η-Cyclopentadienyltungsten Compounds with Vinyl- and Allyl-phosphine Ligands†

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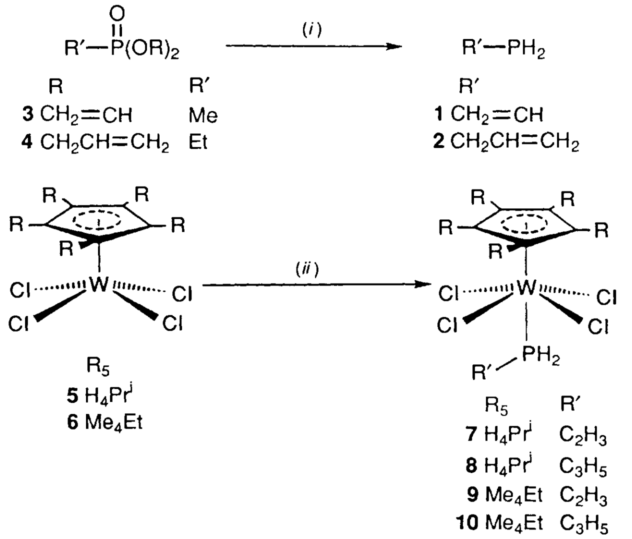
The properties as ligands of the primary phosphines $PH_2(CH{=}CH_2)$ **1** and $PH_2(CH_2CH{=}CH_2)$ **2** have been studied. The new compounds $[W(\eta\text{-}C_5R_5)Cl_4(PH_2R')]$ ($R_5 = H_4Pr^i$, $R' = CH{=}CH_2$ **7** or $CH_2CH{=}CH_2$ **8**; $R_5 = Me_4Et$, $R' = CH{=}CH_2$ **9** or $CH_2CH{=}CH_2$ **10**), $[W_2(\eta\text{-}C_5H_4Pr^i)_2X_4(\mu\text{-}H)(\mu\text{-}PHR)]$ (X = Cl, $R = CH{=}CH_2$ **12** or $CH_2CH{=}CH_2$ **13**; X = Br, $R = CH{=}CH_2$ **15**), $[W_2(\eta\text{-}C_5Me_5)_2Cl_4(\mu\text{-}H)(\mu\text{-}PHC_2H_3)]$ **17** and $[W_2(\eta\text{-}C_5Me_5)_2Cl_2(\mu\text{-}Cl)(\mu\text{-}PHC_2H_3)]$ **18** have been prepared. The crystal structures of compounds **10** and **17** have been determined.

The primary phosphines $PH_2(CH{=}CH_2)$ **1** and $PH_2(CH_2CH{=}CH_2)$ **2** have been described[1–3] and are available in gram quantities. Both these phosphines are bifunctional and have the potential to act as ligands to transition metals by co-ordination using the phosphorus atom or the carbon–carbon double bond, or both. Here we describe an exploratory synthetic study of the reactivity of these phosphines towards the tungsten centre of the tungsten compounds in the classes $[W(\eta\text{-}C_5R_5)Cl_4]$ and $[W_2(\eta\text{-}C_5H_4Pr^i)_2X_4]$ (X = Cl or Br).

Results and Discussion

The reported syntheses of vinylphosphine **1** and allylphosphine **2** proceed by the reduction under reduced pressure (5×10^{-3}–10^{-5} mbar) using $AlHCl_2$,[4] which is formed *in situ*, of the corresponding vinyl- and allyl-phosphonate esters $R'P(O)(OR')_2$ ($R = CH{=}CH_2$, R' = Me **3**; $R = CH_2CH{=}CH_2$, R' = Et **4**) (Scheme 1).[3] The solvent used was the high boiling tetraglyme $[Me(OCH_2CH_2)_4OMe]$ and the pure phosphines were distilled from the reaction mixture as they formed. Although an excellent regioselectivity (90–95%) was observed, the presence (5–10%) of phosphines $R''PH_2$ (R'' = Et or Pr^n) resulting from further reductions of the phosphonate starting materials could not be avoided. This was mainly due to the inability to carry out the reduction below *ca.* −10 °C since at that temperature the reaction mixture was highly viscous. We have modified this synthesis using the apparatus described in the Experimental section. We found that by decreasing the vacuum to 10^{-2} mbar and using triglyme $[Me(OCH_2CH_2)_3OMe]$ as solvent it was possible to lower the reaction temperature to −40 °C. This resulted in a higher regioselectivity of the reduction (> 99%) with similar yields (60–65%). Under these conditions the phosphines **1** and **2** were readily prepared on a scale of 10–20 g.



Scheme 1 (*i*) $AlCl_3$ in triglyme, $LiAlH_4$, at −45 °C; (*ii*) PH_2R, $R = CH{=}CH_2$ or $CH_2CH{=}CH_2$, in thf at −40 °C. Yields *ca.* 80%

Treatment of the tetrahalide monomers $[W(\eta\text{-}C_5R_5)Cl_4]$ ($R_5 = H_4Pr^i$ **5** or Me_4Et **6**) with one equivalent of vinyl- or allyl-phosphine gave a change from red to green (for **5**) or from green to red (for **6**) and the mono-adducts $[W(\eta\text{-}C_5R_5)Cl_4(PH_2R')]$ ($R_5 = H_4Pr^i$, R' = vinyl **7**; $R_5 = H_4Pr^i$, R' = allyl **8**; $R_5 = Me_4Et$, R' = vinyl **9**; $R_5 = Me_4Et$, R' = allyl **10**), were isolated in *ca.* 80% yields. The new paramagnetic (NMR) compounds **7**–**10** are air sensitive. They have been characterised by elemental analysis and by infrared spectroscopy (Tables 1 and 2). The infrared spectra confirm the presence of both ν(P–H) and ν(C=C) absorptions (Table 1). All the compounds **7**–**10** show bands assignable to ν(P–H) in the range 2392–2396 cm^{-1}, each band exhibiting a shoulder. The values for ν(P–H) are *ca.* 100 cm^{-1} lower than those for the corresponding unco-ordinated phosphines[1,3] (Table 1). We note that the ν(P–H) absorptions for the previously described $[W(CO)_5(PH_2C{\equiv}CH)]$[5] and $[Mo(CO)_3(PH_2CH_2CH{=}CH_2)_3]$,[6] are also shifted to longer wavenumbers, compared to ν(P–H) of the free phosphines. Surprisingly the compound $[W(\eta\text{-}C_5Me_5)Cl_4(PH_2Ph)]$ shows essentially no shift of ν(P–H) (see Table 1).[7,8]

Bands assignable to ν(C=C) are observed at *ca.* 1597 cm^{-1} for the vinyl compounds **7** and **9**, and at *ca.* 1630 cm^{-1} for the allyl derivatives **8** and **10**. There is little change in the ν(C=C) absorption band on complexation of the phosphine ligands indicating the C=C groups are not bonding to the tungsten centre.

