Diphosphine and Diarsine Complexes of Chromium(III). Crystal and Molecular Structure of $[NPr^n_4][Cr(cis\text{-}Ph_2PCHCHPPh_2)Cl_4]$ †

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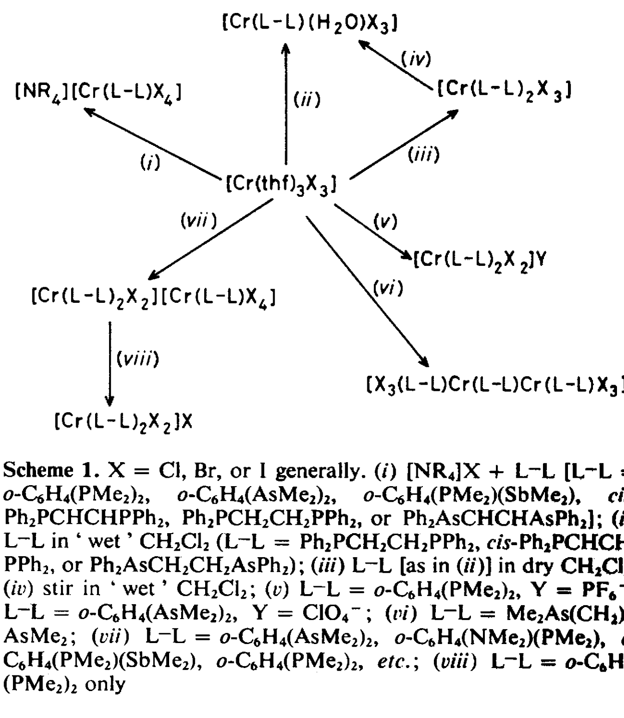
cis-$[Cr(L\text{-}L)X_4]^-$ ions (X = Cl, Br, or I; L–L = diphosphine or diarsine) have been isolated as tetra-alkylammonium salts by reaction of $[NR_4]X$, $[Cr(thf)_3X_3]$ (thf = tetrahydrofuran), and L–L. The reaction of $[Cr(thf)_3X_3]$ with L–L' in CH_2Cl_2 gave $Cr(L\text{-}L')_{1.5}X_3$ [L–L' = *o*-$C_6H_4(AsMe_2)_2$, *o*-$C_6H_4(AsMe_2)(PMe_2)$, *o*-$C_6H_4(NMe_2)(PMe_2)$, or *o*-$C_6H_4(PMe_2)(SbMe_2)$], which are formulated as *trans*-$[Cr(L\text{-}L')_2X_2]$*cis*-$[Cr(L\text{-}L')X_4]$. In the case of *o*-$C_6H_4(PMe_2)_2$ only, it is possible to isolate both $Cr[o\text{-}C_6H_4(PMe_2)_2]_{1.5}X_3$ and $[Cr\{o\text{-}C_6H_4(PMe_2)_2\}_2X_2]X$ depending upon the Cr : L–L ratio. The ligand $Me_2As(CH_2)_3AsMe_2$ gave $Cr(L\text{-}L)_{1.5}X_3$ (X = Cl or Br) complexes for which a ligand-bridged structure is proposed $[X_3(L\text{-}L)Cr(L\text{-}L)Cr(L\text{-}L)X_3]$. Weaker donors ($Ph_2PCH_2CH_2PPh_2$, *cis*-$Ph_2PCHCHPPh_2$, or $Ph_2AsCH_2CH_2AsPh_2$) react with $[Cr(thf)_3X_3]$ to give $[Cr(L\text{-}L)_2X_3]$ which contain one uni- and one bi-dentate diphosphine or diarsine, and in the presence of moisture $[Cr(L\text{-}L)(H_2O)X_3]$ can be isolated. The complexes $[Cr(L\text{-}L)_2X_2]Y$ [X = Cl or Br; Y = ClO_4^- or PF_6^-; L–L = *o*-$C_6H_4(AsMe_2)_2$ or *o*-$C_6H_4(PMe_2)_2$] have also been obtained The complexes have been characterised by analysis, conductance, i.r. and electronic spectroscopy, and the electronic spectra analysed (d^3) to produce *Dq*, *B'*, and β_{35}. The title complex is triclinic, a = 17.534(3), b = 11.930(2), c = 11.108(3) Å, α = 116.30(2), β = 75.12(2), γ = 110.61(1)°, and Z = 2; space group $P\bar{1}$ (no. 2). 1 757 Reflections were refined to R = 0.0656 (R' = 0.0658). The structure consists of tetrahedral $NPr^n_4{}^+$ cations, and pseudo-octahedral $[Cr(Ph_2PCHCHPPh_2)Cl_4]^-$ anions. In the anion Cr–P = 2.485(4) and 2.511(4) Å; Cr–Cl = 2.331(4), 2.319(4), 2.318(4), and 2.316(4) Å; P–Cr–P = 81.2°. The diphosphine does not exert any *trans* influence, consistent with weak binding to the hard Cr^{III} ion.

There are few reported [1-5] complexes of chromium(III) with bidentate phosphines or arsines, and only the *o*-phenylenebis-(dimethylarsine) complexes $[Cr\{o\text{-}C_6H_4(AsMe_2)_2\}_2X_2]ClO_4$, $Cr\{o\text{-}C_6H_4(AsMe_2)_2\}_{1.5}X_3$ and $[\{Cr[o\text{-}C_6H_4(AsMe_2)_2]X_3\}_n]$ (X = Cl, Br, or I) have received more than cursory study. Since *o*-$C_6H_4(AsMe_2)_2$ is in many respects an atypical soft donor, we have examined the complexes formed by various types of diphosphines and diarsines, which in addition to their intrinsic interest, are relevant to a study of the ability of early transition metal complexes to bind small molecules (*e.g.* O_2 or SO_2). A preliminary account of some of this work has appeared [6] in which it was shown that the compounds $Cr\{o\text{-}C_6H_4(AsMe_2)_2\}_{1.5}X_3$ should be formulated $[Cr\{o\text{-}C_6H_4(AsMe_2)_2\}_2X_2][Cr\{o\text{-}C_6H_4(AsMe_2)_2\}X_4]$. We have described elsewhere [7] the synthesis of chromium(III) complexes of multidentate phosphines and arsines (L) of the type $[CrLX_3]$, which have P_3X_3 or As_3X_3 donor sets, and $[CrL'X_2]BF_4$ {L' = $P(CH_2CH_2PPh_2)_3$, $As(CH_2CH_2CH_2AsMe_2)_3$, or $[\text{-}CH_2P(Ph)CH_2CH_2PPh_2]_2$}.



Scheme 1. X = Cl, Br, or I generally. (*i*) $[NR_4]X$ + L–L [L–L = *o*-$C_6H_4(PMe_2)_2$, *o*-$C_6H_4(AsMe_2)_2$, *o*-$C_6H_4(PMe_2)(SbMe_2)$, *cis*-$Ph_2PCHCHPPh_2$, $Ph_2PCH_2CH_2PPh_2$, or $Ph_2AsCHCHAsPh_2$]; (*ii*) L–L in 'wet' CH_2Cl_2 (L–L = $Ph_2PCH_2CH_2PPh_2$, *cis*-$Ph_2PCHCHPPh_2$, or $Ph_2AsCH_2CH_2AsPh_2$); (*iii*) L–L [as in (*ii*)] in dry CH_2Cl_2; (*iv*) stir in 'wet' CH_2Cl_2; (*v*) L–L = *o*-$C_6H_4(PMe_2)_2$, Y = PF_6^-; L–L = *o*-$C_6H_4(AsMe_2)_2$, Y = ClO_4^-; (*vi*) L–L = $Me_2As(CH_2)_3AsMe_2$; (*vii*) L–L = *o*-$C_6H_4(AsMe_2)_2$, *o*-$C_6H_4(NMe_2)(PMe_2)$, *o*-$C_6H_4(PMe_2)(SbMe_2)$, *o*-$C_6H_4(PMe_2)_2$, *etc.*; (*viii*) L–L = *o*-$C_6H_4(PMe_2)_2$ only

Results and Discussion

Chromium(III) forms a variety of complexes with bidentate phosphorus or arsenic donor ligands (Scheme 1), the type(s) obtained being dependent upon the ligand involved, but independent of the halide (Cl, Br, or I) present. It is convenient to discuss the different types separately.

