Polyhedron Vol. 8, No. 10, pp. 1261–1277, 1989
Printed in Great Britain

0277–5387/89 $3.00+.00

TUNGSTEN COMPLEXES WITH STRONG π-DONOR AND π-ACCEPTOR LIGANDS: $W(E)Cl_2(L)(PR_3)_2$ (E = O, NR, S, AND L = CO, CNR, $CH_2{=}CHR$ AND $O{=}CHMe$)

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(*Received* 17 *September* 1988; *accepted* 23 *November* 1988)

Abstract—The synthesis and characterization of a series of tungsten complexes, $W(E)Cl_2(L)(PR_3)_2$, containing both a π-donor group (E = oxo, imido, or sulphido) and a π-acceptor ligand (L = CO, CN^tBu, $CH_2{=}CHR$, $O{=}CHMe$) is reported ($PR_3 = PMe_3$, $PMePh_2$). The compounds are prepared by substitution of a phosphine ligand in $W(E)Cl_2(PR_3)_3$ by L and by oxidative addition of heterocumulenes E=L, epoxides or episulphides to $WCl_2(PMePh_2)_4$. All of the compounds have an octahedral structure with the π-donor and π-acceptor ligands *cis*, according to spectroscopic data and X-ray crystal structures of oxo–carbonyl (**4**), oxo-ethylene (**7**) and imido–carbonyl (**25**) complexes. The ethylene ligands are oriented perpendicular to the tungsten–oxygen, –nitrogen, or –sulphur multiple bond, and are non-fluxional by NMR. These geometrical features are a direct result of the electronic structure of the d^2 metal centre. The dihapto coordination of acetaldehyde shows the substantial π-basicity of the tungsten(IV)–oxo centre. The CO stretching frequencies indicate that the donor abilities are in the order: oxo < sulphido < imido (< alkylidene < alkylidyne). Complexes **4**, **7** and **25** are significantly distorted from octahedral geometry, also due to the electronic influence of two π-bonding ligands. The structure of $WCl_2(PMePh_2)_4$ (**1**) shows smaller distortions, a result of the steric bulk of the four phosphine ligands. Crystallographic data for **1**: $P\bar{1}$, $a = 11.7401(13)$, $b = 14.2555(12)$, $c = 17.5922(12)$ Å, $\alpha = 76.226(6)$, $\beta = 70.891(7)$, $\gamma = 83.476(8)°$, $Z = 2$; for **25**: *Pbcn*, $a = 17.764(2)$, $b = 15.821(6)$, $c = 23.829(3)$ Å, $Z = 8$.

Metal–ligand π-bonding can be divided into two types. π-Donor ligands, such as terminal oxo (O^{2-}), imido (NR^{2-}), and sulphido (S^{2-}) groups, form multiple bonds with transition metal centres, formally by donation of electrons to empty metal *d* orbitals.[1] Because of the need for empty *d* orbitals, these groups are found as terminal ligands predominantly in high oxidation state complexes, with d^0, d^1 or d^2 electronic configurations. In contrast, the π-acceptor (π-acid) ligands: carbon monoxide, isonitriles and olefins require filled *d* orbital(s) of π-symmetry for productive π-bonding.[2] The filled d_π orbital must in addition be high enough in energy to interact strongly with the ligand acceptor orbital(s), so that π-acid ligands are found mostly in low-valent complexes. Since the two classes of ligands have conflicting requirements, few examples of complexes containing both types have been reported.[3]

This report describes the synthesis and characterization of a series of tungsten(IV) complexes with both a π-donor oxo, imido, or sulphido group and a π-acid carbonyl, isonitrile or ethylene ligand.[4] These are the first isolated examples of olefin complexes with terminal oxo, sulphido or imido ligands,[5] and of oxo–carbonyl and sulphido–carbonyl species. The compounds are prepared by substitution and/or by oxidative addition to a tungsten(II) complex. The electronic structure of these compounds is discussed in light of their structure and reactivity, with the conclusion that the d^2 configuration is ideal for molecules with both classes of ligands.

The oxo– and imido–olefin complexes are of particular interest because species of this kind have been suggested as intermediates in olefin oxidation reactions by metal reagents (osmium tetroxide,

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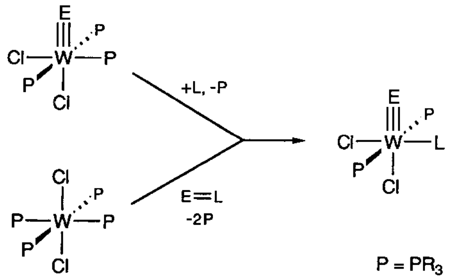
chromyl chloride, etc.) and by metalloenzymes.[1,6] Similarly, oxo–carbonyl species may be intermediates in the oxidation of CO by metal oxides.[7] Indeed, the oxidative addition of epoxides and carbon dioxide to form oxo–olefin and oxo-carbonyl complexes reported here is the reverse of olefin or CO oxidation.

RESULTS

Synthesis

Two synthetic routes have been used to prepare the tungsten(IV) oxo, imido, and sulphido complexes: substitution of a phosphine ligand in the tris-phosphine complexes $W(E)Cl_2(PR_3)_3$ (E = O, S, NR) and oxidative addition of epoxides, episulphides and heterocumulenes to $WCl_2(PR_3)_4$ (**1**) [eq. (1)].



(1)

E = O, S, N^{t}Bu, NPh, N-*p*-Tol, $NSiMe_3$; $PR_3 = PMePh_2$, PMe_3; L = CO, CN^{t}Bu, $CH_2{=}CH_2$, $CH_2{=}CHR$, $PhC{\equiv}CH$.

Many of the compounds have been prepared by both routes. The molybdenum oxo–carbonyl complex $Mo(O)Cl_2(CO)(PMePh_2)_2$ is also formed by displacement of a phosphine ligand in $Mo(O)Cl_2(PMePh_2)_3$ with CO. The isolated compounds are listed in Table 1, together with the compound numbers and the method(s) of synthesis. The last column indicates the reagent used in the oxidative addition reaction.

Ligand substitution is the most straightforward procedure, since facile routes to $W(O)Cl_2(PR_3)_3$ [$PR_3 = PMePh_2$ (**2**), PMe_3 (**3**)][8] and $W(NPh)Cl_2(PR_3)_3$ [$PR_3 = PMePh_2$ (**19**), PMe_3 (**20**)][9] have been reported. Preparation of the sulphido complex $W(S)Cl_2(PMePh_2)_3$ (**13**) is reported below. Carbon monoxide, *t*-butylisonitrile and ethylene all readily displace $PMePh_2$ from $W(E)Cl_2(PMePh_2)_3$ (E = O, S, NPh). The reactions are equilibria, however, and addition of excess $PMePh_2$ to the CO, CN^{t}Bu and $CH_2{=}CH_2$ complexes in a sealed NMR tube in general forms a small amount of the tris-$PMePh_2$ complexes. The formation of PMe_3–carbonyl and –ethylene complexes from **3** is less favourable: $W(O)Cl_2(CH_2{=}CH_2)(PMe_3)_2$ has been observed in the presence of excess ethylene, but we have been unable to isolate it because the equilibrium is unfavourable. In contrast, PMe_3 is readily displaced from the imido complex **20** by ethylene.

Terminal olefins such as propylene do not bind as strongly to the tungsten–oxo centre and can be completely displaced by excess $PMePh_2$. Internal olefins do not react with $W(O)Cl_2(PMePh_2)_3$ (**2**). This pattern of binding $CH_2{=}CH_2 > CH_2{=}CHR > RHC{=}CHR$, is typical of transition metal olefin complexes.[10] Butadiene, vinyl fluoride and allyl alcohol displace phosphine from **2**, but the electron rich olefin ethyl–vinyl–ether does not, indicating that π-backbonding is important in stabilizing the olefin complexes (see below). The π-basicity of the tungsten(IV) centre is especially evident in the formation of the η^2-acetaldehyde complex, **12**, by reaction of **2** with $O{=}CHMe$. η^2-Aldehyde complexes are rare;[11] the η^2-form is favoured over the η^1-linkage isomer only by metal centres that have a strong preference for a π-acid ligand.

The oxidative addition reactions of $WCl_2(PMePh_2)_4$ (**1**)[12] generally require a few hours at ambient temperatures in benzene solution. $PMePh_2$ is the ligand of choice because its large size favours dissociation; PMe_3 is more difficult to substitute because of its small size and greater donor ability.[13] The difference between the two ligands is observed both in the thermodynamics of the ligand substitution reactions, as described above, and in the reaction kinetics. $WCl_2(PMe_3)_4$ reacts very slowly at ambient temperatures with CO_2, and reactions of $W(NPh)Cl_2(PR_3)_3$ occur at 25°C for $PR_3 = PMePh_2$ but only at elevated temperatures for the PMe_3 derivative.

Epoxides react with **1** to give an apparent equilibrium mixture of tungsten(IV) oxo complexes. Thus ethylene oxide gives predominantly the oxo–ethylene complex **7**, propylene oxide gives a mixture of the propylene and phosphine complexes **8** and **2**, and epoxides of internal olefines (2-butene oxides, tetramethylethylene oxide) give only the tris-phosphine complex **2**. The rate of equilibration among the oxo complexes is comparable to or faster than the rate of oxidative addition. Ethylene sulphide reacts with **1** to give the sulphido ethylene complex **16** as the major product when the stoichiometry is 1 : 1, but ethylene sulphide reacts further with **16** to give unidentified tungsten product(s) and $MePh_2PS$.