It is notable that treatment **5** or **6** with excess of vinyl- or

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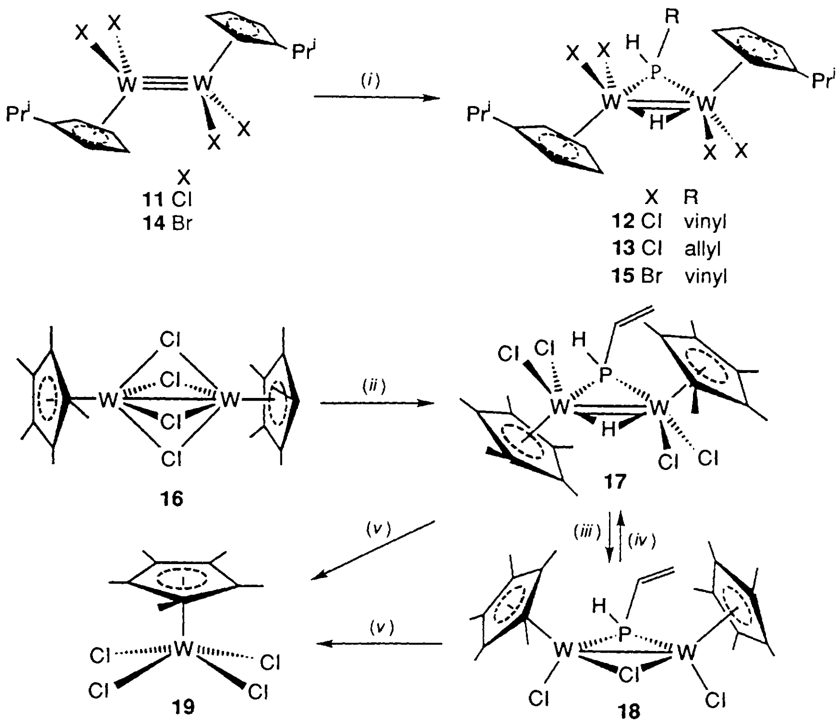
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: bar = 10^5 Pa.



Scheme 2 (*i*) PH_2R, R = $CH{=}CH_2$ or $CHCH{=}CH_2$, in thf at −40 °C, > 80%; (*ii*) $PH_2CH{=}CH_2$ in thf at r.t., 98%; (*iii*) $NMe(SiMe_3)_2$ (or NEt_3) in thf at −20 °C; warm to 45 °C, 55%; (*iv*) 1 equivalent HCl gas in thf, *ca.* 30%; (*v*) excess of HCl gas in thf at r.t., *ca.* 60%

Table 1 A comparison of the ν(P–H) and ν(C=C) frequencies for various free or co-ordinated multiply-bonded primary phosphines

Compound	Ref.	ν(P–H)	ν(C=C)
$PH_2(CH{=}CH_2)$	1, 3	2295	1595
$PH_2(CH_2CH{=}CH_2)$	2	2290	1633
$PH_2C{\equiv}CH$	5	2300	—
PH_2Ph	8	2295	—
$[W(CO)_5(PH_2C{\equiv}CH)]$	5	2338	—
$[Mo(CO)_3(PH_2CH_2CH{=}CH_2)_3]$	6	2302, 2294	1633
$[W(\eta\text{-}C_5Me_5)Cl_4(PH_2Ph)]$	7	2300	—
7		2396 (sh)	1598
8		2392 (sh)	1632
9		2392 (sh)	1597
10		2396 (sh)	1630
12		2333	1628
13		2334	1632
15		2329	1635
17		2335	1639
18		2296	1633

allyl-phosphine produced only **7**–**10** as described above, whereas treatment of **5** with an excess of PMe_3 causes displacement of the η-cyclopentadienyl ring giving the compound $[W(PMe_3)_3Cl_4]$.[9]

The crystal structure of $[W(\eta\text{-}C_5Me_4Et)Cl_4(PH_2C_3H_5)]$ **10** has been determined. The molecular structure of **10** is shown in Fig. 1, and selected bond lengths and angles are listed in Table 3; fractional atomic coordinates are given in Table 4. The structure of **10** can be described as distorted octahedral with the four chlorine atoms lying in the equatorial plane. The molecular structure shows W–P [2.554(2)], W–Cl [2.385–2.410(2)] and P–C [1.77(1) Å] bond lengths which are consistent with those reported for other similar structures. The short length of C(2)–C(3) [1.20(2) Å] is consistent with the presence of a double bond.

Comparison of complex **10** with the crystallographically characterised $[W(\eta\text{-}C_5H_4Pr^i)Cl_4]$[9] **5** shows that all the Cp_{cent}–W(1)–Cl angles are more acute in the case of the former. The average value for **5** is 110°, whereas for **10** it is 105°. Correspondingly the Cl(1)–W–Cl(3) angle is 10° more acute in the case of the latter compound. The angle Cp_{cent}–W–P(1) 176.4° indicates that the phosphorus is located as far away from the C_5Me_4Et ligand as possible. The bond angle Cl(3)–W–P(1) 78.26(9)° is significantly greater than that for the other three Cl atoms; this reflects the position of the C(1) of the allyl group which is pointing towards Cl(3). Finally, a similar distorted octahedral geometry can be seen in the dimeric structure of $[\{WCl_4(PMe_3)\}_2(C_5Me_5CH_2CH_2C_5Me_5)]$.[10]

Treatment of the W≡W triply bonded dimer $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ **11** in tetrahydrofuran (thf) with vinylphosphine **1** or allylphosphine **2** gave the μ-phosphido derivatives $[W_2(\eta\text{-}C_5H_4Pr^i)_2X_4(\mu\text{-}H)(\mu\text{-}PHR)]$ (X = Cl, R = vinyl **12**; X = Cl, R = allyl **13**), respectively. Similarly, treatment of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Br_4]$ **14** with vinylphosphine gave $[W_2(\eta\text{-}C_5H_4Pr^i)_2Br_4(\mu\text{-}H)(\mu\text{-}PHC_2H_3)]$ **15**, in high yield.

The new compounds **12**, **13** and **15** have been characterised by elemental analysis, by ^1H, ^{13}C and ^{31}P NMR spectroscopy and by infrared spectroscopy (Tables 1 and 2). The proposed structures are shown in Scheme 2. The ^1H NMR spectra of **12**, **13** and **15** show two inequivalent diastereotopic $\eta\text{-}C_5H_4Pr^i$ ligands (proximal to either the PH or PR functionality). For each compound there are eight resonances occurring between δ 6.2 and δ 4.6, each integrating as one H atom, assignable to four different hydrogens of each $\eta\text{-}C_5H_4$ fragment. Similar observations have been reported for other oxidative-addition reaction products of W≡W triply bonded dimers. The ^1H NMR spectrum of **12** shows a doublet of doublets $[^3J(^1H\text{-}^1H) = 10.3$ and $^1J(^{31}P\text{-}^1H) = 424$ Hz] at δ 9.48, which integrates as one H atom and is assignable to the P–H group. Similar low-field resonances are observed in the spectra of **13** and **15** at δ 9.14 and 10.28, respectively. For all the three compounds **12**, **13** and **15** an additional signal at high field, at about δ −1.7, with a $^2J(^{31}P\text{-}^1H)$ coupling constant of *ca.* 5.5 Hz and which integrates as one H atom is characteristic of a W–H–W hydrogen. These signals show ^{183}W satellites of the intensity expected for a hydrogen atom bonded to two tungsten atoms

