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Organoimido complexes of tungsten-(VI) and -(V): correlation between relative orientation of π-donor ligands and electron configuration of the metal‡

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The high-yield synthesis of the monomeric five-co-ordinate arylimido complex $[WCl_3(NPh)(OC_6H_3Pr^i_2\text{-}2,6)]$ was achieved starting from $[\{WCl_3(NPh)\}_2(\mu\text{-}Cl)_2]$. The adducts $[WCl_3(NPh)(OC_6H_3Pr^i_2\text{-}2,6)L]$ (L = tetrahydrofuran, pyridine (py) or 4-*tert*-butylpyridine) of the monoalkoxide have been synthesized and the constitution of the pyridine adduct determined by X-ray crystallography. The reduction of the monoalkoxide with 1 equivalent of sodium amalgam in the presence of pyridine or triethylphosphine leads to the paramagnetic adducts $[WCl_2(NPh)(OC_6H_3Pr^i_2\text{-}2,6)L_2]$ (L = py or PEt_3) which were characterized. A *trans* configuration was found for the two chlorine atoms and the two σ-donor ligands in the structure analysis. Reorganization of the two π-donor ligands (aryloxide and NPh) from a *cis* arrangement in the complex with d^0 electron configuration to a *trans* arrangement in the d^1 configurated complexes is found and verified by X-ray diffraction analyses.

The correlation between the relative orientation of two π-donor ligands in octahedrally co-ordinated complexes and the electron configuration of the metal centre is well established by several theoretical and preparative studies.[1–4] Mingos[1] had discussed in 1979 the *cis* preference of the MO_2 moiety in d^0 L_4MO_2 octahedra and the *trans* preference in d^2 L_4MO_2 octahedra using the $[MoO_2(PH_3)_4]^{n+}$ ($n = 2$ or 0) system on the basis of extended-Hückel molecular orbital calculations. Similar arguments hold for the alkylimide ligand which is isoelectronic to the oxide ligand and acts as a 4e π donor exhibiting a M−N−C angle of *ca.* 180°. Several examples for the *cis*-$M(NR)_2$ preference in d^0 complexes are known.[3,5–8] In 1989 Wigley and co-workers[3] presented an example of the confirmation of this phenomenon in a tantalum(V) phenylimidoaryloxide. That work clearly shows the *cis* orientation of the aryloxide and phenylimide ligands in the d^0 complex $[TaCl_2(NR)(OC_6H_3Pr^i_2\text{-}2,6)(py)_2]$ ($R = 2,6\text{-}Pr^i_2C_6H_3$, py = pyridine) and the *trans* stereochemistry in the reduced d^2 complex $[Ta(NR)(OC_6H_3Pr^i_2\text{-}2,6)(EtC{\equiv}CEt)(py)_2]$. The *cis* configuration of two π donors in complexes with d^0 electron configuration allows all three metal d_π orbitals to accept π donation from the π-donor ligands. In complexes with d^1 and d^2 electron configuration the π-donor ligands prefer the *trans* configuration because the electrons can reside in the lone d_π orbital which is not destabilized by the π donation.

We are interested in the synthesis and reduction of tungsten(VI) phenylimidoaryloxides which are known to react together with SnR_3H as catalysts for ring-opening metathesis polymerization of cyclic alkenes.[9] The organoimide ligand, which has become very popular in the last years, provides electronic flexibility and steric control. The structures of organoimido complexes in the solid state and solution have been studied very extensively.[8] Mono- as well as di-meric complexes are known.[8,10] In comparison to the many organoimido complexes of tungsten(VI), there are few of tungsten(V). Nearly all the latter are of the general composition $[WCl_3(NR)L_2]$, with L being a σ-donor ligand.[11–13]

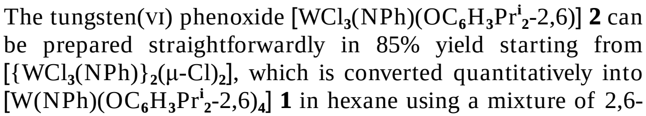
In this work another example of the dependence of the relative orientation of two π-donor ligands on the electronic configuration is presented. The synthesis of three tungsten(VI) complexes, $[WCl_3(NPh)(OC_6H_3Pr^i_2\text{-}2,6)L]$ [L = tetrahydrofuran (thf), py or 4-*tert*-butylpyridine (bpy)], and two tungsten(V) complexes, $[WCl_2(NPh)(OC_6H_3Pr^i_2\text{-}2,6)L_2]$ (L = py or PEt_3), is described. The solid-state structure of the d^0 complex $[WCl_3(NPh)(OC_6H_3Pr^i_2\text{-}2,6)(py)]$ and of the d^1 complex $[WCl_2(NPh)(OC_6H_3Pr^i_2\text{-}2,6)(py)_2]$ are also discussed.

