mining whether the third-row transition metals that activate C–H bonds[13] might behave differently, perhaps because they have filled 4f orbitals shielding the 5d electrons.

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Articles

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Mononuclear Chromium Complexes of the Tripod Ligand (Tripod = 1,1,1-Tris((dimethylphosphino)methyl)ethane)

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Tripod (tripod = 1,1,1-tris((dimethylphosphino)methyl)ethane) reacts with anhydrous $CrCl_3$ or $CrCl_3(THF)_3$ in THF or CH_2Cl_2 to give $CrCl_3$(tripod), which may be crystallized from CH_2Cl_2 as a dichloromethane solvate, *fac*-$CrCl_3$(tripod)·CH_2Cl_2 (**1**), in high yield (>95%). All three phosphorus atoms are coordinated to the Cr atom. The reaction of anhydrous $CrCl_2$ with 2 equiv of tripod in THF yields *trans*-$CrCl_2(\text{tripod})_2$ (**2**) in 96% yield. In **2**, each tripod behaves as a bidentate ligand with one uncoordinated $-PMe_2$ group. The reduction of **2** with Na/Hg in THF yields $Cr(\text{tripod})_2$ (**3**) in 70% yield. The coordination geometry about Cr in **3** is that of a trigonal antiprism. X-ray diffraction studies have been performed on *fac*-$CrCl_3$(tripod)·CH_2Cl_2 (**1**), $CrCl_2(\text{tripod})_2$ (**2**), and $Cr(\text{tripod})_2$ (**3**). Crystal data for **1** ($CrCl_5P_3C_{12}H_{29}$): $M_r = 495.55$, orthorhombic, *Pbca* (No. 61), $a = 15.602$ (2) Å, $b = 16.718$ (5) Å, $c = 17.030$ (2) Å, $V = 4442$ Å^3, $d_{calcd} = 1.482$ g/cm^3, $Z = 8$, $\lambda(\text{Mo K}\alpha) = 0.710\,73$ Å (graphite monochromator), $\mu(\text{Mo K}\alpha) = 13.2$ cm^{-1}, final $R = 0.046$ ($R_w = 0.049$) from 2351 observed reflections ($I > 3\sigma(I)$) of 4351 measured. Crystal data for **2** ($CrCl_2P_6C_{22}H_{54}$): $M_r = 627.42$, monoclinic, $P2_1/c$ (No. 14), $a = 8.305$ (1) Å, $b = 20.528$ (3) Å, $c = 10.008$ (2) Å, $\beta = 103.799$ (13)°, $V = 1658$ Å^3, $d_{calcd} = 1.257$ g/cm^3, $Z = 2$, $\lambda(\text{Mo K}\alpha) = 0.710\,73$ Å (graphite monochromator), $\mu(\text{Mo K}\alpha) = 8.0$ cm^{-1}, final $R = 0.059$ ($R_w = 0.071$) from 1397 observed reflections ($I > 3\sigma(I)$) of 1546 measured. Crystal data for **3** ($CrP_6C_{22}H_{54}$): $M_r = 556.52$, orthorhombic, *Pnnm* (No. 58), $a = 9.964$ (2) Å, $b = 10.709$ (2) Å, $c = 13.723$ (3) Å, $V = 1464$ Å^3, $d_{calcd} = 1.262$ g/cm^3, $Z = 2$, $\lambda(\text{Mo K}\alpha) = 0.710\,73$ Å (graphite monochromator), $\mu(\text{Mo K}\alpha) = 7.1$ cm^{-1}, final $R = 0.063$ ($R_w = 0.067$) from 815 observed reflections ($I > 3\sigma(I)$) of 1511 measured. Complexes **1**–**3** have also been characterized spectroscopically.

Introduction

The coordination chemistry of potentially multidentate phosphine ligands with transition-metal carbonyl species has been well established.[1] Several complexes involving metals in higher oxidation states have been prepared for the late, first-row transition metals. Examples are known for Ni(I), Ni(II), Co(I), and Co(II) with potentially tri- and quadridentate phosphines, arsines, thioethers, and amide ligands as well as mixed ligands.[2] To date, most examples of chromium halide complexes bearing multidentate phosphines have involved Cr(III). These include CrX_3E (X = F, Cl, Br, I; E = multidentate arsine, phosphine, or thioether).[3] Related chromium(II) halide complexes with multidentate ligands include $[Cr(\text{tetraphos})X]BPh_4$ (X = Cl, Br, I; tetraphos = tris(2-(diphenylphosphino)ethyl)phosphine),[4] $[Cr(QP_3)X]BPh_4$ (X = Cl, Br, I; QP_3 = tris(2-(dicyclohexylphosphino)ethyl)amine), and $[Cr(NP_3)X]PF_6$ (X = Cl, Br; NP_3 = tris(2-(dimethylphosphino)ethyl)amine).[5] This report describes the synthesis and X-ray structures of three tripod (tripod = 1,1,1-tris((dimethylphosphino)methyl)ethane) complexes of Cr(0), Cr(II), and Cr(III). Only three examples of stable Cr(0) hexaphosphorus compounds have previously been described: $Cr(\text{dmpe})_3$[6] (dmpe = 1,2-bis(dimethylphosphino)ethane), $Cr(PF_3)_6$,[7] and $Cr[P(OR)_3]_6$ (R = alkyl group), the last compound being prepared by metal-vapor synthesis.[8] The Cr(0) hexakis(trimethyl phosphite) complex is reportedly active as a catalyst for the hydrogenation of olefins.[8] To our knowledge, $Cr(\text{tripod})_2$ (**3**), reported here, represents the first structurally characterized example of a Cr(0) hexakis(trialkylphosphine) complex.

