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Co-ordination Behaviour of Potentially Tridentate Diphosphinoamido Ligands: Synthesis and Crystal Structures of the Complexes $[CrCl\{N(CH_2CH_2PMe_2)_2\}_2]$, $[Cr_2Cl_3\{N(CH_2CH_2PMe_2)_2\}\{CH_2P(Me)CH_2CH_2NCH_2CH_2PMe_2\}]$ and $[Cr_2Cl_4\{N(CH_2CH_2PPr^i_2)_2\}_2]$ †

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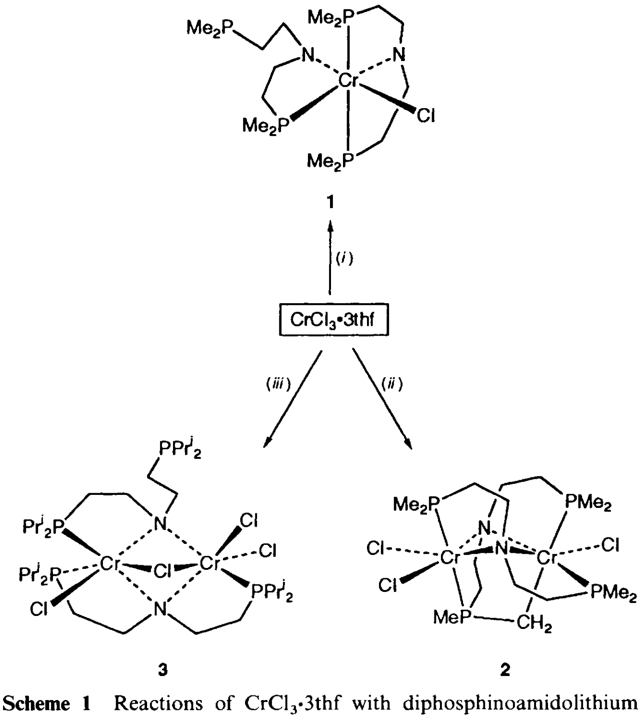
The reaction of $CrCl_3{\cdot}3thf$ (thf = tetrahydrofuran) with bis(2-dialkylphosphinoethyl)amidolithium reagents, $LiN(CH_2CH_2PR_2)_2$, resulted in the formation of the new compounds $[CrCl\{N(CH_2CH_2PMe_2)_2\}_2]$ **1**, $[Cr_2Cl_3\{N(CH_2CH_2PMe_2)_2\}\{CH_2P(Me)CH_2CH_2NCH_2CH_2PMe_2\}]$ **2** and $[Cr_2Cl_4\{N(CH_2CH_2PPr^i_2)_2\}_2]$ **3** depending on reaction conditions and stoichiometry. Thus, if 2 equivalents (per Cr) of $LiN(CH_2CH_2PMe_2)_2$ are used **1** may be isolated where chromium is bound to two amido ligands each in different co-ordination modes (bi- and tri-dentate). With 1.5 equivalents of $LiN(CH_2CH_2PMe_2)_2$, **2** is formed which has a binuclear structure with bridging amido ligands and an unusual α-metallated PCH_2 group. With the more bulky $LiN(CH_2CH_2PPr^i_2)_2$, **3** may be isolated in which a binuclear structure is bridged by both bi- and tri-dentate amido ligands. All complexes have been characterised by analysis, mass spectroscopy, and single-crystal X-ray crystallography.

Although chromium dialkylamides have been known for some time, there are few examples of ternary complexes also containing other ligands.[1] We have reported that the application of potentially tridentate diaminoamido and diphosphinoamido ligands to electropositive transition metals in Groups 4 and 5 has provided reactive ternary complexes.[2] Previously, the only other classes of partially substituted dialkylamido complexes for these metals were stabilised by bulky ligands which commonly render the complexes kinetically inert. Ligands of this type appear to be versatile and readily stabilise new unusual classes of metal amido complexes but their behaviour has not been explored and investigation of the co-ordination behaviour and properties of complexes of these ligands is of interest. In this paper we describe the reactions of $CrCl_3{\cdot}3thf$ (thf = tetrahydrofuran) with two different diphosphinoamido ligands and show that the outcome varies markedly as a result of changes in reaction conditions as well as the bulk of the tertiary phosphine donors.

Results and Discussion

Synthesis and Spectroscopy.—Details of the routes to the new compounds reported and diagrammatic representations of their structures are in Scheme 1.

$[CrCl\{N(CH_2CH_2PMe_2)_2\}_2]$ **1**. The reaction of $CrCl_3{\cdot}3thf$ with 2 mole equivalents of $LiN(CH_2CH_2PMe_2)_2$ results in dark brown solutions from which crude complex **1** may be isolated and recrystallised from cold light petroleum as brown-green paramagnetic prisms. The complex is stable for a long period under an inert atmosphere at room temperature and for a short period in air without significant apparent decomposition. The empirical formula was established by analysis as well as the mass spectrum in which the molecular parent-ion cluster centred at *m*/*z* 472 (3%) was observed. The most intense chromium-containing ion was $[M - N(CH_2CH_2PMe_2)_2]^+$ (*m*/*z* 280, 10.0%) while the base peak can be assigned to $[N(CH_2CH_2PMe_2)_2 - Me]^+$ (*m*/*z* 178, 100.0%). A peak at *m*/*z* 268 (2.3%) may be assigned to the ion $[CrCl_2Me\{N(CH_2CH_2PMe_2)_2 - PMe_2\}]^+$ and may be evidence of a methyl-migration reaction during the fragmentation of **1** in the mass spectrometer.



Scheme 1 Reactions of $CrCl_3{\cdot}3thf$ with diphosphinoamidolithium reagents. (*i*) 2 equivalents of $LiN(CH_2CH_2PMe_2)_2$ in toluene–Et_2O; (*ii*) 1.5 equivalents of $LiN(CH_2CH_2PMe_2)_2$ in toluene; (*iii*) 1 equivalent of $LiN(CH_2CH_2PPr^i_2)_2$ in thf

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

The ESR spectrum of complex **1** in frozen toluene shows a broad six-line pattern with no nitrogen or phosphorus superhyperfine structure. The absence of superhyperfine structure reduces the diagnostic value of the spectrum; ESR spectra of Cr^{3+} [^{53}Cr ($I = \frac{3}{2}$), 9.54%] complexes frequently show a strong central line with few distinct features.[3] The IR spectrum exhibited bands characteristic of Cr–Cl stretches (in the region 300–400 cm^{-1});[4] a band at 510 cm^{-1} can be assigned to ν(Cr–N) and a strong band at 485 cm^{-1} to ν(Cr–P).[5]

$[Cr_2Cl_3\{N(CH_2CH_2PMe_2)_2\}\{CH_2P(Me)CH_2CH_2NCH_2CH_2PMe_2\}]\cdot 0.5C_6H_5Me$ **2**. If less than 2 mole equivalents of $LiN(CH_2CH_2PMe_2)_2$ are treated with $CrCl_3\cdot 3thf$ in toluene a brown-red slurry results from which dark red prisms can be isolated. An X-ray diffraction study revealed that one phosphorus-bound methyl group is metallated to form a Cr–C σ bond, and that the complex crystallises as a 2 : 1 toluene solvate.

