Synthesis and characterisation of $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}PH_2)(\mu\text{-}H)]$ (M = Mo, W); a new route to μ-PH_2 complexes involving novel activation of a bridging diphosphorus ligand

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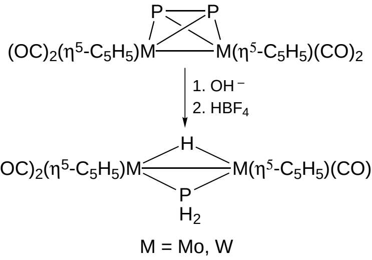
Reaction of the known diphosphorus complexes $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ (M = Mo 1a, W 1b) with M′OH (M′ = Na, K) in thf–water followed by addition of HBF_4 affords the new phosphido complexes $[M_2(\eta^5C_5H_5)_2(CO)_4(\mu\text{-}PH_2)(\mu\text{-}H)]$ (M = Mo 3a, W 3b) in good yield; 3a is the subject of a single-crystal X-ray diffraction study.

The preparation and characterisation of complexes containing naked group 15 ligands has been an active area of research for some years now,[1] although the subsequent reactivity of these complexes has been relatively poorly investigated, being in the main restricted to the coordination of 16-electron fragments to lone pairs present on the main-group fragment.[2] We recently showed with the formation of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_3\{\mu,\eta^3\text{-}PPh_2C(H)SP_2S\}]$ from $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu,\eta^2\text{-}P^2)]$ **1a** the hitherto unsuspected potential of naked P_n ligands as precursors to otherwise inaccessible ligands.[3] We now report that the reaction of $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ (M = Mo **1a**, W **1b**) with M′OH (M′ = Na, K) in thf–H_2O gives the dimetallic anions $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}PH_2)]^-$ (M = Mo **2a**, W **2b**).† Protonation of **2a**,**b** then affords the new phosphido complexes $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}PH_2)(\mu\text{-}H)]$ (M = Mo **3a**, W **3b**) in typically 70–80% yield based on **1a**,**b** (Scheme 1). This new route to μ-PH_2 complexes avoids the potentially hazardous use of PH_3 gas often used in previous syntheses,[4] and to our knowledge there are no previous examples of the preparation of μ-PH_2 complexes from complexes containing naked phosphorus ligands.



Scheme 1

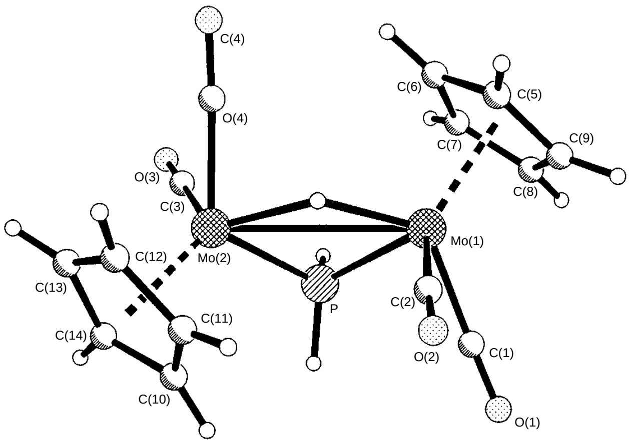


Fig. 1 Molecular structure of **3a**. Selected bond lengths (Å) and angles (°): Mo(1)–Mo(2) 3.2818(9), Mo(1)–P 2.403(2), Mo(2)–P 2.401(2), Mo(1)–P–Mo(2) 86.19(5), P–Mo(1)–Mo(2) 46.88(4), P–Mo(2)–Mo(1) 46.93(4).

Reaction of a solution of **1a** (400 mg, 0.806 mmol), synthesised by the method of Scherer *et al.*,[5] in thf (80 ml)–water (0.2 ml) with a large excess of M′OH pellets at 80 °C affords an air-sensitive purple solution of $[M']^+[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}PH_2)]^-$ **2a**. Filtration through a glass sinter followed by addition of a slight excess of $HBF_4\cdot OEt_2$ and filtration through silica affords **3a** (289 mg, 0.617 mmol, 77%) as the only isolable product. Similar treatment of a solution of **1b** (400 mg, 0.604 mmol) affords **3b** (268 mg, 0.416 mmol, 69%).

The structure of **3a** has been determined by X-ray diffraction analysis.‡ The molecular structure is shown in Fig. 1, and includes selected bond parameters. The spectroscopic data† for **3a** are consistent with this structure. An 18-electron configuration is achieved at each Mo atom only if an Mo–Mo bond is proposed; the metal–metal distance is increased from 3.0406(8) Å in **1a**[5] to 3.2818(9) Å in **3a**, this being slightly longer than the 3.244(1) Å distance observed in the diphenylphosphido analogue $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}PPh_2)(\mu\text{-}H)]$ **4**.[6] The MoHMoP core of the complex is essentially planar. The Mo–P bond distances [av. 2.402(1) Å] are slightly shorter than in **4**; this may reflect the reduced steric bulk of the PH_2 fragment as compared to the PPh_2 fragment.

