

Pentamethylcyclopentadienyl tungsten complexes containing imido, hydrazido and amino acid derived N–O chelate ligands †

Carl Redshaw,^{*,a} Vernon C. Gibson,^a William Clegg,^b Andrew J. Edwards^b and Benedict Miles^b

^a Department of Chemistry, Imperial College, South Kensington, London, UK SW7 2AY

^b Department of Chemistry, University of Newcastle, Newcastle upon Tyne, UK NE1 7RU

Reactions of $[W(\eta\text{-C}_5\text{Me}_5)\text{Cl}_4]$ with a number of functionalised amines have been studied. With 2 equivalents of the dianiline 2,2'-($\text{H}_2\text{NC}_6\text{H}_4$)₂C₂H₄ the *ansa*-bis(imido)tungsten complex $[W(\eta\text{-C}_5\text{Me}_5)\text{Cl}\{2,2'-(\text{NC}_6\text{H}_4)_2\text{CH}_2\text{CH}_2\}]$ **1** was obtained. Analogous treatment with 2-diphenylphosphinoaniline gave the 2-diphenylphosphine-substituted imidometal species $[W(\eta\text{-C}_5\text{Me}_5)\text{Cl}(\text{NC}_6\text{H}_4\text{PPh}_2)_2]$ **2**. The pendant tertiary phosphine groups do not interact with the metal centre. 1,1-Diphenylhydrazine hydrochloride reacted with $[W(\eta\text{-C}_5\text{Me}_5)\text{Cl}_4]$ to give $[W(\eta\text{-C}_5\text{Me}_5)\text{Cl}_3(\text{NNPh}_2)]$ **3**. Reactions of $[W(\eta\text{-C}_5\text{Me}_5)\text{Cl}_4]$ with the amino acid 2,2-diphenylglycine or tyrosine afforded the tungsten(v) complexes $[W(\eta\text{-C}_5\text{Me}_5)\text{Cl}_3(\text{NH}_2\text{C}(\text{Ph})_2\text{CO}_2)]$ **4** and $[W(\eta\text{-C}_5\text{Me}_5)\text{Cl}_3\{\text{NH}_2\text{CH}(\text{CH}_2\text{C}_6\text{H}_4\text{-OH-}p)\text{CO}_2\}]$ **5** respectively. Complexes **1** to **5** have been structurally characterised.

The chemistry of imido transition-metal complexes bearing simple alkyl or aryl substituents is relatively well developed.¹ By contrast, there have been few reports of imidometal complexes in which the imido substituent carries one or more heteroatom functionalities.^{2–4} In recent work we have been investigating routes to highly functionalised imidometal systems, for example derivatives containing Brønsted acid substituents such as CO₂H and SO₃H.⁵ We have also recently described the first chelating or *ansa* bis(imido)metal derivatives.⁶

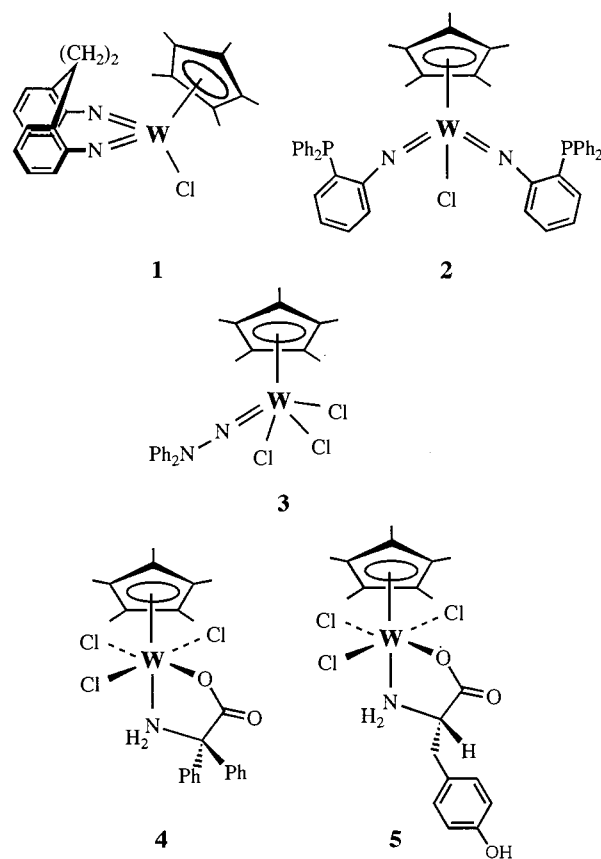
Although the chemistry of $[W(\text{C}_5\text{Me}_5)\text{Cl}_4]$ is relatively unexplored it is known to provide an entry into half-sandwich tungsten systems.⁷ We therefore decided to investigate its reactions with a number of bifunctional amino-containing reagents with the aim of generating novel functionalised imidometal species. We thus describe herein several unusual products, including a further example of an *ansa*-bis(imido)metal complex, a tertiary phosphine-derivatised bis(imido) derivative, a hydrazido(2–) species and N–O chelate complexes derived from amino acids. The products are summarised in Scheme 1. We also note that a number of simple organoimido half-sandwich complexes of molybdenum and tungsten have been described by Sundermeyer *et al.*^{8a} and Green *et al.*^{8b}