Results and Discussion

Syntheses

The tungsten(VI) phenoxide $[WCl_3(NPh)(OC_6H_3Pr^i_2\text{-}2,6)]$ **2** can be prepared straightforwardly in 85% yield starting from $[\{WCl_3(NPh)\}_2(\mu\text{-}Cl)_2]$, which is converted quantitatively into $[W(NPh)(OC_6H_3Pr^i_2\text{-}2,6)_4]$ **1** in hexane using a mixture of 2,6-diisopropylphenol and diethylamine (Scheme 1).§,[14] The diethylamine hydrochloride was filtered off and the solvent was changed to toluene. Owing to the high solubility of the tetraaryloxide even in hexane, crystallization at −30 °C affords crystals of **1** in only 28% yield. Therefore we developed a method to use the crude reaction product, which is pure on the basis of ^1H NMR spectroscopy. The crude toluene solution of the tetraaryloxide **1** was treated with 1.5 equivalents of $[\{WCl_3(NPh)\}_2(\mu\text{-}Cl)_2]$ resulting in a redistribution to give the monoaryloxide $[WCl_3(NPh)(OC_6H_3Pr^i_2\text{-}2,6)]$ **2**. Redistribution reactions have previously been shown to be a versatile method for the syntheses of phenylimidoaryloxides.[15]

The monomeric five-co-ordinate compound **2** reacts with σ donors like thf, pyridine or 4-*tert*-butylpyridine to form the six-co-ordinate complexes $[WCl_3(NPh)(OC_6H_3Pr^i_2\text{-}2,6)L]$ (L = thf **3**, py **4** or bpy **5**) (Scheme 2).[16] The monoaryloxide **2** is readily reduced by 1 equivalent of sodium amalgam in the presence of 2 equivalents of the desired σ-donor ligand (L = py or PEt_3) using toluene–tetrahydrofuran (3 : 1) as solvent. The pyridine



Scheme 1 $R = 2,6\text{-}Pr^i_2C_6H_3$. (*i*) 8ROH, $8NEt_2H$; (*ii*) $3[\{WCl_3(NPh)\}_2(\mu\text{-}Cl)_2]$

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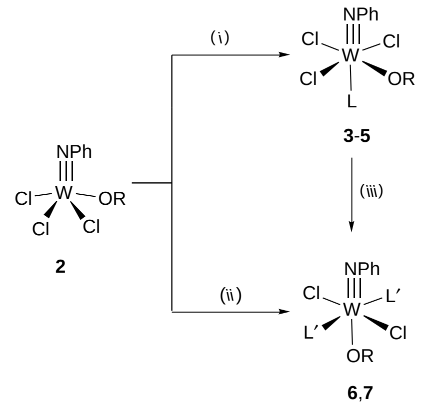
‡ *Non-SI units employed*: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}; G = 10^{-4} T.

§ Proposed monomeric structure of **1**, in the case of the analogue oxoaryloxide complex $[WO(OC_6H_3Pr^i_2\text{-}2,6)_4]$ the monomeric square-pyramidal structure has been demonstrated by a crystal structure analysis.[14]



Scheme 2 R = 2,6-Pr^i_2-C_6H_3. (*i*) L = thf, py or bpy; (*ii*) Na–Hg, 2L′ (L′ = py or PEt_3); (*iii*) Na–Hg, L = L′ = py

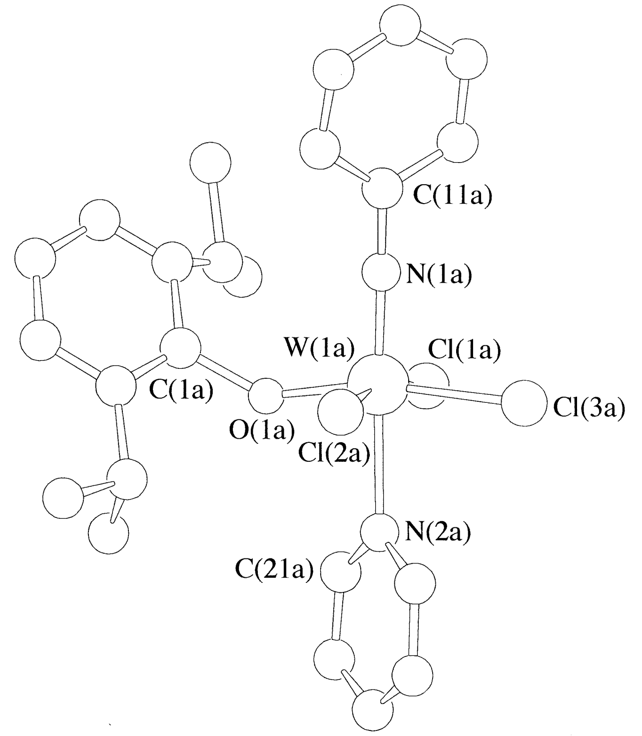


Fig. 1 A SCHAKAL plot of $[WCl_3(NPh)(OC_6H_3Pr^i_2\text{-}2,6)(py)]$ **4**

adduct $[WCl_2(NPh)(OC_6H_3Pr^i_2\text{-}2,6)(py)_2]$ **6** was obtained as dark green crystals in 77% yield and the triethylphosphine adduct $[WCl_2(NPh)(OC_6H_3Pr^i_2\text{-}2,6)(PEt_3)_2]$ **7** as red crystals in 62% yield. The reduction of $[WCl_3(NPh)(OC_6H_3Pr^i_2\text{-}2,6)(py)]$ **4** with 1 equivalent of sodium amalgam in the presence of pyridine also leads to the paramagnetic pyridine adduct **6**.