$[NR_4][Cr(L\text{-}L)X_4]$ (L–L = *Diphosphine or Diarsine*; X = Cl, Br, *or* I).—This type of complex was obtained with most ligands studied, by reaction of $[NR_4]X$, L–L, and $[Cr(thf)_3X_3]$ [8] (thf = tetrahydrofuran) in a 1 : 1 : 1 ratio in dry CH_2Cl_2 (Table 1). These are rare examples of substituted halogeno-anions of the 3*d* transition metals. Attempts to isolate analytically pure complexes with *o*-$C_6H_4(NMe_2)(PMe_2)$, *o*-$C_6H_4(AsMe_2)(NMe_2)$, or *o*-$C_6H_4(SMe)_2$ failed due to the extremely moisture-sensitive nature of the products. $[NBu^n_4][Cr\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}Cl_4]$, containing the first example of a Cr^{III}–Sb linkage, was prepared. The isolated complexes

† Tetra-n-propylammonium [*cis*-1,2-bis(diphenylphosphino)-ethylene]tetrachlorochromate(III).

Supplementary data available (No. SUP 23736, 15 pp.): calculated H-atom co-ordinates, atomic thermal parameters, observed and calculated structure factors. See Instructions for Authors, Section 4.0, *J. Chem. Soc., Dalton Trans.*, 1983, Issue 3, p. xvii.

Table 1. Analytical and physical data

		Analysis [a] (%)					
Complex	Colour	C	H	N	X [b]	Λ_M [c]	ν(CrX) [d]/cm^{-1}
$[NPr^n_4][Cr\{o\text{-}C_6H_4(PMe_2)_2\}Cl_4]$	Purple	45.3 (45.6)	7.9 (7.6)	2.2 (2.4)	24.3 (24.6)	122	355m, 330s, 305 (sh)
$[NPr^n_4][Cr\{o\text{-}C_6H_4(AsMe_2)_2\}Cl_4]$	Blue	39.4 (39.6)	6.1 (6.6)	2.0 (2.1)	21.8 (21.3)	61	358 (sh), 333m, 325s, 312 (sh)
$[PPh_3(CH_2Ph)][Cr\{o\text{-}C_6H_4(AsMe_2)_2\}Br_4]$	Blue	41.8 (41.5)	3.6 (3.8)	—	30.9 (31.7)	89	312m, 285s, 258s
$[NBu^n_4][Cr\{o\text{-}C_6H_4(AsMe_2)_2\}I_4]$	Yellow-green	30.3 (30.1)	5.0 (5.0)	1.5 (1.5)	—	decomp.	—
$[NBu^n_4][Cr\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}Cl_4]$	Blue	43.2 (43.0)	7.0 (7.2)	2.6 (1.9)	—	70	354, 326s, 302s
$[NPr^n_4][Cr\{Me_2As(CH_2)_3AsMe_2\}Cl_4]\cdot H_2O$	Blue	34.9 (35.0)	7.5 (7.4)	2.1 (2.2)	21.0 (21.8)	49	326s, 319s
$[NPr^n_4][Cr(Ph_2PCHCHPPh_2)Cl_4]$	Purple	58.4 (58.7)	6.7 (6.4)	1.9 (1.8)	17.9 (18.3)	100	340s, 315s
$[NBu^n_4][Cr(Ph_2PCHCHPPh_2)Br_4]$	Blue	50.0 (49.9)	5.6 (5.7)	1.5 (1.4)	—	103	284s, 259s, 250 (sh)
$[NPr^n_4][Cr(Ph_2PCH_2CH_2PPh_2)Cl_4]$	Purple	58.6 (58.6)	6.7 (6.7)	1.9 (1.8)	17.0 (18.2)	79	366 (sh), 340m, 315 (sh), 300s
$[NBu^n_4][Cr(Ph_2PCH_2CH_2PPh_2)Br_4]$	Blue	49.0 (49.8)	6.2 (5.9)	1.2 (1.4)	—	decomp.	284s, 255s
$[NBu^n_4][Cr(Ph_2PCH_2CH_2PPh_2)I_4]$	Yellow	42.4 (42.0)	5.0 (5.0)	1.2 (1.2)	—	decomp.	—
$[NPr^n_4][Cr(Ph_2AsCHCHAsPh_2)Cl_4]$	Purple	52.2 (52.8)	5.4 (5.8)	1.7 (1.6)	16.2 (16.4)	92	346m, 335s, 302s
$[Cr\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]Cl$	Purple-brown	44.0 (43.3)	5.9 (5.7)	—	—	insol.	355m
$[Cr\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]PF_6$	Pink-brown	36.1 (36.1)	4.8 (4.8)	—	—	insol.	355m
$[Cr\{o\text{-}C_6H_4(PMe_2)_2\}_2Br_2]PF_6$	Green	32.0 (31.9)	4.1 (4.2)	—	—	insol.	282m
$[Cr\{o\text{-}C_6H_4(PMe_2)_2\}_2Br_2]Br$	Green	35.1 (34.9)	4.6 (4.65)	—	—	insol.	280m
$[Cr\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]ClO_4$	Bright green	30.3 (30.2)	4.3 (4.0)	—	—	90	380m
$[Cr\{o\text{-}C_6H_4(AsMe_2)_2\}_2Br_2]ClO_4$	Bright green	27.2 (27.2)	3.6 (3.6)	—	—	105	320m
$[Cr(Ph_2PCH_2CH_2PPh_2)_2Cl_3]$	Green	64.9 (65.4)	5.0 (5.0)	—	10.5 (11.2)	10.5	362, 340w, 316
$[Cr(Ph_2PCH_2CH_2PPh_2)_2Br_3]$	Green	57.0 (57.4)	4.2 (4.2)	—	—	decomp.	290, 250
$[Cr(Ph_2PCH_2CH_2PPh_2)_2I_3]$	Yellow	50.0 (50.8)	3.8 (3.9)	—	—	decomp.	—
$[Cr(Ph_2PCHCHPPh_2)_2Cl_3]$	Blue	65.9 (65.6)	4.4 (4.6)	—	11.0 (11.2)	10.4	366, 336, 316
$[Cr(Ph_2PCHCHPPh_2)_2Br_3]$	Green	58.2 (57.6)	4.0 (4.1)	—	—	decomp.	298, 252
$[Cr(Ph_2AsCH_2CH_2AsPh_2)_2Cl_3]$	Green	55.7 (55.2)	4.8 (4.2)	—	9.4 (9.4)	18	375, 324
$[Cr(Ph_2PCHCHPPh_2)(H_2O)Cl_3]$	Blue	54.6 (54.5)	3.5 (4.2)	—	—	insol.	349, 336, 317
$[Cr(Ph_2PCHCHPPh_2)(H_2O)Br_3]$	Blue	44.8 (44.2)	3.2 (3.4)	—	—	insol.	269, 250
$[Cr(Ph_2PCH_2CH_2PPh_2)(H_2O)Cl_3]$	Green	54.0 (54.3)	3.6 (3.5)	—	—	—	337br
$Cr[o\text{-}C_6H_4(PMe_2)_2]_{1.5}Br_3$	Blue	31.0 (30.5)	4.2 (4.1)	—	—	—	290 (sh), 275s
$Cr[o\text{-}C_6H_4(PMe_2)_2]_{1.5}Cl_3$	Pink	39.9 (39.5)	5.4 (5.2)	—	—	70 [e]	355m, 352 (sh), 338m, 306 (sh)
$Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}Cl_3$	Green	30.5 (30.7)	4.0 (4.1)	—	18.0 (18.1)	41 [e]	380m, 333 (sh), 321s, 307 (sh)
$Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}Br_3$	Green	25.4 (25.0)	3.8 (3.3)	—	32.6 (33.3)	40 [e]	314, 285s, 258 (sh)
$Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}I_3$	Yellow-brown	21.2 (20.9)	3.0 (2.8)	—	—	decomp.	—
$Cr[o\text{-}C_6H_4(AsMe_2)(PMe_2)]_{1.5}Cl_3$	Purple	34.0 (34.5)	4.9 (4.6)	—	21.6 (21.4)	39 [e]	375 (sh), 352s, 338, 320 (sh), 308 (sh)
$Cr[o\text{-}C_6H_4(AsMe_2)(PMe_2)]_{1.5}Br_3$	Blue-purple	27.6 (27.5)	3.8 (3.7)	—	—	insol.	306, 295s, 275s

