Reactions of Bis[1,2-bis(dimethylphosphino)ethane]-bis(dinitrogen)chromium(0) and -bis(carbonyl)chromium(0) with Acids and Oxidizing Agents. *X*-Ray Crystal Structures of *trans*-$Cr^{II}(O_2CCF_3)_2(dmpe)_2$, *trans*-$[Cr^{II}(NCR)_2(dmpe)_2][CF_3SO_3]_2$ (R = Me or Et), *trans*-$[Cr^{III}Cl_2(dmpe)_2]BPh_4 \cdot CH_2Cl_2$, *trans*-$[Cr^{I}(CO)_2(dmpe)_2]BPh_4$, and $[Cr^{0}H(CO)_2(dmpe)_2]BPh_4$†

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The interaction of *trans*-$Cr(N_2)_2(dmpe)_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane] with hydrogen chloride gives the eight-co-ordinate chromium(IV) species $CrH_2Cl_2(dmpe)_2$ whereas CF_3CO_2H gives *trans*-$Cr(O_2CCF_3)_2(dmpe)_2$. Protonation by CF_3SO_3H of *trans*-$CrL_2(dmpe)_2$ (L = N_2 or C_2H_4) in MeCN or EtCN gives the chromium(II) octahedral nitrile species *trans*-$[Cr(NCR)_2(dmpe)_2]^{2+}$ (R = Me or Et). The electron spin resonance spectra of the latter are attributed to trace impurities of a chromium(I) nitrile species; the main quintet is typical of Cr^{I} with four equivalent phosphorus ligands but hyperfine splitting is ascribed to interaction of CH_3 groups of MeCN and CH_2 groups of EtCN with the 17-electron chromium(I) atom. The interaction of *trans*-$Cr(N_2)_2(dmpe)_2$, *trans*-$CrCl_2(dmpe)_2$, or $CrH_4(dmpe)_2$ with CH_3I or I_2 in methanol leads to compounds of general formula *trans*-$[Cr^{III}X_2(dmpe)_2]X'$ (X = Cl or I, X' = I or BPh_4). The interaction of *cis*-$Cr(CO)_2(dmpe)_2$ with CF_3SO_3H followed by treatment with $NaBPh_4$ in MeOH leads to the seven-co-ordinate $[CrH(CO)_2(dmpe)_2]BPh_4$, while treatment of the dicarbonyl with one equivalent of $AgCF_3SO_3$ leads to *trans*-$[Cr(CO)_2(dmpe)_2]BPh_4$. *X*-Ray structures of the following compounds have been determined: *trans*-$Cr(O_2CCF_3)_2(dmpe)_2$, *trans*-$[Cr(NCR)_2(dmpe)_2][CF_3SO_3]_2$ (R = Me or Et), *trans*-$[CrCl_2(dmpe)_2]BPh_4 \cdot CH_2Cl_2$, $[CrH(CO)_2(dmpe)_2]BPh_4$, and *trans*-$[Cr(CO)_2(dmpe)_2]BPh_4$.

We have previously described the synthesis of 1,2-bis(dimethylphosphino)ethane (dmpe) complexes of chromium in oxidation states 0 to IV.[1,2] We now discuss the action of protic acids on *trans*-$CrL_2(dmpe)_2$ (L = N_2 or C_2H_4) and on *cis*-$Cr(CO)_2(dmpe)_2$. The reactions studied are summarized in the Scheme.

Results and Discussion

The protonation of dinitrogen compounds, especially those of Mo and W of the type *trans*-$M(N_2)_2(P-P)_2$ [P–P = $Ph_2PCH_2CH_2PPh_2$ (dppe) or $Et_2PCH_2CH_2PEt_2$ (depe)] has been much studied.[3–6] For some compounds, and depending on conditions such as the nature of the acid or solvent, (*a*) N–H or M–H bonds are formed, (*b*) the compound is oxidized with loss of hydrogen, or (*c*) eight-co-ordinate M^{IV} compounds are produced.

Hydrogen Chloride.—Interaction of *trans*-$Cr(N_2)_2(dmpe)_2$ with two equivalents of HCl in Et_2O at low temperature leads to the loss of N_2 and formation of a yellow solid that analyses closely for $CrH_2Cl_2(dmpe)_2$. Attempts to recrystallize the solid from a variety of solvents were unsuccessful, gas being evolved and *trans*-$CrCl_2(dmpe)_2$ being formed. The compound is presumably similar to $MoH_2Cl_2(P-P)_2$[5,6] and formed by a similar route. The only other eight-co-ordinate Cr^{IV} species, $CrH_4(dmpe)_2$, has been characterized by *X*-ray diffraction.[1] The i.r. spectrum of the chloride hydride has two Cr–H stretches at 2 075 and 1 980 cm^{-1} and the compound reacts with CCl_4 to give $CHCl_3$ essentially quantitatively corresponding to two hydrogen atoms as determined by n.m.r. study; the orange solid produced in this reaction is similar to that obtained in the reaction of $CrH_4(dmpe)_2$ with CCl_4 and appears to be $CrCl_4(dmpe)_2$.[1]

Trifluoroacetic Acid.—The interaction of the dinitrogen complex with CF_3CO_2H in thf leads to isolation of the first example of a chromium(II) carboxylate[7] with tertiary phosphine ligands, *trans*-$Cr(O_2CCF_3)_2(dmpe)_2$. The i.r. stretch at 1 680 cm^{-1} indicates a unidentate carboxylate as confirmed by *X*-ray crystallographic study (Figure 1); selected bond lengths and angles are in Table 1. Considerable difficulties were experienced in the refinement of this structure due to severe orientational disorder of the unidentate O_2CCF_3 groups in a channel along the O–Cr–O axis, formed by the methyl groups of the dmpe ligands. Accordingly, in Figure 1 the positions shown for the atoms of the trifluoroacetate are idealized, and were obtained using molecular modelling procedures[8] (see Experimental section). Although the chelating dmpe groups also show signs of

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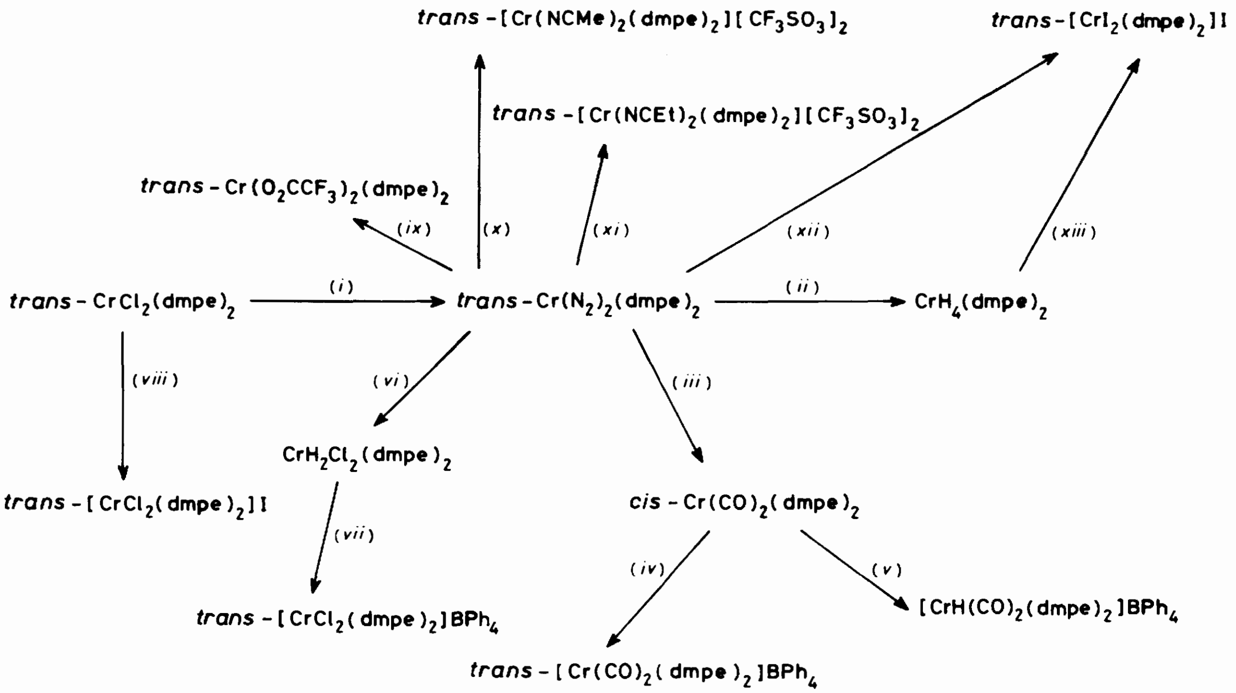
† *trans*-Bis[1,2-bis(dimethylphosphino)ethane]bis(trifluoroacetato)-chromium(II), *trans*-bis(acetonitrile)bis[1,2-bis(dimethylphosphino)-ethane]chromium(II) trifluoromethanesulphonate, *trans*-bis[1,2-bis(dimethylphosphino)ethane]bis(propionitrile)chromium(II) trifluoromethanesulphonate, *trans*-bis[1,2-bis(dimethylphosphino)ethane]dichlorochromium(III) tetraphenylborate–dichloromethane (1/1), *trans*-bis[1,2-bis(dimethylphosphino)ethane]dicarbonylchromium(I) tetraphenylborate, and bis[1,2-bis(dimethylphosphino)ethane]dicarbonylhydridochromium tetraphenylborate.

Supplementary data available (No. SUP 56503, 11 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. units employed: B.M. = 9.274×10^{-24} J T^{-1}, G = 10^{-4} T, p.s.i. = 6.7×10^3 N m^{-2}.



Scheme. Reaction of 1,2-bis(dimethylphosphino)ethane compounds of chromium: (*i*) Na–Hg, thf, N_2 (70 p.s.i.); (*ii*) *hν*, hexane, H_2 (100 p.s.i.); (*iii*) *hν*, hexane, CO (100 p.s.i.); (*iv*) $AgCF_3SO_3$, CH_3CN; $NaBPh_4$, MeOH; (*v*) CF_3SO_3H, CH_3CN; $NaBPh_4$, MeOH; (*vi*) HCl, Et_2O; (*vii*) CH_3CN; $NaBPh_4$, MeOH; (*viii*) MeI, *hν*, toluene; MeOH; (*ix*) CF_3CO_2H, thf; CH_2Cl_2; (*x*) CF_3SO_3H, MeCN; (*xi*) CF_3SO_3H, EtCN; (*xii*) I_2, MeOH or MeI, MeOH; (*xiii*) I_2, CH_2Cl_2 or MeI, toluene

Table 1. Bond lengths (Å) and angles (°) for $Cr(O_2CCF_3)_2(dmpe)_2$

O(1)–Cr(1)	2.085(31)	P(1)–Cr(1)	2.387(11)
C(11)–P(1)	1.711(49)	C(12)–P(1)	1.964(73)
C(13)–P(1)	1.784(55)		
P(1)–Cr(1)–O(1)	88.8(6)	P(1)–Cr(1)–P(1)	83.6(7)
P(1)–Cr(1)–P(1)	96.5(7)		
C(11)–P(1)–Cr(1)	124.0(18)	C(12)–P(1)–Cr(1)	111.9(23)
C(12)–P(1)–C(11)	94.8(34)	C(13)–P(1)–Cr(1)	117.9(27)

conformational disorder, with large thermal anisotropy in the carbon atoms, the phosphorus atoms refined well, and we consider the e.s.d.s assigned to the Cr–P bond lengths (Table 1) to be meaningful. Thus the values found for these distances show them to be consistent with, although slightly larger than, those found for other well defined $Cr^{II}(dmpe)_2$ complexes (see below).

The dinitrogen complex does not react with acetic, benzoic, or pivalic acids. In MeCN as solvent CF_3CO_2H also gives the carboxylate, in contrast to the protonation using CF_3SO_3H (see below). The formation of the chromium(II) complex is probably due to the ability of $CF_3CO_2^-$ to co-ordinate giving initially $CrH(O_2CCF_3)(dmpe)_2$ which then loses hydrogen on further protonation.

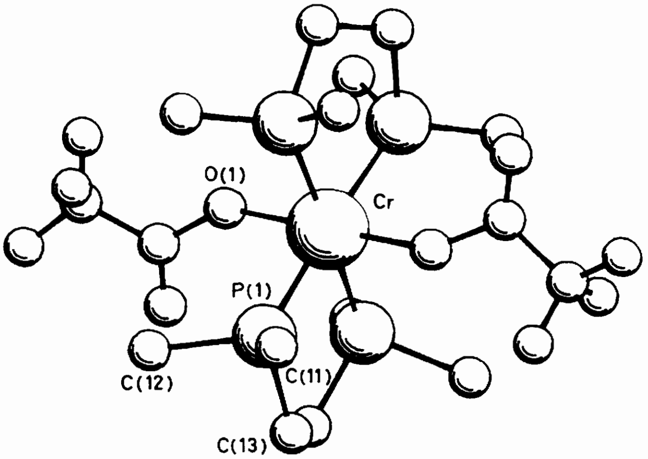


Figure 1. The molecular structure of *trans*-$Cr(O_2CCF_3)_2(dmpe)_2$

Trifluoromethanesulphonic Acid.—The interaction of *trans*-$Cr(N_2)_2(dmpe)_2$ in diethyl ether with CF_3SO_3H gives an immediate tan precipitate that is insoluble in organic solvents with which it does not react. Analyses indicate the approximate stoicheiometry $[Cr(NNH_2)(dmpe)_2][CF_3SO_3]_2$. Diprotonation of dinitrogen has evidently occurred with loss of one N_2 molecule; comparison of the i.r. spectrum with those of similar Mo and W compounds[3–6] suggests the presence of the N-NH_2 group as there are two broad bands at 3 242 and 3 080 cm^{-1} (NH_2) and a sharp band at 1 618 cm^{-1} (N–N stretch).

