Chromium(III) Complexes of Multidentate Phosphines, Arsines, and Thioethers. Crystal and Molecular Structure of the Complex *mer*-$[Cr\{P(CH_2CH_2PPh_2)_3\}Cl_3]$ †

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Octahedral chromium(III) complexes *mer*-$[CrLX_3]$ {X = Cl or Br; L = $PPh(CH_2CH_2PPh_2)_2$, $P(CH_2CH_2PPh_2)_3$, $[-CH_2P(Ph)CH_2CH_2PPh_2]_2$, or $S(CH_2CH_2CH_2SMe)_2$} and *fac*-$[CrLX_3]$ [L = $CMe(CH_2PPh_2)_3$, $CMe(CH_2AsMe_2)_3$, $CMe(CH_2SMe)_3$, $AsMe(CH_2CH_2CH_2AsMe_2)_2$, or $As(CH_2CH_2CH_2AsMe_2)_3$] have been prepared from $[Cr(thf)_3X_3]$ (thf = tetrahydrofuran) and L in CH_2Cl_2 under anhydrous conditions. Chromium(III) fluoride complexes $[CrLF_3]$ [L = $PPh(CH_2CH_2PPh_2)_2$, $P(CH_2CH_2PPh_2)_3$, or $CMe(CH_2AsMe_2)_3$] are obtained by reaction of $[Cr(thf)_3Cl_3]$ with AgF in thf, followed by addition of the ligand. The reactions with $[Cr(thf)_3I_3]$ differ in that both $[CrLI_3]$ [L = *e.g.* $PPh(CH_2CH_2PPh_2)_2$ or $CMe(CH_2AsMe_2)_3$] and CrL_2I_3 can be isolated depending upon the Cr : L ratio. The $[CrLX_3]$ complexes, which have been characterised by i.r. and electronic spectroscopy, conductance and molecular weight measurements, have P_3X_3, As_3X_3, or S_3X_3 (X = F, Cl, Br, or I) donor sets. The electronic spectra were analysed to produce *Dq*, *B'*, and β_{35}. Treatment of $[CrLCl_3]$ {L = $P(CH_2CH_2PPh_2)_3$, $As(CH_2CH_2CH_2AsMe_2)_3$, or $[-CH_2P(Ph)CH_2CH_2PPh_2]_2$} with $AgBF_4$ in CH_2Cl_2 produced *cis*-$[CrLCl_2]BF_4$ (P_4Cl_2 or As_4Cl_2 donor sets). The title complex is monoclinic, a = 14.787(6), b = 21.617(4), c = 14.474(4) Å, β = 113.43(3)°, and Z = 4; space group $P2_1/a$ (no. 14). 2 101 Reflections were refined to R = 0.075 (R' = 0.079). The molecular complex has a *mer* octahedral structure (P_3Cl_3 co-ordination) with $Cr-P(Ph_2)$ 2.466(5) and 2.489(6); $Cr-P(CH_2)_3$ 2.399(4); Cr–Cl 2.306(4), 2.292(6), and 2.320(5) Å. The long Cr–P bonds are due both to the steric crowding, and the relatively weak binding of the phosphorus donors to the hard metal, and both these points are also evident in the electronic spectral parameters.

Many chromium(III) complexes of nitrogen- and oxygen-donor ligands are known, and as a result of the kinetically inert nature of the d^3 configuration, numerous isomers and mixed-ligand complexes can be isolated.[1,2] Few complexes of soft donor ligands have been studied in detail, although some data on complexes of $P(o\text{-}C_6H_4PPh_2)_3$,[3,4] $PPh(o\text{-}C_6H_4PPh_2)_2$,[3,4] $AsMe(CH_2CH_2CH_2AsMe_2)_2$,[5] $AsMe(o\text{-}C_6H_4AsMe_2)_2$,[6] and $CMe(CH_2AsMe_2)_3$ [5] have been published. Here the properties of some tri- and quadri-dentate P-, As-, and S-donor ligands with chromium(III) are described.

Results and Discussion

$[CrLX_3]$ (L = *polydentate ligand*, X = Cl *or* Br).—The intractable nature of chromium(III) halides makes them unsuitable starting materials, and the readily soluble $[Cr(thf)_3X_3]$ (thf = tetrahydrofuran, X = Cl or Br) [7,8] were used. Although other workers [3] have prepared and used these complexes *in situ*, isolation of the $[Cr(thf)_3X_3]$ and reaction with the ligand (L) in methylene chloride solution is preferable, in that the Cr : L ratio is more readily controlled ‡ and the presence of a large excess of O-donor solvent which can compete for the hard Cr^{III} is avoided. In this way the 1 : 1 (L : Cr) complexes $[CrLX_3]$ (Table 1) were obtained. The trithioether complexes are extremely moisture sensitive, the phosphine and arsine complexes less so, with the *fac* isomers generally more sensitive than the *mer*. No 2 : 1 (L : Cr) complexes could be obtained, although species of the type CrN_6^{3+} are readily obtained with triamines.[1] The complexes are non-electrolytes in freshly prepared 1,2-dichloroethane and nitromethane solutions, showing that the halides are co-ordinated, and molecular weight measurements on representative examples confirm they are monomers (Table 1). Since the electronic spectra (below) are consistent with a pseudo-octahedral structure, all contain E_3X_3 donor sets (E = P, As, or S; X = Cl or Br). The failure to prepare 2 : 1 complexes and the binding of the potentially quadridentate ligands as tridentates demonstrates that the hard Cr^{III} prefers to bind Cl^- or Br^- ions rather than more than three soft donors. The 'tripod' quadridentates, $As(CH_2CH_2CH_2AsMe_2)_3$ or $P(CH_2CH_2PPh_2)_3$, form octahedral complexes in contrast to the trigonal-bipyramidal structures they promote with many 3*d* metal halides.[9] Attempts to convert $[CrLCl_3]$ to the bromide or iodide by metathesis with LiX were unsuccessful.

