Inorg. Chem. **2003**, *42*, 6876–6885

Inorganic Chemistry
Article

Chromium(II) and Chromium(III) Complexes Supported by Tris(2-pyridylmethyl)amine: Synthesis, Structures, and Reactivity

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Received May 16, 2003

This report describes the synthesis, structural characterization, and polymerization behavior of a series of chromium(II) and chromium(III) complexes ligated by tris(2-pyridylmethyl)amine (TPA), including chromium(III) organometallic derivatives. For instance, the combination of TPA with $CrCl_2$ yields monomeric (TPA)$CrCl_2$ (**1**). A similar reaction of $CrCl_2$ with TPA, followed by chloride abstraction with $NaBPh_4$ or $NaBAr^F_4$ ($Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$), provides the weakly associated cationic dimers $[(TPA)CrCl]_2[BPh_4]_2$ (**2A**) and $[(TPA)CrCl]_2[BAr^F_4]_2$ (**2B**), respectively. X-ray crystallographic analysis reveals that each chromium(II) center in **1**, **2A**, and **2B** is a tetragonally elongated octahedron; such Jahn–Teller distortions are consistent with the observed high spin ($S = 2$) electronic configurations for these chromium(II) complexes. Likewise, reaction of $CrCl_3(THF)_3$ with TPA, followed by anion metathesis with $NaBPh_4$ or $NaBAr^F_4$, yields the monomeric, cationic chromium(III) complexes $[(TPA)CrCl_2][BPh_4]$ (**4A**) and $[(TPA)CrCl_2][BAr^F_4]$ (**4B**), respectively. Treatment of **4A** with methyl and phenyl Grignard reagents produces the cationic chromium(III) organometallic derivatives $[(TPA)Cr(CH_3)_2][BPh_4]$ (**5**) and $[(TPA)CrPh_2][BPh_4]$ (**6**), respectively. Similar reactions of **4A** with organolithium reagents leads to intractable solids, presumably due to overreduction of the chromium(III) center. X-ray crystallographic analysis of **4A**, **5**, and **6** confirms that each possesses a largely undistorted octahedral chromium center, consistent with the observed $S = {}^3/_2$ electronic ground states. Compounds **1**, **2A**, **2B**, **4A**, **4B**, **5**, and **6** are all active polymerization catalysts in the presence of methylalumoxane, producing low to moderate molecular weight high-density polyethylene.

Introduction

Chromium-based polymerization catalysts play a central role in commercial polyethylene production. For example, silica-supported chromium oxide catalysts[1] (Phillips catalysts) are responsible for the production of billions of pounds of high-density polyethylene (HDPE) per year. The active site is thought to be a low-valent chromium species bound to silica, but the coordination sphere and mechanism of activation are not well understood, even after years of study.[2] A class of Unipol catalyst, formed by adsorption of chromocene (Cp_2Cr, Cp = cyclopentadienyl) onto dehydroxylated silica,[3] is also used to prepare commercially significant quantities of HDPE. The active site of the chromocene catalyst presumably comprises a chromium atom covalently bonded to the silica surface (via a Si–O–Cr linkage) and to a single Cp ligand,[4] although the metal's oxidation state and coordination geometry are not well defined.

These ambiguities have spurred considerable effort directed toward the synthesis of discrete chromium compounds to serve as models of the commercial systems and as potential single-site catalysts. For example, Theopold's group has prepared a large family of mono-Cp chromium complexes,[5] of which the coordinately unsaturated Cp* chromium(III) alkyl derivatives (Cp* = C_5Me_5) are particularly active homogeneous catalysts.[6−8] In addition, deposition of these

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10.1021/ic034530i CCC: $25.00

Cp* chromium alkyl complexes onto dehydroxylated silica, alumina, and aluminum phosphate supports yields highly active *heterogeneous* polymerization catalysts.[9] More recently, Jolly,[10−13] Bazan,[14,15] and others[16,17] have prepared mono-Cp chromium(III) derivatives containing an additional neutral donor (i.e., amine or phosphine) that binds to the chromium center. In the presence of methylalumoxane (MAO) or borane activators, highly active catalysts are formed, resulting in the production of polyethylene or α-olefin products whose properties depend on the nature of the neutral donor and the activator employed.

In addition to Cp ligated compounds, transition-metal complexes containing non-Cp ligands have enjoyed recent success in polymerization catalysis. Several excellent reviews have appeared on the use of non-Cp ligands to produce both early and late metal catalysts.[18−21] Chromium complexes with non-Cp ligands include those coordinated by anionic salicylaldiminato,[22] reduced Schiff-base,[23] imino-pyrrolide,[24,25] β-diketiminate ("nacnac"),[25−28] and bis(phosphoranimine)-methanide[29] ligands. Furthermore, chromium(III) derivatives supported by neutral triazacyclohexane,[30] pyridine bis(imine),[31] pyridine bis(oxazolinyl),[32] triphosphacyclododecane,[33] bis(imidazole),[34] amine bis(thioether),[35] and certain bridged-diphosphine[36,37] ligands are known. When combined with the appropriate activator, these complexes polymerize ethylene to form polymeric or oligomeric products with properties dependent on the identity of the chromium compound.

A focus of our research group is the synthesis of monomeric chromium species bound by chelating, nitrogen-based ligands. Of particular interest are tetradentate ligands that yield monomeric octahedral transition-metal complexes with reactive sites in a cis configuration. The cis orientation is ideal for coordination/insertion polymerization; olefin binding cis to the growing polymer chain allows for rapid olefin insertion into the chain and high catalyst activity. Tetradentate ligands, such as tris(2-pyridylmethyl)amine (TPA), would yield such cis-ligated octahedral complexes. The TPA ligand has a long and productive history in the construction of functional models for various non-heme iron mono-oxygenases and other oxygen-activating enzymes,[38,39] but it has yet to be explored in the context of polymerization catalysis. With respect to chromium chemistry, a few dimeric chromium(III)−TPA complexes (with bridging oxo and hydroxo groups) are known and have been structurally characterized.[40] In this report, we describe the synthesis, X-ray structural characterization, and polymerization behavior of a series of monomeric (or weakly associated dimeric) chromium(II) and chromium(III) complexes supported by TPA. Among these complexes are thermally robust, cationic chromium(III) dimethyl and diphenyl derivatives. All complexes possess labile or reactive coordination sites in a cis

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arrangement and all are active polymerization catalysts in the presence of MAO.

Experimental Section

Materials and Methods. Unless otherwise stated, all operations were carried out in an argon-filled glovebox or using standard Schlenk techniques. Tetrahydrofuran, diethyl ether, dichloromethane, and acetonitrile were purified by standard drying procedures and distilled under argon prior to use. Furthermore, acetonitrile was stored over activated molecular sieves in the glovebox. Anhydrous high-performance liquid chromatography grade benzene and toluene were degassed prior to use and stored over molecular sieves. Chlorobenzene was degassed and dried over molecular sieves. Anhydrous chromium(II) chloride, chromium(III) chloride, sodium tetraphenylborate ($NaBPh_4$), 1,4-dioxane, and Grignard reagents were purchased from Aldrich or Acros Organics and used as received. Chromium(III) chloride tris(tetrahydrofuran),[41] tris(2-pyridylmethyl)amine (TPA),[42] and sodium tetrakis(3,5-bis(trifluoromethyl)phenyl) borate ($NaBAr^F_4$)[43] were prepared as described in the literature. Galbraith Laboratories, Inc. (Knoxville, TN), and Atlantic Microlab, Inc. (Norcross, GA), performed elemental analyses. Magnetic susceptibilities were determined at room temperature using a Johnson Matthey magnetic susceptibility balance, and electronic absorption spectra were recorded on a Hewlett-Packard 8453 spectrophotometer (190−1100 nm range). Samples for IR were dispersed in KBR, and spectra were recorded on a Nicolet 5DXC spectrometer with a diffuse reflectance (DRIFTS) attachment. Polymer analysis, including gel permeation chromatography (GPC), high temperature ^{13}C NMR, and differential scanning calorimetry (DSC) experiments were performed at W. R. Grace & Co. GPC measurements were made with a Waters 150 C GPC operating at 140 °C using 1,2,4-trichlorobenzene as solvent. ^{13}C NMR experiments were conducted at 120 °C in 1,1,2,2-tetrachloroethane using a Bruker ACE 300 spectrometer.