This solid readily dissolves in acetonitrile or propionitrile with evolution of dinitrogen and crystals of the alkyl nitrile complexes $[Cr(NCR)_2(dmpe)_2][CF_3SO_3]_2$ (R = Me or Et) can be isolated. These complexes are more readily obtained directly from either *trans*-$Cr(N_2)_2(dmpe)_2$ or *trans*-$Cr(C_2H_4)_2(dmpe)_2$* with two equivalents of CF_3SO_3H in

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* Interaction of CF_3CO_2H with *trans*-$Mo(C_2H_4)_2(dppe)_2$ in benzene gives $[MoH(C_2H_4)_2(dmpe)_2]^+$; J. W. Byrne, H. U. Blaser, and J. A. Osborn, *J. Am. Chem. Soc.*, 1975, **97**, 3871.

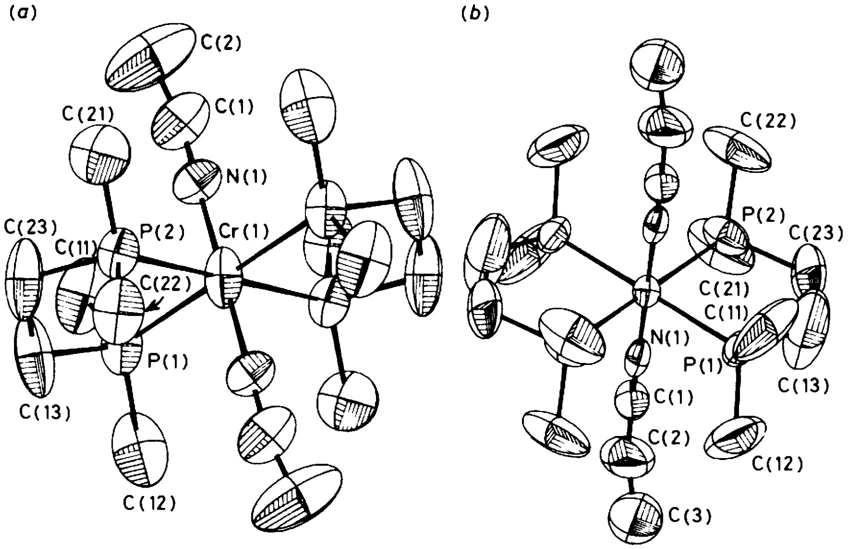


Figure 2. The structure of the cations (*a*) *trans*-[Cr(NCMe)$_2$(dmpe)$_2$]$^{2+}$, (*b*) *trans*-[Cr(NCEt)$_2$(dmpe)$_2$]$^{2+}$ in the trifluoromethanesulphonate salts

MeCN or EtCN at −30 °C. We have been unable to isolate comparable complexes from benzonitrile or pivalonitrile. The trifluoromethanesulphonates are 1:2 electrolytes in MeCN; the green solutions are very air sensitive, turning red.

The structures of the trifluoromethanesulphonate salts of the MeCN and EtCN complexes have been determined. Figure 2(*a*) and (*b*) show the structures of the cations whilst selected bond lengths and angles are given in Table 2. As with the previous structure, disorder and/or high thermal motion, this time involving the $CF_3SO_3^-$ anions in both structures, caused difficulties in achieving the desired levels of refinements, although fortunately the most important parts of the structures, the cations, are least affected.

The acetonitrile complex contains two crystallographically independent cations each lying on centres of symmetry; the one propionitrile cation is similarly positioned. Not unexpectedly, the geometry parameters around the chromium centres are very close, with the Cr–P distances again similar to those found for other Cr^{II}(dmpe)$_2$ species. These results will be discussed in more detail below. The Cr–N distances are slightly longer than those in *trans*-Cr(N$_2$)$_2$(dmpe)$_2$,[1] but shorter than the Cr–C distance in *trans*-CrMe$_2$(dmpe)$_2$[2] and the Cr–O distance in the trifluoroacetate above.

The band at 2 280 cm^{-1} in the i.r. spectrum is normal for co-ordinated nitriles, being slightly lower than the free nitrile as expected, the +2 charge on the metal centre having an additional lowering effect on the vibrational frequency.

The formation of the complexes by dissolution of the tan solid in the nitrile presumably involves initial co-ordination of one nitrile molecule, followed by loss of dihydrogen along with dinitrogen. The chromium(II) centre will finally co-ordinate a second nitrile molecule to complete the octahedral geometry. The direct synthesis from the bis(dinitrogen) or bis(ethylene) complexes in the nitrile could involve initial protonation of the metal, loss of N$_2$ or C$_2$H$_4$, co-ordination by one nitrile molecule, formation and loss of dihydrogen and final co-ordination of the second nitrile molecule. It is possible that there is an initial dissociation of N$_2$ or C$_2$H$_4$ (L): equation (1). Such dissociation

$$trans\text{-CrL}_2(\text{dmpe})_2 + \text{RCN} \rightleftharpoons trans\text{-CrL(NCR)(dmpe)}_2 + \text{L} \quad (1)$$

occurs in nitrile substitution reactions of *trans*-Mo(N$_2$)$_2$(dppe)$_2$.[9] However, dissociation is unlikely as dinitrogen- or ethylene-chromium complexes do not undergo substitution even on refluxing in MeCN or EtCN. On u.v. irradiation in MeCN, *trans*-Cr(N$_2$)$_2$(dmpe)$_2$ produces a brown solid that may be polymeric with HCrCH$_2$CN groups since 'activation' of CH$_3$CN to give H–M–CH$_2$CN moieties has been shown to occur in the reaction of HM(C$_{10}$H$_7$)(dmpe)$_2$ (M = Fe, Ru, or Os; C$_{10}$H$_7$ = 2-naphthyl) with CH$_3$CN, CH$_3$NO$_2$, *etc.*[10]

Both nitrile compounds have magnetic moments corresponding to two unpaired electrons in the solid state. The somewhat higher values (3.3 and 3.1 B.M.) than those for CrX$_2$(dmpe)$_2$ (X = Cl or Me), 2.8 B.M.,[2] is probably due to there always being a small amount of a Cr^I species present (see below). Since the Cr^{II} species with $S = 1$ are e.s.r. silent, the e.s.r. spectra found for the complexes are best attributed to this Cr^I component.

Electron Spin Resonance Spectra of Nitrile Complexes.—In frozen nitrile solution both the nitrile compounds show e.s.r. spectra with sharp binomial quintets, Figure 3 and Table 3, that are characteristic for the single electron on chromium(I) complexes split by four equivalent phosphorus atoms. Such spectra have been observed[11] for *trans*-[Cr(CO)$_2$(dmpe)$_2$]$^+$ and for a chromium(I) species formed when solutions of [CrH(CO)$_2$(dppm)$_2$]$^+$ were allowed to stand.[12] Single-crystal spectra of the nitrile complexes at room temperature also show the binomial quintets, and unusually, the satellites[13] due to ^{53}Cr ($I = \frac{3}{2}$, 10%) are also observed with $A_{av.}$(Cr) = 39 G. In nitrile solution at room temperature in a flat cell additional hyperfine structure is apparent (Figure 3). For the MeCN compound this is a quintet of quartets and for the EtCN compound a quintet of triplets. In the MeCN case, this hyperfine splitting, A_{iso}(H) = 6 G, is clearly due to the three hydrogen atoms of a methyl group on MeCN since it disappears when the spectrum of [Cr(NCMe)$_2$(dmpe)$_2$]$^{2+}$ is obtained in CD$_3$CN. Note that there is no exchange of CD$_3$CN with the MeCN in *trans*-[Cr(NCMe)$_2$(dmpe)$_2$]$^{2+}$ which can be crystallized from CD$_3$CN. For the EtCN compound, the hyperfine splitting can be ascribed to the hydrogens of the CH$_2$ group.

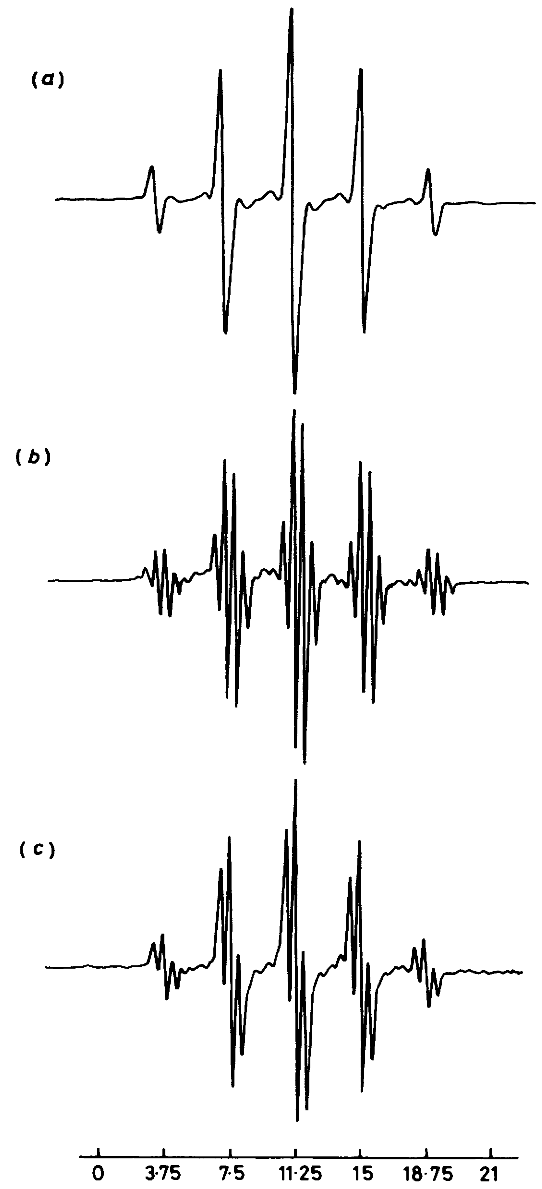


Figure 3. Electron spin resonance spectra of chromium(I) minor component in *trans*-$[Cr(NCR)_2(dmpe)_2][CF_3SO_3]_2$ (R = Me or Et). (*a*) R = Me in CD_3CN, (*b*) R = Me in MeCN, (*c*) R = Et in EtCN MeCN: quintet, $g = 2.0062$ $A_{iso}(P) = 37.5$ G; hyperfine $A_{iso}(H) = 6.0$ G. EtCN: quintet, $g = 2.0025$, $A_{iso}(P) = 37.5$ G; hyperfine $A_{iso}(H) = 6.0$ G

Since the Cr^I species are always present and co-crystallize with the nitrile complexes, the best candidates appear to be *trans*-$[Cr(NCR)_n(dmpe)_2]^+$ (n = 1 or 2, R = Me or Et). Such cations could well be present in small amounts, formed by competitive oxidation of *trans*-$Cr(L)_2(dmpe)_2$ (L = N_2 or C_2H_4) in nitrile solutions by CF_3SO_3H. Protonation using either CF_3SO_3D or CF_3SO_3H in acetonitrile produces the same hyperfine splitting showing that it is the nitrile that is responsible for the hyperfine interaction with the 17-electron chromium(I) centre.

