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Chromium(II) Organochromates. Preparation, Characterization, and Stability

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The synthesis, characterization, and stability properties of a novel series of Cr(II) alkylchromates together with their transformation into unprecedented alkylidene (Schrock-type) Cr(III) species and Cr(II) and Cr(III) metallacycles is described. Reaction of $CrCl_2(THF)_2$ with 4 equiv of RLi [R = Me, $PhCH_2$, $(CH_3)_3CCH_2$, $(CH_3)_2C(Ph)CH_2$] led to the initial formation of the corresponding $R_8Cr_2Li_4(THF)_4$ (**1**) which were isolated as thermally labile and almost diamagnetic crystalline solids. Treatment of these complexes with TMEDA [*N*,*N*,*N'*,*N'*-tetramethylethylenediamine] gave different species containing either Cr(II) or Cr(III), depending on the nature of the alkyl. While in the case of the methyl derivative the monomeric $Me_4Cr[Li(TMEDA)]_2$ (**2**) was reversibly formed, another diamagnetic Cr(II) complex $(PhCH_2)_6Cr_2[Li(TMEDA)]_2$ (**3**), likely dimeric, was obtained in the case of the benzyl derivative. Addition of TMEDA to the in situ prepared diamagnetic $[(CH_3)_3CCH_2]_8Cr_2[Li(THF)]_4$ gave the chromacyclobutane species $[(CH_3)_3CCH_2]_2[CH_2C(CH_3)_2CH_2]Cr[Li(TMEDA)]_2$ (**4**). In the case of the corresponding neophyl derivative a Cr(III) complex $[o\text{-}C_6H_4C(CH_3)_2CH_2]_2Cr(TMEDA)][Li(TMEDA)_2]$ (**5**) was obtained via an unexplained oxidation reaction. The utilization of a RLi:Cr stoichiometric ratio of 2:1, in the presence of TMEDA, led to the formation of the corresponding paramagnetic dialkyl species $(TMEDA)CrR_2$ [R = CH_2Ph (**7**), $CH_2C(CH_3)_3$ (**8**), $CH_2C(Ph)(CH_3)_2$ (**9**)]. In these three cases there is evidence that the reaction proceeds via formation of the intermediate monosubstitution product $(TMEDA)CrR(\mu\text{-}Cl)[LiCl(TMEDA)]$. In the case of the crystalline benzyl derivative (**6**) the product was isolated in analytically pure form. Finally, the employment of a $PhCH_2Li$:Cr stoichiometric ratio of 3:1 formed a Cr(III) complex, probably an alkylidene species $(TMEDA)Cr(CHPh)CH_2Ph$ (**10**). The structures of **4–7**, **9**, and **10** were clarified by X-ray analysis. Crystal data are as follows. **4**: $C_{27}H_{64}N_4Li_2Cr$, $M = 510.71$, monoclinic, $C2/c$, $a = 14.72(4)$ Å, $b = 14.100(6)$ Å, $c = 16.94(2)$ Å, $\beta = 106.6(1)°$, $V = 3367$ Å^3, $Z = 4$, $T = -160$ °C, Mo Kα, $R = 0.061$, $R_w = 0.047$ for 1197 reflections out of 1726 unique. **5**: $C_{38}H_{72}N_6CrLi$, $M = 671.96$, monoclinic, $P2_1/n$, $a = 11.629(2)$ Å, $b = 23.259(5)$ Å, $c = 15.726(3)$ Å, $\beta = 107.89(1)°$, $V = 4048(1)$ Å^3, $Z = 4$, $T = -160$ °C, Mo Kα, $R = 0.059$, $R_w = 0.069$ for 4003 reflections out of 7344 unique. **6**: $C_{25}H_{55}N_6CrCl_3Li_2$, $M = 611.99$, triclinic, $P\bar{1}$, $a = 11.976(5)$ Å, $b = 17.251(5)$ Å, $c = 8.828(3)$ Å, $\alpha = 92.43(3)°$, $\beta = 101.79(3)°$, $\gamma = 84.05(3)°$, $V = 1775(1)$ Å^3, $Z = 2$, $T = -160$ °C, Mo Kα, $R = 0.066$, $R_w = 0.071$ for 4189 reflections out of 6258 unique. **7**: $C_{20}H_{30}N_2Cr$, $M = 350.47$, monoclinic, $P2_1/n$, $a = 9.596(1)$ Å, $b = 18.128(2)$ Å, $c = 11.803(1)$ Å, $\beta = 110.692(9)°$, $V = 1980.8(4)$ Å^3, $Z = 4$, $T = -157$ °C, Mo Kα, $R = 0.029$, $R_w = 0.041$ for 2901 reflections out of 3503 unique. **9**: $C_{26}H_{42}N_2Cr$, $M = 434.63$, orthorhombic, $Pbcn$, $a = 15.808(8)$ Å, $b = 9.562(4)$ Å, $c = 16.036(5)$ Å, $V = 2424(3)$ Å^3, $Z = 4$, $T = -160$ °C, Mo Kα, $R = 0.041$, $R_w = 0.057$ for 1604 reflections out of 2439 unique; **10**: $C_{20}H_{29}N_2Cr$, $M = 349.46$, orthorhombic, $Pbca$, $a = 23.085(5)$ Å, $b = 14.455(6)$ Å, $c = 11.243(3)$ Å, $V = 3751(3)$ Å^3, $Z = 8$, $T = -158$ °C, Mo Kα, $R = 0.064$, $R_w = 0.072$ for 2477 reflections out of 3725 unique.

Introduction

Metallacycle[1] and Schrock-type carbenes[2] of Mo and W play a fundamental role in a series of synthetically useful transformations[3] and some important catalytic processes.[4] By way of contrast, chromacyclobutane species and chromium alkylidenes remain almost unknown[5] despite the remarkable devleopment of the chemistry of Fisher-type chromium(II) carbenes.[6,7] Since these species are

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currently used in quite a number of stoichiometric metal-promoted transformations,[8] we became interested in the preparation of low- and medium-valent chromium alkylidenes (Schrock-type). An electron-rich configuration of the chromium atom is in fact expected to offer a variety of reactivity patterns due to the ability of the low-valent metal to perform oxidative addition reactions, thus further extending the range of reactivity and catalytic performances. Since Cr(II) alkyls are the most obvious precursors for the preparation of Cr(II) carbenes and metallacycles, and since examples of divalent chromium organometallics remain relatively rare[9] (apart from the quadruply bonded systems), we have recently undertaken a systematic synthetic study to clarify the structure, synthesis, and stability features of these species.

Last, but not least, interest in the chemistry of divalent chromium alkyls is attracted by the behavior of the few existing dinuclear Cr(II) complexes of nonchelating alkyls. A literature survey suggested that monodentate alkyls might possess a unique ability to bridge dichromium species, thus favoring the occurrence of short or extremely short Cr–Cr contacts.[9h–j,10] In an attempt to understand this important characteristic, we have recently revisited the chemistry of $Me_8Cr_2[Li(THF)]_4$,[11] finding, despite the presence of a very short intermetallic contact, that no significant Cr–Cr bond exists in this species.[12] While the factors which are capable of enforcing the remarkably short Cr–Cr distance remain to be identified, the crystal structure of the monomeric $Me_4Cr[Li(TMEDA)]_2$[12] suggests the attractive possibility that Li···H(Me) agostic interactions might be capable of assembling dimeric structures and enforcing very short Cr–Cr contacts. Therefore, since the presence of α-hydrogen atoms seems to be a prerequisite for the occurrence of bonding interaction with the alkali-metal cation, we have selected for this preliminary study alkyls such as CH_2Ph, $CH_2(t\text{-}Bu)$, and $CH_2C(Ph)Me_2$. The most attractive characteristic of these alkyls, however, is provided by their well-known ability to undergo α-hydrogen abstraction to form alkylidene and/or metallacyclobutane species, as indicated by the chemistry of high-valent Mo and W congeners.

In this paper, we describe the synthesis, characterization, and stability properties of a novel series of Cr(II) alkyl complexes together with their transformation into unprecedented Cr(III) alkylidene derivatives and Cr(II) and Cr(III) metallacycles.

