

Synthesis of chloro and methyl imido cyclopentadienyl molybdenum and tungsten complexes. X-ray molecular structures of $[\text{WCp}^*\text{Cl}_3(\text{N}^t\text{Bu})]$, $[\text{MoCp}^*\text{ClMe}_2(\text{N}^t\text{Bu})]$ and $[\text{WCp}^*\text{ClMe}_2(\text{N}^t\text{Bu})]$ ¹

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Abstract

Alternative methods to prepare $[\text{MCp}'\text{Cl}_4]$, $[\text{MCp}'\text{Cl}_2(\text{N}^t\text{Bu})]$ and $[\text{MCp}'\text{Cl}_3(\text{N}^t\text{Bu})]$ [$\text{M} = \text{Mo}$, $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$ (Cp^*); $\text{M} = \text{W}$, $\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$ (Cp), $\eta^5\text{-C}_5\text{Me}_5$ (Cp^*)] in high yields are reported. Alkylation of $[\text{MCp}'\text{Cl}_3(\text{N}^t\text{Bu})]$ with stoichiometric amounts of LiMe or MeMgCl under appropriate conditions leads to the dimethyl $[\text{MCp}'\text{ClMe}_2(\text{N}^t\text{Bu})]$ and trimethyl $[\text{MCp}'\text{Me}_3(\text{N}^t\text{Bu})]$, ($\text{M} = \text{Mo}$, $\text{Cp}' = \text{Cp}^*$; $\text{M} = \text{W}$, $\text{Cp}' = \text{Cp}$, Cp^*) complexes. The 18-electron trimethyltungsten complex $[\text{WCp}^*\text{Me}_3(\text{N}^t\text{Bu})]$ reacts very slowly with $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ to give the insertion product $[\text{WCp}^*\{\text{C}(\text{Me}) = \text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}\text{Me}_2(\text{N}^t\text{Bu})]$. All of the new compounds reported were characterized by elemental analyses, IR and NMR spectroscopy and the X-ray molecular structures of $[\text{WCp}^*\text{Cl}_3(\text{N}^t\text{Bu})]$, $[\text{MoCp}^*\text{ClMe}_2(\text{N}^t\text{Bu})]$ and $[\text{WCp}^*\text{ClMe}_2(\text{N}^t\text{Bu})]$ have been determined by diffraction methods. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The chemistry of organoimido molybdenum and tungsten complexes has received much attention in the last few years because the imido ligand provides the desired electronic and steric control for molybdenum complexes to act as catalysts for ring-opening metathesis polymerization (ROMP) of cyclic olefins [1] and cyclopolymerization of acetylenes [2]. Formation of imido species has also been proposed as an intermediate step in the ammonoxidation of olefins [3]. Numerous terminal and bridging imido complexes of molybdenum [4] and tungsten [5] have been reported and the synthesis, structural characterization and reactivity of these types of compounds have been reviewed [6]. Related imido cyclopentadienyl complexes have also been studied, and a number of molybdenum and tungsten compounds have been reported [7]. We have previously reported the synthesis and reactivity of new tantalum [8], molybdenum and tungsten

[9] derivatives. In this work we present the results of our studies on the synthesis of chloro imido cyclopentadienyl molybdenum and tungsten(V) and (VI) compounds, their alkylation with Grignard and lithium reagents and the X-ray crystal structures of three of the new complexes.

2. Results and discussion

2.1. Synthesis of $[\text{MCp}'\text{Cl}_2(\text{N}^t\text{Bu})]$

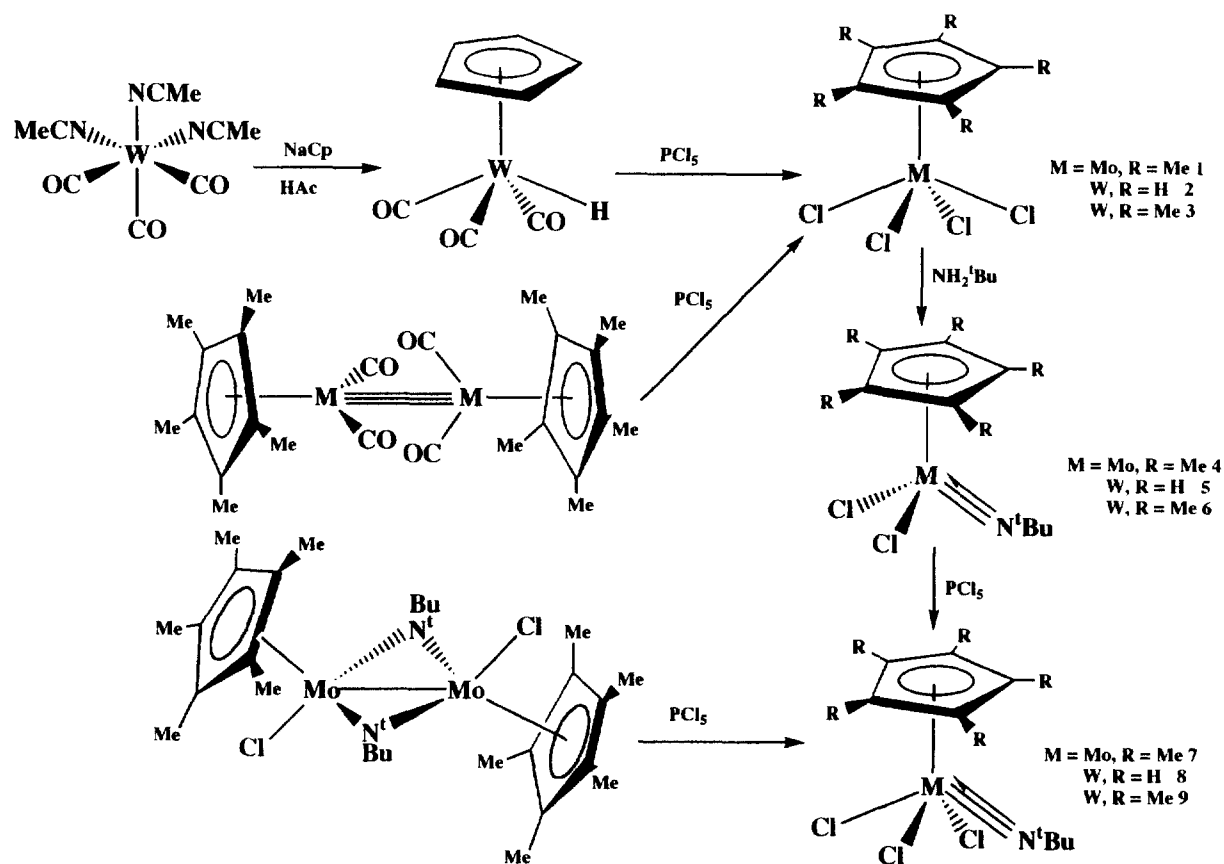
The best method to prepare cyclopentadienyltungsten(V) chlorides is the oxidation of low valent tungsten carbonyls based on the method first reported by Schrock and co-workers [10] to obtain $[\text{WCpCl}_4]$ by chlorination of $[\text{WCp}(\text{CO})_3\text{-Me}]$ with PCl_5 . However, the tedious isolation of the methyl carbonyl complex can be avoided, and the same method has subsequently been extended [11] to many other carbonyl derivatives which can be easily oxidized in a similar reaction. Using a modification of the method previously reported [12] we isolated the complex $[\text{W}(\text{CO})_3(\text{NCMe})_3]$ and used this compound instead of $\text{W}(\text{CO})_6$ [13] to prepare $[\text{WCp}(\text{CO})_3\text{H}]$ in yields higher than 95% by reaction with