A complex of the type CrE_3X_3 can exist in two isomeric forms, *mer* (C_{2v}) or *fac* (C_{3v}). The extensive literature [1,2] on chromium complexes shows that usually one isomer is favoured, and even in cases like $[Cr(dien)Cl_3]$ [10] (dien = diethylenetriamine) where both isomers are known, they are obtained by different synthetic routes. In the present case the data suggest that only one isomer is obtained from each reaction. The structure of $[Cr\{P(CH_2CH_2PPh_2)_3\}Cl_3]$ was established as *mer* by an *X*-ray study (below), and those of the other complexes were identified by far-i.r. spectroscopy (Table 1). Theory predicts three i.r. active Cr–Cl stretches for *mer* isomers ($2A_1 + B_1$) and two for *fac* ($A_1 + E$), based upon local symmetry. The steric constraints of the tripodal tridentates $CMe(CH_2PPh_2)_3$, $CMe(CH_2AsMe_2)_3$, and $CMe(CH_2SMe)_3$ are such that monomeric complexes must be facial isomers, and this is borne out by the i.r. data. It is notable that for any particular ligand the complexes $[CrLCl_3]$ and $[CrLBr_3]$ form as the same isomer, and with the

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† *mer*-Trichloro[tris(2-diphenylphosphinoethyl)phosphine]chromium(III).

Supplementary data available (No. SUP 23748, 18 pp.): atomic thermal parameters, observed and calculated structure factors, full electronic spectral data and parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. unit employed: 1 B.M. = 9.274×10^{-24} J T^{-1}.

‡ Anhydrous CrX_3 rarely dissolve completely in thf, making the Cr : L ratio difficult to control in *in situ* preparations.

Table 1. Analytical and physical data

Complex	Colour	Analysis (%) [a]			Λ_M [b]	M [a,c]	$\mu_{eff.}$ [d]	$\nu(Cr-X)/cm^{-1}$	Isomer
		C	H	X					
[$CrLCl_3$]									
L									
$PPh(CH_2CH_2PPh_2)_2$	Blue	59.0 (58.9)	4.8 (4.8)	—	8	—	3.8	362, 342, 320	*mer*
[–$CH_2P(Ph)CH_2CH_2PPh_2]_2$	Blue	60.6 (60.9)	4.9 (5.1)	12.2 (12.9)	7	—	3.8	354, 334, 320 (sh)	*mer*
$P(CH_2CH_2PPh_2)_3$	Purple	61.0 (60.9)	5.3 (5.1)	12.9 (12.9)	2	746 (828)	4.0	360 (sh), 340, 318	*mer*
$CMe(CH_2PPh_2)_3$	Blue-green	62.0 (62.8)	5.0 (5.0)	13.4 (13.6)	decomp.	—	4.1	350, 334	*fac*
$AsMe(CH_2CH_2CH_2AsMe_2)_2$	Purple	24.2 (24.4)	5.1 (5.0)	19.6 (19.7)	1	461 (542)	3.8 [e]	346br	*fac*
$As(CH_2CH_2CH_2AsMe_2)_3$	Purple	26.7 (26.7)	5.4 (5.3)	15.8 (15.8)	4	628 (674)	3.7 [e]	346, 340 (sh)	*fac*
$CMe(CH_2AsMe_2)_3$	Blue-purple	24.2 (24.3)	5.0 (5.0)	19.5 (19.6)	1.5	—	3.9	333 (sh), 326	*fac*
$S(CH_2CH_2CH_2SMe)_2$	Green	25.9 (26.1)	5.0 (4.9)	27.9 (28.9)	—	—	—	368, 353, 312	*mer*
$CMe(CH_2SMe)_3$	Pink	25.7 (26.1)	5.2 (4.9)	27.7 (28.9)	—	—	—	356, 326	*fac*
[–$CH_2SCH_2CH_2SMe]_2$	Pink-purple	23.6 (23.9)	4.4 (4.5)	26.5 (26.6)	—	—	3.8	353, 340	*fac*
[$CrLBr_3$]									
L									
$PPh(CH_2CH_2PPh_2)_2$	Blue	49.2 (49.4)	4.1 (3.9)	—	1 [c]	—	—	298, 265, 230	*mer*
[–$CH_2P(Ph)CH_2CH_2PPh_2]_2$	Blue	51.9 (52.4)	4.3 (4.4)	24.9 (24.9)	1 [c]	—	3.8	305, 282	*mer*
$P(CH_2CH_2PPh_2)_3$	Blue	52.8 (52.4)	4.3 (4.4)	—	9	948 (962)	—	290 (sh), 263, 245 (sh)	*mer*
$CMe(CH_2PPh_2)_3$	Green	52.9 (53.7)	4.3 (4.3)	—	decomp.	—	—	290, 256	*fac*
$AsMe(CH_2CH_2CH_2AsMe_2)_2$	Purple	19.2 (19.5)	4.0 (4.0)	—	4	—	—	288br	*fac*
$As(CH_2CH_2CH_2AsMe_2)_3$	Purple	22.0 (22.3)	4.5 (4.5)	30.8 (29.7)	9	851 (808)	3.8 [c]	286br	*fac*
$CMe(CH_2AsMe_2)_3$	Blue	18.0 (19.5)	3.8 (4.0)	34.3 (35.3)	insol.	—	3.7	298, 278	*fac*
$S(CH_2CH_2CH_2SMe)_2$	Grey-pink	18.6 (19.1)	3.6 (3.6)	—	—	—	—	328, 307, 285	*mer*
$CMe(CH_2SMe)_3$	Fawn	18.8 (19.1)	3.7 (3.6)	—	—	—	—	305, 292	*fac*
[$CrLF_3$]									
L									
$PPh(CH_2CH_2PPh_2)_2$	Blue	64.5 (63.4)	5.3 (5.2)	—	insol.	—	3.6	544, 517, 505	*mer*
$P(CH_2CH_2PPh_2)_3$	Purple	65.1 (64.7)	5.6 (5.4)	—	5 [c]	—	—	542, 519, 507	*mer*
$CMe(CH_2AsMe_2)_3$	Blue	27.0 (26.8)	5.5 (5.5)	—	insol.	—	4.0	538, 492	*fac*
[$CrLI_3$]									
L									
$PPh(CH_2CH_2PPh_2)_2$	Blue	42.3 (42.2)	3.3 (3.4)	—	—	—	—		
$P(CH_2CH_2PPh_2)_3$	Blue	45.3 (45.7)	3.7 (3.8)	—	—	—	—		
$AsMe(CH_2CH_2CH_2AsMe_2)_2$	Buff	16.2 (16.2)	3.1 (3.3)	—	—	—	—		
$As(CH_2CH_2CH_2AsMe_2)_3$	Yellow-fawn	18.8 (19.0)	3.6 (4.0)	—	—	—	—		
$CMe(CH_2AsMe_2)_3$	Yellow-green	15.9 (16.2)	3.1 (3.3)	—	—	—	—		

