The Chemistry of Chromium Nitrile Complexes of 1,2-Bis(dimethylphosphino)-ethane. X-Ray Crystal Structures of trans-[Cr^{IV}Cl(NEt)(dmpe)$_2$]CF$_3$SO$_3$, trans-[Cr^{IV}(N=CHMe)$_2$(dmpe)$_2$][BPh$_4$]$_2$, and trans-[Co^0(H·NCMe)$_2$(dmpe)$_2$][BPh$_4$]$_2$†

Andrew R. Barron, Julian E. Salt, and Geoffrey Wilkinson *
Chemistry Department, Imperial College, London SW7 2AY
Majid Motevalli and Michael B. Hursthouse *
Chemistry Department, Queen Mary College, London E1 4NS

The interaction of CrCl$_2$(dmpe)$_2$ with NaBPh$_4$ in MeCN at room temperature gives the partially substituted complex trans-[Cr^{II}Cl(NCMe)(dmpe)$_2$]BPh$_4$; when the reaction is carried out in refluxing MeCN the product is the previously characterised trans-[Cr^{II}(NCMe)$_2$(dmpe)$_2$][BPh$_4$]$_2$. The interaction of both nitrile complexes with methanol has been studied, and the X-ray structures of the products, trans-[Cr^{IV}Cl(NEt)(dmpe)$_2$]CF$_3$SO$_3$ and trans-[Cr^{IV}(N=CHMe)$_2$(dmpe)$_2$][BPh$_4$]$_2$ respectively, have been determined. These are the first octahedral Cr^{IV} complexes. The interaction of trans-[Cr(NCMe)$_2$(dmpe)$_2$][BPh$_4$]$_2$ with H$_2$ leads to a complex of stoicheiometry trans-[Cr-(H·NCMe)$_2$(dmpe)$_2$][BPh$_4$]$_2$, whose structure has been confirmed by X-ray crystallography. Although hydrogens bound to acetonitrile were not detected either crystallographically or spectroscopically, the diamagnetism together with the values of the Cr–P distances eliminate the possibility of a Cr^{II} species and confirm the presence of Cr^0. Two weakly acidic protons have been shown to be present chemically, and its is proposed that H$^+$ is located on the electron density in the C≡N bond. The chromium(III) complex trans,trans-[{Cr(NCMe)(dmpe)$_2$}$_2$(μ-O)]$^{4+}$ is also described.

We have described the synthesis of 1,2-bis(dimethylphosphino)ethane (dmpe) complexes of chromium in oxidation states 0 to IV,[1-3] including the synthesis of salts of the cations trans-[Cr(NCR)$_2$(dmpe)$_2$]$^{2+}$ (R = Me or Et) from trans-Cr(N$_2$)$_2$(dmpe)$_2$.[3]

We now report a simplified synthesis of the bis(acetonitrile) complex, along with that of the partially substituted analogue. Interaction of the complexes with MeOH, H$_2$, and O$_2$ is discussed.

The reactions studied are summarised in Scheme 1.

Results and Discussion

Interaction of trans-CrCl$_2$(dmpe)$_2$[2] with one equivalent of NaBPh$_4$ in MeCN, at room temperature, leads to a golden-brown solution from which the complex trans-[CrCl(NCMe)(dmpe)$_2$]BPh$_4$ (1) can be isolated. However, when two equivalents of NaBPh$_4$ are used and the solution refluxed the product is the previously reported[3] trans-[Cr(NCMe)$_2$-(dmpe)$_2$][BPh$_4$]$_2$ (2). The complexes can be isolated with other counter ions, PF$_6^-$, CF$_3$SO$_3^-$, and BF$_4^-$, although ion exchange cannot be carried out in MeOH solution (see below).

The above reactions have to be carried out with rigorous exclusion of atmospheric oxygen. If this is not the case the product is the previously reported complex trans-[CrCl$_2$(dmpe)$_2$]BPh$_4$[3] whose octahedral Cr^{III} centre is substitution inert.

The i.r. spectra of (1) and (2) are similar, both contain a strong band (2 250 cm^{-1}) due to the co-ordinated nitrile [v(C≡N)].

In addition the spectrum of (1) contains a band at 340 cm^{-1} [v(Cr–Cl)]; a similar band is observed in trans-CrCl$_2$(dmpe)$_2$.[2]

Both nitrile complexes are paramagnetic showing very broad ^{1}H n.m.r. spectra. However, no e.s.r. spectra are observed on account of the Cr^{II} (S = 1) ground state, confirmed by magnetic susceptibility measurments [(1), μ_B = 2.9; (2), μ_B = 2.8]. None of the minor Cr^I species,[3] detected by e.s.r. spectra formed together with (2) in the protonation of trans-Cr(N$_2$)$_2$(dmpe)$_2$ with CF$_3$SO$_3$H in MeCN, was detected in samples prepared by the present procedure.

Reaction of trans-[Cr(NCMe)$_2$(dmpe)$_2$]$^{2+}$ *with* O$_2$.—A MeCN solution of (2) on exposure to air yields a deep red solution, from which a red solid (3) can be precipitated by the addition of Et$_2$O.

The i.r. spectrum is almost identical to that obtained for (2) but with addition of a band at 860 cm^{-1} assigned to a Cr–O–Cr stretch.[4] The magnetic susceptibility is very low, μ_B = 1.82 per Cr, suggesting interaction between the Cr^{III} centres. Both homo- and hetero-binuclear μ-oxo complexes have been observed[4] including those of Cr^{III}. Analytical, magnetic, and conductivity data indicate that (3) is a dimer, trans,trans-[{Cr^{III}(NCMe)-(dmpe)$_2$}$_2$(μ-O)][BPh$_4$]$_4$.

The structure of the related oxo-bridged complex tetracation, [Mo$^{III}_2$O(NCMe)$_{10}$]$^{4+}$, has been confirmed by X-ray crystallography[5a] as containing a linear Mo–O–Mo unit, while a peroxo-bridged complex trans-[{Co^{III}(Me$_2$SO)(dmpe)$_2$}$_2$(μ-O$_2$)]$^{4+}$ has been made by air oxidation of [Co(dmpe)$_2$]$^+$.[5b]

Reaction of trans-[CrCl(NCMe)(dmpe)$_2$]$^+$ *and* trans-[Cr(NCMe)$_2$(dmpe)$_2$]$^{2+}$ *with Methanol.*—In attempting anion exchange of the tetraphenylborates of (1) and (2) in methanol solution, it was observed that the co-ordinated acetonitrile is rapidly attacked by MeOH.

