

Organoimido-complexes of Tungsten-(vi) -(v), and -(iv): Crystal and Molecular Structures of $[W(NPh)Cl_3(PPh_3)_2]$ and $[W(NPh)Cl_2(PMe_3)_3]$ †

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Reaction of $RNCO$ ($R = Ph$ or Et) with $WOCl_4$ gave the tungsten(vi) imido-compounds $[W(NR)Cl_4]$ which, in further reactions, gave $[W(NR)Cl_4(thf)]$ ($thf =$ tetrahydrofuran) and $[W(NPh)(\mu-O)Me_2(PMe_3)_3]$. In the presence of phosphine ligands ($L = PPh_3$ or PMe_2Ph ; $L_2 = Ph_2PCH_2CH_2PPh_2$), in boiling benzene, reduction occurred forming the paramagnetic tungsten(v) compounds $[W(NPh)Cl_3L_2]$. More powerful reduction (sodium amalgam) in the presence of ligands ($L = PMe_3$, PMe_2Ph , and $CNBu^†$) gave the tungsten(iv) compounds $[W(NR)Cl_2L_3]$. Other reactions led to cleavage of the organoimido-group from the tungsten. An X-ray structure determination of $[W(NPh)Cl_3(PPh_3)_2]$ showed the meridional configuration of chlorines with mutually *trans*-phosphines. The short $W-N$ bond length (1.742 Å) and practically linear WNC (172.3°) suggest that the imido-group is acting as a four-electron ligand. Structure determination of $[W(NPh)Cl_2(PMe_3)_3]$ shows that the three phosphines are meridional, and all *cis* to the $W=N-Ph$ unit. Although the imido-function seems to exert a small *trans*-lengthening influence on the relevant $W-Cl$ bond, in the trichloride, this effect does not seem to be present in the dichloride.

The resurgence of interest in organoimido-transition-metal complexes was clearly shown in a recent review article.¹ The alkyl- or aryl-imido-ligand NR may act as a two-electron non-bridging bent (with $MNC \leq 180^\circ$) or bridging (μ) ligand or alternatively as a four-electron non-bridging (linear MNC) or bridging (μ or μ_3) ligand. Prior to 1980 most published work on organoimido-complexes concerned Mo , W , Re , and Os and mainly involved these metals in d^0 or d^2 configurations.

Organoimidotungsten compounds have been synthesized by reactions of amines or lithium diethylamide with WCl_6 ,²⁻⁴ or from $NMe(SiMe_3)_2$ or primary amines with WF_6 .^{5,6} Other routes have used organonitriles⁷ or aryl azides.⁸ Chatt and co-workers¹ have also established a number of novel syntheses of hydrazido-compounds containing the $W=N-NX_2$ moiety by means of reactions involving dinitrogen complexes such as *trans*- $[W(N_2)_2(dppe)_2]$ ($dppe = Ph_2PCH_2CH_2PPh_2$).

We were interested in developing further the chemistry of tungsten imido-compounds in various valence states and have found that the organoimidotungsten tetrachloride $[W(NR)Cl_4]$ is very suitable for this purpose since it can be conveniently prepared from $WOCl_4$ and $RNCO$. This paper gives an account of our results covering organoimido-compounds of tungsten-(vi), -(v), and -(iv) as depicted in the Scheme.

Results and Discussion

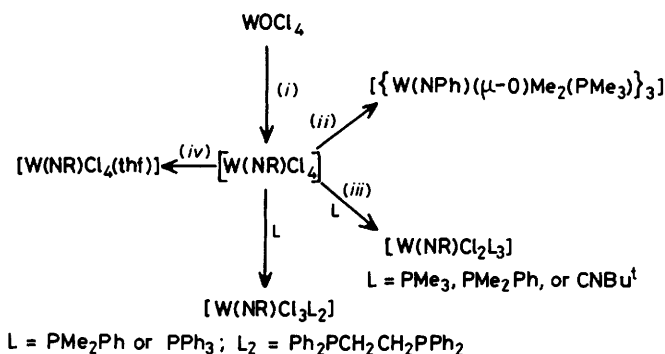
Tungsten(vi) Compounds.—Following the work of Volpin and co-workers⁹ who prepared arylimidorhenium(v) compounds by treating oxorhenium compounds with aryl isocyanate, we have found that $WOCl_4$ reacts similarly to give organoimidotungsten tetrachlorides (Table 1), equation (1).



The phenylimido-compound $[W(NPh)Cl_4]$ is a dark green

† *mer*-Trichloro(phenylimido)bis(triphenylphosphine)tungsten(v) and *mer*-dichloro(phenylimido)tris(trimethylphosphine)tungsten-(iv).

Supplementary data available (No. SUP 23731, 52 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles, structure factors. See Instructions for Authors, Section 4.0, *J. Chem. Soc., Dalton Trans.*, 1983, Issue 3, p. xvii.



Scheme. (i) $RNCO$ ($R = Ph$ or Et); (ii) $MgMe_2 + PMe_3$; (iii) sodium amalgam; (iv) thf

