# The First Stable Transition Metal (Molybdenum or Tungsten) Complexes Having a Metal–Phosphorus(III) Double Bond: the Phosphorus Analogues of Metal Aryl- and Alkyl-imides; *X*-Ray Structure of $[Mo(\eta\text{-}C_5H_5)_2(=PAr)]$ ($Ar = C_6H_2Bu^t{}_3\text{-}2,4,6$)†

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Arylphosphinylidenemetal complexes $[M(\eta\text{-}C_5H_5)_2(=PAr)]$ [M = Mo (**1**) or W (**2**), $Ar = C_6H_2Bu^t{}_3\text{-}2,4,6$] and an alkyl analogue $[W(\eta\text{-}C_5H_5)_2(=PR)]$ [$R = CH(SiMe_3)_2$(**3**)] have been prepared from $[\{M(\eta\text{-}C_5H_5)_2HLi\}_4]$ and $PCl_2R'$ (R′ = Ar or R), and show low-field $^{31}P$ chemical shifts: $\delta(^{31}P\{^1H\})$ ($C_6D_6$) (**1**) +799.5 [$J(^{31}P\text{–}^1H)$ 4 Hz (involving only one of the two $C_5H_5$ rings)]; (**2**) +666.1 [$J(^{31}P\text{–}^{183}W)$ 153.5 Hz, $J(^{31}P\text{–}^1H)$ 4 Hz]; and (**3**) +679.6 [$J(^{31}P\text{–}^{183}W)$ 144.1 Hz]. Compound (**1**) has an Mo–P bond length of 2.370(2) Å and a Mo–P–C bond angle of 115.8(2)°.

There has been much recent interest in multiply bonded compounds involving a second row or a heavier element. Examples of *X*-ray-characterised molecules relevant to the present study include ArP=PAr ($Ar = C_6H_2Bu^t{}_3\text{-}2,4,6$)[1] and $R_2M'=M'R_2$ [M′ = Ge or Sn, $R = CH(SiMe_3)_2$];[2] for a review, see ref. 3.

We now report the synthesis [equation (i)] and n.m.r. characterisation‡ of the first stable transition metal (M) compounds containing an M=P multiple bond and having two-co-ordinate phosphorus. These hydrocarbon-soluble complexes have the formula $[M(\eta\text{-}C_5H_5)_2(=PR')]$ [R′ = Ar and M = Mo (**1**) or W (**2**); or R′ = R and M = W (**3**)] and may be named as aryl- or alkyl-phosphinylidenemetal complexes, the P analogues of $[M(L_n)(=NR')]$. The *X*-ray structure for the crystalline molybdenum compound (**1**) is illustrated in Figure 1.§

$$\tfrac{1}{4}[\{M(\eta\text{-}C_5H_5)_2HLi\}_4] \xrightarrow{PCl_2R'} [M(\eta\text{-}C_5H_5)_2(=PR')] \qquad \text{(i)}$$

(ref. 4)

(**1**) M = Mo, R′ = Ar, red, m.p. *ca.* 65 °C (decomp.)
(**2**) M = W, R′ = Ar, red, m.p. *ca.* 102 °C (decomp.)
(**3**) M = W, R′ = R, red oil

The $^{31}P$ chemical shifts‡ for $C_6D_6$ solutions of the complexes (**1**)—(**3**) are at very low field, +666.1 to +799.5 p.p.m. This may be compared with $\delta(^{31}P)$ for some main group compounds $L_nM''=PAr$ [$L_nM$ = ArP +494,[3] $(Me_3Si)_3CP$ +533.1 (PAr), RP +495 (PAr) and +508.3 (PR), RAs +575, RSb +620, $(2,4,6\text{-}Me_3C_6H_2)_2Si$ +136,[5] $(2,4,6\text{-}Me_3C_6H_2)_2Ge$ +175.4,[6] and $R_2Sn$ +204.7 p.p.m.;[7] of these, only those with $L_nM$ = ArP or RAs are *X*-ray characterised].[3] The previously recorded lowest field $^{31}P$ signal for a two co-ordinate phosphorus compound appears to be +954 p.p.m. in $[Fe(\eta\text{-}C_5H_5)(CO)_2(P=NPr^i{}_2)]$ $[PF_6]$.[8]

