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FULL PAPER

Regiospecific influences of phenyl ring substituents in monoimido complexes of tantalum and tungsten and bis imido complexes of molybdenum

Alastair J. Nielson,*[a] Mark W. Glenny,[b] Clifton E. F. Rickard[b] and Joyce M. Waters[a]

[a] *Chemistry, Institute of Fundamental Sciences, Massey University at Albany, Private Bag 102904, North Shore Mail Centre, Auckland, New Zealand*
[b] *Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand*

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Imido exchange of $[TaCl_3(NCMe_3)(py)_2]$ with 2-*tert*-butylaniline in refluxing benzene and crystallisation of the product from CH_2Cl_2 gave the anionic complex $[Hpy][TaCl_4(C_6H_4CMe_3\text{-}2)(py)]$ **1**. X-Ray structural analysis shows that with the Ta–N–C bond angle at 165.1(5)° two of the *tert*-butyl substituent methyl groups sit above two meridional chloro ligands but NMR spectroscopy indicates that the *tert*-butyl group can still rotate in solution. Reaction of isocyanates ArNCO [Ar = $C_{10}H_7$ (naphthyl), $C_6H_4CMe_3$-2 or C_6H_4Ph-2] with $WOCl_4$ in refluxing benzene gave $[\{WCl_4(NC_{10}H_7)\}_x]$ **2**, $[\{WCl_4(NC_6H_4CMe_3\text{-}2)\}_x]$ **3**, and $[\{WCl_4(NC_6H_4Ph\text{-}2)\}_x]$ **4** which NMR spectra show convert from two species into one in $CDCl_3$. In refluxing toluene, 2-*tert*-butylphenyl isocyanate also forms the metallacyclic amido complex $[WCl_4\{NHC_6H_4(CMe_2CH_2)\text{-}2(C,N)\}]$ **5**. The d^1 complexes $[WCl_3(NC_{10}H_7)(PMe_3)_2]$ **6**, $[WCl_3(NC_6H_4CMe_3\text{-}2)(PMe_3)_2]$ **7**, $[WCl_3(NC_6H_4Ph\text{-}2)(PMe_3)_2]$ **8**, $[WCl_3(NC_{10}H_7)(PMe_2Ph)_2]$ **9** and $[WCl_3(NC_{10}H_7)(PMePh_2)_2]$ **10** were prepared, and show hindered imido ligand aryl C–N bond rotation. A crystal structure determination of **6** shows the naphthyl ring C-8 proton positioned between a chloro and phosphine ligand. Also prepared to demonstrate hindered aryl C–N bond rotation were the d^2 complexes $[WCl_2(NC_{10}H_7)(PMe_3)_3]$ **11**, $[WCl_2(NC_6H_4CMe_3\text{-}2)(PMe_3)_3]$ **12**, $[WCl_2(NC_6H_4Ph\text{-}2)(PMe_3)_3]$ **13** and $[WCl_2(NC_{10}H_7)(PMe_2Ph)_3]$ **14**. Crystal stucture determinations show the *tert*-butyl group in **12** located above a chloro ligand and the phenyl group in **13** located between a chloro and phosphine ligand. They also show the methyl and isopropyl substituents in $[MoCl_2(NC_6H_3Me\text{-}2\text{-}Pr^i\text{-}6)_2(dme)]$ **15** form an *anti* configuration and in $[MoCl_2(NC_6H_4CMe_3\text{-}2)_2(dme)]$ **16** a *syn* configuration is identified where the Mo–N–C bond angles are determined by steric effects and crystal packing forces.

Introduction

In co-ordination chemistry it is often difficult to achieve specific environments if a constrained ligand system is not used. Regiospecifically to influence sections of a complex it may then be necessary to restrict certain bond rotations so that steric interactions can be localised. In the field of organoimido chemistry, use of the symmetrically substituted 2,6-di-isopropylphenylimide ligand has given rise to a variety of bis and tris complexes which involve low co-ordination numbers.[1] Monoimido complexes of tungsten containing this ligand do not show steric properties different from those of the unsubstituted phenylimide,[2] whereas attempts to form complexes with 2,6-di-*tert*-butyl substituents have been unsuccessful[3] and only one complex is known which contains 2,6-diphenyl substituents.[4] Recent work on d^2 complexes of molybdenum containing the mesitylimide ligand ($NC_6H_3Me_2$-2,6) shows that free rotation about the imido C–N bond can be restricted at low temperatures[5] but most imido complexes reported to date lack regiospecific influence. Use of a single sterically bulky substituent in the 2 position of a phenylimide ring appears one way of achieving this. There is also the possibility of unusual complex formation and the observance of M–N–C bond angles which are directly related to steric interactions of the substituent with other parts of the molecule.[6,7] We report here the results of studies directed towards assessing how ligands of this type regiospecifically influence molecular structure.

Results and discussion

Monoimidotantalum(V)

Tantalum d^0 phenylimido complexes can be prepared from $TaCl_5$ and silylated arylamines[8] but we were interested to establish whether imido exchange[9] (eqn. 1) could be used to introduce a 2-substituted phenylimide, given the ease of preparation of *tert*-butylimido complexes of tantalum.[10,11] In a series of preliminary investigations it was found by $^{13}C\text{-}\{^1H\}$ NMR spectroscopy that $[TaCl_3(NCMe_3)(py)_2]$[11]/2-*tert*-butylaniline mixtures required refluxing in benzene or toluene to exchange the imido ligand. This contrasts with the reaction of the d^0 titanium complex $[TiCl_2(NCMe_3)(py)_3]$ with 2,6-diisopropylamine where refluxing is not needed.[12] When the tantalum product was recrystallised from CH_2Cl_2 the analytical data (Table 1) and NMR spectra (Table 2) were inconsistent with the expected complex $[TaCl_3(NC_6H_4CMe_3\text{-}2)(py)_2]$. However X-ray structural analysis showed that the complex was $[Hpy][TaCl_4(NC_6H_4CMe_3\text{-}2)(py)]\cdot CH_2Cl_2$ **1** (Fig. 1). Further work is in progress to establish the role of CH_2Cl_2 during the crystallisation process. The structure of the anion in **1** is a distorted octahedron with the py ligand lying *trans* to the imido function and the four chloro ligands lying in the equatorial plane. Selected bond lengths and angles are shown in Table 3. The imido phenyl ring is rotated so that two *tert*-butyl substituent methyls [C(8) and C(10)] lie over Cl(1) and Cl(2) respectively with the C(8)···Cl(1) and C(10)···Cl(2) contacts being 3.73 and and 3.77 Å respectively. This positioning appears to have no effect on the Ta–N bond length [1.779(5) Å] which is similar to those found in a variety of other imido complexes of

$$[TaCl_3(NCMe_3)(L)_2] + ArNH_2 \longrightarrow [TaCl_3(NAr)(L)_2] + Me_3CNH_2 \quad (1)$$

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Table 1 Physical and analytical data

Complex	Yield(%)	Colour	Analyses[a](%) C	H	N
1 [Hpy][$TaCl_4(C_6H_4CMe_3$-2)(py)][b]	66	Orange	37.2 (36.7)	4.1 (3.8)	6.1 (6.3)
2 [{$WCl_4(NC_{10}H_7)$}$_x$]	85	Brown	26.1 (25.7)	1.4 (1.5)	3.1 (3.0)
3 [{$WCl_4(NC_6H_4CMe_3$-2)}$_x$]	70	Brown	24.6 (25.4)	2.8 (2.8)	2.6 (3.0)
4 [{$WCl_4(NC_6H_4Ph$-2)}$_x$]	90	Brown	29.4 (29.2)	1.5 (1.8)	2.6 (2.8)
5 [WCl_4{$HNC_6H_4(CMe_2CH_2)$-2(*C*,*N*)}]	76	Dark brown	25.2 (25.4)	2.7 (2.8)	3.1 (3.0)
6 [$WCl_3(NC_{10}H_7)(PMe_3)_2$][c]	79	Brown	30.3 (30.5)	4.2 (4.1)	2.1 (2.1)
7 [$WCl_3(NC_6H_4CMe_3$-2)$(PMe_3)_2$][b]	80	Brown	31.6 (31.4)	5.3 (5.1)	2.1 (2.3)
8 [$WCl_3(NC_6H_4Ph$-2)$(PMe_3)_2$]	69	Brown	35.7 (35.5)	5.1 (4.5)	1.7 (2.3)
9 [$WCl_3(NC_{10}H_7)(PMe_2Ph)_2$][d]	61	Brown	43.2 (43.5)	4.2 (4.1)	1.8 (1.9)
10 [$WCl_3(NC_{10}H_7)(PMePh_2)_2$]	57	Brown	51.6 (52.0)	3.9 (4.0)	1.7 (1.7)
11 [$WCl_2(NC_{10}H_7)(PMe_3)_3$]	66	Purple	36.2 (36.6)	5.2 (5.5)	2.4 (2.2)
12 [$WCl_2(NC_6H_4CMe_3$-2)$(PMe_3)_3$][c]	80	Purple	33.8 (33.6)	6.2 (5.9)	2.0 (2.0)
13 [$WCl_2(NC_6H_4Ph$-2)$(PMe_3)_3$]	77	Purple	39.1 (38.8)	5.3 (5.6)	2.1 (2.2)
14 [$WCl_2(NC_{10}H_7)(PMe_2Ph)_3$]	89	Yellow	50.1 (50.4)	5.0 (5.0)	1.7 (1.7)
15 [$MoCl_2(NC_6H_3Me$-2-Pr^i-6)$_2$(dme)]	63	Deep red	52.2 (52.3)	6.6 (6.6)	5.3 (5.1)
16 [$MoCl_2(NC_6H_4CMe_3$-2)$_2$(dme)]	68	Purple red	51.6 (52.3)	6.6 (6.6)	5.2 (5.1)

[a] Calculated values given in parentheses. [b] Calculated values for 0.5 CH_2Cl_2 solvate. [c] Calculated values for CH_2Cl_2 solvate. [d] Calculated values for 0.17 CH_2Cl_2 solvate.

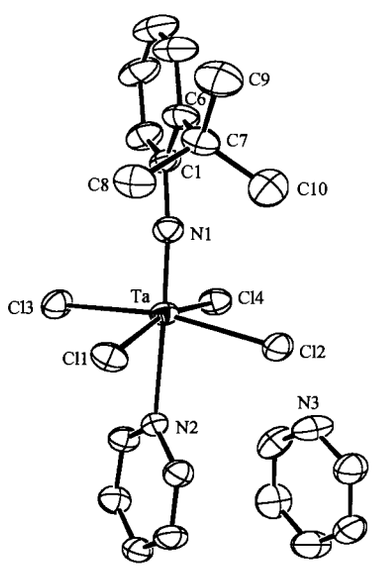


Fig. 1 Molecular structure of the anion of complex **1**, without H atoms and with key atoms labelled.

tantalum such as [$Ta(NCMe_3)(NMe_2)_3$] [1.77(2) Å],[13] [$TaCl_3(NC_6H_5)(PEt_3)$(thf)] [1.765(5) Å][14] and [$TaCl_2(NC_6H_3Pr^i_2$-2,6)(C_5Me_5)] [1.780(5) Å].[15] The Ta–Cl bond lengths lie in the range 2.391(2)–2.445(2) Å.