This metallation reaction presumably results from base abstraction of a proton from one P-methyl group of a co-ordinated $N(CH_2CH_2PMe_2)_2$ ligand. That it is not observed when a larger ligand to chromium ratio is used in the preparation of complex **1** is surprising. It may be that the rate of deprotonation becomes more favourable under these reaction conditions (*i.e.* less-polar solvent system) or alternatively the pseudo-octahedral d^3 chromium(III) centre in **1** is presumably kinetically inert and in the presence of sufficient amide it may be formed rapidly enough to render a competing deprotonation less significant. However, examples of deprotonation of alkyl groups adjacent to heteroatoms are numerous. In a closely related ligand system, Fryzuk *et al.*[6] observed that treatment of a hexane solution of $[MCl\{N(SiMe_2)CH_2PMe_2\}_2]$ (M = La or Lu) with LiPh affords a cyclometallated complex in which a methylene proton (β to phosphorus) was abstracted from the ligand backbone. The solid-state magnetic susceptibility of **2** (μ_{eff} = 2.9 μ_B) is again significantly lower than the theoretical spin-only value for a d^3 ion and may reflect some spin interaction by metal–metal bonding or by antiferromagnetic coupling *via* the bridging amido ligands.

Although no parent ion could be detected, the mass spectrum of complex **2** showed more chromium-containing fragments than for **1** or **3**, the peak at highest mass and the base peak corresponding to $[M - PMe]^+$ and $[CrCl\{N(CH_2CH_2PMe_2)_2\}]^+$ respectively. In addition, the base peaks observed in the mass spectra of the other complexes reported here were due to the species resulting from fragmentation of the organic ligands. Fragmentations with methyl migration from the ligand to the metal atoms were indicated by the peaks observed at *m/z* 309 $[CrClMe_2\{N(CH_2CH_2PMe_2)\}_2{}^+$, 2%] and 268 $[CrCl_2Me\{N(CH_2CH_2PMe_2)_2 - PMe_2\}^+$, 38%]. Fragments observed between *m/z* 194 and 47 are identical with those observed in the mass spectrum of the free amine $NH(CH_2CH_2PMe_2)_2$.

$[Cr_2Cl_4\{N(CH_2CH_2PPr^i_2)_2\}_2]$ **3**. With the more bulky $Li(NCH_2CH_2PPr^i_2)_2$, $CrCl_3\cdot 3thf$ reacts to give a dark slurry from which blue paramagnetic prisms of complex **3** could be obtained and recrystallised from a C_6H_5Me–Et_2O mixture. The complex was characterised by elemental analysis, solid-state magnetic susceptibility and a single-crystal X-ray structure analysis. Its paramagnetism is in accordance with the presence of two unpaired electrons (μ_{eff} = 2.7 μ_B) per chromium atom. This may indicate a direct orbital overlap between the two chromium(III) ions [Cr ··· Cr 2.811(3) Å] although antiferromagnetic spin pairing *via* bridging amido-nitrogens cannot be ruled out. The poor solubility of **2** and **3** at ambient temperature precluded accurate measurement of the magnetic susceptibility by Evans' method.[7] In the infrared spectrum, bands observed at 360, 340, 320 and 290 cm^{-1} can be assigned to Cr–Cl stretching vibrations.[4] Those at 540 and 475 cm^{-1} can be attributed to ν(Cr–N) and ν(Cr–P) respectively.

Although no parent molecular ion was observed, the mass spectrum of complex **3** showed a relatively intense group of peaks centred at *m/z* 462 (31%), 427 (79%), 390 (66%) and 346 (34%) corresponding to chromium-containing ions. The peak at highest mass may be assigned to $[M - \{Cl + N(CH_2CH_2PPr^i_2)_2\}]^+$ whereas the most abundant peak corresponds to $[M - \{2Cl + N(CH_2CH_2PPr^i_2)_2\}]^+$. The base peak observed at *m/z* 188 (100%) corresponds to $[N(CH_2CH_2PPr^i_2)_2 - PPr^i_2]^+$.

Crystal Structures.—Compound **1**. Fig. 1 shows the molecular structure of complex **1** with the atom labelling scheme. The crystal is composed of discrete monomeric molecules of formula $[CrCl\{N(CH_2CH_2PMe_2)_2\}]$ with six-co-ordinate chromium(III). The geometry around the chromium atom can be described as distorted octahedral with *cis* amido-nitrogen atoms. One of the two amide ligands is co-ordinated in a bidentate fashion, the other in a tridentate fashion with *trans* phosphine donors. The distortion of octahedral co-ordination around Cr, in respect of the deviation of bond angle from ideal values of 90 and 180°, and non-equivalence of chromium–ligand bond distances is not unexpected given the steric demands and the flexibility of the tridentate amido ligand.[8]

Relevant intramolecular bond distances and bond angles are listed in Table 1. The chromium–nitrogen bond lengths are non-equivalent: Cr–N(2) [1.996(2) Å] is shorter than Cr–N(1) [2.017(2) Å] by 10σ; Cr–N(2) is also significantly shorter than Cr–N distances in comparable tertiary amine complexes (see Table 2). The geometry of the amido nitrogen in the bidentate ligand is tending towards planarity [sum of angles around

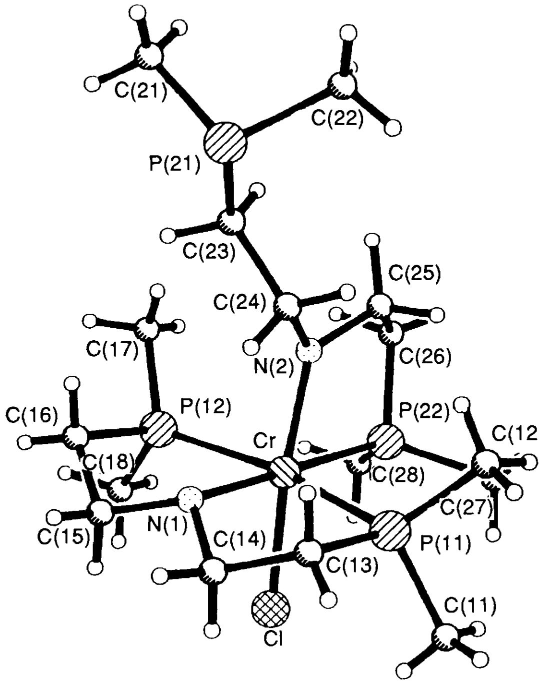

Fig. 1 Molecular structure and atom labelling scheme of $[CrCl\{N(CH_2CH_2PMe_2)_2\}_2]$ **1**

Table 1 Important bond distances (Å) and angles (°) in compound **1**

Cr–N(1)	2.017(2)	Cr–P(12)	2.444(1)
Cr–N(2)	1.996(2)	Cr–P(22)	2.429(1)
Cr–Cl	2.401(1)	$C–P_{co\text{-}ord}$	1.815 (average)
Cr–P(11)	2.435(1)	$C–P_{unco\text{-}ord}$	1.833 (average)
P(11)–Cr–P(12)	164.7(1)	C(25)–N(2)–Cr	122.4(1)
P(22)–Cr–N(1)	179.5(1)	C(25)–N(2)–C(24)	109.9(2)
Cl–Cr–N(2)	168.7(1)	C(24)–N(2)–Cr	122.6(2)
P(11)–Cr–N(1)	82.1(1)	C(22)–P(21)–C(21)	100.3(2)
P(12)–Cr–N(1)	82.6(1)	$C–P_{co\text{-}ord}–C$	102.7 (average)
P(22)–Cr–N(2)	80.4(1)		

Table 2 Comparison of important intramolecular parameters of selected chromium compounds

