Organoimido Complexes of Tungsten(IV) containing π-Olefin Ligands. The *X*-Ray Crystal Structure of Dichloro(2-methylpropene)(phenylimido)bis(trimethylphosphine)tungsten(IV), $[WCl_2(NPh)(Me_2C{=}CH_2)(PMe_3)_2]$†

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Reduction of $[WCl_3(NPh)(PMe_3)_2]$ in benzene with Na–Hg amalgam under ethylene gave $[WCl_2(NPh)(CH_2{=}CH_2)(PMe_3)_2]$ (**1**) for which i.r. and n.m.r. spectral data indicated *cis*-chloro and *trans*-phosphine ligands. Similar complexes were prepared from propene, *cis*- and *trans*-but-2-ene, and 2-methylpropene. The complex $[WCl_2(NPh)(MeCH{=}CH_2)(PMe_3)_2]$ (**2**) forms two isomers in which the olefin methyl groups lie either above or below the equatorial co-ordination plane. The reduction reaction with *trans*-but-2-ene and 2-methylpropene also produces $[\{WCl_2(NPh)(PMe_3)_2\}_2]$ (**5**) (16 and 19%, respectively). 2-Methylbut-2-ene and 2,3-dimethylbut-2-ene do not form identifiable π-olefin complexes but complex (**5**) is produced in 27 and 70% yield, respectively. The n.m.r. spectra of $[WCl_2(NPh)(MeCH{=}CH_2)(PMe_3)_2]$ (**2**), $[WCl_2(NPh)(trans\text{-}MeCH{=}CHMe)(PMe_3)_2]$ (**4**), and $[WCl_2(NPh)(Me_2C{=}CH_2)(PMe_3)_2]$ (**6**) show non-equivalent *trans*-phosphine ligands. The $^1J(PW)$ values [*e.g.* 243.7 and 228.8 Hz for (**6**)] suggest small differences in the W–P bond lengths. The structure of (**6**) was determined by *X*-ray crystallography. The complex has a distorted octahedral geometry with *trans*-phosphines, *cis*-chloro ligands, and mutually *cis* orientated phenylimido and 2-methylpropene ligands. The W–P bond lengths are significantly different at 2.564(5) and 2.522(6) Å, the longer of the two lying adjacent to the two methyl groups of the $Me_2C{=}CH_2$ ligand. The W–C bond lengths are 2.25(2) and 2.30(2) Å and the olefinic C–C bond length is 1.45(3) Å. The W–C–CH_3 bond angles are 110.9(14) and 118.1(15)° and the upper and lower methyl groups incline away to different extents from the C=C bond [CH_3–C–C bond angles 113(2) and 124(2)°].

The interaction of olefins with high-valent metal compounds is of considerable importance both in industrial applications such as oxidation or ammoxidation reactions[1] and laboratory syntheses such as the Sharpless oxidation and oxyamination processes.[2] Theoretical studies indicate that, for oxidation of alkenes by OsO_4, reaction is possible at the olefin and oxo ligand interface with the metal acting as an electron sink.[3] Co-ordination of the olefin to the metal is thus not necessary although such intermediates have been suggested in these oxidations.[1,4] Olefins are π-acceptor ligands and as such require filled *d* orbitals of π symmetry on the metal before co-ordination is possible making conventional π bonding of an olefin to a d^0 complex unlikely. However, where d^1 or d^2 complexes have orbitals of sufficient energy to overlap strongly with an olefin acceptor orbital, π-olefin complexes may be stabilised. We have been interested in the co-ordination chemistry of complexes containing the strong π-donor organoimido ligand (≡NR)[5] which in conjunction with a strong σ-donor phosphine ligand was expected to give rise to a suitable electronic environment for stable olefin co-ordination in a d^1 or d^2 system. To date, $[TaCl(NPh)(RCH{=}CH_2)(PMe_3)_3]$ (R = H or Ph) are the only complexes known containing both a π-olefin and an organoimido ligand.[6] We report here the preparation and characterisation of phenylimido complexes of tungsten(IV) containing π-bound olefin ligands in which the size of the olefin is gradually increased. A preliminary account of this work has appeared.[7]

Results and Discussion

Reactions leading to the formation of phenylimido complexes of tungsten(V) containing ethylene or other olefins have so far proven unsuccessful. However, reduction of $[WCl_3(NPh)(PMe_3)_2]$[8,9] in benzene solution with 1 equivalent of sodium–mercury amalgam under ethylene at low pressure (2.5 lbf in^{-2}) led to the tungsten(IV) olefin complex $[WCl_2(NPh)(CH_2{=}CH_2)(PMe_3)_2]$ (**1**) in near quantitative yield. Complex (**1**) also formed when $[WCl_2(NPh)(PMe_3)_3]$[9,10] was refluxed in benzene under an ethylene atmosphere but the reaction did not go to completion.‡ Similarly, reduction of $[\{WCl_4(NPh)\}_2]$[9,10] under ethylene in benzene with 2 equivalents of sodium–mercury amalgam in the presence of exactly 2 equivalents of PMe_3 gave $[WCl_2(NPh)(CH_2{=}CH_2)(PMe_3)_2]$ (**1**) (62%) and $[WCl_2(NPh)(PMe_3)_3]$ (38%). When this reduction was carried out with 3 equivalents of PMe_3 only $[WCl_2(NPh)(PMe_3)_3]$ was formed.

