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S_2CPR_3 Adducts as Binucleating Ligands. Novel Heterobimetallic Complexes with S_2CPR_3 Bridges of Eight and Six Electrons. X-ray Structure of [MnMo(CO)$_6$(μ-Br)(μ-$S_2CPPr^i_3$)] and [MnMo(CO)$_5$(μ-Br)(μ-S_2CPCy_3)(μ-tedip)]

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[Mn(CO)$_3$(S_2CPR_3)Br] complexes react with [Mo(CO)$_3$(NCMe)$_3$] in CH_2Cl_2 to afford a novel class of heterodinuclear complexes of the general formula [MnMo(CO)$_6$(μ-Br)(μ-S_2CPR_3)] [R = cyclohexyl (Cy), **2a**; or isopropyl (Pr^i), **2b**] containing one bromide bridge and one S_2CPR_3 bridging ligand which is coordinated as a η^2(S,S′) chelate to manganese and as a η^3(S,C,S′) pseudoallyl to molybdenum, as shown by an X-ray determination of the derivative with R = Pr^i (**2b**, monoclinic, space group $P2_1/c$, a = 9.065 (1) Å, b = 19.579 (5) Å, c = 13.398 (3) Å, β = 106.67 (2)°, Z = 4, R = 0.032, R_w = 0.033). Hexacarbonyls **2a,b** undergo substitution of one carbonyl group on the molybdenum atom, upon treatment with monodentate P-donor ligands in CH_2Cl_2 at room temperature, producing pentacarbonyls [MnMo(CO)$_5$(L)(μ-Br)(μ-S_2CPR_3)] (L = PEt_3, P(OMe)$_3$) which have been characterized by analytical and spectroscopic methods. Reaction of **2a,b** with bidentate ligands produces the substitution of one carbonyl group on the Mo atom and the displacement of one of the sulfur atoms bonded to the manganese, affording pentacarbonyls [MnMo(CO)$_5$(μ-P-P)(μ-Br)(μ-S_2CPR_3)] [P-P = tetraethylpyrophosphite (tedip), bis(dimethylphosphino)methane (dmpm), or bis(diphenylphosphino)methane (dppm)]. An X-ray determination of derivative **4a** (R = Cy, L-L = tedip; monoclinic, space group $P2_1/c$, a = 14.827 (9) Å, b = 15.097 (9) Å, c = 19.566 (10) Å, β = 103.19 (7)°, Z = 4, R = 0.060, R_w = 0.059) showed that the coordination mode of the S_2CPR_3 ligand changes from η^2(S,S′),η^3(S,C,S′) to η^1(S),η^3(S,C,S′). The analogy between this rearrangement and ring-opening processes of chelate S_2CPR_3 ligands in mononuclear complexes is examined.

Introduction

Several families of complexes containing S_2CPR_3 acting as bridges have been reported in the past 10 years.[1-9] However, the chemical behavior of the S_2CPR_3 adducts as bridging ligands remains essentially unexplored. As far as we know, most of the complexes prepared have not been further studied, probably due to the fragility of the bridges. Thus, compounds with S_2CPR_3 bridges of type η^1(S),η^1(S′) and η^1(S),η^2(C,S′) have been reported to be unstable in solution,[1] or to undergo splitting into two mononuclear complexes either by treatment with PR_3 ligands[5] or even upon attack by donor solvents such as acetone, nitromethane, or diethyl ether.[2] Additionally, in many cases the complexes are produced through spontaneous dimerization, thus leading to symmetrical homobinuclear species.[1,5]

In contrast, we have found that S_2CPR_3 ligands are able to form very stable η^2(S,S′),η^3(S,C,S′) bridges across a Mn–Mn[8] or a Re–Mn[9] bond and that their reactivity toward nucleophiles is qualitatively different from that previously known for the same ligands when acting as chelate in mononuclear complexes.[10] All these facts prompted us to design ways of rational synthesis of binuclear complexes with S_2CPR_3 bridges which, being stable enough to maintain the binuclear arrangement, could serve as substrates to explore the chemistry of coordinated S_2CPR_3 ligands.

Here we wish to report a facile, high-yield synthesis of a new class of heterodinuclear hexacarbonyl complexes containing one bridging bromide and one η^2(S,S′),η^3(S,C,S′) S_2CPR_3 bridge between Mn^I and Mo^0 not directly bonded, by using the (S,C,S′,Br) donor set of [Mn(CO)$_3$(S_2CPR_3)(Br)][11] as a sort of polydentate ligand donating six electrons to a Mo^0L_3 fragment. Several reactions of carbonyl

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substitution by P-donor ligands show the stability of the binuclear unit. A preliminary account of part of this work has been published.[12]

Experimental Section

All reactions were carried out in dry solvents under a nitrogen atmosphere. Literature procedures for the preparation of starting materials are quoted in each case. Ligands and other reagents were purchased and used without purification unless otherwise stated. Infrared spectra (in CH_2Cl_2 solutions) were recorded on a Perkin-Elmer FT1720-X instrument. ^1H NMR (300.1 MHz, δ, ppm from internal TMS), $^{31}P\{^1H\}$ NMR (125.5 MHz, δ, ppm to higher frequencies from external 85% H_3PO_4), and $^{13}C\{^1H\}$ NMR (75.5 MHz, δ, ppm from internal TMS) spectra (from CD_2Cl_2 solutions) were recorded on a Bruker AC300 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 240B analyzer. The complexes *fac*-$[Mn(CO)_3(S_2CPR_3)Br]$ were prepared as previously described.[11]

$[MnMo(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPCy_3)]$ (2a). A solution of $[Mo(CO)_3(NCMe)_3]$ was prepared by heating $[Mo(CO)_6]$ (0.200 g, 0.758 mmol) in acetonitrile (15 mL) for 3 h at reflux temperature. The solvent was evaporated in vacuo and $[Mn(CO)_3(S_2CPCy_3)Br]$[11] (0.345 g, 0.758 mmol) was added to the dry residue. The mixture of solids was dissolved in CH_2Cl_2 (15 mL), and the resulting solution was stirred for 15 min and then filtered. The filtrate was concentrated in vacuo to ca. 5 mL. Addition of hexane (10 mL) and slow concentration gave **2a** as a red microcrystalline solid. Yield 0.409 g, 85%. Anal. Calcd for $C_{25}H_{33}BrMnMoO_6PS_2$: C, 39.75; H, 4.40. Found: C, 39.12; H, 4.37.

$[MnMo(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPPr^i_3)]$ (2b). Compound **2b** was prepared by the same method as described above by using $[Mo(CO)_6]$ (0.200 g, 0.785 mmol), and $[Mn(CO)_3(S_2CPPr^i_3)Br]$ (0.436 g, 0.758 mmol). The product **2b** was obtained as red microcrystals. Yield: 0.526 g, 92%. Anal. Calcd for $C_{16}H_{21}BrMnMoO_6PS_2$: C, 30.25; H, 3.33. Found: C, 30.20; H, 3.32. Crystals suitable for an X-ray determination were grown by slow diffusion of hexane into a concentrated solution of **2b** in CH_2Cl_2.