Table 2 Analytical and spectroscopic data

Compound	Colour	Analysis[a] (%) C	H	Halide	NMR[b]
8	Brown	25.65 (26.05)	3.65 (3.60)	27.5 (28.0)	Paramagnetic
7	Green-brown	24.60 (24.35)	3.35 (3.25)	29.05 (28.75)	Paramagnetic
10	Red	30.85 (30.65)	4.40 (4.45)	26.0 (26.0)	Paramagnetic
9	Brown	29.05 (29.20)	4.13 (4.15)	26.05 (26.15)	Paramagnetic
12	Green-brown	27.80 (27.60)	3.45 (3.45)	18.0 (18.0)	^{1}H:^{c} 9.48 [1 H, dd, $^{3}J(^{1}$H–^{1}H) 10.3, $^{1}J(^{31}$P–^{1}H) 424, μ-P*H*CH=CH$_2$], 6.72 (1 H, m, μ-PHC*H*=CH$_2$), 6.22 (2 H, m, η-C$_5$*H*$_4$Pr^{i}), 6.02 (2 H, m, μ-PHCH=C*H*$_2$), 5.87 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 5.81 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 5.14 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 5.09 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 4.72 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 4.68 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 2.46 [2 H, overlapping 2 × spt, $^{3}J(^{1}$H–^{1}H) 7.3, C*H*Me$_2$], 0.92 (12 H, qd, CH*Me*$_2$), −1.66 [1 H, d, $^{2}J(^{31}$P–^{1}H) 6.2, $^{1}J(^{183}$W–^{1}H) 95.5 (combined area is *ca.* 28%), W(μ-H)W] ^{13}C-{^{1}H}:^{c} 140.6 [d, $^{1}J(^{31}$P–^{13}C) 55.9 PH*C*H=CH$_2$], 136.1, 135.1 [*C*Pr^{i}, η-C$_5$H$_4$Pr^{i}], 130.4 (PHCH=*C*H$_2$), 104.0, 103.2, 101.9, 101.3, 95.6, 94.7, 92.8, 91.8 (*C*H, η-C$_5$H$_4$Pr^{i}), 28.0 (*C*HMe$_2$), 22.6, 21.5 (CH*Me*$_2$) ^{31}P-{^{1}H}:^{c} 258.3 [$^{1}J(^{31}$P–^{183}W) 226 (combined area is *ca.* 28%)]
13	Green	29.55 (28.5)	3.80 (3.65)	17.5 (18.0)	^{1}H:^{c} 9.14 [1 H, dt, $^{3}J(^{1}$H–^{1}H) 5.6, $^{1}J(^{31}$P–^{1}H) 418, μ-P*H*C$_3$H$_5$], 6.16 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 6.05 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 6.03 (1 H, m, μ-PHCH$_2$C*H*=CH$_2$), 5.84 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 5.78 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 5.72 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 5.16 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 5.08 (2 H, m, μ-PHCH$_2$CH=C*H*$_2$), 4.70 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 4.60 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 3.82 (1 H, m, μ-PHC*H*$_2$CH=CH$_2$), 2.95 (2 H, m, μ-PHC*H*$_2$CH=CH$_2$), 2.44 [2 H, overlapping 2 × spt, $^{3}J(^{1}$H–^{1}H) 7.3, C*H*Me$_2$], 1.21 (12 H, qd, CH*Me*$_2$), −1.80 [1 H, d, $^{2}J(^{31}$P–^{1}H) 5.3, $^{1}J(^{183}$W–^{1}H) 95.3 (combined area is *ca.* 28%), W(μ-H)W] ^{13}C-{^{1}H}:^{c} 136.0, 135.3 (*C*Pr^{i}, η-C$_5$H$_4$Pr^{i}), 133.7 [d, $^{2}J(^{31}$P–^{13}C) 10.0, PHCH$_2$*C*H=CH$_2$], 119.8 [d, $^{3}J(^{31}$P–^{13}C) 10.0, PHCH$_2$CH=*C*H$_2$], 102.7, 102.5, 101.8, 101.7, 95.3, 95.1, 91.6 (*C*H, η-C$_5$H$_4$Pr^{i}), 35.8 [d, $^{1}J(^{31}$P–^{13}C) 28.5, PH*C*H$_2$CH=CH$_2$], 27.9, 27.8 (*C*HMe$_2$), 22.2, 21.2 (CH*Me*$_2$) ^{31}P-{^{1}H}:^{c} 258.15 [$^{1}J(^{31}$P–^{183}W) 220.8 (combined area is *ca.* 28%)]
15	Green	22.80 (22.50)	2.90 (2.85)	33.0 (33.0)	^{1}H:^{c} 10.28 [1 H, dd, $^{3}J(^{1}$H–^{1}H) 11.3, $^{1}J(^{31}$P–^{1}H) 433, μ-P*H*CH=CH$_2$], 6.80 (1 H, m, μ-PHC*H*=CH$_2$), 6.23 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 6.20 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 6.00 (2 H, m, μ-PHCH=C*H*$_2$), 5.84 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 5.78 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 5.72 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 5.16 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 4.70 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 4.60 (1 H, virtual q, η-C$_5$*H*$_4$Pr^{i}), 2.60 [2 H, overlapping 2 × spt, $J(^{1}$H–^{1}H) 7.3, C*H*Me$_2$], 0.83 (12 H, qd, CH*Me*$_2$), −1.78 [1 H, d, $^{2}J(^{31}$P–^{1}H) 5.2, $^{1}J(^{183}$W–^{1}H) 99.5 (combined area is *ca.* 28%), W(μ-H)W] ^{13}C-{^{1}H}:^{c} 140.6 [d, $^{1}J(^{31}$P–^{13}C) 51.3, PH*C*H=CH$_2$), 135.6, 133.9 (*C*Pr^{i}, η-C$_5$H$_4$Pr^{i}), 130.4 (PHCH=*C*H$_2$), 103.4, 103.1, 102.7, 96.2, 95.3, 92.6, 92.0 (*C*H, η-C$_5$H$_4$Pr^{i}), 28.5 (*C*HMe$_2$), 22.6, 21.5, 21.4 (CH*Me*$_2$) ^{31}P-{^{1}H}:^{c} 261.0 [$^{1}J(^{31}$P–^{183}W) 231 (combined area is *ca.* 28%)]
17	Green	31.65 (31.45)	4.20 (4.20)	17.0 (17.0)	^{1}H:^{d} 9.46 [1 H, dd, $^{3}J(^{1}$H–^{1}H) 11.2, $^{1}J(^{31}$P–^{1}H) 416, μ-P*H*CH=CH$_2$], 6.80 (1 H, m, μ-PHC*H*=CH$_2$), 6.63 [1 H, dd, $^{3}J(^{31}$P–^{1}H$_{trans}$) 46.8, $^{3}J(^{1}$H–^{1}H$_{cis}$) 18.0, μ-PHCH=C*H*$_2$], 6.30 [1 H, dd, $^{3}J(^{31}$P–^{1}H$_{cis}$) 17.7, $^{3}J(^{1}$H–^{1}H$_{trans}$) 26.7, μ-PHCH=C*H*$_2$], 2.10 (d, 30 H, C$_5$Me$_5$), −1.28 [1 H, d, $^{2}J(^{31}$P–^{1}H) 5.4, $^{1}J(^{183}$W–^{1}H) 102.6 (combined area is *ca.* 28%), W(μ-H)W] ^{13}C-{^{1}H}:^{d} 139.1 [d, $^{1}J(^{31}$P–^{13}C) 44.5, PH*C*H=CH$_2$], 130.1 (PHCH=*C*H$_2$), 114.2, 114.0 [*C*$_5$Me$_5$], 11.7, 10.7 [C$_5$*Me*$_5$] ^{31}P-{^{1}H}:^{d} 270 [$^{1}J(^{31}$P–^{183}W) 231 (combined area is *ca.* 28%)]
18	Green	32.60 (32.90)	4.25 (4.25)	12.90 (13.25)	^{1}H:^{d} 8.24 [1 H, dd, $^{3}J(^{1}$H–^{1}H) 9, $^{1}J(^{31}$P–^{1}H) 155, μ-P*H*CH=CH$_2$], 6.38 (3 H, m, μ-PHC*H*=C*H*$_2$), 2.21 (30 H, s, C$_5$Me$_5$) ^{13}C-{^{1}H}:^{d} 140.7 [d, $^{1}J(^{31}$P–^{13}C) 58.5, PH*C*H=CH$_2$], 121.5 (PHCH=*C*H$_2$), 103.3 (*C*$_5$Me$_5$), 14.0 (C$_5$*Me*$_5$) ^{31}P-{^{1}H}:^{d} −17.4 [$^{1}J(^{31}$P–^{183}W) 158 (combined area is *ca.* 28%)]

