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Metal–Metal Bond Formation and Rearrangement of the S_2CPR_3 Ligands in Binuclear Manganese–Molybdenum Complexes. X-ray Structure of $[MnMo(SnPh_3)(CO)_6(\mu\text{-}S_2CPPr^i_3)]$

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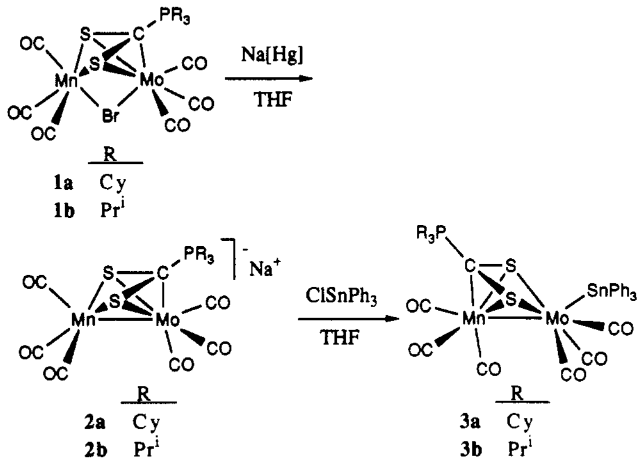
Summary: The reduction of complexes $[MnMo(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)]$ (1) with Na[Hg] produces the anions $[MnMo(CO)_6(\mu\text{-}S_2CPR_3)]^-$ (2), which can be trapped with $ClSnPh_3$ to afford the stable derivatives $[MnMo(SnPh_3)(CO)_6(\mu\text{-}S_2CPR_3)]$ (3). An X-ray structure determination shows the formation of Mn–Mo and Sn–Mo bonds in compounds 3 and also the rearrangement of the S_2CPR_3 bridge: its central carbon, which was bonded to Mo in the starting compounds 1, is now bonded to the Mn atom in complexes 3.

Binuclear complexes containing η^2:η^3-S_2CPR_3 bridges straddling a Mn–Mn bond[1] have proved to display interesting reactivity in reduction and hydride addition reactions.[2] We have recently reported a convenient synthetic way to obtain heterodinuclear complexes containing manganese and molybdenum, in which the metals, not directly bonded, are bridged by a halide and a S_2CPR_3 ligand which acts as η^2(S,S′) chelate (to Mn) and as η^3-(S,C,S′) pseudoallyl (to Mo).[3] The generality of the method has been demonstrated by the preparation of similar complexes with other combinations of metals such as Ru/Mo and Ru/W.[4] The presence of the halide bridge in these families of complexes prompted us to explore the possibility of forming a direct bond between the metals by reduction reactions. Herein we wish to report the first results of such work, which has led to the preparation of very reactive heterodinuclear carbonyl anions which can be used *in situ* to obtain neutral, stable complexes containing Mn–Mo and Mo–Sn bonds. The scarcity of heterodinuclear carbonyl anions, when compared to the number of homodinuclear anions or heterodinuclear neutral complexes, has been recently pointed out by Hersh *et al.*[5]

The reaction of compounds $[MnMo(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)]$ (**1a,b** in Scheme I)[3] with excess 1% sodium amalgam in THF at room temperature for 50 min leads to the formation of anionic species which, on the basis of their IR spectra, are formulated as $[MnMo(CO)_6(\mu\text{-}S_2CPR_3)]^-$ (**2a,b** in Scheme I). The reactive character of these anions precluded their isolation as Na^+, PPN^+, or NEt_4^+ salts. However, fresh solutions of those anions **2a,b** can be reacted *in situ* with $ClSnPh_3$ to afford stable derivatives which can be isolated as red crystalline solids in good yields (70–80%).[6] Their analytical and spectroscopic data[7] suggested the formulation $[MnMo(SnPh_3)(CO)_6(\mu\text{-}S_2CPR_3)]$ (**3a,b** in Scheme I). The exact details of the structure, however, could not be inferred from spectroscopic data alone and, therefore, an X-ray determination was carried out on a crystal of the derivative **3b**.[8] As can be seen in Figure 1, the molecule of **3b** consists of the fragments $Mn(CO)_3$ and $Mo(CO)_3(SnPh_3)$ bridged by a S_2CPR_3 ligand. The Mo–Mn distance of 2.877(1) Å is within the range expected for a direct bond between the metals, as required by the EAN rule. There are two interesting features in the structure of **3b**: first, the triphenyltin group is bonded to molybdenum (Mo–Sn

