Formation of Enol and Acyl Phosphine Ligands *via* Alkylation of a Tungsten Phosphaallyl complex: Crystal Structures of $[WI\{C_6H_4(PH_2)[PMeC(O)CH_2(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]\cdot 0.5C_4H_8O$ and $[WI\{C_6H_4(PH_2)[P\{(CH_2)_4I\}C(O)CH_2(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$†

James E. Denison, John C. Jeffery,* Suanna Harvey and K. D. Vinindra Weerasuria
Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 1TS, UK

The π-phosphaallyl complex $[W\{\sigma,\eta^3\text{-}C_6H_4(PH_2)[PC(OH)CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$ **1** has an unused lone pair of electrons on the central phosphorus atom of the chelate ring and like a conventional PR_3 ligand will undergo facile P-alkylation reactions. Methylation (Me_3OBF_4, CH_2Cl_2, 20 °C) at the allylic phosphorus affords the co-ordinated enol–phosphine salt $[W\{\sigma^2,\eta^2\text{-}C_6H_4(PH_2)\text{-}[PMeC(OH)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$ **2**. Complex **2** is stable in CH_2Cl_2 but MeCN displaces the enol group (1 d, 20 °C), affording $[W\{\sigma^2\text{-}C_6H_4(PH_2)[PMeC(OH)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(MeCN)(CO)(\eta\text{-}C_5H_5)]^+$ **3**, which subsequently undergoes very slow (10 d, 20 °C) enol–keto tautomerisation to the ketone isomer $[W\{\sigma^2\text{-}C_6H_4(PH_2)[PMeC(O)CH_2(C_6H_4Me\text{-}4)]\text{-}1,2\}(MeCN)\text{-}(CO)(\eta\text{-}C_5H_5)]^+$ **4**. Deprotonation of the hydroxyl group in **2** (Et_3N, MeCN) affords the neutral metallaphosphacyclobutanone complex $[W\{\sigma^3\text{-}C_6H_4(PH_2)[PMeC(O)CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$ **5** which undergoes facile O-methylation (Me_3OBF_4, CH_2Cl_2) affording $[W\{\sigma^2,\eta^2\text{-}C_6H_4(PH_2)[PMeC(OMe)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$ **6**, a methoxy derivative of the hydroxy precursor **2**. The methoxyvinyl group in **6** is slowly displaced by MeCN (3 d, 20 °C), affording the cation $[W\{\sigma^2\text{-}C_6H_4(PH_2)[PMeC(OMe)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(MeCN)(CO)(\eta\text{-}C_5H_5)]^+$ **7**. The presence of the methoxy group in **7** prevents enol–keto tautomerisation. The reaction of complex **1** with MeI (CH_2Cl_2, 20 °C) initially affords a yellow precipitate of $[W\{\sigma^2,\eta^2\text{-}C_6H_4(PH_2)\text{-}[PMeC(OH)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]I$ **8** which then slowly dissolves and simultaneously isomerises to $[WI\{\sigma^2\text{-}C_6H_4(PH_2)[PMeC(O)CH_2(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$ **9**. The related reaction of **1** with 1,4-diiodobutane gives $[WI\{\sigma^2\text{-}C_6H_4(PH_2)[P\{(CH_2)_4I\}C(O)CH_2(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)\text{-}(\eta\text{-}C_5H_5)]$ **10**, an *n*-butyl iodide analogue of **9**. The molecular structures of **9** and **10** have been established by single-crystal X-ray diffraction studies and are extremely similar. The tungsten atoms carry a cyclopentadienyl ring and are ligated by the *o*-phenylene bidentate phosphine, iodide, and CO ligands. In both cases the iodide ligand lies *trans* to the PH_2 end of the bidentate phosphine ligand. The alkylated phosphorus atom of the bidentate phosphine ligand carries a methyl (**9**) or an *n*-butyl iodide (**10**) group, and an acyl group $C(O)CH_2C_6H_4Me\text{-}4$ which has arisen from isomerisation of the enol moiety $C(OH)=C(H)C_6H_4Me\text{-}4$ in the precursor **1**. The alkyl groups lie *syn* to the cyclopentadienyl rings which is consistent with stereospecific alkylation of the phosphorus lone pair in complex **1**. Spectroscopic data (IR and ^1H, $^{13}C\text{-}\{^1H\}$, and ^{31}P NMR) for the new tungsten complexes are discussed and mechanisms proposed to account for their formation.

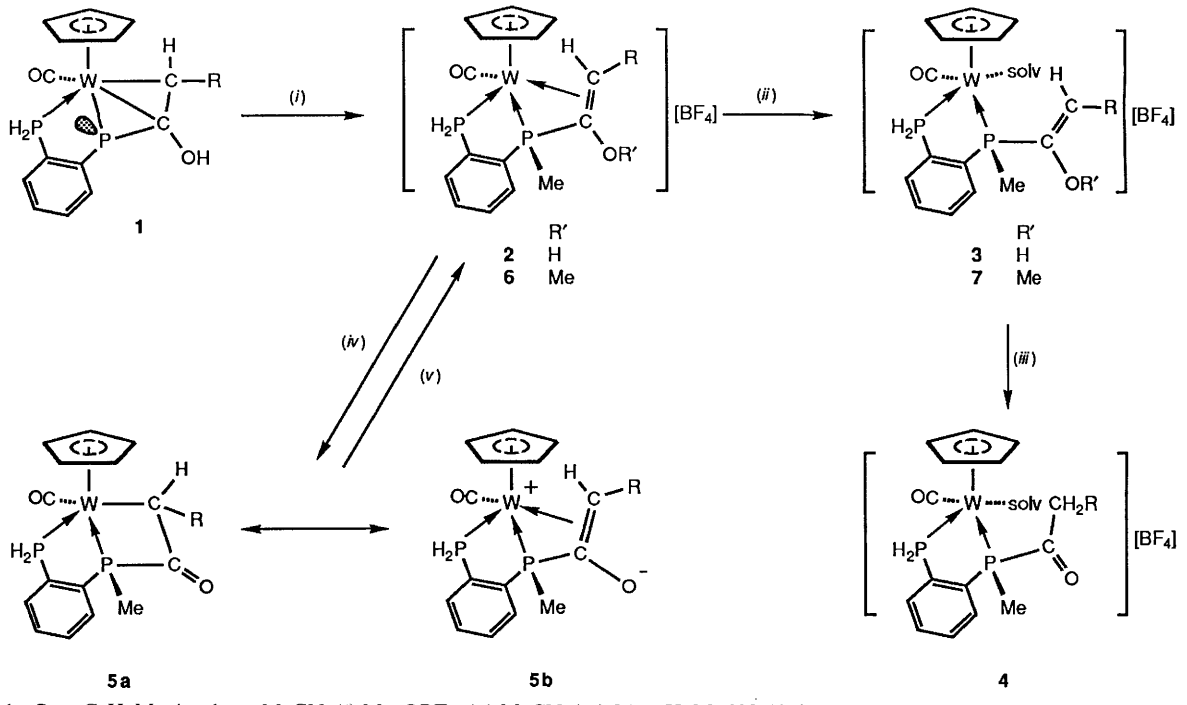
The alkylidyne complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4, Me, C_6H_4OMe-2, or $C_6H_4CH_2OMe$-2) and $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ react with the bidentate primary phosphine $C_6H_4(PH_2)_2$-1,2 to give the metallaphosphine complexes $[M\{\sigma,\eta^3\text{-}C_6H_4(PH_2)[PC(OH)CHR]\text{-}1,2\}\text{-}(CO)(\eta\text{-}C_5H_5)]$ (M = W or Mo).[1,2] The molecular structure of the tungsten derivative $[W\{\sigma,\eta^3\text{-}C_6H_4(PH_2)[PC(OH)CH\text{-}(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$ **1** shows that the central phosphorus atom of the chelate chain is part of a π-phosphaallyl moiety and as such it has an unused pair of electrons available for bonding. The complex as a whole may therefore be viewed as a novel metallaphosphine ligand and will substitute CO ligands in transition-metal complexes. Thus, treatment of the tricobalt alkylidyne clusters $[Co_3(\mu_3\text{-}CR)(CO)_9]$ (R = H or Me) with 1 equivalent of **1** gives deep green solutions of the complexes $[WCo_3(\mu_3\text{-}CR)\{\mu\text{-}C_6H_4(PH_2)[PC(OH)CH(C_6H_4\text{-}Me\text{-}4)]\text{-}1,2\}(CO)_9(\eta\text{-}C_5H_5)]$ in which complex **1** has replaced an equatorial CO ligand in the parent Co_3 complexes.[1] The central phosphorus atom in **1** could also be viewed as a Lewis base and should therefore react with organic electrophiles. In this paper we show that complex **1** will undergo facile electrophilic P-alkylation reactions, thus confirming its Lewis basicity. Some of the work described in this paper has appeared in a preliminary communication.[1]

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Carbonyl (η-cyclopentadienyl)iodo-{1-[methyl(*o*-phosphinophenyl-κ*P*)phosphino-κ*P*]propanone}tungsten–tetrahydrofuran (1/0.5) and -{1-(4-iodobutyl)(*o*-phosphinophenyl-κ*P*)phosphino-κ*P*]propanone}-tungsten.