Compound[a]	Cr–P/Å	Cr–Cl(t)/Å	Cr–N/Å	Cr–C/Å	Chelate angle (°)	Ref.
1	2.429–2.444	2.401	1.996–2.017		81.7 (average)	This work
2	2.363–2.564	2.345–2.372	2.092–2.120	2.141–2.154	83.8	This work
3	2.483–2.558	2.306–2.330	2.054–2.101		83.3 (average)	This work
$[CrCl_3(tren)]$		2.303–2.325	2.08–2.1		83.3 (average)	10
$[CrCl_2(cyclam)]^+$		2.333–2.347	2.06–2.065		85.04, 94.96	11, *b*
$[Cr_2(PhNNNPh)_4]$			2.058–2.1			12
$[Cr(PhNNNPh)_3]$			2.000			12
$[(tren)Cr(\mu\text{-}CO_3)(\mu\text{-}OH)Cr(tren)]^{3+}$			2.061		82.95 (average)	13
$[Cr(en)_3][Co(CN)_6]$			2.08		81.81 (average)	14
$[CrCl_2(4\text{-}MeC_6H_4)]\cdot 3thf$		2.307–2.331		2.014		15(*a*)
$Cr[N(SiMe_3)_2]_2\cdot 2thf$			2.090			16
$CrPh_3\cdot 3thf$				2.06		15(*b*)
$[Cr(CH_2SiMe_3)_2(bipy)_2]^+$			2.103–2.156	2.107		15(*c*)
$[Cr_2Me_8]^{4-}$				2.199		17
$[Cr_2\{Me_2P(CH_2)_2\}_4]$				2.22		18
$[CrPh_2(bipy)_2]^+$			2.087–2.147	2.087	77.6, 77.65	19
$[Cr(2\text{-}MeOC_6H_4)(bipy)_2]^+$			2.071–2.156	2.101		20
$[CrMe_2(dmpe)_2]$	2.342–2.349			2.168	82.7	15(*c*)
$[CrCl_2(dmpe)_2]$	2.371–2.365	2.348			82.7	15(*c*)
$[Cr(CO)_3\{NEt(CH_2CH_2PPh)_2\}]$	2.375–2.387		2.31		81.9	21
$[Cr(CO)_3(tren)]$			2.1		83.5	22
$[Cr(py)_4F_2]PF_6$			2.09			23
$[Cr(py)_4][PF_6]_2\cdot py$			2.113			23
$[Cr(bipy)_3]^{3+}$			2.08		79.80	24
$Cr(NPr^i{}_2)_3$			1.87			9
$[CrCl_4\{(H_2N)_2C_6H_4\}]^-$		2.341–2.356	2.094–2.108		82.10	3(*c*)

[a] tren = Tris(2-aminoethyl)amine; cyclam = 1,4,8,11-tetrazacyclotetradecane; en = ethane-1,2-diamine; bipy = 2,2′-bipyridine; dmpe = $Me_2PCH_2CH_2PMe_2$; py = pyridine. [b] The first angle is the average for the five-membered chelates, the second the average for the six-membered chelates.

N(2) is 354.9°] whereas that in the tridentate ligand is more pyramidal [sum of angles around N(1) is 341.8°]. These observations are indicative of ligand-to-metal p_π–d_π bonding.[1,9] The puckering of the three chelate rings can be seen in Fig. 1; the carbons α to the amido nitrogen, N(2), of the tridentate ligand are both orientated away from the pendant phosphino donor attached to N(1). Compound **1** is then the first example of a bis(dialkylamido) complex with both a σ- and a π-bonded amido ligand in the same molecule, although there is one example of a dialkylphosphido complex exhibiting similar behaviour that has been structurally characterised.[25] It is also noteworthy that the Cr–Cl bond distance [2.401(1) Å] *trans* to N(2) is significantly longer than would be expected for terminal chromium chlorides; thus it appears that in this case the π-bonded amido ligand has a significant *trans* influence.

In spite of the obvious variation in the cone angles[26,27] and in the σ-donating ability[1,27] of $RPMe_2$, $RPPr^i{}_2$, $RPPh_2$, $RNEt_2$ and RNH_2 (R = alkyl), chelating angles are in the narrow range of 81.9–83.5° in five-membered rings for a series of complexes of aliphatic linear ligands, while in complexes with macrocyclic or aromatic diimine ligands they vary considerably due to constraints imposed by the chelate-ring size and ligand structure (see Table 2). The analogous angles formed by the tridentate ligand in complex **1** [P(12)–Cr–N(1) 82.6(1) and P(11)–Cr–N(1) 82.1(1)°] probably represent the ideal value for the chelating angles of five-membered aliphatic heterocyclic rings in chromium(III) complexes. However, the chelating angle [P(22)–Cr–N(2)] formed by the bidentate ligand is somewhat smaller [80.4(1)°], probably due to the relative shortening of the Cr–N(2) bond relative to Cr–N(1). Co-ordination of phosphine donors to the metal and the subsequent steric repulsion between the substituents on the phosphorus atom affects the geometries and bond lengths around the co-ordinated in comparison to the unco-ordinated phosphorus atoms. For example, the average P–C bond distance for the unco-ordinated P(21) is 1.833 Å, whereas the analogous value for the co-ordinated phosphine donors is 1.815 Å. The metal–phosphine bond distances are almost identical within experimental error and fall in the range 2.38–2.52 Å observed for comparable complexes.[27]

Compound **2**. The asymmetric unit of complex **2** comprises two crystallographically unrelated molecules (A and B) which exhibit only minor differences in molecular geometry, apparently due to crystal-packing forces, and one molecule of toluene. Molecule B is shown in Fig. 2; the atom numbering scheme in molecule A is similar. In both molecules, both six-co-ordinated chromium atoms are bridged by two amido-nitrogen atoms with Cr ··· Cr distances of 2.972(1) (molecule A) and 2.990(1) Å (B) (Table 3). Thus the co-ordination around each Cr atom can be described as octahedral, the octahedra sharing the N(1) ··· N(2) edge and distorted due to steric overcrowding and constraints imposed by the chelate rings.

A striking feature disclosed by the structure determination is the deprotonation of the methyl group, C(27), linked to P(22) and the formation of a carbon–chromium σ bond [C(27)–Cr(1) 2.141(6)–2.154(6) Å] and a unique phosphadichroma(III) heterocycle. Thus the tridentate amide containing C(27) becomes a dianionic tetradentate ligand, whereas the other amide ligand retains tridentate co-ordination. The conformations of the ligand backbone carbons enable the ligands to bridge the two metals in a 'helical' manner allowing approximate tetrahedral geometry around the bridging nitrogens and staggered terminal donors. This arrangement is very similar to that observed for the analogous phosphidodiphosphino ligand in $[Zr_2Cl_3\{P(CH_2CH_2PMe_2)_2\}_3]$.[2b] The chromium–phosphorus bond distances include two normal [Cr(1)–P(11) and Cr(2)–P(12) 2.410–2.498 Å], one slightly lengthened [Cr(1)–P(21) 2.548–2.564 Å], and one relatively short [Cr(2)–P(22) 2.363–2.388 Å]. The elongation of the Cr(1)–P(21) bond may result from the *trans* influence of C(27). The *trans* influence of σ-bonded carbon atoms (alkyl or aryl group) on the bond distances between chromium and *trans*-disposed oxygen- or nitrogen-bonded ligands is well documented.[15]

All chelating angles, except N(2)–Cr(2)–P(22), are identical within experimental error and fall in the expected range of

