

Synthesis and Reactions of d^0 Imido Aryl Derivatives of Chromium, Molybdenum, and Tungsten. Crystal Structures of $\text{Cr}(\text{NBU}^t)_2(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2$, $\text{Mo}(\text{NBU}^t)_2(\text{C}_6\text{H}_3\text{Me}_2\text{-2,6})_2$, and $\text{Cr}(\text{NBU}^t)_2[\text{C}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})=\text{NBU}^t](\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})^\dagger$

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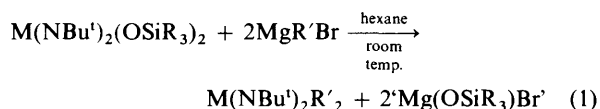
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The compounds $\text{M}(\text{NBU}^t)_2\text{R}'_2$ ($\text{M} = \text{Cr, Mo, or W}$, $\text{R}' = \text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$ or $\text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$; $\text{M} = \text{Mo}$, $\text{R}' = \text{C}_6\text{H}_4\text{Me-}o$) have been prepared from $\text{M}(\text{NBU}^t)_2(\text{OSiR}_3)_2$ ($\text{M} = \text{Cr or Mo}$, $\text{R} = \text{Me}$; $\text{M} = \text{W}$, $\text{R} = \text{Ph}$) and appropriate Grignard reagents. $\text{Cr}(\text{NBU}^t)_2(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2$ reacts with CO to give a thermally unstable bis(acyl) complex $\text{Cr}(\text{NBU}^t)_2(\text{COC}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2$ which eliminates the amide $\text{HN}(\text{BU}^t)(\text{COC}_6\text{H}_2\text{Me}_3\text{-2,4,6})$ possibly *via* acyl migration to the imido nitrogen. Cyclic voltammetry on $\text{Cr}(\text{NBU}^t)_2(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2$ shows a quasi-reversible one-electron reduction, $E_3^{\text{red}} = -1.31$ V. Reaction of compounds $\text{M}(\text{NBU}^t)_2\text{R}'_2$ ($\text{M} = \text{Cr, Mo, or W}$, $\text{R}' = \text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$; $\text{M} = \text{Mo}$, $\text{R}' = \text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$) with *t*-butyl isocyanide gives the corresponding η^2 -iminoacyls $\text{M}(\text{NBU}^t)_2[\text{C}(\text{R}')=\text{NBU}^t]\text{R}'$. The X-ray crystal structures of $\text{Cr}(\text{NBU}^t)_2(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2$, $\text{Mo}(\text{NBU}^t)_2(\text{C}_6\text{H}_3\text{Me}_2\text{-2,6})_2$, and $\text{Cr}(\text{NBU}^t)_2[\text{C}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})=\text{NBU}^t](\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})$ have been determined. The first two consist of monomeric distorted tetrahedra in which one *o*-methyl group on each aryl ligand is positioned close to the metal atom. In the latter compound the structure is best described in terms of a distorted tetrahedron, with the η^2 -iminoacyl occupying one split site.

This paper deals with the synthesis, properties and some chemistry of a group of imido aryl derivatives of Cr^{VI} , Mo^{VI} , and W^{VI} . Prior to this work there were apparently no d^0 σ -organo-chromium, or d^0 aryltungsten compounds although $\text{MoO}_2(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2$ had been prepared¹ from MoO_2Cl_2 and the Grignard reagent $\text{Mg}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})\text{Br}$. Many of the known alkyl or aryl compounds of transition metals in high oxidation states have imido or oxo groups present, for example, $[\text{M}(\text{NBU}^t)_2\text{Me}_2]_2$ ($\text{M} = \text{Mo}^2$ or W^3), $\text{Os}(\text{NMe})(\text{CH}_2\text{SiMe}_3)_4$,⁴ $[\text{NBU}_4][\text{RuN}(\text{CH}_2\text{SiMe}_3)_4]$,⁵ ReO_2Me_3 ,⁶ $\text{OsO}_2(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2$,⁷ and $[\text{WO}_2(\text{OCMe}_2\text{CMe}_2\text{O})\text{CH}_2\text{-BU}^t]^-$;⁸ there are also compounds which are either catalysts or precatalysts for the metathesis of olefins, namely $\text{WO}(\text{CH}_2\text{Bu}^t)_4$,⁹ $\text{WCl}_3\text{OMe}(\text{OEt}_2)$,¹⁰ and $\text{W}(\text{NC}_6\text{H}_3\text{Pr}^i\text{-2,6})[\text{OC}(\text{Me})(\text{CF}_3)_2]_2(\text{CHBU}^t)$.¹¹

Results and Discussion

Compounds (1)–(7) in Table 1 were prepared from $\text{M}(\text{NBU}^t)_2(\text{OSiR}_3)_2$ ($\text{M} = \text{Cr or Mo}$, $\text{R} = \text{Me}$; $\text{M} = \text{W}$, $\text{R} = \text{Ph}$ ¹²) and appropriate Grignard reagents ($\text{R}' = \text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$ or $\text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$) by the reaction (1). The compounds $\text{Cr}(\text{NBU}^t)_2\text{R}'_2$ ($\text{R}' = \text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$ or $\text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$) are the first σ -organo derivatives of chromium(vi) and a preliminary



[†] Dimesityldi(*t*-butylimido)chromium(vi), di(*t*-butylimido)di(2,6-xylyl)molybdenum(vi), and mesityl[mesityl(*t*-butylimino)methyl]di(*t*-butylimido)chromium(vi) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

Non-S.I. units employed: $\text{lb in}^{-2} \approx 7.031 \times 10^2 \text{ kg m}^{-2}$, $\text{eV} \approx 1.60 \times 10^{-19} \text{ J}$.

account has appeared.¹³ Both are remarkably stable to air as solids or in hydrocarbon or ether solutions but decompose slowly in halogenated solvents. Concentrated solutions of $\text{Cr}(\text{NBU}^t)_2(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2$ (1) in hexane give deep red needles when cooled at -21 °C. The crude $\text{Cr}(\text{NBU}^t)_2(\text{C}_6\text{H}_3\text{Me}_2\text{-2,6})_2$ (2), a deep red oil, failed to crystallise from hexane but deep red crystalline material was obtained from cooled hexamethyl-disiloxane solutions. Attempts to prepare the analogous phenyl or *o*-tolyl derivatives using appropriate Grignard reagents were unsuccessful.

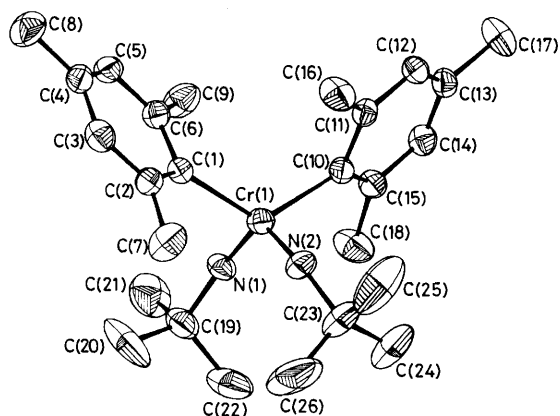
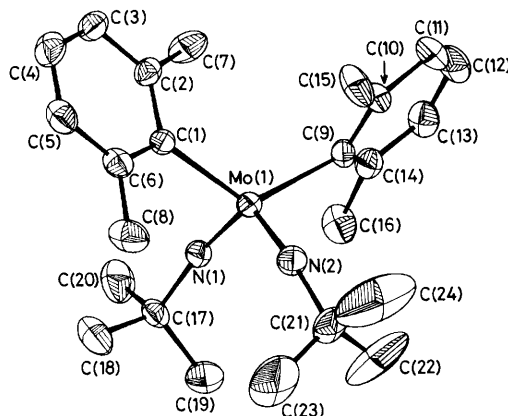
Nugent and Harlow² have reported the formation of *t*-butyl-phenylamine and biphenyl in the reaction between $\text{Cr}(\text{NBU}^t)_2(\text{OSiMe}_3)_2$ and diphenylzinc, invoking a phenyl migration to the electron-deficient imido nitrogen to account for the amine. The stability of $\text{Cr}(\text{NBU}^t)_2\text{R}'_2$ is doubtless due to the steric protection afforded by the *o*-methyls on the aromatic rings by inhibiting migratory reactions to the imido group and attack by oxygen or water. Attempts to obtain isolable compounds by methods similar to those using MoO_2Cl_2 , Re_2O_7 , and OsO_4 and Grignard reagents, which give $\text{MoO}_2(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2$,¹ $\text{ReO}(\text{C}_6\text{H}_4\text{Me-}o)_4$, and $\text{OsO}_2(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2$,⁷ were unsuccessful. Thus interaction of CrO_2Cl_2 or CrO_3 and two equivalents of mesitylmagnesium bromide led only to unisolable reduced Cr^{III} and Cr^{V} species as indicated by e.s.r. spectra of frozen tetrahydrofuran (thf) solutions. In the reaction between CrO_3 and triphenylaluminium etherate an amorphous black solid, presumably a chromium oxide, and biphenyl were produced.