Experimental Section

All operations were performed under an inert atmosphere in a nitrogen-filled drybox (Vacuum Atmosphere) or by using standard Schlenk techniques. **(WARNING: all the complexes prepared in this work were extremely air-sensitive and pyrophoric. Appropriate precautions should be taken for their safe manipulation.)** $CrCl_2(THF)_2$,[13] $PhCH_2Li$,[14] and $PhCH_2Li(TMEDA)$[15] [TMEDA = *N,N,N′,N′*-tetramethylethylenediamine] were prepared following published procedures. $(CH_3)_3CCH_2Li$ and $Ph(CH_3)_2CCH_2Li$ were prepared from metallic lithium and the appropriate organic halide (Aldrich) in hexane by following standard procedures. $(CH_3)_8Cr_2[Li(THF)]_4$ (**1a**) was prepared with minor modification of a published procedure.[11] TMEDA was chromatographed over Al_2O_3 and distilled over molten potassium after refluxing; pyridine was refluxed over CaH_2 and distilled under nitrogen using a Vigreux column. Infrared spectra were recorded on a Perkin-Elmer 283 instrument from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were weighed inside a drybox equipped with an analytical balance and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated following standard methods[16] and corrections for underlying diamagnetism were applied to data.[17] Elemental analysis of C, H, and N was carried out with combustion techniques. The thermal instability of **1b**, **1c**, **1d**, and **3** prevented any analytical determination.

Preparation of $CrCl_2(TMEDA)$. A suspension of $CrCl_2(THF)$ (1.67 g, 6.2 mmol) in THF (100 mL) was treated with neat TMEDA (3 mL, 20.7 mmol). The initially light-green solid became bright light-blue during 1 h of stirring. The solid was isolated by filtration and stored in ampules under nitrogen without further purification (1.5 g, 6.2 mmol, 98%). IR [Nujol, KBr, cm^{-1}], ν: 1460 (s), 1385 (s), 1290 (m), 1250 (w), 1200 (w), 1170 (w), 1130 (w), 1050 (sh), 1030 (s), 1010 (m), 960 (s), 890 (m), 880 (m), 810 (s), 780 (m), 730 (br), 590 (w), 500 (br) [$\mu_{eff} = 4.80\ \mu_B$]. Anal. (Calcd) found for $C_6H_{16}N_2CrCl_2$: C (30.14), 29.77; H (6.75), 6.66; N (11.72), 11.28; Cr (21.75), 21.19.

Preparation of $(CH_3)_8Cr_2[Li(THF)]_4$ (1a). Solid $CrCl_2(THF)_2$ (4.4 g, 16.5 mmol) was added to a stirred solution of

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CH_3Li (47 mL, 1.4 M, 65.8 mmol) in Et_2O (200 mL) at −30 °C. The light-blue starting material slowly disappeared forming a deep-yellow solution. The insoluble residue was filtered out and the resulting solution concentrated to a small volume. Bright-yellow pyrophoric crystals of **1a** (3.1 g, 5.7 mmol, 69%) were obtained upon standing overnight at −30 °C. IR [Nujol, KBr, cm^{-1}], ν: 1340 (m), 1250 (w), 1220 (w), 1180 (m), 1045 (w), 1040 (vs), 920 (vs), 890 (vs), 670 (m), 610 (s), 420 (vs). ^1H NMR [C_6D_6, 200 MHz, 25 °C], δ: 3.95 (m, 2H, THF), 1.32 (m, 2H, THF), −0.35 (s, 3H, CH_3). Anal. (Calcd) found for $C_{24}H_{56}Cr_2Li_4O_4$: C (53.34), 52.99; H (10.44), 10.25; Cr (19.24), 19.07.

Preparation of $(CH_3)_8Cr_2[Li(pyridine)]_4$ (1a′). Neat pyridine (0.25 g, 3.2 mmol) was added to a bright-yellow solution of **1a** (0.43 g, 0.80 mmol) in toluene (80 mL) at room temperature. Pyrophoric, yellow microcrystals of **1a′** separated almost immediately (0.4 g, 0.70 mmol, 88%). IR [Nujol, KBr, cm^{-1}], ν: 2780 (sh), 1596 (m), 1460 (s), 1220 (w), 1150 (w), 1070 (m), 1036 (m), 1005 (m), 750 (s), 700 (s), 620 (m), 420 (sh). ^1H NMR [C_6D_6, 200 MHz, 25 °C], δ: 8.81 (m, 2H, Py), 6.80 (m, 1H, Py), 6.59 (m, 2H, Py), 0.01 (s, 6H, CH_3). Anal. (Calcd) found for $C_{28}H_{44}N_4Cr_2Li_4$: C (59.16), 58.98; H (7.80), 7.77; N (9.86), 9.57; Cr (18.29), 18.01.

Attempted Isolation of $[PhCH_2]_8Cr_2[Li(THF)]_4$ (1b). Solid $CrCl_2(THF)_2$ (1.6 g, 6.0 mmol) was added at −60 °C to a stirred solution of $PhCH_2Li$ in ether (24.1 mL, 1.0 M, 24.1 mmol). A deep-red-brown color started to develop immediately while the insoluble starting material disappeared. Stirring was continued for 1 h at −30 °C. The solution was filtered while cold, rapidly concentrated to a small volume and allowed to stand overnight at the same temperature. Pyrophoric deep-orange well-formed crystals separated upon cooling at −50 °C. The product rapidly decomposed at room temperature, forming a black paramagnetic oil, thus preventing further characterization.

Preparation of $[(CH_3)_3CCH_2]_8Cr_2[Li(Et_2O)]_4$ (1c). Solid $CrCl_2(THF)_2$ (1.6 g, 6.0 mmol) was added at −50 °C to a stirred solution of $(CH_3)_3CCH_2Li$ (1.84 g, 23.6 mmol) in Et_2O (50 mL). The color turned red upon mixing and stirring was continued for 1 h at low T. The orange microcrystalline **1c** which separated out during the stirring was collected on a filtration column cooled at −40 °C and then dried at room temperature (0.4 g, 0.39 mmol, 15%). Dry solid samples were stable at room temperature for a few hours. IR [Nujol, KBr, cm^{-1}], ν: 1360 (s), 1235 (m), 1205 (m), 1110 (w), 1085 (w), 1045 (s), 990 (w), 925 (w), 890 (s), 740 (m), 660 (w), 605 (w), 535 (w), 450 (sh) [$\mu_{eff} = 1.72\ \mu_B$].

Preparation of $[Ph(CH_3)_2CCH_2]_8Cr_2[Li(Et_2O)]_4$ (1d). Solid $CrCl_2(THF)_2$ (1.2 g, 4.5 mmol) was added to a solution of $Ph(CH_3)_2CCH_2Li$ (2.6 g, 18.6 mmol) in Et_2O (80 mL) cooled at −40 °C. Stirring was continued for 2 h at low temperature until the starting $CrCl_2(THF)_2$ disappeared completely from the reaction mixture. The initial green color of the suspension slowly turned red and finally deep-yellow. The gray insoluble material was eliminated by filtration, and the resulting solution was allowed to stand overnight at −30 °C, upon which yellow microcrystalline **1d** separated out (0.5 g, 1.4 mmol, 15%). The solid slowly decomposed at room temperature under nitrogen. IR [Nujol, KBr, cm^{-1}], ν: 3040 (sh), 1565 (m), 1420 (sh), 1360 (sh), 1265 (w), 1235 (w), 1220 (w), 1190 (w), 1170 (m), 1120 (w), 1090 (w), 1070 (w), 1045 (s), 920 (sh), 890 (s), 770 (s), 720 (s), 700 (w), 560 (w), 450 (sh) [$\mu_{eff} = 0.55\ \mu_B$].

