DALTON

Metallation of the μ-phosphido bridging ligand in the reaction of the anion [M₂Cp₂(CO)₄(μ-PH₂)]⁻ (M = Mo or W; Cp = η⁵-C₅H₅) with organometallic monohalides; synthesis and characterisation of [M₂Cp₂(CO)₄(μ-H){μ-PH(M′Lₙ)}] [M′Lₙ = Mn(CO)₅, FeCp(CO)₂, MoCp(CO)₃ or WCp(CO)₃] †

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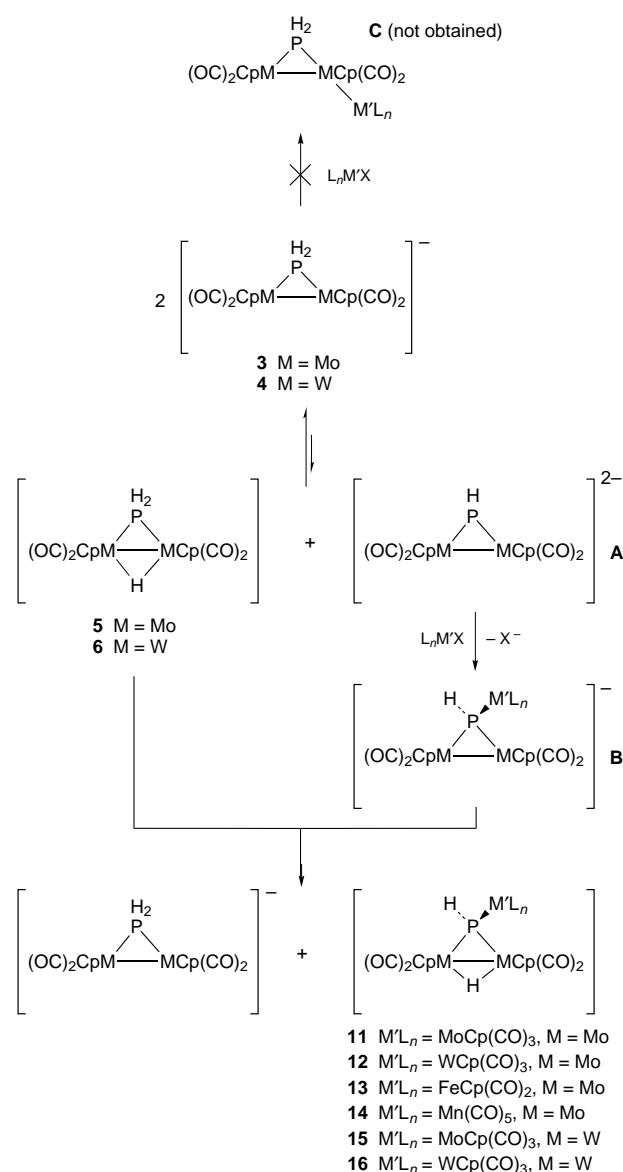*Department of Chemistry, Lensfield Road, Cambridge, UK CB2 1EW*

The anions $[M_2Cp_2(CO)_4(\mu\text{-}PH_2)]^-$ (M = Mo or W; Cp = η^5-C₅H₅) reacted with the organometallic halides $[M'L_nX]$ [M′Lₙ = Mo(CO)₃Cp, X = Cl; M′Lₙ = W(CO)₃Cp, X = Cl; M′Lₙ = Fe(CO)₂Cp, X = Cl or M′Lₙ = Mn(CO)₅, X = Br] to afford the new complexes $[M_2Cp_2(CO)_4(\mu\text{-}H)\{\mu\text{-}PH(M'L_n)\}]$ together with $[L_nM'\text{–}M'L_n]$, each in low yield. The crystal structure of $[W_2Cp_2(CO)_4(\mu\text{-}H)\{\mu\text{-}PH[MoCp(CO)_3]\}]$ has been determined.