Both the general applicability of this new, convenient high-yield synthesis of μ-PH_2 complexes and a comparison of their chemistry to that of the well studied μ-PR_2 complexes is in progress.

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Footnotes

† *Selected spectroscopic data*: [IR (ν_{CO}/cm^{-1}) recorded in thf (**2a**, **2b**) or CH_2Cl_2 (**3a**, **3b**) solution; ^1H, ^{13}C and ^{31}P NMR recorded in $CDCl_3$ solution; ^{31}P NMR shifts recorded relative to $P(OMe)_3$ at δ 0.0 with upfield shifts negative; *J* in Hz]. For **2a**: ν_{CO} 1843vs, 1798s; ^1H NMR 4.81 (s, 10 H, C_5H_5), 4.17 (d, 2 H, $^1J_{HP}$ 319, PH_2); ^{31}P NMR −89.7 (s, PH_2). For **2b**: ν_{CO} 1835vs, 1789s; ^1H NMR 4.90 (s, 10 H, C_5H_5), 4.56 (d, 2 H, $^1J_{HP}$ 336, PH_2); ^{31}P NMR −89.7 (s, PH_2, $^1J_{PW}$ 728). For **3a**: ν_{CO} 1940vs, 1875s; ^1H NMR 5.14 (s, 10 H, C_5H_5), 4.82 (d, 2 H, $^1J_{HP}$ 353, PH_2), −12.97 (d, 1 H, $^2J_{HP}$ 39, MoHMo); ^{13}C NMR 90.1 (C_5H_5), 235.4 (s, CO), 240.6 (d, $^2J_{CP}$ 92, CO); ^{31}P NMR −107.3 (s, PH_2); FABMS 468 (M^+); 440, 412, 384 ($M^+ - n$CO, n = 1–3); microanalysis (calculated values in parentheses) C, 35.79 (35.90); H, 2.71 (2.78); P, 6.33 (6.62). For **3b**: ν_{CO} 1929vs, 1861vs; ^1H NMR 5.27 (s, 10 H, C_5H_5), 4.90 (d, 2 H, $^1J_{HP}$ 373, PH_2), −15.52 (d, 1 H, $^2J_{HP}$ 28, $^1J_{HW}$ 28.4, WHW); ^{31}P NMR −180.7 (s, $^1J_{PW}$ 508); FABMS 644 (M^+); microanalysis (calculated values in parentheses) C, 25.57 (26.09); H, 2.17 (2.02); P, 4.40 (4.73).

‡ *Crystal data*: suitable crystals of **3a** were grown by diffusion of hexane into a concentrated dichloromethane solution at room temp. $C_{14}H_{13}Mo_2O_4P$, M = 468.09, monoclinic, space group $P2_1/n$, a = 9.071(2), b = 15.667(3), c = 11.010(2) Å, β = 97.32(2)°, U = 1551.9(6) Å^3 (by least-squares refinement on diffractometer angles from 25 centred reflections $25 < 2\theta < 30°$), T = 150 K, graphite-monochromated Mo-Kα radiation, λ = 0.710 73 Å, Z = 4, D_c = 2.003 Mg m^{-3}, $F(000)$ = 912, orange block 0.20 × 0.18 × 0.17 mm, μ(Mo-Kα) = 1.729 mm^{-1}, semi-empirical absorption correction based on ψ-scans, relative transmission 0.940–0.997, Rigaku AFC7R diffractometer, ω–2θ scans, data collection range $5.20 < 2\theta < 55.0°$, $+h$, $+k$, $\pm l$, three standard reflections measured at intervals of 200 reflections showed no significant variation in intensity. 3784 reflections measured, 3565 unique (R_{int} = 0.037) used in all calculations. Solution by direct methods (SHELXTL-PLUS)[7] and subsequent Fourier-difference syntheses, anisotropic full-matrix least-squares refinement on F^2 (SHELXL 93).[8] Cyclopentadienyl hydrogen atoms placed in geometrically idealised positions and included using riding model. Phosphido hydrogen atoms located in final difference density map and coordinates were allowed to refine. The bridging hydride was located using the program HYDEX.[9] Final $wR(F^2)$ = 0.110 on all data, conventional $R(F)$ = 0.040 for 2903 observed reflections [$I > 2\sigma(I)$]; weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (0.0423P)^2 + 4.63P]$ where $P = (F_o^2 + 2F_c^2)/3$, 196 parameters, GOF = 1.046, maximum Δ/σ = 0.002, max, min $\Delta\rho$ = 1.16, −1.03 e Å^{-3}.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/349.

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