Crystal structures

Brown single crystals of $[WCl_3(NPh)(OC_6H_3Pr^i_2\text{-}2,6)(py)]$ **4** suitable for structure analysis were grown from benzene–hexane–diethyl ether (1:2:2) at −6 °C. Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with two independent molecules (named A and B). Both have a disordered group: in molecule A the $OC_6H_3Pr^i_2$ and in B the NPh group have two alternative positions. A SCHAKAL[17] plot of A is shown in Fig. 1; the disordered moiety was omitted for clarity. Selected bond lengths and angles are compiled in Tables 1 and 2. Obviously the disorder of the two groups is correlated, otherwise short intermolecular distances would occur (shortest C–C distance *ca.* 2.8 Å). The disorder in molecule A shows for the important angles of the $OC_6H_3Pr^i_2$ part [W(1a)–O(1a)–C(1a) 142(2) and W(1a)–O(1a)–C(1a*) 161(3)°] a difference of 19(5)°. In the other disordered group, the NPh in molecule B, the difference is 19(5)° too [W(1b)–N(1b)–C(11b) 172(2) and W(1b)–N(1b)–C(11b*) 153(3)°]. It seems likely that the two moieties avoid each other. There is a meridional arrangement of the three

Table 1 Selected bond lengths (Å) for compounds **4*** and **6**

$[WCl_3(NPh)(OC_6H_3\text{-}Pr^i_2\text{-}2,6)(py)]$ **4**		$[WCl_2(NPh)(OC_6H_3\text{-}Pr^i_2\text{-}2,6)(py)_2]$ **6**	
W(1a)–Cl(1a)	2.325(5)	W–Cl(1)	2.400(3)
W(1b)–Cl(1b)	2.358(6)		
W(1a)–Cl(2a)	2.350(6)	W–Cl(2)	2.406(3)
W(1b)–Cl(2b)	2.337(6)		
W(1a)–Cl(3a)	2.381(5)		
W(1b)–Cl(3b)	2.365(6)		
W(1a)–O(1a)	1.85(1)	W–O	1.969(8)
W(1b)–O(1b)	1.82(1)		
W(1a)–N(1a)	1.78(1)	W–N(1)	1.75(1)
W(1b)–N(1b)	1.70(2)		
W(1a)–N(2a)	2.32(2)	W–N(2)	2.18(1)
W(1b)–N(2b)	2.31(2)		
		W–N(3)	2.18(1)
N(1a)–C(11a)	1.34(2)	N(1)–C(11)	1.38(1)
N(1b)–C(11b)	1.62(5)		
N(1b)–C(11b*)	1.24(5)		
O(1a)–C(1a)	1.53(5)	O–C(1)	1.33(1)
O(1a)–C(1a*)	1.26(5)		
O(1b)–C(1b)	1.40(2)		
N(2a)–C(21a)	1.30(3)	N(2)–C(21)	1.34(1)
N(2b)–C(21b)	1.33(3)		
		N(3)–C(31)	1.34(2)

* Indices a and b indicate the two independent molecules A and B, an asterix the second different position of the disordered groups.

Table 2 Selected bond angles (°) for compounds **4** and **6**

4		**6**	
Cl(1a)–W(1a)–Cl(2a)	168.2(2)	Cl(1)–W–Cl(2)	174.1(1)
Cl(1b)–W(1b)–Cl(2b)	168.2(2)		
Cl(1a)–W(1a)–Cl(3a)	87.0(2)		
Cl(1b)–W(1b)–Cl(3b)	85.7(2)		
Cl(2a)–W(1a)–Cl(3a)	87.8(2)		
Cl(2b)–W(1b)–Cl(3b)	87.7(2)		
Cl(1a)–W(1a)–O(1a)	91.7(4)	Cl(1)–W–O	87.6(3)
Cl(1b)–W(1b)–O(1b)	89.7(4)		
Cl(2a)–W(1a)–O(1a)	91.0(4)	Cl(2)–W–O	86.5(2)
Cl(2b)–W(1b)–O(1b)	93.9(3)		
Cl(3a)–W(1a)–O(1a)	167.3(4)		
Cl(3b)–W(1b)–O(1b)	163.5(4)		
Cl(1a)–W(1a)–N(1a)	98.6(5)	Cl(1)–W–N(1)	94.6(3)
Cl(1b)–W(1b)–N(1b)	94.4(6)		
Cl(1a)–W(1a)–N(2a)	85.1(4)	Cl(1)–W–N(2)	89.7(3)
Cl(1b)–W(1b)–N(2b)	84.8(4)		
Cl(2a)–W(1a)–N(1a)	92.2(4)	Cl(2)–W–N(1)	91.3(3)
Cl(2b)–W(1b)–N(1b)	95.7(6)		
Cl(2a)–W(1a)–N(2a)	83.8(5)	Cl(2)–W–N(2)	90.4(3)
Cl(2b)–W(1b)–N(2b)	84.6(4)		
Cl(3a)–W(1a)–N(1a)	92.8(4)		
Cl(3b)–W(1b)–N(1b)	94.1(7)		
Cl(3a)–W(1a)–N(2a)	83.9(4)		
Cl(3b)–W(1b)–N(2b)	81.9(4)		
		Cl(1)–W–N(3)	85.9(3)
		Cl(2)–W–N(3)	93.5(3)
O(1a)–W(1a)–N(1a)	99.9(5)	O–W–N(1)	177.8(4)
O(1b)–W(1b)–N(1b)	102.1(8)		
O(1a)–W(1a)–N(2a)	83.4(6)	O–W–N(2)	88.0(3)
O(1b)–W(1b)–N(2b)	81.9(5)		
		O–W–N(3)	86.6(3)
N(1a)–W(1a)–N(2a)	174.9(6)	N(1)–W–N(2)	91.8(4)
N(1b)–W(1b)–N(2b)	176.0(8)		
		N(1)–W–N(3)	93.8(4)
		N(2)–W–N(3)	173.1(4)
W(1a)–O(1a)–C(1a)	142(2)	W–O–C(1)	168.3(7)
W(1a)–O(1a)–C(1a*)	161(3)		
W(1b)–O(1b)–C(1b)	151(1)		
W(1a)–O(1a)–C(11a)	175(2)	W–N(1)–C(11)	175.7(9)
W(1b)–N(1b)–C(11b)	172(2)		
W(1b)–N(1b)–C(11b*)	153(3)		