Table 2. Selected bond lengths and angles for $[Cr(NCMe)_2(dmpe)_2][CF_3SO_3]_2$ and $[Cr(NCEt)_2(dmpe)_2][CF_3SO_2]_2$

$[Cr(NCMe)_2(dmpe)_2][CF_3SO_3]_2$			
P(1)–Cr(1)	2.364(3)	P(2)–Cr(1)	2.378(3)
N(1)–Cr(1)	1.906(6)	P(3)–Cr(2)	2.392(3)
P(4)–Cr(2)	2.381(3)	N(2)–Cr(2)	1.994(6)
C(11)–P(1)	1.810(9)	C(12)–P(1)	1.803(9)
C(13)–P(1)	1.820(9)	C(21)–P(2)	1.808(9)
C(22)–P(2)	1.779(9)	C(23)–P(2)	1.831(8)
C(31)–P(3)	1.814(9)	C(32)–P(3)	1.813(9)
C(33)–P(3)	1.827(8)	C(41)–P(4)	1.813(8)
C(42)–P(4)	1.820(9)	C(43)–P(4)	1.826(9)
C(1)–N(1)	1.220(8)	C(3)–N(2)	1.168(7)
C(2)–C(1)	1.232(12)	C(4)–C(3)	1.404(9)
C(23)–C(13)	1.470(11)	C(43)–C(33)	1.494(10)
$[Cr(NCEt)_2(dmpe)_2][CF_3SO_3]_2$			
P(1)–Cr(1)	2.359(4)	P(2)–Cr(1)	2.369(4)
N(1)–Cr(1)	1.938(8)	C(11)–P(1)	1.759(13)
C(12)–P(1)	1.822(16)	C(13)–P(1)	1.679(14)
C(21)–P(2)	1.776(12)	C(22)–P(2)	1.803(13)
C(23)–P(2)	1.903(12)	C(23)–C(13)	1.362(14)
C(1)–N(1)	1.212(9)	C(2)–C(1)	1.410(14)
C(3)–C(2)	1.330(18)		
$[Cr(NCMe)_2(dmpe)_2][CF_3SO_3]_2$			
P(2)–Cr(1)–P(1)	82.9(2)	N(1)–Cr(1)–P(1)	90.3(3)
N(1)–Cr(1)–P(2)	89.6(3)		
P(4)–Cr(2)–P(3)	82.1(2)	N(2)–Cr(2)–P(3)	90.0(2)
N(2)–Cr(2)–P(4)	91.1(2)		
C(11)–P(1)–Cr(1)	115.9(4)	C(12)–P(1)–Cr(1)	120.1(4)
C(12)–P(1)–C(11)	103.8(5)	C(13)–P(1)–Cr(1)	108.3(3)
C(13)–P(1)–C(11)	103.1(5)	C(13)–P(1)–C(12)	103.7(5)
C(21)–P(2)–Cr(1)	121.1(3)	C(22)–P(2)–Cr(1)	117.8(3)
C(22)–P(2)–C(21)	102.9(5)	C(23)–P(2)–Cr(1)	107.2(3)
C(23)–P(2)–C(21)	102.2(5)	C(23)–P(2)–C(22)	103.3(4)
C(31)–P(3)–Cr(2)	115.9(3)	C(32)–P(3)–Cr(2)	122.0(4)
C(32)–P(3)–C(31)	103.0(4)	C(33)–P(3)–Cr(2)	108.6(3)
C(33)–P(3)–C(31)	102.5(4)	C(33)–P(3)–C(32)	102.5(4)
C(41)–P(4)–Cr(2)	116.4(3)	C(42)–P(4)–Cr(2)	120.6(3)
C(42)–P(4)–C(41)	103.0(4)	C(43)–P(4)–Cr(2)	107.8(3)
C(43)–P(4)–C(41)	103.9(4)	C(43)–P(4)–C(42)	103.3(5)
C(1)–N(1)–Cr(1)	177.3(6)	C(3)–N(2)–Cr(2)	177.1(4)
C(2)–C(1)–N(1)	161.4(11)	C(4)–C(3)–N(2)	174.9(7)
C(23)–C(13)–P(1)	111.5(6)	C(13)–C(23)–P(2)	111.6(6)
C(43)–C(33)–P(3)	110.0(5)	C(33)–C(43)–P(4)	111.2(6)
$[Cr(NCEt)_2(dmpe)_2][CF_3SO_3]_2$			
P(2)–Cr(1)–P(1)	83.7(2)	N(1)–Cr(1)–P(1)	89.0(3)
N(1)–Cr(1)–P(2)	90.1(3)		
C(11)–P(1)–Cr(1)	117.4(4)	C(12)–P(1)–Cr(1)	117.9(5)
C(12)–P(1)–C(11)	100.7(8)	C(13)–P(1)–Cr(1)	109.5(5)
C(13)–P(1)–C(11)	102.5(9)	C(13)–P(1)–C(12)	107.3(9)
C(21)–P(2)–Cr(1)	117.3(5)	C(22)–P(2)–Cr(1)	119.5(5)
C(22)–P(2)–C(21)	103.6(6)	C(23)–P(2)–Cr(1)	105.3(4)
C(23)–P(2)–C(21)	104.2(7)	C(23)–P(2)–C(22)	105.2(7)
C(23)–C(13)–P(1)	122.0(11)	C(13)–C(23)–P(2)	116.2(9)
C(1)–N(1)–Cr(1)	179.0(6)	C(2)–C(1)–N(1)	169.7(10)
C(3)–C(2)–C(1)	126.5(15)		

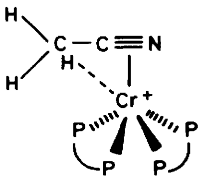
It seems unlikely that the CH_3 or CH_2 group on a normal N-bonded nitrile would be sufficiently close to the metal atom for interaction to occur. This problem has been considered for the bonding of acetonitrile on flat, stepped and stepped, kinked metal surfaces,[14] but the models proposed for close approach of the H atoms to the surface, facilitating C–H bond cleavage, seem inappropriate in a mononuclear species.

There is no need for more than one bound nitrile to be

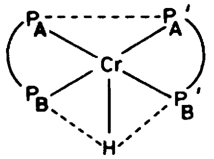
Table 3. Electron spin resonance spectra of the chromium(I) minor constituent in chromium nitrile and carbonyl complexes in MeCN at 90 K

Complex	Quintet *g* value (Cr^I)	$A_{iso}(P)/G$	$A_{iso}(H)/G$
$[Cr(NCMe)_2(dmpe)_2]^{2+\,a}$	2.0062	37.5	6.0
$[Cr(NCEt)_2(dmpe)_2]^{2+\,a}$	2.0025	37.5	6.0
$[CrH(CO)_2(dmpe)_2]^{+\,b}$	2.0166	37.5	

[a] $CF_3SO_3^-$ salt. [b] BPh_4^- salt; the spectra of the paramagnetic minor component and that of *trans*-$[Cr(CO)_2(dmpe)_2]^+$ are identical.



(1)



(2)

involved if dissociation occurs to give a five-co-ordinate Cr^I species, equation (2), in which case the interacting nitrile could

$$trans\text{-}[Cr(NCMe)_2(dmpe)_2]^+ \rightleftharpoons [Cr(NCMe)(dmpe)_2]^+ + MeCN \quad (2)$$

be π-bonded as in (**1**). The disappearance of the hyperfine splitting in CD_3CN noted above confirms this dissociation. Complexes with η^2-RCN are known,[15] *e.g.* $M(\eta^5\text{-}C_5H_5)_2(NCMe)$ (M = Mo or W). Free rotation about the C–C bond would then allow interaction between the metal and CH_3 or CH_2 groups of MeCN and EtCN respectively.

Interactions of C–H bonds on ligands with metal centres including electron deficient ones is a well known phenomenon [2,16] and can sometimes be detected by low C–H stretching frequencies in the i.r. spectra but in the present case the concentration is too low for detection. As far as we are aware, evidence for M–H–C interaction from e.s.r. spectra has not previously been observed.

Attempts to isolate the Cr^I species have been unsuccessful. Oxidation of *trans*-$Cr(N_2)_2(dmpe)_2$ in MeCN by $AgCF_3SO_3$ led to decomposition, while oxidation by I_2 in MeOH gave *trans*-$[CrI_2(dmpe)_2]I$. Careful oxidation of *trans*-$Cr(N_2)_2(dmpe)_2$ in MeCN with air gave a solution showing an e.s.r. spectrum similar to that in Figure 3, but further oxidation readily occurred. Cyclic voltametric study of the *trans*-$[Cr(NCMe)_2(dmpe)_2]^{2+}$ ion in MeCN shows a reversible one-electron reduction, but attempts to isolate a reduced species showing the Cr^I e.s.r. spectrum by controlled potential electrolytic reduction or chemically, using $Co(\eta^5\text{-}C_5H_5)_2$, were unsuccessful.

Interaction of *trans*-$Cr(N_2)_2(dmpe)_2$, *trans*-$CrCl_2(dmpe)_2$, *and* $CrH_4(dmpe)_2$ *with* CH_3I *or* I_2 *in Polar Solvents.*—The interaction of *trans*-$Cr(N_2)_2(dmpe)_2$ with CH_3I in hexane under irradiation gives a yellow precipitate which, on crystallization from methanol, gives the green salt *trans*-$[CrI_2(dmpe)_2]I$, a 1 : 1 electrolyte in methanol. The magnetic susceptibility (3.83 B.M.) indicates a d^3 high-spin Cr^{III} system; the e.s.r. spectrum has a broad feature at $g = 3.56$ and a better defined peak at $g = 2.03$ characteristic of octahedral Cr^{III}. This salt is also produced both by the interaction of $CrH_4(dmpe)_2$ with an excess of methyl iodide in a hexane–toluene mixture and by the action of iodine on the dinitrogen complex in methanol. In the former reaction methyl iodide may react with the tetrahydride generating methane and $CrI_4(dmpe)_2$ which loses iodine to give *trans*-$[CrI_2(dmpe)_2]I$.

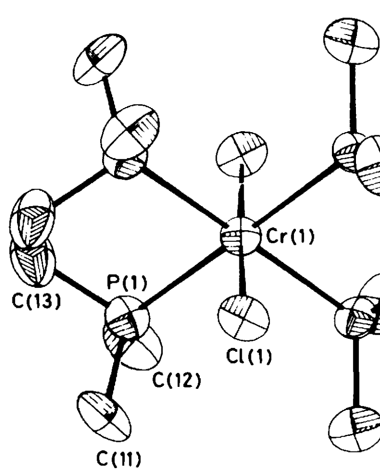


Figure 4. The structure of the cation in *trans*-$[CrCl_2(dmpe)_2]BPh_4$

A similar complex, *trans*-$[CrCl_2(dmpe)_2]I$ is obtained from the interaction of CH_3I and *trans*-$CrCl_2(dmpe)_2$ and the corresponding tetraphenylborate is obtained from $CrH_2Cl_2(dmpe)_2$ by dissolution in MeCN followed by removal of solvent and addition of methanolic $NaBPh_4$. Crystals of the tetraphenylborate salt were suitable for an *X*-ray study, which confirms the *trans* structure.

A diagram of the $[CrCl_2(dmpe)_2]^+$ ion, which has a two-fold axis of symmetry perpendicular to the Cl–Cr–Cl axis and relating the two dmpe ligands, is shown in Figure 4; selected bond lengths and angles are given in Table 4. The geometry parameters for this species are discussed below.

The structure of a related compound, *trans*-$[WCl_2(dppe)_2]BF_4\cdot0.33CH_2Cl_2$ has recently been reported,[17a] and *trans*-$CrI_2(dmpe)_2$ has also been made by interaction of MeI and $Cr(dmpe)_3$.[17b]

Interaction of *cis*-$Cr(CO)_2(dmpe)_2$ *with* CF_3SO_3H.—Although n.m.r. evidence has been obtained[11,12] for the protonation of *cis*-$Cr(CO)_2(dppm)_2$ to give $[CrH(CO)_2(dppm)_2]^+$, similar to known Mo and W species, the complex was not isolated, nor is the dmpe analogue fully characterised.

Treatment of *cis*-$Cr(CO)_2(dmpe)_2$[1,11,18] with two equivalents of CF_3SO_3H in MeCN gives a yellow solution from which crystals of $[CrH(CO)_2(dmpe)_2]CF_3SO_3$ can be obtained.* As *X*-ray quality crystals could not be obtained, the anion was exchanged for BPh_4^- which led to pale green crystals from MeCN. The n.m.r. spectra are discussed later.

The compound also shows an e.s.r. spectrum but this is due to trace amounts of *trans*-$[Cr(CO)_2(dmpe)_2]^+$ impurity (see below); in the solid state the compound appears diamagnetic by bulk susceptibility measurement.

It may be noted that protonation of *cis*-$Mo(CO)_2(dppe)_2$ with HBF_4 or H_2SO_4[6a] gave the cation *trans*-$[Mo(CO)_2(dppe)_2]^+$ and it was suggested that the proton first attacked the metal centre finally giving an oxidized species with the release of hydrogen; no metal hydride could be detected by n.m.r.

As noted earlier, e.s.r. spectra for Cr^I are well established as a binomial quintet centred around $g = 2.00$ in *trans*-$[Cr(CO)_2(dppm)_2]^+$ and in aged solutions of [CrH-

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* Although this ion could be formulated as a Cr^{II} species we prefer to consider it as Cr^0 by comparison with the protonation of, *e.g.*, NH_3 to give NH_4^+ or of $ReH(\eta^5\text{-}C_5H_5)_2$ to give $[ReH_2(\eta^5\text{-}C_5H_5)_2]^+$ (J. M. Birmingham and G. Wilkinson, *J. Am. Chem. Soc.*, 1955, **77**, 3421).