$[MnMo(CO)_5(\mu\text{-}Br)(\mu\text{-}S_2CPCy_3)\{P(OMe)_3\}]$ (3a). To a solution of **2a** (0.200 g, 0.265 mmol) in CH_2Cl_2 (15 mL) was added $P(OMe)_3$ (31 μL, 0.265 mmol). The mixture was stirred for 15 min and then hexane (10 mL) was added. Slow evaporation in vacuo gave **3a** as deep-red microcrystals. Yield: 0.178 g, 79%. Anal. Calcd for $C_{27}H_{42}BrMnMoO_8P_2S_2$: C, 38.09; H, 4.97. Found: C, 37.93; H, 4.90.

$[MnMo(CO)_5(\mu\text{-}Br)(\mu\text{-}S_2CPPr^i_3)\{P(OMe)_3\}]$ (3b). Compound **3b** was prepared by the same method as described for **3a** by using **2b** (0.200 g, 0.315 mmol) and $P(OMe)_3$ (37 μL, 0.315 mmol). Yield: 0.157 g, 68%. Anal. Calcd for $C_{18}H_{30}BrMnMoO_8P_2S_2$: C, 29.56; H, 4.13. Found: C, 29.46; H, 4.08.

$[MnMo(CO)_5(\mu\text{-}Br)(\mu\text{-}S_2CPCy_3)(PEt_3)]$ (3c). Compound **3c** was prepared by the same method as described for **3a** by using **2a** (0.200 g, 0.265 mmol) and PEt_3 (40 μL, 0.265 mmol). Yield: 0.179 g, 80%. Anal. Calcd for $C_{30}H_{48}BrMnMoO_5P_2S_2$: C, 42.61; H, 5.72. Found: C, 42.73; H, 5.70.

$[MnMo(CO)_5(\mu\text{-}Br)(\mu\text{-}S_2CPPr^i_3)(PEt_3)]$ (3d). Compound **3d** was prepared by the same method as described for **3a** by using **2b** (0.200 g, 0.315 mmol) and PEt_3 (46 μL, 0.315 mmol). Yield: 0.174 g, 76%. Anal. Calcd for $C_{21}H_{36}BrMnMoO_5P_2S_2$: C, 34.77; H, 5.00. Found: C, 34.51; H, 4.92.

$[MnMo(CO)_5(\mu\text{-}Br)(\mu\text{-}S_2CPCy_3)(\mu\text{-tedip})]$ (4a). A mixture of **2a** (0.200 g, 0.265 mmol) and tetraethylpyrophosphite (tedip; 65 μL, 0.265 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 20 min. The solvent was evaported under reduced pressure to ca. 5 mL. Addition of hexane (10 mL) gave **4a** as a red solid which was recrystallized from CH_2Cl_2/hexane. Yield: 0.198 g, 76%. Anal. Calcd for $C_{32}H_{53}BrMnMoO_{10}P_3S_2$: C, 39.00; H, 5.42. Found: C, 39.52; H, 5.44. Crystals suitable for an X-ray determination were grown by slow diffusion of hexane into a concentrated solution of **4a** in CH_2Cl_2.

$[MnMo(CO)_5(\mu\text{-}Br)(\mu\text{-}S_2CPPr^i_3)(\mu\text{-tedip})]$ (4b). Compound **4b** was prepared as described above for **4a** by using **2b** (0.200 g, 0.315 mmol) and tedip (77 μL, 0.315 mmol). Yield: 0.191 g, 70%. Anal. Calcd for $C_{23}H_{41}BrMnMoO_{10}P_3S_2$: C, 31.92; H, 4.77. Found: C, 32.05; H, 4.80.

$[MnMo(CO)_5(\mu\text{-}Br)(\mu\text{-}S_2CPCy_3)(\mu\text{-dmpm})]$ (4c). To a cooled (−78 °C) solution of **2a** (0.200 g, 0.265 mmol) in THF (20 mL) was added dmpm (40 μL, 0.256 mmol). After stirring at −78 °C for 5 min, the mixture allowed to warm up slowly to room temperature (ca. 20 min). The solvent was evaporated in vacuo, and the residue was taken up in CH_2Cl_2 (5 mL) and filtered. Addition of hexane (15 mL) to the filtrate produced **4c** as a red solid. Yield: 0.167 g, 73%. Anal. Calcd for $C_{29}H_{47}BrMnMoO_5P_3S_2$: C, 40.34; H, 5.49. Found: C, 40.76; H, 5.53.

$[MnMo(CO)_5(\mu\text{-}Br)(\mu\text{-}S_2CPPr^i_3)(\mu\text{-dmpm})]$ (4d). Compound **4d** was prepared as described for **4c** by using **2b** (0.200 g, 0.315 mmol) and dmpm (47 μL, 0.300 mmol). Yield: 159 mg, 68%. Anal. Calcd for $C_{20}H_{35}BrMnMoO_5P_3S_2$: C, 32.32; H, 4.75. Found: C, 31.98; H, 4.83.

$[MnMo(CO)_5(\mu\text{-}Br)(\mu\text{-}S_2CPCy_3)(\mu\text{-dppm})]$ (4e). A mixture of **2a** (0.200 g, 0.265 mmol) and dppm (0.102 g, 0.265 mmol) in THF (20 mL) was refluxed for 5 h and then filtered. Addition of hexane (15 mL) to the filtrate produced **4c** as a greenish solid. (Crude yield: 0.241 g, 82%). Analytically pure samples of the compound could be obtained only after repeated crystallization from CH_2Cl_2/hexane mixtures, thus resulting in a low yield of the product (8–15%). Anal. Calcd for $C_{49}H_{55}BrMnMoO_5P_3S_2$: C, 52.93; H, 4.99. Found: C, 53.04; H, 4.86. ^1H NMR (CD_2Cl_2): δ 7.84–6.86 (m, 20 H, C_6H_5 of dppm), 4.94 (m, 1 H, PCH_2P of dppm)], 3.81 (m, 1 H, PCH_2P of dppm), 2.58 (m, 3 H, CH of Cy), 2.07–1.24 (m, 30 H, CH_2 of Cy).

$[MnMo(CO)_5(\mu\text{-}Br)(\mu\text{-}S_2CPPr^i_3)(\mu\text{-dppm})]$ (4f). Compound **4f** was prepared as described above for **4e**, by using **2b** (0.200 g, 0.315 mmol) and dppm (0.121 g, 0.315 mmol) in THF (20 mL). Crude yield: 0.231 g, 74%. As for **4c**, successive crystallizations from CH_2Cl_2/hexane were needed to obtain pure samples of the compound, resulting in low yield of the product (10–15%). Anal. Calcd for $C_{40}H_{43}BrMnMoO_5P_3S_2$: C, 48.45; H, 4.37. Found: C, 48.44; H, 4.35. ^1H NMR (CD_2Cl_2): δ 7.99–6.88 (m, 20 H, C_6H_5 of dppm), 5.05 (m, 1 H, PCH_2P of dppm), 3.87 (m, 1 H, PCH_2P of dppm), 2.97 (m, 3 H, CH of Pr^i), 1.76–1.44 (m, 18 H, CH_3 of Pr^i).