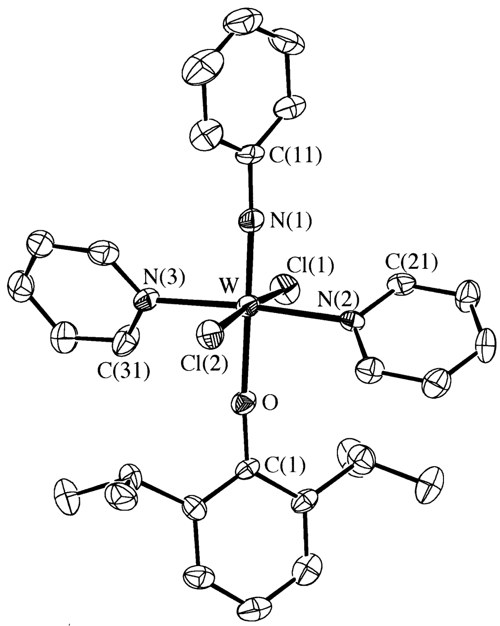


Fig. 2 A PLATON[18] drawing of $[WCl_2(NPh)(OC_6H_3Pr^i_2\text{-}2,6)(py)_2]$ **6**

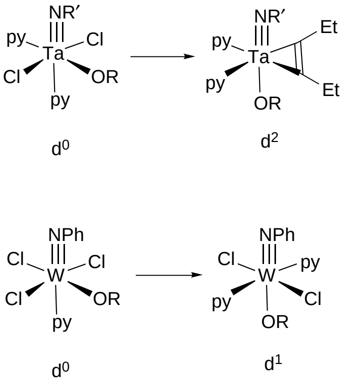
chloride ligands and a *cis* arrangement of the phenylimide and aryloxide π-donor ligands at the tungsten centre.

Green single crystals of $[WCl_2(NPh)(OC_6H_3Pr^i_2\text{-}2,6)(py)_2]$ **6** were grown from a benzene–hexane solution at room temperature. The molecular structure is shown in Fig. 2. Selected bond lengths and angles are in Tables 1 and 2. The tungsten atom adopts a distorted-octahedral configuration with a *trans* arrangement of the arylimide and aryloxide ligands. A *trans* arrangement is also found for the two chlorine atoms and two pyridine ligands.

The short W–N(1) distance [1.75(1) Å] and the almost linear W–N(1)–C(11) angle [175.7(9)°] clearly indicate that the organoimido group functions as a four-electron donor.[19] The W–O distance of the aryloxide moiety is 1.969(8) Å, which is in the middle of the range for other known aryloxide W–O distances, *e.g.* 2.129(8) Å in $[WH_3(OPh)(PMe_3)_4]$,[20] 1.966(4) Å in $[WCl_2(OR)_2(PMe_2Ph)_2]$ (R = 2,6-$Ph_2C_6H_3$),[21] 1.849(5)–1.866(5) Å in $[W(OC_6H_3Pr^i_2\text{-}2,6)_4]$[22] and 1.853(4) and 1.877(4) Å in $[WCl_3(OR)_2(PMe_2Ph)]$.[21] The large W–O–C(1) angle of 168.3(7)° together with the W–O distance indicate a weak π-donor character of the aryloxide ligand. Steric interactions between the isopropyl groups of the aryloxide and the equatorial ligands (py, Cl) have also to be taken into consideration for the W–O–C(1) angle enlargement.

Owing to poor crystal quality the data set for the structure determination of $[WCl_2(NPh)(OC_6H_3Pr^i_2\text{-}2,6)(PEt_3)_2]$ **7** did not allow an anisotropic refinement of all non-hydrogen atoms. Therefore the bond lengths and angles will not be discussed. However the *trans* arrangement of the arylimide and aryloxide ligands at the octahedrally co-ordinated tungsten centre was unambiguously demonstrated. The *cis* arrangement in d^0 and the *trans* arrangement in d^n transition-metal complexes (n = 1 or 2) of two π-donor ligands has been observed in several examples (Table 3).