The chemistry of complexes featuring μ-PR₂ bridges (R = alkyl or aryl) has been the subject of extensive study in recent years, principally because such bridges often confer stability on di- and poly-nuclear complexes with respect to fragmentation.[1] By contrast, the reactivity of complexes containing μ-PH₂ ligands has been the subject of relatively few investigations in the literature, possibly due to the inconvenience and hazards associated with the use of phosphine gas, the conventional route to such species.[2] We recently reported, however, a preparation of μ-PH₂ complexes avoiding the use of PH₃.[3] Thus, reaction of $[M_2Cp_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ (1, M = Mo or 2, M = W; Cp = η⁵-C₅H₅) with the hydroxides of alkali metals afforded in good yield the phosphido bridged anions $[M_2Cp_2(CO)_4(\mu\text{-}PH_2)]^-$ (3, M = Mo or 4, M = W) which on treatment with acid afforded the corresponding hydrides $[M_2Cp_2(CO)_4(\mu\text{-}H)(\mu\text{-}PH_2)]$ (5, M = Mo or 6, M = W).[3] The chemistry of species with bonds to hydrogen often differs significantly from that of analogous species with bonds to alkyl or aryl groups. Accordingly, it seemed of interest to examine the reactivity of complexes featuring the μ-PH₂ ligand, and in this paper the reactivity of the anions 3 and 4 towards a variety of halide-containing organometallic species is reported. It is shown that such reactions lead to metallation of the phosphido ligand and regeneration of a bridging hydride ligand.

Discussion

The air-sensitive anions **3** and **4** are conveniently prepared from tetrahydrofuran (thf) solutions of complexes **5** and **6** respectively by addition of 1 equivalent of LiBuᵗ. The reaction of the anions **3** and **4** with a range of organometallic monohalides [M′LₙX] {[MoCp(CO)₃Cl] **7**, [WCp(CO)₃Cl] **8**, [FeCp(CO)₂Cl] **9** or [Mn(CO)₅Br] **10**} leads to metallation of the phosphido ligand and regeneration of a bridging hydride between the two bonded metal centres giving the new complexes **11–16** (Scheme 1). A similar reaction, in which two Os₃ triangles were linked by utilising the reactivity of a μ-PH₂ ligand co-ordinated to one of them has previously been reported by Lewis and co-workers,[4a] other metallated phosphido complexes have been prepared by deprotonation of complexes of the μ-PHPh ligand followed by reaction with organometallic halides.[4b] The spectroscopic data for the new complexes **11–16** are shown in Table 1 and are in accord with the proposed structures, shown in Scheme 1.

† In memory of Sir Geoffrey Wilkinson, who first aroused my interest in organometallic chemistry.

11 M′Lₙ = MoCp(CO)₃, M = Mo
12 M′Lₙ = WCp(CO)₃, M = Mo
13 M′Lₙ = FeCp(CO)₂, M = Mo
14 M′Lₙ = Mn(CO)₅, M = Mo
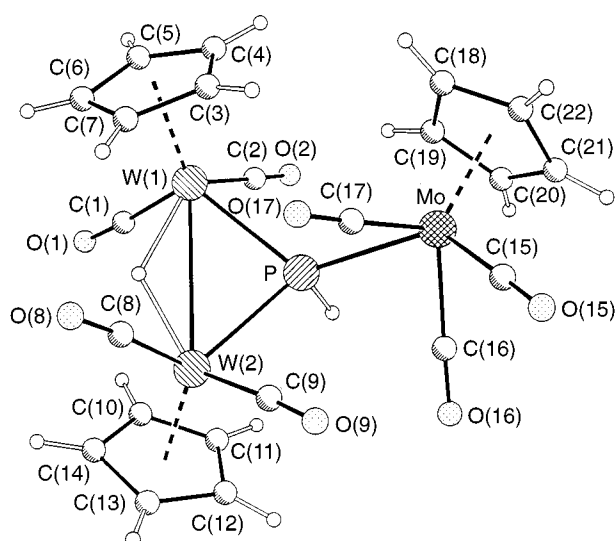**15** M′Lₙ = MoCp(CO)₃, M = W
16 M′Lₙ = WCp(CO)₃, M = W