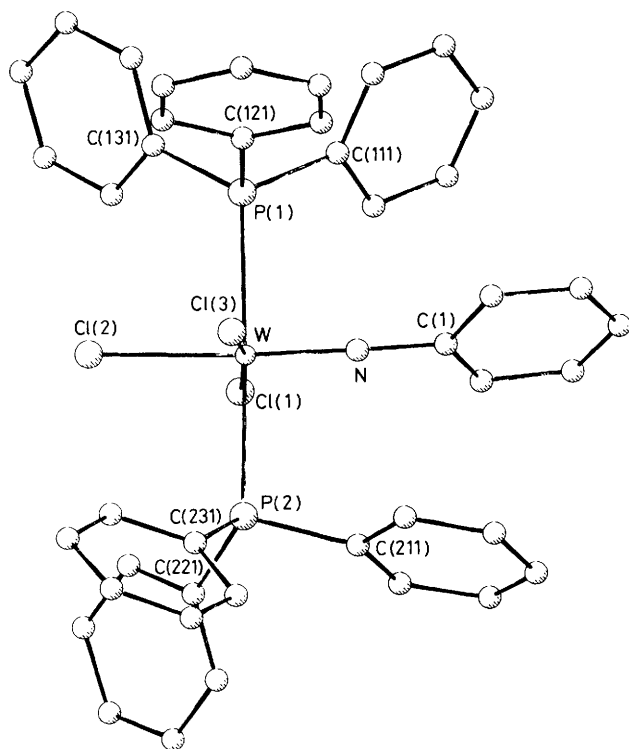
solid sparingly soluble in chlorinated hydrocarbons and practically insoluble in benzene. A weak i.r. band at 1160 cm^{-1} may be due to the $\nu(WN)$ stretching vibration and the strong band at 350 cm^{-1} is probably due to $\nu(WCl)$. The compound was insufficiently soluble for n.m.r. spectroscopy. The ethylimido-compound $[W(NEt)Cl_4]$ is an orange solid, slightly more soluble than the phenyl derivative, and gave corresponding i.r. bands at 1104 and 341 cm^{-1} . Its 1H n.m.r. spectrum in $(CD_3)_2CO$ gave a methylene quartet with a large downfield chemical shift (δ 7.1) and a methylene triplet at δ 1.45. This downfield chemical shift of the methylene group is consistent with triple-bond character in the tungsten-nitrogen bond and is comparable with the corresponding value (δ 7.3, $CDCl_3$) for $[W(O)(NEt)Cl(NHEt)]_n$.¹⁰ Although a molecular ion peak did not appear in the mass spectrum there was a very intense peak ($m/e = 332$ for ^{184}W and ^{35}Cl) corresponding to $[W(NEt)Cl_3]^+$. From the reaction of $WOCl_4$ and $Bu^†NCO$ a black solid was obtained but it exhibited i.r. bands suggesting the presence of $N-H$ groups and its analysis did not accord with the requirements of $[W(NBu^†)Cl_4]$.

The imido-compounds $[W(NR)Cl_4]$ ($R = Ph$ or Et) dissolved in tetrahydrofuran (thf) and gave the 1:1 adducts $[W(NPh)Cl_4(thf)]$ [green solid: $\nu(WN)$ 1158 ; $\nu(WCl)$ 352 cm^{-1}] and $[W(NEt)Cl_4(thf)]$ [lemon-yellow solid: $\nu(WN)$ 1135 ;

Table 1. Physical data for organoimido-complexes of tungsten

Complexes	Colour	M.p. (°C)	Infrared bands (cm ⁻¹) ^a	
			$\nu(\text{W}=\text{N})^b$	$\nu(\text{W}-\text{Cl})$
(a) Tungsten(vi)				
[W(NPh)Cl ₄]	Dark green	decomp. 100	1 160	350
[W(NPh)Cl ₄ (thf)]	Green	decomp. 110	1 158	352
[W(NEt)Cl ₄]	Orange	225 ^c	1 104	341, 282
[W(NEt)Cl ₄ (thf)]	Lemon-yellow	decomp. 135	1 135	342
(b) Tungsten(v)				
[W(NPh)Cl ₃ (PPh ₃) ₂ (C ₆ H ₅ Me)]	Brown	decomp. 120	1 115 ^d	305
[W(NPh)Cl ₃ (PMe ₂ Ph) ₂]	Green	decomp. 84	1 130	300
[W(NPh)Cl ₃ (Ph ₂ PCH ₂ CH ₂ PPh ₂)]	Green	decomp. 45	1 099	320, 295
[W(NEt)Cl ₃ (PMe ₂ Ph) ₂]	Red	152	1 133	293, 280
(c) Tungsten(iv)				
[W(NPh)Cl ₂ (PMe ₂ Ph) ₂ (C ₆ H ₅ Me)]	Green	148	1 095	248
[W(NPh)Cl ₂ (PMe ₃) ₃]	Purple	110 ^c	1 070	255
[W(NPh)Cl ₂ (CNBu ^t) ₃]	Red-brown	146	<i>d</i>	270, 255
[W(NEt)Cl ₂ (PMe ₂ Ph) ₂]	Red-brown	135	1 070	270, 248
[W(NEt)Cl ₂ (PMe ₃) ₃]	Purple-red	93–96	1 080	263, 245
[W(NEt)Cl ₂ (CNBu ^t) ₃]	Red-brown	decomp. 124	<i>d</i>	268

^a Some i.r. data are from KBr discs and hence the frequencies may vary by a few wavenumbers compared to those from Nujol mulls. ^b Tentative assignment. ^c Melts with decomposition. ^d Obscured by other ligand absorptions.

**Figure 1.** The molecular structure of [W(NPh)Cl₃(PPh₃)₂]

$\nu(\text{WCl})$ 342 cm⁻¹. We suppose these adducts involve six-coordinated tungsten and presume that the [W(NR)Cl₄] compounds may be dimeric in the solid state through chlorine bridges.