Results and Discussion

Methylation of complex **1** (Me_3OBF_4, CH_2Cl_2, 20 °C) occurs at the allylic phosphorus atom affording a yellow precipitate of the co-ordinated enol–phosphine cation $[W\{\sigma^2,\eta^2\text{-}C_6H_4\text{-}(PH_2)[PMeC(OH)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]^+$ **2** (Scheme 1). Spectroscopic and analytical data for **2** and the



Scheme 1 R = C_6H_4Me-4, solv = MeCN. (*i*) Me_3OBF_4; (*ii*) MeCN; (*iii*) R′ = H, MeCN, 10 d; (*iv*) Et_3N, MeCN; (*v*) Me_3OBF_4, CH_2Cl_2

Table 1 Analytical and other data

Compound	Colour	Yield (%)	ν_{max}(CO)[a] (cm^{-1})	Analysis (%)[b] C	H
2 $[W\{\sigma^2,\eta^2\text{-}C_6H_4(PH_2)[PMeC(OH)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$	Yellow	90	1932s[c]	40.2 (40.5)	3.6 (3.6)
3 $[W\{\sigma^2\text{-}C_6H_4(PH_2)[PMeC(OH)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(MeCN)(CO)(\eta\text{-}C_5H_5)][BF_4]$[d]	Yellow	—	1888s[e]	—	—
4 $[W\{\sigma^2\text{-}C_6H_4(PH_2)[PMeC(O)CH_2(C_6H_4Me\text{-}4)]\text{-}1,2\}(MeCN)(CO)(\eta\text{-}C_5H_5)][BF_4]$[d]	Yellow	—	1888s[f]	—	—
5 $[W\{\sigma^3\text{-}C_6H_4(PH_2)[PMeC(O)CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$	Yellow	95	1854s[g]	45.6 (46.8)	4.0 (3.9)
6 $[W\{\sigma^2,\eta^2\text{-}C_6H_4(PH_2)[PMeC(OMe)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$[h]	Orange	80	1976s	38.6 (38.4)	3.8 (3.6)
7 $[W\{\sigma^2\text{-}C_6H_4(PH_2)[PMeC(OMe)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(MeCN)(CO)(\eta\text{-}C_5H_5)][BF_4]$[d]	Yellow	—	1884s[i]	—	—
8 $[W\{\sigma^2,\eta^2\text{-}C_6H_4(PH_2)[PMeC(OH)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]I$[h]	Yellow	57	1939s[c]	35.8 (35.6)	3.6 (3.2)
9 $[WI\{\sigma^2\text{-}C_6H_4(PH_2)[PMeC(O)CH_2(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$	Orange	81	1862s[j]	38.2[k] (38.2)	3.6 (3.4)
10 $[WI\{\sigma^2\text{-}C_6H_4(PH_2)[P\{(CH_2)_4I\}C(O)CH_2(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$	Red	30	1864s[l]	34.9 (34.9)	3.5 (3.3)

[a] In CH_2Cl_2 unless otherwise noted. [b] Calculated values in parentheses. [c] In Nujol. [d] Not isolated, see text. [e] ν(C=C) 1605w cm^{-1}. [f] ν(C=O) 1684m cm^{-1}. [g] ν(C=O) 1598m(br) cm^{-1}. [h] Crystallises with one molecule of CH_2Cl_2. [i] ν(C=C) 1682w cm^{-1}. [j] ν(C=O) 1692m cm^{-1}. [k] I, 18.6 (18.3%). [l] ν(C=O) 1689m cm^{-1}.

other new complexes described in this paper are given in Tables 1–3. The Nujol mull IR spectrum of **2** shows a single absorption at 1932 cm^{-1} due to the terminal CO ligand. This band occurs at an appreciably higher wavenumber than that of the CO ligand in the neutral precursor **1** [ν(CO) 1862 cm^{-1}], which is consistent with the formation of a cationic complex. The ^1H-coupled ^{31}P NMR spectrum was particularly informative showing resonances at δ −37.5 [ddd, *J*(PP) 15, *J*(HP) 479, 403, *J*(WP) 286 Hz] and 11.9 [d, *J*(PP) 15 Hz] which may be assigned to the PH_2 and PMe phosphorus atoms, respectively. The chemical shift of the former resonance is similar to that found for the PH_2 group in **1** (δ −28.3) but the PMe resonance no longer exhibits the pronounced deshielding which is characteristic of the allylic phosphorus atom in **1** (δ −52.6)[2] and related π-phospha complexes such as $[W(\eta^3\text{-}RPCHCH_2)(CO)(\eta\text{-}C_5H_5)]$ [R = $C_6H_2(CMe_3)_3$-2,4,6].[3] The ^1H NMR spectrum shows resonances at δ 2.97 and 4.55 [dd, *J*(PH) 8, 3 Hz] which may be assigned to the OH and *CH*R protons of the co-ordinated enol ligand and the presence of a doublet for the PMe group at δ 2.15 [*J*(PH) 12 Hz] confirms that methylation has occurred at phosphorus. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum the resonances for the CHR and COH groups of the co-ordinated enol occur as doublets at δ 35.4 [*J*(PC) 25] and 96.8 [*J*(PC) 24 Hz]. The latter resonance is substantially more shielded than that found for the COH in **1** (δ 142.1) and this reflects the loss of allylic delocalisation which occurs on P-methylation.

Complex **2** is only sparingly soluble in CH_2Cl_2, but is stable in this solvent. In contrast, it dissolves readily in the more strongly co-ordinating solvent MeCN, which then slowly (1 d, 20 °C) displaces co-ordination of the enol moiety affording the MeCN cation $[W\{\sigma^2\text{-}C_6H_4(PH_2)[PMeC(OH)=CH(C_6H_4Me\text{-}$

Table 2 Proton and ^{13}C NMR data[a]