Scheme 1 Proposed mechanism for the formation of complexes **11–16**

In each case, all Cp ligands present in a given complex are observed to be in distinct environments on the NMR spectro-

Table 1 Spectroscopic data for complexes **11**–**16**

Complex	ν_{CO}/cm^{-1}	^{1}H NMR	^{31}P NMR	FAB mass spectra	Microanalysis * (%)		
					C	H	P
11	2023s, 1943vs, 1921s, 1858s	5.65 (s, 5 H, Cp), 5.27 (d, 1 H, $^1J_{HP}$ 269, PH), 5.21 (s, 5 H, Cp), 5.08 (s, 5 H, Cp), −11.96 (d, 1 H, $^2J_{HP}$ 32, MoHMo)	−74.7 (s)	712 (M^+), 626, 598, 570, 542, 514 ($M^+ - n$CO, $n = 3$–7)	36.88 (37.08)	2.29 (2.39)	4.22 (4.21)
12	2019s, 1938vs, 1929vs, 1857s	5.76 (s, 5 H, Cp), 5.21 (s, 5 H, Cp), 5.07 (s, 5 H, Cp), 4.87 (d, 1 H, $^1J_{HP}$ 273, PH), −11.91 (d, 1 H, $^2J_{HP}$ 32, MoHMo)	−116.8 (s)	800 (M^+)	32.90 (33.00)	2.12 (2.13)	3.88 (3.88)
13	2021m, 1974m, 1938w, 1918s, 1853s	5.71 (d, 1 H, $^1J_{HP}$ 263, PH), 5.19 (s, 5 H, Cp), 5.11 (s, 5 H, Cp), 5.09 (s, 5 H, Cp), −11.64 (d, 1 H, $^2J_{HP}$ 29, MoHMo)	−16.34 (s)	644 (M^+), 588, 532, 476 ($M^+ - n$CO, $n = 2, 4, 6$)	Not recrystallised due to instability in solution		
14	2111m, 2023vs, 1940w, 1925s, 1858m	5.24 (s, 5 H, Cp), 5.14 (s, 5 H, Cp), 4.79 (d, 1 H, $^1J_{HP}$ 266, PH), −11.88 (d, 1 H, $^2J_{HP}$ 30, MoHMo)	−75.4 (s)	662 (M^+), 634, 606, 549, 521, 494, 466, 438, 410 ($M^+ - n$CO, $n = 1, 2, 4$–9)	Not recrystallised due to instability in solution		
15	2023s, 1939vs, 1912vs, 1844s	5.64 (s, 5 H, Cp), 5.32 (s, 5 H, Cp), 5.22 (s, 5 H, Cp), 5.08 (d, 1 H, $^1J_{HP}$ 282, PH), −14.26 (d, 1 H, $^2J_{HP}$ 21, $^1J_{HW}$ 42.2, WHW)	−180.0 (s)	888 (M^+)	30.16 (29.73)	2.04 (1.91)	3.54 (3.49)
16	2019s, 1935s, 1910s, 1844s	5.76 (s, 5 H, Cp), 5.31 (s, 5 H, Cp), 5.21 (s, 5 H, Cp), −14.25 (d, 1 H, $^2J_{HP}$ 22, $^1J_{HW}$ 43, WHW)	−220.6 (s)	977 ($M^+ + 1$), 948, 920, 892, 864, 836 ($M^+ - n$CO, $n = 1$–5)	27.10 (27.05)	1.79 (1.74)	3.22 (3.18)

* Calculated values in parentheses.