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¹ Dedicated to a good scientist and good friend, Ivano Bertini.

² X-ray diffraction studies.

³ X-ray diffraction studies.



NaCp and subsequent addition of acetic acid in THF without isolation (Scheme 1). The compounds $[\text{MCp}^*(\text{CO})_2]_2$ ($\text{M} = \text{Mo}, \text{W}$) were prepared as previously described [14].

Treatment of $[\text{WCp}(\text{CO})_3\text{H}]$ and $[\text{MCp}^*(\text{CO})_2]_2$ ($\text{M} = \text{Mo}, \text{W}$) with an excess of PCl_5 in dichloromethane and toluene respectively followed by filtration afforded the almost insoluble complexes $[\text{MCp}'\text{Cl}_4]$, ($\text{M} = \text{Mo}, \text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$ (**1**) [10a]; $\text{M} = \text{W}, \text{Cp}' = \eta^5\text{-C}_5\text{H}_5$ (**2**) [11], $\eta^5\text{-C}_5\text{Me}_5$ (**3**) [10b]) in yields higher than 90%.

Reaction of complexes **1–3** with tert-butylamine led to the reported complexes $[\text{MCp}'\text{Cl}_2(\text{N}^t\text{Bu})]$ ($\text{M} = \text{Mo}, \text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$ (**4**) [7e,15]; $\text{M} = \text{W}, \text{Cp}' = \eta^5\text{-C}_5\text{H}_5$ (**5**) [7a,16], $\eta^5\text{-C}_5\text{Me}_5$ (**6**) [7e]).

2.2. Oxidation of $[\text{MCp}'\text{Cl}_2(\text{N}^t\text{Bu})]$

Addition of 0.5 mol of PCl_5 to a dichloromethane solution of complex $[\text{MoCp}^*\text{Cl}_2(\text{N}^t\text{Bu})]$ (**4**) led to the formation of the trichloro imido molybdenum(VI) complex $[\text{MoCp}^*\text{Cl}_3(\text{N}^t\text{Bu})]$ (**7**) [7a], which could also be obtained by reaction of the imido molybdenum(IV) derivatives *cis-trans*- $[\text{MoCp}^*\text{Cl}(\text{N}^t\text{Bu})]_2$ [15] with 1 mol of PCl_5 . Oxidation of complexes **5–6** with 1 equiv. of PCl_5 led to the formation of the reported [7a] $[\text{WCp}'\text{Cl}_3(\text{N}^t\text{Bu})]$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$ (**8**), $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$ (**9**)) (Scheme 1). Related molybdenum and tungsten complexes containing different cyclopentadienyl rings were also isolated using chlorine gas as the oxi-

dizing agent [16] and by selective reaction of the diimidometal(VI) derivatives $[\text{MCp}^*\text{Cl}(\text{N}^t\text{Bu})_2]$ with HCl [7a]. However, the oxidation of the imidomolybdenum(V) complexes described here is the most direct and easiest method to prepare the corresponding molybdenum(VI) compounds in high yield.

Complexes **7–9** were isolated as crystalline solids which were characterized by elemental analysis and IR and NMR spectroscopy (see Section 3) and the molecular structure of complex **9** was studied by X-ray diffraction methods.

The molecular structure of complex **9** is shown in Fig. 1 along with the labelling scheme. Selected bond distances and angles are presented in Table 1. The molecule shows a pseudo-square pyramidal coordination where the four square planar positions are occupied by the three chlorine atoms and the nitrogen atom of the imido N^tBu group.

The Cp(centroid)–W distance is a normal 2.121 Å, but the W–C(Cp) distances range from 2.297(6) to 2.595(6), showing an important *trans* influence of the N^tBu substituent which is responsible for the longest C3–W1 distance. All the W–Cl distances are similar. The W1–N1 distance of 1.736(4) Å and the W1–N1–C21 angle 174.8(4)° confirm the linear coordination of the formally triple bonded imido group. This structure is similar to that found for $\text{MoCp}^*\text{Cl}_3(\text{N}^t\text{Bu})$. The W1–N1 distance is even shorter than that found [17] for $\text{W}(\eta^5\text{-C}_5\text{Me}_5)(=\text{NAr})_2\text{Cl}$ where the

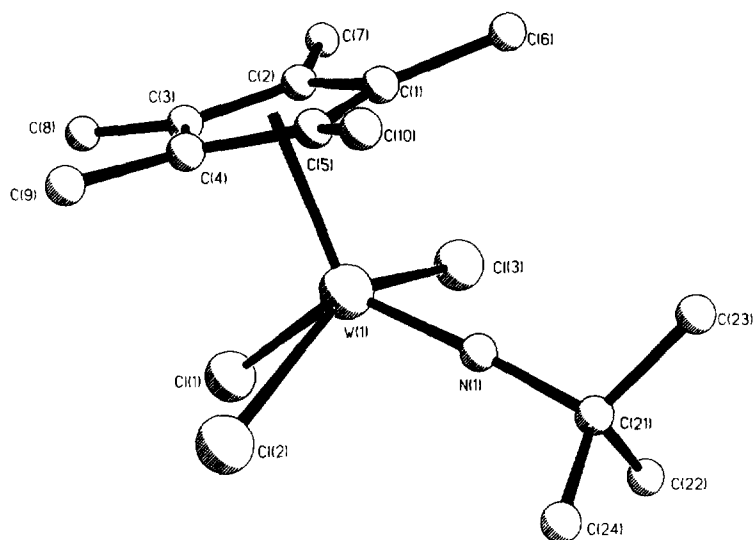


Fig. 1. Perspective view of the molecular structure of $[WCp^*Cl_3(N'Bu)]$ (**9**) with the atom-numbering scheme. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for **9**