Compound	$\delta(^1H)$[b]	$\delta(^{13}C)$[c]
2	2.15 [d, 3 H, PMe, *J*(PH) 12], 2.33 (s, 3 H, Me-4), 2.97 (s, 1 H, OH), 4.55 (dd, 1 H, C*H*R, *J*(PH) 8, 3], 5.38 [d, 5 H, C_5H_5, *J*(PH) 1], 6.23 [d, 2 H, PH_2, *J*(PH) 457], 7.10 [d, 2 H, C_6H_4Me-4, *J*(HH) 8], 7.31 [d, 2 H, C_6H_4Me-4, *J*(HH) 8], 7.80 (m, 2 H, $P_2C_6H_4$), 8.15 (m, 1 H, $P_2C_6H_4$), 8.29 (m, 1 H, $P_2C_6H_4$)	20.9 (Me-4), 21.0 [d, PMe, *J*(PC) 26], 35.4 [d, *C*HR, *J*(PC) 25], 89.3 (C_5H_5), 96.8 [d, *C*OH, *J*(PC) 24], 129.0 [C^3, $C^5(C_6H_4Me\text{-}4)$], 129.3 [C^2, $C^6(C_6H_4Me\text{-}4)$], 130.0–141.0 [m, C^1, $C^4(C_6H_4Me\text{-}4)$, $P_2C_6H_4$], 224.6 [d, WCO, *J*(PC) 12]
3	1.95 (s, 3 H, MeCN), 2.24 [d, 3 H, PMe, *J*(PH) 9], 2.31 (s, 3 H, Me-4), 2.96 (s, 1 H, OH), 5.37 [d, 5 H, C_5H_5, *J*(PH) 1], 6.06 [d, 1 H, C*H*R, *J*(PH) 8], 6.15 [ddd, 1 H, PH_2, *J*(PH) 362, 6, *J*(HH) 2], 6.56 [dd, 1 H, PH_2, *J*(PH) 398, *J*(HH) 2], 7.17 [d, 2 H, C_6H_4Me-4, *J*(HH) 8], 7.61 [d, 2 H, C_6H_4Me-4, *J*(HH) 8], 7.67 (m, 2 H, $P_2C_6H_4$), 8.03 (m, 2 H, $P_2C_6H_4$)	[d] 19.8 [d, PMe, *J*(PC) 32], 21.2 (Me-4), 89.3 (C_5H_5), 114.1 [d, *C*HR, *J*(PC) 16], 129.5 [C^3, $C^5(C_6H_4Me\text{-}4)$], 130 [C^2, $C^6(C_6H_4Me\text{-}4)$],131.3–143.3[m,C^1,$C^4(C_6H_4Me\text{-}4)$,$P_2C_6H_4$], 147.5 [d, COH, *J*(PC) 46], 235.7 [d, WCO, *J*(PC) 24]
4	1.95 (s, 3 H, MeCN), 2.11 [d, 3 H, PMe, *J*(PH) 9], 2.24 (s, 3 H, Me-4), 3.31 [d, 1 H, CH_2, *J*(HH) 16], 3.64 [d, 1 H, CH_2, *J*(HH) 16], 5.38 [d, 5 H, C_5H_5, *J*(PH) 3], 6.30 [m, 1 H, PH_2, *J*(PH) 365], 6.75 [d, 2 H, C_6H_4Me-4, *J*(HH) 8], 6.93 [m, 1 H, PH_2, *J*(PH) 385], 7.03 [d, 2 H, C_6H_4Me-4, *J*(HH) 8], 7.67 (m, 2 H, $P_2C_6H_4$), 7.92 (m, 1 H, $P_2C_6H_4$), 8.03 (m, 1 H, $P_2C_6H_4$)	[d] 14.2 [d, PMe, *J*(PC) 32], 20.6 (Me-4), 46.0 [d, CH_2, *J*(PC) 42], 89.4 (C_5H_5), 129.5 [C^3,$C^5(C_6H_4Me\text{-}4)$], 130.0 [C^2,$C^6(C_6H_4Me\text{-}4)$], 131.0–140.6 [m, C^1, $C^4(C_6H_4Me\text{-}4)$, $P_2C_6H_4$], 217.2 [d, C=O, *J*(PC) 10], 234.1 [d, WCO, *J*(PC) 22]
5	[e] 2.06 [d, 3 H, PMe, *J*(PH) 11], 2.28 (s, 3 H, Me-4), 4.97 (s, 1 H, CHR), 5.09 [d, 5 H, C_5H_5, *J*(PH) 2], 6.52 [dd, 1 H, PH_2, *J*(PH) 381, 7], 6.87 [d, 1 H, PH_2, *J*(PH) 323], 7.02 [d, 2 H, C_6H_4Me-4, *J*(HH) 8], 7.33 [d, 2 H, C_6H_4Me-4, *J*(HH) 8], 7.60 (m, 2 H, $P_2C_6H_4$), 8.02 (m, 2 H, $P_2C_6H_4$)	[e] 7.7 [d, PMe, *J*(PC) 22], 21.0 (Me-4), 38.1 [d, *C*HR, *J*(PC) 56], 87.8 (C_5H_5), 127.3 [C^3, $C^5(C_6H_4Me\text{-}4)$], 128.4 [C^2, $C^6(C_6H_4Me\text{-}4)$], 130.7–145.6 [m, C^1, $C^4(C_6H_4Me\text{-}4)$, $P_2C_6H_4$], 162.3 [d, C=O, *J*(PC) 12], 232.3 [d, WCO, *J*(PC) 20]
6	2.19 [d, 3 H, PMe, *J*(PH) 13], 2.33 (s, 3 H, Me-4), 3.26 (s, 3 H, OMe), 4.19 [d, 1 H, CHR, *J*(PH) 9], 5.38 [d, 5 H, C_5H_5, *J*(PH) 1], 6.23 [m, 2 H, PH_2, *J*(PH) 457], 7.10 [d, 2 H, C_6H_4Me-4, *J*(HH) 8], 7.31 [d, 2 H, C_6H_4Me-4, *J*(HH) 8], 7.80 (m, 2 H, $P_2C_6H_4$), 8.15 (m, 1 H, $P_2C_6H_4$), 8.29 (m, 1 H, $P_2C_6H_4$)	20.9 (Me-4), 21.1 [d, PMe, *J*(PC) 24], 35.3 [d, *C*HR, *J*(PC) 27], 60.3 (OMe), 89.3 (C_5H_5), 96.9 [d, *C*OMe, *J*(PC) 22], 129.0 [C^3, $C^5(C_6H_4Me\text{-}4)$], 129.3 [C^2, $C^6(C_6H_4Me\text{-}4)$], 131.4–141.0 [m, C^1, $C^4(C_6H_4Me\text{-}4)$, $P_2C_6H_4$], 224.0 [d, WCO, *J*(PC) 17]
7	1.95 (s, 3 H, MeCN), 2.19 [d, 3 H, PMe, *J*(PH) 13], 2.33 (s, 3 H, Me-4), 3.23 (s, 1 H, OMe), 5.38 (s, 5 H, C_5H_5), 6.39 [d, 1 H, CHR, *J*(PH) 7], 6.69 [m, 1 H, PH_2, *J*(PH) 395], 7.19 [d, 2 H, C_6H_4Me-4, *J*(HH) 8], 7.47 [d, 2 H, C_6H_4Me-4, *J*(HH) 8], 7.48 [m, 1 H, PH_2, *J*(PH) 385], 7.67 (m, 2 H, $P_2C_6H_4$), 8.15 (m, 2 H, $P_2C_6H_4$)	[d] 20.0 [d, PMe, *J*(PC) 29], 21.2 (Me-4), 60.3 (OMe), 89.3 (C_5H_5), 114.2 (CHR), 128.8–147.8 [m, C_6H_4Me-4, $P_2C_6H_4$, *C*OMe], 235.8 [d, WCO, *J*(PC) 22]
9	[e] 2.20 [d, 3 H, PMe, *J*(PH) 7], 2.21 (s, 3 H, Me-4), 3.30 [d, 1 H, CH_2, *J*(HH) 16], 3.94 [d, 1 H, CH_2, *J*(HH) 16], 5.13 (s, 5 H, C_5H_5), 6.08 [ddd, 1 H, PH_2, *J*(PH) 343, 13, *J*(HH) 3], 6.55 [d, 2 H, C_6H_4Me-4, *J*(HH) 8], 6.87 [d, 2 H, C_6H_4Me-4, *J*(HH) 8], 7.01 [dd, 1 H, PH_2, *J*(PH) 385, *J*(HH) 3], 7.47 (m, 2 H, $P_2C_6H_4$), 7.62 (m, 1 H, $P_2C_6H_4$), 7.95 (m, 1 H, $P_2C_6H_4$)	[e] 16.1 [d, PMe, *J*(PC) 34], 20.8 (Me-4), 44.7 [d, CH_2, *J*(PC) 43], 87.3 (C_5H_5), 128.7 [C^3, $C^5(C_6H_4Me\text{-}4)$], 129.4 [C^2, $C^6(C_6H_4Me\text{-}4)$], 130.0–145.4 [m, C^1, $C^4(C_6H_4Me\text{-}4)$, $P_2C_6H_4$], 218.6 [d, C=O, *J*(PC) 17], 229.4 [d, WCO, *J*(PC) 22]
10	[e] 1.37 [m, 2 H, $P(CH_2)_4I$], 1.93 [m, 2 H, $P(CH_2)_4I$], 2.21 (s, 3 H, Me-4), 2.68 [m, 2 H, $P(CH_2)_4I$], 3.20 [m, 2 H, $P(CH_2)_4I$], 3.25 [d, 1 H, CH_2, *J*(HH) 17], 3.97 [d, 1 H, $C(O)CH_2$, *J*(HH) 17], 5.20 (s, 5 H, C_5H_5), 6.11 [ddd, 1 H, PH_2, *J*(PH) 340, 10, *J*(HH) 3], 6.56 [d, 2 H, C_6H_4Me-4, *J*(HH) 8], 6.88 [d, 2 H, C_6H_4Me-4, *J*(HH) 8], 6.98 [dd, 1 H, PH_2, *J*(PH) 385, *J*(HH) 3], 7.50 (m, 3 H, $P_2C_6H_4$), 7.95 (m, 1 H, $P_2C_6H_4$)	[e] 7.5 [$P(CH_2)_4I$], 21.1 (Me-4), 25.2 [$P(CH_2)_4I$], 27.7 [$P(CH_2)_4I$], 34.8 [d, $P(CH_2)_4I$, *J*(PC) 17], 45.0 [d, $C(O)CH_2$, *J*(PC) 42], 87.2 (C_5H_5), 138.9–145.0 [m, C_6H_4Me-4, $P_2C_6H_4$], 219.2 [d, $C(O)CH_2$, *J*(PC) 17], 229.1 [d, WCO, *J*(PC) 22]