Preparation of $(CH_3)_4Cr[Li(TMEDA)]_2$ (2). Method A. A light-yellow solution of **1a′** (0.8 g, 1.5 mmol) in Et_2O (200 mL) was treated with neat TMEDA (20 mL). The resulting orange solution was concentrated to a small volume, and a small amount of insoluble material was eliminated by filtration. Extremely air-sensitive orange-yellow crystals of **2** (0.6 g, 1.7 mmol, 57% yield) were obtained upon standing overnight at −30 °C. Satisfactory analytical results were obtained. IR [Nujol mull, cm^{-1}, KBr], ν: 1360 (s), 1295 (s), 1260 (m), 1180 (m), 1160 (s), 1135 (s), 1100 (m), 1070 (s), 1040 (s), 1020 (s), 950 (s), 840 (w), 790 (s), 770 (s), 720 (w), 615 (s), 590 (sh) [$\mu_{eff} = 4.98\ \mu_B$]. Anal. (Calcd) found for $C_{16}H_{44}N_4CrLi_2$: C (53.62), 53.44; H (12.37), 12.28; N (15.63), 15.44; Cr (14.51), 14.35.

Method B. A suspension of $CrCl_2(THF)_2$ (12.4 g, 46 mmol) in neat TMEDA (400 mL) was refluxed overnight, forming a blue insoluble solid. The resulting mixture was cooled to −50 °C, and a solution of MeLi in Et_2O (130 mL, 1.4 M) was added dropwise by syringe. The green solid initially formed disappeared upon stirring at room temperature, forming an orange suspension. The solid was isolated by filtration and recrystallized from neat TMEDA (80 °C), yielding bright-orange octahedral crystals (10 g, 28 mmol, 61% yield).

Preparation of $(PhCH_2)_6Cr_2][Li(TMEDA)]_2$ (3). A suspension of $CrCl_2(THF)_2$ (1.46 g, 5.5 mmol) in ether (200 mL) was cooled at −50 °C. Solid $PhCH_2Li(TMEDA)$ (4.61 g, 21.5 mmol) was added to the mixture, and the resulting suspension was vigorously stirred while slowly warming to room temperature. The diamagnetic, brick-red and poorly soluble **3** (1.3 g, 1.44 mmol, 53%) was collected on a filtration column and washed with two portions of toluene. IR [Nujol, KBr, cm^{-1}], ν: 3050 (m), 1580 (s), 1460 (s), 1370 (m), 1290 (m), 1240 (w), 1220 (m), 1180 (m), 1160 (w), 1130 (w), 1030 (w), 1010 (sh), 980 (w), 950 (m), 890 (m), 820 (w), 790 (s), 740 (s), 690 (s), 600 (w), 510 (w). ^1H NMR [C_6D_6, 200 MHz, 25 °C], δ: 7.10–6.70 (m, 15H, phenyl), 2.20 (s, 4H, CH_2 TMEDA), 2.05 (s, 12H, CH_3 TMEDA) 1.36 (s, 6H, benzyl).

Preparation of $[(CH_3)_3CCH_2]_2[CH_2C(CH_3)_2CH_2]Cr[Li(TMEDA)]_2$ (4). A suspension of $CrCl_2(THF)_2$ (1.7 g, 6.4 mmol) in hexane (80 mL) was stirred at −50 °C in the presence of $(CH_3)_3CCH_2Li$ (2.13 g, 27.3 mmol). The light-green solid slowly dissolved, forming a yellow solution which became red after 1 h. When all the starting material had disappeared, the addition of TMEDA (4 mL) to the cold solution turned the color deep-green. The temperature was allowed to rise to ambient values and the insolubles were eliminated by filtration. Deep-red crystals of **4** (0.29 g, 0.58 mmol, 9%) separated from the resulting solution after concentration to a small volume and upon standing overnight at −30 °C [$\mu_{eff} = 4.66\ \mu_B$]. Anal. (Calcd) found for $C_{27}H_{64}N_4CrLi_2$: C (63.50), 63.11; H (12.63), 12.38; N (10.97), 10.88; Cr (10.18), 9.91.

Preparation of $[o\text{-}C_6H_4(CH_3)_2CCH_2]_2Cr(TMEDA)][Li(TMEDA)_2]$ (5). An ether solution (100 mL) of $Ph(CH_3)_2CCH_2Li$ (2.72 g, 19.4 mmol) cooled at −50 °C was treated with $CrCl_2(THF)_2$ (1.32 g, 4.9 mmol). The mixture was stirred at low temperature until the starting $CrCl_2(THF)_2$ disappeared, forming a deep-green solution with a bright-yellow suspension. The addition of neat TMEDA (3 mL) to the cold mixture formed a green solid which, when isolated, melted into a green oil at room temperature. The red mother liquor, which became green at room temperature, was decanted, concentrated, and cooled to −30 °C. A small amount of gray solid (ca. 0.3 g) which separated upon standing overnight at −30 °C, was eliminated by filtration. The resulting dark-red solution was concentrated and allowed to stand 2 days at −30 °C, upon which deep-red crystals of **5** separated (1.4 g, 2.0 mmol, 41%). IR [Nujol, KBr, cm^{-1}], ν: 3030 (sh), 2780 (sh), 1560 (w), 1360 (sh), 1340 (sh), 1290 (s), 1270 (w), 1250 (m), 1230 (w), 1210 (w), 1190 (w), 1160 (m), 1130 (m), 1100 (w), 1090 (w), 1075 (m), 1035 (s), 1015 (s), 990 (w), 960 (sh), 950 (s), 935 (sh), 800 (s), 790 (sh), 770 (s), 730 (s), 600 (m), 570 (m), 510 (m), 490 (m), 465 (m) [$\mu_{eff} = 3.52\ \mu_B$]. Anal. (Calcd) found for $C_{38}H_{72}N_6CrLi$: C (67.92), 67.78; H (10.80), 10.66; N (12.51), 12.43; Cr (7.74), 7.17.

Preparation of $(TMEDA)Cr(CH_2Ph)Cl(\mu\text{-}Cl)[Li(TMEDA)]\cdot{}^1/_2[LiCl(TMEDA)]_2$ (6). A suspension of $CrCl_2(THF)_2$ (2.36 g, 8.8 mmol) in THF (100 mL) was cooled to −40 °C and treated with $PhCH_2Li(TMEDA)$ (2.01 g, 9.4 mmol). The stirring of the resulting slurry for 1 h at −40 °C formed a dark greenish-blue solution. The suspension was evaporated to dryness and the residual oil redissolved in Et_2O (120 mL). The solution was filtered, concentrated, and allowed to stand overnight at −30 °C upon which deep-blue crystals of **6** separated out (1.4 g, 2.3 mmol, 26%). IR [Nujol, KBr, cm^{-1}], ν: 3060 (sh), 1585 (s), 1295 (sh), 1285 (m), 1265 (w), 1250 (w), 1205 (s), 1180 (m), 1155 (w), 1125 (w), 1105 (w), 1065 (w), 1050 (w), 1020 (s), 1000 (m), 955 (sh), 940 (s), 880 (m), 840 (w), 800 (s), 790 (s), 785 (w), 740 (s), 695 (s), 595 (m), 500 (w), 430 (m) [$\mu_{eff} = 5.10\ \mu_B$]. Anal. (Calcd) found for

Table 1. Crystal Data and Structural Analysis Results

	4	5	6	7	9	10
formula	$C_{27}H_{64}Li_2CrN_4$	$C_{38}H_{72}CrLiN_6$	$C_{25}H_{55}Cl_3CrN_6Li_2$	$C_{20}H_{30}CrN_2$	$C_{26}H_{42}CrN_2$	$C_{20}H_{29}CrN_2$
fw	510.71	671.96	611.99	350.47	434.63	349.46
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic	orthorhombic
space group	$C2/c$	$P2_1/n$	$P\bar{1}$	$P2/n$	*Pbcn*	*Pbca*
a (Å)	14.743(3)	11.629(2)	11.976(5)	9.596(1)	15.808(8)	23.085(5)
b (Å)	14.090(4)	23.259(5)	17.251(5)	18.128(2)	9.562(4)	14.455(6)
c (Å)	16.919(4)	15.726(3)	8.828(3)	11.803(1)	16.036(5)	11.243(3)
α (deg)			92.43(3)			
β (deg)	106.58(1)	107.89(1)	101.79(3)	110.692(9)		
γ (deg)			84.05(3)			
V (Å^3)	3368(2)	4048(1)	1775(1)	1920.8(4)	2424(3)	3751(3)
Z	4	4	2	4	4	8
radiation (Mo Kα) (Å)	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69
T (°C)	−160	−160	−160	−157	−160	−158
D_{calcd} (g cm^{-3})	1.007	1.102	1.145	1.212	1.191	1.237
μ_{calcd} (cm^{-1})	3.48	3.05	5.63	5.82	4.73	5.96
R_F, R_w	0.061, 0.047	0.059, 0.069	0.066, 0.071	0.029, 0.041	0.041, 0.057	0.064, 0.072
GoF	3.20	1.79	3.62	1.81	2.34	6.29

$C_{25}H_{55}N_6CrLi_2Cl_3$: C (49.07), 48.81; H (9.06), 9.00; N (13.73), 13.65; Cr (8.50), 8.13.