W(1)–N(1)	1.736(4)	W(1)–Cl(1)	2.410(2)
W(1)–Cl(2)	2.402(2)	W(1)–Cl(3)	2.402(2)
W(1)–C(1)	2.302(5)	W(1)–C(2)	2.496(5)
W(1)–C(3)	2.595(5)	W(1)–C(4)	2.488(5)
W(1)–C(5)	2.297(5)	N(1)–C(21)	1.444(7)
C(1)–C(5)	1.416(8)	C(1)–C(2)	1.425(8)
C(2)–C(3)	1.416(8)	C(3)–C(4)	1.407(8)
C(4)–C(5)	1.425(8)	C(21)–C(22)	1.529(11)
C(21)–C(23)	1.509(12)	C(21)–C(24)	1.473(12)
W(1)–Cp(1)	2.121		
N(1)–W(1)–Cl(2)	86.4(2)	N(1)–W(1)–Cl(3)	87.1(2)
Cl(2)–W(1)–Cl(3)	145.77(7)	N(1)–W(1)–Cl(1)	128.8(2)
Cl(2)–W(1)–Cl(1)	79.03(7)	Cl(3)–W(1)–Cl(1)	79.11(8)
C(21)–N(1)–W(1)	174.8(4)		

Cp(1) is the centroid of the C(1) to C(5) ring.

W–N distance is 1.785(4) Å and the proposed bond order is greater than two.

2.3. Alkylation of $[MCp^*Cl_3(N'Bu)]$

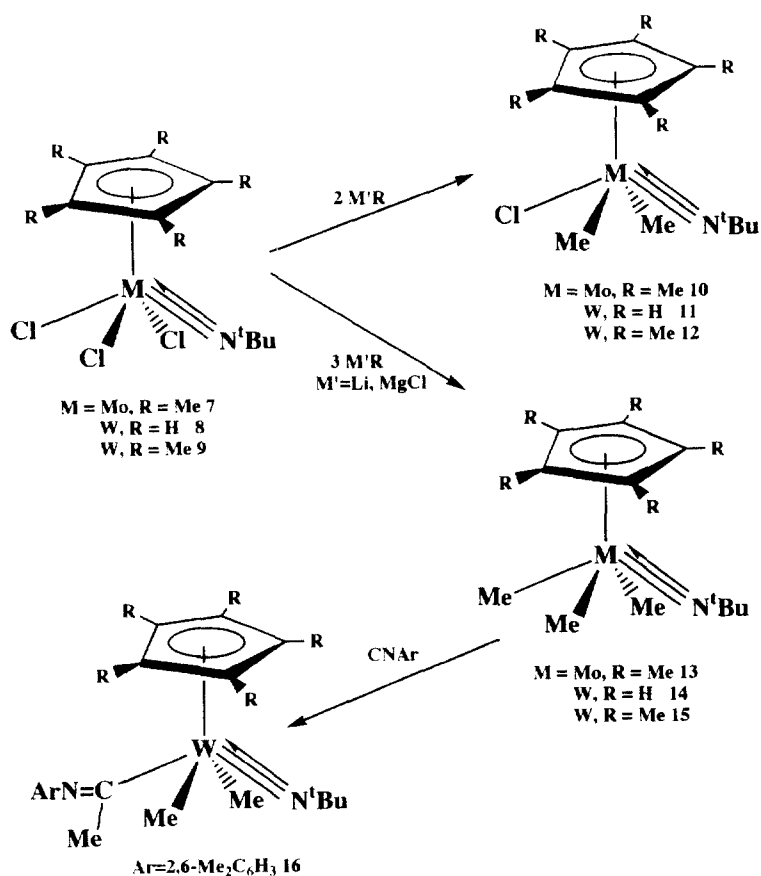
Alkylation of complex **7** with 2 equiv. of LiMe in diethyl-ether gave the dimethyl complex $[MoCp^*ClMe_2(N'Bu)]$ (**10**), which was isolated as a crystalline yellow solid after cooling the solution to $-78^\circ C$ (Scheme 2). The analogous reaction using 3 equiv. of the same alkylating agent led to the trimethyl complex $[MoCp^*Me_3(N'Bu)]$ (**13**) as a micro-crystalline orange solid. Both alkyl compounds **10** and **13** were moderately air-stable in the solid and very soluble in all organic solvents although they decomposed on heating their solutions above $70^\circ C$ to give unidentified brown paramagnetic products. They were characterized by elemental analyses, IR and NMR spectroscopy and the molecular structure of complex **10** was determined by X-ray diffraction.

The molecular structure of **10** is shown in Fig. 2, along with the labelling scheme. Only one of the enantiomers was

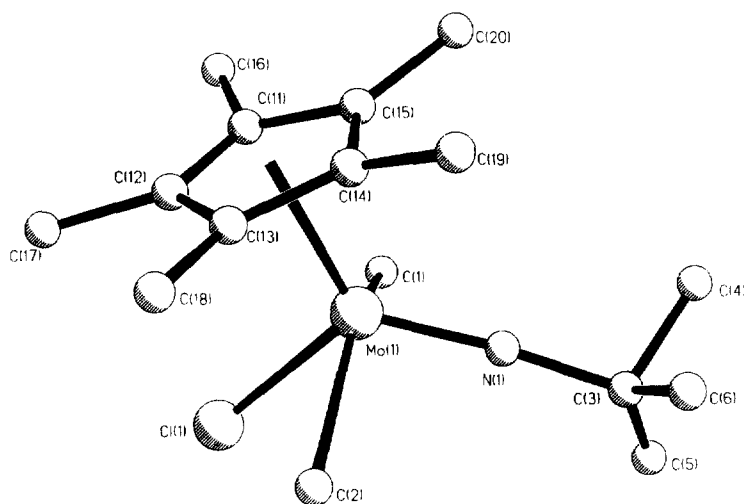
observed. Selected bond distances and angles are presented in Table 2.