The N(1)–Ta–Cl(1) and N(1)–Ta–Cl(2) bond angles [98.8(2) and 98.6(2)° respectively] widen out a little under the influence of the *tert*-butyl substituent methyl groups [*cf*. N(1)–Ta–Cl(3), 94.3(2)° and N(1)–Ta–Cl(4), 96.4(2)°] and the angle C(8)–C(7)–C(10) at 109.9(6)° is a little larger than the 107.7(6) and 107.1(7)° observed for C(8)–C(7)–C(9) and C(9)–C(7)–C(10) respectively as a result of the proximity of Cl(1) and Cl(2). The *tert*-butyl substituent is thus easily accommodated without forcing the Ta–N(1)–C(1) bond angle to bend more than the observed 165.1(5)°. This latter angle is not very different from those found in other tantalum complexes which contain more symmetrical imido ligands (*e.g.* Ta–N–C bond angles of 171.4(5)° in [$TaCl_2(NC_6H_3Pr^i_2$-2,6)(C_5Me_5)][15] and 165.8° in [$TaCl(NCMe_3)${$N(SiMe_3)_2$}$_2$][16]) hence the *tert*-butyl substituent does not distort this angle unduly. For organoimido ligands in general, it has been recognised that M–N–C bond angles as low as *ca*. 150° can be achieved from crystal packing and intramolecular effects without involving electronic changes to the imido linkage.[6,7] In both the ^{1}H and ^{13}C-{^{1}H} NMR spectra the *tert*-butyl group resonances appear as narrow singlets indicating that the group is free to rotate in solution. Since the structure of complex **1** shows the *tert*-butyl substituent is easily accommodated in the molecule, rotation about the N(1)–C(1) bond should be uninhibited.

Each pyridinium cation ring interleaves between a co-ordinated pyridine and an imido ligand phenyl ring, a sequence which is extended by back-to-back approaches of co-ordinated pyridine rings for two adjacent complexes related by a centre of symmetry. However the stacking arrangement is marred by the interplanar angles between the co-ordinated pyridines and also between the pyridinium ion and the imido ligand rings of 11.3 and 21.2° respectively. Thus a perfectly parallel set of aromatic rings is not achieved. The distances between adjacent aromatic rings in the series vary from 3.5 to a little over 4.0 Å. The pyridinium cation nitrogen atom [N(3)] makes contact with Cl(4) and Cl(2) at 3.38 and 3.46 Å respectively, distances which are slightly longer than those recognised as involving strong hydrogen bonding in an N–H · · · Cl system.[17] N(3) makes even longer contacts with Cl(4) and Cl(2) [3.62 and 3.70 Å respectively] on an adjacent anion.

Monoimido tungsten-(VI), -(V) and -(IV)

The reaction of an isocyanate with $WOCl_4$ in benzene solution[18–20] was used to prepare the complexes [{$WCl_4(NC_{10}H_7)$}$_x$] **2**, [{$WCl_4(NC_6H_4CMe_3$-2)}$_x$] **3**, and [{$WCl_4(NC_6H_4Ph$-2)}$_x$] **4**. Non-crystalline solids were formed which are expected to be chloro-bridged dimers based on the crystal structures of like molecules.[21] However, ^{1}H NMR spectra of the naphthylimide complex **2** in $CDCl_3$ showed two C-8 proton resonances (δ 9.22 and 9.10) in a ratio 1:4 slowly converting in the $CDCl_3$ solution to the less predominant form over time (24 h). This process was also evident in the ^{13}C-{^{1}H} NMR spectrum in which one set of resonances converted into another over time. Addition of thf (tetrahydrofuran) to the NMR tube containing complex **2** led to only one set of resonances in both spectra (expected to be the monomeric thf adduct [$WCl_4(NC_{10}H_7)$(thf)]) where the single C-8 proton resonance position (δ 9.08) is similar to that found for the transforming [{$WCl_4(NC_{10}H_7)$}$_x$] species.

The 2-*tert*-butylphenylimido and 2-phenylphenylimido tungsten complexes show similar NMR spectral features to those of **2**. Initially there are two *tert*-butyl resonances in the spectra of complex **3** and two doublets for the *ortho*-protons of the phenyl substituent for **4**. The NMR spectra of complex **3** indicate that the *tert*-butyl group rotates since there are no diastereotopic

Table 2 Selected NMR spectroscopic data (δ, J/Hz)[a]

Complex	^{1}H[b]	^{13}C-{^{1}H}
1	1.61 (s, 9 H, CMe_3); 5.5 (s, 1 H, CH_2Cl_2); 6.81 [td, ^3J(HH) 7.7, ^4J(HH) 1.2, 1 H]; 7.20 [td, ^3JHH) 7.7, ^4J(HH) 1.2, 2 H]; 7.30 [dd, ^3J(HH) 7.7, ^4J(HH) 1.2, 1 H]; 7.41 [prt, 2 H, β-H py or Hpy]; 7.48 [prt, 2 H, β-H Hpy or py]; 7.90 (m, 2 H, χ-H py and Hpy); 8.80 [d, ^3J(HH) 5.2, 3 H, α-H py or Hpy and NH]; 9.25 (bd, 2 H, α-H py or Hpy)	30.9 (CMe_3); 35.1 (C); 124.8 (CH); 124.9 (CH); 125.5 (CH); 125.6 (CH); 128.3 (CH); 133.1 (CH); 139.0 (CH); 140.2 (CH); 146.3 (*o*-C); 151.9 (CH); 152.2 (CH); 152.4 (*ipso*-C)
2	7.22–7.40 (m); 7.50–7.86 (m); 7.88–8.23 (m); 9.10 [d, ^3J(HH) 8.3, 1 H, H^8 (major)]; 9.22 [d, ^3J(HH) 8.2, 1 H, H^8 (minor)]	122.5 (CH minor); 122.7 (CH major); 123.3 (CH major); 123.7 (CH major); 124.9 (CH minor); 126.3 (CH minor); 127.5 (CH major); 128.0 (C minor); 128.5 (CH minor); 129.2 (CH minor); 129.6 (CH minor); 130.1 (CH major); 130.6 (CH major); 131.6 (C minor); 132.2 (CH minor); 135.0 (C major); 135.4 (CH major); 136.0 (C major); 136.9 (*ipso*-C minor); 137.8 (*ipso*-C major)
3	1.59 [s, 18 H, CMe_3 (major)]; 1.67 [s, 18 H, CMe_3 (minor)]; 6.85 [t, ^3J(HH) 7.4, 1 H, *p*-H (major)]; 7.30–7.75 (m, aromatics)	30.7 [CMe_3 (major)]; 31.1 [CMe_3 (minor)]; 34.7 [C (minor)]; 35.1 [C (major)]; 124.9 [CH (major)]; 126.1 [CH (major)]; 128.4 [CH (major)]; 128.5 [CH (minor)]; 129.9 [CH (minor)]; 131.5 [CH (minor)]; 135.6 [CH (major)]; 144.7 [CH minor)]; 150.1 [C (major)]; 150.9 [*ipso*-C (major)]; 153.2 [C (major)]; 154.1 [*ipso*-C (minor)]
4[c]	7.32–7.74 (m, aromatics); 7.93 [t, ^3J(HH) 7.7, 2 H, *p*-H]; 8.46 [d, ^3J(HH) 8.1, 2 H, *o*-H (major)]; 8.55 [d, ^3J(HH) 7.9, 2 H, *o*-H (minor)]	117.9 (CH); 123.1 (CH); 123.4 (CH); 124.1 (CH); 124.5 (CH); 125.1 (CH); 125.6 (CH); 127.6 (CH); 127.8 (CH); 128.7 (CH); 128.9 (CH); 129.1 (CH); 129.4 (CH); 130.0 (CH); 130.1 (C); 130.2 (C); 130.6 (C); 134.5 (C); 153.8 (*ipso*-C); 163.2 (*ipso*-C)
5	1.46 (s, 6 H, CMe_2); 1.62 (s, 2 H, CH_2); 7.26 [prt, 1 H, *p*-H]; 7.36 [d, ^3J(HH) 7.1, 1 H, *m*-H]; 7.48 [d, ^3J(HH) 7.1, 1 H, *m*-H]; 7.66 [m, 1 H, *o*-H]; 9.27 (bs, 1 H, NH)	30.1 (CH_2); 32.0 (CMe_2); 32.8 (C); 124.2 (CH); 125.6 (CH); 128.5 (CH); 130.2 (CH); 134.4 (*ortho*-C); 141.8 (*ipso*-C)
11	1.61 [t, ^2J(HP) 3.7, 18 H, PMe_3]; 1.90 [d, ^2J(HP) 8.3, 9 H, PMe_3]; 7.20 [d, ^3J(HH) 7.9, 2 H, H^4 and H^5]; 7.44 [d, ^3J(HH) 7.4, 1 H, H^2]; 7.57 [t, ^3J(HH) 7.4, 1 H, H^3]; 7.75 [t, ^3J(HH) 7.4, 2 H, H^6 and H^7]; 8.90 [d, ^3J(HH) 7.4, 1 H, H^8]	17.8 [t, ^1J(HP) 13.5, PMe_3]; 26.8 [d, ^1J(HP) 28.8, PMe_3]; 121.5 (CH); 123.9 (CH); 125.3 (CH); 126.1 (CH); 126.3 (CH); 126.9 (CH); 127.2 (CH); 129.7 (C); 134.1 (C); 153.7 (*ipso*-C)
12	1.33 (s, 9 H, CMe_3); 1.52 [t, ^2J(HP) 3.7, 18 H, PMe_3]; 1.72 [d, ^2J(HP) 8.0, 9 H, PMe_3]; 7.02 [td, ^3J(HH) 7.4, ^4J(HH) 1.4, 1 H, *p*-H]; 7.09 [td, ^3J(HH) 7.4, ^4J(HH) 1.4, 1 H, *m*-H]; 7.14 [dd, ^3J(HH) ^3J(HH) 7.4, ^4J(HH) 1.4, 1 H, *m*-H]; 7.18 [dd, ^3J(HH) 7.4, ^4J(HH) 1.4, 1 H, *o*-H]	17.2 [t, ^1J(HP) 13.4, PMe_3]; 26.0 [d, ^1J(HP) 28.5, PMe_3]; 30.4 (CMe_3); 35.7 (C); 124.1 (*p*-CH); 126.1 (*m*-CH); 126.4 (*m*-CH); 138.29 (*o*-CH); 143.3 (*o*-C); 155.5 (*ipso*-C)
13	1.34 [t, ^2J(HP) 3.7, 18 H, PMe_3]; 1.60 [d, ^2J(HP) 8.1, 9 H, PMe_3]; 7.04 [bt, 2 H, *m*- and *p*-H (imido)]; 7.10–7.18 [m, 2 H, *m*- and *o*-H (imido)]; 7.21 [t, ^3J(HH) 7.5, 1 H, *p*-H (phenyl)]; 7.35 [t, ^3J(HH) 7.5, 2 H, *m*-H (phenyl)]; 7.46 [d, ^3J(HH) 7.5, 2 H, *o*-H (phenyl)]	17.8 [t, ^1J(HP) 13.5, PMe_3]; 26.3 [d, ^1J(HP) 28.3, PMe_3]; 124.3 [*p*-CH (imido)]; 127.2 and 127.3 [*m*-CH (imido) and *p*-CH (phenyl)]; 128.2 [*m*-CH (phenyl)]; 129.0 [*o*-CH (phenyl)]; 131.4 [*m*-CH (phenyl)]; 133.3 [*o*-CH (imido)]; 136.3 [*ipso*-C (phenyl)]; 139.1 [*o*-C (imido)]; 153.5 [*ipso*-C (imido)]
15	1.06 [d, ^3J(HH) 6.9, 12 H, $CHMe_2$]; 2.43 (s, 6 H, *o*-Me); 3.75 (bs, 4 H, CH_2CH_2); 3.83 (obsc. sept, 2 H, $CHMe_2$); 3.87 (bs, 6 H, OMe); 6.91 (m, 4 H, *m*-H); 7.05 (m, 2 H, *p*-H)	18.7 (*o*-Me); 24.3 (Me); 27.5 (CH); 62.0 (OMe); 71.2 (CH_2); 122.8 (*m*-CH); 126.9 (*p*-CH); 127.4 (*m*-CH); 134.7 [*o*-C(Me)]; 144.2 (*o*-C($CHMe_2$)]; 154.6 (*ipso*-C)
16	1.39 [s, 18 H, CMe_3 (*anti*)]; 1.44 [s, 18 H, CMe_3 (*syn*)]; 3.73 [bs, 6 H, OMe (*anti* and *syn*)]; 3.90 [bs, 4 H, CH_2CH_2 (*anti* and *syn*)]; 6.85 [t, ^3J(HH) 7.4, 4 H, *m* and *p*-H (*syn*)]; 7.00 [t, ^3J(HH) 7.5, 2 H, *p*-H (*anti*)]; 7.02 [obsc, 2 H, *m*-H (*syn*)]; 7.08 [t, ^3J(HH) 7.5, 2 H, *m*-H (*anti*)]; 7.21 [d, ^3J(HH) 7.5, 2 H, *m*-H (*anti*)]; 7.27, [obsc. d, 2 H, *o*-H (*syn*)]; 7.67 [d, ^3J(HH) 7.5, 2 H, *o*-H (*anti*)]	30.4 [Me (*anti*)]; 31.5 [Me (*syn*)]; 34.3 [C (*syn*)]; 35.1 [C (*anti*)]; 62.3 [b, OMe (*syn* and *anti*)]; 71.4 [CH_2 (*syn* and *anti*)]; 125.0 [CH (*anti*)]; 125.5 [CH (*syn*)]; 126.2 [CH (*anti*)]; 126.7 [CH (*syn*)]; 126.9 [CH (*syn*)]; 128.1 [b, 2CH (*anti*)]; 129.7 [CH (*syn*)]; 140.4 [*o*-C (*anti*)]; 141.6 [*o*-C (*syn*)]; 154.9 [*ipso*-C (*syn*)]; 155.2 [*ipso*-C (*anti*)