Results and Discussion

Imido complexes

The diamagnetic tungsten(vi) complex $[W(\eta\text{-C}_5\text{Me}_5)\text{Cl}\{2,2'-(\text{NC}_6\text{H}_4)_2(\text{CH}_2\text{CH}_2)\}]$ **1** is obtained upon reaction of $[W(\eta\text{-C}_5\text{Me}_5)\text{Cl}_4]$ with 2 equivalents of the diamine 2,2'-($\text{H}_2\text{NC}_6\text{H}_4$)₂C₂H₄ in refluxing toluene. Brown-orange blocks suitable for an X-ray diffraction study were grown from acetonitrile and the molecular structure is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. The co-ordination geometry is best described as distorted tetrahedral with the C₅Me₅ ring occupying one position; angles at W range from 99.8(1) to 117.6(1)°.

For the chelating diimide ligand the C–N–W angles are 163.4(3) and 166.3(3)° with corresponding W–N distances of 1.795(3) and 1.776(3) Å. An approximate non-crystallographic mirror plane bisects the molecule passing through C(19), C(20), W, Cl and the centre of the ethanediyl bridge, the main distortion from the symmetry being in this bridge. The only other structurally characterised compound containing a chelating bis-



Scheme 1

(imido) ligand derived from 2,2'-($\text{H}_2\text{NC}_6\text{H}_4$)₂C₂H₄ is $[\text{MoCl}_2\text{-}\{2,2'-(\text{NC}_6\text{H}_4)_2\text{CH}_2\text{CH}_2\}(\text{dme})]$ (dme = 1,2-dimethoxyethane),⁶ for which the bite angle is 107.13(7)° [*cf.* 107.2(1)° in **1**]. There is clear evidence of C₅Me₅ ring slippage in **1**; the W–C distances differ significantly, from 2.359(4) [for C(16)] to 2.498(4) Å [for C(20)]. This effect is summarised later for all the structures. A similar situation occurs in the complex $[W(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2\{1,2-(\text{HN})_2\text{C}_6\text{H}_4\}]$; interestingly here the use of 1,2-phenylenediamine results only in a diamido chelate most probably due to the restricted angles at the metal-bound nitrogen atoms which prevent the pseudo-linear M–N–C imido ligand arrangement being attained.^{7a}

It was envisaged that an *o*-diphenylphosphine substituted

† Dedicated to the memory of Professor Sir Geoffrey Wilkinson.

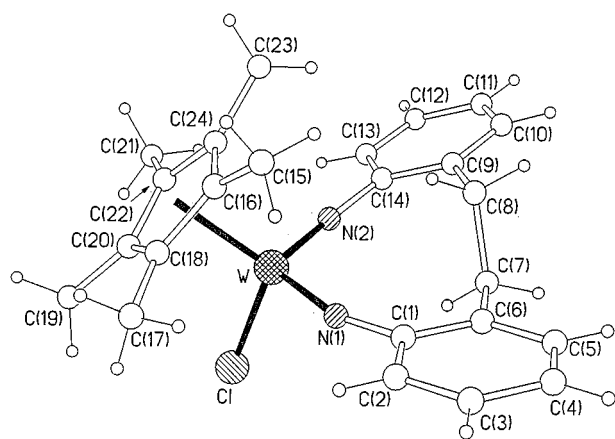
Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

W–N(1)	1.795(3)	W–N(2)	1.776(3)
W–Cl	2.3499(9)	W–C(16)	2.359(4)
W–C(24)	2.366(4)	W–C(22)	2.450(4)
W–C(18)	2.466(4)	W–C(20)	2.498(4)
W–Cent	2.105(4)	N(1)–C(1)	1.367(5)
N(2)–C(14)	1.380(5)		
N(2)–W–N(1)	107.2(1)	N(1)–W–Cl	102.8(1)
N(2)–W–Cl	99.8(1)	Cent–W–N(1)	117.6(1)
Cent–W–N(2)	115.2(1)	Cent–W–Cl	112.1(1)
C(1)–N(1)–W	163.4(3)	C(14)–N(2)–W	166.3(3)

In the tables, Cent is the centroid of the C₅Me₅ ring.