Compound (1) undergoes a reversible one-electron reduction at a Pt electrode in $0.2 \text{ mol dm}^{-3} [\text{NBU}^t]_4[\text{PF}_6]^-$ thf supporting electrolyte solution, with $E_3^{\text{red}} = -1.31$ V *versus* a standard Ag/AgCl electrode (against which ferrocene is oxidised at $E_{1/2} = +0.34$ V). A thf solution of (1) containing less than one equivalent of sodium dihydronaphthylide gave an e.s.r. spectrum with a sharp signal ($g_{\text{av.}} \approx 1.96$) indicative of d^1 Cr^{V} species flanked by a broad signal with the appearance of a Cr^{III} species. Neither species was isolated.

Table 1. Analytical data for the new chromium, molybdenum, and tungsten compounds

Compound	Colour	M.p. (°C)	Analysis* (%)		
			C	H	N
(1) Cr(NBu ^t) ₂ (C ₆ H ₂ Me ₃ -2,4,6) ₂	Dark red	146	71.9 (72.2)	9.1 (9.3)	6.3 (6.4)
(2) Cr(NBu ^t) ₂ (C ₆ H ₃ Me ₂ -2,6) ₂	Dark red	106	71.1 (71.2)	9.3 (9.0)	6.9 (6.9)
(3) Mo(NBu ^t) ₂ (C ₆ H ₂ Me ₃ -2,4,6) ₂	Yellow	124	65.0 (65.5)	8.5 (8.4)	5.9 (5.9)
(4) Mo(NBu ^t) ₂ (C ₆ H ₃ Me ₂ -2,6) ₂	Yellow	100 (decomp.)	64.1 (64.3)	8.1 (8.1)	6.2 (6.2)
(5) Mo(NBu ^t) ₂ (C ₆ H ₄ Me- <i>o</i>) ₂	Orange (oil)				
(6) W(NBu ^t) ₂ (C ₆ H ₂ Me ₃ -2,4,6) ₂	Pale orange	92 (decomp.)	51.4 (55.4)	6.8 (7.1)	4.6 (5.0)
(7) W(NBu ^t) ₂ (C ₆ H ₃ Me ₂ -2,6) ₂	Pale yellow	90 (decomp.)	52.9 (53.7)	6.7 (6.8)	5.1 (5.2)
(8) Cr(NBu ^t) ₂ (COC ₆ H ₂ Me ₃ -2,4,6) ₂	Yellow	98 (decomp.)	68.8 (68.8)	8.3 (8.2)	5.6 (5.7)
(9) Cr(NBu ^t) ₂ [C(C ₆ H ₂ Me ₃ -2,4,6)=NBu ^t](C ₆ H ₂ Me ₃ -2,4,6)	Yellow	120 (decomp.)	72.5 (72.2)	9.6 (9.6)	8.2 (8.2)
(10) Mo(NBu ^t) ₂ [C(C ₆ H ₂ Me ₃ -2,4,6)=NBu ^t](C ₆ H ₂ Me ₃ -2,4,6)	Cream	186	66.5 (66.5)	8.8 (8.8)	7.5 (7.5)
(11) W(NBu ^t) ₂ [C(C ₆ H ₂ Me ₃ -2,4,6)=NBu ^t](C ₆ H ₂ Me ₃ -2,4,6)	Colourless	168	57.2 (57.5)	7.7 (7.6)	6.2 (6.5)
(12) Mo(NBu ^t) ₂ [C(C ₆ H ₄ Me- <i>o</i>)=NBu ^t](C ₆ H ₄ Me- <i>o</i>)	Tan	68	63.1 (64.4)	8.1 (8.2)	8.6 (8.4)

* Calculated values given in parentheses.

**Figure 1.** The molecular structure of Cr(NBu^t)₂(C₆H₂Me₃-2,4,6)₂ (1)**Figure 2.** The molecular structure of Mo(NBu^t)₂(C₆H₃Me₂-2,6)₂ (4)

The arylmetal derivatives Mo(NBu^t)₂(C₆H₂Me₃-2,4,6)₂ (3), Mo(NBu^t)₂(C₆H₃Me₂-2,6)₂ (4), and W(NBu^t)₂(C₆H₃Me₂-2,6)₂ (7) are obtained from hexane solutions as yellow air-sensitive crystals. Mo(NBu^t)₂(C₆H₄Me-*o*)₂ (5) could not be crystallised from a range of solvents and W(NBu^t)₂(C₆H₂Me₃-2,4,6)₂ (6) obtained in the first instance as a pale orange waxy solid was recrystallised from hexamethyldisiloxane. Like the chromium aryls the molybdenum and tungsten species are quite thermally stable, but readily attacked by oxygen presumably because of their larger covalent radii. All of the compounds except (7) were obtained in high yield and all display high solubility in aromatic and aliphatic hydrocarbons but decompose slowly in halogenated solvents. The ¹H n.m.r. spectra show that there is free rotation at the metal-carbon bonds in each case.

X-Ray diffraction studies showed compounds (1) and (4) to be monomeric with a distorted tetrahedral geometry, as shown in Figures 1 and 2. Selected bond lengths and angles are given in

Tables 2 and 3. The molecular structures are very similar and contain normal linear *t*-butylimido functions. The M-N and M-C bond lengths show a slightly larger difference for Mo-C *vs.* Cr-C than for Mo=N *vs.* Cr=N.

Perhaps the most interesting common feature of the structures is the distribution of the angles in the distorted MC₂N₂ tetrahedra. In both molecules the N=M=N angles are smaller than the C-M-C angles (see Tables 2 and 3). This contrasts with most structures containing two neighbouring multiply bonded functions [*e.g.*, M(NR)₂, M(O)₂] where the repulsion between the π-electron density in the two bonds leads to an opening up of the interbond angle from idealised values. In our earlier preliminary presentation of the structure of the chromium complex¹³ we suggested that the unexpectedly small N-M-N angle might be ascribed to steric effects, with the positioning of the methyl substituents on the aryl functions dominant in deciding the geometry.

