Synthesis and Characterisation of 1,2-Bis(dimethylphosphino)ethane (dmpe) Complexes of Chromium-(0) and -(IV): *X*-Ray Crystal Structures of *trans*-$Cr(N_2)_2(dmpe)_2$, *cis*-$Cr(CO)_2(dmpe)_2$, $Cr(C_2Ph_2)_2(dmpe)$, and $CrH_4(dmpe)_2$†

Julian E. Salt, Gregory S. Girolami, and Geoffrey Wilkinson*
Chemistry Department, Imperial College of Science and Technology, London SW7 2AY
Majid Motevalli, Mark Thornton-Pett, and Michael B. Hursthouse*
Chemistry Department, Queen Mary College, London E1 4NS

The reduction of *trans*-$CrCl_2(dmpe)_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane] in tetrahydrofuran by sodium amalgam under dinitrogen leads to the complex *trans*-$Cr(N_2)_2(dmpe)_2$, under carbon monoxide to the known *cis*-$Cr(CO)_2(dmpe)_2$, and in presence of Bu^{t}NC to *trans*-$Cr(CNBu^t)_2(dmpe)_2$. Interaction of *trans*-$Cr(N_2)_2(dmpe)_2$ with ethylene, buta-1,3-diene, diphenylacetylene, and hydrogen (under irradiation) gives, respectively, *trans*-$Cr(C_2H_4)_2(dmpe)_2$, *cis*-$Cr(\eta^4\text{-}C_4H_6)(dmpe)_2$, $Cr(PhC{\equiv}CPh)_2(dmpe)$, and $CrH_4(dmpe)_2$. Infrared and nuclear magnetic resonance spectra are reported together with *X*-ray crystal structures of four of the complexes. The *trans*-bis(dinitrogen) complex is centrosymmetric with octahedral geometry and Cr–N and Cr–P distances of 1.874(3) and 2.296(1) Å, respectively. The N–N bond length, 1.122(3) Å, is normal. The *cis*-dicarbonyl complex is also octahedral with a Cr–C distance of 1.812(6) Å; the Cr–P distances are different at 2.343(3) Å *trans* to CO and 2.278(3) Å *trans* to P, reflecting large differences in *trans* influence between CO and phosphine. The diphenylacetylene complex has π-bonded acetylene groups with Cr–C distances in the range 1.886(5)—1.980(5) Å and a chelating dmpe ligand, with Cr–P distances of 2.280(3), 2.298(3) Å. The chromium(IV) hydride has a dodecahedral structure with phosphines occupying the *B* sites [Cr–P 2.255(3) Å] and the hydrogen atoms the *A* sites [Cr–H 1.57(3) Å].

In a preliminary note[1] we have described some 1,2-bis(dimethylphosphino)ethane (dmpe) complexes of chromium-(0), -(II), and -(IV). Details of some of this work are now given; the synthesis of the starting material, *trans*-$CrCl_2(dmpe)_2$, and the corresponding dimethyl are described separately.[2]

Results and Discussion

1. trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*bis*(*dinitrogen*)*chromium*(0). — Reduction of $CrCl_2(dmpe)_2$ with five equivalents of sodium amalgam under dinitrogen gives initially a brown, and subsequently, a red-orange solution. Interruption of the reduction at the brown stage followed by work-up of the products gives a mixture of *trans*-$Cr(N_2)_2(dmpe)_2$ and darker coloured crystals which appear to be the *cis* isomer. These can be separated by hand picking (not by fractional crystallisation). The more vigorous the stirring and the longer the reaction time, the less *cis* isomer is formed. The orange-red solution after evaporation and extraction into light petroleum produces large red prisms of *trans*-$Cr(N_2)_2(dmpe)_2$ in high yield.

For the *trans* isomer, the i.r. band at 1 930 cm^{-1} is very broad in the Nujol mull but in hexane solution the band at 1 932 cm^{-1} is very sharp. The ^1H n.m.r. spectrum shows only a singlet at 1.29 p.p.m. for both the CH_3 and CH_2 groups of dmpe while the $^{31}P\text{-}\{^1H\}$ spectrum has a sharp singlet at 69.3 p.p.m. confirming the equivalence of the equatorial P atoms in the *trans* structure. The i.r. spectrum of the *cis* isomer shows two bands, at 1 920 and 1 895 cm^{-1}, while that of the *trans* isomer has one; these are clearly the dinitrogen stretches.

Previously known chromium complexes of N_2 have been either unstable or unisolable[3–5] and except for *cis*-$Cr(N_2)_2(PMe_3)_4$[4] all contain CO or arene ligands.[5] The dmpe ligand presumably stabilizes the $Cr(N_2)_2$ unit by its basic nature and chelation.

Since the initial *X*-ray structural determination at room temperature (see later) indicated an abnormally short N–N bond distance,[1] the photoelectron and Raman spectra of the *trans* complex were determined. The values for the N(1*s*) binding energies (corrected by calibration to the known binding energy of chromium metal) were 398.4 and 399.75 eV. The lower value was probably due to ionization of the 1*s* electron from the terminal nitrogen as this has a tendency to be more negative;[3] both values are similar to those in, for example, *trans*-$Mo(N_2)_2(dppe)_2$ [dppe = 1,2-bis(diphenylphosphino)ethane] (399.6 and 398.6 eV),[3] for which N–N = 1.118(9) Å.[6]

Similarly, the Raman data in the solid at 80 K appeared normal with N–N$_{sym}$ 2 001.65, Cr–N$_{sym}$ 408.35, and Cr–P$_{sym}$ 942.43 cm^{-1}.

The *X*-ray structure shows that the molecule lies on a centre of symmetry and contains conformationally frozen chelating dmpe groups (Figure 1). The revised bond lengths and angles for the structure at room temperature (see Experimental section) are given in Table 1. Compared with our previously reported results,[1] the N–N distance of 1.122(3) Å is now normal, thus accounting for the normality of the spectroscopic data, and the Cr–N distance has shortened to 1.874(3) Å. This and the shortness of the Cr–P distances when compared with those of 2.345(3) Å in the octahedral chromium(II) complex, $CrMe_2(dmpe)_2$,[2] indicates significant metal–ligand π back-bonding in this 18-electron complex. Part of the difference

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† Bis[1,2-bis(dimethylphosphino)ethane]bis(dinitrogen)chromium(0), *cis*-bis[1,2-bis(dimethylphosphino)ethane]dicarbonylchromium(0), 1,2-bis(dimethylphosphino)ethanebis(diphenylacetylene)chromium(0), and bis[1,2-bis(dimethylphosphino)ethane]tetrahydridochromium(IV).

Supplementary data available (No. SUP 56139, 10 pp.): anisotropic and isotropic thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. units employed: atm = 101 325 N m^{-2}, eV ≈ 1.60 × 10^{-19} J.