[a] Spectra obtained in $CDCl_3$ solution. [b] b = broad, bd = broad doublet, bs = broad singlet, bt = broad triplet, d = doublet, dd = doublet of doublets, m = multiplet, obsc = obscured, obsc d = obscured doublet, obsc sept = obscured septet, prt = poorly resolved triplet, s = singlet, t = triplet, td = triplet of doublets. [c] Major and minor components not distinguishable in ^{13}C-{^{1}H} NMR spectrum.

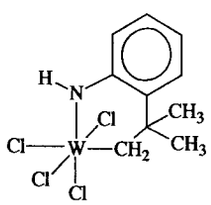
Table 3 Selected bond lengths (Å) and bond angles (°) for [Hpy][$TaCl_4(C_6H_4CMe_3$-2)(py)]·CH_2Cl_2 **1**

Ta–N(1)	1.779(5)	Ta–Cl(2)	2.420(2)
Ta–N(2)	2.437(5)	Ta–Cl(3)	2.421(2)
Ta–Cl(1)	2.391(2)	Ta–Cl(4)	2.445(2)
N(1)–Ta–Cl(1)	98.8(2)	N(2)–Ta–Cl(1)	82.1(1)
N(1)–Ta–Cl(2)	98.6(2)	N(2)–Ta–Cl(2)	84.0(1)
N(1)–Ta–Cl(3)	94.3(2)	N(2)–Ta–Cl(3)	83.1(1)
N(1)–Ta–Cl(4)	96.4(2)	N(2)–Ta–Cl(4)	82.7(1)
Cl(1)–Ta–Cl(2)	91.15(6)	Cl(1)–Ta–Cl(3)	91.06(6)
Cl(1)–Ta–Cl(4)	164.77(5)	Cl(2)–Ta–Cl(3)	166.44(6)
Cl(2)–Ta–Cl(4)	86.20(6)	Cl(3)–Ta–Cl(4)	88.18(6)
Ta–N(1)–C(1)	165.1(5)	C(1)–C(6)–C(7)	123.0(5)
C(5)–C(6)–C(7)	121.5(6)	C(6)–C(7)–C(8)	108.7(6)
C(6)–C(7)–C(9)	112.2(6)	C(6)–C(7)–C(10)	111.1(6)
C(8)–C(7)–C(9)	107.7(6)	C(8)–C(7)–C(10)	109.9(6)
C(9)–C(7)–C(10)	107.1(7)	N(1)–Ta–N(2)	177.3(2)
N(1)–C(1)–C(2)	115.5(6)	N(1)–C(1)–C(6)	124.5(6)

methyl groups observed. Low temperature studies of this feature have been hampered by low solubility in non-coordinating solvents. When thf was added to the 2-*tert*-butylphenylimido complex **3** and the solvent removed the NMR spectra showed only one set of resonances characteristic of the adduct [$WCl_4(NC_6H_4CMe_3$-2)(thf)]. Addition of Et_4NCl to **3** gave [NEt_4][$WCl_4(NC_6H_4CMe_3$-2)] which NMR spectra also showed as a single compound. Previously we have not observed the formation of two species in the NMR spectra of other [{$WCl_4(NR)$}$_x$] complexes which suggests that in the present complexes there are either some rotational differences regarding the position of the imido ligands if a dimer persists in solution or dimer–monomer solution dynamics is involved.

In the preparations of complexes **2**–**4** the product usually precipitates from the benzene reaction medium in high yield. When the reaction of 2-*tert*-butylphenyl isocyanate and $WOCl_4$ was carried out in the higher boiling solvent toluene a significant portion of the product remained in solution. A dark

brown solid was isolated which analysed as [{$WCl_4(NC_6H_4$-CMe_3-2)}] but which had completely different NMR spectra from those of complex **3**. In the ^{1}H NMR spectrum there were resonances at δ 1.46 and 1.62 in a ratio of 3:1 consistent with 2 methyl and one methylene group and there was a broad 1-proton resonance at δ 9.27 assigned as an NH proton. The *ortho*-proton of the aromatic ring apparently couples to this NH proton since there is a multiplet present and not the expected doublet. The ^{13}C-{^{1}H} NMR spectrum contained a resonance for the methyl groups and also a resonance at δ 30.1 shown to be a methylene group by DEPT-135. The NMR spectra thus show the metallacycle amide complex [WCl_4-{$NHC_6H_4(CMe_2CH_2)$-2(*C*,*N*)}] **5** (structure **I**) forming at the elevated temperature of the toluene solvent. Simple molecular models indicate that the NH proton for this complex lies in the same plane as the *ortho*-proton of the aromatic ring which may explain the coupling observed in the ^{1}H NMR spectrum. The reaction represents the first example of a cyclometallation observed during the interaction of an isocyanate and a metal oxo complex. As yet, we have been unable to obtain the cyclometallate by refluxing complex **3** in toluene for extended periods.



I

Reduction of complexes **2**–**4** with one equivalent of Na/Hg amalgam in the presence of 2 equivalents of PMe_3 [19,20] gave the d^1 complexes [$WCl_3(NC_{10}H_7)(PMe_3)_2$] **6**, [$WCl_3(NC_6H_4CMe_3$-2)$(PMe_3)_2$] **7**, and [$WCl_3(NC_6H_4$Ph-2)$(PMe_3)_2$] **8** for which simple molecular models indicate rotation about the aryl C–N bond will be hindered by steric interaction of the imido ligand with the PMe_3 ligand methyls. The naphthylimido ligand is expected to produce the least steric constraint and hence the more bulky phosphine derivatives [$WCl_3(NC_{10}H_7)(PMe_2Ph)_2$] **9** and [$WCl_3(NC_{10}H_7)(PMePh_2)_2$] **10** were prepared. A crystal structure determination of the trimethylphosphine complex **6** was carried out to assess the steric contribution a naphthyl ligand makes in the presence of the smaller PMe_3 ligand.

Complex **6** shows a distorted octahedral geometry with *trans* phosphines, *trans* chloro ligands and a third chloro ligand lying *trans* to the naphthylimido ligand (Fig. 2). Selected bond lengths and angles are contained in Table 4. The W–N bond length [1.707(13) Å] is not significantly different from those found in [$WCl_3(NC_6H_5)(PMe_3)_2$] [1.731(6) Å] [19] and [WCl_3-$(NC_6H_3Pr^i_2$-2,6$)(PMe_3)_2$] [1.750(6) Å] [2] nor is the P(1)–W–P(2) bond angle [173.4(1)° in **6**] compared with that in the phenylimido complex [172.3(1)°] but this angle is slightly smaller [169.5(1)°] in the 2,6-diisopropylphenylimido complex. The imido ligand in **6** tilts away from Cl(3) [W–N–C(1) bond angle 167.4(1)°] more than in the phenylimido or 2,6-diisopropylphenylimido complexes [W–N–C bond angles 175.8(6) and 178.0(5)° respectively]. As well, the naphthyl group twists slightly to the P(1) side of Cl(3) in **6** to reduce contact between the C(8) proton and Cl(3) as similarly found in the 2,6-diisopropylphenylimido complex, but the N–W–Cl(3) bond angle in **6** is much larger [99.3(5) and 90.8(5)° respectively] showing that Cl(3) still needs to move away from the C(8) proton. The calculated Cl(3)···H(8) distance is 3.04 Å which is slightly less than the sum of the van der Waals radius of these atoms (3.18 Å). Thus the widening out of the N–W–Cl(3) bond angle is accompanied by a bend in the N–W–Cl(1) bond angle

Table 4 Selected bond lengths (Å) and bond angles (°) for [WCl_3-$(NC_{10}H_7)(PMe_3)_2$] **6**

W–N	1.707(13)	W–Cl(3)	2.379(4)
W–Cl(1)	2.451(4)	W–P(1)	2.531(3)
W–Cl(2)	2.407(4)	W–P(2)	2.536(4)
N–W–Cl(1)	173.7(5)	Cl(1)–W–P(1)	86.5(2)
N–W–Cl(2)	91.2(5)	Cl(1)–W–P(2)	87.0(2)
N–W–Cl(3)	99.3(5)	Cl(2)–W–P(1)	88.7(1)
N–W–P(1)	95.2(4)	Cl(2)–W–P(2)	91.6(1)
N–W–P(2)	91.2(4)	Cl(3)–W–P(1)	90.1(1)
P(1)–W–P(2)	173.4(1)	Cl(3)–W–P(2)	88.5(2)
Cl(1)–W–Cl(2)	82.7(2)	Cl(2)–W–Cl(3)	169.4(2)
Cl(1)–W–Cl(3)	86.8(2)	W–N–C(1)	167.4(1)
N–C(1)–C(2)	123.3(15)	N–C(1)–C(9)	119.3(13)

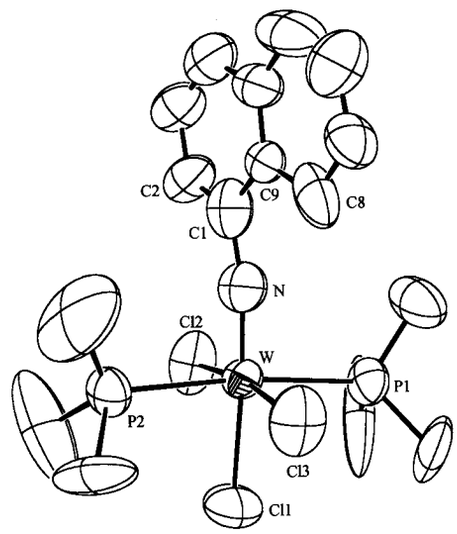


Fig. 2 Molecular structure of complex **6**, without H atoms and with key atoms labelled.