Table 2. Selected bond lengths (Å) and angles (°) for (1)

N(1)–Cr(1)	1.628(5)	N(2)–Cr(1)	1.623(5)	C(15)–C(10)	1.412(6)	C(12)–C(11)	1.392(6)
C(1)–Cr(1)	2.032(6)	C(10)–Cr(1)	2.035(6)	C(16)–C(11)	1.509(8)	C(13)–C(12)	1.371(7)
C(19)–N(1)	1.449(6)	C(23)–N(2)	1.449(6)	C(14)–C(13)	1.368(6)	C(17)–C(13)	1.502(8)
C(2)–C(1)	1.413(6)	C(6)–C(1)	1.404(6)	C(15)–C(14)	1.379(6)	C(18)–C(15)	1.510(8)
C(3)–C(2)	1.375(7)	C(7)–C(2)	1.496(7)	C(20)–C(19)	1.472(9)	C(21)–C(19)	1.540(10)
C(4)–C(3)	1.380(7)	C(5)–C(4)	1.366(7)	C(22)–C(19)	1.502(9)	C(24)–C(23)	1.489(8)
C(8)–C(4)	1.483(7)	C(6)–C(5)	1.378(7)	C(25)–C(23)	1.521(11)	C(26)–C(23)	1.493(10)
C(9)–C(6)	1.515(8)	C(11)–C(10)	1.410(6)				
N(2)–Cr(1)–N(1)	114.5(3)	C(1)–Cr(1)–N(1)	100.8(3)	C(15)–C(10)–C(11)	117.3(4)	C(12)–C(11)–C(10)	120.1(5)
C(1)–Cr(1)–N(2)	109.7(3)	C(10)–Cr(1)–N(1)	110.1(3)	C(16)–C(11)–C(10)	122.4(5)	C(16)–C(11)–C(12)	117.5(5)
C(10)–Cr(1)–N(2)	101.1(3)	C(10)–Cr(1)–C(1)	121.2(2)	C(13)–C(12)–C(11)	122.4(5)	C(14)–C(13)–C(12)	117.0(5)
C(19)–N(1)–Cr(1)	159.6(3)	C(23)–N(2)–Cr(1)	159.7(3)	C(17)–C(13)–C(12)	122.0(5)	C(17)–C(13)–C(14)	121.0(5)
C(2)–C(1)–Cr(1)	127.7(4)	C(6)–C(1)–Cr(1)	114.4(4)	C(15)–C(14)–C(13)	123.7(5)	C(14)–C(15)–C(10)	119.5(5)
C(6)–C(1)–C(2)	117.7(5)	C(3)–C(2)–C(1)	119.2(5)	C(18)–C(15)–C(10)	122.1(5)	C(18)–C(15)–C(14)	118.4(5)
C(7)–C(2)–C(1)	122.2(5)	C(7)–C(2)–C(3)	118.6(5)	C(20)–C(19)–N(1)	108.0(5)	C(21)–C(19)–N(1)	106.3(5)
C(4)–C(3)–C(2)	123.8(5)	C(5)–C(4)–C(3)	115.9(5)	C(21)–C(19)–C(20)	110.7(7)	C(22)–C(19)–N(1)	111.5(5)
C(8)–C(4)–C(3)	121.6(6)	C(8)–C(4)–C(5)	122.5(6)	C(22)–C(19)–C(20)	112.6(6)	C(22)–C(19)–C(21)	107.7(6)
C(6)–C(5)–C(4)	123.7(5)	C(5)–C(6)–C(1)	119.6(5)	C(24)–C(23)–N(2)	108.6(5)	C(25)–C(23)–N(2)	106.3(6)
C(9)–C(6)–C(1)	122.2(5)	C(9)–C(6)–C(5)	118.2(5)	C(25)–C(23)–C(24)	110.7(7)	C(26)–C(23)–N(2)	111.2(6)
C(11)–C(10)–Cr(1)	115.7(4)	C(15)–C(10)–Cr(1)	126.9(4)	C(26)–C(23)–C(24)	109.7(6)	C(26)–C(23)–C(25)	110.3(7)

Table 3. Selected bond lengths (Å) and angles (°) for (4)

N(1)–Mo(1)	1.733(7)	N(2)–Mo(1)	1.708(7)	C(10)–C(9)	1.401(9)	C(14)–C(9)	1.417(8)
C(1)–Mo(1)	2.161(7)	C(9)–Mo(1)	2.162(7)	C(11)–C(10)	1.391(9)	C(15)–C(10)	1.518(11)
C(17)–N(1)	1.461(8)	C(21)–N(2)	1.480(9)	C(12)–C(11)	1.359(11)	C(13)–C(12)	1.371(10)
C(2)–C(1)	1.418(8)	C(6)–C(1)	1.404(9)	C(14)–C(13)	1.364(9)	C(16)–C(14)	1.515(11)
C(3)–C(2)	1.391(9)	C(7)–C(2)	1.486(10)	C(18)–C(17)	1.519(11)	C(19)–C(17)	1.503(11)
C(4)–C(3)	1.382(10)	C(5)–C(4)	1.358(11)	C(20)–C(17)	1.516(12)	C(22)–C(21)	1.466(15)
C(6)–C(5)	1.386(10)	C(8)–C(6)	1.494(10)	C(23)–C(21)	1.467(15)	C(24)–C(21)	1.456(14)
N(2)–Mo(1)–N(1)	112.5(3)	C(1)–Mo(1)–N(1)	101.1(3)	C(14)–C(9)–C(10)	117.5(6)	C(11)–C(10)–C(9)	121.0(7)
C(1)–Mo(1)–N(2)	109.3(3)	C(9)–Mo(1)–N(1)	109.0(3)	C(15)–C(10)–C(9)	121.1(6)	C(15)–C(10)–C(11)	117.9(7)
C(9)–Mo(1)–N(2)	102.6(3)	C(9)–Mo(1)–C(1)	122.6(3)	C(12)–C(11)–C(10)	119.1(7)	C(13)–C(12)–C(11)	121.7(7)
C(17)–N(1)–Mo(1)	161.1(4)	C(21)–N(2)–Mo(1)	160.1(5)	C(14)–C(13)–C(12)	120.1(7)	C(13)–C(14)–C(9)	120.6(7)
C(2)–C(1)–Mo(1)	114.8(5)	C(6)–C(1)–Mo(1)	127.7(5)	C(16)–C(14)–C(9)	122.2(6)	C(16)–C(14)–C(13)	117.2(7)
C(6)–C(1)–C(2)	117.5(6)	C(3)–C(2)–C(1)	120.3(7)	C(18)–C(17)–N(1)	107.4(6)	C(19)–C(17)–N(1)	111.3(6)
C(7)–C(2)–C(1)	121.5(6)	C(7)–C(2)–C(3)	118.1(7)	C(19)–C(17)–C(18)	112.3(7)	C(20)–C(17)–N(1)	108.4(6)
C(4)–C(3)–C(2)	120.0(7)	C(5)–C(4)–C(3)	120.6(7)	C(20)–C(17)–C(18)	107.1(7)	C(20)–C(17)–C(19)	110.2(7)
C(6)–C(5)–C(4)	120.6(7)	C(5)–C(6)–C(1)	120.9(7)	C(22)–C(21)–N(2)	107.1(8)	C(23)–C(21)–N(2)	111.3(8)
C(8)–C(6)–C(1)	121.4(7)	C(8)–C(6)–C(5)	117.7(7)	C(23)–C(21)–C(22)	107.0(13)	C(24)–C(21)–N(2)	107.8(9)
C(10)–C(9)–Mo(1)	113.7(5)	C(14)–C(9)–Mo(1)	128.5(5)	C(24)–C(21)–C(22)	107.8(12)	C(24)–C(21)–C(23)	115.4(13)

However, close examination of the completed structure showed that an alternative explanation may be possible. In both molecules we find that one *o*-methyl group on each aryl ligand is in reasonably close contact with the metal atom and that one C–H bond on each methyl seems to be oriented to interact with the metal. It is pertinent to note here that hydrogens in these methyl groups were among those detected experimentally. Unfortunately no indications of such interactions could be detected in the i.r. spectra of the complexes. A further feature of the structure which could be consistent with the presence of attractive M...H interactions is the tilting of the aryl ligands in directions which correspond to a pulling in of the methyl group towards the metal: *cf.* the M–C–C angles of *ca.* 114–116 and 127–128°. On the other hand, it could equally be argued that the bulky *t*-butyl groups are in fact pushing the aryl ligands in the observed direction, an explanation more in keeping with the character expected for a 16-electron metal centre, which would not be expected to participate in significant agostic interactions. In order to examine this possibility we have made some simple steric energy calculations on the chromium complex. In these we assumed that all atom–atom interactions between ligands or between ligand and metal (except of course for the bonded