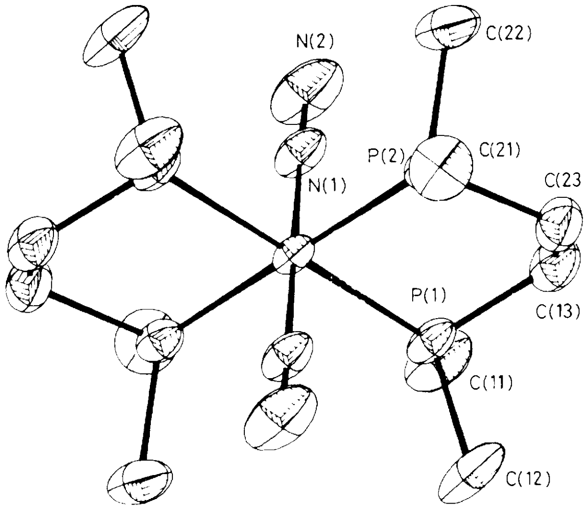

Figure 1. The structure of *trans*-$Cr(N_2)_2(dmpe)_2$

Table 1. Bond lengths (Å) and angles (°) for *trans*-$Cr(N_2)_2(dmpe)_2$

N(1)–Cr(1)	1.874(3)	P(1)–Cr(1)	2.294 0(5)
P(2)–Cr(1)	2.297 0(5)		
N(2)–N(1)	1.122(3)		
C(11)–P(1)	1.830(4)	C(12)–P(1)	1.829(4)
C(13)–P(1)	1.851(4)	C(23)–C(13)	1.514(4)
C(21)–P(2)	1.830(4)	C(22)–P(2)	1.830(4)
C(23)–P(2)	1.858(4)		
P(1)–Cr(1)–N(1)	88.10(5)	P(2)–Cr(1)–N(1)	89.30(5)
P(2)–Cr(1)–P(1)	83.40(5)		
N(2)–N(1)–Cr(1)	178.2(1)		
C(11)–P(1)–Cr(1)	123.1(2)	C(12)–P(1)–Cr(1)	119.6(2)
C(12)–P(1)–C(11)	100.4(2)	C(13)–P(1)–Cr(1)	109.2(2)
C(13)–P(1)–C(11)	99.4(2)	C(13)–P(1)–C(12)	101.5(2)
C(23)–C(13)–P(1)	109.5(2)	C(21)–P(2)–Cr(1)	123.1(2)
C(22)–P(2)–Cr(1)	118.0(2)	C(22)–P(2)–C(21)	100.6(2)
C(23)–P(2)–Cr(1)	110.8(2)	C(23)–P(2)–C(21)	99.7(2)
C(23)–P(2)–C(22)	101.2(2)	P(2)–C(23)–C(13)	109.4(2)

however, may also be due to an increase in the metal radius in the Cr^{II} complex resulting from the metal spin state.

The *trans* complex is relatively unreactive. It does not react with CO or H_2 at 25 °C and 7 atm except under u.v. irradiation (see later) where facile reactions occur probably due to dissociation of N_2 to give the co-ordinatively unsaturated 14-electron species $Cr(dmpe)_2$, similar to the species '$Mo(dppe)_2$' proposed by Graff *et al.*,[7] and the '$W(dppe)_2$' detected by flash photolysis of $WH_4(dppe)_2$[8] [dppe = 1,2-bis(diphenylphosphino)ethane].

Photolysis in the presence of other potential ligands, *e.g.*, excess PMe_3, cyclo-octa-1,5-diene, and phenylacetylene gave no identifiable new species. The major difficulty is that when an extended photolysis time is required (due to unreactivity of the incoming ligand), the formation of $Cr(dmpe)_3$ always occurs.

2. cis-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dicarbonylchromium*(0).—This compound has been previously prepared by the action of dmpe on $Cr_2(CO)_6(dmpe)_3$, which in turn was prepared from $Cr(CO)_3(C_7H_8)$.[9] It is also readily obtained either by reduction, using Na/Hg, of *trans*-$CrCl_2(dmpe)_2$ under carbon monoxide or carbon dioxide, by photolysis of *trans*-$Cr(N_2)_2(dmpe)_2$ under CO, or by interaction of *trans*-$CrMe_2(dmpe)_2$[2] with CO. The last reaction is quite slow but proceeds essentially quantitatively at 10 atm: *trans*-$CrMe_2(dmpe)_2 + 3CO \longrightarrow$ *cis*-$Cr(CO)_2(dmpe)_2 + Me_2CO$. Similar carbonylations of methyl compounds to give acetone have been noted for Ta,[10a] Mo,[10b] W,[10c] and Co.[10d]

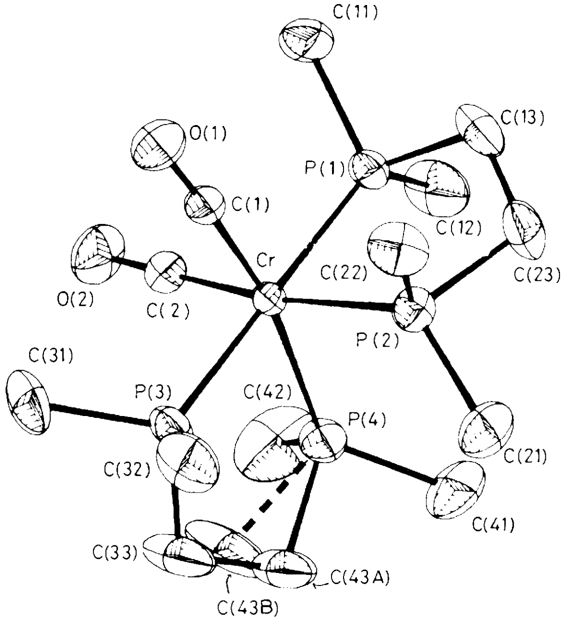

Figure 2. The structure of *cis*-$Cr(CO)_2(dmpe)_2$

The structure of the dicarbonyl is shown in Figure 2, whilst selected bond lengths and angles are given in Table 2. The molecule has the *cis* octahedral structure expected on the basis of i.r. and ^{31}P n.m.r. data with angles distorted only by the restricted bite (82.5 ± 0.1°) of the dmpe ligands. The bond lengths in the molecule make interesting comparisons with those in the isoelectronic (18-electron), but not isostructural *trans*-dinitrogen complex (see above). Thus the Cr–C distances are shorter than the Cr–N distances by *ca.* 0.06 Å, whilst the Cr–P distances in the dicarbonyl are, on average slightly longer but individually longer or shorter than in the dinitrogen complex. The quite significant difference is probably a reflection of the relative *trans* influences of the CO and P bonds, with the carbonyls inducing a considerable lengthening of *ca.* 0.06 Å in the Cr–P bonds to which they are *trans*. These results reflect the much greater π-acceptor capability of the CO molecule when compared with N_2.

3. trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*bis*(t-*butyl isocyanide*)*chromium*(0).—Sodium amalgam reduction of *trans*-$CrCl_2(dmpe)_2$ in presence of two equivalents of Bu^tNC in tetrahydrofuran gives a red-yellow solution from which red prisms of the bis(isocyanide) complex can be obtained. The $^{31}P-\{^1H\}$ n.m.r. spectrum has a singlet at 71.8 p.p.m. in accord with the proposed structure while the i.r. spectrum also has a single C–N stretch at 2 055 cm^{-1}.

4. *Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]-*bis*(*ethylene*)-*chromium*(0) *and* -(η^4-*buta*-1,3-*diene*)*chromium*(0).—Thermal reactions of *trans*-$Cr(N_2)_2(dmpe)_2$ with ethylene and buta-1,3-diene under mild pressure lead to the corresponding bis(ethylene) and butadiene complexes in quantitative yields.