Fig. 1 Molecular structure of complex **15**, showing the atom labelling scheme adopted

Table 2 Selected bond lengths (Å) and angles (°) for complex **15**

W(1)–W(2)	3.2770(13)	W(1)–H(2)	1.85
W(1)–P	2.466(3)	W(2)–H(2)	1.85
W(2)–P	2.443(3)	P–H(1)	1.39(13)
P–Mo	2.599(3)		
P–W(1)–W(2)	47.82(8)	P–W(2)–W(1)	48.43(8)
P–W(1)–H(2)	75.4	W(2)–P–W(1)	83.75(10)
P–W(2)–H(2)	76.1	W(1)–H(2)–W(2)	124.8
W(1)–P–Mo	123.90(14)	W(2)–P–Mo	130.27(14)

scopic time-scale, as compared to **3**–**6** for which only one signal is observed. There is a reduction in overall symmetry (loss of C_2 axis) as compared to **3**–**6** on conversion of the μ-PH$_2$ ligand to a species that can be regarded as a μ-PH(M′L$_n$) ligand; the *trans* geometry of the Cp ligands observed in the solid state in **3**[3] is presumably retained in solution for the μ-PH(M′L$_n$) complexes. This then results in one of the Cp ligands being nearer the phosphorus-bound H atom and the other being nearer the newly introduced M′L$_n$ moiety.

The crystal structure of [W$_2$Cp$_2$(CO)$_4$(μ-H){μ-PH[MoCp-(CO)$_3$]}] **15** has been determined by X-ray diffraction. The molecular structure is shown in Fig. 1; selected bond lengths and angles are given in Table 2. The complex shows a *trans* orientation of the Cp ligands in the W$_2$Cp$_2$(CO)$_4$ fragment,

consistent with NMR spectroscopic evidence indicating their magnetic inequivalence; the Cp ligands are similarly *trans* in the μ-PH$_2$ complex **3**.[3] The W–W bond length of 3.2770(13) Å is indicative of a single metal–metal bond, as required for each tungsten atom to satisfy the 18-electron rule. The WHWP core of the molecule is essentially planar, as also observed in **3**,[3] with the bridging phosphorus occupying a slightly asymmetric position [W(1)–P(1) 2.466(3), W(2)–P(1) 2.443(3) Å]; these bonds are both rather shorter than the Mo–P distance of 2.599(3) Å. The major residual electron density peaks after the final refinement are in the vicinity of the tungsten atoms and do not correspond to any chemically sensible moiety.

Scheme 1 shows a plausible mechanism for the formation of complexes **11**–**16**. It is suggested that the phosphido anion [M$_2$Cp$_2$(CO)$_4$(μ-PH$_2$)]$^-$ (**3**, M = Mo or **4**, M = W) is in equilibrium with [M$_2$Cp$_2$(CO)$_4$(μ-H)(μ-PH$_2$)] (**5**, M = Mo or **6**, M = W) and the dianion [M$_2$Cp$_2$(CO)$_4$(μ-PH)]$^{2-}$ **A**. This dianion will be more nucleophilic than [M$_2$Cp$_2$(CO)$_4$(μ-PH$_2$)]$^-$ and will in consequence react more readily with the organometallic halide L$_n$M′X to displace X$^-$. The resulting metallated anion **B** could then accept a proton from the neutral hydride to afford the observed metallated product and regenerate 1 equivalent of [M$_2$Cp$_2$(CO)$_4$(μ-PH$_2$)]$^-$. The NMR spectroscopic studies on the anions **3** and **4** did not reveal the presence of any hydride-containing species in solution, suggesting the proportion of intermediate **A** present in solution is very small. This

is in accord with the fact that the reaction is relatively slow. Direct reaction of the phosphido anions **3** and **4** with mononuclear organometallic halides might be expected to lead to a trimetallic chain complex of type **C** (Scheme 1), but no compound with such a formulation was observed. It is probable that the steric bulk of the organometallic halide and of the Cp and CO ligands present in the anions both render initial attack of the metal halide at a metal centre on the anions more difficult than attack at the phosphorus atom. When the anions are treated with a small, hard electrophile such as H^+, reaction occurs essentially instantaneously even at 0 °C and presumably takes place at the metal centres to regenerate the neutral hydride directly.[3] Treatment of the neutral hydrides with a large excess of LiBu^t affords deep orange solutions, for which a number of IR bands in the 1600–1700 cm^{-1} region are observed, suggesting further deprotonation to give **A** may have occurred, but these solutions have as yet proved too unstable to characterise further.