Synthesis of Chromium Complexes. (TPA)CrCl$_2$ (1). A mixture of anhydrous $CrCl_2$ (0.085 g, 0.69 mmol) and tris(2-pyridylmethyl)amine (0.200 g, 0.69 mmol) was stirred overnight in 15 mL of tetrahydrofuran, resulting in a purple-gray precipitate. The solid was collected, dissolved in a minimum of acetonitrile, and filtered. Deep-purple crystals were obtained by ether diffusion into the acetonitrile solution (0.186 g, 65%). Completely satisfactory elemental analysis could not be obtained; however, an X-ray crystal structure determination confirmed the identity of **1**. Fourier transform (FT)IR (KBr): 3055, 3020, 2944, 2915, 1602, 1474, 1439, 1287, 1048, 1024, 773 cm^{-1}. UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 375 (2400). Anal. Calcd (found) for $C_{18}H_{18}N_4Cl_2Cr$: C, 52.32 (50.37); H, 4.39 (4.64); N, 13.56 (13.94). $\mu_{eff} = 4.6\ \mu_B$.

[(TPA)CrCl]$_2$[BPh$_4$]$_2$ (2A). A mixture of tris(2-pyridylmethyl)amine (0.300 g, 1.03 mmol), anhydrous $CrCl_2$ (0.127 g, 1.03 mmol), and $NaBPh_4$ (0.354 g, 1.03 mmol) was stirred overnight in 15 mL of tetrahydrofuran, yielding a red-brown solid. The solid was collected and dissolved in 100 mL of acetonitrile, and the solution was heated to 70 °C, and filtered. The filtrate was concentrated in vacuo until reaching the saturation point and slowly cooled to room temperature. The dark-red-brown crystals that formed were collected and dried under vacuum (0.350 g, 49%). FTIR (KBr): 3048, 2999, 2978, 1945, 1883, 1818, 1610, 1483, 1438, 1426, 1291, 1262, 1156, 1029, 841, 735, 702, 612 cm^{-1}. UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 382 (2500). Anal. Calcd (found) for $C_{84}H_{76}N_8B_2Cl_2Cr_2$: C, 72.37 (72.12); H, 5.50 (5.47); N, 8.04 (8.15). $\mu_{eff} = 4.6\ \mu_B$.

[(TPA)CrCl]$_2$[BAr$^F_4$]$_2$ (2B). Tris(2-pyridylmethyl)amine (0.200 g, 0.69 mmol), anhydrous $CrCl_2$ (0.085 g, 0.69 mmol), and $NaBAr^F_4$ (0.610 g, 0.69 mmol) were stirred overnight in 15 mL of tetrahydrofuran. The solvent was removed in vacuo, yielding a dark-brown solid. The solid was dissolved in a minimum (ca. 5 mL) of diethyl ether, and the solution was filtered and layered with an equal volume of pentane. A dark-brown crystalline solid formed after 2 days. The solid was isolated and dried under vacuum (0.325 g, 38%). FTIR (KBr): 3072, 3040, 2929, 1785, 1610, 1438, 1356, 1279, 1123, 886, 837, 768, 715, 681, 670 cm^{-1}. UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 360 (1500). Anal. Calcd (found) for $C_{100}H_{60}N_8B_2Cl_2F_{48}Cr_2$: C, 48.39 (47.50); H, 2.43 (2.44); N, 4.51 (4.39). $\mu_{eff} = 3.9\ \mu_B$.

[(TPA)CrCl$_2$][BPh$_4$]·MeCN (4A). Sodium tetraphenylborate (0.236 g, 0.69 mmol), tris(2-pyridylmethyl)amine (0.200 g, 0.69 mmol), and $CrCl_3(THF)_3$ (0.258 g, 0.69 mmol) were combined in 15 mL of tetrahydrofuran. A green-brown solution formed immediately, which gradually formed a flocculent purple solid after overnight stirring. The solid was collected and dissolved in 100 mL of acetonitrile, and the solution was filtered to remove a small amount of white solid (presumably NaCl). The resulting purple solution was heated to 70 °C, concentrated in vacuo until the saturation point, and slowly cooled to room temperature yielding (0.179 g, 34%) of deep-purple crystals of **4A** (acetonitrile monosolvate). Further concentration of the remaining filtrate deposited an additional 0.149 g of product (total yield = 0.328 g, 61%). FTIR (KBr): 3049, 3031, 2985, 1958, 1888, 1830, 1608, 1479, 1444, 1281, 1159, 1053, 1030, 768, 738, 703, 610 cm^{-1}. UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 421 (170). Anal. Calcd (found) for $C_{44}H_{41}N_5BCl_2Cr$: C, 68.32 (68.18); H, 5.34 (5.42); N, 9.05 (8.91). $\mu_{eff} = 3.5\ \mu_B$.

[(TPA)CrCl$_2$][BAr$^F_4$] (4B). Tris(2-pyridylmethyl)amine (0.200 g, 0.69 mmol), $CrCl_3(THF)_3$ (0.258 g, 0.69 mmol), and $NaBAr^F_4$ (0.610 g, 0.69 mmol) were stirred overnight in 15 mL of tetrahydrofuran. The solvent was removed under vacuum yielding a dark-purple solid. The solid was dissolved in a minimum of diethyl ether, and the solution was filtered and layered with an equal volume of pentane. A deep-purple crystalline solid formed after 2 days. It was isolated and dried under vacuum (0.672 g, 76%). FTIR (KBr): 3078, 2973, 2938, 1614, 1444, 1357, 1281, 1112, 884, 838, 768, 709, 668 cm^{-1}. UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 421 (180). Anal. Calcd (found) for $C_{50}H_{30}N_4BCl_2F_{24}Cr$: C, 47.05 (46.82); H, 2.37 (2.38); N, 4.39 (4.27). $\mu_{eff} = 3.9\ \mu_B$.

[(TPA)CrMe$_2$][BPh$_4$]·0.5CH$_2$Cl$_2$ (5). Tris(2-pyridylmethyl)amine (0.500 g, 1.73 mmol), $CrCl_3(THF)_3$ (0.645 g, 1.72 mmol), and $NaBPh_4$ (0.589 g, 1.73 mmol) were stirred overnight in 20 mL of tetrahydrofuran. The resulting solid was collected, washed with diethyl ether, and dried under vacuum, yielding 1.40 g of a (presumably) 1:1 mixture of [(TPA)CrCl$_2$][BPh$_4$] and NaCl. This precursor was used as a convenient starting material in the synthesis of both **5** and **6**. A 0.200 g portion of the precursor (0.25 mmol) was slurried in tetrahydrofuran at room temperature and slowly treated with CH_3MgCl (0.52 mmol, 0.17 mL of a 3.03 M solution), resulting in a red-brown solution. The solution was stirred at room temperature for 1.5 h and treated with 0.50 mL of 1,4-dioxane (99.8%, anhydrous). The resulting mixture was stirred an additional 30 min, filtered, and taken to dryness, yielding a light-brown solid. The solid was dissolved in about 5 mL of dichloromethane and filtered to remove a small amount of insoluble material. Slow

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Table 1. Summary of X-ray Crystallographic Data for Chromium−TPA Complexes **1**, **2A**, **2B**, **4A**, **5**, and **6**[a]