Heterocumulenes $X{=}C{=}Y$ react with **1** with cleavage of one double bond, forming a tungsten–X multiple bond and a $C{\equiv}Y$ ligand. When X and

Table 1. Compounds prepared and synthetic procedures

Number	Compound	Prepared by Substitution	Oxidative addition, $WCl_2(PMePh_2)_4$ (1)+
2	$W(O)Cl_2(PMePh_2)_3$[a,b]		
3	$W(O)Cl_2(PMe_3)_3$[a]		
4	$W(O)Cl_2(CO)(PMePh_2)_2$	√	CO_2
5	$W(O)Cl_2(CO)(PMe_3)_2$	√	CO_2
6	$W(O)Cl_2(CN^tBu)(PMePh_2)_2$	√	
7	$W(O)Cl_2(CH_2{=}CH_2)(PMePh_2)_2$	√	$\overline{OCH_2C}H_2$
8	$W(O)Cl_2(CH_2{=}CHMe)(PMePh_2)_2$	√	$\overline{OCH_2C}HMe$[c]
9	$W(O)Cl_2(CH_2{=}CHCH{=}CH_2)(PMePh_2)_2$	√	
10	$W(O)Cl_2(CH_2{=}CHCH_2OH)(PMePh_2)_2$	√	
11	$W(O)Cl_2(PhC{\equiv}CH)(PMePh_2)_2$	√	
12	$W(O)Cl_2(O{=}CHMe)(PMePh_2)_2$	√	
13	$W(S)Cl_2(PMePh_2)_3$		$MePh_2PS$
14	$W(S)Cl_2(CO)(PMePh_2)_2$	√	OCS
15	$W(S)Cl_2(CN^tBu)(PMePh_2)_2$	√	SCN^tBu
16	$W(S)Cl_2(CH_2{=}CH_2)(PMePh_2)_2$	√	$\overline{SCH_2C}H_2$[d]
17	$W(N^tBu)Cl_2(CO)(PMePh_2)_2$		OCN^tBu
18	$W(N^tBu)Cl_2(CN^tBu)(PMePh_2)_2$		$^tBuNCN^tBu$
19	$W(NPh)Cl_2(PMePh_2)_3$		
20	$W(NPh)Cl_2(PMe_3)_3$[e]		
21	$W(NPh)Cl_2(CO)(PMePh_2)_2$	√	
22	$W(NPh)Cl_2(CO)(PMe_3)_2$	√	
23	$W(NPh)Cl_2(CH_2{=}CH_2)(PMePh_2)_2$	√	
24	$W(NPh)Cl_2(CH_2{=}CH_2)(PMe_3)_2$	√	
25	$W(N\text{-}p\text{-}Tol)Cl_2(CO)(PMePh_2)_2$		$OCN\text{-}p\text{-}Tol$
26	$W(NSiMe_3)Cl_2(CO)(PMePh_2)_2$		$OCNSiMe_3$
27	$Mo(O)Cl_2(CO)(PMePh_2)_2$	√	

[a] Reference 8.

[b] Also formed from **1**+ sterically crowded epoxides, see text.

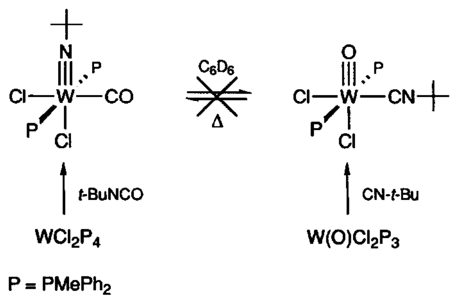
[c] Formed together with **2**.

[d] A number of products are formed in the reaction.

[e] Reference 9.

Y are different the reactions are regioselective: isocyanates yield only tungsten–imido–carbonyl complexes, and SCO and SCN^tBu give the sulphido–carbonyl and sulphido–isonitrile compounds. The weaker double bond of the heterocumulene appears to be cleaved in each case. The reaction of **1** with CS_2 gave only $MePh_2PS$ and uncharacterized tungsten product(s).

The oxidative addition of heterocumulenes is an irreversible reaction. Isomeric oxo–isonitrile (**6**) and imido–carbonyl (**17**) species have been isolated and they do not interconvert, even after a week at 70°C [eq. (2)].



(2)

^{13}C enrichment of the oxo–carbonyl complex **4** is not observed on reaction with $^{13}CO_2$ for a week at 25°C.

The oxidative addition reaction appears to be a powerful route to high oxidation state tungsten compounds. We have, for instance, recently reported the addition of ketones to **1**, forming oxo–alkylidene compounds.[14] This route has also been used to prepare the sulphido tris(phosphine) complex **13** from the phosphine sulphide [eq. (3)]:

$$\underset{(\mathbf{1})}{WCl_2(PMePh_2)_4} + MePh_2PS \longrightarrow \underset{(\mathbf{13})}{W(S)Cl_2(PMePh_2)_3} + 2PMePh_2. \quad (3)$$

Phosphinimines (e.g. $MePh_2P{=}N$-*p*-Tol) also react with **1** to form imido complexes, but oxygen atom transfer from phosphine oxides has not been observed.

Characterization

Compounds **2–27** have been characterized by NMR and IR spectroscopies (Table 2), analytical data, and by X-ray crystal structures of **4**, **7** and **25**. The data are consistent with a common geometry for all the complexes: octahedral with *trans*-phosphines, *cis*-chlorides and *cis*-π-donor and -acceptor ligands. Thus all the compounds (except those with unsymmetrical olefin, acetylene and aldehyde ligands **8–12**) show a virtual triplet for the phosphine methyl groups, indicative of two *trans*-phosphine ligands. The ^{13}C resonances for the carbonyl and isonitrile carbons are binomial triplets. The phenyl groups of $PMePh_2$ are observed to be diastereotopic (when not obscured by overlapping resonances), consistent with the only molecular symmetry element being a mirror plane that relates the two phosphines. The α-olefin, phenylacetylene and acetaldehyde complexes **8–12**, which contain no symmetry element, shown an AB pattern in the ^{31}P NMR and the phosphorus methyl groups appear as two doublets in the ^1H NMR.

The butadiene ligand in **9** is bound in an η^2-fashion, as indicated by its NMR spectra. For instance, four ^{13}C signals are observed for the butadiene, two in the olefinic region and two quite close to those observed for the propylene complex, **8**.

The ^1H NMR spectra of the ethylene complexes **7**, **16**, **23** and **24** all show two signals for the ethylene hydrogens, indicating that the ethylene ligands do not rotate on the NMR timescale. The barriers to ethylene rotation are significant, greater than 16 kcal mol^{-1} from variable temperature NMR data.[15] The phenylacetylene complex is also non-fluxional at 25°C.

The presence of a single ^{13}C resonance for the ethylene carbons shows that these carbons are related by the mirror plane. Therefore the ethylene ligands are oriented perpendicular to the metal–oxo, –sulphido and –imido multiple bonds, consistent with the structure of **7** in the solid state (Fig. 2).

The fluxionality of the complexes of α-olefins and acetaldehyde (**8–10**, **12**) cannot be determined from the NMR spectra. The substituted carbon is a chiral centre so the phosphines are diastereotopic, independent of olefin or aldehyde rotation. Two isomers are possible: the substituent can either point towards the oxo group or away. The observation of only one species by NMR seems to indicate that one isomer is strongly preferred, although it is possible that rotation, which would interconvert the isomers, is much more facile for these ligands. Rapid isomer interconversion via olefin or aldehyde dissociation is ruled out by the presence of inequivalent phosphines and by separate resonances for bound and free ligands.

The dihapto bonding mode of acetaldehyde in **12** is indicated by the lack of a high energy (> 1500 cm^{-1}) C═O stretching mode in its IR spectrum and by its NMR spectra. An η^1-structure would be expected to have free rotation about the W—OCHMe bond and would therefore show equivalent phosphine ligands, in contrast to the asymmetric structure observed. Both the aldehyde carbon and hydrogen atoms show coupling to the phosphorus atoms that are bound to tungsten, indicative of W—C bonding. The observed C—H and H—H coupling shows that the acetaldehyde group is intact in **12**, ruling out, for instance, an alternative hydrido–acyl structure.

Compounds **4**,[4b] **7**[4a] and **25** have been characterized by X-ray crystal structures (Figs 1–3): a comparison of the bond distances and angles is given in Table 3. The three complexes adopt similar octahedral structures, with an approximate mirror plane containing the tungsten and the *cis*-chlorides. The presence of this mirror plane is consistent with the spectroscopic data, which indicate equivalent phosphine ligands. The tungsten–oxygen distances of 1.689(6) (**4**) and 1.714(6) Å (**7**) are typical of mono-oxo tungsten compounds: the mean W—O distance in 34 mono-oxo structures is 1.699 Å[16] (compare also the value of 1.67(1) Å in **3**[17]). The W—N distance of 1.754(6) Å and W—N—C angle of 171.6(5)° in **25** are very similar to those in the phenylimido complex **20** (1.755(3) Å, 179.5(3)°).[18] On the basis of tungsten–chloride distances, the order of the *trans* influence appears to be: oxo > imido > carbon monoxide ≈ ethylene, consistent with previous suggestions.[19] A shorter tungsten–carbonyl distance is found in the imido complex (1.983(8) Å) than in the oxo species (2.029(9) Å),

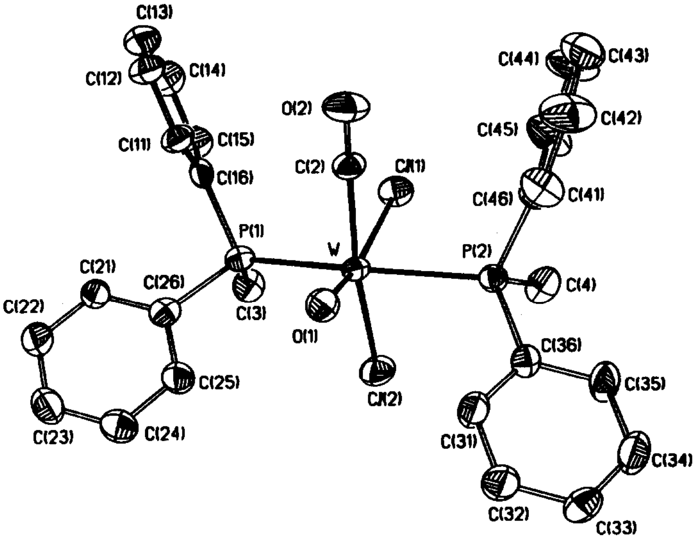


Fig. 1. Perspective drawing of $W(O)Cl_2(CO)(PMePh_2)_2$ (**4**) with hydrogen atoms omitted for clarity.