The addition of a methanolic solution of Ba(CF$_3$SO$_3$)$_2$ to a MeCN solution of (1) yields a light green precipitate, which on

---

† trans-Bis[1,2-bis(dimethylphosphino)ethane]chloro(ethylimido)-chromium(IV) trifluoromethanesulphonate, trans-bis[1,2-(dimethyl-phosphino)ethane]bis(ethylideneamido)chromium(IV) bis(tetraphenyl-borate), and trans-bis[1,2-(dimethylphosphino)ethane]bis(ethylidyne-ammonium)chromium(0) bis(tetraphenylborate) respectively.
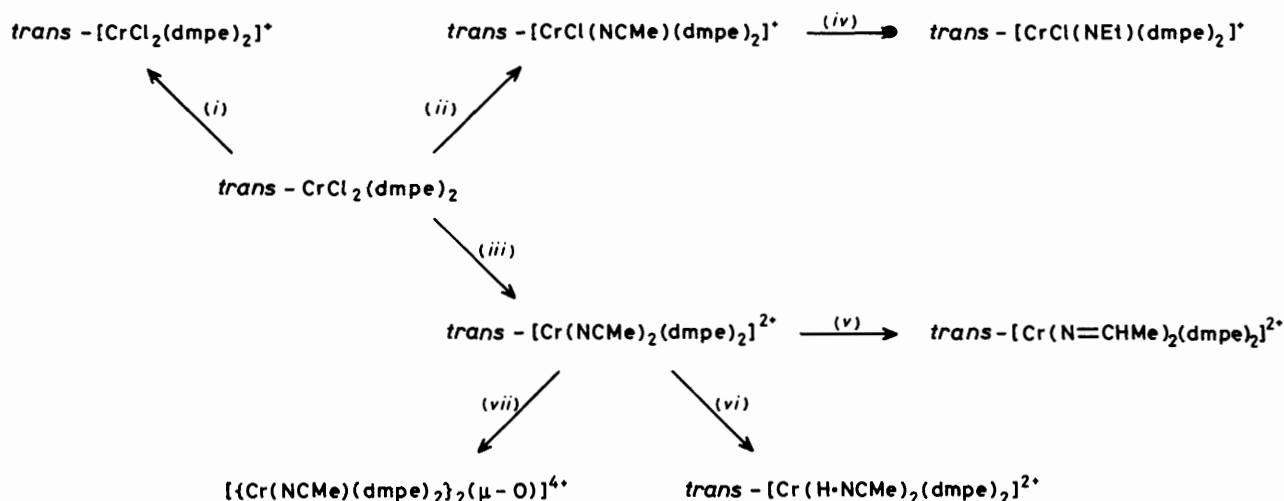
Scheme 1. (*i*) NaBPh$_4$, MeCN, O$_2$; (*ii*) NaBPh$_4$, MeCN; (*iii*) NaBPH$_4$, MeCN, reflux, 12 h; (*iv*) MeOH, Ba(CF$_3$SO$_3$)$_2$; (*v*) MeOH; (*vi*) MeCN, H$_2$ (40 atm), 100 °C; (*vii*) O$_2$
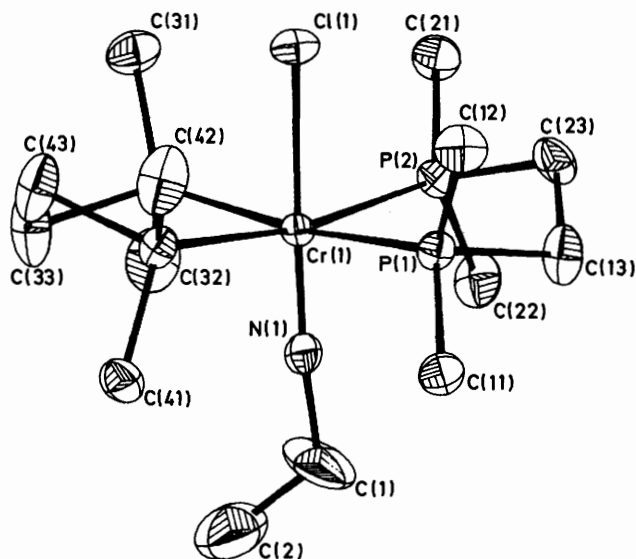
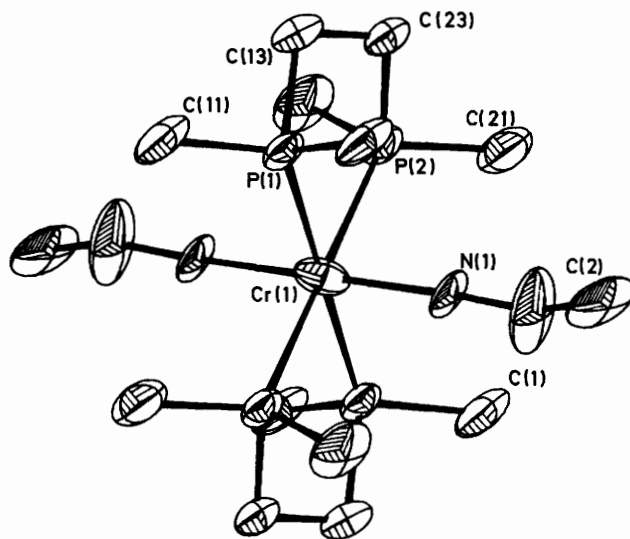**Figure 1.** The structure of the cation [CrCl(NEt)(dmpe)$_2$]$^+$

Figure 2. The structure of the cation [Cr(N≡CHMe)$_2$(dmpe)$_2$]$^{2+}$

recrystallization from MeCN, yields green crystals of the ethylimido complex *trans*-[CrCl(NEt)(dmpe)$_2$]CF$_3$SO$_3$ (4) whose structure has been confirmed by *X*-ray crystallography (see below). The complex is diamagnetic (Cr^{IV}, d^2). The protons of the ethylimido group are observable in the ^{1}H n.m.r. spectrum, as a quartet [δ 3.30 p.p.m., *J*(H–H) = 7.3 Hz, CH$_2$] and a triplet [δ 1.00 p.p.m., *J*(H–H) = 7.3 Hz, CH$_3$]. The Cr–Cl stretch, 340 cm^{-1}, is still present in the i.r. spectrum.

The addition of MeOH to an MeCN solution of (2), by contrast, yields the ethylideneamido (azomethine) complex *trans*-[Cr(N≡CHMe)$_2$(dmpe)$_2$][BPh$_4$]$_2$ (5), whose crystal structure is discussed below.

The methyl of the N≡CHMe group is observed in the ^{1}H n.m.r. spectrum; the resonance of the H atom on carbon is obscured by the signal due to the BPh$_4^-$ ions although observable as a broad quartet [δ 7.36 p.p.m., *J*(H–H) = 7.0 Hz] in the PF$_6^-$ salt (see Experimental section).

In the i.r. spectrum no C≡N bands were observed in the region 1 680—1 700 cm^{-1} for linear M–N≡CHR groups.[6,7] Interestingly, the C–N stretching frequency for the cluster compound

Fe$_3$H(N≡CHMe)(CO)$_9$[8] was given as 1 325 cm^{-1}, a position intermediate between that expected for ν(C–N) at 1 100 cm^{-1} and ν(C≡N) at 1 640 cm^{-1}.[9] However, no reason was given for this shift, although subsequent crystallographic work [10] showed the imine to be π-bonded to one of the three iron atoms and hence μ$_3$-η^2-co-ordinated.

Both compounds (4) and (5) are stable in air and are respectively 1:1 and 2:1 electrolytes in MeCN solution.