Table 4. Selected bond lengths (Å) and angles (°) for $[CrCl_2(dmpe)_2]BPh_4$

Cl(1)–Cr(1)	2.293(4)	P(1)–Cr(1)	2.443(5)
P(2)–Cr(1)	2.447(5)		
C(11)–P(1)	1.800(13)	C(12)–P(1)	1.809(11)
C(13)–P(1)	1.815(14)	C(21)–P(2)	1.819(12)
C(22)–P(2)	1.807(13)	C(23)–P(2)	1.830(12)
C(13)–C(13a)*	1.538(23)	C(23)–C(23a)*	1.484(20)
P(1)–Cr(1)–Cl(1)	90.8(2)	P(2)–Cr(1)–Cl(1)	88.6(2)
P(2)–Cr(1)–P(1)	97.4(2)	P(1)–Cr(1)–P(1)	82.2(2)
P(2)–Cr(2)–P(1)	83.0(2)		
C(11)–P(1)–Cr(1)	117.8(5)	C(12)–P(1)–Cr(1)	117.9(5)
C(12)–P(1)–C(11)	103.4(7)	C(13)–P(1)–Cr(1)	106.3(5)
C(13)–P(1)–C(11)	104.9(8)	C(13)–P(1)–C(12)	105.0(7)
C(21)–P(2)–Cr(1)	117.5(5)	C(22)–P(2)–Cr(1)	119.3(5)
C(22)–P(2)–C(21)	104.0(7)	C(23)–P(2)–Cr(1)	104.8(4)
C(23)–P(2)–C(21)	104.3(7)	C(23)–P(2)–C(22)	105.4(7)

* Symmetry operation relating designated atoms to reference atoms at *x,y,z* is 1.0 − *x,y*, 1.5 − *z*.

$(CO)_2(dppm)_2]^+$.[11,12] For $[CrH(CO)_2(dmpe)_2]^+$ a similar spectrum is always observed even when light was excluded and hence the Cr^I impurity probably arises from oxidation competitive with protonation (*cf.* ref. 6*a*), equation (3).

$$2\,cis\text{-}Cr(CO)_2(dmpe)_2 + 2\,H^+ \longrightarrow 2\,trans\text{-}[Cr(CO)_2(dmpe)_2]^+ + H_2 \quad (3)$$

Integration of the e.s.r. signal of the tetraphenylborate in MeCN at room temperature against a standard Cu^{2+} ethylenediaminetetra-acetic acid solution indicated that the Cr^I component was in *ca.* 3% concentration.

The *trans*-$[Cr(CO)_2(dmpe)_2]^+$ ion was first obtained by $AgBF_4$ oxidation of *cis*-$Cr(CO)_2(dmpe)_2$ and characterized by i.r. and e.s.r. spectra, but not isolated;[11] *trans*-$[Cr(CO)_2(dppm)_2]^+$ was isolated as I_3^- and PF_6^- salts.[11,12] Oxidation of *cis*-$Cr(CO)_2(dmpe)_2$ by $AgCF_3SO_3$ in MeCN and conversion of the triflate into the BPh_4^- salt leads to large orange crystals of *trans*-$[Cr(CO)_2(dmpe)_2]BPh_4$, whose structure has been determined as discussed later.

The *cis–trans* stereochemical change in several $M(CO)_2(P–P)_2$ complexes has been associated with electron-transfer reactions, either chemical or electrochemical.[19] For oxidations using Ag^+, an equally satisfactory alternative would be initial electrophilic attack (*cf.* that of H^+) to give a non-rigid seven-co-ordinate species, *e.g.* $[CrAg(CO)_2(dmpe)_2]^+$, which on elimination of Ag^0 would lead to isomerization. Electrophilic attacks by $[Cu(MeCN)_4]^+$, NO^+, or I_2 are equally feasible especially for complexes where the metal atom is more electron-rich due to greater basicity of the phosphine ligands. It may be noted also that attack on $[CrH(CO)_2(dmpe)_2]^+$ by LiMe in thf gives CH_4, and the *cis*-dicarbonyl complex.

The *X*-ray structure analysis of $[CrH(CO)_2(dmpe)_2]BPh_4$ (Figure 5) showed the cation to have an almost octahedral structure with *trans*-OC–Cr–CO and with, at first sight, no clear-cut indication as to the site of the metal-bound hydrogen. The possible location of the hydrogen in seven-co-ordinate species of the type $MH(CO)_2(P–P)_2$ has been much discussed on the basis of detailed n.m.r. studies (see below), but *X*-ray data are sparse.

Meakin *et al.*[20] attempted to determine the structure of $TaH(CO)_2(dmpe)_2$, but serious disorder reduced the accuracy of the determinations. Nevertheless, there were strong indications to support a capped octahedral structure; in particular, the OC–Ta–CO unit appeared to be significantly bent, with an angle at Ta of 163°. Hanckel and Darensbourg[21] recently reported the structure determination of the complex $[MoH(CO)_2(dppe)_2]AlCl_4$ [dppe = 1,2-bis(diphenylphosphino)ethane]. In this structure, the $Mo(CO)_2P_4$ unit in the cation is considerably distorted, with clear indications that the hydrogen, which was not directly located, lay at one corner of an equatorial girdle of a pentagonal bipyramidal structure. Thus the two dppe chelates are compressed together to take up two sides of a pentagon, leading to non-chelating P–Mo–P angles of 89.6 and 114.6°, the hydrogen presumably being located in the large P–Mo–P angle. Additionally, the two CO groups are slightly tilted over towards the hydrogen side, which is presumably less crowded, giving a C–Mo–C angle of 175.4(3)°. One final very significant structural feature is that the Mo–P bond lengths lie in two groups: 2.466(1) and 2.468 (2) Å, *cis*, and 2.574(2) and 2.583(2) Å, *trans*, to the hydrogen.

For $[CrH(CO)_2(dmpe)_2]^+$ the OC–Cr–CO unit is almost linear with an angle of 177.4(2)°. There also appears to be some swinging round of the two chelating dmpe ligands to give different non-chelate P–Cr–P angles, 94.0(2) and 105.7(2)°, clearly a significant difference, but much smaller than in the Mo complex discussed above. If the hydride is truly located in the equatorial plane, then the much smaller deformation in this Cr complex could relate to the shorter Cr–P bonds and the difficulty in squeezing together the non-connected phosphorus atoms, although, of course, much closer approach does occur *within* the chelate ring. One further point is that if the hydride is localized in the equatorial girdle then it does not seem to be causing any significant structural *trans* influence, since the Cr–P distances are all quite similar (Table 5). The indications are, therefore, that in this chromium complex, the hydride does not seem to be exerting the usual expected stereochemical activity.

The isolation of BPh_4^- salts of both $[CrH(CO)_2(dmpe)_2]^+$ and $[Cr(CO)_2(dmpe)_2]^+$ allows a unique comparison to be made, the only difference between them being the presence of one hydrogen atom. The two compounds are crystallographically isostructural and the cation $[Cr(CO)_2(dmpe)_2]^+$ has essentially the same structure, Figure 5, as the hydride species. However, as can be seen from Table 5 and from the cell dimensions in Table 7, there are significant differences between the two structures; there is no possibility that the crystal of $[CrH(CO)_2(dmpe)_2]BPh_4$ examined could have accidentally been one of $[Cr(CO)_2(dmpe)_2]BPh_4$ present as impurity. The most noticeable differences are the basic symmetry of the equatorial girdle, in which the two non-chelating P–Cr–P angles are now equal, at *ca.* 96°, and the Cr–P bond lengths, which are significantly longer, by *ca.* 0.030(3) Å in $[Cr(CO)_2(dmpe)_2]BPh_4$.

In discussing the relationship between the geometry parameters of these two structures, it is convenient now to consider also the relationship between the structures of the compounds of the general type $CrX_2(dmpe)_2$ described in this and previous papers.[1,2] For convenience we have collected together (Table 6) the Cr–P and Cr–X distances, and other relevant data.

The variation in Cr–P distances is particularly revealing. To a first degree of approximation (with just two exceptions: the hydrides) this parameter changes systematically with oxidation state of chromium but in the opposite sense to that expected for normal σ-bonding; that is, the bond length *increases* with *increasing* oxidation state whereas we would normally expect a decrease. This variation we believe to be in part a consequence of $Cr \longrightarrow P$ π-back bonding, with the d^6 Cr^0 centre showing significant shortening in its bonds to the phosphorus atoms. Some idea of the effect of this interaction is gained by comparing the change in Cr–Cl bond lengths in the Cr^{II} and Cr^{III} species, where the difference is *ca.* −0.055 Å, virtually identical to the value of 0.05 Å often used as the expected difference between

Table 5. Selected bond lengths (Å) and angles (°) for $[CrH(CO)_2(dmpe)_2]BPh_4$ and $[Cr(CO)_2(dmpe)_2]BPh_4$

$[CrH(CO)_2(dmpe)_2]BPh_4$

P(1)–Cr(1)	2.332(4)	C(31)–P(3)	1.837(9)	P(2)–Cr(1)	2.332(4)	C(32)–P(3)	1.780(10)
P(3)–Cr(1)	2.331(4)	C(33)–P(3)	1.830(8)	P(4)–Cr(1)	2.364(4)	C(41)–P(4)	1.811(10)
C(1)–Cr(1)	1.857(8)	C(42)–P(4)	1.797(9)	C(2)–Cr(1)	1.875(8)	C(43)–P(4)	1.806(8)
		C(23)–C(13)	1.480(10)			C(43)–C(33)	1.392(10)
C(11)–P(1)	1.798(9)			C(12)–P(1)	1.825(9)		
C(13)–P(1)	1.822(9)	C(1)–O(1)	1.104(8)	C(21)–P(2)	1.792(11)	C(2)–O(2)	1.115(8)
C(22)–P(2)	1.834(12)			C(23)–P(2)	1.818(10)		

$[Cr(CO)_2(dmpe)_2]BPh_4$

P(1)–Cr(1)	2.379(3)	C(22)–P(2)	1.833(9)	P(2)–Cr(1)	2.361(3)	C(23)–P(2)	1.833(7)
P(3)–Cr(1)	2.360(3)	C(31)–P(3)	1.838(8)	P(4)–Cr(1)	2.366(3)	C(32)–P(3)	1.792(8)
C(1)–Cr(1)	1.842(7)	C(33)–P(3)	1.819(7)	C(2)–Cr(1)	1.877(7)	C(41)–P(4)	1.819(8)
		C(42)–P(4)	1.812(7)			C(43)–P(4)	1.809(7)
C(11)–P(1)	1.818(7)	C(1)–O(1)	1.155(7)	C(12)–P(1)	1.820(6)	C(2)–O(2)	1.136(6)
C(13)–P(1)	1.831(7)	C(23)–C(13)	1.528(9)	C(21)–P(2)	1.804(8)	C(43)–C(33)	1.331(9)

$[CrH(CO)_2(dmpe)_2]BPh_4$

P(2)–Cr(1)–P(1)	80.1(2)	C(11)–P(1)–Cr(1)	120.8(4)	P(3)–Cr(1)–P(1)	105.7(2)	C(12)–P(1)–Cr(1)	115.9(4)
P(3)–Cr(1)–P(2)	174.3(1)	C(12)–P(1)–Cr(11)	102.3(5)	P(4)–Cr(1)–P(1)	173.6(1)	C(13)–P(1)–Cr(1)	111.7(3)
P(4)–Cr(1)–P(2)	94.0(2)	C(13)–P(1)–Cr(11)	102.4(4)	P(4)–Cr(1)–P(3)	80.3(2)	C(13)–P(1)–C(12)	101.1(5)
C(1)–Cr(1)–P(1)	92.0(3)	C(21)–P(2)–Cr(1)	120.9(4)	C(1)–Cr(1)–P(2)	88.6(3)	C(22)–P(2)–Cr(1)	117.4(5)
C(1)–Cr(1)–P(3)	90.8(3)	C(22)–P(2)–Cr(21)	103.1(6)	C(1)–Cr(1)–P(4)	90.3(3)	C(23)–P(2)–Cr(1)	108.7(4)
C(2)–Cr(1)–P(1)	90.6(3)	C(23)–P(2)–Cr(21)	102.2(6)	C(2)–Cr(1)–P(2)	91.9(3)	C(23)–P(2)–C(22)	102.0(6)
C(2)–Cr(1)–P(3)	88.5(3)	C(31)–P(3)–Cr(1)	117.1(4)	C(2)–Cr(1)–P(4)	87.2(3)	C(32)–P(3)–Cr(1)	119.8(4)
C(2)–Cr(1)–C(1)	177.4(2)	C(32)–P(3)–Cr(31)	102.2(5)			C(33)–P(3)–Cr(1)	111.6(3)
		C(33)–P(3)–Cr(31)	100.9(5)	O(2)–C(2)–Cr(1)	177.0(6)	C(33)–P(3)–C(32)	102.8(5)
O(1)–C(1)–Cr(1)	179.1(7)	C(41)–P(4)–Cr(1)	119.8(4)			C(42)–P(4)–Cr(1)	118.5(4)
		C(42)–P(4)–Cr(41)	103.2(5)	C(13)–C(23)–P(2)	108.1(6)	C(43)–P(4)–Cr(1)	110.0(3)
C(23)–C(13)–P(1)	107.7(5)	C(43)–P(4)–Cr(41)	97.6(5)	C(33)–C(43)–P(4)	113.3(6)	C(43)–P(4)–C(42)	105.0(5)
C(43)–C(33)–P(3)	114.1(6)						