Table 1 (*continued*)

Complex	Colour	Analysis [a] (%) C	H	N	X [b]	Λ_M [c]	ν(CrX) [d]/cm⁻¹
$Cr[o-C_6H_4(PMe_2)(SbMe_2)]_{1.5}Cl_3$	Grey-green	29.4 (29.9)	4.6 (4.8)	—	—	insol.	375w, 345s, 333 (sh), 308m
$Cr[o-C_6H_4(PMe_2)(SbMe_2)]_{1.5}Br_3$	Yellow-brown	24.7 (24.8)	3.5 (3.3)	—	—	insol.	320br, 280s
$Cr[o-C_6H_4(NMe_2)(PMe_2)]_{1.5}Cl_3$	Blue	42.1 (41.9)	5.4 (5.6)	5.9 (4.9)	24.8 (25.8)	insol.	370 (sh), 345s, 306s
$Cr[o-C_6H_4(AsMe_2)(NMe_2)]_{1.5}Cl_3$	Green	35.9 (36.3)	4.9 (4.8)	4.2 (4.2)	20.6 (21.5)	insol.	375 (sh), 345 (sh), 340 (sh), 315m
$Cr[Me_2As(CH_2)_3AsMe_2]_{1.5}Cl_3$	Blue	23.1 (23.5)	4.9 (5.0)	—	19.5 (19.0)	insol.	350s, 338s
$Cr[Me_2As(CH_2)_3AsMe_2]_{1.5}Br_3$	Purple	18.8 (18.8)	4.0 (4.0)	—	—	insol.	290br

[a] Calculated values are in parentheses. [b] Halogen. [c] Values in Ω^{-1} cm² mol⁻¹, in 10^{-3} mol dm⁻³ CH_3NO_2 (1 : 1 electrolytes have Λ_M = 70—120 Ω^{-1} cm² mol⁻¹: ref. 15); insol. = insoluble; decomp. = decomposes. [d] Nujol mulls. [e] Λ_M for $[Cr(L-L)_2X_2][Cr(L-L)X]_4$ formulation.

Table 2. Electronic spectral data

Complex	Medium [a]	$10^{-3}\nu_1$ [b]/cm⁻¹ (ε/dm³ mol⁻¹ cm⁻¹)	$10^{-3}\nu_2$ [c]/cm⁻¹ (ε/dm³ mol⁻¹ cm⁻¹)	B'/cm⁻¹	β_{35} [d]	Dq/cm⁻¹
$[NPr^n_4][Cr\{o-C_6H_4(PMe_2)_2\}Cl_4]$	d.r	15.58	19.84	420	0.46	1 558
$[NPr^n_4][Cr\{o-C_6H_4(AsMe_2)_2\}Cl_4]$	CH_2Cl_2	15.00 (502)	19.30 (328)	416	0.45	1 500
$[PPh_3(CH_2Ph)][Cr\{o-C_6H_4(AsMe_2)_2\}Br_4]$	CH_2Cl_2	14.80 (993)	18.00 (601)	308	0.34	1 480
$[NBu^n_4][Cr\{o-C_6H_4(AsMe_2)_2\}I_4]$	d.r.	13.44	16.45	280	0.31	1 344
$[NBu^n_4][Cr\{o-C_6H_4(PMe_2)(SbMe_2)\}Cl_4]$	CH_2Cl_2	15.53 (n.m.)	20.80 (n.m.)	535	0.58	1 553
$[NPr^n_4][Cr(Ph_2PCHCHPPh_2)Cl_4]$	CH_2Cl_2	14.66 (378)	19.50 (170)	473	0.52	1 466
$[NBu^n_4][Cr(Ph_2PCHCHPPh_2)Br_4]$	CH_2Cl_2	14.80 (408)	19.00 (150)	410	0.45	1 480
$[NPr^n_4][Cr(Ph_2PCH_2CH_2PPh_2)Cl_4]$	CH_2Cl_2	14.70 (543)	19.70 (343)	507	0.55	1 470
$[NBu^n_4][Cr(Ph_2PCH_2CH_2PPh_2)Br_4]$	CH_2Cl_2	14.70 (402)	18.80 (337)	408	0.44	1 470
$[NBu^n_4][Cr(Ph_2PCH_2CH_2PPh_2)I_4]$	d.r.	14.49	17.54	290	0.32	1 449
$[NPr^n_4][Cr(Ph_2AsCHCHAsPh_2)Cl_4]$	d.r.	14.00	18.20	400	0.44	1 400
$[NPr^n_4][Cr\{Me_2As(CH_2)_3AsMe_2\}Cl_4]\cdot H_2O$	CH_2Cl_2	15.25 (367)	19.60 (273)	425	0.46	1 525
$[Cr(Ph_2PCH_2CH_2PPh_2)_2Cl_3]$	CH_2Cl_2	15.66 (253)	21.66 (173)	625	0.68	1 566
$[Cr(Ph_2PCH_2CH_2PPh_2)_2Br_3]$	d.r.	14.79	19.46	462	0.50	1 479
$[Cr(Ph_2PCH_2CH_2PPh_2)_2I_3]$	d.r.	14.97	18.24	372	0.34	1 497
$[Cr(Ph_2PCHCHPPh_2)_2Cl_3]$	CH_2Cl_2	15.66 (352)	21.00 (163)	540	0.59	1 566
$[Cr(Ph_2PCHCHPPh_2)_2Br_3]$	CH_2Cl_2	15.15 (206)	20.40 (110)	540	0.59	1 515
$[Cr(Ph_2AsCH_2CH_2AsPh_2)_2Cl_3]$	d.r.	15.80	21.30	565	0.61	1 580
$[Cr(Ph_2PCHCHPPh_2)(H_2O)Cl_3]$	d.r.	16.13	20.83	450	0.49	1 613
$[Cr(Ph_2PCHCHPPh_2)(H_2O)Br_3]$	d.r.	15.82	20.00	405	0.44	1 582
$[Cr_2\{Me_2As(CH_2)_3AsMe_2\}_3Cl_6]$	d.r.	14.50, 17.00	21.00	508	0.55	1 575
$[Cr_2\{Me_2As(CH_2)_3AsMe_2\}_3Br_6]$	d.r.	14.12, 17.00	20.00	490	0.47	1 556
$[Cr\{o-C_6H_4(PMe_2)_2\}_2Cl_2]Cl$ [e]	d.r.	*ca.* 16.1 (sh), 18.3 (sh)	20.00, 22.53	412	0.45	1 830
$[Cr\{o-C_6H_4(PMe_2)_2\}_2Cl_2]PF_6$	d.r.	*ca.* 16.2 (sh), 18.4 (sh)	19.96, 22.70	402	0.44	1 840
$[Cr\{o-C_6H_4(PMe_2)_2\}_2Br_2]PF_6$ [f]	d.r.	16.61 (sh), 18.15	21.3 (sh), 22.83	432	0.47	1 815
$[Cr\{o-C_6H_4(PMe_2)_2\}_2Br_2]Br$	d.r.	16.72 (sh), 18.18	21.4 (sh), 22.70	423	0.46	1 818
$[Cr\{o-C_6H_4(AsMe_2)_2\}_2Cl_2]ClO_4$ [g]	d.r.	15.97 (sh), 17.01	21.5 (sh), 24.00	605	0.66	1 701
$[Cr\{o-C_6H_4(AsMe_2)_2\}_2Br_2]ClO_4$ [h]	d.r.	15.3 (sh), 16.55	*ca.* 20.00 (sh), 22.60	430	0.47	1 655