X-ray Diffraction Studies of 2b and 4a. Crystals suitable for an X-ray determination were grown by slow diffusion of hexane into concentrated solutions of the compounds in CH_2Cl_2. Relevant crystallographic details are given in Table II. 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 controls. Significant decay was not observed. Heavy atoms were located from a Patterson synthesis and the remaining non-hydrogen atoms by DIRDIF.[13] Full-matrix least-squares refinements for both structures were made with SHELX.[14] After isotropic refinement, an additional absorption correction was applied with DIFABS.[15] In the structure of **2b**, all non-hydrogen atoms were refined anisotropically. In the structure of **4a**, it was found that the carbon atoms of the ethoxy groups attached to P(2) on the tedip ligand were affected by some degree of conformational disorder which could not be modeled satisfactorily. Therefore, they were refined as rigid groups with fixed distances (C–O, 1.40 Å; C–C, 1.42 Å). Due to the poor quality of the crystal, and in order to keep an acceptable data-to-parameter ratio, the carbon

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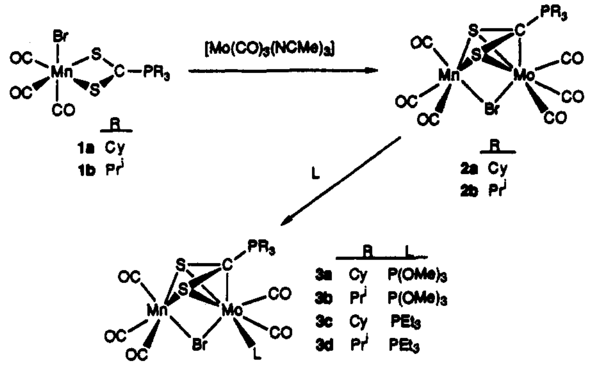
Scheme I



atoms of the cyclohexyl rings of PCy_3 and those of the ethyl groups of tedip were refined isotropically. The remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms in both structures were geometrically positioned and were given a common isotropic temperature factor, which was refined. The carbon and hydrogen atoms on the ethyl groups, refined as rigid groups in **4a**, were given fixed isotropic temperature factors of 0.12 Å^2. Torsion angles, least-squares planes, and other calculations were determined with PARST.[16] Crystallographic drawings were made with PLUTO.[17]

Results and Discussion

The complexes *fac*-$[Mn(CO)_3(S_2CPR_3)Br]$[11] (R = cyclohexyl, Cy, **1a**; isopropyl, Pr^i, **1b**) quickly react with $[Mo(CO)_3(NCMe)_3]$ in CH_2Cl_2 or THF to give purple-red solutions from which air-stable, deep-red crystalline solids of the general formula $[MnMo(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)]$ (**2a,b**, see Scheme I) can be isolated in high yields (85–95%). Spectroscopic data are collected in Tables I and II. The IR spectra of complexes **2a,b** show five bands in the ν(CO) region, with a pattern consistent with a $M_2(CO)_6$ unit, and the $^{31}P\{^1H\}$ NMR spectra show one sharp singlet for the phosphorus of the S_2CPR_3 ligand. The $^{13}C\{^1H\}$ NMR spectra show the signal of the central carbon of the S_2CPR_3 ligand as a doublet at 96.2 ppm for **2a**, and at 95.9 ppm for **2b**, suggesting that the carbon is directly bonded to one metal atom. These data suggested that the S_2CPR_3 ligand was coordinated as η^3(S,C,S′). However, from analytical and spectroscopic data alone it was not possible to fully establish the structure of these complexes. An X-ray determination was carried out on a crystal of derivative **2b**. Crystal and refinement data are given in Table III, atomic coordinates in Table IV, and selected bond lengths and angles in Table V. A perspective view can be seen in Figure 1. The molecule can be described as consisting of two $M(CO)_3$ units held together by a bridging bromide and by a $S_2CPPr^i_3$ ligand which is bonded as a η^2(S,S′) chelate to Mn and as a η^3(S,C,S′) pseudoallyl to Mo. The spectroscopic data obtained from solutions of **2a** and **2b** are in agreement with the solid-state structure. Although we had already found such type of $\eta^2\eta^3$ coordination in the Mn–Mn and the Mn–Re complexes mentioned above, **2a,b** are among the first examples[18] containing this type of bridging mode in molecules without a direct metal-to-metal bond. Assuming that S_2CPR_3 donates four electrons to each metal atom, as it does in $[Mn_2(CO)_6(\mu\text{-}S_2CPR_3)]$ and its derivatives, the electron count in **2b** does not require the existence of a Mn–Mo direct bond. Consistent with this, the Mn–Mo distance of 3.235 (1) Å is somewhat longer than that expected for a normal bonding interaction between the two metals. However, it is not very different from the values found in complexes with Mn–Mo bonds such as $[Cp(CO)_2Mo(\mu\text{-}AgPPh_3)(\mu\text{-}PPh_2)Mn(CO)_4]$ [3.190 (2) Å].[19] The distances Mn–Br [2.657 (1) Å] and Mo–Br [2.669 (1) Å] are close to the mean values found in Mn and Mo complexes containing bromide bridges,[20] the slight asymmetry of the M–Br distances in **2b** reflecting the different covalent radii of the metals. The manganese atom lies in an octahedral environment, slightly distorted due to the small bite angle formed by the two sulfur atoms [S(1)–Mn–S(2) 73.4 (1)°]. The sulfur atoms, two carbonyl carbons [C(6) and C(7)], and Mn display a fairly planar arrangement, the maximum deviation corresponding to C(6), at 0.124 (6) Å from the best plane. The ring Mn–S(1)–C(1)–S(2) is close to planarity, being only slightly folded [8.0 (2)°] over the line joining S(1) and S(2). The Mn–S and S–C distances and the S–C–S angle in **2b** are close to the values found in mononuclear complexes of Mn(I) containing S_2CPR_3 as η^2(S,S′) chelate.[11,22]

The η^3(S,C,S′) pseudoallyl coordination of the S_2CPR_3 ligands had only been found to date in complexes of molybdenum or manganese. Therefore, the S_2CPR_3 ligand might have been expected to be coordinated in this fashion to either Mn or Mo in **2a,b**. It is remarkable that, in the reaction between $[Mo(CO)_3(NCMe)_3]$ and **1a** (or **1b**), the binuclear complex **2a** (or **2b**) is formed as the only product, as shown by the $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixtures. Interestingly, the selective formation of the product with a Mo–C bond suggests a stronger preference for molybdenum attachment to the central carbon of the S_2CPR_3 ligand than for manganese attachment.[23] We have recently found a similar selectivity in the formation of a Mn–C (but not a Re–C) bond in the complex $[MnRe(CO)_6(\mu\text{-}S_2CPCy_3)]$,[7] the reasons for such discrimination remaining, so far, unclear. In the case of **2a,b** the behavior seems to be somewhat easier to rationalize assuming the formal oxidation states Mn^I and Mo^0 in the complexes. The S_2CPR_3 ligand would prefer to coordinate the electron richer metal fragment in the pseudoallyl fashion. In fact, in all the known complexes in which the S_2CPR_3 ligand is bonded either as η^3(S,C,S′)[2,6,7,21] or as η^2(S,C),[1] the metal atom is in the formal oxidation state zero.

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(18) As a matter of fact, in a parallel work we have prepared, by different synthetic procedures, a family of complexes of the general formula $[Mo(CO)_2(PR_3)(\mu\text{-}Cl)(\mu\text{-}S_2CPR_3)SnCl_2Bu]$ which contains an unsymmetrically placed Cl bridge and a S_2CPR_3 ligand bonded as η^2(S,S′) to Sn and as a η^3(S,C,S′) pseudoallyl to Mo. Due to the special character of the structure of these complexes, they have been published (see ref 9) separately after the preliminary report of this work, and they will not be discussed further here.

