Diphosphine and Diarsine Complexes of Chromium(III). Crystal and Molecular Structure of [NPr^{*}4][Cr(*cis*-Ph₂PCHCHPPh₂)Cl₄] †

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cis-[Cr(L-L)X₄]⁻ ions (X = Cl, Br, or I; L-L = diphosphine or diarsine) have been isolated as tetra-alkylammonium salts by reaction of [NR₄]X, [Cr(thf)₃X₃] (thf = tetrahydrofuran), and L-L. The reaction of [Cr(thf)₃X₃] with L-L' in CH₂Cl₂ gave Cr(L-L')_{1.5}X₃ [L-L' = o-C₆H₄(AsMe₂)₂, o-C₆H₄-(AsMe₂)(PMe₂), o-C₆H₄(NMe₂) (PMe₂), or o-C₆H₄(PMe₂)(SbMe₂)], which are formulated as *trans*-[Cr(L-L')₂X₂]*cis*-[Cr(L-L')X₄]. In the case of o-C₆H₄(PMe₂)₂ only, it is possible to isolate both Cr[o-C₆H₄(PMe₂)₂]_{1.5}X₃ and [Cr{o-C₆H₄(PMe₂)₂]₂X₂]X depending upon the Cr : L-L ratio. The ligand Me₂As(CH₂)₃AsMe₂ gave Cr(L-L)_{1.5}X₃ (X = Cl or Br) complexes for which a ligand-bridged structure is proposed [X₃(L-L)Cr(L-L)Cr(L-L)X₃]. Weaker donors (Ph₂PCH₂CH₂PPh₂, *cis*-Ph₂PCHCHPPh₂, or Ph₂AsCH₂CH₂AsPh₂) react with [Cr(thf)₃X₃] to give [Cr(L-L)₂X₃] which contain one uni- and one bi-dentate diphosphine or diarsine, and in the presence of moisture [Cr(L-L)(H₂O)X₃] can be isolated. The complexes [Cr(L-L)₂X₂]Y [X = Cl or Br; Y = ClO₄⁻ or PF₆⁻; L-L = o-C₆H₄(AsMe₂)₂ or o-C₆H₄(PMe₂)₂] have also been obtained. The complexes have been characterised by analysis, conductance, i.r. and electronic spectroscopy, and the electronic spectra analysed (d³) 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 PT (no. 2). 1757 Reflections were refined to R = 0.0656 (R' = 0.0658). The structure consists of tetrahedral NPrⁿ₄⁺ cations, and pseudo-octahedral [Cr(Ph₂PCHCHPPh₂)Cl₄]⁻ 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; Y-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 $[Cr{o-C_6H_4(AsMe_2)_2}_2X_2]ClO_4$, $Cr\{o-C_6H_4(AsMe_2)_2\}_{1.5}X_3$ and $[\{Cr[o-C_6H_4(AsMe_2)_2]X_3\}_n]$ (X = Cl, Br, or I) have received more than cursory study. Since $o-C_{6}H_{4}(AsMe_{2})_{2}$ 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 $Cr\{o-C_6H_4(AsMe_2)_2\}_{1,5}X_3$ should be formulated [$Cr\{o-C_6H_4(AsMe_2)_2\}_{1,5}X_3$] $C_6H_4(AsMe_2)_2 X_2 [Cr\{o-C_6H_4(AsMe_2)_2\}X_4]$. We have described elsewhere 7 the synthesis of chromium(III) complexes of multidentate phosphines and arsines (L) of the type [CrLX₃], 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 $[-CH_2P(Ph) CH_2CH_2PPh_2]_2$.

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.

 $[NR_4][Cr(L-L)X_4]$ (L-L = Diphosphine or Diarsine; X = Cl, Br, or 1).—This type of complex was obtained with most