Olefin complex (**1**) is air stable in contrast to $[WCl_2(NPh)(PMe_3)_3]$, but slowly decomposes in solution. The i.r. spectrum exhibits a strong absorption at 1 345 cm^{-1} characteristic of the imido ligand [ν_{sym}(W–N–C)][13] and two W–Cl stretches indicate *cis* orientated chloro ligands[14] (Table 1). The ^1H n.m.r. spectrum (Table 2) shows a virtually coupled triplet for the PMe_3 protons indicative of a *trans*-phosphine geometry[15] and there are two multiplets for the ethylene protons similar to that found for $[WCl_2(O)(CH_2{=}CH_2)(PMePh_2)_2]$ where ethylene rotation up to 80 °C is very slow on the n.m.r. time-scale.[16] A *trans*-phosphine geometry in (**1**) is also indicated by a singlet in

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.

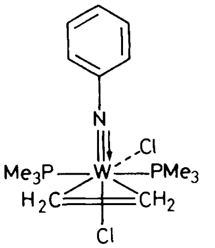
Non-S.I. unit employed: lbf in^{-2} ≈ 6 895 Pa.

‡ During the course of this work we became aware this reaction had been undertaken by other workers.[11] It has recently been reported.[12]

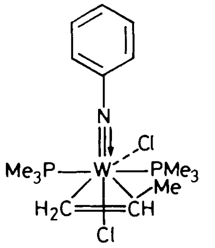
Table 1. Physical data

Complex	Yield (%)	M.p. (° C)	Analysis (%)[a] C	H	N	I.r. (cm^{-1}) ν_{sym}(W–N–C)	ν(W–Cl) (*cis*)
(**1**) [$WCl_2(NPh)(CH_2{=}CH_2)(PMe_3)_2$]	92	142	32.4 (32.0)	5.3 (5.2)	2.4 (2.7)	1 345	285, 245
(**2**) [$WCl_2(NPh)(MeCH{=}CH_2)(PMe_3)_2$]	92	*b*	33.0 (33.4)	5.6 (5.4)	2.5 (2.6)	1 335	280, 275, 248, 242
(**3**) [$WCl_2(NPh)$(*cis*-$MeCH{=}CHMe)(PMe_3)_2$]	78	142	34.5 (34.7)	5.5 (5.6)	2.5 (2.5)	1 354	275, 250
(**4**) [$WCl_2(NPh)$(*trans*-$MeCH{=}CHMe)(PMe_3)_2$]	77	148—152 (decomp.)	35.3 (34.7)	6.1 (5.6)	2.6 (2.5)	1 352	275, 248
(**5**) [$\{WCl_2(NPh)(PMe_3)_2\}_x$][c]	16—70	*d*	29.2 (28.9)	5.1 (4.7)	3.1 (2.8)	1 345	275, 240
(**6**) [$WCl_2(NPh)(Me_2C{=}CH_2)(PMe_3)_2$]	72	132 (decomp.)	34.6 (34.7)	5.8 (5.6)	2.5 (2.5)	1 354	272, 242

[a] Calculated values given in parentheses. [b] Complex consists of two isomers. [c] Complex proposed as a dimer, $x = 2$. [d] Dark red complex showing advanced decomposition above 170 °C.



(**a**)



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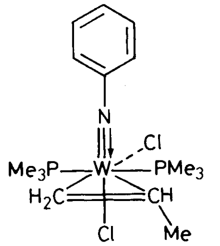

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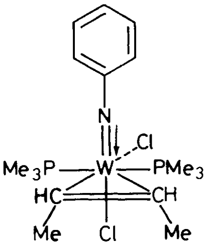
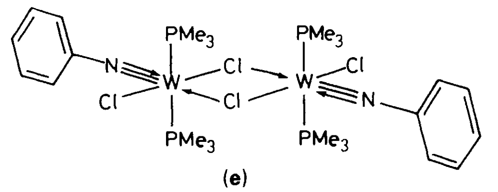


(**d**)



(**e**)

the ^{31}P-{^1H} n.m.r. spectrum and a triplet for the phosphine carbons in the ^{13}C-{^1H} n.m.r. spectrum.[17] The ethylene carbons appear as a triplet for this symmetrical complex with the resonance position (38.4 p.p.m.) lying considerably upfield to that found for [$WCl_2(O)(CH_2{=}CH_2)(PMePh_2)_2$] (53.0 p.p.m.)[16] which may represent an increase in π backbonding to the olefin π* orbital.[18]

Based on the spectroscopic data, complex (**1**) has the *trans*-phosphine, *cis*-chloro structure (**a**). Ethylene binds *cis* to the imido function which is the geometry expected on simple molecular-orbital grounds. With the two *d* electrons lying paired in an orbital perpendicular to the metal–nitrogen multiple bond, π-backbonding to the olefin is maximised. This orbital occupancy has been established in oxo-olefin and oxoacetylene complexes for which structures have been verified by *X*-ray crystallography.[16,19]

In the presence of propene, reduction of [$WCl_3(NPh)(PMe_3)_2$] with sodium–mercury amalgam gave [$WCl_2(NPh)(MeCH{=}CH_2)(PMe_3)_2$] (**2**) consisting of two isomeric forms. The i.r. spectrum showed two sets of *cis*-chloro ligands and the proton, carbon, and phosphorus resonances in the ^1H, ^{13}C-{^1H}, and ^{31}P-{^1H} n.m.r. spectra each appeared as two doublet of doublet sets. The ^{31}P-{^1H} n.m.r. resonance sets appeared as two separate AB systems with ^{31}P coupling constants [^2J(PP) 177.4 and 162.9 Hz] consistent with *trans* orientated PMe_3 ligands.[20] Co-ordination of the unsymmetrical propene ligand thus leads to asymmetry in the complex resulting in non-equivalent *trans*-phosphines. The two P–W coupling constants observed for each isomer are significantly different (14.5 Hz) which may represent small differences in the two W–P bond lengths.[21,22]

Formation of isomers in complex (**2**) is expected to arise when the propene methyl group lies either above or below the equatorial plane. The ^1H n.m.r. spectrum shows two methyl group resonances each of which couple to the adjacent CH proton. Decoupling experiments show that the CH_2 and CH proton resonances for isomer (**2a**) (54%) lie separately downfield from the two methyl resonances and for isomer (**2b**) (46%) they lie collectively upfield. In the ^{13}C-{^1H} n.m.r. spectrum there are two sets of ^{31}P-coupled resonances for the CH_2, CH, and CH_3 carbons. Coupling ^{13}C–^{183}W is only observed for the CH_2 and CH carbons. The CH carbons lie to lower field than the CH_2 carbons, the set for (**2a**) lying further downfield than for (**2b**), but as the origin of these features is not apparent assigning specific orientations of the propene ligand is not possible.