$[Cr(CO)_2(dmpe)_2]BPh_4$

P(2)–Cr(1)–P(1)	83.4(.5)	C(11)–P(1)–Cr(1)	122.5(3)	P(3)–Cr(1)–P(1)	95.9(.5)	C(12)–P(1)–Cr(1)	117.9(3)
P(3)–Cr(1)–P(2)	179.2(1)	C(12)–P(1)–C(1))	101.3(4)	P(4)–Cr(1)–P(1)	179.6(.5)	C(13)–P(1)–Cr(1)	107.5(3)
P(4)–Cr(1)–P(2)	96.9(.5)	C(13)–P(1)–C(11)	102.9(3)	P(4)–Cr(1)–P(3)	83.8(.5)	C(13)–P(1)–C(12)	102.1(4)
P(1)–Cr(1)–P(1)	89.8(2)	C(21)–P(2)–Cr(1)	121.0(3)	C(1)–Cr(1)–P(2)	89.3(3)	C(22)–P(2)–Cr(1)	119.8(4)
C(1)–Cr(1)–P(3)	91.0(3)	C(22)–P(2)–C(21)	102.3(5)	C(1)–Cr(1)–P(4)	89.9(3)	C(23)–P(2)–Cr(1)	105.3(3)
C(2)–Cr(1)–P(1)	91.9(2)	C(23)–P(2)–C(21)	103.1(4)	C(2)–Cr(1)–P(2)	91.2(3)	C(23)–P(2)–C(22)	102.6(4)
C(2)–Cr(1)–P(3)	88.5(3)	C(31)–P(3)–Cr(1)	118.4(3)	C(2)–Cr(1)–P(4)	88.3(2)	C(32)–P(3)–Cr(1)	121.0(3)
C(2)–Cr(1)–C(1)	178.3(2)	C(32)–P(3)–C(31)	101.3(5)			C(33)–P(3)–Cr(1)	107.2(3)
		C(33)–P(3)–C(31)	101.7(5)	C(13)–C(23)–P(2)	108.3(5)	C(33)–P(3)–C(32)	105.1(5)
C(23)–C(13)–P(1)	109.1(4)	C(41)–P(4)–Cr(1)	119.7(3)	C(33)–C(43)–P(4)	119.3(6)	C(42)–P(4)–Cr(1)	120.5(3)
C(43)–C(33)–P(3)	121.0(6)	C(42)–P(4)–C(41)	101.6(5)			C(43)–P(4)–Cr(1)	107.9(3)
		C(43)–P(4)–C(41)	100.9(5)			C(43)–P(4)–C(42)	103.5(4)
		O(1)–C(1)–Cr(1)	178.8(5)			O(2)–C(2)–Cr(1)	177.1(4)

covalent radii for neighbouring oxidation states in a common co-ordination geometry.

As mentioned above, the exceptions to this trend are the two hydride structures. The change in Cr–P distances between the Cr^{III} chloride and Cr^{IV} hydride is quite dramatic, and although the shortness of these bonds has previously been discussed in comparison with distances in the Cr^0 complexes,[1] the determination of structures for the chromium-(I), -(II), and -(III) species serves only to highlight what now must be considered exceptionally short Cr^{IV}–P bonds. The most logical explanation for these differences may lie in the fact that the two hydrides are diamagnetic, with the associated spin pairing producing a reduction in the 'equatorial' Cr bonding radius. It is also possible that this effect will contribute to the shortness of the Cr–P lengths in the Cr^0 species. It is also pertinent to note that on magnetochemical and bond-length considerations, the two hydrides associate most closely with the Cr^0 species. This again is consistent with the idea that the carbonyl hydride may be considered to be a protonated Cr^0 species.

Nuclear Magnetic Resonance Spectra.—There have been extensive variable-temperature n.m.r. studies on non-rigid seven-co-ordinate hydride species of the type $MH(CO)_2(P\text{–}P)_2$ and associated discussion of possible structures. Thus studies on $TaH(CO)_2(dmpe)_2$,[20] $[MoH(CO)_2(dmpe)_2]^+$,[22] $[MH(CO)_2(dppm)_2]^+$ (M = Cr or Mo),[12] and especially the extensive ^1H, ^{31}P, and ^{13}C n.m.r. spectra of several chelating diphosphine species,[23] $[MoH(CO)_2(diphos)_2]^+$, indicated that a monocapped octahedral structure was preferred. Evidence[23] for monocapped octahedron–pentagonal bipyramid conversion was also obtained; for $[CrH(CO)_2(dppm)_2]^+$ a pentagonal bipyramidal structure could not be excluded.[12] As noted above, the crystal structure of $[MoH(CO)_2(dppe)_2]AlCl_4$[21] has provided the first example of two dppe ligands occupying the plane of a pentagonal bipyramidal structure in this type of compound and the hydride position was inferred to be between two P atoms and in or very near the MoP_4 plane.

The variable-temperature ^1H, $^{31}P\text{-}\{^1H\}$, and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of $[CrH(CO)_2(dmpe)_2]^+$ (Figure 6) suggest that at low

Table 6. Structural data for $(dmpe)_2CrX_2$ species

Compound	Formal oxidation state	Cr–P/Å	Cr–X/Å	Ref.
$Cr(N_2)_2(dmpe)_2$	0	2.296(1)	1.874(3)	1
$Cr(C_2Ph)_2(dmpe)_2$	0	2.280(3)		1
cis-$Cr(CO)_2(dmpe)_2$	0	2.278(3)—2.343(3)	1.812(6)	1
trans-$[Cr(CO)_2(dmpe)_2]^+$	1	2.360(3)—2.379(3)	1.842(7)—1.877(7)	This work
$CrCl_2(dmpe)_2$	2	2.365(3)—2.371(3)	2.345(3)—2.351(3)	2
$CrMe_2(dmpe)_2$	2	2.342(1)—2.349(1)	2.168(4)	2
$Cr(O_2CCF_3)_2(dmpe)_2$	2	2.39(1)	2.09(3)	This work
$[Cr(NCMe)_2(dmpe)_2]^{2+}$	2	2.364(3)—2.392(3)	1.906(6)—1.994(6)	This work
$[Cr(NCEt)_2(dmpe)_2]^{2+}$	2	2.359(4)—2.369(4)	1.938(8)	This work
$[CrH(CO)_2(dmpe)_2]^+$	'2'	2.331(4)—2.364(4)	1.857(8)—1.875(8)	This work
$[CrCl_2(dmpe)_2]^+$	3	2.443(5)—2.447(5)	2.293(4)	This work
$CrH_4(dmpe)_2$	4	2.255(3)	1.57(3)	1

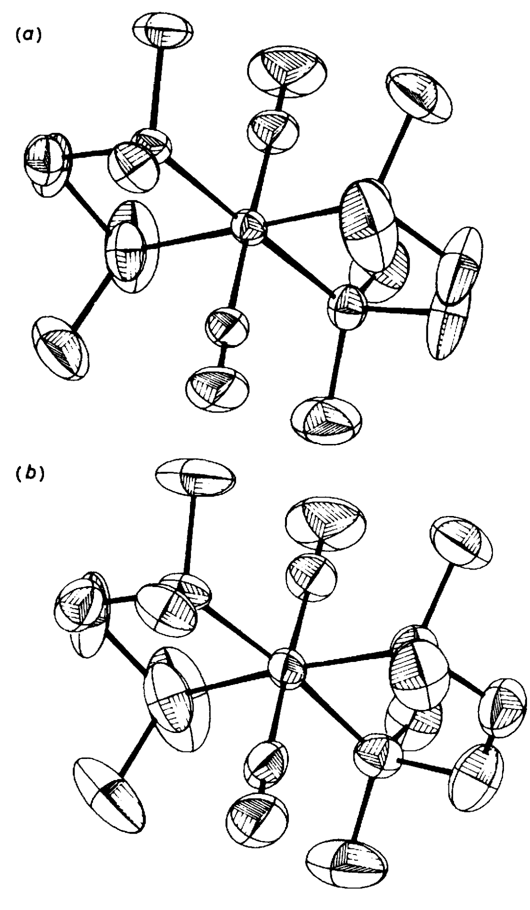

Figure 5. The structure of the cations (*a*) *trans*-$[Cr(CO)_2(dmpe)_2]^+$ and (*b*) $[CrH(CO)_2(dmpe)_2]^+$ in the tetraphenylborate salts

temperature the hydrogen atom is located in the plane of a pentagonal bipyramidal structure in agreement with the conclusion drawn from the *X*-ray studies. For a hydrogen atom in the plane with the four phosphorus atoms as an AA′BB′ system (**2**) the ^1H n.m.r. spectrum would be a triplet of triplets; such spectra have been observed previously,[12,22,23] but they are not unique to a pentagonal bipyramid and would also be given by a capped octahedral structure. At 233 K there is a triplet of triplets centred at −9.14 p.p.m., $J(P_A–H) = 90$, $J(P_B–H) = 14$ Hz. The substantial difference in these P–H coupling constants lends credence to the location of the H in the plane, since one pair of phosphorus atoms, P_AP_A', will be '*trans*' and the other pair '*cis*' to H.

At higher temperatures proton site exchange in the pentagonal plane presumably occurs with retention of the two types of phosphorus atoms. This results in a broad triplet which sharpens to a binomial quintet at 343 K where the P–H coupling constant (53 Hz) is an average of the two low-temperature *J* values, so that at this temperature the P atoms appear equivalent.

The ^{31}P-{^1H} spectrum at 233 K is a doublet of triplets with $J(P–P) = 45$ Hz and consistent with two sets of different phosphorus pairs as in (**2**). At higher temperatures fluxionality leads eventually to a singlet at 343 K with all P atoms appearing equivalent. The presence of two distinct phosphorus sites in solid $[CrH(CO)_2(dmpe)_2]CF_3SO_3$ has been further confirmed by solid-state magic angle spinning n.m.r. spectra (see Experimental section).

The ^{13}C-{^1H} spectrum of the dmpe ligand provides additional evidence for the location of the hydride in the plane of a pentagonal bipyramid. Over the range 343—233 K the peak for the ligand splits on cooling. This can be interpreted as being due to the H in the CrP_4 plane forcing the distortion of the dmpe leading to a difference in the CH_3 and CH_2 carbon atoms of the ligand. Extra hyperfine structure within each of these two new peaks may be attributed to the slightly conformationally different methyl and methylene groups. The resonance at 21.9 p.p.m. is assigned to the methylene carbons (CH_2), while the resonance at 16.7 p.p.m. is assigned to the methyl carbons (CH_3). The signal for the axial carbon monoxide carbons however remains largely unchanged over the temperature range employed. An extended scan of this signal at room temperature showed it to be a binomial quintet caused by coupling to four equivalent phosphorus atoms. All the spectroscopic evidence suggests that proton tunnelling is much faster than the relaxation time for ^{13}CO. Ideally, a low-temperature extended scan would perhaps show inequivalent phosphorus coupling to the axial carbon monoxides, but this is difficult technically.

Experimental

Microanalyses were by Pascher, Bonn, and Imperial College Laboratories. All manipulations were performed under oxygen-free nitrogen or argon or *in vacuo*; melting points were determined in sealed capillaries under argon. Solvents were dried over sodium (except dichloromethane, which was dried over P_2O_5 and nitriles, which were dried over CaH_2) and distilled from sodium–benzophenone under nitrogen immediately before use. The petroleum used had b.p. 40—60 °C. The trifluoromethanesulphonic acid was used as a stock solution in diethyl ether.