[a] Given as: Found (calc.) %. [b] Data for ^{1}H given as: chemical shift (δ) [relative intensity, multiplicity (*J* in Hz), assignment], *etc.* [c] In C$_6$D$_6$. [d] In CD$_2$Cl$_2$.

[$^{1}J(^{183}$W–^{1}H) *ca.* 95 Hz; *ca.* 28% of the total signal intensity]. The ^{31}P-{^{1}H} NMR spectra of **12**, **13** and **15** each show one signal at *ca.* δ 260, with the expected ^{183}W satellites [$^{1}J(^{183}$W–^{1}H) *ca.* 225 Hz]. In the ^{1}H coupled spectra the aforementioned signals are split into doublets with the same $^{1}J(^{31}$P–^{1}H) coupling constant confirming that only one H atom is bonded to the phosphorus atom.

The ^{13}C-{^{1}H} NMR spectra of **12**, **13** and **15** in association with the distortionless enhancements by polarization transfer (DEPT) pulse sequence ^{13}C experiments have proved to be particularly useful for the characterisation of these compounds. They show sets of signals corresponding to the two diastereotopic C$_5$H$_4$Pr^{i} groups. For **12** and **15** the carbon atoms of the vinyl group exhibit resonances at δ 140.6 [CH, $^{1}J(^{31}$P–^{13}C) *ca.* 55 Hz] and 130.4 [CH$_2$, $^{2}J(^{31}$P–^{13}C) ≈ 0 Hz]. The complexation of the phosphorus atom to the tungsten centres does not seem to have an effect on the $^2J(^{31}P-^{13}C)$ coupling constant which is similar to that of the free phosphines. However, as expected, the value of the $^1J(^{31}P-^{13}C)$ coupling constant lies between those reported for free vinylphosphines (P^{III}, *ca.* 10–20 Hz) and vinylphosphonates (P^{V}, *ca.* 100–120 Hz). For compound **13**, the two carbons of the double-bond function give more shielded signals, as compared to the resonances of those of the vinyl group in **12** and **15**, at δ 133.7 and 119.8 [$^2J(^{31}P-^{13}C) = {^3J}(^{31}P-^{13}C) = 10.0$ Hz], while the aliphatic CH_2 next to the phosphorus atom gives a signal at δ 35.8 [$^1J(^{31}P-^{13}C) = 28.5$ Hz]. The infrared spectra of compounds **12**, **13** and **15** show bands assignable to ν(P–H) absorption in the range 2329–2334 cm^{-1} (Table 1).

In contrast to compounds $[W_2(\eta-C_5H_4Pr^i)_2Cl_4]$ **11** and $[W_2(\eta-C_5H_4Pr^i)_2Br_4]$ **14**, compound $[W_2(\eta-C_5Me_5)_2Cl_4]$ **16** very rarely undergoes oxidative-addition chemistry. However, treatment of **16** with a thf solution of vinylphosphine caused a slow colour change from apple green to emerald green and green crystals of $[W_2(\eta-C_5Me_5)_2Cl_4(\mu-H)(\mu-PHC_2H_3)]$ **17** separated. This compound has been characterised by elemental analysis, by ^1H, ^{13}C and ^{31}P NMR spectroscopy and by infrared spectroscopy (Tables 1 and 2). The well resolved ^1H NMR spectrum allowed us to determine the different coupling constants for the vinyl moiety. Comparison with those of the free vinylphosphine[1,3] (Table 5), shows that, as expected, complexation has enhanced the coupling constants, particularly those between the phosphorus atom and the proton H_a and H_b. The crystal structure of **17** has been determined. The molecular structure is shown in Fig. 2, bond lengths and angles are listed in Table 6 and fractional atomic coordinates in Table 7. The W–W bond length [2.681(1) Å] is in the range expected for W=W double-bond structure and lies between values reported for triply bonded W≡W dimers *e.g.* for $[W_2(\eta-C_5H_4Pr^i)_2Cl_4]$ **11** [W≡W 2.3678(6) Å] and singly bonded W–W bonds *e.g.* for $[W_2(\eta-C_5H_4Me)_2Cl_4(\mu-C_4Me_4)]$ [W–W 2.9295(7) Å].[11] The bond angle P(1)–C(11a)–C(12) 118.9(3)° is close to the value of 120° expected for sp^2 hybridisation of the alkene group.

Treatment of $[W_2(\eta-C_5Me_5)_2Cl_4(\mu-H)(\mu-PHC_2H_3)]$ **17** in thf with 1 equivalent of $NMe(SiMe_3)_2$ or NEt_3 at 50 °C caused a slow colour change from emerald green to dark green and $[W_2(\eta-C_5Me_5)_2Cl_2(\mu-Cl)(\mu-PHC_3H_3)]$ **18** was isolated as a green powder. The ^1H NMR spectrum of **18** shows a doublet of doublets at δ 8.24 [$^1J(^{31}P-^1H) = 155$ Hz, $^3J(^1H-^1H) = 9$ Hz] which integrate as one H atom per molecule and is assignable to

Table 3 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for $[W(\eta-C_5Me_4Et)Cl_4(PH_2C_2H_3)]$ **10**; Cp_{cent} refers to the computed $\eta-C_5Me_4Et$ ring centroid

W–P(1)	2.554(2)	W–Cl(1)	2.409(2)
W–Cl(2)	2.410(2)	W–Cl(3)	2.398(2)
W–Cl(4)	2.385(2)	W–Cp_{cent}	2.081
P(1)–C(1)	1.77(1)	C(1)–C(2)	1.48(2)
C(2)–C(3)	1.20(2)		
Cl(1)–W–Cl(2)	84.3(1)	Cl(2)–W–Cl(3)	84.8(1)
Cl(3)–W–Cl(4)	87.1(1)	Cl(4)–W–Cl(1)	87.5(1)
Cl(1)–W–Cl(3)	149.2(1)	Cl(2)–W–Cl(4)	148.6(1)
Cl(1)–W–P(1)	71.1(1)	Cl(2)–W–P(1)	74.9(1)
Cl(3)–W–P(1)	78.3(1)	Cl(4)–W–P(1)	73.8(1)
Cp_{cent}–W–Cl(1)	105.6	Cp_{cent}–W–Cl(2)	106.5
Cp_{cent}–W–Cl(3)	105.1	Cp_{cent}–W–Cl(4)	104.9
Cp_{cent}–W–P(1)	176.4	C(1)–C(2)–C(3)	129.7(2)

