solution, although not in the same molar ratio as in the crystal. In the present case there is no second isomer in the solution or in the crystal (i.e., no disorder in the crystal). Why should this be so?

Inspection of Figure 6 will reveal the answer. Neither of the two molecules that can be obtained from the one that is found by changing the orientation of the Mo_2 within the ligand cage is a β isomer. Both are α isomers, and in fact, they are identical. Evidently the energy difference between the β and α isomers is so great as to disfavor the α isomer altogether.

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Supplementary Material Available: Complete tables of anisotropic thermal parameters, bond distances, bond angles, and torsional angles for the central portion of the molecule and schematic figures of the 10 possible isomers (11 pages); listings of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Tertiary Phosphine Complexes of Chromium(III): Syntheses, Magnetic Properties, and Single-Crystal Structure Studies on $Cr_2Cl_6(PMe_3)_4$, $Cr_2Cl_6(PEt_3)_4$, and $Cr_2Cl_6(dmpm)_2$

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Anhydrous chromium(III) chloride reacts, in appropriate solvents at reflux temperatures, with each of the monodentate tertiary phosphines PMe_3 and PEt_3 and with the bidentate tertiary phosphine bis(dimethylphosphino)methane (dmpm) to form $Cr_2Cl_6(PMe_3)_4$ (**1**), $Cr_2Cl_6(PEt_3)_4$ (**2**) and $Cr_2Cl_6(dmpm)_2$ (**3**), respectively. Complex **1** was also obtained from the reaction of $Cr_2(OAc)_4$, Me_3SiCl, and PMe_3. The magnetic susceptibility of **2** varies with temperature in the range 5–300 K, in agreement with the Curie–Weiss law, and this indicates no significant interaction between the Cr atoms. However, the magnetic properties of **3** suggest that there may be an antiferromagnetic interaction between the Cr atoms at low temperatures (1.3–10 K). The $Cr\cdots Cr$ distances are as follows: **1**, 3.587 (5) Å; **2**, 3.637 (2) Å; **3**, 3.480 (1) Å. Crystal data: $Cr_2Cl_6(PMe_3)_4$ (**1**), orthorhombic, space group *Pmcn*, $a = 13.452$ (3) Å, $b = 18.292$ (3) Å, $c = 11.317$ (2) Å, $V = 2784.7$ (9) Å^3, $Z = 4$, $R = 0.064$ ($R_w = 0.092$) for 877 data with $F_o^2 > 3\sigma(F_o^2)$; $Cr_2Cl_6(PEt_3)_4$ (**2**), orthorhombic, space group *Pnma*, $a = 20.184$ (3) Å, $b = 19.066$ (2) Å, $c = 10.642$ (1) Å, $V = 4095.3$ (9) Å, $Z = 4$, $R = 0.0498$ ($R_w = 0.072$) for 1889 data with $F_o^2 = 3\sigma(F_o^2)$; $Cr_2Cl_6(dmpm)_2$ (**3**), monoclinic, space group $P2_1/a$, $a = 8.505$ (2) Å, $b = 20.574$ (2) Å, $c = 8.481$ (1) Å, $\beta = 92.66°$, $V = 1482.4$ (3) Å^3, $Z = 2$, $R = 0.0332$ ($R_w = 0.0423$) for 2099 data with $F_o^2 > 3\sigma(F_o^2)$.

Introduction

Chromium(III) complexes containing monodentate tertiary phosphines have been known for quite some time. These include the dimers $[CrX_3(PR_3)_2]_2$ (X = Cl, R = Et, Bu^n; X = Br, R = Et),[1,2] several polymers $[CrCl_3(PR_3)]_n$ (R = Et, Bu^n, Ph), and the monodentate anionic complex $[PPh_4][CrCl_4(PR_3)_2]$ (R = Et).[2] However, there have not been any prior reports of binuclear chromium(III) complexes containing bidentate tertiary phosphines. In addition, the structures of the binuclear Cr(III) complexes containing P donor atoms have generally been inferred from conductance and molecular weight measurements,[1] and IR and electronic spectra.[2] No single-crystal X-ray data have been reported previously for these Cr dimers.

We report here the preparation and the single-crystal structure determinations of binuclear Cr(III) complexes containing mono- [$Cr_2Cl_6(PMe_3)_4$ (**1**) and $Cr_2Cl_6(PEt_3)_4$ (**2**)] and bidentate tertiary phosphines [$Cr_2Cl_6(dmpm)_2$ (**3**)] and the variable-temperature magnetic susceptibilities of complexes **2** and **3**. The purpose of this work was to see what sort of Cr–Cr interactions might occur in these bridged binuclear systems, as well as to have well-characterized dichromium(III) species as potential synthetic precursors for the preparation of dichromium(II) compounds.

Experimental Section

All operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods and distilled under dinitrogen. Electronic spectra were measured in dichloromethane and benzene solutions with a Cary 17D spectrophotometer. The elemental analysis was done by Galbraith Laboratories, Knoxville, TN. PMe_3, PEt_3, dmpm, and $CrCl_3$ were purchased from Strem Chemicals, and $(CH_3)_3SiCl$ was purchased from Aldrich Chemicals Co.