The two isomers also show specific n.m.r. spectral differences in the region of the phenylimido ligand. The *ortho*-protons appear as two resonances in the ^1H n.m.r. spectrum and in the ^{13}C-{^1H} n.m.r. spectrum there are two sets of *ipso*-, *ortho*-, *meta*-, and *para*-carbon resonances. Structures (**b**) and (**c**) are proposed for the isomers of (**2**) but the n.m.r. features cannot be assigned to individual isomers.

With *cis*-but-2-ene the reduction of [$WCl_3(NPh)(PMe_3)_2$] gave [$WCl_2(NPh)$(*cis*-$MeCH{=}CHMe)(PMe_3)_2$] (**3**) for which spectral data indicated a single isomer with a *cis*-chloro-*trans*-phosphine geometry. The CH protons of the olefin resonate at δ 2.92 in the ^1H n.m.r. spectrum and the methyl groups form a doublet of doublets arising from coupling to the two CH protons. In the ^{13}C-{^1H} n.m.r. spectrum the CH_3 and CH carbons each appear as a single set of ^{31}P-coupled triplets. As no asymmetry is present in the molecule the n.m.r. spectral

Table 2. N.m.r. spectral data[a]

	^{31}P-{^{1}H}				
Complex	δ/p.p.m.	^{2}J(PP)/Hz	^{1}J(PW)/Hz	^{1}H[b]	^{13}C-{^{1}H}[b,c]
(1)	−18.91	—	234.5	1.80 [t, ^{2}J(HP) 4.30, 18 H, 2PMe$_3$], 2.10—2.18 (m, 2 H, CH$_2$), 2.25—2.32 (m, 2 H, CH$_2$), 6.93 [d, ^{3}J(HH) 7.03, 2 H, *o*-H], 7.15—7.29 (m, 3 H, *m*-, *p*-H)	13.5 [t, ^{1}J(CP) 15.02, PMe$_3$], 38.4 [t, ^{2}J(CP) 3.48, ^{1}J(CW) 20.52, CH$_2$], 124.3 [t, ^{4}J(CP) 1.88, ^{3}J(CW) 7.63, *o*-C], 126.0 (*p*-C), 128.4 (*m*-C), 153.7 [t, ^{3}J(CP) 2.16, *ipso*-C]
(2a)[d]	−17.30 −20.26	177.39	244.86 225.84	1.67 and 1.76 [d, ^{2}J(HP) 9.06, 18 H, 2PMe$_3$], 2.36 [d, ^{3}J(HH) 5.76, 3 H, Me], 2.71—2.79 (m, 1 H, CH), 2.79—2.91 (m, 2 H, CH$_2$), 7.04 [d, ^{3}J(HH) 7.37, *o*-H], 7.08—7.20 (m, 3 H, *m*-, *p*-H]	13.0 and 13.3 [d, ^{1}J(CP) 26.62, ^{3}J(CP) 1.05, PMe$_3$], 26.5 [d, ^{3}J(CP) 2.28, Me], 45.7 [d, ^{2}J(CP) 6.84, ^{1}J(CW) 20.28, CH$_2$], 51.2 [d, ^{2}J(CP) 7.20, ^{1}J(CW) 21.54, CH], 124.7 [t, ^{4}J(CP) 1.42, *o*-C], 125.6 (*p*-C), 128.0 (s, *m*-C), 153.4 [t, ^{3}J(CP) 2.0, *ipso*-C]
(2b)[e]	−16.79 −19.41	162.92	245.36 233.68	1.68 and 1.73 [d, ^{2}J(HP) 9.04, 18 H, 2PMe$_3$], 2.24—2.32 (m, 3 H, CH$_2$ and CH), 2.45 [d, ^{3}J(HH) 5.83, 3 H, Me], 6.84 [d, ^{3}J(HH) 7.36, 2 H, *o*-H], 7.08—7.20 (m, 3 H, *m*-, *p*-H)	13.2 and 13.7 [d, ^{1}J(CP) 27.33, ^{3}J(CP) 1.25, PMe$_3$], 22.7 [dd, ^{3}J(CP) 3.79 and 1.18, Me], 44.4 [d, ^{2}J(CP) 7.09, CH$_2$], 47.4 [d, ^{2}J(CP) 7.36, CH], 123.6 [t, ^{4}J(CP) 1.84, *o*-C], 125.7 (*p*-C), 127.8 (*m*-C), 153.6 [t, ^{3}J(CP) 2.14, *ipso*-C]
(3)	−16.41	—	244.31	1.72 [t, ^{2}J(HP) 4.35, 18H, 2PMe$_3$], 2.50 [dd, ^{3}J(HH) 3.74, ^{4}J(HH) 1.73, 6 H, 2Me], 2.86—2.98 (m, 2 H, 2CH), 7.10—7.21 (m, 5 H, aromatic H)	13.5 [t, ^{1}J(CP) 14.78, PMe$_3$], 21.0 (prt, Me), 54.2 [t, ^{2}J(CP) 3.93, ^{1}J(CW) 22.46, CH], 124.9 [t, ^{4}J(CP) 1.61 *o*-C], 125.9 (*p*-C), 128.5 (*m* − C), 154.0 [t, ^{3}J(CP) 1.83, *ipso*-C]
(4)	−17.18 −18.35	173.87	238.65 241.62	1.71 and 1.77 [dd, ^{2}J(HP) 6.3, ^{4}J(HP) 2.19, 18 H, 2PMe$_3$], 2.35 [d, ^{2}J(HH) 1.52, 3 H, Me], 2.37 [d, ^{2}J(HH) 1.16, 3 H, Me], 2.49—2.60 (m, 1 H, CH), 2.81—2.90 (m, 1 H, CH), 7.05—7.07 (m, 2 H, *o*-H), 7.12—7.18 (m, 3 H, *m*-, *p*-H)	14.0 [dd, ^{1}J(CP) 19.87, ^{3}J(CP) 9.09, PMe$_3$], 14.3 [dd, ^{1}J(CP) 20.46, ^{3}J(CP) 8.78, PMe$_3$], 24.5 [d, ^{3}J(CP) 2.62, Me], 28.9 [d, ^{3}J(CP) 1.64, Me], 55.3 [dd, ^{2}J(CP$_{cis}$) 2.69, ^{2}J(CP$_{trans}$) 5.54, CH], 58.5 [dd, ^{2}J(CP$_{cis}$) 2.84, ^{2}J(CP$_{trans}$) 5.78, CH], 125.4 [t, ^{4}J(CP) 1.70, *o*-C], 126.0 (*p*-C), 128.6 (*m*-C), 154.0 [t, ^{3}J(CP) 1.85, *ipso*-C]
(5)[f]	−13.52 −15.62	219.99	297.22 290.01	1.68 [d, ^{2}J(HP) 8.28, 9 H, PMe$_3$], 1.75 [d, ^{2}J(HP) 8.46, 9 H, PMe$_3$], 7.05—7.12 (m, 3 H, aromatic H), 7.26—7.33 (m, 2 H, aromatic H)	14.1 [dd, ^{1}J(CP) 25.61, ^{3}J(CP) 3.48, PMe$_3$], 15.0 [dd, ^{1}J(CP) 26.11, ^{3}J(CP) 3.86, PMe$_3$], 126.5 (*p*-C), 127.5 (*o*-C), 128.4 (*m*-C), 153.7 (*ipso*-C)
(6)	−19.52 −20.83	172.26	243.73 228.76	1.64 and 1.80 [dd, ^{2}J(HP) 7.36, ^{4}J(HP) 1.16, 18 H, 2PMe$_3$], 2.09 [dd, ^{3}J(HP) 8.18, ^{4}J(HH) 3.96, 1 H, CH], 2.44 [d, ^{4}J(HH) 1.06, 6 H, 2 Me], 2.68 [dd, ^{3}J(HP) 6.50, ^{4}J(HH) 3.96, 1 H, CH], 7.02—7.20 (m, 5 H, aromatic H)	13.5 [dd, ^{1}J(CP) 23.63, ^{3}J(CP) 6.37, PMe$_3$] 15.3 [dd, ^{1}J(CP) 21.66, ^{3}J(CP) 6.04, PMe$_3$], 31.9 [d, ^{3}J(CP) 3.00, Me], 37.5 [d, ^{3}J(CP) 1.52, Me], 52.9 [dd, ^{2}J(CP$_{cis}$) 2.52, ^{2}J(CP$_{trans}$) 6.47, CH$_2$], 60.8 [d, ^{2}J(CP) 6.57, C], 125.4 (*o*-C), 126.1 (*p*-C), 128.6 (*m*-C), 154.1 [t, ^{3}J(CP) 4.78, *ipso*-C]