Our structural studies of compounds **4** and **6** together with the direct transformation of the diamagnetic adduct **4** to the paramagnetic product **6** (Scheme 3) by reduction clearly shows that the reorganization of the ligands depends on the electron configuration at the transition-metal centre. Wigley[8] found another example for this dependence during his studies of the chemistry of tantalum(v) phenylimidoaryloxides (Scheme 3). The reduction of the tantalum(v) complex $[TaCl_2(NR')(OC_6H_3Pr^i_2\text{-}2,6)(py)_2]$ (R′ = 2,6-$Pr^i_2C_6H_3$) with *cis* arrangement of the π-donor ligands (NR′ and $OC_6H_3Pr^i_2$) leads to a reorganized reduction product with a *trans* arrangement of the respective π-donor ligands.



Scheme 3 R = R′ = 2,6-$Pr^i_2C_6H_3$

These preparative and structural results are consistent with the theoretical studies of Mingos and co-workers[1,2] on the MO_2 moiety. In octahedrally co-ordinated d^0 complexes a *cis* arrangement of the π-donor ligands is preferred because all three d_π orbitals are allowed to accept π donation from these ligands. A *trans* configuration is favoured by the π-donor ligands in complexes with d^1 and d^2 electron configuration because the valence electrons can reside in the lone d_π orbital which is not destabilized by π donation.

Spectroscopy

The ^1H NMR spectra of complexes **4** and **5** show a significant low-field shift of δ 9.46 and 9.16 for the H_α protons of the co-ordinated pyridine. Three bands are observed in the IR spectra for the W–Cl stretches which is characteristic for a meridional arrangement of the chlorine substituents.[15a] In the case of the reduction products **6** and **7** only one W–Cl stretch at 297 and 282 cm^{-1} can be observed, which is consistent with the *trans* arrangement of the chloride ligands.[25]

The magnetic susceptibility of complex **6** was measured over a temperature range (2–300 K) and the Curie–Weiss relation was obeyed within a small value of θ (5 K). The magnetic moment of 1.58 μ_B (room temperature) is appreciable less than the spin-only value. Apparently spin–orbit coupling is responsible for the low magnetic moment.[26]

Cyclic voltammograms of complexes **6** and **7** were recorded in thf. The voltammogram of ferrocene was used for calibration purposes. Both complexes show a quasi-reversible one-electron reduction (**6**, $E_{\frac{1}{2}} = -1.68$ V; **7**, $E_{\frac{1}{2}} = -1.64$ V, *vs.* ferrocene–ferrocenium)¶ which can be assigned to the couple W^V–W^{IV}.

The new compounds **6** and **7** were also characterized by their X-band EPR spectra. The fluid solution spectrum of **6** [Fig. 3(*a*)] shows an intense peak centred at $g = 1.86$ along with two satellite peaks characteristic of the coupling of a single unpaired electron with the ^{183}W nucleus ($I = \frac{1}{2}$, natural abundance = 14.4%, $A = 60 \times 10^{-4}$ cm^{-1}). In the frozen-solution spectrum of **6** [Fig. 3(*b*)] three different g values were expected due to the C_{2v} symmetry. The spectrum shows only two signals; obviously two g values are not resolvable (g_1, $g_2 = 1.88$, $g_3 = 1.80$). Again the hyperfine splitting for the ^{183}W isotope can be observed as satellites around the main peak. The fluid-solution EPR spectrum of **7** [Fig. 3(*c*)] exhibits a triplet centred at $g = 1.89$, with hyperfine coupling to two equivalent ^{31}P nuclei

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¶ The reference electrode was a saturated calomel electrode (SCE). A platinum-inlay electrode was used as the working electrode and the counter electrode was also platinum. Test solutions contained 1×10^{-3} mol dm^{-3} analyte and 0.1 mol dm^{-3} $[NBu^n_4][PF_6]$ supporting electrolyte. The $E_{\frac{1}{2}}$ values are reported *vs.* ferrocene–ferrocenium as internal standard.

Table 3 Examples of the relative orientation of two π-donor ligands in octahedral complexes

Complex	Electron configuration	Orientation	Ref.
$[WCl_3(NPh)(OC_6H_3Pr^i_2\text{-}2,6)(py)]$	d^0	*cis*	This work
$[TaCl_2(NC_6H_3Pr^i_2\text{-}2,6)(OC_6H_3Pr^i_2\text{-}2,6)(py)_2]$	d^0	*cis*	3
$[ReCl_3(Me)(NC_6H_3Me_2\text{-}2,6)_2]^-$	d^0	*cis*	5
$[WCl_2(NPh)_2(bipy)]$	d^0	*cis*	6
$[WCl_2(NPh)(OC_6H_3Pr^i_2\text{-}2,6)(py)_2]$	d^1	*trans*	This work
$[WCl_2(NPh)(OC_6H_3Pr^i_2\text{-}2,6)(PEt_3)_2]$	d^1	*trans*	This work
$[WCl_3(OC_6H_3Ph_2\text{-}2,6)_2(PMe_2Ph)]$	d^1	*trans*	21
$[Ta(NC_6H_3Pr^i_2\text{-}2,6)(OC_6H_3Pr^i_2\text{-}2,6)(EtC{\equiv}CEt)(py)_2]$	d^2	*trans*	3
$[Re(NC_6H_4Me\text{-}4)(OEt)(S_2CNMe_2)_2]$	d^2	*trans*	23
$[ReCl_2O(OEt)(py)_2]$	d^2	*trans*	24
$[WCl_2(OCH_2Cf_3)_2(PMe_2Ph_3)_2]$	d^2	*trans*	4

bipy = 2,2′-Bipyridine.

