co: Barrado, G.; Li, J.; Miguel, D.; Pérez-Martínez, J. A.; Riera, V.; Bois, Jeannin, Y. *Organometallics* **1994**, *13*, 2330.

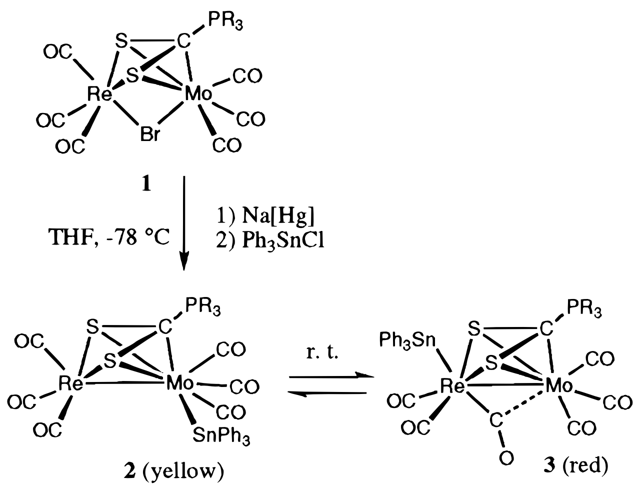
(2) For theoretical studies on the metal preference for η^3(S, C, S′) or η^2(S, S′) coordination, see: (a) Jemmis, E. D.; Subramanian, G.; Prasad, B. V. *Organometallics* **1993**, *12*, 4267. (b) Galindo, A.; Mealli, C.; Cuyás, J.; Miguel, D.; Riera, V.; Pérez-Martínez, J. A.; Bois, C.; Jeannin, Y. *Organometallics* **1996**, *15*, 2735.

(3) Miguel, D.; Pérez-Martínez, J. A.; Riera, V.; García-Granda, S. *Organometallics* **1994**, *13*, 2888.

(4) Miguel, D.; Pérez-Martínez, J. A.; Riera, V.; García-Granda, S. *Organometallics* **1994**, *13*, 4667.

10.1021/om9804273

Scheme 3



carbon from Mo to Mn. Whether the carbon migration takes place prior, subsequently, or simultaneously to the metal−metal bond formation remains an open question.

A parallel behavior could be anticipated for the rhenium analogue $[(CO)_3Re(\mu\text{-}Br)(\mu\text{-}S_2CPCy_3)Mo(CO)_3]$ (**1**).[1f] However, the reaction took a different course. Our findings are the subject of this article.

Results and Discussion

The reaction of $[(CO)_3Re(\mu\text{-}Br)(\mu\text{-}S_2CPCy_3)Mo(CO)_3]$ (**1**)[1f] with Na/Hg in THF gives a solution with carbonyl stretching frequencies considerably lower than those of **1**, indicating reduction to an anionic species. Reaction of this solution with Ph_3SnCl at −80 °C gives a new compound **2**, displaying a pattern of ν(CO) bands that is consistent with a neutral formulation.

When the solution of **2** is allowed to warm, the IR bands of a second neutral species **3** appear. The **3**/**2** ratio grows to reach a value of 4/5 after 1 h at room temperature and then does not change appreciably when the temperature is maintained several hours at 60 °C.

The mixture of **2** and **3** can be isolated as an orange solid with C, H analyses consistent with a formulation $[MoRe(SnPh_3)(CO)_6(S_2CPCy_3)]$, reminiscent of the related MnMo chemistry. Crystallization from CH_2Cl_2/hexane yielded a mixture of yellow and red crystals, which were found to be pure **2** and **3**, respectively. When the crystals of either **2** or **3** are dissolved (CH_2Cl_2 or THF), the composition of the solution evolves to give the **3**/**2** = 4/5 mixture.

Hence, a reversible isomerization takes place between **2** and **3**, and the 4/5 mixture corresponds to the thermodynamic equilibrium. The similar concentrations in the equilibrium reflect the close thermodynamic stabilities of **2** and **3**.