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-Ph₂PCHCHPPh₂, Ph₂PCH₂CH₂PPh₂, or Ph₂AsCHCHAsPh₂]; (ii) L^{-L} in 'wet' CH₂Cl₂ (L^{-L} = Ph₂PCH₂CH₂PPh₂, cis-Ph₂PCHCH-PPh₂, or Ph₂AsCH₂CH₂AsPh₂); (iii) L^{-L} [as in (ii)] in dry CH₄Cl₂; (iv) sir in 'wet' CH₂Cl₂; (v) L^{-L} = o-C₆H₄(PMe₂)₂, Y = PF₆⁻; L^{-L} = o-C₆H₄(ASMe₂)₂, V = CIO₄⁻; (vi) L^{-L} = Me₂As(CH₂)₂, AsMe₂; (vii) L^{-L} = o-C₆H₄(ASMe₂)₂, o-C₆H₄(NMe₂)(PMe₂), o-C₆H₄(PMe₂)₂, etc.; (viii) L^{-L} = o-C₆H₄(PMe₂)₂, orly

ligands studied, by reaction of $[NR_4]X$, L⁻L, and $[Cr(thf)_3X_3]^a$ (thf = tetrahydrofuran) in a 1:1:1 ratio in dry CH₂Cl₂ (Table 1). These are rare examples of substituted halogenoanions 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. $[NBu^n_4]-[Cr{o-C_6H_4(PMe_2)(SbMe_2)}]Cl_4]$, containing the first example of a Cr¹¹¹-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	Н	N	Xb	Λ _M ^c	v(CrX) ^{<i>d</i>} /cm ⁻¹
$[NPr^{n}_{4}][Cr\{o-C_{6}H_{4}(PMe_{2})_{2}\}Cl_{4}]$	Purple	45.3	7.9	2.2	24.3	122	355m, 330s, 305 (sh)
$[NPr^{n}_{4}][Cr\{o-C_{6}H_{4}(AsMe_{2})_{2}\}Cl_{4}]$	Blue	(45.0) 39.4 (39.6)	(7.0) 6.1 (6.6)	(2.4) 2.0 (2.1)	(24.0) 21.8 (21.3)	61	358 (sh), 333m, 325s, 312 (sh)
$[PPh_3(CH_2Ph)][Cr{o-C_6H_4(AsMe_2)_2}Br_4]$	Blue	41.8 (41.5)	3.6 (3.8)		30.9 (31.7)	89	312m, 285s, 258s
$[NBu^{n}_{4}][Cr\{o-C_{6}H_{4}(AsMe_{2})_{2}\}I_{4}]$	Yellow-green	30.3	5.0	1.5	_	decomp.	
$[NBu^{n}_{4}][Cr\{o-C_{6}H_{4}(PMe_{2})(SbMe_{2})\}Cl_{4}]$	Blue	(30.1) 43.2 (43.0)	(5.0) 7.0 (7.2)	(1.5) 2.6 (1.9)		70	354, 326s, 302s
$[NPr^{n}_{4}][Cr\{Me_{2}As(CH_{2})_{3}AsMe_{2}\}Cl_{4}]\cdot H_{2}O$	Blue	(45.0) 34.9 (35.0)	(7.2) 7.5 (7.4)	(1.5) 2.1 (2.2)	21.0	49	326s, 319s
[NPr ⁿ ₄][Cr(Ph ₂ PCHCHPPh ₂)Cl ₄]	Purple	58.4	6.7	1.9	17.9	100	340s, 315s
[NBu ⁿ ₄][Cr(Ph ₂ PCHCHPPh ₂)Br ₄]	Blue	(58.7) 50.0 (49.9)	(6.4) 5.6 (5.7)	(1.8) 1.5 (1.4)	(18.3)	103	284s, 259s, 250 (sh)
[NPr ⁿ ₄][Cr(Ph ₂ PCH ₂ CH ₂ PPh ₂)Cl ₄]	Purple	58.6	6.7 (6.7)	1.9	17.0 (18.2)	79	366 (sh), 340m, 315 (sh), 300s
[NBu ⁿ ₄][Cr(Ph ₂ PCH ₂ CH ₂ PPh ₂)Br ₄]	Blue	49.0 (49.8)	6.2 (5.9)	1.2 (1.4)		decomp.	284s, 255s