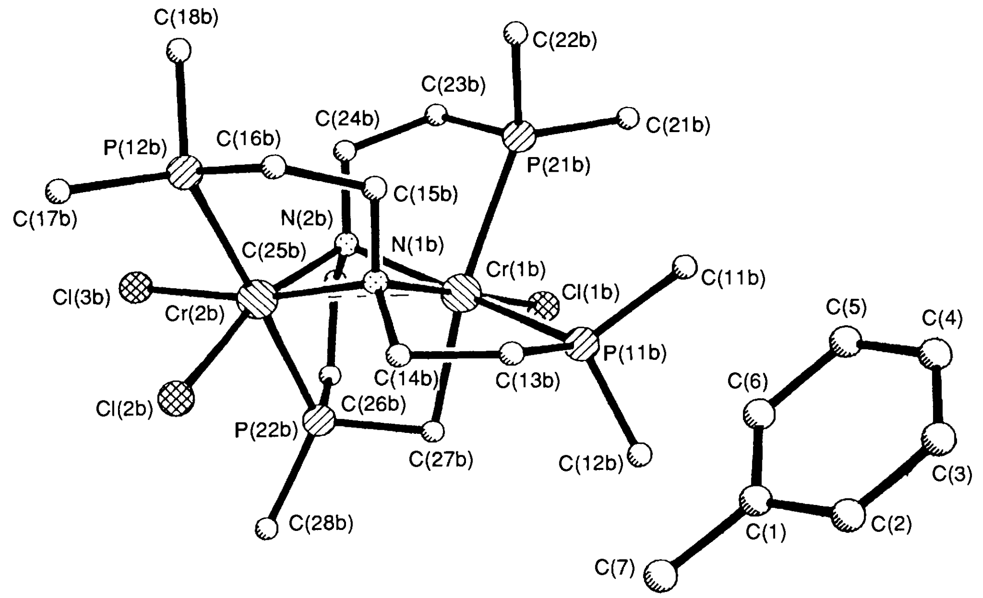

Fig. 2 Molecular structure and atom labelling scheme of $[Cr_2Cl_3\{N(CH_2CH_2PMe_2)_2\}\{CH_2P(Me)CH_2CH_2NCH_2CH_2PMe_2\}]\cdot 0.5C_6H_5Me$ **2**

Table 3 Important bond distances (Å) and angles (°) of two crystallographically independent molecules of complex **2**

	Molecule A	Molecule B
Cr(1)···Cr(2)	2.972(1)	2.990(1)
Cr(1)–P(11)	2.410(2)	2.423(2)
Cr(1)–P(21)	2.548(2)	2.564(2)
Cr(1)–N(1)	2.093(4)	2.093(5)
Cr(1)–N(2)	2.108(4)	2.099(5)
Cr(1)–Cl(1)	2.372(2)	2.365(2)
Cr(1)–C(27)	2.154(6)	2.141(6)
Cr(2)–P(12)	2.498(2)	2.473(2)
Cr(2)–P(22)	2.363(2)	2.388(2)
Cr(2)–N(1)	2.092(4)	2.106(5)
Cr(2)–N(2)	2.115(4)	2.120(5)
Cr(2)–Cl(2)	2.345(2)	2.348(2)
Cr(2)–Cl(3)	2.356(2)	2.346(2)
P(22)–C(27)	1.754(6)	1.768(6)
P(11)–Cr(1)–N(2)	166.6(1)	166.7(2)
P(21)–Cr(1)–C(27)	167.6(2)	167.3(2)
Cl(1)–Cr(1)–N(1)	177.7(1)	177.6(1)
P(22)–Cr(2)–P(12)	175.3(1)	175.0(1)
Cl(3)–Cr(2)–N(1)	171.6(1)	168.7(1)
Cl(2)–Cr(2)–N(2)	164.4(1)	164.5(2)
Cr(2)–P(22)–C(27)	103.8(2)	103.3(2)
Cr(2)–P(22)–C(28)	122.5(2)	126.5(3)
C(27)–P(22)–C(28)	114.8(3)	111.9(4)
Cr(1)–C(27)–P(22)	98.0(3)	98.8(3)
Cr(1)–N(1)–Cr(2)	89.9(2)	90.4(2)
Cr(1)–N(2)–Cr(2)	90.1(2)	90.6(2)
P(21)–Cr(1)–P(11)	95.5(1)	98.4(1)
N(1)–Cr(1)–P(11)	83.4(1)	83.5(1)
N(1)–Cr(2)–P(12)	83.8(1)	83.5(1)
N(2)–Cr(2)–P(22)	75.6(1)	75.5(1)
N(2)–Cr(1)–P(21)	84.5(1)	84.3(1)
N(1)–Cr(1)–N(2)	83.4(2)	83.3(2)
N(2)–Cr(2)–N(1)	83.3(2)	82.5(2)
C–P–C (average)*	99.5–102.8	98.8–102.1

* For co-ordinated phosphine functions.

81.7–84.0°. The combination of the narrow chelating angle involving P(22) [N(2)–Cr(2)–P(22) 75.6°], short P(22)–Cr(2) bond distance and the P(22)–C(27) bond distance of 1.754–1.768 Å intermediate between double P=C (1.66–1.74 Å) and single P–C (1.80–1.85 Å)[28] bond distances imply some ylidic character.[18] The average P–C bond distances and C_{Me}–P–C_{Me} bond angles, except those involving P(22), are similar to the corresponding parameters observed in compounds **1** and **2**.

Notwithstanding the differences in the σ-donating ability and the cone angles between $RPMe_2$ and $RPPr^i_2$, the substituents attached to the phosphorus atom have no influence upon the Cr–P bond lengths and chelating angles in agreement with the observations of Cotton[29] and Mason[8] and co-workers.

Compound **3**. A view of the molecular structure of complex **3** and atom labelling scheme is displayed in Fig. 3. The two chromium atoms are bridged by N(1), N(2) and Cl(12). The overall geometry of the dinuclear co-ordination centre can be regarded as a distorted face-sharing bioctahedron. Important bond distances and bond angles are given in Table 4. In addition, the molecular structure shows that the potentially tridentate amido ligands adopt two different chelating modes (tri- *vs.* bi-dentate) in the same molecule. The tridentate bridging ligand adopts a conformation similar to that in **2** with a staggered arrangement of terminal donors and an approximately tetrahedral amido nitrogen atom; the bidentate ligand has a puckered chelate ring and an approximately tetrahedral nitrogen where the C(25), N(2), C(24) plane is approximately orthogonal to the Cr(1), N(2), Cr(2) plane.

The metal–metal bond distance [2.811(3) Å] in complex **3**, and the solid-state paramagnetism (μ_{eff} = 2.7 μ_B), which is close to the expected value (2.83 μ_B) of the spin-only magnetic moment for two unpaired electrons, may be consistent with the formation of a Cr–Cr single bond. A comparison between selected structural parameters of **2** and **3** with the previously reported diamagnetic chromium(III) compound, $[Cr_2(\eta\text{-}C_5H_5)_2\{N(SiMe_3)\}_4]$[30] **4** is informative. Thus the Cr–Cr distance in **4** [2.569(4) Å] is significantly shorter than those in **2** (average 2.981 Å) and **3** [2.811(3) Å] and the angle N–Cr–N is significantly larger in **4** [average 94.0(1)°] than in **2** [average 85.7(4)°] and **3** (average 83.2°). This indicates that the relatively short Cr–Cr bond distance and the wider N–Cr–N angle in **4** may result from its higher Cr–Cr bond order than in **3**[31] and is then consistent with the paramagnetism observed for **2** and **3**. The effect of the metal–metal interaction on the angles subtended at the metal atom in a bridging frame (or complex core) of the binuclear complex has been previously used to prove or to dismiss the possible presence of a metal–metal interaction.[32]

Owing to steric crowding, there are significant deviations in Cr–P distances within complex **3** [Cr(2)–P(11) 2.483(4) Å

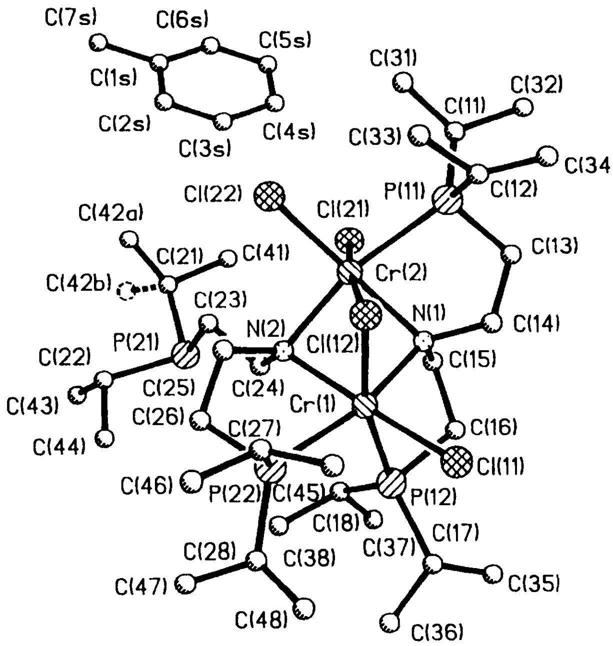

Fig. 3 Molecular structure and atom labelling scheme of $[Cr_2Cl_4\{N(CH_2CH_2PPr^i_2)_2\}_2]\cdot 0.5C_6H_5Me$ **3**