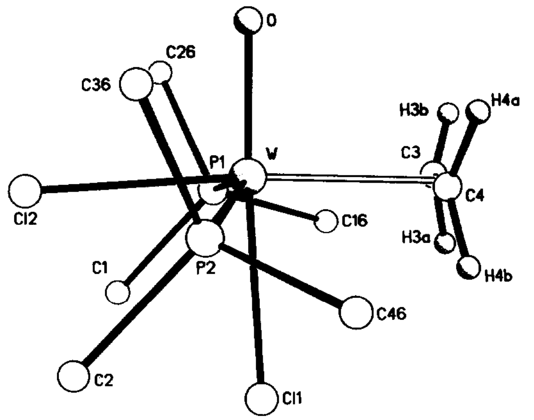


Fig. 2. Perspective drawing of $W(O)Cl_2(CH_2{=}CH_2)(PMePh_2)_2$ (**7**) with hydrogen atoms (except on the ethylene ligand) omitted and only the *ipso*-carbons of the phenyl rings shown.

indicating stronger backbonding in the imido derivative (see Discussion).

The coordination geometries in **4**, **7** and **25** are best described as distorted octahedral, with *cis* angles varying from 75.5(3) to 104.1(2)° and *trans* angles as low as 154.7(1)°. In all three structures the π-acid ligand lies almost exactly at a right angle to the metal–oxo/imido multiple bond ($\angle$E—W—L = 88.9(3)–90.7(4)°, E = oxo or imido), but the phosphines and the *cis*-chloride ligand have moved away from the oxo or imido group ($\angle$E—W—L = 93.0(2)–104.1(2)°). Thus the "*trans*" P—W—P angles are significantly less than 180° (154.7(1)–168.5(1)°). In **4** and **25** the phosphines bend primarily away from the oxo or imido ligand; in **7** the distortion is away from the ethylene as well. The Cl—W—Cl angle is approximately 90° in all three structures, presumably to keep the Cl···Cl non-bonded distance at ~3.5 Å. The movement of Cl(2) away from the oxo or imido thus results in Cl(1) being close to the carbonyl or ethylene ligands, with Cl(1)—W—$C_{carbonyl}$ angles of 75.5(3) (**4**) and 78.0(2)° (**25**).

$WCl_2(PMePh_2)_4$ (**1**) has a more regular octahedral structure, with *trans*-chlorides ($\angle$Cl—W—Cl = 179.6(1)°) and four phosphines in the equatorial plane (Fig. 4, Table 4). The steric crowding caused by the presence of four large $PMePh_2$ ligands (cone angle 136°[13]) is partially relieved by a ruffling of the four phosphines. Two phosphines lie above the equatorial plane and two below, with Cl(1)—W—P angles of 94.8, 84.7, 95.4 and 84.8(1)°. This gives an approximate S_4 axis, and the molecule as a whole has roughly D_{2d} symmetry. Similar structures have been reported for a number of $MoCl_2L_4$ molecules (L = PMe_3, L_2 = diphos, dmpe, 1,2-$C_6H_4(PPh_2)_2$) and the disordered $MCl_2(PMe_3)_4$—$M(N_2)_2(PMe_3)_4$ (M = Mo, W).[20] The facile loss of $PMePh_2$ from **1**, and therefore its high reactivity, is undoubtedly due to this steric crowding.

The $PMePh_2$ cone angle is not a good measure of the crowding in **1** because the phenyl rings interleave and stack [Fig. 4(a)]. The eight phenyls form four pairs in which the rings are roughly parallel, with interplanar distances from 3.2 to 3.5 Å. These distances indicate an attractive stacking interaction; the interlayer distance in graphite, for example, is 3.35 Å.[21]

Table 2. Selected NMR and IR data for the complexes $W(E)Cl_2L(PR_3)_2$ (**2–27**)[a]

Ligands			$^{31}P\{^1H\}$		$^{13}C\{^1H\}$ NMR				^1H NMR: $PC\mathit{H}_3$			^1H NMR: Others					IR	
E	L	No.	∂	J_{WP}	∂	m	J_{PC}	Assignment	∂	m	J_{PC}	∂	m	J	Int	Assignment	ν(CX)	ν(WE)
O	$PMePh_2$	**2**[b]	0.0	340					2.22	t	4	1.67	d	8	3H	$\mathrm{PC}\mathit{H}_3\mathrm{Ph}_2$		945
			−16.7	413					1.67	d	8							
O	CO	**4**	4.6	331	234.4	t	5	$\mathit{C}\mathrm{O}$	2.22	t	4						2006	955
					13.7	t	15	$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$										
O	CO	**5**							1.31	t	4						1995	955
O	CN—*t*-Bu	**6**	0.7	339	14.4	t	15	$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$	2.40	t	4	0.66	s		9H	$\mathrm{C(C}\mathit{H}_3)_3$	2120	955
O	$CH_2{=}CH_2$	**7**	8.5	266	53.8[c]			$=\mathit{C}\mathrm{H_2}$[c]	2.43	t	6	2.77	m		2H	$\mathrm{C}\mathit{H}\mathrm{H{=}C}\mathit{H}\mathrm{H}$		960
					14.0	t	15	$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$				2.24	m		2H	$\mathrm{CH}\mathit{H}\mathrm{{=}CH}\mathit{H}$		
O	$CH_2{=}CHMe$	**8**	9.1[d]		27.1	s		$\mathit{C}\mathrm{H_3}$	2.40	d	8	2.39	d	3	3H	$\mathrm{C}\mathit{H}_3$		960
			9.4[d]		60.2	s		$=\mathit{C}$	2.54	d	8	2.58	m		1H	$=\mathrm{C}\mathit{H}\mathrm{H}$		
					65.8	s		$=\mathit{C}$				2.78	m		1H	$=\mathrm{CH}\mathit{H}$		
												3.45	m		1H	$\mathrm{C}\mathit{H}\mathrm{Me}$		
O	$CH_2{=}CHCH{=}CH_2$	**9**[e]	6.3[f]	279	12.9	d	27	$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$	2.38	d	8				[e]			960
			9.2[f]	263	13.6	d	27	$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$	2.52	d	8							
O	$CH_2{=}CHCH_2OH$	**10**[g]	9.4[h]						2.40	d	9				[g]			960
			9.4[h]						2.48	d	9							
O	$PhC{\equiv}CH$	**11**	10.5[h]	255					2.17	d	10	9.88	dd[i]		1H	$\equiv\mathrm{C}\mathit{H}$		940
			12.7[h]	236					2.52	d								
O	$O{=}CHMe$	**12**	9.5[j]	273	23.2	s		$\mathrm{C}\mathit{C}\mathrm{H_3}$	2.48	d	11	2.50	d	5	3H	$\mathrm{C}\mathit{H}_3$		
			14.2[j]	276	93.1	d	9	$\mathrm{O}\mathit{C}\mathrm{HMe}$	2.37	d	11	4.41	m			$\mathrm{OC}\mathit{H}\mathrm{Me}$		
S	$PMePh_2$	**13**	−22.3	270	18.6	t	15	$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$	2.24	t	4							
			−37.6	320	26.6	d	33	$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$	2.01	d	8							
S	CO	**14**	4.0	266	16.2	t	16	$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$	2.18	t	4						1986	524
S	CN—*t*-Bu	**15**	−4.1	276	16.7	t	15	$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$	2.32	t	3	0.72	s		9H	$\mathrm{C(C}\mathit{H}_3)_3$	2127	519
S	$CH_2{=}CH_2$	**16**	8.1	208	14.7	t	16	$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$	2.32	t	4	3.17	m		2H	$\mathrm{C}\mathit{H}\mathrm{H{=}C}\mathit{H}\mathrm{H}$		515
					53.2	s		$=\mathit{C}\mathrm{H_2}$				2.63	m		2H	$\mathrm{CH}\mathit{H}\mathrm{{=}CH}\mathit{H}$		
N—*t*-Bu	CO	**17**	4.2	298	14.6	t	15	$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$	2.34	t	4	0.74	s		9H	$\mathrm{C(C}\mathit{H}_3)_2$	1966	1098
					30.1	s		$\mathrm{NC(}\mathit{C}\mathrm{H_3)_3}$										
					69.7	s		$\mathrm{N}\mathit{C}\mathrm{Me_3}$										

N—*t*-Bu	CN—*t*-Bu	**18**	6.0	308					2.48	t	4	0.77	s	9H		2090[k]	
												0.99	s	9H			
N—Ph	$PMePh_2$	**19**[l]	−4.2	300					2.37	t	4	7.05	m	5H	N—*Ph*		
			1.2	386					1.88	d	8	7.31	m				
N—Ph	CO	**21**	3.2	290	240.5	s			2.30	t	4	7.03	m	5H	N—*Ph*	1964	1101
					14.5	t	15	PCH_3Ph_2									
N—Ph	CO	**22**	−20.3	288	248.8	s			1.35	t	4	6.97	m	5H	N—*Ph*	1946	1070
					15.3	t	15	$P(CH_3)_3$				6.84	m				
N—Ph	$CH_2{=}CH_2$	**23**	4.1	232	13.2	t	15	PCH_3Ph_2	2.42	t	4	2.27	m	2H	C*H*H=C*H*H		1099
					48.0	s		$=CH_2$				2.24	m	2H	CH*H*=CH*H*		
												7.05	m	5H	N—*Ph*		
												7.36	m				
N—Ph	$CH_2{=}CH_2$	**24**	2.6	232	13.9	t	15	$P(CH_3)_3$	1.39	t	4	2.25	m	2H	C*H*H=C*H*H		1156
					39.4	s		$=CH_2$				2.30		2H	CH*H*=CH*H*		
												6.79	m	5H	N—*Ph*		
N—*p*-Tol																	
	CO	**25**	3.5	292	13.6	t		PCH_3Ph_2	2.32	t	4	1.76	s	3H	$C_6H_4CH_3$	1964[k]	1099
					21.5	s		$C_6H_4CH_3$									
$NSiMe_3$	CO	**26**	6.5	307					2.31	t	4	−0.33	s	9H	$NSi(CH_3)_3$	1976[k]	
Mo(O)[m]	CO	**27**							2.21	t	4					2130[k]	950

[a] Taken in C_6D_6 at ambient temperature at 500 or 300 MHz (^1H), and 121.4 MHz (^{31}P). Taken in CD_2Cl_2 or C_6D_6 at 75.4 MHz (^{13}C). Coupling constants are reported in Hz. Resonances in the aromatic region are not reported. ^1H and ^{13}C chemical shifts (∂) are in ppm downfield from TMS and are referenced to solvent resonances. ^{31}P spectra are internally referenced to $PMePh_2$, ∂ −27.6, relative to H_3PO_4. IR spectra obtained as Nujol mulls except where indicated, values given in cm^{-1}. Complete IR spectra are given in the Experimental.