Experimental Section

General Procedures. All operations were performed under nitrogen or vacuum. Microanalyses were by Schwarzkopf Microanalytical Laboratory, Woodside, NY. THF and hexane were dried over sodium and distilled from the sodium/benzophenone ketyl radical under nitrogen immediately prior to use. Toluene was distilled from sodium, and methylene chloride was dried and distilled from calcium hydride under nitrogen. All solvents were degassed prior to use. $CrCl_3(THF)_3$[9] was

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Table I. Summary of Crystal Data, Data Collection Parameters, and Least-Squares Residuals for Compounds **1**–**3**

	1	**2**	**3**
formula	$CrCl_5P_3C_{12}H_{29}$	$CrCl_2P_6C_{22}H_{54}$	$CrP_6C_{22}H_{54}$
fw	495.55	627.42	556.52
space group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)	*Pnnm* (No. 58)
a, Å	15.602 (2)	8.305 (1)	9.964 (2)
b, Å	16.718 (5)	20.528 (3)	10.709 (2)
c, Å	17.030 (2)	10.008 (2)	13.723 (3)
β, deg		103.799 (13)	
V, Å^3	4442	1658	1464
Z	8	2	2
d_{calcd}, g/cm^3	1.482	1.257	1.262
cryst size, mm	0.50 × 0.25 × 0.15	0.55 × 0.22 × 0.15	0.35 × 0.18 × 0.10
μ(Mo Kα), cm^{-1}	13.2	8.0	7.1
radiation (Mo Kα), Å	0.71073	0.71073	0.71073
ω scan width, deg	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
% decay of stds	<0.1	8.2	9.9
std reflcns	195, 339	126, 513	255, 345
2θ range, deg	2–50	2–50	2–50
octants collected	$+h,+k,+l$	$+h,+k,\pm l$	$+h,+k,+l$
no. of reflcns measd (unique)	4351	1546	1511
no. of reflcns obsd	2351	1397	815
data omission	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
data/parameter	7.68	9.63	6.22
no. of params varied	306	145	131
R^a	0.046	0.059	0.063
$R_w{}^a$	0.049	0.071	0.067

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

prepared by the literature method, and $CrCl_2$ was prepared from $[Cr(OAc)_2]_2$ in THF by the addition of anhydrous HCl to a 0 °C THF solution of chromous acetate; 1,1,1-tris((dimethylphosphino)methyl)ethane (tripod) was prepared from the reaction of potassium dimethylphosphide[11] with 1,1,1-tris(chloromethyl)ethane.[12]

Spectroscopy. Magnetic susceptibilities were determined by Evans' method,[13] and ^{1}H NMR data were obtained on a Varian EM-390 spectrometer (90.0 MHz). ^{31}P NMR spectra were recorded on a Varian FT80A spectrometer (32.384 MHz). NMR spectra for diamagnetic species were obtained in toluene-d_8 as the solvent. ^{1}H NMR spectra were referenced to the residual proton resonance of benzene-d_6, at 7.15 ppm relative to $SiMe_4$. ^{31}P NMR spectra were referenced to external 85% H_3PO_4(aq) (δ 0.0) with positive values to high frequency. All NMR spectra were obtained at ambient temperature (35 ± 2 °C).

Infrared spectra were recorded on a Perkin-Elmer 1330 spectrometer and calibrated to the 1601-cm^{-1} stretch for a polystyrene film standard.

ESR spectra were recorded on a Varian E-9 EPR spectrometer. Samples of paramagnetic compounds were dissolved in methanol or methylene chloride at room temperature, and spectra were recorded as frozen samples at 77 K.

[1,1,1-Tris((dimethylphosphino)methyl)ethane]chromium(III) Chloride–Methylene Chloride (1). $CrCl_3$(tripod), tripod = 1,1,1-tris((dimethylphosphino)methyl)ethane, was obtained in quantitative yield from the reaction of tripod with $CrCl_3$ or $CrCl_3(THF)_3$ as a suspension or solution in THF or methylene chloride, respectively. In a typical preparation, $CrCl_3$ (0.786 g, 4.96 mmol) was suspended in THF (50 mL). Tripod (1.25 g, 4.96 mmol) was added as a standard solution in toluene to the magnetically stirred mixture at −78 °C. The mixture was allowed to warm slowly to room temperature and then stirred an additional 12 h. At this stage a blue solution with a suspended blue precipitate was obtained. All volatile materials were removed under vacuum followed by washing the solid with hexane (15 mL). The powder was sufficiently pure for use in subsequent reactions without further purification. Crystals were obtained by extracting the blue powder with methylene chloride (2 × 40 mL). The combined extracts were reduced in volume (ca. 40 mL) and then cooled (−20 °C). Deep blue crystals were obtained, which were isolated by decanting the mother liquor: yield 2.00 g (99%); mp >360 °C (1 atm of N_2, uncorrected). IR (Nujol mull, KBr plates): 2876 (s), 1412 (m), 1297 (m), 1283 (m), 1242 (w), 1230 (w), 1155 (br, w), 1106 (w), 1056 (w), 942 (s), 926 (s), 888 (m), 841 (w), 817 (w), 730 (m), 721 (m) cm^{-1}. μ_{eff} = 3.52 μ_B (MeOH, 298 K, Evans' method). Anal. Calcd for $CrCl_5P_3C_{12}H_{29}$: C, 29.09; H, 5.09; Cl, 35.77; P, 18.75. Found: C, 28.71; H, 4.93; Cl, 35.44; P, 18.60. ESR: λ = 9.323 GHz; power = 0.044 mW; methylene chloride in a 3 mm glass tube at 77 K; *g* = 2.001; no hyperfine coupling observed.