[a] d.r. = diffuse reflectance; CH_2Cl_2 = solution spectrum. [b] $^4A_{2g} \longrightarrow {}^4T_{2g}$; in *trans*-$[Cr(L-L)_2X_2]^+$, $^4T_{2g}$ splits into ^4E_g and $^4B_{2g}$; n.m. = ε not measured. [c] $^4A_{2g} \longrightarrow {}^4T_{1g}(F)$; in *trans*-$[Cr(L-L)_2X_2]^+$, $^4T_{1g}$ splits into $^4A_{2g}$ and ^4E_g. [d] Free-ion value = 918 cm⁻¹. [e] Dt = 251, Ds = 508 cm⁻¹. [f] Dt = 172, Ds = 290 cm⁻¹. [g] Dt = 119, Ds = 433 cm⁻¹. [h] Dt = 143, Ds = 463 cm⁻¹.

(Table 1) are approximately 1 : 1 electrolytes in 10^{-3} mol dm⁻³ $MeNO_2$, except for the iodo-complexes and $[NBu^n_4][Cr(Ph_2PCH_2CH_2PPh_2)Br_4]$ which are unstable in solution. The steric constraints of the bidentate ligands require the anions to be *cis* isomers, and this is confirmed by the presence of generally three or four bands in the far-i.r. spectra assignable as ν(CrX) (theory, $2A_1 + B_1 + B_2$; all i.r. active), and by the *X*-ray study of $[NPr^n_4][Cr(Ph_2PCHCHPPh_2)Cl_4]$ (see below). These complexes are the first examples of *cis*-$[CrP_2X_4]^-$ type co-ordination, although a number of *trans*-$[Cr(PR_3)_2Cl_4]^-$ complexes have been reported previously.[9] Although the anions are decomposed by water or alcohols, attempts to replace one chlorine in $[Cr\{o-C_6H_4(AsMe_2)_2\}Cl_4]^-$ by soft donors such as $AsMe_2Ph$, PMe_2Ph, or SMePh (L) by refluxing them together in toluene or CH_2Cl_2 solutions failed to give $[Cr\{o-C_6H_4(AsMe_2)_2\}LCl_3]$, most of the starting materials being recovered unchanged. Attempts to oxidise $[Cr\{o-C_6H_4(AsMe_2)_2\}Cl_4]^-$ to Cr^{IV} either chemically or electrochemically were unsuccessful.

The electronic spectra of these anions have been analysed in the usual way [7] to give the ligand field parameters Dq, B', and β_{35} (Table 2). The parameters are internally consistent, al-

Table 3. Selected bond lengths (Å), bond angles (°), and non-bonded distances (Å)

(*a*) Anion

Cr–Cl(1)	2.331(4)	Cr–P(1)	2.485(4)
Cr–Cl(2)	2.319(4)	Cr–P(2)	2.511(4)
Cr–Cl(3)	2.318(4)		
Cr–Cl(4)	2.316(4)	C(1)–C(2)	1.31(2)
P(1)–C(1)	1.82(1)	P(2)–C(2)	1.81(1)
P(1)–C(11)	1.82(1)	P(2)–C(31)	1.83(1)
P(1)–C(21)	1.82(1)	P(2)–C(41)	1.82(1)

Cl · · · Cl	max.	3.54
	min.	3.35
Cl · · · P	max.	3.42
	min.	3.18
P(1) · · · P(2)		3.25
C–C (aromatic)		1.395 (fixed)

Cl(1)–Cr–Cl(2)	94.7(2)	Cl(2)–Cr–P(1)	89.2(2)
Cl(1)–Cr–Cl(4)	93.6(2)	Cl(3)–Cr–Cl(4)	92.6(2)
Cl(1)–Cr–P(1)	86.7(1)	Cl(3)–Cr–P(1)	85.9(1)
Cl(1)–Cr–P(2)	81.9(1)	Cl(3)–Cr–P(2)	89.0(1)
Cl(2)–Cr–Cl(3)	93.2(2)	Cl(4)–Cr–P(2)	90.2(2)
Cl(2)–Cr–Cl(4)	99.5(2)	P(1)–Cr–P(2)	81.2(1)
Cr–P(1)–C(1)	107.0(4)	Cr–P(2)–C(2)	107.1(4)
Cr–P(1)–C(11)	118.7(3)	Cr–P(2)–C(31)	120.6(3)
Cr–P(1)–C(21)	123.0(3)	Cr–P(2)–C(41)	119.1(3)
P(1)–C(1)–C(2)	123(1)	P(2)–C(2)–C(1)	122(1)

C–P–C	max.	104.2(5)
	min.	100.1(5)

(*b*) Cation

N–C	max.	1.53(2)
	min.	1.52(2)
C–C	max.	1.53(2)
	min.	1.46(2)
C–N–C	max.	112(1)
	min.	108(1)

though the data for the iodides are less reliable since the *d–d* bands are ill defined and superimposed on the tail of higher energy charge-transfer bands.

Structure of $[NPr^n_4][Cr(Ph_2PCHCHPPh_2)Cl_4]$.—The structure consists of discrete tetrahedral cations and pseudo-octahedral anions. Selected bond lengths and angles are given in Table 3 and Figures 1 and 2 show the discrete anion and the packing respectively.

