Polyhedron Vol. 9, No. 21, pp. 2625–2634, 1990
Printed in Great Britain

0277-5387/90 \$3.00+.00

t-BUTYLIMIDO COMPLEXES OF CHROMIUM. X-RAY CRYSTAL STRUCTURES OF $Cr(NBu^t)_2(PMe_2Ph)Cl_2$ AND $[Cr(NBu^t)_2(C_5H_4N)_2(\eta^1\text{-}O_3SCF_3)]O_3SCF_3$

ANDREAS A. DANOPOULOS, WA-HUNG LEUNG and
GEOFFREY WILKINSON†

Johnson Matthey Laboratory, Chemistry Department, Imperial College,
London SW7 2AY, U.K.

and

BILQUIS HUSSAIN-BATES and MICHAEL B. HURSTHOUSE†

Chemistry Department, Queen Mary and Westfield College, Mile End Road,
London E1 4NS, U.K.

(*Received* 22 *June* 1990; *accepted* 5 *July* 1990)

Abstract—The compound $Cr(NBu^t)_2Cl_2$ has been synthesized and converted to $Cr(NBu^t)_2(NHBu^t)Cl$, $Cr(NBu^t)_2(NHBu^t)_2$ and $Li_2Cr(NBu^t)_4$, the latter completing the series of Group 6 compounds, $Li_2M(NBu^t)_4$, M = Cr, Mo, W. The five-coordinate adducts, $Cr(NBu^t)_2Cl_2L$, L = PMe_3, PMe_2Ph and Bu^tNC, have been characterized as well as $[Cr(NBu^t)_2Cl_2]_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)$ and the six-coordinate $Cr(NBu^t)_2Cl_2(2,2'\text{-bipyridyl})$. Chloride substitution reactions of $Cr(NBu^t)_2Cl_2$ lead to the compounds, $Cr(NBu^t)_2(\eta^1\text{-}O_2CMe)_2$, $[Cr(NBu^t)_2(PMe_3)_2](O_3SCF_3)_2\cdot 0.5MeCN$, $[Cr(NBu^t)_2py_2(\eta^1\text{-}O_3SCF_3)]SO_3CF_3$ and $[Cr(NBu^t)_2(bpy)_2](PF_6)_2$. The isocyanide, $[Cr(NBu^t)_2Cl_2(Bu^tNC)]$, with MeLi gives the η^2-iminoacyl $Cr(NBu^t)_2[\eta^2\text{-}(Bu^tN{=}CMe)]Cl$. Interaction of $Cr(NBu^t)_2Cl_2$ with alkylating agents at low temperatures gives the chromium(V) dimer $[Cl(Bu^tN)Cr(\mu\text{-}NBu^t)]_2$ in a one-electron per chromium reduction and the same product is obtained by reduction of the dihalide with $(\eta^5\text{-}C_5H_5)_2Co$. X-ray structures of compounds listed in the title have been determined.

In previous papers we have described the synthesis, X-ray structures and some reactions of the lithium derivatives of the species $[M(NBu^t)_4]^{2-}$, M = Mo and W,[1] and $[Re(NBu^t)_4]^-$.[1a,2] A preliminary note on the chromium(VI) analogue[3] is now expanded and this paper also includes a number of reactions of $Cr(NBu^t)_2Cl_2$.[3]

We have also previously described the chromium(VI) diaryls, $Cr(NBu^t)_2Ar_2$, Ar = $C_6H_2Me_3$-2,4,6(mesityl, mes), $C_6H_3Me_2$-2,6, the X-ray structures of the mesityl and of the reaction product with Bu^tNC, i.e. $Cr(NBu^t)_2[\eta^2\text{-mesC}{=}NBu^t]mes$; an unstable acyl from the reaction with CO, $Cr(NBu^t)_2(COmes)_2$ was characterized spectroscopically.[4] After completion of the present study, a recent paper has described $Cr(NBu^t)_2X_2(py)$, X = Cl, Br, some bulky dialkyls, e.g. $Cr(NBu^t)_2(CH_2SiMe_3)_2$, similar to the aryls, and η^5-cyclopentadienyl compounds of the type $Cr(\eta^5\text{-}C_5H_5)(NBu^t)_2R$, R = alkyl or bromide.[5]

Analytical and physical data for new compounds are collected in Table 1. Reactions of $Cr(NBu^t)_2Cl_2$ are summarized in Scheme 1.

RESULTS AND DISCUSSION

(1) *Bis*(*t-butylimido*)*dichlorochromium*(VI)

As in previous work,[4,5] the starting material is $Cr(NBu^t)_2(OSiMe_3)_2$[6] from which, by interaction

---

† Authors to whom correspondence should be addressed.