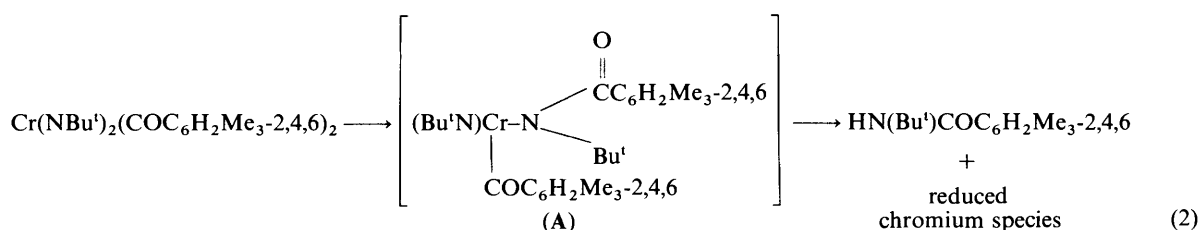
atoms) were normal non-bonding van der Waals interactions. The tilting of the aryl groups about the C...M bonds was removed by setting both M–C–C angles to 120° and the interligand steric interactions minimised by allowing torsion angle changes about all formally single bonds. The overall 'steric energy' was reduced by *ca.* 60 kJ mol⁻¹, a large proportion of which (*ca.* 37 kJ mol⁻¹) was due to removal of the M...H–C interaction. For this calculation the metal atom was defined as a spherical methyl group with a radius of 1.3 Å. Clearly the energy sum will be significantly affected by any change in the assignment of parameters to the metal atom, but the calculation does show that regardless of the way in which the metal atom is treated, the aryl ligands are not being forced into their tilted mode of bonding by the other ligands. It is possible therefore that these ligands are indeed being pulled into the positions found. More detailed molecular mechanics and extended Hückel molecular orbital calculations are in progress to investigate this system further.

Insertion Reactions of the Imido Aryl Compounds.—The bright yellow bis(acyl) complex Cr(NBu^t)₂(COC₆H₂Me₃-2,4,6)₂ (8) is obtained on treatment of hexane solutions of (1)

with CO (80 lb in⁻²) for 2 h at room temperature. The ¹H n.m.r. spectrum shows that the mesityl groups are equivalent but shifted slightly downfield while the t-butyl protons appear at slightly higher field than in the parent compound. In the ¹³C-¹H spectrum the carbonyl carbon peak occurs at 264.13 p.p.m. which is higher field than found in some η²-systems,¹⁴⁻¹⁷ although probably at sufficiently low field to indicate η²-type bonding. Curiously, the i.r. spectrum (Nujol mull), shows three strong bands (1 545, 1 630, and 1 650 cm⁻¹) in the acyl region.

This appears to be the highest oxidation state acyl derivative of chromium but d⁰ acyls of titanium,^{18,19} zirconium,^{15,18,19} and hafnium^{18,19} are also known. Bis(acyl) formation is also an unusual feature, mono-insertions being more commonly observed in systems with more than one metal-carbon bond present, for example Zr(η⁵-C₅H₅)₂RR' (R = R' = CH₂SiMe₃, Me, or C₆H₄Me-*o*; R = CH₂SiMe₃, R' = Me or CH₂Bu^t),¹⁵ but a few bis(acyl) complexes are known, namely *cis*-Os(COEt)₂(CO)₄²⁰ and the anionic *cis*-[Mn(COME)₂(CO)₄]⁻.²¹

The bis(acyl) compound is thermally unstable and eliminates HN(Bu^t)COC₆H₂Me₃-2,4,6²² if the solid or solutions are heated or left standing at room temperature. According to e.s.r. spectra, a mixture of paramagnetic chromium species appears to be present in the dark residues after elimination of amide has taken place. These species have not been characterised. The exact nature of the mechanism of amide elimination is not clear but possibly the initial step requires migration of the acyl group to the electron-deficient imido nitrogen with formation of an intermediate carboxamido derivative (A) as in equation (2).



A further transformation is necessary to provide a hydride for the elimination of the amide. This may be abstracted either from the mesityl or t-butyl groups which are the only sources of hydrogen present in the solid (hexane was the only solvent used). In an attempt to stabilise the postulated intermediate (A) the bis(acyl) complex was dissolved in PMe₃ at -78 °C and subsequently stirred at room temperature, but once again the main product was the amide HN(Bu^t)COC₆H₂Me₃-2,4,6. When the molybdenum compound (3) was similarly treated with CO (80 lb in⁻², 2 h or 12 h) substantial quantities of the amide HN(Bu^t)COC₆H₂Me₃-2,4,6 were produced, but no intermediate molybdenum acyl species could be isolated.

An acyl migration of the type proposed here from a metal to imido nitrogen function has not to our knowledge been previously observed. Azacarbonylations²³ usually proceed by CO insertion in metal-nitrogen bonds or attack of acyl moieties by amines. However some carbocarbonylation²³ reactions involving 1,2-metal acyl additions to unsaturated carbon-carbon bonds, for instance the addition of the cobalt complex Co{C(O)OMe}(CO)₄ to butadiene with formation of the π-allylic complex Co{η³-C₃H₄[CH₂C(O)OMe]}(CO)₃,²⁴ are related to the present work. More directly related is the ester migration from cobalt to co-ordinated nitrogen in the one-electron electrochemical oxidation of ethoxycarbonyl-[5,10,15,20-tetraphenylporphyrinato]cobalt(III) to [N-ethoxycarbonyl-5,10,15,20-tetraphenylporphyrinato]cobalt(II).²⁵ Intramolecular acyl shifts in purely organic molecules are of course well known.²⁶

Reactions between the d⁰ imido aryls M(NBu^t)₂R'₂ (M = Cr, Mo, or W, R' = C₆H₂Me₃-2,4,6; M = Mo, R' = C₆H₄Me-*o*) and t-butyl isocyanide proceed cleanly and rapidly at room temperature; only mono-inserted products, M(NBu^t)₂[C(R')=NBu^t]R', were isolated even when excess isocyanide was used. The i.r. bands were in the range 1 650—1 715 cm⁻¹ suggesting η²-co-ordination of the iminoacyl groups. The ¹H n.m.r. spectra show two sets of resonances for the mesityl and *o*-tolyl groups. For the aryl groups attached to the imine functions, the *o*-methyls are shifted to high field, the *m*-protons shifted to low field, and the *para* position is unaffected in accord with the expected shielding and deshielding effects of the η²-C=N moiety.

High-oxidation-state iminoacyl derivatives with the iminoacyl function η²-bound have been described for titanium,^{27,28} zirconium,^{15,29} uranium,³⁰ and recently tantalum.³¹ While there are no d⁰ iminoacyls known for the chromium group (a complicated insertion and rearrangement occurs in reactions of WMe₆ with Bu^tNC),³² compounds with metals in lower oxidation states containing this functionality have been prepared, for example, by alkylation of complexed methyl isocyanide as in Mo(η⁵-C₅H₅)(CO)₂(η²-MeCNMe),³³ or by action of imidoyl chlorides on anions as in W(η⁵-C₅H₅)(CO)₃(CPhNPh).³⁴ The mass spectra of mesityl-chromium and -molybdenum iminoacyls give parent ions while for the tungsten compound the base peak represents the parent ion less t-butyl. There is no evidence in the mass spectra for species resulting from iminoacyl migration, akin to the acyl migration proposed above, to account for thermal elimination of the amide HN(Bu^t)COC₆H₂Me₃-2,4,6 from Cr(NBu^t)₂(C₆H₂Me₃-2,4,6)₂.