Preparation of (TMEDA)Cr(CH$_2$Ph)$_2$ (7). A suspension of $CrCl_2(THF)_2$ (1.8 g, 6.7 mmol) in THF (100 mL) was stirred at −40 °C for 1 h with $PhCH_2Li(TMEDA)$ (2.7 g, 12.8 mmol). The resulting dark greenish-blue solution was evaporated to dryness and the residual oil redissolved in Et_2O (120 mL). The solution was filtered, concentrated, and allowed to stand overnight at −30 °C upon which deep-purple crystals of 7 separated out (0.7 g, 2.0 mmol, 30%). IR [Nujol, KBr, cm^{-1}], ν: 3060 (sh), 1585 (s), 1410 (w), 1350 (w), 1295 (m), 1285 (m), 1240 (w), 1210 (s), 1190 (w), 1180 (m), 1165 (m), 1120 (m), 1070 (m), 1050 (w), 1025 (s), 1000 (sh), 940 (s), 920 (sh), 870 (s), 795 (s), 770 (w), 740 (s), 700 (s), 620 (w), 600 (m), 570 (w), 540 (w), 520 (m), 485 (w), 470 (w), 450 (w), 400 (sh) [μ_{eff} = 4.68 μ_B]. Anal. (Calcd) found for $C_{20}H_{30}N_2Cr$: C (68.54), 68.35; H (8.63), 8.44; N (7.99), 7.71; Cr (14.84), 14.67.

Preparation of (TMEDA)Cr[CH$_2$C(CH$_3$)$_3$]$_2$ (8). A suspension of $CrCl_2(THF)_2$ (1.96 g, 7.3 mmol) in THF (100 mL) was stirred for 1 h at room temperature in the presence of TMEDA (2 mL). After cooling to −30 °C, the addition of $(CH_3)_3CCH_2Li$ (1.07 g, 13.7 mmol) to the resulting bright-blue suspension turned the color red. After stirring for another hour at room temperature, the solvent was removed in vacuo and the residual oil redissolved in hexane (140 mL). The solution was filtered, concentrated, and allowed to stand overnight at −50 °C upon which deep-red crystals of 8 separated out (1.4 g, 4.5 mmol, 62%). IR [Nujol, KBr, cm^{-1}], ν: 2760 (sh), 1405 (w), 1345 (s), 1280 (s), 1260 (w), 1245 (w), 1225 (s), 1200 (s), 1160 (w), 1120 (m), 1095 (m), 1090 (sh), 1060 (s), 1040 (w), 1025 (s), 1010 (s), 995 (sh), 955 (s), 900 (w), 795 (vs), 770 (m), 740 (m), 620 (sh), 595 (m), 530 (m), 480 (w), 440 (m), 380 (sh) [μ_{eff} = 4.99 μ_B]. Anal. (Calcd) found: C (62.71), 62.61; H (11.18), 11.00; N (9.14), 9.01; Cr (16.97), 16.71.

Preparation of (TMEDA)Cr[CH$_2$C(CH$_3$)$_2$Ph]$_2$ (9). A suspension of $CrCl_2(THF)_2$ (2.6 g, 9.7 mmol) in toluene (100 mL) was stirred in the presence of TMEDA (2 mL). After stirring 1 h at room temperature, the resulting bright-blue suspension was cooled to −30 °C. After addition of $Ph(CH_3)_2CCH_2Li$ (2.76 g, 19.7 mmol), the resulting red mixture was allowed to warm to room temperature. The suspension was filtered, concentrated and cooled to −30 °C, upon which deep-red crystals of 9 (1.1 g, 2.5 mmol, 26%) separated out. IR [Nujol, KBr, cm^{-1}], ν: 3060 (sh), 3040 (sh), 1595 (m), 1575 (w), 1490 (sh), 1410 (w), 1365 (sh), 1350 (m), 1280 (s), 1240 (w), 1170 (w), 1160 (w), 1120 (w), 1110 (m), 1080 (w), 1055 (w), 1020 (s), 1005 (s), 950 (s), 905 (w), 795 (s), 765 (s), 730 (w), 700 (s), 610 (w), 590 (m), 490 (w), 430 (w) [μ_{eff} = 4.97 μ_B]. Anal. (Calcd) found for $C_{26}H_{42}N_2Cr$: C (71.85), 71.66; H (9.74), 9.51; N (6.45), 6.29; Cr (11.96), 11.71.

Preparation of (TMEDA)Cr(=CHPh)(CH$_2$Ph) (10). A suspension of $CrCl_2(THF)_2$ (5.5 g, 20 mmol) in THF (100 mL) was treated at −40 °C with $PhCH_2Li(TMEDA)$ (12.8 g, 60.0 mmol). After stirring 1 h at −40 °C, the resulting slurry formed a dark greenish-blue solution. The suspension was evaporated to dryness and the residual oil redissolved in Et_2O (150 mL). The solution was filtered, concentrated, and allowed to stand overnight at −30 °C upon which orange crystals of 10 separated out (4.2 g, 12.0 mmol, 60%). IR [Nujol, KBr, cm^{-1}], ν: 3060 (w), 1590 (s), 1470 (sh), 1405 (w), 1360 (sh), 1300 (w), 1285 (m), 1210 (s), 1180 (w), 1125 (w), 1020 (m), 1000 (w), 950 (s), 880 (m), 795 (s), 770 (w), 740 (s), 695 (s), 595 (w), 570 (w), 550 (w), 525 (w), 450 (w) [μ_{eff} = 3.96 μ_B]. Anal. (Calcd) found for $C_{20}H_{29}N_2Cr$: C (68.74), 68.59; H (8.36), 8.18; N (8.02), 7.88; Cr (14.88), 14.69.

Cyclic Voltammetry. Cyclic voltammograms were recorded in THF solutions using tetrabutylammonium tetrafluoborate ($TBABF_4$) (Aldrich) as a supporting electrolyte. All the solutions and the electrochemical cell were prepared in a drybox. The experiments were performed under nitrogen in an airtight cell equipped with a 0.5-mm-diameter Pt wire as a working electrode. A silver wire in contact with a THF solution of $TBABF_4$ (0.2 M) and saturated with AgCl was used as a reference electrode. The contact with the cell was realized through a porous Vycor frit. THF solutions were 0.01 M of each complex and 0.2 M of $TBABF_4$. Potentials were referenced to the ferrocenium/ferrocene potential obtained under identical conditions. A PAR 273 potentiostat/signal generator in combination with Headstart software was employed for the measurements.

X-ray Crystallography. Air-sensitive crystals were selected in a drybox equipped with a stereomicroscope and glued on a glass fiber with a small amount of silicone grease. Data were collected at temperatures in the range −157 to −160 °C using the ω–2θ scan technique to a maximum 2θ value of 50.0°. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 carefully centered high-angle reflections. Redundant reflections were removed from the data set. The intensities of three representative reflections were measured after every 150 reflections to monitor crystal and instrument stability. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps and refined isotropically in the case of a favorable observation:parameter ratio. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with $I > 2.5\sigma(I)$. Neutral atomic scattering factors were taken from Cromer and Waber.[18] Anomalous dispersion effects were included in F_c. All calculations were performed using the TEXSAN package on a Digital VAX station. Details on data collection and structure refinement are reported in Table 1. The final atomic coordinates are given as supplementary material. Selected bond distances and angles are given in Table 2.