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(23) One reviewer pointed out, quite rightly, that this statement would be true only if the formation of **2b** is thermodynamically controlled. Although we have no conclusive evidence about such a point, we think that this is the case, since complexes **2** can be heated in refluxing THF for several hours without change (IR monitoring). When heated in refluxing toluene, IR monitoring shows the dissapaerance of the bands of **2** without any indication of the formation of other, thermodynamically favored product. The decomposition is almost complete in ca. 2 h.

Table I. IR and $^{31}P\{^1H\}$ NMR Data for the New Complexes

compound	IR (CH_2Cl_2), ν(CO), cm^{-1}	$^{31}P\{^1H\}$, CD_2Cl_2, δ, ppm (S_2CP)	Mo–P	Mn–P
2a $[MnMo(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPCy_3)]$	2036 (m), 2016 (vs), 1950 (s), 1912 (m), 1864 (m)	34.85		
2b $[MnMo(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPPr^i_3)]$	2037 (m), 2017 (vs), 1951 (s), 1914 (m), 1867 (m)	46.82		
3a $[MnMo(CO)_5\{P(OMe)_3\}(\mu\text{-}Br)(\mu\text{-}S_2CPCy_3)]$	2022 (s), 1936 (s), 1907 (m), 1827 (m)	34.29	158.63	
3b $[MnMo(CO)_5\{P(OMe)_3\}(\mu\text{-}Br)(\mu\text{-}S_2CPPr^i_3)]$	2023 (s), 1937 (vs), 1909 (m), 1828 (m)	45.45	158.14	
3c $[MnMo(CO)_5(PEt_3)(\mu\text{-}Br)(\mu\text{-}S_2CPCy_3)]$	2020 (s), 1932 (vs), 1909 (m), 1801 (m)	34.24	25.19	
3d $[MnMo(CO)_5(PEt_3)(\mu\text{-}Br)(\mu\text{-}S_2CPPr^i_3)]$	2021 (s), 1933 (vs), 1910 (m), 1803 (m)	45.22	25.61	
4a $[MnMo(CO)_5(\mu\text{-}Br)(\mu\text{-}S_2CPCy_3)(\mu\text{-}tedip)]$	2034 (m), 1963 (m), 1823 (s), 1795 (m)	39.87	165.36[a]	148.98[a]
4b $[MnMo(CO)_5(\mu\text{-}Br)(\mu\text{-}S_2CPPr^i_3)(\mu\text{-}tedip)]$	2035 (m), 1964 (m), 1824 (s), 1795 (m)	50.07	163.99[b]	148.44[b]
4c $[MnMo(CO)_5(\mu\text{-}Br)(\mu\text{-}S_2CPCy_3)(\mu\text{-}dmpm)]$	2020 (s), 1945 (s), 1905 (s), 1775 (m)	39.27	12.64[c]	15.88 (br)
4d $[MnMo(CO)_5(\mu\text{-}Br)(\mu\text{-}S_2CPPr^i_3)(\mu\text{-}dmpm)]$	2020 (s), 1944 (s), 1906 (s), 1776 (m)	49.02	12.19[d]	15.72 (br)
4e $[MnMo(CO)_5(\mu\text{-}Br)(\mu\text{-}S_2CPCy_3)(\mu\text{-}dppm)]$	2024 (s), 1951 (s), 1907 (s), 1772 (m)	38.74	37.14[e]	35.74 (br)
4f $[MnMo(CO)_5(\mu\text{-}Br)(\mu\text{-}S_2CPPr^i_3)(\mu\text{-}dppm)]$	2026 (s), 1954 (s), 1909 (s), 1771 (m)	48.93	36.86[f]	35.71 (br)

[a] d, J(P–P) = 36 Hz. [b] d, J(P–P) = 33 Hz. [c] d, J(P–P) = 14 Hz. [d] d, J(P–P) = 15 Hz. [e] d, J(P–P) = 22 Hz. [f] d, J(P–P) = 25 Hz.

Table II. ^1H and $^{13}C\{^1H\}$ NMR Data for the New Complexes[a]

compd	δ, ppm[b] ^1H NMR	$^{13}C\{^1H\}$ NMR
2a	2.52 (m, 3 H, CH of Cy), 1.93–1.33 (m, br, 30 H, CH_2 of Cy)	242.0 [d (5), 2MoCO], 223.7 (s, br, MnCO), 217.1 (s, br, 2MnCO), 216.6 (s, MoCO), 96.2 [d (39), S_2CP], 33.9 [d, (38), C^1 or Cy], 27.8 (s, C^3 and C^5 of Cy), 27.1 [d (12), C^2 and C^6 of Cy], 25.6 (s, C^4 of Cy)
2b	2.82 (m, 3 H, CH of Pr^i), 1.47 (m, 18 H, CH_3 of Pr^i)	242.2 [d (6), 2MoCO], 223.3 (s, br, MnCO), 216.8 (s, br, 2MnCO), 216.3 (s, MoCO), 95.9 [d (39), S_2CP], 24.0 [d (41), CH of Pr^i], 18.2 [d (3), CH_3 or Pr^i]
3a	3.78 [d (5), 9 H, POCH_3], 2.53 (m, 3 H, CH of Cy), 1.93–1.33 (m, br, 30 H, CH_2 of Cy)	249.4 [d (27), MoCO], 228.3 [d (5), MoCO], 224.5 (s, br, MnCO), 217.1 (s, br, MnCO), 216.3 (s, br, MnCO), 91.1 [d (46), S_2CP], 52.4 [d (3), POCH_3], 33.5 [d (42), C^1 of Cy], 27.5 (s, C^3 and C^5 of Cy), 26.9 [d (10), C^2 and C^6 of Cy], 25.5 (s, C^4 of Cy)
3b	3.79 [d (10), 3 H, POCH_3], 2.83 (m, 3 H, CH or Pr^i), 1.51 (m, 18 H, CH_3 of Pr^i)	251.3 (s, br, MoCO), 228.4 (s, MoCO), 227.9 (s, br, MnCO), 218.6 (s, br, MnCO), 216.4 (s, MnCO), 90.3 [dd (42 and 5), S_2CP], 52.6 [d (3), POCH_3], 23.8 [d (42), CH or Pr^i], 18.1 [d (3), CH_3 of Pr^i]
3c	2.51–1.18 (m, br, Et and Cy)	254.4 [dd (22 and 7), MoCO], 231.0 [d (6), MoCO], 224.1 (s, br, MnCO), 217.5 (s, br, MnCO), 216.7 (s, br, MnCO), 89.6 [d (42), S_2CP], 33.9 [d (40), C^1 of Cy], 27.6 (s, C^3 and C^5 of Cy), 26.9 [d (12), C^2 and C^6 of Cy], 25.5 (s, C^4 of Cy), 17.9 [d (23), CH_2 of PEt_3], 7.7 (s, CH_3 of PEt_3)
3d	2.26 (m, 3 H, CH of Pr^i), 1.87 (m, 6 H, CH_2 of Et), 1.03 (m, 18 H, CH_3 of Pr^i), 0.84 (m, 9 H, CH_3 of Et)	254.5 [d (22), MoCO], 229.4 (s, MoCO), 223.5 (s, br, MnCO), 216.9 (s, br, MnCO), 215.8 (s, MnCO), 88.7 [d (44), S_2CP], 52.6 [d (3), POCH_3], 31.0 [d (42), CH of Pr^i], 18.2 (s, CH_3 of Pr^i), 17.6 [d (23), CH_2 of PEt_3], 7.7 (s, CH_3 of PEt_3)
4a	4.33 (m, 8 H, CH_2 of tedip), 2.63 (m, 3 H, CH of Cy), 2.09–1.27 (m, br, 42 H, CH_2 of Cy and CH_3 of tedip)	244.7 [dd (23 and 5), MoCO], 227.7 [d (9), MoCO], 218.6 [d (15) MnCO], 218.0 [d (34), MnCO], 214.1 [d (31), MnCO], 80.33 [ddd (57, 16, and 7), S_2CP], 63.8–61.4 (m, CH_2 of tedip), 34.8 [d (39), C^1 of Cy], 28.2 (s, C^3 and C^5 of Cy), 27.4 [d (11), C^2 and C^6 of Cy], 26.2 (s, C^4 of Cy), 16.8–16.4 (m, CH_3 of tedip)
4b	4.34 (m, 8 H, CH_2 of tedip), 2.91 (m, 3 H, CH of Pr^i), 1.45–1.40 (m, 30 H, CH_3 of Pr^i and tedip)	244.9 [d (26), MoCO], 226.7 [d (8), MoCO], 218.0 [d (32), Mn CO], 217.4 [d (51), MnCO], 213.6 [d (31), MnCO], 79.1 [ddd (58, 15, and 7), S_2CP], 63.4–61.0 (m, CH_2 of tedip), 24.6 [d (42), CH of Pr^i], 18.3 (s, CH_3 of Pr^i), 16.2 (m, CH_3 of tedip)
4c	3.30 (m, 1 H, PCH_2P of dmpm), 2.65 (m, 4 H, CH of Cy, and PCH_2P of dmpm), 2.11–1.24 (m, br, 42 H, CH_2 of Cy and CH_3 of dmpm)	248.3 [dd (19 and 4), MoCO], 230.7 [d (7), MoCO], 218.5 [d (31) Mn CO], 218.0 [d (34), MnCO], 215.8 [d (21), MnCO], 76.61 [ddd (58, 14, and 5), S_2CP], 38.7 [t (12), CH_2 of dmpm], 34.5 [d (40), C^1 of Cy], 28.1 (s, C^3 and C^5 of Cy), 27.2 [d (11), C^2 and C^6 of Cy], 26.2 (s, C^4 of Cy), 20.5–16.2 (m, CH_3 of dmpm)
4d	3.28 (m, 1 H, PCH_2P of dmpm), 2.91 (m, 1 H, PCH_2P of dmpm), 1.93–1.36 (m, 30 H, CH_3 of dmpm and Pr^i)	248.05 [dd (18 and 5), MoCO], 230.3 [d (7), MoCO], 219.9 [d (23), Mn CO], 218.1 [d (31), MnCO], 215.6 [d (19), MnCO], 75.9 [ddd (61, 15, and 5), S_2CP], 38.56 [t (12), CH_2 of dmpm], 24.7 [d (42), CH of Pr^i], 18.1 (s, CH_3 of Pr^i), 20.6–16.2 (m, CH_3 of dmpm)