The coordination of the Mo atoms is similar to that described for complex **9**. In this case the unique chlorine atom is located *trans* to the N'Bu group and together with the other two *trans* methyl groups complete the square base of the pseudo-square pyramid whose apex is occupied by the η^5 -pentamethylcyclopentadienyl ligand. The Cp(centroid)–Mo–Cl1 and Cp(centroid)–Mo–N angles are 110.3 and 126.3° , respectively. They are larger than the other two (mean 108.0°) and the N atom is slightly out-of-the plane of the base of the pyramid, probably due to the steric requirement of the bulky N'Bu group. The *trans* influence due to the imido N'Bu is also remarkable, giving rise to the largest Mo–C12(Cp) distance of 2.53(1) Å. The Mo(1)–C(methyl) distances of 2.25(1) Å, correspond to normal single bonds and the Mo(1)–N(1) distance of 1.706(8) Å and the Mo–N(1)–C(3) angle of $175.1(9)^\circ$ are consistent with the triple bond character of the Mo–N bond.

The methylation of complexes **8** and **9** was studied using different molar ratios of LiMe and MgClMe as alkylating agents. Addition of 1 equiv. of the alkylating agent to suspensions of complexes **8** and **9** in THF or toluene always led to unresolvable mixtures containing the unreacted starting complex and variable amounts of the dialkyl and trialkyl derivatives together with traces of a paramagnetic component, which is probably the reduced tungsten(V) complex when LiMe was used. The addition of 2 equiv. of MgClMe to a toluene suspension of $[WCpCl_3(N'Bu)]$ (**8**) led after stirring for 16 h at room temperature to a green solution, which after purification by chromatography afforded the dimethyl complex $[WCpClMe_2(N'Bu)]$ (**11**) as a green crystalline solid in 40% yield. The same reaction carried out with $[WCp^*Cl_3(N'Bu)]$ (**9**) in THF allowed us to isolate the related complex $[WCp^*ClMe_2(N'Bu)]$ (**12**) as yellow crystals in 45% yield. LiMe can be alternatively used to prepare complex **12** under the same conditions, whereas a



Scheme 2.

Fig. 2. Perspective view of the molecular structure of $[\text{MoCp}^*\text{ClMe}_2(\text{N}^t\text{Bu})]$ (**10**) with the atom-numbering scheme. Hydrogen atoms are omitted for clarity.

lower yield due to the formation of other unidentified products was obtained when this alkylating agent was used to prepare complex **11**. Addition of 3 equiv. of MgClMe to a THF suspension of $[\text{WCpCl}_3(\text{N}^t\text{Bu})]$ (**8**) led to an unresolvable mixture of alkylated products, but the related trimethyl derivative $[\text{WCpMe}_3(\text{N}^t\text{Bu})]$ (**14**) could be easily prepared in 50% yield as a yellow-brown solid by reacting the previously isolated dimethyl complex **11** with 1 equiv. of MgClMe in toluene. The same methylation of $[\text{WCp}^* -$

$\text{Cl}_3(\text{N}^t\text{Bu})]$ (**9**) with 3 equiv. of MgClMe or LiMe produced an initially green solution, which after warming and stirring at 0°C changed to give a brown solution which after purification by chromatography provided yellow crystals of the trimethyl complex $[\text{WCp}^*\text{Me}_3(\text{N}^t\text{Bu})]$ **15** [18] in 35% yield. Complex **15** is a rather stable 18-electron compound, which reacts very slowly with an excess of $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ when heated in a sealed ampoule to 65°C for more than 10 days, affording the *trans*-dimethyliminoacyl

Table 2
Selected bond lengths (Å) and angles (°) for **10**

Mo(1)–N(1)	1.706(8)	Mo(1)–C(1)	2.252(12)
Mo(1)–C(2)	2.256(13)	Mo(1)–Cl(1)	2.481(3)
Mo(1)–C(11)	2.46(1)	Mo(1)–C(12)	2.53(1)
Mo(1)–C(13)	2.40(1)	Mo(1)–C(14)	2.31(1)
Mo(1)–C(15)	2.34(1)	N(1)–C(3)	1.46(2)
C(3)–C(5)	1.27(3)	C(3)–C(6)	1.38(3)
C(3)–C(4)	1.50(3)	C(11)–C(12)	1.38(2)
C(11)–C(15)	1.47(2)	C(12)–C(13)	1.36(2)
C(13)–C(14)	1.40(2)	C(14)–C(15)	1.40(2)
Mo(1)–Cp(1)	2.096		
N(1)–Mo(1)–C(1)	88.4(5)	N(1)–Mo(1)–C(2)	88.6(5)
C(1)–Mo(1)–C(2)	137.1(5)	N(1)–Mo(1)–Cl(1)	123.3(3)
C(1)–Mo(1)–Cl(1)	73.1(4)	C(2)–Mo(1)–Cl(1)	73.2(4)
C(3)–N(1)–Mo(1)	175.1(9)	Cp(1)–Mo(1)–Cl(1)	110.3
Cp(1)–Mo(1)–N(1)	126.3	Cp(1)–Mo(1)–C(1)	108.5
Cp(1)–Mo(1)–C(2)	107.5		

Cp(1) is the centroid of the C(11) to C(15) ring.

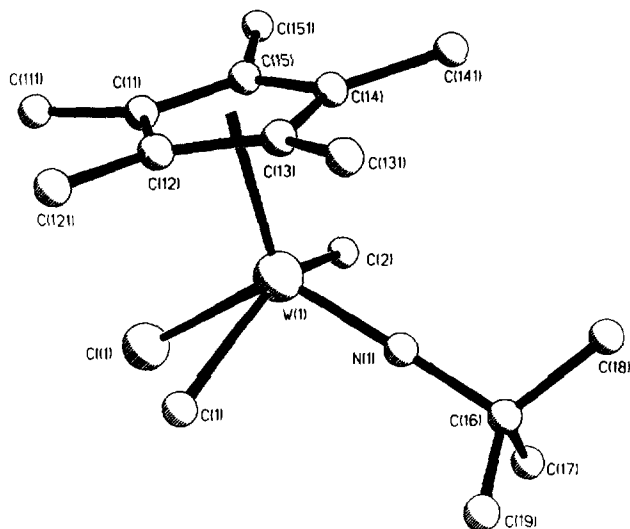


Fig. 3. Perspective view of the molecular structure of $[\text{WCp}^*\text{Cl-Me}_2(\text{N}'\text{Bu})]$ (**12**) with the atom-numbering scheme. Hydrogen atoms are omitted for clarity.

complex $[\text{WCp}^*\{\text{C}(\text{Me})=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}\text{Me}_2(\text{N}'\text{Bu})]$ (**16**) as a red crystalline solid. Formulation of complex **16** containing the monohapto-coordinated iminoacyl ligand and two *trans* W-bonded methyl groups is consistent with its analytical composition and the observed ^1H and ^{13}C NMR spectra which show the low-field resonance of the migrated methyl group displaced to δ 2.39, one singlet at δ 1.15 for the other two equivalent metal-bonded methyl substituents and the low-field resonance due to the iminoacyl carbon atom at δ 230.0. Complex **16** is a very air-sensitive compound soluble in all alkanes and aromatic solvents.