	1	**2A**	**2B**	**4A**	**5**	**6**
empirical formula	$C_{18}H_{18}Cl_2CrN_4$	$C_{42}H_{38}BClCrN_4$	$C_{54}H_{40}BClCrF_{24}N_4O$	$C_{44}H_{41}BCl_2CrN_5$	$C_{44.50}H_{45}BClCrN_4$	$C_{56}H_{51}BCrN_5$
fw	413.26	697.02	1315.16	773.53	734.10	856.83
cryst syst	monoclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1$
a (Å)	15.195(3)	9.426(2)	13.645(3)	13.807(2)	9.839(1)	10.6190(4)
b (Å)	8.7230(10)	11.868(1)	13.759(3)	10.145(1)	22.339(3)	14.1215(6)
c (Å)	29.260(5)	16.663(2)	17.522(3)	28.569(3)	18.064(2)	15.1598(6)
α (deg)	90	71.02(1)	92.43(2)	90	90	90
β (deg)	97.31(2)	82.66(1)	107.85(2)	95.95(1)	92.21(1)	103.8810(10)
γ (deg)	90	82.61(1)	114.36(2)	90	90	90
V (Å^3)	3846.8(11)	1740.7(4)	2798.9(10)	3980.2(8)	3967.4(8)	2206.92(15)
Z	8	2	2	4	4	2
d_{calcd} (mg m^{-3})	1.427	1.330	1.561	1.291	1.229	1.289
cryst size (mm)	0.58 × 0.30 × 0.20	0.46 × 0.32 × 0.15	0.42 × 0.38 × 0.35	0.50 × 0.42 × 0.35	0.42 × 0.40 × 0.35	0.310 × 0.188 × 0.146
abs. coeff. (mm^{-1})	0.880	0.442	0.376	0.459	0.391	0.305
2θ max (deg)	49.96	50.06	49.98	50.10	50.08	64.12
transmission range	1.0−0.9199	1.0−0.9295	1.0−0.9334	1.0−0.9148	1.0−0.9564	
no. reflns collected	7001	6534	10264	7327	7436	28957
no. indep reflns	6743	6127	9816	7016	7001	14897
no. obsd reflns	4026	4371	6625	4450	4126	7177
no. variables	451	442	827	478	471	834
R1 (wR2)[b] [$I > 2\sigma(I)$]	0.0741 (0.1331)	0.0554 (0.0986)	0.0631 (0.1606)	0.0659 (0.1153)	0.0784 (0.1489)	0.0406 (0.0878)
GOF (F^2)	1.033	1.024	1.032	1.030	1.022	1.039
diff. peaks (e$^-$·Å^{-3})	1.004, −0.308	0.236, −0.238	0.505, −1.120	0.222, −0.369	0.332, −0.427	0.621, −0.336

[a] See Experimental Section for additional data collection, reduction, and structure solution and refinement details. [b] $R1 = \sum ||F_o| - |F_c||/\sum |F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]]^{1/2}$ where $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$.

diffusion of diethyl ether into the dichloromethane solution resulted in the formation of red-orange crystals and a small amount of off-white solid. The crystals were separated from the off-white solid, washed with diethyl ether, and dried under vacuum to give **5** as a dichloromethane hemisolvate (0.123 g, 64%). FTIR (KBr): 3055, 2996, 2909, 2856, 2792, 1946, 1888, 1824, 1608, 1479, 1439, 1421, 1281, 1030, 768, 733, 703, 610, 487 cm^{-1}. UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 328 (sh, 1700). Anal. Calcd (found) for $C_{44.5}H_{45}N_4BClCr$: C, 72.81 (72.18); H, 6.18 (6.20); N, 7.63 (7.72). $\mu_{eff} = 3.5\ \mu_B$.

[(TPA)CrPh$_2$][BPh$_4$]·CH$_3$CN (6). A 0.400 g portion (0.50 mmol) of the [(TPA)$CrCl_2$][BPh_4]·NaCl precursor, prepared as for compound **5** above, was slurried in 20 mL of tetrahydrofuran and treated slowly with C_6H_5MgCl (1.0 mmol, 0.50 mL of a 2.0 M solution) at room temperature. A red-brown precipitate formed after the mixture was stirred for 2 h at room temperature. The precipitate was isolated by filtration, washed with diethyl ether, and dissolved in a minimum of acetonitrile. The red-orange solution was heated to 70 °C, filtered, and slowly cooled to room temperature, resulting in the deposition of 0.141 g of red-orange blocks (33%). FTIR (KBr): 3055, 2985, 2921, 2255, 1952, 1882, 1812, 1608, 1479, 1433, 1281, 1059, 756, 733, 709, 610, 464 cm^{-1}. UV−vis (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 374 (sh, 1800). Anal. Calcd (found) for $C_{56}H_{51}N_5BCr$: C, 78.50 (78.45); H, 6.00 (5.99); N, 8.17 (8.27). $\mu_{eff} = 3.5\ \mu_B$.

X-ray Crystallography. Single crystals of **1**, **2A**, **4A**, and **5** were mounted in thin-walled glass capillaries and transferred to an Enraf-Nonius CAD4 X-ray diffractometer for data collections at 298(2) K. Data for complex **2B** were collected at 173(2) K using a Bruker-Nonius MACH3/S diffractometer, and data for **6** were collected at 100(2) K using a Bruker SMART APEX CCD-based diffractometer system. All data were collected using graphite monochromated Mo Kα radiation. Unit cell constants for **1**, **2A**, **2B**, **4A**, and **5** were determined from a least-squares refinement of the setting angles of 25 intense, high-angle reflections, while the unit cell constants for **6** are based upon the refinement of the XYZ-centroids of 7177 reflections above 20 $\sigma(I)$. Intensity data for **1**, **2A**, **2B**, **4A**, and **5** were collected using the $\omega/2\theta$ scan technique to a maximum 2θ value of 50−52°, while data for **6** were harvested from a total of 1800 frames collected with a scan width of 0.3° in ω to a maximum 2θ angle of 64.12°. Absorption corrections for **1**, **2A**, **2B**, **4A**, and **5** were applied based on azimuthal scans of several reflections for each sample, while the absorption correction for **6** was performed using an empirical method (SADABS). Space groups were determined based on systematic absences and intensity statistics. Successful direct-methods solutions were calculated for each compound using the SHELXTL suite of programs. Any non-hydrogen atoms not identified from the initial E-map were located after several cycles of structure expansion and full matrix least squares refinement on F^2. Hydrogen atoms were added geometrically. All non-hydrogen atoms were refined with anisotropic displacement parameters, while hydrogen atoms were refined using a riding model with group isotropic displacement parameters. Relevant crystallographic information for the compounds is summarized in Table 1, and selected interatomic distances and angles are provided in Table 2. Complete crystallographic data for each compound are provided as Supporting Information in CIF and PDF format.

The asymmetric unit of **1** contains two crystallographically independent yet metrically similar neutral molecules. The unit cells of **2B**, **4A**, **5**, and **6** each contain uncoordinated solvent molecules (**2B**, Et_2O; **4A** and **6**, CH_3CN; **5**, 0.5CH_2Cl_2). These solvates are fully ordered in **2B** and **4A** but disordered in **5** (statistically disordered about an inversion center) and **6** (found in two overlapping orientations sharing a common internal carbon atom). Four of the eight −CF_3 groups of the anion in **2B** are rotationally disordered. Split-atom models and geometric constraints were applied to these disordered groups. The tetraphenylborate anion in **6** is disordered, occupying two positions separated by a distance of ~0.5 Å with site occupancy factors of 0.53 and 0.47. Geometric constraints were applied to these two independent anions.