The $^1H$ n.m.r. spectra of $C_6D_6$ solutions of complex (**1**) or (**2**) at 80 MHz at 305 K revealed that the two cyclopentadienyl rings are non-equivalent, with one only showing through-space coupling, $J(^{31}P\text{–}^1H)$ 4 Hz. This coupling was not observed when the spectrum was run at 360 MHz. The effect is

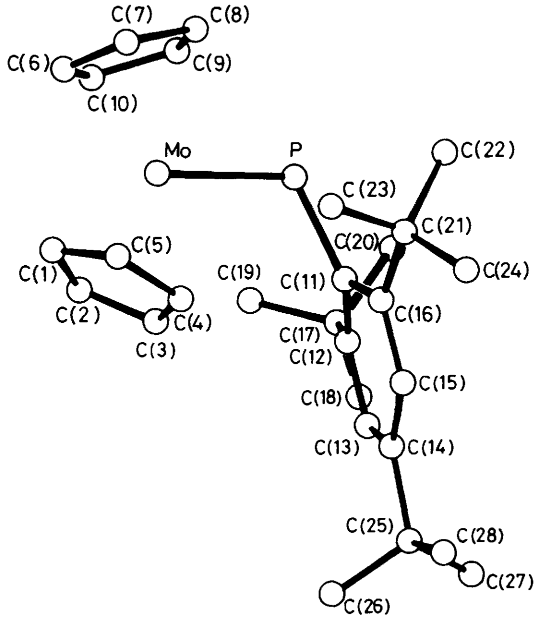

**Figure 1.** The molecular structure and atom numbering scheme for $[Mo(\eta\text{-}C_5H_5)_2(=PAr)]$ ($Ar = C_6H_2Bu^t{}_3\text{-}2,4,6$) (**1**). Some important bond distances and angles are: Mo–P 2.370(2), P–C(11) 1.858(7), Mo–cp(1) 1.966, Mo–cp(2) 1.962 Å; Mo–P–C(11) 115.8(2), cp(1)–Mo–cp(2) 144.6, P–Mo–cp(1) 113.0, P–Mo–cp(2) 102.4°; cp(1) and cp(2) are the centroids of the rings C(1) to C(5), and C(6) to C(10), respectively.

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† No reprints available.

‡ *Selected n.m.r. data* [$^{31}P$ at 32.4 MHz (δ in p.p.m. rel. to 85% $H_3PO_4$), $^1H$ at 80 or 360 MHz, $^{13}C$ at 20.1 MHz, in $C_6D_6$ at 305 K]: (**1**) $^{31}P\{^1H\}$ δ +799.5 p.p.m; $^1H$ (80 MHz) 1.54 (9H, s, $Bu^t$), 1.60 (18H, s, $Bu^t$), 4.36 (5H, s, $C_5H_5$), 4.98 [5H, d, $C_5H_5$, $J(^{31}P\text{–}^1H)$ 4 Hz], and 7.60 (2H, s, $C_6H_2$); $^1H$ (360 MHz) 1.45 (9H, s, $Bu^t$), 1.52 (18H, s, $Bu^t$), 4.30 (5H, s, $C_5H_5$), 4.90 (5H, s, $C_5H_5$), and 7.50 (2H, s, $C_6H_2$); $^{13}C\{^1H\}$ 31.8 and 32.6 $[C(CH_3)_3]$, 87.1 ($C_5H_5$), 88.7 ($C_5H_5$), 126.8, 128.1, 129.3, and 187.6 ($C_6H_2$); (**2**) $^{31}P\{^1H\}$ δ +661.1 p.p.m. [$J(^{31}P\text{–}^{183}W)$ 153.5 Hz]; $^1H$ (80 MHz) 1.40 (9H, s, $Bu^t$), 1.53 (18H, s, $Bu^t$), 4.30 (5H, s, $C_5H_5$), 4.82 [5H, d, $C_5H_5$, $J(^{31}P\text{–}^1H)$ 4 Hz], and 7.35 (2H, s, $C_6H_2$); $^1H$ (360 MHz) 1.36 (9H, s, $Bu^t$), 1.50 (18H, s, $Bu^t$), 4.26 (5H, s, $C_5H_5$), 4.80 (5H, s, $C_5H_5$), and 6.93 and 7.06 (2H, $C_6H_2$); $^{13}C\{^1H\}$ 35.4 and 35.7 $[C(CH_3)_3]$, 66.9 ($C_5H_5$), 81.2 ($C_5H_5$), 127.1, 128.3, and 129.8 ($C_6H_2$); (**3**) $^{31}P\{^1H\}$ δ +679.6 p.p.m. [$J(^{31}P\text{–}^{183}W)$] 144.1 Hz]; $^1H$ (80 MHz) 0.18 (18H, s, $Me_3Si$), 4.06 (5H, s, $C_5H_5$) and 4.79 [5H, d, $C_5H_5$, $J(^{31}P\text{–}^1H)$ 3.4 Hz]; $^1H$ (360 MHz), 0.18 (18H, s, $Me_3Si$), 4.06 (5H, s, $C_5H_5$), and 4.80 (5H, s, $C_5H_5$).