Table I. Crystallographic Data for Compounds **1–3**

	1	**2**	**3**
formula	$C_{12}H_{36}Cl_6Cr_2P_4$	$C_{24}H_{60}Cl_6Cr_2P_4$	$C_{10}H_{28}Cl_6Cr_2P_4\cdot 2CH_2Cl_2$
fw	621.0	789.35	758.81
space group	*Pmcn* (No. 62)	*Pnma* (No. 62)	$P2_1/a$ (No. 14)
a, Å	13.452 (3)	20.184 (3)	8.505 (3)
b, Å	18.292 (3)	19.066 (2)	20.574 (5)
c, Å	11.317 (3)	10.642 (3)	8.481 (1)
α, deg	90	90	90
β, deg	90	90	94.66 (2)
γ, deg	90	90	90
V, Å^3	2784.7 (9)	4095.3 (9)	1482.4 (3)
Z	4	4	2
T, °C	21	20	−80
λ, Å	0.71073	0.71073	0.71073
ρ_{obs}, g/cm^3	1.487	1.285	1.706
μ, cm^{-1}	15.705	10.819	18.445
trans coeff	1.00–0.77	1.00–0.82	1.00–0.83
$R(F_o)^a$	0.064	0.050	0.033
$R_w(F_o)^b$	0.092	0.072	0.042

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Preparation of $Cr_2Cl_6(PMe_3)_4$ (1). The complex $Cr_2Cl_6(PMe_3)_4$ (**1**) was obtained as a byproduct from the reaction of a mixture of $Cr_2(OAc)_4$,[3] 4 equiv of PMe_3, and excess Me_3SiCl in THF.[4] Crystals suitable for the X-ray analysis were obtained by the slow diffusion of hexane into a THF solution of the residue from the above reaction. A high yield of compound **1** can be obtained by reacting $CrCl_3$ with PMe_3.[1]

Preparation of $Cr_2Cl_6(PEt_3)_4$ (2). This was prepared by the method of Issleib and Froehlich.[1,2] A 0.64-g (4.0-mmol) sample of anhydrous chromium(III) chloride was reacted with 1.1 mL (7.6 mmol) of PEt_3 in

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Table II. Positional Parameters and Their Estimated Standard Deviations for $Cr_2Cl_6(PMe_3)_4$ (**1**)[a]

atom	x	y	z	B, Å^2
Cr(1)	0.2500	0.5752 (2)	0.0787 (2)	2.43 (8)
Cr(2)	0.2500	0.4273 (2)	0.2872 (2)	2.59 (8)
Cl(1)	0.1321 (2)	0.5012 (2)	0.1829 (3)	3.35 (7)
Cl(2)	0.6225 (3)	0.1377 (2)	0.5084 (4)	4.3 (1)
Cl(3)	0.7500	0.4980 (3)	0.5507 (5)	5.1 (2)
Cl(4)	0.2500	0.1624 (3)	0.6458 (5)	5.1 (2)
P(1)	0.2500	0.4927 (3)	−0.0940 (5)	3.5 (1)
P(2)	0.2500	0.6708 (3)	0.2313 (5)	3.3 (1)
P(3)	0.1138 (4)	0.3605 (2)	0.3837 (4)	4.6 (1)
C(11)	0.7500	0.454 (2)	0.231 (2)	5.2 (8)
C(12)	0.363 (1)	0.066 (1)	0.393 (1)	5.5 (5)
C(21)	0.7500	0.263 (1)	0.332 (2)	4.2 (5)*
C(22)	0.644 (1)	0.3300 (9)	0.670 (2)	6.1 (5)
C(31)	0.385 (2)	0.349 (2)	0.539 (2)	17 (1)
C(32)	0.501 (2)	0.396 (2)	0.350 (3)	22 (2)
C(33)	0.412 (3)	0.273 (2)	0.337 (4)	30 (2)

[a] Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. Starred values denote atoms that were refined isotropically.

Table III. Positional Parameters and Their Estimated Standard Deviations for $Cr_2Cl_6(PEt_3)_4$ (**2**)[a]

atom	x	y	z	B, Å^2
Cr(1)	0.06018 (7)	0.250	0.0994 (1)	3.75 (3)
Cr(2)	−0.08960 (7)	0.250	−0.0905 (2)	3.76 (3)
Cl(1)	0.0280 (1)	0.250	−0.1196 (2)	4.17 (5)
Cl(2)	−0.0593 (1)	0.250	0.1258 (2)	4.81 (6)
Cl(3)	0.06560 (9)	0.36977 (9)	0.1102 (2)	5.67 (5)
Cl(4)	−0.1061 (2)	0.250	−0.3029 (3)	6.08 (8)
Cl(5)	−0.1997 (1)	0.250	−0.0406 (3)	6.59 (8)
P(1)	0.0736 (2)	0.250	0.3343 (3)	7.3 (1)
P(2)	0.1792 (1)	0.250	0.0281 (3)	5.31 (7)
P(3)	−0.09704 (9)	0.11862 (9)	−0.0980 (2)	5.47 (5)
C(111)	0.138 (3)	0.319 (2)	0.384 (3)	9 (1)
C(112)	0.137 (1)	0.335 (2)	0.535 (2)	10.6 (8)
C(121)	−0.006 (1)	0.293 (1)	0.409 (2)	10.2 (9)
C(122)	−0.021 (1)	0.367 (2)	0.388 (2)	12 (1)
C(131)	0.083 (2)	0.178 (2)	0.420 (3)	14 (1)
C(132)	0.144 (2)	0.151 (2)	0.417 (5)	12 (1)
C(211)	0.1925 (9)	0.294 (1)	−0.131 (2)	7.1 (5)
C(212)	0.182 (2)	0.376 (2)	−0.131 (5)	10 (2)
C(221)	0.2328 (8)	0.301 (1)	0.140 (2)	9.9 (7)
C(222)	0.306 (1)	0.306 (1)	0.092 (2)	12.4 (8)
C(231)	0.216 (1)	0.162 (1)	−0.003 (3)	12 (1)
C(232)	0.177 (2)	0.129 (2)	−0.110 (3)	14 (1)
C(311)	−0.1066 (5)	0.0720 (5)	0.054 (1)	8.0 (3)
C(312)	−0.1695 (6)	0.0896 (7)	0.128 (1)	11.9 (4)
C(321)	−0.1699 (4)	0.0935 (4)	−0.194 (1)	8.1 (3)
C(322)	−0.1832 (6)	0.0123 (5)	−0.199 (1)	12.4 (5)
C(331)	−0.0267 (4)	0.0687 (4)	−0.165 (1)	7.6 (3)
C(332)	−0.0132 (7)	0.0816 (7)	−0.299 (1)	11.3 (4)