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**·MeCN

W–N(1)	1.783(3)	W–N(2)	1.775(3)
W–Cl	2.3257(9)	W–C(37)	2.319(3)
W–C(39)	2.427(3)	W–C(45)	2.427(3)
W–C(41)	2.470(3)	W–C(43)	2.475(3)
W–Cent	2.100(3)	N(1)–C(1)	1.368(4)
N(2)–C(19)	1.378(4)		
N(2)–W–N(1)	104.0(1)	N(1)–W–Cl	103.8(1)
N(2)–W–Cl	103.4(1)	Cent–W–N(1)	117.3(1)
Cent–W–N(2)	117.7(1)	Cent–W–Cl	108.9(1)
C(1)–N(1)–W	157.9(2)	C(19)–N(2)–W	165.1(3)

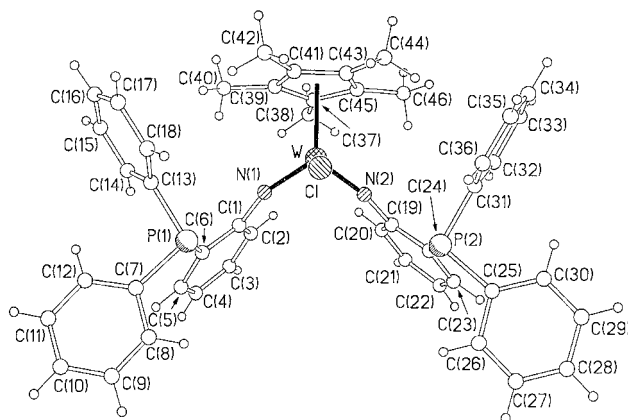
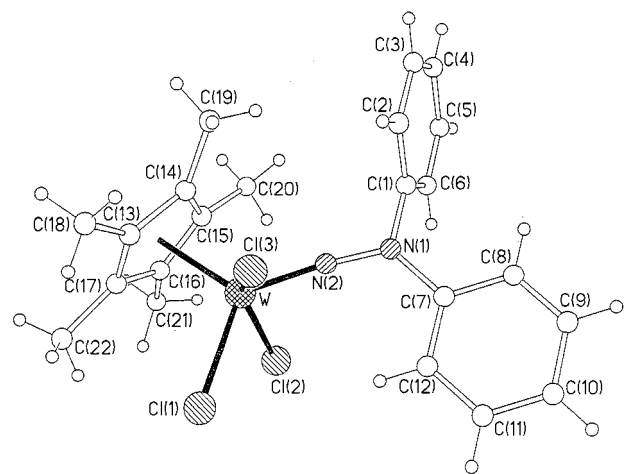
**Fig. 1** Molecular structure of complex **1**

aniline might afford a chelating imidophosphine or alternatively an amidophosphine species. The reaction of [W(η -C₅Me₅)Cl₄] with 1,2-(H₂N)(Ph₂P)C₆H₄ in refluxing toluene gave after work-up orange needles in ca. 30% isolated yield. Analytical and spectroscopic data were not consistent with either an imido- or amido-phosphine chelate complex and hence its structure was determined by X-ray diffraction. The molecular structure of **2**, determined as a 1 : 1 MeCN solvate, is shown in Fig. 2; selected bond lengths and angles are given in Table 2.

Again the molecule has a pseudo-tetrahedral geometry with a non-crystallographic mirror plane passing through Cl, W and the C₅Me₅ ring. Interestingly, in contrast to **1**, the imido ligand is not a chelate, preferring instead to form a linear WNR group with a pendant and non-co-ordinated Ph₂P group [W–N–C 157.9(2) and 165.1(3)°; W–N 1.783(3) and 1.775(3) Å]. Its structure bears close resemblance to the bis(arylimido) complex [W(η -C₅Me₅)(NR)₂Cl] (R = C₆H₃Prⁱ₂-2,6) structurally characterised by Wigley and co-workers.⁹ It is noteworthy that Dilworth and co-workers¹⁰ have structurally characterised a rhenium complex, [ReCl₂(NC₆H₄PPh₂-2)(HNC₆H₄PPh₂-2)], which is found to contain a bidentate bonding mode for this ligand, though ³¹P NMR data indicate that the monodentate