[173.7(5)°] in comparison with the 2,6-diisopropylphenylimido complex [N–W–Cl(1) bond angle 178.0(5)°]. The W–Cl(3) bond length [2.379(4) Å] is marginally shorter in terms of 3σ than the W–Cl(2) bond length [2.407(4) Å] whereas in the phenylimido and 2,6-diisopropylphenylimido complexes these bond lengths are similar [2.387(2), 2.390(2) and 2.387(3), 2.382(3) Å respectively].

Simple molecular models indicate that the N–W–P(1) bond angle would need to open significantly for the C(8) proton to rotate over the phosphine ligand and such a rotation would need the C(8) and C(2) protons to enter the space between the phosphine carbons at the same time (geared rotation [5]). This suggests that the naphthylimido ligand is regiospecific to Cl(3). It is also noted that whereas an isopropyl group itself can rotate to remove contacts, the naphthyl ligand offers a much more rigid system and can thus be expected to exert different steric properties.

Reduction of complexes **2**–**4** with two equivalents of Na/Hg amalgam in the presence of 3 equivalents of PMe_3 [19,20] gave the d^2 complexes [$WCl_2(NC_{10}H_7)(PMe_3)_3$] **11**, [$WCl_2(NC_6H_4CMe_3-2)(PMe_3)_3$] **12**, and [$WCl_2(NC_6H_4$Ph-2$)(PMe_3)_3$] **13**. The complex [$WCl_2(NC_{10}H_7)(PMe_2Ph)_3$] **14** could be prepared but the reaction failed with $PMePh_2$. Complexes **11–13** all show a doublet and a triplet for the PMe_3 ligands in the ^{1}H NMR and ^{13}C-{^{1}H} NMR spectra and **14** shows two triplets for the phosphine methyls. These features are consistent with a *mer*-phosphine arrangement. [18,19] Naphthylimido complex **11** shows a doublet for the C(8) proton at δ 8.90 in the ^{1}H NMR spectrum and is expected to show a similar interaction and ligand rotational properties to those of the d^1 complex **6**. There is only one resonance in the ^{1}H NMR and ^{13}C-{^{1}H} NMR spectra for the CMe_3 group in complex **12** indicating that the *tert*-butyl

Table 5 Selected bond lengths (Å) and bond angles (°) for $[WCl_2(NC_6H_4CMe_3\text{-}2)(PMe_3)_3]$ **12**

W–N	1.770(3)	W–P(1)	2.5039(10)
W–Cl(1)	2.4974(9)	W–P(2)	2.5074(10)
W–Cl(2)	2.5096(9)	W–P(3)	2.4845(10)
N–W–Cl(1)	177.5(5)	Cl(1)–W–Cl(2)	83.62(3)
N–W–Cl(2)	98.9(1)	Cl(1)–W–P(1)	82.75(3)
N–W–P(1)	98.0(1)	Cl(1)–W–P(2)	81.31(3)
N–W–P(2)	98.2(1)	Cl(1)–W–P(3)	86.45(3)
N–W–P(3)	91.1(1)	Cl(2)–W–P(1)	86.20(3)
P(1)–W–P(2)	162.99(3)	Cl(2)–W–P(2)	86.17(3)
P(1)–W–P(3)	92.57(3)	Cl(2)–W–P(3)	170.07(3)
P(2)–W–P(3)	92.33(3)	W–N–C(1)	172.9(3)
N–C(1)–C(2)	115.9(3)	N–C(1)–C(6)	124.8(3)
C(1)–C(6)–C(7)	123.5(3)	C(5)–C(6)–C(7)	120.3(3)
C(6)–C(7)–C(8)	109.5(3)	C(6)–C(7)–C(9)	109.3(3)
C(6)–C(7)–C(10)	107.3(3)	C(8)–C(7)–C(9)	111.7(3)
C(8)–C(7)–C(10)	106.5(3)	C(9)–C(7)–C(10)	107.3(3)

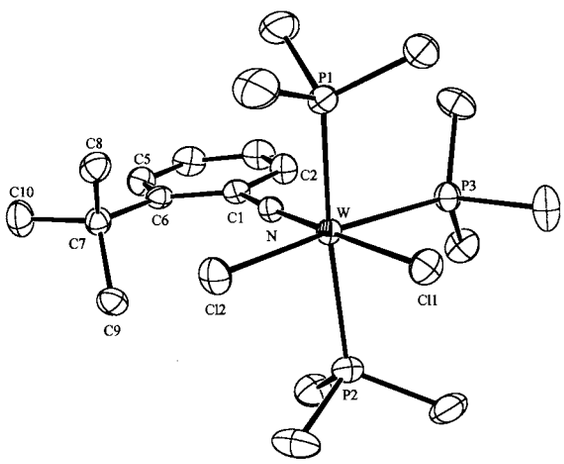


Fig. 3 Molecular structure of complex **12**, without H atoms and with key atoms labelled.

group is able to rotate. The *ortho*-protons of the phenyl substituent in **13** show a doublet in the ^{1}H NMR spectrum which suggests rapid rotation of this group.

A crystal structure determination of the 2-*tert*-butylphenylimido complex **12** showed a distorted octahedral geometry (Fig. 3) similar to that found for $[WCl_2(NC_6H_5)(PMe_3)_3]$.[19] Selected bond lengths and angles are contained in Table 5. The W–N bond lengths are similar in both complexes [1.770(3) and 1.755(3) Å respectively] as are the W–Cl(1) bond lengths for the chloro ligand lying *trans* to the imido ligand [2.497(1) and 2.501(1) Å respectively]. The W–Cl(2) bond in which the chloro ligand lies *cis* to the imido group is marginally longer where the *tert*-butyl substituent is present [2.510(1) and 2.494(1) Å respectively] as are the W–P bonds for the *trans* phosphines [W–P(1) bond lengths 2.504(1) and 2.483(1) Å respectively; W–P(2) 2.507(1) and 2.497(1) Å]. The W–P(3) bond is significantly longer with a *tert*-butyl substituent present [2.485(1) and 2.453(1) Å respectively].

The 2-*tert*-butyl substituent in complex **12** has a pronounced effect on the orientation of the imido ligand phenyl ring and the bond angles. Two of the *tert*-butyl group methyls straddle Cl(2) [C(8)···Cl(2) and C(9)···Cl(2) contacts 3.55 and 3.58 Å respectively] which brings the phenyl ring close to the plane of the atoms P(3), W, Cl(2) and N. The best fit for these two methyls with the phosphine methyls on P(1) and P(2) is where one P–C bond eclipses the W–N bond, whereas the best fit of the phenyl group C(2) proton with P(3) forces two of its methyls to adopt a staggered conformation with respect to the W–N bond. In $[WCl_2(NC_6H_5)(PMe_3)_3]$ the phenyl group swings around so that the hydrogen in the 2 position falls over and between P(1) and Cl(2) and that in the 6 position over and

Table 6 Selected bond lengths (Å) and bond angles (°) for $[WCl_2(NC_6H_4Ph\text{-}2)(PMe_3)_3]$ **13**

W–N	1.764(3)	W–P(1)	2.5010(10)
W–Cl(1)	2.4989(8)	W–P(2)	2.5148(9)
W–Cl(2)	2.4918(7)	W–P(3)	2.4581(10)
N–W–Cl(1)	171.84(9)	Cl(1)–W–Cl(2)	84.28(3)
N–W–Cl(2)	102.79(9)	Cl(1)–W–P(1)	89.28(3)
N–W–P(1)	95.29(9)	Cl(1)–W–P(2)	87.02(3)
N–W–P(2)	89.97(9)	Cl(1)–W–P(3)	79.45(3)
N–W–P(3)	93.57(9)	Cl(2)–W–P(1)	85.41(3)
P(1)–W–P(2)	166.79(3)	Cl(2)–W–P(2)	81.61(3)
P(1)–W–P(3)	92.55(3)	Cl(2)–W–P(3)	163.63(3)
P(2)–W–P(3)	99.22(3)	W–N–C(1)	171.84(9)
N–C(1)–C(2)	118.6(3)	N–C(1)–C(6)	122.2(3)
C(1)–C(6)–C(7)	123.0(3)	C(5)–C(6)–C(7)	118.4(3)

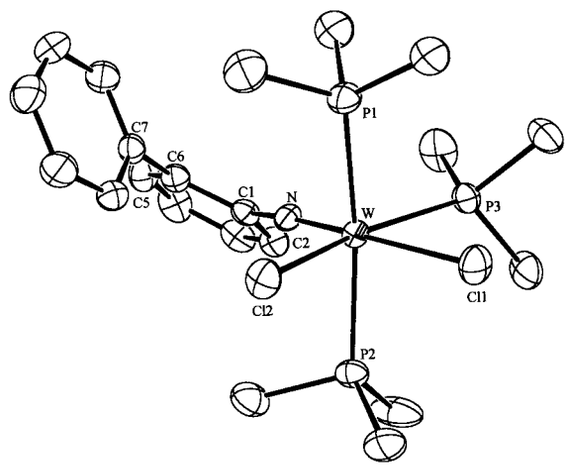


Fig. 4 Molecular structure of complex **13**, without H atoms and with key atoms labelled.

between P(2) and P(3). The best fit of these hydrogens with the phosphine methyls is in a staggered arrangement with the W–N bond for the *trans* phosphines [P(1) and P(2)] and eclipsed with P(3).

In complex **12** the effect of the *tert*-butyl group is to push P(1) and P(2) towards P(3) more than is observed in $[WCl_2(NC_6H_5)(PMe_3)_3]$ [P(1)–W–P(2) angles 162.99(3) and 169.1(1)° respectively] and also towards Cl(1). Interestingly, the N(1)–W–Cl(2) and N(1)–W–P(3) angles in complex **12** [98.9(1) and 91.1(1)° respectively] are smaller than in the phenylimido complex [103.3(1) and 95.2(1)° respectively]. The ^{1}H NMR spectrum indicates that in solution the *tert*-butyl group itself is able to rotate so there is apparently room for the methyls to move over the top of Cl(2). However molecular models show that it is unlikely that C(1)–N bond rotation occurs easily to allow the *tert*-butyl group to pass over the phosphine ligands. Low temperature studies in CD_2Cl_2 down to −75 °C show no broadening of the *tert*-butyl group resonance that would indicate geared rotation[5] and no changes were observed in the aromatic region of the spectrum.