[a] Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$.

Table IV. Positional Parameters and Their Estimated Standard Deviations for $Cr_2Cl_6(dmpm)_2{\cdot}2CH_2Cl_2$[a] (**3**)

atom	x	y	z	B, Å^2
Cr	0.10838 (5)	0.43352 (2)	0.57042 (5)	1.098 (8)
Cl(1)	−0.11756 (8)	0.49246 (3)	0.64444 (8)	1.34 (1)
Cl(2)	0.08156 (9)	0.36734 (4)	0.78259 (9)	1.99 (1)
Cl(3)	0.32578 (9)	0.38107 (4)	0.4882 (1)	1.97 (1)
P(1)	0.26243 (9)	0.51318 (4)	0.73197 (9)	1.36 (1)
P(2)	−0.06185 (9)	0.36675 (4)	0.39134 (9)	1.33 (1)
C(11)	0.2067 (4)	0.5184 (2)	0.9349 (4)	2.10 (6)
C(12)	0.4720 (4)	0.4979 (2)	0.7525 (4)	2.21 (6)
C(13)	0.2550 (3)	0.5970 (1)	0.6578 (4)	1.50 (5)
C(21)	0.0219 (4)	0.3489 (2)	0.2036 (4)	2.22 (6)
C(22)	−0.1132 (4)	0.2874 (2)	0.4635 (4)	2.26 (7)
C(1)	0.4757 (4)	0.3001 (2)	0.8752 (4)	2.49 (7)
Cl(11)	0.4241 (1)	0.32565 (5)	1.0645 (1)	3.20 (2)
Cl(12)	0.6665 (1)	0.32778 (5)	0.8335 (1)	3.30 (2)

[a] Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$.

Table V. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $Cr_2Cl_6(PMe_3)_4$ (**1**)[a]

Bond Distances			
Cr(1)–Cr(2)	3.587 (5)	Cr(2)–P(3)	2.459 (6)
Cr(1)–Cl(1)	2.398 (5)	P(1)–C(11)	1.84 (2)
Cr(1)–Cl(2)	2.286 (5)	P(1)–C(12)	1.84 (2)
Cr(1)–P(1)	2.480 (7)	P(2)–C(21)	1.81 (3)
Cr(1)–P(2)	2.458 (7)	P(2)–C(22)	1.83 (2)
Cr(2)–Cl(1)	2.391 (5)	P(3)–C(31)	1.80 (2)
Cr(2)–Cl(3)	2.278 (7)	P(3)–C(32)	1.72 (3)
Cr(2)–Cl(4)	2.295 (8)	P(3)–C(33)	1.75 (3)

Bond Angles			
Cl(1)–Cr(1)–Cl(1)′	82.8 (2)	P(3)–Cr(2)–P(3)′	96.1 (2)
Cl(1)–Cr(1)–Cl(2)′	172.7 (2)	Cr(1)–Cl(1)–Cr(2)	97.0 (2)
Cl(1)–Cr(1)–Cl(2)	89.9 (2)	Cr(1)–P(1)–C(11)	109.0 (8)
Cl(1)–Cr(1)–P(1)	92.4 (2)	Cr(1)–P(1)–C(12)	114.9 (6)
Cl(1)–Cr(1)–P(2)	93.3 (2)	C(11)–P(1)–C(12)	103.9 (7)
Cl(2)–Cr(1)–Cl(2)′	97.5 (2)	C(12)–P(1)–C(12)′	109.1 (9)
Cl(2)–Cr(1)–P(1)	87.9 (2)	Cr(1)–P(2)–C(21)	112.5 (9)
Cl(2)–Cr(1)–P(2)	87.0 (2)	Cr(1)–P(2)–C(22)	116.0 (6)
P(1)–Cr(1)–P(2)	172.4 (3)	C(21)–P(2)–C(22)	104.2 (8)
Cl(1)–Cr(2)–Cl(1)′	83.1 (2)	C(22)–P(2)–C(22)′	102.6 (9)
Cl(1)–Cr(2)–Cl(3)	93.6 (2)	Cr(2)–P(3)–C(31)	120 (1)
Cl(1)–Cr(2)–Cl(4)	93.3 (2)	Cr(2)–P(3)–C(32)	113 (1)
Cl(1)–Cr(2)–P(3)	90.4 (2)	Cr(2)–P(3)–C(33)	120 (1)
Cl(1)–Cr(2)–P(3)′	173.5 (2)	C(31)–P(3)–C(32)	105 (1)
Cl(3)–Cr(2)–Cl(4)	170.8 (3)	C(31)–P(3)–C(33)	95 (2)
Cl(3)–Cr(2)–P(3)	86.7 (2)	C(32)–P(3)–C(33)	101 (2)
Cl(4)–Cr(2)–P(3)	87.1 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits

benzene at reflux temperature for 2 days, resulting in a green solution. Crystals suitable for the X-ray analysis were obtained by the slow diffusion of hexane into the filtered green solution from the above reaction.