[a] Chemical shifts in ppm, coupling constants in Hz, with measurements at room temperature. [b] Measured in CD_3CN unless otherwise noted. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$ (0.0 ppm), with measurements in CD_3CN unless otherwise noted. [d] The peaks of co-ordinated MeCN are masked by those of the solvents. [e] Measured in CD_2Cl_2.

Table 3 Phosphorus-31 NMR data

Compound	$\delta(^{31}P)$[a]
2	−37.5 [ddd, PH_2, *J*(PP) 15, *J*(HP) 479, 403, *J*(WP) 286], 11.9 [d, PMe, *J*(PP) 15]
3	−17.7 [ddd, PH_2, *J*(PP) 22, *J*(HP) 398, 362, *J*(WP) 234], 51.6 [d, PMe, *J*(PP) 22]
4	−19.4 [ddd, PH_2, *J*(PP), 22, *J*(HP) 385, 365], 58.0 [d, PMe, *J*(PP) 22]
5	[b] −26.0 [ddd, PH_2, *J*(PP) 22, *J*(HP) 381, 323, *J*(WP) 286], 57.0 [d, PMe, *J*(PP) 22]
6	−41.9 [dd, PH_2, *J*(HP) 457, 457, *J*(WP) 264], −1.7 (s, PMe)
7	−19.2 [ddd, PH_2, *J*(PP) 29, *J*(HP) 395, 385], 43.8 [d, PMe, *J*(PP) 29]
9	[b] −12.3 [ddd, PH_2, *J* (PP) 22, *J*(HP) 385, 343, *J*(WP) 264], 46.1 [d, PMe, *J*(PP) 22, *J*(WP) 316]
10	[b] −11.5 [ddd, PH_2, *J*(PP) 22, *J*(HP) 385, 340, *J*(WP) 264], 56.6 [d, $P(CH_2)_4I$, *J*(PP) 22, *J*(WP) 315]

[a] Hydrogen-1 coupled spectra, chemical shifts are positive to high frequency of 85% H_3PO_4 (external), *J* values in Hz. Measured in CD_3CN unless otherwise noted. [b] Measured in CD_2Cl_2.

4)]-1,2}(MeCN)(CO)(η-C_5H_5)]$^+$ **3**. Complex **3** subsequently undergoes very slow (10 d, 20 °C, MeCN) enol–keto tautomerisation, affording the isomeric ketone [W{σ^2-$C_6H_4(PH_2)$-[PMeC(O)$CH_2(C_6H_4Me\text{-}4)$]-1,2}(MeCN)(CO)(η-C_5H_5)]$^+$ **4**. The complexes **2**–**4** provide an interesting demonstration of the kinetically controlled synthesis of a co-ordinated enol and its subsequent isomerisation to the thermodynamically favoured ketone. Despite repeated attempts, **3** and **4** could not be isolated as crystalline solids and when MeCN solutions of these species were evaporated they gave yellow oils which slowly decomposed *in vacuo*. However, these complexes were readily identified from their solution spectroscopic data.

The IR spectrum of complex **3** shows an absorption at 1888 cm^{-1} due to the terminal CO ligand and a weak band at 1605

cm^{-1} tentatively ascribed to the C=C stretch of the free enol group. The ^1H NMR spectrum has resonances at δ 1.95 and 2.96 which may be attributed to the co-ordinated MeCN ligand and the hydroxyl group of the enol. Moreover, the vinylic *CH*R proton appears as a characteristically deshielded resonance at δ 6.06 [d, *J*(PH) 8 Hz] which is consistent with the presence of a non-co-ordinated enol group. In the ^{13}C-{^1H} NMR spectrum resonances at δ 114.1 [d, *J*(PC) 16 Hz] and 147.5 [d, *J*(PC) 46 Hz] are attributed to the *C*HR and COH carbon atoms of the free enol group and as expected these values are appreciably more deshielded than those found at δ 35.4 [d, *C*HR, *J*(PC) 25] and 96.8 [d, COH, *J*(PC) 24 Hz] for the co-ordinated enol precursor **2**.

The IR spectrum of the isomeric ketone **4** has a carbonyl absorption at 1888 cm^{-1} identical to that observed for the enol precursor **3**. Moreover, the ^1H-coupled ^{31}P NMR spectra for complexes **3** and **4** are also extremely similar, and these data confirm that there has been no change in co-ordination at the tungsten atom. The IR spectrum also shows an absorption at 1684 cm^{-1} which may be attributed to the ketonic C=O stretch of the $C(O)CH_2C_6H_4Me$-4 group. In the ^1H NMR spectrum doublets at δ 3.31 [*J*(HH) 16 Hz] and 3.64 [*J*(HH) 16 Hz] are observed for the diastereotopic protons of the $C(O)CH_2R$ fragment and the ^{13}C-{^1H} NMR spectrum shows a pair of doublets at δ 217.2 [*J*(PC) 10 Hz] and 46.0 [*J*[PC) 42 Hz] which are assigned to the C(O) and CH_2R atoms of the ketone group.

The cationic complex $[W\{\sigma^2,\eta^2\text{-}C_6H_4(PH_2)[PMeC(OH)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$ **2** has potentially acidic PH_2 and COH protons and its reactions with bases were therefore studied. Tretment of an MeCN solution of **2** with Et_3N immediately deprotonates the hydroxyl ligand affording a yellow precipitate of the neutral cyclic ketone derivative $[W\{\sigma^3\text{-}C_6H_4(PH_2)[PMeC(O)CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$ **5**. Unfortunately it was not possible to grow crystals of **5** suitable for an X-ray diffraction study and its structure has therefore been tentatively assigned from an analysis of its spectroscopic data. The IR spectrum has bands at 1854 and 1598 cm^{-1} which may be assigned to a terminal CO ligand and to the C=O group of the metallaphosphacyclobutanone ring system. The latter absorption lies at the low end of that expected for ketone groups and it is possible that the bonding in **5** has contributions from both ketone **5a** and enolate anion **5b** resonance hybrids. The ^1H-coupled ^{31}P NMR spectrum showed the expected resonances for the ligated PH_2 and PMe phosphorus atoms and in the ^{13}C-{^1H} NMR spectrum doublets at δ 38.1 [*J*(PC) 56 Hz] and 162.3 [*J*(PC) 12 Hz] are ascribed to the *C*HR and C=O groups, respectively. The latter ketonic resonance is significantly more shielded than that observed at δ 217.2 [d, *J*(PC) 10 Hz] for the acyclic $C(O)CH_2R$ group in complex **4**. This may reflect the constraints of the cyclic metallaphosphacyclobutanone ring system or be indicative of a contribution from the previously noted enolate anion resonance structure **5b**.