[b] Reference 8.

[c] t, $^1J_{CH} = 156$.

[d] Doublet (part of an AB pattern), $^2J_{PP} = 161$.

[e] Complete ^1H and ^{13}C NMR data are given in the Experimental.

[f] Doublet (part of an AB pattern), $^2J_{PP} = 163$.

[g] Complete ^1H NMR data are given in the Experimental.

[h] Part of an AB pattern, only the two large peaks are reported, J_{PP} not determined.

[i] $J_{PH} = 17$, $J_{PH} = 5$.

[j] Doublet (part of an AB pattern), $^2J_{PP} = 175$.

[k] IR spectrum taken in C_6D_6 solution.

[l] Reference 9.

[m] *Mo*(O)Cl_2(CO)($PMePh_2$)$_2$.

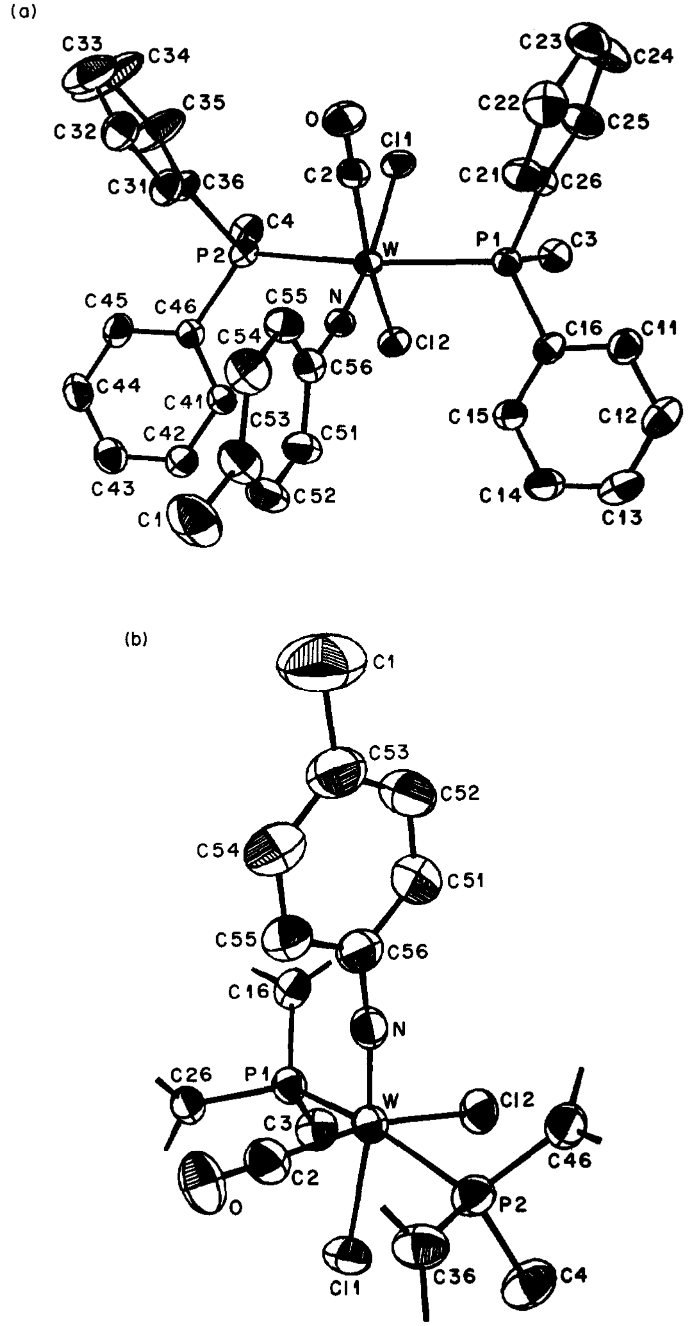


Fig. 3. Perspective drawings of W(N-*p*-Tol)Cl_2(CO)$(PMePh_2)_2$ (**25**) with hydrogen atoms omitted; in (b) only the *ipso*-carbons of the phenyl rings are shown.

Reactions

The oxo–carbonyl, oxo–isonitrile and oxo–ethylene complexes are thermally stable, exhibiting less than 10% decomposition after a day at 90°C in C_6D_6 solution. Solutions of the α-olefin complexes, however, are substantially decomposed within 24 h at 40°C, and the acetaldehyde complex decomposes within a few hours at 25°C. These processes appear to occur via loss of the π-acid ligand. Reaction of complexes **4**–**10** with an excess of CO, CN^{t}Bu, or C_2H_4 results in ligand exchange, consistent with the suggestion above that the ligand exchange reactions are equilibria.

Dissociation of coordinated carbon monoxide or ethylene in **4** or **7** can also be promoted photochemically. Irradiation of **7** in the presence of $PMePh_2$, for instance, gives **2** [eq. (4)]:

Table 3. Selected bond lengths and angles in $W(O)Cl_2(CO)(PMePh_2)_2$ (**4**), $W(O)Cl_2(CH_2CH_2)(PMePh_2)_2$ (**7**) and $W(N\text{-}p\text{-}Tol)Cl_2(CO)(PMePh_2)_2$ (**25**)[a]

	$W(O)Cl_2(CO)L_2$ (**4**)	$W(O)Cl_2(C_2H_4)L_2$ (**7**)	$W(NTol)Cl_2(CO)L_2$ (**25**)
W=E	1.689(6)	1.714(6)	1.754(6)
W—Cl(1)	2.504(2)	2.495(3)	2.476(2)
W—Cl(2)	2.411(3)	2.444(3)	2.455(2)
W—P	2.538, 2.539(2)	2.594, 2.575(3)	2.521, 2.526(2)
W—C(2)	2.029(9)	2.218, 2.221(12)	1.983(8)
C(2)—O(2)	1.142(11)		1.139(8)
C(3)—C(4)		1.404(17)	
E—W—C(2)	89.6(3)	90.6, 90.7(4)	88.9(3)
E—W—P	98.3, 97.4(2)	98.8, 98.3(2)	98.3(2), 93.0(2)
E—W—Cl(1)	165.1(2)	176.1(2)	166.9(2)
E—W—Cl(2)	103.4(2)	94.2(2)	104.1(2)
P—W—Cl(1)	82.4, 83.9(1)	82.1, 82.1(1)	83.4(1), 86.2(1)
C(2)—W—Cl(1)	75.5(3)	85.8, 85.5(3)	78.0(2)
P(1)—W—P(2)	163.2(1)	154.7(1)	168.5(1)
Cl(1)—W—Cl(2)	91.6(1)	89.6(1)	89.0(1)
P—W—Cl(2)	84.2, 86.5(1)	80.4, 79.8(1)	86.9, 87.8(1)
C(2)—W—Cl(2)	166.8(3)	175.0(3)[b]	166.9(2)
P—W—C(2)	93.9, 92.0(2)	99.2, 99.2(3)[b]	90.8, 92.0(2)
W—C(2)—O(2)	177.0(7)		178.5(7)
W—N—C(56)			171.6(5)

[a] Bond distances in Å, angles in degrees; E represents O(1) in **4**, O in **7** and N in **25**. When P is given, the bond length or angle to both P(1) and P(2) is listed.

[b] Angle involving the ethylene centroid.

$$\underset{(\mathbf{7})}{W(O)Cl_2(CH_2{=}CH_2)(PMePh_2)_2} + PMePh_2 \xrightarrow{h\nu} \underset{(\mathbf{2})}{W(O)Cl_2(PMePh_2)_3} + CH_2{=}CH_2. \quad (4)$$

No evidence of olefin oxidation or oxygen atom transfer to phosphine was obtained.