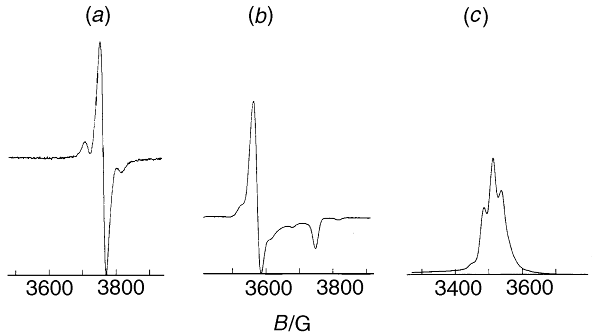

Fig. 3 The EPR spectra (X-band) of (*a*) complex **6** in toluene at room temperature (first derivative), (*b*) **6** in toluene at 136 K (first derivative) and (*c*) **7** in toluene at room temperature

($A = 28 \times 10^{-4}$ cm^{-1}) which is in the range found for other complexes.[27]

Experimental

Materials

2,6-Diisopropylphenol, bpy and py were obtained from Aldrich. Triethylphosphine[28] and $[\{WCl_3(NPh)\}_2(\mu\text{-}Cl)_2]$[15b] were prepared according to literature procedures. Hexane was distilled from potassium, benzene and thf from sodium–benzophenone and toluene from sodium. All distillations and bench-top manipulations were carried out under nitrogen.

Physical measurements

Infrared spectra were recorded on a Perkin-Elmer FT-IR 1720 X spectrometer, NMR spectra with Bruker WP 80 PFT (^{1}H, 80 MHz), WH-250 PFT (^{1}H, 250; ^{13}C, 62.9 MHz) and Varian VXR 300 (^{1}H, 300; ^{13}C, 75.4 MHz) spectrometers. Cyclic voltammetry was performed using an EG&G 173 potentiostat and a 175 programmer with a normal three-electrode configuration. The EPR spectra were obtained with a Bruker ER 200D/ESP 3220 spectrometer. Samples were prepared as ≈1 mmol dm^{-3} solutions in toluene (using diphenylpicrylhydrazyl for calibration). A gaseous nitrogen cryostat was used for low-temperature (136 K) studies. Magnetic measurements on a polycrystalline sample were carried out with a SQUID magnetometer (Quantum design). Liquid secondary ion mass spectra were obtained with a Finnigan MAT 95 instrument. Elemental analyses were performed by Mikroanalytisches Labor Pascher (D 53424 Remagen) and for complexes **2**, **3** and **5** with a Carlo-Erba Elemental Analyzer.

Syntheses

$[W(NPh)(OC_6H_3Pr^i_2\text{-}2,6)_4]$ 1. A hexane suspension of $[\{WCl_3(NPh)\}_2(\mu\text{-}Cl)_2]$ (9.06 g, 10.9 mmol) was cooled to 0 °C and treated with a mixture of diethylamine (6.36 g, 87 mmol) and 2,6-diisopropylphenol (15.5 g, 87.0 mmol). The reaction mixture was stirred for 15 h at room temperature. Diethylamine hydrochloride was separated by filtration, the hexane solution was concentrated *in vacuo* (removal of hexane *in vacuo* results in a highly viscous red oil, ⩾95% pure according to ^{1}H NMR spectroscopy) and cooled to −30 °C to give red crystals which were filtered off (5.95 g, 28%). NMR ($CDCl_3$): ^{1}H (300 MHz), δ 7.47 (m, 2 H, NPh), 7.12–7.02 (m, 3 H, NPh), 7.01 [d, 8 H, ^3J(HH) = 7.4, $H^{3,5}$ of aryloxide], 6.85 [dd, 4 H, ^3J(HH) = 7.1, 8.1, H^4 of aryloxide], 3.52 [spt, 8 H, ^3J(HH) = 6.7, $CHCH_3$] and 0.92 [d, 48 H, ^3J(HH) = 6.7 Hz, $CHCH_3$]; ^{13}C-{^{1}H} (75.4 MHz), δ 159.1 (C_{ipso} of aryloxide), 153.5 (C_{ipso} of NPh), 138.1 ($C^{2,6}$ of aryloxide), 127.7, 127.6, 127.0, 123.3, 123.1 (NPh, aryloxide), 26.5 ($CHCH_3$) and 23.9 ($CHCH_3$). Mass spectrum (SIMS): *m*/*z* 806 [$M^+ - OC_6H_3Pr^i_2$] (Found: C, 65.8; H, 7.75. Calc. for $C_{54}H_{73}NO_4W$: C, 65.9; H, 7.5%).