Scheme I



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[6] A solution of **1a** (0.189 g, 0.25 mmol) in THF (15 mL) was stirred with excess 1% Na[Hg] (2 g) until the IR monitoring showed exclusively the bands of the anion **2a** (40–50 min). The color changed from red to yellow. The mixture was allowed to settle for several minutes, and the supernatant solution was then transferred under nitrogen to another flask containing solid $ClSnPh_3$ (0.096 g, 0.25 mmol). The color changed instantaneously to red, and IR monitoring showed complete reaction. Solvent was evaporated in vacuo, and the red residue was extracted with CH_2Cl_2 and filtered through alumina (activity III, 2 × 15 cm column). To the filtrate (ca. 35 mL) was added hexane (15 mL). Slow concentration in vacuo gave **3a** as a red microcrystalline solid, yield 0.20 g (79%). The anion **2b** and its derivative **3b** were prepared by similar procedures, by using **1b** (0.16 g, 0.25 mmol): isolated yield of **3b** 0.17 g (73%).

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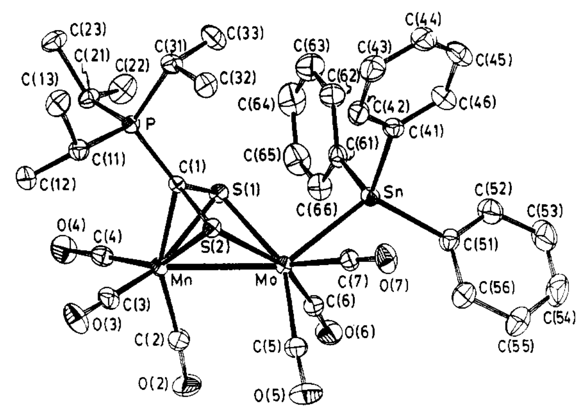

Figure 1. Perspective view (EUCLID package)[18] of $[MnMo(SnPh_3)(CO)_6(\mu\text{-}S_2CPPR^i{}_3)]$ (**3b**), showing the atom numbering. Selected bond distances (Å) and angles (deg): Mn–Mo = 2.877(1), Mo–Sn = 2.810(1), Mo–S(1) = 2.453(1), Mo–S(2) = 2.464(1), Mn–S(1) = 2.377(1), Mn–S(2) = 2.352(1), Mn–C(1) = 2.029(4), Mn–C(2) = 1.805(5), Mn–C(3) = 1.784(5), Mn–C(4) = 1.790(5), Mo–C(5) = 1.976(5), Mo–C(6) = 1.981(5), Mo–C(7) = 1.944(5); Sn–Mo–Mn = 134.96(6), S(1)–Mn–S(2) = 73.44(7), S(1)–Mo–S(2) = 70.20(6), S(2)–C(1)–S(1) = 105.7(2), C(1)–Mn–C(2) = 153.7(2), C(3)–Mn–C(1) = 110.2(2), C(4)–Mn–C(1) = 102.8(2), C(5)–Mo–C(6) = 78.2(2), C(5)–Mo–C(7) = 76.0(2), C(6)–Mo–C(7) = 105.3(2), Sn–Mo–C(5) = 124.6(1), Sn–Mo–C(6) = 71.4(1), Sn–Mo–C(7) = 69.2(1). C(carbonyl)–Mn–C(carbonyl) angles range from 89.7(2) to 93.6(2)°.