All the new complexes **11**–**16** are sensitive to air, being more so in solution. From the reactions leading to complexes **11**, **12**, **15** and **16** we have also been able to isolate in low yield the green trimetallic species $[Mo_{3-n}W_nCp_3(CO)_6(\mu_3\text{-PO})]$ (**17**, $n = 0$; **18**, $n = 1$; **19**, $n = 2$ or **20**, $n = 3$) respectively, although analogous μ_3-PO complexes were not isolated during the preparation of complexes **13** or **14**. The phosphorus monoxide complexes were identified by comparison of their IR and NMR spectra to those previously reported in the literature.[5] A plausible route to the transformation of the metallated phosphido complexes into the phosphorus monoxide complexes would involve the initial reaction of O_2 with the μ-P(H)(ML$_n$) and hydride ligands to form a molecule of water and a μ_3-PO ligand by oxidation of the phosphorus atom. Subsequent loss of carbon monoxide and metal–metal bond formation would then yield the observed tetrahedrane.

Experimental

All reactions were performed under an atmosphere of dry oxygen-free nitrogen, using solvents which had been freshly distilled from the appropriate drying agent. Infrared spectra were recorded in dichloromethane solution in 0.5 mm NaCl cells, using a Perkin-Elmer 1710 Fourier-transform spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS890 instrument using 3-nitrobenzyl alcohol as a matrix. Proton and ^{31}P NMR spectra were recorded on either a Bruker WM250 or AM-400 spectrometer; ^{31}P NMR spectroscopy chemical shifts are referenced to P(OMe)$_3$ at δ 0.0 with upfield shifts negative. Microanalyses were performed by the microanalytical department, University of Cambridge. Preparative TLC was carried out on 1 mm silica plates prepared at the University of Cambridge. Products are given in order of decreasing R_f values. The complexes $[M_2Cp_2(CO)_4(\mu\text{-H})(\mu\text{-PH}_2)]$ (**5**, M = Mo or **6**, M = W),[3] [MoCp(CO)$_3$Cl] **7**,[6] [WCp(CO)$_3$Cl] **8**[6] and [FeCp(CO)$_2$Cl] **9**[7] were prepared by literature methods; [Mn(CO)$_5$Br] **10** was purchased from Strem Chemicals Inc. and used without further purification.

Reaction of $[Mo_2Cp_2(CO)_4(\mu\text{-H})(\mu\text{-PH}_2)]$ 5 with LiBu^t

To a solution of complex **5** (306 mg, 0.667 mmol) in thf (25 cm^3) was added LiBu^t (0.41 cm^3 as 1.7 M solution, 0.697 mmol). The solution changed immediately from orange to purple, and was identified by ^{31}P and ^{1}H NMR spectroscopy as containing $[Mo_2Cp_2(CO)_4(\mu\text{-PH}_2)]^-$ **3**.[3]

Reaction of $[W_2Cp_2(CO)_4(\mu\text{-H})(\mu\text{-PH}_2)]$ 6 with LiBu^t

To a solution of complex **6** (355 mg, 0.550 mmol) in thf (25 cm^3) was added LiBu^t (0.35 cm^3 as 1.7 M solution, 0.585 mmol). The solution changed immediately from orange to

pink-purple, and was identified by ^{31}P and ^{1}H NMR spectroscopy as containing $[W_2Cp_2(CO)_4(\mu\text{-PH}_2)]^-$ **4**.[3]

Reaction of $[Mo_2Cp_2(CO)_4(\mu\text{-PH}_2)]^-$ 3 with [MoCp(CO)$_3$Cl] 7

To a solution of **3** [prepared from complex **5** (354 mg, 0.756 mmol)] in thf (25 cm^3) was added complex **7** (216 mg, 0.770 mmol) and the solution heated to reflux for 2 min. The colour of the solution became dark orange. The solvent was removed and the residue redissolved in the minimum quantity of dichloromethane and applied to the base of TLC plates. Elution with hexane–dichloromethane (1:1) afforded [Mo$_2$Cp$_2$(CO)$_6$] (50 mg, 0.102 mmol, 13%), **3** (trace), [Mo$_2$Cp$_2$(CO)$_4$(μ-H){μ-PH[MoCp(CO)$_3$]}] **11** (44 mg, 0.062 mmol, 8%) and unreacted **7** (trace). Subsequent elution with hexane–acetone (1:2) afforded green [Mo$_3$Cp$_3$(CO)$_6$(μ_3-PO)] **17** (22 mg, 0.032 mmol, 4%).