Reactions of [W(NPh)Cl₄] with alcohols, phenols, and carboxylic acids appeared to cause loss of the phenylimido-group and were not pursued further. With the lithium derivative of *p*-*t*-butylphenol a yellow solid was obtained

Table 2. Selected bond lengths (Å) and angles (°) for [W(NPh)Cl₃(PPh₃)₂]

W-Cl(1)	2.405(2)	W-Cl(2)	2.443(3)
W-Cl(3)	2.368(3)	W-P(1)	2.590(3)
W-P(2)	2.590(3)	W-N	1.742(8)
P(1)-C(av.)	1.833(5)	P(2)-C(av.)	1.822(8)
Cl(1)-W-Cl(2)	85.1(1)	Cl(1)-W-Cl(3)	171.4(1)
Cl(2)-W-Cl(3)	87.9(1)	P(1)-W-Cl(1)	93.9(1)
P(1)-W-Cl(2)	88.1(1)	P(1)-W-Cl(3)	90.8(1)
P(2)-W-Cl(1)	90.2(1)	P(2)-W-Cl(2)	90.4(1)
P(2)-W-Cl(3)	84.9(1)	P(2)-W-P(1)	175.4(1)
N-W-Cl(1)	92.1(2)	N-W-Cl(2)	175.4(3)
N-W-Cl(3)	95.2(3)	N-W-P(1)	88.3(2)
N-W-P(2)	93.4(3)	W-N-C(1)	172.3(7)
W-P(1)-C(111)	113.5(3)	W-P(2)-C(211)	104.3(3)
W-P(1)-C(121)	108.1(3)	W-P(2)-C(221)	120.8(3)
W-P(1)-C(131)	120.0(3)	W-P(2)-C(231)	116.6(3)

which had an ¹H n.m.r. spectrum suggesting it was [W(NPh)(OC₆H₄Bu^t-*p*)₄] [$\nu(\text{WN})$ 1 100 cm⁻¹] but the elemental analysis was unsatisfactory.

In a more drastic reaction which was expected to alkylate and reduce the tungsten, [W(NPh)Cl₄] was treated with MgMe₂ and PMe₃. Several products were formed and a small amount of the crystalline trimer [(W(NPh)(μ-O)Me₂(PMe₃))₃] was isolated. Its crystal structure has been reported previously.¹¹

Tungsten(v) Compounds.—In attempting to form phosphine adducts of [W(NPh)Cl₄] it was found that in boiling benzene reduction occurred and the tungsten(v) complexes [W(NPh)Cl₃L₂] (L = PPh₃ or PMe₂Ph; L₂ = Ph₂PCH₂CH₂PPh₂) and [W(NEt)Cl₃(PMe₂Ph)₂] were isolated. These compounds are of interest by virtue of being the first *d*¹ organoimido-complexes of tungsten thus filling the gap in the [M(NR)Cl₃L₂] series between the *d*⁰ (Ta) and *d*² (Re) compounds. They are paramagnetic solids, moderately stable in air, and have i.r. bands (see Table 1) around 1 100–1 130 cm⁻¹ [probably $\nu(\text{W}=\text{N})$ stretching] and 285–320 cm⁻¹ [$\nu(\text{W}-\text{Cl})$ stretching]. A single

Table 3. Structural data on $[M(NR)Cl_3L_2]$ complexes

Compound	$M\equiv N$ (Å)	MNC (°)	$M-Cl^a$ (Å)	$M-Cl^b$ (Å)	$M-P$ (Å)	Ref.
$[W(NPh)Cl_3(PPh_3)_2]$	1.742(8)	172.3(7)	2.368(3) 2.405(2)	2.443(3)	2.590(3)	This paper
$[Re(NC_6H_4OMe-p)Cl_3(PEt_2Ph)_2]$	1.709(4)	175.8(1)	2.421(1)	2.432(2)	2.470(1)	12
$[Re(NC_6H_4COMe-p)Cl_3(PEt_2Ph)_2]$	1.690(5)	171.8(4)	2.433(3) 2.399(3)	2.410(3)	2.457(4) 2.461(4)	12
$[Re(NMe)Cl_3(PEtPh_2)_2]$	1.685(11)	173(1)	2.408(6) 2.428(6)	2.411(6)	2.482(7) 2.486(7)	13

^a Chlorine *cis* to imido-nitrogen. ^b Chlorine *trans* to imido-nitrogen.

crystal of $[W(NPh)Cl_3(PPh_3)_2(C_6H_5Me)]$ was grown from toluene solution and subjected to X-ray crystal structure determination.

The structure (Figure 1, Table 2) is a slightly distorted octahedron with a meridional arrangement of the three chlorines and *trans*-phosphines analogous to the configuration well established for the d^2 complexes $[Re(NR)Cl_3L_2]$ ($R = C_6H_4OMe-p$ or $C_6H_4COMe-p$; $L = PEt_2Ph$ or $PEtPh_2$) by Bright and Ibers.^{12,13} In the tungsten(v) compound the phenylimido-group ($W-N$ 1.742 Å, WNC 172.3°) behaves as a four-electron donor whilst the chlorines *cis* to nitrogen ($W-Cl$ 2.368, 2.405 Å) are slightly closer to tungsten than the *trans*-chlorine ($W-Cl$ 2.443 Å). Thus the imido-ligand in this d^1 complex appears to exert a small *trans* influence whereas the rhenium(v) d^2 complexes (Table 3) show no *trans* influence. It would be most instructive to obtain structural parameters for an analogous tantalum(v) d^0 complex. In fact Rocklage and Schrock¹⁴ have prepared the compounds $[Ta(NPh)Cl_3L_2]$ ($L = thf, PMe_3,$ and PEt_3) and have made provisional structural assignments on the basis of n.m.r. spectra. For $[Ta(NPh)Cl_3(PMe_3)_2]$ which has non-equivalent phosphines they propose a *mer* configuration of the three chlorines (*cis* to the phenylimido-nitrogen) and *cis*-phosphines (one *trans* and one *cis* to nitrogen). If this structure is correct then there appears to be a *trans* effect because the *trans*-phosphine exchanges more rapidly with excess of PMe_3 than the *cis*-phosphine. The complex $[Ta(NPh)Cl_3(thf)_2]$ also has the *cis-mer* configuration but $[Ta(NPh)Cl_3(PEt_3)_2]$ with two equivalent phosphines appears to have either the *trans-mer* or the *cis-fac* configuration. Recently the structure of $[Ta(NPh)Cl_3(PEt_3)(thf)]$ has been determined by Churchill and Wasserman.¹⁵ This molecule has a linear phenylimidotantalum group ($TaNC$ 173.3°) with a meridional configuration of three chlorines all *cis* to the imido-group which is *trans* to the thf molecule.