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(18) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table 2. Selected Bond Distances (Å) and Angles (deg)

4	5	6	7	9	10
Cr1–C1 = 2.267(6) Å	Cr1–N1 = 2.335(4)	Cr1–N1 = 2.209(6)	Cr1–N1 = 2.227(2)	Cr1–N1 = 2.249(3)	Cr1–C6 = 2.170(7)
Cr1–C6 = 2.198(7)	Cr1–N2 = 2.328(4)	Cr1–N2 = 2.184(6)	Cr1–N2 = 2.225(2)	Cr1–C1 = 2.146(3)	Cr1–C13 = 2.169(7)
Cr1···Li1 = 2.70(1)	Cr1–C1 = 2.083(5)	Cr1–C1 = 2.141(7)	Cr1–C8 = 2.177(2)	N1–Cr1–C1 = 92.8(1)	C6–H26 = 1.14
Li1–N1 = 2.15(1)	Cr1–C23 = 2.172(5)	C41–Cl1 = 2.425(2)	C1–C2 = 1.477(3)	N1–Cr1–C1a = 158.0(1)	C13–H26 = 2.10
Li1–C1 = 2.29(1)	Cr1–C7 = 2.162(5)	Cl1–Li1 = 2.34(1)	C8–C9 = 1.474(3)	N1–Cr1–N1a = 79.6(1)	Cr1–N1 = 2.228(5)
Li1–C6 = 2.12(1)	Cr1–C8 = 2.093(5)	Cr1···Cl2 = 2.671(2)	N1–Cr1–N2 = 80.15(6)	Cr1–C1–C2 = 118.2(2)	Cr1–N2 = 2.209(5)
Li1–H32 = 1.93	C8–Cr1–N2 = 165.4(2)	Cl2–Li1 = 2.34(1)	N1–Cr1–C1 = 95.58(7)		Cr1–C6–C7 = 115.5(4)
Li1–H33 = 2.24	C1–Cr1–C23 = 80.0(2)	Li1–N3 = 2.07(1)	C1–Cr1–C8 = 165.10(8)		Cr1–C13–C14 = 120.9(5)
Li1–H34 = 2.39	C1–Cr1–N1 = 166.0(2)	Li1–N4 = 2.06(1)	N2–Cr1–C8 = 91.02(7)		N1–Cr1–N2 = 79.9(2)
Cr1–C6–C7 = 91.6(4)	C7–Cr1–C23 = 175.4(2)	C1–Cr1–Cl2 = 97.6(2)	N1–Cr1–C8 = 165.10(8)		N1–Cr1–C6 = 94.0(2)
Cr1–C6–Li1 = 77.4(4)	C7–Cr1–C8 = 79.8(2)	N1–Cr1–N2 = 81.8(2)	Cr1–C8–C9 = 111.9(1)		N1–Cr1–C13 = 174.6(2)
C6–C7–C6a = 108.2(7)	N1–Cr1–N2 = 79.3(1)	C1–Cr1–N2 = 95.8(2)	Cr1–C8–C9 = 111.9(1)		N1–Cr1–C13 = 174.6(2)
Cr1–C1–Li1 = 72.5(3)	Cr1–C7–C14 = 113.0(3)	C1–Cr1–Cl1 = 92.1(2)			N2–Cr1–C6 = 173.9(2)
C1–Cr1–C6 = 164.2(3)	Cr1–C23–C24 = 112.6(3)	C1–Cr1–N1 = 170.9(3)			N2–Cr1–C13 = 94.7(2)
C11–Li1–C6 = 102.3(5)	C1–C6–C24–C23 = 17.2(6)	Cl1–Cr1–N2 = 165.1(2)			
Li1–Cr1–Li1a = 167.9(5)		Cr1–C1–C2 = 116.5(4)			
Cr1–C1–C2 = 113.9(4)		Cr1–Cl1–Li1 = 85.3(3)			
C6–Cr1–C6a = 68.5(4)		Cl1–Cr1–Cl2 = 91.40(7)			
C1–Cr1–C1a = 92.1(3)		N1–Cr1–Cl2 = 91.4(2)			
N1–Li1–N2 = 84.5(4)		Cl2–Cr1–N2 = 100.0(2)			
N1–Li1–C1 = 113.2(5)					
Cr1–C6–C7–C6 = 0.0					
Cr1–C1–Li1–C6 = 20.4(4)					

Results and Discussion

As illustrated in Schemes 1 and 2, the result of the reaction of $CrCl_2(THF)_2$ with RLi [R = CH_2Ph, Me, $CH_2C(CH_3)_3$, $CH_2C(CH_3)_2Ph$] was determined by both the RLi/Cr stoichiometric ratio and the presence in the reaction mixture of a chelating Lewis base (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine). In the cases where a molar ratio of 4 was employed (Scheme 1), the reactions led to the initial formation of bright-yellow-orange, poorly-soluble and almost diamagnetic materials. Unfortunately, in contrast to $Me_8Cr_2Li_4(THF)_4$ (**1a**), which is thermally stable, the benzyl (**1b**), neopentyl (**1c**), and neophyl (**1d**) analogues are very labile, thus preventing analytical determinations. In all cases, the complexes had to be isolated from reaction mixtures kept at temperatures below −40 °C to avoid a rapid decomposition with formation of deeply-colored intractable solutions. A similar behavior was also observed in the solid state where crystalline samples of **1b** and **1d** decomposed within a few hours at temperatures about −20 °C. Although the formulation is not proven, we speculate that these complexes are isostructural with $Me_8Cr_2Li_4(THF)_4$, since they showed the same residual paramagnetism which has been determined in the dimeric $Me_8Cr_2Li_4(THF)_4$, and in general for the quadruply bonded systems.

The behavior of the diamagnetic and dimeric $R_8Cr_2Li_4(THF)_4$ (**1**) with respect to the coordination of Lewis bases is somewhat surprising. In the case of the methyl derivative **1a**, displacement of THF from the coordination sphere of lithium takes place with a monodentate ligand such as pyridine, without significant modification of the molecular structure and of the magnetic properties of the product. Only a slow decomposition was observed upon heating **1a** in the presence of a large excess of pyridine. In contrast, treatment with a chelating diamine such as TMEDA, gave a reversible reaction where the dinuclear frame was cleaved to form the monomeric and paramagnetic $Me_4CrLi_2(TMEDA)_2$ (**2**). The isolation and crystal structure determination of this complex have been described previously.[12]

Similar attempts to cleave the dinuclear structures of **1b**, **1c**, and **1d** via reaction with TMEDA gave an unpredictable trend of reactions. The addition of TMEDA to **1b** or reaction of $CrCl_2(THF)_2$ with 4 equiv of $PhCH_2Li(TMEDA)$ complex gave the moderately stable $(PhCH_2)_6Cr_2Li_2(TMEDA)_2$ (**3**) as a diamagnetic reddish-brown crystalline solid. The dimeric structure is indicated by the diamagnetism observed in both solid state and solution, while the formulation is suggested by the integration of the NMR resonances. This type of dinuclear structure is also suggested by the analogy with the chemistry of dinuclear Cr(II) aryloxo lithium chromates.[19]

In the case of the $(CH_3CCH_2)_8Cr_2Li_4(THF)_4$ derivative, the reaction proceeded in a similar manner when either the preformed complex was resuspended in THF containing TMEDA or neat TMEDA was added to the crude reaction mixture from the preparation of **1c** maintained at −50 °C. After the addition of TMEDA, the reaction was allowed to reach room temperature. Subsequent cooling gave a poor yield of deep-orange crystals of the metallacycle derivative $[(CH_3)_3CCH_2]_2[CH_2C(CH_3)_2CH_2]Cr[Li(TMEDA)]_2$ (**4**).