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

W–N(2)	1.769(2)	W–Cl(1)	2.4043(7)
W–Cl(2)	2.4270(7)	W–Cl(3)	2.4235(7)
W–C(14)	2.281(3)	W–C(15)	2.300(3)
W–C(13)	2.427(3)	W–C(16)	2.459(3)
W–C(17)	2.522(3)	W–Cent	2.068(3)
N(1)–N(2)	1.296(3)	N(1)–C(1)	1.440(3)
N(1)–C(7)	1.440(3)		
N(2)–W–Cl(1)	126.3(1)	N(2)–W–Cl(2)	82.8(1)
N(2)–W–Cl(3)	84.4(1)	Cl(1)–W–Cl(2)	80.8(1)
Cl(1)–W–Cl(3)	80.8(1)	Cl(2)–W–Cl(3)	144.8(1)
Cent–W–N(2)	123.6(1)	Cent–W–Cl(1)	110.0(1)
Cent–W–Cl(2)	106.0(1)	Cent–W–Cl(3)	108.4(1)
N(2)–N(1)–C(1)	117.9(2)	N(2)–N(1)–C(7)	120.2(2)
C(1)–N(1)–C(7)	121.8(2)	N(1)–N(2)–W	173.8(2)

**Fig. 2** Molecular structure of complex **2****Fig. 3** Molecular structure of complex **3**

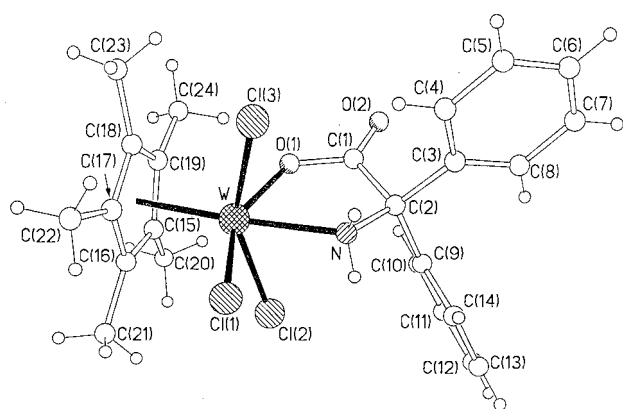
co-ordination mode prevails in solution. For **2** we observe the opposite trend, the solid-state structure showing the monodentate co-ordination mode, the solution ³¹P NMR spectrum revealing two resonances, at δ +39.5 and –15.0, consistent with the presence of one co-ordinated and one non-co-ordinated phosphine group.

Hydrazido complex

Treatment of [W(η -C₅Me₅)Cl₄] with 1,1-diphenylhydrazine hydrochloride, Ph₂NNH₂·HCl, affords after work-up dark brown blocks of [W(η -C₅Me₅)Cl₃(NNPh₂)] **3**. Complex **3** shows a single ν_{NN} stretch at 1585 cm⁻¹. Crystals suitable for an X-ray analysis were grown from MeCN at room temperature; the molecular structure is shown in Fig. 3. Selected bond lengths and angles are given in Table 3.

Table 4 Selected bond lengths (Å) and angles (°) for complex **4**

W–O(1)	2.023(1)	W–N	2.244(2)
W–Cl(1)	2.3879(5)	W–Cl(2)	2.4101(6)
W–Cl(3)	2.4187(5)	W–C(16)	2.346(2)
W–C(15)	2.385(2)	W–C(17)	2.386(2)
W–C(19)	2.438(2)	W–C(18)	2.451(2)
W–Cent	2.075(2)	O(1)–C(1)	1.310(2)
O(2)–C(1)	1.210(3)	N–C(2)	1.504(2)
C(1)–C(2)	1.543(3)		
O(1)–W–N	73.2(1)	O(1)–W–Cl(1)	149.9(1)
N–W–Cl(1)	76.7(1)	O(1)–W–Cl(2)	87.7(1)
N–W–Cl(2)	76.2(1)	Cl(1)–W–Cl(2)	85.7(1)
O(1)–W–Cl(3)	86.8(1)	N–W–Cl(3)	76.3(1)
Cl(1)–W–Cl(3)	85.7(1)	Cl(2)–W–Cl(3)	152.4(1)
Cent–W–O(1)	102.7(1)	Cent–W–N	175.8(1)
Cent–W–Cl(1)	107.4(1)	Cent–W–Cl(2)	104.6(1)
Cent–W–Cl(3)	103.0(1)	C(1)–O(1)–W	127.1(2)
C(2)–N–W	116.3(2)	O(2)–C(1)–O(1)	122.8(2)
O(2)–C(1)–C(2)	121.7(2)	O(1)–C(1)–C(2)	115.6(2)
N–C(2)–C(1)	105.6(2)		