Table 1. Analytical and physical data for chromium compounds

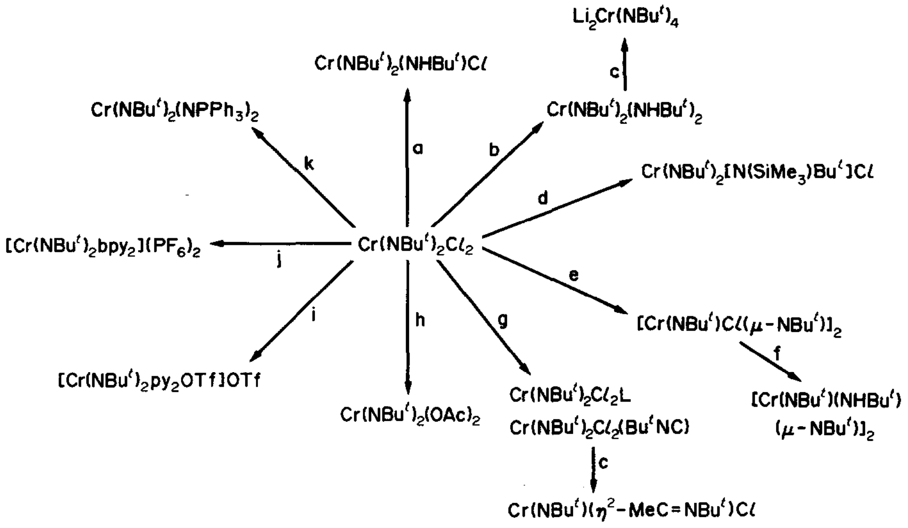
Compound	Colour	Melting point (°C)	Analysis (%)[a] C	H	N	Cl
$\mathrm{Cr(NBu^t)_2Cl_2}$ **(1)**	Red	68–70	36.4	6.8	10.5	
			(36.2)	(6.8)	(10.5)	
$\mathrm{Cr(NBu^t)_2(NHBu^t)Cl}$ **(2)**	Orange	148–150	47.6	9.4	13.8	12.1
			(47.8)	(9.3)	(13.9)	(11.7)
$\mathrm{Cr(NBu^t)_2(NHBu^t)_2}$ **(3)**	Red–purple	57–60	55.9	11.0	16.0	
			(56.8)	(11.2)	(16.5)	
$\mathrm{Cr(NBu^t)_2[N(SiMe_3)Bu^t)]Cl}$ **(4)**	Red	165–170	48.0	9.5	11.0	
			(48.2)	(9.6)	(11.3)	
$\mathrm{Li_2Cr(NBu^t)_4}$ **(5)**	Red	> 250[b]	53.8	10.5	16.0	
			(54.9)	(10.3)	(15.9)	
$\mathrm{Cr(NBu^t)_2Cl_2(PMe_2Ph)}$ **(6)**	Dark yellow	164[b]	47.6	7.3	6.9	
			(47.6)	(7.2)	(6.9)	
$\mathrm{Cr(NBu^t)_2Cl_2(PMe_3)}$ **(7)**	Yellow	142[b]	29.6	5.2	7.8	
			(29.8)	(5.0)	(7.7)	
$\mathrm{Cr(NBu^t)_2Cl_2(CNBu^t)}$ **(8)**	Orange	130[b]	44.8	7.8	11.9	
			(44.8)	(7.8)	(12.0)	
$\mathrm{Cr_2(NBu^t)_4Cl_4(\mu\text{-dppe})}$ **(9)**	Yellow	192[b]	54.1	6.5	6.0	
			(54.2)	(6.5)	(6.0)	
$\mathrm{Cr(NBu^t)_2Cl_2(bpy)}$ **(10)**	Orange–yellow	141[b]	51.4	6.1	13.0	
			(51.3)	(6.2)	(13.3)	
$\mathrm{Cr(NBu^t)_2(O_2CMe)_2}$ **(11)**	Dark orange	63–64	46.0	7.5	8.7	
			(46.2)	(7.7)	(9.0)	
$\mathrm{[Cr(NBu^t)_2py_2(OTf)]OTf}$ **(12)**[c]	Orange	161[b]	37.1	4.3	8.7	
			(37.8)	(4.4)	(8.8)	
$\mathrm{Cr(NBu^t)(PMe_3)_2(OTf)_2(MeCN)_{0.5}}$ **(13)**	Pale green	131[b]	30.7	5.8	5.4	
			(30.7)	(5.6)	(5.3)	
$\mathrm{[Cr(NBu^t)_2(bpy)_2](PF_6)_2}$ **(14)**	Purple	175–176[b]	42.2	4.1	10.2	
			(42.2)	(4.2)	(10.5)	
$\mathrm{Cr(NBu^t)_2(Bu^tNCMe)Cl}$ **(15)**	Dark yellow	90–92	51.1	9.0	12.9	
			(51.3)	(9.2)	(12.8)	
$\mathrm{Cr(NBu^t)_2(NPPh_3)_2}$ **(16)**	Red–purple	190–193	71.4	6.5	7.4	
			(70.8)	(6.4)	(7.5)	
$\mathrm{[(Bu^tN)ClCr(\mu\text{-}NBu^t)]_2}$ **(17)**	Yellow–green	225–227	45.0	8.1	12.9	16.0
			(45.4)	(8.5)	(13.2)	(16.7)
$\mathrm{[Cr(NBu^t)(NHBu^t)(\mu\text{-}NBu^t)]_2}$ **(18)**	Green	175–176	53.8	10.5	15.7	
			(54.1)	(10.5)	(15.7)	

[a] Calculated values given in parentheses.

[b] Decomposes.

[c] OTf = $\mathrm{CF_3SO_3}$.

with boron trichloride in dichloromethane, the chloride, $\mathrm{Cr(NBu^t)_2Cl_2}$ **(1)**, can be prepared in multigram quantities. The reaction is very sensitive to conditions; longer reaction times or higher temperatures than those specified in the Experimental lead to reduced yields, possibly due to polymer formation and/or reduction by chloride ion (cf. reduction of $\mathrm{CrO_2Cl_2}$ by $\mathrm{BCl_3}$[7]). Other main group or transition metal halides ($\mathrm{AlCl_3}$, $\mathrm{PCl_5}$, $\mathrm{TiCl_4}$, $\mathrm{ZrCl_4}$) react similarly but the products are difficult to separate and $\mathrm{BCl_3}$ is the preferred reagent because of the ease of removal of excess chlorinating agent and side products. The chloride **(1)** has been claimed previously,[5,8] but the materials reported were evidently impure oils; our product is a red crystalline solid that can be conveniently purified by sublimation. It is extremely sensitive to moisture; it is less oxidizing than $\mathrm{CrO_2Cl_2}$ as is evident from its reactivity and this is doubtless due to increased π-donation to the metal by the imido group.[6b] The ^{1}H NMR spectrum is strongly dependent on the nature of the solvent; aromatic solvents induce upfield shifts, possibly due to weak complex formation (cf. the adduct with pyridine[5]). In the ^{13}C-{^{1}H} NMR



Scheme 1. Reactions of $Cr(NBu^t)_2Cl_2$. (a) Bu^tNH_2 or $Bu^tNH(SiMe_3)$; (b) Bu^tNHLi (2 eq); (c) MeLi, Et_2O; (d) $LiN(SiMe_3)(Bu^t)\cdot Et_2O$; (e) $Zn(CH_2CMe_3)_2$, *CpLi or Cp_2Co; (f) Bu^tNHLi; (g) L = PMe_2Ph, PMe_3, Bu^tNC, bpy; (h) AgOAc; (i) $AgSO_3CF_3$+py; (j) bpy, $AgCF_3SO_3$, PF_6^-; (k) $LiNPPh_3$.

spectrum the Δ parameter[6b,9] ($\Delta = 53$ ppm) indicates the presence of electrophilic, probably linear, $MNBu^t$ groups and the high order of the Cr—N bond is supported by the IR stretching frequency.

(2) *Bis(t-butylimido)(t-butylamido)chlorochromium* (VI) (2), *bis(t-butylimido)bis(t-butylamido)chromium*(VI) (3), *bis(butylimido)[t-butyl(trimethylsilyl) amido]chlorochromium*(VI) (4) *and dilithium tetrakis (t-butylimido)chromate*(VI) (5)

The interaction of the dichloride with excess Bu^tNH_2 proceeds according to eq. (1):

$$Cr(NBu^t)_2Cl_2 + 2Bu^tNH_2 = Cr(NBu^t)_2(Bu^tNH)Cl + Bu^tNH_3Cl. \quad (1)$$

Further substitution does not occur even under forcing conditions, while the use of less bulky amines gives intractable products.

t-Butylsilylamine reacts similarly only to give the monoamido species (2), eq. (2):

$$Cr(NBu^t)_2Cl_2 + Bu^tNH(SiMe_3) = Cr(NBu^t)_2(Bu^tNH)Cl + SiMe_3Cl. \quad (2)$$

Compound **2** is monomeric (mass spectrum) and remarkably inert towards substitution of the chloride by a variety of nucleophiles. Methyllithium gives intractable products and there is no reaction with more bulky alkyl lithium or Grignard reagents. The compound can be recovered after treatment with Na/Hg or Mg in tetrahydrofuran.