Preparation of $Cr_2Cl_6(dmpm)_2$ (3). Anhydrous chromium(III) chloride (0.22 g, 1.44 mmol) was reacted with dmpm (240 μL, 1.44 mmol) at reflux temperature in a mixture of benzene (15 mL) and toluene (15 mL). The mixture was refluxed overnight, resulting in the formation of a green precipitate, yield 0.30 g (73.4%). Crystals of **3** were obtained by slow crystallization from a saturated solution of **3** in CH_2Cl_2. A green crystal from this crop was used for the X-ray diffractometric study. Anal. Calcd for $C_{10}H_{28}Cl_6Cr_2P_4$: C, 20.47; H, 4.75. Found: C, 19.30; H, 4.90. UV-visible spectroscopic properties in CH_2Cl_2: λ_{max} = 620, 480 nm. This complex was barely soluble in CH_2Cl_2 and insoluble in the other common organic solvents.

X-ray Crystallography. Suitable green crystals of complexes **1** and **2** were mounted inside Lindemann capillaries and that of **3** was affixed to the top of a glass fiber by using epoxy resin. All relevant crystallographic information is given in Table I. Accurate unit cell parameters were obtained by means of a least-squares fitting of 25 reflections in all cases. Intensity data on each compound were then collected by utilizing the options specified in Table S1 (Supplementary Material) and the general procedures for data collection as previously described.[5] All data sets were corrected for decay and Lorentz and polarization effects. In addition, absorption corrections were also applied by using an empirical method based on ψ scans for χ angles near 90°.[6] Heavy atoms (Cr, Cl, P) in all cases were located from a three-dimensional Patterson function. The remaining non-hydrogen atoms were found by alternating least-squares full-matrix cycles of refinement and difference Fourier maps. For this the Enraf-Nonius SDP software was employed. The models were first refined with isotropic and then anisotropic thermal parameters to convergence. In compound **2**, the carbon atoms of the ethyl groups belonging to the two phosphorus atoms of the triethylphosphine ligands on the crystallographic mirror plane were disordered. This disorder was modelled successfully with SHELXS-76[7] by fixing the distance between

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Table VI. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $Cr_2Cl_6(PEt_3)_4$ (**2**)^a

Bond Distances			
Cr(1)-Cr(2)	3.637 (2)	Cr(2)-P(3)	2.511 (2)
Cr(1)-Cl(1)	2.419 (3)	P(1)-C(111)	1.92 (5)
Cr(1)-Cl(2)	2.427 (3)	P(1)-C(121)	1.97 (2)
Cr(1)-Cl(3)	2.289 (2)	P(1)-C(131)	1.65 (4)
Cr(1)-P(1)	2.514 (4)	P(2)-C(211)	1.89 (2)
Cr(1)-P(2)	2.519 (3)	P(2)-C(221)	1.88 (2)
Cr(2)-Cl(1)	2.393 (3)	P(2)-C(231)	1.86 (2)
Cr(2)-Cl(2)	2.382 (3)	P(3)-C(311)	1.858 (10)
Cr(2)-Cl(4)	2.284 (3)	P(3)-C(321)	1.851 (9)
Cr(2)-Cl(5)	2.285 (3)	P(3)-C(331)	1.851 (9)

Bond Angles			
Cl(1)-Cr(1)-Cl(2)	81.05 (9)	P(3)-Cr(2)-P(3)′	172.24 (9)
Cl(1)-Cr(1)-Cl(3)	93.52 (7)	Cr(1)-Cl(1)-Cr(2)	98.2 (1)
Cl(1)-Cr(1)-P(1)	170.6 (1)	Cr(1)-Cl(2)-Cr(2)	98.3 (1)
Cl(1)-Cr(1)-P(2)	88.1 (1)	Cr(1)-P(1)-C(111)	110 (1)
Cl(2)-Cr(1)-Cl(3)	92.39 (6)	Cr(1)-P(1)-C(121)	108.3 (5)
Cl(2)-Cr(1)-P(1)	89.6 (1)	Cr(1)-P(1)-C(131)	124 (1)
Cl(2)-Cr(1)-P(2)	169.1 (1)	C(111)-P(1)-C(121)	99 (2)
Cl(3)Cr(1)-Cl(3)′	172.0 (1)	C(111)-P(1)-C(131)	110 (2)
Cl(3)-Cr(1)-P(1)	86.83 (7)	C(121)-P(1)-C(131)	102 (2)
Cl(3)-Cr(1)-P(2)	88.26 (6)	Cr(1)-P(2)-C(211)	113.7 (5)
P(1)-Cr(1)-P(2)	101.3 (1)	Cr(1)-P(2)-C(221)	111.0 (5)
Cl(1)-Cr(2)-Cl(2)	82.53 (9)	Cr(1)-P(2)-C(231)	115.8 (8)
Cl(1)-Cr(2)-Cl(4)	91.0 (1)	C(211)-P(2)-C(221)	104.5 (8)
Cl(1)-Cr(2)-Cl(5)	174.0 (1)	C(211)-P(2)-C(231)	100 (1)
Cl(1)-Cr(2)-P(3)	93.17 (5)	C(221)-P(2)-C(231)	111 (1)
Cl(2)-Cr(2)-Cl(4)	173.5 (1)	Cr(2)-P(3)-C(311)	117.1 (3)
Cl(2)-Cr(2)-Cl(5)	91.5 (1)	Cr(2)-P(3)-C(321)	108.8 (3)
Cl(2)-Cr(2)-P(3)	92.63 (7)	Cr(2)-P(3)-C(331)	118.6 (3)
Cl(4)-Cr(2)-Cl(5)	95.1 (1)	C(311)-P(3)-C(321)	105.8 (4)
Cl(4)-Cr(2)-P(3)	87.71 (7)	C(311)-P(3)-C(331)	99.8 (4)
Cl(5)-Cr(2)-P(3)	87.09 (5)	C(321)-P(3)-C(331)	105.4 (4)

