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Novel heterobimetallic complexes with $S_2CPR_3(\kappa\text{-}S,S')$-$(\kappa\text{-}S,C,S')$ bridges. X-Ray structure of $[MnMo(CO)_6(\mu\text{-}Br)$-$(\mu\text{-}S_2CP^iPr_3)]$

Daniel Miguel, Julio A. Pérez-Martínez, Víctor Riera*
Departamento de Quimica Organometálica, Universidad de Oviedo, 33071 Oviedo (Spain)

Santiago García-Granda
Departamento de Quimica Física y Analítica, Universidad de Oviedo, 33071 Oviedo (Spain)

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Abstract

Reaction of *fac*-$[Mn(CO)_3(S_2CPR_3)(Br)]$ with $[Mo(CO)_3(NCMe)_3]$ produces a member of a novel class of heterodinuclear complex $[MnMo(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)]$ (R = Cy, ^{i}Pr), which contains S_2CPR_3 bridging ligands, acting as an $(\kappa S,S')$ chelate towards Mn, and as an $(\kappa\text{-}S,C,S')$ pseudoallyl group to Mo, without a direct Mo–Mn bond. One carbonyl group in $[MnMo(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)]$ can be easily displaced at room temperature by neutral ligands such as PEt_3 and $P(OMe)_3$, affording pentacarbonyl complexes, $[MnMo(CO)_5(L)(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)]$.

Trialkylphosphine-carbon disulphide adducts, S_2CPR_3, have been used as ligands for a long time. However, despite the great number of complexes prepared, only a few cases are known containing S_2CPR_3 as bridging ligands [1–9]. We have reported recently the preparation and characterisation of the first examples of S_2CPR_3 acting as $(\kappa\text{-}S,S')$, $(\kappa\text{-}S,C,S')$ bridges across a Mn–Mn or a Mn–Re bond [6,7]. Here we wish to report a facile, high yield synthesis of a new class of hetero-dinuclear complex containing $(\kappa\text{-}S,S')$, $(\kappa\text{-}S,C,S')$ S_2CPR_3 bridges between Mn^I and Mo^0 not directly bonded by using the (S,C,S,Br) donor set of $[Mn(CO)_3(S_2CPR_3)(Br)]$ as a tripod ligand donating 6 electrons to Mo.

Compounds *fac*-$[Mn(CO)_3(S_2CPR_3)(Br)]$ (R = Cy, **1a**; ^{i}Pr, **1b**) [10] react with $[Mo(CO)_3(NCMe)_3]$ in THF at room temperature to give purple-red solutions from which air-stable, deep red crystalline solids of formula $[MnMo(CO)_6(Br)(S_2CPR_3)]$ (R = Cy, **2a**; ^{i}Pr, **2b**) can be isolated in virtually quantitative yield. On the bases of analytical and spectroscopic data it was not possible to fully establish the structure of the complexes, so an X-ray structure determination was carried out on a crystal of **2b** (see below). The molecule (Fig. 1) can be described as containing two *fac*-$M(CO)_3$ units held together by a bridging bromide and a S_2CPR_3 bridging ligand which is bonded as $(\kappa\text{-}S,S')$ to manganese, and as $(\kappa\text{-}S,C,S')$ pseudoallyl to

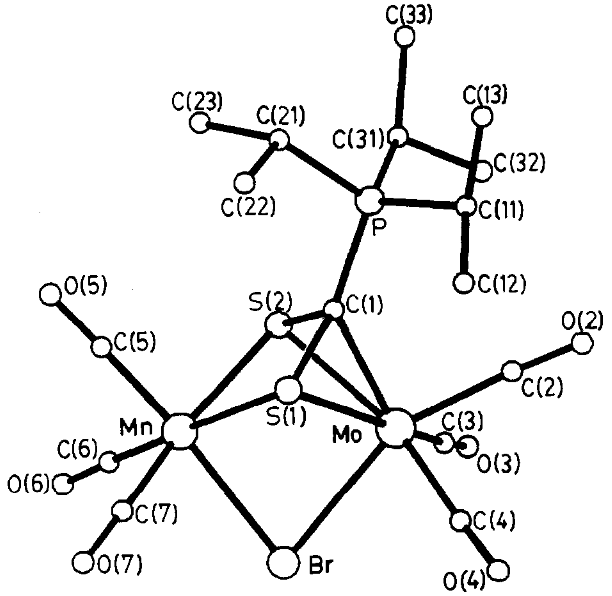
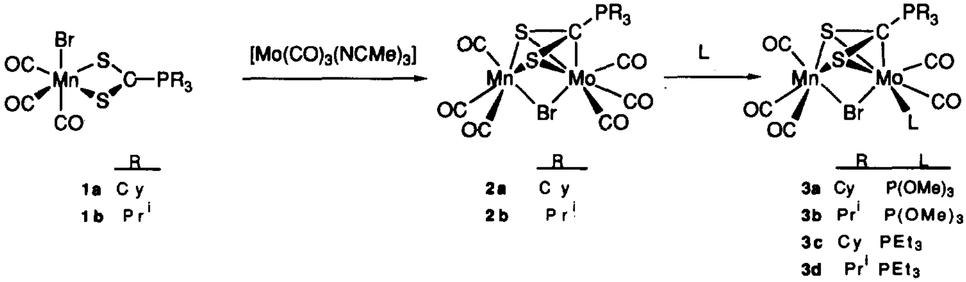