A crystal structure determination shows that the 2-phenylphenylimido complex **13** (Fig. 4) is more like $[WCl_2(NC_6H_5)(PMe_3)_3]$ than 2-*tert*-butylphenylimido complex **12**. Selected bond lengths and angles for **13** are contained in Table 6. The W–N bond lengths are similar [1.764(3) and 1.755(3) Å respectively], as are the W–Cl(1) bond lengths [2.499(1) and 2.501(1) Å] and W–Cl(2) bond lengths [2.492(1) and 2.494(1) Å]. However, the W–P bonds for the *trans* phosphines in **13** are more similar in length to those in 2-*tert*-butylphenylimido complex **12** [W–P(1) and W–P(2) 2.504(1) and 2.507(1) Å for **12** and 2.501(1), 2.515(1) Å for **13** respectively] whereas the W–P(3) bonds in **13** are more like those in the phenylimido complex [2.458(1) and 2.453(1) Å respectively].

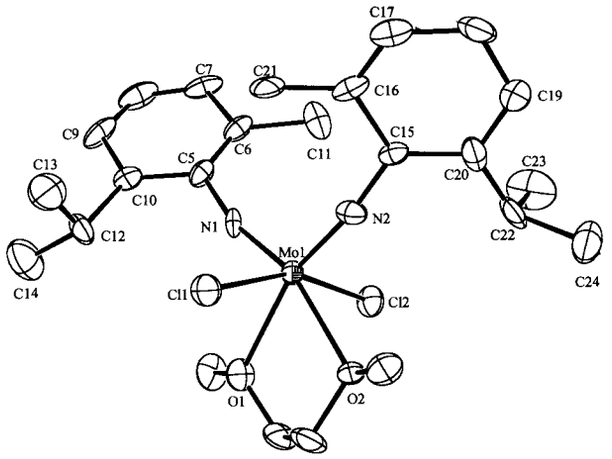
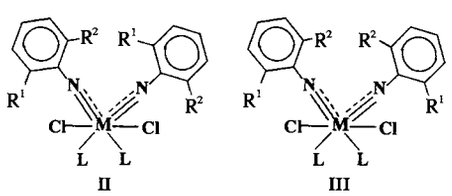


Fig. 5 Molecular structure of complex **15**, without H atoms and with key atoms labelled.

The 2-phenyl substituent in complex **13** lies over and between P(1) and Cl(2) to avoid placing the aromatic ring over Cl(2) and this places the C(2) proton over and between P(2) and P(3). The phenylimide ring orientation is thus similar to that found in the phenylimido complex. So also are the configurations of the PMe_3 ligands where two of the P(1) and P(2) methyls are staggered with respect to the W–N bond and a P(3) methyl is eclipsed. Whereas the N–W–P(2) bond angles are similar in complex **13** and the phenylimido complex [89.9(1) and 90.0(1)° respectively], the 2-phenyl substituent forces the N–W–P(1) angle to widen [95.3(1) and 89.7(1)° for the respective complexes] but the N–W–P(3) angles are similar [93.6(1) and 95.2(1)°] as are the N–W–Cl(2) angles [102.8(1) and 103.2(1)°]. The 2-phenyl substituent thus does not appear to influence the molecule drastically since there is room for the imido ligand to bend back between P(2) and P(3) in the absence of a substituent at C(2). The ^{1}H NMR spectrum shows that rotation of the 2-phenyl group is possible but molecular models suggest it is unlikely that it will pass easily over the phosphines. It should be noted that the absence of C–N bond rotations in the d^2 molecules is predicted on the basis of structural data and an analysis of simple molecular models. The NMR spectra observed could arise from either locked or free C–N bond rotation and it would be difficult to differentiate between the two unless locking gave rise to asymmetry in the molecules.

Bis(imido)molybdenum(VI)

In bis-imido complexes with different phenyl ring *ortho*-substituents there is the possibility of forming *syn* and *anti* type isomers (structures **II** and **III**) if rotation of the imido C–N



bonds is impeded. Preparation of $[MoCl_2(NC_6H_3Me\text{-}2\text{-}Pr^i\text{-}6)_2(dme)]$ **15** was carried out by treating the arylamine with Na_2MoO_4 in dimethoxymethane in the presence of Me_3SiCl and Et_3N.[22] The ^{1}H and ^{13}C-{^{1}H} NMR spectra of **15** show the presence of what appears to be only one isomer in solution with one set of resonances for the isopropyl and methyl group substituents on the imido ligand phenyl ring.

A crystal structure determination of complex **15** shows a distorted octahedral molecule (Fig. 5) which has bond distances and bond angles (Table 7) little different from a variety of bis-imido complexes of the same type.[6,22–24] The phenyl rings of the imido ligands lie with isopropyl and methyl groups of the two rings opposite to each other thus forming the *anti* type isomer. Whereas the methyl groups lie almost over and above the two chloro ligands, the isopropyl groups lie over, but between, a chloro ligand and a methyl group of the dme ligand. These methyl groups push away towards the chloro ligand side of the molecule to relieve interaction with the isopropyl methine proton. Based on the crystal structure and an analysis of simple molecular models it appears unlikely that the imido ligands are able to rotate since it would be difficult for the isopropyl and methyl groups to pass over the dme ligand methyls without the Mo–N–C bond angles [165.8(6) and 171.3(6)°] bending considerably which in turn would force the other *ortho* substituent into the π-electron density of an adjacent phenyl ring. In 5-co-ordinate bis-imido complexes where the dme ligand is not present the N–M–N bond angles can open out more than in **15** [bond angle 105.4(1)°] and allow an *ortho* substituent to pass over an adjacent phenyl ring without overdue M–N–C bond angle bending.[25]

$[MoCl_2(NC_6H_4CMe_3\text{-}2)_2(dme)]$ **16** has been prepared before.[26] The NMR spectra of this complex prepared in the present work indicated that two isomers were present in $CDCl_3$ solution (ratio 8.3 : 1.7). When a concentrated dme solution was allowed to stand a small quantity of crystalline material was produced and no more was formed after filtering and concentrating the solution further. NMR spectra of the solid obtained from this solution showed the minor component of the original mixture to be almost absent. A crystal structure determination of the minor component **16a** showed two crystallographically distinct but chemically similar molecules, A and B, in the asymmetric unit. Each molecule exhibits a distorted octahedral structure (Fig. 6 for molecule A) in which both *tert*-butyl substituents of the phenyl rings lie on the same side of the molecule characteristic of the *syn*-type isomer. A similar structure has been found for $[MoCl_2(NC_6H_4CN\text{-}2)_2(dme)]$[26] but the ^{1}H NMR spectrum reported does not indicate the presence of *syn* and *anti* isomers.

There is very little difference in the bond lengths between complexes **16a** (Table 8) and **15** except that the two Mo–N bonds are more similar [1.773(2),1.773(2) and 1.746(2), 1.739(2) Å in **16a**; 1.769(7) and 1.718(7) Å in **15**]. The N–Mo–N bond angles are not very different in both complexes [104.6(1), 102.9(1)° in **16a** and 105.4(1)° in **15**] but the *tert*-butyl groups in **16a** push away from the adjacent chloro ligand [Cl(1) in A and Cl(3) in B],opening out the N–Mo–Cl bond angles [N(1)–Mo(1)–Cl(1), 98.4(1); N(3)–Mo(2)–Cl(3) 99.3(1); *cf.* N(2)–Mo(1)–Cl(2), 93.4(1); N(4)–Mo(2)–Cl(4) 91.5(1)°]. These

Table 7 Selected bond lengths (Å) and bond angles (°) for $[MoCl_2(NC_6H_3Me\text{-}2\text{-}Pr^i\text{-}6)_2(dme)]$ **15**

Mo(1)–N(1)	1.769(7)	Mo(1)–Cl(2)	2.415(2)
Mo(1)–N(2)	1.718(7)	Mo(1)–O(1)	2.317(6)
Mo(1)–Cl(1)	2.415(2)	Mo(1)–O(2)	2.372(5)
N(1)–Mo(1)–N(2)	105.4(1)	N(2)–Mo(1)–O(2)	92.4(3)
N(1)–Mo(1)–Cl(1)	96.2(2)	Cl(1)–Mo(1)–O(1)	82.6(2)
N(1)–Mo(1)–Cl(2)	96.8(3)	Cl(1)–Mo(1)–O(2)	79.2(2)
N(1)–Mo(1)–O(1)	92.2(3)	Cl(1)–Mo(1)–Cl(2)	158.57(2)
N(1)–Mo(1)–O(2)	162.2(3)	Cl(2)–Mo(1)–O(1)	80.0(2)
N(2)–Mo(1)–Cl(1)	97.2(3)	Cl(2)–Mo(1)–O(2)	82.7(2)
N(2)–Mo(1)–Cl(2)	95.7(3)	Mo(1)–N(1)–C(5)	165.8(6)
N(2)–Mo(1)–O(1)	162.3(3)	Mo(1)–N(2)–C(15)	171.3(6)
N(1)–C(5)–C(6)	121.8(7)	N(2)–C(15)–C(16)	117.4(7)
N(1)–C(5)–C(10)	115.2(8)	N(2)–C(15)–C(20)	122.3(8)
C(5)–C(6)–C(11)	123.9(6)	C(15)–C(16)–C(21)	118.1(7)
C(7)–C(6)–C(11)	116.9(7)	C(17)–C(16)–C(21)	124.8(7)
C(5)–C(10)–C(12)	121.8(8)	C(15)–C(20)–C(22)	120.5(8)
C(9)–C(10)–C(12)	123.8(8)	C(19)–C(20)–C(22)	119.8(8)
C(10)–C(12)–C(13)	108.8(8)	C(20)–C(22)–C(23)	109.5(8)
C(10)–C(12)–C(14)	110.6(8)	C(20)–C(22)–C(24)	115.4(9)
C(13)–C(12)–C(14)	110.3(9)	C(23)–C(22)–C(24)	110.8(9)

Table 8 Selected bond lengths (Å) and bond angles (°) for [$MoCl_2$-($NC_6H_4CMe_3$-2)$_2$(dme)] **16**