The structures of **2** and **3** were determined by X-ray diffraction. In both compounds, a S_2CPCy_3 ligand bridges the $Mo(CO)_3$ and $Re(CO)_3$ fragments, coordinating Mo through the two sulfur atoms and the central carbon, and Re through the two sulfur atoms. A terminal $SnPh_3$ group is bonded to Mo in **2** and to Re in **3**.

In **3**, one of the carbonyl ligands bonded to rhenium shows a considerable deviation from linearity [Re−C(1)−O(1) = 156.0(32)° and 157.4(30)°], and the carbon atom C(1) is near Mo [2.60(3) and 2.51(3) Å]. As expected for a semibridging carbonyl, the Re−C distance [2.00(4) and 2.06(3) Å] is slightly longer than in terminal carbonyl ligands.

The coordination of this carbonyl follows the pattern expected for semibridging carbonyl ligands in asymmetric binuclear compounds:[5] the electron count is 16 for Mo and 18 for Re; then, a dative Mo−Re bond must be considered. This would leave Re(+) and Mo(−) charges. The semibridging CO ligand mitigates this charge separation by allowing an empty orbital of CO to accept electron density from a filled Mo orbital.

The comparison of the structural parameters in both isomers reveals several features of interest: in the first place the Mo−Re distance is slightly shorter (about 0.152 Å, ca. 5%) in the structure of **3** (average 2.919 Å), containing a dative Re→Mo bond and a semibridging carbonyl, than in **2** (3.071 Å), with a normal Re−Mo bond and without a semibridging carbonyl. The presence of an unsupported dative bond usually produces a significant elongation of the M−M distance when compared to a “normal” bond.[6] However, there is a fairly wide range of complexes of the “ferrole” type with, and without, a semibridging carbonyl. In most cases those compounds containing a semibridging carbonyl display Fe−Fe dative bonds which are slightly shorter than the Fe−Fe bonds in similar complexes without a semibridging carbonyl.[7] Therefore, we ascribe the small shortening of the Re→Mo distance to the effect of the semibridging carbonyl, which compensates the elongation that would be expected for the dative bond.

Other minor differences concern the metal−sulfur distances: the Re−S distances in **2** (average 2.411 Å) are slightly shorter than those in **3** (average 2.459 Å), while the Mo−S distances in **2** (average 2.530 Å) are slightly longer than those in **3** (average 2.505 Å). It seems that the coordination of $SnPh_3$ to the metal produces a slight elongation of the M−S distances. For the remaining structural parameters, the differences found are well within the experimental error ($\pm 3\sigma$ range).

Two features are remarkable in the structure of **2**: (a) both the $SnPh_3$ ligand and the PCy_3-bonded carbon coordinate the same metal. Avoidance of such a congested arrangement was considered to be partially responsible for the observed structure of $[(CO)_3(Ph_3Sn)Mo(\mu\text{-}S_2CPCy_3)Mn(CO)_3]$.[3] (b) The central carbon of the S_2CPCy_3 ligand prefers to bind the metal in the higher formal oxidation state, in contrast with all our previous findings.[3,4] No product with the central S_2CPCy_3 carbon bonded to Re is observed, in contrast with the related MnMo chemistry.

All this indicates the preference of the central carbon of the S_2CPCy_3 ligand to bind Mo rather than Re and the fact that this preference overcomes the tendency of that carbon to bind the metal in the lower formal oxidation state and the destabilizing effect of having two

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(5) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988; p 1030

(6) See description of the structure of $[(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5]$, the first complex with an unbridged dative bond between two different metals: Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *Organometallics* **1985**, *4*, 250.

(7) Fehlhammer, W. P.; Stolzenberg, H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol 4, pp 548−555.