The structures of the complex cations in (4) and (5) are shown in Figures 1 and 2; selected bond lengths and angles are given in Tables 1 and 2. Both molecules have the now typical[1–3] octahedral structures with two 'equatorial' (dmpe) ligands and two axial ligands. The cation in (5) lies on a crystallographic centre of symmetry. The geometry parameters found for these structures provide an interesting addendum to our earlier results on Cr(dmpe)$_2$ complexes. In the previous paper in this series,[3] we showed how the Cr–P bond length, in particular, might be used as an indicator of the formal oxidation state of the Cr centre in these complexes. In summary, for Cr^0, Cr–P distances were 2.278—2.343(3), for Cr^I 2.360—2.379(3), for

Table 1. Selected bond lengths and angles for compound (4)

Bond lengths (Å)

P(1)–Cr(1)	2.362(3)	C(31)–P(3)	1.808(13)	P(2)–Cr(1)	2.352(4)	C(23)–P(2)	1.806(11)
P(3)–Cr(1)	2.355(5)	C(33)–P(3)	1.834(12)	P(4)–Cr(1)	2.343(5)	C(32)–P(2)	1.796(13)
C(11)–P(1)	1.818(11)	C(42)–P(4)	1.811(12)	N(1)–Cr(1)	1.622(9)	C(41)–P(4)	1.813(14)
C(13)–P(1)	1.832(11)	C(1)–N(1)	1.463(12)	C(12)–P(1)	1.739(13)	C(43)–P(4)	1.821(12)
C(22)–P(2)	1.805(13)	C(23)–C(13)	1.557(14)	C(21)–P(2)	1.826(12)	C(2)–C(1)	1.303(18)
Cl(1)–Cr(1)	2.425(4)						

Bond angles (°)

P(2)–Cr(1)–P(1)	83.5(2)	C(23)–P(2)–Cr(1)	108.5(4)	P(3)–Cr(1)–P(1)	172.6(1)	C(22)–P(2)–C(21)	102.9(6)
P(3)–Cr(1)–P(2)	95.9(2)	C(23)–P(2)–C(22)	102.7(6)	P(4)–Cr(1)–P(1)	96.1(2)	C(23)–P(2)–C(21)	101.3(6)
P(4)–Cr(1)–P(2)	169.5(1)	C(32)–P(3)–Cr(1)	117.5(5)	P(4)–Cr(1)–P(3)	83.2(2)	C(31)–P(3)–Cr(1)	120.5(5)
Cl(1)–Cr(1)–P(1)	86.4(2)	C(33)–P(3)–Cr(1)	108.2(4)	Cl(1)–Cr(1)–P(2)	84.9(2)	C(32)–P(3)–C(31)	103.4(6)
Cl(1)–Cr(1)–P(3)	86.1(2)	C(33)–P(3)–C(32)	102.8(7)	Cl(1)–Cr(1)–P(4)	84.5(2)	C(33)–P(3)–C(31)	102.2(6)
N(1)–Cr(1)–P(1)	91.8(4)	C(42)–P(4)–Cr(1)	122.0(5)	N(1)–Cr(1)–P(2)	94.7(3)	C(41)–P(4)–Cr(1)	114.3(5)
N(1)–Cr(1)–P(3)	95.7(4)	C(43)–P(4)–Cr(1)	108.9(4)	N(1)–Cr(1)–P(4)	95.8(3)	C(42)–P(4)–C(41)	102.4(6)
N(1)–Cr(1)–Cl(1)	178.2(3)	C(43)–P(4)–C(42)	102.9(6)	C(11)–P(1)–Cr(1)	118.5(5)	C(43)–P(4)–C(41)	104.5(7)
C(12)–P(1)–Cr(1)	122.1(5)	C(2)–C(1)–N(1)	122.9(14)	C(12)–P(1)–C(11)	102.1(6)	C(1)–N(1)–Cr(1)	175.3(7)
C(13)–P(1)–Cr(1)	106.2(4)	C(13)–C(23)–P(2)	108.3(7)	C(13)–P(1)–C(11)	102.6(6)	C(23)–C(13)–P(1)	108.5(7)
C(13)–P(1)–C(12)	102.7(6)	C(33)–C(43)–P(4)	108.5(8)	C(21)–P(2)–Cr(1)	122.9(5)	C(43)–C(33)–P(3)	107.7(8)
C(22)–P(2)–Cr(1)	115.9(5)						

Table 2. Selected bond lengths and angles for compound (5)

Bond lengths (Å)

P(1)–Cr(1)	2.372(3)	P(2)–Cr(1)	2.365(3)
N(1)–Cr(1)	1.865(5)	C(11)–P(1)	1.816(7)
C(12)–P(1)	1.798(6)	C(13)–P(1)	1.839(6)
C(21)–P(2)	1.808(7)	C(22)–P(2)	1.811(7)
C(23)–P(2)	1.847(6)	C(1)–N(1)	1.265(7)
C(2)–C(1)	1.336(7)	C(23)–C(13)	1.513(8)

Bond angles (°)

P(2)–Cr(1)–P(1)	83.2(0.5)	N(1)–Cr(1)–P(1)	92.6(2)
N(1)–Cr(1)–P(2)	89.3(2)	C(11)–P(1)–Cr(1)	122.1(2)
C(12)–P(1)–Cr(1)	116.0(2)	C(12)–P(1)–C(11)	102.2(3)
C(13)–P(1)–Cr(1)	108.2(2)	C(13)–P(1)–C(11)	102.3(3)
C(13)–P(1)–C(12)	103.9(3)	C(21)–P(2)–Cr(1)	120.3(2)
C(22)–P(2)–Cr(1)	116.8(3)	C(22)–P(2)–Cr(21)	104.2(3)
C(23)–P(2)–Cr(1)	107.7(2)	C(23)–P(2)–C(21)	103.2(3)
C(23)–P(2)–C(22)	102.3(3)	C(1)–N(1)–Cr(1)	176.5(4)
C(2)–C(1)–N(1)	148.0(7)	C(23)–C(13)–P(1)	109.5(4)
C(13)–C(23)–P(2)	110.4(4)		

Cr^{II} 2.359—2.392(3), and for Cr^{III} 2.443—2.447(5) Å. This unusual increase in effective Cr covalent radius with increasing oxidation state was attributed to a significant contribution from π-bonding in the Cr–P interaction, which is maximised in the (d^6) Cr^0 case and reduced sharply as the oxidation state increases.

In the present structures, the values found for the Cr–P distances in (4) and (5) indicate that the oxidation state *versus* Cr–P bond length curve has peaked at Cr^{III} and is now decreasing. One important additional factor to be considered however, is that (4) and (5) are diamagnetic; a much reduced Cr^{IV} radius was also found for the diamagnetic tetrahydride $CrH_4(dmpe)_2$.[3] Several other features of the structures are worthy of mention. In (4), the Cr–Cl distance is longer than those found in the Cr^{II} or Cr^{III} species studied earlier,[3] but this may be ascribed to a strong *trans* influence from the ethylimido function. For the EtN group the Cr–N distance is very short, as would be expected, whilst the apparent shortening of the ethyl C–C distance must be due to high thermal motion or disorder, since the spectroscopic results preclude the presence of a C=C grouping at this position. In (5), the geometry of the ethylidene-

amido ligand is similar to that found for the analogous ligand in $Zr(\eta\text{-}C_5H_5)_2(Cl)(N=CHPh)$,[6] with an *sp*-hybridised N atom and the Cr–N–C system behaving as a heteroallenic group. The Cr–N distance is compatible with some degree of multiple bonding and the C–N distance is very similar to that found for the Zr complex, 1.259(7) Å.