Table 1 (*continued*)

Complex		Colour	Analysis (%) ^{a}			Λ_M ^{b}	M ^{a,c}	$\mu_{eff.}$ ^{d}	ν(Cr–X)/cm^{-1}	Isomer
			C	H	X					
CrL_2I_3										
L										
$PPh(CH_2CH_2PPh_2)_2$		Blue	54.7	4.6	—	—	—	—		
			(54.3)	(4.4)						
$CMe(CH_2AsMe_2)_3$		Green	21.8	4.3	—	59.5	—	—		
			(22.0)	(4.5)						
$S(CH_2CH_2CH_2SMe)_2$		Dark green	22.5	4.3	—	insol.	—	—		
			(22.5)	(4.5)						
$[CrLX_2]BF_4$										
L	X									
$P(CH_2CH_2PPh_2)_3$	Cl	Dark blue	57.1	5.0	—	60	—	—	350, 310	*cis*
			(57.2)	(4.8)						
$P(CH_2CH_2PPh_2)_3$	Br	Dark blue	51.5	4.3	—	70	—	—	296, 255	*cis*
			(52.0)	(4.3)						
$P(CH_2CH_2PPh_2)_3$	I	Turquoise	48.0	4.1	—	insol.	—	—	—	*cis*
			(47.4)	(4.0)						
$[\text{-}CH_2P(Ph)CH_2CH_2PPh_2]_2$	Cl	Dark blue	56.8	5.0	—	61	—	—	347, 318	*cis*
			(57.2)	(4.8)						
$As(CH_2CH_2CH_2AsMe_2)_3$	Cl	Purple	25.0	4.7	—	62	—	3.7	346, 326	*cis*
			(24.8)	(5.0)						

[a] Calculated values in parentheses. [b] Values in Ω^{-1} cm^2 mol^{-1} in $MeNO_2$ (10^{-3} mol dm^{-3}); 1 : 1 electrolytes in $MeNO_2$ have Λ_M = 60—115 Ω^{-1} cm^2 mol^{-1} and in $C_2H_4Cl_2$ Λ_M = 10—24 Ω^{-1} cm^2 mol^{-1} (W. J. Geary, *Coord. Chem. Rev.*, 1971, 7, 81). [c] In $ClCH_2CH_2Cl$ (10^{-3} mol dm^{-3}). [d] ±0.1 B.M.; Gouy method. [e] Evans method.

flexible ligands which could in principle produce either isomer, it seems that the phosphines produce *mer*, and the arsines *fac* complexes (Table 1).

In an attempt to obtain a second (*fac*) isomer of $[Cr\{PPh(CH_2CH_2PPh_2)_2\}X_3]$, the reaction of *fac*-$[Cr(CO)_3\{PPh(CH_2CH_2PPh_2)_2\}]$ [11] with dihalogens under various conditions was examined. All of the products had i.r. spectra showing removal of all the carbonyl groups, but also having strong bands at *ca.* 1 150 cm^{-1} characteristic of phosphine oxide groups. It was concluded that both the metal and the phosphine were oxidised. Similar attack on the ligand is reported for $[CrL(CO)_3]$, L = $AsMe(CH_2CH_2CH_2AsMe_2)_2$,[12] but $[CrLX_3]$ (X = Cl, Br, or I) have been made by a similar route for L = $AsMe(o\text{-}C_6H_4AsMe_2)_2$ [6] and possibly $P(o\text{-}C_6H_4PPh_2)_3$ [4] (products identified in solution by u.v.–visible spectra).

$[CrLF_3]$.—Neither anhydrous CrF_3 nor hydrated $CrF_3\cdot3.5H_2O$ react with soft donors, and attempts [8] to isolate $[Cr(thf)_3F_3]$ have been unsuccessful. However, the green thf solution produced on reaction of $[Cr(thf)_3Cl_3]$ with three equivalents of AgF [8] reacted (after removal of the AgCl precipitate) *in situ* with $PPh(CH_2CH_2PPh_2)_2$, $P(CH_2CH_2PPh_2)_3$, or $CMe(CH_2AsMe_2)_3$ to give $[CrLF_3]$. The complexes of $Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2$ or $As(CH_2CH_2CH_2AsMe_2)_3$ could not be isolated. Treatment of $[CrLCl_3]$ in CH_2Cl_2 or thf with AgF was not a viable route to the $[CrLF_3]$ compounds.

$[CrLI_3]$ *and* CrL_2I_3.—The reaction of $[Cr(thf)_3I_3]$ with multidentate ligands in a 1 : 1 ratio gave $[CrLI_3]$ complexes [L = $PPh(CH_2CH_2PPh_2)_2$, $P(CH_2CH_2PPh_2)_3$, $CMe(CH_2AsMe_2)_3$, $AsMe(CH_2CH_2CH_2AsMe_2)_2$, or $As(CH_2CH_2CH_2AsMe_2)_3$] (Table 1). The complexes of the tridentate ligands, and $[Cr\{P(CH_2CH_2PPh_2)_3\}I_3]$ which is a non-electrolyte, are analogous to the other halide adducts having E_3I_3 donor sets. The complex $Cr\{As(CH_2CH_2CH_2AsMe_2)_3\}I_3$ is too insoluble for conductivity studies, but its similarity to that of the linear tridentate arsine suggests it too is of this type (As_3I_3). The isomers present in these complexes have not been identified.