^{a}Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VII. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $Cr_2Cl_6(dmpm)_2{\cdot}2CH_2Cl_2$ (**3**)^a

Bond Distances			
Cr-Cr′	3.480 (1)	P(1)-C(11)	1.809 (3)
Cr-Cl(1)	2.381 (1)	P(1)-C(12)	1.811 (3)
Cr-Cl(1)′	2.379 (1)	P(1)-C(13)	1.837 (3)
Cr-Cl(2)	2.276 (1)	P(2)-C(13)	1.834 (3)
Cr-Cl(3)	2.278 (1)	P(2)-C(21)	1.812 (3)
Cr-P(1)	2.473 (1)	P(2)-C(22)	1.804 (3)
Cr-P(2)	2.467 (1)		

Bond Angles			
Cl(1)-Cr-Cl(1)′	86.07 (3)	Cr-Cl(1)-Cr′	93.93 (3)
Cl(1)-Cr-Cl(2)	89.11 (3)	Cr-P(1)-C(11)	114.3 (1)
Cl(1)-Cr-Cl(3)	176.82 (3)	Cr-P(1)-C(12)	115.6 (1)
Cl(1)-Cr-P(1)	85.97 (3)	Cr-P(1)-C(13)	115.1 (1)
Cl(1)-Cr-P(2)	89.32 (3)	C(11)-P(1)-C(12)	102.6 (2)
Cl(1)′-Cr-Cl(2)	175.19 (3)	C(11)-P(1)-C(13)	105.3 (2)
Cl(1)′-Cr-Cl(3)	90.74 (3)	C(12)-P(1)-C(13)	102.3 (1)
Cl(1)′-Cr-P(1)	87.98 (3)	Cr-P(2)-C(13)	114.1 (1)
Cl(1)′-Cr-P(2)	85.65 (3)	Cr-P(2)-C(21)	114.2 (1)
Cl(2)-Cr-Cl(3)	94.07 (3)	Cr-P(2)-C(22)	116.1 (1)
Cl(2)-Cr-P(1)	91.63 (3)	C(13)-P(2)-C(21)	105.5 (1)
Cl(2)-Cr-P(2)	94.36 (3)	C(13)-P(2)-C(22)	102.5 (1)
Cl(3)-Cr-P(1)	93.83 (3)	C(21)-P(2)-C(22)	103.1 (2)
Cl(3)-Cr-P(2)	90.54 (3)	P(1)-C(13)-P(2)′	118.4 (2)
P(1)-Cr-P(2)	172.32 (3)		

^{a}Numbers in parentheses are estimated standard deviations in the least significant digits.

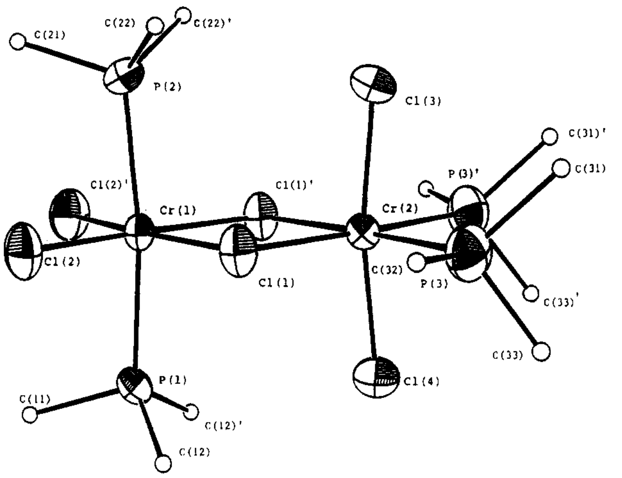

Figure 1. ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 50% probability level. Carbon atoms are represented as circles with arbitrary radii. Singly primed atoms are related to unprimed atoms by a mirror plane.