The bis-amido compound, $Cr(NBu^t)_2(NHBu^t)_2$ (**3**) is obtained from $Cr(NBu^t)_2Cl_2$ with two equivalents of $LiNHBu^t$ in toluene but in rather low yield evidently because of competing reduction reactions. The bis-amido compound could not be obtained either at elevated temperature or by use of more polar solvents.

Attempts to obtain $Cr(NBu^t)_3$ (the isoelectronic analogue of CrO_3) from **2** via α-elimination of HCl by thermal or photochemical treatment or by interaction with strong neutral (Et_3N, proton sponge) or anionic (Bu^tLi) bases were unsuccessful and the starting material is recovered. A possible alternative route involved synthesis of $Cr(NBu^t)_2[N(SiMe_3)Bu^t]Cl$ (**4**) by interaction of $Cr(NBu^t)_2Cl_2$ with $LiNBu^t(SiMe_3)\cdot Et_2O$ but thermolysis in THF or toluene gives a green material from which, on work-up, only orange crystals of $Cr(NBu^t)_2(NHBu^t)Cl$ can be isolated; the solvent evidently acts as a source of hydride. There was no reaction in hexane.

Deprotonation of **3** with lithium alkyls under conditions similar to those used for synthesis of the molybdenum and tungsten analogues[1c] gives $Li_2Cr(NBu^t)_4$ (**5**).

Although crystals of **5** suitable for X-ray study could not be obtained, the compound is evidently isostructural with the molybdenum and tungsten analogues[1] and can be formulated as $(Bu^tN)_2Cr(\mu\text{-}NBu^tLi)_4Cr(NBu^t)_2$, as the spectroscopic properties of the three compounds are very similar. Thus the ^1H NMR spectrum of **5** has two singlets (ratio 1 : 3) at 1.60 and 1.30 ppm corresponding to linear and bent metal–imido groups, respectively (cf. W, 1.67, 1.48 ; Mo, 1.66, 1.47 ppm). The IR bands for linear and bent groups are at 1230 and 1190 cm^{-1}, respectively.

(3) *Adducts and chloride-substituted compounds from* $Cr(NBu^t)_2Cl_2$

(a) *Adducts.* The pyridine compound, $Cr(NBu^t)_2Cl_2(py)$, was obtained from $Cr(NBu^t)_2(OSiMe_3)_2$ by action of HCl in Et_2O followed by pyridine.[5] Interaction of $Cr(NBu^t)_2Cl_2$ with PMe_2Ph, PMe_3 and Bu^tNC readily gives rise to the corresponding mono-adducts (**6**, **7** and **8**), as expected for addition to the 16-electron Lewis acid (**1**). These adducts are insoluble in toluene but are fairly soluble in THF or in CH_2Cl_2 in which they are non-conductors. There is no evidence even in refluxing THF for transfer of an imido group to the phosphine as occurs for the monoimido tetraphenylporphyrin complex of chromium(IV),[10] where the phosphineimide and chromium(II) porphyrin are obtained. Interaction of **1** with $Ph_2P(CH_2)_2PPh_2$ (dppe) formed a dppe bridged dimer (**9**) which again has five-coordinate chromium(VI). The reluctance to give an octahedral species may be attributed to the strong *trans* influence of the imido ligand[6b] which precludes having a phosphorus atom *trans* to it (cf. similar observations for tungsten imido complexes[11]). However, interaction with 2,2′-bipyridyl (bpy) does give a six-coordinate adduct $Cr(NBu^t)_2Cl_2(bpy)$ (**10**) which can be converted to the cation, $[Cr(NBu^t)_2(bpy)_2]^{2+}$, as discussed below.

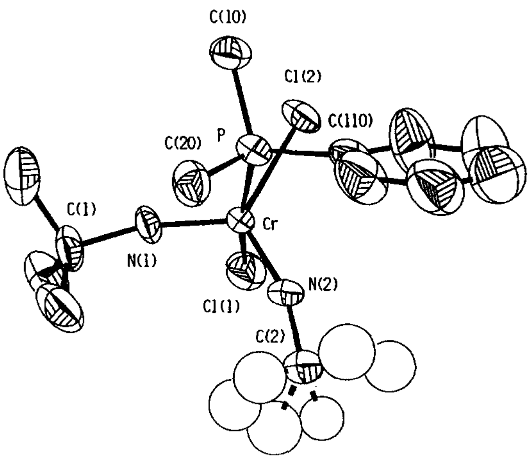


Fig. 1. The structure of $Cr(NBu^t)_2Cl_2(PMe_2Ph)$.

The structure of $Cr(NBu^t)_2Cl_2(PMe_2Ph)$ has been determined by X-ray crystallography.

A diagram of the molecule is shown in Fig. 1 and selected bond lengths and angles are given in Table 2. The geometry is quite clearly best described as trigonal bipyramidal, with the phosphine and one chlorine occupying the axial sites. The Cr—Cl_{ax} and Cr—Cl_{eq} distances are very similar, reflecting the lack of any *d* electrons and Cr—P π-bonding. One surprising feature is that in the equator, the N—Cr—N angle is the smallest, whereas repulsions between the electron density in the imido bonds might be expected to require enlargement of this. A similar feature has been found in the trigonal

Table 2. Selected bond lengths (Å) and bond angles (°) for $Cr(NBu^t)_2Cl_2(PMe_2Ph)$

Bond lengths			
P(1)—Cr(1)	2.392(5)	Cl(1)—Cr(1)	2.351(5)
Cl(2)—Cr(1)	2.342(5)	N(1)—Cr(1)	1.638(11)
N(2)—Cr(1)	1.641(12)	C(10)—P(1)	1.799(15)
C(20)—P(1)	1.812(15)	C(110)—P(1)	1.816(12)
C(1)—N(1)	1.453(17)	C(2)—N(2)	1.446(17)
C(12)—C(1)	1.529(24)	C(13)—C(1)	1.572(25)
C(11)—C(1)	1.480(22)		
Bond angles			
Cl(1)—Cr(1)—P(1)	167.1(1)	Cl(2)—Cr(1)—P(1)	81.5(2)
Cl(2)—Cr(1)—Cl(1)	86.4(2)	N(1)—Cr(1)—P(1)	93.2(4)
N(1)—Cr(1)—Cl(1)	95.3(4)	N(1)—Cr(1)—Cl(2)	122.3(5)
N(2)—Cr(1)—P(1)	91.6(5)	N(2)—Cr(1)—Cl(1)	93.1(5)
N(2)—Cr(1)—Cl(2)	124.1(5)	N(2)—Cr(1)—N(1)	113.4(6)
C(10)—P(1)—Cr(1)	115.2(6)	C(20)—P(1)—Cr(1)	111.6(6)
C(20)—P(1)—C(10)	103.8(8)	C(110)—P(1)—Cr(1)	112.5(5)
C(1)—N(1)—Cr(1)	166.4(10)	C(2)—N(2)—Cr(1)	163.6(10)

bipyramidal $\mathrm{Re(NBu^t)_2Cl_3}$.[2] The Cr–imido functions have normal geometries with short Cr—N bonds (1.635 Å) and slight bends of *ca* 14° in the Cr—N—C group. Both imido groups are required to act as 4e donors to provide an 18e configuration at chromium.

