The Chemistry of Chromium Nitrile Complexes of 1,2-Bis(dimethylphosphino)ethane. X-Ray Crystal Structures of *trans*-[Cr^{IV}Cl(NEt)(dmpe)₂]CF₃SO₃, *trans*-[Cr^{IV}(N=CHMe)₂(dmpe)₂][BPh₄]₂, and *trans*-[Co⁰(H·NCMe)₂(dmpe)₂][BPh₄]₂†

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The interaction of $CrCl_2(dmpe)_2$ with NaBPh₄ in MeCN at room temperature gives the partially substituted complex *trans*- $[Cr^{11}Cl(NCMe)(dmpe)_2]BPh_4$; when the reaction is carried out in refluxing MeCN the product is the previously characterised *trans*- $[Cr^{11}(NCMe)_2(dmpe)_2][BPh_4]_2$. The interaction of both nitrile complexes with methanol has been studied, and the X-ray structures of the products, *trans*- $[Cr^{1V}Cl(NEt)(dmpe)_2]CF_3SO_3$ and *trans*- $[Cr^{1V}(N=CHMe)_2(dmpe)_2][BPh_4]_2$ respectively, have been determined. These are the first octahedral Cr^{1V} complexes. The interaction of *trans*- $[Cr(NCMe)_2(dmpe)_2][BPh_4]_2$ with H₂ leads to a complex of stoicheiometry *trans*- $[Cr-(H\cdot NCMe)_2(dmpe)_2][BPh_4]_2$, 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 Cr¹¹ species and confirm the presence of Cr⁰. 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*- $[{Cr(NCMe)(dmpe)_2}_2(\mu-O)]^{4+}$ is also

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(N₂)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-CrCl₂(dmpe)₂² with one equivalent of NaBPh₄ in MeCN, at room temperature, leads to a goldenbrown solution from which the complex trans-[CrCl(NCMe)-(dmpe)₂]BPh₄ (1) can be isolated. However, when two equivalents of NaBPh₄ are used and the solution refluxed the product is the previously reported ³ trans-[Cr(NCMe)₂-(dmpe)₂][BPh₄]₂ (2). The complexes can be isolated with other counter ions, PF₆⁻, CF₃SO₃⁻, and BF₄⁻, 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)].

Non-S.I. unit employed: atm = 101 325 Pa.

In addition the spectrum of (1) contains a band at 340 cm⁻¹ [v(Cr-Cl)]; a similar band is observed in *trans*-CrCl₂(dmpe)₂.²

Both nitrile complexes are paramagnetic showing very broad ¹H 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), $\mu_B = 2.9$; (2), $\mu_B = 2.8$]. None of the minor Cr^I species,³ detected by e.s.r. spectra formed together with (2) in the protonation of *trans*-Cr(N₂)₂(dmpe)₂ with CF₃SO₃H in MeCN, was detected in samples prepared by the present procedure.

Reaction of trans- $[Cr(NCMe)_2(dmpe)_2]^{2+}$ with O₂.—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 Et₂O.

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, $\mu_B = 1.82$ per Cr, suggesting interaction between the Cr^{III} centres. Both homoand hetero-binuclear μ -oxo complexes have been observed⁴ 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)][BPh₄]₄.

The structure of the related oxo-bridged complex tetracation, $[Mo^{III}_2O(NCMe)_{10}]^{4+}$, has been confirmed by X-ray crystallography 5a as containing a linear Mo–O–Mo unit, while a peroxobridged complex *trans*-[{Co^{III}(Me₂SO)(dmpe)₂}₂(μ -O₂)]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 $Ba(CF_3SO_3)_2$ to a MeCN solution of (1) yields a light green precipitate, which on

[†] *trans*-Bis[1,2-bis(dimethylphosphino)ethane]chloro(ethylimido)chromium(1v) trifluoromethanesulphonate, *trans*-bis[1,2-bis(dimethylphosphino)ethane]bis(ethylideneamido)chromium(1v) bis(tetraphenylborate), and *trans*-bis[1,2-(dimethylphosphino)ethane]bis(ethylidyneammonium)chromium(0) bis(tetraphenylborate) respectively.

Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1987, Issue 1, pp. xvii—xx.