Table 2. Bond lengths (Å) and angles (°) for *cis*-$Cr(CO)_2(dmpe)_2$

P(1)–Cr(1)	2.280(3)	P(2)–Cr(1)	2.347(3)
P(3)–Cr(1)	2.275(3)	P(4)–Cr(1)	2.339(3)
C(1)–Cr(1)	1.812(6)	C(2)–Cr(1)	1.812(6)
C(11)–P(1)	1.831(7)	C(12)–P(1)	1.833(7)
C(13)–P(1)	1.842(7)	C(23)–C(13)	1.527(9)
C(21)–P(2)	1.840(7)	C(22)–P(2)	1.823(7)
C(23)–P(2)	1.870(7)		
C(31)–P(3)	1.817(7)	C(32)–P(3)	1.817(7)
C(33)–P(3)	1.841(7)	C(43B)–C(33)	1.427(14)
C(43A)–C(33)	1.436(11)		
C(41)–P(4)	1.820(7)	C(42)–P(4)	1.832(8)
C(43A)–P(4)	1.968(10)	C(43B)–P(4)	1.848(14)
O(1)–C(1)	1.170(6)	O(2)–C(2)	1.170(6)
P(2)–Cr(1)–P(1)	82.60(5)	P(3)–Cr(1)–P(1)	178.3(1)
P(3)–Cr(1)–P(2)	96.20(5)	P(4)–Cr(1)–P(1)	99.00(5)
P(4)–Cr(1)–P(2)	95.60(5)	P(4)–Cr(1)–P(3)	82.40(5)
C(1)–Cr(1)–P(1)	91.3(2)	C(1)–Cr(1)–P(2)	90.2(2)
C(1)–Cr(1)–P(3)	87.4(2)	C(1)–Cr(1)–P(4)	168.7(1)
C(2)–Cr(1)–P(1)	89.3(2)	C(2)–Cr(1)–P(2)	171.6(1)
C(2)–Cr(1)–P(3)	91.8(2)	C(2)–Cr(1)–P(4)	87.8(2)
C(2)–Cr(1)–C(1)	87.7(3)		
C(11)–P(1)–Cr(1)	117.8(3)	C(12)–P(1)–Cr(1)	121.6(3)
C(12)–P(1)–C(11)	100.3(4)	C(13)–P(1)–Cr(1)	112.0(3)
C(13)–P(1)–C(11)	100.6(4)	C(13)–P(1)–C(12)	101.2(4)
C(23)–C(13)–P(1)	108.0(4)		
C(21)–P(2)–Cr(1)	126.8(3)	C(22)–P(2)–Cr(1)	117.3(3)
C(22)–P(2)–C(21)	99.6(3)	C(23)–P(2)–Cr(1)	108.9(3)
C(23)–P(2)–C(21)	99.8(4)	C(23)–P(2)–C(22)	100.5(4)
P(2)–C(23)–C(13)	109.2(4)		
C(31)–P(3)–Cr(1)	115.8(3)	C(32)–P(3)–Cr(1)	122.2(3)
C(32)–P(3)–C(31)	98.2(4)	C(33)–P(3)–Cr(1)	113.9(3)
C(33)–P(3)–C(31)	101.8(4)	C(33)–P(3)–C(32)	101.8(4)
C(43A)–C(33)–P(3)	109.1(6)	C(43B)–C(33)–P(3)	111.9(7)
C(41)–P(4)–Cr(1)	127.9(3)	C(42)–P(4)–Cr(1)	118.2(3)
C(42)–P(4)–C(41)	97.8(4)	C(43A)–P(4)–Cr(1)	106.2(4)
C(43A)–P(4)–C(41)	91.6(4)	C(43A)–P(4)–C(42)	112.1(5)
C(43B)–P(4)–Cr(1)	108.1(5)	C(43B)–P(4)–C(41)	111.8(6)
C(43B)–P(4)–C(42)	84.7(5)	P(4)–C(43A)–C(33)	109.0(6)
P(4)–C(43B)–C(33)	116.1(8)		
O(1)–C(1)–Cr(1)	176.8(4)	O(2)–C(2)–Cr(1)	179.0(4)

The ethylene complex has i.r. bands at 3 032, 3 020 (C–H), and 1 168 cm^{-1} (C=C) while the ^1H n.m.r. spectrum shows a broad band at 1.28 p.p.m. due to bound ethylene; the broadness of the peak, coupled with a peak at 5.24 p.p.m. due to free ethylene indicates dissociation and exchange broadening in solution at room temperature. The $^{31}P-\{^1H\}$ spectrum at −80 °C has a sharp singlet as expected for the *trans* configuration. Good quality crystals were obtained but due to crystallographic problems, presumably similar to those for the *cis*-$(N_2)_2$ complex, the structure was unresolvable.

The butadiene complex, which is very sensitive to oxygen even in the solid state, has three multiplets in the ^1H n.m.r. spectrum at 4.00, 0.81, and −1.75 p.p.m. assignable to η^4-C_4H_6,[11] while the $^{31}P-\{^1H\}$ spectrum has a broad singlet at 77.8 p.p.m. at room temperature.

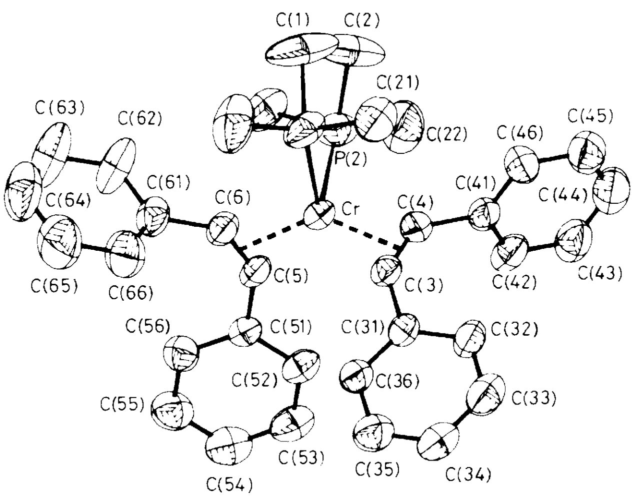

Figure 3. The structure of $Cr(PhC{\equiv}CPh)_2(dmpe)$

5. 1,2-*Bis(diphenylphosphino)ethanebis(diphenylacetylene)-chromium*(0).—Although traces of this acetylene complex were isolated in a photolysis reaction, it is readily obtained by interaction of the acetylene and *trans*-$Cr(N_2)_2(dmpe)_2$ on heating in hexane.

The *X*-ray structure is shown in Figure 3 and selected bond distances and angles in Table 3. The Cr–P distances are very similar to those found for the dinitrogen and carbonyl complexes. The difference between the two values, *ca.* 0.02 Å, may be due to steric interactions involving the acetylene carbon atoms since in the structure as found, the two groups of P ··· C contacts for the two P atoms are very similar indeed. There also exists a slight asymmetry in the bonding of the acetylene groups with one short [1.902(5), 1.886(5) Å] and one long [1.961(5), 1.980(5) Å] Cr–C bond to each group. Again, intermolecular steric factors may be responsible.

The bonding of the two acetylenes, which act as 4-electron donors, has occurred with substantial bending back of the attached phenyl groups [Ph–C≡C = 136.9(3)—141.3(3)°], and lengthening of the C≡C bonds to 1.307(5) and 1.310(5) Å. These features indicate significant contributions from the metallacyclopropenyl form of bonding for these ligands.

6. *Bis*[1,2-*bis(dimethylphosphino)ethane*]*tetrahydridochromium*(IV).—Interaction of a slurry of *trans*-$CrCl_2(dmpe)_2$ in light petroleum with two equivalents of LiBu^n under hydrogen produces an orange-red solution from which yellow crystals of $CrH_4(dmpe)_2$ may be isolated. Since the tetrahydride is also formed under argon, the complex probably results from initial formation of the n-butyl, followed by a β-hydride transfer with olefin elimination to give a dihydride which may abstract hydrogen from the solvent. The tetrahydride can also be obtained in quantitative yield by photolysis of $Cr(N_2)_2(dmpe)_2$ in hexane under hydrogen for *ca.* 5 min.