[a] From CD_2Cl_2 solutions. Due the limited solubility of complexes **4e,f**, it was not possible to obtain informative ^{13}C NMR spectra for them. Their ^1H NMR spectra are in the Experimental Section. [b] For data in brackets, J values (in hertz) are given in parentheses.

Compounds **2a,b** react with monodentate phosphorus ligands in CH_2Cl_2 at room temperature to afford pentacarbonyl complexes of the general formula $[MnMo(CO)_5(L)(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)]$ (**3a–d**, see Scheme I). The reactions are virtually instantaneous and the products **3a–d** can be isolated, in high yields, as red crystalline solids from CH_2Cl_2 mixtures. Analytical and spectroscopic data (Tables I and II) support the structures depicted for these complexes in Scheme I. Their IR spectra in solution display four ν(CO) absorptions, with a pattern consistent with a $M_2(CO)_5$ arrangement, and the $^{31}P\{^1H\}$ NMR spectra display the signal of the entering ligand in the region expected for a phosphorus bonded to Mo rather than to Mn. The signals of the CO groups in the $^{13}C\{^1H\}$ NMR are more informative, those attributable to the carbonyls bonded to the Mo atom being very close to those found in complexes $[Mo(CO)_2(PR_3)(\mu\text{-}Cl)(\mu\text{-}S_2CPR_3)SnCl_2Bu]$, the structure of which has been established by X-ray crystallography for R = Cy.[9] Such coincidence support both the consistency of the assignments and the spatial arrangement of the carbonyl and phosphine ligands around the molybdenum atom.

Hexacarbonyl complexes **2a,b** react with bidentate ligands such as tetraethylpyrophosphite, $(EtO)_2POP(OEt)_2$ (tedip), bis(dimethylphosphino)methane (dmpm), or bis(diphenylphosphino)methane (dppm), to afford

Table III. Crystal Data and Refinement Details for [MnMo(CO)$_6$(μ-Br)(μ-S$_2$CPPr$^i_3$)] (2b) and [MnMo(CO)$_4$(μ-Br)(μ-S$_2$CPCy$^i_3$)(μ-tedip)] (4a)

	compound **2b**	compound **4a**
formula	$C_{16}H_{21}BrMnMoO_6PS_2$	$C_{32}H_{53}BrMnMoO_{10}P_3S_2$
fw	635.21	985.59
cryst syst, space group	monoclinic, $P2_1/c$ (No. 14)	
a, Å	9.065 (1)	14.827 (9)
b, Å	19.579 (5)	15.097 (9)
c, Å	13.398 (3)	19.566 (10)
β, deg	106.67 (2)	103.19 (7)
V, Å^3	2293 (1)	4264 (4)
molecules/cell	4	4
T, K	200	293
ρ_{calc}, g cm^{-3}	1.84	1.53
F(000)	1256	2016
λ(MoKα), Å	0.710 73	0.710 73
μ, cm^{-1}	30.61	17.51
method of collection	$\omega/2\theta$ scan	$\omega/2\theta$ scan
scan range, deg	$0 \le \theta \le 25$	$0 \le \theta \le 22$
drift corrections max, min	1.04, 0.98	1.11, 0.97
no. of rflns measd	4008	5206
no. of rflns obsd $I \ge 3\sigma(I)$	2646	1584
abs cor	empirical (ψ scan)	
factors: max, min	0.999, 0.965	0.999, 0.938
no. of params	263	292
weighting scheme	$w = [\sigma^2(F) + gF^2]^{-1}$	
g	0.0004	0.0006
residuals R, R_w	0.032, 0.033	0.060, 0.059