[a] Spectra obtained in CDCl$_3$ solution. [b] d = Doublet, dd = doublet of doublets, m = multiplet, prt = poorly resolved triplet, t = triplet, *J* in Hz. [c] Aromatic ring resonances assignments: *ortho*-carbons coupling to ^{31}P and shift from δ 128.5 p.p.m., *meta*-carbons based on δ 128.5, *para*-carbons made from relative peak height. δ in p.p.m., *J* in Hz. [d] Assignment as major component (54%). [e] Assignment as minor component (46%). [f] Complex proposed as dimeric, $x = 2$.

features indicate only one orientation of the *cis*-but-2-ene ligand. Structure (**d**) is proposed for this complex in which the olefin methyl groups lie below the equatorial plane where no steric interaction with the phenylimido group is present.

Reduction of [WCl$_3$(NPh)(PMe$_3$)$_2$] under *trans*-but-2-ene led to two complexes. The major component was [WCl$_2$(NPh)(*trans*-MeCH=CHMe)(PMe$_3$)$_2$] (**4**), which again exhibited i.r. and n.m.r. spectral characteristics consistent with a *cis*-chloro–*trans*-phosphine structure. The ^{31}P-{^{1}H} n.m.r. spectrum showed only one isomer, represented by an AB system with ^{2}J(PP) of 173.9 Hz consistent with *trans* orientated PMe$_3$ ligands. With this geometry the inequivalence observed in the spectrum must again arise from asymmetry associated with co-ordination of the olefin ligand. However, the ^{1}J(PW) values (238.7 and 241.6 Hz) are only slightly different so that in solution W–P bond differences are small.[21,22] The appearance of the spectrum also indicates that olefin rotation is slow on the n.m.r. time-scale.

In the ^{1}H and ^{13}C-{^{1}H} spectra the PMe$_3$ resonances also reflect the asymmetry, appearing as eight lines apparently a doublet of doublets with each line split into a further doublet. For the *trans*-but-2-ene ligand the ^{1}H n.m.r. spectrum showed two methyl resonances vicinally coupled to the CH protons. One CH proton resonance lies at δ 2.86 and is likely to arise from an olefinic proton lying above the equatorial plane on the basis of a similar resonance position for complex (**3**). In the ^{13}C-{^{1}H} n.m.r. spectrum of (**4**) the methyl group carbons appeared as two ^{31}P-coupled doublets. However, the olefinic carbons appeared as two doublet of doublets, the fine structure of each arising from different couplings to the phosphines lying either *cis* or *trans* to the respective olefinic carbons.