Reaction of $[Mo_2Cp_2(CO)_4(\mu\text{-PH}_2)]^-$ 3 with [WCp(CO)$_3$Cl] 8

To a solution of **3** [prepared from complex **5** (318 mg, 0.679 mmol)] in thf (25 cm^3) was added complex **8** (256 mg, 0.694 mmol) and the solution heated to reflux for 3 min. The colour of the solution became dark orange. The solvent was removed and the residue redissolved in the minimum quantity of dichloromethane and applied to the base of TLC plates. Elution with hexane–dichloromethane (1:1) afforded [W$_2$Cp$_2$(CO)$_6$] (54 mg, 0.081 mmol, 12%), **5** (trace), [Mo$_2$Cp$_2$(CO)$_4$(μ-H){μ-PH[WCp(CO)$_3$]}] **12** (60 mg, 0.075 mmol, 11%) and unreacted **8** (trace). Subsequent elution with hexane–acetone (1:2) afforded green [Mo$_2$WCp$_3$(CO)$_6$(μ_3-PO)] **18** (31 mg, 0.039 mmol, 6%).

Reaction of $[Mo_2Cp_2(CO)_4(\mu\text{-PH}_2)]^-$ 3 with [FeCp(CO)$_2$Cl] 9

To a solution of **3** [prepared from complex **5** (301 mg, 0.643 mmol)] in thf (25 cm^3) was added complex **9** (136 mg, 0.640 mmol) and the solution heated to reflux for 3 min. The colour of the solution became dark orange. The solvent was removed and the residue redissolved in the minimum quantity of dichloromethane and applied to the base of TLC plates. Elution with hexane–dichloromethane (1:1) afforded **5** (trace), orange [Mo$_2$Cp$_2$(CO)$_4$(μ-H){μ-PH[FeCp(CO)$_2$]}] **13** (46 mg, 0.071 mmol, 11%) and [Fe$_2$Cp$_2$(CO)$_4$] (39 mg, 0.110 mmol, 17%).

Reaction of $[Mo_2Cp_2(CO)_4(\mu\text{-PH}_2)]^-$ 3 with [Mn(CO)$_5$Br] 10

To a solution of **3** [prepared from complex **5** (298 mg, 0.637 mmol)] in thf (25 cm^3) was added complex **10** (175 mg, 0.636 mmol) and the mixture stirred at room temperature for 3 d. The colour of the solution slowly became dark orange. The solvent was removed and the residue redissolved in the minimum quantity of dichloromethane and applied to the base of TLC plates. Elution with hexane–dichloromethane (1:1) afforded [Mn$_2$(CO)$_{10}$] (20 mg, 0.051 mmol, 16%), **5** (34 mg, 0.073 mmol, 11%) and orange [Mo$_2$Cp$_2$(CO)$_4$(μ-H){μ-PH[Mn(CO)$_5$]}] **14** (20 mg, 0.030 mmol, 5%).

Reaction of $[W_2Cp_2(CO)_4(\mu\text{-PH}_2)]^-$ 4 with [MoCp(CO)$_3$Cl] 7

To a solution of **4** [prepared from complex **2** (291 mg, 0.452 mmol)] in thf (25 cm^3) was added **7** (129 mg, 0.459 mmol) and the solution heated to reflux for 3 min. The colour of the solution became dark orange. The solvent was removed and the residue redissolved in the minimum quantity of dichloromethane and applied to the base of TLC plates. Elution with hexane–dichloromethane (1:1) afforded [Mo$_2$Cp$_2$(CO)$_6$] (25 mg, 0.051 mmol, 22%), **2** (trace), [W$_2$Cp$_2$(CO)$_4$(μ-H){μ-PH[MoCp(CO)$_3$]}] **15** (39 mg, 0.044 mmol, 10%) and unreacted **7** (trace). Subsequent elution with hexane–acetone (1:2) afforded green-brown [MoW$_2$Cp$_3$(CO)$_6$(μ_3-PO)] **19** (20 mg, 0.023 mmol, 5%).