The compound is the first chromium(IV) hydrido-species and the first example of eight-co-ordinate Cr^{IV}.

The structure of this complex is shown in Figure 4, whilst selected bond lengths and angles are given in Table 4. The molecular geometry is dodecahedral, with the phosphorus atoms occupying the *B* sites and the hydrogens the *A* sites, and the structure corresponds to the D_{2d} isomeric form of a ML_2D_2 system (L = mono-, D = bi-dentate ligand). The chelation produces a small amount of distortion from the idealised geometry, with an intertrapezial plane angle of 82.9°. The groups making up the two trapezia [P(1),H(1),H(2),P(3)] and

Table 3. Bond lengths (Å) and angles (°) for $Cr(C_2Ph_2)_2(dmpe)$

P(1)–Cr(1)	2.280(3)	P(2)–Cr(1)	2.298(3)
C(3)–Cr(1)	1.902(5)	C(4)–Cr(1)	1.961(5)
C(5)–Cr(1)	1.886(5)	C(6)–Cr(1)	1.980(5)
C(1)–P(1)	1.831(7)	C(11)–P(1)	1.846(8)
C(12)–P(1)	1.815(6)	C(2)–P(2)	1.831(7)
C(21)–P(2)	1.820(6)	C(22)–P(2)	1.814(7)
C(2)–C(1)	1.484(9)		
C(4)–C(3)	1.307(5)	C(31)–C(3)	1.467(5)
C(41)–C(4)	1.461(5)	C(6)–C(5)	1.310(5)
C(51)–C(5)	1.459(5)	C(61)–C(6)	1.462(5)
C(32)–C(31)	1.389(5)	C(36)–C(31)	1.380(5)
C(33)–C(32)	1.373(6)	C(34)–C(33)	1.350(6)
C(35)–C(34)	1.374(6)	C(36)–C(35)	1.375(6)
C(42)–C(41)	1.385(6)	C(46)–C(41)	1.386(5)
C(43)–C(42)	1.383(6)	C(44)–C(43)	1.367(7)
C(45)–C(44)	1.346(7)	C(46)–C(45)	1.373(6)
C(52)–C(51)	1.386(5)	C(56)–C(51)	1.386(5)
C(53)–C(52)	1.364(6)	C(54)–C(53)	1.351(6)
C(55)–C(54)	1.379(6)	C(56)–C(55)	1.377(6)
C(63)–C(61)	1.386(6)	C(66)–C(61)	1.363(6)
C(63)–C(62)	1.385(7)	C(64)–C(63)	1.318(9)
C(65)–C(64)	1.356(8)	C(66)–C(65)	1.384(7)
P(2)–Cr(1)–P(1)	82.90(5)	C(3)–Cr(1)–P(1)	106.9(2)
C(3)–Cr(1)–P(2)	126.2(2)	C(4)–Cr(1)–P(1)	103.1(2)
C(4)–Cr(1)–P(2)	86.7(2)	C(4)–Cr(1)–C(3)	39.5(1)
C(5)–Cr(1)–P(1)	128.3(2)	C(5)–Cr(1)–P(2)	108.3(2)
C(5)–Cr(1)–C(3)	105.5(2)	C(5)–Cr(1)–C(4)	127.2(2)
C(6)–Cr(1)–P(1)	88.9(2)	C(6)–Cr(1)–P(2)	104.8(2)
C(6)–Cr(1)–C(3)	127.6(2)	C(6)–Cr(1)–C(4)	164.4(1)
C(6)–Cr(1)–C(5)	39.5(1)		
C(1)–P(1)–Cr(1)	111.1(3)	C(11)–P(1)–Cr(1)	123.2(3)
C(11)–P(1)–C(1)	105.2(4)	C(12)–P(1)–Cr(1)	112.9(2)
C(12)–P(1)–C(1)	101.7(3)	C(12)–P(1)–C(11)	100.3(3)
C(2)–P(2)–Cr(1)	109.6(3)	C(21)–P(2)–Cr(1)	114.8(3)
C(21)–P(2)–C(2)	101.9(3)	C(22)–P(2)–Cr(1)	125.2(3)
C(22)–P(2)–C(2)	103.2(4)	C(22)–P(1)–C(21)	99.1(3)
C(2)–C(1)–P(1)	110.1(4)	C(1)–C(2)–P(2)	110.4(5)
C(4)–C(3)–Cr(1)	72.7(3)	C(31)–C(3)–Cr(1)	149.6(2)
C(31)–C(3)–C(4)	137.5(3)	C(3)–C(4)–Cr(1)	67.8(3)
C(41)–C(4)–Cr(1)	155.1(2)	C(41)–C(4)–C(3)	136.9(3)
C(6)–C(5)–Cr(1)	74.1(3)	C(51)–C(5)–Cr(1)	144.4(2)
C(51)–C(5)–C(6)	141.3(3)	C(5)–C(6)–Cr(1)	66.3(3)
C(61)–C(6)–Cr(1)	155.9(2)	C(61)–C(6)–C(5)	137.7(3)
C(32)–C(31)–C(3)	121.4(4)	C(36)–C(31)–C(3)	121.3(4)
C(36)–C(31)–C(32)	117.3(4)	C(33)–C(32)–C(31)	120.6(4)
C(34)–C(33)–C(32)	121.2(4)	C(35)–C(34)–C(33)	119.4(5)
C(36)–C(35)–C(34)	119.8(4)	C(35)–C(36)–C(31)	121.6(4)
C(42)–C(41)–C(4)	119.2(4)	C(46)–C(41)–C(4)	123.4(4)
C(46)–C(41)–C(42)	117.4(4)	C(43)–C(42)–C(41)	120.6(5)
C(44)–C(43)–C(42)	120.1(5)	C(45)–C(44)–C(43)	120.2(5)
C(46)–C(45)–C(44)	120.3(5)	C(45)–C(46)–C(41)	121.4(5)
C(52)–C(51)–C(5)	119.9(4)	C(56)–C(51)–C(5)	121.9(4)
C(56)–C(51)–C(52)	118.3(4)	C(53)–C(52)–C(51)	120.3(4)
C(54)–C(53)–C(52)	120.6(4)	C(55)–C(54)–C(53)	121.2(4)
C(56)–C(55)–C(54)	118.2(4)	C(55)–C(56)–C(51)	121.4(4)
C(62)–C(61)–C(6)	122.5(4)	C(66)–C(61)–C(6)	121.1(4)
C(66)–C(61)–C(62)	116.4(5)	C(63)–C(62)–C(61)	120.4(6)
C(64)–C(63)–C(62)	121.6(6)	C(65)–C(64)–C(63)	120.0(5)
C(66)–C(65)–C(64)	119.3(6)	C(65)–C(66)–C(61)	122.3(6)

[P(2),H(3),H(4),P(4)] are themselves quite planar (sum of angles = 360.1° and 360.6° respectively).