An *X*-ray crystal structure determination of complex (**4**)[23] has shown an octahedral array with *trans*-phosphines, *cis*-chloro ligands, and mutually *cis* orientated phenylimido and *trans*-but-2-ene ligands. Structural determinations carried out both at ambient and low temperature led to unacceptable high thermal parameters for all atoms as a result of disorder problems. However, the structure does confirm the position of the phosphine ligands so that the non-equivalence observed in the n.m.r. spectra must be associated with asymmetry in the molecule arising from co-ordination of the *trans*-but-2-ene ligand.

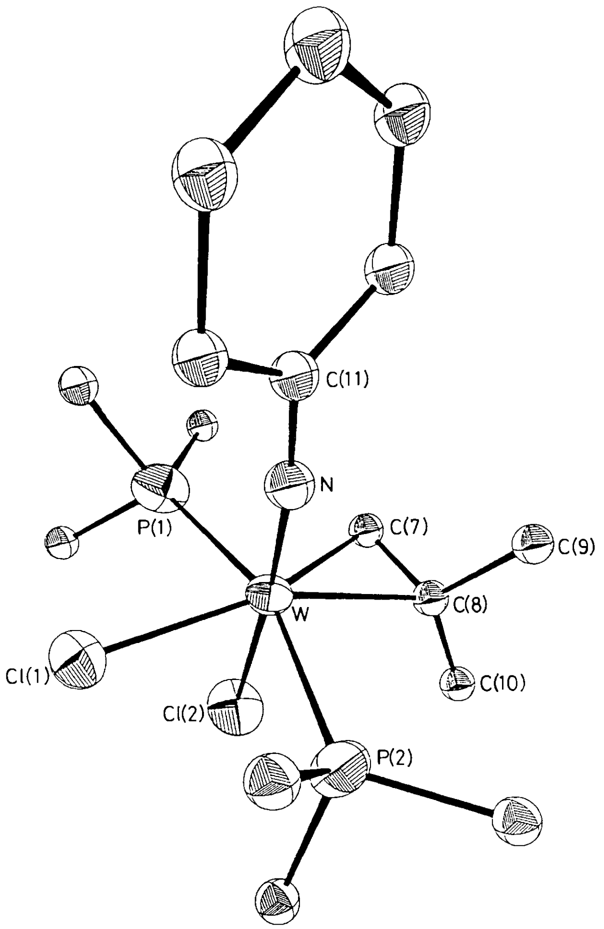


Figure. Molecular structure of complex (**6**)

Table 3. Selected bond lengths (Å) and angles (°) for complex (**6**)

W-Cl(1)	2.499(5)	W-C(8)	2.30(2)
W-Cl(2)	2.474(5)	C(7)-C(8)	1.45(3)
W-P(1)	2.522(6)	C(8)-C(9)	1.65(4)
W-P(2)	2.564(5)	C(8)-C(10)	1.46(3)
W-N	1.778(14)	C(11)-N	1.34(2)
W-C(7)	2.25(2)		
Cl(1)-W-Cl(2)	82.3(2)	C(7)-W-N	96.5(8)
Cl(1)-W-P(1)	80.3(2)	C(8)-W-N	97.8(7)
Cl(1)-W-P(2)	79.3(2)	C(7)-W-C(8)	37.1(8)
Cl(2)-W-P(1)	85.2(2)	C(9)-C(8)-W	110.9(14)
Cl(2)-W-P(2)	90.0(2)	C(10)-C(8)-W	118.1(15)
P(1)-W-P(2)	159.4(2)	C(9)-C(8)-C(7)	113(2)
Cl(1)-W-N	93.9(5)	C(10)-C(8)-C(7)	124(2)
Cl(2)-W-N	175.7(5)	C(10)-C(8)-C(9)	114(2)
P(1)-W-N	92.1(5)	C(11)-N-W	173.1(14)
P(2)-W-N	91.5(5)		

The reduction of [$WCl_3(NPh)(PMe_3)_2$] under *trans*-but-2-ene in addition to (**4**) gave a dark red complex analysing as [$WCl_2(NPh)(PMe_3)_2\}_x$] (**5**). In the i.r. spectrum the W-Cl stretches were poorly defined but the $^{31}P-\{^1H\}$ n.m.r. spectrum showed only one isomer, represented by an AB pattern. The phosphine protons appeared as a doublet of doublets in the ^1H n.m.r. spectrum but as the $^2J(PP)$ value in the $^{31}P-\{^1H\}$ n.m.r. spectrum is 219.99 Hz, non-equivalent *trans*-phosphine ligands are again preferred. Suitable crystals for structural studies have not been obtained and the complex is not sufficiently soluble for molecular-weight studies. However, a chloro-bridged dimer [structure (**e**)] is proposed for the complex on the basis of the phenylimido ligand *ipso*-carbon resonance position (153.7 p.p.m.) which is consistent with a terminal phenylimido ligand.[24] Distortions in the chloro-bridge structure could then give rise to the non-equivalent PMe_3 ligands evident in the n.m.r. spectra. The complex does not react with excess of PMe_3 in toluene at ambient temperature but heating the mixture gives rise to [$WCl_2(NPh)(PMe_3)_3$].