However, there are peaks in the spectrum of Cr(NBu^t)₂[C(C₆H₂Me₃-2,4,6)=NBu^t](C₆H₂Me₃-2,4,6) corresponding to the imine Bu^tN=C(C₆H₂Me₃-2,4,6)₂ and suggesting that an intermediate Cr^{IV} species Cr(NBu^t)₂[η²-C(C₆H₂Me₃-2,4,6)₂=NBu^t] may be formed. Noteworthy in this respect is the thermal rearrangement of the compounds Ta(OR')₂(η²-CMe=NR')₂Me (R' = C₆H₃-Me₂-2,6) to Ta(OR')₂[N(R')CMe₂CMe=NR'], for which the intermediate Ta(OR')₂(η²-CMe=NR')(η²-CMe₂=NR') is suggested³¹ (cf. also ref. 32).

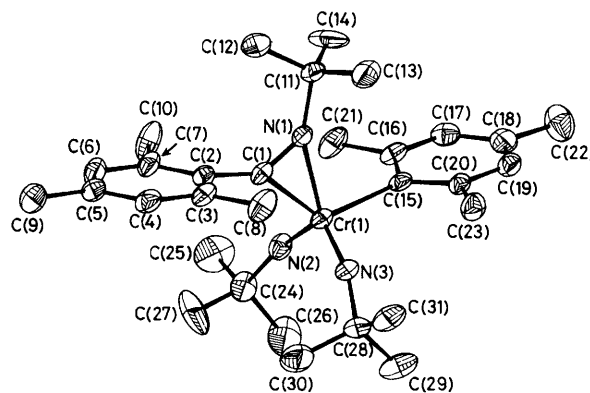


Figure 3. The molecular structure of Cr(NBu^t)₂[C(C₆H₂Me₃-2,4,6)NBu^t](C₆H₂Me₃-2,4,6) (9)

Table 4. Selected bond lengths (Å) and angles (°) for (9)

N(1)–Cr(1)	2.057(6)	N(2)–Cr(1)	1.628(6)	C(13)–C(11)	1.497(10)	C(14)–C(11)	1.516(11)
N(3)–Cr(1)	1.630(6)	C(1)–Cr(1)	1.982(7)	C(16)–C(15)	1.406(8)	C(20)–C(15)	1.404(8)
C(15)–Cr(1)	2.134(7)	C(1)–N(1)	1.244(7)	C(17)–C(16)	1.395(9)	C(21)–C(16)	1.494(9)
C(11)–N(1)	1.502(9)	C(24)–N(2)	1.465(8)	C(18)–C(17)	1.383(10)	C(19)–C(18)	1.376(9)
C(28)–N(3)	1.456(8)	C(2)–C(1)	1.465(8)	C(22)–C(18)	1.518(11)	C(20)–C(19)	1.380(9)
C(3)–C(2)	1.397(9)	C(7)–C(2)	1.399(9)	C(23)–C(20)	1.494(9)	C(25)–C(24)	1.505(12)
C(4)–C(3)	1.367(9)	C(8)–C(3)	1.502(10)	C(26)–C(24)	1.490(12)	C(27)–C(24)	1.507(12)
C(5)–C(4)	1.371(9)	C(6)–C(5)	1.368(9)	C(29)–C(28)	1.525(11)	C(30)–C(28)	1.509(11)
C(9)–C(5)	1.531(10)	C(7)–C(6)	1.387(9)	C(31)–C(28)	1.521(11)		
C(10)–C(7)	1.498(9)	C(12)–C(11)	1.524(11)				
N(2)–Cr(1)–N(1)	121.7(3)	N(3)–Cr(1)–N(1)	116.2(3)	C(12)–C(11)–N(1)	111.3(6)	C(13)–C(11)–N(1)	106.0(6)
N(3)–Cr(1)–N(2)	112.8(3)	C(1)–Cr(1)–N(1)	35.8(2)	C(13)–C(11)–C(12)	112.3(7)	C(14)–C(11)–N(1)	107.1(6)
C(1)–Cr(1)–N(2)	103.4(3)	C(1)–Cr(1)–N(3)	104.0(3)	C(14)–C(11)–C(12)	110.3(6)	C(14)–C(11)–C(13)	109.5(7)
C(15)–Cr(1)–N(1)	90.2(3)	C(15)–Cr(1)–N(2)	104.6(3)	C(16)–C(15)–Cr(1)	119.7(5)	C(20)–C(15)–Cr(1)	124.0(5)
C(15)–Cr(1)–N(3)	106.4(3)	C(15)–Cr(1)–C(1)	125.8(3)	C(20)–C(15)–C(16)	116.3(6)	C(17)–C(16)–C(15)	120.6(6)
C(1)–N(1)–Cr(1)	68.8(4)	C(11)–N(1)–Cr(1)	157.7(4)	C(21)–C(16)–C(15)	122.9(6)	C(21)–C(16)–C(17)	116.4(6)
C(11)–N(1)–C(1)	133.3(5)	C(24)–N(2)–Cr(1)	162.8(4)	C(18)–C(17)–C(16)	122.1(6)	C(19)–C(18)–C(17)	116.9(7)
C(28)–N(3)–Cr(1)	161.5(4)	N(1)–C(1)–Cr(1)	75.4(4)	C(22)–C(18)–C(17)	121.1(8)	C(22)–C(18)–C(19)	121.9(8)
C(2)–C(1)–Cr(1)	145.9(4)	C(2)–C(1)–N(1)	138.7(5)	C(20)–C(19)–C(18)	122.4(7)	C(19)–C(20)–C(15)	121.3(6)
C(3)–C(2)–C(1)	119.8(6)	C(7)–C(2)–C(1)	119.7(6)	C(23)–C(20)–C(15)	122.9(6)	C(23)–C(20)–C(19)	115.8(6)
C(7)–C(2)–C(3)	120.4(6)	C(4)–C(3)–C(2)	118.5(6)	C(25)–C(24)–N(2)	111.5(7)	C(26)–C(24)–N(2)	107.7(7)
C(8)–C(3)–C(2)	120.1(6)	C(8)–C(3)–C(4)	121.4(7)	C(26)–C(24)–C(25)	110.2(8)	C(27)–C(24)–N(2)	108.2(6)
C(5)–C(4)–C(3)	122.8(7)	C(6)–C(5)–C(4)	118.0(7)	C(27)–C(24)–C(25)	107.9(8)	C(27)–C(24)–C(26)	111.4(9)
C(9)–C(5)–C(4)	120.9(7)	C(9)–C(5)–C(6)	121.1(7)	C(29)–C(28)–N(3)	108.9(6)	C(30)–C(28)–N(3)	109.3(6)
C(7)–C(6)–C(5)	122.5(7)	C(6)–C(7)–C(2)	117.8(6)	C(30)–C(28)–C(29)	111.0(7)	C(31)–C(28)–N(3)	109.3(6)
C(10)–C(7)–C(2)	121.0(6)	C(10)–C(7)–C(6)	121.1(7)	C(31)–C(28)–C(29)	108.1(7)	C(31)–C(28)–C(30)	110.2(7)

All four iminoacyl compounds $M(\text{NBu}^t)_2[\text{C}(\text{R}')=\text{NBu}^t]\text{R}'$ are air-sensitive crystalline solids. The structure of the chromium compound was determined and the η^2 -co-ordination confirmed. A diagram of the molecular structure is shown in Figure 3; selected bond lengths and angles are given in Table 4. The co-ordination geometry can be described most conveniently as pseudo-tetrahedral with the η^2 -aminoacyl group occupying a split site. The geometry of attachment of the η^2 -ligand is different to that found for the Ta complexes mentioned previously, in that the Cr–C bond is shorter than the Cr–N bond here; the opposite is true for the Ta compounds. The Cr≡N bond lengths are very similar to those in the diaryldi-imido complexes described earlier, whereas the Cr–C(aryl) bond is *ca.* 0.1 Å longer in the present complex.