[NBu ⁿ ₄][Cr(Ph ₂ PCH ₂ CH ₂ PPh ₂)I ₄]	Yellow	42.4 (42.0)	5.0 (5.0)	1.2 (1.2)	_	decomp.	—
[NPr ⁿ ₄][Cr(Ph ₂ AsCHCHAsPh ₂)Cl ₄]	Purple	52.2	5.4	1.7	16.2 (16.4)	92	346m, 335s, 302s
$[Cr{o-C_6H_4(PMe_2)_2}_2Cl_2]Cl$	Purple-brown	(32.8) 44.0 (43.3)	5.9 (5.7)			insol.	355m
$[Cr{o-C_6H_4(PMe_2)_2}_2Cl_2]PF_6$	Pink-brown	36.1 (36.1)	4.8			insol.	355m
$[Cr{o-C_6H_4(PMe_2)_2}_2Br_2]PF_6$	Green	32.0 (31.9)	4.1 (4.2)	_		insol.	282m
$[Cr{o-C_6H_4(PMe_2)_2}_2Br_2]Br$	Green	35.1 (34.9)	4.6 (4.65)	—		insol.	280m
$[Cr{o-C_6H_4(AsMe_2)_2}_2Cl_2]ClO_4$	Bright green	30.3 (30.2)	4.3 (4.0)	-		90	380m
$[Cr{o-C_6H_4(AsMe_2)_2}_2Br_2]ClO_4$	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 ₂ PCH ₂ CH ₂ PPh ₂) ₂ Br ₃]	Green	57.0 (57.4)	4.2 (4.2)	_		decomp.	290, 250
[Cr(Ph ₂ PCH ₂ CH ₂ PPh ₂) ₂ I ₃]	Yellow	50.0 (50.8)	3.8 (3.9)			decomp.	
[Cr(Ph ₂ PCHCHPPh ₂) ₂ Cl ₃]	Blue	65.9 (65.6)	4.4 (4.6)	—	11.0 (11.2)	10.4	366, 336, 316
[Cr(Ph ₂ PCHCHPPh ₂) ₂ Br ₃]	Green	58.2 (57.6)	4.0 (4.1)			decomp.	298, 252
[Cr(Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂ Cl ₃]	Green	55.7	4.8		9.4 (9.4)	18	375, 324
[Cr(Ph ₂ PCHCHPPh ₂)(H ₂ O)Cl ₃]	Blue	54.6 (54.5)	3.5 (4.2)		—	insol.	349, 336, 317
[Cr(Ph ₂ PCHCHPPh ₂)(H ₂ O)Br ₃]	Blue	44.8	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
$Cr[o-C_{6}H_{4}(PMe_{2})_{2}]_{1.5}Br_{3}$	Blue	31.0 (30.5)	4.2 (4.1)		_		290 (sh), 275s
$Cr[o-C_{6}H_{4}(PMe_{2})_{2}]_{1.5}Cl_{3}$	Pink	39.9 (39.5)	5.4 (5.2)		—	70 ^e	355m, 352 (sh), 338m, 306 (sh)
$Cr[o-C_6H_4(AsMe_2)_2]_{1.5}Cl_3$	Green	30.5 (30.7)	4.0		18.0 (18.1)	41 ^e	380m, 333 (sh), 321s, 307 (sh)
$Cr[o-C_{6}H_{4}(AsMe_{2})_{2}]_{1.5}Br_{3}$	Green	25.4 (25.0)	3.8		32.6	40 ^e	314, 285s, 258 (sh)
$Cr[o-C_{6}H_{4}(AsMe_{2})_{2}]_{1.5}I_{3}$	Yellow-brown	21.2 (20.9)	3.0 (2.8)			decomp.	—
$Cr[o-C_6H_4(AsMe_2)(PMe_2)]_{1.5}Cl_3$	Purple	34.0	4.9	—	21.6	39 e	375 (sh), 352s, 338, 320 (sh) 308 (sh)
$Cr[o-C_6H_4(AsMe_2)(PMe_2)]_{1.5}Br_3$	Blue-purple	(34.3) 27.6 (27.5)	3.8 (3.7)	_	(21.4)	insol.	306, 295s, 275s