In the presence of 2-methylpropene, reduction of [$WCl_3(NPh)(PMe_3)_2$] gave [$WCl_2(NPh)(Me_2C{=}CH_2)(PMe_3)_2$] (**6**) and also [$\{WCl_2(NPh)(PMe_3)_2\}_x$] (**5**) which was produced in 19% yield (*cf.* 16% for the *trans*-but-2-ene reaction). Spectral data indicate the complex has the usual *cis*-chloro–*trans*-phosphine geometry. The phosphines are however again non-equivalent, as evidenced by the AB system in the $^{31}P-\{^1H\}$ n.m.r. spectrum and well separated doublet of doublets in the ^1H and $^{13}C-\{^1H\}$ n.m.r. spectra. The olefin ligand shows some special n.m.r. features: for the methyl groups, a single resonance in the ^1H n.m.r. spectrum and in the $^{13}C-\{^1H\}$ n.m.r. spectrum two doublets which have different $^{13}C-^{31}P$ coupling constants. The olefinic protons appear in the ^1H n.m.r. spectrum at δ 2.09 and 2.68 consistent with positions above and below the equatorial plane but the two $^3J(HP)$ values are different. In the $^{13}C-\{^1H\}$ n.m.r. spectrum the CH_2 carbon couples differently to the two phosphines which lie *cis* and *trans* to it, while the olefinic quaternary carbon only couples significantly to one phosphine. These n.m.r. features again point to lack of rotation of the olefin.

The overall geometry of complex (**6**) was obtained from an *X*-ray crystal structure determination. The molecule (Figure) consists of a a distorted octahedral array with *trans*-phosphines, *cis*-chloro ligands, and mutually *cis* orientated phenylimido and 2-methylpropene ligands. Selected bond lengths and angles are contained in Table 3. The bond lengths and angles associated with the phenylimido and chloro ligands are normal, being similar to those found for [$WCl_2(NPh)(PMe_3)_3$].[9] However the two W–P bond lengths are significantly different with the longer of the two lying adjacent to the two methyl groups of the olefin ligand. The tungsten atom is displaced out of the plane made by the equatorial ligands and the PMe_3 ligands are pushed back from the olefin, the P(1)–W–P(2) bond angle being 159.4(2)°. In contrast, the Cl(2)–W–N bond angle is 175.7(5)°. The C(7)–W–N and C(8)–W–N bond angles of 96.5(8) and 97.8(7)° and P(1)–W–N and P(2)–W–N bond angles of 92.1(5) and 91.5(5)° show the olefin co-ordinates parallel to and slightly below the equatorial plane. The W–C bond lengths [2.25(2) and 2.30(2) Å] are not significantly different to those found for [$WCl_2(O)(CH_2{=}CH_2)(PMePh_2)_2$].[16]

Several features concerning the bond angles associated with the 2-methylpropene ligand are unusual. The W–C–CH_3 bond angles are different at 110.9(14) and 118.1(15)°, whereby the smaller angle is made by the methyl group lying above the equatorial plane. The angles at which the upper and lower methyl groups incline away from the olefinic C–C bond are also different at 113(2) and 124(2)°. Overall, the structural features indicate that the methyl groups of the olefin severely affect the adjacent P–W bond length which in solution is reflected in the $^{31}P-\{^1H\}$ n.m.r. spectrum by the difference in magnitude of the two $^1J(PW)$ values (15 Hz).

When reductions of [$WCl_3(NPh)(PMe_3)_2$] were carried out in the presence of 2-methylbut-2-ene or 2,3-dimethylbut-2-ene identifiable olefin complexes were not obtained but the yields of [$\{WCl_2(NPh)(PMe_3)_2\}_x$] (**5**) increased to 27 and 70%, respectively. Reduction of [$WCl_3(NPh)(PMe_3)_2$] in the absence of an alkene led to an intractable material without complex (**5**) being formed, showing that the olefin is necessary for the reaction to proceed.

In a preliminary investigation of the co-ordinating properties of α,β-unsaturated systems, $[WCl_3(NPh)(PMe_3)_2]$ was reduced with sodium–mercury amalgam in the presence of MeCH=$CHCO_2Me$ which led to a non-crystalline solid analysing as $[WCl_2(NPh)(MeCH{=}CHCO_2Me)(PMe_3)_2]\cdot\frac{1}{6}C_6H_6$. The $^{31}P-\{^1H\}$ n.m.r. spectrum appears to show two isomeric forms but the complex rapidly deteriorates in solution so that further characterisation has not been possible.

Conclusion

The results of this work indicate that olefins will bind to tungsten in a d^2 electron configuration when the strong π-donating phenylimido ligand is present. Reduction of the d^1 tungsten complex $[WCl_3(NPh)(PMe_3)_2]$ provides the position *cis* to the imido function necessary for olefin co-ordination. The size of the olefin has a direct effect on the reaction leading to increasing amounts of the non-olefin-containing product $[\{WCl_2(NPh)(PMe_3)_2\}_x]$ as the number of methyl groups increases. The olefin complexes are stable and initial studies show no tendency for the organoimido ligand to interact with the unsaturated ligand.

Experimental

All preparations and manipulations were carried out under dry oxygen-free nitrogen using standard bench-top air-sensitive techniques.[25] The compound $[\{WCl_4(NPh)\}_2]$ was prepared from $[WCl_4(O)]$ and phenyl isocyanate,[9] and PMe_3 by reaction of MgMeI on triphenyl phosphite.[26]

Commercial mercury was distilled twice before use. Ethylene, propene, *cis*- and *trans*-but-2-ene, and 2-methylpropene were commercially available gases of purity greater than 98% and were used as supplied. 2-Methylbut-2-ene and 2,3-dimethylbut-2-ene were passed through a small alumina column before use. Tetrahydrofuran was distilled from sodium dihydronaphthylide and benzene and diethyl ether from sodium wire. Infrared spectra were recorded on a Perkin-Elmer 597 spectrometer as Nujol mulls between CsI plates, ^1H, $^{13}C-\{^1H\}$, and $^{31}P-\{^1H\}$ n.m.r. spectra on a Bruker AM400 spectrometer in $CDCl_3$ solution. Analytical data were obtained by Professor A. C. Campbell and associates, University of Otago, New Zealand. Melting points were determined in sealed tubes under N_2 on an electrothermal melting-point apparatus and are uncorrected.