(b) *Chloride substitution reactions*. Some of these have been noted above. Interaction of **1** with silver acetate gives $\mathrm{Cr(NBu^t)_2(\eta^1\text{-}O_2CMe)_2}$ (**11**) as a low melting solid, readily soluble in organic solvents. The η^1-coordination is in accord with both IR and NMR data.

Interaction of **1** with silver trifluoromethanesulphonate (AgOTf) in acetonitrile removes $\mathrm{Cl^-}$ as AgCl and the adduct $\mathrm{Cr(NBu^t)_2(MeCN)_{\mathit{n}}(OTf)_2}$ is obtained, but only as an orange oil that has not crystallized; addition of pyridine or $\mathrm{PMe_3}$ allows isolation of the respective crystalline products, **12**, **13**. In the latter case the analysis corresponds to $\mathrm{[Cr(NBu^t)_2(PMe_3)_2](OTf)_2 \cdot 0.5MeCN}$ (**13**) and the presence of MeCN was also confirmed by IR and ^{1}H NMR spectra. From spectroscopic data the pyridine complex (**12**) is clearly $\mathrm{[Cr(NBu^t)_2py_2(\eta^1\text{-}OTf)](OTf)}$, with one η^1-triflate bound to five-coordinate chromium(VI); in MeCN at 25°C the molar conductivity (183 Ω^{-1} cm^2 mol^{-1}) is somewhat higher than usual for a 1 : 1 electrolyte which suggests some dissociation of coordinated triflate in dilute solution. The X-ray structure of the salt is shown in Fig. 2 and bond lengths and angles are given in Table 3.

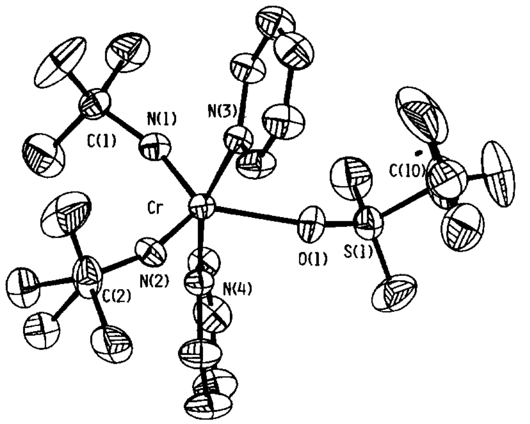


Fig. 2. The structure of the cation in $\mathrm{[Cr(NBu^t)_2(C_5H_4N)_2(\eta^1\text{-}O_3SCF_3)]CF_3SO_3}$.

The geometry of the cation is again suitably described as trigonal bipyramidal, this time with the axial sites occupied by the pyridine donors. The distribution of ligands in the equator reflects that found in the dichloro complex described above, with the smallest angle between the two imido bonds. The Cr—N—C groups are again slightly bent, with angles of *ca* 163°, although normal Cr≡NR interactions are again required to provide an 18e configuration for chromium. It may be noted that a similar tungsten compound $\mathrm{W(NBu^t)_2(NH_2Bu^t)_2(\eta^1\text{-}OTf)_2}$ is octahedral with *cis*-η^1-$\mathrm{O_3SCF_3}$ groups.[1b,c]

Interaction of $\mathrm{Cr(NBu^t)_2Cl_2(bpy)}$ (**10**) with AgOTf and additional bpy in MeCN leads to the cation $\mathrm{[Cr(NBu^t)_2(bpy)_2]^{2+}}$ that can be precipitated as its $\mathrm{PF_6^-}$ salt (**14**), which is sparingly soluble in THF and $\mathrm{CH_2Cl_2}$ but very soluble in MeCN in which $\Lambda_M = 250\ \Omega^{-1}$ cm^2 mol^{-1} (1 : 2 electrolyte). The solid salt is unaffected by water, methanol or dilute normal acids. The *cis* geometry for the two $\mathrm{NBu^t}$ ligands in the octahedral complex is suggested

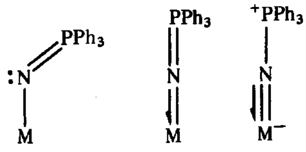
Table 3. Selected bond lengths (Å) and bond angles (°) for $\mathrm{[Cr(NBu^t)_2py_2(\eta^1\text{-}OTf)]^+}$

Bond lengths			
O(1)—Cr(1)	2.028(7)	N(1)—Cr(1)	1.629(7)
N(2)—Cr(1)	1.615(7)	N(3)—Cr(1)	2.062(7)
N(4)—Cr(1)	2.067(7)	O(1)—S(1)	1.466(6)
Bond angles			
N(1)—Cr(1)—O(1)	127.1(3)	N(2)—Cr(1)—O(1)	121.0(3)
N(2)—Cr(1)—N(1)	111.8(4)	N(3)—Cr(1)—O(1)	79.6(3)
N(3)—Cr(1)—N(1)	96.4(3)	N(3)—Cr(1)—N(2)	93.9(3)
N(4)—Cr(1)—O(1)	82.8(3)	N(4)—Cr(1)—N(1)	94.8(3)
N(4)—Cr(1)—N(2)	94.5(3)	N(4)—Cr(1)—N(3)	162.4(2)
S(1)—O(1)—Cr(1)	137.3(3)	C(1)—N(1)—Cr(1)	163.2(5)
C(2)—N(2)—Cr(1)	161.9(5)	C(31)—N(3)—Cr(1)	121.4(5)
C(35)—N(3)—Cr(1)	120.9(5)	C(41)—N(4)—Cr(1)	121.8(5)
C(45)—N(4)—Cr(1)	120.1(5)		

by two types of C_5H_4N rings of the bpy ligands (two N atoms *trans* to $\mathrm{NBu^t}$) according to the NMR data.