Attempts to insert other small molecules have been made: compound (1) failed to react with C_2H_4 , CO_2 , or CS_2 although weak complexation with the last in solution was suggested by upfield shifts of the mesityl resonances. There was, however, no evidence for complexation with PMe_3 or pyridine presumably because of crowding at the metal centre. Hexane or toluene solutions of the chromium compound reacted rapidly with nitric oxide (25 lb in⁻², room temperature) to give deep red paramagnetic materials with a strong band in the i.r. at 1750 cm^{-1} indicating co-ordinated NO, but no crystalline material could be obtained. Likewise, reactions with SO_2 proceeded rapidly to give an insoluble pale creamy white solid which apart from the mesityl bands had a strong i.r. band in the range 925–985 cm^{-1} probably indicating $^{28}\text{O}=\text{CrOSC}_6\text{H}_2\text{Me}_3\text{-2,4,6}$ linkage but again no pure material could be obtained.

Experimental

Microanalyses were by Imperial College and Pascher, Bonn. Spectrometers: i.r., Perkin-Elmer 683 (spectra in Nujol mulls; values in cm^{-1}); n.m.r., Perkin-Elmer R32 (90 MHz; CW) and Bruker WM-250 (in C_6D_6 ; data in p.p.m. relative to SiMe_4); e.s.r., Varian E-12 (X-band); mass, Kratos MS-902 (recorded at 70 eV). Cyclic voltammetry: E.G. and G Par model 174A polarographic analyser.

Table 5. Crystallographic data

	(1)	(4)	(9)
(a) Crystal data			
Formula	$\text{C}_{26}\text{H}_{40}\text{CrN}_2$	$\text{C}_{24}\text{H}_{36}\text{MoN}_2$	$\text{C}_{31}\text{H}_{49}\text{CrN}_3$
<i>M</i>	432.611	448.502	515.744
Crystal system	Monoclinic	Orthorhombic	Monoclinic
<i>a</i> /Å	9.145(2)	14.047(7)	26.909(5)
<i>b</i> /Å	18.893(3)	16.511(7)	10.050(2)
<i>c</i> /Å	15.226(4)	20.847(4)	23.689(4)
α /°	90	90	90
β /°	91.49(2)	90	101.55(2)
γ /°	90	90	90
<i>U</i> /Å ³	2 629.8(1.0)	4 835.0(3.3)	6 276.6(2.1)
Space group	$P2_1/n$	<i>Pbca</i>	<i>C2/c</i>
<i>D</i> _c /g cm ⁻³	1.09	1.23	1.09
<i>Z</i>	4	8	8
<i>F</i> (000)	936	1 888	2 240
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	4.36	5.38	3.75
(b) Data collection			
$\theta_{\text{min.}}$, $\theta_{\text{max.}}$ /°	1.5, 25	2.0, 28	1.5, 23
Total data measured	5 189	6 840	4 881
Total data unique	4 620	5 825	4 351
Total data observed	2 673	2 894	2 219
Significance test	$F_o > 5\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$
(c) Refinement			
No. of parameters	263	245	316
Weighting scheme	0.0001	0.0006	0.0005
parameter <i>g</i> ^a			
Final <i>R</i> ^b	0.0507	0.0451	0.0483
Final <i>R'</i> ^c	0.0536	0.0565	0.0577

$$^a w = 1/[\sigma^2(F_o) + gF_o^2]. \quad ^b R = \Sigma|\Delta F|/\Sigma|F_o|. \quad ^c R' = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2}.$$

All manipulations were carried out under argon or *in vacuo*. Solvents were dried by standard methods and degassed prior to use. Melting points were determined in sealed capillaries and are uncorrected. $\text{Cr}(\text{NBu}^t)_2(\text{OSiMe}_3)_2$, $\text{Mo}(\text{NBu}^t)_2(\text{OSiMe}_3)_2$, and

Bu¹N(SiMe₃)H were prepared by the published methods. The procedure for W(NBu¹)₂(OSiPh₃)₂ was modified to give an improved (75%) yield by carrying out the reaction in toluene at ca. 70 °C with the Bu¹NH₂ being continually swept from the system as it was formed.

Physical and analytical data of the new compounds are given in Table 1.

Dimesityldi(t-butylimido)chromium(vi), (1).—To a stirred solution of Cr(NBu¹)₂(OSiMe₃)₂ (0.96 g, 2.5 mmol) in hexane (20 cm³) was added mesitylmagnesium bromide (5 cm³ of 1.0 mol dm⁻³ solution in Et₂O, 5 mmol) at room temperature. An instant and slightly exothermic reaction occurred with deposition of a red solid. The mixture was stirred overnight and then the solvents were removed under vacuum. The residue was extracted with hexane (15 cm³) and the filtered red solution concentrated to ca. 7 cm³ and cooled (-21 °C) to give fine red needles. Yield: 0.7 g, (65%). ¹H N.m.r.: δ 1.35 (18 H, s, Bu¹), 2.15 (6 H, s, 4-Me), 2.6 (12 H, s, 2,6-Me₂), and 6.75 (4 H, s, C₆H₂).

Di(t-butylimido)di(2,6-xylyl)chromium(vi), (2).—A stirred solution of Cr(NBu¹)₂(OSiMe₃)₂ (1.65 g, 4.4 mmol) in hexane (20 cm³) at -40 °C was treated with 2,6-xylylmagnesium bromide (11 cm³ of 0.8 mol dm⁻³ solution in Et₂O, 8.8 mmol). The solution rapidly darkened with precipitation of a solid on warming to room temperature. After stirring for several hours the solvent was pumped off and the residue extracted with hexane (20 cm³). The deep red filtered hexane solution was evaporated and the oily residue dissolved in hexamethyldisiloxane (15 cm³). Cooling this solution at -21 °C gave the product as dark red crystals. Yield: 1.23 g, 69%. ¹H N.m.r.: δ 1.39 (18 H, s, Bu¹), 2.64 (12 H, s, 2,6-Me₂), and 6.97 (6 H, m, C₆H₃).

Dimesityldi(t-butylimido)molybdenum(vi), (3).—To a stirred solution of Mo(NBu¹)₂(OSiMe₃)₂ (1.24 g, 2.97 mmol) in hexane (20 cm³) was added slowly at room temperature mesitylmagnesium bromide (6 cm³ of 1.0 mol dm⁻³ solution in Et₂O, 6 mmol). The yellow solution became deep orange with deposition of a yellow precipitate. After stirring for a further 2 h the solvent was removed under vacuum and the residue extracted with hexane (20 cm³). The filtered yellow hexane solution was pumped dry to give the pure (by n.m.r.) product, a yellow solid. Yield: 1.2 g, 85%. Crystalline material was obtained by cooling concentrated hexane solutions of the product at -21 °C. ¹H N.m.r.: δ 1.35 (18 H, s, Bu¹), 2.05 (6 H, s, 4-Me), 2.55 (12 H, s, 2,6-Me₂), and 6.8 (4 H, br s, C₆H₂).

Di(t-butylimido)di(2,6-xylyl)molybdenum(vi), (4).—This was prepared as for (1), from Mo(NBu¹)₂(OSiMe₃)₂ (0.85 g, 2.04 mmol) and 2,6-xylylmagnesium bromide (5.1 cm³ of 0.8 mol dm⁻³ solution in Et₂O, 4.08 mmol). The yellow solid obtained was crystallised from hexane as yellow plates. Yield: 0.49 g, 54%. ¹H N.m.r.: δ 1.42 (18 H, s, Bu¹), 2.59 (12 H, s, 2,6-Me₂), and 6.97 (6 H, m, C₆H₃).

Di(t-butylimido)di(o-tolyl)molybdenum(vi), (5).—This was prepared as for (1), from Mo(NBu¹)₂(OSiMe₃)₂ (1.42 g, 3.4 mmol) and *o*-tolylmagnesium bromide (11.4 cm³ of 0.6 mol dm⁻³ solution in Et₂O, 6.8 mmol) with the exception that the addition of Grignard reagent was carried out at -78 °C. The product, a red-orange waxy solid, could not be crystallised. Yield: 0.97 g, 68%. ¹H N.m.r.: δ 1.5 (18 H, s, Bu¹), 2.7 (6 H, s, *o*-Me), 7.1 and 8.15 (m, C₆H₄).