All the di- and tri-methyl tungsten complexes **11–12**, **14–15** were characterized by their analytical composition and IR, ^1H and ^{13}C NMR spectroscopies, and the molecular structure of the dimethyl complex **12** was studied by X-ray diffraction methods. The molecular structure is shown in Fig. 3 with the

Table 3
Selected bond lengths (Å) and angles (°) for **12**

W(1)–N(1)	1.739(6)	W(1)–C(1)	2.205(8)
W(1)–C(2)	2.221(8)	W(1)–Cl(1)	2.474(2)
W(1)–C(11)	2.539(7)	N(1)–C(16)	1.439(11)
C(11)–C(12)	1.412(11)	C(11)–C(15)	1.414(10)
C(12)–C(13)	1.424(11)	C(13)–C(14)	1.437(11)
C(14)–C(15)	1.410(11)	C(16)–C(19)	1.47(2)
C(16)–C(18)	1.53(2)	C(16)–C(17)	1.54(2)
W(1)–Cp(1)	2.097		
N(1)–W(1)–C(1)	88.2(3)	N(1)–W(1)–C(2)	88.4(3)
C(1)–W(1)–C(2)	140.0(4)	N(1)–W(1)–Cl(1)	123.4(2)
C(1)–W(1)–Cl(1)	73.9(3)	C(2)–W(1)–Cl(1)	75.0(3)
W(1)–N(1)–C(16)	177.2(6)	Cp(1)–W(1)–Cl(1)	111.1
Cp(1)–W(1)–N(1)	125.5	Cp(1)–W(1)–C(1)	106.8
Cp(1)–W(1)–C(2)	107.5		

Cp(1) is the centroid of the C(11) to C(15) ring.

labelling scheme employed and selected bond distances and angles are presented in Table 3.

Complex **12** shows a pseudo-square pyramidal coordination analogous to that described for complex **10**, with the chlorine atom *trans* to the imido N'Bu group with the N atom out of the plane defined by the other three ligands. The W–N1 bond distance of 1.739(6) Å is almost the same as that found for complex **9** and the W–N1–C16 bond angle of 177.2(6)° is slightly larger. The only remarkable difference is the W–Cl bond distance which at 2.474(2) Å, is significantly larger than the distance observed in complex **9** (mean 2.404 Å) consistent with the shorter Cp*(centroid)–W distance of 2.097 Å.

3. Experimental

All manipulations were carried out under a dry argon atmosphere either in a Vacuum Atmosphere Dri-lab or by standard Schlenk techniques. Solvents were dried and freshly distilled: hexane from sodium–potassium alloy, diethyl ether and THF from sodium–benzophenone, toluene from sodium and dichloromethane from calcium hydride. Reagent grade LiMe (1.6 M in OEt₂, Aldrich), MgClMe (3.0 M in THF), PCl₅ (Aldrich), acetic acid (Panreac) and N'BuH₂ (Aldrich) were purchased from commercial sources and were used without further purification. NaCp and the complexes MoCp*Cl₂(N'Bu) [7e], [MoCp*Cl(N'Bu)]₂ [15], W(CO)₃–(NCMe)₃ [12], WCpCl₂(N'Bu) [16], [MoCp*(CO)₂]₂ and [WCp*(CO)₂]₂ [14b] were prepared following modified reported methods. IR spectra were recorded on a Perkin-Elmer 583 spectrophotometer (4000–200 cm^{–1}) as Nujol mulls between CsI or polyethylene pellets. ^1H and ^{13}C NMR spectra were recorded on Varian Unity VXR 300 MHz and Varian Unity FT 500 MHz instruments. Chemical shifts were measured relative to residual resonances in the deuterated solvents C₆D₆ (δ 7.15), CDCl₃ (δ 7.24) and C₆D₆ (δ 128.0), CDCl₃ (δ 77.0), respectively. Mass spectra were recorded

on an HP 5988 A instrument. C, H, and N analyses were carried out with a Perkin-Elmer 240C microanalyzer.

3.1. Preparation of $[\text{WCp}(\text{CO})_3\text{H}]$

This compound was isolated by a method analogous to that reported by Fischer [13], using $\text{W}(\text{CO})_3(\text{NCMe})_3$ instead of $\text{W}(\text{CO})_6$. To a suspension of $\text{W}(\text{CO})_3(\text{NCMe})_3$ (6.00 g, 15.3 mmol) in THF (200 ml) was added freshly prepared NaCp (1.35 g, 15.3 mmol) and the mixture was stirred at 25°C for 2 h. The mixture was then treated with acetic acid (0.92 g, 0.88 ml, 15.3 mmol) and vigorously stirred for 10 min. After elimination of volatiles under vacuum the solid residue was extracted into pentane (2 × 25 ml) to give a solution which by evaporation under vacuum afforded a yellow crystalline solid identified as $\text{WCp}(\text{CO})_3\text{H}$ by elemental analysis and comparison of its IR and NMR spectra with reported data [13]. Yield 4.86 g, 14.6 mmol, 95%.

3.2. Preparation of $[\text{MoCp}^*\text{Cl}_4] (\mathbf{1})$

A solution of $[\text{MoCp}^*(\text{CO})_2]_2$ (1.00 g, 1.72 mmol) in toluene (40 ml) was slowly added to a solution of PCl_5 (1.50 g, 7.2 mmol) in toluene (50 ml) and the mixture was stirred at 25°C for 2 h and then at 75°C for 1 day to give a purple solid which was filtered, washed with dichloromethane (2 × 10 ml) and dried under vacuum to be characterized as the title compound. Yield 1.20 g, 1.61 mmol, 93%. *Anal. Calc.* for $\text{C}_{10}\text{H}_{15}\text{Cl}_4\text{Mo}$: C, 32.19; H, 4.02. Found: C, 31.74; H, 4.00%.