Table 1 (continued)

Complex	Colour	Ċ	Н	N	Xb	Λ_{M}^{c}	v(CrX) ^{<i>d</i>} /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 CH₃NO₂ (1:1 electrolytes have $\Lambda_M = 70-120 \ \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$; ref. 15); insol. = insoluble; decomp. = decomposes. ^{*d*} Nujol mulls. ^{*e*} Λ_M for [Cr(L⁻L)₂X₂][Cr(L⁻L)X]₄ formulation.

Table 2. Electronic spectral data

		$10^{-3}v_1 / cm^{-1}$	$10^{-3}v_2 c/cm^{-1}$			
Complex	Medium ^a	$(\epsilon/dm^3 mol^{-1} cm^{-1})$	$(\varepsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1})$	<i>B′</i> /cm⁻¹	β35 ^d	Dq/cm^{-1}
$[NPr_{4}][Cr_{0}-C_{6}H_{4}(PMe_{2})_{2}]Cl_{4}]$	d.r	15.58	19.84	420	0.46	1 558
$[NPr_{4}][Cr{o-C_{6}H_{4}(AsMe_{2})_{2}}Cl_{4}]$	CH ₂ Cl 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 ₂ Cl 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
$[NBu^{n}_{4}][Cr\{o-C_{6}H_{4}(PMe_{2})(SbMe_{2})\}Cl_{4}]$	CH ₂ Cl ₂	15.53 (n.m.)	20.80 (n.m.)	535	0.58	1 553
[NPr ⁿ ₄][Cr(Ph ₂ PCHCHPPh ₂)Cl ₄]	CH_2Cl_2	14.66 (378)	19.50 (170)	473	0.52	1 466
[NBu ⁿ ₄][Cr(Ph ₂ PCHCHPPh ₂)Br ₄]	CH ₂ Cl ₂	14.80 (408)	19.00 (150)	410	0.45	1 480
[NPr ⁿ ₄][Cr(Ph ₂ PCH ₂ CH ₂ PPh ₂)Cl ₄]	CH ₂ Cl ₂	14.70 (543)	19.70 (343)	507	0.55	1 470
[NBu ⁿ ₄][Cr(Ph ₂ PCH ₂ CH ₂ PPh ₂)Br ₄]	CH ₂ Cl ₂	14.70 (402)	18.80 (337)	408	0.44	1 470
[NBu ⁿ ₄][Cr(Ph ₂ PCH ₂ CH ₂ PPh ₂)I ₄]	d.r.	14.49	17.54	290	0.32	1 449
[NPr ⁿ ₄][Cr(Ph ₂ AsCHCHAsPh ₂)Cl ₄]	d.r.	14.00	18.20	400	0.44	1 400
$[NPr_4][Cr{Me_2As(CH_2)_3AsMe_2}Cl_4]H_2O$	CH ₂ Cl ₂	15.25 (367)	19.60 (273)	425	0.46	1 525
[Cr(Ph ₂ PCH ₂ CH ₂ PPh ₂) ₂ Cl ₃]	CH ₂ Cl ₂	15.66 (253)	21.66 (173)	625	0.68	1 566
[Cr(Ph ₂ PCH ₂ CH ₂ PPh ₂) ₂ Br 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 ₂ PCHCHPPh ₂) ₂ Cl ₃]	CH ₂ Cl ₂	15.66 (352)	21.00 (163)	540	0.59	1 566
[Cr(Ph ₂ PCHCHPPh ₂) ₂ Br ₃]	CH ₂ Cl ₂	15.15 (206)	20.40 (110)	540	0.59	1 515
[Cr(Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂ Cl ₃]	d.r.	15.80	21.30	565	0.61	1 580
[Cr(Ph ₂ PCHCHPPh ₂)(H ₂ O)Cl ₃]	d.r.	16.13	20.83	450	0.49	1 613
[Cr(Ph ₂ PCHCHPPh ₂)(H ₂ O)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),	20.00, 22.53	412	0.45	1 830
		18.3 (sh)				
$[Cr{o-C_6H_4(PMe_2)_2}_2Cl_2]PF_6$	d.r.	ca. 16.2 (sh),	19.96, 22.70	402	0.44	1 840
		18.4 (sh)				
$[Cr{o-C_6H_4(PMe_2)_2}_2Br_2]PF_6$	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	1818
$[Cr{o-C_6H_4(AsMe_2)_2}_2Cl_2]ClO_4$	d.r.	15.97 (sh), 17.01	21.5 (sh), 24.00	605	0.66	1 701
$[Cr{o-C_6H_4(AsMe_2)_2}_2Br_2]ClO_4$ "	d.r.	15.3 (sh), 16.55	ca. 20.00 (sh),	430	0.47	1 655
			22.60			