Table IV. Atomic Coordinates (Esd's in Parentheses) for Non-Hydrogen Atoms in [MnMo(CO)$_6$(μ-Br)(μ-S$_2$CPPr$^i_3$)] (2b)

atom	x	y	z
Mo(1)	0.11519 (5)	0.09200 (2)	0.28308 (4)
Br(1)	0.23760 (7)	0.21294 (3)	0.25258 (5)
C(2)	−0.0285 (7)	0.0326 (3)	0.3259 (4)
O(2)	−0.1178 (5)	0.0019 (2)	0.3535 (3)
C(3)	−0.0825 (7)	0.1291 (3)	0.1905 (5)
O(3)	−0.1928 (5)	0.1483 (2)	0.1317 (4)
C(4)	0.1251 (7)	0.1304 (3)	0.4255 (5)
O(4)	0.1296 (6)	0.1498 (2)	0.5058 (4)
Mn(1)	0.41290 (9)	0.11836 (4)	0.20108 (7)
C(5)	0.5339 (6)	0.0602 (3)	0.1580 (5)
O(5)	0.6119 (5)	0.0247 (2)	0.1277 (4)
C(6)	0.4063 (7)	0.1739 (3)	0.0915 (5)
O(6)	0.4097 (5)	0.2102 (2)	0.0262 (4)
C(7)	0.5762 (7)	0.1638 (3)	0.2793 (5)
O(7)	0.6845 (5)	0.1930 (2)	0.3283 (4)
C(1)	0.2284 (6)	0.0034 (3)	0.2474 (4)
S(1)	0.3853 (2)	0.04593 (7)	0.3379 (1)
S(2)	0.1892 (2)	0.04900 (7)	0.1280 (1)
P(1)	0.2011 (2)	−0.08774 (7)	0.2477 (1)
C(11)	0.1572 (7)	−0.1156 (3)	0.3667 (4)
C(12)	0.2453 (7)	−0.0786 (3)	0.4651 (4)
C(13)	0.1738 (7)	−0.1934 (3)	0.3807 (5)
C(21)	0.3708 (6)	−0.1334 (3)	0.2339 (5)
C(22)	0.5177 (7)	−0.1213 (4)	0.3218 (5)
C(23)	0.4011 (7)	−0.1187 (4)	0.1291 (5)
C(31)	0.0418 (6)	−0.1090 (3)	0.1315 (4)
C(32)	−0.1148 (6)	−0.0826 (3)	0.1393 (5)
C(33)	0.0291 (7)	−0.1840 (3)	0.1014 (5)

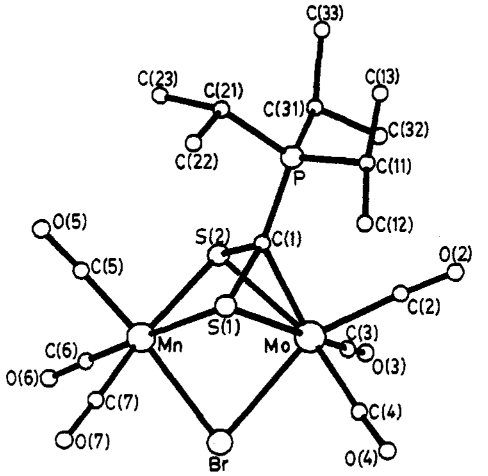
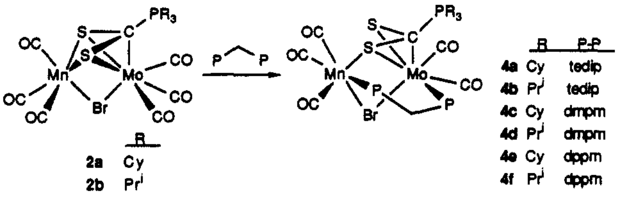


Figure 1. Perspective view of [MnMo(CO)$_6$(μ-Br)(μ-S$_2$CPPr$^i_3$)] (**2b**), showing the atom numbering.

Table V. Selected Bond Lengths (Å) and Angles (deg) for [MnMo(CO)$_6$(μ-Br)(μ-S$_2$CPPr$^i_3$)] (2b)

Mo–Br	2.696 (1)	Mn–Br	2.657 (1)
Mo–S(1)	2.513 (1)	Mo–S(2)	2.506 (1)
Mo–C(1)	2.138 (5)	Mn–S(1)	2.387 (2)
Mn–S(2)	2.403 (2)	Mo–C(2)	1.951 (6)
Mo–C(3)	1.999 (6)	Mo–C(4)	2.028 (7)
Mn–C(5)	1.788 (6)	Mn–C(6)	1.815 (6)
Mn–C(7)	1.786 (6)	C(2)–O(2)	1.152 (6)
C(3)–O(3)	1.145 (7)	C(4)–O(4)	1.132 (7)
C(5)–O(5)	1.146 (7)	C(6)–O(6)	1.134 (7)
C(7)–O(7)	1.162 (7)	C(1)–S(1)	1.787 (5)
C(1)–S(2)	1.776 (5)	C(1)–P(1)	1.802 (5)
Mn–Br–Mo	74.4 (1)	S(1)–Mo–Br	87.2 (1)
S(2)–Mo–Br	87.1 (1)	S(1)–Mo–C(1)	44.3 (1)
S(2)–Mo–C(1)	44.1 (1)	S(2)–Mo–S(1)	69.6 (1)
C(1)–Mo–Br	115.7 (1)	C(1)–Mo–C(2)	89.2 (2)
C(1)–Mo–C(3)	123.9 (2)	C(1)–Mo–C(4)	128.1 (2)
S(1)–Mo–C(2)	112.2 (2)	S(2)–Mo–C(2)	113.8 (2)
S(1)–Mo–C(3)	159.3 (2)	S(2)–Mo–C(3)	90.8 (2)
S(1)–Mo–C(4)	94.7 (2)	S(2)–Mo–C(4)	162.7 (2)
C(2)–Mo–Br	155.1 (2)	C(3)–Mo–Br	85.5 (2)
C(3)–Mo–C(2)	81.0 (2)	C(4)–Mo–Br	84.7 (2)
C(4)–Mo–C(2)	78.3 (2)	C(4)–Mo–C(3)	103.8 (2)
O(2)–C(2)–Mo	174.9 (5)	O(3)–C(3)–Mo	175.2 (5)
O(4)–C(4)–Mo	177.8 (6)	S(2)–Mn–S(1)	73.4 (1)
S(1)–Mn–Br	90.7 (1)	S(2)–Mn–Br	90.1 (1)
S(1)–Mn–C(5)	94.5 (2)	S(2)–Mn–C(5)	91.9 (2)
S(1)–Mn–C(6)	172.4 (2)	S(2)–Mn–C(6)	100.5 (2)
S(1)–Mn–C(7)	95.6 (2)	S(2)–Mn–C(7)	168.8 (2)
C(5)–Mn–Br	174.8 (2)	C(6)–Mn–Br	84.8 (2)
C(6)–Mn–C(5)	90.1 (3)	C(7)–Mn–Br	87.5 (2)
C(7)–Mn–C(5)	91.5 (3)	C(7)–Mn–C(6)	90.3 (3)
Mn–S(1)–Mo	82.6 (1)	Mn–S(2)–Mo	82.4 (1)
O(5)–C(5)–Mn	177.4 (6)	O(6)–C(6)–Mn	176.2 (5)
O(7)–C(7)–Mn	178.1 (6)	S(2)–C(1)–S(1)	106.9 (3)
P(1)–C(1)–Mo	136.7 (3)	S(1)–C(1)–Mo	79.1 (2)
S(2)–C(1)–Mo	79.0 (2)		

Scheme II



complexes [MnMo(CO)$_5$(μ-Br)(μ-S$_2$CPR$_3$)(μ-P-P)] (**4a–f** in Scheme II), which have been isolated as red crystalline solids. The IR spectra of complexes **4a–f** in CH_2Cl_2 solution show four ν(CO) absorptions suggesting the presence of five carbonyls. This is confirmed by the $^{13}C\{^1H\}$ NMR spectra of the tedip and dmpm derivatives, which display five signals for the carbonyl groups (see Table II). On the other hand, the $^{31}P\{^1H\}$ NMR spectra of the complexes show, apart from the signal of the P atom of S_2CPR_3, two doublets for the P-P ligand: one of them is sharp and can be assigned to a phosphorus bonded to Mo; the other, broad, fits well for a P atom bonded to manganese, the broadening of the signal being a typical consequence of the nuclear quadrupole of ^{55}Mn. All spectroscopic data indicated simultaneously the presence of five carbonyls, and the formation of the Mn–P–P–Mo