**Fig. 4** Molecular structure of complex **4**

The molecular geometry is best described as a distorted square-based pyramid with the centroid of the C_5Me_5 ligand at the apex. The $NNPh_2$ unit is linear [$W-N(2)-N(1)$ 173.8(2)°] with short $W-N$ [1.769(2) Å] and long $N-N$ [1.296(3) Å] bonds and a trigonal-planar arrangement at the $N(1)$ atom. The N_2Ph_2 ligand may be regarded as lying closer to the hydrazido(2-) rather than an isodiazeno description and thus the tungsten centre may be formally regarded as being in the +6 oxidation state.¹¹ The $W-C$ bond lengths are notably different; both $W-C(14)$ and $W-C(15)$ are short consistent with the presence of either a η^2 - or η^4 - C_5Me_5 ligand. Although the solid-state structure shows inequivalent phenyl rings, solution 1H and ^{13}C NMR data show only one set of signals, a consequence of rapid rotation about the $N(1)-N(2)$ bond.

Reactions with amino acids

Reaction of $[W(\eta-C_5Me_5)Cl_4]$ with 2,2-diphenylglycine (2 equivalents) in refluxing toluene (12 h) affords, after work-up, large green needles of $[WCl_3(\eta-C_5Me_5)(NH_2CPh_2CO_2)]$ **4** in good yield. The IR spectrum of **4** contains two sharp stretches in the $N-H$ region, at 3326 and 3269 cm^{-1} , characteristic of the NH_2 group. The 1H NMR spectrum is broad and uninformative while the X-band EPR spectrum is sharp with $g_{iso} = 1.870$; there is no observable hyperfine splitting. The molecular structure of **4** is shown in Fig. 4, with selected bond lengths and angles given in Table 4. The amino acid residue binds to the tungsten centre as an aminocarboxylate chelate ligand. Both hydrogen atoms were experimentally located on $N(1)$.

The $W-N(1)$ distance [2.2437(17) Å] is consistent with a coordinated amine. The geometry about the tungsten centre is best described as pseudo-octahedral with a *mer*-arrangement of

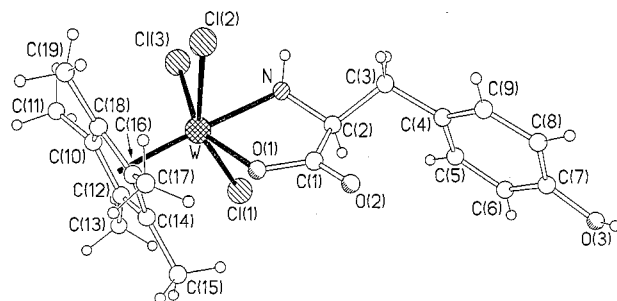
Table 5 Selected bond lengths (Å) and angles (°) for complex **5**· CH_2Cl_2

W–O(1)	2.053(2)	W–N	2.200(3)
W–Cl(1)	2.4266(9)	W–Cl(2)	2.436(1)
W–Cl(3)	2.3785(8)	W–C(14)	2.334(4)
W–C(16)	2.335(4)	W–C(18)	2.426(4)
W–C(12)	2.429(4)	W–C(10)	2.477(3)
W–Cent	2.074(4)	O(1)–C(1)	1.301(4)
O(2)–C(1)	1.213(4)	O(3)–C(7)	1.361(5)
N–C(2)	1.491(4)	C(1)–C(2)	1.518(5)
O(1)–W–N	73.8(1)	O(1)–W–Cl(1)	85.5(1)
N–W–Cl(1)	74.7(1)	O(1)–W–Cl(2)	82.9(1)
N–W–Cl(2)	76.9(1)	O(1)–W–Cl(3)	150.9(1)
N–W–Cl(3)	77.2(1)	Cl(1)–W–Cl(2)	151.4(1)
Cl(1)–W–Cl(3)	89.2(1)	Cl(2)–W–Cl(3)	88.4(1)
Cent–W–O(1)	104.0(1)	Cent–W–N	177.4(1)
Cent–W–Cl(1)	103.9(1)	Cent–W–Cl(2)	104.3(1)
Cent–W–Cl(3)	105.1(1)	C(1)–O(1)–W	124.5(2)
C(2)–N–W	114.5(2)	O(2)–C(1)–O(1)	122.3(3)
O(1)–C(1)–C(2)	115.0(3)	O(2)–C(1)–C(2)	122.6(3)
N–C(2)–C(1)	106.9(3)		