Treatment of complex **2** with $NaBH_4$ also leads to deprotonation and formation of **5** and attempts to synthesise a WCo dimetal species by treating **2** with an equivalent of $[Co(CO)_4]^-$ also gave **5** as the only isolable metal complex. Not surprisingly, protonation of **5** (HBF_4·Et_2O) regenerates **2** but more interestingly complex **5** undergoes facile O-methylation (Me_3OBF_4, Et_2O) affording $[W\{\sigma^2,\eta^2\text{-}C_6H_4(PH_2)\text{-}[PMeC(OMe)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$ **6**, a methoxy derivative of the hydroxy precursor **2**. Surprisingly, the latter reaction is also reversible and treatment of an MeCN solution of **6** with Et_3N regenerates **5**. The spectroscopic data for complex **6** are extremely similar to those of the hydroxy analogue **2** and the presence of the methoxy ligand was firmly established by the observation of appropriate resonances for the methyl group in both the ^1H and ^{13}C-{^1H} NMR spectra.

It was previously noted that MeCN displaces co-ordination of the enol moiety in complex **2** affording the MeCN cation **3**. The co-ordination of the methoxyvinyl group in **6** is similarly, albeit more slowly (3 d, 20 °C), displaced by MeCN affording the solvated cation $[W\{\sigma^2\text{-}C_6H_4(PH_2)[PMeC(OMe)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(MeCN)(CO)(\eta\text{-}C_5H_5)][BF_4]$ **7**. Spectroscopic data for **7** are comparable with those of the hydroxy analogue **3**, but the presence of the methoxy group in **7** prevents the enol–keto tautomerisation which occurs for **3**.

The reaction of the complex **1** with MeI was also investigated to allow comparison with the results obtained with Me_3OBF_4. An excess of MeI (CH_2Cl_2, 20 °C) affords a bright yellow precipitate of the iodide salt $[W\{\sigma^2,\eta^2\text{-}C_6H_4(PH_2)[PMeC(OH)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]I$ **8** (Scheme 2). Complex **8** is stable in the solid state and almost insoluble in CH_2Cl_2. On stirring in CH_2Cl_2 the complex slowly dissolves and simultaneously isomerises to the co-ordinated iodide complex $[WI\{\sigma^2\text{-}C_6H_4(PH_2)[PMeC(O)CH_2(C_6H_4Me\text{-}4)]\text{-}1,2\}\text{-}(CO)(\eta\text{-}C_5H_5)]$ **9**. It was therefore not possible to obtain solution spectroscopic data for complex **8** but the Nujol mull IR spectrum shows a single band at 1939 cm^{-1} which is very similar to that observed at 1932 cm^{-1} for the terminal CO ligand in the analogous BF_4^- salt **2**. The related reaction with 1,4-diiodobutane was also carried out in the hope of obtaining dimetal species from metallation of both ends of the diiodide chain. Unfortunately, the only product isolated from this reaction was the mononuclear tungsten complex $[WI\{\sigma^2\text{-}C_6H_4(PH_2)[P\{(CH_2)_4I\}C(O)CH_2(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$ **10**, an *n*-butyl iodide analogue of the methyl complex **9**.

The molecular structures of complexes **9** and **10** are shown in Figs. 1 and 2 and selected bond lengths and angles are given in Tables 4 and 5, respectively. The two structures are extremely similar. The tungsten atoms carry a cyclopentadienyl ring and are ligated by the *o*-phenylene bidentate phosphine, iodide, and CO ligands. In both cases the iodide ligand lies *trans* to the PH_2 end of the bidentate phosphine ligand and the W–PH_2 separations [2.377(2) in **9** and 2.388(4) Å in **10**] are significantly shorter than those to the phosphorus atoms which lie *trans* to the CO ligands [2.435(2) in **9** and 2.433(3) Å in **10**]. These W–P separations are typical of σ-bound phosphorus ligands and may be contrasted with the significantly longer W–P(allyl) π interaction [2.506(1) Å] observed in the phosphaallyl precursor **1**.[2] Few complexes with a $WI(\eta\text{-}C_5H_5)$ core have been structurally characterised and the W–I separations in **9** and **10** [2.856(1) Å] are somewhat longer than found in the related complexes $[WI\{=C(H)C_6H_4Me\text{-}4\}(CO)_2(\eta\text{-}C_5H_5)]$[4] [W–I 2.847(2) Å], $[WI\{=C(Ph)C(Ph)CH(C_6H_4Me\text{-}4)\}(CO)\text{-}(\eta\text{-}C_5H_5)]$[5] [W–I 2.832(1) Å], and $[WI(NO)(\eta^3\text{-}C_3H_5)]$[6] [W–I 2.8026(5) Å]. Interest centres on the alkylated phosphorus atom of the bidentate phosphine ligand which carries a methyl (**9**) or an *n*-butyl iodide (**10**) group, and an acyl group $C(O)CH_2C_6H_4Me$-4 which has arisen from isomerisation of the enol moiety $C(OH)=C(H)C_6H_4Me$-4 in the precursor **1**. The alkyl groups lie *syn* to the cyclopentadienyl rings which is consistent with stereospecific alkylation of the phosphorus lone pair in complex **1**. Phosphine ligands with acyl groups are rare but the P–C(acyl) and C=O separations in **9** [P–C 1.906(6), C=O 1.208(6) Å] and **10** [P–C 1.90(1), C=O 1.22(2) Å] are comparable with those found in the complexes $[MnBr\{PPh_2\text{-}C(O)CH_2CHClMe\}(CO)_4]$[7] [P–C 1.89(1), C=O 1.17(1) Å] and $[MnBr\{PPhMeC(O)CCl_3\}(CO)_4]$[8] [P–C 1.898(4), C=O 1.191(5) Å], whilst somewhat shorter P–C separations are found in the dipivaloylphosphido complex $[Ru\{P[C(O)Bu^t]_2\}\text{-}(CO)_2(\eta\text{-}C_5Me_5)]$[9] [P–C 1.873(3), 1.873(4); C=O 1.205(4), 1.205(5) Å]. In complex **9** the centroids of the C_6H_4Me-4 and *o*-phenylene arene ring systems are separated by 4.12 Å and the angle between the normals to the planes of these aromatic ring systems is 29.8°. This suggested the interesting possibility that complex **9** might act as a bidentate π-arene ligand to a second transition-metal atom but initial attempts to insert Cr or Mo atoms between these aromatic rings were unsuccessful.

Spectroscopic data for complexes **9** and **10** are consistent with

Table 4 Selected internuclear distances (Å) and angles (°) for [WI{$C_6H_4(PH_2)$[PMeC(O)$CH_2(C_6H_4Me$-4)]-1,2}(CO)(η-C_5H_5)] **9** with estimated standard deviations (e.s.d.s) in parentheses

W–I	2.856(1)	W–P(1)	2.435(2)	W–P(2)	2.377(2)	W–C(1)	1.936(5)
P(1)–C(2)	1.906(6)	P(1)–C(3)	1.824(5)	P(1)–C(21)	1.831(5)	P(2)–H(1)	1.32(5)
P(2)–H(2)	1.33(6)	P(2)–C(26)	1.806(5)	O(1)–C(1)	1.159(6)	O(2)–C(2)	1.208(6)
C(2)–C(10)	1.512(7)	C(10)–C(11)	1.503(8)				
I–W–P(1)	76.1(1)	I–W–P(2)	139.8(1)	P(1)–W–P(2)	77.2(1)	I–W–C(1)	81.7(1)
P(1)–W–C(1)	107.1(2)	P(2)–W–C(1)	78.1(1)	W–P(1)–C(2)	119.9(2)	W–P(1)–C(3)	118.5(2)
C(2)–P(1)–C(3)	100.1(2)	W–P(1)–C(21)	113.1(2)	C(2)–P(1)–C(21)	98.3(2)	C(3)–P(1)–C(21)	104.0(2)
W–P(2)–H(1)	127(2)	W–P(2)–H(2)	116(3)	W–P(2)–C(26)	116.0(2)	H(1)–P(2)–C(26)	96(3)
H(2)–P(2)–C(26)	100(3)	W–C(1)–O(1)	177.2(4)	P(1)–C(2)–O(2)	120.1(4)	P(1)–C(2)–C(10)	117.6(4)
O(2)–C(2)–C(10)	122.2(5)	C(2)–C(10)–C(11)	112.3(4)	P(1)–C(21)–C(22)	123.8(4)	P(1)–C(21)–C(26)	116.5(4)
C(22)–C(21)–C(26)	119.7(5)	P(2)–C(26)–C(21)	116.0(4)	P(2)–C(26)–C(25)	124.0(3)	C(21)–C(26)–C(25)	120.0(5)