Bis[1,1,1-tris((dimethylphosphino)methyl)ethane]chromium(II) Dichloride (2). $CrCl_2(tripod)_2$ was prepared from the reaction of $CrCl_2$ with 2 mol equiv of tripod. In a typical preparation, $CrCl_2$ (0.54 g, 4.39 mmol) was suspended in THF (40 mL). Tripod (2.21 g, 6.78 mmol) was added to the stirred mixture at −78 °C. A yellow color developed immediately, and the solid $CrCl_2$ slowly dissolved. The mixture was slowly warmed to room temperature and stirred an additional 8 h. Volatile materials were removed under vacuum, and the remaining sticky yellow solid was washed and hexane (10 mL). Extraction of the residue with toluene (40 mL) followed by evaporation under vacuum (20 mL) and cooling (−20 °C) gave yellow cube-shaped crystals. Drying of the crystals under vacuum resulted in loss of crystallinity, leaving a golden yellow powder: yield 2.65 g (96%); mp 209–212 °C (1 atm of N_2, uncorrected). IR (Nujol mull, KBr plates): 2895 (s), 1294 (m), 1278 (m), 1239 (w), 1206 (w), 1157 (m, br), 1120 (w), 1101 (w), 1063 (w), 939 (m), 907 (m), 877 (w), 840 (w), 768 (w), 718 (m), 704 (w), 684 (w), 669 (w) cm^{-1}. μ_{eff} = 2.72 μ_B (MeOH, 298 K, Evans' method). Anal. Calcd for $CrCl_2P_6C_{22}H_{54}$: C, 42.15; H, 8.68; Cl, 11.30; P, 29.62. Found: C, 42.09; H, 8.59; Cl, 11.23; P, 29.42. ESR: λ = 9.325 GHz (power = 5.00 mW); methanol solvent in a 3-mm glass tube as a frozen sample at 77 K; *g* = 2.002; no hyperfine coupling observed.

Bis[1,1,1-tris((dimethylphosphino)methyl)ethane]chromium(0) (3). The reduction of **2** in THF at room temperature with excess Na/Hg gives $Cr(tripod)_2$ (**3**). In a typical preparation, **2** (1.0 g, 1.59 mmol) was dissolved in THF (30 mL). The solution was added to a stirred suspension of Na/Hg (5 equiv of Na) in THF (40 mL) and stirred (4 h). The cloudy green solution was filtered, and all volatile materials were removed under vacuum. The sticky solid was washed with cold (0 °C) hexane (10 mL). Extraction with toluene (40 mL) followed by evaporation of the solvent under vacuum (ca. 15 mL) and cooling (−20 °C afforded yellow crystals. Crystallinity is lost if the crystals are removed from toluene vapor or dried under vacuum: yield 0.62 g (70%); mp 290–291 °C dec (1 atm of N_2, uncorrected). IR (Nujol mull, KBr plates): 2895 (s), 1290 (m), 1274 (w), 1258 (m), 1151 (w) 1098 (m, br), 1059 (w), 1015 (m, br), 936 (s), 905 (s), 874 (m), 798 (m), 718 (m), 702 (m), 683 (w), 667 (w) cm^{-1}. ^{1}H NMR: δ 1.20 (s, 36 H, P-CH_3), 1.03 (s, 6 H, CH_3), 0.90 (m, 12 H, CH_2, J_{PH} = 0.2 Hz). ^{31}P{^{1}H} NMR: δ 56.50 (s). Anal. Calcd for $CrP_6C_{22}H_{54}$: C, 47.48; H, 9.78; P, 33.39 Found: C, 47.52; H, 9.69; P, 33.12.

X-ray Crystallography. General Procedures. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. Final lattice parameters were determined from 25

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(11) Potassium dimethylphosphide was prepared from the following steps: $(P(S)Me_2)_2$ + $(n\text{-}Bu)_3P \rightarrow P_2Me_4$ (Maier, L. *J. Inorg. Nucl. Chem.* **1962**, *24*, 275); P_2Me_4 + K $\rightarrow$ $KPMe_2$ (Whitesides, G. M. *J. Am. Chem. Soc.* **1971**, *93*, 1379–1389).