General Ethylene Polymerization Procedure. In a glovebox, the chromium complex precatalyst (10−50 μmol) was dissolved in 100 mL of the appropriate solvent (dichloromethane, chlorobenzene, or toluene) and placed in a Fisher−Porter bottle adapted with stainless steel valving and connections. The required cocatalyst was

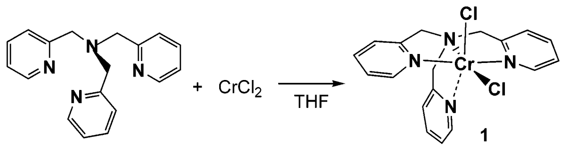
Table 2. Selected Distances (Å) and Angles (deg) for Structurally Characterized Complexes[a]

Complex **1**[b]							
molecule 1				molecule 2			
Cr(1)−N(1)	2.474(6)	Cr(1)−N(4)	2.164(5)	Cr(1a)−N(1a)	2.633(6)	Cr(1a)−N(4a)	2.152(5)
Cr(1)−N(2)	2.123(6)	Cr(1)−Cl(1)	2.619(2)	Cr(1a)−N(2a)	2.105(5)	Cr(1a)−Cl(1a)	2.646(2)
Cr(1)−N(3)	2.122(5)	Cr(1)−Cl(2)	2.3783(19)	Cr(1a)−N(3a)	2.110(5)	Cr(1a)−Cl(2a)	2.375(2)
N(1)−Cr(1)−N(2)	81.7(2)	N(2)−Cr(1)−Cl(2)	102.42(18)	N(1a)−Cr(1a)−N(2a)	92.99(18)	N(2a)−Cr(1a)−Cl(2a)	100.77(15)
N(1)−Cr(1)−N(3)	95.94(19)	N(3)−Cr(1)−N(4)	77.8(2)	N(1a)−Cr(1a)−N(3a)	79.90(19)	N(3a)−Cr(1a)−N(4a)	79.52(19)
N(1)−Cr(1)−N(4)	75.98(19)	N(3)−Cr(1)−Cl(1)	90.97(14)	N(1a)−Cr(1a)−N(4a)	74.92(19)	N(3a)−Cr(1a)−Cl(1a)	90.96(15)
N(1)−Cr(1)−Cl(1)	165.40(14)	N(3)−Cr(1)−Cl(2)	100.82(15)	N(1a)−Cr(1a)−Cl(1a)	164.59(13)	N(3a)−Cr(1a)−Cl(2a)	100.85(16)
N(1)−Cr(1)−Cl(2)	89.87(14)	N(4)−Cr(1)−Cl(1)	93.02(15)	N(1a)−Cr(1a)−Cl(2a)	91.43(14)	N(4a)−Cr(1a)−Cl(1a)	91.32(15)
N(2)−Cr(1)−N(3)	156.6(2)	N(4)−Cr(1)−Cl(2)	165.46(15)	N(2a)−Cr(1a)−N(3a)	157.4(2)	N(4a)−Cr(1a)−Cl(2a)	166.13(15)
N(2)−Cr(1)−N(4)	79.1(2)	Cl(1)−Cr(1)−Cl(2)	101.48(7)	N(2a)−Cr(1a)−N(4a)	77.90(18)	Cl(1a)−Cr(1a)−Cl(2a)	102.53(7)
N(2)−Cr(1)−Cl(1)	86.86(16)			N(2a)−Cr(1a)−Cl(1a)	90.80(14)		
Complex **2A**[c]							
Cr(1)−N(1)	2.100(3)	Cr(1)−N(4)	2.131(3)	N(2)−Cr(1)−N(3)	83.09(11)	N(3)−Cr(1)−Cl(1)	98.57(7)
Cr(1)−N(2)	2.100(3)	Cr(1)−Cl(1)	2.3528(9)	N(2)−Cr(1)−N(4)	80.18(12)	N(3)−Cr(1)−Cl(1a)	166.83(7)
Cr(1)−N(3)	2.370(3)	Cr(1)−Cl(1a)	2.9388(11)	N(2)−Cr(1)−Cl(1)	100.82(8)	N(4)−Cr(1)−Cl(1)	176.71(9)
N(1)−Cr(1)−N(2)	158.09(12)	N(1)−Cr(1)−Cl(1)	99.72(10)	N(2)−Cr(1)−Cl(1a)	86.40(8)	N(4)−Cr(1)−Cl(1a)	92.03(8)
N(1)−Cr(1)−N(3)	101.29(11)	N(1)−Cr(1)−Cl(1a)	85.66(8)	N(3)−Cr(1)−N(4)	78.40(11)	Cl(1)−Cr(1)−Cl(1a)	91.17(3)
N(1)−Cr(1)−N(4)	79.73(13)						
Complex **2B**[c]							
Cr(1)−N(1)	2.129(4)	Cr(1)−N(4)	2.177(3)	N(2)−Cr(1)−N(3)	95.09(13)	N(3)−Cr(1)−Cl(1)	100.45(10)
Cr(1)−N(2)	2.274(4)	Cr(1)−Cl(1)	2.3708(15)	N(2)−Cr(1)−N(4)	78.32(12)	N(3)−Cr(1)−Cl(1a)	89.21(10)
Cr(1)−N(3)	2.116(4)	Cr(1)−Cl(1a)	2.7642(15)	N(2)−Cr(1)−Cl(1)	99.93(9)	N(4)−Cr(1)−Cl(1)	178.00(10)
N(1)−Cr(1)−N(2)	84.05(13)	N(1)−Cr(1)−Cl(1)	101.69(10)	N(2)−Cr(1)−Cl(1a)	167.97(9)	N(4)−Cr(1)−Cl(1a)	91.55(9)
N(1)−Cr(1)−N(3)	157.65(14)	N(1)−Cr(1)−Cl(1a)	87.69(10)	N(3)−Cr(1)−N(4)	78.82(13)	Cl(1)−Cr(1)−Cl(1a)	90.30(5)
N(1)−Cr(1)−N(4)	79.15(14)						
Complex **4A**							
Cr(1)−N(1)	2.053(3)	Cr(1)−N(4)	2.082(3)	N(2)−Cr(1)−N(3)	85.28(13)	N(3)−Cr(1)−Cl(1)	173.96(9)
Cr(1)−N(2)	2.060(3)	Cr(1)−Cl(1)	2.2951(15)	N(2)−Cr(1)−N(4)	80.23(13)	N(3)−Cr(1)−Cl(2)	92.25(9)
Cr(1)−N(3)	2.074(3)	Cr(1)−Cl(2)	2.2717(13)	N(2)−Cr(1)−Cl(1)	91.74(11)	N(4)−Cr(1)−Cl(1)	91.86(10)
N(1)−Cr(1)−N(2)	160.35(13)	N(1)−Cr(1)−Cl(1)	88.88(10)	N(2)−Cr(1)−Cl(2)	99.50(10)	N(4)−Cr(1)−Cl(2)	174.71(11)
N(1)−Cr(1)−N(3)	92.16(13)	N(1)−Cr(1)−Cl(2)	100.06(10)	N(3)−Cr(1)−N(4)	82.47(13)	Cl(1)−Cr(1)−Cl(2)	93.43(5)
N(1)−Cr(1)−N(4)	80.12(13)						
Complex **5**							
Cr(1)−N(1)	2.077(4)	Cr(1)−N(4)	2.157(4)	N(2)−Cr(1)−N(3)	83.45(16)	N(3)−Cr(1)−C(100)	171.04(18)
Cr(1)−N(2)	2.061(4)	Cr(1)−C(100)	2.078(5)	N(2)−Cr(1)−N(4)	80.27(15)	N(3)−Cr(1)−C(101)	95.35(17)
Cr(1)−N(3)	2.167(4)	Cr(1)−C(101)	2.095(4)	N(2)−Cr(1)−C(100)	88.55(19)	N(4)−Cr(1)−C(100)	95.63(18)
N(1)−Cr(1)−N(2)	158.66(16)	N(1)− Cr(1)−C(100)	90.55(18)	N(2)−Cr(1)−C(101)	102.61(19)	N(4)−Cr(1)−C(101)	173.48(18)
N(1)−Cr(1)−N(3)	95.43(15)	N(1)−Cr(1)−C(101)	98.72(19)	N(3)−Cr(1)−N(4)	79.08(14)	C(100)− Cr(1)−C(101)	90.3(2)
N(1)−Cr(1)−N(4)	78.61(15)						
Complex **6**							
Cr(1)−N(1)	2.0797(14)	Cr(1)−N(4)	2.1455(14)	N(2)−Cr(1)−N(3)	97.01(5)	N(3)−Cr(1)−C(19)	90.41(6)
Cr(1)−N(2)	2.1967(13)	Cr(1)−C(19)	2.1015(16)	N(2)−Cr(1)−N(4)	79.23(5)	N(3)−Cr(1)−C(25)	99.80(5)
Cr(1)−N(3)	2.0928(13)	Cr(1)−C(25)	2.0743(14)	N(2)−Cr(1)−C(19)	167.43(5)	N(4)−Cr(1)−C(19)	92.58(5)
N(1)−Cr(1)−N(2)	78.66(5)	N(1)−Cr(1)−C(19)	90.69(5)	N(2)−Cr(1)−C(25)	95.95(5)	N(4)−Cr(1)−C(25)	174.07(5)
N(1)−Cr(1)−N(3)	158.23(5)	N(1)−Cr(1)−C(25)	101.86(5)	N(3)−Cr(1)−N(4)	77.54(5)	C(19)−Cr(1)−C(25)	92.74(6)
N(1)−Cr(1)−N(4)	80.69(5)						

[a] Estimated standard deviations are indicated in parentheses. [b] Two crystallographically independent molecules are present in the asymmetric unit. [c] Atoms labeled with an "a" are related to atoms not so labeled by a crystallographic inversion center.

added to this solution, and the bottle was sealed, placed in a 40 °C water bath, and connected to a constant 20 psig ethylene supply. The solution was stirred with a magnetic stir bar. Polymerizations were halted after 1 h by venting the reactor and treating the reactor contents with 30 mL of 6 M HCl and 200 mL of methanol. Polymeric product was collected by filtration, washed with methanol, and dried under vacuum.

