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Preliminary communication

Synthesis and reactivity of the unsaturated dimolybdenum compound $[\text{Mo}_2(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_2]$. Crystal structure of $[\text{Mo}_2(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-I})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_2][\text{TlI}_4] \cdot \text{CH}_2\text{Cl}_2$

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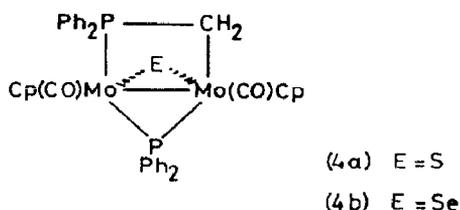
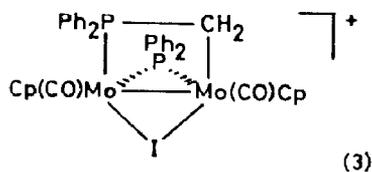
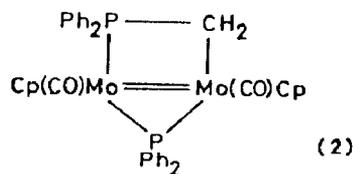
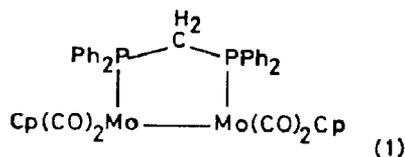
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Abstract

The unsaturated compound $[\text{Mo}_2\text{Cp}_2(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_2]$ (Cp = $\eta\text{-C}_5\text{H}_5$) has been prepared by heating $[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]$ in tetrahydrofuran at 60 °C. This compound reacts with elemental E (E = S, Se) to yield $[\text{Mo}_2\text{Cp}_2(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\mu\text{-E})(\text{CO})_2]$, and with iodine to give the cation $[\text{Mo}_2\text{Cp}_2(\mu\text{-I})(\mu\text{-CH}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_2]^+$ the crystal structure of which as the $[\text{TlI}_4]^-$ salt has been determined by an X-ray diffraction study.

The use of bidentate phosphorus ligands of the type A_2PXPA_2 (A = R, OR; X = O, NR', CH₂) in holding transition-metal atoms together is now well established [1]. The ligand $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) is probably the most commonly used for this purpose [2], but P–C bond cleavage can occur in this ligand and related ligands (tertiary phosphines in general), usually at moderately high temperatures (80–100 °C), and these processes have been shown to play a relevant role in deactivation of phosphorus-containing transition metal catalysts [2,3].

During a general study of the synthesis and reactivity of dppm-bridged dimolybdenum compounds we found that a clean P–C(sp³) bond cleavage in this ligand can be modily brought about by gentle heating at 60 °C of a tetrahydrofuran (thf) solution of $[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\mu\text{-dppm})]$ (1) [4], which gives air-sensitive, brown



[Mo₂Cp₂(μ-CH₂PPh₂)(μ-PPh₂)(CO)₂] (**2**) in 75% yield *. This process is related to those reported for some diphosphine bridged diiron complexes [5], which, however, invariably yielded saturated species.

The unsaturation present in **2** allows for study of a range of reactions under mild conditions. Thus, addition of iodine (Et₂O solution) to an Et₂O solution of **2** at room temperature gives an almost immediate precipitate of the cation [Mo₂Cp₂(μ-I)(μ-CH₂PPh₂)(μ-PPh₂)(CO)₂]⁺ (**3**) as its iodide salt. The structure of this cation was confirmed by an X-ray diffraction study ** on its [TlI₄]⁻ salt (accidentally formed upon treatment of the iodide salt with TlPF₆ in CH₂Cl₂ and crystallization from CH₂Cl₂/Et₂O), and is shown in Fig. 1. The Mo-Mo distance, 3.001(2) Å, is consistent with the presence of a single metal-metal bond (for example, 3.008(2) Å in *cis*-[Mo₂Cp₂(μ-S^tBu)₂(CO)₄]²⁺ [6]) and so the cation can be viewed as resulting