Table 4 Important bond distances (Å) and angles (°) for complex **3**

Cr(1)···Cr(2)	2.811(3)	Cr(2)–Cl(21)(t)	2.306(4)
Cr(1)–P(22)	2.507(4)	Cr(2)–Cl(22)(t)	2.323(4)
Cr(1)–P(12)	2.558(4)	Cr(2)–N(2)	2.100(9)
Cr(1)–N(1)	2.054(10)	Cr(2)–N(1)	2.101(9)
Cr(1)–N(2)	2.054(10)	Cr(2)–P(11)	2.483(4)
Cr(1)–Cl(1)(t)	2.330(4)	C–$P_{co\text{-}ord}$ (average)	1.843
Cr(1)–Cl(12)(b)	2.385(4)	C–$P_{unco\text{-}ord}$ (average)	1.866
Cr(2)–Cl(12)(b)	2.417(4)		
N(2)–Cr(1)–Cl(11)	172.3(3)	Cr(1)–Cl(12)–Cr(2)	71.7(1)
P(22)–Cr(1)–N(1)	167.8(3)	P(12)–Cr(1)–P(22)	102.5(1)
P(12)–Cr(1)–Cl(12)	165.5(1)	N(2)–Cr(1)–N(1)	86.3(4)
Cl(21)–Cr(2)–Cl(12)	172.2(1)	N(1)–Cr(2)–N(2)	85.2(4)
Cl(22)–Cr(2)–N(1)	173.6(3)	N(2)–Cr(1)–Cl(12)	81.0(3)
P(11)–Cr(2)–N(2)	165.8(3)	N(2)–Cr(2)–Cl(12)	80.3(3)
P(11)–Cr(2)–N(1)	83.6(3)	N(1)–Cr(2)–Cl(12)	80.2(3)
P(22)–Cr(1)–N(2)	82.6(3)	N(1)–Cr(1)–Cl(12)	81.9(3)
P(12)–Cr(1)–N(1)	85.2(3)	P(22)–Cr(1)–P(12)	102.5(1)
P(22)–Cr(1)–P(12)	102.5(1)	C–$P_{co\text{-}ord}$–C (average)	113.0
Cr(1)–N(1)–Cr(2)	85.1(3)	C–$P_{unco\text{-}ord}$–C	98.9(8)
Cr(1)–N(2)–Cr(2)	84.0(3)		

while Cr(1)–P(12) and Cr(1)–P(22) are 2.558(4) and 2.507(4) Å respectively] and the angle P(12)–Cr(1)–P(22) [102.5(1)°] deviates considerably from the ideal 90° in octahedral geometry. The chelating angles P(12)–Cr(1)–N(1) [85.2(3)°] and P(11)–Cr(2)–N(1) [83.6(3)°] formed by the same ligand and Cr(2) are similar to those observed in other chromium chelates with aliphatic linear ligands (see Table 2). Although there are small variations in Cr–N bond lengths (2.054–2.102 Å) within **3**, they compare favourably with other observed Cr–N distances.[1] As would be expected, the terminal Cr–Cl bond distances (2.306–2.330 Å) are shorter than the bridging Cr–Cl bond distances (2.385–2.417 Å). Although molecules of **3** occupy a general position, the structure contains a disordered toluene molecule on an inversion centre (Fig. 4).

Conclusion

Application of the potentially tridentate ligands $N(CH_2CH_2PR_2)_2^-$ (R = Me or Pr^i) to transition metals can lead to the isolation of new kinetically stabilised metal complexes containing halide or other functions. These materials are potentially versatile precursors for a range of studies. The co-ordination chemistry of these ligands is poorly understood. It is becoming clear that they are capable of stabilising complex stereochemistries which may be imposed by requirements of both the metal and the ligand. The versatility of these ligands gives access to new classes of complexes with unusual co-ordination properties. The effects of the variation of the ligand substituents (R) on the nature of the metal complex are apparently non-trivial; differences in relative kinetic stabilisation lead not only to differences in stereochemistries but also in degrees of substitution. These features are of value in the design of mono- and bi-metallic transition-metal complexes. Although $N(CH_2CH_2PR_2)_2^-$ and $N(SiMe_2CH_2PR_2)_2^-$ ligands appear to have comparable properties in mononuclear complexes, the former has allowed stabilisation and isolation of unusual dimeric complexes in which it bridges two metal centres, whereas no such dimeric complexes have yet been reported for the latter ligand despite the large number of d- and f-block element derivatives reported.[33] The lack of bridging derivatives of $N(SiMe_2CH_2PR_2)_2^-$ is likely due to the bulkiness of the $SiMe_2$ unit and its electronic influence on the nitrogen lone pair of electrons and metal–nitrogen bonding.[15] Further studies into the properties of complexes of these and related ligands are in progress.

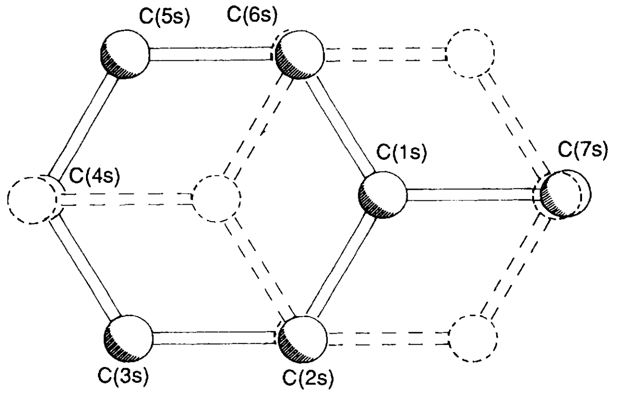

Fig. 4 Two-site occupancy for the disordered toluene molecule of solvation in compound **3**

Experimental

Synthetic Studies.—Manipulations throughout were performed using a vacuum atmospheres HE-43-2 glove-box or standard Schlenk techniques. The compounds $CrCl_3\cdot 3thf$,[34] $NH(CH_2CH_2PR_2)_2$ and $LiN(CH_2CH_2PR_2)_2$ (R = Me or Pr^i)[35] were prepared according to published methods; other reagents were obtained from commercial sources. All reactions involving secondary phosphines or 2-chloroethylamines were carried out in a well ventilated fume cupboard. Solvents were rigorously dried over an appropriate reagent and distilled under high-purity dinitrogen prior to use. Yields quoted are for the analytically pure isolated material based on the metal halides used, unless otherwise stated.