$[WCl_3(NPh)(OC_6H_3Pr^i_2\text{-}2,6)]$ 2. The red viscous oil of complex **1** (21.4 g, 21.7 mmol) (not crystallized from hexane for this preparation) was dissolved in toluene and treated with $[\{WCl_3(NPh)\}_2(\mu\text{-}Cl)_2]$ (27.2 g, 32.6 mmol) at room temperature. The mixture was stirred overnight, concentrated *in vacuo*, cooled to −30 °C and the brown microcrystals filtered off (41.3 g, 85%). NMR: ^{1}H (250 MHz, $CDCl_3$), δ 7.9–7.1 (m, 8 H, NPh, aryloxide), 3.45 [spt, 2 H, ^3J(HH) = 6.8, $CHCH_3$] and 1.29 [d, 12 H, ^3J(HH) = 6.8 Hz, $CHCH_3$]. Mass spectrum (SIMS): *m*/*z* 557 (M^+). Molecular weight determination (vapour-pressure osmometry, 32.35 mg in 1.1870 g CH_2Cl_2): *M* = 555. Calc. 558.59 (Found: C, 38.45; H, 4.05; N, 2.5. Calc. for $C_{18}H_{22}Cl_3NOW$: C, 38.7; H, 3.95; N, 2.5%).

$[WCl_3(NPh)(OC_6H_3Pr^i_2\text{-}2,6)(thf)]$ 3. A solution of complex **2** (0.5 g, 0.4 mmol) in thf (10 cm^3) was stirred overnight at room temperature. The solvent was removed *in vacuo*. Slow diffusion from hexane into a diethyl ether solution of **2** gave the product as a dark red microcrystalline powder (0.5 g, 96%). NMR ($CDCl_3$): ^{1}H (80 MHz), δ 7.6–6.8 (m, 8 H, aryloxide, NPh), 4.5–4.0 (br s, 4 H, H_α of thf), 3.84 [spt, 2 H, ^3J(HH) = 6.8, $CHCH_3$], 2.2–1.8 (m, 4 H, H_β of thf) and 1.23 [d, 12 H, ^3J(HH) = 6.8 Hz, $CHCH_3$]; ^{13}C-{^{1}H} (62.9 MHz), δ 160.0 (C_{ipso} of aryloxide), 151.0 (C_{ipso} of NPh), 138.3 ($C^{2,6}$ of aryloxide), 131.9, 129.6, 127.4, 126.2, 123.7 (NPh, aryloxide), 70.0 (br, C_α of thf), 26.1 ($CHCH_3$), 25.6 (C_β of thf) and 24.5 ($CHCH_3$) (Found: C, 41.2; H, 4.85; N, 2.25. Calc. for $C_{22}H_{30}Cl_3NO_2W$: C, 41.9; H, 4.8; N, 2.2%).

$[WCl_3(NPh)(OC_6H_3Pr^i_2\text{-}2,6)(py)]$ 4. A solution of complex **2** (1.45 g, 1.3 mmol) in thf (10 cm^3) was treated with pyridine (0.21 cm^3, 2.6 mmol) and stirred for 30 min at room temperature. The solvent was removed *in vacuo.* Recrystallization from benzene–hexane–diethyl ether (1 : 2 : 2) gave the complex as dark brown crystals (1.27 g, 77%). IR: $\tilde{\nu}_{max}$/cm^{-1} (CsI) 337, 322 and

Table 4 Crystallographic data for complexes **4** and **6***

	4	**6**
Formula	$C_{23}H_{27}Cl_3N_2OW$	$C_{28}H_{32}Cl_2N_3OW$
M	637.69	681.34
Crystal size/mm	0.20 × 0.20 × 0.20	0.25 × 0.20 × 0.15
a/Å	15.483(8)	9.815(2)
b/Å	17.886(8)	15.965(3)
c/Å	18.315(9)	11.7752(5)
β/°	93.42(5)	92.09(2)
U/Å^3	5063(8)	2780(2)
D_c/g cm^{-3}	1.673	1.628
Z	8	4
μ(Mo-Kα)/cm^{-1}	50.0	44.6
T/K	203	253
Scan mode	ω–2θ	ω
Scan range/°	$3 < \theta < 25$	$3 < \theta < 28$
Total data	9579	5278
No. unique observed data $[I > 1.0\sigma(I)]$	4386	2709
No. variables	523	316
R, *R′*	0.084, 0.062	0.046, 0.048
Goodness of fit	1.189	1.113
Maximum residual density/e Å^{-3}	2.01 [1.02 Å from W(1a)]	0.96 (0.96 Å from W)

* Details in common: monoclinic, space group $P2_1/c$; weighting scheme $w = 1/\sigma^2(F_o)$.

288 (WCl). NMR (C_6D_6): ^{1}H (250 MHz), δ 9.46 [dd, 2 H, ^3J(HH) = 6.5, ^4J(HH) = 1.5, H_α of py], 7.15–6.35 (m, 11 H, aryloxide, NPh, py), 3.72 [spt, 2 H, ^3J(HH) = 6.8, C*H*CH$_3$] and 1.03 [d, 12 H, ^3J(HH) = 6.8 Hz, CHC*H*$_3$]; ^{13}C-{^{1}H} (62.9 MHz), δ 159.8 (C_{ipso} of aryloxide), 151.5 (C_α of py), 150.9 (C_{ipso} of NPh), 139.2 ($C^{2,6}$ of aryloxide), 138.8 (C_γ of py), 131.6, 130.0, 128.5, 126.5, 124.4, 124.3 (NPh, aryloxide, C_γ of py), 26.3 (*C*HCH$_3$) and 24.7 (CH*C*H$_3$) (Found: C, 43.95; H, 4.45. Calc. for $C_{23}H_{27}Cl_3N_2OW$: C, 43.3; H, 4.25%).