Table 4 Fractional atomic coordinates for $[W(\eta-C_5Me_4Et)Cl_4(PH_2C_2H_3)]$ **10**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W	0.077 66(3)	0.248 51(3)	0.103 99(1)
P(1)	0.167 5(4)	0.358 4(2)	0.002 0(2)
Cl(1)	0.046 1(4)	0.403 6(2)	0.108 3(2)
Cl(2)	0.322 7(3)	0.326 1(2)	0.178 5(2)
Cl(3)	0.263 2(4)	0.147 2(2)	0.053 7(2)
Cl(4)	−0.112 9(4)	0.223 2(2)	−0.021 7(1)
C(1)	0.289(2)	0.314(9)	−0.064 4(8)
C(2)	0.328(2)	0.396(1)	−0.116 6(9)
C(3)	0.457(3)	0.434(1)	−0.118(1)
C(11)	0.026 7(9)	0.230 7(4)	0.233 6(4)
C(12)	−0.125 2(8)	0.216 3(6)	0.178 8(5)
C(13)	−0.118 1(9)	0.130 4(6)	0.134 8(5)
C(14)	0.044(1)	0.092 4(5)	0.162 5(5)
C(15)	0.130 6(9)	0.152 5(6)	0.223 2(4)
C(21)	0.064(1)	0.305 1(7)	0.298 4(5)
C(22)	−0.280(1)	0.271 3(7)	0.177 2(7)
C(23)	−0.259(1)	0.081 3(7)	0.079 6(6)
C(24)	0.096(1)	−0.003 5(6)	0.138 1(6)
C(25)	0.298(1)	0.131 5(8)	0.274 4(6)
C(26)	−0.335(2)	0.009(1)	0.127 9(8)

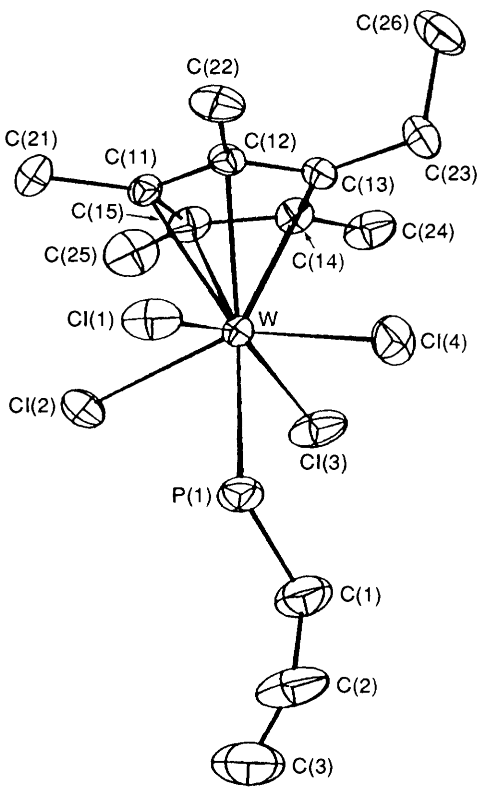
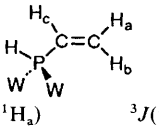


Fig. 1 The molecular structure of complex **10**. The thermal ellipsoids are drawn at the 25% probability level. The hydrogen atoms are omitted for clarity

Table 5 A comparison of selected coupling constants (Hz) for the vinylphosphine moiety of **17** in conjunction with those of the free vinylphosphine **1**



Compound	$^3J(^{31}P-^1H_a)$	$^3J(^{31}P-^1H_b)$	$^3J(^1H_c-^1H_a)$	$^3J(^1H_c-^1H_a)$
$[W_2(\eta-C_5Me_5)_2Cl_4(\mu-H)(\mu-PHC_2H_3)]$ **17**	46.8	17.7	18.0	26.7
$PH_2CH{=}CH_2$ **1**	13.5	6.5	9.4	17.3

Table 6 Bond lengths (Å) and selected angles (°) with e.s.d.s in parentheses for [$W_2(\eta$-$C_5Me_5)_2Cl_4(\mu$-H)(μ-PHC_2H_3)] **17**

W(1)–W(2)	2.681(1)	W(2)–Cl(3)	2.422(6)
W(1)–Cl(1)	2.420(7)	W(2)–Cl(4)	2.436(7)
W(1)–Cl(2)	2.441(7)	W(2)–P(1)	2.369(7)
W(1)–P(1)	2.363(6)	C(11a)–C(12)	1.47(5)
P(1)–C(11a)	1.60(4)		
Cl(1)–W(1)–W(2)	101.5(1)	Cl(3)–W(2)–W(1)	117.9(2)
Cl(2)–W(1)–W(2)	118.4(1)	Cl(4)–W(2)–W(1)	102.8(1)
Cl(1)–W(1)–Cl(2)	80.8(2)	Cl(3)–W(2)–Cl(4)	80.6(3)
P(1)–W(1)–W(2)	55.6(2)	P(1)–W(2)–W(1)	55.4(2)
P(1)–W(1)–Cl(1)	135.7(2)	P(1)–W(2)–Cl(3)	78.7(3)
P(1)–W(1)–Cl(2)	80.1(3)	P(1)–W(2)–Cl(4)	135.2(3)
W(1)–P(1)–C(11a)	130.0(2)	W(2)–P(1)–C(11a)	138.6(2)
W(1)–P(1)–W(2)	69.0(2)	P(1)–C(11a)–C(12)	118.9(3)

Table 7 Fractional atomic co-ordinates for [$W_2(\eta$-$C_5Me_5)_2Cl_4$-(μ-H)(μ-PHC_2H_3)] **17**

Atom	*X/a*	*Y/b*	*Z/c*
W(1)	0.000 7(1)	0.048 3(1)	0.220 1(1)
Cl(1)	0.018 2(7)	0.118 0(3)	0.100 2(3)
Cl(2)	0.231 2(7)	−0.007 6(3)	0.188 9(4)
C(1)	−0.098 1(27)	−0.071 7(11)	0.163 7(12)
C(2)	−0.192 5(26)	−0.017 7(11)	0.124 1(11)
C(3)	−0.262 8(22)	0.023 1(12)	0.180 5(11)
C(4)	−0.205 5(28)	−0.009 0(12)	0.258 2(11)
C(5)	−0.102 3(25)	−0.067 9(11)	0.246 5(11)
C(1a)	−0.016 6(31)	−0.132 6(12)	0.126 8(14)
C(2a)	−0.230 2(31)	−0.007 6(16)	0.034 4(12)
C(3a)	−0.380 7(30)	0.082 1(15)	0.162 2(15)
C(4a)	−0.272 0(28)	0.003 3(14)	0.332 1(13)
C(5a)	−0.040 1(28)	−0.127 1(13)	0.307 8(12)
W(2)	0.028 8(1)	0.157 1(1)	0.330 1(1)
Cl(3)	−0.017 1(10)	0.125 8(4)	0.462 2(3)
Cl(4)	−0.230 1(8)	0.203 2(3)	0.317 8(4)
C(6)	0.169 4(30)	0.256 8(14)	0.411 7(14)
C(7)	0.078 9(28)	0.291 5(13)	0.346 7(15)
C(8)	0.112 7(29)	0.264 7(13)	0.271 3(14)
C(9)	0.237 8(29)	0.213 6(12)	0.293 6(15)
C(10)	0.269 7(35)	0.207 2(14)	0.379 3(15)
C(6a)	0.177 4(42)	0.272 7(18)	0.497 3(16)
C(7a)	−0.032 8(34)	0.352 7(14)	0.353 7(18)
C(8a)	0.042 9(35)	0.293 9(15)	0.194 3(15)
C(9a)	0.340 8(31)	0.185 6(16)	0.238 7(18)
C(10a)	0.412 3(32)	0.172 6(16)	0.427 9(20)
P(1)	0.147 1(10)	0.038 7(4)	0.350 5(4)
C(11a)	0.313 3(49)	0.004 9(23)	0.379 6(23)
C(11b)	0.178 4(74)	−0.018 3(22)	0.423 1(29)
C(12)	0.337 0(44)	−0.049 9(17)	0.445 3(17)