Table 1. Crystal Data and Refinement Details for $[(CO)_3Re(\mu\text{-}S_2CPCy_3)Mo(SnPh_3)(CO)_3]\cdot H_2O$ (2) and $[(CO)_3(Ph_3Sn)Re(\mu\text{-}S_2CPCy_3)Mo(CO)_3]$ (3)

	2	**3**
formula	$C_{43}H_{50}MoO_7PReS_2Sn$	$C_{43}H_{48}MoO_6PReS_2Sn$
fw	1174.79	1156.8
cryst syst, space group	triclinic, $P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	10.844(5)	21.149(5)
b, Å	14.511(9)	11.425(2)
c, Å	16.192(9)	39.260(9)
α, deg	79.91(6)	90
β, deg	70.32(4)	97.75(3)
γ, deg	74.72(5)	90
V, Å^3	2304(44)	9400(7)
Z	2	8
T, K	293	293
ρ_{calc}, g cm^{-3}	1.69	1.63
$F(000)$	1144	4128
λ (Mo Kα), Å	0.710 69	0.710 69
cryst size, mm; color	0.6 × 0.5 × 0.3, orange	0.70 × 0.30 × 0.15, red
μ, cm^{-1}	36.23	35.48
method of collection	$\omega/2\theta$ scan	$\omega/2\theta$ scan
scan range, deg	$1 \leq \theta \leq 25$	$1 \leq \theta \leq 25$
no. of reflns measd	8401	14 052
no. of reflns obsd, $I \geq 3\sigma(I)$	3457	4987
function minimized	$\sum w(F_o - \lvert F_c\rvert)^2$	$\sum w(F_o - \lvert F_c\rvert)^2$
weighting scheme	Chebyshev polynomial[a]	units
no. of params	503	632
residuals R, R_w[b]	0.058, 0.067	0.063, 0.071

[a] $w = w'[1 - ((|F_o - |F_c||)/6\sigma(F_o))^2]^2$; $w' = 1/\sum_{r=1}A_rT_r(X)$, $X = F_o/F_o(\max)$, with three coefficients, 5.87, −3.23, and 4.05, for the Chebyshev series. [b] $R = \sum(|\Delta F|)/\sum|F_o|$, $R_w = [\sum w(|\Delta F)^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) in $[(CO)_3Re(\mu\text{-}S_2CPCy_3)Mo(SnPh_3)(CO)_3]$ (2)

Re(1)−Mo(1)	3.071(2)	Re(1)−S(1)	2.417(4)
Re(1)−S(2)	2.404(4)	Re(1)−C(1)	1.84(2)
Re(1)−C(2)	1.94(2)	Re(1)−C(3)	1.90(2)
Mo(1)−Sn(1)	2.866(2)	Mo(1)−S(1)	2.535(4)
Mo(1)−S(2)	2.525(4)	Mo(1)−C(4)	1.97(2)
Mo(1)−C(5)	1.95(2)	Mo(1)−C(6)	1.96(2)
Mo(1)−C(7)	2.18(1)	S(1)−C(7)	1.78(2)
S(2)−C(7)	1.75(1)	P(1)−C(7)	1.82(1)

Mo(1)−Re(1)−S(1)	53.4(1)	Mo(1)−Re(1)−S(2)	53.3(1)
S(1)−Re(1)−S(2)	71.9(1)	Mo(1)−Re(1)−C(1)	152.6(6)
S(1)−Re(1)−C(1)	108.6(6)	S(2)−Re(1)−C(1)	104.0(6)
Mo(1)−Re(1)−C(2)	111.0(6)	S(1)−Re(1)−C(2)	164.3(6)
Mo(1)−Re(1)−C(3)	108.3(5)	S(2)−Re(1)−C(3)	161.4(5)
Re(1)−Mo(1)−Sn(1)	87.89(5)	Re(1)−Mo(1)−S(1)	50.0(1)
S(1)−Mo(1)−S(2)	68.0(1)	Re(1)−Mo(1)−C(4)	141.5(5)
S(1)−Mo(1)−C(4)	146.2(5)	Re(1)−Mo(1)−C(5)	139.4(5)
Sn(1)−Mo(1)−C(5)	121.0(5)	S(2)−Mo(1)−C(5)	144.1(5)
S(1)−Mo(1)−C(6)	99.1(5)	S(2)−Mo(1)−C(6)	134.2(6)
C(4)−Mo(1)−C(6)	111.6(7)	Sn(1)−Mo(1)−C(7)	132.3(4)
C(4)−Mo(1)−C(7)	104.9(6)	C(5)−Mo(1)−C(7)	102.8(6)
C(6)−Mo(1)−C(7)	142.7(7)	Mo(1)−C(7)−S(1)	78.8(5)
Mo(1)−C(7)−S(2)	79.1(5)	S(1)−C(7)−S(2)	106.2(8)
Mo(1)−C(7)−P(1)	140.1(8)	S(1)−C(7)−P(1)	120.2(8)
S(2)−C(7)−P(1)	121.5(8)		