Reaction of $[W_2Cp_2(CO)_4(\mu\text{-}PH_2)]^-$ 4 with $[WCp(CO)_3Cl]$ 8

To a solution of **4** [prepared from complex **2** (404 mg, 0.627 mmol)] in thf (25 cm^3) was added **8** (238 mg, 0.646 mmol) and the solution heated to reflux for 3 min. The colour of the solution became dark orange. The solvent was removed and the residue redissolved in the minimum quantity of dichloromethane and applied to the base of TLC plates. Elution with hexane–dichloromethane (1:1) afforded $[W_2Cp_2(CO)_6]$ (42 mg, 0.063 mmol, 20%), **2** (trace), $[W_2Cp_2(CO)_4(\mu\text{-}H)$-$\{\mu\text{-}PH[WCp(CO)_3]\}]$ **16** (53 mg, 0.054 mmol, 9%) and unreacted **8** (trace). Subsequent elution with hexane–acetone (1:2) afforded green-brown $[W_3Cp_3(CO)_6(\mu_3\text{-}PO)]$ **20** (40 mg, 0.042 mmol, 7%).

Crystal-structure determination of $[W_2Cp_2(CO)_4(\mu\text{-}H)$-$\{\mu\text{-}PH[MoCp(CO)_3]\}]$ 15

Single crystals of complex **15** suitable for X-ray diffraction studies were grown by slow diffusion of hexane into a dichloromethane solution under a nitrogen atmosphere at 0 °C. Data were collected on an orange crystal, $0.10 \times 0.15 \times 0.15$ mm in dimensions, by the ω–2θ scan method on a Rigaku AFC7R four-circle diffractometer.

Crystal data. $C_{22}H_{17}MoO_7PW_2$ **15**: $M = 887.97$, triclinic, space group $P\bar{1}$, $a = 10.047(4)$, $b = 15.409(5)$, $c = 7.653(3)$ Å, $\alpha = 94.22(3)$, $\beta = 103.73(3)$, $\gamma = 90.42(3)°$, $U = 1152.0(7)$ Å^3, $T = 150(2)$ K, graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\,713$ Å, $Z = 2$, $D_c = 2.560$ Mg m^{-3}, $F(000) = 820$, μ(Mo-Kα) = 10.608 mm^{-1}, relative transmission 1.000–0.845. Data collection range $5.30 < 2\theta < 55.02°$, $0 \leqslant h \leqslant 13$, $-20 \leqslant k \leqslant 20$, $-9 \leqslant l \leqslant 9$, 5558 reflections collected of which 5259 were independent ($R_{int} = 0.0797$) used in all calculations. Three standard reflections were monitored at intervals of 200 reflections. Cell parameters were obtained by least-squares refinement on diffractometer angles from 25 centred reflections ($15 < 2\theta < 20°$). A semiempirical absorption correction based on ψ-scan data was applied. The structure was solved by direct methods (SIR 92)[8] and subsequent Fourier-difference syntheses and refined anisotropically on all non-hydrogen atoms by full-matrix least-squares on F^2 (SHELXL 93).[9] Cyclopentadienyl hydrogen atoms were placed in idealised positions and refined using a riding model; the coordinates of H(1) were refined freely and the bridging hydride located using the program HYDEX.[10] In the final cycles of refinement a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$ was introduced which produced a flat analysis of variance. Final $wR(F^2)$ on all data 0.134, $R1 = 0.053$ on 3852 reflections with $I > 2\sigma(I)$, 301 parameters, goodness of fit 1.047, greatest peak and hole in final electron density map 3.023 and -2.403 e Å^3.

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