Table 6 Distortions in $M-C_5Me_5$ bonding

Compound	$\Delta M/\text{Å}$	$\Delta X/\text{Å}$	$\tau/^\circ$	Pattern of M–C
1	0.139	0.160	4.4	ss mm l
2	0.156	0.152	4.3	s mm ll
3	0.241	0.265	7.4	ss mm l
4	0.105	0.112	3.1	s mm ll
5	0.143	0.169	4.7	ss mm l

ΔM = Difference between longest and shortest $W-C$ bond; ΔX = distance between ring centroid and the point where the tungsten–ring normal meets the mean plane (direct measure of ring slippage); τ = angle between ring-plane normal and metal–centroid vector.

**Fig. 5** Molecular structure of complex **5**

chlorines; the amino group of the glycine is *trans* to the C_5Me_5 ligand, an arrangement often seen in $M(C_5H_5)X_4L$ species.¹² The $W-C$ distances for the latter are consistent with a slipped $3e^-, \eta^3$ group in which the planarity and delocalisation of the C_5 ring is largely preserved.

Similar treatment of $[W(\eta-C_5Me_5)Cl_4]$ with tyrosine, $HCO_2-CH(NH_2)CH_2C_6H_4OH-p$, affords after work-up red-brown prisms of $[W(\eta-C_5Me_5)Cl_3\{NH_2CH(CH_2C_6H_4OH-p)CO_2\}]$ **5**. The molecular structure of **5**, determined as a 1:1 CH_2Cl_2 solvate, is shown in Fig. 5, with selected bond lengths and angles in Table 5. As in **4**, the tungsten has a distorted-octahedral geometry with a *mer* arrangement of chlorines and a chelating aminocarboxylate ligand. It is noteworthy that the essential features of the amino acid are retained, in particular the survival of the *p*-hydroxy substituent of the tyrosine residue.

Several features emerge from the above structural studies regarding 'ring slippage', see Table 6. In three cases (**1**, **3** and **5**) there are two short (s), two medium (m) and one long (l) $W-C$ bond. The remaining two complexes, **2** and **4**, have one short, two medium and two long $W-C$ bonds. The former pattern (ss mm l) is consistent with a tendency towards $3e^-, \eta^3$ co-

Table 7 Crystallographic data

	Compound				
	1	2 ·MeCN	3	4	5 ·CH ₂ Cl ₂
Formula	C ₂₄ H ₂₇ ClN ₂ W	C ₄₆ H ₄₃ ClN ₂ P ₂ W·C ₂ H ₃ N	C ₂₂ H ₂₅ Cl ₃ N ₂ W	C ₂₄ H ₂₇ Cl ₃ NO ₂ W	C ₁₉ H ₂₅ Cl ₃ NO ₃ W·CH ₂ Cl ₂
<i>M</i>	562.8	946.1	607.6	651.7	690.5
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pna</i> 2 ₁	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	7.2357(8)	20.6098(10)	18.0769(17)	12.9084(10)	8.7042(8)
<i>b</i> /Å	15.9110(17)	25.2500(12)	8.0405(8)	8.9263(7)	12.7368(11)
<i>c</i> /Å	18.452(2)	8.1256(4)	15.6714(15)	20.4865(15)	21.7816(19)
β/°	94.283(2)			100.264(2)	
<i>U</i> /Å ³	2118.3(4)	4228.5(4)	2277.8(4)	2322.8(3)	2414.8(4)
<i>Z</i>	4	4	4	4	4
<i>D</i> _c /g cm ⁻³	1.765	1.486	1.772	1.863	1.899
μ/mm ⁻¹	5.59	2.91	5.43	5.34	5.36
<i>F</i> (000)	1104	1904	1184	1276	1348
Crystal size/mm	0.48 × 0.40 × 0.18	0.28 × 0.16 × 0.12	0.38 × 0.36 × 0.22	0.42 × 0.33 × 0.26	0.24 × 0.18 × 0.16
θ _{max} /°	28.3	28.5	28.4	28.3	28.3
Maximum <i>hkl</i> indices	9, 21, 24	27, 33, 10	23, 10, 20	17, 11, 27	11, 16, 27
Reflections measured	14 041	25 500	13 790	16 049	14 923
Unique reflections	4769	9271	4962	5329	5382
<i>R</i> _{int}	0.0478	0.0291	0.0199	0.0188	0.0245
Transmission	0.186–0.431	0.746–0.862	0.265–0.356	0.331–0.492	0.699–0.831
Extinction coefficient <i>x</i>	0	0.000 12(5)	0.001 94(8)	0.002 03(8)	0.000 86(8)
Weighting parameters	0.0396, 0	0.0274, 0	0.0058, 0	0.0134, 1.9002	0.0225, 0.6868
<i>a</i> , <i>b</i>					
No. refined parameters	258	503	259	294	289
<i>wR</i> 2 (all data)	0.0754	0.0512	0.0352	0.0382	0.0507
<i>R</i> 1 ('observed' data)	0.0300 (4279)	0.0241 (7836)	0.0153 (4817)	0.0164 (5122)	0.0207 (5206)
Goodness of fit	1.042	0.837	1.042	1.135	1.080
Maximum, minimum electron density/e Å ⁻³	1.97, -2.94	1.08, -0.73	0.74, -0.70	0.60, -0.79	1.06, -1.16