In marked contrast to the other halides, reaction of $[Cr(thf)_3I_3]$ with two equivalents of the tridentates $PPh(CH_2CH_2PPh_2)_2$, $S(CH_2CH_2CH_2SMe)_2$, and $CMe(CH_2AsMe_2)_3$ readily gave CrL_2I_3 complexes. The triphosphine complex has a high conductivity in CH_2Cl_2, and its electronic spectra both in the solid state and solution are identical with that of $[Cr\{PPh(CH_2CH_2PPh_2)_2\}_2][BF_4]_3$ which has CrP_6^{3+} co-ordination,[13] and hence the iodo-complex is formulated similarly. In contrast $Cr\{CMe(CH_2AsMe_2)_3\}_2I_3$ is a 1 : 1 electrolyte in nitromethane, and its electronic spectrum differs from that [13] of $[Cr\{CMe(CH_2AsMe_2)_3\}_2][BF_4]_3$, but resembles that of $[Cr\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]^+$.[14] On this basis it is formulated as $[Cr\{CMe(CH_2AsMe_2)_3\}_2I_2]I$, with the triarsines bound as bidentates. Similar bidentate behaviour of this ligand has been proposed in the $[NiL_2X_2]$ (X = Cl, Br, or I) complexes.[15] The nature of the insoluble trithioether complex is unclear; its electronic spectrum differs from that of $[Cr\{S(CH_2CH_2CH_2SMe)_2\}_2][BF_4]_3$[13] suggesting some iodide co-ordination here also.

The different behaviour of the chromium(III) iodide system to that of the other halides is readily rationalised in terms of the weaker affinity of the hard Cr^{III} for the soft iodide ligands. From the results with the triphosphine and triarsine it seems that the affinity of Cr^{III} for P, As, or I donors is similar, the donor set being influenced by the steric and electronic properties of the individual multidentate ligand.

Structure of $[Cr\{P(CH_2CH_2PPh_2)_3\}Cl_3]$.—The *X*-ray study revealed a distorted octahedral arrangement composed of three chlorine and three phosphorus atoms in *mer* relationships about the chromium (Figure 1). This complex is both the first structurally characterised chromium(III) phosphine complex, and the first example of this tetraphosphine binding as a tridentate ligand Several structures containing the same phosphine bound as a quadridentate ligand have been reported and all of them are five-co-ordinate, *viz.* $[Co\{P(CH_2CH_2PPh_2)_3\}Br]PF_6$,[16] $[Fe\{P(CH_2CH_2PPh_2)_3\}Br]BPh_4$,[17] $[Fe\{P(CH_2CH_2PPh_2)_3\}(SH)]BPh_4$,[18] $[Co\{P(CH_2CH_2PPh_2)_3\}(OH)]BF_4$,[19] and $[Co\{P(CH_2CH_2PPh_2)_3\}(H_2O)][BF_4]_2$.[19] The

Table 2. Selected bond lengths (Å), non-bonded distances (Å) and angles (°) for [Cr{P($CH_2CH_2PPh_2$)$_3$}Cl_3]

Cr–Cl(1)	2.306(4)	Cr–P(1)	2.399(4)	Cl(1) · · · Cl(2)	3.38	Cl(2) · · · P(1)	3.28
Cr–Cl(2)	2.292(6)	Cr–P(2)	2.466(5)	Cl(1) · · · Cl(3)	3.40	Cl(2) · · · P(2)	3.46
Cr–Cl(3)	2.320(5)	Cr–P(3)	2.489(6)	Cl(1) · · · P(2)	3.61	Cl(2) · · · P(3)	3.48
P(1)–C(1)	1.82(2)	P(3)–C(2)	1.87(1)	Cl(1) · · · P(3)	3.66	Cl(3) · · · P(1)	3.09
P(1)–C(3)	1.83(1)	P(3)–C(31)	1.79(1)	P(1) · · · P(2)	3.15	Cl(3) · · · P(2)	3.23
P(1)–C(5)	1.81(2)	P(3)–C(41)	1.79(1)	P(1) · · · P(3)	3.18	Cl(3) · · · P(3)	3.28
P(2)–C(4)	1.84(1)	P(4)–C(6)	1.83(2)	C(1)–C(2)	1.53(2)	C–C(aromatic)	1.395 (fixed)
P(2)–C(11)	1.80(1)	P(4)–C(51)	1.85(1)	C(3)–C(4)	1.55(3)	C–H	1.08 (fixed)
P(2)–C(21)	1.82(2)	P(4)–C(61)	1.79(1)	C(5)–C(6)	1.56(2)		

Cl(1)–Cr–Cl(2)	94.6(2)	Cr–P(1)–C(1)	107.9(4)	Cl(2)–Cr–P(1)	88.8(2)
Cl(1)–Cr–Cl(3)	94.7(2)	Cr–P(1)–C(3)	106.7(4)	Cl(2)–Cr–P(2)	93.2(2)
Cl(2)–Cr–Cl(3)	170.7(2)	Cr–P(1)–C(5)	120.9(5)	Cl(2)–Cr–P(3)	93.4(2)
Cl(1)–Cr–P(1)	176.6(2)	Cr–P(2)–C(4)	108.3(6)	Cl(3)–Cr–P(1)	81.9(2)
Cl(1)–Cr–P(2)	98.3(2)	Cr–P(2)–C(11)	119.9(4)	Cl(3)–Cr–P(2)	84.8(2)
Cl(1)–Cr–P(3)	99.4(2)	Cr–P(2)–C(21)	115.8(4)	Cl(3)–Cr–P(3)	85.8(2)
P(1)–Cr–P(2)	80.8(2)	C(1)–P(1)–C(3)	112.2(8)	Cr–P(3)–C(2)	106.2(6)
P(1)–Cr–P(3)	81.0(2)	C(1)–P(1)–C(5)	104.8(7)	Cr–P(3)–C(31)	122.5(5)
P(2)–Cr–P(3)	160.5(2)	C(3)–P(1)–C(5)	104.4(7)	Cr–P(3)–C(41)	112.9(4)