(12) 1,1,1-tris(chloromethyl)ethane was prepared from 2-(hydroxymethyl)-2-methylpropanediol-1,3 as described by: Urry, W. H.; Eiszner, J. R. *J. Am. Chem. Soc.* **1952**, *74*, 5822–5826.

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strong reflections ($26 < 2\theta < 28°$). Data were collected by the $\omega/2\theta$ scan technique at 23 ± 2 °C. Details of the standard data collection methods were similar to those outlined in ref 14. All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius software package "SDS-PLUS" (B.A. Frenz and Associates, College Station, TX 77840; 4th ed., 1981). Scattering factors were taken from ref 16.

$CrCl_3(tripod)\cdot CH_2Cl_2$ (1). The data crystal was mounted in a Lindemann glass capillary under a CH_2Cl_2 atmosphere. Relevant crystal and data collection parameters and details of the refinement are collected in Table I. Systematic absences ($hk0$, $h = 2n + 1$; $h0l$, $l = 2n + 1$; $0kl$, $k = 2n + 1$) uniquely defined the space group as *Pbca* (No. 61). The data were corrected for absorption by an empirical ψ-scan method (program EAC) (transmission: minimum 88.60%, maximum 99.92%, average 95.46%) as well as for Lorentz and polarization effects.

The structure was solved by direct methods (MULTAN).[15] Successive difference Fourier maps followed by least-squares refinement based on 2351 observed reflections ($I > 3\sigma(I)$) gave all non-hydrogen atom positions. Hydrogen atoms were not located, and all atoms were refined anisotropically. A weighting scheme using a non-Poisson contribution with an experimental instability factor, *P*, of 0.05 was employed. *P* is used in the calculation of $\sigma(I)$ to downweight intense reflections in the least-squares refinement. The function minimized was $\sum w(|F_o| - |Fc|)^2$ where $w = 4(F_o)^2[\sum(F_o)^2]^2$ and $[\sum(F_o)^2]^2 = [S^2(C + R^2B) + (P(F_o)^2)^2]/(Lp)^2$, where *S* is the scan rate, *C* is the total integrated peak count, *R* is the ratio of scan time to background counting time, *B* is the total background count, and *Lp* is the Lorentz–polarization factor. The highest peak in the final difference Fourier was 0.479 e/Å^3, located 2.029 Å from C(12).

$CrCl_2(tripod)_2$ (2). The data crystal was mounted in a Lindeman glass capillary under a toluene atmosphere. Relevant crystallographic information is collected in Table I. Systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) uniquely defined the space group as $P2_1/c$ (No. 14). The data were corrected for absorption (EAC) (transmission: minimum 90.08%, maximum 99.91%, average 95.93%) and Lorentz and polarization effects. An anisotropic decay correction was also applied (decay 8.2%). The agreement factors for equivalent reflections that were merged were 0.022 (on intensity) and 0.017 (on F_o).

The structure was solved by direct methods (MULTTAN).[15] All non-hydrogen atoms were located and refined by successive difference Fourier maps followed by least-squares refinement based on 1397 observed reflections ($I > 3\ \sigma(I)$). Hydrogen atoms were not located. Unit weights were used throughout. All atoms were refined with the use of anisotropic thermal parameters. The highest peak in the final difference Fourier was 0.561 e/Å^3, located 1.117 Å from C(10).

$Cr(tripod)_2$ (3). The data crystal was mounted in a Lindemann glass capillary under a toluene atmosphere. Relevant crystallographic information is collected in Table I. Systematic absences ($h0l$, $h + l = 2n + 1$; $0kl$, $k + l = 2n + 1$) indicated a choice of either *Pnnm* (No. 58) or *Pnn*2 (No. 34) as the space group. *Pnnm* was chosen on the basis of a successful refinement. Data were corrected for absorption (EAC) (transmission: minimum 82.03%, maximum 99.35%, average 91.79%) and for Lorentz and polarization effects. The structure was solved by direct methods (MULTAN).[15] Successive difference Fourier maps followed by least-squares refinement based on 815 observed reflections ($I > 3\sigma(I)$) gave all non-hydrogen atom positions. Most hydrogen atoms were located; those not found were placed in fixed positions and refined isotropically; all other atoms were refined anisotropically. An anisotropic decay correction was applied (decay 9.9%). A weighting scheme using a non-Poisson contribution with a *P* factor of 0.06 was employed. The highest peak in the final difference Fourier was 0.957 e/Å^3 and was located 1.109 Å from Cr.

Thermal parameters and tables of observed and calculated structure factors are available as supplementary material for compounds **1**–**3**.[17]

Results and Discussion

Synthesis of Chromium Phosphine Complexes. Complex 1. The tripod ligand reacts quantitatively with $CrCl_3$ or $CrCl_3(THF)_3$ as a slurry or suspension in THF or CH_2Cl_2, respectively. Recently, Levason and co-workers reported similar reactions whereby a number of chromium halide/multidentate phosphine complexes were prepared in which the phosphorus atoms bear two phenyl groups.[3] Related arsine and thioether complexes of Cr(III) are also known.[3] In all cases reported, the phosphine, arsine, and thioether ligands exhibit tridentate behavior even when there is a potential for a higher coordination number. The blue crystalline paramagnetic complex (**1**) is air-stable and can be crystallized as the dichloromethane solvate $CrCl_3(tripod)\cdot CH_2Cl_2$ (**1**). The magnetic moment ($\mu_{eff} = 3.52\ \mu_B$ 298 K) is consistent with the presence of three unpaired electrons as expected for an octahedral d^3 ion.