distance 2.810(1) Å) and, second, the central carbon of the S_2CPR_3 ligand is now bonded to manganese (Mn–C(1) distance 2.029(4) Å), while in the starting complex **1b** it was bonded to molybdenum.[3] These two facts may be related to each other and deserve some discussion. It is remarkable that complexes **3a,b** are obtained as the only products from the reaction sequence outlined in Scheme I: the IR and ^{31}P NMR spectra of the crude reaction mixtures showed no formation of other products which could contain a Mn–Sn bond or one with the S_2CPR_3 ligand η^3(S,C,S′) bonded to molybdenum. It seems that complexes **3** are produced through a regiospecific electrophilic addition of the triphenyltin group to the molybdenum atom in the intermediate anions **2**, in which the molybdenum atom would support most of the charge. This leads to the assignment of formal oxidation states[12] Mn^0 and Mo^{-I} in the anions **2**, which are thus isoelectronic (and, most probably, also isostructural) with the neutral dimanganese complexes $[Mn_2(CO)_6(\mu\text{-}S_2CPR_3)]$.[1] In complexes **3**, the well-established practice of considering the tin ligand as anionic triphenylstannate(II) leads to the assignment of oxidation numbers[12] Mn^0 and Mo^I. At this point, the migration of the central carbon of the S_2CPR_3 ligand from molybdenum in the starting **1** to manganese in the final product **3** can be rationalized by considering either electronic or steric factors. We have already shown that the central carbon of the S_2CPR_3 ligand displays a definite preference for one of the metals when coordinated in the η^2(S,S′):η^3(S,C,S′) fashion to a heterobimetallic template, either with a metal–metal bond, as in $[MnRe(CO)_6(\mu\text{-}S_2CPR_3)]$,[13] or without a metal–metal bond, as in the starting complexes **1**.[3] While the reasons of the preference for Mn rather than for Re are unclear so far, we have advanced an explanation for such preference, in complexes **1**, based on the different oxidation states in both metals. Thus, in **1a,b** and in their substituted derivatives, the center carbon of the ligand is bonded to Mo(0) rather than to Mn(I).[3] This explanation was supported by the fact that, for all the reported complexes in which the S_2CPR_3 is bonded either as η^3(S,C,S′)[1,3,4,13–16] or as η^2(S,C),[17] the metal atom is in the formal oxidation state 0. From the picture of the molecule of **3b** in Figure 1, it is clear that the bulkiness of the $SnPh_3$ group would create a great steric congestion around the molybdenum atom if the S_2CPR_3 ligand were to remain bonded as η^3-(S,C,S′) toward Mo and, probably, the observed rearrangement of the ligand should be taken as a result of the cooperative effect of both electronic and steric factors pushing in the same direction.

The structure of anions **2**, depicted in Scheme I, is tentatively proposed on the basis of keeping the carbon atom of the S_2CPR_3 ligand bonded to the metal with lower oxidation number. Unfortunately, all the attempts to