One unusual feature of the N=CHMe ligand is the large N–C–C angle of *ca.* 150° and an associated short CH–CH₃ bond. Again, some thermal or positional disorder may be occurring.
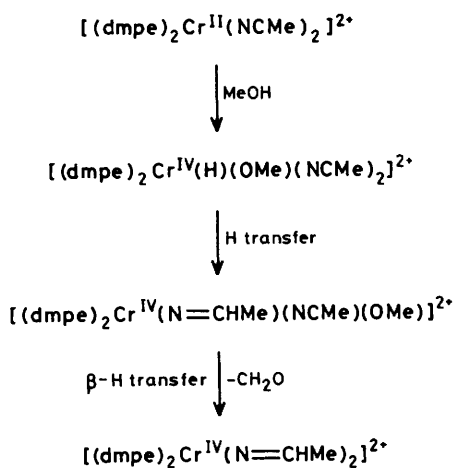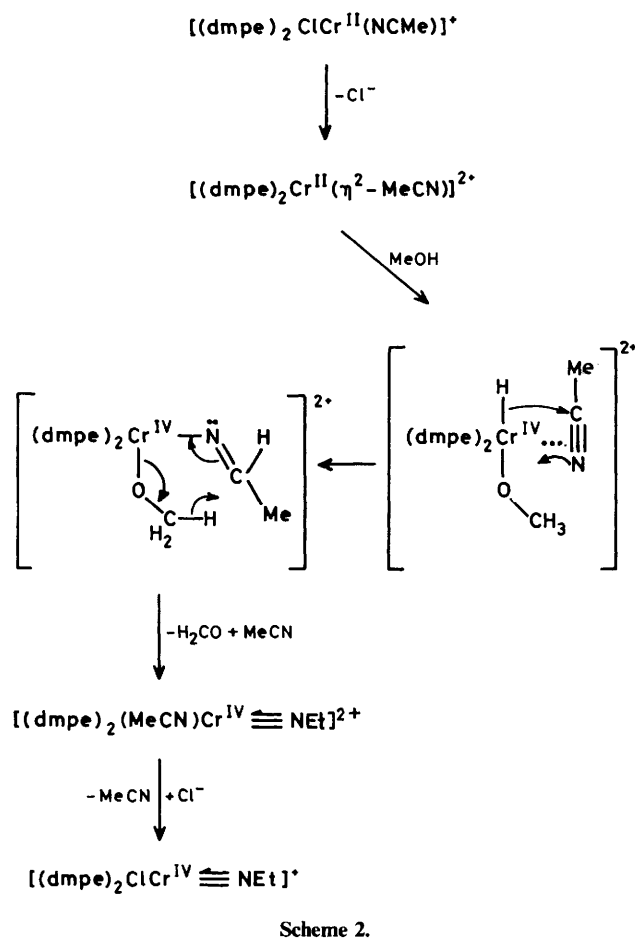
The nucleophilic attack of methanol on co-ordinated nitriles to give M–N(H)C(OMe)R groups has been extensively studied[11] but the present reactions appear to be unique in leading to oxidation of the metal and to hydrogen transfer to carbon.

In the reaction leading to (4), we assume that dissociation of chloride provides for the possibility of the η^2-bonding of MeCN (now fully established by X-ray crystallography;[12] see also ref. 3) we consider necessary for H transfer and that oxidative addition of methanol as H and MeO, which also has a precedent,[13] is facilitated.

Transfer of the hydride on Cr^{IV} to carbon of η^2-MeCN then leads to a non-linear N=C(H)Me group (*cf.* refs. 6 and 7). A second hydride transfer from the methyl group of the methoxide, probably *via* a cyclic transition state, then gives the $Cr\equiv N\text{-}CH_2CH_3$ moiety, with elimination of formaldehyde. Final reassociation of chloride leads to the formation of (4) (Scheme 2).

The reaction of $[Cr(NCMe)_2(dmpe)_2]^{2+}$ with methanol is presumably similar. However, it seems unlikely that dissociation of MeCN occurs since no exchange of co-ordinated MeCN with CD_3CN was observed for the cation.[3] Assuming as above initial oxidative addition of MeOH to give an eight-co-ordinate Cr^{IV} species, hydride transfer from Cr–H to MeCN will then give the first N=C(H)Me group; now, assuming that dissociation of one MeCN from this eight-co-ordinate species can occur, generation of an η^2-MeCN is possible. A β-hydride transfer from the methoxide then generates a second Cr–H with elimination of formaldehyde; subsequent H transfer to η^2-MeCN gives the second N=C(H)Me group (Scheme 3).

Interaction of trans-$[Cr(NCMe)_2(dmpe)_2]^{2+}$ *with Hydrogen.*—There has been considerable study of non-catalytic

[(dmpe)$_2$ClCr^{II}(NCMe)]$^+$

$\downarrow$ $-$Cl$^-$

[(dmpe)$_2$Cr^{II}(η^2-MeCN)]$^{2+}$

$\searrow$ MeOH

$$\left[(dmpe)_2Cr^{IV}-\!\!\!\!\overset{\overset{\cdot\cdot}{N}}{\underset{\underset{H_2}{C-H}}{\overset{|}{O}}}\!\!\!\!\overset{H}{\underset{Me}{C}}\right]^{2+} \longleftarrow \left[(dmpe)_2Cr^{IV}\cdots\underset{\underset{CH_3}{O}}{\overset{\overset{Me}{\overset{|}{C}}}{\underset{N}{|||}}}\right]^{2+}$$

$\downarrow$ $-$H$_2$CO + MeCN

[(dmpe)$_2$(MeCN)Cr^{IV} $\equiv$ NEt]$^{2+}$

$\downarrow$ $-$MeCN $\Big|$ +Cl$^-$

[(dmpe)$_2$ClCr^{IV} $\equiv$ NEt]$^+$

Scheme 2.

[(dmpe)$_2$Cr^{II}(NCMe)$_2$]$^{2+}$

$\downarrow$ MeOH

[(dmpe)$_2$Cr^{IV}(H)(OMe)(NCMe)$_2$]$^{2+}$

$\downarrow$ H transfer

[(dmpe)$_2$Cr^{IV}(N=CHMe)(NCMe)(OMe)]$^{2+}$

β-H transfer $\Big|$ $-$CH$_2$O

[(dmpe)$_2$Cr^{IV}(N=CHMe)$_2$]$^{2+}$

Scheme 3.

hydrogenation of nitriles by H$_2$ mostly with cluster complexes of iron, ruthenium, and osmium.[8,10,14–16] Intermediates with cluster-bound groups of the type μ_3-η^2-N=CHR, μ_3-η^2-NH=CHR have been characterised.

Although catalytic reductions of nitriles have been reported,[7,17] only recently has the stepwise catalytic hydrogenation been observed for the Sc(η-C$_5$H$_5$)$_2$H system.[7]

Neither [Cr(NCMe)$_2$(dmpe)$_2$]$^{2+}$ nor [CrCl(NCMe)(dmpe)$_2$]$^+$ catalyses hydrogenation of MeCN even under pressure at elevated temperatures. Small quantities of NH$_2$Et

Table 3. Selected bond lengths and angles for compound (6)

Bond lengths (Å)

P(1)–Cr(1)	2.265(3)	P(2)–Cr(1)	2.268(3)
N(1)–Cr(1)	1.900(5)	C(11)–P(1)	1.816(7)
C(12)–P(1)	1.807(8)	C(13)–P(1)	1.829(8)
C(21)–P(2)	1.827(7)	C(22)–P(2)	1.812(7)
C(23)–P(2)	1.815(8)	C(1)–N(1)	1.151(6)
C(2)–C(1)	1.448(7)		

Bond angles (°)