Complex **7** reacts with 1 equivalent of trimethylaluminium to form the oxo–methyl complex, **28**, which has been characterized spectroscopically [eq. (5)]:

$$\underset{(\mathbf{7})}{W(O)Cl_2(CH_2{=}CH_2)(PMePh_2)_2} + AlMe_3 \longrightarrow \underset{(\mathbf{28})}{W(O)(Me)Cl(CH_2{=}CH_2)(PMePh_2)_2}. \quad (5)$$

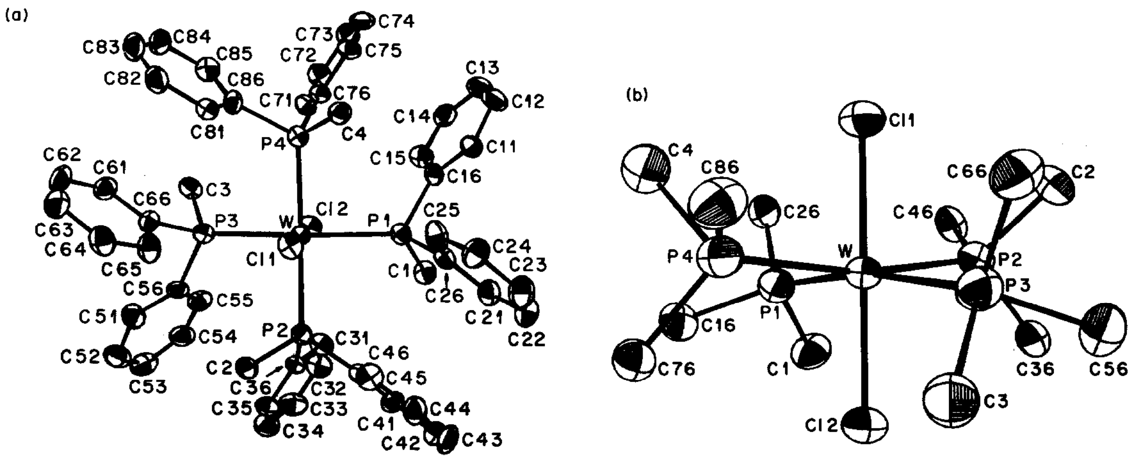


Fig. 4. Perspective drawings of $WCl_2(PMePh_2)_4$ (**1**) with hydrogen atoms omitted; in (b) only the *ipso*-carbons of the phenyl rings are shown.

Table 4. Selected bond lengths and angles in $WCl_2(PMePh_2)_4$ (**1**)[a]

W—Cl(1)	2.423(2)	W—C(2)	2.432
W—P(1)	2.531(3)	W—P(2)	2.539
W—P(3)	2.540(3)	W—P(4)	2.539
Cl(1)—W—Cl(2)	179.57(11)		
Cl(1)—W—P(1)	94.75(9)	Cl(2)—W—P(1)	84.82(9)
Cl(1)—W—P(2)	84.74(9)	Cl(2)—W—P(2)	95.18(9)
Cl(1)—W—P(3)	95.44(9)	Cl(2)—W—P(3)	84.99(9)
Cl(1)—W—P(4)	84.81(9)	Cl(2)—W—P(4)	95.26(9)
P(1)—W—P(2)	90.03(9)	P(1)—W—P(3)	169.80(8)
P(1)—W—P(4)	90.67(9)	P(2)—W—P(4)	169.55(8)
P(2)—W—P(3)	91.39(9)	P(3)—W—P(4)	89.79(9)

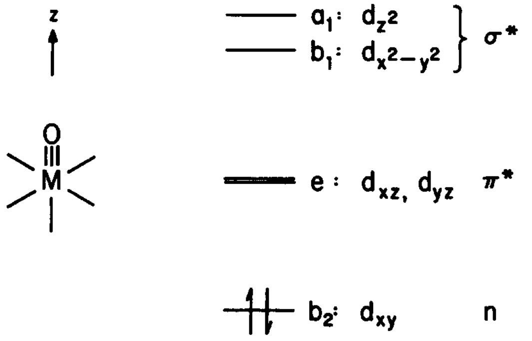
[a] Bond distances in Å, angles in degrees.

The carbonyl and isonitrile complexes **4** and **6** do not react with $AlMe_3$, although the ethylene ligand in **28** can be substituted for CO and CN^tBu to form $W(O)(Me)Cl(L)(PMePh_2)_2$ [L = CO (**29**); CN^tBu (**30**)]. The methyl derivatives are less stable than the dichloride analogues, decomposing in solution at ambient temperatures. A major product of the decomposition of the methyl–ethylene complex **28**, is the *di*chloride–ethylene complex, **7**. The ^1H NMR of **28**–**30** show a triplet for the tungsten methyl groups (J_{PH} = 10 Hz), in addition to resonances similar to those for **4**, **6** and **7**. The methyl group is believed to be *trans* to the oxo ligand, given the large oxo *trans* influence, but this cannot be determined from the spectral data.

DISCUSSION

The stability of this wide range of tungsten(IV) olefin and carbonyl complexes is remarkable, given that these ligands do not often form high oxidation state complexes.[3,22] The tungsten(IV)–oxo, –sulphido, or –imido centre clearly has a high affinity for a π-acid ligand. This is perhaps most evident in the formation of the η^2-acetaldehyde complex **12**. The origin of this stability lies in the electronic structure of the tungsten(IV) d^2 centre.

The electronic configuration of d^2 mono-oxo and related species is well established.[23] The two d electrons are paired in the HOMO, which is the d_{xy} orbital (the z axis is taken as coincident with the metal–ligand multiple bond, Scheme 1). The LUMO is usually the metal–ligand π^*-orbitals, the antibonding combination of the metal d_{xz} and d_{yz} with the ligand p_π orbitals. Oxo, sulphido and imido ligands form strong triple bonds in octahedral symmetry only in electron counts of d^0, d^1 or d^2, because additional d electrons would have to occupy strongly antibonding[24] π^*-orbitals.[23] The d^2 configuration is therefore ideal for the π-donor/π-acceptor molecules reported here: a W≡E triple bond can be formed and two electrons (one pair) are available for backbonding to the π-acid ligand.



Scheme 1.

Since the two d electrons are in the d_{xy} orbital, the π-acid ligand (carbon monoxide, ethylene, etc.) must bind *cis* to the tungsten–E multiple bond. In addition, an olefin ligand with only one acceptor orbital has only one orientation that allows favourable overlap with d_{xy}:

Thus, the unsaturated organic ligand lies perpendicular to the tungsten–E bond, as observed in complexes **7**–**12**, **16**, **23** and **24**. The large barrier to ethylene rotation is due to loss of the π-backbonding interaction on turning the ethylene 90°. This orbital description is similar to that used to explain the geometry and lack of rotation in d^2 oxo–acetylene[25] and oxo–carbene compounds,[26] and is supported by two recent theoretical studies.[27]

The high barriers to olefin rotation indicate that π-backbonding is an important interaction for these complexes. Significant backbonding is also implied by the CO stretching frequencies (Table 5). This conclusion is somewhat surprising since the tungsten centre is in the +4 oxidation state, with two chloride ligands and an oxo, sulphido, or imido group. However, the tungsten(IV) centre is a reasonable reducing agent,[28a] implying that the two d electrons are at fairly high energy and are available for backbonding. Weaker backbonding is seen in the molybdenum oxo–carbonyl complex **27** (compare $\nu(CO) = 2130\ cm^{-1}$ for **27**, $2006\ cm^{-1}$ for **4**), because molybdenum is a less electropositive metal and molybdenum(IV) is a poorer reducing agent than tungsten(IV).[28]

The CO stretching frequency can be used as a measure of the electron density at the metal centre. For instance, because PMe_3 is a stronger donor than $PMePh_2$, the PMe_3 complexes **5** and **22** have lower CO stretching frequencies than **4** and **21**, by 11 and 18 cm^{-1}. This enables a comparison of the electron donor abilities of the multiply bonded ligands (Table 5). The oxo ligand is the least electron donating, then sulphido, and the imido group is the most donating. This order does not simply parallel the donor atom electronegativity, O (3.5) > N (3.0) > S (2.5).[29] It is reasonable that oxygen is the weakest donor, but the poor donation from the sulphido ligand is surprising. The presence of the imido substituent may complicate the comparison, but the substituent does not seem to have a substantial influence on ν(CO). The poor donation from the sulphido ligand may indicate that π-bonding involving the third row element sulphur is not as effective as π-interactions involving oxygen and nitrogen. This is also suggested by the electronic spectra: the lowest energy transition, believed to be $d_{xy} \rightarrow d_{xz}d_{yz}$ ($n \rightarrow \pi^*$),[23] is in the range 492–544 nm in the oxo– and imido–carbonyl complexes, but is at much lower energy (696 nm) in the sulphido–carbonyl compound **14**.

Table 5. Comparison of C—O stretching frequencies

Compound	ν(CO) (cm^{-1})
$W(O)Cl_2(CO)(PMePh_2)_2$ (**4**)	2006
$W(S)Cl_2(CO)(PMePh_2)_2$ (**13**)	1986
$W(NSiMe_3)Cl_2(CO)(PMePh_2)_2$ (**26**)	1976
$W(N^tBu)Cl_2(CO)(PMePh_2)_2$ (**17**)	1966
$W(N\text{-}p\text{-}Tol)Cl_2(CO)(PMePh_2)_2$ (**25**)	1964
$W(NPh)Cl_2(CO)(PMePh_2)_2$ (**21**)	1964
$W(CPMePh_2)Cl_2(CO)(PMePh_2)_2$[a]	1903
$W(O)Cl_2(CO)(PMe_3)_2$ (**5**)	1995
$W(NPh)Cl_2(CO)(PMe_3)_2$ (**22**)	1946
$W(CHPh)Cl_2(CO)(PMe_3)_2$[b]	1939
$W(CPh)Cl(CO)[P(OMe)_3](PMe_3)_2$[b]	1919

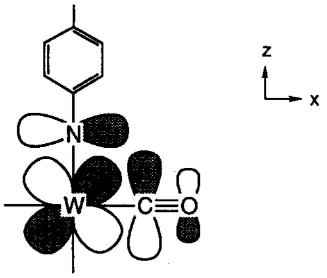
[a] G. Hillhouse, unpublished results.

[b] A. Mayr, M. F. Asaro, M. A. Kjelsberg, K. S. Lee and D. V. Engen, *Organometallics* 1987, **6**, 432.