Instruments.—Solid-state IR spectra were obtained on a 577 Perkin Elmer grating spectrophotometer, 4000–200 cm^{-1}, as Nujol mulls using CsI plates and referenced to polystyrene (1601 cm^{-1}); absorptions are quoted in cm^{-1}. Mass spectra were performed on a VG Mass Lab. GC/MS instrument at the SERC Mass Spectrometry Centre, Swansea. Samples were introduced as solids. Only the most intense peak is quoted for each isotopometric cluster of ions. Melting and decomposition points were measured in sealed capillaries and are uncorrected. The ESR spectra were obtained on a Varian E109 X-band instrument at 9.4 GHz at low temperature (100 K)

Table 5 Crystal data and details of refinement of compounds **1–3** *

	1	**2**	**3**
Colour	Brown-green	Dark-red	Blue
Empirical formula	$C_{16}H_{40}ClCrN_2P_4$	$C_{16}H_{39}Cl_3Cr_2N_2P_4{\cdot}0.5C_7H_8$	$C_{32}H_{78}Cl_4Cr_2N_2P_4{\cdot}0.5C_7H_8$
M	471.8	639.8	906.8
Crystal size/mm	0.5 × 0.7 × 1.0	0.5 × 0.5 × 0.75	0.25 × 0.30 × 0.32
a/Å	10.215(4)	20.142(4)	13.817(5)
b/Å	11.774(3)	18.756(5)	13.892(5)
c/Å	20.767(10)	15.991(4)	24.696(8)
β/°	91.07(3)	95.67(2)	92.40(3)
U/Å^3	2497(2)	6012(3)	4736(3)
Z	4	8	4
D_c/g cm^{-3}	1.255	1.414	1.263
$F(000)$	1004	2664	1916
μ/mm^{-1}	0.824	1.214	0.845
2θ Range/°	3.0–45.0	3.0–44.0	3.0–42.0
Index ranges	$0 \leqslant h \leqslant 13, 0 \leqslant k \leqslant 15, -26 \leqslant l \leqslant 26$	$0 \leqslant h \leqslant 21, 0 \leqslant k \leqslant 21, -17 \leqslant l \leqslant 17$	$0 \leqslant h \leqslant 13, 0 \leqslant k \leqslant 14, -24 \leqslant l \leqslant 24$
Minimum/maximum transmission	0.4895, 0.5574	0.1370, 0.1900	0.6723, 0.7987
No. of unique reflections	5727	7405	4955
R_{int}	0.013	0.027	0.026
No. of obs. reflections, $I > 2\sigma(I)$	4273	5239	2828
Data-to-parameter ratio	11.3:1	9.5:1	8.8:1
ρ_{min}, ρ_{max}/e Å^{-3}	−0.27, 0.33	−0.35, 0.41	−0.75, 0.57
Maximum shift-to-error ratio	0.057	0.001	0.001
Weighting scheme parameter			
g in $w = 1/[\sigma^2(F) + gF^2]$	0.0003	0.0003	0.0004
R	0.034	0.044	0.076
R'	0.039	0.045	0.077
Goodness of fit	1.42	1.59	2.05

* Details in common: monoclinic, space group $P2_1/c$; ω scan range 0.60°; semiempirical absorption correction.

Table 6 Atomic coordinates (× 10^4) of compound **1**

Atom	x	y	z
Cr	1741(1)	2003(1)	1331(1)
Cl	968(1)	81(1)	1388(1)
P(11)	−234(1)	2529(1)	728(1)
P(12)	3934(1)	1358(1)	1649(1)
P(21)	4243(1)	6125(1)	490(1)
P(22)	931(1)	2301(1)	2410(1)
N(1)	2429(2)	1759(1)	437(1)
N(2)	2303(2)	3610(1)	1468(1)
C(11)	−1661(3)	1611(4)	747(2)
C(12)	−951(4)	3943(3)	743(2)
C(13)	401(3)	2392(3)	−82(1)
C(14)	1464(3)	1498(2)	−66(1)
C(15)	3520(3)	982(2)	379(1)
C(16)	4612(3)	1325(3)	846(1)
C(17)	5066(4)	2220(3)	2119(2)
C(18)	4237(5)	−57(3)	1968(3)
C(21)	5927(4)	6485(4)	733(2)
C(22)	3347(5)	7222(3)	917(2)
C(23)	3991(2)	4923(2)	1036(1)
C(24)	2665(2)	4349(2)	939(1)
C(25)	1869(3)	4282(2)	2005(1)
C(26)	1739(3)	3619(3)	2617(1)
C(27)	−808(3)	2534(4)	2526(2)
C(28)	1355(5)	1304(5)	3049(2)

in quartz tubes. Solid-state magnetic susceptibilities were measured on a Johnson-Matthey magnetic susceptibility balance at ambient temperature, and standardised against mercury tetrathiocyanatocobalate(II). Microanalyses were by CHN Analysis (Leicester, UK).

Preparations.—$[\mathrm{CrCl\{N(CH_2CH_2PMe_2)_2\}_2}]$ **1**. A solution of $\mathrm{LiN(CH_2CH_2PMe_2)_2}$ (1.035 g, 5.34 mmol) in toluene (20 cm^3) was slowly added to a cold (−78 °C) stirred suspension of $\mathrm{CrCl_3{\cdot}3thf}$ (1 g, 2.67 mmol) in toluene–$\mathrm{Et_2O}$ (7:1, 80 cm^3); after 15 min the mixture was allowed to warm to ambient temperature. After stirring (48 h), the solvents were removed *in vacuo* and the residue washed with cold (−78 °C) light petroleum (2 × 5 cm^3, b.p. 40–60 °C). Recrystallisation from cold (−20 °C) light petroleum gave brownish green prisms which were suitable for single-crystal X-ray diffraction. Overall yield: 0.6 g (46%), m.p. 120 °C. Analysis [calc. (found)] for $\mathrm{C_{16}H_{40}ClCrN_2P_4}$: C, 40.7 (40.9); H, 8.5 (8.5); N, 5.9 (6.1%). IR: 1525m, 1460vs, 1415m, 1405m, 1370s, 1340m, 1330m, 1310s, 1285m, 1275m, 1265m, 1260m, 1205s, 1180m, 1160s, 1140w, 1120(sh), 1095(sh), 1085vs, 1055m, 1040s, 995vs, 975m, 940vs, 915s, 900s, 850m, 825s, 800m(br), 765m, 730vs, 715vs, 660m, 595vw, 560s, 510(sh), 485vs, 440vs, 360m, 330s, 310m and 230m(br). Mass spectrum: *m/z* 472, M^+, 3; 434, $[M - \mathrm{Cl}]^+$, 2.5; 280, $[M - \mathrm{N(CH_2CH_2PMe_2)_2}]^+$, 10.0]; 268, $[\mathrm{CrCl_2Me\{N(CH_2CH_2PMe_2)_2 - PMe_2\}}]^+$, 2.3; 254, $[\mathrm{CrCl_2\{N(CH_2CH_2PMe_2)_2 - PMe_2\}}]^+$, 4.0; 238, $[\mathrm{CrCl_2\{N(CH_2CH_2PMe_2)_2 - (PMe_2 + Me)\}^+}]$, 2.1; 206, $[\mathrm{CrCl\{N(CH_2CH_2PMe_2)_2 - (PMe_2 + Me)\}}]^+$, 1.1; 194, $[\mathrm{N(CH_2CH_2PMe_2)_2}]^+$, 55.3; 178, $[\mathrm{N(CH_2CH_2PMe_2)_2 - Me}]^+$, 100; 150, $[\mathrm{N(CH_2CH_2PMe_2)_2 - PMe}]^+$, 3.4; 132, $[\mathrm{N(CH_2CH_2PMe_2)_2 - PMe_2}]^+$, 35.7; 118, $[\mathrm{N(CH_2CH_2PMe_2)_2 - CH_2PMe_2}]^+$, 28.1; 104, $[\mathrm{N(CH_2CH_2PMe_2)_2 - CH_2CH_2PMe_2}]^+$, 4.4; 89, $[\mathrm{N(CH_2CH_2PMe_2)_2 - NCH_2CH_2PMe_2}]^+$, 85.5; 75, $[\mathrm{CH_2PMe_2}]^+$, 10.2; 61, $[\mathrm{PMe_2}]^+$, 20.0; and 47, $[\mathrm{PMe}]^+$, 5.6%.