3.3. Preparation of $[\text{WCpCl}_4] (\mathbf{2})$

This compound was prepared following a method similar to that described by Green et al. [11] but using $\text{WCp}(\text{CO})_3\text{H}$ instead of $\text{WCp}(\text{CO})_3\text{Me}$. A solution of $\text{WCp}(\text{CO})_3\text{H}$ (4.00 g, 12.0 mmol) in dichloromethane (100 ml) was added dropwise to a stirring solution of phosphorus pentachloride (7.48 g, 36.0 mmol) in the minimum amount of dichloromethane at 25°C with evolution of a colourless gas. The mixture was stirred for 20 h. Then the solvent was removed by filtration leaving a red-brown solid which was washed with dichloromethane (3 × 20 ml) dried in vacuo and identified as complex **2** by elemental analysis and comparison of its IR spectrum with reported data [11]. Yield 4.59 g, 11.5 mmol, 98%.

3.4. Preparation of $[\text{WCp}^*\text{Cl}_4] (\mathbf{3})$

A solution of $[\text{WCp}^*(\text{CO})_2]_2$ (2.00 g, 2.66 mmol) in toluene (40 ml) was slowly added to a solution of PCl_5 (2.35 g, 11.3 mmol) in toluene (50 ml) and the mixture was stirred at 25°C for 2 h and then at 75°C for 2 days to give a yellow-orange solid which was filtered, washed with dichloromethane (2 × 10 ml) and dried under vacuum to be characterized as the title compound. Yield 2.25 g, 2.44 mmol,

92%. *Anal. Calc.* for $\text{C}_{10}\text{H}_{15}\text{Cl}_4\text{W}$: C, 26.05; H, 3.25. Found: C, 26.03; H, 3.61%.

3.5. Preparation of $[\text{MoCp}^*\text{Cl}_3(\text{N}^i\text{Bu})] (\mathbf{7})$

A CH_2Cl_2 (50 ml) solution of complex **4** (0.59 g, 1.58 mmol) was prepared and the stoichiometric amount of PCl_5 (0.17 g, 0.81 mmol) was added. The solution colour changed quickly from the initial brown to orange-red. The solution was stirred for 2 h and then filtered. After removal of the solvent, an orange-red solid was obtained. The residue was washed with ~15 ml of pentane and extracted with toluene (2 × 30 ml). The solution was concentrated to give a microcrystalline orange solid identified as **7**. Yield 0.56 g, 1.37 mmol, 87%. The same procedure can also be used starting from the imidomolybdenum(IV) complex $[\text{MoCp}^*\text{-Cl}(\text{N}^i\text{Bu})]_2$ [15]. IR (Nujol mull, $\nu(\text{cm}^{-1})$): 1212 (sh), 1201 (vs), 1031 (m), 793 (m), 369 (w), 349 (s), 324 (vs), 297 (w). ^1H NMR (δ ppm, in C_6D_6): 1.79 (s, 15H, C_5Me_5), 1.23 (s, 9H, NCMe_3). *Anal. Calc.* for $\text{C}_{14}\text{H}_{24}\text{NCl}_3\text{Mo}$: C, 41.13; H, 5.87; N, 3.43. Found: C, 41.33; H, 5.93; N, 3.29%.

3.6. Preparation of $[\text{WCpCl}_3(\text{N}^i\text{Bu})] (\mathbf{8})$

Following the method reported by Green et al. [16], $\text{WCpCl}_2(\text{N}^i\text{Bu})$ was prepared by addition of NH_2^iBu (2.52 g, 3.6 ml, 34.5 mmol) to a toluene (150 ml) solution of WCpCl_4 (4.5 g, 11.5 mmol) and used in situ by adding PCl_5 (1.20 g, 5.8 mmol). After stirring for 20 h at 25°C the insoluble residue was removed by filtration and the toluene solution together with that obtained after washing the solid with dichloromethane (2 × 50 ml) was evaporated to dryness to afford a solid, which after being washed with pentane was identified as complex **8** (4.17 g, 9.8 mmol, 81% yield). ^1H NMR (δ ppm, in CDCl_3): 6.69 (s, 5H, C_5H_5), 1.51 (s, 9H, NCMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ ppm, in CDCl_3): 115.2 (s, C_5H_5), 77.5 (s, CMe_3), 28.4 (s, CMe_3). *Anal. Calc.* for $\text{C}_9\text{H}_{14}\text{Cl}_3\text{NW}$: C, 25.41; H, 3.32; N, 3.31. Found: C, 26.06; H, 3.75; N, 3.50%.

3.7. Preparation of $[\text{WCp}^*\text{Cl}_3(\text{N}^i\text{Bu})] (\mathbf{9})$

A solution of $\text{WCp}^*\text{Cl}_2(\text{N}^i\text{Bu})$ prepared by reacting WCp^*Cl_4 (1.00 g, 2.2 mmol) with NH_2^iBu (0.69 ml, 6.6 mmol) in toluene (50 ml) was treated with PCl_5 (0.23 g, 1.08 mmol). The colour of the solution changed from green to yellow and after stirring for 4 h at 25°C the insoluble solid was removed by filtration. The toluene solution was cooled to -35°C to give orange crystals of complex **9** (1.0 g, 2.0 mmol, 92%). ^1H NMR (δ ppm, in CDCl_3): 1.96 (s, 15H, C_5Me_5), 1.22 (s, 9H, NCMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ ppm, in CDCl_3): 125.4 (s, C_5Me_5), 76.0 (s, CMe_3), 28.9 (s, CMe_3), 12.7 (s, C_5Me_5). *Anal. Calc.* for $\text{C}_{14}\text{H}_{40}\text{Cl}_3\text{NW}$: C, 33.87; H, 4.83; N, 2.82. Found: C, 34.16; H, 4.82; N, 2.97%.

3.8. Preparation of $[MoCp^*ClMe_2(N^iBu)]$ (**10**)

A suspension of **7** (0.40 g, 0.98 mmol) in Et_2O (60 ml) was cooled to approximately $-65^\circ C$, then 2 equiv. (1.22 ml) of a LiMe (1.6 M in Et_2O) solution were added. The mixture was stirred at room temperature for 3 h. After filtration the solution was concentrated to ~ 10 ml giving an orange crystalline compound identified as complex **10** (0.31 g, 80% yield). 1H NMR (δ ppm, in C_6D_6): 1.55 (s, 15H, C_5Me_5), 1.99 (s, 9H, $NCMe_3$), 1.53 (s, 6H, $Mo-Me_2$). *Anal. Calc.* for $C_{16}H_{30}NCiMo$: C, 52.25; H, 8.16; N, 3.81. Found: C, 52.41; H, 8.11; N, 3.89%.