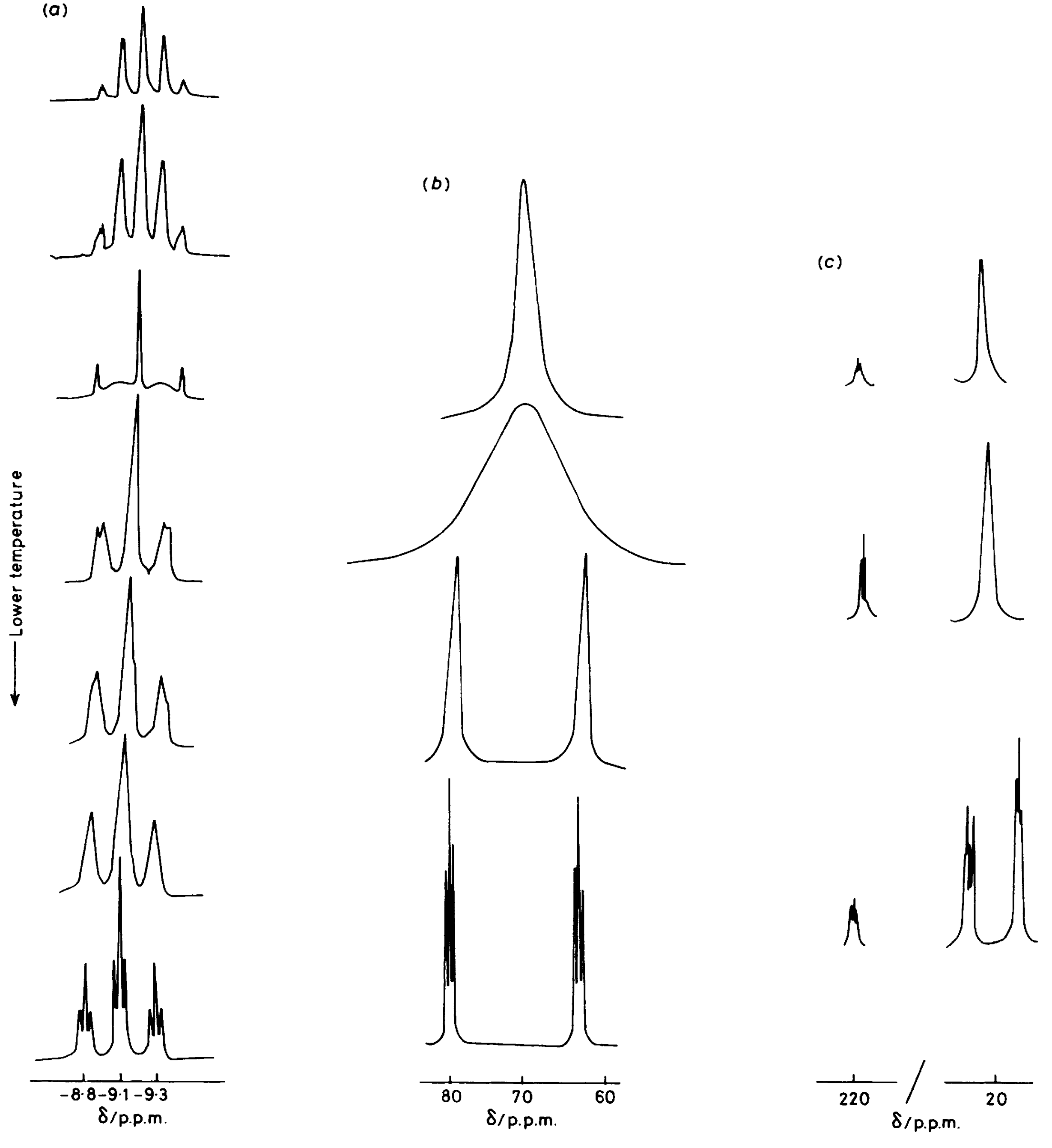

Figure 6. Nuclear magnetic resonance spectra of $[CrH(CO)_2(dmpe)_2]CF_3SO_3$ in $[^2H_6]$acetone. (*a*) ^1H spectra at 343, 333, 298, 273, 263, 253, and 233 K; (*b*) $^{31}P-\{^1H\}$ spectra at 343, 297, 253, and 233 K; (*c*) $^{13}C-\{^1H\}$ spectra at 343, 298, and 233 K

Spectrometers.—N.m.r.: Bruker WM-250 and JEOL FX-90Q; ^1H and ^{13}C (δ/p.p.m.) referenced to $SiMe_4$ and ^{31}P to external H_3PO_4 (*J* values in Hz). E.s.r.: Varian E12 (*X*-band); spectra in frozen nitrile solutions at 90 K, in flat cells at ambient temperature and in single crystals. I.r.: Perkin-Elmer 693; spectra (cm^{-1}) in Nujol mulls unless otherwise stated.

Conductivities were determined in acetonitrile unless otherwise stated on a Data Scientific PTI-18 instrument.

Magnetic susceptibilities were determined in solution by a modification of the Evans' method and in the solid state at ambient temperature on an Evans' balance.

1. *Interaction of trans*-$Cr(N_2)_2(dmpe)_2$ with HCl.—Two equivalents of hydrogen chloride (3.6 cm^3, 0.5 mol dm^{-3} in Et_2O) were added to a solution of *trans*-$Cr(N_2)_2(dmpe)_2$ (0.38 g, 0.93 mmol) in Et_2O (50 cm^3) at −78 °C. The yellow precipitate of $CrH_2Cl_2(dmpe)_2$ that formed immediately was washed with cooled diethyl ether (2 × 10 cm^3) and vacuum dried. Yield: 0.37 g, 95% (Found: C, 33.1; H, 7.5; Cl, 17.0; N, 0.5; P, 28.1. $C_{12}H_{34}Cl_2CrP_4$ requires C, 33.9; H, 8.1; Cl, 16.7; P, 29.1%). I.r.: 2 075, 1 980 cm^{-1} (Cr–H).

2. trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*bis*(*trifluoroacetato*)*chromium*(II).—To *trans*-$Cr(N_2)_2(dmpe)_2$ (0.4 g, 1 mmol) in thf (50 cm^3) at 78 °C were added two equivalents of CF_3CO_2H (2.8 cm^3, 0.7 mol dm^{-3} in Et_2O). On warming to

Table 7. Crystallographic data

Formula	Cr(O$_2$CCF$_3$)-(dmpe)$_2$	[Cr(NCMe)$_2$(dmpe)$_2$]-[CF$_3$SO$_3$]$_2$	[Cr(NCEt)$_2$(dmpe)$_2$]-[CF$_3$SO$_3$]$_2$	[CrCl$_2$(dmpe)$_2$]-BPh$_4$·CH$_2$Cl$_2$	[CrH(CO)$_2$(dmpe)$_2$]-BPh$_4$	[Cr(CO)$_2$(dmpe)$_2$]-BPh$_4$
M	578.30	732.46	762.54	872.32	728.49	727.48
System	Tetragonal	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	9.467(2)	9.806(2)	8.835(3)	15.443(8)	19.995(2)	20.027(3)
b/Å	9.467	13.126(3)	11.959(4)	21.914(5)	13.055(2)	12.898(1)
c/Å	14.876(4)	14.413(6)	16.696(7)	12.780(4)	15.854(1)	15.981(3)
α/°	90	84.58(3)	90	90	90	90
β/°	90	73.84(3)	93.50(4)	97.27(3)	108.26(1)	107.07(2)
γ/°	90	70.66(2)	90	90	90	90
U/Å	1 333.5	1 681.1	1 760.8	4 293.4	3 930.1	3 946.2
Space group	$P\bar{4}n2$	$P\bar{1}$	$P2_1/c$	$C2/c$	$P2_1/n$	$P2_1/c$
D_c/g cm^{-3}	1.44	1.44	1.40	1.28	1.23	1.22
Z	2	2	2	4	4	4
μ(Mo-K_α)/cm^{-1}	6.65	6.56	6.28	6.82	4.35	4.34
$\theta_{min.}$, $\theta_{max.}$	a	a	a	a	a	a
T/K	293	293	293	293	293	275
Data measured	1 386	6 447	3 493	4 190	7 718	7 523
Data unique	1 182	5 892	3 087	3 775	6 896	6 923
Data observed	825	3 916	1 935	1 793	4 544	4 399
Cut-off	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$
No. parameters	44	507	229	256	499	407
Weight parameter[b]	Unit	0.0005	0.0001	Unit	0.0001	0.0005
H-Atom treatment	None	c	d	e	e	f
Final R[g]	0.186	0.059	0.071	0.057	0.069	0.051
Final R'[h]		0.056	0.068	0.057	0.066	0.056

[a] Values are 1.5, 25.0° for all compounds. [b] Parameter g in $w = 1/[\sigma^2(F_o) + gF_o^2]$. [c] Free refinement with common group U_{iso}. [d] Methylene-H atoms idealized, some methyl-H included with free refinement and common group U_{iso}, other methyl-H omitted. [e] Phenyl-H idealized, others refined freely with group U_{iso}. [f] All H atoms refined as part of rigid group with group U_{iso}. [g] $\Sigma|\Delta F|/\Sigma F_o$. [h] $[\Sigma w\Delta F^2/\Sigma wF_o^2]^{\frac{1}{2}}$.

room temperature the solution slowly changes from a deep red to orange. After stirring for *ca.* 12 h the solvent was removed *in vacuo* and the orange-green solid extracted with CH$_2$Cl$_2$ (30 cm^3). Filtration and concentration of the red-green solution followed by cooling to −20 °C produced dichroic red-green crystals. Yield: 0.35 g, 65%; m.p. 232 °C (decomp.) (Found: C, 33.3; H, 5.4; F, 19.8; N, 0.3; P, 21.4. C$_{16}$H$_{32}$CrF$_6$O$_4$P$_4$ requires C, 33.2; H, 5.6; F, 19.7; P, 21.4%). I.r.: 1 680s (CF$_3$CO$_2$); 1 185s, 1 142s cm^{-1} (CF$_3$). Magnetic susceptibility: $\mu_{eff.}$ = 2.7.

3. trans-*Bis(acetonitrile)bis*[1,2-*bis(dimethylphosphino)-ethane*]*chromium*(II) *Trifluoromethanesulphonate*.—*Method* 1. Two equivalents of trifluoromethanesulphonic acid (11.8 cm^3, 0.2 mol dm^{-3} in Et$_2$O) were added to a solution of *trans*-Cr(N$_2$)$_2$(dmpe)$_2$ (0.48 g, 1.1 mmol) in Et$_2$O (75 cm^3) at −78 °C. The tan precipitate was collected and washed with cooled Et$_2$O (2 × 10 cm^3). Yield: 0.8 g, 90%; m.p. 330 °C (decomp.) (Found: C, 23.3; H, 4.7; N, 2.5; P, 15.8; S, 10.7. C$_{14}$H$_{34}$CrF$_6$N$_2$O$_6$P$_4$S$_2$ requires C, 24.7; H, 5.0; N, 4.1; P, 16.2; S, 9.4%). The tan solid dissolved in MeCN (30 cm^3) with gas evolution to give an amber-brown solution which on concentration and cooling to −20 °C gave yellow-green prisms of *trans*-[Cr(NCMe)$_2$-(dmpe)$_2$][CF$_3$SO$_3$]$_2$. Yield: 0.5 g, 95%; m.p. 330 °C (decomp.) (Found: C, 29.3; H, 5.3; N, 3.9; P, 17.1. C$_{18}$H$_{38}$CrF$_6$N$_2$O$_6$P$_4$S$_2$ requires C, 29.5; H, 5.2; N, 3.8; P, 16.9%). I.r.: 2 380m, 2 280m cm^{-1} (CN). Conductivity (MeCN): Λ_M = 234 ohm^{-1} cm^2 mol^{-1}. Magnetic susceptibility: $\mu_{eff.}$ = 3.3.

Method 2. *trans*-Cr(N$_2$)$_2$(dmpe)$_2$ (10.33 g, 0.8 mmol) in MeCN (40 cm^3) was cooled to −40 °C and CF$_3$SO$_3$H (2 mol equiv., 4.5 cm^3, 0.36 mol dm^{-3} in Et$_2$O) added to give immediately a golden colour. The solution was stirred for several hours at room temperature, filtered and concentrated to *ca.* 10 cm^3; cooling to −20 °C produced gold-green crystals identical to those obtained as above. Yield *ca.* 95%.

Table 8. Fractional atomic co-ordinates (× 10^4) for Cr(O$_2$CCF$_3$)$_2$-(dmpe)$_2$

Atom	x	y	z
Cr(1)	0*	5 000*	2 500*
P(1)	1 223(20)	6 152(16)	3 697(7)
C(11)	960(60)	7 877(48)	3 996(25)
C(12)	3 240(77)	6 392(109)	3 429(42)
C(13)	423(74)	6 151(89)	4 782(29)
O(1)	1 558(22)	8 442(22)	2 500*

* Invariant parameter.

Method 3. To *trans*-Cr(C$_2$H$_4$)$_2$(dmpe)$_2$ (0.3 g, 0.74 mmol) in MeCN (30 cm^3) at −30 °C were added two equivalents of CF$_3$SO$_3$H (1.6 cm^3, 0.93 mol dm^3 in Et$_2$O). An immediate orange-green colour developed and remained as the solution warmed to room temperature. The solution was filtered, concentrated and cooled to −20 °C to give crystals as above. Yield: 0.4 g, 70%.