Scheme 1. (i) NaBPh₄, MeCN, O₂; (ii) NaBPh₄, MeCN; (iii) NaBPH₄, MeCN, reflux, 12 h; (iv) MeOH, Ba(CF₃SO₃)₂; (v) MeOH; (vi) MeCN, H₂ (40 atm), 100 °C; (vii) O₂



Figure 1. The structure of the cation [CrCl(NEt)(dmpe)₂]⁺

C(23)

C(2

Figure 2. The structure of the cation $[Cr(N=CHMe)_2(dmpe)_2]^{2+1}$

C(13)

PIT

Cr(1)

C(11)

recrystallization from MeCN, yields green crystals of the ethylimido complex *trans*-[CrCl(NEt)(dmpe)₂]CF₃SO₃ (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 ¹H n.m.r. spectrum, as a quartet [δ 3.30 p.p.m., J(H–H) = 7.3 Hz, CH₂] and a triplet [δ 1.00 p.p.m., J(H–H) = 7.3 Hz, CH₃]. 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 ¹H n.m.r. spectrum; the resonance of the H atom on carbon is obscured by the signal due to the BPh₄⁻ ions although observable as a broad quartet [δ 7.36 p.p.m., J(H-H) = 7.0 Hz] in the PF₆⁻ 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

Fe₃H(N=CHMe)(CO)₉⁸ was given as 1 325 cm⁻¹, a position intermediate between that expected for v(C-N) at 1 100 cm⁻¹ and v(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 Cr⁰, Cr–P distances were 2.278—2.343(3), for Cr¹ 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) 2.343(5) P(3)-Cr(1) 1.796(13) 2.355(5) C(33)-P(3) 1.834(12) P(4)-Cr(1) C(32)-P(2) 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)C(12)-P(1) 1.463(12) 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) 169.5(1) C(32)-P(3)-Cr(1) 83.2(2) P(4)-Cr(1)-P(2)117.5(5) P(4)-Cr(1)-P(3)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) Cl(1)-Cr(1)-P(4)102.8(7) C(33)-P(3)-C(31) 84.5(2) 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) 95.8(3) N(1)-Cr(1)-P(3)95.7(4) C(43)-P(4)-Cr(1)108.9(4) N(1)-Cr(1)-P(4)C(42)-P(4)-C(41) 102.4(6)N(1)-C(1)-Cl(1)178.2(3) 102.9(6) C(43)-P(4)-C(42)C(11)-P(1)-Cr(1)118.5(5) C(43)-P(4)-C(41)104.5(7) 175.3(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)C(13)-P(1)-Cr(1)C(13)-C(23)-P(2) 106.2(4) 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) 107.7(8) 108.5(8) C(21)-P(2)-Cr(1)122.9(5) C(43)-C(33)-P(3) C(22)-P(2)-Cr(1) 115.9(5)

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

Bond	lengths	(Å)
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	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)
Bc	ond 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}) Cr⁰ 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 ethylideneamido ligand is similar to that found for the analogous ligand in $Zr(\eta-C_5H_5)_2(Cl)(N=CHPh)$,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 studied¹¹ 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 n^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=N-CH₂CH₃ 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 CD₃CN 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).

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

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 $[Cr(H \cdot NCMe)_2(dmpe)_2]^{2+}$

can be detected from the reaction at $100 \,^{\circ}\text{C}/40$ 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 CF₃SO₃⁻ 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 BPh₄⁻ 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(0) complexes,¹ and in this case it is necessary to







MeOH



[(dmpe)₂(MeCN)Cr^{IV} NEt]²⁺

Scheme 2.

H transfer

$$[(dmpe)_{\circ}Cr^{IV}(N = CHMe)(NCMe)(OMe)]^{2*}$$

$$\beta$$
-H transfer $\sqrt{-CH_2O}$
[(dmpe)₂Cr^{IV}(N=CHMe)₂]²

Scheme 3.

hydrogenation of nitriles by H₂ 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 $Sc(\eta-C_5H_5)_2H$ system.⁷

ation been observed for the $Sc(\eta-C_5H_5)_2H$ system.⁷ Neither $[Cr(NCMe)_2(dmpe)_2]^{2+}$ nor $[CrCl(NCMe)_2(dmpe)_2]^+$ catalyses hydrogenation of MeCN even under pressure at elevated temperatures. Small quantities of NH₂Et 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 BPh₄⁻ peaks (Experimental section) there is a sharp singlet for co-ordinated MeCN at δ 2.01 p.p.m. Addition of *ca*. 0.1 cm³ of CD₃OD produces a broad singlet at δ 4.10 p.p.m. due to CD₃OH, the intensity of which is constant on further addition of CD₃OD. Integration of the peak gives a value *ca*. 1/12 that of the CH₃ 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(dimethylamino)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=N triple bonds (see below; cf. the well known mercurinium ions formed by electrophilic attacks of Hg^{2+} on C=C bonds¹⁸).

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 cannot 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=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 (CCl₄ reaction); further, the $Cr(P_2)_2$ unit is symmetrical by virtue of its crystallographic positioning, the ${}^{31}P-{}^{1}H$ 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 Cr¹ and Cr⁰ species failed. Similarly attempts to isolate Cr⁰(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 PMe₃, 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

		Analysis" (%)			
	Compound	С	H	N	
(1)	[CrCl(NCMe)(dmpe) ₂][BPh ₄]	59.8	7.3	1.8	
07		(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),]CF ₃ SO 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 Re	quired values in parentheses. ^b O, 0.70 (0	.75%).			