[WCl$_3$(NPh)(OC$_6$H$_3$Pr$^i_2$-2,6)(bpy)] 5. This complex was prepared in the same manner as for **4** using **2** (1.30 g, 2.3 mmol). Yield 1.31 g (81%). IR: $\tilde{\nu}_{max}$/cm^{-1} (CsI) 339, 325 and 288 (WCl). NMR (CDCl$_3$): ^{1}H (250 MHz), δ 9.16 [dd, 2 H, ^3J(HH) = 5.4, ^4J(HH) = 1.3, H_α of bpy], 7.5–6.9 (m, 10 H, aryloxide, NPh, bpy), 3.27 [spt, 2 H, ^3J(HH) = 6.8, C*H*CH$_3$], 1.26 (s, 9 H, CCH$_3$) and 0.85 [d, 12 H, ^3J(HH) = 6.8 Hz, CHC*H*$_3$]; ^{13}C-{^{1}H} (62.9 MHz), δ 164.3, 159.4, 150.5 (C_{ipso} of aryloxide, NPh, bpy), 151.0 (C_α of bpy), 138.8 ($C^{2,6}$ of aryloxide), 131.8, 130.0, 127.5, 126.2, 123.8, 121.8 (aryloxide, NPh, C_β of bpy), 35.4 [*C*(CH$_3$)$_3$], 30.3 [C(*C*H$_3$)$_3$], 26.0 (*C*HCH$_3$) and 24.5 (CH*C*H$_3$) (Found: C, 46.2; H, 5.4, N, 3.95. Calc. for $C_{27}H_{35}Cl_3N_2OW$: C, 46.75; H, 5.1; N, 4.05%).

[WCl$_2$(NPh)(OC$_6$H$_3$Pr$^i_2$-2,6)(py)$_2$] 6. A solution of complex **2** (6.49 g, 5.81 mmol) in thf (10 cm^3) and toluene (30 cm^3) was cooled to 0 °C and treated with pyridine (1.84 g, 2.23 mmol). After 5 min sodium amalgam (Na, 267 mg, 11.6 mmol; Hg, 52 g) was added. The mixture was stirred vigorously overnight at room temperature, filtered and the solvent removed *in vacuo*. Recrystallization from benzene–hexane gave the complex as dark green crystals (6.1 g, 77%). IR: $\tilde{\nu}_{max}$/cm^{-1} (CsI) 297 (WCl). Mass spectrum (SIMS): *m*/*z* 683 (M^+), 646 ($M^+ - $ Cl), 604 ($M^+ - $ py) and 505 ($M^+ - OC_6H_3Pr^i_2$) (Found: C, 49.35; H, 4.75. Calc. for $C_{28}H_{32}Cl_2N_3OW$: C, 49.35; H, 4.75%).

[WCl$_2$(NPh)(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$(PEt$_3$)$_2$] 7. To a solution of complex **2** (3.12 g, 2.79 mmol) in thf (10 cm^3) and toluene (30 cm^3) was added sodium amalgam (Na, 129 mg, 5.6 mmol; Hg, 25 g) at 0 °C. The resulting mixture was stirred for 1 h at room temperature and triethylphosphine (1.33 g, 11.21 mmol) was added at 0 °C. The mixture was stirred vigorously overnight at room temperature, filtered and the solvent removed *in vacuo*. Recrystallization of the product from toluene gave the complex as red crystals (2.63 g, 62%). IR: $\tilde{\nu}_{max}$/cm^{-1} (CsI) 282 (WCl). Mass spectrum (SIMS): *m*/*z* 758 (M^+), 724 ($M^+ - $ Cl), 642 ($M^+ - PEt_3$) and 583 ($M^+ - OC_6H_3Pr^i_2$) (Found: C, 47.6; H, 6.9. Calc. for $C_{30}H_{52}Cl_2NOP_2W$: C, 47.45; H, 6.9%).

Crystallography

Crystals of complexes **4** and **6** were mounted on a glass fibre under a stream of nitrogen. Geometry and intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.710 73 Å). Crystal data and the parameters of data collection and structure refinement[29] are compiled in Table 4. Structure **4** was solved by direct methods[30] and **6** by the Patterson method. The remaining atom positions resulted from subsequent refinement cycles and Fourier-difference syntheses. In the final least-squares full-matrix refinement (based on *F*) all non-hydrogen atoms were refined with anisotropic thermal displacement parameters except for the disordered parts of structure **4** which were refined isotropically. All hydrogen atoms of both structures were treated as riding atoms with an idealized geometry (C–H 0.98 Å, $B_H = 1.3B_C$). For **4** an empirical absorption correction was applied (ψ scans).[31]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/368.

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