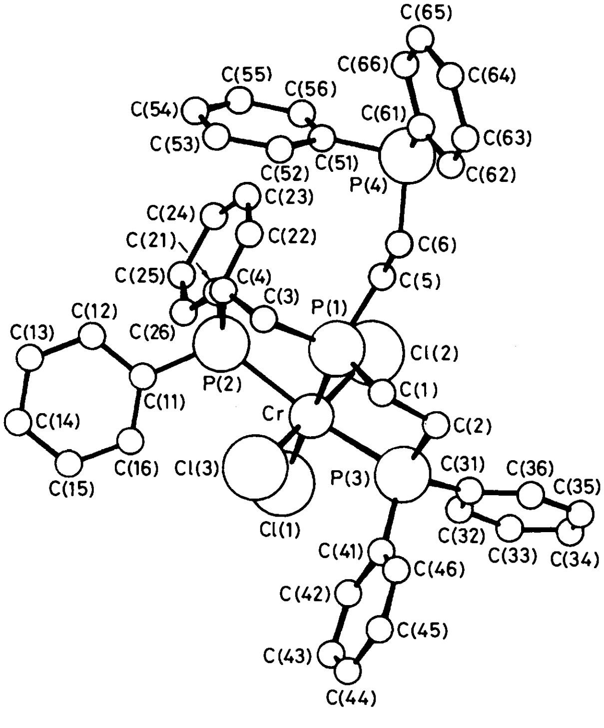


Figure 1. Discrete molecule of [Cr{P($CH_2CH_2PPh_2$)$_3$}Cl_3] showing the atom numbering scheme and excluding H atoms

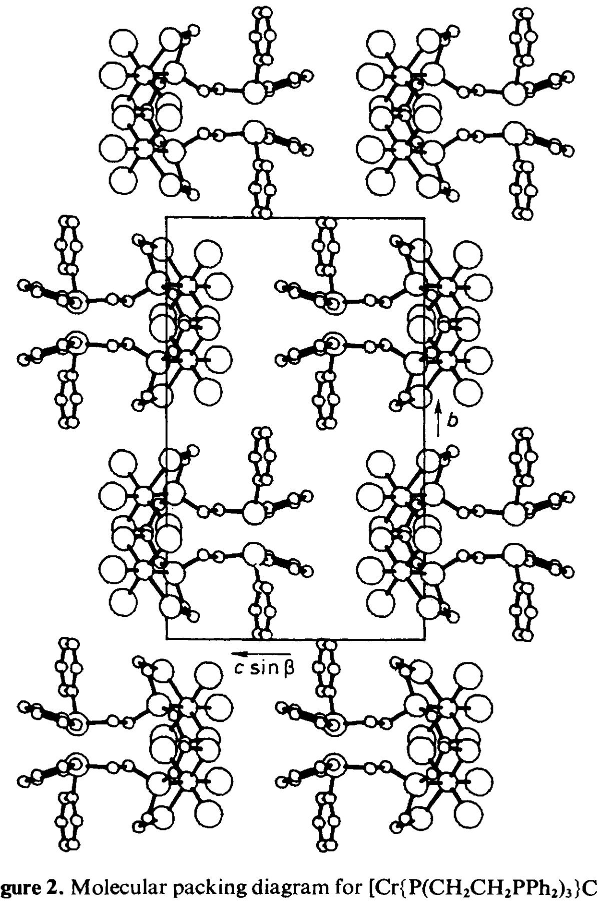


Figure 2. Molecular packing diagram for [Cr{P($CH_2CH_2PPh_2$)$_3$}Cl_3] viewed from the *a* direction. All H atoms and the phenyl groups on the co-ordinated P atoms have been excluded for clarity

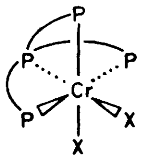
first point of note about the title complex is the long Cr–P bonds: Cr–P(2) 2.466(5), Cr–P(3) 2.489(6), Cr–P(1) 2.399(4) Å (Table 2). In the five-co-ordinate complexes the M–P-(Ph_2) distances are in the range *ca.* 2.25—2.36 Å and M–P-(central) is *ca.* 2.14—2.25 Å. A useful comparison is with [Fe{PPh($CH_2CH_2PPh_2$)$_2$}$_2$$Cl_2$] which is octahedral with the triphosphines bound as bidentates,[20] in which the very long Fe–P distances [2.665(3) and 2.713(3) Å] are attributable both to the steric repulsions within this very crowded molecule, and to the weak binding of the phosphine to the hard (high-spin) Fe^{II}. The steric interactions are also evident in the present chromium complex, and since Cr^{III} is a hard metal ion, the electronic factors also favour weak binding of the phosphines. The shorter Cr–P(1) distance compared with Cr–P(2) and Cr–P(3) is consistent with stronger binding of the trialkyl-substituted P(1) compared to the diaryl(alkyl)-substituted P(2) and P(3).[16–18] The free arm of the chelate is bent away from the metal [Cr–P(1)–C(5) 120.9(5)°] probably due to non-bonded interactions (Figure 2), but also serves to reduce the crowding at the metal. The Cr–Cl distances are normal: Cr–Cl-(*trans* Cl) 2.320(5), 2.292(6) Å and Cr–Cl(*trans* P) 2.306(4) Å.

Comparable Cr–Cl(*trans* Cl) distances are 2.32 Å in *trans*-$[Cr(H_2NCH_2CH_2NH_2)_2Cl_2]^+$,[21] 2.286(1) Å in *trans*-$[Cr(H_2O)_4Cl_2]^+$,[22] and 2.34(1) Å in *mer*-trichloro(*NN*-dimethylformamide)(1,10-phenanthroline)chromium(III).[23]

The angles at the chromium differ by up to 9.4° from the idealised 90°, and inspection of the values shows an approximate mirror in the Cl(1)Cl(2)Cl(3)P(1) plane but not in the Cl(1)P(1)P(2)P(3) plane. The non-bonded distances in the CrP_3Cl_3 octahedron vary from 3.09 [Cl(3) $\cdots$ P(1)] to 3.66 Å [Cl(1) $\cdots$ P(3)]. The smallest value probably arises from the steric requirements of C(5) in matching the inherent three-fold symmetry of the phosphine ligand to the four-fold symmetry of the acceptor grouping, and gives rise to the differences (5σ) in the Cr–Cl(*trans* Cl) bond lengths [Cr–Cl(3) > Cr–Cl(2)].

In view of the distortion it is not possible to establish whether the phosphine exerts a measurable *trans* influence.

