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## Preliminary Communication

### Transition-metal derivatives of the cyclopentadienylphosphine ligands

#### IX \*. Molecular structure of [Mo<sub>2</sub>(μ-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub>] and first account of its redox properties

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#### Abstract

A new route for the preparation of the homobimetallic complex [Mo<sub>2</sub>(μ-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub>] in good yield (90%) is described and its X-ray structure is reported, together with some spectroscopic data and its redox properties.

Numerous heterodifunctional phosphines, including, for example, phosphines with an oxygen function [1], aminophosphines [2], phosphine functionalized dipodal macrocycles [3], may be used for synthesizing homo- and hetero-dimetallic complexes. Cyclopentadienylphosphines have recently been of widespread interest as they contain two constituting moieties, *viz.* the cyclopentadienyl and phosphine fragments, both suitable for binding to reactive metal species [4–6].

Moreover, from our studies of rhodium dinuclear complexes we elucidated an interesting and specific property of the double-bridge (μ-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub> which provides a very flexible joint between the two molecular moieties. The resultant flexibility appears to be a determining factor of both the chemical and the redox behaviour of these Group 9 bimetallic complexes [6,7].

The recent publication by Duckworth *et al.* [8] of the synthesis and properties of some dinuclear metal-metal bonded complexes of molybdenum and tungsten bridged by the heterodifunctional ligand C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>, prompts us to report some of our results in the same field. These concern mainly the new compound

[Mo<sub>2</sub>(μ-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub>], **1**, which we have prepared [9] from the mononuclear hydride complex [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)(CO)<sub>3</sub>H], **3**, in excellent yield (90%), its molecular structure, and some of its electrochemical properties.

The preparation of **1** is from the tricarbonylcycloheptatriene derivative [Mo(η<sup>6</sup>-C<sub>7</sub>H<sub>8</sub>)(CO)<sub>3</sub>] as starting material which reacts in THF at 70°C with lithium (diphenylphosphino)cyclopentadienide, affording Li[Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)(CO)<sub>3</sub>], **2**. Treatment of a toluene solution of **2** with one molar equivalent of glacial acetic acid at room temperature for 1 h afforded the hydride **3** which has been fully characterized. The hydride solution was then irradiated with a Hg lamp under slow flow of argon. This caused H<sub>2</sub> and CO elimination. The solvent was evaporated and the resulting red powder washed with pentane. Table 1 gives the spectroscopic data for these three complexes.

Brown-red crystals of [Mo<sub>2</sub>(μ-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub>], **1**, suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether in a dichloromethane solution. The molecular structure \* of **1** is shown in Fig. 1, together with some important bond parameters. Our determination confirms the proposal of Duckworth *et al.* [8] based on spectroscopic data and analogous with our previous X-ray determination of the structure of [Rh<sub>2</sub>(μ-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>] [6]. The metal-metal distance (3.2767(5) Å) is slightly longer than that in [Mo<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>6</sub>] (3.235(1) Å), whereas this distance in the singly bridged [Mo<sub>2</sub>(μ-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>5</sub>] (3.255(2) Å) [8] is between these two values.

\* Crystal data for [Mo<sub>2</sub>(μ-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>(CO)<sub>4</sub>], **1**: C<sub>38</sub>H<sub>28</sub>O<sub>4</sub>P<sub>2</sub>Mo<sub>2</sub>, *M* = 802.5, monoclinic, space group *P*2<sub>1</sub>/*n* (non-standard no. 14), *a* = 12.576(1), *b* = 16.101(2), *c* = 16.660(2) Å, β = 96.28(1)°, *V* = 3353(1) Å<sup>3</sup>, *D*<sub>c</sub> = 1.59 g cm<sup>-3</sup>, *Z* = 4, *F*(000) = 1608, λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 8.6 cm<sup>-1</sup>. Brown-red parallelepipeds, crystal dimensions: 0.400 × 0.200 × 0.075 mm. 5260 unique reflexions measured on a CAD4 Enraf-Nonius four-circle diffractometer (3° < 2θ < 48°), corrected for absorption (ψ-scan method) and 3627 with *I* > 3σ(*I*). Structure solved by the Patterson method and refined by full-matrix least-squares techniques, with non-H atoms anisotropic except those of phenyl rings. All H atoms were introduced in calculated positions. The weighting scheme was *w* = [σ<sup>2</sup>(*F*) + 0.0005 *F*<sup>2</sup>]<sup>-1</sup>. The final residuals were *R* = 0.029 and *R*<sub>w</sub> = 0.032. Full lists of atomic coordinates, bond lengths and angles, and temperature factors have been deposited with the Cambridge Crystallographic Data Centre.