Table 5 also contains CO stretching frequencies for related alkylidene and alkylidyne complexes. Because of the low electronegativity of carbon (2.5), an alkylidene would be expected to be a very strong donor, but phenylimido is almost as donating as benzylidene. The difference in bond polarity is probably offset by the difference in bond order, an M≡NPh triple bond versus an M=CHPh double bond. The alkylidyne ligand provides a comparison of triple bonds but, because the alkylidyne is a trivalent group, the compounds are not strictly analogous. One of the alkylidyne complexes in Table 5 has an unusual phosphinium–alkylidyne moiety, and in the other a phosphite ligand is in place of one of the chlorides. The list of analogous compounds illustrates the similarities among metal–ligand multiple bonds. Imido and carbene or alkylidene ligands are not as different as is implied by the oxidation state formalism of NR^{2-} as a π-donor and CR_2, a neutral π-acid ligand.

The above discussion used the electronic structure of the parent oxo, sulphido or imido complex and added the π-acid ligand as a small perturbation. The solid state structures and the spectroscopic data are consistent with this approach: The molecules are not distorted towards bound epoxide, η^2-CO_2 or η^2-OCNR forms—there is no evidence for bonding between the π-donor and π-acceptor ligands. The angle between the ligands is very close to 90° in all three cases, and the carbonyl ligands are essentially linear (W—C—O = 177.0(7), 178.5(7)° for **4** and **25**).

There is, however, a short contact between the carbonyl carbon and the oxo or imido nitrogen atom in **4** and **25**, due to the short W—CO and W≡O or W≡NR bonds. These distances, $O \cdots C = 2.63$ Å and $N \cdots C = 2.62$ Å, are much longer than a bond (compare 1.163 Å in CO_2),[30] but are substantially shorter than the sum of the van der Waals radii (C, 1.7; N, 1.55; O, 1.5 Å).[31] Thus, there is probably overlap of the oxygen or nitrogen p_x orbital with the carbonyl π^*-orbital in the xz plane, in addition to the overlap with the tungsten d_{xz} (Scheme 2). One effect of this three orbital–two electron situation is to lower the energy of the filled W—O or W—N π_x-orbital compared to the π_y. This is consistent with the orientation of



Scheme 2. A schematic drawing of the interaction of the tungsten d_{xz}, nitrogen p_x and carbonyl π^* orbitals in $W(N\text{-}p\text{-}Tol)Cl_2(CO)(PMePh_2)_2$ (**25**).

the tolyl group in **25**, in the xz plane: the empty aromatic π^*-orbital(s) of the tolyl ring overlap better with the filled M—N π_y-orbital than the lower energy π_x. This is a weak interaction, however, since rapid rotation about the C—N bond is observed in the ^1H NMR at $-90°C$ ($\Delta G^\ddagger < 9$ kcal mol^{-1}). The π-donor acetylene ligand in **11**, *cis* to the oxo, has a larger effect: in this three orbital–*four* electron case the acetylene competes for the tungsten d_{xz} orbital, as noted in other oxo–acetylene compounds.[25] As a result, the W—O bond order is lower and complex **11** has the lowest W—O stretching frequency of the oxo compounds reported here.

The presence of two π-bonding ligands also seems to be the origin of the significant distortions from octahedral geometry. Closely related d^0 dioxo[32] and d^4 dicarbonyl[33] complexes also adopt highly distorted structures, the distortions resulting from the presence of *cis*-π-bonding ligands.

EXPERIMENTAL

General considerations

All manipulations were carried out using either high vacuum line or glovebox techniques except as indicated. Solvents were vacuum transferred from sodium benzophenone (diethyl ether, THF), calcium hydride (benzene, toluene, petroleum ether, heptane and pentane), or 4 Å sieves (methylene chloride) immediately before use. Deuterated solvents were dried and transferred from activated 4 Å sieves. Gaseous reagents were obtained from Matheson and used without further purification. Complexes **1**,[12] **2**, **3**,[8] **20**,[9] and $Mo(O)Cl_2(PMePh_2)_3$[34] and $MePh_2PS$[35] were prepared following literature procedures.

Elemental analyses were performed by Canadian Microanalytical Service Ltd, Vancouver, British Columbia. NMR spectra were taken using Varian CFT-20 and VXR-300, and Bruker CXP-200 and WM-500 spectrometers. Variable temperature NMR was performed on the VXR-300. IR spectra were obtained as Nujol mulls (unless otherwise noted) using Perkin–Elmer 225, 283 or 1640 spectrometers, and are reported in cm^{-1}. Selected NMR and IR spectra are given in Table 2, the remainder below. The NMR data are reported below as: chemical shift (multiplicity, integral, coupling constant in Hz, assignment). UV–vis spectra were recorded on a Hewlett–Packard 8450A spectrophotometer, and are reported as: UV–vis: λ_{max} (ε).

$W(O)Cl_2(CO)(PMePh_2)_2$ (4)

This was prepared from CO in 70% yield as red–purple crystals following the procedure for **7**. Complex **4** was also observed in > 95% yield (together with < 5% **2**) by NMR when CO_2 (127 torr in 7.5 cm^3) was was exposed to **1** (27 mg) for 3 h in C_6D_6 in a sealed NMR tube. IR: $\nu(CO) = 2006$, $\nu(^{13}CO) = 1985$. Found: C, 46.6; H, 3.9. Calc. for $C_{27}H_{26}Cl_2O_2P_2W$: C, 46.4; H, 3.7%. UV–vis: 498 nm (86). **4**—^{13}CO was prepared in a sealed NMR tube from 10 mg of **2** in C_6D_6 and ^{13}CO (Cambridge Isotope).

$W(O)Cl_2(CO)(PMe_3)_2$ (5)

This was prepared in a sealed tube containing 10 mg of **3** in C_6D_6 and 20 equivalents of CO.

$W(O)Cl_2(CN^tBu)(PMePh_2)_2$ (6)

CN^tBu (0.02 cm^3, 0.26 mmol) was added to a stirred solution of **2** (0.2 g, 0.23 mmol) in benzene (15 cm^3). The purple solution was filtered and the volume was reduced to 1 cm^3. Petroleum ether (5 cm^3) was added. The purple crystals were isolated and dried *in vacuo*; yield 0.11 g (70%). ^1H NMR: 7.02–7.95 (br m, 12, PMe*Ph*$_2$, *p* and *m*), 7.70 (m, 4, PMe*Ph*Ph′, *o*), 8.11 (m, 4, PMePh*Ph′*, *o*). UV–vis: 552 nm (110).

$W(O)Cl_2(CH_2{=}CH_2)(PMePh_2)_2$ (7)

A suspension of **2** (0.35 g, 0.4 mmol) in benzene (20 cm^3) was stirred at 40°C under 1 atm of ethylene for 30 min. Filtration, evaporation of most of the solvent and addition of petroleum ether gave 0.25 g (74%) of yellow crystals. **7** was also formed in ~ 80% yield (together with ~ 10% of **2**, by NMR) when ethylene oxide (6 torr in 25 cm^3) was exposed to **1** (9 mg) for 3 h in C_6D_6 in a sealed NMR tube.

^{1}H NMR: 6.94 (m, 6, PMe*Ph*Ph′, *p* and *m*), 7.04 (m, 6, PMePh*Ph′*, *p* and *m*), 7.40 (m, 4, PMe*Ph*Ph′, *o*), 7.98 (m, 4, PMePh*Ph′*, *o*). Found: C, 48.5; H, 4.5. Calc. for $C_{28}H_{30}Cl_2OP_2W$: C, 48.1; H, 4.3%. UV–vis: 358 nm (240).

$W(O)Cl_2(C_2H_4)(PMe_3)_2$

The compound was detected by ^{1}H NMR in a sealed tube when $W(O)Cl_2(PMe_3)_2$ (10 mg) dissolved in C_6D_6 was exposed to 20 equivalents of C_2H_4. IR (C_6D_6): 960 br [ν(WO)]. ^{1}H NMR: 1.42 (t, $J_{PH} = 4$, P*Me*$_3$), 2.60 (m, 2, *C*HH′*C*HH′), 2.64 (m, 2, CH*H′*CH*H′*).

$W(O)Cl_2(CH_2{=}CHMe)(PMePh_2)_2$ (8)

Compound **8** was prepared from propylene and **2** in 65% yield as yellow crystals following the procedure for **7**. **8** was also formed in ~ 15% yield (together with ~ 75% of **2**, by NMR) when propylene oxide (10 torr in 25 cm^3, Aldrich) was exposed to **1** (9 mg) for 3 h in C_6D_6 in a sealed NMR tube. ^{1}H NMR: 6.94–7.11 (br m, 12, PMe*Ph*$_2$, *p* and *m*), 7.43 (m, 2, PMe*Ph*$_2$, *o*), 7.67 (m, 2, PMe*Ph*$_2$, *o*), 8.02 (m, 4, PMe*Ph*$_2$, *o*). Found: C, 48.8; H, 4.7. Calc. for $C_{29}H_{32}Cl_2OP_2W$: C, 48.4; H, 4.5%.

$W(O)Cl_2(CH_2{=}CHCH{=}CH_2)(PMePh_2)_2$ (9)

Compound **9** was prepared from butadiene and **2** in 50% yield as yellow crystals following the procedure for **7**. ^{1}H NMR: 2.61 (m, 1, WC*H*H′CH CHCH$_2$), 3.00 (m, 1, WCH*H′*CHCHCH$_2$), 3.68 (d, 1, $J = 17$, WCH$_2$CHCHC*H*H′), 4.25 (m, 1, WCH$_2$ *C*HCHCH$_2$), 4.28 (d, 1, $J = 11$, WCH$_2$CHCH CH*H′*), 5.97 (dt, 1, $J = 17$, 10, WCH$_2$CHC*H*CH$_2$), 6.94–7.11 (br m, 12, PMe*Ph*$_2$, *p* and *m*), 7.36 (m, 2, PMe*Ph*$_2$, *o*), 7.69 (m, 2, PMe*Ph*$_2$, *o*), 7.91 (m, 4, PMe*Ph*$_2$, *o*). ^{13}C{^{1}H} NMR: 57.8 (s, W*C*H$_2$ CHCHCH$_2$), 71.7 (s, WCH$_2$*C*HCHCH$_2$), 113.9 (s, WCH$_2$CHCH*C*H$_2$), 145.7 (s, WCH$_2$CH*C*HCH$_2$). Found: C, 50.3; H, 4.6. Calc. for $C_{30}H_{32}Cl_2OP_2W$: C, 49.7; H, 4.4%.