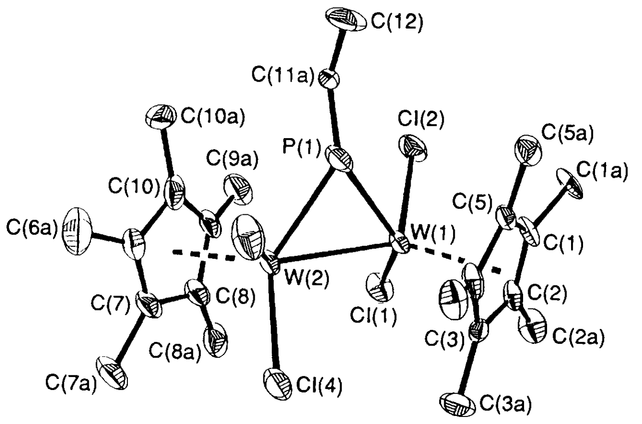


Fig. 2 The molecular structure of complex **17** is shown with one orientation of the vinyl group, and omitting the hydrogen atoms. The thermal ellipsoids are drawn at the 30% probability level

the hydrogen bonded to the phosphorus atom. It is notable that this signal occurs at a higher field than for the parent compound **17** (δ 9.46) and that the coupling constant $^1J(^{31}P-^1H)$ = 155 Hz is much smaller (416 Hz for **17**). There was no resonance assignable to a W–H–W hydrogen.

A striking feature is the chemical shift observed in the ^{31}P NMR spectrum: δ −17.4 as compared to δ 270 for **17**. This signal possesses the expected sets of ^{183}W satellites of the intensity expected for a phosphorus atom bonded to two tungsten atoms [$^1J(^{31}P-^{183}W)$ *ca.* 158 Hz, *ca.* 28% of the total signal intensity]. The infrared spectrum of **18** shows the ν(P–H) absorption at 2296 cm^{-1}. Treatment of **18** with *ca.* 1 equivalent of HCl at room temperature for 2 h gave compound **17** (^{31}P NMR spectrum). Treatment of **18** with an excess of HCl gas gave [W(η-C_5Me_5)Cl_4] **19** as the only tractable product in *ca.* 30% yield.

In conclusion, the new reactions and the structures proposed for the new compounds are shown in the Schemes 1 and 2. It can be seen that the unsaturated vinyl and allyl groups attached to the phosphorus ligands play no direct part in the chemistry of the binuclear metal system.

Experimental

All manipulations and reactions were carried out using either standard Schlenk-vessel and vacuum-line techniques under an atmosphere of dinitrogen, which had been purified by passage over MnO (or a BASF catalyst) and 4 Å molecular sieves, or in a dry box containing dinitrogen.

Solvents were pre-dried over activated 4 Å molecular sieves and then distilled under an atmosphere of dinitrogen from phosphorus pentoxide (dichloromethane), potassium (thf), sodium (toluene, triglyme), sodium–potassium alloy (1 : 3 w/w) [light petroleum (b.p. 40–60 °C), diethyl ether, pentane]. Deuteriated solvents (Aldrich) for NMR studies were stored in Young's ampoules under an atmosphere of dinitrogen over sodium–potassium alloy ([$^2H_6$]benzene) or dried using calcium hydride (CD_2Cl_2) and transferred by vacuum distillation.

Proton, ^{13}C and ^{31}P NMR spectra were recorded using a Brüker AM 300 spectrometer (^1H 300, ^{13}C 75.5, ^{31}P 121.6 MHz). The ^{13}C NMR spectra were recorded using a gated sequence to give nuclear Overhauser enhancement. Spectra were referenced internally using residual protio solvent resonances (^1H and ^{13}C) relative to tetramethylsilane (δ 0) or externally using trimethyl phosphate in D_2O (^{31}P). All chemical shifts are quoted in δ and coupling constants in Hz. Signals are expressed as position, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, spt = septet, m = multiplet), coupling constant, relative integration and assignment.

Infrared spectra were recorded on a Perkin Elmer 1510 FT interferometer or, in the region below 400 cm^{-1}, on a Perkin Elmer 457 grating spectrometer. Data are expressed as wavenumber (cm^{-1}) with relative intensity in parentheses (s = strong, m = medium, w = weak, sh = shoulder).

Elemental analyses were performed by the Microanalytical Department of this laboratory. The compounds [W(η-C_5R_5)-X_4] and [$W_2(\eta$-$C_5R_5)_2X_4$] (R_5 = H_4Pr^i, Me_5 or Me_4Et; X = Cl or Br) were prepared as described.[9,11]

Preparations.—*Vinyl- and allyl-phosphines* **1** *and* **2**. The vinyl- and allyl-phosphines were prepared by modification of the procedure set out by Cabioch and Denis.[3] The apparatus is shown in Fig. 3. A quantity of $LiAlH_4$ (2.5 g, 66 mmol) was placed in the three-necked round-bottom flask, $AlCl_3$ (27 g, 200 mmol) in the solid-addition vessel, and the vinyl- or allyl-phosphonate ester RP(O)(OR')$_2$ (76 mmol) (R = CH=CH_2, R' = Me **3**; R = CH_2CH=CH_2, R' = Et **4**) in the dropping