Molecule A		Molecule B	
Mo(1)–N(1)	1.773(2)	Mo(2)–N(3)	1.773(2)
Mo(1)–N(2)	1.746(2)	Mo(2)–N(4)	1.739(2)
Mo(1)–Cl(1)	2.3957(7)	Mo(2)–Cl(3)	2.3984(8)
Mo(1)–Cl(2)	2.4277(8)	Mo(2)–Cl(4)	2.4102(8)
Mo(1)–O(1)	2.324(2)	Mo(2)–O(3)	2.324(2)
Mo(1)–O(2)	2.395(2)	Mo(2)–O(4)	2.435(2)
N(1)–Mo(1)–N(2)	104.62(11)	N(3)–Mo(2)–N(4)	102.89(12)
N(1)–Mo(1)–Cl(1)	98.36(8)	N(3)–Mo(2)–Cl(3)	99.30(8)
N(1)–Mo(1)–Cl(2)	92.89(8)	N(3)–Mo(2)–Cl(4)	93.61(8)
N(1)–Mo(1)–O(1)	96.71(9)	N(3)–Mo(2)–O(3)	97.07(10)
N(1)–Mo(1)–O(2)	166.92(9)	N(3)–Mo(2)–O(4)	167.06(10)
N(2)–Mo(1)–Cl(1)	99.88(8)	N(4)–Mo(2)–Cl(3)	100.23(8)
N(2)–Mo(1)–Cl(2)	93.40(8)	N(4)–Mo(2)–Cl(4)	91.47(8)
N(2)–Mo(1)–O(1)	157.73(9)	N(4)–Mo(2)–O(3)	158.64(10)
N(2)–Mo(1)–O(2)	88.19(9)	N(4)–Mo(2)–O(4)	89.74(10)
Cl(1)–Mo(1)–Cl(2)	159.78(3)	Cl(3)–Mo(2)–Cl(4)	160.12(3)
Cl(1)–Mo(1)–O(1)	83.00(5)	Cl(3)–Mo(2)–O(3)	83.78(6)
Cl(1)–Mo(1)–O(2)	81.68(5)	Cl(3)–Mo(2)–O(4)	80.93(6)
Cl(2)–Mo(1)–O(1)	79.02(6)	Cl(4)–Mo(2)–O(3)	79.66(6)
Cl(2)–Mo(1)–O(2)	83.59(5)	Cl(4)–Mo(2)–O(4)	83.13(6)
O(1)–Mo(1)–O(2)	70.28(7)	O(3)–Mo(2)–O(4)	70.05(7)
Mo(1)–N(1)–C(5)	146.6(2)	Mo(2)–N(3)–C(35)	141.0(2)
Mo(1)–N(2)–C(15)	167.4(2)	Mo(2)–N(4)–C(45)	165.1(2)
N(1)–C(5)–C(6)	116.1(3)	N(3)–C(35)–C(36)	116.5(3)
N(1)–C(5)–C(10)	123.5(3)	N(3)–C(35)–C(40)	123.0(3)
C(5)–C(10)–C(11)	122.5(3)	C(35)–C(40)–C(41)	122.5(3)
C(9)–C(10)–C(11)	121.1(3)	C(39)–C(40)–C(41)	121.6(3)
C(10)–C(11)–C(12)	109.9(2)	C(40)–C(41)–C(42)	110.7(3)
C(10)–C(11)–C(13)	111.9(3)	C(40)–C(41)–C(43)	109.4(3)
C(10)–C(11)–C(14)	110.0(2)	C(40)–C(41)–C(44)	112.3(3)
C(12)–C(11)–C(13)	107.7(3)	C(42)–C(41)–C(43)	110.2(3)
C(12)–C(11)–C(14)	110.1(3)	C(42)–C(41)–C(44)	107.1(3)
C(13)–C(11)–C(14)	107.2(3)	C(43)–C(41)–C(44)	107.0(3)
N(2)–C(15)–C(16)	114.7(3)	N(4)–C(45)–C(46)	114.6(3)
N(2)–C(15)–C(20)	124.1(3)	N(4)–C(45)–C(50)	124.1(3)
C(15)–C(20)–C(21)	122.8(2)	C(45)–C(50)–C(51)	122.8(3)
C(19)–C(20)–C(21)	121.5(3)	C(49)–C(50)–C(51)	121.5(3)
C(20)–C(21)–C(22)	108.3(2)	C(50)–C(51)–C(52)	108.6(2)
C(20)–C(21)–C(23)	111.4(2)	C(50)–C(51)–C(53)	112.5(2)
C(20)–C(21)–C(24)	111.7(3)	C(50)–C(51)–C(54)	111.3(3)
C(22)–C(21)–C(23)	110.1(3)	C(52)–C(51)–C(53)	109.2(3)
C(22)–C(21)–C(24)	107.9(3)	C(52)–C(51)–C(54)	108.8(3)
C(23)–C(21)–C(24)	107.3(3)	C(53)–C(51)–C(54)	106.4(2)

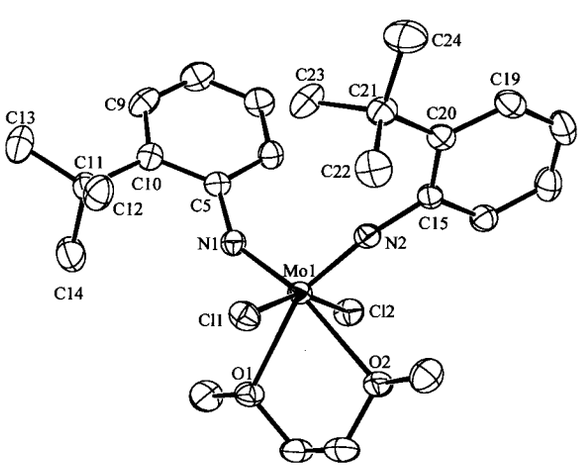


Fig. 6 Molecular structure of complex **16a**, without H atoms and with key atoms labelled.

widened angles are slightly greater than that observed for N(1)–Mo(1)–Cl(1) in complex **15** [96.2(2)°]. However, the Cl–Mo–Cl bond angles are very similar [158.57(2) in **15** and 159.78(3), 160.12(3)° in **16a**]. It is apparent from the structure of complex **16a** and from a consideration of simple molecular models that the *tert*-butyl groups cannot easily pass over dme ligand methyls if the *ortho*-proton of either imido ligand were to pass over the face of the adjacent imido phenyl ring. Thus imido ligand N–C bond rotation is unlikely to occur indicating that interconversion of the *syn* and *anti* forms of [$MoCl_2$-($NC_6H_4CMe_3$-2)$_2$(dme)] is not easy. This is also apparent from the absence of *syn* [$MoCl_2(NC_6H_4CMe_3$-2)$_2$(dme)] from NMR studies after crystallisation.

In general, M–N bond lengths and M–N–C bond angles are of interest in applications of imido complexes as nitrene transfer reagents.[1,27] In complex **16a** the two imido bond lengths are clearly different (*ca.* 0.02 Å). The longer Mo–N bond [bond length 1.773(2) Å for molecules A and B] is no different from that of the electronically controlled 1σ–2π W–N bond in the bis-imide [$WCl_2(NC_6H_3Pr^i_2$-2,6)(NCOC$_6H_4$Me-4)($OPMe_3$)-(PMe_3)][28] [bond length 1.769(5) Å] (Mo and W have similar atomic radii[29]) whereas the Mo–N–C bond angle [146.6(2) and 141.0(2)° for A and B] is much reduced in comparison with this tungsten complex [174.5(5)°]. The Mo–N bond length and Mo–N–C bond angle in molecule B are very similar to those found for the "bent" imido ligand in the classic "linear" and "bent" imido ligands in [$MoCl_2(NC_6H_5)_2(S_2CNEt_2)_2$][7,30] for which studies of related compounds point to the bending arising from crystal packing effects.[7]

Analysis of the structure of complex **16a** points to steric and crystal packing effects for this bending. From the diagram it can be seen that in molecule A the puckering of the dme ligand brings C(4) forward and C(1) back. As a result, C(22) and C(23) of the N(2) *tert*-butyl group straddle Cl(1) with contacts of 3.74 and 4.24 Å respectively. These approaches contribute to the bending of the Mo(1)–N(2)–C(15) angle [167.4(2)°] but there is an intermolecular contact of 3.64 Å [C(23)···C(48)] which also must have an effect. For the other phenylimido ligand [N(1)] the Mo(1)–N(1)–C(5) angle is even lower [146.6(2)°] and this appears to result from steric pressures between the *tert*-butyl group and Cl(1) as well as a crystal packing effect [C(12)···C(16)′, 3.51 Å]. With the bending of this phenyl imido ligand, C(6) of the aromatic ring approaches to within 3.69 Å of Cl(2) so that there is little leeway for this angle to reduce still further, although in molecule B a value of 141.0(2)° is observed. The lower angle is apparently accommodated by small changes elsewhere in the molecule. The crystal structure of [$MoCl_2(NC_6H_4CN$-2)$_2$(dme)][24] also shows a *syn* arrangement of the *ortho* substituents but with the less bulky cyano groups present there is more room on the substituent side of the complex and the Mo–N–C bond angles are 166.5(3) and 158.4(3)°. A steric effect responsible for "linear" bis-imide ligands has been identified in [$Mo(NC_6H_3Pr^i_2$-2,6)$_2$(S_2CNEt_2)$_2$].[31]

Conclusion

The results of this work show that, to restrict phenylimido ligand C–N bond rotation with a large *ortho* substituent, ligands larger than the 4 chloro groups in [Hpy][$TaCl_4$-($NC_6H_4CMe_3$-2)(py)] **1** are needed. This type of substituent leads to solution dynamics in the [{WCl_4(NAr)}$_x$] complexes and cyclometallation is possible during complex formation with the isocyanate reaction. The substituted phenylimido ligands are easily accommodated in the relative d^1 [WCl_3(NAr)($P)_2$] and d^2 [WCl_2(NAr)($P)_3$] complexes by small distortions within the molecules and a suitable positioning of the imido phenyl ring substituent over, but between, phosphine and chloro ligands (naphthylimido and 2-phenylphenylimido complexes **6** and **13**) or over a chloro ligand (2-*tert*-butylphenylimido complex **12**). The naphthylimido ligand is similar in effect to an isopropyl group as seen in a 2,6-diisopropylphenylimide but is much more rigid and operates sterically in one direction only. Structural analysis and simple molecular models indicate that movement of substituents over the phosphines is unlikely. Recent theoretical calculations on [WCl_3(NPh)($PH_3)_2$] show that even an unsubstituted phenylimido ligand experiences unfavourable

steric effects as it rotates over a PH_3 ligand.[32] Low temperature NMR studies indicate that geared rotation does not occur for the 2-*tert*-butylphenylimido complex **12**. With the bis-imido molybdenum complexes **15** and **16** where unsymmetrically substituted imido ligands could give rise to rapid *syn*- and *anti*-type isomer interconversion, if imido ligand N–C bond rotation occurred, the studies indicate that both these isomer types can exist independently where the imido ligand phenyl ring contains a 2-*tert*-butyl substituent.

Experimental

All preparations and manipulations were carried out under dry oxygen-free nitrogen using standard bench-top techniques for air-sensitive substances. 2-*tert*-Butylaniline, 2-aminobiphenyl, 2-isopropyl-6-methylaniline and 1-naphthyl isocyanate were obtained from Aldrich. Chlorotrimethylsilane was distilled before use and trimethylamine dried over and distilled from freshly ground CaH_2. Trimethylphosphine was prepared by reaction of MgMeI with $P(OPh)_3$ in di-*n*-butyl ether[33] and PMe_2Ph by the reaction of MgMeI with PCl_2Ph. Na_2MoO_4 was obtained by drying $Na_2MoO_4 \cdot 2H_2O$ under vacuum with a heat gun. [$\{WCl_4(O)_x\}$] was prepared by refluxing H_2WO_3 in thionyl chloride.[34] [$TaCl_3(NCMe_3)(py)_2$] was prepared by a literature procedure.[11] Phosgene $COCl_2$ was obtained from Matheson Gases and used as supplied. Light petroleum (bp 40–60 °C), benzene, toluene and dimethoxyethane were distilled from sodium wire and dichloromethane from freshly ground CaH_2. ^1H and ^{13}C-{^1H} NMR spectra were recorded at 400 and 100 MHz respectively on a Bruker AM400 spectrometer. C, H and N analyses were determined by Dr A. Cunninghame and associates, University of Otago, New Zealand.