We expect to obtain more information concerning the electronic structure of $[W(NPh)Cl_3(PPh_3)_2]$ from its e.s.r. spectrum. Preliminary results show a complex spectrum involving a modified triplet primarily due to superhyperfine coupling of the d electron to two equivalent ^{31}P nuclei.

Tungsten(IV) Compounds.—Encouraged by the robust nature of the phenylimido-group bonded to W^{VI} and W^V we carried out reductions with sodium amalgam and obtained the d^2 tungsten(IV) compounds $[W(NR)Cl_2L_3]$ ($R = Ph$ or Et ; $L = PMe_2Ph, PMe_3,$ and $CNBU^t$). These moderately air-sensitive solids gave i.r. bands (see Table 1) around 1 070—1 095 cm^{-1} [possibly $\nu(W\equiv N)$ stretching] and 245—270 cm^{-1} [$\nu(W-Cl)$ stretching]. They are diamagnetic compounds and the 1H n.m.r. spectrum of $[W(NEt)Cl_2(PMe_2Ph)_3]$ showed in [2H_8]toluene: δ 1.38, d, 6, PMe_2Ph ; 1.80, d, 12, PMe_2Ph that the three phosphine ligands (2 : 1 ratio) were non-equivalent. This non-equivalence could occur in *mer* or *fac* configurations of phosphines and there are two *mer* isomers with *cis*- or

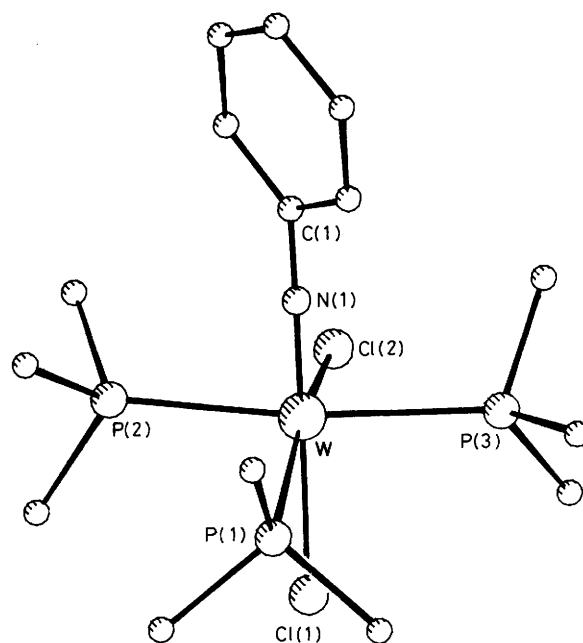


Figure 2. The molecular structure of $[W(NPh)Cl_2(PMe_3)_3]$

trans-chlorines. However, a *mer* configuration would require a triplet and a doublet in 2 : 1 ratio and the observed pair of doublets for $[W(NEt)Cl_2(PMe_2Ph)_3]$ suggests a *fac* configuration. However, by analogy with the isoelectronic rhenium(v) nitrido-complex $[Re(N)Cl_2(PEt_2Ph)_3]$ whose structure was shown by Ibers and co-workers¹⁶ to have a *mer*-phosphine configuration with *cis*-chlorines, it would be reasonable to expect a similar configuration for the $[W(NR)Cl_2L_3]$ complexes. The nitridorhenium compound exhibited a large *trans* influence with $Re-Cl$ distances of 2.45 Å (*cis* to N) and 2.56 Å (*trans* to N) and also a surprisingly long $Re\equiv N$ bond (1.788 Å). The complex $[W(NEt)Cl_2(PMe_2Ph)_3]$ exhibits i.r. bands at 268 and 245 cm^{-1} which would be due to $W-Cl$ stretching frequencies of two mutually *cis*-chlorines. Interestingly, Chatt and co-workers¹⁷ found that the analogous oxo-complex $[WOCl_2(PMe_2Ph)_3]$ exhibited the *mer*-phosphine-*cis*-chlorine configuration.

The situation has been somewhat clarified with the X-ray structure determination of $[W(NPh)Cl_2(PMe_3)_3]$. This molecule (Figure 2, Table 4) has the expected octahedral structure with a meridional arrangement of the phosphines, all of which are *cis* to the $W-NPh$ bond, leaving one of the chlorine atoms to occupy the *trans* position. In comparison with $[W(NPh)Cl_3L_2]$, described above, a number of features are noteworthy. The $W\equiv N$ bond, at 1.755(3) Å, is a little longer than in the previous compound and this may reflect the change

Table 4. Selected bond lengths (Å) and angles (°) for [W(NPh)Cl₂(PMe₃)₃]

W-Cl(1)	2.501(1)	W-Cl(2)	2.491(1)
W-P(1)	2.453(1)	W-P(2)	2.483(1)
W-P(3)	2.497(1)	W-N(1)	1.755(3)
P(1)-C(av.)	1.824(6)	P(2)-C(av.)	1.825(6)
Cl(1)-W-Cl(2)	84.3(1)	Cl(1)-W-P(1)	77.2(1)
Cl(1)-W-P(2)	91.4(1)	Cl(1)-W-P(3)	90.5(1)
Cl(1)-W-N(1)	172.5(1)	Cl(2)-W-P(1)	161.6(1)
Cl(2)-W-P(2)	86.2(1)	Cl(2)-W-P(3)	82.3(1)
Cl(2)-W-N(1)	103.2(1)	P(1)-W-P(2)	93.8(1)
P(1)-W-P(3)	98.0(1)	P(1)-W-N(1)	95.2(1)
P(2)-W-P(3)	168.1(1)	P(2)-W-N(1)	89.7(1)
P(3)-W-N(1)	89.9(1)	W-N(1)-C(1)	179.5(3)
W-P(1)-C(11)	118.3(2)	W-P(2)-C(21)	115.3(2)
W-P(1)-C(12)	118.9(2)	W-P(2)-C(22)	119.5(2)
W-P(1)-C(13)	113.4(2)	W-P(2)-C(23)	115.3(2)
W-P(3)-C(31)	115.4(2)	W-P(3)-C(33)	123.2(2)
W-P(3)-C(32)	108.2(2)		