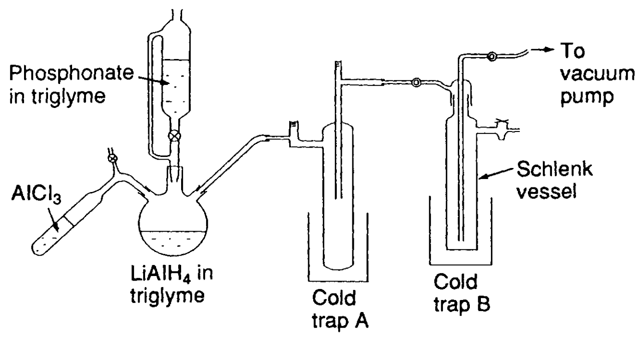


Fig. 3 Apparatus used for the synthesis of **1** and **2**

funnel, and hydroquinone (Aldrich, *ca.* 1 mg) in the Schlenk vessel. The apparatus was degassed under vacuum, and filled with dinitrogen. Triglyme (150 cm^3) was then added to the $LiAlH_4$ at −45 °C while a vigorous stirring was maintained, and also to the phosphonate (50 cm^3). The apparatus was evacuated to *ca.* 5×10^{-2} mbar and the reaction flask was cooled to −40 °C. The $AlCl_3$ was then added in small portions over a period of 30 min, volatile products, such as traces of HCl gas, being removed as they evolved. The reaction mixture was allowed to warm to room temperature and was stirred at this temperature for 15 min. The mixture was then cooled to −40 °C and traps A and B were both cooled to liquid-nitrogen temperature and the phosphonate solution was added dropwise over a period of 15 min. The phosphine distilled from the reaction mixture as it was formed and was trapped in the cold traps A and B. After the addition of the phosphonate was complete the reaction mixture was allowed to warm to room temperature and was stirred for 2 h. The temperature was increased to *ca.* 35–40 °C using a water-bath and the mixture was stirred for another 30 min. The liquid-nitrogen bath under the trap A was then removed while the temperature of trap B was kept at 77 K. The apparatus was evacuated for a further 2 h. The Schlenk vessel (second one) was then separated from the apparatus and solvent (thf, toluene or diethyl ether) was added to the Schlenk vessel (same one) which contained the pure phosphine. The concentration of product in the resulting solution was estimated by ^{31}P NMR spectroscopy by comparison of peak intensity with that of added Ph_3PO as an internal reference. Yield: *ca.* 60–65%, purity >99%. The phosphines were characterized by comparison of their spectroscopic data with those reported in the literature. ^{31}P NMR ([$^2H_6$]benzene–thf 1 : 1 v/v): vinylphosphine **1**: δ −139 [t, $^1J(^{31}P-^1H)$ 214 Hz]; allylphosphine **2**: δ −136 [t, $^1J(^{31}P-^1H)$ 220 Hz].

$[W(\eta\text{-}C_5H_4Pr^i)Cl_4(PH_2C_2H_3)]$ **7**. Compound $[W(\eta\text{-}C_5H_4Pr^i)Cl_4]$ **5** (2.1 g, 4.85 mmol) in thf (20 cm^3) at −40 °C was treated with vinylphosphine (11.55 cm^3 of a 0.42 mol dm^{-3} solution in thf) at −40 °C. The reaction mixture was allowed to warm to room temperature. The colour changed from deep red to dark green and stirring was maintained at room temperature for another 30 min. The volatiles were removed under reduced pressure and the residue was extracted with toluene (35 cm^3). After filtration the filtrate was concentrated to *ca.* 15 cm^3 and cooled to −80 °C giving green-brown crystalline $[W(\eta\text{-}C_5H_4Pr^i)Cl_4(PH_2C_2H_3)]$. Yield: 2 g, 85%.

$[W(\eta\text{-}C_5H_4Pr^i)Cl_4(PH_2C_3H_5)]$ **8**. Compound $[W(\eta\text{-}C_5H_4Pr^i)Cl_4]$ **5** (3.2 g, 7.4 mmol) in thf (35 cm^3) at −20 °C was treated with allylphosphine (12.8 cm^3 of a 0.58 mol dm^{-3} solution in thf) at −20 °C. The reaction mixture was allowed to warm to room temperature and progressively turned from deep red to green. After a further stirring at room temperature for 30 min, the volatiles were removed under reduced pressure and the residue was extracted into diethyl ether (2 × 25 cm^3) to give a green-red dichroic solution. After concentration to *ca.* 25 cm^3, this solution was cooled to −25 °C giving brown feather-like microcrystals of $[W(\eta\text{-}C_5H_4Pr^i)Cl_4(PH_2C_3H_5)]$. Yield: 3.1 g, 82%.

$[W(\eta\text{-}C_5Me_4Et)Cl_4(PH_2C_2H_3)]$ **9**. Compound $[W(\eta\text{-}C_5Me_4Et)Cl_4]$ **6** (1 g, 2.1 mmol) in thf (10 cm^3) at −40 °C was treated with vinylphosphine (35 cm^3 of a 0.06 mol dm^{-3} solution in thf) at −40 °C. The reaction mixture was allowed to warm to room temperature. The colour turned from green to red and stirring was maintained at room temperature for 2 h. The volatiles were removed under reduced pressure and the residue was extracted into toluene (15 cm^3). The extract was filtered and concentrated to *ca.* 10 cm^3 and then cooled to −80 °C giving light brown crystalline $[W(\eta\text{-}C_5Me_4Et)Cl_4(PH_2C_2H_3)]$. Yield: 0.91 g, 81%.

$[W(\eta\text{-}C_5Me_4Et)Cl_4(PH_2C_3H_5)]$ **10**. Compound $[W(\eta\text{-}C_5Me_4Et)Cl_4]$ **6** (1.5 g, 3.16 mmol) in thf (10 cm^3) at −20 °C was treated with allylphosphine (6 cm^3 of a 0.58 mol dm^{-3} solution in thf) at −20 °C. The reaction mixture was then allowed to warm to room temperature. The colour changed from green to red and stirring was maintained at room temperature for 4 h. The volatiles were removed under reduced pressure and the residue was extracted into diethyl ether (15 cm^3). After filtration the filtrate was concentrated (to 10 cm^3) and cooled to 0 °C giving red crystals of $[W(\eta\text{-}C_5Me_4Et)Cl_4(PH_2C_3H_5)]$. Yield: 1.33 g, 77%.

$[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}H)(\mu\text{-}PHC_2H_3)]$ **12**. A solution of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ **11** (500 mg, 0.7 mmol) in thf (25 cm^3) at −40 °C was treated with vinylphosphine (19 cm^3 of a 0.038 mol dm^{-3} solution in thf) at −40 °C. The reaction mixture was allowed to warm to room temperature and the colour changed from green to red. After stirring for a further 1 h, the volatiles were removed under reduced pressure leaving a brown solid. Extraction with toluene (20 cm^3) gave a red-green solution, which on cooling to −25 °C yielded air-sensitive green-brown crystals of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}H)(\mu\text{-}PHC_2H_3)]$. Yield: 466 mg, 85%.

$[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}H)(\mu\text{-}PHC_3H_5)]$ **13**. A solution of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4]$ **11** (200 mg, 0.28 mmol) in thf (10 cm^3) at −40 °C was treated with allylphosphine (6 cm^3 of a 0.048 mol dm^{-3} solution in thf) at −40 °C. The reaction mixture was allowed to warm to room temperature and the colour changed from green to green-red. After stirring for a further 1 h, the volatiles were removed under reduced pressure leaving a pale brown solid. Extraction with diethyl ether (10 cm^3) gave a green solution. This was filtered and cooled to −25 °C giving green crystalline $[W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}H)(\mu\text{-}PHC_3H_5)]$. Yield: 184 mg, 84%.

$[W_2(\eta\text{-}C_5H_4Pr^i)_2Br_4(\mu\text{-}H)(\mu\text{-}PHC_2H_3)]$ **15**. A solution of $[W_2(\eta\text{-}C_5H_4Pr^i)_2Br_4]$ **14** (400 mg, 0.44 mmol) in thf (10 cm^3) at −80 °C was treated with vinylphosphine (7.4 cm^3 of a 0.06 mol dm^{-3} solution in thf) at −80 °C. The reaction mixture was then allowed to warm to room temperature and the colour changed from green-brown to green-red. After stirring for a further 2 h, the volatiles were removed under reduced pressure leaving a dark brown solid. Extraction with diethyl ether (15 cm^3) gave a green solution. This was filtered and cooled to −80 °C giving green microcrystalline $[W_2(\eta\text{-}C_5H_4Pr^i)_2Br_4(\mu\text{-}H)(\mu\text{-}PHC_2H_3)]$. Yield: 340 mg, 82%.