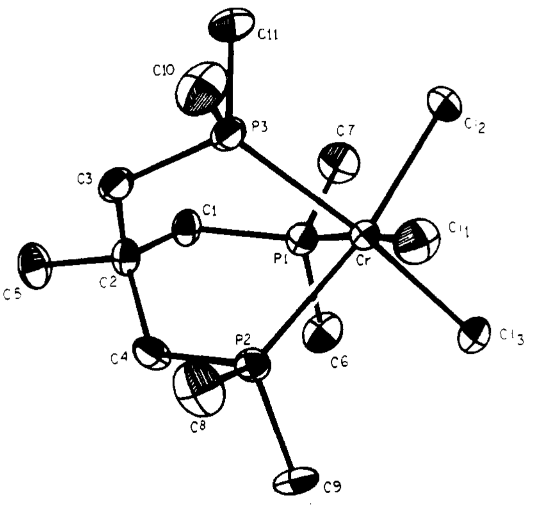

Figure 1. ORTEP view of $CrCl_3(tripod)\cdot CH_2Cl_2$ (**1**).

Complex 2. $CrCl_2$ reacts readily in a variety of solvents (e.g., toluene, Et_2O, THF, CH_2Cl_2, or MeOH) to give the trans dichloride $CrCl_2(tripod)_2$ (**2**). Crystals of **2** can be obtained from toluene and are highly solvent-dependent. Removal of solvent results in an appearance change from translucent yellow to a cloudy golden color. The molecular geometry of this paramagnetic complex is a distorted octahedron (see below). The magnetic moment ($\mu_{eff} = 2.72\ \mu_B$) is consistent with the presence of two unpaired electrons and a low-spin d^4 electronic configuration. The 16-electron complex is thermally unstable at room temperature and slowly disproportionates into a mixture of **1** and **3**. This process is accelerated by refluxing **2** in toluene (eq 1).

$$\underset{\mathbf{2}}{3\mathrm{CrCl_2(tripod)_2}} \xrightarrow[\mathrm{PhMe}]{\Delta} 2\mathrm{CrCl_3(tripod)} + \underset{\mathbf{3}}{\mathrm{Cr(tripod)_2}} \qquad (1)$$

Attempts to replace the Cl ligands of **2** with a variety of other anionic substituents have, with the exception of SH^-,[19] led to reduction and formation of the stable 18-electron complex **3** (eq 2), where R = alkoxy, alkyl, or aryl and M = Li or MgX (X = Cl, Br)).

$$\underset{\mathbf{2}}{\mathrm{CrCl_2(tripod)_2}} + \mathrm{R{-}M} \xrightarrow[\mathrm{THF}]{\mathrm{Et_2O\ or}} \underset{\mathbf{3}}{\mathrm{Cr(tripod)_2}} + \mathrm{Cl{-}M} \qquad (2)$$

The driving force of such a reaction is undoubtedly due to salt elimination and the presence of the free $-PMe_2$ group on each bidentate tripod in **2**, which can sterically hinder the incoming R group. Once Cl^- has been lost, the free $-PMe_2$ units merely have to swing into the vacant coordination sites in order to form the stable 18-electron complex **3**. In the presence of transition-metal carbonyls, e.g. $Cr(CO)_6$, $W(CO)_6$, and $[Rh(CO)_2Cl]_2$, the disproportionation reaction shown in eq 1 is accelerated.

Complex 3. This complex may be prepared from **2** conveniently by the reaction with excess Na/Hg in THF. **3** is a diamagnetic, 18-electron Cr(0) speices with a low-spin d^6 electronic configuration. Crystals of **3** were obtained from hexane or toluene. X-ray-suitable crystals could only be obtained from toluene and are highly solvent-dependent, rapidly becoming a powder in the

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Table II. Positional Parameters and Their Estimated Standard Deviations for **1**[a]