^{*a*} d.r. = diffuse reflectance; CH₂Cl₂ = solution spectrum. ${}^{b}{}^{4}A_{2g} \longrightarrow {}^{4}T_{2g}$; in *trans*-[Cr(L-L)₂X₂]⁺, ${}^{4}T_{2g}$ splits into ${}^{4}E_{g}$ and ${}^{4}B_{2g}$; n.m. = ε not measured. ${}^{c}{}^{4}A_{2g} \longrightarrow {}^{4}T_{1g}(F)$; in *trans*-[Cr(L-L)₂X₂]⁺, ${}^{4}T_{1g}$ splits into ${}^{4}A_{2g}$ and ${}^{4}E_{g}$. 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 MeNO₂, except for the iodo-complexes and [NBuⁿ₄][Cr(Ph₂-PCH₂CH₂PPh₂)Br₄] 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 v(CrX) (theory, $2A_1 + B_1 + B_2$; all i.r. active), and by the X-ray study of [NPrⁿ₄][Cr(Ph₂PCHCHPPh₂)Cl₄] (see below). These complexes are the first examples of *cis*-[Cr(PR₃)₂Cl₄]⁻ 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^{1V} 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-

bonded distance	s (A)		
(a) Anion			• • • • • • •
Cr-Cl(1)	2.331(4)	Cr - P(1)	2.485(4)
Cr = Cl(2)	2.319(4) 2.318(4)	$Cr^{-}P(2)$	2.511(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)
	$Cl \cdots Cl$	max. 3.54	
		min. 3.35	
	$Cl \cdots P$	max. 3.42	
		min. 3.18	
	$P(1) \cdots P(2)$	3.25	
	C-C (aromatic)	1.395 (fixed)	
C(1) = Cr = C(2)) 947(2)	C(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)
	107 0(4)		107 1 (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)	C(2) = C(41) P(2) = C(2) = C(1)	119.1(3)
P(1)=C(1)=C(2)	.) 123(1)	P(2)=C(2)=C(1)	122(1)
	C-P-C ma	x. 104.2(5) n. 100.1(5)	
(b) Cation			
	N-C m	ax. 1.53(2)	
	m	in. 1.52(2)	
	C-C m	ax. 1.53(2)	
	m	in. 1.46(2)	
	C-N-C ma	ax. 112(1)	
	m	in. 108(1)	

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

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 $[NPr_4][Cr(Ph_2PCHCHPPh_2)Cl_4]$.—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 $[Cr{P(CH_2CH_2PPh_2)_3}]$ -Cl₃],⁷ [Hg(Ph₂PCHCHPPh₂)Br₂],¹⁰ [Pd(Ph₂PCHCHPPh₂)I₄],¹¹ and especially with the high-spin d⁶ complex [Fe(Ph₂PCHCH- $PPh_2_2Cl_2$.¹² In the present complex the P(1)-Cr-P(2) angle is 81.2°, the P-Cr-Cl(cis to P) angles are $\leq 90^\circ$, and all Cl-Cr-Cl angles are $>90^\circ$. The Cr-P bond lengths of 2.485(4) and 2.511(4) Å are slightly longer on average than those in [Cr{P(CH₂CH₂PPh₂)₃}Cl₃]⁷ [2.399(4)-2.489(6) Å] attributable to the weak binding of the (aryl)₂P(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 $P(2) \cdots Cl(1)$ (3.18 Å). The



Figure 1. The anion in $[NPr_4][Cr(Ph_2PCHCHPPh_2)Cl_4]$ showing the atom-labelling scheme and excluding H atoms for clarity

Cr-Cl(1) bond is *ca*. 4 σ 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 Cr¹¹¹ 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 $[L^-L = o - C_6 H_4 (A_5 Me_2)_2,$ $o-C_6H_4(AsMe_2)(PMe_2)$, $o-C_6H_4(PMe_2)(SbMe_2),$ o-C₆H₄- $(AsMe_2)(NMe_2)$, $o-C_6H_4(NMe_2)(PMe_2)$, or $Me_2As(CH_2)_3$ -AsMe₂] in thf or CH₂Cl₂ 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 $Cr[o-C_6H_4(AsMe_2)_2]_{1.5}X_3$ (X = Cl or Br) as trans- $[Cr{o-C_{6}H_{4}(AsMe_{2})_{2}}_{2}X_{2}]^{+}cis-[Cr{o-C_{6}H_{4}(AsMe_{2})_{2}}X_{4}]^{-}$ 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 $Cr[Me_2As(CH_2)_3-$ AsMe₂]_{1.5}X₃, are formulated similarly. Slight differences in the v(CrX) frequencies observed in some cases between the two ions in $Cr(L-L)_{1.5}X_3$ and the values in the [NR₄][Cr(L-L)X₄] or $[Cr(L-L)_2X_2]Y$ (Y = ClO₄⁻, PF₆⁻, 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 v(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 [X₃(L-L)Cr(L-L)Cr(L-L)X₃] 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 $[NPr^{n}_{4}][Cr(Ph_{2}PCHCHPPh_{2})Cl_{4}]$ viewed from the *c* direction; H atoms and the phenyl groups on the ligand have been excluded