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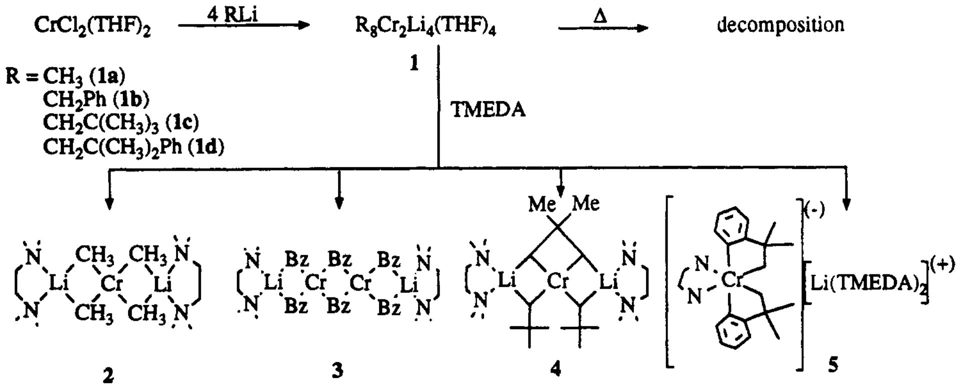
(19) Edema, J. J. H.; Meetsma, A.; Gambarotta, S.; Khan, S. I.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1991**, *30*, 3639.

Scheme 1



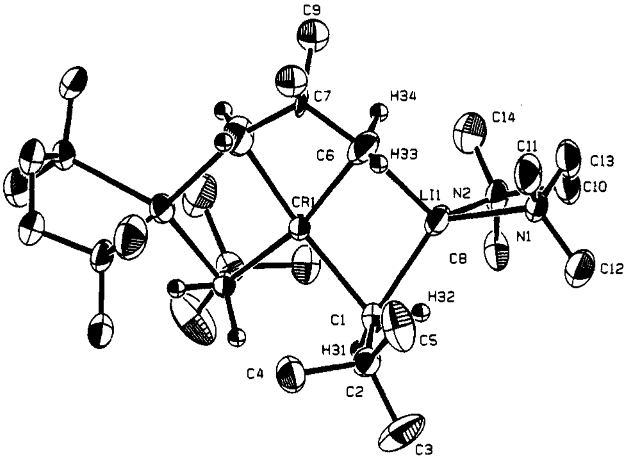


Figure 1. ORTEP plot of 4. Thermal ellipsoids are drawn at the 50% probability level.

The complex is monomeric and consists of one chromium atom bound to two neopentyl groups and to the two terminal carbon atoms of a $CH_2C(CH_3)_2CH_2$ unit, forming a chromacyclobutane ring (Figure 1). Two Li(TMEDA) moieties are connected to the central organochromium core by the bridging carbon atoms of the neopentyl and cyclobutane ring. The backbone of the molecule is formed by an almost linear Li–Cr–Li array [Li1–Cr1–Li1a = 167.9(5)°] with the chromium atom placed in the center of a distorted square plane defined by four bridging carbon atoms. Of these four bridging carbon atoms, two are provided by two bridging neopentyl groups placed in *cis* position with respect to the square-planar chromium and with the bulky *t*-Bu moieties pointing in opposite directions with respect to the molecular plane [Cr1–C1–C2 = 113.9(4)°]. The remaining two bridging carbon atoms are provided by one metallacyclobutane moiety. The plane defined by the four bridging carbon atoms [Cr1–C1 = 2.267(6) Å, Cr1–C6 = 2.198(7) Å], the two lithiums [Li1–C1 = 2.29(1) Å, Li1–C6 = 2.12(1) Å], and chromium is rather twisted. In contrast to the crystallographically imposed planarity of the central metallacyclobutane core [Cr1–C6–C7–C6 = 0.0°, Cr1–C6–C7 = 91.6(4)°, C6–C7–C6 = 108.2(7)°], the two $LiCrC_2$ cores are significantly folded [Cr1–C1–Li1–C6 = 20.4(4)°, Cr1–C6–Li1 = 77.4(4)°, C6–Li1–C1 = 102.3(5)°, Cr1–C1–Li1 = 72.5(3)°], forming a rather short Cr–Li nonbonding Distance [Cr1–Li1 = 2.70(1) Å]. The coordination geometry of the chromium atom is distorted square-planar [C1–Cr1–C6 = 164.2(3)°, C1–Cr1–C1a = 92.1(3)°, C6–Cr1–C6a = 68.5(4)°], while that of the two alkali cations is distorted tetrahedral [N1–Li1–N2 = 84.5(4)°, N1–Li1–C1 = 113.2(5)°]. Similar to the case of the monomeric $Me_4CrLi[(TMEDA)]_2$, short contacts have been found between one of the two α-hydrogens of the neopentyl group (the position of which was isotropically refined) and the alkali-metal cation [Li1–H32 = 1.93 Å]. This contact is also significantly shorter than the Li–C distance of the corresponding carbon atom [Li1–C1 = 2.29(1) Å]. This suggests that a fairly strong Li–H agostic interaction may be the factor which holds together the heterodimetallic frame and which also folds the $CrLiC_2$ core. Conversely, the hydrogen atoms of the two bridging carbons of the metallacyclobutane moiety are almost equidistant from the lithium atom [Li1–H33 = 2.24 Å, Li1–H34 = 2.39 Å], while the distance from the corresponding carbon atom [Li1–C6 = 2.12(1) Å] appears to be the shortest contact. The methyl group of the metallacyclobutane group displayed large thermal parameters, possibly indicating some disorder. The disorder has been modeled by assigning an occupancy of 33% of the carbon atom over three positions (C9, C15, C16), as revealed by the difference Fourier maps. The significant improvement of the residual values supports the accuracy of the model.

In the initial step, the reaction probably formed anionic metallates analogous to the cases of 2 or 3, which produce the metallacyclobutane via γ-hydrogen abstraction and consequent elimination of neopentane. The divalent oxidation state of the chromium atom of complex 4 is indicated by both the solid state crystal structure and confirmed by the magnetic moment, which is as expected for a Cr(II) d^4 high-spin electronic configuration. This species is a rare example of metallacyclobutane species and a very unique case in the chemistry of Cr(II).

In the case of the neophyl derivative $[(CH_3)_2PhCCH_2]_8Cr_2Li_4(THF)_4$ (**1d**), the reaction with TMEDA led to the formation of anionic Cr(III) species $[o\text{-}C_6H_4C(CH_3)_2CH_2]_2Cr(TMEDA)][Li(TMEDA)_2]$ (**5**) where the two aromatic rings of both neophyl groups have been metalated in the *ortho* position. The octahedral coordination geometry, characteristic of Cr(III), is completed by one molecule of TMEDA. A lithium cation coordinated to two molecules of TMEDA was found in the crystal structure in a stoichiometric ratio of 1:1 with chromium, thus indicating a formal oxidation state of +III for the metal. The oxidation state of the transition metal has been further confirmed by the measurement of the magnetic moment, which is consistent with a Cr(III) d^3 high-spin electronic configuration. Although it is unclear how the oxidation of the metal center occurs in this case, a disproportionation reaction is the most likely possibility. This is also suggested

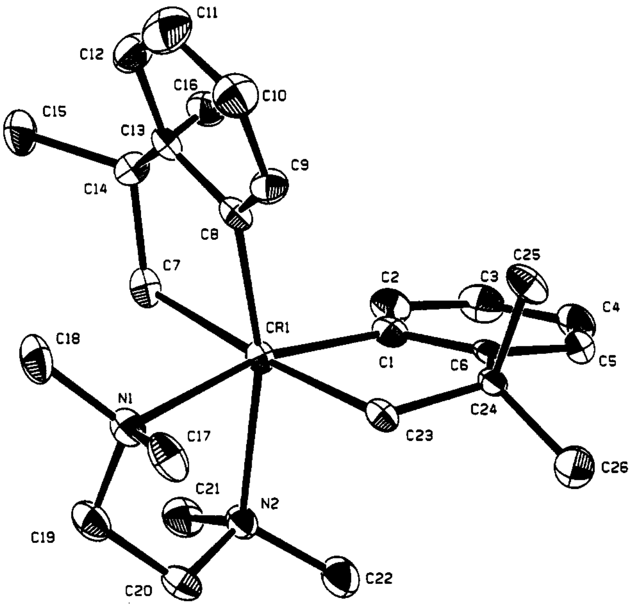


Figure 2. ORTEP plot of **5** (anionic moiety). Thermal ellipsoids are drawn at the 50% probability level.