in oxidation state. The W-Cl bonds in the present compound are also significantly longer than in the trichloride, with differences of 0.05–0.15 Å. Surprisingly, however, there seems to be no significant *trans* influence in the present case, since the two W-Cl bonds, one *cis* and one *trans* to W≡NPh, are equal within experimental limits. Even more surprising is the fact that the W-P bonds in the present complex which show differences arising mainly from a chlorine *trans* influence are much shorter than in the bis(phosphine): 2.453(1)–2.497(1) *vs.* 2.590(3) Å. Although M → P d_{π} - d_{π} bonding would be enhanced for the lower oxidation state, the differences between the two compounds is only one *d* electron and this would not be expected to produce such a change in bond lengths. Differences in the steric size of the PMe₃ and PPh₃ groups could also be important. In conclusion it should be pointed out that the tantalum(v) imido-compounds [Ta(NR)Cl₃(PMe₃)₂] (R = Ph or Me) were reduced by sodium amalgam to the *d*² tantalum(III) species [Ta(NR)Cl(PMe₃)₄] in which it was shown by n.m.r. that the chlorine is *trans* to the organoimido-nitrogen.¹⁴

Experimental

Analytical data (C, H, N, and P) were obtained from the University College Microanalytical Department and tungsten analyses were carried out by Dr. Halina Chudzynska. Melting points were determined on a Electrothermal melting-point apparatus. Infrared spectra were recorded as Nujol mulls or pressed KBr discs on a Perkin-Elmer 577 spectrometer and ¹H n.m.r. spectra on a Bruker WP-80 spectrometer. Solvents were dried over sodium dihydronaphthylide or sodium wire and were distilled under nitrogen, immediately prior to use. The compound WOCl₄ was prepared by refluxing WO₃ in thionyl chloride.¹⁸ All experiments were carried out under strictly anaerobic anhydrous conditions.

Tetrachloro(phenylimido)tungsten(vi).—Tungsten tetrachloride oxide (40 g, 1.2 mol) and phenyl isocyanate (12.7 cm³, 1.2 mol) were refluxed in benzene (120 cm³) for 24 h. The cooled solution was filtered and the solid washed several times with aliquot portions of benzene (5 cm³) and dried *in vacuo* to give a dark green solid (43 g, 86% yield). The compound does not mull in Nujol and reacts with KBr {Found: C, 17.0; H, 1.2; Cl, 33.9; N, 3.4; W, 43.3. [W(NPh)Cl₄] requires C, 17.3; H, 1.2; Cl, 34.0; N, 3.4; W, 44.0%}.

Tetrachloro(ethylimido)tungsten(vi).—Tungsten tetrachloride oxide (40 g, 0.12 mol) and ethyl isocyanate (8.8 cm³, 0.12 mol) were refluxed in benzene (150 cm³) for 18 h. The solution was filtered while hot and the solvent removed to give an orange-red crystalline solid (42.4 g, yield 98%). The compound was sufficiently pure for further use, but may be recrystallized from hot benzene. Infrared spectrum (Nujol mull): 1644w, 1586w, 1418m, 1314w, 1277s, 1242m, 1104m, 1063m, 986w, 958w, 949w, 789w, 738w, 617w, 503m, 386s, 354s, 341s, and 282s cm⁻¹. ¹H N.m.r. [(CD₃)₂CO]: δ 1.45 (t, 3, Me) and 7.1 (q, 2, CH₂) {Found: C, 6.7; H, 1.6; Cl, 38.2; N, 4.0. [W(NEt)Cl₄] requires C, 6.5; H, 1.4; Cl, 38.5; N, 3.8%}.

Tetrachloro(phenylimido)(tetrahydrofuran)tungsten(vi).—Tetrachloro(phenylimido)tungsten(vi) was dissolved in thf and the solution stirred for 15 min to give a green solution. The solvent was removed giving the complex as a green solid (100% yield). Infrared spectrum (Nujol): 3100w, 3050w, 2715w, 1574w, 1341w, 1323w, 1167w, 1158m, 1086w, 1060w, 1039w, 1025m, 999m, 993m, 956w, 922w, 836s, 755s, 738w, 721w, 675s, 667m, 623w, 557m, 536w, 467w, 394w, 361m, 352s, and 280m cm⁻¹ {Found: C, 29.0; H, 4.3; Cl, 19.6; N, 2.9; W, 36.7. [W(NPh)Cl₄(thf)] requires C, 28.8; H, 4.0; Cl, 21.2; N, 2.8; W, 36.7%}.

Tetrachloro(ethylimido)(tetrahydrofuran)tungsten(vi).—This was obtained as lemon-yellow crystals by dissolving [W(NEt)Cl₄] in thf followed by evaporation *in vacuo*. Infrared spectrum (Nujol): 1645w, 1590w, 1455vs(br), 1411s, 1373s, 1363s, 1341m, 1318w, 1286vs, 1250w(sh), 1175w, 1135m, 1040w, 1003s, 920m, 845vs, 790w(sh), 723m, 675m, 628w, 490w, 400w, 342s, and 327vs cm⁻¹ {Found: C, 15.5; H, 2.8; Cl, 30.8; N, 2.8. [W(NEt)Cl₄(thf)] requires C, 16.3; H, 3.0; Cl, 32.1; N, 3.2%}.