$W(O)Cl_2(CH_2{=}CHCH_2OH)(PMePh_2)_2$ (10)

Compound **10** was prepared from allyl alcohol (0.05 cm^3) in 45% yield as pale yellow crystals following the procedure for **6**. IR: 3450 (br, OH). ^{1}H NMR: 1.0 (br m, 1, CH$_2$CHCH$_2$O*H*), 2.35 (br m, 1, *C*HH′CHCH$_2$OH), 2.70 (br m, 1, CH*H′*CH CH$_2$OH), 3.52 (br m, 2, CH$_2$CHC*H*$_2$OH), 4.36 (br m, 1, CH$_2$C*H*CH$_2$OH).

$W(O)Cl_2(PhC{\equiv}CH)(PMePh_2)_2$ (11)

Compound **11** was prepared from phenylacetylene (0.05 cm^3) in 65% yield as light yellow crystals following the procedure for **6**.

$W(O)Cl_2(O{=}CHMe)(PMePh_2)_2$ (12)

Acetaldehyde (0.5 cm^3, Aldrich) was added to a suspension of **1** (0.20 g) in benzene (1 cm^3). On stirring for 2 h, some blue solids were observed to form on the reaction walls. Pentane (5 cm^3) was added and the resulting white solids filtered and dried *in vacuo* for 3 h, yielding 0.045 g (27%) of **12**. IR: 1192, 1113 vs, 1076 s, 953 s, 923 s, 896 vs, 746, 722, 692 vs.

$W(S)Cl_2(PMePh_2)_3$ (13)

Complex **1** (0.41 g) was added to MePh$_2$PS (0.09 g) in 10 cm^3 of toluene and stirred for 3 h. The reaction mixture was concentrated to 2 cm^3 and heptane (10 cm^3) was added. The resulting solids were filtered, washed with pentane (5 cm^3) and dried *in vacuo* for 18 h, yielding 0.245 g (71%) of green **13**. Found: C, 51.9; H, 4.4. Calc. for $C_{39}H_{39}Cl_2P_2SW$: C, 52.8; H, 4.4%. IR: 1282, 1095, 1028, 1000 w, 890 vs, 741 s, 694 vs, 507 vs, 480, 441 w.

$W(S)(CO)Cl_2(PMePh_2)_2$ (14)

Carbonyl sulphide (66 torr in 25 cm^3, K&K) was added to a suspension of **1** (75 mg) in benzene (12 cm^3) and stirred for 1 h. Volatiles were pumped away and Et$_2$O (2 cm^3) was added to dissolve the residue, and pentane (15 cm^3) was added. The resulting solids were filtered and dried *in vacuo* for 2 h, yielding 17 mg (33%) of green **14**. Found: C, 45.0; H, 3.9. Calc. for $C_{27}H_{26}Cl_2OP_2SW$: C, 45.3; H, 3.7%. IR: 1986 [ν(CO)], 1280 w, 1092, 1034, 893 vs, 741 s, 729 s, 689 s, 524 s ν(W=S), 508 s, 480, 457 s, 291 w ν(WCl). UV–vis: 696 nm (82).

$W(S)(CN^tBu)Cl_2(PMePh_2)_2$ (15)

t-Butyl isothiocyanate (0.011 cm^3, Aldrich) was added to a suspension of **1** (89 mg) in benzene (10 cm^3) and stirred for 2.5 h. The reaction mixture was concentrated to 4 cm^3 and pentane (10 cm^3) was added. The resulting solids were filtered and dried *in vacuo* for 2 h, yielding 44 mg (68%) of yellow–green **15**. Found: C, 48.2; H, 4.6; N, 1.7; S, 4.4. Calc. for $C_{31}H_{35}Cl_2NP_2SW$: C, 48.3; H, 4.6; N, 1.8; S, 4.2%. IR: 2127 [ν(CN)], 1239, 1190, 1101, 1090, 1028, 893 vs, 795 s, 739 vs, 695 s, 519 s ν(W=S), 510 s, 488, 480, 420, 347 w, 277 ν(WCl).

$W(S)(CH_2{=}CH_2)Cl_2(PMePh_2)_2$ (16)

Complex **13** (0.125 g) was stirred under 1 atm of ethylene in toluene (8 cm^3) for 1 h. The reaction mixture was concentrated to 2 cm^3 and heptane (10 cm^3) was added. The resulting solids were filtered and dried *in vacuo* for 18 h, yielding 0.075 g (74%) of grey **16**. Found: C, 46.9; H, 4.2. Calc. for $C_{28}H_{30}Cl_2P_2SW$: C, 47.0; H, 4.2%. IR: 1284, 1186, 1100, 1027 w, 965 w, 901 s, 890 vs, 753, 737 s, 693 vs, 515 s, 447.

$W(N^tBu)(CO)Cl_2(PMePh_2)_2$ (17)

t-Butyl isocyanate (0.013 cm^3, Strem) was added to a suspension of **1** (0.14 g) in benzene (10 cm^3) and stirred for 90 min. Volatiles were pumped away and Et_2O (4 cm^3) and pentane (5 cm^3) were added. The resulting solids were filtered and dried *in vacuo* for 2 h, yielding 0.055 g (55%) of red **17**. Found: C, 49.5; H, 4.7; N, 1.6. Calc. for $C_{31}H_{35}Cl_2NOP_2W$: C, 49.4; H; 4.7; N, 1.9%. IR: 1966 vs ν(CO), 1281 w, 1252 s, 1098 ν(WNC), 1029 w br, 893 vs, 740 s, 727 s, 690 s, 508 s, 489, 454 w, 287 w, 254 w. UV–vis: 501 nm (56).

$W(N^tBu)(CN^tBu)Cl_2(PMePh_2)_2$ (18)

t-Butyl carbodiimide (0.002 cm^3, Aldrich) was exposed to **1** (15 mg) for 1 week in C_6D_6 in a sealed NMR tube. IR (C_6D_6): 2090 s ν(CN), 1262, 1185 br, 1120 s br, 1100 s br, 890 vs br, 740 vs, 693 vs.

$W(NPh)Cl_2(PMePh_2)_3$ (19)

This complex was prepared following the reported procedure for **20**.[9] Excess $PMePh_2$ (2.2 cm^3, 11.7 mmol) was added by syringe to a benzene solution of $W(NPh)Cl_4$ (1.18 g, 2.83 mmol). Sodium amalgam (Na 0.196 g, 8.52 mmol; Hg 19.8 g) was then added by syringe. The solution was stirred at room temperature for 12 h, filtered, and most of the volatiles were removed *in vacuo*. Petroleum ether was added and 2.0 g (75%) of brown **19** was isolated by filtration. IR: 1279 w, 1094 w, 1025 w, 892, 748, 738, 724, 695, 506. UV–vis: 542 nm (260).

$W(NPh)Cl_2(CO)(PMePh_2)_2$ (21)

Following the procedure for **22**, 0.4 g (0.43 mmol) of **19** was stirred under 1 atm of CO at room temperature for 2 days. Evaporation of the solvent and addition of petroleum ether gave 0.27 g (83%) of purple **21**. IR: 1964 ν(CO), 1101, 906, 893, 770, 746, 736, 723, 696, 505, 483, 455, 446. UV–vis: 508 nm (100).

$W(NPh)Cl_2(CO)(PMe_3)_2$ (22)

A suspension of **20** (0.25 g, 0.44 mmol) in benzene (25 cm^3) was stirred under 1 atm CO at 65°C for a day. Evaporation of most of the solvent and addition of Et_2O gave 0.11 g (69%) of purple **22**. IR: 1946 ν(CO), 1303, 1282, 1070, 950, 773, 743, 723, 555, 465, 379. Found: C, 29.8; H, 4.3; N, 2.5. Calc. for $C_{13}H_{23}Cl_2NOP_2W$: C, 29.7; H, 4.4; N, 2.7%. UV–vis: 492 nm (220).

$W(NPh)Cl_2(CH_2{=}CH_2)(PMePh_2)_2$ (23)

Following the procedure for **20**, 0.3 g (0.32 mmol) of **19** gave 0.14 g (49%) of **23**. IR: 1653, 1582, 1188, 1156, 1104, 1093, 1072, 999, 990, 891, 767, 739, 697, 618, 507, 484, 446, 437.

$W(NPh)Cl_2(CH_2{=}CH_2)(PMe_3)_2$ (24)

A solution of **24** (0.35 g, 0.9 mmol) in benzene (15 cm^3) was stirred at 70°C under 1 atm of ethylene for 1 h. Evaporation of most of the solvent and addition of petroleum ether gave 0.18 g (38%) of yellow **24**. IR: 1282, 1168, 1069, 1023, 950, 861, 773, 743, 723, 691, 567, 555, 542. Found: C, 31.8; H, 5.1; N, 2.6. Calc. for $C_{14}H_{27}Cl_2NOP_2W$: C, 31.9; H, 5.1; N, 2.7%.