atom	*x*	*y*	*z*	*B*, Å^2
Cr	0.98929 (6)	0.21622 (6)	0.49283 (6)	2.01 (2)
Cl(1)	0.9709 (1)	0.1535 (1)	0.6140 (1)	3.39 (4)
Cl(2)	1.0815 (1)	0.3149 (1)	0.5395 (1)	3.77 (4)
Cl(3)	1.0968 (1)	0.1289 (1)	0.4513 (1)	3.12 (4)
Cl(4)	0.6182 (2)	0.0384 (1)	0.3065 (2)	6.34 (7)
Cl(5)	0.7617 (2)	−0.0008 (2)	0.2046 (2)	7.28 (7)
P(1)	0.9881 (1)	0.2759 (1)	0.3612 (1)	2.41 (3)
P(2)	0.8763 (1)	0.1304 (1)	0.4371 (1)	2.45 (3)
P(3)	0.8701 (1)	0.3086 (1)	0.5170 (1)	2.54 (3)
C(1)	0.8823 (5)	0.3100 (4)	0.3277 (4)	2.8 (1)
C(2)	0.8020 (4)	0.2719 (4)	0.3629 (4)	2.3 (1)
C(3)	0.7825 (4)	0.3030 (4)	0.4451 (4)	2.9 (1)
C(4)	0.8099 (4)	0.1788 (4)	0.3612 (4)	2.8 (1)
C(5)	0.7257 (5)	0.2933 (5)	0.3112 (4)	3.7 (2)
C(6)	1.0225 (5)	0.2098 (5)	0.2821 (4)	4.0 (2)
C(7)	1.0584 (5)	0.3618 (5)	0.3442 (5)	4.5 (2)
C(8)	0.7983 (5)	0.0918 (5)	0.5055 (5)	4.3 (2)
C(9)	0.9108 (5)	0.0387 (4)	0.3889 (5)	3.9 (2)
C(10)	0.8173 (6)	0.2984 (5)	0.6109 (5)	4.4 (2)
C(11)	0.8989 (5)	0.4146 (4)	0.5178 (5)	4.3 (2)
C(12)	0.6483 (6)	0.0041 (5)	0.2131 (4)	5.5 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Selected Bond Lengths (Å) for **1**

Cr–Cl(1)	2.333 (2)	Cr–P(3)	2.452 (2)
Cr–Cl(2)	2.328 (2)	P(1)–C(1)	1.838 (7)
Cr–Cl(3)	2.334 (2)	P(2)–C(4)	1.834 (7)
Cr–P(1)	2.454 (2)	P(3)–C(3)	1.838 (7)
Cr–P(2)	2.463 (2)		

Table IV. Selected Bond Angles (deg) for **1**

Cl(1)–Cr–Cl(2)	95.32 (8)	Cl(2)–Cr–P(1)	91.64 (7)
Cl(1)–Cr–Cl(3)	94.30 (7)	Cl(2)–Cr–P(2)	170.50 (8)
Cl(2)–Cr–Cl(3)	95.91 (7)	Cl(2)–Cr–P(3)	87.98 (7)
Cl(3)–Cr–P(1)	89.02 (7)	P(1)–Cr–P(2)	83.06 (7)
Cl(3)–Cr–P(2)	91.89 (7)	P(1)–Cr–P(3)	83.76 (6)
Cl(3)–Cr–P(2)	171.90 (8)	P(2)–Cr–P(3)	83.62 (7)
Cl(1)–Cr–P(1)	171.93 (8)	Cr–P(1)–C(1)	114.6 (2)
Cl(1)–Cr–P(2)	89.48 (7)	Cr–P(2)–C(4)	114.6 (2)
Cl(1)–Cr–P(3)	92.40 (7)	Cr–P(3)–C(3)	114.9 (2)

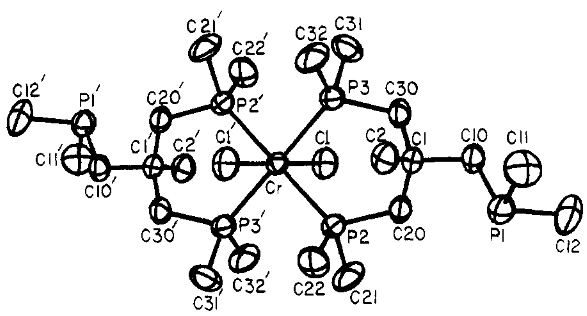

Figure 2. ORTEP view of $CrCl_2(tripod)_2$ (**2**).

Table V. Positional Parameters and Their Estimated Standard Deviations for **2**[a]

atom	*x*	*y*	*z*	*B*, Å^2
Cr	1.000	0.000	0.500	2.57 (4)
Cl	1.2311 (3)	0.0680 (1)	0.5281 (3)	4.33 (6)
P(1)	0.4869 (4)	0.2567 (1)	0.5128 (3)	4.08 (6)
P(2)	0.8700 (3)	0.0691 (1)	0.6398 (3)	3.18 (5)
P(3)	0.8476 (3)	0.0570 (1)	0.2974 (3)	3.35 (5)
C(1)	0.670 (1)	0.1519 (5)	0.4263 (9)	3.0 (2)
C(2)	0.813 (1)	0.2007 (5)	0.437 (1)	4.1 (2)
C(10)	0.499 (1)	0.1893 (5)	0.392 (1)	3.6 (2)
C(11)	0.498 (2)	0.3286 (6)	0.403 (1)	5.5 (3)
C(12)	0.256 (1)	0.2562 (7)	0.493 (1)	6.3 (3)
C(20)	0.679 (1)	0.1152 (5)	0.562 (1)	3.8 (2)
C(21)	0.786 (1)	0.0279 (6)	0.774 (1)	5.7 (3)
C(22)	1.000 (1)	0.1330 (6)	0.742 (1)	5.1 (3)
C(30)	0.660 (1)	0.1047 (5)	0.305 (1)	3.8 (2)
C(31)	0.741 (1)	0.0062 (6)	0.150 (1)	5.4 (3)
C(32)	0.963 (1)	0.1153 (6)	0.212 (1)	5.4 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table VI. Selected Bond Distances (Å) for **2**