The isocyanide complex, $\mathrm{Cr(NBu^t)_2Cl_2(CNBu^t)}$ (**8**), was treated with MeLi in diethyl ether in the expectation that nucleophilic attack might lead to a carbene complex. However, the product was the η^2-iminoacyl complex, $\mathrm{[Cr(NBu^t)_2(\eta^2\text{-}Bu^tN{=}CMe)Cl]}$ (**15**), that was characterized spectroscopically. A related iminoacyl,[4] characterized crystallographically, was obtained by transfer of a mesityl group in $\mathrm{Cr(NBu^t)_2(mes)_2}$ to the carbon atom of $\mathrm{Bu^tNC}$ in an "insertion" reaction. The present complex is presumably formed by methyl transfer to the isocyanide carbon atom in an intermediate $\mathrm{Cr(NBu^t)_2Cl(Me)(CNBu^t)}$. The IR spectrum has a characteristic ν(C=N) stretch at 1760 $\mathrm{cm^{-1}}$ (cf. refs 2 and 4).

The interaction of $\mathrm{Cr(NBu^t)_2Cl_2}$ with two equivalents of $\mathrm{LiN{=}PPh_3}$ in toluene gives the bis-phosphineiminato compound, $\mathrm{Cr(NBu^t)_2(NPPh_3)_2}$ (**16**). Although phosphineiminato complexes are well established,[12] the use of $\mathrm{LiNPPh_3}$ as a phosphineiminato transfer agent is not common. From the three resonance forms possible for the metal–ligand system, viz.



(I) **(II)** **(III)**

We consider that form **I** contributes more in the present case in view of the IR absorption (1075 $\mathrm{cm^{-1}}$) at the lower limit of the ν(P—N) region, 1050–1200 $\mathrm{cm^{-1}}$.[12]

Complex **16**, although it reacts with high oxidation state oxo compounds like $\mathrm{CrO_2Cl_2}$, $\mathrm{CrO_2(OSiMe_3)_2}$, $\mathrm{OsO_4}$ or $\mathrm{MoO_2(S_2CNEt_2)_2}$, does not form a nitrido-bridged dimer with elimination of $\mathrm{Ph_3PO}$; such a reaction occurs with free phosphine imines and the oxo species, $\mathrm{OsO_4}$ and $\mathrm{OsO_3NBu^t}$.[13]

(4) *Reduction reactions of* $\mathrm{Cr(NBu^t)_2Cl_2}$

The dialkyls[5] such as the neopentyl were obtained by alkylation of $\mathrm{Cr(NBu^t)_2(py)Br_2}$ and the authors state that "The choice of alkylating agent is clearly critical in order to prevent reduction". We had independently shown that $\mathrm{Cr(NBu^t)_2Cl_2}$ at 0–5°C in diethyl ether with $\mathrm{LiCH_2CMe_3}$ and $\mathrm{LiCH_2SiMe_3}$ gives the dialkyls identical to those described.[5] However, we find additionally that at low temperatures the diamagnetic chromium(V) dimer, $\mathrm{[(Bu^tN)ClCr(\mu\text{-}NBu^t)]_2}$ (**17**), only is obtained; the same product is obtained by reaction of **1** with $\mathrm{LiC_5Me_5}$. An oxo analogue of this imido species is not known. It seems reasonable to assume that reduction (with Li or Mg alkyls acting as one-electron reductants) and alkylation, are competing reactions, with substitution being kinetically favoured, while the thermodynamically preferred product is **17**. (cf. The similar rhenium(VI) compound[2].)

The confirmation of a one-electron reduction process is shown by the reaction of **1** with $\mathrm{(\eta^5\text{-}C_5H_5)_2Co}$ [eq. (3)]:

$$\mathrm{2Cr(NBu^t)_2Cl_2 + 2Cp_2Co} = \mathrm{2Cp_2Co^+Cl^- + [Cl(NBu^t)Cr(\mu\text{-}NBu^t)]_2}. \quad (3)$$

So far, attempts to reduce $\mathrm{Cr(NBu^t)_2Cl_2}$ in the presence of various O, N and P donors, alkenes, etc., by use of Na/Hg or Mg, have given only brown intractable products.

The dimer **17** reacts with $\mathrm{LiNHBu^t}$ in diethyl ether to give the first imido amido complex of chromium(V), namely $\mathrm{[Cr(NBu^t)(NHBu^t)(\mu\text{-}NBu^t)]_2}$ (**18**); the high solubility of the compound in hexane, even at −78°C, makes isolation in high yields difficult. The ^{1}H NMR spectrum of the diamagnetic compound consists of six singlets, which on close examination are found to comprise two sets of three singlets. A similar spectrum has been observed for the isoelectronic vanadium analogue,[14] $\mathrm{[V(NBu^t)(NHBu^t)(\mu\text{-}NBu^t)]_2}$, which is also highly petroleum soluble. The spectra probably result from the double bond character of the $\mathrm{Cr{\leftrightharpoons}NHBu^t}$ bond which restricts rotation about the Cr—N bond,[15] giving two sets of isomers.

We have been unable to obtain X-ray quality crystals of compounds **17** and **18** due to twinning. However, the structures with bridged $\mathrm{NBu^t}$ groups are well established by IR and NMR spectra. The chromium(V) atom is thus four-coordinate in both cases and there could be a metal–metal interaction, although this seems unlikely. The diamagnetism of the compounds is presumably due to superexchange interaction of unpaired electron density on each metal atom via the imido bridge. The situation is thus similar to that found for the rhenium(VI) compound, $\mathrm{[(Bu^tN)_2(\mu\text{-}Bu^tN)Re]_2}$, which has been characterized by X-ray diffraction.[2]

EXPERIMENTAL

Experimental procedures and instrumentation have been described.[2,16] The following starting materials were prepared by literature methods:

$Cr(NBu^t)_2(OSiMe_3)_2$,[6a] $Zn(CH_2CMe_3)_2$[17] and $(C_6H_5)_3P{=}NH$,[18] $LiNHBu^t$ was prepared by interaction of Bu^tNH_2 with Bu^nLi in hexane at −78°C and $LiNBu^t(SiMe_3)\cdot Et_2O$ by deprotonation of $Bu^tNHSiMe_3$ with LiMe in Et_2O. In mass spectra (EI at 70 eV) all m/e values show appropriate isotopic envelopes due to chromium isotopes. NMR data are in ppm relative to Me_4Si in C_6D_6 unless otherwise stated; ^{31}P spectra are referenced to external H_3PO_4. IR data are in cm^{-1} in Nujol mulls unless otherwise stated.