bulky groups close on the coordination sphere of the same metal. It must be noted that the fact that the central carbon is bonded to Mo in **1**, **2**, and **3** cannot be attributed to a high kinetic barrier for Mo−C cleavage, since that cleavage does occur in the sequence mentioned above to afford the Mn−C bonded complex $[(CO)_3(Ph_3Sn)Mo(\mu\text{-}S_2CPCy_3)Mn(CO)_3]$.[3]

According to IR monitoring at low temperature, the reaction of the anion with Ph_3SnCl affords **2**, with a Mo−Sn bond, which then slowly and partially rearranges to **3**. This suggests that the nucleophilic character of the anion is concentrated on Mo. If a similar pathway operates for the MoMn system, formation of the Mo−Mn and Mo−Sn bond would take place in a first step to give a MoMn complex isostructural with **2**. This undetected species would rapidly rearrange to the observed $[(CO)_3(Ph_3Sn)Mo(\mu\text{-}S_2CPCy_3)Mn(CO)_3]$ (**D**).[3]

Although there is some precedent of migration of stannyl groups from a metal to a cyclopentadienyl group,[8] this is the first example, as far as we know, of a reversible migration of a stannyl group between two metals. There are two previous reports describing the migration of silyl groups from Fe to Pt (irreversible), in $[FePt(\mu\text{-}PPh_2)(CO)_4(PPh_3)(SiR_3)]$,[9] and between two Ru atoms (reversible), in $[Ru_2(\mu\text{-}CH_2)Cp_2(CO)_2(H)(SiR_3)]$.[10]

Experimental Section

General conditions and methods were given elsewhere.[1f]

$[(CO)_3Re(\mu\text{-}S_2CPCy_3)Mo(SnPh_3)(CO)_3]$ (2) and $[(CO)_3(Ph_3Sn)Re(\mu\text{-}S_2CPCy_3)Mo(CO)_3]$ (3). A solution of $[(CO)_3Mo(\mu\text{-}Br)(\mu\text{-}S_2CPCy_3)Re(CO)_3]$ (**1**)[1f] (0.177 g, 0.20 mol) in THF (20 mL) was stirred with 5% sodium amalgam (excess). In about 30 min, the IR spectrum showed the disappearance of the bands of **1** and the presence of bands at lower frequency, corresponding to the species $Na[Mo(CO)_3(\mu\text{-}S_2CPCy_3)Re(CO)_3]$ (νCO (THF): 1989s, 1895vs, 1885s, 1867m, 1805m, 1761m, cm^{-1}). Then, the solution was filtered to another flask through a cannula with filter paper at one end using positive nitrogen pressure. A solution of Ph_3SnCl (0.077 g, 0.20 mmol) in THF (5 mL) was cooled to −80 °C and added via cannula to the cooled (−80 °C) solution of the anionic complex. The reaction mixture was stirred at −80 °C for 30 min. An IR taken at this point showed only the bands of **2**. The solvent was removed in vacuo, the solid residue was extracted with CH_2Cl_2 (10 mL) at −80 °C, and the solution was filtered with cannula/paper as before to another flask, layered with hexanes, and kept at −30 °C several days. Yellow crystals of **2** were obtained and were used to obtain spectroscopic data and for X-ray studies. When this procedure was repeated without cooling, the crystallization yielded a mixture of yellow crystals of **2** and dark red crystals of **3**. Crystals of **3** were hand-picked and used to obtain spectra and for X-ray studies.