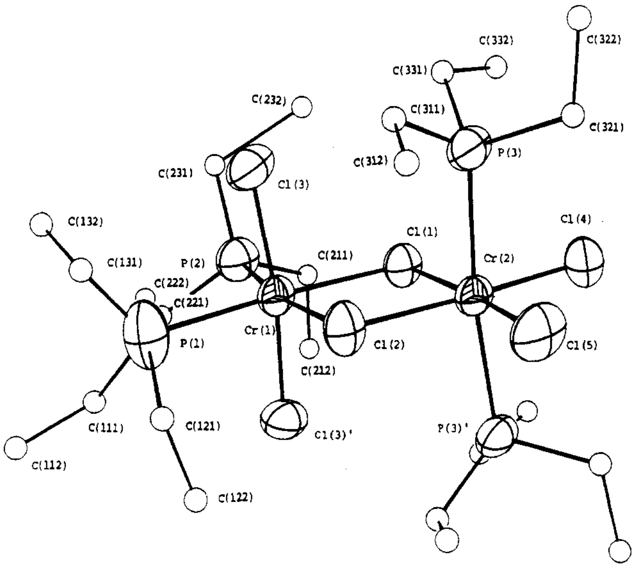

Figure 2. ORTEP drawing of **2**. Singly primed atoms are related to unprimed atoms by a mirror plane.

phosphorus and α-carbon atoms and between the α-carbon and β-carbon atoms and refining the resulting 12 C atoms at 50% occupancies. In the final stages of refining compound **3** peaks that indicated a carbon and two chloride atoms of a solvent molecule (CH_2Cl_2) appeared in the final difference map and were refined anisotropically. In all cases H atoms were inserted at calculated positions and thermal parameters constrained to one value, which was refined. The final results are summarized in Table I. The atomic positional parameters are listed in Tables II–IV, and selected bond distances and angles are listed in Tables V–VII for **1**–**3**, respectively.

Magnetic Measurements. Crystalline samples of the complexes were measured with a SQUID (superconducting quantum interference device) at Michigan State University operating at measuring fields of 5 and 7 kG. The measurement and calibration techniques are reported elsewhere.[8] The molar magnetic susceptibility data for each of the complexes were corrected for the diamagnetism of the constituent atoms using Pascal's constants. The magnetic data for $Cr_2Cl_6(PEt_3)_4$ and $Cr_2Cl_6(dmpm)_2$ are submitted as supplementary material.

Results and Discussion

Preparation. Complex $Cr_2Cl_6(PMe_3)_4$ (**1**) was obtained as a byproduct from the reaction of $Cr_2(acetate)_4$ with 4 equiv of PMe_3 and excess Me_3SiCl in THF. This is unlike the reactions of $Mo_2(OAc)_4$, PR_3, and Me_3SiCl where the quadruply bonded $Mo_2Cl_4(PR_3)_4$ species are obtained.[4] A high yield of pure **1** can also be obtained by reacting $CrCl_3$ and PMe_3 directly.[1] A similar procedure using PEt_3 was employed to synthesize **2**, and the reaction of $CrCl_3$ with the bidentate phosphine dmpm leads to the new complex **3**.

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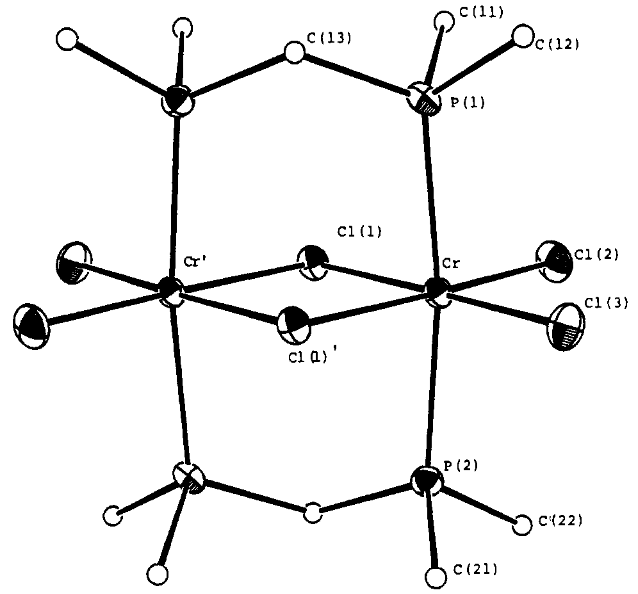


Figure 3. ORTEP drawing of **3**. Singly primed atoms are related to unprimed atoms by an inversion center located at the midpoint of the Cr–Cr line.

Table VIII. Averaged Bond Distances (Å) and Angles (deg)[a]

	1	**2**	**3**
Cr···Cr	3.587 (5)	3.637 (2)	3.480 (1)
Cr–Cl_b[b]	2.395 [4]	2.406 [11]	2.381 (1)
Cr–Cl_t	2.286 [5]	2.286 [2]	2.277 [3]
Cr–P	2.466 [7]	2.515 [3]	2.470 [3]
Cr–Cl_b–Cr	97.0 [2]	98.2 [1]	93.93 (3)
Cl_b–Cr–Cl_b	83.0 [2]	81.8 [8]	86.07 [3]
P_t–Cr–P_t	172.4 [3]	172.24 [9]	172.32 [3]

[a] Brackets signify the variance, viz., $[(\sum\Delta_i^2)/n(n-1)]^{1/2}$. [b] Cl_b = bridge Cl; Cl_t = terminal Cl; P_t = P trans to P.

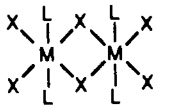
Structural Results. ORTEP drawings of the structures of complexes **1–3** are given in Figures 1–3, respectively. Averaged bond distances and angles are compared in Table VIII. Compounds **1** and **2** crystallize in the same space group, *Pnma*, although a nonstandard setting was adopted for **1**. In each case there are only four molecules in the unit cell, and there is a crystallographic mirror plane passing through the molecule so as to include the two Cr atoms. However, in **1** the mirror plane contains the axial phosphorus atoms while in **2** it contains the equatorial ones. The molecules of **3** reside on inversion centers.