quadri-dentate arsines (L') form fac-[CrL'X₃] complexes.⁷ The failure of Me₂As(CH₂)₃AsMe₂ to form [Cr(L-L)₂X₂]⁺ 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 $[Cr(L-L)(H_2O)X_3]$ $(L-L = Ph_2PCH_2-PCH_2)$ CH2PPh2, Ph2AsCH2CH2AsPh2, or cis-Ph2PCHCHPPh2).-These weaker σ -donor bidentates react with [Cr(thf)₃X₃] under rigorously anhydrous conditions in CH₂Cl₂ to give $[Cr(L-L)_2X_3]$ complexes. In the presence of moisture the products are [Cr(L-L)(H₂O)X₃], 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 $[Cr{o-C_6H_4(AsMe_2)_2}(H_2O)X_3]$, 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 Cr¹¹¹ ion in a cationic species. The reaction of Ph₂P(CH₂)₂PPh₂ with hydrated chromium(III) halides in propan-2-ol is reported ⁵ to give $Cr(L-L)_{1.5}X_3$. 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)X₄]⁻ 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 ophenylenebis(dimethylphosphine) gave trans-[Cr(L-L)₂X₂]X directly when reacted with [Cr(thf)₃X₃] in a ratio Cr : L-L <1:2, the closely related $o-C_6H_4(A_5Me_2)_2$ and $o-C_6H_4(NMe_2)-$ (PMe₂) gave only $Cr(L-L)_{1.5}X_3$ even with a large excess of ligand. The complexes $[Cr{o-C_6H_4(PMe_2)_2}_2X_2]PF_6$ were obtained by reaction of the ligand, CrX₃·nH₂O, and NaPF₆ in propan-2-ol and the long known 1,3 complexes [Cr{o-C₆H₄- $(AsMe_2)_2$ ₂X₂ClO₄ are easily made from Cr[o-C₆H₄(As- $Me_{2}_{2}_{1,5}X_{3}$ and aqueous 40% HClO₄, 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 = ClO₄⁻, BPh₄⁻, BF₄⁻, etc.) by treatment of Cr(L-L)_{1.5}X₃ in thf-CH₂Cl₂ with 70% HClO₄ (CAUTION: explosion hazard), LiClO₄, NaBPh₄, etc. or by reaction of mixtures of [Cr(thf)₃X₃] and LiClO₄, NaBF₄, 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 $[Cr\{o-C_6H_4(AsMe_2)_2\}_2X_2]^+$ have been reported previously,³ and for X = Cl analysed in D_{4h} symmetry (Figure 3). This assignment was ${}^{4}B_{1g} \longrightarrow {}^{4}E_{g}$ (17 000 cm⁻¹), $\longrightarrow {}^{4}B_{2g}$ (20 800 cm⁻¹), $\longrightarrow {}^{4}A_{2g}$ (23 600 cm⁻¹), $\longrightarrow {}^{4}E_{g}$ (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-C_6H_4(AsMe_2)_2}_3]³⁺ (1 633 cm⁻¹). We propose an alternative assignment (Table 2) for these complexes, which places $o-C_6H_4(AsMe_2)_2$ [and $o-C_6H_4(PMe_2)_2$] lower in the spectrochemical series, on this hard metal, where π -







0_h D_{4h}

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 ${}^{4}T_{2g}$ and ${}^{4}T_{1g}$ 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 $[Cr\{o-C_6H_4(PMe_2)_2\}_2Cl_2]^+$ 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 (H₂O <10 p.p.m.). The complexes [Cr(thf)₃X₃] were prepared as described elsewhere.⁸ Ligands were prepared by literature routes. Tetrahydrofuran was dried by distillation from LiAlH₄; CH₂Cl₂ was distilled from CaH₂. [NPrⁿ₄]Cl and [NBuⁿ₄]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 drybox techniques, and representative procedures are described below.