Dimesityldi(t-butylimido)tungsten(vi), (6).—To a solution of W(NBu¹)₂(OSiPh₃)₂ (0.92 g, 1.06 mmol) in hexane (20 cm³) was added mesitylmagnesium bromide (3.6 cm³ of 0.6 mol dm⁻³ solution in Et₂O, 2.16 mmol) at room temperature. The mixture

was stirred for 3 h and the solvent removed under vacuum. The residue was extracted with hexane (20 cm³) and the filtered hexane extract dried under vacuum. The oily material obtained was dissolved in hexamethyldisiloxane (ca. 5 cm³) and the solution cooled to give small clumps of pale orange crystals. The mother-liquor was decanted and the product dried under vacuum to give a pale orange powder. Yield: 0.35 g, 58%. ¹H N.m.r.: δ 1.5 (18 H, s, Bu¹), 2.15 (6 H, s, 4-Me), 2.7 (12 H, s, 2,6-Me₂), 6.9 (4 H, br, s, C₆H₂). The mass spectrum shows a molecular ion at 70 eV, P⁺ [*m/e* 564 (42%)] along with fragments (P - Me)⁺ [549 (19.6)], and (P - Bu¹)⁺ [507 (10.6)], with a base peak at *m/e* 147 possibly due to (C₆H₂Me₃-N≡N)⁺.

Di(t-butylimido)di(2,6-xylyl)tungsten(vi), (7).—A solution of W(NBu¹)₂(OSiPh₃)₂ (0.54 g, 0.6 mmol) in hexane (15 cm³) was treated with 2,6-xylylmagnesium bromide (1.5 cm³ of 0.8 mol dm⁻³ solution in Et₂O, 1.2 mmol) at room temperature. After stirring for 2 h the solvent was removed under vacuum and the residue stirred in hexane (20 cm³) overnight. The yellow hexane solution was filtered and pumped dry to give a pale yellow solid. This was extracted with hexane (5 cm³) and the filtered solution cooled to give pale yellow plates. Yield 0.12 g, 38%. ¹H N.m.r.: δ 1.4 (18 H, s, Bu¹), 2.56 (12 H, s, 2,6-Me₂), and 7.05 (6 H, s, C₆H₃).

Di(mesitylformyl)di(t-butylimido)chromium(vi), (8).—A solution of (1) (0.35 g, 0.81 mmol) in hexane (10 cm³) was stirred for 2 h under CO (140 lb in⁻²) at room temperature. No colour change was observed. The reaction mixture was transferred to a Schlenk tube under argon. On standing, yellow needles of the product began to form on the sides of the flask. The solution was cooled to ca. -10 °C and after 30 min the mother-liquor was decanted and the yellow crystalline residue washed with hexane. Yield: 0.09 g, 25%. ¹H N.m.r.: δ 1.28 (18 H, s, Bu¹), 2.08 (6 H, s, 4-Me), 2.68 (12 H, s, 2,6-Me₂), and 6.68 (4 H, s, C₆H₂). ¹³C-{¹H} N.m.r. (C₇D₈, -40 °C): δ 31.49 (s, CMe₃), 72.27 (s, CMe₃), and 264.13 (s, C=O); the aromatic mesityl carbon atoms are masked by the C₇D₈ peaks. I.r.: 1 650s, 1 630s, 1 610m, 1 545s, 1 355w, 1 290m, 1 220s, 1 160m, 875m, 820s, 720m, and 610m. The HN(Bu¹)C₆H₂Me₃-2,4,6 formed on decomposition was identified by n.m.r., i.r., mass spectrum, m.p. and analysis which were identical to literature values.²²

Mesityl[mesityl(t-butylimino)methyl]di(t-butylimido)chromium(vi), (9).—A solution of (1) (0.31 g, 0.72 mmol) in hexane (10 cm³) was treated with *t*-butyl isocyanide (0.16 g, 1.9 mmol). The solution changed instantly from deep red to golden brown. Filtration and concentration to half-volume, followed by further filtration and cooling at -21 °C, gave a mass of yellow plate-like crystals. Yield: 0.3 g, 83%. I.r.: 1 715s, 1 610w, 1 365m, 1 350s, 1 230s, 1 210s, 1 195s, 1 115m, 1 015m, 1 000m, 890m, 855m, 840m, 830w, 805w, 725w, 710w, 665w, 615w, and 555w. ¹H N.m.r.: δ 0.88 (9 H, s, C=NBU¹), 1.33 (18 H, s, NBU¹), 2.14 (3 H, s, NCC₆H₂Me-4), 2.22 (6 H, s, NCC₆H₂Me₂-2,6), 2.43 (3 H, s, 4-Me), 2.75 (6 H, s, 2,6-Me₂), and 6.74 (2 H, br s, C₆H₂); the other aromatic protons (NCC₆H₂) are masked by the C₆D₅H peak. The mass spectrum (*m/e*) shows a molecular ion at 70 eV, P⁺ [*m/e* 515 (25.8%)] and the fragments [(C₆H₂Me₃)₂C=NBU¹]⁺ [321 (73.1)], [(C₆H₂Me₃)₂C=N]⁺ [264 (94.6%)]. The base peak at *m/e* 144 is probably due to [Bu¹N(H)NBU¹H]⁺ [144 (100%)].

Mesityl[mesityl(t-butylimino)methyl]di(t-butylimido)molybdenum(vi), (10).—This was prepared as for (9), from (3) (0.54 g, 1.13 mmol) and *t*-butyl isocyanide (0.23 g, 2.83 mmol). The product was a cream coloured crystalline solid. Yield: 0.46 g, 73%. I.r.: 1 670s, 1 610w, 1 365m, 1 350s, 1 245s, 1 205vs, 1 165s, 900m, 840m, 805m, 740w, 720w, 705w, 595w. ¹H N.m.r.: 0.98

Table 6. Fractional atomic co-ordinates ($\times 10^4$) for compound (1)

Atom	x	y	z	Atom	x	y	z
Cr(1)	1 960(1)	2 041(0.5)	556(0.5)	C(13)	1 305(5)	415(2)	2 986(3)
N(1)	3 651(4)	2 300(2)	483(2)	C(14)	2 662(5)	496(2)	2 644(3)
N(2)	1 338(4)	1 598(2)	-287(2)	C(15)	2 945(4)	922(2)	1 932(3)
C(1)	914(4)	2 988(2)	621(2)	C(16)	-951(5)	1 579(3)	1 465(3)
C(2)	50(5)	3 320(2)	-42(3)	C(17)	1 070(5)	-61(3)	3 759(3)
C(3)	-736(5)	3 916(3)	163(2)	C(18)	4 491(5)	955(3)	1 611(3)
C(4)	-743(5)	4 215(2)	989(3)	C(19)	4 986(6)	2 552(3)	96(3)
C(5)	127(5)	3 893(2)	1 614(3)	C(20)	4 588(7)	3 099(4)	-556(5)
C(6)	975(4)	3 306(2)	1 455(3)	C(21)	5 918(6)	2 872(3)	853(5)
C(7)	-36(6)	3 047(3)	-964(3)	C(22)	5 842(6)	1 956(4)	-292(4)
C(8)	-1 648(5)	4 845(3)	1 182(4)	C(23)	1 307(6)	1 107(3)	-1 019(3)
C(9)	1 944(5)	3 025(3)	2 197(3)	C(24)	2 325(8)	512(3)	-809(4)
C(10)	1 791(4)	1 309(2)	1 527(2)	C(25)	-261(8)	842(4)	-1 110(5)
C(11)	381(4)	1 216(2)	1 861(3)	C(26)	1 751(10)	1 462(5)	-1 847(4)
C(12)	176(4)	779(2)	2 583(3)				