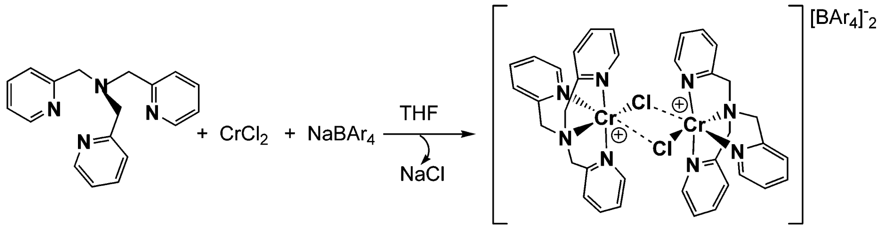
Scheme 1



Results and Discussion

Synthesis and Structural Characterization of (TPA)-$CrCl_2$ (1). Treatment of anhydrous $CrCl_2$ with 1 equiv of tris(2-pyridylmethyl)amine (TPA) in tetrahydrofuran, followed by recrystallization from acetonitrile, generated (TPA)-$CrCl_2$ (**1**) in good yield (Scheme 1). Figure 1 shows the molecular structure of **1** as determined by X-ray crystallography; selected bond distances and angles are summarized in Table 2. This complex crystallizes with two independent molecules in the asymmetric unit. The two molecules are similar except for one significantly longer Cr−N bond length in molecule 2, Cr(1a)−N(1a) = 2.633 Å versus Cr(1)−N(1) = 2.474 Å. At best, N(1) and N(1a) are only weakly associated with their respective chromium centers, resulting in a tetragonally elongated octahedral geometry around each chromium atom with cis disposed chloride ligands. A slight ruffling of the equatorial plane (defined by N(2), N(3), N(4), and Cl(2)) is also observed, with the mean deviation of these

Scheme 2



2A: $BAr_4^- = BPh_4^-$
2B: $BAr_4^- = BAr^F{}_4^-$

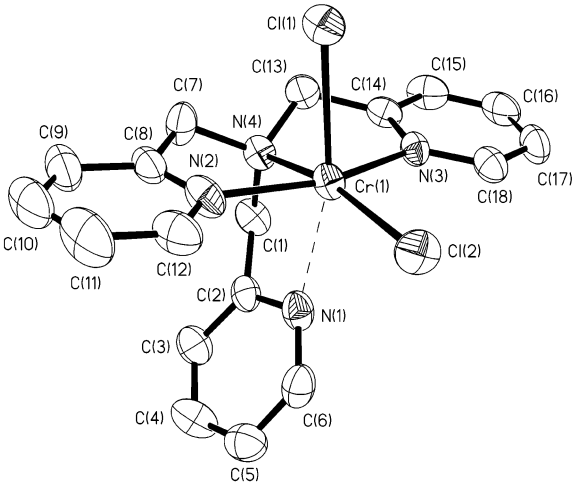


Figure 1. Thermal ellipsoid representation (35% probability boundaries) of the X-ray crystal structure of **1**. Hydrogen atoms are omitted for clarity.

atoms from the plane being 0.14 Å. Moreover, the chromium atom is displaced 0.14 Å out of this plane toward the axial chloride.

The full extent of tetragonal distortion is evidenced by the large difference in axial and equatorial Cr−N and Cr−Cl bond lengths (Table 2). For molecule 1, the $Cr-N_{ax}$ bond length is 0.34 Å longer than the average of its equatorial counterparts, and the $Cr-Cl_{ax}$ bond is 0.24 Å longer than $Cr-Cl_{eq}$. Similar statements can be made for molecule 2, except that the difference between $Cr-N_{ax}$ and $Cr-N_{eq}$ bond lengths is even more striking (0.51 Å difference). The structure of **1** is consistent with the Jahn−Teller distortions[44] expected for a high-spin d^4 complex, and the room-temperature magnetic moment ($\mu_{eff} = 4.6\ \mu_B$) of **1** agrees with the high-spin ($S = 2$) configuration. As expected, the average $Cr-N_{eq}$ bond length in **1** is longer than that in the known dimeric chromium(III)−TPA complexes,[45] consistent with the larger atomic radius of chromium(II).

Thus far, attempts to synthesize neutral chromium(II) organometallic derivatives, such as $(TPA)CrR_2$ or (TPA)-Cr(Cl)R, have led to highly soluble but intractable residues. For example, treatment of **1** with organolithium or Grignard (alkyl or aryl) reagents at low temperature (−70 °C) resulted in red-brown solutions that formed deep-green-blue mixtures upon warming to room temperature. The residues, though highly soluble in tetrahydrofuran and diethyl ether, did not yield isolable products, perhaps hinting at the instability of organometallic chromium(II) species containing the TPA framework.

Synthesis and Structural Characterization of $[(TPA)CrCl]_2[BPh_4]_2$ (2A) and $[(TPA)CrCl]_2[BAr^F{}_4]_2$ (2B). The long axial Cr−Cl bond in **1** suggested that this chloride might be abstracted and replaced with a noncoordinating anion, generating a cationic species with a vacant coordination site cis to the remaining chloride. Halide abstraction (anion exchange) with sodium tetraphenylborate, $NaBPh_4$, is a convenient way to generate coordinatively unsaturated metal centers.[19,46] Indeed, treatment of $CrCl_2$ with 1 equiv each of TPA and $NaBPh_4$ (Scheme 2) in tetrahydrofuran generated monochloro complex **2A**. Substitution of the sodium salt of tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ($NaBAr^F{}_4$) for $NaBPh_4$ in Scheme 2 resulted in the formation of the significantly more soluble $BAr^F{}_4^-$ analogue, **2B**. For **2A**, the red-brown solid, isolated in nearly quantitative yield from the reaction mixture, can be recrystallized from acetonitrile to give analytically pure material in moderate yield (49%). The isolated yield of **2A** was reduced, in part, due to the simultaneous formation of a cationic chromium(III) μ-oxo dimer, $\{[(TPA)CrCl]_2(\mu\text{-}O)\}[BPh_4]_2$ (**3**). The dimer (whose identity was confirmed by an X-ray crystallographic study)[47] was deposited as dark-green crystals after further concentration of the filtrate remaining after crystallization of **2A**. Compound **3** presumably formed by reaction of **2A** with trace water or oxygen impurities in the solvent. Fortunately, dimer **3** is sufficiently more soluble than **2A** to allow for the latter's isolation in analytically pure form.

The solid-state structure of **2A** consists of well-separated cations and anions. The cationic portion, shown in Figure 2, consists of a weakly associated dimer of mononuclear

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(44) (a) Jahn, H. A.; Teller, E. *Proc. R. Soc.* **1937**, *A161*, 220. (b) Ballhausen, C. J. *Introduction to Ligand Field Theory*; McGraw-Hill: New York, 1962; p 193.

(45) For example, the average Cr−N bond length in $[Cr_2(TPA)_2(\mu\text{-}OH)_2]Br_4 \cdot 8H_2O$ is 2.048 Å (ref 40b) compared to 2.136 Å (average of the three $Cr-N_{eq}$ bonds) in **1**.