Fig. 1. Perspective view of the molecule of **2b**, showing the atom numbering. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (**3**): Mo–Br 2.696(1), Mn–Br 2.657(1), Mo–S(1) 2.513(1), Mo–S(2) 2.506(1), Mo–C(1) 2.138(5), Mn–S(1) 2.387(2), Mn–S(2) 2.403(2), C(1)–P 1.802(5), distances Mo–C(carbonyl) range from 1.951(6) to 2.028(7), distances Mn–C(carbonyl) from 1.786(6) to 1.815(6). Mn–Br–Mo 74.40(1), S(1)–Mo–Br 87.20(1), S(2)–Mo–Br 87.10(1), S(1)–Mn–Br 90.70(1), S(2)–Mn–Br 90.10(1), Mn–S(1)–Mo 82.60(1), Mn–S(2)–Mo 82.40(1), S(2)–C(1)–S(1) 106.9(3), C(3)–Mo–C(2) 81.0(2), C(4)–Mo–C(2) 78.3(2), C(4)–Mo–C(3) 103.8(2), angles C(carbonyl)–Mn–C(carbonyl) range from 90.1(3) to 91.5(3).

molybdenum. The spectroscopic data obtained from solutions of **2a** and **2b** are consistent with the solid state structure.

Although η^2,η^3 coordination had already been found in the Mn–Mn [6] and Mn–Re [7] complexes mentioned above, **2a,b** are the first examples containing this type of bridging bonding mode in molecules without a direct metal-to-metal bond. It is remarkable that, in the reaction between $[Mo(CO)_3(NCMe)_3]$ and **1a** (or **1b**), the binuclear **2a** (or **2b**) is formed as the only product, as shown by the $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixtures. The (κ-*S*,*C*,*S'*) pseudoallyl coordination of the S_2CPR_3 ligand has only been found to date in complexes of molybdenum [2,13] and manganese [6,7], both in formal oxidation state zero. Thus, the S_2CPR_3 might be expected to be coordinated pseudoallyl-fashion to either Mn or Mo in **2a,b**. Interestingly, the selective formation of the product with a Mo–C bond suggest a stronger preference for molybdenum attachment to the central carbon of the S_2CPR_3 ligand than for manganese. 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]. In **2a,b** the coordination of the S_2C pseudoallyl system to Mo may be rationalised assuming the formal oxidation states Mn^I and Mo^0. That is consistent with the fact that we have not found this type of η^3 coordination in Mn^I complexes. If we assume 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 [6,7],



Scheme 1

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 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 $[(\eta^5\text{-}C_5H_5)(CO)_2Mo\{\mu\text{-}Ag(PPh_3)\}(\mu\text{-}PPh_2)Mn(CO)_4]$ [3.190(2) Å] [11]. On the other hand, the Mo–Br [2.669(1) Å] and Mn–Br [2.657(1) Å] are close to the mean values found in Mn and Mo complexes containing bromide bridges [12]. The slight asymmetry of the M–Br distances in **2b** may reflect the difference in covalent radii of the metals.

Treatment of **2a,b** with a molar equivalent of a monodentate phosphorus ligand, L, at room temperature displaces one carbonyl group, leading to the pentacarbonyl complexes $[MnMo(CO)_5(L)(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)]$ (**3a–d**) (see Scheme 1). The analytical and spectroscopic data of the products (see below) support the structure proposed for them in Scheme 1, in which one carbonyl group of the molybdenum atom has been replaced by the entering ligand L. According to the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra, the bridging disposition of the S_2CPR_3 ligand remains unchanged after the reactions leading from **2a,b** to **3a–d**, consistent with a reasonable stability of the bridge.