Table 7. Fractional atomic co-ordinates ($\times 10^4$) for compound (4)

Atom	x	y	z	Atom	x	y	z
Mo(1)	1 647(0.5)	4 336(0.5)	6 650(0.5)	C(12)	-155(5)	2 183(4)	5 563(4)
N(1)	2 816(3)	4 386(3)	6 389(2)	C(13)	684(5)	2 408(4)	5 279(3)
N(2)	1 028(4)	5 205(3)	6 496(2)	C(14)	1 209(4)	3 028(4)	5 530(3)
C(1)	1 846(4)	4 211(3)	7 673(2)	C(15)	-394(5)	3 646(5)	6 927(4)
C(2)	1 908(4)	3 401(4)	7 895(3)	C(16)	2 115(5)	3 258(5)	5 180(3)
C(3)	2 041(5)	3 241(4)	8 543(3)	C(17)	3 738(4)	4 712(4)	6 193(3)
C(4)	2 152(5)	3 873(5)	8 972(3)	C(18)	4 045(5)	5 317(5)	6 701(4)
C(5)	2 104(5)	4 653(5)	8 769(3)	C(19)	3 686(6)	5 086(5)	5 536(4)
C(6)	1 947(4)	4 831(4)	8 128(3)	C(20)	4 460(5)	4 029(5)	6 199(4)
C(7)	1 890(5)	2 704(4)	7 443(3)	C(21)	711(6)	5 952(4)	6 167(4)
C(8)	1 904(5)	5 703(4)	7 939(3)	C(22)	765(12)	5 796(8)	5 475(6)
C(9)	892(4)	3 447(3)	6 083(3)	C(23)	1 352(14)	6 632(6)	6 303(9)
C(10)	20(4)	3 210(3)	6 350(3)	C(24)	-285(10)	6 084(11)	6 330(9)
C(11)	-494(5)	2 566(4)	6 093(4)				

Table 8. Fractional atomic co-ordinates ($\times 10^4$) for compound (9)

Atom	x	y	z	Atom	x	y	z
Cr(1)	1 448(0.5)	2 231(1)	5 897(0.5)	C(15)	1 145(2)	2 669(6)	5 014(2)
N(1)	809(2)	3 008(4)	6 125(2)	C(16)	821(2)	1 750(6)	4 676(3)
N(2)	1 556(2)	637(4)	5 909(2)	C(17)	656(2)	1 956(6)	4 085(3)
N(3)	1 965(2)	3 110(4)	6 076(2)	C(18)	797(3)	3 067(7)	3 810(3)
C(1)	1 094(2)	2 497(5)	6 547(3)	C(19)	1 090(2)	4 000(6)	4 149(3)
C(2)	1 116(2)	2 307(6)	7 164(2)	C(20)	1 252(2)	3 836(6)	4 735(3)
C(3)	1 362(2)	3 249(6)	7 557(3)	C(21)	634(3)	518(7)	4 918(3)
C(4)	1 413(2)	2 993(7)	8 133(3)	C(22)	642(3)	3 225(8)	3 161(3)
C(5)	1 230(2)	1 860(7)	8 340(3)	C(23)	1 547(3)	4 967(7)	5 046(3)
C(6)	984(3)	957(6)	7 949(3)	C(24)	1 801(3)	-667(6)	6 018(3)
C(7)	925(2)	1 136(6)	7 359(3)	C(25)	1 422(4)	-1 781(7)	5 881(4)
C(8)	1 555(3)	4 518(7)	7 345(3)	C(26)	2 190(4)	-771(9)	5 652(5)
C(9)	1 297(3)	1 616(8)	8 989(3)	C(27)	2 039(4)	-752(8)	6 649(4)
C(10)	647(3)	138(6)	6 943(3)	C(28)	2 496(2)	3 469(8)	6 269(3)
C(11)	315(2)	3 749(6)	6 053(3)	C(29)	2 782(3)	3 147(8)	5 792(4)
C(12)	89(3)	3 642(7)	6 592(3)	C(30)	2 713(3)	2 710(9)	6 812(4)
C(13)	431(3)	5 157(7)	5 918(4)	C(31)	2 537(2)	4 959(7)	6 383(3)
C(14)	-41(2)	3 143(8)	5 541(3)				

(9 H, s, C=NBU¹), 1.51 (18 H, s, NBU¹), 2.2 (3 H, s, NCC₆H₂Me-4), 2.25 (6 H, s, NCC₆H₂Me₂-2,6), 2.43 (3 H, s, 4-Me), 2.85 (6 H, s, 2,6-Me₂), 6.72 (2 H, s, C₆H₂), and 7.12 (2 H, s, NCC₆H₂). The mass spectrum shows a molecular ion at 70 eV, M⁺ [m/e 559 (19.2%)] and the base peak (M - BU¹)⁺ [504 (100)].

Mesityl[mesityl(t-butylimino)methyl]di(t-butylimido)-tungsten(vi), (11).—This was prepared as for (9), from (6) (0.35

g, 0.62 mmol) and t-butyl isocyanide (0.1 g, 1.32 mmol). The product was obtained as colourless crystals. Yield: 0.21 g, 52%. I.r.: 1 655m, 1 650w, 1 615w, 1 600w, 1 370m, 1 360s, 1 280s, 1 235vs, 1 215s, 1 195m, 1 114w, 1 100br, m, 1 025br, m, 915w, 850m, 810s, 745w, 730w, 715w, 590w, and 570w. ¹H N.m.r.: δ 0.9 (9 H, s, C=NBU¹), 1.46 (18 H, s, NBU¹), 2.15 (3 H, s, NCC₆H₂Me-4), 2.23 (6 H, s, NCC₆H₂Me₂-2,6), 2.37 (3 H, s, 4-Me), 2.85 (6 H, s, 2,6-Me₂), and 6.71 (2 H, s, C₆H₂). The other aromatic protons

(NCC₆H₂) are masked by the C₆D₅H signal. The mass spectrum shows a base peak at 70 eV for (M - Bu)⁺ [*m/e* 590 (100%)].

Di(t-butylimido)(o-tolyl)[o-tolyl(t-butylimino)methyl]-molybdenum(vi), (12).—A solution of (5) (0.35 g, 0.83 mmol) in hexane (10 cm³) was treated at room temperature with *t*-butyl isocyanide (0.2 g, 2.5 mmol). The mixture was stirred for 2 h. Filtration followed by removal of solvent gave a tan coloured solid; this was recrystallised from hexamethyldisiloxane. Yield: 0.23 g, 57%. I.r.: 1 660vs, 1 575w, 1 370s, 1 355vs, 1 295vs (sh), 1 265vs, 1 220s (sh), 1 215vs, 1 210vs, 1 045s, 1 025s, 920m, 840w, 810vs, 760vs, 740vs, 720s, 680w, 570w, and 440m cm⁻¹. ¹H N.m.r.: δ 0.9 (9 H, s, C=NBU⁺), 1.35 (18 H, s, NBU⁺), 2.1 (3 H, s, NCC₆H₄Me-*o*), 3.58 (3 H, s, *o*-Me), and 6.97 and 8.4 (m, NCC₆H₄ and C₆H₄).

Crystallographic Studies.—All crystallographic measurements were made on crystals sealed under argon in glass capillaries, using a CAD4 diffractometer operating in the ω/2θ scan mode with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) as previously described.³⁵ The structures were solved *via* standard heavy-atom procedures and refined using full-matrix least-squares methods,³⁶ with scattering factors calculated using data from ref. 37. All non-hydrogen atoms were refined with anisotropic displacement factors; many hydrogens were identified in difference maps and included with geometrical constraints whilst others were similarly included in geometrically required positions. However, no hydrogen atoms on some of the *t*-butyl methyl groups could be detected and were thus omitted. Details of the crystal data, intensity recording and refinements are given in Table 5. Final fractional atomic co-ordinates are given in Tables 6–8.

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