Table 5 Selected internuclear distances (Å) and angles (°) for [WI{σ^2-$C_6H_4(PH_2)$[P{$(CH_2)_4$I}C(O)$CH_2(C_6H_4Me$-4)]-1,2}(CO)(η-C_5H_5)] **10** with e.s.d.s in parentheses

W–I(1)	2.856(1)	W–P(1)	2.388(4)	W–P(2)	2.433(3)	W–C(1)	1.93(2)
I(2)–C(5)	2.14(2)	I(2)···O	2.31(2)	P(1)–C(21)	1.81(1)	P(2)–C(2)	1.84(1)
P(2)–C(26)	1.84(1)	P(2)–C(29)	1.90(1)	C(1)–O(1)	1.16(2)	C(2)–C(3)	1.52(2)
C(3)–C(4)	1.50(2)	C(4)–C(5)	1.45(3)	C(29)–O(29)	1.22(2)	C(29)–C(30)	1.52(2)
C(30)–C(31)	1.53(2)						
I(1)–W–P(1)	140.6(1)	I(1)–W–P(2)	80.1(1)	P(1)–W–P(2)	77.2(1)	I(1)–W–C(1)	78.2(4)
P(1)–W–C(1)	77.8(4)	P(2)–W–C(1)	106.1(4)	C(5)–I(2)···O	78.0(7)	W–P(1)–C(21)	116.4(5)
W–P(2)–C(2)	119.0(5)	W–P(2)–C(26)	113.3(4)	C(2)–P(2)–C(26)	100.7(6)	W–P(2)–C(29)	119.8(4)
C(2)–P(2)–C(29)	101.3(6)	C(26)–P(2)–C(29)	99.4(6)	W–C(1)–O(1)	179(1)	P(2)–C(2)–C(3)	115.4(9)
C(2)–C(3)–C(4)	114(1)	C(3)–C(4)–C(5)	117(2)	I(2)–C(5)–C(4)	115(1)	P(1)–C(21)–C(22)	125(1)
P(1)–C(21)–C(26)	116(1)	C(22)–C(21)–C(26)	120(1)	P(2)–C(26)–C(21)	117(1)	P(2)–C(26)–C(25)	125(1)
C(21)–C(26)–C(25)	118(1)	P(2)–C(29)–O(29)	120(1)	P(2)–C(29)–C(30)	116(1)	O(29)–C(29)–C(30)	124(1)
C(29)–C(30)–C(31)	116(1)						

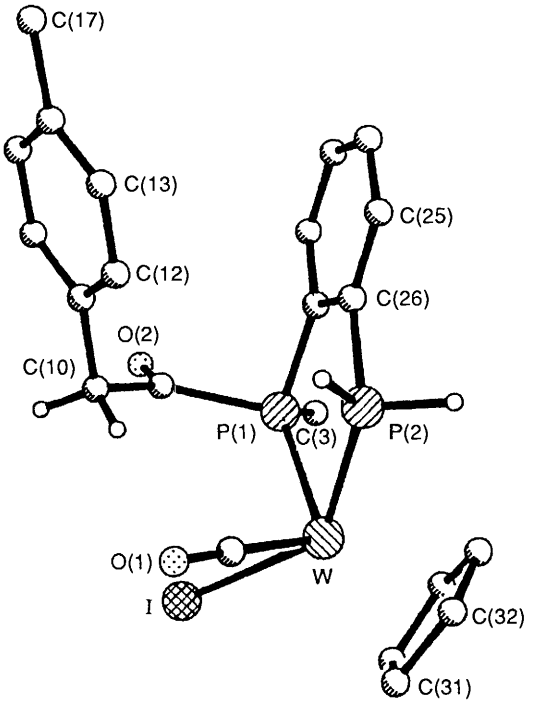


Fig. 1 The molecular structure of [WI{$C_6H_4(PH_2)$[PMeC(O)CH_2-(C_6H_4Me-4)]-1,2}(CO)(η-C_5H_5)] **9** showing the crystallographic numbering scheme

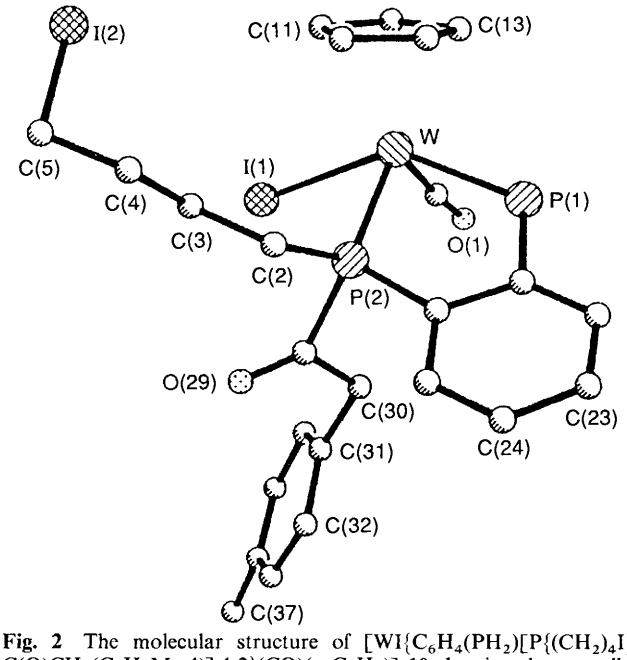
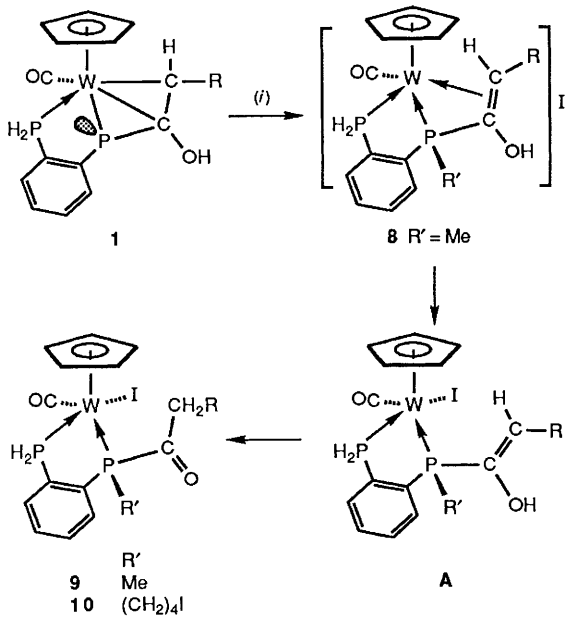


Fig. 2 The molecular structure of [WI{$C_6H_4(PH_2)$[P{$(CH_2)_4$I}-C(O)$CH_2(C_6H_4Me$-4)]-1,2}(CO)(η-C_5H_5)] **10** showing the crystallographic numbering scheme

the structures determined in the solid state by X-ray diffraction. These data have obvious similarities with those previously described for the structurally related cationic MeCN complex **4** and require no further comment. A mechanism which accounts for the formation of complexes **9** and **10** is shown in Scheme 2. Initial P-alkylation of complex **1** affords an iodide salt, which due to its poor solubility may be isolated for the methyl derivative **8**. Dissociation of the co-ordinated enol and attack of I^- would give a neutral enol intermediate **A**. Subsequent enol–keto tautomerisation would then afford the observed ketone complex **9** or **10**. There are obvious parellels in this mechanism with the conversion of complex **1** into **4** *via* the enol cations **2** and **3**. However, the final enol–keto tautomerisation of **3** to **4** is extremely slow, whilst the conversion of the proposed enol intermediate **A** into **9** or **10** must be extremely fast because we were unable to detect this species in solution. It is therefore possible that the final tautomerisation of **A** to **9** or **10** is base catalysed by the presence of iodide ions in the solution.