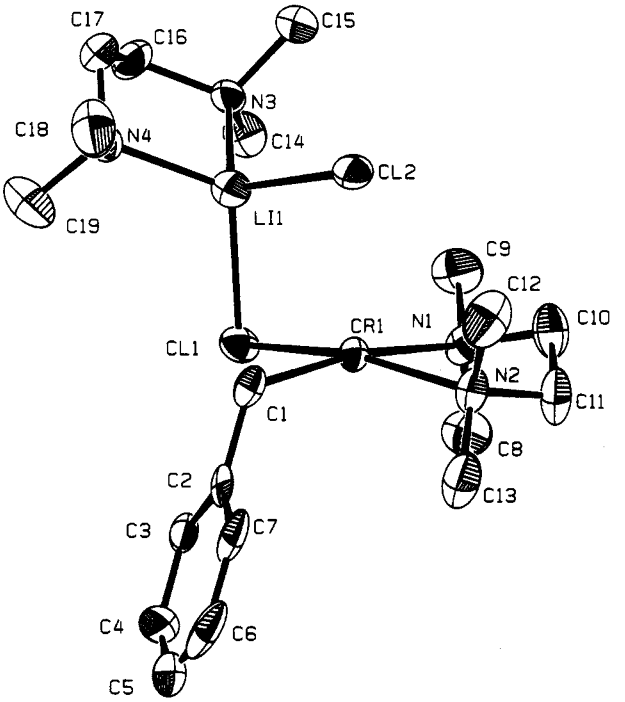


Figure 3. ORTEP plot of **6** (first molecule). Thermal ellipsoids are drawn at the 50% probability level.

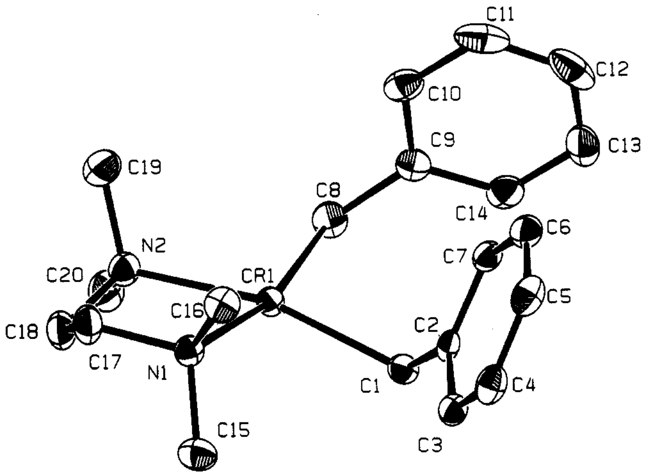
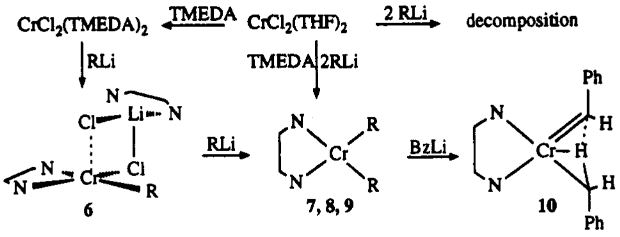


Figure 4. ORTEP plot of **7**. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 2



by the rather poor yield, which indicates the likelihood of more products being present in the reaction mixture.

The structure of **5** consists of two separate ionic fragments. The anion (Figure 2) is composed of a slightly distorted octahedral Cr(III) atom with the coordination octahedron defined by the two nitrogen atoms of one chelated TMEDA molecule (Cr1–N1 = 2.335(4) Å, Cr1–N2 = 2.328(4) Å] and four carbon atoms of two neophyl groups [C1–Cr1–N1 = 166.0(2)°, C7–Cr1–C23 = 175.4(2)°, C8–Cr1–N2 = 165.4(2)°]. Each neophyl group is bound to chromium through the methylene carbon atom and one *ortho* carbon atom of each phenyl group [Cr1–C1 = 2.083(5) Å, Cr1–C23 = 2.172(5) Å]. Each neophyl group works as a chelating ligand, forming slightly twisted five-membered rings with the central metal atom [C1–C6–C24–C23 = 17.2(6)°]. The metallocycles are coplanar with the corresponding phenyl ring of the neophyl group. The two methyl groups borne by the two neophyl β-carbon atoms point in opposite directions with respect to the metallocycle plane. The methylene carbon atoms are in *trans* positions with respect to each other, while the two aromatic carbons occupy the *cis* positions, probably to minimize steric repulsions. The cationic fragment is formed by one tetrahedral lithium cation surrounded by two chelating TMEDA molecules (see supplementary material). No significant intermolecular contacts have been found between the two ionic units.

The utilization of a RLi:Cr stoichiometric ratio of 2:1 in the reaction of $CrCl_2(THF)_2$ with RLi [R = $PhCH_2$, $(CH_3)_3CCH_2$, $Ph(CH_3)_2CCH_2$] gave a substantially different reactivity pattern (Scheme 2). While only decomposition was obtained from the reaction carried out at −60 °C in the absence of TMEDA, clean and reproducible reactions were obtained when reaction with RLi [R = $CH_2C(CH_3)_3$, $CH_2C(CH_3)_2Ph$, CH_2Ph] was carried out on the preformed $(TMEDA)CrCl_2$ complex. The reaction led to the initial formation of an intense deep-green color. With the exception of **8**, the color did not change upon reaching room temperature and crystals of $(TMEDA)CrR_2$ [R = $PhCH_2$ (**7**), $(CH_3)_3CCH_2$ (**8**), $(CH_3)_2PhCCH_2$ (**9**)] were isolated at −30 °C from the corresponding toluene solutions. All these complexes have magnetic moments in common, as expected for a high-spin Cr(II) d^4 electronic configuration.

The structures of **7** and **9** have been demonstrated by X-ray analysis. In complex **7** the tetrahedrally-distorted square-planar coordination geometry of chromium [N1–Cr1–N2 = 80.15(6)°, N1–Cr1–C1 = 95.58(7)°, C1–Cr1–C8 = 165.10(8)°, N2–Cr1–C8 = 91.02(7)°, N1–Cr1–C8 = 165.10(8)°] (Figure 4) is defined by two nitrogen atoms of one chelated TMEDA molecule [Cr1–N1 = 2.227(2) Å, Cr1–N2 = 2.225(2) Å] and by two methylene groups of each benzyl group [Cr1–C1 = 2.185(2) Å, Cr1–C8 = 2.177-

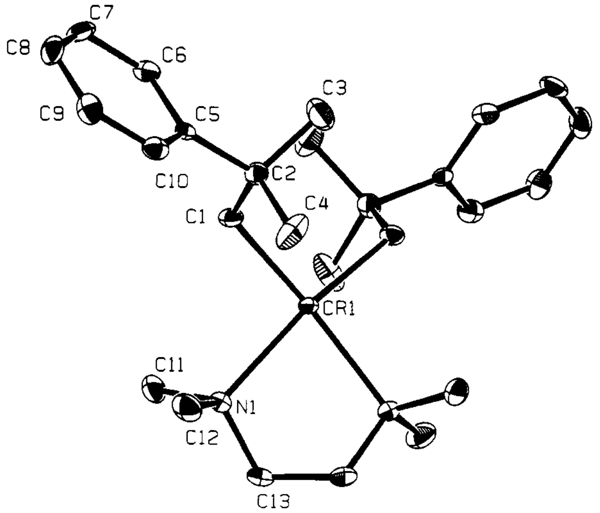


Figure 5. ORTEP plot of **9**. Thermal ellipsoids are drawn at the 50% probability level.