4. trans-*Bis*[1,2-*bis(dimethylphosphino)ethane*)*bis(propionitrile)chromium*(II) *Trifluoromethanesulphonate*.—To *trans*-Cr(N$_2$)$_2$(dmpe)$_2$ (10.45 g, 1.1 mmol) in EtCN (30 cm^3) at −40 °C was added CF$_3$SO$_3$H (2 mol equiv., 2.4 cm^3, 0.93 mol dm^{-3} in Et$_2$O). The solution which immediately became green

Table 9. Fractional atomic co-ordinates (× 10^4) for $[Cr(NCMe)_2(dmpe)_2][CF_3SO_3]_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cr(1)	0*	10 000*	0*	C(33)	−296(7)	3 257(5)	3 481(5)
Cr(2)	0*	5 000*	5 000*	C(41)	3 053(7)	2 595(6)	4 179(5)
P(1)	366(2)	8 128(1)	190(1)	C(42)	1 164(9)	2 277(5)	6 000(5)
P(2)	1 442(2)	9 671(1)	1 142(1)	C(43)	104(7)	2 553(5)	4 305(5)
P(3)	−1 191(2)	4 661(1)	3 876(1)	S(1)	−4 080(2)	11 930(2)	6 299(2)
P(4)	1 131(2)	3 090(1)	4 906(1)	O(11)	−4 106(9)	11 165(7)	7 071(5)
N(1)	−1 782(5)	10 295(4)	1 034(3)	O(12)	−5 450(7)	12 466(7)	6 186(6)
N(2)	1 653(5)	5 208(3)	3 906(3)	O(13)	−3 053(8)	12 451(6)	6 290(5)
C(1)	−2 951(9)	10 471(7)	1 670(5)	C(5)	−3 208(9)	11 075(7)	5 304(7)
C(2)	−3 844(15)	10 512(12)	2 470(9)	F(51)	−1 841(7)	10 501(5)	5 230(6)
C(3)	2 665(7)	5 298(5)	3 284(4)	F(52)	−3 049(7)	11 664(6)	4 474(4)
C(4)	3 966(8)	5 346(7)	2 586(5)	F(53)	−3 956(7)	10 493(5)	5 129(5)
C(11)	−1 241(9)	7 756(6)	894(6)	S(2)	6 584(2)	6 831(2)	−1 059(1)
C(12)	1 077(10)	7 266(6)	−856(6)	O(21)	7 194(8)	7 641(5)	−1 007(4)
C(13)	1 740(8)	7 561(6)	884(6)	O(22)	7 464(7)	6 070(6)	−1 797(4)
C(21)	790(9)	10 475(7)	2 225(5)	O(23)	5 040(6)	7 132(6)	−1 016(5)
C(22)	3 348(8)	9 623(6)	709(5)	C(6)	6 766(9)	6 049(6)	7(6)
C(23)	1 572(8)	8 314(6)	1 632(5)	F(61)	6 208(7)	5 269(5)	89(5)
C(31)	−3 139(7)	4 738(7)	4 358(5)	F(62)	8 104(6)	5 681(4)	98(5)
C(32)	−1 184(8)	5 389(6)	2 742(5)	F(63)	5 988(7)	6 666(6)	783(4)

* Invariant parameter.

Table 10. Fractional atomic co-ordinates (× 10^4) for $[Cr(NCEt)_2(dmpe)_2][CF_3SO_3]_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cr(1)	0*	0*	0*	C(2)	−3 111(17)	2 775(9)	767(7)
P(1)	1 612(2)	501(2)	1 121(1)	C(3)	−2 508(20)	3 747(12)	1 005(10)
P(2)	−1 000(3)	−1 293(2)	904(2)	S(1)	−3 959(3)	3 635(2)	−1 806(2)
C(11)	3 523(13)	89(13)	1 120(8)	O(1)	−3 416(8)	2 873(5)	−1 205(4)
C(12)	1 825(20)	1 983(12)	1 357(10)	O(2)	−5 566(9)	3 739(6)	−1 906(5)
C(13)	1 030(18)	−136(14)	1 944(7)	O(3)	−3 203(11)	3 567(6)	−2 517(5)
C(21)	−2 920(13)	−1 113(10)	1 137(8)	C(4)	−3 377(12)	4 957(9)	−1 412(6)
C(22)	−858(15)	−2 771(9)	711(9)	F(1)	−3 908(8)	5 188(6)	−714(3)
C(23)	124(14)	−1 058(9)	1 898(5)	F(2)	−1 921(8)	5 044(6)	−1 317(5)
N(1)	−1 437(6)	1 118(5)	315(3)	F(3)	−3 856(9)	5 784(5)	−1 887(4)
C(1)	−2 319(9)	1 828(7)	512(4)				

* Invariant parameter.

was stirred for several hours at room temperature, filtered and concentrated to *ca.* 10 cm^3. Cooling to −20 °C produced green crystals. Yield: 0.4 g, 60%; m.p. 202 °C (decomp.) (Found: C, 31.4; H, 5.8; N, 3.7; P, 16.3. $C_{20}H_{42}CrF_6N_2O_6P_4S_2$ requires C, 31.5; H, 5.8; N, 3.7; P, 16.3%). I.r.: 2 278m, 2 262m (CN); 1 265s (SO_3); 1 150s cm^{-1} (CF_3). Conductivity (EtCN): Λ_M = 217 ohm^{-1} cm^2 mol^{-1}. Magnetic susceptibility: $\mu_{eff.}$ = 3.1.

5. trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*di-iodochromium*(III) *Iodide*.—*Method* 1. An excess of methyl iodide was added to a petroleum solution of *trans*-$Cr(N_2)_2(dmpe)_2$ (0.5 g, 1.22 mmol) cooled to −78 °C. No reaction occurred even upon warming but irradiation of the solution produced a flocculent yellow-green precipitate. The collected solid was extracted into methanol (40 cm^3) giving a green solution which on filtration, concentration (*ca.* 10 cm^3) and cooling to −20 °C produced green crystals of *trans*-$[CrI_2(dmpe)_2]I$. Yield: 0.61 g, 70%; m.p. 300 °C (decomp.) (Found: C, 19.8; H, 4.4; I, 51.5; P, 16.8. $C_{12}H_{32}CrI_3P_4$ requires C, 19.7; H, 4.4; I, 51.9; P, 16.9%). I.r.: 1 405, 1 145, 1 000, 950, 935, 925, 895, 890, 845, 805, 740, 710, 645 cm^{-1}. E.s.r. (PhMe-MeCN): *g* = 3.56, 2.03. Magnetic susceptibility (MeOH): $\mu_{eff.}$ = 3.83. Conductivity (MeOH): Λ_M = 99.98 ohm^{-1} cm^2 mol^{-1}.

Method 2. To *trans*-$Cr(N_2)_2(dmpe)_2$ (0.5 g, 1.22 mmol) was added iodine (2 mol equiv., 0.62 g). The mixture of solids was cooled to −78 °C and toluene added (30 cm^3). After *ca.* 1 h the solution was evaporated to dryness and the orange solid dissolved in methanol (40 cm^3). Slowly the orange solid dissolved to give a green solution which, after a few hours stirring was filtered, concentrated and cooled to −20 °C, producing dark green crystals. Yield: 0.6 g, 60%.

Method 3. Excess methyl iodide was added to a toluene–hexane solution of $CrH_4(dmpe)_2$ (0.3 g, 0.75 mmol) cooled to −78 °C. The solution was allowed to warm to room temperature slowly, with some evolution of gas. After *ca.* 1 h a brown-red solid had appeared, but this soon turned into a yellow-green solid. After stirring for several hours the solvent was removed and the resulting solid extracted into hot CH_2Cl_2 (60 cm^3). Concentration and cooling of the green solution to −20 °C produced green microcrystals. Yield: 0.5 g, 80%.

6. trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dichlorochromium*(III) *Iodide and Tetraphenylborate*.—(*a*) *Iodide*. Excess methyl iodide was added to a cooled (−78 °C) solution of *trans*-$CrCl_2(dmpe)_2$ (0.5 g, 1.18 mmol) in toluene (40 cm^3). No reaction occurred until the solution had warmed to room temperature, when a yellow solid precipitated. The mixture was stirred for *ca.* 2 d to give a red solution together with a little yellow-green precipitate. The solution was filtered and evaporated in vacuum. Extraction of the residue into methanol (40 cm^3), concentration and cooling to −20 °C produced red-green crystals of *trans*-$[CrCl_2(dmpe)_2]I$. Yield: 0.44 g, 70%; m.p.

Table 11. Fractional atomic co-ordinates (× 10^4) for $[\mathrm{CrCl_2(dmpe)_2}]\mathrm{BPh_4{\cdot}CH_2Cl_2}$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cr(1)	5 000*	3 822(1)	7 500*	C(34)	7 316(3)	6 345(2)	7 896(3)
Cl(1)	4 943(1)	3 836(1)	5 699(1)	C(35)	6 978(3)	6 567(2)	8 784(3)
P(1)	3 953(1)	2 981(1)	7 395(2)	C(36)	6 253(3)	6 952(2)	8 665(3)
P(2)	3 942(1)	4 658(1)	7 361(2)	C(31)	5 865(3)	7 114(2)	7 658(3)
C(11)	3 356(9)	2 810(7)	6 127(9)	C(42)	5 823(3)	8 237(3)	6 178(4)
C(12)	3 115(7)	3 001(6)	8 263(9)	C(43)	5 850(3)	8 672(3)	5 384(4)
C(13)	4 580(7)	2 297(5)	7 765(12)	C(44)	5 077(3)	8 927(3)	4 890(4)
C(21)	3 422(8)	4 836(6)	8 524(10)	C(45)	4 277(3)	8 748(3)	5 190(4)
C(22)	3 050(7)	4 654(7)	6 299(10)	C(46)	4 251(3)	8 314(3)	5 984(4)
C(23)	4 579(6)	5 340(5)	7 149(9)	C(41)	5 024(3)	8 059(3)	6 477(4)
B(1)	5 000*	7 584(6)	7 500*	Cl(2)	4 068(2)	10 079(2)	7 346(3)
C(32)	6 203(3)	6 892(2)	6 770(3)	C(1)	5 000*	9 615(7)	7 500*
C(33)	6 928(3)	6 507(2)	6 890(3)				

* Invariant parameter.

Table 12. Fractional atomic co-ordinates (× 10^4) for $[\mathrm{CrH(CO)_2(dmpe)_2}]\mathrm{BPh_4}$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cr(1)	3 997(1)	7 354(1)	1 132(1)	C(53)	1 106(2)	4 988(2)	10 511(2)
P(1)	4 745(1)	8 263(1)	2 234(1)	C(54)	1 659(2)	4 783(2)	11 283(2)
P(2)	3 659(1)	9 025(1)	672(1)	C(55)	2 029(2)	3 863(2)	11 366(2)
P(3)	4 258(1)	5 631(1)	1 457(1)	C(56)	1 845(2)	3 148(2)	10 678(2)
P(4)	3 159(1)	6 598(1)	−108(1)	C(51)	1 292(2)	3 353(2)	9 906(2)
O(1)	5 027(3)	7 462(5)	140(3)	C(62)	181(2)	2 593(2)	7 412(2)
O(2)	2 913(3)	7 159(5)	2 060(4)	C(63)	−512(2)	2 586(2)	6 847(2)
C(1)	4 643(3)	7 414(5)	509(4)	C(64)	−1 070(2)	2 627(2)	7 199(2)
C(2)	3 319(4)	7 260(5)	1 720(4)	C(65)	−934(2)	2 676(2)	8 116(2)
C(11)	4 754(4)	8 011(6)	3 443(4)	C(66)	−241(2)	2 683(2)	8 682(2)
C(12)	5 679(4)	8 227(8)	2 426(5)	C(61)	317(2)	2 641(2)	8 330(2)
C(13)	4 572(4)	9 635(5)	2 218(4)	C(72)	1 348(2)	593(3)	8 748(2)
C(21)	3 498(8)	9 402(7)	−461(6)	C(73)	1 291(2)	−452(3)	8 897(2)
C(22)	2 900(6)	9 554(8)	940(6)	C(74)	1 085(2)	−781(3)	9 616(2)
C(23)	4 361(6)	9 893(5)	1 261(5)	C(75)	936(2)	−65(3)	10 185(2)
C(31)	5 129(4)	5 179(6)	1 460(6)	C(76)	993(2)	980(3)	10 036(2)
C(32)	4 192(5)	5 105(6)	2 464(5)	C(71)	1 199(2)	1 309(3)	9 317(2)
C(33)	3 682(4)	4 794(5)	611(5)	C(82)	1 655(2)	3 793(3)	8 052(2)
C(41)	2 240(4)	6 956(8)	−388(6)	C(83)	2 203(2)	4 178(3)	7 776(2)
C(42)	3 319(5)	6 631(6)	−1 162(5)	C(84)	2 858(2)	3 695(3)	8 039(2)
C(43)	3 058(4)	5 257(5)	104(5)	C(85)	2 965(2)	2 828(3)	8 579(2)
B(1)	1 146(3)	2 548(5)	9 032(4)	C(86)	2 417(2)	2 443(3)	8 855(2)
C(52)	922(2)	4 273(2)	9 823(2)	C(81)	1 762(2)	2 926(3)	8 592(2)

295 °C (decomp.) (Found: C, 25.9; H, 5.8; Cl, 12.2; I, 25.0; P, 22.4. $\mathrm{C_{12}H_{32}Cl_2CrIP_4}$ requires C, 26.2; H, 5.9; Cl, 12.9; I, 23.1; P, 22.5%). I.r.: 1 415, 1 400, 1 305, 1 295, 1 290, 1 280, 1 130, 1 090, 985, 945, 925, 890, 870, 860, 840, 795, 750, 715, 645, 595 cm^{-1}. E.s.r. (PhMe–MeCN): $g = 3.29, 1.99$. Magnetic susceptibility (MeOH): $\mu_{\mathrm{eff.}} = 3.80$. Conductivity (MeOH): $\Lambda_M = 134.5$ ohm^{-1} cm^2 mol^{-1}.