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\* For Part VIII, see ref. 9.

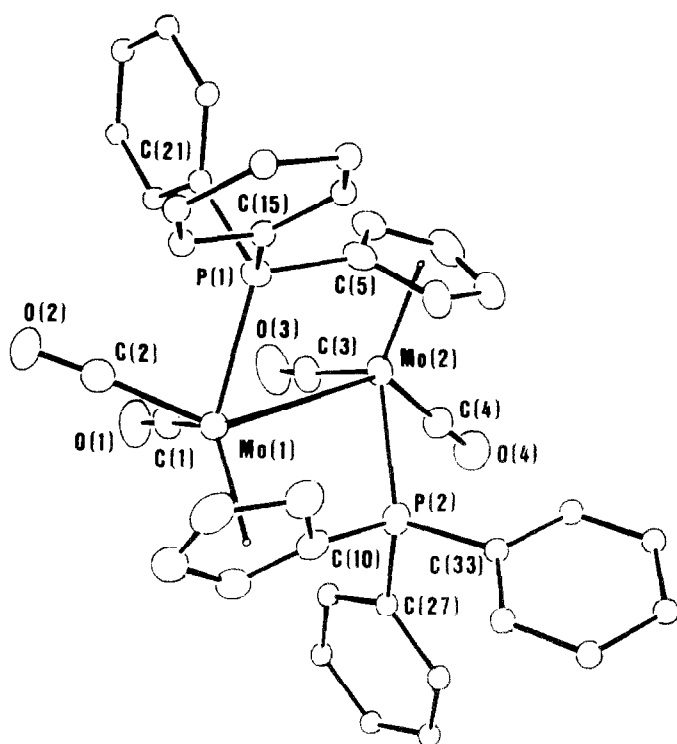


Fig. 1. The molecular structure of  $[\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2(\text{CO})_4]$ , **1**. Bond lengths (Å) and angles ( $^\circ$ ). Mo(1)–Mo(2) = 3.2767(5), Mo(1)–P(1) = 2.404(1), Mo(2)–P(2) = 2.417(1), Mo(1)–Cp(2) = 1.974(5), Mo(2)–Cp(1) = 1.987(5), P(1)–C(5) = 1.797(4), P(2)–C(10) = 1.807(4).  $\langle\text{Mo}-\text{C}(\text{cyclopentadienyl})\rangle = 2.315(5)$ ,  $\langle\text{Mo}-\text{C}(\text{carbonyl})\rangle = 1.941(5)$ ,  $\langle\text{C}(\text{carbonyl})-\text{O}\rangle = 1.152(6)$ ,  $\langle\text{P}-\text{C}(\text{phenyl})\rangle = 1.823(4)$ ,  $\langle\text{C}-\text{C}(\text{cyclopentadienyl})\rangle = 1.409(7)$ ,  $\langle\text{C}-\text{C}(\text{phenyl})\rangle = 1.389(7)$ , C(1)–Mo(1)–C(2) = 78.5(2), C(3)–Mo(2)–C(4) = 77.4(2), C(1)–Mo(1)–P(1) = 107.8(1), C(3)–Mo(2)–P(2) = 108.8(1), C(1)–Mo(1)–Cp(2) = 125.4(2), C(3)–Mo(2)–Cp(1) = 124.0(2), C(2)–Mo(1)–P(1) = 81.4(1), C(4)–Mo(2)–P(2) = 78.9(2), C(2)–Mo(1)–Cp(2) = 116.2(2), C(4)–Mo(2)–Cp(1) = 119.7(2), P(1)–Mo(1)–Cp(2) = 125.8(2), P(2)–Mo(2)–Cp(1) = 126.2(1),  $\langle\text{Mo}-\text{C}(\text{carbonyl})-\text{O}\rangle = 175.4(4)$ ,  $\langle\text{Mo}-\text{P}-\text{C}(\text{cyclopentadienyl})\rangle = 109.0(2)$ ,  $\langle\text{Mo}-\text{P}-\text{C}(\text{phenyl})\rangle = 118.5(1)$ . Cp(1) and Cp(2) are the centroids of cyclopentadienyl rings.