(46) For a recent example, see: Aneetha, H.; Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P.; Mereiter, K. *Organometallics* **2003**, *22*, 1779−1782.

(47) X-ray crystallographic data for complex **3**, $\{[(TPA)CrCl]_2(\mu\text{-}O)\}[BPh_4]_2$, $C_{84}H_{76}B_2Cl_2Cr_2N_8O$: monoclinic, $P2_1/n$, with $a = 10.137(2)$ Å, $b = 23.295(3)$ Å, $c = 15.472(3)$ Å, $\beta = 90.43(4)°$, $V = 3653.5(11)$ Å^3, and $Z = 2$ at 25 °C. Full-matrix least-squares refinement based on F^2 provided current residuals of R1 = 0.0608 and wR2 = 0.1097 with GOF = 1.022 for 6441 reflections with $I > 2\sigma(I)$ and 448 variables. Full details of the structure determination will be reported elsewhere.

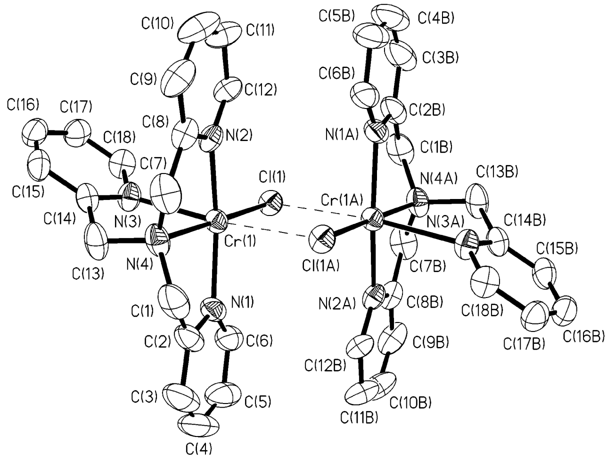


Figure 2. Thermal ellipsoid representation (35% probability boundaries) of the X-ray crystal structure of **2A**. Hydrogen atoms and tetraphenylborate counterions are omitted for clarity.

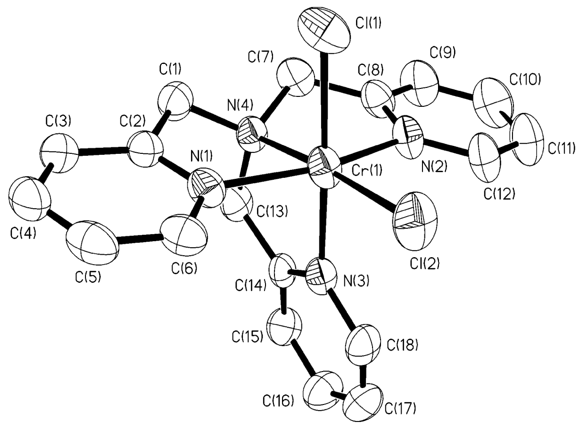


Figure 3. Thermal ellipsoid representation (35% probability boundaries) of the X-ray crystal structure of **4A**. Hydrogen atoms, the tetraphenylborate counterion, and the acetonitrile solvent molecule are omitted for clarity.

$[(TPA)CrCl]^+$ fragments that are related by a crystallographically imposed inversion center. Important distances and angles are collected in Table 2. Each monomeric chromium center can be described as a tetragonally distorted octahedron, with Cr(1), N(1), N(2), N(4), and Cl(1) residing in the equatorial plane, and N(3) and the bridging Cl(1a) (from the neighboring monomer) occupying the axial sites. Again, the full extent of tetragonal distortion is shown by comparing the long $Cr-Cl_{ax}$ (2.9388(11) Å) and short $Cr-Cl_{eq}$ (2.3528(9) Å) bond lengths, as well as the long $Cr-N_{ax}$ (2.370(3) Å) and short $Cr-N_{eq}$ (2.100(3), 2.100(3), and 2.131(3) Å) distances. Alternatively, the geometry around chromium can be described as square pyramidal, with N(1), N(2), N(4), and Cl(1) in the basal plane and N(3) in the apical site. In any event, the plane defined by N(1), N(2), N(4), and Cl(1) is modestly ruffled, with the mean deviation of these atoms from the plane being 0.10 Å. Given the asymmetry in axial ligation, it is somewhat surprising that the chromium atom is only raised 0.04 Å out of the plane toward N(3).

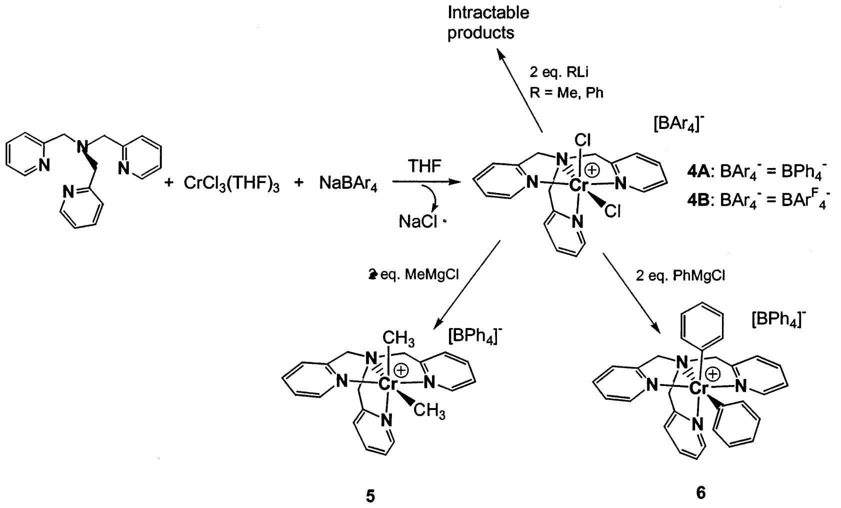
For either description, the tetragonal distortion from purely octahedral geometry is consistent with that expected for a high-spin chromium(II) center. Moreover, the room-temperature magnetic moment for **2A** is in line with magnetically isolated, high-spin ($S = 2$) chromium centers ($\mu_{eff} = 4.6\ \mu_B$ per Cr). The long Cr$\cdots$Cr (3.727(1) Å) and Cr$\cdots$Cl distances presumably preclude any significant magnetic coupling between the chromium centers. The structure of **2B** ($BAr^F{}_4{}^-$ counterion) was also determined by X-ray crystallography. The cationic portion was found to be similar to that of **2A**, except for shorter Cr$\cdots$Cl and Cr$\cdots$Cr distances in **2B** (0.17 and 0.10 Å shorter, respectively). Interestingly, the room-temperature magnetic moment of **2B** (3.9 μ_B per Cr) was lower than that of **2A**. Although the shorter Cr$\cdots$Cr and Cr$\cdots$Cl distances in **2B** might enhance antiferromagnetic coupling between the chromium centers, we have not performed a detailed magnetic susceptibility study to determine if this is indeed the case.

For **2A** and **2B**, we found it somewhat surprising that recrystallization from acetonitrile did not generate monomeric $[(TPA)CrCl(MeCN)]^+$ cations, products that would form by solvolysis of the weakly associated dimers. Equally surprising, we observed that treatment of **2A** with 1 equiv of the strong donor ligand 4-(dimethylamino)pyridine (DMAP) left **2A** unaltered. Thus, binding of neutral ligands to the cationic chromium(II) centers appears to be weak, a feature that forebodes relatively modest polymerization catalyst activity (vide infra). On the basis of these observations, we believe that crystal-packing effects are largely responsible for the presence of bridging chloride ligands in the solid-state structures for **2A** and **2B** and not any strong tendency for chromium(II) to bind ligands at the axial site.

As found for **1**, treatment of **2A** with organolithium or Grignard reagents at low temperature led to intractable, oily residues upon warming to room temperature. Furthermore, complexes **2A** and **2B** were unstable in dichloromethane, undergoing what appeared to be oxidative halide abstraction from the solvent to form the corresponding chromium(III) complexes, **4A** and **4B**. Alternative syntheses of **4A** and **4B**, along with structural characterization data, are provided in the following section.