Table 6 Atomic positional parameters (fractional coordinates × 10^4) for compound **9** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
W	8 237(1)	−156(1)	7 907(1)
I	5 226(1)	913(1)	8 313(1)
P(1)	6 469(1)	−2 041(1)	8 054(1)
P(2)	9 765(1)	−1 407(1)	6 824(1)
O(1)	8 578(5)	1 721(4)	5 851(3)
O(2)	3 551(5)	−2 378(4)	7 840(3)
C(1)	8 410(5)	1 012(5)	6 623(3)
C(2)	4 794(6)	−1 783(5)	7 436(4)
C(3)	5 428(6)	−2 953(6)	9 289(3)
C(10)	5 118(7)	−889(5)	6 410(4)
C(11)	5 545(6)	−1 669(5)	5 611(4)
C(12)	7 056(7)	−1 633(6)	5 043(4)
C(13)	7 449(7)	−2 348(7)	4 301(4)
C(14)	6 367(7)	−3 095(6)	4 090(4)
C(15)	4 834(7)	−3 137(7)	4 658(5)
C(16)	4 447(6)	−2 433(6)	5 394(4)
C(17)	6 800(8)	−3 843(7)	3 257(5)
C(21)	7 422(6)	−3 346(5)	7 453(3)
C(22)	6 702(7)	−4 597(5)	7 537(4)
C(23)	7 475(8)	−5 485(5)	7 023(5)
C(24)	8 989(7)	−5 153(6)	6 406(4)
C(25)	9 707(6)	−3 938(5)	6 324(4)
C(26)	8 935(6)	−3 029(5)	6 860(3)
C(31)	9 453(8)	1 320(6)	8 542(4)
C(32)	10 517(6)	372(6)	8 221(4)
C(33)	9 956(7)	−894(6)	8 829(4)
C(34)	8 576(7)	−727(6)	9 529(4)
C(35)	8 268(7)	629(7)	9 343(4)
C(98)	11 064(19)	4 645(15)	9 371(12)
C(99)	9 512(33)	4 712(20)	9 368(16)
O(50)	11 233(23)	4 591(23)	10 207(19)



Scheme 2 R = C_6H_4Me-4, R′ = Me or $(CH_2)_4I$. (*i*) MeI or $I(CH_2)_4I$

Experimental

All experiments were carried out under dry oxygen-free nitrogen using Schlenk-tube techniques. Light petroleum refers to that fraction of b.p. 40–60 °C. All solvents were dried and deoxygenated before use. Products were separated by column chromatography on BDH Florosil (100–200 mesh). NMR spectra were recorded with JEOL JNM FX90Q, GX270 and GX400 spectrometers, and IR spectra with Nicolet MX5 or Perkin-Elmer 1600 spectrophotometers. The compound

Table 7 Atomic positional parameters (fractional coordinates × 10^4) for compound **10** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
W	10 308(1)	1 141(1)	1 180(1)
I(1)	8 760(1)	660(1)	1 115(1)
I(2)	8 190(1)	3 792(2)	321(1)
P(1)	11 376(2)	983(3)	1 849(2)
P(2)	9 867(2)	1 750(2)	2 173(2)
C(1)	10 355(8)	−122(11)	1 297(6)
O(1)	10 400(7)	−876(7)	1 364(6)
C(2)	9 494(7)	2 878(9)	2 188(6)
C(3)	8 839(8)	3 055(9)	1 743(7)
C(4)	8 620(11)	4 004(11)	1 696(8)
C(5)	8 013(12)	4 212(14)	1 269(10)
C(11)	10 013(11)	1 830(17)	229(8)
C(12)	10 487(13)	1 155(13)	97(7)
C(13)	11 142(10)	1 383(13)	389(8)
C(14)	11 031(11)	2 211(12)	708(7)
C(15)	10 329(12)	2 473(12)	608(8)
C(21)	11 303(8)	1 462(9)	2 625(6)
C(22)	11 876(7)	1 504(10)	3 055(7)
C(23)	11 768(9)	1 896(12)	3 644(7)
C(24)	11 076(10)	2 224(13)	3 800(8)
C(25)	10 515(9)	2 209(12)	3 366(7)
C(26)	10 605(8)	1 830(9)	2 772(6)
C(29)	9 128(8)	1 137(10)	2 644(6)
O(29)	8 573(5)	1 523(7)	2 831(5)
C(30)	9 306(8)	184(10)	2 802(7)
C(31)	8 670(9)	−340(10)	3 103(6)
C(32)	8 462(10)	−155(11)	3 725(7)
C(33)	7 906(11)	−631(12)	4 001(8)
C(34)	7 563(9)	−1 321(11)	3 677(9)
C(35)	7 785(10)	−1 491(11)	3 080(8)
C(36)	8 327(10)	−1 031(12)	2 797(7)
C(37)	6 997(10)	−1 896(12)	4 045(9)
O	9 172(15)	4 760(12)	471(6)

$[W\{\sigma,\eta^3\text{-}C_6H_4(PH_2)[PC(OH)CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$ **1** was prepared as previously described.[1,2] Analytical and other data for the new complexes are listed in Tables 1–3.

Alkylation Reactions of $[W\{\sigma,\eta^3\text{-}C_6H_4(PH_2)[PC(OH)CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$ **1**.—(*i*) A solution of complex **1** (0.125 g, 0.23 mmol) in CH_2Cl_2 (15 cm^3) was treated with Me_3OBF_4 (0.035 g, 0.23 mmol) and stirred at room temperature for 1 h. The yellow precipitate was collected by filtration and washed with CH_2Cl_2 (3 × 5 cm^3). Drying *in vacuo* yielded bright yellow microcrystals of $[W\{\sigma^2,\eta^2\text{-}C_6H_4(PH_2)[PMeC(OH)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$ **2** (0.13 g).

A solution of complex **2** in MeCN left at room temperature for 1 d rearranges to $[W\{\sigma^2\text{-}C_6H_4(PH_2)[PMeC(OH)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(MeCN)(CO)(\eta\text{-}C_5H_5)][BF_4]$ **3**. If complex **3** is left in MeCN for 10 d it undergoes enol–keto tautomerism to $[W\{\sigma^2\text{-}C_6H_4(PH_2)[PMeC(O)CH_2(C_6H_4Me\text{-}4)]\text{-}1,2\}(MeCN)(CO)(\eta\text{-}C_5H_5)][BF_4]$ **4**.

(*ii*) A solution of complex **1** (0.25 g, 0.45 mmol) in CH_2Cl_2 (10 cm^3) was treated with an excess of methyl iodide (0.5 cm^3) and stirred at room temperature. After *ca.* 5 min bright yellow microcrystals were deposited. The reaction mixture was left to stand for 45 min and yellow *microcrystals* of $[W\{\sigma^2,\eta^2\text{-}C_6H_4(PH_2)[PMeC(OH)=CH(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]I$ **8** (0.18 g) were obtained by filtration. Solvent was removed from the residual mother-liquor *in vacuo* and the residue was dissolved in the minimum volume of CH_2Cl_2–tetrahydrofuran (95:5). Chromatography on a Florosil column (2 × 40 cm) using the same solvent mixture afforded an orange band which was collected. Removal of the solvents *in vacuo* gave orange *microcrystals* of the complex $[WI\{\sigma^2\text{-}C_6H_4(PH_2)[PMeC(O)CH_2(C_6H_4Me\text{-}4)]\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$

9 (0.125 g). The orange-red crystals used for the X-ray diffraction studies were obtained by recrystallisation from tetrahydrofuran–CH_2Cl_2.

Complex **9** may be prepared in better yield by refluxing a CH_2Cl_2 solution of **8** for 15 min. Following chromatography as described above, complex **9** was obtained in *ca.* 80% yield. Solution spectroscopic data for complex **8** could not be recorded because as it dissolves in organic solvents it isomerises to **9**.