The Cr–P distances, 2.252—2.258(3) Å are shorter than in the two octahedral complexes described above, and although this might be expected on account of the smaller radius of the Cr^{IV}

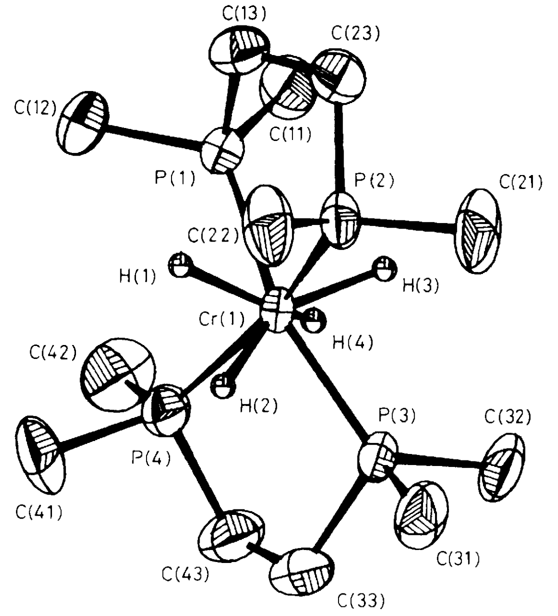

Figure 4. The structure of the eight-co-ordinate $CrH_4(dmpe)_2$

Table 4. Bond lengths (Å) and angles (°) for $CrH_4(dmpe)_2$

Cr(1)–P(1)	2.258(3)	Cr(1)–P(2)	2.252(3)
Cr(1)–P(3)	2.258(3)	Cr(1)–P(4)	2.252(3)
Cr(1)–H(1)	1.60(3)	Cr(1)–H(2)	1.56(3)
Cr(1)–H(3)	1.53(3)	Cr(1)–H(4)	1.59(4)
P(1)–C(11)	1.824(6)	P(2)–C(21)	1.827(6)
P(1)–C(12)	1.832(6)	P(2)–C(22)	1.825(6)
P(1)–C(13)	1.848(5)	P(2)–C(23)	1.860(6)
P(3)–C(31)	1.832(6)	P(4)–C(41)	1.830(7)
P(3)–C(32)	1.823(6)	P(4)–C(42)	1.839(6)
P(3)–C(33)	1.859(7)	P(4)–C(43)	1.849(7)
P(2)–Cr(1)–P(1)	84.80(5)	P(3)–Cr(1)–P(1)	159.00(5)
P(3)–Cr(1)–P(2)	99.80(5)	P(4)–Cr(1)–P(1)	98.40(5)
P(4)–Cr(1)–P(2)	157.90(5)	P(4)–Cr(1)–P(3)	85.10(5)
H(1)–Cr(1)–P(1)	67(1)	H(1)–Cr(1)–P(2)	78(1)
H(1)–Cr(1)–P(3)	134(1)	H(1)–Cr(1)–P(4)	84(1)
H(2)–Cr(1)–P(1)	132(1)	H(2)–Cr(1)–P(2)	84(1)
H(2)–Cr(1)–P(3)	68(1)	H(2)–Cr(1)–P(4)	78(1)
H(2)–Cr(1)–H(1)	65(2)	H(3)–Cr(1)–P(1)	77(1)
H(3)–Cr(1)–P(2)	71(1)	H(3)–Cr(1)–P(3)	85(1)
H(3)–Cr(1)–P(4)	131(1)	H(3)–Cr(1)–H(1)	134(2)
H(3)–Cr(1)–H(2)	140(2)	H(4)–Cr(1)–P(1)	85(1)
H(4)–Cr(1)–P(2)	135(1)	H(4)–Cr(1)–P(3)	77(1)
H(4)–Cr(1)–P(4)	68(1)	H(4)–Cr(1)–H(1)	137(2)
H(4)–Cr(1)–H(2)	133(2)	H(4)–Cr(1)–H(3)	64(2)
C(11)–P(1)–Cr(1)	120.3(2)	C(12)–P(1)–Cr(1)	122.3(3)
C(12)–P(1)–C(11)	99.6(3)	C(13)–P(1)–Cr(1)	109.9(2)
C(13)–P(1)–C(11)	101.9(3)	C(13)–P(1)–C(12)	99.2(3)
C(21)–P(2)–Cr(1)	123.7(3)	C(22)–P(2)–Cr(1)	119.7(2)
C(22)–P(2)–C(21)	100.7(4)	C(23)–P(2)–Cr(1)	109.1(2)
C(23)–P(2)–C(21)	98.5(3)	C(23)–P(2)–C(22)	101.2(3)
C(31)–P(3)–Cr(1)	123.8(3)	C(32)–P(3)–Cr(1)	120.1(2)
C(32)–P(3)–C(31)	99.1(3)	C(33)–P(3)–Cr(1)	109.3(2)
C(33)–P(3)–C(31)	99.2(3)	C(33)–P(3)–C(32)	101.6(4)
C(41)–P(4)–Cr(1)	119.5(3)	C(42)–P(4)–Cr(1)	123.8(3)
C(42)–P(4)–C(41)	99.9(4)	C(43)–P(4)–Cr(1)	109.3(2)
C(43)–P(4)–C(41)	103.2(4)	C(43)–P(4)–C(42)	97.4(3)

centre compared with Cr^0, competing factors would be the higher co-ordination number and fewer electrons available for back-bonding. These distances may therefore additionally reflect both the small steric influence of the hydrogen atoms (with a cone angle of *ca.* 64°) and the loss of two competing π-acceptor ligands (N_2 and CO).

It is interesting to compare this d^2 structure with that of the related molecule $ZrMe_4(dmpe)_2$ [12] which is also dodecahedral but which has the dmpe ligands bridging the two pairs of *A* sites leaving the methyl groups to occupy the *B* sites.

The i.r. and n.m.r. spectra are consistent with the structure determined by *X*-ray diffraction. There are Cr–H stretches in the i.r. spectrum at 1 757m, 1 725s, and 1 701m cm^{-1} while the ^1H n.m.r. spectrum shows a binomial quintet centred at −6.91 p.p.m. The proton-coupled ^{31}P n.m.r. spectrum also shows a binomial quintet at 78.8 p.p.m., J(P–H) = 56.1 Hz. Apart from slight broadening due to viscosity effects, there is no change in the ^{31}P spectrum on cooling to −80 °C suggesting non-rigidity in solution.

Experimental

Microanalyses were by Pascher, Bonn. All manipulations were performed under oxygen-free nitrogen or argon or *in vacuo*. All chemicals used were of reagent grade. Melting points were determined in sealed capillaries under argon. Solvents were dried over sodium (except dichloromethane, which was dried over P_2O_5) and distilled from sodium benzophenone under nitrogen immediately before use. The light petroleum used had b.p. 40—60 °C.

Spectrometers.—N.m.r.: JEOL FX-90Q (^{13}C, 22.51 MHz) and Bruker WM250 (^1H, 250 MHz; ^{31}P, 36.21 MHz). Data are given in δ (p.p.m.); ^1H and ^{13}C are referenced to $SiMe_4$ and ^{31}P to external 85% H_3PO_4 [*via* internal $P(OMe)_3$]; solvent C_6D_6 unless otherwise stated. I.r.: Perkin-Elmer 683; spectra (cm^{-1}) determined in Nujol mulls unless otherwise specified. Mass: V.G. Micromass 7070 and MS-9. Raman: SPEX 1401 double monochromator in conjunction with Coherent Radiation model CR500K krypton-ion laser; detection of the scattered radiation was by standard photon counting techniques employing RCA C31034 photomultipliers and an exciting line of 647 nm. Wavenumber measurements were calibrated by reference to the emission spectrum of neon. KBr discs were cooled to 80 K using a liquid-nitrogen dewar assembly. Photoelectron: ESCALAB Mark 2, V.G. Scientific.

Reactions requiring pressure were made in glass pressure bottles. Photolysis reactions were normally carried out at 0 °C in these bottles using a 250-W u.v. lamp.