ordination; in each case the longest W–C bond is found 'cis' to a W–Cl bond. For the latter (s mm ll), Δ*X* is smaller and the situation is less clear; **2** has a short W–C 'trans' to a W–Cl bond, whereas in **4** there are no distinct W–Cl bonds close to 'cis' or 'trans' positions relative to the shortest W–C.

Experimental

General

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the micro-analytical services of the Department of Chemistry at Imperial College. The NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400.0 (¹H) and 75.0 MHz (¹³C); chemical shifts are referenced to the residual protio impurity of the deuterated solvent. Infrared spectra (Nujol mulls, KBr windows) were obtained on Perkin-Elmer 577 and 457 grating spectrophotometers. The ligand 1,2-(H₂N)(Ph₂P)C₆H₄ was prepared by a previously published procedure.¹³ The ligand 2,2'-(H₂NC₆H₄)₂C₂H₄ was obtained as its diphosphate salt and extracted from aqueous alkaline solution into ethyl acetate, dried (MgSO₄) and recrystallised from isopropyl alcohol. The complex [W(η-C₅Me₅)Cl₄] was prepared by the literature method.¹⁴ All other chemicals were obtained commercially and used as received unless stated otherwise.

Preparations

[W(η-C₅Me₅)Cl₄CH(2,2'-(NC₆H₄)₂(CH₂CH₂))] 1. The complex [W(η-C₅Me₅)Cl₄] (1.0 g, 2.16 mmol) and the diamine 2,2'-(H₂NC₆H₄)₂C₂H₄ (0.92 g, 4.33 mmol) were refluxed in toluene (40 cm³) for 12 h. Volatiles were removed *in vacuo*, and the residue was extracted into hot MeCN (50 cm³) affording on cooling to room temperature (1–2 d) large brown-red prisms.

Yield 0.56 g, 46% (Found: C, 51.2; H, 4.9; N, 5.0. C₂₄H₂₇ClN₂W requires C, 51.0; H, 4.9; N, 5.2%). IR: 2360m, 2342m, 1588w, 1352m, 1315m, 1261s, 1089s, 1022s, 939w, 867w, 800s, 764m, 741m, 723m and 669w cm⁻¹. ¹H NMR [(CD₃)₂SO]: δ 7.35–6.88 (m, 8 H, aryl H), 2.80 (m, 2 H, CH₂), 2.14 (m, 2 H, CH₂) and 2.08 (s, 15 H, C₅Me₅).

[W(η-C₅Me₅)Cl₃(NC₆H₄PPh₂)₂] 2. Analogous conditions were employed to those described for the preparation of complex **1**, using [W(η-C₅Me₅)Cl₄] (0.25 g, 0.54 mmol) and 2-diphenylphosphinoaniline (0.30 g, 1.08 mmol). Recrystallisation from MeCN or CH₂Cl₂ afforded **2** as orange needles. Yield 0.16 g, 30% (Found: C, 57.4; H, 4.7; N, 2.8. C₄₈H₄₆ClN₂P₂W·CH₂Cl₂ requires C, 56.9; H, 4.6; N, 2.8%). IR: 1615w, 1585w, 1568w, 1435m, 1351w, 1321m, 1261s, 1092s, 1021s, 977w, 940w, 896w, 867w, 800s, 766m, 747m, 721w, 709w, 696m, 566w, 543w, 520w, 497w, 485w and 468w cm⁻¹. ¹H NMR (CD₃CN): δ 7.68–6.61 (m, 28 H, aryl H) and 2.23 (s, 15 H, C₅Me₅). ³¹P-{¹H} NMR (CD₃CN): δ 39.5 (s) and -15.0 (s).