The UV-visible spectrum of **1** in THF [530 nm ( $\epsilon = 340 \text{ l cm}^{-1} \text{ mol}^{-1}$ ), 388 nm ( $\epsilon = 9800 \text{ l cm}^{-1} \text{ mol}^{-1}$ )] is consistent with the presence of a Mo–Mo bond, as inferred in the parent dimolybdenum compound  $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6]$  [512 nm ( $\epsilon = 1720 \text{ l cm}^{-1} \text{ mol}^{-1}$ ), 388 nm ( $\epsilon = 20400 \text{ l cm}^{-1} \text{ mol}^{-1}$ )] [10] and its mass spectrum (DCI/ $\text{NH}_3$ ) shows an isotopic pattern at  $M + 1 = 803$ , characteristic of a dimolybdenum complex.

The electrochemical properties of reduction and oxidation of **1** were determined using various electrochemical techniques in  $\text{CH}_2\text{Cl}_2$  ( $\text{Bu}_4\text{N}$ ,  $\text{ClO}_4$ , 0.1 M). The dinuclear **1** is reduced by an overall two-electron ECE mechanism at  $E_p = -1.67 \text{ V}$  like the previously reported  $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6]$  [11], but its oxidation occurs in two steps: the first, quasi-reversible at  $E_{ox} = 0.48 \text{ V}$ , corresponds to the formation of the monocationic dinuclear which is now under investigation, the second, irreversible, at  $E_p = 0.86 \text{ V}$ , presumably leads to the cleavage of the dinuclear. The occurrence of a monocationic step contrasts with the case of the non-bridged complex and emphasizes the influence of the double bridge ( $\mu\text{-C}_5\text{H}_4\text{PPh}_2$ )<sub>2</sub> as already exemplified by the rhodium analogous complex [7].

## References

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TABLE 1. IR,  $^{31}\text{P}$   $\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectroscopic data for the compounds **1–3**

Products	$\nu(\text{CO})^a$ ( $\text{cm}^{-1}$ )	$\delta(^{31}\text{P})^b$ (ppm)	$\delta(^1\text{H})^b$ (ppm)
$\text{Li}[\text{Mo}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_3]$	1909(vs), 1813 (vs), 1790(s), 1724(s)	–18.2 (s)	7.70 and 7.46 (2m, <i>ortho</i> ), 7.14 (m, <i>meta</i> and <i>para</i> ), 5.5 (s, $\text{C}_5\text{H}_4\text{P}$ )
$[\text{Mo}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\text{CO})_3\text{H}]$	2024(s), 1937(s)	–19.5 (s)	7.70 and 7.45 (2m, <i>ortho</i> ), 7.20 (m, <i>meta</i> and <i>para</i> ), 4.98 ( $\alpha$ , $\text{C}_5\text{H}_4\text{P}$ ), 4.74 ( $\beta$ , $\text{C}_5\text{H}_4\text{P}$ ), –5.26 (H–Mo)
$[\text{Mo}_2(\mu\text{-C}_5\text{H}_4\text{PPh}_2)_2(\text{CO})_4]$	1941(s), 1896(s), 1865(m), 1843(m), 1951(s), 1906(s), 1858(m) <sup>c</sup>	68.2 (s)	7.90 and 7.75 (2m, <i>ortho</i> ), 7.13 (m, <i>meta</i> and <i>para</i> ), 4.89, 4.42, 3.73, 3.15 (4m, $\text{C}_5\text{H}_4\text{P}$ )

<sup>a</sup> Recorded in THF solution. <sup>b</sup> Recorded at 298 K in  $\text{C}_6\text{D}_6$  solution. <sup>c</sup> Recorded in hexadecane solution.

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