Preparations.—$[WCl_3(NPh)(PMe_3)_2]$. This complex was prepared by a modification of the published procedure.[8] The compound $[\{WCl_4(NPh)\}_2]$ (6.0 g, 14.4 mmol) was dissolved in tetrahydrofuran (120 cm^3) and the mixture was transferred to a pressure bottle. Trimethylphosphine (5.5 cm^3, 50.0 mmol) was added and the mixture stirred and heated to 80 °C for 8 h. The solution was filtered, the solvent removed *in vacuo*, and the residue extracted with hot toluene (140 cm^3). The volume of solvent was reduced and the complex crystallised at −20 °C by successive cropping. Yield: 6.8 g (90%).

$[WCl_2(NPh)(CH_2{=}CH_2)(PMe_3)_2]$ (**1**). A solution of $[WCl_3(NPh)(PMe_3)_2]$ (2.0 g, 3.7 mmol) in benzene (100 cm^3) was added to a pressure bottle containing sodium–mercury amalgam (0.1 g Na, 5.0 mmol; 70 g Hg) and vented twice with ethylene gas. The mixture was stirred rapidly and ethylene gas added until a constant pressure of 2.5 lbf in^{-2} was obtained in the pressure bottle. The mixture was stirred for 5 h, filtered, and the residue extracted with benzene (3 × 20 cm^3). The extracts were combined and the solvent removed to give a yellow gum which solidified on standing overnight. The complex was recrystallised from diethyl ether at −20 °C to give yellow crystals. Yield: 1.8 g (92%). I.r. spectrum (Nujol): 1 560w, 1 448s, 1 405s, 1 345s, 1 295m, 1 275s, 1 238w, 1 160m, 1 060w, 1 012w, 940s, 845m, 838m, 765s, 725s, 683m, 664w, 590w, 548w, 530w, 385w, 342w, 285s, and 245s cm^{-1}.

$[WCl_2(NPh)(MeCH{=}CH_2)(PMe_3)_2]$ (**2**). A solution of $[WCl_3(NPh)(PMe_3)_2]$ (1.5 g, 2.8 mmol) in benzene (80 cm^3) was reduced with sodium–mercury amalgam (0.1 g Na, 5.0 mmol; 60 g Hg) under propene using the method employed for (**1**). The complex is not particularly stable in solution and was recrystallised quickly at −20 °C from diethyl ether. Yield: 1.4 g (92%). I.r. spectrum (Nujol): 1 565w, 1 445s, 1 405s, 1 335s, 1 285m, 1 265s, 1 250m, 1 195w, 1 135w, 1 080w, 1 054w, 1 030w, 1 012m, 993w, 972m, 930s, 840m, 790w, 754s, 722s, 700m, 678s, 658m, 610w, 554w, 535w, 352w, 280s, 275s, 248s, and 242s cm^{-1}.

$[WCl_2(NPh)(cis\text{-}MeCH{=}CHMe)(PMe_3)_2]$ (**3**). The complex $[WCl_3(NPh)(PMe_3)_2]$ (1.0 g, 1.9 mmol) in benzene (75 cm^3) was reduced with sodium–mercury amalgam (0.05 g Na, 2.2 mmol) under *cis*-but-2-ene using the method employed for (**1**). Recrystallisation from diethyl ether gave yellow crystals. Yield: 0.81 g (78%). I.r. spectrum (Nujol): 1 585w, 1 480s, 1 354s, 1 310m, 1 290m, 1 284m, 1 215m, 1 075w, 1 048w, 1 035w, 1 015w, 995w, 950s, 870w, 855w, 830w, 780s, 750m, 740s, 704s, 680w, 567w, 358w, 275m, and 250m cm^{-1}.

$[WCl_2(NPh)(trans\text{-}MeCH{=}CHMe)(PMe_3)_2]$ (**4**) *and* $[\{WCl_2(NPh)(PMe_3)_2\}_x]$ (**5**). The complex $[WCl_3(NPh)(PMe_3)_2]$ (1.0 g, 1.9 mmol) was reduced under *trans*-but-2-ene as for complex (**3**) giving an orange-red solution. Reducing the volume of the diethyl ether extract and cooling to −20 °C gave complex (**4**) as yellow crystals. Yield: 0.8 g (77%). I.r. spectrum (Nujol): 1 585w, 1 480s, 1 420s, 1 352s, 1 305m, 1 285m, 1 264w, 1 235w, 1 155w, 1 135w, 1 072w, 1 050w, 1 030w, 990w, 945s, 902w, 855w, 770s, 740s, 690m, 675w, 560w, 390w, 350w, 275s, and 248s cm^{-1}.

The red residue from the above reaction was extracted with hot benzene (50 cm^3), the solution filtered, and the volume reduced to *ca.* 20 cm^3. Addition of diethyl ether (50 cm^3) gave complex (**5**) as a dark red solid. Yield: 0.15 g (16%). I.r. spectrum (Nujol): 1 585w, 1 490s, 1 420w, 1 345m, 1 290w, 1 100w, 1 025w, 990w, 950s, 860w, 850w, 780m, 770m, 750m, 695m, 560w, 545w, 345w, 290m, 275m, and 240m cm^{-1}.

