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Domination of Electronic Factors in the Selective Metal to Carbon Bond Formation in Binuclear Manganese−Molybdenum Complexes with S_2CPR_3 Bridges

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Summary: Reactions of the heterodinuclear anion $[MnMo(CO)_6(\mu\text{-}S_2CPPr^i_3)]^-$ *(**2**) with PhSeI and* Ph_2PCl *produce the hexacarbonyls* $[MnMo(CO)_6(\mu\text{-}SePh)(\mu\text{-}S_2CPPr^i_3)]$ *(**4**; monoclinic, space group* $P2_1/n$, $a = 10.334(2)$ Å, $b = 12.901(3)$ Å, $c = 20.367(3)$ Å, $\beta = 96.15(1)°$, $V = 2700(1)$ Å^3, $Z = 4$, $R = 0.028$, $R_w = 0.027$ *for 2886 reflections) and* $[MnMo(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}S_2CPPr^i_3)]$ *(**5**), which does not have an Mn−Mo bond and in which the central carbon of* $S_2CPPr^i_3$ *is bonded to Mo. On standing in solution, hexacarbonyl **5** loses CO to afford the pentacarbonyl* $[MnMo(CO)_5(\mu\text{-}PPh_2)(\mu\text{-}S_2CPPr^i_3)]$ *(**6**; monoclinic, space group* $P2_1/n$, $a = 10.413(2)$ Å, $b = 13.734(4)$ Å, $c = 21.761(8)$ Å, $\beta = 101.01(2)°$, $V = 3055(2)$ Å^3, $Z = 4$, $R = 0.045$, $R_w = 0.045$ *for 2464 reflections), which contains a direct Mn−Mo bond and in which the central carbon of* $S_2CPPr^i_3$ *is bonded to Mn. An analysis of the structures of **4**−**6** shows that the rearrangement of* S_2CPR_3 *is induced by electronic effects. Thus, a change in the electron distribution within the heterobimetallic complex (as it occurs in the reaction from **5** to **6**) forces the central carbon of* S_2CPR_3 *to migrate to the metal with the lowest oxidation number.*

Heterobimetallic complexes are the subject of continuing attention, mainly because it is expected that the association of two different metals may induce a kind of reactivity qualitatively different from that of related homonuclear compounds.[1] Particularly interesting in organometallic chemistry are the reactions of metal−carbon bond formation and cleavage. Although the initial interest was stimulated by the potential catalytic applications, the more recent use of transition-metal complexes in the synthesis of organic molecules makes it desirable to obtain experimental information about the differential behavior of metal−ligand fragments. In this paper we report the preparation of heterobinuclear complexes in which manganese and molybdenum are held together by a $\mu\text{-}\eta^3{:}\eta^2\text{-}S_2CPPr^i_3$ ligand of 8 e, and by an additional bridge of 3 e (phenylselenyl or diphenylphosphide). The spectroscopic data available, in addition to the X-ray determinations of two derivatives, show that the changes of oxidation states within the bimetallic system promote the rearrangement of the S_2CPR_3 ligand, involving the cleavage, and subsequent formation, of a metal−carbon bond.

We have recently reported that the reduction of compounds $[MnMo(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)]$ (**1**) with Na[Hg] in THF produces the highly reactive, heterobinuclear anions $[MnMo(CO)_6(\mu\text{-}S_2CPR_3)]^-$ (**2**) which, upon reaction with $ClSnPh_3$, afford the neutral derivatives $[MnMo(SnPh_3)(CO)_6(\mu\text{-}S_2CPR_3)]$ (**3**) (see Scheme 1).[2] In this reaction, we observed a change in the coordination mode of the S_2CPR_3 ligand: its central carbon was initially bonded to molybdenum in the starting **1**, while in the final product **3** it is bonded to manganese. We have proposed an explanation to account for the migration of the central carbon of the S_2CPR_3 ligand: it prefers to bind the metal atom with the lower oxidation number. Such a hypothesis is consistent with our previous observations of the selective formation of a bond between a metal atom and the central carbon of S_2CPR_3 in several families of binuclear complexes containing two metals in different oxidation states.[3−5] In the production of **3**, the argument of the oxidation numbers was not conclusive since the bulkiness of the $SnPh_3$ group could also influence the rearrangement of the S_2CPR_3 bridge.[2] In the course of a systematic exploration of the reactivity of anionic compounds **2**, we have found experimental evidence which strongly supports the argument based on the oxidation numbers. Thus, reaction of anion **2** with PhSeI at −78 °C affords a red solution from which, after workup, the hexacarbonyl $[MnMo(CO)_6(\mu\text{-}SePh)(\mu\text{-}S_2CPPr^i_3)]$ (**4** in Scheme 1) is obtained as red crystals.[6] Analytical and spectroscopic data,[7] and an X-ray determination (Figure 1),[8] showed that **4** contains a bridging $S_2CPPr^i_3$ ligand which is bonded as an η^2(S,S′) chelate