$[CrLX_2]BF_4$.—Although $[Cr\{As(CH_2CH_2CH_2AsMe_2)_3\}Cl_3]$ is a non-conductor in freshly prepared $MeNO_2$ solution, on standing the conductivity increases, and after about 4 h reaches *ca.* 60% of the expected value for a 1 : 1 electrolyte. A similar but smaller increase in conductance occurred with $[Cr\{P(CH_2CH_2PPh_2)_3\}Cl_3]$, but that of $[Cr\{AsMe(CH_2CH_2CH_2AsMe_2)_2\}Cl_3]$ showed no change over the same period. This suggests that in a polar solvent the quadridentate ligand complexes may partially ionise to form a species of the type $CrE_4X_2^+$. Attempts to isolate these by addition of $LiClO_4$ failed. However, treatment of $[Cr\{P(CH_2CH_2PPh_2)_3\}X_3]$ (X = Cl, Br, or I), $[Cr\{\text{-}CH_2P(Ph)CH_2CH_2PPh_2\}_2Cl_3]$, or $[Cr\{As(CH_2CH_2CH_2AsMe_2)_3\}Cl_3]$ in CH_2Cl_2 with one mol equiv. of $AgBF_4$ gave a solution from which the required $[CrLX_2]BF_4$ complexes were isolated (Table 1). These are 1 : 1 electrolytes in $MeNO_2$, except for $[Cr\{P(CH_2CH_2PPh_2)_3\}I_2]BF_4$ which was insufficiently soluble for measurement. The tripod quadridentates can only bind as in (I) to octahedral metal ions, and this structure was confirmed by the presence of two ν(Cr–X) stretches in the far-i.r. spectra ($A_1 + B_1$). The i.r. spectrum of the linear tetraphosphine complex (Table 1) is very similar to those of the other chloro-complexes and hence it is also the *cis* complex.



(I)

Electronic Spectra.—For Cr^{III} (d^3) in O_h symmetry three spin allowed *d*–*d* bands are predicted,[24] assigned as $^4A_{2g} \longrightarrow {}^4T_{2g}$ (ν_1), $^4A_{2g} \longrightarrow {}^4T_{1g}(F)$ (ν_2), and $^4A_{2g} \longrightarrow {}^4T_{1g}(P)$ (ν_3). In practice ν_3 is obscured by more intense charge-transfer bands. The spectra of the $[CrLX_3]$ and $[CrLX_2]BF_4$ complexes were analysed by the standard treatment [24] and *Dq*, *B′*, and β_{35} obtained. Full details of the spectra and the derived parameters are in SUP 23748. The lower actual symmetry of these complexes results in some splitting of the bands, and this coupled with the broadness and overlapping of the bands introduces some inaccuracy, but the assignments are generally clear. The $[CrLI_3]$ complexes gave very ill defined absorptions in the range 14 000—19 000 cm^{-1} superimposed on the tail of the higher energy charge-transfer bands, and in view of the poor spectral quality have not been included.

The $[CrLX_3]$ complexes produce the expected trends in *Dq* (N > P ~ As > S > F ~ Cl > Br), and the Racah parameter *B′* is greatly reduced from the free ion value (918 cm^{-1}) in the order P ~ As > S. The individual *B′* values may be of low accuracy (as is often the case [24]), since they were each derived from a single calculation and small changes in ν_1 and ν_2 energies produce significant shifts in *B′*. Assignment of the charge-transfer bands has not been attempted, although we note that $[CrLCl_3]$ have very intense bands at *ca.* 33 000 cm^{-1}, and $[CrLBr_3]$ have similar absorptions at *ca.* 28 000—30 000 cm^{-1}, in good agreement with the predictions for $X(\pi) \longrightarrow Cr(t_{2g})$ transitions using a $\chi_{opt.}$ of 1.9 for Cr^{III}.[24] Comparison of the spectral parameters for $[CrLX_2]^+$ with those of $[CrLX_3]$ reveal little change in *Dq* or *B′*. Probably the expected increase in *Dq* and decrease in *B′* on replacement of X by P or As is off-set by the effect of the charge on the cation, which would result in a contraction of the chromium *d* orbitals (a ‘ hardening ’ of the Cr) and less effective interaction with the soft donor.

Experimental

Electronic spectra were obtained on a Perkin-Elmer 554 spectrometer. Other physical measurements were made as described previously.[25] 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] The ligands $P(CH_2CH_2PPh_2)_3$, $PPh(CH_2CH_2PPh_2)_2$, and $CMe(CH_2PPh_2)_3$ were purchased from the Strem Chemical Co.; other ligands were made by literature routes.[9,26] Tetrahydrofuran was dried by distillation from $LiAlH_4$, other solvents over molecular sieves.

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

$[Cr\{PPh(CH_2CH_2PPh_2)_2\}X_3]$ (X = Cl *or* Br).—$[Cr(thf)_3X_3]$ (2 mmol) was dissolved in dichloromethane and filtered. Bis(2-diphenylphosphinoethyl)phenylphosphine (1.07 g, 2 mmol) was dissolved in dichloromethane (*ca.* 40 cm^3) and added under nitrogen to the filtrate. A dark blue solution formed immediately. 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 blue solid was isolated by filtration and dried *in vacuo*.

$[CrLX_3]$ {L = $P(CH_2CH_2PPh_2)_3$, $[\text{-}CH_2P(Ph)CH_2CH_2PPh_2]_2$, $CMe(CH_2PPh_2)_3$, $AsMe(CH_2CH_2CH_2AsMe_2)_2$, $As(CH_2CH_2CH_2AsMe_2)_3$, $CMe(CH_2AsMe_2)_3$, $S(CH_2CH_2SMe)_2$, $CMe(CH_2SMe)_3$, or $[\text{-}CH_2SCH_2CH_2SMe]_2$; X = Cl or Br} were prepared similarly. Liquid ligands were added undiluted to the filtered solution of $[Cr(thf)_3X_3]$ under nitrogen.

$[CrLI_3]$ [L = $PPh(CH_2CH_2PPh_2)_2$, $P(CH_2CH_2PPh_2)_3$, $AsMe(CH_2CH_2CH_2AsMe_2)_2$, $As(CH_2CH_2CH_2AsMe_2)_3$, *or* $CMe(CH_2AsMe_2)_3$].—$[Cr(thf)_3I_3]$ (0.325 g, 0.5 mmol) was dissolved in CH_2Cl_2 and filtered. Ligand (0.5 mmol) was added under nitrogen to the filtrate and the solution stirred for *ca.* 30 min. The solution was concentrated *in vacuo* at room temperature and the resulting oil/solid stirred under dry light petroleum (b.p. 40—60 °C) containing a few drops of 1,2-dichloroethane. The solid obtained was filtered off and dried *in vacuo*.