Synthesis and Structural Characterization of $[(TPA)CrCl_2][BPh_4]$ (4A). The relatively straightforward synthesis of **2**, via formal chloride abstraction from $(TPA)CrCl_2$, suggested that a similar strategy could be used in conjunction with $CrCl_3$ to prepare cationic chromium(III) dichloride derivatives $[(TPA)CrCl_2][BAr_4]$. Treatment of $CrCl_3(THF)_3$ with 1 equiv each of $NaBPh_4$ and TPA in tetrahydrofuran produced monomeric **4A** (Scheme 3), with concomitant formation of insoluble NaCl. Recrystallization from acetonitrile yielded analytically pure **4A** as the acetonitrile monosolvate. As observed in the synthesis of **2** (Scheme 2), substitution of $NaBAr^F{}_4$ for $NaBPh_4$ in Scheme 3 afforded the more soluble $BAr^F{}_4{}^-$ analogue, **4B**. The structure of **4A** (acetonitrile solvate), as determined by X-ray crystallography, is depicted in Figure 3; important distances and angles are provided in Table 2. The crystal lattice consists of a roughly octahedral cationic chromium center along with well-separated $BPh_4{}^-$ and solvent molecules. In contrast to the severe tetragonal distortion exhibited by **1** and **2**, complex **4A** is largely octahedral with Cr−N (2.053(3)−2.082(3) Å) and Cr−Cl (2.2717(13)−2.2951(15) Å) bond lengths varying

Scheme 3



over a narrow range. The room-temperature magnetic moment ($\mu_{\text{eff}} = 3.9\ \mu_B$, $S = {}^3/_2$) and the lack of significant tetragonal distortion are consistent with the d^3 electronic configuration for **4A**. Moreover, relative to complex **1**, the equatorial plane defined by N(1), N(2), N(4), and Cl(2) displays minimal ruffling (mean deviation from the plane is 0.04 Å) and Cr(1) is displaced only 0.06 Å from this plane toward the axial chloride (Cl(1)). It should be noted that compounds **1** and **4A** provide examples of chromium(II) and chromium(III) complexes with identical inner coordination spheres, containing four nitrogens from the tetradentate TPA framework and two chloride ligands. The striking difference in axial Cr−N and Cr−Cl bond lengths between **1** and **4A** (see Table 2) underscores the significant structural reorganization that accompanies the chromium(III) + $e^- \rightarrow$ chromium(II) transition.

Synthesis and Structural Characterization of [(TPA)-Cr(CH$_3$)$_2$][BPh$_4$] (5) and [(TPA)CrPh$_2$][BPh$_4$] (6). Attempts to form cationic organometallic complexes by treating **4A** with 2.0 equiv of alkyl- or aryllithium reagents led to the formation of deep-blue-green, intractable residues, perhaps due to reduction of the chromium(III) center by the strongly reducing organolithium reagents. These residues were reminiscent of those resulting from attempted alkylation of chromium(II) derivatives **1** and **2** (vide supra). However, use of 2.0 equiv of milder alkylating/arylating reagents, such as MeMgCl and PhMgCl, allowed for generation and isolation of stable, cationic organometallic derivatives [(TPA)-Cr(CH$_3$)$_2$][BPh$_4$] (**5**) and [(TPA)CrPh$_2$][BPh$_4$] (**6**), respectively (Scheme 3). For **5**, addition of 1,4-dioxane facilitated the removal of MgCl$_2$ from the reaction mixture. For **6**, the diphenyl complex precipitated out of tetrahydrofuran solution, allowing for its separation from the more soluble MgCl$_2$ coproduct. In either case, the red-brown solids that were ultimately isolated were readily recrystallized from dichloromethane or acetonitrile to give analytically pure crystalline material. The structures of dimethyl complex **5** (methylene chloride hemisolvate) and diphenyl complex **6** (acetonitrile solvate) were confirmed by X-ray crystallography. Selected bond lengths and angles are given in Table 2.

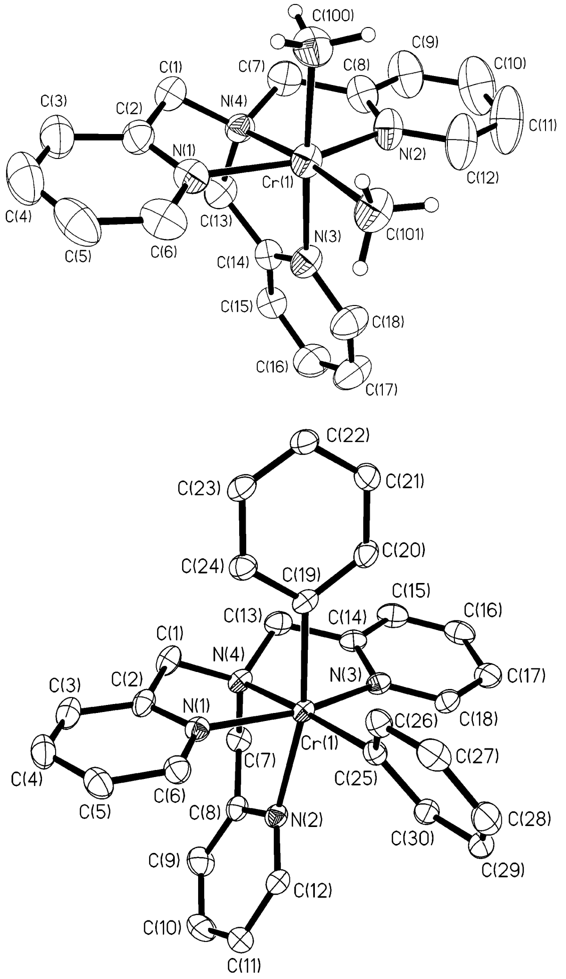


Figure 4. Thermal ellipsoid representation (35% probability boundaries) of the X-ray crystal structures of **5** (top) and **6** (bottom). Tetraphenylborate counterions, solvent molecules, and most hydrogen atoms are omitted for clarity.

Except for the substitution of carbon for chloride (and the necessarily shorter Cr−C bond lengths), the basic octahedral geometry of **5** (Figure 4) is similar to that of **4A**. However, the Cr−N bond lengths in **5** (2.061−2.167 Å) vary over a somewhat wider range than those in **4A** (2.053(3)−2.082(3) Å) with the longest Cr−N bonds (2.157(4) and 2.167(4) Å)

Table 3. Results of Polymerization Experiments[a]

run no.	catalyst system	Cr, μmol	Co−cat/Cr mole ratio	yield, g	activity[b]	M_w	M_w/M_n	T_m, °C
1	**1**, MAO	50	200	1.09	16.0	9000	2.8	127.9
2	**2A**, MAO[c]	10	200	0.14	10.3	11300	2.5	
3	**2A,** Et_2AlCl[c]	10	20	trace	∼0			
4	**2B**, MAO[c]	10	200	0.15	11.0	41900	7.5	130.0
5	**2B**, TMSMLi[d,e]	10	10	trace	∼0			
6	**2B**, $Al(i\text{-}Bu)_3$[d]	10	20	trace	∼0			
7	**4A**, MAO	50	200	0.65	9.6	3600	2.0	123.9
8	**4B**, MAO	50	200	1.11	16.3	5800	2.4	126.0
9	**5**, MAO[c]	10	200	0.30	22.0	34600	7.2	131.7
10	**5**, MAO	50	200	1.13	16.6	5600	2.5	
11	**6**, MAO	50	200	1.35	19.8	11200	3.5	128.7

[a] See the Experimental Section for details. Polymerizations performed in dichloromethane unless stated otherwise. [b] Activity expressed in g PE produced per (mmol Cr-atm-hr). [c] Polymerization performed in chlorobenzene. [d] Polymerization performed in toluene. [e] TMSMLi = trimethylsilylmethyllithium ($(CH_3)_3SiCH_2Li$).

trans to the methyl carbon atoms, C(100) and C(101). The presence of longer Cr−N bonds opposite the methyl groups is consistent with the methyl group's strong σ-donor ability. The Cr−CH_3 distances in **5** (2.078(5) and 2.095(4) Å) are fairly typical of other methylchromium(III) complexes found in the literature,[48] including those in the structurally related chromium(III) trispyrazolylborate complex, $Tp^*Cr(CH_3)_2(DMAP)$ (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate).[49] In the latter compound, the facially coordinating Tp* ligand forces the two methyl groups into a cis arrangement with a C−Cr−C angle of 91.2(5)°. The corresponding angle in **5** is 90.3(2)°. As observed for **5**, the two longest Cr−N bonds in $Tp^*Cr(CH_3)_2(DMAP)$ (2.179(9) and 2.202(9) Å) are those trans to the Cr−methyl linkages.