(*b*) *Tetraphenylborate.* $\mathrm{CrH_2Cl_2(dmpe)_2}$ (0.39 g, 0.7 mmol) was dissolved in acetonitrile (30 cm^3) at low temperature (−40 °C). On warming to room temperature gas was evolved and after stirring for *ca.* 1 h the amber solution was evaporated to dryness. A methanolic solution of sodium tetraphenylborate was then added to the solid, and the yellow precipitate was washed with methanol (2 × 15 cm^3) and dried. Crystallization from $\mathrm{CH_2Cl_2}$ after concentration, filtration and cooling to −20 °C gave pink crystals of *trans*-$[\mathrm{CrCl_2(dmpe)_2}]\mathrm{BPh_4}$. Yield: 0.2 g, 35%; m.p. 280 °C (decomp.) (Found: C, 57.6; H, 7.0; B, 1.4; Cl, 9.8; P, 16.5. $\mathrm{C_{56}H_{52}BCl_2CrP_4}$ requires C, 58.1; H, 7.2; B, 1.4; Cl, 9.5; P, 16.7%). I.r.: 3 050, 3 030, 1 580, 1 430, 1 420, 1 305, 1 290, 940, 930, 890, 855, 800, 745, 730, 720, 710, 625, 615, 600, 370 cm^{-1}. Magnetic susceptibility: $\mu_{\mathrm{eff.}} = 3.86$. Conductivity (MeCN): $\Lambda_M = 96.1$ ohm^{-1} cm^2 mol^{-1}.

7. *Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dicarbonylhydridochromium*(0) *Trifluoromethanesulphonate and Tetraphenylborate.*—To *cis*-$\mathrm{Cr(CO)_2(dmpe)_2}$ (0.6 g, 1.47 mmol) in MeCN (30 cm^3) at −30 °C were added two equivalents of $\mathrm{CF_3SO_3H}$ (4.1 cm^3, 0.93 mol dm^{-3} in $\mathrm{Et_2O}$). The initial yellow solution became colourless, then after *ca.* 15 min orange-green. The solution was stirred at room temperature overnight, filtered, concentrated to *ca.* 10 cm^3 and cooled at −20 °C to produce yellow crystals of $[\mathrm{CrH(CO)_2(dmpe)_2}]\mathrm{CF_3SO_3}$. Yield: 0.5 g, 48%; m.p. 213 °C (decomp.) (Found: C, 31.5; H, 5.8; F, 11.1; P, 20.0. $\mathrm{C_{15}H_{33}CrF_3O_5P_4S}$ requires C, 32; H, 5.9; F, 10.2; P, 22.2%). I.r.: 1 940s (Cr–H), 1 830s br (CO), 1 265s ($\mathrm{SO_3}$), 1 150s cm^{-1} ($\mathrm{CF_3}$). Conductivity (MeCN): $\Lambda_M = 83$ ohm^{-1} cm^2 mol^{-1}. N.m.r.: ^{1}H (343 K), 1.83s ($\mathrm{PCH_2}$), 1.51s ($\mathrm{PMe_2}$), −9.14 [quintet, J(P–H) = 53, Cr–H]; ^{1}H (233 K), 1.83s ($\mathrm{PCH_2}$), 1.51s ($\mathrm{PMe_2}$), −9.14 ['triplet of triplets', $J(\mathrm{P_A}\text{–H}) = 90$, $J(\mathrm{P_B}\text{–H}) = 14$, Cr–H]; ^{31}P-{^{1}H} (343 K), 70.95s ($w_{\frac{1}{2}} = 250$ Hz); ^{31}P-{^{1}H} (233 K), AA′BB′, 78.7 (t, $\mathrm{P_A}$), 63.2 (t, $\mathrm{P_B}$) [$J(\mathrm{P_A}\text{–}\mathrm{P_B}) = 45$]; ^{13}C-{^{1}H} (343 K), 222.2 [quin, J(P–C) = 15.2, Cr–CO], 23.2 (s, $\mathrm{PCH_2}$ and $\mathrm{PMe_2}$); ^{13}C-{^{1}H} (233 K), 218.5 [quin, J(P–C) = 14.2, Cr–CO], 21.9 ['quintet', $\mathrm{PCH_2}$, J(P–C) = 9], 16.7 ['triplet', $\mathrm{PMe_2}$, J(P–C) = 10.4].

Table 13. Fractional atomic co-ordinates (× 10^4) for $[Cr(CO)_2(dmpe)_2]BPh_4$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cr(1)	3 962(.5)	7 424(1)	1 082(.5)	C(3A)	1 096(1)	5 001(2)	10 507(2)
P(1)	4 745(1)	8 234(1)	2 324(1)	C(4A)	1 645(1)	4 799(2)	11 260(2)
P(2)	3 657(1)	9 150(1)	641(1)	C(5A)	2 015(1)	3 870(2)	11 337(2)
P(3)	4 273(1)	5 707(1)	1 544(1)	C(6A)	1 837(1)	3 143(2)	10 662(2)
P(4)	3 191(1)	6 611(1)	−153(1)	C(1A)	1 288(1)	3 345(2)	9 909(2)
O(1)	5 062(2)	7 514(4)	155(3)	C(8A)	199(1)	2 572(2)	7 462(2)
O(2)	2 814(2)	7 275(4)	1 944(3)	C(9A)	−488(1)	2 548(2)	6 918(2)
C(1)	4 641(3)	7 468(4)	516(3)	C(10A)	−1 042(1)	2 578(2)	7 279(2)
C(2)	3 254(2)	7 353(4)	1 633(3)	C(11A)	−910(1)	2 732(2)	8 185(2)
C(11)	4 736(3)	7 960(4)	3 437(3)	C(12A)	−224(1)	2 657(2)	8 729(2)
C(12)	5 675(2)	8 168(5)	2 438(4)	C(7A)	331(1)	2 626(2)	8 368(2)
C(13)	4 578(3)	9 631(4)	2 224(3)	C(14A)	1 380(2)	561(2)	8 760(2)
C(21)	3 534(5)	9 554(5)	−475(4)	C(15A)	1 332(2)	−498(2)	8 910(2)
C(22)	2 916(4)	9 767(6)	899(5)	C(16A)	1 114(2)	−836(2)	9 616(2)
C(23)	4 398(3)	9 940(4)	1 260(4)	C(17A)	944(2)	−116(2)	10 173(2)
C(31)	5 134(3)	5 225(5)	1 530(5)	C(18A)	993(2)	943(2)	10 023(2)
C(32)	4 241(5)	5 262(5)	2 593(5)	C(13A)	1 211(2)	1 281(2)	9 316(2)
C(33)	3 689(4)	4 852(5)	756(5)	C(20A)	1 645(1)	3 827(2)	8 067(2)
C(41)	2 257(3)	6 864(7)	−430(6)	C(21A)	2 184(1)	4 234(2)	7 778(2)
C(42)	3 339(4)	6 699(5)	−1 216(3)	C(22A)	2 838(1)	3 757(2)	8 015(2)
C(43)	3 213(5)	5 231(4)	56(4)	C(23A)	2 953(1)	2 874(2)	8 541(2)
B(1)	1 148(2)	2 538(4)	9 043(3)	C(24A)	2 415(1)	2 467(2)	8 831(2)
C(2A)	918(1)	4 274(2)	9 832(2)	C(19A)	1 761(1)	2 944(2)	8 594(2)

To the $CF_3SO_3^-$ salt in methanol (30 cm^3) was added an excess of $NaBPh_4$ in methanol (20 cm^3). The greenish white precipitate was collected, and washed with methanol (3 × 10 cm^3). The solid was extracted into acetonitrile (50 cm^3) and the solution concentrated and cooled to −20 °C to yield small pale green prisms of $[CrH(CO)_2(dmpe)_2]BPh_4$. Yield: 0.38 g, 95%; m.p. 234 °C (decomp.) (Found: C, 62.6; H, 7.4; P, 17.3. $C_{38}H_{53}BCrO_2P_4$ requires C, 62.6; H, 7.3; P, 17.0%). I.r.: 3 180m, 1 570m (phenyl), 1 940s (Cr–H), 1 830s cm^{-1} (CO). Conductivity (MeCN): Λ_M = 83.1 ohm^{-1} cm^2 mol^{-1}.

8. trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dicarbonylchromium*(I) *Tetraphenylborate*.—To *cis*-$Cr(CO)_2(dmpe)_2$ (0.48 g, 1.2 mmol) in MeCN (30 cm^3) at −30 °C in the dark was added one equivalent of $AgCF_3SO_3$ (0.3 g, 1.2 mmol). After *ca.* 15 min the pale yellow solution was filtered from silver metal and evaporated. To the residue dissolved in methanol (20 cm^3) was added $NaBPh_4$ (1 mol equiv., 0.4 g) in methanol (20 cm^3). After stirring for *ca.* 15 min the precipitate was collected, washed with methanol (2 × 20 cm^3), dried and extracted into MeCN (20 cm^3). Concentration to *ca.* 5 cm^3 and cooling to −20 °C produced large orange prisms. Yield: 0.7 g, 90%; m.p. 277 °C (decomp.) (Found: C, 63.4; H, 7.3; P, 17.5. $C_{38}H_{52}BCrO_2P_4$ requires C, 62.7; H, 7.2; P, 17.0%). I.r. (MeCN): 3 120m (phenyl), 1 830vs cm^{-1} (CO). Conductivity (MeCN): Λ_M = 83 ohm^{-1} cm^2 mol^{-1}. Magnetic susceptibility: $\mu_{eff.}$ = 1.67.

Solid-state N.M.R. on $[CrH(CO)_2(dmpe)_2]CF_3SO_3$.—The ^{31}P magic angle spinning n.m.r. spectrum was measured at 80.76 MHz (25 °C, Bruker MSL300) by Dr. I. J. P. Poplett of the B.P. Research Centre, Sunbury-on-Thames. The chemical shift anisotropy of the two ^{31}P resonances was calculated from the intensities of the spinning sidebands using the notation below

$$|\sigma_{zz} - \sigma_{iso}| \geqslant |\sigma_{xx} - \sigma_{iso}| \geqslant |\sigma_{yy} - \sigma_{iso}|$$

where σ_{iso} is the isotropic chemical shift. The chemical shift anisotropies were as follows. Site A: $\sigma_{iso} = 75.6 + 0.3$ p.p.m., $\sigma_{xx} = +30 + 30$ p.p.m., $\sigma_{yy} = -62 + 30$ p.p.m., $\sigma_{zz} = -195 + 30$ p.p.m. Site B: $\sigma_{iso} = -60.7$ p.p.m., $\sigma_{xx} = +70 + 50$ p.p.m., $\sigma_{yy} = -56 + 40$ p.p.m., $\sigma_{zz} = -196 + 40$ p.p.m.

The most negative value corresponds to the most shielded component of the chemical shift tensor and most positive value, to the least shielded component.

An attempt to obtain ^{13}C data for CO at 50.1 MHz on the same sample was unsuccessful as the fast relaxation of protons prevents a good contact between ^1H and ^{13}C nuclei in CO. Only ^{13}C resonances of the CH_3 and CH_2 groups on dmpe were observed.

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 (λ = 0.710 69 Å) as previously described.[24] The structures were solved *via* standard heavy-atom procedures and refined using full-matrix least squares,[25] with scattering factors calculated using data from ref. 26. In a number of cases, disorder caused problems during structure solution and refinement.

The bis(trifluoroacetate) complex crystallizes in the tetragonal system with Laue symmetry and absences indicating membership of the *P*4/**n** set of space groups. Attempts to develop a structure in each member of the set proved successful only for space group *P*4*n*2, in which the Cr atom is at a position of site symmetry 222, with the CrP_4 group oriented parallel to the $1\bar{1}0$ plane. The unique atoms from the dmpe ligands were refined successfully, although the carbon atoms showed high thermal parameters. An oxygen atom of the O_2CCF_3 ligand was located on the two-fold axis perpendicular to the CrP_4 plane and although other peaks were present in the difference map in a channel around this two-fold axis, it was not possible to recognise the requisite connectivity for the remainder of the ligand. Indeed, even insertion of suitable 'fractional' atoms at sites of significant electron density failed to produce any real reduction in the *R* value.

In an attempt to explore the possible configuration of the trifluoroacetate groups we have used model-building and steric-energy minimization methods, but these have so far been inconclusive, with suggestions of several allowable orientations of the ligands. Accordingly, the results presented in Table 7 correspond to the inclusion of the metal, atoms of the dmpe ligands and the one trifluoroacetate oxygen.

Disorder, but of a rather less serious nature, also seems to be affecting the structures of the two trifluoromethanesulphonates, where highly anisotropic thermal motion was found for atoms of these anions. As a result, the *R* values for these structures remained higher than we would expect judging from the apparent good quality of the data.

Details of the crystal data, intensity recording and refinements are given in Table 7. Final atomic fractional co-ordinates are given in Tables 8—13.

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