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[7] *Analytical and Spectroscopic Data.* $^{31}P\{^1H\}$ NMR (121.5 MHz, 85% H_3PO_4 standard), ^1H (300 MHz, TMS standard), and $^{13}C\{^1H\}$ NMR (75.5 MHz, TMS standard) spectra were taken from CD_2Cl_2 solutions. **2a**: IR (THF, cm^{-1}) ν(CO) 1971 s, 1898 vs, 1875 s, 1792 m, 1749 m. **2b**: IR (THF, cm^{-1}) ν(CO) 1973 s, 1898 vs, 1876 s, 1793 m, 1751 m. **3a**: IR (CH_2Cl_2, cm^{-1}) ν(CO) 2009 vs, 1978 vs, 1919 s (br), 1885 m; ^1H NMR δ 7.56–7.31 [m, 15H, 3 × C_6H_5], 2.33 [m, 3H, C^1H of Cy], 1.95–1.19 [m (br), 30 H, CH_2 of Cy]; $^{31}P\{^1H\}$ NMR δ 34.5; $^{13}C\{^1H\}$ NMR δ 226.3 [s (br), Mn–CO], 224.1 [s, Mo–CO], 144.2 [s, $J(^{119}SnC)$ = 397 Hz, $J(^{117}SnC)$ = 376 Hz, C^1 of SnC_6H_5], 137.2 [s, J(SnC) = 37 Hz, C^2 of SnC_6H_5], 128.7 [s, J(SnC) = 47 Hz, C^3 of SnC_6H_5], 128.8 [s, C^4 of SnC_6H_5], 90.0 [d, J(PC) = 49 Hz, S_2CP], 35.1 [d, J(PC) = 40 Hz, C^1 of Cy], 27.8 [s, C^2 and C^6 of C_6H_{11}], 27.1 [d, J(PC) = 12 Hz, C^3 and C^5 of C_6H_{11}], 25.5 [s, C^4 of C_6H_{11}]. Anal. Found: C, 50.43; H, 4.99. Calcd for $C_{43}H_{48}MnMoO_6PS_2Sn$: C, 50.36; H, 4.72. **3b**: IR (CH_2Cl_2, cm^{-1}) ν(CO) 2010 vs, 1979 vs, 1920 s (br), 1884 m; ^1H NMR δ 7.55–7.31 [m 15H, 3 × C_6H_5], 2.56 [m, 3H, CH of Pr^i], 1.28 [m, 18 H, CH_3 of Pr^i]; $^{31}P\{^1H\}$ NMR δ 44.9; $^{13}C\{^1H\}$ NMR δ 226.2 [s (br), Mn-CO], 223.5 [s, Mo–CO], 144.1 [s, $J(^{119}SnC)$ = 400 Hz, $J(^{117}SnC)$ = 382 Hz, C^1 of SnC_6H_5], 137.2 [s, J(PSn) = 37 Hz, C^2 of SnC_6H_5], 128.6 [s, J(PSn) = 47 Hz, C^3 of SnC_6H_5], 128.8 [s, C^4 of SnC_6H_5], 87.5 [d, J(PC) = 50 Hz, S_2CP], 24.4 [d, J(PC) = 43 Hz, PCH of Pr^i], 17.76 [d, J(PC) = 3 Hz, CH_3 of Pr^i]. Anal. Found: C, 45.37; H, 4.21. Calcd for $C_{34}H_{36}MnMoO_6PS_2Sn$: C, 45.11; H, 4.01.

[8] *Crystal Data for compound **3b**:* $C_{34}H_{36}MnMoO_6PS_2Sn$, M_r = 905.32, triclinic, space group $P\bar{1}$, a = 10.720(2) Å, b = 11.000(2) Å c = 18.363(7) Å, α = 76.67(2)°, β = 82.04(2)°, γ = 61.72(2)°, V = 1854.4(8) Å^3, D_c = 1.62 g cm^{-3}, Z = 2, $F(000)$ = 904, λ(Mo Kα) = 0.710 73 Å, μ(Mo Kα) = 15.09 cm^{-1}, room temperature yellow-orange prismatic crystal (0.13 × 0.13 × 0.1 mm), Enraf-Nonius CAD4 diffractometer, ω–2θ scan technique, 6522 reflections measured ($0 \le \theta \le 25°$), 4722 ($I \ge 3\sigma(I)$) used in the refinement, heavy atoms located from a Patterson synthesis and the remaining non-H atoms by DIRDIF.[9] Full-matrix least-squares refinements were made with SHELX76.[10] After isotropic refinement, an additional absorption correction was applied with DIFABS[11] (correction factors: minimum 0.88, maximum 1.18). All non-H atoms were refined anisotropically. H atoms were geometrically placed, and a common isotropic temperature factor was refined: number of parameters 416, R = 0.029 (R_w = 0.030).

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isolate and characterize those anions have been fruitless so far, due to their high reactivity.

Additonal work is now in progress to explore the chemistry of anions **2** toward other electrophiles.

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Supplementary Material Available: Complete tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for the structure of **3b** (5 pages). Ordering information is given on any current masthead page. A list of structure factor amplitudes is available from the authors.

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