Trichlorobis(dimethylphenylphosphine)(phenylimido)tungsten(v).—The preparation of this complex is typical for all of the tungsten(v) organoimido-complexes. Phenylimidotungsten tetrachloride (1.2 g, 2.8 mmol) was suspended in benzene (50 cm³) and refluxed with dimethylphenylphosphine (1 cm³) for 3 d. The solvent was removed *in vacuo* leaving a green gum which was extracted with hot toluene (40 cm³) and the solution cooled to -25 °C giving the complex as green crystals (1.43 g, yield 79%). Infrared spectrum (KBr disc): 3042m, 2900w, 1565w, 1475s, 1428s, 1418m, 1408m, 1395m, 1342s, 1325m, 1292s, 1280m, 1170m, 1130s, 1100s, 1025w, 990w, 945s, 905s, 872m, 841m, 775s, 748s, 720m, 685s, 551m, 485s, 448m, 411m, 384w, and 300s cm⁻¹ {Found: C, 41.1; H, 4.4; Cl, 15.9; N, 2.0; P, 9.5. [W(NPh)Cl₃(PMe₂Ph)₂] requires C, 40.2; H, 4.1; Cl, 16.2; N, 2.1; P, 9.4%}.

Trichloro(phenylimido)bis(triphenylphosphine)tungsten(v)-Toluene (1/1).—This was obtained from the reaction of [W(NPh)Cl₄] and PPh₃ in boiling benzene and isolated as a dark red solid. Infrared spectrum (Nujol): 1890w, 1808w, 1765w, 1660w, 1580m, 1566m, 1470s(sh), 1430vs, 1355(sh), 1310w, 1275w, 1260w, 1186m, 1150s, 1115vs(br), 1086vs, 1023s, 990s, 970s(sh), 920w, 850w, 770s, 743vs, 688vs, 617w, 536vs, 521vs, 508vs, 490vs, 447s, 386m, 305vs(br), 283(sh), and 253s cm⁻¹ {Found: C, 59.1; H, 4.6; Cl, 10.8; N, 1.4. [W(NPh)Cl₃(PPh₃)₂(C₆H₅Me)] requires C, 59.0; H, 4.4; Cl, 10.7; N, 1.4%}.

[1,2-Bis(diphenylphosphino)ethane]trichloro(phenylimido)tungsten(v).—This was obtained as a green solid from the reaction of [W(NPh)Cl₄] and Ph₂PCH₂CH₂PPh₂. Infrared spectrum (Nujol): 1963w, 1890w, 1770w, 1585m, 1520w(sh),

Table 5. Atom co-ordinates ($\times 10^4$) for $[\text{W}(\text{NPh})\text{Cl}_3(\text{PPh}_3)_2]$

Atom	x	y	z	Atom	x	y	z
W	1 571(0.2)	1 562(0.2)	1 661(0.2)	C(134)	5 185(13)	3 333(6)	637(8)
Cl(1)	1 071(2)	1 476(1)	359(1)	C(135)	4 055(12)	3 094(7)	369(7)
Cl(2)	1 403(2)	2 757(1)	1 451(2)	C(136)	3 629(10)	2 597(6)	716(6)
Cl(3)	1 870(2)	1 782(1)	2 913(1)	C(211)	-889(8)	614(5)	1 690(6)
P(1)	3 786(2)	1 672(1)	1 817(1)	C(212)	-1 363(9)	217(5)	1 091(6)
P(2)	-617(2)	1 499(1)	1 604(1)	C(213)	-1 441(10)	-468(6)	1 177(7)
N	1 769(6)	708(4)	1 769(4)	C(214)	-1 057(10)	-754(6)	1 861(8)
C(1)	1 946(9)	27(4)	1 761(6)	C(215)	-554(10)	-366(6)	2 442(7)
C(2)	1 496(9)	-323(5)	1 144(6)	C(216)	-452(9)	317(6)	2 368(6)
C(3)	1 747(12)	-1 000(6)	1 160(8)	C(221)	-1 745(8)	1 778(5)	794(5)
C(4)	2 425(13)	-1 289(6)	1 765(10)	C(222)	-2 879(9)	1 571(5)	655(6)
C(5)	2 866(16)	-932(7)	2 373(10)	C(223)	-3 740(10)	1 811(7)	64(7)
C(6)	2 635(11)	-260(6)	2 401(7)	C(224)	-3 454(10)	2 281(6)	-377(6)
C(111)	4 432(8)	932(4)	1 528(5)	C(225)	-2 339(10)	2 514(6)	-242(6)
C(112)	3 775(9)	573(5)	938(5)	C(226)	-1 456(9)	2 260(5)	355(6)
C(113)	4 242(10)	12(6)	716(7)	C(231)	-1 048(8)	1 917(5)	2 327(5)
C(114)	5 350(10)	-195(6)	1 066(6)	C(232)	-751(10)	2 593(6)	2 446(6)
C(115)	5 999(10)	169(6)	1 646(7)	C(233)	-1 121(12)	2 945(7)	2 959(7)
C(116)	5 553(8)	726(5)	1 874(6)	C(234)	-1 764(11)	2 625(9)	3 354(6)
C(121)	4 522(8)	1 774(5)	2 778(5)	C(235)	-2 049(11)	1 989(8)	3 243(6)
C(122)	4 837(9)	1 231(6)	3 236(6)	C(236)	-1 707(8)	1 630(6)	2 725(6)
C(123)	5 325(10)	1 321(7)	3 970(6)	C(20)	6 873(36)	4 869(17)	-765(16)
C(124)	5 479(9)	1 953(7)	4 253(6)	C(21)	7 391(24)	4 790(11)	-10(9)
C(125)	5 155(9)	2 498(6)	3 809(6)	C(22)	6 988(24)	5 022(11)	559(9)
C(126)	4 689(9)	2 417(5)	3 078(5)	C(23)	7 578(24)	4 855(11)	1 275(9)
C(131)	4 330(8)	2 349(5)	1 370(5)	C(24)	8 571(24)	4 457(11)	1 422(9)
C(132)	5 468(9)	2 577(5)	1 633(6)	C(25)	8 974(24)	4 225(11)	853(9)
C(133)	5 884(11)	3 065(6)	1 275(7)	C(26)	8 384(24)	4 391(11)	137(9)