Preparations

[Hpy][$TaCl_4(C_6H_4CMe_3$-2)(py)] 1. A solution of 2-*tert*-butylaniline (0.28 g, 1.88 mmol) in benzene (20 cm^3) was added to a solution of [$TaCl_3(NCMe_3)(py)_2$] (1.07 g, 2.07 mmol) in benzene (40 cm^3) and the mixture refluxed for 14 h. The cooled solution was filtered and the solvent removed giving an orange microcrystalline solid after drying *in vacuo*. The solid was extracted into CH_2Cl_2 and the solution cooled to −20 °C giving 0.43 g of the complex as orange needles. X-Ray structural analysis showed this material to be [Hpy][$TaCl_4(C_6H_4CMe_3$-2)(py)]·CH_2Cl_2. Under vacuum some CH_2Cl_2 is lost and the solid analyses as [Hpy][$TaCl_4(C_6H_4CMe_3$-2)(py)]·$0.5CH_2Cl_2$ (see Table 1).

Isocyanates. *Method A: 2-tert-butylphenyl isocyanate.* 2-*tert*-Butylaniline (7.96 g, 53.3 mmol) was dissolved in toluene (150 cm^3) in a 500 cm^3 two necked round bottom flask containing a magnetic stirring bar and equipped with a gas tap and a reflux condenser to which a balloon was attached at the top as well as a ventilating gas tap. **CAUTION**: phosgene is an extremely toxic gas and should be used in a well ventillated hood. Traces of the gas produce a smell similar to that formed by rotting hay. Phosgene was passed into the system *via* the gas tap to blow the balloon to approximately 500 cm^3 (judged by comparison with the size of the reaction vessel) and the gas tap turned off. The solution was stirred until the balloon had collapsed and the process repeated 4 times more. (This method ensures that more than the required 2 equivalents of phosgene dissolve in the toluene solution.) The mixture was heated to reflux and the HCl gas vented from the balloon *via* the gas tap attached to the reflux condenser until gas production ceased. The balloon was filled with 500 cm^3 of phosgene and the solution refluxed for 1h. Distillation (42–44 °C, 0.2 mmHg) gave 15.7 g (85%) of the isocyanate.

Method B: 2-phenylphenyl isocyanate. 2-Aminobiphenyl (6.76 g, 39.9 mmol) in toluene (100 cm^3) was treated with phosgene (approximately 2 L) as for the synthesis above. Distillation (118–119 °C, 0.8 mmHg) gave 6.35 g (82%) of the isocyanate.

[$\{WCl_4(NC_{10}H_7)\}_x$] 2. 1-Naphthyl isocyanate (5.3 cm^3, 36.9 mmol) was added to a suspension of $WOCl_4$ (12.6 g, 36.9 mmol) in benzene (100 cm^3) and the mixture refluxed for 14 h. The solution was filtered and the solid washed twice with benzene (20 cm^3) followed by light petroleum (30 cm^3) and dried under vacuum to give 14.7 g of product.

[$\{WCl_4(NC_6H_4CMe_3$-2)$\}_x$] 3. 2-*tert*-Butylphenyl isocyanate (5.3 g, 30.4 mmol) and $WOCl_4$ (10.4 g, 30.4 mmol) were refluxed in benzene (60 cm^3) for 14 h. The solution was filtered and the solid washed twice with benzene (15 cm^3) followed by light petroleum (20 cm^3) and dried under vacuum to give 10 g of product.

[$\{WCl_4(NC_6H_4Ph$-2)$\}_x$] 4. 2-Phenylphenyl isocyanate (2.0 g, 10.2 mmol) and $WOCl_4$ (3.5 g, 10.2 mmol) were refluxed in toluene (90 cm^3) for 15 h. The solution was filtered and the solid washed twice with light petroleum (15 cm^3) and dried under vacuum to give 4.5 g of product.

[WCl_4{$HNC_6H_4(CMe_2CH_2)$-2(*C*,*N*)}] 5. 2-*tert*-Butylphenyl isocyanate (3.55 g, 20.3 mmol) and $WOCl_4$ (6.7 g, 19.6 mmol) were refluxed in toluene (60 cm^3) for 14 h. The solution was filtered and the solid washed with toluene (7 cm^3) followed by light petroleum (20 cm^3) and dried under vacuum to give 3 g (32%) of complex **2**. The solvent was removed from the reaction filtrate leaving an oil which on washing with toluene (10 cm^3) and light petroleum (20 cm^3) gave the metallacyclic amide (4 g).

[$WCl_3(NC_{10}H_7)(PMe_3)_2$] 6. A suspension of [$\{WCl_4(NC_{10}H_7)\}_2$] (1.2 g,1.3 mmol) in benzene (80 cm^3) was added to sodium–mercury amalgam (Na, 0.060 g, 2.6 mmol; Hg, 26 g) under benzene (20 cm^3) containing PMe_3 (0.54 cm^3, 5.3 mmol) using a cannula and the mixture stirred for 1.5 h. The solution was filtered, the solvent removed, and the solid recrystallised from toluene at −20 °C to give 1.2 g of the product. Crystals for X-ray analysis and the analytical sample were grown from a dichloromethane solution layered with light petroleum.

[$WCl_3(NC_6H_4CMe_3$-2)$(PMe_3)_2$] 7. A suspension of [$\{WCl_4(NC_6H_4CMe_3$-2)$\}_2$] (1.5 g,1.6 mmol) in benzene (80 cm^3) was added to sodium–mercury amalgam (Na, 0.080 g, 3.3 mmol; Hg, 29 g) under benzene (10 cm^3) containing PMe_3 (0.71 cm^3, 6.4 mmol) using a cannula and the mixture stirred for 7 h. The solution was filtered, the solvent removed and the solid recrystallised from CH_2Cl_2 and light petroleum to give 1.5 g of product.

[$WCl_3(NC_6H_4Ph$-2)$(PMe_3)_2$] 8. A suspension of [$\{WCl_4(NC_6H_4Ph$-2)$\}_2$] (0.7 g, 0.71 mmol) in benzene (40 cm^3) was added to sodium–mercury amalgam (Na, 0.038 g, 1.7 mmol; Hg, 23 g) under benzene (10 cm^3) containing PMe_3 (0.71 cm^3, 6.4 mmol) using a cannula and the mixture stirred for 14 h. The solution was filtered, the solvent removed and the solid recrystallised from CH_2Cl_2 and light petroleum to give 0.5 g of product.

[$WCl_3(NC_{10}H_7)(PMe_2Ph)_2$] 9. A suspension of [$\{WCl_4(NC_{10}H_7)\}_2$] (1.3 g, 1.4 mmol) in benzene (50 cm^3) was added to sodium–mercury amalgam (Na, 0.066 g, 2.9 mmol; Hg, 25 g) under benzene (10 cm^3) containing PMe_2Ph (0.78 cm^3, 5.6 mmol) using a cannula and the mixture stirred for 5 h. The solution was filtered, the solvent removed and the solid recrystallised from CH_2Cl_2 and light petroleum to give 1.2 g of the product.

[$WCl_3(NC_{10}H_7)(PMePh_2)_2$] 10. A suspension of [$\{WCl_4(NC_{10}H_7)\}_2$] (1.0 g, 1.1 mmol) in benzene (50 cm^3) was added to

Table 9 Crystallographic data for compounds

	1	6	12	13	15	16
Formula	$[C_{15}H_{18}Cl_4N_2Ta]$-$[C_5H_6N]\cdot CH_2Cl_2$	$C_{16}H_{25}Cl_3P_2W$	$C_{19}H_{40}Cl_2NP_3W\cdot 0.5\ C_7H_8$	$C_{21}H_{36}Cl_2NP_3W$	$C_{24}H_{36}Cl_2MoN_2O_2$	$C_{24}H_{36}Cl_2MoN_2O_2$
M	714.10	583.51	675.74	650.17	551.39	551.39
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$	Cc	$P\bar{1}$
a/Å	8.3472(1)	8.618(1)	8.6878(8)	9.1057(1)	17.5980(1)	8.7929(1)
b/Å	10.0506(2)	27.756(4)	9.4309(1)	15.0474(1)	10.0198(2)	16.8765(1)
c/Å	16.8679(2)	9.486(2)	19.9949(8)	19.8071(1)	14.9081(3)	18.3315(2)
α/°	100.66(1)	90.00(1)	90.391(8)	90.0	90.0	76.505(1)
β/°	93.253(1)	103.90(2)	94.694(1)	90.0	99.119(1)	88.259(1)
γ/°	93.475(1)	90.00(1)	116.93(1)	90.0	90.0	86.306(1)
U/Å^3	1384.82(4)	2202.7(7)	1453.94(3)	2713.91(4)	2595.50(8)	2639.34(4)
Z	2	4	2	4	4	4
D_c/g cm^3	1.713	1.760	1.544	1.591	1.411	1.388
μ(Mo-Kα)/mm^{-1}	4.562	5.752	4.332	4.638	0.733	0.721
T/K	203(2)	293(2)	203(2)	203(2)	203(2)	203(2)
R_1, $wR2$ [$I > 2\sigma(I)$]	0.0427, 0.1107	0.0603, 0.1560	0.0261, 0.0675	0.0206, 0.0465	0.0198, 0.0526	0.0344, 0.0749
R_1, $wR2$ (all data)	0.0507, 0.1157	0.0933, 0.1756	0.0275, 0.0683	0.0216, 0.0468	0.0230, 0.0543	0.0499, 0.0914
Data, parameters	6022, 283	4268, 255	6288, 263	6009, 262	3639, 281	11281, 559
Observed data [$I > 2\sigma(I)$]	5279	3106	6046	5817	3347	9295

sodium–mercury amalgam (Na, 0.041 g, 2.1 mmol; Hg, 27 g) under benzene (10 cm^3) containing $PMePh_2$ (0.8 cm^3, 4.2 mmol) using a cannula and the mixture stirred for 2 h. The solution was filtered, the solvent removed and the solid recrystallised from CH_2Cl_2 and light petroleum to give 1.0 g of the product.

$[WCl_2(NC_{10}H_7)(PMe_3)_3]$ 11. A suspension of $[\{WCl_4(NC_{10}H_7)\}_2]$ (1.35 g, 1.5 mmol) in benzene (80 cm^3) was added to sodium–mercury amalgam (Na, 0.141 g, 6.1 mmol; Hg, 105 g) under benzene (20 cm^3) containing PMe_3 (1.0 cm^3, 9.7 mmol) using a cannula and the mixture stirred for 4 h. The solution was filtered, the solvent removed and the solid recrystallised from CH_2Cl_2 and light petroleum to give 1.2 g of the product.

$[WCl_2(NC_6H_4CMe_3\text{-}2)(PMe_3)_3]$ 12. A suspension of $[\{WCl_4(NC_6H_4CMe_3\text{-}2)\}_2]$ (2.5 g, 2.64 mmol) in toluene (120 cm^3) was added to sodium–mercury amalgam (Na, 0.080 g, 3.3 mmol; Hg, 29 g) under toluene (10 cm^3) containing PMe_3 (1.3 cm^3, 7.9 mmol) using a cannula and the mixture stirred for 14 h. The solution was filtered and the solvent removed giving 2.9 g of the product. Recrystallisation from CH_2Cl_2 layered with light petroleum gave the analytical sample and the crystals used for X-ray crystallography were obtained from toluene.