P(2)–Cr(1)–P(1)	95.1(0.5)	N(1)–Cr(1)–P(1)	89.8(2)
N(1)–Cr(1)–P(2)	89.0(2)	C(11)–P(1)–Cr(1)	120.7(3)
C(12)–P(1)–Cr(1)	117.5(3)	C(12)–P(1)–C(11)	103.6(4)
C(13)–P(1)–Cr(1)	108.6(3)	C(13)–P(1)–C(11)	100.7(4)
C(13)–P(1)–C(12)	103.2(4)	C(21)–P(2)–Cr(1)	122.6(3)
C(22)–P(2)–Cr(1)	116.2(3)	C(22)–P(2)–C(21)	101.9(4)
C(23)–P(2)–Cr(1)	109.9(3)	C(23)–P(2)–C(21)	98.7(4)
C(23)–P(2)–C(22)	104.9(4)	C(1)–N(1)–Cr(1)	177.7(3)
C(2)–C(1)–N(1)	178.6(5)		
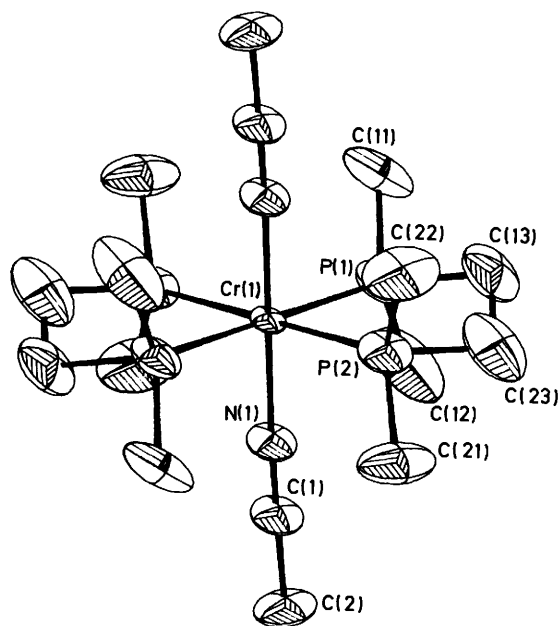
Figure 3. The structure of the cation [Cr(H·NCMe)$_2$(dmpe)$_2$]$^{2+}$

can be detected from the reaction at 100 °C/40 atm using the bis(acetonitrile) complex. The original complex is not, however, recovered from the residual red solution but instead bright yellow crystals of a new complex (6), are obtained. The structure of the complex has been determined by X-ray study and a diagram of the cation is given in Figure 3; selected bond lengths and angles are given in Table 3.

At first sight, this species appears to be [Cr(N≡C–Me)$_2$-(dmpe)$_2$]$^{2+}$ with the geometry of the Cr–N≡C–Me unit very similar to those found in the cations [Cr(N≡CR)$_2$(dmpe)$_2$]$^{2+}$ (R = Me or Et) in the CF$_3$SO$_3^-$ salts studied earlier.[3] However, these salts and their solutions are green, whilst the present complex is yellow. The complex is clearly different to the Cr^{II} species {and it is pertinent to note that BPh$_4^-$ salts of the [Cr(NCR)$_2$(dmpe)$_2$]$^{2+}$ ions cannot be obtained crystalline} and further examination of the geometry gives a clue to the possible solution. The key parameters are the Cr–P distances which are most compatible with values found earlier for chromium(o) complexes,[1] and in this case it is necessary to

postulate that the two positive charges in the form of two protons needed to balance the presence of the anions must lie elsewhere.

The formulation of the cation with Cr^0 is supported by the sharpness of ^1H n.m.r. spectra in MeCN and its diamagnetism. In addition to dmpe and BPh_4^- peaks (Experimental section) there is a sharp singlet for co-ordinated MeCN at δ 2.01 p.p.m. Addition of ca. 0.1 cm^3 of CD_3OD produces a broad singlet at δ 4.10 p.p.m. due to CD_3OH, the intensity of which is constant on further addition of CD_3OD. Integration of the peak gives a value ca. 1/12 that of the CH_3 peak of dmpe, suggesting that there are indeed two acidic hydrogen atoms present. These cannot however be detected in the ^1H n.m.r. spectrum, possibly due to rapid exchange.

The relative acidity of these two protons can be estimated by titration of an MeCN solution of (6) with 1,8-bis(dimethyl-amino)naphthalene ('proton sponge') in MeCN. The titration curve shows two equivalence points indicating that (6) is a weak dibasic acid ($pK_1 = 4.9$, $pK_2 = 5.1$; corrected to aqueous medium). The similarlity of the pK values indicates that the protons on (6) are bonded to each nitrile.

We suggest that these protons are located on the position of greatest electron density, namely the $C\equiv N$ triple bonds (see below; cf. the well known mercurinium ions formed by electro-philic attacks of Hg^{2+} on $C=C$ bonds[18]).

$$Cr \longleftarrow N \overset{.\overset{\text{H}}{.}..}{\equiv} C \longrightarrow Me$$
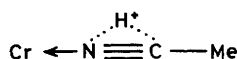
Such protonation, which is probably asymmetric, accounts for the $2+$ charge on the ion, the zero oxidation state of the metal, and the acidity. The X-ray crystallographic results can-not provide any further positive evidence for such a structure, but do not preclude its existence. Obviously the protons could be sited at any position around the cylindrical $N\equiv C$ bond, and so their presence may not be detectable through deformations in other parts of the structure. It is highly unlikely that the protons are bound to the metal as in $[CrH(CO)_2(dmpe)_2]^+$.[3] There is no evidence for Cr–H bonds spectroscopically or chemically (CCl_4 reaction); further, the $Cr(P_2)_2$ unit is symmetrical by virtue of its crystallographic positioning, the $^{31}P-\{^1H\}$ spectrum is a sharp singlet, and there are no indications of displacement disorder in the low anisotropy of the P atoms. Clearly the true picture may be clarified only via neutron diffraction analysis, and such studies are planned.

Although in the i.r. spectrum the $C\equiv N$ stretches in complexes (2) and (6) are very similar, the relative intensity in the latter is much decreased, suggesting some alteration of the dipole moment along the $C\equiv N$ bond axis such as might be produced by protonation. The formation of the complex by hydrogen reduction then can be written as given below.

$$[Cr^{II}(NCMe)_2(dmpe)_2]^{2+} + H_2 \longrightarrow$$
$$[Cr^0(H\cdot NCMe)_2(dmpe)_2]^{2+}$$
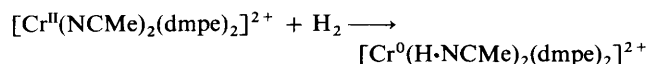
Cyclic voltametric study of $[Cr(NCMe)_2(dmpe)_2][CF_3SO_3]_2$ in MeCN, where hydride transfer cannot of course occur, shows a one-electron reversible reduction at -1.3 V (vs. hydrogen electrode) with a second irreversible one-electron reduction at -1.7 V. Attempts to isolate the presumed Cr^I and Cr^0 species failed. Similarly attempts to isolate $Cr^0(NCMe)_2(dmpe)_2$ by reduction of the dication (2) by sodium or by the addition of 'proton sponge' to (6), even in the presence of excess PMe_3, failed.

The small amount of NH_2Et formed in addition to (6) in the hydrogenation is probably due to the direct reduction of co-ordinated MeCN and is unrelated to the formation of (6).

Table 4. Analytical data for chromium complexes

| Compound | Analysis[a] (%) | | |
	C	H	N
(1) $[CrCl(NCMe)(dmpe)_2][BPh_4]$	59.8	7.3	1.8
	(61.0)	(7.4)	(1.9)
(2) $[Cr(NCMe)_2(dmpe)_2][BPh_4]_2$	72.0	7.5	2.3
	(71.6)	(7.3)	(2.6)
(3) $[\{Cr(NCMe)(dmpe)_2\}_2(\mu-O)][BPh_4]_4$[b]	72.0	7.2	1.2
	(71.6)	(7.2)	(1.3)
(4) $[CrCl(NEt)(dmpe)_2]CF_3SO_3$	33.3	6.4	3.0
	(33.9)	(7.0)	(2.6)
(5a) $[Cr(N=CHMe)_2(dmpe)_2][BPh_4]_2$	71.7	7.5	2.6
	(71.5)	(7.4)	(2.6)
(5b) $[Cr(N=CHMe)_2(dmpe)_2][PF_6]_2$	25.6	5.3	3.9
	(26.4)	(5.5)	(3.8)
(6) $[Cr(H\cdot NCMe)_2(dmpe)_2][BPh_4]_2$	70.9	7.3	2.6
	(71.6)	(7.4)	(2.6)

[a] Required values in parentheses. [b] O, 0.70 (0.75%).