$[\mathrm{Cr_2Cl_3\{N(CH_2CH_2PMe_2)_2\}\{CH_2P(Me)CH_2CH_2NCH_2CH_2PMe_2\}}]{\cdot}0.5\mathrm{C_6H_5Me}$ **2**. A solution of $\mathrm{LiN(CH_2CH_2PMe_2)_2}$ (0.797 g, 4.00 mmol) in toluene (30 cm^3) was added to a suspension of $\mathrm{CrCl_3{\cdot}3thf}$ (1 g 2.67 mmol) in toluene (80 cm^3) with stirring at −78 °C. The reaction mixture was allowed to warm to ambient temperature and then stirred for 48 h. The resultant brownish red slurry was evaporated to dryness *in vacuo*. The residue was washed with $\mathrm{Et_2O}$ (20 cm^3) and then extracted with warm (60 °C) toluene (3 × 30 cm^3). On concentration and standing at −10 °C, the dark red toluene solution gave dark red prisms in 0.31 g (20%) yield, m.p. (decomp.) 230 °C. Analysis [calc. (found)] for $\mathrm{C_{16}H_{39}Cl_3Cr_2N_2P_4{\cdot}0.5C_7H_8}$: C, 36.6 (36.1); H, 6.7 (6.5); N, 4.4 (4.6%). Mass spectrum: M^+, not present; *m/z* 546, $[M - \mathrm{PMe}]^+$, 4; 508, $[M - (\mathrm{Me} + 2\mathrm{Cl})]^+$, 6; 470, $[\mathrm{CrCl\{N(CH_2CH_2PMe_2)_2\}}]^+$, 2; 449, $[M - (5\mathrm{Me} + 2\mathrm{Cl})]^+$, 5; 439, [Cr{N-

Table 7 Atomic coordinates (× 10^4) of compound **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cr(1A)	8 708(1)	5 326(1)	1 631(1)	Cr(1B)	3 533(1)	5 256(1)	2 825(1)
Cr(2A)	9 049(1)	3 977(1)	2 550(1)	Cr(2B)	4 676(1)	5 961(1)	2 095(1)
Cl(1A)	8 343(1)	5 587(1)	208(1)	Cl(1B)	3 200(1)	5 224(1)	4 201(1)
Cl(2A)	10 080(1)	3 783(1)	3 334(1)	Cl(2B)	5 427(1)	5 352(1)	1 318(1)
Cl(3A)	8 872(1)	2 760(1)	2 240(1)	Cl(3B)	5 426(1)	6 876(1)	2 528(1)
P(11A)	9 227(1)	6 460(1)	1 977(1)	P(11B)	3 039(1)	4 140(1)	2 316(1)
P(12A)	8 565(1)	3 828(1)	3 918(1)	P(12B)	4 385(1)	6 631(1)	778(1)
P(21A)	7 524(1)	5 740(1)	1 803(1)	P(21B)	2 464(1)	6 002(1)	2 613(1)
P(22A)	9 595(1)	4 116(1)	1 319(1)	P(22B)	5 002(1)	5 237(1)	3 295(1)
N(1A)	9 061(2)	5 071(2)	2 870(3)	N(1B)	3 868(2)	5 301(3)	1 628(3)
N(2A)	8 293(2)	4 294(2)	1 634(3)	N(2B)	4 012(3)	6 248(3)	2 976(3)
C(11A)	8 741(3)	7 247(3)	2 160(5)	C(11B)	2 139(3)	4 068(4)	2 055(5)
C(12A)	9 849(3)	6 798(3)	1 332(4)	C(12B)	3 236(4)	3 303(4)	2 852(5)
C(13A)	9 668(3)	6 248(3)	3 003(4)	C(13B)	3 405(4)	4 073(4)	1 318(4)
C(14A)	9 703(3)	5 435(3)	3 140(4)	C(14B)	3 992(3)	4 579(3)	1 293(4)
C(15A)	8 608(3)	5 217(3)	3 531(4)	C(15B)	3 433(3)	5 670(4)	960(4)
C(16A)	8 730(3)	4 728(3)	4 305(4)	C(16B)	3 808(3)	5 988(4)	264(4)
C(17A)	8 963(4)	3 212(4)	4 679(5)	C(17B)	5 042(4)	6 799(5)	112(5)
C(18A)	7 695(4)	3 684(4)	4 060(5)	C(18B)	3 921(4)	7 473(4)	693(5)
C(21A)	7 106(3)	6 388(4)	1 087(4)	C(21B)	1 761(3)	5 823(4)	3 218(5)
C(22A)	7 147(3)	5 964(4)	2 751(4)	C(22B)	2 001(3)	6 325(4)	1 646(4)
C(23A)	7 161(3)	4 885(3)	1 480(4)	C(23B)	2 879(3)	6 799(3)	3 083(4)
C(24A)	7 601(3)	4 291(3)	1 890(4)	C(24B)	3 571(3)	6 855(3)	2 740(4)
C(25A)	8 271(3)	3 902(3)	822(4)	C(25B)	4 341(4)	6 398(4)	3 825(4)
C(26A)	8 960(3)	3 848(3)	497(4)	C(26B)	4 848(3)	5 830(4)	4 141(4)
C(27A)	9 655(3)	5 043(3)	1 206(4)	C(27B)	4 359(3)	4 594(3)	3 274(4)
C(28A)	10 341(3)	3 628(3)	1 143(4)	C(28B)	5 816(3)	4 846(5)	3 567(5)
C(1)	2 664(4)	1 854(4)	203(4)	C(5)	1 638(4)	2 428(5)	430(5)
C(2)	2 289(4)	1 331(4)	−243(5)	C(6)	2 326(4)	2 402(4)	532(5)
C(3)	1 606(5)	1 379(4)	−334(5)	C(7)	3 402(4)	1 828(5)	309(5)
C(4)	1 297(4)	1 916(5)	6(5)				

$(CH_2CH_2PMe_2)_2\}_2]^+$, 7; 309, $[CrClMe_2\{N(CH_2CH_2PMe_2)_2\}]^+$, 2; 298, $[CrCl_2\{N(CH_2CH_2PMe_2)_2 - Me\}]^+$, 18; 280, $[CrCl\{N(CH_2CH_2PMe_2)_2\}]^+$, 100; 268, $[CrCl_2Me\{N(CH_2CH_2PMe_2)_2 - PMe_2\}]^+$, 38; 254, $[CrCl_2\{N(CH_2CH_2PMe_2)_2 - PMe_2\}]^+$, 42; 238, $[CrCl_2\{N(CH_2CH_2PMe_2)_2 - (PMe_2 + Me)\}]^+$, 13; 228, $[Cr\{N(CH_2CH_2PMe_2)_2 - Me\}]^+$, 16; 218, $[CrCl\{N(CH_2CH_2PMe_2)_2 - PMe_2\}]^+$, 43; 204, $[CrCl\{N(CH_2CH_2PMe_2)_2 - (PMe_2 + Me)\}]^+$, 16; 194, $N(CH_2CH_2PMe_2)_2{}^+$, 40; 178, $[N(CH_2CH_2PMe_2)_2 - Me]^+$, 9; 132, $[N(CH_2CH_2PMe_2)_2 - PMe_2]^+$, 74; 118, $[N(CH_2CH_2PMe_2)_2 - CH_2PMe_2]^+$, 60; 89, $[N(CH_2CH_2PMe_2)_2 - NCH_2CH_2PMe_2]^+$, 27; and 104, $[N(CH_2CH_2PMe_2)_2 - CH_2CH_2PMe_2]^+$, 3%.