Cr–Cl(1)	2.336 (2)	P(3)–C(30)	1.861 (6)
Cr–P(2)	2.420 (2)	C(1)–C(2)	1.537 (8)
Cr–P(3)	2.421 (3)	C(1)–C(10)	1.537 (8)
P(1)–C(10)	1.857 (7)	C(1)–C(20)	1.537 (8)
P(2)–C(20)	1.851 (6)	C(1)–C(30)	1.538 (9)

Table VII. Selected Bond Angles (deg) for **2**

Cl–Cr–P(2)	92.69 (6)	C(2)–C(1)–C(30)	111.3 (5)
Cl–Cr–P(3)	93.54 (6)	C(10)–C(1)–C(20)	106.7 (5)
P(2)–Cr–P(3)	89.11 (6)	C(10)–C(1)–C(30)	104.9 (5)
Cr–P(2)–C(20)	120.7 (2)	C(20)–C(1)–C(30)	111.5 (6)
Cr–P(3)–C(30)	119.7 (2)	P(1)–C(10)–C(1)	114.1 (4)
C(2)–C(1)–C(10)	109.7 (5)	P(2)–C(20)–C(1)	118.9 (4)
C(2)–C(1)–C(20)	112.4 (5)	P(3)–C(30)–C(1)	118.5 (4)

absence of toluene or hexane vapor. **3** exhibits thermochromic behavior when heated under nitrogen, turning from yellow to orange at ca. 150 °C; this process may be reversed on cooling. Further heating results in a red color prior to decomposition at 200 °C.

The $^{31}P\{^1H\}$ and ^1H NMR spectra of **3** are straightforward. The methyl groups on phosphorus appear as a broad singlet (δ 1.20), and the $-CH_2$ units as a multiplet (δ 0.90). The $^{31}P\{^1H\}$ spectrum is a singlet (δ 56.50), consistent with the symmetrical trigonal-antiprismatic geometry as found in the solid state.

X-ray Crystallographic Results for 1–3. $CrCl_3(tripod)\cdot CH_2Cl_2$. **1** crystallizes in the orthorhombic space group *Pbca*. The molecular geometry is *fac* about Cr(III). A view of the molecule is shown in Figure 1. Atomic positional parameters and selected bond lengths and angles are presented in Tables II, III, and IV, respectively. Interestingly, Levason and co-workers[3] obtained exclusively the *mer* isomer for $CrCl_3E$ phosphine complexes (where E = $PPh(CH_2CH_2PPh_2)_2$, $[-CH_2P(Ph)CH_2CH_2PPh_2]_2$, and $P(CH_2CH_2PPh_2)_3$) and the *fac* isomer for complexes where E = $MeC(CH_2PPh_2)_3$ and related arsine ligands. This difference for the phosphines could be due to the extra methylene group in the ligand backbones of the phenyl-substituted ligands as compared to a single methylene in tripod. This would allow more flexibility in the coordination geometry of the phosphorus groups about the metal center.

The average P–Cr bond distance of 2.456 (2) Å is relatively long and is similar to the P–Cr bond lengths in $Cr\{P(CH_2CH_2PPh_2)_3\}Cl_3$ (**4**) (average 2.451 Å).[3] This could be due to relatively weak binding of the phosphine, since the Cr(III) ion is a "hard" acceptor and the P atoms are considered "soft" donors. The average Cr–Cl bond distance of 2.332 (2) Å is normal and is similar to those observed in **4** (average Cr–Cl = 2.306 Å). The Cr–P(1)–C(1), Cr–P(2)–C(4), and Cr–P(3)–C(3) bond angles fall within the narrow range 114.6–113.9° (average 114.7 (2)°), which reflects the symmetrical binding of the tripod ligand.

$CrCl_2(tripod)_2$. This complex crystallizes in the centrosymmetric space group $P2_1/c$. The coordination geometry about the Cr atom is roughly octahedral. The two tripod ligands act as bidentate 4-electron donors, each with an uncoordinated-PMe_2 group. The Cr atom lies on a crystallographically imposed inversion center. A view of the molecule is shown in Figure 2. Atomic positional parameters and selected bond lengths and angles are given in Tables V, VI, and VII, respectively.

The average P–Cr bond distance in **2** is 2.420 (2) Å, which is relatively long but somewhat shorter than the observed average for **1** (2.456 (2) Å). It may be compared to that recently reported

Table VIII. Positional Parameters and Their Estimated Standard Deviations for **3**[a]

atom	*x*	*y*	*z*	*B*, Å^2
Cr	1.000	0.000	1.000	2.11 (4)
P(1)	1.1664 (3)	0.0361 (3)	1.1110 (2)	5.93 (6)
P(2)	0.9833 (5)	0.2131 (3)	1.000	6.6 (1)
C(1)	1.283 (1)	0.169 (1)	1.0915 (9)	7.3 (3)
C(2)	1.270 (1)	0.243 (1)	1.000	4.4 (3)
C(3)	1.136 (2)	0.311 (1)	1.000	6.1 (4)
C(4)	1.383 (2)	0.342 (1)	1.000	6.0 (4)
C(5)	1.277 (2)	−0.066 (2)	1.167 (2)	7.3 (4)
C(6)	1.107 (2)	0.106 (3)	1.236 (1)	6.7 (6)
C(7)	0.901 (2)	0.296 (1)	1.093 (2)	7.8 (6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table IX. Selected Bond Lengths (Å) for **3**