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*bis*(*dinitrogen*)-*chromium*(0).—$CrCl_2(dmpe)_2$ [1,2] (4.01 g, 9.5 mmol) in nitrogen-saturated tetrahydrofuran (130 cm^3) was transferred to a glass pressure bottle containing sodium amalgam (5 equiv. Na per Cr) which had been cooled to −78 °C. The bottle was pressurised with nitrogen (5 atm) and the solution allowed to warm slowly to room temperature with stirring. After *ca.* 1 h the solution turned brown, eventually becoming orange-red after *ca.* 12 h. Excess nitrogen was vented and the solution allowed to stand for 1 h, then filtered and evaporated in vacuum. Extraction of the red-orange solid with light petroleum (70 cm^3), followed by filtration, concentration, and subsequent cooling to −20 °C produced red-orange *prisms* of the complex. Yield: 3 g, 77%, m.p. >350 °C [Found: C, 34.8; H, 7.9; N, 11.5; P, 29.0. $C_{12}H_{32}CrN_4P_4$ requires C, 35.3; H, 7.9; N, 13.7; P, 30.3%]. I.r. (hexane): 1 932 (N–N_{asym}) cm^{-1}. Raman (KBr disc): 2 001.65 (N–N_{sym}), 942.43 (Cr–P_{sym}), 408.35 cm^{-1} (Cr–N_{sym}). Electronic spectrum (light petroleum): $\lambda_{max.}$ 400s, 470br, 545w (sh) nm. N.m.r.: ^1H, 1.29 (br s, PMe_2 and PCH_2); ^{31}P-{^1H}, 69.3 (s).

cis-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dicarbonyl*-*chromium*(0).—*Method 1.* A solution of *trans*-$Cr(N_2)_2(dmpe)_2$ (*ca.* 0.3 g) in light petroleum (50 cm^3) was pressurised to 7 atm with CO; no reaction occurred over a period of several hours but upon irradiation the red solution rapidly turned pale yellow. Concentration of the solution and cooling to −20 °C afforded yellow prisms in quantitative yield, m.p. >350 °C [Found: C, 40.8; H, 7.8; P, 29.3. $C_{14}H_{32}CrO_2P_4$ requires C, 41.0; H, 7.9; P, 30.3%]. I.r.: 1 920w, 1 820s br, 1 755s br; in hexane, 1 820, 1 755 cm^{-1}. N.m.r.: ^1H, 1.65 [d, J(P–H) = 7.0 Hz, PMe_2], 1.35 (m, PCH_2), 1.22 [d, J(P–H) = 5.2 Hz, PMe_2], 1.08 [d, J(P–H) = 5.0 Hz, PMe_2], 0.72 [d, J(P–H) = 4.2 Hz, PMe_2]; ^{13}C-{^1H}, 33.0 ['quintet', J(P–C) = 8.6 Hz, PCH_2], 22.6 (s, PMe_2), 20.9 (s, PMe_2), 20.7 (s, PMe_2), 20.5 (s, PMe_2); ^{31}P-{^1H} (AA′BB′), 73.2 (A), 49.6 [B, 'J(A–B)' = 20.7 Hz].

Method 2. *trans*-$CrCl_2(dmpe)_2$ (0.5 g, 1.18 mmol) was dissolved in tetrahydrofuran (50 cm^3) and transferred *via* cannula to a pressure bottle containing excess sodium amalgam (1 g in 5 cm^3). The bottle was pressurised to 30 atm with CO and allowed to stir for several hours. The solvent was removed and the residue dissolved in light petroleum (30 cm^3); after filtering, the solution was concentrated to *ca.* 10 cm^3 and cooled to −20 °C to give the dicarbonyl in essentially quantitative yield.

Method 3. A solution of $CrMe_2(dmpe)_2$ [1,2] (0.35 g, 0.92 mmol) in benzene (10 cm^3) was transferred to a pressure bottle and treated with carbon monoxide (10 atm). After 12 h the solution had changed from orange to yellow; the excess CO was vented, the solution transferred to a flask, and the volatile material condensed under vacuum into a separate receiver. A ^1H n.m.r. spectrum of a portion of the condensate showed the presence of acetone (0.88 mmol, 96% yield, by integration *vs.* the benzene peak). The solid residue from the carbonylation reaction was extracted with light petroleum (50 cm^3), and the filtered extract concentrated to *ca.* 10 cm^3 and cooled to −20 °C to give pale yellow prisms of *cis*-$Cr(CO)_2(dmpe)_2$. Yield: 0.23 g, 62%.

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*bis*(*t-butyl isocyanide*)*chromium*(0).—To a solution of $CrCl_2(dmpe)_2$ (0.58 g, 1.37 mmol) in tetrahydrofuran (50 cm^3) was added t-butyl isocyanide (0.25 cm^3, 2.56 mmol), and the solution transferred *via* cannula to excess sodium amalgam (1 g in 5 cm^3). After 1 h, the red-yellow solution was decanted from the excess amalgam, the solvent removed, and the residue extracted with light petroleum (50 cm^3). The filtered extract was concentrated to *ca.* 10 cm^3, refiltered, and cooled to −20 °C to give red prisms of the complex. Yield: 0.19 g, 32% [Found: C, 50.3; H, 9.7; N, 5.3; P, 23.6. $C_{22}H_{40}CrN_2P_4$ requires C, 50.9; H, 9.7; N, 5.4; P, 23.9%]. I.r.: 2 085 (sh), 2 055vs cm^{-1}. N.m.r.: ^1H, 1.49 (s, PMe_2 and PCH_2), 1.12 (s, Me_3CNC); ^{13}C-{^1H}, 166.2 (s, $Me_3CN\mathit{C}$), 57.0 (s, $Me_3\mathit{C}NC$), 32.7 (s, PCH_2), 31.9 (s, Me_3CNC), 21.4 (m, $P\mathit{Me}_2$); ^{31}P-{^1H}, 71.8 (s).

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*]*bis*(*ethylene*)-*chromium*(0).—A solution of *trans*-$Cr(N_2)_2(dmpe)_2$ (0.3 g, 0.73 mmol) in hexane (50 cm^3) was pressurised with ethylene (5 atm) and warmed slowly with vigorous stirring. At *ca.* 75 °C the solution gradually changed from red to orange. The solution was filtered, concentrated, and cooled to −20 °C to give golden crystals. Yield: 0.3 g, 100%, m.p. 138 °C (decomp.) [Found: C, 46.5; H, 9.9; P, 30.4. $C_{16}H_{40}CrP_4$ requires C, 47.0; H, 9.9; P, 30.3%]. I.r.: 3 032m, 3 020 (sh) (C–H stretch), 1 168 cm^{-1} (C=C). N.m.r.: ^1H, 0.72 (s, PMe_2), 1.13 (s, PCH_2), 1.28 (br, C_2H_4), 5.24 (s, free C_2H_4); ^{31}P-{^1H}, 72.5 (s); ^{13}C-{^1H}, 35.0 (m, C_2H_4), 30.9 (m, PCH_2), 20.2 (s, PMe_2), 9.6 (s, PMe_2).