(*iii*) A solution of complex **1** (0.20 g, 0.36 mmol) in CH_2Cl_2–Et_2O (15 cm^3, 1:2) was treated with 1,4-diiodobutane (0.15 g, excess) and stirred at room temperature for 48 h. The solvents were removed *in vacuo* and the resulting red solid was redissolved in CH_2Cl_2 (10 cm^3) and chromatographed on a Florosil column (3 × 40 cm) Elution with CH_2Cl_2–light petroleum (1:1) afforded a red band which was collected. Removal of the solvents *in vacuo* afforded red *microcrystals* of [WI{σ^2-$C_6H_4(PH_2)$[P{$(CH_2)_4I$}C(O)$CH_2(C_6H_4Me$-4)]-1,2}(CO)(η-C_5H_5)] **10** (0.095 g). Crystals for the X-ray diffraction study were obtained by recrystallisation from tetrahydrofuran-Et_2O.

Reaction of [W{σ^2,η^2-$C_6H_4(PH_2)$[PMeC(OH)=CH(C_6H_4-Me-4)]-1,2}(CO)(η-C_5H_5)][BF_4] **2** *with Triethylamine.*—A solution of complex **2** (0.120 g, 0.18 mmol) in MeCN (3 cm^3) was treated with triethylamine (0.030 g, 0.3 mmol) and shaken. On standing for 15 min a yellow crystalline product precipitated and was collected by filtration. The product was washed with MeCN (3 × 2 cm^3) and dried *in vacuo* to give yellow *microcrystals* of [W{σ^3-$C_6H_4(PH_2)$[PMeC(O)CH(C_6H_4Me-4)]-1,2}(CO)(η-C_5H_5)] **5** (0.098 g).

Reaction of [W{σ^3-$C_6H_4(PH_2)$[PMeC(O)CH(C_6H_4Me-4)]-1,2}(CO)(η-C_5H_5)] **5** *with* Me_3OBF_4.—A solution of complex **5** (0.10 g, 0.18 mmol) in CH_2Cl_2 (15 cm^3) was treated with Me_3OBF_4 (0.027 g, 0.18 mmol) and stirred at room temperature for 1 h. The resulting orange precipitate was collected by filtration and washed with CH_2Cl_2–Et_2O (3 × 5 cm^3, 1:1). Drying *in vacuo* yielded orange microcrystals of [W{σ^2,η^2-$C_6H_4(PH_2)$[PMeC(OMe)=CH(C_6H_4Me-4)]1,2}(CO)(η-C_5H_5)][BF_4] **6** (0.095 g). A solution of complex **6** in MeCN left at room temperature for 4 d rearranges to [W{σ^2-$C_6H_4(PH_2)$[PMeC(OMe)=CH(C_6H_4Me-4)]-1,2}(MeCN)(CO)(η-C_5H_5)][BF_4] **7**.

Crystal Structure Determinations.—Data were collected using Nicolet $P2_1$ or $P\bar{3}$ diffractometers (293 K, Mo-Kα X-radiation, graphite monochromator, $\bar{\lambda}$ = 0.710 69 Å). They were corrected for Lorentz, polarisation and X-ray absorption effects. The structures were solved by conventional heavy-atom or direct methods and successive Fourier difference syntheses were used to locate all non-hydrogen atoms. Final refinements by blocked-cascade or full-matrix least-squares procedures were performed on Data General 'Eclipse' or μ-Vax computers with the SHELXTL system of programs.[10] Scattering factors with corrections for anomalous dispersion were taken from ref. 11. Atom coordinates are given in Tables 6 and 7.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

[WI{σ^2-$C_6H_4(PH_2)$[PMeC(O)$CH_2(C_6H_4$Me-4)]-1,2}(CO)(η-C_5H_5)]·0.5C_4H_8O **9**. Crystals of complex **9** were grown from tetrahydrofuran-CH_2Cl_2 mixtures as dark red plates (crystal dimensions *ca.* 0.45 × 0.30 × 0.25 mm). Of the 4826 data collected (WycKoff ω scans, $2\theta \leqslant 50°$), 3982 unique data had $F \geqslant 5\sigma(F)$, and only these were used for structure solution and refinement. An empirical absorption correction was applied using a method based upon azimuthal scan data.

Crystal data. $C_{22}H_{23}IO_2P_2W$·(0.5C_4H_8O), M = 728.2, triclinic, space group $P\bar{1}$, a = 8.892(3), b = 10.232(3), c = 14.315(6) Å, α = 77.60(3), β = 75.31(3), γ = 89.68(3)°, U = 1228.8(8) Å^3, Z = 2, D_c = 1.97 g cm^{-3}, $F(000)$ = 696, μ(Mo-Kα) = 61.9 cm^{-1}.

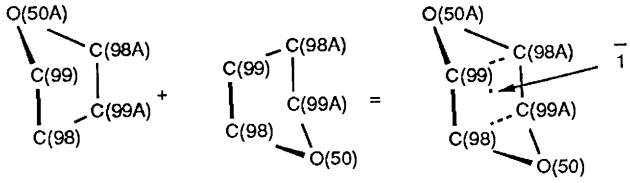


Fig. 3 Disordered tetrahydrofuran in complex **9**

All non-hydrogen atoms were refined with anisotropic thermal parameters. The PH_2 hydrogen atoms were located from a final electron-density difference synthesis and their positions were refined with fixed isotropic thermal parameters (U = 0.06 Å^2). All other hydrogen atoms were included in calculated positions (C–H 0.96 Å) with either fixed isotropic thermal parameters (U = 0.08 Å^2; C_6H_4, $CH_2C_6H_4$Me-4, and η-C_5H_5) or a common refined isotropic thermal parameter (Me-4, PMe, and $CH_2C_6H_4$Me-4). Final R = 0.024 (R' = 0.026) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0003\ |F|]^2]$. The final electron-density difference synthesis showed no peaks >0.61 or < −0.78 e Å^{-3}.

The asymmetric unit contains half a molecule of tetrahydrofuran which is disordered about the inversion centre (1, 0.5, 1). The nature of the disorder is shown in Fig. 3, atoms generated by symmetry being indicated by the suffix A. The CH_2 carbon atoms C(98) and C(99) were refined with unit site occupation whilst O(50) was given a site occupancy of 0.5. The marked deviations from the expected geometry and the comparatively large thermal parameters reflect the fact that the separations C(98)–C(99A) and C(99)–C(98A) represent bonding interactions in one of the disordered components and non-bonded separations in the other. We were unable to resolve alternative sites for these atoms and, in view of the distorted geometry, solvent hydrogen atoms were not included in the refinement.

[WI{σ^2-$C_6H_4(PH_2)$[P{$(CH_2)_4I$}C(O)$CH_2(C_6H_4$Me-4)]-1,2}(CO)(η-C_5H_5)]·H_2O **10**. Crystals of complex **10** were grown from tetrahydrofuran–Et_2O mixtures as dark red prisms (crystal dimensions *ca.* 0.62 × 0.35 × 0.30 mm). Of the 5803 data collected (WycKoff ω scans, $2\theta \leqslant 50°$), 3215 unique data had $F \geqslant 5\sigma(F)$, and only these were used for structure solution and refinement. An empirical absorption correction was applied using a method based upon azimuthal scan data.

Crystal data. $C_{25}H_{28}I_2O_2P_2W$·H_2O, M = 878.1, orthorhombic, space group *Pbca*, a = 17.819(4), b = 15.157(3), c = 21.256(6) Å, U = 5741(2) Å^3, Z = 8, D_c = 2.03 g cm^{-3}, $F(000)$ = 3312, μ(Mo-Kα) = 63.7 cm^{-1}.

The atoms of the $(CH_2)_4I$ group have comparatively large thermal parameters, the greatest thermal motion being observed for the terminal iodine atom I(2). It was not possible to resolve separate disordered components for these chain atoms. The iodine atom I(2) is hydrogen-bonded to a molecule of H_2O. All non-hydrogen atoms were refined with anisotropic thermal parameters. The PH_2 and H_2O hydrogen atoms could not be located in a final electron-density difference synthesis and they were not included in the refinement. All other hydrogen atoms were included in calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters (U = 0.08 Å^2). Final R = 0.049 (R' = 0.049 with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0004\ |F|^2]$. The final electron-density difference synthesis showed no peaks >1.44 or < −2.28 e Å^{-3}, the latter peaks lying in the vicinity of the iodine atom attached to the alkyl chain.

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