CrL_2I_3 [L = $PPh(CH_2CH_2PPh_2)_2$, $CMe(CH_2AsMe_2)_3$, *or* $S(CH_2CH_2CH_2SMe)_2$].—These complexes were prepared using the same general method as for $[CrLI_3]$, but using 0.5 mmol of $[Cr(thf)_3I_3]$ and 1.0 mmol of ligand. $Cr[PPh(CH_2CH_2PPh_2)_2]_2I_3$: $\Lambda_M = 78\ \Omega^{-1}\ cm^2\ mol^{-1}$ for 10^{-3} mol dm^{-3}

Table 3. Final atomic co-ordinates ($\times 10^4$) for $[Cr\{P(CH_2CH_2PPh_2)_3\}Cl_3]$ with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cr	1 745(2)	1 621(1)	878(2)	C(26)	3 636(8)	789(5)	−482(8)
Cl(1)	3 341(3)	1 629(2)	2 073(3)	C(31)	1 418(8)	3 151(4)	1 955(8)
Cl(2)	2 022(3)	2 360(2)	−114(3)	C(32)	2 428(8)	3 264(4)	2 303(8)
Cl(3)	1 208(3)	862(2)	1 676(3)	C(33)	2 793(8)	3 859(4)	2 600(8)
P(1)	67(3)	1 558(2)	−318(3)	C(34)	2 148(8)	4 341(4)	2 550(8)
P(2)	1 909(3)	762(2)	−166(3)	C(35)	1 138(8)	4 228(4)	2 202(8)
P(3)	989(3)	2 370(2)	1 668(3)	C(36)	773(8)	3 633(4)	1 905(8)
P(4)	−1 768(4)	2 016(3)	−3 462(4)	C(41)	1 007(8)	2 104(5)	2 847(6)
C(1)	−723(11)	1 809(7)	309(11)	C(42)	1 918(8)	1 935(5)	3 588(6)
C(2)	−339(11)	2 436(7)	790(11)	C(43)	1 978(8)	1 726(5)	4 522(6)
C(3)	−154(10)	750(6)	−728(11)	C(44)	1 129(8)	1 685(5)	4 716(6)
C(4)	672(10)	546(7)	−1 068(11)	C(45)	218(8)	1 853(5)	3 976(6)
C(5)	−352(11)	1 996(8)	−1 477(11)	C(46)	158(8)	2 063(5)	3 041(6)
C(6)	−1 483(11)	1 947(8)	−2 112(11)	C(51)	−1 304(9)	1 250(5)	−3 643(9)
C(11)	2 478(7)	49(4)	420(8)	C(52)	−1 730(9)	701(5)	−3 506(9)
C(12)	2 442(7)	−455(4)	−197(8)	C(53)	−1 357(9)	133(5)	−3 648(9)
C(13)	2 907(7)	−1 008(4)	229(8)	C(54)	−557(9)	114(5)	−3 929(9)
C(14)	3 406(7)	−1 058(4)	1 271(8)	C(55)	−130(9)	664(5)	−4 066(9)
C(15)	3 442(7)	−554(4)	1 887(8)	C(56)	−504(9)	1 232(5)	−3 923(9)
C(16)	2 978(7)	−1(4)	1 462(8)	C(61)	−3 072(7)	1 881(6)	−4 007(9)
C(21)	2 632(8)	927(5)	−902(8)	C(62)	−3 664(7)	2 040(6)	−3 496(9)
C(22)	2 215(8)	1 211(5)	−1 843(8)	C(63)	−4 686(7)	1 977(6)	−3 971(9)
C(23)	2 802(8)	1 357(5)	−2 365(8)	C(64)	−5 115(7)	1 756(6)	−4 957(9)
C(24)	3 806(8)	1 219(5)	−1 945(8)	C(65)	−4 522(7)	1 598(6)	−5 468(9)
C(25)	4 223(8)	935(5)	−1 004(8)	C(66)	−3 501(7)	1 660(6)	−4 993(9)

Carbon atoms of the phenyl groups are labelled C(*ij*) where *i* (1—6) indicates the ring and *j* (1—6) the atoms within a ring.

solution in CH_2Cl_2 (1 : 1 electrolytes in CH_2Cl_2 have Λ_M = 20—28 Ω^{-1} cm^2 mol^{-1} [27,28]). Nujol mull diffuse reflectance spectrum, $\nu_{max.}$ (10^3 cm^{-1}) = 16.39, 22.73; in CH_2Cl_2 solution, $\nu_{max.}$ (10^3 cm^{-1}) ($\varepsilon_{mol.}$/dm^3 mol^{-1} cm^{-1}) = 16.39 (220), 17.0 (220), 21.55 (127), 22.22 (120). $[Cr\{CMe(CH_2AsMe_2)_3\}_2I_2]I$: Nujol mull diffuse reflectance spectrum, $\nu_{max.}$ (10^3 cm^{-1}) = 16.00, 19.60, 20.83, 24.40; in CH_2Cl_2 solution, $\nu_{max.}$ (10^3 cm^{-1}) ($\varepsilon_{mol.}$/dm^3 mol^{-1} cm^{-1}) = 15.62 (284), 18.31 (266), 20.41 (294), 24.39 (412). $Cr\{S(CH_2CH_2CH_2SMe)_2\}_2I_3$: Nujol mull diffuse reflectance spectrum, $\nu_{max.}$ (10^3 cm^{-1}) = 15.02 (sh), 16.26, 21.46, 22.73, 25.25 (last three bands on charge-transfer tail).

$[Cr\{P(CH_2CH_2PPh_2)_3\}X_2]BF_4$ (X = Cl, Br, *or* I).—A methylene chloride solution of $[Cr\{P(CH_2CH_2PPh_2)_3\}X_3]$ (0.5 mmol) was prepared *in situ* as above. After stirring under nitrogen for *ca.* 20 min, solid $AgBF_4$ (0.098 g, 0.5 mmol) was added followed by dry thf (*ca.* 20 cm^3). The mixture was stirred under nitrogen overnight, then filtered and the resulting dark blue (X = Cl or Br) or light blue (X = I) solution concentrated *in vacuo* to yield a blue oil. This was stirred under light petroleum (b.p. 40—60 °C), filtered and dried. The complexes $[Cr\{P(CH_2CH_2PPh_2)_3\}X_2]BF_4$ were recrystallised by dissolving in the minimum amount of methylene chloride, filtering and concentrating the filtrate *in vacuo*.