A similar reaction of hydrogen with $[Fe(MeCN)_2(dmpe)_2]$ -[BPh₄]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

Microanalyses were by Imperial College and Pascher (Bonn) Laboratories. Melting points were determined in sealed capillaries and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 683 grating spectrometer in Nujol mulls (4 000--200 cm⁻¹), or on a Perkin-Elmer 983 spectrometer as a KBr disc (4 000-600 cm⁻¹). N.m.r. spectra (in CD₃CN) were recorded on JEOL FX90Q or Bruker WM-250 spectrometers; δ in p.p.m. relative to SiMe₄ (¹H) or external 85% H₃PO₄ (³¹P). Magnetic suseptibilities were determined in the solid state at ambient temperatures on an Evans' balance.²⁰ Conductivities were determined in acetonitrile on a Data Scientific PTI-18 instrument. Electrochemical studies employed an E.G. and G PAR 174A polarographic analyser and NBuⁿ₄BF₄ (0.20 mol dm⁻³) in MeCN at room temperature with Pt working and auxiliary electrodes, and a saturated calomel reference electrode (against which ferrocene is oxidised at $E_{\star} = +0.65$ V).

High-pressure reactions were carried out in a Berghof autoclave. All manipulations were carried out under argon. Solvents were distilled and degassed before use. Analytical data are given in Table 4.

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 cm³), was added NaBPh₄ (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): $\Lambda_{\rm M} = 138$ ohm⁻¹ cm² 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 cm³), was added NaBPh₄ (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

Compound	(4)	(5)	(6)
Formula	$[CrCl(NEt)(dmpe)_2]CF_3SO_3 C_{11}H_{25}ClCrF_3O_3P_4S$	$[Cr(N=CHMe)_2(dmpe)_2][BPh_4]_2 C_{64}H_{80}B_2CrN_2P_4$	$[Cr(H \cdot NCMe)_2(dmpe)_2][BPh_4]_2$ $C_{64}H_{80}B_2CrN_2P_4$
Crystal data			04 00 2 2 4
М	579.861	1 074.86	1 074 86
a/Å	9.189 0(5)	12.247(5)	12.246(3)
b/Å	17.500(4)	13.109(6)	13.118(6)
c/Å	16.414(4)	12.102(9)	12.201(5)
α/°	90	116.27(5)	116.28(4)
β/°	90.60(1)	119.18(3)	118.98(3)
$\gamma/^{\circ}$	90	64.16(3)	62.97(3)
$U/Å^3$	2 639.35	1 459.82	1 463.68
System	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	PĨ	ΡĪ
$D_{\rm c}/{\rm g~cm^{-3}}$	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	$F_{\rm o}>4\sigma(F_{\rm o})$	$F_{\rm o} > 4\sigma(F_{\rm o})$	$F_{\rm o} > 4\sigma(F_{\rm o})$
Refinement			
No. of parameters	390	475	487
Weighting scheme	$1/[\sigma^2(F_{o}) + 0.000 \ 01F_{o}^2]$	$1/[\sigma^2(F_{\rm c}) + 0.0001F^2]$	$1/[\sigma^2(F_{\star})] + 0.000 01F^2$
Final $R = \Sigma F / \Sigma F_{-} $	0.0609	0.0543	0.0468
Final $R' = [\Sigma w (\Delta F)^2 / \Sigma w F_o^2]^{\frac{1}{2}}$	0.0557	0.0561	0.0438

Table 5. Crystal data	, intensity data,	collection parameters	and	details of	refinement
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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): $\Lambda_{M} = 230 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Both the above complex cations can be obtained as the corresponding trifluoromethanesulphonates or hexafluorophosphates by using either $Ba(CF_3SO_3)_2$ 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 cm³) of [Cr(NCMe)₂-(dmpe)₂][BPh₄]₂ (0.4 g, 0.37 mmol) for 5 min. The solution, which rapidly became dark red, was reduced to *ca*. 5 cm³ and the oil tritiated with Et₂O to leave a red microcystalline 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): $\Lambda_{M} = 523$ ohm⁻¹ cm² mol⁻¹ {*cf.* conductivity of [Mo₂O(MeCN)₁₀]-[BF₄]₄, $\Lambda_{M} = 552$ ohm⁻¹ cm² mol⁻¹}.

trans-Bis[1,2-bis(dimethylphosphino)ethane]chloro(ethyl-

imido)chromium(IV) Trifluoromethanesulphonate, (4).—To an MeCN (20 cm³) solution of [CrCl(NCMe)(dmpe)₂]BPh₄ (0.43 g, 0.58 mmol) was added a MeOH (20 cm³) solution of Ba(CF₃SO₃)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 cm³). The dried solid was extracted into acetonitrile (60 cm³) which was then reduced to *ca*. 15 cm³ 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, 790w, 740m, 705m, 630s, 520w, 340w cm⁻¹. ¹H N.m.r.: δ 3.30 [q, J(H–H) = 7.3 Hz, NCH₂CH₃], 1.50 (m, P–CH₃), 1.30 (m, PCH₂), 1.0 [t, J(H–H) = 7.3 Hz, NCH₂CH₃]. Conductivity (MeCN): $\Lambda_{\rm M}$ = 149 ohm⁻¹ cm² mol⁻¹.