§ *Crystal data* for (**1**): $C_{28}H_{39}MoP\cdot C_6H_6$, *M* 580.7, orthorhombic, space group $P2_12_12_1$, $a = 16.209(8)$, $b = 20.994(6)$, $c = 8.978(5)$ Å; $U = 3055.2$ Å$^3$, $Z = 4$, $D_c = 1.26$ g cm$^{-3}$, Mo-$K_\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 4.9$ cm$^{-1}$. The structure was solved by routine heavy atom methods and refined by full-matrix least-squares procedures with anisotropic temperature factors for the non-hydrogen atoms, and no absorption correction to $R = 0.050$, $R' = 0.066$, using 2602 reflections with $|F^2| > \sigma(F^2)$. The crystal contains discrete molecules of the metal complex and the benzene of solvation with no intermolecular contacts to Mo shorter than 4 Å. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

attributed to the chemical shift anisotropy of the phosphorus, which at 360 MHz results in an efficient relaxation mechanism [$T_1$ *ca.* 0.06 s; $1/T_1 \gg J(^{31}\text{P}–^1\text{H})$], whereas at 80 MHz, the anisotropy is reduced and relaxation is sufficiently slow ($T_1$ *ca.* 0.75 s) for coupling to be observed.

The *X*-ray structure of (**1**) shows an Mo–P distance of 2.370(2) Å, rather short for a $d^2$ $\text{Mo}^{\text{IV}}$ complex; *cf.*,[9] 2.54(1) Å in $[\overline{\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\{\text{P(H)–P}}\text{H}\}]$. On the basis of the PP distance of 2.034(2) Å in ArP=PAr,[1] an average Mo–Cl bond length of 2.471(5) Å in $[\text{Mo}(\eta\text{–C}_5\text{H}_5)_2\text{Cl}_2]$,[10] and the covalent radius of Cl (0.99 Å), the calculated Mo=P length in (**1**) is 2.50 Å; that this distance is significantly longer than the experimentally observed MoP bond length suggests that complex (**1**) might best be considered as a hybrid, Mo=PAr ⟷ (Mo←PAr). The angular arrangement at P in (**1**), Mo–P–C 115.8(2)°, is also consistent with there being an Mo=P double bond and a stereochemically active lone pair at phosphorus.

Transient phosphinylidenemetal complexes $[\text{M(CO)}_5(=\text{PR}')]$ (M = Cr, Mo, or W; R′ = Me or Ph) have been studied by Mathey and his co-workers.[11] Others have described transition metal complexes $[\text{M(L}_n)(\text{PR}'_2)]$ having trigonal planar P as containing M=P bonds (phosphorus donor), as in the *X*-ray-characterised $[\text{W}(\eta\text{–C}_5\text{H}_5)(\text{CO})_2\{\overline{\text{POCMe}_2\text{CMe}_2\text{O}}\}]$, which has $\delta(^{31}\text{P}\{^1\text{H}\})$ +226.8 p.p.m., $J(^{31}\text{P}–^{183}\text{W})$ 847 Hz.[12]

The reactivity of the complexes (**1**)—(**3**) and of similar compounds is being investigated, as well as the general implications of metathetical reactions related to those of equation (i).

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