$[WCl_2(NPh)(Me_2C{=}CH_2)(PMe_3)_2]$ (**6**). The complex $[WCl_3(NPh)(PMe_3)_2]$ (1.0 g, 1.9 mmol) was reduced under 2-methylpropene using the conditions employed for complex (**3**) giving a red-brown solution. Reducing the volume of the diethyl ether extract and cooling to −20 °C gave complex (**6**) as yellow-brown crystals. Yield: 0.75 g (72%). I.r. spectrum (Nujol): 1 590w, 1 485s, 1 425m, 1 354s, 1 325w, 1 310m, 1 290m, 1 175w, 1 160w, 1 110w, 1 090w, 1 055w, 1 030m, 1 012w, 992w, 955s, 860w, 775s, 740m, 695s, 680w, 560w, 355w, 280w, 272m, and 242m cm^{-1}.

Complex (**5**) was precipitated from the benzene-soluble residue by addition of diethyl ether. Yield: 0.18 g (19%).

$[WCl_2(NPh)(MeCH{=}CHCO_2Me)(PMe_3)_2]\cdot\frac{1}{6}C_6H_6$. The complex $[WCl_3(NPh)(PMe_3)_2]$ (0.9 g, 1.7 mmol) was reduced in benzene (80 cm^3) with sodium–mercury amalgam (0.05 g Na, 2.2 mmol; 40 g Hg) in the presence of methyl crotonate (0.18 cm^3, 1.7 mmol) for 2 h. The product was obtained as a yellow non-crystalline solid from the diethyl ether extract (Found: C, 35.5; H, 6.0; N, 2.5. $C_{18}H_{32}Cl_2NO_2P_2W$ requires C, 35.4; H, 5.3; N, 2.3%).

Reduction of $[WCl_3(NPh)(PMe_3)_2]$.—In the presence of 2-methylbut-2-ene. A solution of $[WCl_3(NPh)(PMe_3)_2]$ (1.0 g, 1.9 mmol) and 2-methylbut-2-ene (0.4 cm^3, 3.8 mmol) in benzene (80 cm^3) was added to sodium–mercury amalgam (0.05 g Na, 2.2 mmol; 50 g Hg) and the mixture was stirred for 5 h giving a red solution. The solution was filtered and the solvent removed to give a gum. Extraction with ether left complex (**5**) as a dark red solid. Yield: 0.25 g (27%).

Table 4. Fractional atomic co-ordinates for complex (**6**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W	0.155 53(3)	0.080 76(2)	0.250 00(0)
Cl(1)	0.243 11(18)	0.082 95(14)	0.333 1(7)
Cl(2)	0.151 3(2)	0.030 26(15)	0.435 9(7)
P(1)	0.147 2(2)	0.123 67(17)	0.470 2(7)
P(2)	0.195 2(2)	0.036 03(14)	0.063 6(7)
N	0.162 1(5)	0.118 6(4)	0.124 7(17)
C(1)	0.182 7(15)	0.168 2(11)	0.433(5)
C(2)	0.092 8(18)	0.142 7(14)	0.536(8)
C(3)	0.184 6(15)	0.112 5(11)	0.632(5)
C(4)	0.247 5(10)	0.057 5(7)	−0.025(3)
C(5)	0.164 1(10)	0.014 0(8)	−0.097(4)
C(6)	0.222 6(9)	−0.003 9(7)	0.153(3)
C(7)	0.073 7(9)	0.085 7(7)	0.279(3)
C(8)	0.081 6(7)	0.058 8(5)	0.162(2)
C(9)	0.070 0(10)	0.075 2(7)	−0.006(4)
C(10)	0.071 2(10)	0.019 2(7)	0.179(3)
C(11)	0.169 4(7)	0.149 5(5)	0.044(2)
C(12)	0.128 8(6)	0.170 9(5)	−0.018(2)
C(13)	0.138 5(7)	0.202 8(5)	−0.100(2)
C(14)	0.186 2(9)	0.212 1(7)	−0.137(3)
C(15)	0.223 7(10)	0.191 9(7)	−0.086(3)
C(16)	0.218 5(8)	0.158 7(5)	0.008(4)

In the presence of 2,3-*dimethylbut*-2-*ene*. Reduction of $[WCl_3(NPh)(PMe_3)_2]$ with this alkene as above gave a dark red solution from which complex (**5**) was obtained. Yield: 0.65 g (70%).

Crystallography.—A crystal of complex (**6**) was mounted on a glass fibre and data were collected using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) in a ω—2θ scan mode. The intensity data were corrected for Lorentz, polarisation and absorption effects. Absorption corrections were by empirical psi scans, maximum and minimum corrections being 0.996 and 0.774 respectively.

Crystal data. $C_{16}H_{31}Cl_2NP_2W$, M = 554.22, orthorhombic, space group *Fdd2*, a = 27.209(3), b = 36.034(4), c = 8.992(5) Å, U = 8 815.92 Å^3, Z = 16, D_c = 1.670 g cm^{-3}, $F(000)$ = 4 384, μ(Mo-K_α) = 59.2 cm^{-1}.

Structure solution and refinement. The structure was solved by conventional Patterson and Fourier techniques and refined by full-matrix least-squares methods. The heavier atoms were assigned anisotropic thermal parameters, the light atoms being refined isotropically. There is some evidence for disorder in one trimethylphosphine group as evidenced by the larger thermal parameters for those carbon atoms. Hydrogen atoms were not resolved and were not included. The diagram (Figure) does not imply a particular enantiomer.

The final R and R' values were 0.0471 and 0.0476 {1 837 observed data with $I > 3\sigma(I)$, 2 522 measured, weights $w = [\sigma(F)^2 + 0.001F^2]^{-1}$}. Final atomic co-ordinates are given in Table 4. Scattering factors for neutral atoms were from ref. 27. Programs used were the SDP suite[28] on a PDP-11 for data reduction and SHELX 76[29] implemented on an IBM 4341 computer for structure solution and refinement.

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