$[CrLX_2]BF_4$ {L = $[^-CH_2P(Ph)CH_2CH_2PPh_2]_2$ or $As(CH_2CH_2CH_2AsMe_2)_3$, X = Cl} were prepared similarly.

Halogenation of fac-$[Cr(CO)_3\{PPh(CH_2CH_2PPh_2)_2\}]$.—The tricarbonyl complex was prepared by the standard literature route.[26] *fac*-$[Cr(CO)_3\{PPh(CH_2CH_2PPh_2)_2\}]$ (0.19 g, 0.28 mmol) was dissolved in chloroform and three equivalents of bromine in chloroform (1 cm^3 of a solution containing 2.3 cm^3 bromine in 97.7 cm^3 $CHCl_3$) added under nitrogen. A green solution was initially obtained, but this rapidly became blue on stirring and then pink-brown. Concentration *in vacuo* gave a purple-brown solid.

Similar attempted oxidations with iodine yielded brown oils that were stirred under dry light petroleum (b.p. 40—60 °C) before isolating a brown solid.

$[CrLF_3]$ [L = $PPh(CH_2CH_2PPh_2)_2$, $P(CH_2CH_2PPh_2)_3$, *or* $CMe(CH_2AsMe_2)_3$].—$[Cr_3(thf)_3Cl]$ (0.187 g, 0.5 mmol) in thf was stirred with excess silver(I) fluoride (at least 2.5 mmol) until a pale green solution was obtained. This reaction seems to work better if the AgF is slightly damp, aiding solubility. The AgCl which precipitated was removed by filtration and the ligand (0.5 mmol) added to the filtrate. After overnight stirring, the solution was concentrated *in vacuo*, the oil obtained stirred under dry light petroleum (b.p. 40—60 °C) and the resulting solid filtered off and dried *in vacuo*.

Crystal Structure Determination of $[Cr\{P(CH_2CH_2PPh_2)_3\}Cl_3]$.—Air-stable crystals were grown by slow diffusion of pentane into a methylene chloride solution of the compound over a period of a few days. Preliminary *X*-ray photographic examination established the crystal system and approximate cell dimensions and accurate cell dimensions were obtained from the setting angles of 25 accurately centred reflections on the diffractometer.

Crystal data. $C_{42}H_{42}Cl_3CrP_4$, M = 829.0, Monoclinic, a = 14.787(6), b = 21.617(4), c = 14.474(4) Å, β = 113.43(3)°, U = 4 245.1 $Å^3$, D_m (flotation) = 1.32(2) g cm^{-3}, Z = 4, D_c = 1.297 g cm^{-3}, $F(000)$ = 1 716, Mo-K_α radiation (λ = 0.7107 Å), μ = 5.83 cm^{-1}, space group $P2_1/a$ (no. 14). Systematic absences ($h0l$, $h \neq 2n$; $0k0$, $k \neq 2n$) unambiguously established the centrosymmetric space group $P2_1/a$.

Data collection. Using graphite-monochromated Mo-K_α radiation, 8 208 reflections were recorded ($1.5 < \theta < 25°$) on a room-temperature crystal (0.5 × 0.1 × 0.1 mm) using an Enraf-Nonius CAD-4 diffractometer. The check reflections showed no change during the course of the experiment and an empirical psi-scan absorption correction was applied. After averaging multiply measured reflections (merging R = 0.009) there remained 7 427 unique reflections whose normalised structure factors (E's) suggested a centrosymmetric space group in accord with the absences. The width of the peaks during the initial diffractometer peak search indicated rather poor crystallinity and the data included a large number of weak reflections [57% with $F < 3\sigma(F)$]. It was found necessary (see later section) to introduce a lower $\theta_{\text{max.}}$ limit during the analysis and this was later set to 20.5° ($\sin\theta < 0.35$), eliminating 3 175 reflections. Eliminating those reflections where $F < 5\sigma(F)$ left 2 101 reflections which were used in the refinement.

Structure analysis and refinement. The structure was solved by conventional Patterson methods. Both Cr–Cr and Cr–Cl(P) vectors were located with appropriate heights. Introducing Cr into a structure factor calculation followed by an electron-density calculation located the Cl and P atoms and repetition of this process rapidly located the remaining non-hydrogen atoms. Least squares refinement [all data ($\theta_{\text{max.}} = 25°$), omitting $F < 3\sigma(F)$, isotropic atoms] reduced R to *ca.* 0.12 but subsequent attempts to improve the data fit failed to lower the residual. A difference electron-density synthesis showed no missing or misplaced atoms and an alternative empirical absorption correction failed to improve matters. Since the distinction between $P2_1/a$ and Pa depends critically on a small number of $0k0$ reflections, refinement was also attempted in space group Pa (with two molecules in the asymmetric unit) with no improvement.

Successful refinement was achieved in space group $P2_1/a$ by introducing a maximum θ value of 20.5° ($\sin\theta < 0.35$).

Least-squares refinement using anisotropic temperature factors for Cr, P, and Cl atoms, isotropic carbon atoms, rigid C_6 groups (C–C 1.395 Å), empirical weights $\{w = 1/[\sigma^2(F) + AF^2], A = 0.0009\}$, hydrogen atoms in calculated positions [d(C–H) = 1.08 Å] slowly converged to a final $R = 0.075$ ($R' = 0.079$). The ratio of reflections (2 101) to parameters (169) is 12.4 and a final difference electron-density synthesis showed all features in the range +1.27 to −0.41 e Å^{-3}.

The final atomic co-ordinates are given in Table 3 and selected bond lengths and angles in Table 2.

Scattering factors for neutral atoms and anomalous dispersion corrections were taken from ref. 29 (Cr) and SHELX [30] (Cl, P, C, H). All calculations were carried out on an ICL2970 computer using the programs SHELX,[30] PLUTO,[31] XANADU [32] and various local programs.

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