Table 6. Atom co-ordinates for $[\text{W}(\text{NPh})\text{Cl}_2(\text{PMe}_3)_3]$

Atom	x	y	z	Atom	x	y	z
W	0.052 62(3)	0.176 30(2)	0.343 46(2)	C(5)	-0.308 9(12)	0.384 7(9)	0.481 7(6)
Cl(1)	0.207 4(3)	0.128 2(2)	0.252 5(1)	C(6)	-0.229 2(11)	0.344 4(8)	0.433 1(5)
Cl(2)	0.012 0(3)	-0.005 3(2)	0.352 4(1)	C(11)	0.086 3(13)	0.374 7(7)	0.212 2(5)
P(1)	0.141 3(2)	0.336 4(2)	0.307 1(1)	C(12)	0.340 6(11)	0.357 6(8)	0.318 5(6)
P(2)	0.266 1(3)	0.153 7(2)	0.445 1(1)	C(13)	0.078 9(15)	0.440 9(7)	0.354 5(7)
P(3)	-0.177 2(2)	0.164 2(2)	0.248 6(1)	C(21)	0.303 4(13)	0.257 3(9)	0.507 5(6)
N(1)	-0.051 4(7)	0.226 2(5)	0.404 4(3)	C(22)	0.449 7(12)	0.129 3(10)	0.425 2(6)
C(1)	-0.132 6(8)	0.265 7(6)	0.453 1(4)	C(23)	0.245 2(13)	0.054 0(10)	0.509 2(6)
C(2)	-0.117 3(10)	0.226 2(8)	0.523 1(5)	C(31)	-0.164 5(13)	0.082 2(9)	0.172 1(5)
C(3)	-0.197 4(12)	0.266 4(10)	0.570 7(5)	C(32)	-0.319 9(12)	0.106 7(11)	0.288 9(6)
C(4)	-0.291 7(12)	0.345 7(10)	0.551 3(6)	C(33)	-0.273 5(13)	0.271 9(9)	0.205 2(6)

1 475s, 1 432vs, 1 412m, 1 346m, 1 336m(sh), 1 312w, 1 193m, 1 170m, 1 130m, 1 099s, 1 025w, 992w, 909w, 870w, 826m, 766m, 751s, 739s, 709s, 690vs(br), 662w, 550m, 523vs, 496s, 433w, 385w, 320s, 295m, 280m and 250m(br) cm^{-1} {Found: C, 48.7; H, 4.0; Cl, 14.5; N, 1.8. $[\text{W}(\text{NPh})\text{Cl}_3(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$ requires C, 49.3; H, 3.7; Cl, 13.7; N, 1.8%}.

Trichlorobis(dimethylphenylphosphine)(ethylimido)tungsten(v).—This was obtained as a red solid from the reaction of $[\text{W}(\text{NEt})\text{Cl}_4]$ and PMe_2Ph . Infrared spectrum (Nujol): 1 650w(br), 1 587w, 1 485w, 1 475w, 1 432s, 1 420m, 1 408m, 1 319s, 1 290vs, 1 280s, 1 260w(sh), 1 133vs, 1 110vs(br), 945s, 907vs, 872m, 840w, 745vs, 694vs, 618w, 488s, 436w, 412w, 390w, 293s, and 280s cm^{-1} {Found: C, 35.8; H, 4.4; Cl, 17.7; N, 2.2. $[\text{W}(\text{NEt})\text{Cl}_3(\text{PMe}_2\text{Ph})_2]$ requires C, 35.5; H, 4.5; Cl, 17.4; N, 2.3%}.

Dichloro(phenylimido)tris(trimethylphosphine)tungsten(iv).—This purple solid was obtained by sodium amalgam reduction of $[\text{W}(\text{NPh})\text{Cl}_4]$ in benzene in the presence of PMe_3 . Infrared spectrum (Nujol): 1 705vw, 1 580s, 1 479vs, 1 420s(sh),

1 353vs, 1 298m, 1 280s, 1 260m, 1 165w, 1 151w(sh), 1 140w(sh), 1 070s(br), 1 020s(br), 947vs, 850w, 800m, 765s, 693w, 672w, 542w, 400w(br), 380, 345w, 285w(sh), and 255w(br) cm^{-1} {Found: C, 32.2; H, 5.6; Cl, 11.8; N, 2.7; P, 15.5. $[\text{W}(\text{NPh})\text{Cl}_2(\text{PMe}_3)_3]$ requires C, 31.4; H, 5.6; Cl, 12.3; N, 2.4; P, 16.2%}.

Dichlorotris(dimethylphenylphosphine)(ethylimido)tungsten(iv).—The preparation of this complex is typical for the imidotungsten(iv) complexes. Tetrachloro(ethylimido)tungsten(vi) (1.15 g, 3.1 mmol) and dimethylphenylphosphine (1.21 cm^3) were stirred in benzene (50 cm^3) over 2% sodium amalgam (0.3 g) for 6 h giving a reddish brown solution. The solution was evaporated to a gum, the solid washed with pentane and extracted with toluene. Cooling the solution to -25°C gave the complex as brown crystals (1.65 g, yield 93%). Infrared spectrum (Nujol): 1 582w, 1 578w, 1 485m, 1 430s, 1 412s, 1 324m, 1 294s, 1 285s, 1 270s, 1 195w, 1 159w, 1 070s, 990m, 970m, 938s, 902s, 838m, 792s, 690s, 675s, 618m, 485s, 418s, 385w, 352w, 347s, 325w, 270m, and 248m cm^{-1} . ^1H N.m.r. [$^2\text{H}_8$]toluene: δ 0.83 (t, 3, ethyl- CH_3), 1.38 (d, 6,

2Me), 1.80 (d, 12, 4Me), and 7.1—7.35 (m, 5, aromatics) {Found: C, 43.8; H, 5.6; Cl, 9.8; N, 2.0; W, 25.7. [W(NEt)Cl₂-(PMe₂Ph)₃] requires C, 43.8; H, 5.6; Cl, 9.9; N, 2.0; W, 25.8%}.