The anion has a distorted octahedral arrangement of two *cis* phosphorus and four chlorine atoms. Comparisons can be made with the data obtained on $[Cr\{P(CH_2CH_2PPh_2)_3\}Cl_3]$,[7] $[Hg(Ph_2PCHCHPPh_2)Br_2]$,[10] $[Pd(Ph_2PCHCHPPh_2)I_4]$,[11] and especially with the high-spin d^6 complex $[Fe(Ph_2PCHCHPPh_2)_2Cl_2]$.[12] In the present complex the P(1)–Cr–P(2) angle is 81.2°, the P–Cr–Cl(*cis* to P) angles are $\leqslant 90°$, and all Cl–Cr–Cl angles are $>90°$. The Cr–P bond lengths of 2.485(4) and 2.511(4) Å are slightly longer on average than those in $[Cr\{P(CH_2CH_2PPh_2)_3\}Cl_3]$ [7] [2.399(4)—2.489(6) Å] attributable to the weak binding of the (aryl)$_2$P(alkenyl) donors to the hard chromium. In the Fe^{II} complex [12] Fe–P = 2.532—2.675(1) Å. The difference (*ca.* 6σ) between Cr–P(1) and Cr–P(2) appears to be due to the steric demand of the rigid diphosphine with the longer Cr–P(2) bond correlating with a short non-bonded contact P(2) · · · Cl(1) (3.18 Å). The

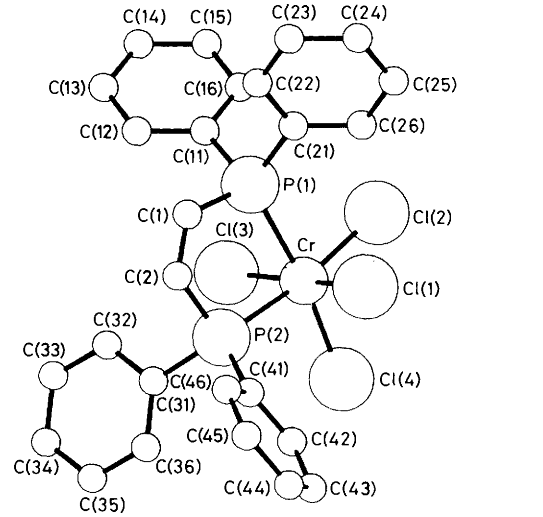


Figure 1. The anion in $[NPr^n_4][Cr(Ph_2PCHCHPPh_2)Cl_4]$ showing the atom-labelling scheme and excluding H atoms for clarity

Cr–Cl(1) bond is *ca.* 4σ longer than Cr–Cl(2,3,4) which are not significantly different. The diphosphine does not exert a measurable *trans* influence, in marked contrast to phosphorus ligands bound to later transition metals, where M–Cl(*trans* to P) > M–Cl(*trans* to Cl) by *ca.* 0.05—0.1 Å.[13] The relatively weak binding of the diphosphine to Cr^{III} is also evident in the electronic spectral parameters (Table 2).

$Cr(L-L)_{1.5}X_3$.—The reaction of $[Cr(thf)_3X_3]$ with excess of the stronger σ-donor bidentates [L–L = o-$C_6H_4(AsMe_2)_2$, o-$C_6H_4(AsMe_2)(PMe_2)$, o-$C_6H_4(PMe_2)(SbMe_2)$, o-C_6H_4-$(AsMe_2)(NMe_2)$, o-$C_6H_4(NMe_2)(PMe_2)$, or $Me_2As(CH_2)_3$-$AsMe_2$] in thf or CH_2Cl_2 gave materials of composition $Cr(L-L)_{1.5}X_3$ (Table 1). *o*-Phenylenebis(dimethylphosphine) gave $Cr(L-L)_{1.5}X_3$ complexes with a Cr : L–L ratio of 1 : 1.5, but an excess of the ligand gave $[Cr(L-L)_2X_2]X$. The formulation of $Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}X_3$ (X = Cl or Br) as *trans*-$[Cr\{o\text{-}C_6H_4(AsMe_2)_2\}_2X_2]^+$*cis*-$[Cr\{o\text{-}C_6H_4(AsMe_2)_2\}X_4]^-$ on the basis of far-i.r. spectra has been discussed elsewhere,[6] and in view of the similar pattern of Cr–X stretching vibrations, the other complexes, with the exception of $Cr[Me_2As(CH_2)_3$-$AsMe_2]_{1.5}X_3$, are formulated similarly. Slight differences in the ν(CrX) frequencies observed in some cases between the two ions in $Cr(L-L)_{1.5}X_3$ and the values in the $[NR_4][Cr(L-L)X_4]$ or $[Cr(L-L)_2X_2]Y$ (Y = ClO_4^-, PF_6^-, *etc.*) are attributable to the effect of the counter ions.[14] Many of the $Cr(L-L)_{1.5}X_3$ complexes are poorly soluble in common solvents, a factor which contributes to their ready isolation and stability, but restricts physical measurements. For example, only in a few cases were molar conductances measured, and the values are rather low for 1 : 1 electrolytes, presumably attributable to the size of the ions.[15]

The complexes $Cr[Me_2As(CH_2)_3AsMe_2]_{1.5}X_3$ (X = Cl or Br) have far-i.r. spectra which were considerably simpler than those of the other complexes of this stoicheiometry. Moreover, the bands at 350s and 338s cm^{-1} assigned as ν(CrCl) in the chloro-complex compare with bands at 326s and 319s cm^{-1} in $[Cr\{Me_2As(CH_2)_3AsMe_2\}Cl_4]^-$, inconsistent with the presence of this anion in $Cr[Me_2As(CH_2)_3AsMe_2]_{1.5}Cl_3$. An alternative formulation, tentatively proposed for these two complexes is $[X_3(L-L)Cr(L-L)Cr(L-L)X_3]$ with a diarsine bridge and *fac* halides, structure (I). The insolubility of these complexes in common solvents prevented both conductance and molecular weight measurements. It is noteworthy however that tri- and

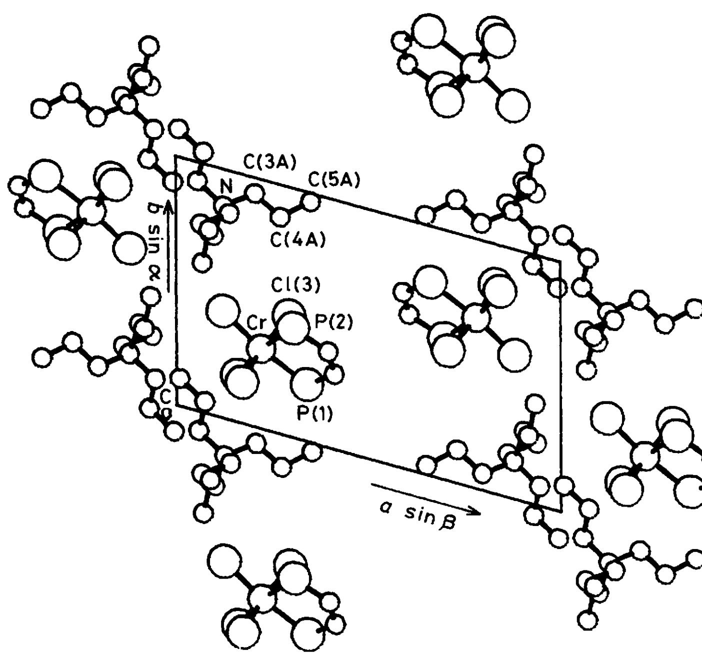
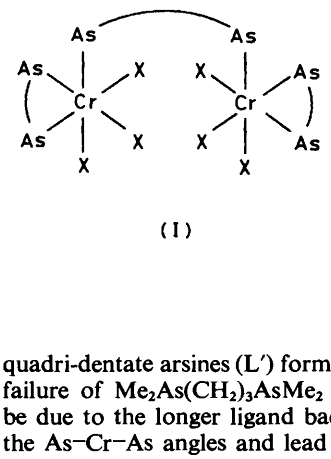
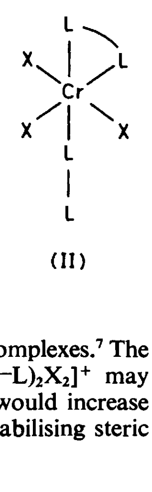


Figure 2. Packing diagram of $[NPr^n_4][Cr(Ph_2PCHCHPPh_2)Cl_4]$ viewed from the *c* direction; H atoms and the phenyl groups on the ligand have been excluded



(I)



(II)

quadri-dentate arsines (L′) form *fac*-$[CrL'X_3]$ complexes.[7] The failure of $Me_2As(CH_2)_3AsMe_2$ to form $[Cr(L{-}L)_2X_2]^+$ may be due to the longer ligand backbone which would increase the As–Cr–As angles and lead to greater destabilising steric interactions.