* Selected spectroscopic data. NMR chemical shifts in ppm relative to internal TMS (¹H, ¹³C) or external 85% H₃PO₄ in H₂O (³¹P), coupling constants in Hz; ν(CO) in cm⁻¹:

Compound **2**: ν(CO)(thf): 1835msh and 1807sbr; ¹H(C₆D₆): δ 4.81 (s, Cp, 5H), 4.75(s, Cp, 5H), 2.61 (dd, *J*(HH) 11, *J*(PH) 4, CH₂, 1H) and 1.99(ddd, *J*(HH) 11, *J*(PH) 17 and 3, CH₂, 1H); ³¹P{¹H}(C₆D₆): δ 92.1(d, *J*(PP) 16, μ-PPh₂) and 46.8(d, μ-PPh₂CH₂); ¹³C{¹H}(C₆D₆): δ 233.0 (t, *J*(PC) 14, MoCO), 231.6(dd, *J*(PC) 18 and 3, MoCO) and 1.0(d, *J*(PC) 8, MoCH₂).

Compound **3** (iodide salt): ν(CO)(CH₂Cl₂): 1960s and 1903vs; ³¹P{¹H}(CDCl₃): δ 151.4(d, *J*(PP) 14, μ-PPh₂) and -1.1(d, μ-PPh₂CH₂). ¹³C{¹H}(thf/C₆D₆): δ -21.4(br, MoCH₂).

Compound **4a**: ν(CO)(CH₂Cl₂): 1899s and 1846vs; ¹H(CDCl₃): δ 5.20(s, Cp, 5H), 4.44(t, *J*(PH) 2, Go, 5H) 1.82(dd, *J*(HH) 10, *J*(PH) 14, CH₂, 1H) and 1.66(ddd, *J*(PH) 4 and 2, CH₂, 1H); ³¹P{¹H}(CDCl₃): δ 90.7(d, *J*(PP) 60, μ-PPh₂) and 27.6(d, μ-PPh₂CH₂). Compound **4b**: ν(CO)(CH₂Cl₂): 1885s and 1842vs; ³¹P{¹H}(C₆D₆): δ 96.2(d, *J*(PP) 50, *J*(⁷⁷Se-³¹P) 25, μ-PPh₂) and 21.5(d, *J*(Se-P) 39, μ-PPh₂CH₂); ¹³C{¹H}(CH₂Cl₂/C₆D₆): δ -2.9(d, *J*(PC) 26, MoCH₂).

** Crystal data for **3**: C₃₇H₃₂I₅O₂P₂TlMo₂·CH₂Cl₂, *M* = 1686.5, monoclinic, space group *Cc*, *a* 29.973(9), *b* 12.678(2), *c* 15.579(4) Å, β 129.92(2)°, *V* 4540(2) Å³, *Z* 4, *D_c* 2.03 g cm⁻³, μ 40.5 cm⁻¹, *F*(000) = 3088. Final *R* = 0.043 (*R_w* = 0.055) for 3787 independent absorption corrected data (1 < θ < 25°, *F* ≥ 3σ(*F*)) with Mo *K_α* radiation and graphite monochromator, collected at room temperature on a Nonius CAD4 (ω-2θ mode). The structure was solved by direct methods and subsequent Fourier maps. Least squares refinements were in three blocks (469 parameters). Hydrogen atoms were placed at calculated positions and given an overall isotropic thermal parameter.