(1) *Bis*(*t-butylimido*)*dichlorochromium*(VI) (**1**)

To a solution of $Cr(NBu^t)_2(OSiMe_3)_2$ (6.0 g, 0.016 mol) in CH_2Cl_2 (60 cm^3) at 0°C was added dropwise with stirring over 5 min a solution of BCl_3 in hexane (32 cm^3 of 1M solution; 0.032 mol). The solution becomes slightly darker in colour and after addition of BCl_3 was allowed to warm to room temperature and stirred for 2 h. Longer reaction times depress the yield. Volatiles were recovered in vacuum leaving an oily residue which after *ca* 1 h in vacuum solidifies. The solid was extracted with hot hexane until the extracts were colourless (*ca* 4 × 50 cm^3); removal of solvent left a red residue which was sublimed (80–100°C/0.01 mm Hg) to a cold probe. Yield 55–65%.

MS: 264(M^+); 249($M^+ - Me$); 233($M^+ - MeNH_2$). NMR ^1H: 1.14s; ($CDCl_3$) 1.60 s; ^{13}C-$\{^1H\}$ ($CDCl_3$): 30.4, $C(CH_3)_3$; 82.5 $C(Me_3)$. IR: 1258 (NBu^t); 358 (CrCl).

(2) *Bis*(*t-butylimido*)(*t-butylamido*)*chlorochromium* (VI) (**2**)

Method A. A solution of **1** (1.0 g, 3.8 mmol) and $Bu^tNH(SiMe_3)$ (1.45 g, 10 mmol) in hexane (30 cm^3) was refluxed (*ca* 12 h) when the colour changed from dark red to orange–red. After removal of volatiles in vacuum the orange solid was crystallized from hot hexane. Yield: 0.75 g (66%).

Method B. To **1** (0.5 g, 1.9 mmol) in hexane (10 cm^3) was added Bu^tNH_2 (2 cm^3) and the solution refluxed for 8 h. Work-up as above gave 0.2 g (35%) of product, spectroscopically identical with that prepared as above. MS: 301 (M^+); 286 ($M^+ - Me$); 271 ($M^+ - 2Me$); 230 ($M^+ - NBu^t$). NMR ^1H: 1.30 [s, 18H, $NC(CH_3)_3$]; 1.21 [s, 9H, $NHC(CH_3)_3$]. IR: 3250 (NH), 1202 (NBu^t), 358 (CrCl).

(3) *Bis*(*t-butylimido*)*bis*(*t-butylamido*)*chromium*(VI) (**3**)

A toluene (20 cm^3) solution of **1** (0.5 g, 1.89 mmol) at −78°C was added via a cannula to a cold (−78°C) solution of $LiNHBu^t$ (0.3 g, 3.77 mmol) in toluene (20 cm^3) over *ca* 10 min and the mixture allowed to warm over 12 h, during which time the colour changed from orange–red to dark purple. The volatiles were removed and the residue extracted with hexane (3 × 20 cm^3); the filtered extracts were evaporated and the residue sublimed (80°C/0.05 mm Hg) to give a red–purple crystalline solid. Yield: 0.25 g (40%).

MS: 338 (M^+); 323 ($M^+ - Me$); 308 ($M^+ - 2Me$). NMR ^1H: 1.39 [s, 18H, $NHBu^t$]; 1.35 [s, 18H, (NBu^t)].

(4) *Bis*(*t-butylimido*)[*t-butyl*(*trimethylsilyl*)*amido*] *chlorochromium* (**4**)

To **1** (0.3 g, 1.13 mmol) in toluene (30 cm^3) at −78°C was added dropwise via a cannula, a solution of $LiNBu^t(SiMe_3)\cdot Et_2O$ (0.26 g, 1.13 mmol) in toluene (20 cm^3) and the mixture allowed to warm to room temperature with stirring (12 h). Removal of volatiles and extraction of the residue with hexane (2 × 20 cm^3), filtration and evaporation of the solution left a red–purple solid which was sublimed (100°C/0.05 mm Hg). Yield: 0.18 g (*ca* 45%).

NMR ^1H ($CDCl_3$): 1.60 {s, 9H, $N(SiMe_3)[C(CH_3)_3]$}; 1.54 [s, 18H, $NC(CH_3)_3$]; 0.51 [s, 9H, $SiMe_3$].

(5) *Dilithium tetrakis*(*t-butylimido*)*chromate*(VI) (**5**)

To a solution of $Cr(NBu^t)_2(NHBu^t)_2$ (0.3 g, 0.9 mmol) in hexane–ether (3 : 1, 20 cm^3) at −78°C was added dropwise a solution of Bu^nLi (0.65 cm^3 of a 2.68 M solution). After stirring for 10 min at −78°C the mixture was allowed to warm (1 h) and then was heated (30°C, 0.5 h), after which volatiles were removed and the residue extracted with hexane (3 × 10 cm^3); concentration (5 cm^3) and cooling (−20°C, 2 days) gave red crystals which could be recrystallized from Et_2O. Yield: 0.03 g (*ca* 10%).

IR: 1224 (linear $CrNBu^t$); 1184 (bent $CrNBu^t$). NMR ^1H: 1.30 [s, 27H, (bent imido)]; 1.60 [s, 9H (linear imido)]. In $CDCl_3$ values are 1.40 and 1.56.

(6) *Bis*(*t-butylimido*)(*dimethylphenylphosphine*)*dichlorochromium*(VI) (**6**)

To a solution of **1** (0.2 g, 0.75 mmol) in toluene (10 cm^3) was added PMe_2Ph (0.1 cm^3, 1.5 mmol). The resulting mixture was stirred at room temperature for 3 h. The yellow precipitate was collected, washed with hexane and recrystallized from THF at −20°C. Yield: 0.13 g (52%).

NMR ^1H ($CDCl_3$): 1.52 (s, 18H, NBu^t); 2.08 (6H, d, PMe_2, $^3J_{P—H} = 11.95$ Hz) and aromatic protons; $^{31}P-\{^1H\}$ ($CDCl_3$): 30.67.

(7) *Bis(t-butylimido)(trimethylphosphine)dichlorochromium*(VI) (**7**)

This was prepared as for **6** from **1** (0.2 g, 0.75 mmol) and PMe_3 (0.075 cm^3) in toluene. Recrystallization from THF at −20°C afforded a yellow microcrystalline solid. Yield: 0.14 g (60%).

NMR ^{1}H ($CDCl_3$): 1.54 (s, 18H, NBu^t); 1.83 (d, 9H, PMe_3); $^{31}P-\{^1H\}$ ($CDCl_3$): 28.72.

(8) *Bis(t-butylimido)(t-butylisocyanide)dichlorochromium*(VI) (**8**)

This was prepared as for **6** from **1** (0.2 g, 0.75 mmol) and Bu^tNC (0.1 cm^3) in toluene. Recrystallization from THF–hexane at −20°C gave an orange microcrystalline solid. Yield: 0.12 g (45%).

IR (Nujol and KBr disk): 2237 (NC).