A similar reaction of hydrogen with $[Fe(MeCN)_2(dmpe)_2]$-$[BPh_4]_2$ yields $[Fe(NH_2Et)_2(dmpe)_2][BPh_4]_2$ from which ethylamine can be liberated on refluxing the complex in MeCN.[19]

Experimental

trans-Acetonitrilebis[1,2-bis(dimethylphosphino)ethane]-(chloro)chromium(II) Tetraphenylborate, (1).—To $CrCl_2(dmpe)_2$ (0.35 g, 0.83 mmol) in MeCN (50 cm^3), was added $NaBPh_4$ (0.29 g, 0.84 mmol). The solution rapidly changed from green to orange-brown and NaCl precipitated. After stirring for 12 h the solution was filtered, concentrated, and cooled to -20 °C to yield a golden-brown microcrystalline powder. Yield: 0.51 g, 83%; m.p. >300 °C. I.r.: 3 020m, 3 010m, 2 250m, 1 945w, 1 870w, 1 820w, 1 755w, 1 575m, 1 425s, 1 300m, 1 285m, 1 260m, 1 140m, 1 030w, 1 040m, 935s, 925s, 885m, 840m, 730s, 700s, 610s, 460m, 375w, 340m cm^{-1}. Magnetic moment: $\mu_{eff.} = 2.9$. Conductivity (MeCN): $\Lambda_M = 138$ ohm^{-1} cm^2 mol^{-1}.

trans-Bis(Acetonitrile)bis[1,2-bis(dimethylphosphino)ethane]-chromium(II) Bis(tetraphenylborate), (2).—To $CrCl_2(dmpe)_2$ (0.92 g, 2.17 mmol) in MeCN (75 cm^3), was added $NaBPh_4$ (1.49 g, 4.35 mmol). The solution was refluxed gently for 12 h then cooled and the golden-green solution filtered; removal of the

Table 5. Crystal data, intensity data, collection parameters, and details of refinement

Compound	(4)	(5)	(6)
	[CrCl(NEt)(dmpe)$_2$]CF$_3$SO$_3$	[Cr(N=CHMe)$_2$(dmpe)$_2$][BPh$_4$]$_2$	[Cr(H·NCMe)$_2$(dmpe)$_2$][BPh$_4$]$_2$
Formula	C$_{11}$H$_{25}$ClCrF$_3$O$_3$P$_4$S	C$_{64}$H$_{80}$B$_2$CrN$_2$P$_4$	C$_{64}$H$_{80}$B$_2$CrN$_2$P$_4$
Crystal data			
M	579.861	1 074.86	1 074.86
$a/\text{Å}$	9.189 0(5)	12.247(5)	12.246(3)
$b/\text{Å}$	17.500(4)	13.109(6)	13.118(6)
$c/\text{Å}$	16.414(4)	12.102(9)	12.201(5)
$\alpha/^\circ$	90	116.27(5)	116.28(4)
$\beta/^\circ$	90.60(1)	119.18(3)	118.98(3)
$\gamma/^\circ$	90	64.16(3)	62.97(3)
$U/\text{Å}^3$	2 639.35	1 459.82	1 463.68
System	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
$D_c/\text{g cm}^{-3}$	1.46	1.22	1.22
Z	4	1	1
$F(000)$	1 208	572	572
μ/cm^{-1}	8.77	3.37	3.37
Data collection			
Total data measured	5 326	5 340	5 373
Total data unique	4 622	5 127	5 147
Total data observed	2 875	3 824	3 380
Significance test	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$
Refinement			
No. of parameters	390	475	487
Weighting scheme	$1/[\sigma^2(F_o) + 0.000\,01F_o^2]$	$1/[\sigma^2(F_o) + 0.0001F_o^2]$	$1/[\sigma^2(F_o) + 0.000\,01F_o^2]$
Final $R = \Sigma|F|/\Sigma|F_o|$	0.0609	0.0543	0.0468
Final $R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}$	0.0557	0.0561	0.0438

solvent gave a golden solid. Yield: 2.26 g, 97%; m.p. >300 °C. I.r.: 3 025m, 3 015m, 2 250m, 1 950w, 1 875w, 1 820w, 1 750w, 1 575m, 1 415s, 1 300m, 1 275s, 1 260m, 1 170w, 1 140m, 1 090w, 1 030m, 935s, 885m, 845m, 740s, 705s, 610s, 470w cm^{-1}. Magnetic moment: $\mu_{eff.}$ = 2.8. Conductivity (MeCN): Λ_M = 230 ohm^{-1} cm^2 mol^{-1}.

Both the above complex cations can be obtained as the corresponding trifluoromethanesulphonates or hexafluorophosphates by using either Ba(CF$_3$SO$_3$)$_2$ or NaPF$_6$ in place of NaBPh$_4$.

μ-*Oxo-bis{acetonitrilebis[1,2-bis(dimethylphosphino)ethane]-chromium(III)}* *Tetrakis(tetraphenylborate)*, (**3**).—Oxygen was bubbled through a MeCN solution (20 cm^3) of [Cr(NCMe)$_2$-(dmpe)$_2$][BPh$_4$]$_2$ (0.4 g, 0.37 mmol) for 5 min. The solution, which rapidly became dark red, was reduced to *ca.* 5 cm^3 and the oil tritiated with Et$_2$O to leave a red microcrystalline solid. Yield: 0.36 g, 96%; m.p. 176 °C (decomp.). I.r.: 3 020m, 3 010m, 2 245m, 1 945w, 1 870w, 1 820w, 1 755w, 1 575m, 1 425s, 1 305m, 1 285m, 1 260m, 1 145w, 1 040m, 1 030w, 935s, 925s, 880m, 860s, 835m, 730s, 700s, 610s, 460m cm^{-1}. Magnetic moment: $\mu_{eff.}$ = 1.82 per Cr. Conductivity (MeCN): Λ_M = 523 ohm^{-1} cm^2 mol^{-1} {*cf.* conductivity of [Mo$_2$O(MeCN)$_{10}$]-[BF$_4$]$_4$, Λ_M = 552 ohm^{-1} cm^2 mol^{-1}}.

trans-Bis[1,2-bis(dimethylphosphino)ethane]chloro(ethyl-imido)chromium(IV) *Trifluoromethanesulphonate*, (**4**).—To an MeCN (20 cm^3) solution of [CrCl(NCMe)(dmpe)$_2$]BPh$_4$ (0.43 g, 0.58 mmol) was added a MeOH (20 cm^3) solution of Ba(CF$_3$SO$_3$)$_2$ (0.13 g, 0.30 mmol). A pale green precipitate was formed immediately; the mixture was stirred for several hours, after which the precipitate was collected and washed with MeOH (2 × 10 cm^3). The dried solid was extracted into aceto-nitrile (60 cm^3) which was then reduced to *ca.* 15 cm^3 and cooled (−20 °C) to give blue-green crystals. Yield 0.28 g, 84%;

m.p. 190 °C. I.r.: 1 420s, 1 300m, 1 255s, 1 240m, 1 220m, 1 145s, 1 025s, 980w, 940s, 930 (sh), 890m, 835m, 790m, 740m, 705m, 630s, 520w, 340w cm^{-1}. ^{1}H N.m.r.: δ 3.30 [q, J(H–H) = 7.3 Hz, NCH$_2$CH$_3$], 1.50 (m, P–CH$_3$), 1.30 (m, PCH$_2$), 1.0 [t, J(H–H) = 7.3 Hz, NCH$_2$CH$_3$]. Conductivity (MeCN): Λ_M = 149 ohm^{-1} cm^2 mol^{-1}.