$[Cr_2Cl_4\{N(CH_2CH_2PPr^i{}_2)_2\}_2]\cdot 0.5C_6H_5Me$ **3**. A solution of $LiN(CH_2CH_2PPr^i{}_2)_2$ (0.83 g, 2.67 mmol) in toluene (30 cm^3) was slowly added to a stirred suspension of $CrCl_3\cdot 3thf$ (1 g, 2.67 mmol) in thf (100 cm^3) held at −78 °C. The resulting dark slurry was warmed slowly to ambient temperature and stirred (24 h). The residue was evaporated and washed as above and extracted into toluene–Et_2O (6 : 1, 2 × 30 cm^3). After standing at ambient temperature for 12 h blue prisms were deposited. Overall yield 0.66 g (30%), m.p. 150 °C, $\mu_{eff} = 2.7\ \mu_B$. Analysis [calc. (found)] for $C_{32}H_{78}Cl_4Cr_2N_2P_4\cdot 0.5C_7H_8$: C, 47.0 (46.6); H, 9.0 (8.8); N, 3.1 (3.3%). IR: 3190m(br), 1730w, 1465vs, 1410m, 1380s, 1360w, 1255s, 1220m, 1190m, 1165m, 1090(sh), 1065s, 1035(sh), 960s, 930w, 890m(br), 830m, 725(sh), 705s, 655m(br), 630m, 540m(br), 475w, 430m, 360m, 340m, 320m and 290m. Mass spectrum: M^+ not present; m/z 462, $[M - \{Cl + N(CH_2CH_2PPr^i{}_2)_2\}]^+$, 31; 427, $[M - \{2Cl + N(CH_2CH_2PPr^i{}_2)_2\}]^+$, 79; 390, $[M - \{3Cl + N(CH_2CH_2PPr^i{}_2)_2\}]^+$, 66; 346, $[CrCl\{N(CH_2CH_2PPr^i{}_2)_2 - Pr^i\}]^+$, 34; 306, $N(CH_2CH_2PPr^i{}_2)_2{}^+$, 91; 273, $[N(CH_2CH_2PPr^i{}_2)_2 - (2Me + H)]^+$, 2; 262, $[N(CH_2CH_2PPr^i{}_2)_2 - Pr^i]^+$, 58; 220, $[N(CH_2CH_2PPr^i{}_2)_2 - 2Pr^i]^+$, 5; 188, $[N(CH_2CH_2PPr^i{}_2)_2 - PPr^i{}_2]^+$, 100; 174, $[N(CH_2CH_2PPr^i{}_2)_2 - CH_2PPr^i{}_2]^+$, 74; 160, $[N(CH_2CH_2PPr^i{}_2)_2 - CH_2CH_2PPr^i{}_2]^+$, 3; 145, $[CH_2CH_2PPr^i{}_2]^+$, 59; 117, $[PPr^i{}_2]^+$, 40; 102, $[CH_2CH_2PPr^i]^+$, 12; 89, $[CH_2PPr^i]^+$, 8; 75, $[PPr^i]^+$, 20; 61, $[PPr^i - CH_2]^+$, 5; and 43, Pr^{i+}, 29%.

X-Ray Single-crystal Diffraction Studies.—Single well defined crystals of complexes **1**–**3**, which appeared representative of the sample as a whole, were mounted inside thin-walled glass Lindemann capillaries and sealed under purified oxygen-free dry dinitrogen. These manipulations were performed on a double-fold vacuum-nitrogen line. Data were recorded at ambient temperature (293 K) on a Siemens P3m/V automated four-circle diffractometer using Mo-Kα radiation (λ = 0.710 73 Å) and Wyckoff (limited ω) scan technique. During data collection three standard reflections were remeasured every 97 and no significant fluctuations in their intensities were observed. All calculations were carried out on a DEC μ-VaxII computer using the SHELXTL PLUS system of programs.[36] Crystal data, details of the experiment, structure solution and refinement are presented in Table 5. After the initial atomic coordinates of the chromium atoms were derived by direct methods, the remaining non-hydrogen atoms were located from a series of least-squares refinement cycles followed by Fourier difference maps. All non-hydrogen atoms in **1**, **2** and (except for the disordered ones) in **3** were refined with anisotropic thermal parameters. In **1** all hydrogens atoms were refined independently in isotropic approximation; for **2** and **3** all hydrogen atoms were treated by a riding model (in calculated positions). For compound **2** the structural study revealed that the asymmetric unit contains two crystallographically independent, discrete dinuclear chromium molecules together with one molecule of toluene. That of **3** revealed a solvate molecule of toluene which is situated at an inversion centre and disordered over two symmetrically related positions (see Fig. 4). In the molecule of **3**, one methyl carbon atom, C(42) of an isopropyl group on P(21), is disordered over two positions [C(42a) and C(42b)] with equal occupancy factors (50%), as was confirmed by their independent refinement. These atoms were refined in isotropic approximation and the toluene molecule was treated as a rigid

Table 8 Atomic coordinates (× 10^4) of compound **3**

Atom	*x*	*y*	*z*
Cr(1)	4 432(1)	1 950(1)	1 930(1)
Cr(2)	5 713(1)	599(2)	1 507(1)
Cl(11)	2 875(2)	1 722(3)	2 234(2)
Cl(12)	5 013(2)	539(2)	2 387(1)
Cl(21)	6 168(2)	639(3)	620(1)
Cl(22)	7 225(2)	80(3)	1 835(2)
P(11)	5 091(3)	−1 052(3)	1 322(2)
P(12)	3 569(3)	3 155(3)	1 293(2)
P(21)	7 464(3)	3 681(3)	659(2)
P(22)	4 981(3)	2 990(3)	2 714(2)
N(1)	4 284(6)	1 007(7)	1 291(4)
N(2)	5 900(7)	2 041(7)	1 744(4)
C(11)	5 632(9)	−1 774(10)	785(6)
C(12)	4 823(14)	−1 849(12)	1 908(7)
C(13)	3 912(8)	−700(9)	1 039(5)
C(14)	3 578(8)	200(8)	1 331(5)
C(15)	4 078(9)	1 488(9)	757(5)
C(16)	3 225(9)	2 203(9)	800(5)
C(17)	2 411(11)	3 693(11)	1 518(7)
C(18)	4 212(9)	4 036(9)	858(5)
C(21)	8 418(13)	3 096(14)	266(7)
C(22)	8 258(14)	4 491(12)	1 100(7)
C(23)	7 243(9)	2 710(9)	1 155(5)
C(24)	6 188(8)	2 719(9)	1 314(5)
C(25)	6 533(8)	2 215(9)	2 240(5)
C(26)	6 228(8)	3 111(9)	2 531(5)
C(27)	5 094(10)	2 373(10)	3 366(5)
C(28)	4 468(10)	4 195(11)	2 794(7)
C(31)	6 656(12)	−2 049(13)	918(7)
C(32)	5 007(11)	−2 538(11)	533(6)
C(33)	5 722(12)	−2 027(13)	2 264(7)
C(34)	4 146(15)	−2 562(16)	1 854(9)
C(35)	1 587(15)	3 586(16)	1 117(9)
C(36)	2 464(13)	4 708(13)	1 715(8)
C(37)	3 584(11)	4 454(12)	385(6)
C(38)	4 698(11)	4 840(11)	1 175(6)
C(41)	7 899(13)	2 397(13)	−126(7)
C(42A)	9 264(26)	2 643(25)	503(14)
C(42B)	9 047(29)	3 730(31)	44(16)
C(43)	8 649(19)	5 254(20)	736(11)
C(44)	7 647(14)	5 006(14)	1 496(9)
C(45)	4 142(10)	1 877(11)	3 539(6)
C(46)	5 566(11)	2 952(11)	3 827(6)
C(47)	5 116(13)	4 963(13)	2 965(7)
C(48)	3 522(10)	4 169(11)	3 074(6)
C(1S)	10 482	105	4
C(2S)	9 910	393	427
C(3S)	8 925	169	413
C(4S)	8 512	−343	−24
C(5S)	9 084	−631	−447
C(6S)	10 069	−407	−433
C(7S)	11 544	347	20

body (fixed). All attempts to improve the thermal parameters of the carbon atoms of the isopropyl groups and toluene during the refinement of the structure were unsuccessful. The relatively high thermal displacement factors of the carbon atoms of other isopropyl groups in **3** are probably due to positional disorder. Atomic coordinates for compounds **1**–**3** are given in Tables 6–8 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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