(9) *Bis(t-butylimido)[μ-bis(diphenylphosphino)ethane] tetrachlorodichromium*(VI) (**9**)

This was prepared as for **6** from **1** (0.2 g, 0.75 mmol) and dppe (0.3 g, 0.75 mmol) in toluene. Recrystallization from CH_2Cl_2–hexane gave a yellow microcrystalline solid. Yield: 0.2 g (40%).

NMR ^{1}H (CD_2Cl_2): 1.32 (s, 36H, NBu^t); 3.38 (m, 4H, CH_2PPh_2); $^{31}P-\{^1H\}$ (CD_2Cl_2): 50.53.

(10) *Bis(t-butylimido)(2,2′-bipyridyl)dichlorochromium*(VI) (**10**)

As for **6** but from **1** (0.29, 0.75 mmol) and 2,2′-bipyridine (0.12 g, 0.75 mmol) in toluene (20 cm^3). Yield: 0.23 g, (75%).

NMR ^{1}H ($CDCl_3$): 1.62 (s, 18H, NBu^t) and aromatic protons.

(11) *Bis(t-butylimido)di-η^1-acetatochromium*(VI) (**11**)

To a well-stirred suspension of Ag(OAc) (0.25 g, 1.5 mmol) in toluene (10 cm^3) was added $Cr(NBu^t)_2Cl_2$ (0.29, 0.75 mmol) in toluene (10 cm^3). The resulting mixture was stirred at room temperature overnight and filtered. The orange filtrate was evaporated to dryness and the residue extracted with hexane (10 cm^3) which was concentrated (to *ca* 5 cm^3) and cooled at −78°C to give bright orange crystals. Yield: 0.15 g (64%).

MS: 253 ($M^+ - CH_3CO_2$). IR: 1666, 1525, (CO_2). NMR ^{1}H ($CDCl_3$): 1.55 (s, 18H, Bu^t); 2.15 (s, 6H, CH_3CO_2).

(12) *Bis(t-butylimido)bis(pyridine)-η^1-O-trifluoromethylsulphonatochromium*(VI) (*trifluoromethylsulphonate*) (**12**)

To a solution of **1** (0.2 g, 0.75 mmol) in MeCN (10 cm^3) was added AgOTf (0.4 g, 1.5 mmol) in MeCN (10 cm^3). The mixture was stirred at room temperature for 1 h, filtered, and the orange filtrate evaporated. The residue was extracted with CH_2Cl_2 (20 cm^3), then pyridine (0.13 cm^3, 1.5 mmol) was added and the solution stirred for 3 h at room temperature. On reduction of volume (to *ca* 5 cm^3), excess of Et_2O (25 cm^3) was added; the orange precipitate was collected, washed with Et_2O (2 × 5 cm), and recrystallized from CH_2Cl_2–Et_2O. Yield: 0.34 g (73%).

NMR ^{1}H (CD_3CN): 1.66 (s, 18H, NBu^t) and aromatic protons.

(13) *Bis(t-butylimido)bis(trimethylphosphine)chromium*(VI) *bis(trifluoromethylsulphonate)*(0.5 *acetonitrile*) (**13**)

This was prepared as for **12** from **1** (0.2 g, 0.75 mmol), Ag(OTf) (0.4 g, 1.5 mmol) and PMe_3 (0.15 cm, 1.5 mmol). Yield: 0.2 g (40%). Λ_M (MeCN 25°C): 200 Ω^{-1} cm^2 mol^{-1}.

NMR ^{1}H (CD_2Cl_2): 1.61 (s, 18H, NBu^t); 1.92 (d, 18H, $^3J_{P—H} = 12$ Hz; PMe_3). $^{31}P-\{^1H\}$ (CD_2Cl_2): 31.80.

(14) *Bis(t-butylimido)bis(2,2′-bipyridine)chromium* (VI)*bis(hexafluorophosphate)* (**14**)

To a solution of $Cr(NBu^t)_2Cl_2(bpy)$ (0.55 g, 1.3 mmol) in MeCN (10 cm^3) was added 2 equivalents of Ag(OTf) (0.66 g, 2.6 mmol) in MeCN (10 cm^3). The solution was stirred at room temperature for 1 h, filtered and to the filtrate was added another equivalent of bpy (0.2 g). After stirring for an additional 6 h the solution was reduced in volume (5 cm^3) and a saturated methanolic solution of $[Bu^n{}_4N]PF_6$ added. The dark purple precipitate was collected, washed with THF and Et_2O, and recrystallized from MeCN–Et_2O. Yield: 0.4 g (39%).

NMR ^{1}H (CD_3CN): 1.45 (s, 19H, NBu^t) and aromatic protons.

(15) *Bis(t-butylimido)[η^2-methyl(t-butylimino)methyl] chromium*(VI) (**15**)

To a suspension of the isocyanide adduct (**8**) (0.3 g, 1 mmol) in Et_2O (20 cm^3) at −78°C was added MeLi (3 cm^3, 0.33 M in Et_2O) and the mixture slowly warmed to room temperature. After stirring overnight the solution was filtered, evaporated to dryness and the residue extracted with hexane (2×10 cm^3). This extract was concentrated (to *ca* 10 cm^3) and cooled at -20°C to give yellow crystals. Yield: 0.15 g (49%).

IR: 1760 (CN). NMR ^{1}H (C_6D_6): 1.30 (s, 18H, NBu^t); 1.35 (s, 9H, C=N*Bu*^{t}); 2.30 (s, 3H, *Me*—C=N).

(16) *Bis*(*t-butylimido*)*bis*(*triphenylphosphineimino*) *chromium*(VI) (**16**)

A solution of **1** (0.25 g, 9.5 mmol) in toluene (10 cm^3) was added to a suspension of $LiNPPh_3$ (0.54 g, 1.9 mmol) in toluene (20 cm^3) at -78°C. The solution was stirred and allowed to warm overnight; filtration and evaporation of the filtrate gave a residue that was crystallized from Et_2O as dark red needles. Yield: 0.3 g (42%).

IR: 1194 (Bu^{t}N); 1075 (N=P); 712, 694, aromatic CH bands. NMR ^{1}H ($CDCl_3$): 1.28 (s, 18H, NC*Me*$_3$); 7.1, 8.05 (m, 30H, aromatic). ^{31}P-{^{1}H}: 8.93.

(17) *Bis*[*t-butylimido*(*chloro*)(*μ-t-butylimido*)]*dichromium*(V) (**17**)

Method A. To $Cr(NBu^t)_2Cl_2$ (0.2 g, 0.75 mmol) in toluene (20 cm^3) at -78°C was added dineopentylzinc (0.5 g, 2.5 mmol), when the colour changed from red to orange–yellow. After warming with stirring (2 h), volatiles were removed and the residue extracted with hexane (3×5 cm^3); filtration, concentration and cooling (-20°C) gave green–yellow crystals. Yield: 0.06 g (*ca* 35%) based on Cr.