Table 5. Crystallographic data *

Compound	*trans*-$Cr(N_2)_2(dmpe)_2$	*cis*-$Cr(CO)_2(dmpe)_2$	$CrH_4(dmpe)_2$	$Cr(C_2Ph_2)_2(dmpe)$
Formula	$C_{12}H_{32}CrN_4P_4$	$C_{14}H_{32}CrO_2P_4$	$C_{12}H_{36}CrP_4$	$C_{34}H_{36}CrP_2$
M	408.297	408.276	356.288	558.61
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	7.575(1)	13.433(2)	3.396(2)	11.252(4)
b/Å	8.667(2)	17.754(3)	18.004(2)	19.045(11)
c/Å	9.091(1)	9.157(1)	12.522(3)	14.454(8)
α/°	103.80(1)	90	90	90
β/°	106.13(1)	99.18(2)	111.17(2)	92.55(4)
γ/°	103.58(1)	90	90	90
U/Å^3	527.01	2 155.9	1 975.3	3 094.3
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/n$
Z	1	4	4	4
D_c/g cm^{-3}	1.28	1.26	1.20	1.15
μ/cm^{-1}	7.83	7.70	8.24	4.46
$\theta_{min.}$, $\theta_{max.}$/°	1.5, 25.0	1.5, 25.0	1.5, 27.0	1.5, 25.0
Indices		$+h,k,l$	$+h,k,l$	$h,k,+l$
Total unique data	3 067	3 778	4 283	5 452
Total observed	2 674	2 896	3 122	3 356
Significance test	$I > 1.5\sigma(I)$	$I > 1.5\sigma(I)$	$I > 1.5\sigma(I)$	$I > 2\sigma(I)$
Number of parameters	161	311	298	478
Weighting factor, g	0.0005	0.0003	0.0003	0.0005
Final R	0.0243	0.0458	0.0355	0.041
Final R'	0.0254	0.0475	0.0341	0.044

* All measurements at 295 K except for the phenylacetylene complex, where T = 275 K.

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*](η^4-*buta*-1,3-*diene*)-*chromium*(0).—As for the ethylene complex but using excess buta-1,3-diene to give dark red crystals. Yield: *ca.* 100%. The compound is exceedingly air sensitive even in the solid state [m.p. 195 °C (decomp.)]; it decomposes at room temperature on standing so that we have been unable to obtain reliable analyses (mass spectrum: m/e = 406; required, 406.) N.m.r.: ^{1}H, 4.0 (m, C_4H_6), 1.29 (br s, PCH_2), 1.10 (s, PMe_2), 0.81 (m, C_4H_6), −1.75 (m, C_4H_6); ^{31}P-{^{1}H}, 77.8 (br s).

1,2-*Bis*(*dimethylphosphino*)*ethanebis*(*diphenylacetylene*)-*chromium*(0).—To $Cr(N_2)_2(dmpe)_2$ (0.22 g, 0.54 mmol) in light petroleum (30 cm^3) was added two equivalents of diphenylacetylene (0.19 g) in light petroleum (30 cm^3). After 1 h at 75 °C the solution which was dark red was filtered and cooled to −20 °C to yield dark red prisms. Yield: 0.15 g, 40%, m.p. 220 °C (decomp.) [Found: C, 72.0; H, 6.5; P, 11.0. $C_{34}H_{36}CrP_2$ requires C, 73.1; H, 6.5; P, 11.1%]. I.r.: 1 655 (C≡C), 1 589 cm^{-1} (Ph). N.m.r.: ^{1}H, 7.61 (s), 7.54 (s), 7.20 (m, Ph), 1.42 (d, PCH_2), 0.74 (d, PMe_2); ^{31}P-{^{1}H}, 93.0 (s).

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*]*tetrahydridochromium*-(IV).—*Method 1*. A slurry of finely crushed *trans*-$CrCl_2(dmpe)_2$ (0.82 g, 2 mmol) suspended in light petroleum (40 cm^3) was cooled to −78 °C in a pressure bottle and two equivalents of LiBu^n (2.5 cm^3 of 1.90 mol dm^{-3} solution in hexane) added. The bottle was pressurised with hydrogen (10 atm) and the mixture was allowed to warm slowly to room temperature with stirring. After stirring for several hours the red-orange solution was filtered, the solvent removed, and the solid extracted into light petroleum (*ca.* 20 cm^3) which was filtered, concentrated, and cooled to −20 °C for 24 h to give brown-yellow crystals which were collected and dried in vacuum. Yield: *ca.* 25%, m.p. 130 °C (decomp.) [Found: C, 40.7; H, 10.1; P, 34.0. $C_{12}H_{36}CrP_4$ requires C, 40.4; H, 10.2; P, 34.8%]. I.r.: 1 757m, 1 725s, 1 701m (Cr–H stretch) cm^{-1}. N.m.r.: ^{1}H, 1.23 (br s, PMe_2 + PCH_2), −6.91 [quin, J(P–H) = 56.1 Hz, Cr–H].

Method 2. Although a solution of *trans*-$Cr(N_2)_2(dmpe)_2$ (*ca.* 300 mg) in light petroleum (50 cm^3) under hydrogen pressure remains unchanged, upon irradiation at room temperature the red solution became pale yellow within 5 min. Concentration and cooling of the yellow solution produced yellow crystals in essentially quantitative yield.

Crystallography.—Crystals were sealed under argon in Lindemann capillaries. All crystallographic measurements were made using a CAD4 diffractometer, operating in the $\omega/2\theta$ scan mode with graphite monochromated Mo-K_α radiation (λ = 0.710 69 Å) in a manner previously described in detail.[13]

In each case an ω scan width given by $\omega = 0.8 + 0.35 \tan\theta$ was used, and scan times varied from 1.35 to 6.77° min^{-1}. The structures of the *trans*-dinitrogen, the carbonyl, the diphenylacetylene, and the hydride complexes were solved, developed, and refined *via* routine heavy-atom and least-squares methods using standard programs. In the case of the *trans*-dinitrogen complex, the structure was examined three times. From our first analysis,[1] which proceeded quite smoothly to an R value of 0.03, we arrived at a set of geometry parameters which were quite reasonable except for an unusually short N–N distance of 0.985(4) Å, for which we could offer no explanation. The Cr–N distance was 1.957(4) Å. Although our calculations indicated that the N–N distance was not a result of thermal motion shortening, we collected a second, restricted ($1.5 \leqslant \theta \leqslant 22°$) set of data at 193 K. Refinement on this data gave a set of parameters which included a more normal N–N distance of 1.122(4) Å, and a shortened Cr–N distance [1.878(3) Å]. Still unable to account for the first result, we recorded a third data set, again at room temperature, using another crystal. The results of refinement using this set are those reported now (see above) and include a perfectly normal N–N distance. We now consider that the erroneous results of the first room-temperature analysis were most probably due to a small amount of *trans*-$CrCl_2(dmpe)_2$ in the crystal selected. For the carbonyl complex the analyses and refinements proceeded normally except for problems in locating hydrogens on the carbons attached to one of the phosphorus atoms of one dmpe ligand. Indeed, the methylene carbon of this group [C(43)] was representable by two partial atoms (occupancies 0.6 and 0.4), and so we presume there to be rotational disorder in the Me groups. Otherwise hydrogen atoms were located experimentally

Table 6. Fractional atomic co-ordinates ($\times 10^4$) for *trans*-$Cr(N_2)_2(dmpe)_2$

Atom	x	y	z
Cr(1)	0	0	10 000
N(1)	−1 818(2)	1 059(1)	10 321(1)
N(2)	−2 871(2)	1 731(2)	10 524(2)
P(1)	932(1)	1 837(0.5)	8 700(0.5)
C(11)	−799(3)	2 391(3)	7 238(2)
C(12)	2 618(3)	1 527(3)	7 644(3)
C(13)	2 298(3)	3 947(2)	10 211(2)
P(2)	2 341(1)	2 053(0.5)	12 258(0.5)
C(21)	4 407(3)	1 682(3)	13 562(3)
C(22)	1 552(3)	3 208(3)	13 778(2)
C(23)	3 657(3)	3 786(2)	11 698(2)

Table 7. Fractional atomic co-ordinates ($\times 10^4$) for *cis*-$Cr(CO)_2(dmpe)_2$