$[W_2(\eta\text{-}C_5Me_5)_2Cl_4(\mu\text{-}H)(\mu\text{-}PHC_2H_3)]$ **17**. A solution of $[W_2(\eta\text{-}C_5Me_5)_2Cl_4]$ **16** (4 g, 5.13 mmol) in thf (45 cm^3) at room temperature was treated with vinylphosphine (7.65 cm^3 of a 0.69 mol dm^{-3} solution in thf) at room temperature. The reaction mixture was stirred for 5 h resulting in a colour change from apple green to emerald green and separation of a green precipitate. Removal of the volatiles under reduced pressure gave emerald green $[W_2(\eta\text{-}C_5Me_5)_2Cl_4(\mu\text{-}H)(\mu\text{-}PHC_2H_3)]$. Single crystals were obtained by recrystallisation in CH_2Cl_2. Yield: 4.23 g, 98%.

$[W_2(\eta\text{-}C_5Me_5)_2Cl_2(\mu\text{-}Cl)(\mu\text{-}PHC_2H_3)]$ **18**. A stirred solution of $[W_2(\eta\text{-}C_5Me_5)_2Cl_4(\mu\text{-}H)(\mu\text{-}PHC_2H_3)]$ **17** (1 g, 1.2 mmol) in thf (20 cm^3) at −20 °C was treated in a dropwise manner with 1 molar equivalent of $NMe(SiMe_3)_2$ (0.208 g, 0.26 cm^3) or NEt_3

Table 8 Crystal data, details of the data collection and final refinements for [W(η-C_5Me_4Et)Cl_4($PH_2C_2H_3$)] **10** and [W_2(η-C_5Me_5)$_2Cl_4$(μ-H)(μ-PHC_2H_3)] **17**[a]

Compound	10	17
Formula	$C_{14}H_{22}Cl_4PW$	$C_{22}H_{35}Cl_4PW_2$
M	591.02	840.01
Crystal size/mm	0.40 × 0.30 × 0.10	0.40 × 0.20 × 0.15
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	8.378(1)	8.967(2)
b/Å	13.956(2)	17.920(5)
c/Å	17.009(2)	16.993(4)
β/°	103.15(1)	100.62(2)
U/Å^3	1936.5	2683.9
Z	4	4
D_c/g cm^{-3}	1.883	2.074
μ/cm^{-1}	67.23	92.23
F(000)	1060	1584
2θ Limits/°	3–48	3.5–55.0
ω Scan width [+0.35 tan θ]/°	1.2	0.6 + Kα
Zone	−1 to 9, −1 to 16, −20 to 20	0–11, 0–23, −22 to 21
Total data collected	7875	6691
No. of observations [$I > 3\sigma(I)$]	2898	3558
R(merge)	0.031	0.023
Structure solution method	Patterson map	Direct
No. of variables	183	273
Observation/variables	15.8	13.0
Weighting scheme	Chebyshev weighting scheme with the cofficients 34.1, −28.7, 24.3	$w^{-1} = \sigma^2(F) + 0.0006F^2$
Max./min. peaks in final difference map/e Å^{-3}	1.4, −0.9	3.8, −3.3
R[b]	0.034	0.071
R'[c]	0.041	0.090

[a] Comments: C(11a) was disordered (50:50) over two sites. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

(0.12 g, 0.166 cm^3). The reaction mixture was allowed to warm to room temperature and stirred for 2 h. No colour change was observed. The reaction vessel was then placed in warm water (45–50 °C) and the mixture was stirred for another 2 h, resulting in a change from emerald green to dark green. The volatiles were removed under reduced pressure and the residue was extracted with light petroleum (b.p. 40–60 °C, 2 × 10 cm^3) giving a dichroic solution, which on cooling (−80 °C) afforded [W_2(η-C_5Me_5)$_2Cl_2$(μ-Cl)(μ-PHC_2H_3)] as a green solid. Yield: 0.52 g, 55%.

X-Ray Crystal Structure Determination of **10**.—Crystal data and data collection and processing parameters are given in Table 8. The general procedure was as follows. A crystal was sealed in a Lindemann glass capillary and transferred to the goniometer head of an Enraf–Nonius CAD4 diffractometer interfaced to a PDP 11/23 minicomputer. Unit-cell parameters were calculated from the setting angles of 25 carefully centred reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections. The data were measured using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) in the ω–2θ scan mode. The data were corrected for Lorentz and polarisation effects and an empirical absorption correction[12] based on azimuthal scan data was applied. Equivalent reflections were merged and systematically absent reflections rejected. The tungsten atom positions were determined from a Patterson synthesis. Subsequent difference-Fourier syntheses revealed the positions of other non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic thermal parameters by full matrix least-squares procedures. For both molecules, hydrogen atoms were placed in estimated positions (C–H = 0.96 Å) with fixed isotropic thermal parameters and refined riding their supporting carbon atoms. Both hydrogens bonded to the phosphorus atom were not located. All crystallographic calculations were performed using the CRYSTALS suite[13] on a Micro VAX 3800 computer in the Chemical Crystallography Laboratory, Oxford. Neutral-atom scattering factors were taken from the usual sources.[14]

X-Ray Crystal Structure Determination of **17**.—Crystal data, and data collection and processing parameters are given in Table 8. The dark green crystal was sealed in a Lindemann capillary under argon and mounted on a goniometer head. Precession photographs and intensity data were collected on a Nicolet R3m/V diffractometer using graphite-monochromatized Mo-Kα X-rays (λ = 0.710 73 Å). Preliminary investigation revealed some evidence of slight twinning but the crystal was deemed adequate for data collection. Six further crystals were investigated but were found to be more severely twinned. Cell dimensions were obtained from 46 centred reflections with 2θ values from 16 to 30°. Intensity data in the range 3.5 < 2θ < 55° were collected using a θ–2θ scan technique. The intensities of three reflections were measured after every 197 data and showed a decrease of less than 2% over the data collection. Data were corrected for Lorentz and polarisation effects. Neutral-atom scattering factors and complex anomalous-dispersion corrections were taken from the usual sources.[14] A semi-empirical absorption correction was applied using an azimuthal scan technique. The structure was solved by standard heavy-atom routines and refined by full-matrix least-squares methods. All non-hydrogen atoms were given anisotropic thermal parameters. The vinyl carbon atom C(11) was disordered over two positions with equal occupancy and was refined accordingly. The vinylic hydrogen atoms on C(12), C(11a), and C(12b) and the hydrogen atoms on the ring methyl groups were placed in the model at calculated positions (C–H = 0.96 Å) and allowed to ride on their respective carbon atoms. The hydrogen atom on P(1) and the bridging metal hydride atom were not located and were not included in the model. The residual electron density was localised at the two tungsten atoms and reflects the slight twinning present in the crystal. Calculations were performed using SHELXTL PLUS[15] on a MicroVAX II.

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

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