Method B. To a solution of $Cr(NBu^t)_2Cl_2$ (0.2 g, 0.75 mmol) in toluene (10 cm^3) was added $(C_5H_5)_2Co$ (0.15 g, 0.75 mmol) in toluene (10 cm^3). After stirring for *ca* 12 h, the solution was filtered from $(C_5H_5)_2CoCl$ and worked-up as above. Yield: 0.05 g (30%).

MS: 458 (M^+); 443 ($M^+ -$Me); 402 ($M^+ -$iso-

Table 4. Crystal data, details of intensity measurements and structure refinement

Compound	$Cr(NBu^t)_2(PMe_2Ph)Cl_2$	$[Cr(NBu^t)_2py_2(\eta^1\text{-}OTf)]OTf$
Molecular weight	403.295	662.595
Crystal system	Monoclinic	Triclinic
a (Å)	10.227(3)	14.069(2)
b (Å)	18.465(10)	10.879(1)
c (Å)	11.809(2)	9.768(3)
α (°)	90	92.74(3)
β (°)	108.46(2)	89.11(1)
γ (°)	90	93.61(3)
Volume (Å^3)	2115.93	1491.83
Space group	*Cc*	$P\bar{1}$
Z	4	2
D_c (g cm^{-3})	1.266	1.475
μ (cm^{-1})	8.558	5.830
F(000)	848	680
h, *k*, *l* range	$0 \rightarrow 11$	$-15 \rightarrow 15$
	$0 \rightarrow 20$	$0 \rightarrow 11$
	$-13 \rightarrow 13$	$-10 \rightarrow 10$
Total number of reflections	1680	4389
Number of unique reflections	1560	4131
Number of reflections used [$F > 3\sigma(F)$]	1331	2887
Number of parameters	203[a]	442[b]
Weighting scheme paramater g in $w = 1/[\sigma^2(F)+gF_o^2]$	0.002	0.002
Final *R*	0.0511	0.0734
Final R_w	0.0566	0.0813

[a] Methyl carbons of the Bu^t group at C(2) are disordered over orientations.

[b] Methyl carbons of the Bu^t group at C(2) and the fluorines at C(10) in the cation, and the sulphonyl oxygens and the fluorines in the anion are all disordered and represented in each case by four sites with suitable occupancies.

butene); 387 ($M^+ - NBu^t$). NMR ^1H: 1.74 (s, 18H, terminal imido); 1.12 (s, 18H, bridging imido).

(18) *Bis*[(*t-butylamido*)(*t-butylimido*)(*μ-t-butylimido*)] *dichromium*(V) (**18**)

To the chloro compound (**17**) (0.15 g, 0.33 mmol) in Et_2O (10 cm^3) at -78°C was added $LiNHBu^t$ (0.052 g, 0.66 mmol) in Et_2O (10 cm^3). The mixture was slowly warmed to room temperature, stirred overnight and filtered. The bluish-green filtrate was evaporated and the residue was extracted with hexane (10 cm^3). Concentration of the hexane extract (to 5 cm^3) and cooling at -78°C afforded highly-soluble dark green crystals. Yield: 0.08 g (35%).

MS: 532 (M^+); 517 ($M^+ - CH_3$); 502 (M^+ $-$isobutene); 460 ($M^+ - Bu^tNH$); 388 (M^+ $-2Bu^tNH$).

X-ray crystallography

Crystals of both compounds were sealed under argon in glass capillaries. Unit cell and intensity data were obtained using standard procedures on a CAD4 diffractometer. Experimental details are given in Table 4. The structures were solved and developed via the heavy atom method and refined by full-matrix least-squares. Both crystals showed large and variable mosaic spread, indicating lower than preferred crystal quality, and structure refinement was hampered by disorder. Details are given in Table 4. Lists of final coordinates, displacement factor coefficients, bond lengths and angles, together with F_o/F_c values have been deposited as supplementary data with the Editor. Coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgements—We thank the SERC (A.A.D.) and the Croucher Foundation, Hong Kong (W.-H.L.) for support.

REFERENCES

1. A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse: (a) *J. Chem. Soc., Chem. Commun.* 1989, 896; (b) *Polyhedron* 1989, **8**, 2947; (c) *J. Chem. Soc., Dalton Trans.* 1990, 2753.
2. A. A. Danopoulos, C. J. Longley, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *Polyhedron* 1989, **8**, 2657.
3. A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *Polyhedron* 1990, **9**, 1009.
4. A. C. Sullivan, G. Wilkinson, M. Motevalli and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* 1988, 53.
5. N. Meijboom, C. J. Schaverien and A. G. Orpen, *Organometallics* 1990, **9**, 774.
6. (a) W. A. Nugent and R. L. Harlow, *Inorg. Chem.* 1980, **19**, 777; (b) W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*. John Wiley, New York (1988).
7. R. B. Johannesen and H-L. Krauss, *Chem. Ber.* 1964, **97**, 2094.
8. W. A. Nugent, *Inorg. Chem.* 1983, **22**, 965.
9. W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.* 1980, **31**, 123.
10. R. L. Elliot, P. J. Nichols and B. O. West, *Polyhedron* 1987, **6**, 2191.
11. A. J. Nielsen, *Polyhedron* 1987, **6**, 1657.
12. (a) K. Dehnicke and J. Strahle, *Polyhedron* 1989, **8**, 707; (b) B. F. G. Johnson, B. L. Haymore and J. L. Dilworth, in *Comprehensive Coordination Chemistry* (Edited by G. Wilkinson, R. D. Gillard and J. A. McCleverty), Vol. 2, p. 124. Pergamon Press, Oxford (1987).
13. A. O. Chong, K. Oshima and K. B. Sharpless, *J. Am. Chem. Soc.* 1977, **99**, 3420.
14. A. A. Danopoulos and G. Wilkinson, to be published.
15. M. H. Chisholm and I. P. Rothwell, in *Comprehensive Coordination Chemistry* (Edited by G. Wilkinson, R. D. Gillard and J. A. McCleverty), Vol. 2, p. 177. Pergamon Press, Oxford (1987); M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides*, p. 483. Ellis Harwood, Chichester (1980); L. M. Jackman and F. A. Cotton, *Dynamic Nuclear Magnetic Resonance Spectroscopy*. John Wiley, New York (1975).
16. A. A. Danopoulos, A. C. C. Wong, G. Wilkinson, B. Hussain and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* 1990, 315.
17. R. R. Schrock and J. D. Fellman, *J. Chem. Soc.* 1978, **100**, 3359.
18. L. Birkofer, A. R. Her and P. Richter, *Chem. Ber.* 1963, **96**, 2750.