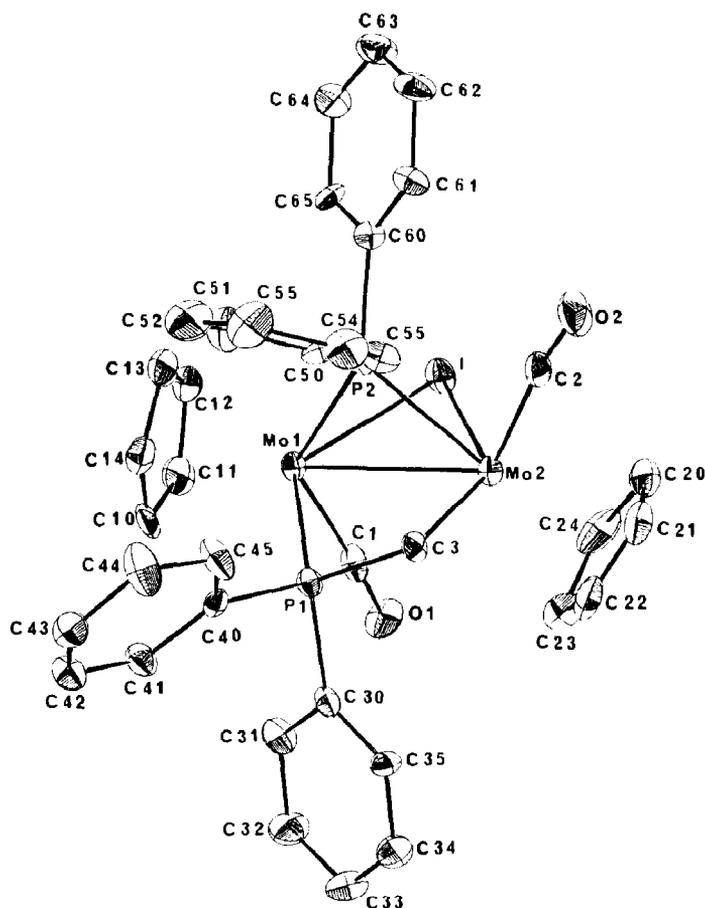


Fig. 1. Structure of the cation **3**. Selected bond distances (Å): Mo(1)–Mo(2) 3.001(2), Mo(1)–I 2.801(1), Mo(2)–I 2.804(2), Mo(1)–P(2) 2.459(4), Mo(2)–P(2) 2.529(4), Mo(1)–P(1) 2.468(4), P(1)–C(3) 1.81(1), Mo(2)–C(3) 2.25(1), Mo(1)–C(1) 2.00(2), Mo(2)–C(2) 1.93(2). Bond angles (°): P(2)–Mo(1)–P(1) 84.8(1), P(1)–Mo(1)–I 126.09(9), C(3)–Mo(2)–P(2) 77.5(4), C(3)–Mo(2)–I 136.1(3), C(3)–Mo(2)–C(2) 98.7(7), and C(2)–Mo(2)–P(2) 68.8(5).

from the addition of “I⁺” to the formal double Mo–Mo bond present in the parent compound **2**. The diphenylphosphinomethyl ligand, the bridging iodide, and the metal atoms define a rather flat, distorted pentagon, whereas the bridging phosphido ligand lies nearly perpendicular to that plane. Surprisingly, the environment around Mo(2) (Fig. 1) is far from the classical “four legged piano stool” arrangement usual for MoCpL₄ complexes (L = monodentate ligand).

Compound **2** reacts with elemental E (E = S, 10 min, Se, 1 h) at room temperature in toluene to give the red-brown compounds [Mo₂Cp₂(μ-CH₂PPh₂)(μ-PPh₂)(μ-E)(CO)₂] (**4a**, **4b**) (E = S (**4a**), Se (**4b**)), which seem to retain a pseudo-*trans* arrangement of the Ph₂PCH₂ and PPh₂ bridges, as indicated by their spectroscopic data. *

In the reactions discussed, compound **2** exhibits definite nucleophilic behaviour. However, we have found that it also shows some electrophilic character, and we are currently examining the reactions of this complex with a wide range of both nucleophilic and electrophilic reagents.

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