 $[NPr^{n}_{4}][Cr(cis-Ph_{2}PCHCHPPh_{2})Cl_{4}].--[Cr(thf)_{3}Cl_{3}]$ (2 mmol, 0.749 g) and $[NPr^{n}_{4}]Cl$ (2 mmol, 0.444 g) were dissolved in dry CH₂Cl₂ (40 cm³) and filtered. The ligand (2 mmol, 0.792 g) was dissolved in CH₂Cl₂ (40 cm³) 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.

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

 $Cr(L-L)_{1.5}X_3$ [L-L = $o-C_6H_4(AsMe_2)_2$, $o-C_6H_4(PMe_2)_2$, $o-C_6H_4(AsMe_2)(PMe_2), o-C_6H_4(PMe_2)(SbMe_2), o-C_6H_4(NMe_2)-$ (PMe₂), $o-C_6H_4(AsMe_2)(NMe_2)$, or Me₂As(CH₂)₃AsMe₂].--The complex $[Cr(thf)_3X_3]$ (1 mmol) was dissolved in dry CH₂Cl₂ (20 cm³), 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 = $o-C_{6}H_{4}(AsMe_{2})_{2}$, 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-C₆H₄(PMe₂)₂, acetone was used instead of CH₂Cl₂. Diffuse reflectance spectra, $10^{-3} \tilde{v}_{max}/cm^{-1}$: Cr[o-C₆H₄(AsMe₂)₂]_{1.5}Cl₃, 13.51, 14.97, 18.38, 23.25, 25.64, and 32.26; Cr[o-C₆H₄-(AsMe₂)₂]_{1.5}Br₃, 14.50, 17.50, 22.60, ca. 28.00, and 30.30; Cr[o-C₆H₄(AsMe₂)(PMe₂)]_{1.5}Cl₃, 15.17, 16.48, 18.76, 21.00, and ca. 29.00; $Cr[o-C_6H_4(AsMe_2)(PMe_2)]_{1.5}Br_3$, 13.59, 17.24, 20.83, 25.00, and 29.85; Cr[o-C₆H₄(PMe₂)(SbMe₂)]_{1.5}Cl₃, 13.59, 15.87, 16.95, 21.00, and 25.00; Cr[o-C₆H₄(PMe₂)-(SbMe₂)]_{1.5}Br₃, 13.90, 16.66 (sh), 17.99, 19.58, 22.73, and 26.32; Cr[o-C₆H₄(NMe₂)(PMe₂)]_{1.5}Cl₃, 14.60, 16.00, 19.70, and 21.80; Cr[o-C₆H₄(AsMe₂)(NMe₂)]_{1.5}Cl₃, 14.80, 16.60, 21.00, and 23.30; Cr[o-C₆H₄(PMe₂)₂]_{1.5}Cl₃ (CH₃CN solution), 16.00, 17.00, and 21.80; Cr[o-C₆H₄(PMe₂)₂]_{1.5}Br₃, 14.88 (sh), 17.00, 18.25, 20.83, and 25.12.

 $[Cr{o-C_{6}H_{4}(PMe_{2})_{2}}_{2}Cl_{2}]Cl.$ —The complex $[Cr(thf)_{3}Cl_{3}]$ (2 mmol, 0.749 g) was dissolved in acetone (30 cm³) and filtered. $o-C_{6}H_{4}(PMe_{2})_{2}$ (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-L)₂X₃] (L-L = cis-Ph₂PCHCHPPh₂, Ph₂PCH₂CH₂-PPh₂, or Ph₂AsCH₂CH₂AsPh₂; X = Cl, Br, or I).—The complex [Cr(thf)₃X₃] (1 mmol) was dissolved in dry CH₂Cl₂ (30 cm³) and filtered. The ligand (2 mmol), dissolved in dry CH₂Cl₂ (30 cm³), was added to the filtrate under nitrogen, and the mixture stirred (30 min). For L-L = cis-Ph₂PCH-CHPPh₂ and X = Br, a small amount of blue solid was filtered off from the solution before [Cr(cis-Ph₂PCHCHPPh₂)₂-Br₃] 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 Ph₂PCH₂CH₂PPh₂ was washed several times with diethyl ether.