$W(N\text{-}p\text{-}Tol)(CO)Cl_2(PMePh_2)_2$ (25)

p-Tolyl isocyanate (0.015 cm^3, Aldrich) was added to a suspension of **1** (105 mg) in benzene (12 cm^3) and stirred for 4 h. The volatiles were pumped away, Et_2O (1 cm^3) was added to dissolve the residue, and pentane (8 cm^3) was added. The resulting solids were filtered and dried *in vacuo* for 2 h, yielding 45 mg (57%) of purple **25**. Found: C, 51.4; H, 4.2; N, 1.7. Calc. for $C_{34}H_{33}Cl_2NOP_2W$: C, 51.8; H, 4.2; N, 1.8%. IR: 1964 vs ν(CO), 1587 w, 1158, 1099 ν(WNC), 892 vs, 821 s, 758 s, 740 s, 731 s, 720 s, 690 vs, 559 w, 515 s, 480, 450 w, 290, 255 w. UV–vis: 544 nm (160).

$W(NSiMe_3)(CO)Cl_2(PMePh_2)_2$ (26)

Trimethylsilyl isocyanate (0.030 cm^3, Aldrich) was added to a suspension of **1** (0.20 g) in benzene (15 cm^3) and stirred for 21 h. The volatiles were pumped away and Et_2O (1 cm^3) and pentane (15 cm^3) were added. The resulting solids were filtered and dried *in vacuo* for 2 h, yielding 0.110 g (75%) of red **26**. IR: 1976 vs ν(CO), 1249, 1129 s, 1118 s, 1098, 890 vs, 838 br, 739 s, 690 vs, 506 s, 455, 273 w, 255 w.

$\mathrm{Mo(O)Cl_2(CO)(PMePh_2)_2}$ (**27**)

This complex was prepared from CO and $\mathrm{Mo(O)Cl_2(PMePh_2)_3}$ in 65% yield as brown crystals following the procedure for **4**, except petroleum ether was added through the side arm of the Schlenk flask instead of by vacuum transfer. ^{1}H NMR: 6.94–7.03 (br m, 12, $\mathrm{PMe}PH_2$, *p* and *m*), 7.55 (m, 4, $\mathrm{PMe}Ph\mathrm{Ph'}$, *o*), 7.92 (m, 4, $\mathrm{PMePh}Ph'$, *o*).

$\mathrm{W(O)Me(Cl)(CH_2{=}CH_2)(PMePh_2)_2}$ (**28**)

A solution of **7** (0.20 g, 0.28 mmol) was dissolved in benzene (20 cm^3), cooled to 10°C, and $\mathrm{AlMe_3}$ (1.0 M in benzene, 0.33 cm^3, 0.33 mmol) was added with stirring. The mixture was filtered and the volume was reduced to 1 cm^3. Ether (10 cm^3) was added and yellow crystals were isolated upon stirring the mixture; yield 0.08 g (40%). IR: 960 ν(W—O). ^{1}H NMR: 1.35 (t, 3, $^3J_{\mathrm{PH}} = 11$, $\mathrm{WC}H_3$), 2.23 (t, 6, $J_{\mathrm{PH}} = 4$, $\mathrm{P}Me\mathrm{Ph_2}$), 2.47 (m, 2, $CH\mathrm{H'}CH\mathrm{H'}$), 2.58 (m, 2, $\mathrm{CH}H'\mathrm{CH}H'$), 6.94–7.06 (br m, 12, $\mathrm{PMe}PhPh'$, *p* and *m*), 7.57 (m, 4, PMe $Ph\mathrm{Ph'}o$), 7.78 (m, 4, $\mathrm{PMePh}Ph'$, *o*). ^{13}C NMR: 11.5 (q of t, $J_{\mathrm{PC}} = 17$, $J_{\mathrm{CH}} = 116$, $\mathrm{W}C\mathrm{H_3}$), 20.65 (q of t, $J_{\mathrm{PC}} = 9$, $J_{\mathrm{CH}} = 121$, $\mathrm{P}C\mathrm{H_3Ph_2}$), 48.99 (t, $J_{\mathrm{CH}} = 158$, $C_2\mathrm{H_4}$). ^{31}P{^{1}H} NMR: 19.5 (s, $J_{\mathrm{WP}} = 274$).

$\mathrm{W(O)Me(Cl)(CO)(PMePh_2)_2}$

This complex was prepared in a sealed tube containing **28** (10 mg) in $\mathrm{C_6D_6}$ and 1 atm CO. IR ($\mathrm{C_6D_6}$): 1985 ν(CO), 960 ν(WO). ^{1}H NMR: 1.72 (t, 3, $^3J_{\mathrm{PH}} = 10$, $\mathrm{WC}H_3$), 2.17 (t, 6, $J_{\mathrm{PH}} = 4$, $\mathrm{P}Me\mathrm{Ph_2}$), 6.94–7.07 (br m, 12, $\mathrm{PMePh}Ph'$, *p* and *m*), 7.67 (m, 4, $\mathrm{PMe}Ph\mathrm{Ph'}$, *o*), 7.75 (m, 4, $\mathrm{PMePh}Ph'$, *o*). ^{13}C{^{1}H} NMR: 236.6 (s, $J_{\mathrm{PC}} = 5$, CO). ^{31}P{^{1}H} NMR: 15.7 (s, $J_{\mathrm{WP}} = 323$, $J_{\mathrm{PC}} = 4$). The ^{13}C and ^{31}P spectra were determined for $\mathrm{W(O)Me(Cl)(^{13}CO)(PMePh_2)_2}$.

$\mathrm{W(O)Cl(Me)(CN^tBu)(PMePh_2)_2}$

$\mathrm{CN^tBu}$ (0.015 cm^3, 0.20 mmol) was added to a stirred solution of **28** (0.10 g, 0.23 mmol) in 15 cm^3 of benzene. The purple solution was filtered and the volume was reduced to 1 cm^3. Petroleum ether (5 cm^3) was added and the purple crystals were isolated and dried *in vacuo*; yield 0.35 g (45%). IR: 2110 ν(CN), 955 ν(WO). ^{1}H NMR: 0.80 (s, 9, $\mathrm{CNC}Me_3$), 2.07 (t, 3, $J_{\mathrm{PH}} = 9$, $\mathrm{WC}H_3$), 2.40 (t, 6, $J_{\mathrm{PH}} = 4$, $\mathrm{P}Me\mathrm{Ph_2}$), 6.97–7.14 (br m, 12, $\mathrm{PMe}Ph_2$, *p* and *m*), 7.70 (m, 4, $\mathrm{PMe}Ph\mathrm{Ph'}$, *o*), 8.11 (m, 4, $\mathrm{PMePh}Ph'$, *o*). ^{13}C{^{1}H} NMR: 15.35 (t, $J_{\mathrm{PC}} = 15$, $\mathrm{P}Me\mathrm{Ph_2}$), 15.45 (t, $J_{\mathrm{PC}} = 6$, $\mathrm{W}C\mathrm{H_3}$), 30.69 (s, $\mathrm{CNC}Me_3$), 57.83 (s, $\mathrm{CH}C\mathrm{Me_3}$), 145.50 (t, $J_{\mathrm{PC}} = 19$, $C\mathrm{NCMe_3}$). ^{31}P{^{1}H} NMR: 16.8 (s, $J_{\mathrm{WP}} = 327$).

X-ray structure determinations for $\mathrm{W(N\text{-}\mathit{p}\text{-}Tol)(CO)Cl_2(PMePh_2)_2}$ (**25**) *and* $\mathrm{WCl_2(PMePh_2)_4}$ (**1**)

Data were collected at room temperature (295 K) on a crystal sealed in a glass capillary (**25**) and on

Table 6. Crystallographic data for $\mathrm{WCl_2(PMePh_2)_4}$ (**1**) and $\mathrm{W(N\text{-}\mathit{p}\text{-}Tol)(CO)Cl_2(PMePh_2)_2}$ (**25**)

Complex	$\mathrm{WCl_2(PMePh_2)_4 \cdot (THF) \cdot (C_6H_6)_{0.5}}$	$\mathrm{W(N\text{-}\mathit{p}\text{-}Tol)(CO)Cl_2(PMePh_2)_2}$
Formula	$\mathrm{C_{59}H_{63}Cl_2OP_2W}$	$\mathrm{C_{34}H_{33}Cl_2NOP_2W}$
f_w	1104.86	788.35
Crystal dimensions	0.28 × 0.23 × 0.21 mm	0.17 × 0.26 × 0.58 mm
Space group	*P*1-bar	*Pbcn*
a (Å)	11.7401(13)	17.764(2)
b (Å)	14.2555(12)	15.821(6)
c (Å)	17.5922(12)	23.829(3)
α (°)	76.226(6)	
β (°)	70.891(7)	
γ (°)	83.476(8)	
V (Å^3)	2700.0(7)	6697(3)
Z	2	8
ρ_{calc} (g cm^{-3})	1.36	1.56
μ (cm^{-1})	23.8	38.1
θ limits (°)	2–25	2–28
Transmission factors		0.794–0.999; av 0.890
Total number of reflections	9954	16,110
	$h, \pm k, \pm l$	$\pm h, k, l$
Data $I > 3\sigma$	5734	3713
Final number of variables	564	370
R	0.054	0.028
R_w	0.065	0.031

a crystal mounted on a glass fiber (**1**) using a CAD4 diffractometer operating in the θ–2θ scan mode with graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å), as previously described.[36] The structures were solved using standard heavy atom methods and refined with full-matrix least-squares, with scattering factors and anomalous dispersion terms taken from standard compilations.[37] All non-hydrogen atoms were refined anisotropically, hydrogen atom positions were calculated (C—H = 0.95 Å). Crystallographic data are given in Table 6. Positional and thermal parameters, complete tabulations of bond lengths and angles, and observed and calculated structure factors are available as supplementary material from the Editor.

Acknowledgements—We would like to thank Lauren Atagi for the photochemical experiments and Don McAlister for his many contributions. This work was supported by the Donors of the Petroleum Research Fund, administered by the American Chemical Society, the University of Washington Graduate School Research Fund (GSRF), the National Science Foundation (CHE-8617965), and the Chevron Research Company. We also acknowledge support for X-ray equipment from the National Science Foundation (CHE-8617023) and the University of Washington GSRF (PHS grant PR-07096).

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