Spectroscopic data for **2**: IR ν(CO) (THF) 2018m, 1981vs, 1933s, 1921m, 1900s, cm^{-1}; ^1H NMR (CH_2Cl_2) δ 7.63 and 7.30 [m, 15H, C_6H_5], 2.54 [m, 3H, CH of Cy], 2.15 to 1.30 [m, 30 H, CH_2 of Cy]; ^{31}P NMR (CH_2Cl_2) δ 42.81. Spectroscopic data for **3**: IR ν(CO) (THF) 2016s, 1983s, 1943s, 1866m (broad), cm^{-1}; ^1H NMR (CH_2Cl_2) 7.74 and 7.31 [m, 15H, C_6H_5], 2.31 [m, 3H, CH of Cy], 2.15 to 1.30 [m, 30 H, CH_2 of Cy]; ^{31}P NMR (CH_2Cl_2) δ 42.95.

A solid consisting of a mixture of composition **3**/**2** = 4/5 could be obtained in good yield (0.195 g, from 0.177 g of **1**, 85%) working at room temperature with the following modification of the previous procedure: after the reaction with Ph_3SnCl is complete (as judged by IR), the resulting solution is filtered with cannula and paper, the THF was removed in vacuo, the residue was extracted in CH_2Cl_2 (20 mL), this solution was filtered through a short column of alumina (activation grade IV), and the solution was concentrated in vacuo to a volume of 5 mL. Hexanes (20 mL) was added with stirring to cause precipitation of an orange solid. The liquid was discarded, and

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(8) See Cervantes, J.; Vincenti, S. P.; Kapoor, R. N.; Pannell, K. H. *Organometallics* **1989**, *8*, 744, and references therein.

(9) Braunstein, P.; Knorr, M.; Hirle, B.; Reinhardt, G.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1583.

(10) Akita, M.; Hua, R.; Oku, T.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1996**, *15*, 4162.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) in [(CO)$_3$(Ph$_3$Sn)Re(μ-S$_2$CPCy$_3$)-Mo(CO)$_3$] (3)