Table IX. Optical Spectral Data for the Chromium (III) Complexes

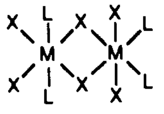
complex	solvent	λ, mm (λ, cm^{-1})		
1	benzene	640 (15 600)	450 (22 200)	300 (33 000)
2	*a*	780 (13 000)	640 (15 600)	490 (20 500)
		430 (23 100)	330 (30 400)	240 (41 000)
3	CH_2Cl_2	620 (16 100)	480 (20 800)	315 (31 700)

[a] Diffuse reflectance spectrum; data taken from ref 2.

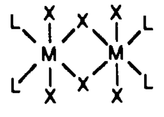
The common feature of the structures is that they all display an edge-sharing bioctahedral configuration. While a structure of this general class had previously been postulated for **1**, the detailed arrangement of ligands that was suggested, namely, all phosphine ligands axial and all chlorine atoms equatorial, I, is not correct. This, of course was to be expected, since no such arrangement has ever been seen when all four neutral ligands are separate monodentate species. Instead, the arrangement II was found for both **1** and **2**. This is by far the most common isomer and previous examples include $Ta_2Cl_6(PMe_3)_4$ (d^2–d^2),[9] $Mo_2Cl_6(PEt_3)_4$,[10] $W_2Cl_6(PEt_3)_4$,[11] and $W_2Cl_6(py)_4$ (d^3–d^3),[12] and $Ru_2Cl_6(PBu_3)_4$ (d^5–d^5).[13] The only other type known, III, is relatively rare, $Zr_2Cl_6(PR_3)_4$ compounds being examples.[14]



I



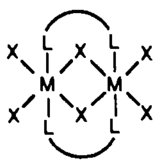
II



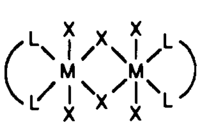
III

In most of these other complexes there are direct metal-metal bonding interactions (usually $d_{M-M} < 2.8$ Å) except for $Mo_2Cl_6(PEt_3)_4$ (d_{Mo-Mo} = 3.730 (1) Å) and $Ru_2Cl_6(PBu_3)_4$ (d_{Ru-Ru} = 3.176 (1) Å). There are also no direct Cr–Cr interaction in **1** (d_{Cr-Cr} = 3.587 (5) Å) and **2** (d_{Cr-Cr} = 3.637 (2) Å), as shown in this study. However, in the case of $W_2Cl_6(PEt_3)_4$ there is a strong metal–metal interaction (d_{W-W} = 2.7397 (7) Å). Thus in the series $M_2Cl_6(PEt_3)_4$ with M = Cr, Mo, and W, the formation of a strong M–M bond occurs only with tungsten.

The structures of complexes of formulae $M_2X_6(L-L)_2$, L–L = a neutral bidentate ligand, depend on the number of carbon atoms between the two phosphorus atoms. Usually when there is only one, i.e., for dmpm or dppm [bis(diphenylphosphino)methane], the structure is of type IV. Examples of these include $Nb_2Cl_6(dmpm)_2$ (d^2–d^2),[15] $Ta_2Cl_6(dmpm)_2$ (d^2–d^2),[16] $Mo_2Cl_6(dppm)_2$ (d^3–d^3),[16] $Re_2Cl_6(dppm)_2$ (d^4–d^4),[17] and $Ru_2Cl_6(dppm)_2$ (d^5–d^5),[16] and these all contain strong metal–metal interactions again by use of the criterion $d_{M-M} < 2.8$ Å. There are, however, a few exceptions in whch dppm gives complexes with structure V. Complexes of structure type V are normally observed when chelating diphosphines of the 1,2-diphosphinoethane type are used, i.e., dppe [1,2-bis(diphenylphosphino)ethane]. Examples are $Nb_2Cl_6(dppe)_2$[18] and $Ta_2Cl_6(dmpe)_2$,[19] where dmpe = 1,2-bis(dimethylphosphino)ethane.



IV



V

Thus complex **3** displays the expected geometry, namely IV, but the Cr–Cr distance of 3.480 (1) Å, though significantly shorter than those of **1** and **2**, suggests a lack of metal–metal interactions.

Other general trends include the following: (1) All Cr–Cl_b distances are consistently about 0.1 Å longer than Cr–Cl_t distances, as is commonly found. (2) The Cr–P distances in **2** are slightly longer with triethylphosphine ligands than those in **1** with trimethylphosphine ligands probably because of steric reasons. (3) The Cr–Cl_b–Cr angles are >90° and Cl_b–Cr–Cl_b angles are <90°, which are indicative of the absence of any M–M bonding forces able to counteract the repulsive forces.[20]

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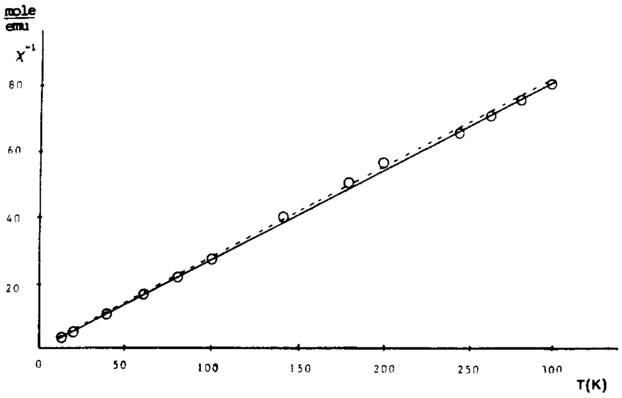

Figure 4. Reciprocal susceptibility, χ^{-1}, versus temperature in $Cr_2Cl_6(PEt_3)_4$ for $\chi = 3.33/(T - 1.32)$ (—) at 5 kG and (---) at 7 kG.