3.9. Preparation of $[WCpClMe_2(N^iBu)]$ (**11**)

To a suspension of $WCpCl_3(N^iBu)$ (1.00 g, 2.34 mmol) in toluene (50 ml) was added a 3.0 M solution of $MgClMe$ in THF (1.56 ml, 0.35 g, 4.68 mmol) at $-78^\circ C$ and the mixture was warmed to $25^\circ C$ and stirred for 4 h. The solution was filtered and the solvent removed under vacuum to give a solid, which after being washed with pentane (2×20 ml) was dissolved in toluene and purified by chromatography (Shedex) using toluene as eluent. The resulting green solution was concentrated and cooled to $-35^\circ C$ to afford complex **11** as a crystalline green solid (0.36 g, 0.94 mmol, 40% yield). 1H NMR (δ ppm, in $CDCl_3$): 5.92 (s, 5H, C_5H_5), 1.28 (s, 9H, $NCMe_3$), 1.23 (s, 6H, $W-Me_2$). $^{13}C\{^1H\}$ NMR (δ ppm, in $CDCl_3$): 104.9 (s, C_5H_5), 70.6 (s, CMe_3), 28.4 (s, CMe_3), 24.4 (s, $W-Me_2$). *Anal. Calc.* for $C_{11}H_{20}ClNW$: C, 34.26; H, 5.23; N, 3.63. Found: C, 32.72; H, 5.00; N, 3.28%.

3.10. Preparation of $[WCp^*ClMe_2(N^iBu)]$ (**12**)

To a solution of $WCp^*Cl_3(N^iBu)$ (**9**) (1.11 g, 2.22 mmol) in THF (50 ml) cooled to $-78^\circ C$ a 3.0 M solution of $MgClMe$ in THF (1.50 ml, 4.47 mmol) was added, then warmed to $25^\circ C$ and stirred for 4 h. The solvent was removed under vacuum and the resulting solid was extracted with pentane to give a red solution. The solution was concentrated under vacuum to give a crystalline yellow solid identified as complex **12** (0.45 g, 0.99 mmol, 44.6% yield). 1H NMR (δ ppm, in $CDCl_3$): 1.63 (s, 15H, C_5Me_5), 1.30 (s, 6H, $W-Me_2$), 1.03 (s, 9H, $NCMe_3$). $^{13}C\{^1H\}$ NMR (δ ppm, in $CDCl_3$): 113.2 (s, C_5Me_5), 70.5 (s, CMe_3), 32.2 (s, $W-Me_2$), 28.7 (s, CMe_3), 11.3 (s, C_5Me_5). *Anal. Calc.* for $C_{16}H_{30}ClNW$: C, 42.19; H, 6.59; N, 3.07. Found: C, 41.40; H, 6.80; N, 2.87%.

3.11. Preparation of $[MoCp^*Me_3(N^iBu)]$ (**13**)

A suspension of complex **7** (0.44 g, 1.077 mmol) in *n*-hexane (50 ml) was prepared and a 1.6 M solution of LiMe in OEt_2 (2.22 ml, 3.55 mmol) was added at $-65^\circ C$. The reaction mixture was warmed to $25^\circ C$ and stirred for 2 h. The red solution was filtered and evaporated to dryness and the

orange oil residue was partially crystallized in the minimum amount of Et_2O by cooling at $-78^\circ C$. 1H NMR (δ ppm, in C_6D_6): 1.55 (s, 15H, C_5Me_5), 1.05 (s, 9H, $NCMe_3$), 0.96 (s, 6H, $Mo-Me_2$), 0.29 (s, 3H, *trans* $Mo-Me$). *Anal. Calc.* for $C_{17}H_{33}NMo$: C, 58.79; H, 9.51; N, 4.03. Found: C, 58.99; H, 9.37; N, 3.99%.

3.12. Preparation of $[WCpMe_3(N^iBu)]$ (**14**)

To a solution of $WCpClMe_3(N^iBu)$ (**12**) (1.5 g, 3.9 mmol) in toluene (50 ml) a 3.0 M solution of $MgClMe$ in THF (0.30 g, 1.3 ml, 3.9 mmol) was added at $-78^\circ C$ and then warmed to $25^\circ C$ and stirred for 4 h. After filtration the solvent was removed under vacuum and the resulting brown solid was extracted into pentane. Evaporation of the solvent afforded a brown solid identified as complex **14** (0.72 g, 1.95 mmol, 50% yield). 1H NMR (δ ppm, in $CDCl_3$): 5.12 (s, 5H, C_5H_5), 1.08 (s, 6H, *cis* $W-Me_2$), 1.02 (s, 9H, $NCMe_3$), 0.79 (s, 3H, *trans* $W-Me$). $^{13}C\{^1H\}$ NMR (δ ppm, in $CDCl_3$): 103.4 (s, C_5H_5), 69.1 (s, CMe_3), 28.8 (s, CMe_3), 21.1 (s, *trans* $W-Me$), 14.3 (s, *cis* $W-Me_2$). *Anal. Calc.* for $C_{12}H_{23}NW$: C, 39.44; H, 6.35; N, 3.84. Found: C, 39.16; H, 6.59; N, 3.73%.

3.13. Preparation of $[WCp^*Me_3(N^iBu)]$ (**15**)

To a solution of $WCp^*Cl_3(N^iBu)$ (**9**) (1.33 g, 2.68 mmol) in THF (50 ml) was added a 3.0 M solution of $MgClMe$ in THF (2.68 ml, 8.04 mmol) at $-78^\circ C$. The mixture was warmed to $25^\circ C$ and stirred for 4 h. After removing the solvent under vacuum the resulting solid residue was extracted into pentane to give a red solution which was evaporated to dryness. The solid was purified by chromatography (florisil) using hexane as eluent to afford after evaporation and cooling a red crystalline solid identified as complex **15** (0.40 g, 0.92 mmol, 35% yield). 1H NMR (δ ppm, in $CDCl_3$): 1.60 (s, 15H, C_5Me_5), 1.09 (s, 9H, $NCMe_3$), 0.89 (s, 6H, *cis* $W-Me_2$), 0.34 (s, 3H, *trans* $W-Me$). $^{13}C\{^1H\}$ NMR (δ ppm, in $CDCl_3$): 109.6 (s, C_5Me_5), 69.8 (s, CMe_3), 28.6 (s, CMe_3), 27.6 (s, *cis* $W-Me_2$), 21.2 (s, *trans* $W-Me$), 10.7 (s, C_5Me_5). *Anal. Calc.* for $C_{17}H_{33}NW$: C, 46.93; H, 7.58; N, 3.22. Found: C, 46.39; H, 7.63; N, 2.90%.