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis(ethylidene-

amido)chromium(1V) Bis(tetraphenylborate), (5a).—Methanol (20 cm³) was added to a solution of [Cr(NCMe)₂(dmpe)₂]-[BPh₄]₂ (0.79 g, 0.74 mmol) in MeCN (20 cm³). 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 cm³); 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, 605s, 445w cm⁻¹. Conductivity (MeCN): $\Lambda_{\rm M} = 283$ ohm⁻¹ cm² 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 NaPF₆, 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. ¹H N.m.r.: 7.36 [br q, J(H-H) = 7.0 Hz, N=CHCH₃], 1.70 [br d, J(H-H) = 7.0 Hz, N=CHCH₃], 1.62 (m, PCH₃), 1.30 (m, PCH₂).

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis(ethylidyneammonium)chromium(0) Bis(tetraphenylborate), (6).—An MeCN(35 cm^3) solution of [Cr(NCMe)₂(dmpe)₂][BPh₄]₂ (0.36 g, 0.34 mmol) was pressurised with H₂ (40 atm) in an autoclave. The temperature was slowly raised to 100 °C and the solution

Atom	x	у	Z	Atom	x	у	Z
Cr(1)	159(1)	-329(1)	2 539(1)	C(31)	-2481(12)	-468(7)	4 157(7)
P(1)	1 866(2)	438(1)	1 850(1)	C(32)	-2 961(13)	-1495(7)	2 851(8)
P(2)	-1548(2)	474(1)	1 890(1)	C(33)	- 568(11)	-1 719(6)	3 930(7)
P(3)	-1536(3)	-971(1)	3 359(2)	C(41)	2 747(12)	-1763(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)	-1371(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)	-1480(7)	1 119(7)	O(1)	4 530(15)	2 613(9)	5 749(6)
C(2)	-22(20)	-2214(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)	-2979(12)	974(7)	2 439(7)	F(2)	5 208(13)	2 499(6)	3 594(5)
C(22)	-2515(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 6. Fractional atomic co-ordinates $(\times 10^4)$ for compound (4)

Table 7. Fractional atomic co-ordinates $(\times 10^4)$ for compound (5)

Atom	x	у	2	Atom	x	У	Ζ
Cr(1)	0*	0*	0*	C(41)	6 840(3)	-3319(3)	643(3)
P(1)	779(1)	1 666(1)	1 533(1)	C(42)	6 916(3)	-3056(3)	-316(3)
P(2)	2 233(1)	-1050(1)	727(1)	C(43)	6 263(3)	-3 474(3)	-1661(3)
N(1)	-186(3)	-271(3)	1 280(3)	C(44)	5 484(4)	-4 186(3)	-2119(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)	-2332(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)	-2754(3)	2 236(4)	C(61)	9 164(3)	-3 067(3)	2 610(3)
C(31)	7 390(3)	-3296(3)	3 108(3)	C(62)	9 804(3)	-3 738(3)	1 717(3)
C(32)	8 248(3)	-4323(3)	3 459(3)	C(63)	11 138(4)	-3 959(4)	2 081(4)
C(33)	8 098(4)	-4778(3)	4 196(4)	C(64)	11 893(3)	-3534(3)	3 376(4)
C(34)	7 056(4)	-4230(3)	4 600(4)	C(65)	11 313(4)	-2913(4)	4 299(4)
C(35)	6 168(4)	-3229(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 $(\times 10^4)$ for compound (6)

Atom	x	У	Ζ	Atom	x	у	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 para	meter.						

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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 °C yielded yellow crystals and further crops were obtained from the filtrate. Yield: 0.21 g, 60%; m.p. > 300 °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. ¹H N.m.r.: δ 7.25, 6.90 (m, BPh₄), 2.15 (m, PCH₂), 2.01 (s, NCCH₃), 1.50 (m, PCH₃). ³¹P-{¹H} 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 p K_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 ($\lambda = 0.71069$ 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 anisotropically, but with the O and F atoms in the $CF_3SO_3^-$ 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=CHCH₃ 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=CH₂CH₃ and N=CHCH₃ 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.

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