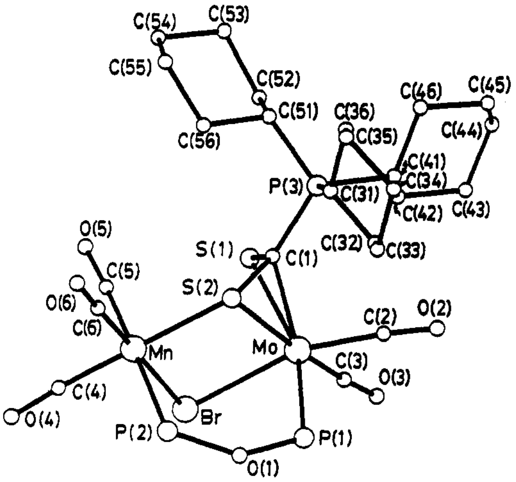


Figure 2. Perspective view of [MnMo(CO)$_5$(μ-Br)(μ-S$_2$CPCy$_3$)(μ-tedip)] (**4a**), showing the atom numbering. The ethoxy groups of the tetraethyldiphosphite (tedip) ligand have been omitted for clarity.

bridge. Having in mind the facile substitution of one carbonyl group of the Mo atom in complexes **2a**,**b** as shown by the reactions with monodentate phosphorus ligands described above, it was straightforward to assume that this was the first step in the reaction with bidentate tedip or diphosphine. The second step, however, posed the question of which ligand had been displaced from manganese, since all three CO groups remained in the final product. There were two possibilities: either one S–Mn or the Br–Mn bond may have been cleaved to allow for the entrance of the phosphorus atom. To establish this point, an X-ray determination was carried out on a crystal of the derivative [MnMo(CO)$_5$(μ-Br)(μ-S$_2$CPCy$_3$)(μ-tedip)] (**4a**). Crystal and refinement data are shown in Table III, and the results are presented in Figure 2 and Tables VI and VII. It can be seen in Figure 2 that the entering P atom of the tedip ligand displaces one sulfur of the S$_2$CPR$_3$ bridge from the coordination sphere of the manganese atom, the distance from Mn to S(1), 3.874 (9) Å, being too long to permit any significant interaction between them. As in the parent complex **2a**, the electron counting for **4a** does not require the presence of a metal–metal bond. In this case the Mn···Mo distance of 3.642 (5) Å is much longer than that expected for a bonding interaction between the metals. The manganese atom forms a nearly planar arrangement with the bridging Br, one P, and two carbonyls [maximum deviation 0.05 (3) Å in relation to C(5)]. One carbonyl and the coordinated sulfur, S(2), complete a fairly regular octahedral environment around manganese. The $\overline{\mathrm{MnBrMoS}}$(2) ring is close to planarity, being only slightly folded [1.3 (2)°] over the line joining Mn and Mo. Additionally, the two metals and the P–O–P atoms of tedip form a fairly planar arrangement which is nearly orthogonal to the $\overline{\mathrm{MnBrMoS}}$(2) ring.

Table VI. Atomic Coordinates (Esd's in Parentheses) for Non-Hydrogen Atoms in [MnMo(CO)$_5$(μ-Br)(μ-S$_2$CPCy$_3$)(μ-tedip)] (4a)

atom	*x*	*y*	*z*
Mo	0.2594 (1)	0.1599 (2)	0.1196 (1)
Br	0.0867 (2)	0.1663 (2)	0.0282 (1)
Mn	0.0540 (3)	0.2984 (3)	0.1004 (2)
S(1)	0.2897 (5)	0.2880 (5)	0.0469 (4)
S(2)	0.2045 (4)	0.2907 (5)	0.1760 (3)
C(1)	0.300 (2)	0.294 (2)	0.138 (1)
C(2)	0.366 (2)	0.122 (2)	0.186 (1)
O(2)	0.433 (1)	0.089 (1)	0.2226 (8)
C(3)	0.306 (2)	0.071 (2)	0.064 (1)
O(3)	0.341 (1)	0.017 (1)	0.035 (1)
C(4)	−0.063 (2)	0.304 (2)	0.050 (2)
O(4)	−0.139 (1)	0.307 (2)	0.022 (1)
C(5)	0.082 (2)	0.379 (2)	0.040 (2)
O(5)	0.099 (2)	0.432 (2)	0.003 (1)
C(6)	0.032 (2)	0.385 (2)	0.153 (2)
O(6)	0.016 (2)	0.444 (2)	0.187 (1)
O(1)	0.081 (1)	0.109 (1)	0.1973 (8)
P(1)	0.1793 (5)	0.0723 (5)	0.1892 (4)
P(2)	0.0150 (5)	0.1933 (6)	0.1718 (4)
P(3)	0.4052 (4)	0.3501 (5)	0.1878 (3)
C(31)	0.396 (2)	0.356 (2)	0.279 (1)
C(32)	0.405 (2)	0.266 (2)	0.316 (1)
C(33)	0.380 (2)	0.277 (2)	0.390 (1)
C(34)	0.447 (2)	0.343 (2)	0.432 (1)
C(35)	0.436 (2)	0.433 (2)	0.398 (1)
C(36)	0.460 (2)	0.424 (2)	0.325 (1)
C(41)	0.513 (1)	0.296 (2)	0.183 (1)
C(42)	0.518 (1)	0.250 (2)	0.116 (1)
C(43)	0.608 (2)	0.199 (2)	0.123 (1)
C(44)	0.692 (2)	0.258 (2)	0.144 (1)
C(45)	0.687 (2)	0.305 (2)	0.213 (1)
C(46)	0.597 (1)	0.358 (2)	0.209 (1)
C(51)	0.407 (2)	0.464 (2)	0.157 (1)
C(52)	0.429 (2)	0.474 (2)	0.084 (1)
C(53)	0.440 (2)	0.577 (2)	0.072 (1)
C(54)	0.348 (2)	0.627 (2)	0.075 (1)
C(55)	0.320 (2)	0.611 (2)	0.143 (1)
C(56)	0.315 (2)	0.510 (2)	0.159 (1)
O(11)	0.149 (1)	−0.029 (1)	0.169 (1)
C(11)	0.136 (2)	−0.065 (2)	0.097 (1)
C(13)	0.208 (2)	−0.134 (2)	0.101 (2)
O(12)	0.232 (1)	0.064 (1)	0.269 (1)
C(12)	0.198 (2)	0.027 (3)	0.323 (2)
C(14)	0.261 (2)	0.037 (2)	0.390 (1)
O(21)	−0.081 (1)	0.146 (1)	0.145 (1)
C(21)	−0.092 (1)	0.062 (1)	0.114 (1)
C(23)	−0.160 (1)	0.011 (1)	0.137 (1)
O(22)	0.003 (2)	0.240 (2)	0.238 (1)
C(22)	−0.019 (2)	0.185 (2)	0.290 (1)
C(24)	0.003 (2)	0.225 (2)	0.357 (1)