Cr–P(1)	2.285 (1)	C(1)–C(2)	1.490 (6)
Cr–P(2)	2.289 (1)	C(2)–C(3)	1.529 (9)
P(1)–C(1)	1.850 (5)	C(2)–C(4)	1.548 (8)
P(2)–C(3)	1.843 (7)		

Table X. Selected Bond Angles (deg) for **3**

P(1)–Cr–P(2)	83.34 (4)	C(1)–C(2)–C(3)	109.0 (4)
Cr–P(1)–C(1)	119.2 (2)	C(1)–C(2)–C(4)	107.8 (3)
Cr–P(2)–C(3)	120.4 (3)	C(3)–C(2)–C(4)	108.1 (6)
P(1)–C(1)–C(2)	118.6 (4)	P(2)–C(3)–C(2)	116.8 (4)
P(1)–Cr–P(1)′	83.6 (3)	P(1)–Cr–P(1)″	96.4 (4)
P(1)″–Cr–P(2)	96.7 (4)		

for $CrCl_2(dmpe)_2$ (**5**) (dmpe = bis(1,2-dimethylphosphino)ethane). The X-ray structure of **5** by Wilkinson and co-workers[18] shows an average Cr–P bond length of 2.369 Å, which is slightly shorter than that observed for **2**. The Cr–P(3) and Cr–P(2) bond lengths of **2** are identical to within experimental error. The Cr–Cl bond length of 2.336 Å in **2** is similar to those reported for **1**, **4** (average 2.306 Å), and **5** (average 2.348 Å).

Cr(tripod)$_2$. Molecules of **3** crystallize from toluene in the centrosymmetric space group *Pnnm*. The Cr atom lies at the origin of the unit cell. There is a mirror plane running through the molecule that contains C(4)″, C(2)″, C(3)″, P(2)″, Cr, P(2), C(3), C(2), and C(4). In addition, there is a twofold axis of rotation perpendicular to this plane that passes through the Cr atom. Thus one-fourth of the molecule generates the other three-fourths by the crystallographically imposed symmetry. A view of the molecule is shown in Figure 3. Atomic positional parameters and selected bond lengths and angles for **3** are presented in Tables VIII, IX, and X, respectively.

The average P–Cr bond distance of 2.287 (1) Å is considerably shorter than the observed P–Cr bond lengths for **1** and **2**, thus reflecting a progressive decrease in the P–Cr length with decreasing Cr oxidation state or increasing "softness" of the metal. This may be due to increased π-back-bonding from the Cr to P as the metal becomes more electron-rich with a lowering of the oxidation state. The two unique angles subtended by one tripod ligand are P(1)–Cr–P(1)′ = 83.6 (3)° and P(1)–Cr–P(2) = 83.34 (4)°. The angles subtended at Cr between the P atoms of the two tripod ligands are P(1)–Cr–P(1)″ = 96.4 (4)° and P(1)″–Cr–P(2) = 96.7 (4)°. Thus, the molecular geometry is best described as a trigonal antiprism as opposed to a regular octahedron. The Cr–P(1)–C(1) and Cr–P(2)–C(3) bond angles of 119.2 (2) and 120.4 (3)°, respectively, are similar to the analogous angles in **2**. The bond angles for groups attached to the C(2) carbon (average 108.3 (4) Å) indicate distortion from an idealized tetrahedral geometry for this atom is minimal.

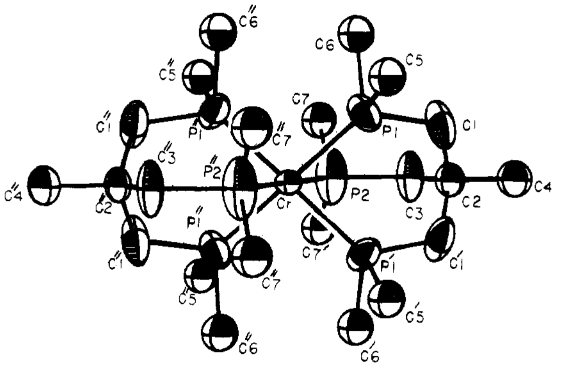

Figure 3. ORTEP view of Cr(tripod)$_2$ (**3**).

To the best of our knowledge, **3** represents the first example of a structurally characterized hexakis(trialkylphosphine)-coordinated Cr(0) atom. Other analogues have been spectroscopically and/or analytically characterized as $Cr(PF_3)_6$[7] (**7**), $Cr[P(OMe)_3]_6$[8] (**8**), and $Cr(dmpe)_3$[6] (**9**). **8** has been reported as a hydrogenation catalyst in the reduction of olefins.

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Registry No. **1**, 100243-99-0; **2**, 100244-00-6; **3**, 100244-01-7.

Supplementary Material Available: Tables of bond distances and angles, atomic thermal parameters, and observed and calculated structure factors for **1**–**3** and a view of the unit cell for **1** (57 pages). Ordering information is given on any current masthead page.