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[6] A solution of **2** (ca. 0.25 mmol)[2] in THF (20 mL) was transferred by cannula to a cooled (−78 °C) solution of PhSeI (0.071 g, 0.25 mmol) in THF (5 mL). The mixture was warmed to room temperature with stirring. The solvent was evaporated in vacuo, and the residue was taken up in CH_2Cl_2 and this solution filtered (alumina, activity III, 1 × 10 cm column). Hexane (10 mL) was added to the filtrate. Slow concentration gave red crystals of **4** (0.15 g, 82%). Similar reaction between **2** (0.25 mmol) and Ph_2PCl (45 μL, 0.25 mmol) gave hexacarbonyl **5** (0.14 g, 76%) as brown microcrystals. Heating a green solution of **5** (0.14 g, 0.19 mmol) in CH_2Cl_2 (10 mL) at reflux temperature afforded a red solution which was concentrated to ca. 2 mL, layered with hexane, and left to stand for 2 days in a refrigerator (−20 ° C), to afford red-black crystals of **6** (0.11 g, 86%).

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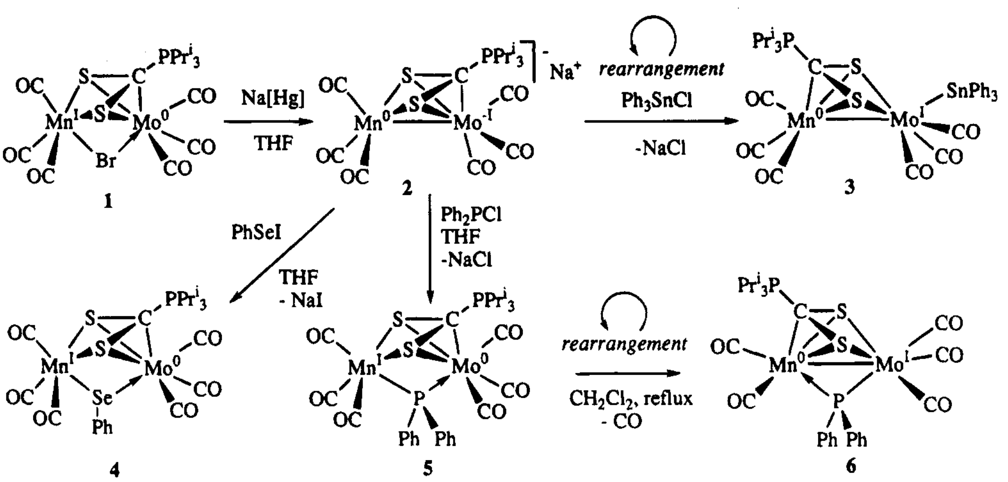
Scheme 1



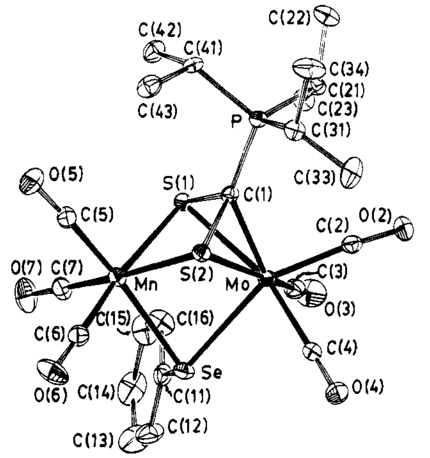


Figure 1. Perspective view (EUCLID package)[15] of [Mn-Mo(CO)$_6$(μ-SePh)(μ-S$_2$CPPr$^i_3$)] (**4**) showing the atom numbering. Selected bond distances (Å) and angles (deg): Mo–Se = 2.655(1), Mn–Se = 2.613(1), Mo–S(1) = 2.499(1), Mo–S(2) = 2.520(1), Mn–S(1) = 2.394(1), Mn–S(2) = 2.409(1), Mo–C(1) = 2.145(5), S(1)–C(1) = 1.793(4), S(2)–C(1) = 1.801(5); Mo–Se–Mn = 75.54(3), C(1)–Mo–Se = 115.8(1), C(2)–Mo–Se = 153.1(2), C(5)–Mn–Se = 175.9(2), S(1)–C(1)–S(2) = 106.1(2).