Work is now being carried out to explore the potential of S_2CPR_3 to bridge other metal–ligand fragments.

Selected spectroscopic data. IR, ν(CO) (CH_2Cl_2, cm^{-1}), **2a**: 2036m, 2016vs, 1950s, 1913m, 1863m. **2b**: 2037m, 2017vs, 1951s, 1914m, 1867m. **3a**: 2022s, 1936vs, 1907m, 1827m. **3b**: 2023s, 1937vs, 1909m, 1828m. **3c**: 2020s, 1932vs, 1909m, 1801m. **3d**: 2021s, 1933vs, 1910m, 1803m.

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz, δ, ppm to high frequencies from external 85% H_3PO_4), **2a**: 34.85 s. **2b**: 46.82 s. **3a**: 158.63 [s, $P(OMe)_3$], 34.29 [s, S_2CP]. **3b**: 158.14 [s, $P(OMe)_3$], 45.45 [s, S_2CP]. **3c**: 34.24 [s, S_2CP], 25.19 [s, PEt_3]. **3d**: 45.22 [s, S_2CP], 25.61 [s, PEt_3].

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz, δ, ppm to high frequencies from internal TMS), **2a**: 242.0 [d, J(PC) 5 Hz, 2 MoCO], 223.7 [s, br, 2 MnCO], 217.1 [s, br, MnCO], 216.6 [s, MoCO], 96.2 [d, J(PC) 39 Hz, S_2CP]. **2b**: 242.2 [d, J(PC) 6 Hz, 2 MoCO], 223.3 [s, br, 2 MnCO], 216.8 [s, br, MnCO], 216.3 [s, MoCO], 95.9 [d, J(PC) 39 Hz, S_2CP]. **3a**: 249.4 [d, J(PC) 27 Hz, MoCO], 228.3 [d, J(PC) 5 Hz, MoCO], 224.5 [s, br, MnCO], 217.1 [s, MnCO], 216.3 [s, MoCO], 91.1 [d, J(PC) 46 Hz, S_2CP]. **3b**: 251.3 [s, br, MoCO], 228.4 [s, MoCO], 227.9 [s, br, MnCO], 218.6 [s, MnCO], 216.4 [s, MoCO], 90.3 [d, J(PC) 43 Hz, S_2CP]. **3c**: 254.4 [d of d, J(PC) 22 and 7 Hz, MoCO], 231.0 [d, J(PC) 6 Hz, MoCO], 224.1 [s, br, MnCO], 217.5 [s, Mn*C*O], 216.7 [s, Mo*C*O], 89.6 [d, *J*(PC) 42 Hz, S_2CP]. **33d**: 254.4 [d, *J*(PC) 22 Hz, Mo*C*O], 229.4 [s, Mo*C*O], 223.5 [s, br, Mn*C*O], 216.9 [s, Mn*C*O], 215.8 [s, Mo*C*O], 88.7 [d, *J*(PC) 44 Hz, S_2CP].

Crystal and refinement data for compound **2b**: $C_{16}H_{21}BrMnMoO_6PS_2$, M = 635.21, monoclinic, space group $P2_1/c$, $a = 9.065(1)$, $b = 19.579(5)$, $c = 13.398(3)$ Å, $\beta = 106.67(2)°$, $V = 2293(1)$ Å^3, $Z = 4$, $D_c = 1.84$ g cm^{-3}, $F(000)$ 1256, λ(Mo-K_α) 0.71073 Å, $\mu = 30.61$ cm^{-1}, 200 K. Dark red prismatic crystal (0.25 × 0.2 × 0.13 mm) grown by slow diffusion of hexane into a concentrated solution of the compound in CH_2Cl_2. Intensities were collected on an Enrag Nonius CAD4 diffractometer, using the $\omega-2\theta$ scan technique. 4008 reflections were measured in the range $0 \leqslant \theta \leqslant 25°$, 2646 with $I \geqslant 3\sigma(I)$ were used in the refinement. Mo and Mn atoms were located from a Patterson synthesis, and the remaining non-hydrogen atoms from DIRDIF [14]. An absorption correction was applied with DIFABS [15]. Full-matrix least squares refinement was made with SHELX76 [16]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were geometrically positioned, and were given an overall isotropic temperature factor which was refined. Final $R = 0.032$ ($Rw = 0.033$). Total number of parameters 263.

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