molecule 1		molecule 2	
Re(1)−Mo(1)	2.914(3)	Re(101)−Mo(101)	2.925(3)
Re(1)−Sn(1)	2.761(2)	Re(101)−Sn(101)	2.763(2)
Re(1)−S(1)	2.432(7)	Re(101)−S(101)	2.468(7)
Re(1)−S(2)	2.468(8)	Re(101)−S(102)	2.467(8)
Re(1)−C(1)	2.00(4)	Re(101)−C(101)	1.89(3)
Re(1)−C(2)	1.86(4)	Re(101)−C(102)	1.81(4)
Re(1)−C(3)	1.85(5)	Re(101)−C(103)	1.77(6)
Mo(1)−S(1)	2.500(8)	Mo(101)−S(101)	2.506(8)
Mo(1)−S(2)	2.507(9)	Mo(101)−S(102)	2.508(8)
Mo(1)−C(1)	2.60(3)	Mo(101)−C(101)	2.51(3)
Mo(1)−C(4)	1.97(3)	Mo(101)−C(104)	1.87(3)
Mo(1)−C(5)	1.97(3)	Mo(101)−C(105)	1.97(4)
Mo(1)−C(6)	2.00(4)	Mo(101)−C(106)	2.06(3)
Mo(1)−C(7)	2.18(3)	Mo(101)−C(107)	2.15(3)
S(1)−C(7)	1.80(3)	S(101)−C(107)	1.77(3)
S(2)−C(7)	1.70(3)	S(102)−C(107)	1.79(3)
P(1)−C(7)	1.83(3)	P(101)−C(107)	1.80(3)
Mo(1)−Re(1)−Sn(1)	144.61(9)	Mo(101)−Re(101)−Sn(101)	145.26(9)
Mo(1)−Re(1)−S(1)	54.9(2)	Mo(101)−Re(101)−S(101)	54.6(2)
Mo(1)−Re(1)−S(2)	54.8(2)	Mo(101)−Re(101)−S(102)	54.6(2)
S(1)−Re(1)−S(2)	71.5(3)	S(101)−Re(101)−S(102)	71.1(2)
Sn(1)−Re(1)−C(1)	154.8(10)	Sn(101)−Re(101)−C(101)	156.6(10)
Mo(1)−Re(1)−C(2)	121.2(11)	Mo(101)−Re(101)−C(102)	123.6(11)
S(1)−Re(1)−C(2)	166.6(9)	S(101)−Re(101)−C(102)	171.7(12)
Mo(1)−Re(1)−C(3)	119.7(10)	Mo(101)−Re(101)−C(103)	121.3(13)
S(2)−Re(1)−C(3)	165.4(13)	S(102)−Re(101)−C(103)	164.2(13)
Re(1)−Mo(1)−C(4)	105.9(9)	Re(101)−Mo(101)−C(104)	110.6(14)
S(2)−Mo(1)−C(4)	158.3(9)	S(102)−Mo(101)−C(104)	162.8(14)
Re(1)−Mo(1)−C(5)	169.4(9)	Re(101)−Mo(101)−C(105)	164.0(10)
S(1)−Mo(1)−C(6)	155.7(10)	S(101)−Mo(101)−C(106)	158.6(8)
C(4)−Mo(1)−C(7)	130.6(12)	C(104)−Mo(101)−C(107)	130.1(14)
C(5)−Mo(1)−C(7)	99.1(12)	C(105)−Mo(101)−C(107)	92.3(11)
C(6)−Mo(1)−C(7)	128.4(12)	C(106)−Mo(101)−C(107)	133.3(11)
Re(1)−C(1)−O(1)	156.0(32)	Re(101)−C(101)−O(101)	157.4(30)
Mo(1)−C(1)−O(1)	125.7(28)	Mo(101)−C(101)−O(101)	120.4(25)
Mo(1)−C(7)−S(1)	77.3(10)	Mo(101)−C(107)−S(101)	78.7(10)
Mo(1)−C(7)−S(2)	79.4(10)	Mo(101)−C(107)−S(102)	78.4(10)
S(1)−C(7)−S(2)	109.7(15)	S(101)−C(107)−S(102)	107.4(14)
Mo(1)−C(7)−P(1)	132.8(15)	Mo(101)−C(107)−P(101)	136.6(14)
S(1)−C(7)−P(1)	119.1(15)	S(101)−C(107)−P(101)	119.7(15)
S(2)−C(7)−P(1)	125.2(16)	S(102)−C(107)−P(101)	123.9(15)

the solid was washed with hexanes (3 × 5 mL) and dried in vacuo. Anal. Calcd for $C_{43}H_{48}MoO_6PReS_2Sn$: C, 44.65; H, 4.18. Found: C, 44.72; H, 4.21.

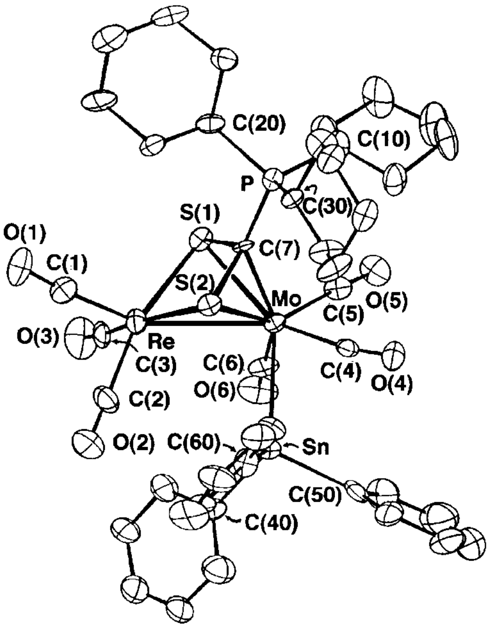

Figure 1. Perspective view (CAMERON)[15] of the structure of [(CO)$_3$Re(μ-S$_2$CPCy$_3$)Mo(SnPh$_3$)(CO)$_3$] (**2**), showing the atom numbering.