In the reaction of **2a** with tedip to give **4a**, the S$_2$CPR$_3$ ligand changes its coordination mode from η^2(S,S′)η^3-(S,C,S′), donating 8e, to η^1(S),η^3(S,C,S′), donating 6e. The latter coordination mode has been observed previously in the complex [Mo$_2$(CO)$_4$(PEt$_3$)$_2$(μ-S$_2$CPEt$_3$)$_2$].[2] Although this is, as far as we know, the first observation of such a change in the coordination mode of the S$_2$CPR$_3$ ligand within a bimetallic complex, the process may not be totally unexpected: from the point of view of the coordination around manganese, it can be considered as the opening of the chelate $\overline{\mathrm{MnSCS}}$ ring upon attack of the entering ligand. In fact, we have observed previously ring-opening processes in the reactivity of mononuclear Mn(I) complexes containing chelate S$_2$CPR$_3$ ligands.[8] In such cases, it was possible to induce additional loss of CO, either thermally or under UV irradiation, resulting in the closing of the $\overline{\mathrm{MnSCS}}$ chelate ring. The complexes bearing an unidentate S$_2$CPR$_3$ ligand, produced in the ring-opening step, can be considered as intermediates in a process which leads, eventually, to an overall substitution of CO. In the case of complexes **4a**–**f**, however, we have failed to obtain stable products in our attempts to promote thermally, photochemically, or by addition of Me$_3$NO the intramolecular displacement of one carbonyl group by the sulfur not coordinate to manganese. From the picture of the structure of **4a** in Figure 2, it can be seen that such displacement would produce, around the Mn atom, a coordination environment severely distorted from its usual

Table VII. Selected Bond Lengths (Å) and Angles (deg) for [MnMo(CO)$_5$(μ-Br)(μ-S$_2$CPCy$_3$)(μ-tedip)] (4a)

Mo–Br	2.770 (3)	Mn–Br	2.553 (6)
Mo–S(1)	2.502 (8)	Mo–S(2)	2.487 (7)
Mo–C(1)	2.12 (2)	Mo–C(2)	1.89 (3)
Mo–C(3)	1.96 (3)	Mo–P(1)	2.398 (8)
Mn–S(2)	2.383 (7)	Mn–C(4)	1.79 (3)
Mn–C(5)	1.81 (4)	Mn–C(6)	1.73 (4)
Mn–P(2)	2.27 (1)	P(3)–C(1)	1.85 (2)
S(1)–C(1)	1.76 (2)	S(2)–C(1)	1.73 (2)
C(2)–O(2)	1.19 (2)	C(3)–O(3)	1.17 (3)
C(4)–O(4)	1.14 (3)	C(5)–O(5)	1.15 (3)
C(6)–O(6)	1.18 (3)	O(1)–P(1)	1.60 (2)
O(1)–P(2)	1.61 (2)		

Mn–Br–Mo	86.2 (1)	S(1)–Mo–Br	82.2 (2)
S(2)–Mo–Br	84.9 (2)	S(2)–Mo–S(1)	76.0 (2)
C(1)–Mo–Br	105.0 (6)	C(1)–Mo–S(1)	43.8 (6)
C(1)–Mo–S(2)	43.3 (6)	C(2)–Mo–Br	163.5 (7)
C(2)–Mo–S(1)	113.1 (8)	C(2)–Mo–S(2)	104.1 (7)
C(3)–Mo–Br	93.5 (7)	C(3)–Mo–S(1)	94.9 (8)
C(3)–Mo–S(2)	170.8 (8)	C(3)–Mo–C(1)	129.2 (9)
P(1)–Mo–Br	83.2 (2)	P(1)–Mo–S(1)	157.8 (3)
P(1)–Mo–S(2)	86.1 (3)	P(1)–Mo–C(1)	125.9 (6)
P(1)–Mo–C(2)	83.6 (7)	P(1)–Mo–C(3)	102.7 (8)
S(2)–Mn–Br	92.1 (2)	C(4)–Mn–S(2)	175 (1)
C(5)–Mn–Br	94 (1)	C(5)–Mn–S(2)	97 (1)
C(5)–Mn–C(4)	87 (1)	C(6)–Mn–Br	177 (1)
C(6)–Mn–S(2)	87 (1)	C(6)–Mn–C(4)	90 (1)
C(6)–Mn–C(5)	89 (2)	P(2)–Mn–Br	84.4 (3)
P(2)–Mn–S(2)	85.3 (3)	P(2)–Mn–C(5)	177 (1)
P(2)–Mn–C(6)	93 (1)	C(1)–S(1)–Mo	56.5 (8)
Mn–S(2)–Mo	96.8 (3)	C(1)–S(2)–Mo	57.0 (8)
C(1)–S(2)–Mn	118.1 (8)	S(1)–C(1)–Mo	79.6 (9)
S(2)–C(1)–Mo	80 (1)	S(2)–C(1)–S(1)	123 (1)
P(3)–C(1)–Mo	134 (1)	P(3)–C(1)–S(1)	115 (1)
P(3)–C(1)–S(2)	118 (1)	O(2)–C(2)–Mo	172 (2)
O(3)–C(3)–Mo	175 (2)	O(4)–C(4)–Mn	176 (3)
O(5)–C(5)–Mn	178 (4)	O(6)–C(6)–Mn	179 (3)
P(2)–O(1)–P(1)	138 (1)		

octahedral geometry, having four donor atoms (two S, P, Br) in one side, and two (two CO) in the opposite side of the metal.

^{31}P{^{1}H} NMR monitoring of the reactions with tedip show the progressive growth of the bands of the products **4a,b**, with the simultaneous dissapearance of the signals of the starting **2a,b**, without any signal attributable to the expected intermediates bearing a monodentate tedip ligand. This behavior is parallel to that observed in the thermal reactions of [Mn$_2$(CO)$_6$(S$_2$CPR$_3$)] with dppm,[6] and suggests that the intramolecular coordination of the second P atom is much faster than the first step (displacement of CO at the Mo atom), which can be considered as the kinetically controlling step of the overall process.

While the reactions of **2a,b** with tedip or dmpm to give **4a–d** are quite fast, being completed within several minutes at room temperature, the progress of the analogous reactions with dppm is much slower, requiring long stirring times (32 h for **4e**) or the heating of the reaction mixtures to the reflux temperature of THF for 5 h. As a result, some impurities, arising probably from decomposition of the reactants, are found in the final mixtures of the reactions with dppm. In the crude products **4e,f**, the amount of impurities is not greater than 10% (according to the ^{31}P NMR spectra). However, several recrystallizations from CH$_2$Cl$_2$/hexane are necessary to obtain analytically pure samples of compounds **4e,f**. This results in a low yield (8–15%) of the purified product.

The slowness of the reactions with dppm, when compared to those with tedip or dmpm, can be attributed to the different sizes of the ligands. It seems that the substitution of CO at the molybdenum atom is somewhat impeded when bulky entering ligands are used. In fact, the hexacarbonyl **2a** does not react with PCy$_3$ after 24 h at room temperature, and the attempts to induce CO substitution by heating in CH$_2$Cl$_2$ led to complex mixtures of products resulting from the degradation of the starting bimetallic compound. In contrast, the reactions discussed above between hexacarbonyls **2a,b** and the smaller PEt$_3$, P(OMe)$_3$, tedip, or dmpm ligands proceed very quickly at room temperature.

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Supplementary Material Available: Complete tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, torsion angles, and least-squares planes for the structures of **2b** and **4a** (18 pages). Ordering information is given on any current masthead page.

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