$[Cr(L{-}L)_2X_3]$ *and* $[Cr(L{-}L)(H_2O)X_3]$ (L–L = $Ph_2PCH_2CH_2PPh_2$, $Ph_2AsCH_2CH_2AsPh_2$, *or cis*-$Ph_2PCHCHPPh_2$).—These weaker σ-donor bidentates react with $[Cr(thf)_3X_3]$ under rigorously anhydrous conditions in CH_2Cl_2 to give $[Cr(L{-}L)_2X_3]$ complexes. In the presence of moisture the products are $[Cr(L{-}L)(H_2O)X_3]$, and these are readily obtained from $[Cr(L{-}L)_2X_3]$ by stirring with wet CH_2Cl_2. The aqua-complexes are analogues of Nyholm's [1] blue complexes $[Cr\{o\text{-}C_6H_4(AsMe_2)_2\}(H_2O)X_3]$, whilst $[Cr(L{-}L)_2X_3]$ are considered to contain one bi- and one uni-dentate diphosphine or diarsine, structure (II). The i.r. spectra of the diphosphine complexes suggest *mer* isomers (Table 1), but the isomer present in $[Cr\{Ph_2As(CH_2)_2AsPh_2\}_2Cl_3]$ is unclear. The formation of $[Cr(L{-}L)_2X_3]$ rather than $[Cr(L{-}L)_2X_2]$ $[Cr(L{-}L)X_4]$ by these ligands probably results from the inability of these weak σ donors to bind to the hard Cr^{III} ion in a cationic species. The reaction of $Ph_2P(CH_2)_2PPh_2$ with hydrated chromium(III) halides in propan-2-ol is reported [5] to give $Cr(L{-}L)_{1.5}X_3\cdot nH_2O$ complexes for which a ligand-bridged dimer structure was proposed. In our hands this route gave materials of rather variable composition, and we have not been able to identify the products satisfactorily.

trans-$[Cr(L{-}L)_2X_2]^+$.—Although these ions are readily obtained in combination with $[Cr(L{-}L)X_4]^-$ anions in the $Cr(L{-}L)_{1.5}X_3$ materials, the presence of the second chromium centre complicates interpretation of the i.r. spectra, and effectively precludes analysis of the electronic spectra. Their isolation with simpler anions was attempted. Only *o*-phenylenebis(dimethylphosphine) gave *trans*-$[Cr(L{-}L)_2X_2]X$ directly when reacted with $[Cr(thf)_3X_3]$ in a ratio Cr : L–L < 1 : 2, the closely related $o\text{-}C_6H_4(AsMe_2)_2$ and $o\text{-}C_6H_4(NMe_2)(PMe_2)$ gave only $Cr(L{-}L)_{1.5}X_3$ even with a large excess of ligand. The complexes $[Cr\{o\text{-}C_6H_4(PMe_2)_2\}_2X_2]PF_6$ were obtained by reaction of the ligand, $CrX_3\cdot nH_2O$, and $NaPF_6$ in propan-2-ol and the long known [1,3] complexes $[Cr\{o\text{-}C_6H_4(AsMe_2)_2\}_2X_2]ClO_4$ are easily made from $Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}X_3$ and aqueous 40% $HClO_4$, but this route gave very small yields or failed completely with other ligands due to greater solubility or instability of the complexes in the aqueous acid. Numerous attempts to obtain other examples of $[Cr(L{-}L)_2X_2]Y$ (Y = ClO_4^-, BPh_4^-, BF_4^-, *etc.*) by treatment of $Cr(L{-}L)_{1.5}X_3$ in thf–CH_2Cl_2 with 70% $HClO_4$ (**CAUTION:** explosion hazard), $LiClO_4$, $NaBPh_4$, *etc.* or by reaction of mixtures of $[Cr(thf)_3X_3]$ and $LiClO_4$, $NaBF_4$, *etc.* with L–L, failed to give analytically pure products, mixtures of $[Cr(L{-}L)_2X_2]Y$ and $[Cr(L{-}L)_2X_2][Cr(L{-}L)X_4]$ being produced.

The electronic spectra of $[Cr\{o\text{-}C_6H_4(AsMe_2)_2\}_2X_2]^+$ have been reported previously,[3] and for X = Cl analysed in D_{4h} symmetry (Figure 3). This assignment was ${}^4B_{1g} \longrightarrow {}^4E_g$ (17 000 cm^{-1}), $\longrightarrow {}^4B_{2g}$ (20 800 cm^{-1}), $\longrightarrow {}^4A_{2g}$ (23 600 cm^{-1}), $\longrightarrow {}^4E_g$ (25 500 cm^{-1}) leading to Dq = 2 080 cm^{-1}, which is very high in comparison with the ligand field splittings produced by other phosphorus and arsenic ligands in halogenochromium(III) complexes,[7,9,16,17] and with the recently prepared [18] $[Cr\{o\text{-}C_6H_4(AsMe_2)_2\}_3]^{3+}$ (1 633 cm^{-1}). We propose an alternative assignment (Table 2) for these complexes, which places $o\text{-}C_6H_4(AsMe_2)_2$ [and $o\text{-}C_6H_4(PMe_2)_2$] lower in the spectrochemical series, on this hard metal, where π-

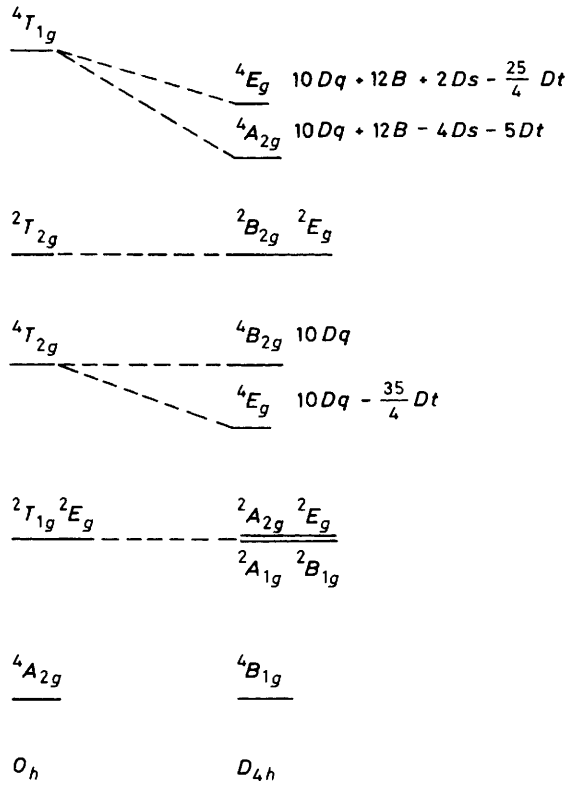


Figure 3. A d^3 ion in O_h and D_{4h} ligand fields

acceptor ability will be less important than with the later transition metals. On this basis the ligands are less far removed from the position of the X^- ions, hence the splittings of the $^4T_{2g}$ and $^4T_{1g}$ levels in the D_{4h} field are much less than proposed previously.[3] In Table 2 are given the values derived for the ligand field parameters *Ds*, *Dt*, *B'*, and β_{35}, which seem reasonable and internally consistent, although the spectral parameters for $[Cr\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]^+$ are less certain since the splittings are not clearly defined in the spectra.