to manganese and as an η^3(S,C,S′) pseudoallyl group to molybdenum. In that coordination mode the S$_2$CPR$_3$ ligands donate four electrons to each metal.[2–5,9,10] The phenylselenyl bridge, a 3e donor, must donate 1e to Mn and 2e to Mo, and the electron counting in **4** does not require the existence of a direct bond between the metals. Accordingly, the observed intermetallic distance of 3.227(1) Å is slightly longer than that expected for a Mo–Mn bond.[11] All these features clearly relate **4** to the starting μ-Br complex **1**: in both compounds the oxidation numbers are Mo^0 and Mn^I and, consistent with our previous observations,[2–5] the central carbon of S$_2$CPR$_3$ is bonded to Mo^0, which is the metal in the lower oxidation state. The same procedure can be used to prepare complexes containing other bridges of three electrons such as thiolate or phosphide. We are now exploring the synthetic potential of the method, and the results will be reported in due course. However, the structures of the complexes with μ-PR$_2$ ligands are relevant to the discussion. The reaction of anion **2** with Ph$_2$PCl produces the hexacarbonyl **5** which, according to analytical and spectroscopic data,[7] is isostructural with compounds **4** (containing μ-SePh) and **1** (containing μ-Br). The most characteristic spectroscopic feature of **5** is the ^{31}P{^{1}H} NMR spectrum, which consists of two bands: one of them, at δ 47.1 ppm, is attributable to the S$_2$CPr$^i_3$ ligand, while the other, at δ −164.8 ppm corresponds to the phosphide and falls in the range (δ −50 to −200 ppm)[12] observed when the μ-PPh$_2$ ligand acts as a bridge between two metal atoms which are not directly bonded. Complex **5** is stable as a solid, under a nitrogen atmosphere. However, on standing in solution for several hours at room temperature, it slowly evolves CO to produce the pentacarbonyl **6**, which can be isolated and characterized. When **5** is heated in refluxing CH$_2$Cl$_2$, the transformation to **6** is produced in a few minutes. Analytical and spectroscopic data,[7] together with an X-ray determination (Figure 2),[8] showed that **6** contains a diphenylphosphido group which bridges the two metal atoms which are directly bonded (distance Mn–Mo = 2.726(2) Å).[13] The formation of the Mn–Mo bond leads us to consider the PPh$_2$ bridge as a 1e donor to Mo and as a 2e donor to Mn, to

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(7) Selected Data. Correct C, H analyses were obtained for **4–6**. IR spectra (cm^{-1}) were measured from CH$_2$Cl$_2$ solutions. ^{31}P{^{1}H} (121.5 MHz) and ^{13}C{^{1}H} NMR (75.5 MHz) spectra were taken from CD$_2$Cl$_2$ solutions. *J*(P–C) values, in Hz, are given in parentheses. Data for **4**: ν(CO) 2023 m, 2005 s, 1938 s, 1909 m, 1870 m; ^{31}P{^{1}H} NMR δ 46.3; ^{13}C{^{1}H} NMR δ 238.1 [d, ^3J(P–C) = 5 Hz, 2 × MoCO], 216.5 [s (broad), 3 × MnCO], 214.3 [s, MoCO], 136.1–128.0 [SeC$_6$H$_5$], 92.6 [d, ^1J(P–C) = 38 Hz, S$_2$CP], 23.3 [d, ^1J(P–C) = 42 Hz, CH of Pr^i], 17.8 [d, ^2J(P–C) = 3 Hz, CH$_3$ of Pr^i]. Data for **5**: ν(CO) 2012 w, 1993 s, 1926 s, 1905 m, 1868 m; ^{31}P{^{1}H} NMR δ 47.1 (S$_2$CP), −164.8 (μ-*P*Ph$_2$). Data for **6**: ν (CO) 1982 m, 1934 s, 1921 (sh), 1882 s, 1866 (sh); ^{31}P{^{1}H} NMR δ 43.0 (S$_2$CP), 253.1 (μ-*P*Ph$_2$); ^{13}C{^{1}H} NMR δ 229.2 [s (br), 2 × MnCO], 223.8 [d, ^2J(P–C) = 13 Hz, 3 × MoCO], 143.1–127.7 [P(C$_6$H$_5$)$_2$], 99.7 [d, ^1J(P–C) = 49 Hz, S$_2$CP], 23.7 [d, ^1J(P–C) = 42 Hz, CH of Pr^i], 17.8 [d, ^2J(P–C) = 3 Hz, CH$_3$ of Pr^i].

(8) Crystal Data for **4**: C$_{22}$H$_{26}$MnMoO$_6$PS$_2$Se, M_r = 711.38, monoclinic, space group $P2_1/n$, a = 10.334(2) Å, b = 12.901(3) Å, c = 20.367(3) Å, β = 96.15(1)°, V = 2700(1) Å^3, Z = 4. A total of 308 parameters were refined to R = 0.028 (R_w = 0.027) for 2886 reflections with $I \geq 3\sigma(I)$. Crystal Data for **6**: C$_{27}$H$_{31}$MnMoO$_5$P$_2$S$_2$, M_r = 712.48, monoclinic, space group $P2_1/n$, a = 10.413(2) Å, b = 13.734(4) Å, c = 21.761(8) Å, β = 101.01(2)°, V = 3055(2) Å^3, Z = 4. A total of 344 parameters were refined to R = 0.045 (R_w = 0.045) for 2464 reflections with $I \geq 3\sigma(I)$.