$[WCl_2(NC_6H_4Ph\text{-}2)(PMe_3)_3]$ 13. A suspension of $[\{WCl_4(NC_6H_4CMe_3\text{-}2)\}_2]$ (1.5 g, 1.5 mmol) in benzene (60 cm^3) was added to sodium–mercury amalgam (Na, 0.15 g, 6.5 mmol; Hg, 46 g) under benzene (20 cm^3) containing PMe_3 (1.0 cm^3, 9.1 mmol) using a cannula and the mixture stirred for 14 h. The solution was filtered and the solvent removed giving 1.5 g of the product. Recrystallisation from toluene at room temperature gave crystals that were used for the analytical sample and one was used for X-ray crystallography.

$[WCl_2(NC_{10}H_7)(PMe_2Ph)_3]$ 14. A solution of $[WCl_3(NC_{10}H_7)(PMePh_2)_2]$ **10** (0.8 g, 1.1 mmol) in benzene (40 cm^3) was added to sodium–mercury amalgam (Na, 0.027 g, 1.2 mmol; Hg, 26 g) under benzene (10 cm^3) containing PMe_2Ph (0.15 cm^3, 1.1 mmol) using a cannula and the mixture stirred for 14 h. The solution was filtered twice and the solvent removed giving 0.8 g of the product. The analytical sample was obtained by recrystallising from a mixture of CH_2Cl_2 and light petroleum.

$[MoCl_2(NC_6H_3Me\text{-}2\text{-}Pr^i\text{-}6)_2(dme)]$ 15. 2-Isopropyl-6-methylaniline (2.46 g, 16.5 mmol) in dme (50 cm^3) was added to a stirred suspension of Na_2MoO_4 (1.7 g, 8.25 mmol) in dme (50 cm^3) followed by triethylamine (4.6 cm^3, 33.0 mmol). Chlorotrimethylsilane (8.4 cm^3, 66.0 mmol) was added dropwise and the mixture stirred for 16 h and refuxed for 8 h. The solution was filtered while hot and the residue washed with hot dme (2 × 50 cm^3). The combined dme solutions were kept hot while the solvent was removed to about 40 cm^3 and on cooling and standing the complex formed as a crystalline solid (2.86 g). A crystal from the sample was used for X-ray crystallography.

$[MoCl_2(NC_6H_4CMe_3\text{-}2)_2(dme)]$ 16. 2-*tert*-Butylaniline (2.46 g, 16.5 mmol) in dme (50 cm^3) was added to a stirred suspension of Na_2MoO_4 (1.7 g, 8.25 mmol) in dme (50 cm^3) followed by triethylamine (4.6 cm^3, 33.0 mmol). Chlorotrimethylsilane (8.4 cm^3, 66.0 mmol) was added dropwise and the mixture stirred for 16 h and refluxed for 8 h. The cooled solution was filtered and the solvent removed giving 4.43 g of crystalline solid. The analytical sample was obtained by dissolving a small portion of this solid in CH_2Cl_2 and layering the solution with light petroleum. The *syn* isomer was obtained by dissolving the remainder of the crude solid in dme (50 cm^3) and reducing the volume (*ca.* 20 cm^3). On standing at room temperature a small quantity of red-purple crystals was obtained one of which was used for X-ray crystallography.

X-Ray crystallography

Data for all structures except **6** were collected on a Siemens SMART diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å). These data collections covered a nominal sphere of reciprocal space by a combination of 4 sets of exposures. Each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. Coverage of the unique data sets was at least 98% complete to 56° in 2θ. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing the duplicate reflections. Unit cell parameters were obtained by a least-squares fit of all the data with $I > 10\sigma(I)$. Lorentz and polarisation corrections were applied and absorption corrections made by the method of Blessing.[35] Data for **6** were collected on a CAD4 diffractometer with graphite monochromated Mo-Kα radiation and ω–2θ scans at variable speed. Lorentz and polarisation corrections were applied using locally written programs and absorption corrections applied from empirical ψ scans. All structures were solved by Patterson and Fourier techniques and refined (on F^2) by full-matrix least-squares methods. All non-hydrogen atoms were allowed to assume anisotropic thermal motion. Hydrogen atoms were placed geometrically and refined with a riding model. In **6**

disorder was observed with the PMe_3 groups. Crystallographic data for the complexes are contained in Table 9. Programs used were SHELXS[36] for structure solution, SHELXL 93[37] for refinement and ORTEP 3[38] for diagrams.

CCDC reference number 186/2226.

See http://www.rsc.org/suppdata/dt/b0/b006420n/ for crystallographic files in .cif format.

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References

1 D. E. Wigley, *Prog. Inorg. Chem.*, 1994, **42**, 239.
2 G. R. Clark, A. J. Nielson and C. E. F. Rickard, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 1907.
3 A. J. Nielson, unpublished work.
4 G. R. Clark, A. J. Nielson and C. E. F. Rickard, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 4265.
5 F. Montilla, A. Galindo, E. Carmona, E. Gutierrez-Puebla and A. Monge, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 1299.
6 A. Bell, W. Clegg. P. W. Dyer, M. R. J. Elsegood, V. C. Gibson and E. L. Marshall, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2247.
7 P. Barrie, T. A. Goffey, G. D. Forster and G. Hogarth, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 4519.
8 Y.-W. Chao, P. A. Wexler and D. E. Wigley, *Inorg. Chem.*, 1989, **32**, 131.
9 M. Jolly, J. P. Mitchell and V. C. Gibson, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 1331.
10 T. C. Jones, A. J. Nielson and C. E. F Rickard, *J. Chem. Soc.*, *Dalton Trans.*, 1984, 205; P. A. Bates, A. J. Nielson and J. M. Waters, *Polyhedron*, 1985, **4**, 1391; A. J. Nielson, *Polyhedron*, 1988, **7**, 67.
11 H.-T. Chiu, S.-H. Chuang, C.-E. Tsai, G.-H. Lee and S.-M. Peng, *Polyhedron*, 1998, **17**, 2187.
12 P. E. Collier, S. C. Dunn, P. Mountford, O. V. Shishkin and D. Swallow, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 3743.
13 W. A. Nugent and R. L. Harlow, *J. Chem. Soc.*, *Chem. Commun.*, 1978, 579.
14 S. M. Rocklage and R. R. Schrock, *J. Am. Chem. Soc.*, 1982, **104**, 3077; M. R. Churchill and H. J. Wasserman, *Inorg. Chem.*, 1982, **21**, 223.
15 D. N. Williams, J. P. Mitchell, A. D. Poole, U. Siemeling, W. Clegg, D. C. R. Hockless, P. A. O'Neil and V. C. Gibson, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 739; T. C. Baldwin, S. R. Huber, M. A. Bruck and D. E. Wigley, *Inorg. Chem.*, 1993, **32**, 5682.
16 D. C. Bradley, M. B. Hursthouse, K. M. A. Malik, A. J. Nielson and G. B. C. Vuru, *J. Chem. Soc.*, *Dalton Trans.*, 1984, 1069.
17 W. C. Hamilton and J. A. Ibers, *Hydrogen Bonding in Solids*, Benjamin, New York, 1968.
18 D. C. Bradley, M. B. Hursthouse, K. M. A. Malik and A. J. Nielson, *J. Chem. Soc.*, *Chem. Commun.*, 1981, 103.
19 D. C. Bradley, M. B. Hursthouse, K. M. A. Malik, A. J. Nielson and R. L. Short, *J. Chem. Soc.*, *Dalton Trans.*, 1983, 2651.
20 A. J. Nielson, R. E. McCarley, S. L. Laughlin and C. D. Carlson, *Inorg. Synth.*, 1986, **24**, 193.
21 B. R. Ashcroft, G. R. Clark, A. J. Nielson and C. E. F. Rickard, *Polyhedron*, 1986, **5**, 2081; W. Clegg and R. J. Errington, *Acta Crystallogr.*, *Sect. C*, 1987, **43**, 2223; D. C. Bradley, R. J. Errington, M. B. Hursthouse and R. L. Short, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 1043.
22 P. W. Dyer, V. C. Gibson, J. A. K. Howard, B. Whittle and C. Wilson, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1666; R. C. B. Copley, P. W. Dyer, V. C. Gibson, J. A. K. Howard, E. L. Marshall, W. Wang and B. Whittle, *Polyhedron*, 1996, **15**, 3001.
23 V. C. Gibson, C. Redshaw, W. Clegg, M. A. J. Elsegood, U. Siemeling and T. Turk, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 4513; E. A. Kretzschmar, J. Kipke and J. Sundermeyer, *Chem. Commun.*, 1999, 2381; D. delRio, F. Montilla, A. Pastor, A. Galindo, A. Monge and E. Gutierrez-Puebla, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 2433.
24 V. C. Gibson, C. Redshaw, W. Clegg and M. R. J. Elsegood, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3207.
25 V. C. Gibson, C. Redshaw, G. L. P. Walker, J. A. K. Howard, V. J. Hoy, J. M. Cole, L. G. Kuzmina and D. S. De Silva, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 161; K. C. Chew, W. Clegg, M. P. Coles, M. R. J. Elsegood, V. C. Gibson, A. J. P. White and D. J. Williams, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2633.
26 H. H. Fox, Y. B. Yap, J. Robbins, S. Cai and R. R. Schrock, *Inorg. Chem.*, 1992, **31**, 2287.
27 W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123; W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley, New York, 1988.
28 A. J. Nielson, P. A. Hunt, C. E. F. Rickard and P. Schwerdtfeger, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3311.
29 R. D. Shannon, *Acta Crystallogr.*, *Sect. A*, 1976, **32**, 751.
30 B. L. Haymore, E. A. Maatta and R. A. D. Wentworth, *J. Am. Chem. Soc.*, 1979, **101**, 2063; E. A. Maatta and R. A. D. Wentworth, *Inorg. Chem.*,1979, **18**, 2409.
31 T. A. Coffey, G. D. Forster, G. Hogarth and A. Sella, *Polyhedron*, 1993, **12**, 2741.
32 G. Hogarth, D. G. Humphrey, N. Kaltsoyannis, W.-S. Kim, M.-Y. Lee, T. Norman and S. P. Redmond, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2705.
33 M. L. Luetkens, Jr., A. P. Sattlebergerer, H. H. Murray, J. D. Basil, J. P. Fackler, Jr., R. A. Jones and P. E. Heaton, *Inorg. Synth.*, 1990, **28**, 305.
34 A. J. Nielson and R. A. Anderson, *Inorg. Synth.*, 1984, **23**, 195.
35 R. H. Blessing, *Acta Crystallogr.*, *Sect. A*, 1995, **51**, 33.
36 G. M. Sheldrick, SHELXS, Institut Für Anorganische Chemie, Universität Göttingen, 1990.
37 G. M. Sheldrick, SHELXL 93, Institut Für Anorganische Chemie, Universität Göttingen, 1993.
38 ORTEP 3 for WINDOWS, Based on ORTEP III, C. K. Johnson and M. N. Burnett, Report ORNL-6895, modified by L. J. Farrugia, University of Glasgow, 1996.