[W(η-C₅Me₅)Cl₃(NNPh₂) 3. As for complex **1**, using [W(η-C₅Me₅)Cl₄] (1.0 g, 2.16 mmol) and Ph₂NNH₂·HCl (0.96 g, 4.3 mmol) afforded **3** as red-brown blocks. Yield: 0.32 g, 31% (Found: C, 43.3; H, 3.1; N, 4.6. C₂₂H₂₅Cl₃N₂W requires C, 43.5; H, 4.1; N, 4.6%). IR: 2361w, 1585w, 1306s, 1262s, 1170m, 1154s, 1069m, 1031m, 969m, 893m, 849w, 802w, 723s, 703m, 684w, 663w and 642m cm⁻¹. ¹H NMR (CDCl₃): δ 7.50–7.47 (m, 4 H, aryl H), 7.29–7.26 (m, 6 H, aryl H) and 2.11 (s, 15 H, C₅Me₅). ¹³C-{¹H} NMR: δ 139.77 (C_{ipso}), 129.60 (C_{meta}), 128.17 (C₅Me₅), 123.26 (C_{para}), 121.52 (C_{ortho}) and 121.8 [C₅(CH₃)₅].

[W(η-C₅Me₅)Cl₃(NH₂CPh₂CO₂)] 4. As for complex **1**, using [W(η-C₅Me₅)Cl₄] (1.0 g, 2.16 mmol) and 2,2-diphenylglycine (0.99 g, 4.36 mmol) afforded **4** as large green needles. Yield: 1.23 g, 88% (Found: C, 44.3; H, 4.2; N, 2.0. C₂₄H₂₇Cl₃NO₂W requires C, 44.2; H, 4.2; N, 2.1%). IR: 3326m, 3269m, 1699s,

1643m, 1632m, 1582m, 1565m, 1542m, 1513m, 1294s, 1272s, 1259s, 1247s, 1196m, 1183s, 1159s, 1089s, 1017s, 973m, 920m, 891m, 849m, 817m, 771m, 756s, 724m, 708m, 698m, 681m, 625m, 603w, 527w, 478w, 429w and 409w cm⁻¹. EPR (solid, 298 K): $g_{\text{iso}} = 1.870$.

[W(η -C₅Me₅)Cl₃{(NH₂)CH(CH₂C₆H₄OH-*p*)CO₂}] **5**. As for complex **1**, using [W(η -C₅Me₅)Cl₃] (0.5 g, 1.08 mmol) and tyrosine (0.39 g, 2.16 mmol) afforded **5** as orange-brown prisms. Crystals suitable for an X-ray analysis were grown from dichloromethane. Yield 0.46 g, 70% (Found: C, 38.9; H, 4.3; N, 4.3. C₁₉H₂₅Cl₃NO₃W·CH₃CN requires C, 39.0; H, 4.4; N, 4.3%). IR: 3268s, 3221s, 2285w, 2250w, 1665s, 1614w, 1592w, 1569w, 1518m, 1333m, 1298w, 1266s, 1231m, 1208m, 1188s, 1171s, 1154s, 1106s, 1076s, 1016s, 917w, 879m, 854w, 832m, 792w, 769w, 721s and 641w cm⁻¹. EPR (solid, 298 K): $g_{\text{iso}} = 1.892$.

X-Ray crystallography

Crystal data and other information on the structure determinations are given in Table 7. All measurements were made at 160 K on a Siemens SMART CCD area detector diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.710$ 73 Å). Cell parameters were refined from the observed ω angles of all strong reflections in each complete data set. Intensities were integrated from sets of exposures each taken over a 0.3° range in ω , covering more than a hemisphere of reciprocal space in each case. Semiempirical absorption corrections were applied, based on repeated and symmetry-equivalent reflections.

The structures were solved by direct methods, and refined by full-matrix least squares on F^2 values, with weighting $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$, where $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were assigned anisotropic displacement parameters, and isotropic hydrogen atoms were included with riding-model constraints and torsional freedom of methyl groups. An isotropic extinction parameter was refined, whereby $F_o' = F_o / (1 + 0.001 \times F_c^2 \lambda^3 / \sin 2\theta)^{1/4}$. Residuals are defined as $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, the latter being calculated only for 'observed' data with $F_o^2 > 2\sigma(F_o^2)$ for comparison with conventional refinements on F values; the goodness of fit was calculated for all F^2 values. The largest residual electron-density peaks lay close to tungsten atoms. Programs used: standard Siemens control (SMART) and integration (SAINT) software, Siemens SHELXTL, and local programs.¹⁵

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