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis(ethylidene-amido)chromium(IV) *Bis(tetraphenylborate)*, (**5a**).—Methanol (20 cm^3) was added to a solution of [Cr(NCMe)$_2$(dmpe)$_2$]-[BPh$_4$]$_2$ (0.79 g, 0.74 mmol) in MeCN (20 cm^3). After stirring for 6 h the solution was green and a small amount of green precipitate had formed. The solvent was removed and the residue extracted with hot MeCN (50 cm^3); reduction in volume and cooling (−20 °C) gave bright green crystals. Yield: 0.58 g, 73%; m.p. 254 °C. I.r.: 3 025m, 3 015m, 1 950w, 1 880w, 1 820w, 1 750w, 1 575m, 1 420s, 1 305m, 1 290s, 1 260m, 1 175w, 1 140m, 1 060m, 1 035m, 940s, 930s, 910w, 885s, 860w, 840m, 790m, 740s, 705s, 645m, 605m, 445w cm^{-1}. Conductivity (MeCN): Λ_M = 283 ohm^{-1} cm^2 mol^{-1}.

The hexafluorophosphate salt (**5b**) was obtained by passing an MeCN solution of the tetraphenylborate salt down an Amberlyst A-26 (B.D.H.) column, saturated with NaPF$_6$, and crystallising. I.r.: 1 425m, 1 305w, 1 290m, 1 255w, 1 220w, 1 100m br, 1 035 (sh), 940s, 895m, 835vs, 745m, 710m, 645m, 560s cm^{-1}. ^{1}H N.m.r.: 7.36 [br q, J(H–H) = 7.0 Hz, N=CHCH$_3$], 1.70 [br d, J(H–H) = 7.0 Hz, N=CHCH$_3$], 1.62 (m, PCH$_3$), 1.30 (m, PCH$_2$).

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis(ethylidyne-ammonium)chromium(0) *Bis(tetraphenylborate)*, (**6**).—An MeCN (35 cm^3) solution of [Cr(NCMe)$_2$(dmpe)$_2$][BPh$_4$]$_2$ (0.36 g, 0.34 mmol) was pressurised with H$_2$ (40 atm) in an autoclave. The temperature was slowly raised to 100 °C and the solution

Table 6. Fractional atomic co-ordinates (× 10⁴) for compound (4)

Atom	x	y	z	Atom	x	y	z
Cr(1)	159(1)	−329(1)	2 539(1)	C(31)	−2 481(12)	−468(7)	4 157(7)
P(1)	1 866(2)	438(1)	1 850(1)	C(32)	−2 961(13)	−1 495(7)	2 851(8)
P(2)	−1 548(2)	474(1)	1 890(1)	C(33)	−568(11)	−1 719(6)	3 930(7)
P(3)	−1 536(3)	−971(1)	3 359(2)	C(41)	2 747(12)	−1 763(7)	2 897(9)
P(4)	1 858(2)	−958(1)	3 376(1)	C(42)	3 371(11)	−460(8)	3 852(7)
Cl(1)	203(2)	642(1)	3 594(1)	C(43)	916(11)	−1 371(7)	4 242(7)
N(1)	164(8)	−961(4)	1 817(4)	S(1)	5 016(4)	2 975(2)	5 069(2)
C(1)	187(19)	−1 480(7)	1 119(7)	O(1)	4 530(15)	2 613(9)	5 749(6)
C(2)	−22(20)	−2 214(9)	1 185(11)	O(2)	6 533(13)	3 114(8)	5 101(8)
C(11)	3 288(11)	−32(6)	1 273(6)	O(3)	4 308(15)	3 594(6)	4 751(8)
C(12)	2 850(12)	1 191(7)	2 352(7)	C(3)	4 970(15)	2 279(8)	4 292(8)
C(13)	843(10)	950(6)	1 057(6)	F(1)	3 616(13)	2 039(8)	4 214(7)
C(21)	−2 979(12)	974(7)	2 439(7)	F(2)	5 208(13)	2 499(6)	3 594(5)
C(22)	−2 515(12)	65(6)	1 032(7)	F(3)	5 586(14)	1 660(5)	4 476(7)
C(23)	−587(10)	1 263(6)	1 434(7)				

Table 7. Fractional atomic co-ordinates (× 10⁴) for compound (5)

Atom	x	y	z	Atom	x	y	z
Cr(1)	0*	0*	0*	C(41)	6 840(3)	−3 319(3)	643(3)
P(1)	779(1)	1 666(1)	1 533(1)	C(42)	6 916(3)	−3 056(3)	−316(3)
P(2)	2 233(1)	−1 050(1)	727(1)	C(43)	6 263(3)	−3 474(3)	−1 661(3)
N(1)	−186(3)	−271(3)	1 280(3)	C(44)	5 484(4)	−4 186(3)	−2 119(4)
C(1)	−357(5)	−493(6)	2 092(5)	C(45)	5 399(4)	−4 491(3)	−1 221(4)
C(2)	−486(5)	−117(6)	3 255(4)	C(46)	6 066(4)	−4 066(3)	125(4)
C(11)	314(4)	2 990(4)	1 086(5)	C(51)	6 982(3)	−1 287(3)	2 672(3)
C(12)	513(4)	2 271(4)	3 064(4)	C(52)	6 276(3)	−591(3)	1 804(3)
C(13)	2 564(4)	1 200(4)	2 048(4)	C(53)	5 848(3)	636(3)	2 208(4)
C(21)	2 757(4)	−2 332(4)	1 259(5)	C(54)	6 094(4)	1 242(3)	3 521(4)
C(22)	3 087(4)	−1 519(5)	−364(5)	C(55)	6 756(4)	606(3)	4 423(4)
C(23)	3 104(4)	−26(4)	2 213(4)	C(56)	7 183(4)	−621(3)	4 004(4)
B(1)	7 583(4)	−2 754(3)	2 236(4)	C(61)	9 164(3)	−3 067(3)	2 610(3)
C(31)	7 390(3)	−3 296(3)	3 108(3)	C(62)	9 804(3)	−3 738(3)	1 717(3)
C(32)	8 248(3)	−4 323(3)	3 459(3)	C(63)	11 138(4)	−3 959(4)	2 081(4)
C(33)	8 098(4)	−4 778(3)	4 196(4)	C(64)	11 893(3)	−3 534(3)	3 376(4)
C(34)	7 056(4)	−4 230(3)	4 600(4)	C(65)	11 313(4)	−2 913(4)	4 299(4)
C(35)	6 168(4)	−3 229(3)	4 256(4)	C(66)	9 992(4)	−2 689(4)	3 916(4)
C(36)	6 335(3)	−2 776(3)	3 526(4)				

* Invariant parameter.