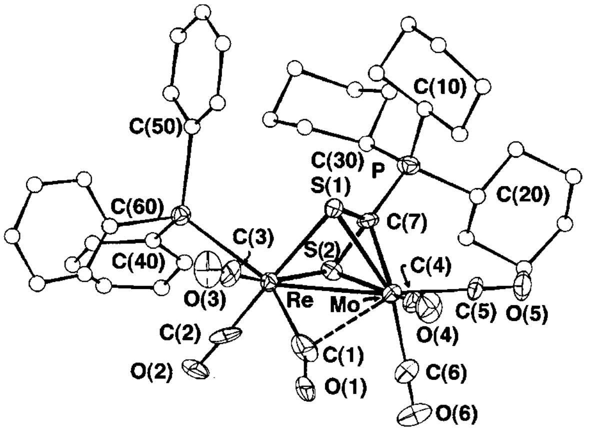

Figure 2. Perspective view (CAMERON)[15] of the structure of [(CO)$_3$(Ph$_3$Sn)Re(μ-S$_2$CPCy$_3$)Mo(CO)$_3$] (**3**), showing the atom numbering.

X-ray Difraction Study of [(CO)$_3$Re(μ-S$_2$CPCy$_3$)Mo(SnPh$_3$)(CO)$_3$] (2) and [(CO)$_3$(Ph$_3$Sn)Re(μ-S$_2$CPCy$_3$)Mo(CO)$_3$] (3). Relevant crystallographic details are given in Table 1. Unit cell parameters were determined from the least-squares refinement of a set of 25 centered reflections. Three reflections were measured every 2 h as orientation and intensity control. Significant decay was not observed for **2**, whereas a correction (30% decay) was necessary for **3**. Corrections were made for Lorentz and polarization effects. An empirical absorption correction was made with DIFABS.[11] An extinction correction was applied for **3**. Computations were performed with CRYSTALS.[12] The structures were solved by direct methods with SHELX86[13] and subsequent Fourier maps. For the structure of **2**, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically positioned, and they were given an overall isotropic thermal parameter. The unit cell was found to contain also two water molecules, related by the inversion center, and linked by hydrogen bonding [O(100)−O(100′) 2.84(7) Å].[14] For the structure of **3**, two independent molecules were found in the asymmetric unit. Due to the low number of observed reflections, and in order to keep aceptable data-to-parameter ratio, only the heavier atoms and C(1)−C(7) were refined anisotropically. The remaining non-hydrogen atoms were refined isotropically, and the hydrogens were not included in the refinement. Drawings in Figures 1 an 2 were made with CAMERON.[15]

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(11) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(12) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS, An Advanced Crystallographic Computer Program*; Chemical Crystallography Laboratory, Oxford University: Oxford, U.K., 1989.

(13) Sheldrick, G. M. *SHELX86, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, 1986.

(14) The presence of the water molecules may be due to condensation during the reaction and manipulation of THF solutions at low temperatures, or during the crystallisation period. A reviewer suggested that the possible presence of hydrogen bridges between the water molecules and **2** may have some effect on the crystallization or in the displacement of the equilibrium between **2** and **3**. Some calculations reveal that the nearest neighbor of the oxygen atom of the water molecule, O(100), is O(2) (from a CO group bonded to Re), the distance being 3.545 Å. This is quite long when compared with the distance of 2.84(7) Å between O(100) and O′(100), which are linked by hydrogen bonds. The hydrogen interactions between water and **2**, if present, should be very weak to have any significant influence in the crystallization. On the other hand, we have checked that the addition of water to the **2**+**3** isomer mixture does not modify the isomer ratio, as judged by the ^{31}P NMR spectra, and produces no better crystallization of isomer **2**.

(15) Pearce, L. J.; Watkin, D. J. *CAMERON*; Chemical Crystallography Laboratory, Oxford University: Oxford, U.K., 1992.

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Supporting Information Available: Complete tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, torsion angles, and least-squares planes for the structure of **2** and **3** (11 pages). Ordering information is given on any current masthead page.

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