Experimental

Electronic spectra were obtained on a Perkin-Elmer 554 spectrometer. Other physical measurements were made as described previously.[19] Samples of the moisture-sensitive materials were made up for spectroscopic measurements in a dry-box (H_2O < 10 p.p.m.). The complexes $[Cr(thf)_3X_3]$ were prepared as described elsewhere.[8] Ligands were prepared by literature routes. Tetrahydrofuran was dried by distillation from $LiAlH_4$; CH_2Cl_2 was distilled from CaH_2. $[NPr^n_4]Cl$ and $[NBu^n_4]X$ (X = Cl, Br, or I) were dried by heating *in vacuo* at 80—90 °C for 2 d.

The complexes were prepared using Schlenk-tube and dry-box techniques, and representative procedures are described below.

$[NPr^n_4][Cr(cis\text{-}Ph_2PCHCHPPh_2)Cl_4]$.—$[Cr(thf)_3Cl_3]$ (2 mmol, 0.749 g) and $[NPr^n_4]Cl$ (2 mmol, 0.444 g) were dissolved in dry CH_2Cl_2 (40 cm^3) and filtered. The ligand (2 mmol, 0.792 g) was dissolved in CH_2Cl_2 (40 cm^3) and added under nitrogen to the filtrate whereupon the purple colour deepened. After stirring under nitrogen (1 h), the solution was concentrated *in vacuo* at room temperature, and the resulting oil/solid stirred under dry light petroleum (b.p. 40—60 °C) overnight. The purple solid was isolated by filtration and dried *in vacuo*.

$[NPr^n_4][Cr(L\text{-}L)Cl_4]$ [L–L = $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$, $Me_2As(CH_2)_3AsMe_2$, $Ph_2PCH_2CH_2PPh_2$, or *cis*-$Ph_2AsCHCHAsPh_2$] and $[NBu^n_4][Cr(L\text{-}L)X_4]$ [L–L = $o\text{-}C_6H_4(AsMe_2)_2$, $o\text{-}C_6H_4(PMe_2)(SbMe_2)$, *cis*-$Ph_2PCHCHPPh_2$, or $Ph_2PCH_2CH_2PPh_2$], and $[PPh_3(CH_2Ph)][Cr\{o\text{-}C_6H_4(AsMe_2)_2\}Br_4]$ were prepared using the same general method. Liquid ligands were added undiluted to the filtered $[NR_4]X$–$[Cr(thf)_3X_3]$ solution under nitrogen.

$Cr(L\text{-}L)_{1.5}X_3$ [L–L = $o\text{-}C_6H_4(AsMe_2)_2$, $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)(PMe_2)$, $o\text{-}C_6H_4(PMe_2)(SbMe_2)$, $o\text{-}C_6H_4(NMe_2)(PMe_2)$, $o\text{-}C_6H_4(AsMe_2)(NMe_2)$, *or* $Me_2As(CH_2)_3AsMe_2$].—The complex $[Cr(thf)_3X_3]$ (1 mmol) was dissolved in dry CH_2Cl_2 (20 cm^3), the solution filtered and the ligand (1.5 mmol) added under nitrogen. The mixture was stirred under nitrogen at room temperature (1 h). For L–L = $o\text{-}C_6H_4(AsMe_2)_2$, green (X = Cl or Br) or yellow (X = I) solids separated and were filtered off, rinsed thoroughly with diethyl ether and dried *in vacuo*. For complexes of the other ligands, a solution was initially obtained which was concentrated to an oil and then stirred under dry light petroleum (b.p. 40—60 °C) before a solid could be isolated. For L–L = $o\text{-}C_6H_4(PMe_2)_2$, acetone was used instead of CH_2Cl_2. Diffuse reflectance spectra, $10^{-3}\ \tilde{\nu}_{max.}/cm^{-1}$: $Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}Cl_3$, 13.51, 14.97, 18.38, 23.25, 25.64, and 32.26; $Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}Br_3$, 14.50, 17.50, 22.60, *ca.* 28.00, and 30.30; $Cr[o\text{-}C_6H_4(AsMe_2)(PMe_2)]_{1.5}Cl_3$, 15.17, 16.48, 18.76, 21.00, and *ca.* 29.00; $Cr[o\text{-}C_6H_4(AsMe_2)(PMe_2)]_{1.5}Br_3$, 13.59, 17.24, 20.83, 25.00, and 29.85; $Cr[o\text{-}C_6H_4(PMe_2)(SbMe_2)]_{1.5}Cl_3$, 13.59, 15.87, 16.95, 21.00, and 25.00; $Cr[o\text{-}C_6H_4(PMe_2)(SbMe_2)]_{1.5}Br_3$, 13.90, 16.66 (sh), 17.99, 19.58, 22.73, and 26.32; $Cr[o\text{-}C_6H_4(NMe_2)(PMe_2)]_{1.5}Cl_3$, 14.60, 16.00, 19.70, and 21.80; $Cr[o\text{-}C_6H_4(AsMe_2)(NMe_2)]_{1.5}Cl_3$, 14.80, 16.60, 21.00, and 23.30; $Cr[o\text{-}C_6H_4(PMe_2)_2]_{1.5}Cl_3$ (CH_3CN solution), 16.00, 17.00, and 21.80; $Cr[o\text{-}C_6H_4(PMe_2)_2]_{1.5}Br_3$, 14.88 (sh), 17.00, 18.25, 20.83, and 25.12.

$[Cr\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]Cl$.—The complex $[Cr(thf)_3Cl_3]$ (2 mmol, 0.749 g) was dissolved in acetone (30 cm^3) and filtered. $o\text{-}C_6H_4(PMe_2)_2$ (4 mmol, 0.792 g) was added to the filtrate under nitrogen, stirred for 30 min, and finally the brown solid filtered off and dried *in vacuo*.

$[Cr(L\text{-}L)_2X_3]$ (L–L = *cis*-$Ph_2PCHCHPPh_2$, $Ph_2PCH_2CH_2PPh_2$, *or* $Ph_2AsCH_2CH_2AsPh_2$; X = Cl, Br, *or* I).—The complex $[Cr(thf)_3X_3]$ (1 mmol) was dissolved in dry CH_2Cl_2 (30 cm^3) and filtered. The ligand (2 mmol), dissolved in dry CH_2Cl_2 (30 cm^3), was added to the filtrate under nitrogen, and the mixture stirred (30 min). For L–L = *cis*-$Ph_2PCHCHPPh_2$ and X = Br, a small amount of blue solid was filtered off from the solution before $[Cr(cis\text{-}Ph_2PCHCHPPh_2)_2Br_3]$ was isolated from the green filtrate. The solids were obtained by concentrating the solutions *in vacuo* at room temperature, stirring under light petroleum and then filtering. The iodide complex of $Ph_2PCH_2CH_2PPh_2$ was washed several times with diethyl ether.