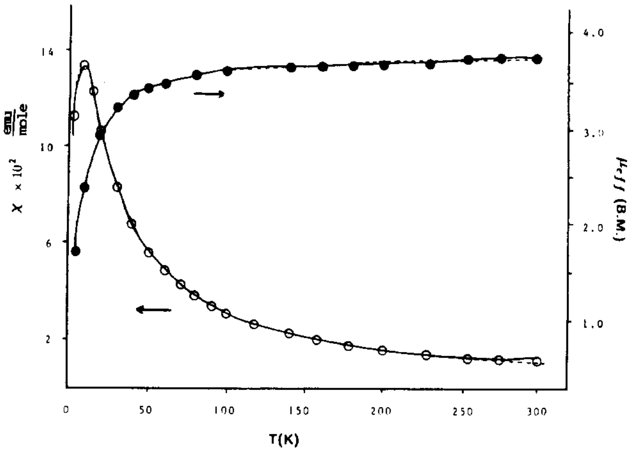

Figure 5. Magnetic susceptibility (○) and effective magnetic moment (•) plotted as a function of temperature for $Cr_2Cl_6(dmpm)_2$. The curve is a fit of the data to the Bleaney–Bowers equation: (—) from 5 kG; (---) from 7 kG.

Electronic Absorption Spectra and Magnetic Properties. Some differences are observed in the electronic absorption spectra for complexes **1**–**3**. The positions of band maxima are collected in Table IX. The lowest energy transitions are entirely consistent with their being assigned as atomic ones, i.e. $t_{2g}{}^3e_g{}^0 \rightarrow t_{2g}{}^2e_g{}^1$, as previously observed for monomeric Cr(III) complexes.[2]

The magnetic susceptibility of **2** was measured between 5 and 300 K at 5 and 7 kG and the data, which are virtually identical at the two field strengths, are plotted in Figure 4. This clearly follows the Curie–Weiss law[21] ($\Theta = +1.32$ K), and suggests that there is negligible interaction between the metal atoms down to 5 K and that these phenomena are also field independent. By employing the Curie–Weiss equation, $\mu_{eff} = 2.828[\chi_M{}^{cor}(T + \Theta)]^{1/2}$, we obtain $\mu_{eff} = 5.39 \pm 0.04\ \mu_B$ for **2**. This corresponds to a value of $3.81 \pm 0.03\ \mu_B$/metal atom, which is consistent with two separate d^3 configurations in **2**.

Since the Cr–Cr distance in **3** is much shorter (0.157 Å) than that in **2**, some interaction beween the metal atoms might be expected for **3**. The data for the magnetic susceptibility of **3** between 1.1 and 300 K at 5 and 7 kG are plotted in Figure 5. In this case there is a deviation from the Curie–Weiss law at low temperatures (<10 K) that could be due to antiferromagnetic interactions between the Cr atoms in **3**. The experimental results are least-squares fitted to the well-known Bleaney–Bowers equation,[8] eq 1, for two exchange-coupled $S = {}^3/_2$ chromium(III)

$$\chi = C\left(\frac{2e^{2x} + 10e^{6x} + 28e^{12x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x}}\right) \qquad (1)$$

$$C = Ng^2\mu_B{}^2/kT \qquad x = J/kT$$

ions. The same negative exchange constant, $J = -1.82$ cm^{-1}, is obtained for the data at the two field strengths, and this again establishes field independence for the observed effects. This is not a large exchange constant, and it could be due either to a weak direct bonding overlap between the two Cr atoms or to superexchange interactions through the bridging Cl atoms, as these have been shown to be a contributor with other dimeric systems.[22]

Conclusions

The preparation and single-crystal X-ray structures of the dinuclear Cr complexes of general form $Cr_2Cl_6(L)_4$ (L = monodentate tertiary phosphines) and $Cr_2Cl_6(LL)_2$ (LL = dmpm) are reported here and provide definitive evidence that these molecules are of the edge-sharing bioctahedral type. The Cr–Cr distances can depend to some extent on the presence of additional bridging groups, such as dmpm, but no chemically significant Cr–Cr interactions are evident even when this strategy is employed. There are magnetic interactions at low temperatures with $Cr_2Cl_6(dmpm)_2$ (**3**) at <10 K, but the cause of these cannot be specified unambiguously.

One can conclude that it is probably not reasonable to expect direct metal–metal interactions with Cr(III) due to contracted valence metal orbitals and also the stability of the two d^3 ground state configurations. The fact that the Cr–Cr distance in **3** is shorter than those in **1** and **2** is probably attributable to the effect of the two bridging dmpm ligands.[23]

Further work in this area is directed toward the syntheses of more reduced Cr dimers where there may be a greater likelihood of metal–metal bonding.

Acknowledgment. We thank the National Science Foundation for financial support. Helpful discussions with Dr. T. Hughbanks and T. Ren are acknowledged.

Supplementary Material Available: Full tables of crystallographic data, bond distances and angles, and anisotropic displacement parameters for complexes **1**–**3**, stereoviews of the crystal packing and unit cells of **1**–**3**, and tables of the magnetic data for **2** and **3** (23 pages); listings of observed and calculated structure factors for **1**–**3** (26 pages). Ordering information is given on any current masthead page.

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