Tris(t-butyl isocyanide)dichloro(phenylimido)tungsten(IV).—This reddish brown solid was obtained by reducing [W(NPh)Cl₄] with sodium amalgam in benzene in the presence of BuⁿCN. Infrared spectrum (Nujol): 2 240vs(br), 2 100vs(sh), 1 680w, 1 620w(br), 1 579s, 1 480vs, 1 395w, 1 350vs, 1 303w, 1 282w, 1 260w, 1 231s, 1 193vs(br), 1 155m, 1 068m, 1 023m, 990w, 855w, 800w, 773s, 694m, 625w, 563m, 522s, 441m, 293s, 283s(sh), 270s, and 255m(sh) cm⁻¹ {Found: C, 41.9; H, 5.3; Cl, 11.6; N, 9.0. [W(NPh)Cl₂(CNBu^t)₃] requires C, 42.4; H, 5.4; Cl, 11.9; N, 9.4%}.

Dichloro(ethylimido)tris(trimethylphosphine)tungsten(IV).—This purple-red compound was obtained by reduction of [W(NEt)Cl₄] by sodium amalgam in benzene in the presence of PMe₃. Infrared spectrum (Nujol): 1 425s, 1 412s, 1 363s, 1 320vs, 1 291vs, 1 280vs, 1 080w, 938vs(br), 852s, 728vs, 711s, 668s, 612w, 480w, 400w, 370w, 347m(br), 263s, 252s, 245s, and 230s cm⁻¹ {Found: C, 25.2; H, 6.3; Cl, 14.4; N, 2.8; P, 16.2. [W(NEt)Cl₂(PMe₃)₃] requires C, 25.1; H, 6.1; Cl, 13.5; N, 2.7; P, 17.7%}.

Tris(t-butyl isocyanide)dichloro(ethylimido)tungsten(IV)-Toluene (1/1).—This red-brown solid was obtained by reduction of [W(NEt)Cl₄] by sodium amalgam in benzene in the presence of BuⁿCN. Infrared spectrum (KBr disc): 2 150vs(sh), 2 110vs, 1 620w, 1 490w, 1 470m, 1 450s, 1 430m(sh), 1 395w, 1 365vs, 1 320s, 1 284vs, 1 231vs, 1 195vs(br), 1 040w, 860w, 817w, 804w(sh), 736w, 700w, 613w, 530s, 522s, 500m(sh), 430m, 420m(sh), 382w, 332w, 310s, 275m(sh), 230s(sh), and 200vs cm⁻¹ {Found: C, 43.5; H, 6.7; Cl, 11.3; N, 8.8. [W(NEt)Cl₂(CNBu^t)₃(C₆H₅Me)] requires C, 44.2; H, 6.2; Cl, 10.9; N, 8.6%}.

Crystallography.—*Crystal data*. [W(NPh)Cl₃(PPh₃)₂-(C₆H₅Me)], Compound A, C₄₉H₄₃Cl₃NP₂W, *M* = 998.05, Monoclinic, *a* = 11.959(3), *b* = 20.167(5), *c* = 19.192(6) Å, β = 106.60(2)°, *U* = 4 435.75 Å³, space group *P*2₁/*n*, *D*_m not measured, *Z* = 4, *D*_c = 1.494 g cm⁻³, *F*(000) = 1 996, μ(Mo-K_α) = 27.5 cm⁻¹.

[W(NPh)Cl₂(PMe₃)₃], Compound B, C₁₅H₃₂Cl₂NP₃W, *M* = 574.11, Monoclinic, *a* = 9.178(3), *b* = 13.511(2), *c* = 18.743(3) Å, β = 100.79(2)°, *U* = 2 283.1 Å³, space group *P*2₁/*n*, *D*_m not measured, *Z* = 4, *D*_c = 1.67 g cm⁻³, *F*(000) = 1 128, μ(Mo-K_α) = 56.1 cm⁻¹.

Data collection. CAD4 diffractometer, graphite monochromated Mo-K_α radiation (λ = 0.710 69 Å), ω-2θ scan mode. Compound A: ω scan width = 0.75 + 0.35 tanθ, scan speed 1.27—6.77° min⁻¹, 1.5 ≤ θ ≤ 23°, 6 736 data measured, 4 942 observed [*I* ≥ 2σ(*I*)]. Compound B: ω scan width 0.8 + 0.3 tan θ, scan speed 1.27—6.77° min⁻¹, 1.5 ≤ θ ≤ 25°, 4 448 data measured, 3 645 observed [*I* ≥ 2σ(*I*)]. Both sets of data were corrected for absorption.

Structure determination and refinement. Heavy-atom, full-

matrix least squares. Non-hydrogen atoms assigned anisotropic thermal parameters, hydrogens isotropic (a single overall value for compound A). The final *R* and *R'* values were 0.056 and 0.066 for compound A, weighting scheme *w* = 1/[σ²(*F*_o) + 0.0015*F*_o²] and 0.041, 0.045 for compound B (unit weights). Computers, programs, and sources of scattering factor data are given in refs. 19*a* (compound A) and 19*b* (compound B). Final atomic positional parameters are given in Tables 5 and 6.

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