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(11) Distances as long as 3.190(2) Å have been observed in compounds in which a direct Mn–Mo bond is assumed. See, for example: Horton, A. D.; Mays, M. J.; Adatia, T.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1987**, 1683.

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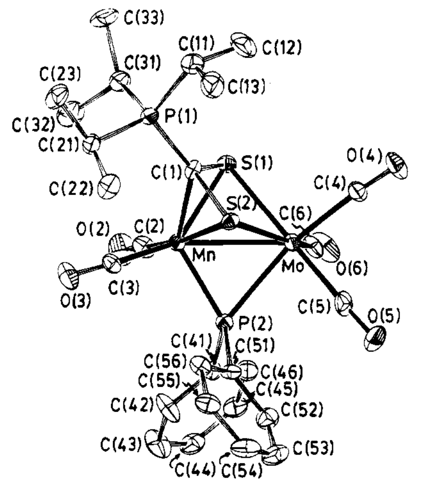

Figure 2. Perspective view (EUCLID package)[15] of [MnMo(CO)$_5$(μ-PPh$_2$)(μ-S$_2$CPPr$^i_3$)] (**6**) showing the atom numbering. Selected bond distances (Å) and angles (deg): Mo–Mn = 2.726(2), Mo–P(2) = 2.485(3), Mn–P(2) = 2.216(3), Mo–S(1) = 2.452(3), Mo–S(2) = 2.584(2), Mn–S(1) = 2.274(3), Mn–S(2) = 2.367(3), Mn–C(1) = 2.052(9), S(1)–C(1) = 1.787(8), S(2)–C(1) = 1.765(9); Mo–P(2)–Mn = 70.6(1), C(1)–Mn–P(2) = 131.8(3), C(4)–Mo–P(2) = 164.4(3), S(1)–C(1)–S(2) = 106.6(5).

result in an 18e count for each metal. This leads to the assignment of oxidation states Mn^0 and Mo^I and, as can be seen in Figure 2, the S$_2$CPPr$^i_3$ ligand has rearranged its coordination mode: the central carbon has migrated from molybdenum to manganese, in agreement with our predictions. It can be seen in Figures 1 and 2 that, in the structures of **4**–**6**, the PhSe or Ph$_2$P bridges are placed in nearly symmetrical positions between the two metals, at opposite sides of the molecule with respect to the S$_2$CPPr$^i_3$ ligand. Therefore, the PhSe or Ph$_2$P bridges cannot induce any significant steric effect on the rearrangement of the S$_2$CPPr$^i_3$ ligand, which appears to be motivated by purely electronic factors. In previous reports of the synthesis of heterobinuclear complexes from two mononuclear blocks, we have shown that the preference of the central carbon of S$_2$CPPr$^i_3$ to bind the metal in the lower oxidation state is able to direct the specific formation of the preferred isomer of the final product. The reactions described here demonstrate that such preference is due to electronic factors and that it is strong enough to induce the migration of the central carbon from one metal to another when a change in the electron distribution within the molecule leads to a change in the oxidation states of the metals. Our explanation cannot be applied when the oxidation numbers in both metals are the same. From orbital overlap arguments, supported by EHMO calculations, it has been predicted that the central carbon of the S$_2$CPR$_3$ ligand would bind the metal atom which offered the more diffuse orbitals: smaller exponents mean more diffuse orbitals. In this case it is molybdenum (smaller exponents) which offers the more diffuse[14] orbitals. Since at the EHMO level the values of the exponents to be used are the same for all Mn–Mo complexes depicted in Scheme 1, the argument offered in ref 14 predicts correctly for compound **1** and for its isostructural homologues **4** and **5** but fails for compounds **3** and **6**. In our opinion, the observed preferences might be a balance between several electronic factors, including the diffuseness of the orbitals and the electron richness of the fragments involved. When the difference in electron richness is so high as to permit the assignment of different oxidation numbers to the metals, this factor overrides the other effects and becomes discriminating. Otherwise, when the oxidation states are the same in both metals, a more detailed study seems to be necessary.

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Supplementary Material Available: Tables of all atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and crystal data and refinement details for the structures of **4** and **6** (11 pages). Ordering information is given on any current masthead page.

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[13] In fact, the distance Mn–Mo of 2.726(2) Å is quite short even for a Mn–Mo bond of order 1. There is only one report of a shorter Mn–Mo distance: 2.680(1) Å in [CpMoMn{μ-CHCHCH$_2$CHPPh$_2$}(CO)$_4$], for which has been proposed some degree of multiple bonding between the metals. See: Caffyn, A. J. M.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1991**, 2349.

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