$[Cr(L\text{-}L)(H_2O)X_3]$ (L–L = *cis*-$Ph_2PCHCHPPh_2$ *or* $Ph_2PCH_2CH_2PPh_2$; X = Cl *or* Br).—These were obtained from the corresponding $[Cr(L\text{-}L)_2X_3]$ complexes by dissolving in 'wet' (*i.e.* not especially dried and distilled) CH_2Cl_2 and filtering off the solid thus precipitated. $[Cr(cis\text{-}Ph_2PCHCHPPh_2)(H_2O)Br_3]$ may also be obtained by carrying out the procedure for the preparation of $[Cr(L\text{-}L)_2X_3]$ complexes in 'wet' CH_2Cl_2 solution, whereupon large amounts of blue

Table 4. Fractional atomic co-ordinates (× 10^4) for $[NPr^n_4][Cr(Ph_2PCHCHPPh_2)Cl_4]$ with estimated standard deviations in parentheses

Atom *	*X/a*	*Y/b*	*Z/c*	Atom *	*X/a*	*Y/b*	*Z/c*
Cr	2 194(1)	3 185(2)	3 298(2)	C(12)	4 811(5)	3 557(9)	973(8)
Cl(1)	1 694(2)	1 628(3)	4 243(4)	C(13)	5 303(5)	3 794(9)	−141(8)
Cl(2)	1 573(2)	1 858(4)	1 339(4)	C(14)	5 026(5)	3 125(9)	−1 411(8)
Cl(3)	2 926(2)	4 808(3)	2 498(4)	C(15)	4 257(5)	2 218(9)	−1 568(8)
Cl(4)	1 204(2)	4 262(4)	4 571(4)	C(16)	3 765(5)	1 981(9)	−453(8)
P(1)	3 386(2)	2 264(4)	2 218(4)	C(21)	3 294(5)	534(6)	1 577(9)
P(2)	3 028(2)	4 360(4)	5 253(4)	C(22)	4 002(5)	137(6)	1 288(9)
N	1 239(7)	8 503(11)	5 911(11)	C(23)	3 946(5)	−1 180(6)	834(9)
C(1)	4 089(8)	2 973(12)	3 487(13)	C(24)	3 182(5)	−2 099(6)	669(9)
C(2)	3 932(8)	3 784(12)	4 722(13)	C(25)	2 473(5)	−1 701(6)	958(9)
C(3A)	2 046(9)	9 322(15)	5 459(16)	C(26)	2 529(5)	−385(6)	1 412(9)
C(3B)	1 368(10)	8 241(16)	7 054(16)	C(31)	3 506(5)	6 117(6)	5 825(9)
C(3C)	960(9)	7 203(14)	4 745(15)	C(32)	4 127(5)	6 570(6)	4 941(9)
C(3D)	582(10)	9 222(15)	6 358(16)	C(33)	4 525(5)	7 895(6)	5 337(9)
C(4A)	2 706(10)	8 689(16)	4 790(18)	C(34)	4 303(5)	8 768(6)	6 616(9)
C(4B)	650(11)	7 504(18)	7 669(18)	C(35)	3 683(5)	8 316(6)	7 500(9)
C(4C)	842(12)	7 297(18)	3 522(18)	C(36)	3 284(5)	6 990(6)	7 104(9)
C(4D)	713(12)	10 451(18)	7 587(19)	C(41)	2 590(5)	4 136(9)	6 831(7)
C(5A)	3 502(11)	9 619(17)	4 447(19)	C(42)	1 824(5)	4 358(9)	7 411(7)
C(5B)	851(12)	7 345(19)	8 790(19)	C(43)	1 482(5)	4 281(9)	8 662(7)
C(5C)	661(11)	5 994(17)	2 395(18)	C(44)	1 907(5)	3 981(9)	9 333(7)
C(5D)	80(12)	11 079(20)	7 736(21)	C(45)	2 673(5)	3 759(9)	8 753(7)
C(11)	4 042(5)	2 650(9)	817(8)	C(46)	3 015(5)	3 836(9)	7 502(7)

* Carbon atoms of the phenyl rings are labelled C(*ij*) where *i* (1—4) indicates the ring and *j* (1—6) the atoms of each ring.

solid $[Cr(cis\text{-}Ph_2PCHCHPPh_2)(H_2O)Br_3]$ may be filtered off from the green solution.

$[Cr\{o\text{-}C_6H_4(AsMe_2)_2\}_2X_2]ClO_4$ (X = Cl or Br).—The complex $Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}X_3$ (1 mmol) was added to 40% aqueous perchloric acid and the mixture stirred for 4—5 h. The bright green solid was separated by filtration and washed with distilled water until the washings were colourless. The solid was rinsed with diethyl ether and dried *in vacuo*.

$[Cr\{o\text{-}C_6H_4(PMe_2)_2\}_2X_2]PF_6$ (X = Cl *or* Br).—The complex $CrX_3{\cdot}6H_2O$ (1.26 mmol) was heated with 2,2-dimethoxypropane (5 cm^3) in refluxing propan-2-ol (50 cm^3) (1 h). The condenser was then removed and some of the solvent boiled off. Anhydrous $NaPF_6$ (0.213 g, 1.26 mmol) was added, followed by addition of the ligand (0.5 g, 2.52 mmol) under nitrogen. The mixture was refluxed gently under nitrogen for 1 h, and the solid which separated on cooling was filtered off and dried *in vacuo*.

Crystal Structure Determination.—Purple air-stable crystals of $[NPr^n_4][Cr(Ph_2PCHCHPPh_2)Cl_4]$ were obtained by vapour diffusion of pentane into methylene chloride solutions of the compound. Preliminary *X*-ray examination established the crystal system and approximate cell dimensions. Accurate cell dimensions were obtained from the setting angles for 25 accurately centred reflections.

Crystal data. $C_{38}H_{50}Cl_4CrNP_2$, M = 776.58, Triclinic, a = 17.534(3), b = 11.930(2), c = 11.108(3) Å, α = 116.30(2), β = 75.12(2), γ = 110.61(1)°, U = 1 935.6 Å^3, D_m (flotation) = 1.37(2) g cm^{-3}, Z = 2, D_c = 1.322 g cm^{-3}, $F(000)$ = 814, λ(Mo-K_α) = 0.7107 Å, μ(Mo-K_α) = 6.27 cm^{-1}, space group $P\bar{1}$ (no. 2).

Using an Enraf-Nonius CAD-4 diffractometer, equipped with graphite-monochromated Mo-K_α radiation, 3 766 reflections ($1.5 \leqslant \theta \leqslant 20°$) were measured from a room temperature crystal (0.15 × 0.15 × 0.05 mm). The check reflections showed no deterioration during the experiment and an empirical ψ-scan absorption correction was applied. After averaging multiply measured reflections (merging R = 0.011), there remained 3 616 reflections; omitting those measurements where $F < 2.5\sigma(F)$ eliminated 1 859 and left 1 757 unique reflections which were used in the structure analysis and refinement. The E's (normalised structure factors) favoured a centrosymmetric space group and the analysis was carried out in the space group $P\bar{1}$.

The structure was solved by conventional heavy-atom methods which readily located an octahedral $CrCl_4P_2$ group. Subsequent structure-factor and electron-density synthesis located the remaining non-hydrogen atoms. An empirical weighting scheme was introduced into the model $\{w = 1/[\sigma^2(F) + AF^2], A = 0.0007\}$ where A was adjusted to give $w\Delta^2$ approximately independent of F, and refinement continued. A difference electron-density synthesis located many of the H atoms and all the H atoms were introduced into the model in geometrically calculated positions [d(C−H) = 1.08 Å], using a common refined temperature factor for methyl hydrogens and another common temperature factor for the remainder (CH and CH_2).

Final refinement {186 variables, anisotropic (Cr, Cl, and P) and isotropic (N, C, and H) atoms, rigid phenyl groups [d(C−C) = 1.395 Å], empirical weights, calculated H-atom positions} converged to a final R of 0.0656 (R' = 0.0658) [$R = \Sigma\Delta/\Sigma F_o$, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$]. A final difference electron-density synthesis showed all features in the range +0.53 to −0.37 e Å^{-3}. Final atomic co-ordinates are given in Table 4.

Scattering factors for neutral atoms and anomalous dispersion terms were taken from SHELX [20] (Cl, P, N, C, and H) and ref. 21 (Cr). All calculations were carried out on an ICL 2970 computer using the programs SHELX,[20] XANADU,[22] and PLUTO [23] and various local programs.

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