Complex **6**, isolated as an acetonitrile solvate, also possesses a slightly distorted octahedral geometry around chromium (Figure 4). As with **5**, the longest Cr−N bonds in **6** (2.1967(13) and 2.1455(14) Å) are those trans to the Cr−C bonds, consistent with the strong σ-donor ability of the phenyl group. For **6**, an additional slight distortion results from the displacement of N(2) away from the C(19)−Cr(1) axis, yielding a slightly more acute C(19)−Cr(1)−N(2) angle (167.43(5)°) compared to the same angle in **5** (C(100)−Cr(1)−N(3) = 171.04(18)°). Similar to dichloro complex **4A**, the equatorial planes in **5** and **6** display minimal ruffling; the mean deviations of the three nitrogen and one carbon atoms from their equatorial planes are 0.07 and 0.04 Å, respectively. Furthermore, the chromium atoms in **5** and **6** are raised only slightly out of their equatorial planes (0.039 and 0.060 Å, respectively). The relatively undistorted structures for **5** and **6**, along with their room-temperature magnetic moments (each 3.5 μ_B) are consistent with the d^3 ($S = {}^3/_2$) electronic configurations expected for octahedral chromium(III) complexes. Finally, although **5** and **6** are formally 15-electron organometallic complexes, they are thermally robust and are relatively air and moisture stable, especially when compared to Cp-containing chromium(III) compounds.[6−8]

Polymerization Experiments. Complexes **1**, **2A**, **2B**, **4A**, **4B**, **5**, and **6** were evaluated as polymerization catalysts in combination with various activators. Table 3 summarizes our findings. It is well-known that transition-metal alkyl complexes possessing vacant or accessible coordination sites cis to the metal−carbon bond are often useful polymerization catalysts. Olefin binding at the vacant site, followed by insertion into the metal−carbon bond, promulgates the chain. Thus, one might have expected that **2A** and **2B**, once alkylated, would generate active catalyst sites. However, treatment of **2A** or **2B** with common alkylating agents such as trimethylsilylmethyllithium ($(CH_3)_3SiCH_2Li$), diethylaluminum chloride, or triisobutylaluminum did not yield active polymerization catalysts (runs 3, 5, and 6). Poor binding of the olefin to chromium, which is consistent with the inability of these cationic chromium(II) centers to bind even strong donor ligands, would contribute to low catalyst activity. Originally, we also wondered whether coordination of the BPh_4^- anion to an alkylated chromium(II) site might interfere with olefin binding and contribute to poor catalyst activity. However, this is probably not the root cause for low activity since complex **2B**, which contains the noncoordinating tetrakis(3,5-bis(trifluoromethyl)phenyl) borate anion, is also inactive in the presence of alkylating cocatalysts (runs 5 and 6).

For complexes **1** and **4A**, treatment with common alkylating agents, such as diethylaluminum chloride and triisobutylaluminum, did not yield active catalysts (data not shown). This is not surprising given that **1** and **4A** are coordinatively saturated. However, one might have predicted that a competent catalyst would form by abstraction of a methyl group from **5** with $B(C_6F_5)_3$, generating a chromium(III)−methyl complex with a vacant coordination site cis to the metal−alkyl bond. Unfortunately, in repeated small-scale polymerization tests, reaction of **5** with 1 equiv of $B(C_6F_5)_3$ did not lead to catalytically active systems.

However, all compounds did produce active catalysts in the presence of MAO (runs 1, 2, 4, 7−11). In all cases, polymerization activity (10−20 g of PE/(mmol of Cr hr atm)) was moderate according to the activity scale proposed by Gibson.[19,20] With regard to polymeric products, GPC, ^{13}C NMR (no branching detected), and polymer melting point

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(48) For example, the Cr−Me bond length in $(cyclo\text{-}C_4H_8NC_2H_4C_5Me_4)CrMe_2$ is 2.080(3) Å (ref 11) and that in $Cp^*CrMe_2(pyridine)$ is 2.091(5) Å (ref 5d).

(49) Mashima, K.; Oshiki, T.; Tani, K.; Aoshima, T.; Urata, H. *J. Organomet. Chem.* **1998**, *569*, 15−19.

data were consistent with the formation of low to moderate molecular weight high-density polyethylene. Polymers produced in dichloromethane (runs 7, 8, and 10) typically possessed lower molecular weight than those produced in chlorobenzene (runs 2, 4, and 9), suggesting that dichloromethane acts as an effective chain termination agent.

Chromium complexes ligated by anionic and neutral non-Cp ligands often yield low to moderate activity catalysts (typically $<$100 g of PE/(mmol of Cr hr atm)) when activated by MAO.[19] However, five reported chromium(III)–ligand combinations are exceptionally active. The five ligands, along with the highest reported activity (in g of product/(mmol of Cr hr atm)), are pyridine bisimine (9000),[31b] salicylaldiminato with bulky ortho substituents (7000),[22b] aminebis(thioether) (300),[35] triazacyclohexane (700),[30] and bis(diarylphosphino)-methylamine (2600).[36] Indeed, it is these exceptions that motivates further work using various chromium–ligand combinations. The activities of the chromium(II) and chromium(III) TPA complexes reported herein are lower than these exceptionally active catalysts but are comparable to, or slightly higher than, MAO-activated chromium catalysts based on β-diketiminate (30),[27] imino-pyrrolide (5),[24,25] bis-(imidazole) (5),[34] pyridine bis(oxazolinyl) (6),[32] and reduced Schiff base (4)[23] ligands. Finally, some of the latter compounds are five-coordinate and are more active with alkyl aluminum chloride cocatalysts (e.g., Et_2AlCl) than with MAO. For example, the activity of chromium(III)-reduced Schiff base complexes increases to 130 g/(mmol of Cr hr atm) when activated by diethylaluminum chloride.[23] In contrast, the chromium TPA complexes, as previously stated, require MAO to form active catalyst systems.

Summary

We have prepared and structurally characterized several chromium(II) and chromium(III) complexes containing the tetradentate TPA ligand. Both neutral (monomeric) and cationic (weakly associated dimeric) chromium(II) complexes were synthesized. Attempts to form stable organometallic chromium(II) species led to intractable products. In the case of cationic chromium(III) derivatives, dichloro as well as dimethyl and diphenyl complexes were prepared, the latter two demonstrating the stability of the chromium(III)–carbon bond in the TPA ligand environment. None of the compounds catalyzed the polymerization of ethylene in the presence of traditional alkylating cocatalysts, but all were active catalysts in the presence of MAO. Catalyst activity was relatively modest, perhaps due to the inability of ethylene to bind appreciably to the rather congested (TPA)Cr centers. Our current research efforts are centered on the preparation of chromium complexes supported by less sterically demanding tridentate bis(2-pyridylmethyl)amine ligands. Results of that work will be the focus of future reports.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 37885-GB3 to M.J.C.), Research Corporation (Cottrell College Science Award to M.J.C.), the National Science Foundation (CHE-0078746 to J.A.H.), and the University of Wisconsin–Eau Claire for financial support of this research. We also wish to thank Albemarle Corporation for providing MAO and tris(pentafluorophenyl)boron and Mr. Walt Dutton, Mr. Gregory Listvoyb, and Dr. Ron Supkowski (W. R. Grace & Co.) for polymer analyses.

Supporting Information Available: Complete X-ray crystallographic information in CIF and PDF format. This material is available free of charge on the Internet at http://pubs.acs.org.

IC034530I