 $[Cr(L-L)(H_2O)X_3]$ (L-L = cis-Ph₂PCHCHPPh₂ or Ph₂-PCH₂CH₂PPh₂; X = Cl or Br).—These were obtained from the corresponding $[Cr(L-L)_2X_3]$ complexes by dissolving in 'wet' (*i.e.* not especially dried and distilled) CH₂Cl₂ and filtering off the solid thus precipitated. $[Cr(cis-Ph_2PCH CHPPh_2)(H_2O)Br_3]$ may also be obtained by carrying out the procedure for the preparation of $[Cr(L-L)_2X_3]$ complexes in 'wet' CH₂Cl₂ solution, whereupon large amounts of blue Table 4. Fractional atomic co-ordinates (\times 10⁴) for [NPr⁴₄][Cr(Ph₂PCHCHPPh₂)Cl₄] 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)
C(1)	1 694(2)	1 628(3)	4 243(4)	C(13)	5 303(5)	3 794(9)	-141(8)
C(2)	1 573(2)	1 858(4)	1 339(4)	C(14)	5 026(5)	3 125(9)	-1411(8)
C(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)
Ň	1 239(7)	8 503(11)	5 911(11)	C(23)	3 946(5)	-1 180(6)	834(9)
$\tilde{\mathbf{C}}(1)$	4 089(8)	2 973(12)	3 487(13)	C(24)	3 182(5)	-2.099(6)	669(9)
$\mathbf{C}(2)$	3 932(8)	3 784(12)	4 722(13)	C(25)	2 473(5)	-1701(6)	958(9)
$\tilde{C}(3A)$	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)
$\tilde{C}(4A)$	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 ator	ns of the phenyl	rings are labelled	C(ij) where $i(1-4)$ in	dicates the ring and	j (16) the at	oms of each rin	g.

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

 $[Cr_{\{o-C_{6}H_{4}(AsMe_{2})_{2}\}_{2}X_{2}]ClO_{4}$ (X = Cl or Br).—The complex $Cr[o-C_{6}H_{4}(AsMe_{2})_{2}]_{1.5}X_{3}$ (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*.

 $[Cr{o-C_6H_4(PMe_2)_2}_2X_2]PF_6 (X = Cl or Br).$ —The complex CrX_3 ' GH_2O (1.26 mmol) was heated with 2,2-dimethoxypropane (5 cm³) in refluxing propan-2-ol (50 cm³) (1 h). The condenser was then removed and some of the solvent boiled off. Anhydrous NaPF₆ (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 $[NPr^{n}_{4}][Cr(Ph_{2}PCHCHPPh_{2})Cl_{4}]$ 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, $\alpha = 116.30(2)$, $\beta = 75.12(2)$, $\gamma = 110.61(1)^\circ$, U = 1.935.6 Å³, D_m (flotation) = 1.37(2) g cm ³, Z = 2, $D_c = 1.322$ g cm⁻³, F(000) = 814, $\lambda(Mo-K_x) = 0.7107$ Å, $\mu(Mo-K_x) = 6.27$ cm⁻¹, space group PI (no. 2).

Using an Enraf-Nonius CAD-4 diffractometer, equipped with graphite-monochromated Mo- K_{α} radiation, 3 766 reflections ($1.5 \le \theta \le 20^{\circ}$) were measured from a room temperature crystal ($0.15 \times 0.15 \times 0.05$ 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 $F \le 2.5\sigma(F)$ 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 $P\overline{I}$.

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 the remainder (CH and CH₂).

Final refinement {186 variables, anisotropic (Cr, Cl, and P) and isotropic (N, C, and H) atoms, rigid phenyl groups $[d(C^-C) = 1.395 \text{ Å}]$, empirical weights, calculated H-atom positions} converged to a final R of 0.0656 (R' = 0.0658) [$R = \Sigma\Delta/\Sigma F_o$, $R' = (\Sigma w \Delta^2 / \Sigma w F_o^2)^{\pm}$]. A final difference electrondensity 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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