Atom	x	y	z
Cr(1)	2 275(0.5)	1 413(0.5)	1 792(1)
P(1)	3 196(1)	2 047(1)	301(1)
C(11)	2 568(4)	2 798(3)	−872(6)
C(12)	3 844(5)	1 554(3)	−1 035(6)
C(13)	4 246(4)	2 576(3)	1 373(6)
P(2)	3 649(1)	1 718(1)	3 617(1)
C(21)	4 369(4)	1 068(4)	4 950(6)
C(22)	3 485(4)	2 497(3)	4 855(6)
C(23)	4 693(4)	2 094(3)	2 698(6)
P(3)	1 362(1)	810(1)	3 328(1)
C(31)	6(4)	946(4)	2 928(7)
C(32)	1 538(5)	955(4)	5 304(6)
C(33)	1 465(5)	−224(3)	5 283(7)
P(4)	2 811(1)	187(1)	1 397(2)
C(41)	4 095(4)	−176(3)	1 692(7)
C(42)	2 386(6)	−248(4)	−410(8)
C(43A)	2 459(7)	−426(5)	3 031(9)
C(43B)	1 923(11)	−476(7)	2 066(12)
C(1)	1 640(3)	2 271(2)	2 190(5)
O(1)	1 187(3)	2 810(2)	2 420(4)
C(2)	1 285(3)	1 281(2)	219(5)
O(2)	636(3)	1 201(2)	−784(4)

Table 8. Fractional atomic co-ordinates ($\times 10^4$) for $Cr(C_2Ph_2)_2(dmpe)$

Atom	x	y	z
Cr(1)	6 263(0.5)	2 542(0.5)	−513(0.5)
P(1)	4 404(1)	2 541(1)	55(1)
P(2)	6 469(1)	1 532(1)	350(1)
C(1)	4 260(4)	1 855(4)	930(4)
C(2)	5 009(5)	1 241(3)	708(4)
C(11)	3 713(4)	3 329(4)	545(4)
C(12)	3 259(4)	2 289(3)	−806(3)
C(21)	7 281(4)	1 683(3)	1 458(3)
C(22)	7 153(6)	726(3)	−33(4)
C(3)	6 067(3)	2 595(2)	−1 842(2)
C(4)	6 086(3)	1 930(2)	−1 602(2)
C(5)	7 553(3)	3 139(2)	−192(2)
C(6)	6 707(3)	3 309(2)	360(2)
C(31)	6 000(3)	3 018(2)	−2 673(2)
C(32)	5 585(3)	2 736(2)	−3 513(2)
C(33)	5 516(4)	3 142(2)	−4 299(3)
C(34)	5 869(4)	3 819(2)	−4 283(3)
C(35)	6 309(4)	4 108(2)	−3 467(3)
C(36)	6 353(4)	3 712(2)	−2 671(2)
C(41)	6 070(3)	1 259(2)	−2 091(2)
C(42)	7 102(4)	1 019(2)	−2 471(2)
C(43)	7 121(4)	378(2)	−2 922(3)
C(44)	6 116(5)	−25(2)	−2 996(3)
C(45)	5 099(4)	203(2)	−2 640(3)
C(46)	5 067(4)	839(2)	−2 195(3)
C(51)	8 747(3)	3 348(2)	−433(2)
C(52)	9 259(3)	3 050(2)	−1 195(2)
C(53)	10 376(3)	3 242(2)	−1 425(3)
C(54)	10 999(3)	3 722(2)	−915(3)
C(55)	10 534(3)	4 026(2)	−145(3)
C(56)	9 404(3)	3 835(2)	86(2)
C(61)	6 515(3)	3 825(2)	1 088(2)
C(62)	6 576(5)	3 652(3)	2 020(3)
C(63)	6 368(6)	4 157(4)	2 684(3)
C(64)	6 089(5)	4 808(3)	2 454(4)
C(65)	6 018(5)	4 999(3)	1 549(4)
C(66)	6 248(5)	4 506(3)	877(3)

Table 9. Fractional atomic co-ordinates ($\times 10^4$) for $CrH_4(dmpe)_2$

Atom	x	y	z
Cr(1)	2 133(0.5)	1 520(0.5)	2 141(0.5)
P(1)	3 320(1)	2 633(0.5)	2 451(1)
C(11)	3 815(6)	3 091(2)	3 838(4)
C(12)	5 087(5)	2 795(3)	2 183(5)
C(13)	2 089(4)	3 335(2)	1 471(4)
P(2)	85(4)	2 163(0.5)	1 014(1)
C(21)	−1 785(4)	2 124(3)	1 150(6)
C(22)	−468(5)	2 119(3)	−539(3)
C(23)	460(4)	3 173(2)	1 277(4)
P(3)	960(1)	501	2 478(1)
C(31)	−784(5)	103(3)	1 437(4)
C(32)	459(7)	452(3)	3 754(4)
C(33)	2 246(5)	−314(2)	2 683(4)
P(4)	4 212(1)	789(0.5)	2 598(1)
C(41)	4 847(7)	453(4)	1 464(6)
C(42)	6 066(5)	1 023(3)	3 701(6)
C(43)	3 867(5)	−78(2)	3 259(4)

and freely refined with isotropic thermal parameters. The refinements for the phenylacetylene complex and the hydride were completed without problems, with all the hydrogen atoms being located and refined isotropically.

Table 5 gives a summary of the relevant data for all the compounds studied crystallographically. Final atomic co-ordinates for the completed structures are given in Tables 6—9.

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References

1 G. S. Girolami, J. E. Salt, G. Wilkinson, M. Thornton-Pett, and M. B. Hursthouse, *J. Am. Chem. Soc.*, 1983, **105**, 5954.
2 G. S. Girolami, G. Wilkinson, M. Thornton-Pett, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, in the press.
3 J. Chatt, J. R. Dilworth, and R. L. Richards, *Chem. Rev.*, 1978, **78**, 589.
4 H. H. Karsch, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 56.
5 D. Sellman and G. Maisel, *Z. Naturforsch., Teil B*, 1972, **27**, 465.
6 Y. Uchida, T. Uchida, M. Hidai, and T. Kodama, *Acta Crystallogr., Sect. B*, 1975, **31**, 1197.
7 J. L. Graff, T. J. Sobieralski, M. S. Wrighton, and G. L. Geoffrey, *J. Am. Chem. Soc.*, 1982, **104**, 7526.
8 R. J. W. Thomas, G. S. Lawrence, and A. A. Diamantis, *Inorg. Chim. Acta*, 1978, **30**, L353.

9 J. A. Connor, G. K. McEwen, and C. J. Rix, *J. Chem. Soc., Dalton Trans.*, 1974, 589.

10 (*a*) C. D. Wood and R. R. Schrock, *J. Am. Chem. Soc.*, 1979, **101**, 542; (*b*) E. Carmona Guzman and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1978, 1139; G. S. Girolami, V. V. Mainz, R. A. Andersen, S. H. Volliner, and V. W. Day, *J. Am. Chem. Soc.*, 1981, **103**, 3953; (*c*) K. W. Chiu, R. A. Jones, G. Wilkinson, A. M. R. Galas, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1981, 2088; (*d*) H-F. Klein and H. H. Karsch, *Chem. Ber.*, 1976, **109**, 1453.

11 See, for example, S. S. Wreford and J. F. Whitney, *Inorg. Chem.*, 1981, **20**, 3918; M. Kotzian, C. G. Kreiter, G. Michael, and S. Ozkar, *Chem. Ber.*, 1983, **116**, 3637.

12 G. S. Girolami, G. Wilkinson, M. Thornton-Pett, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1984, 2789.

13 M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.

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