3.14. Preparation of $[WCp^*Me_2]\eta-C(Me)=N(2,6-Me_2C_6H_3)(N^iBu)]$ (**16**)

An ampoule containing a solution of $WCp^*Me_3(N^iBu)$ (**15**) (0.92 g, 2.12 mmol) and an excess of $CN(2,6-Me_2C_6H_3)$ (1.40 g, 10.56 mmol) in toluene (50 ml) was sealed under vacuum. By heating to $65^\circ C$ a very slow reaction was observed, that required 15 days to be complete, the colour of the solution changing from an orange to a deep red colour. After filtering the solvent was removed under vacuum and the resulting solid residue was recrystallized from hexane to give a red solid identified as complex **16** in 60% yield. 1H NMR (δ ppm, in C_6D_6): 7.10 (d, 2H, *m*-Ph), 6.91 (t, 1H, *p*-

Table 4
Crystal data, experimental data and structure refinement procedures for compounds **9**, **10** and **12**

	9	10	12
Formula	$C_{14}H_{21}Cl_3NW$	$C_{16}H_{26}ClMoN$	$C_{16}H_{30}NClW$
Mw	496.54	367.8	455.71
Crystal habit	prismatic	prismatic	prismatic
Color	orange	orange	yellow
Crystal size (mm)	$0.45 \times 0.38 \times 0.34$	$0.30 \times 0.27 \times 0.20$	$0.40 \times 0.35 \times 0.32$
Symmetry	triclinic, $P-1$	tetragonal $P4_212$	triclinic $P-1$
Unit cell dimensions:			
a (Å)	7.446(1)	11.104(2)	7.639(2)
b (Å)	8.837(2)	11.104(2)	8.900(2)
c (Å)	14.118(4)	30.328(6)	14.114(3)
α (°)	105.38(2)	90.0	104.78(3)
β (°)	98.09(2)	90.0	98.39(3)
γ (°)	96.74(2)	90.0	96.61(3)
V (Å ³)	875.0(3)	3739(1)	906.2(4)
Z	2	8	2
D_{calc} (g cm ⁻³)	1.885	1.307	1.670
$F(000)$	480	1536	448
μ (cm ⁻¹)	70.47	8.34	65.11
Scan mode	ω scans	ω scans	ω scans
θ range (°)	$3.13 < \theta < 27.79$	$2 < \theta < 26$	$2 < \theta < 25$
No. reflections:			
Measured	3810	4174	3466
Independent	3810	3635 ($R_{int} = 0.0516$)	3166 ($R_{int} = 0.0280$)
Observed ($I > 2\sigma(I)$ criterion)	3533	2234	2982
Absorption correction	psi scans DIFABS [19]	n/a	psi scans
Range of hkl	$-9 < h < 9; -10 < k < 10; 0 < l < 18$	$0 < h < 13; 0 < k < 13; 0 < l < 37$	$0 < h < 9; -10 < k < 10; -16 < l < 16$
Standard reflections		3 reflections every 120 minutes, no variation	
$R1$	0.0346	0.0647	0.0410
$wR2$	0.0948	0.1553	0.1172
Parameters for weighting scheme ^a			
w_1, w_2	0.0765, 1.1558	0.0899, 8.3201	0.3141, 79.8920
Goodness of fit indicator	1.026	1.117	1.165
Largest difference peak and hole (e Å ⁻³) near W atom	2.052 and -2.008	0.763, -0.528	1.913, -2.477

Details in common: cell dimensions from least-squares of 25 reflections: $R1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR2 = [\sum (F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

^a Weighting scheme $w = 1 / (\sigma^2(F_o^2) + (AP)^2 + vP^2)$ where $P = (I_o^2 + 2F_o^2) / 3$. Temperature 293(2) K.

Ph), 2.39 (s, 3H, C–Me), 2.33 (s, 6H, Me₂C₆H₃), 1.71 (s, 15H, C₅Me₅), 1.15 (s, 6H, WMe₂), 0.95 (s, 9H, NMe₃). ¹³C{¹H} NMR (δ ppm, in C₆D₆): 230.0 (s, N=CMe), 154.0 (s, N–Ph-*ipso*), 128.0 (s, *o*-Ph), 126.7 (s, *m*-Ph), 120.8 (s, *p*-Ph), 112.1 (s, C₅Me₅), 69.5 (s, CMe₃), 33.0 (s, W–Me₂), 28.9 (s, CMe₃), 19.8 (s, Me₂C₆H₃), 17.0 (s, N=CMe), 10.9 (s, C₅Me₅).

3.15. Crystal structure determinations

Suitably sized orange crystals of **9** were obtained by crystallization from toluene; crystals of **10** were obtained by cooling a diethyl ether solution to –40°C and crystals of **12** were obtained by cooling its hexane solution. The crystals were mounted in sealed tubes under Argon in an Enraf-Nonius CAD-4 automatic four-circle diffractometer with bisecting geometry, using graphite-oriented monochromator and Mo Kα (λ = 0.71073 Å) radiation. Crystallographic and experimental details are summarized in Table 4. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. Absorption was corrected by Psi scans in **9** and **12**. Extinction correction was made in **12** with extinction coefficient of 0.036(3) where $F_c^* = kF_c [1 + 0.001F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$. The structures were solved by a combination of heavy atoms, direct methods, and Fourier synthesis by SHELX90 [20] program and refined on F^2 by full-matrix least-squares calculations (SHELX93) [21]. All non-hydrogen atoms were refined anisotropically. In the last cycle of refinement hydrogen atoms were introduced from geometric calculations and with fixed thermal parameters.

All calculations were performed on an Alpha AXP Digital Workstation.

4. Supplementary material

Tables of atomic coordinates, complete lists of bond distances and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters and structure factors for **9**, **10** and **12** are available from the authors on request.

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