Table 8. Fractional atomic co-ordinates (× 10⁴) for compound (6)

Atom	x	y	z	Atom	x	y	z
Cr(1)	10 000*	5 000*	5 000*	C(41)	8 997(4)	1 767(3)	7 630(4)
P(1)	9 524(1)	3 949(1)	2 860(1)	C(42)	9 906(4)	2 336(4)	8 665(4)
P(2)	10 940(1)	3 377(1)	5 741(1)	C(43)	11 229(4)	1 912(4)	8 850(4)
N(1)	11 667(3)	4 832(3)	5 097(3)	C(44)	11 699(4)	876(4)	7 978(5)
C(1)	12 691(4)	4 737(4)	5 199(4)	C(45)	10 855(4)	278(4)	6 953(5)
C(2)	13 989(4)	4 630(5)	5 364(5)	C(46)	9 537(4)	722(4)	6 798(4)
C(11)	10 777(7)	2 687(5)	2 282(5)	C(51)	6 966(4)	3 745(3)	7 998(4)
C(12)	8 132(7)	3 402(7)	2 083(6)	C(52)	6 148(4)	4 419(4)	8 733(4)
C(13)	9 084(6)	4 929(5)	1 917(5)	C(53)	5 730(4)	5 660(4)	9 148(4)
C(21)	12 285(5)	2 108(5)	5 303(6)	C(54)	6 135(5)	6 296(4)	8 857(4)
C(22)	9 840(5)	2 643(5)	5 452(6)	C(55)	6 964(5)	5 691(4)	8 167(5)
C(23)	11 759(7)	3 800(5)	7 501(5)	C(56)	7 370(5)	4 454(4)	7 767(4)
B(1)	7 428(4)	2 264(4)	7 413(4)	C(61)	6 584(4)	1 927(3)	5 830(4)
C(31)	7 154(4)	1 676(3)	8 164(4)	C(62)	5 664(5)	1 308(4)	5 191(4)
C(32)	8 141(4)	923(4)	8 923(4)	C(63)	4 950(5)	1 079(4)	3 852(4)
C(33)	7 899(5)	466(4)	9 591(5)	C(64)	5 158(5)	1 446(4)	3 086(4)
C(34)	6 645(5)	760(4)	9 526(5)	C(65)	6 076(5)	2 023(4)	3 659(4)
C(35)	5 632(5)	1 479(4)	8 767(4)	C(66)	6 763(4)	2 250(4)	4 986(4)
C(36)	5 886(4)	1 922(4)	8 106(4)				

* Invariant parameter.

stirred for 12 h. After cooling to room temperature and the release of pressure, the solution was transferred to a flask and the volume reduced by about half; cooling to $-20\,^{\circ}\mathrm{C}$ yielded yellow crystals and further crops were obtained from the filtrate. Yield: 0.21 g, 60%; m.p. $>300\,^{\circ}\mathrm{C}$ (decomp.). I.r. (KBr disc): 3 030m, 3 000m, 2 940m, 2 905m, 2 255vw, 1 950w, 1 890w, 1 825w, 1 770w, 1 575m, 1 475m, 1 415s, 1 402s, 1 305m, 1 290s, 1 265m, 1 175w, 1 135m, 1 035m, 935s, 885s, 840m, 735vs, 705vs, 650m cm^{-1}. ^{1}H N.m.r.: δ 7.25, 6.90 (m, BPh$_4$), 2.15 (m, PCH$_2$), 2.01 (s, NCCH$_3$), 1.50 (m, PCH$_3$). ^{31}P-$\{^1$H$\}$ N.m.r.: δ 64.12.

Acid–base titration of the complex was carried out in MeCN using a Data Scientific PT1-15 digital pH-meter and a Russel pH-probe. The pK values were referenced against the pK_a of acetic acid in MeCN and the values given in the text are corrected to aqueous medium.[21]

X-Ray Crystallography.—All crystallographic measurements were made on crystals sealed under argon in glass capillaries using a CAD4 diffractometer operating in the $\omega/2\theta$ scan mode with graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\ 69$ Å) as previously described.[22] The structures were solved *via* the heavy-atom method and refined using full-matrix least-squares methods,[23] with scattering factor data from ref. 24. In general, all non-hydrogen atoms were successfully refined aniso-tropically, but with the O and F atoms in the CF$_3$SO$_3^-$ ion in complex (4) showing signs of severe disorder and anisotropy. Some evidence of disorder was also found for the two carbon atoms of the N=CHCH$_3$ ligand in complex (5). For all complexes all hydrogen atoms were located experimentally and freely refined isotropically, except for those on the carbons of the N=CH$_2$CH$_3$ and N=CHCH$_3$ ligands in (4) and (5), which could not be located and seem to be disordered, and also the two acidic protons in (6). Details of the crystal data, intensity recording and refinement are given in Table 5. Final atomic fractional co-ordinates are given in Tables 6—8.

References
1 J. E. Salt, G. S. Girolami, G. Wilkinson, M. Motevalli, M. Thornton-Pett, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 685.
2 G. S. Girolami, G. Wilkinson, A. M. R. Galas, M. Thornton-Pett, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 1339.
3 J. E. Salt, G. Wilkinson, M. Motevalli, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1986, 1141.
4 B. O. West and D. J. Liston, *Inorg. Chem.*, 1985, 24, 1568; D. J. Liston, B. J. Kennedy, K. S. Murray, and B. O. West, *ibid.*, p. 1561; R. L. Elliot, P. J. Nichols, and B. O. West, *J. Chem. Soc., Chem. Commun.*, 1986, 840.
5 (a) T. C. Wright, M. Motevalli, M. B. Hursthouse, and G. Wilkinson, unpublished work; (b) T. Ohishi, K. Kashiwavara, J. Fujita, S. Ohba, T. Ishi, and Y. Saito, *Bull. Chem. Soc. Jpn.*, 1986, 59, 385.
6 G. Erker, W. Frömberg, J. L. Atwood, and W. E. Hunter, *Angew. Chem., Int. Ed. Engl.*, 1984, 23, 68.
7 J. E. Bercaw, D. L. Davies, and P. T. Wolczanski, *Organometallics*, 1986, 5, 443.
8 M. A. Andrews and H. D. Kaesz, *J. Am. Chem. Soc.*, 1979, 101, 7238, 7255.
9 L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' 3rd edn., Wiley, New York, 1975, pp. 288 and 301.
10 M. A. Andrews, G. van Buskirk, C. B. Knobler, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1979, 101, 7245.
11 B. N. Storhoff and H. C. Lewis, *Coord. Chem. Rev.*, 1977, 23, 1.
12 T. C. Wright, G. Wilkinson, M. Motevalli, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1986, 2017.
13 K. W. Chiu, R. A. Jones, G. Wilkinson, A. M. R. Galas, K. M. A. Malik, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1981, 1204.
14 R. D. Adams and I. T. Horvath, *Prog. Inorg. Chem.*, 1985, 33, 128.
15 Z. Dawoodi, M. J. Mays, and K. Henrick, *J. Chem. Soc., Dalton Trans.*, 1984, 433.
16 W. Bernhardt, C. von Schnering, and H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1986, 25, 279.
17 See, for example, S. Bhaduri and K. R. Sharma, *J. Chem. Soc., Dalton Trans.*, 1982, 727; H. Eckert and Y. Kiesel, *Angew. Chem., Int. Ed. Engl.*, 1981, 20, 473; I. S. Thorburn, S. J. Rettig, and B. R. James, *J. Organomet. Chem.*, 1985, 290, 103.
18 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 4th edn., John Wiley and Sons, New York, 1980, p. 614.
19 A. R. Barron, G. Wilkinson, M. Motevalli, and M. B. Hursthouse, *Polyhedron*, 1987, 6, 1089.
20 D. F. Evans, G. V. Fazakerley, and R. F. Philips, *J. Chem. Soc. A*, 1971, 1931.
21 R. F. Cookson, *Chem. Rev.*, 1974, 74, 5.
22 M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, 101, 4128.
23 G. M. Sheldrick, SHELX 76, program for X-ray structure determination, University of Cambridge, 1976.
24 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.