(2) Å]. The angles subtended at the methylene carbon atom are rather different in the two groups [Cr1–C8–C9 = 111.9(1)°, Cr1–C1–C2 = 120.5(1)°] and are a probable result of steric interactions and crystal packing. Complex **9** is basically isostructural with complex **7** (Figure 5). Two nitrogen atoms of one chelated TMEDA molecule [Cr1–N1 = 2.249(3) Å] and two methylene carbons of two neophyl groups define the tetrahedrally-distorted square-planar coordination geometry of the chromium atom [N1–Cr1–C1 = 92.8(1)°, N1–Cr1–C1a = 158.0(1)°, N1–Cr1–N1a = 79.6(1)°]. The two bulky moieties of the two neophyl groups are oriented in the two opposite directions with respect to the Cr1–N1–N1a plane. The Cr–C distance [Cr1–C1 = 2.146(3) Å] is only slightly shorter than that in the dibenzyl analogue **7**. The angle subtended at the methylene carbon atom [Cr1–C1–C2 = 118.2(2)°] is rather wide, likely as a result of the steric interaction of the two bulky $Ph(CH_3)_2C$ groups.

In the case of the benzyl derivative it was possible to isolate deep-blue crystals from the initial deep-green solution simply by using a stoichiometric ratio $PhCH_2Li$:Cr of 1:1, thus clarifying the structure of the intermediate (TMEDA)CrBzCl(μ-Cl)(LiTMEDA) (**6**) adduct. Attempts to isolate analytically pure complexes in the cases of the neopentyl and neophyl derivatives were unsuccessful, since the reactions gave mixtures of final product, unreacted starting material, and dialkyl species.

The structure of complex **6** consists of one square-planar (TMEDA)Cr(CH_2Ph)Cl moiety where the chlorine atom bridges the chromium and the lithium atom of a tetrahedral (TMEDA)LiCl unit (Figure 3). A molecule of [TMEDA)-Li(μ-Cl)]$_2$ was also found cocrystallized in the unit cell in the stoichiometric ratio 2:1 with the chromium unit. The square plane centered on the chromium atom [N1—Cr1—N2 = 81.8(2)°, C1—Cr1—N2 = 95.8(2)°, C1—Cr1—Cl1 = 92.1(2)°, C1—Cr1—N1 = 170.9(3)°, Cl1—Cr1—N2 = 165.1(2)°] is defined by the two nitrogen atoms of one chelating TMEDA molecule [Cr1—N1 = 2.209(6) Å, Cr1—N2 = 2.184(6) Å], the methylene carbon atom of the benzyl group [Cr1—C1 = 2.141(7) Å, Cr1—C1—C2 = 116.5(4)°], and the bridging chlorine atom [Cr1—Cl1 = 2.425(2) Å, Cl1—Li1 = 2.34(1) Å, Cr1—Cl1—Li1 = 85.3(3)°]. The chromium atom is only slightly elevated above the basal plane [distance from the plane 0.21(3) Å]. The second chlorine atom borne by lithium is positioned on the apex of an ideal square pyramid based on the chromium atom [C1—Cr1—Cl2 = 97.6(2)°, Cl1—Cr1—Cl2 = 91.40(7)°, N1—Cr1—Cl1 = 91.4(2)°, Cl2—Cr1—N2 = 100.0(2)°], forming a fairly short Cr—Cl nonbonding distance [Cr1···Cl2 = 2.671(2) Å]. No intermetallic contacts were observed with [TMEDA)Li(μ-Cl)]$_2$. Details on the geometry of this second fragment are available as supplementary material.

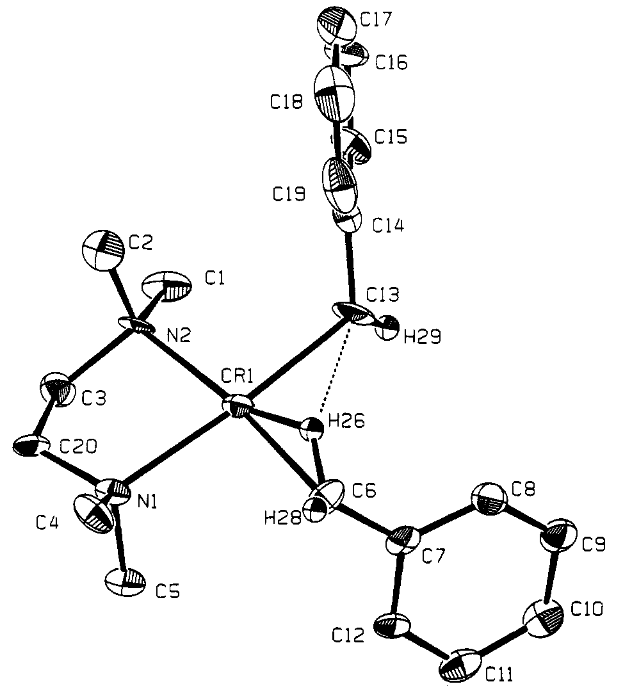


Figure 6. ORTEP plot of **10**. Thermal ellipsoids are drawn at the 50% probability level.

Variable amounts of bright-orange crystals were found in the deep-red crystalline mass of **7**. This orange complex (**10**) turned out to be the only stable product when the ligand replacement reaction was carried out on $CrCl_2$-(TMEDA) by using a stoichiometric ratio $PhCH_2Li$:Cr of 3:1. In one case, the crystals were of sufficient quality to undertake an X-ray crystal structure determination in spite of an unfavorable flat shape. The chemical connectivity is remarkably similar to that of **7** (Figure 6). Apart from the different orientations of the two phenyl rings and the geometry of the chromium atom (square-planar rather than flattened tetrahedral), the bond distances and angles are very comparable in the two complexes. Different from **7**, however, the coordination geometry of chromium, as defined by the two nitrogens of the chelating TMEDA and the two carbon atoms of the benzylidene and benzyl units, is square-planar [C6–Cr1–N2 = 173.9(2)°, N1–Cr1–C13 = 174.6(3)°, N1–Cr1–C6 = 94.0(2)°]. The benzylidene and benzyl groups form identical Cr–C distances [Cr1–C6 = 2.170(7) Å, Cr1–C13 = 2.169(7) Å] which also compare well with those of complex **7**. The orientation of the two phenyl rings marks the most significant difference between the two complexes (on the same side of the molecule instead of transoid with respect to the molecular plane, as might be expected). Different from complex **7**, the angles subtended at the methylene carbon atoms are similar [Cr1–C6–C7 = 115.7(4)°, Cr1–C13–C14 = 120.9(5)°]. This is likely the result of the position of one hydrogen atom of the benzyl group, which was located and refined in a position intermediate between chromium and the corresponding carbon atom [Cr1–H26 = 1.31 Å, C6–H26 = 1.14 Å], and not far from the carbon atom of the benzylidene group [C13–H26 = 2.10 Å].

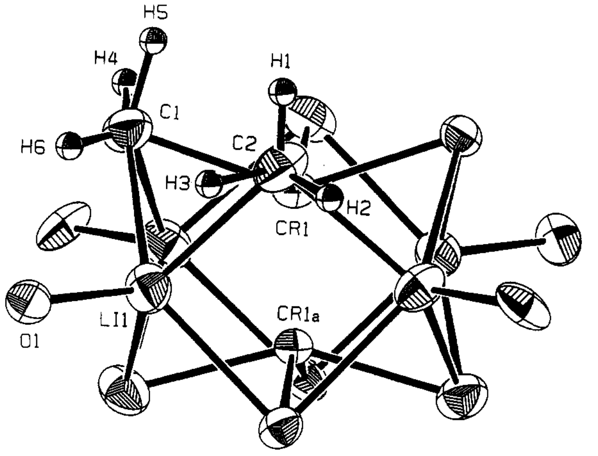


Figure 7. ORTEP plot of **1a**. Thermal ellipsoids are drawn at the 50% probability level. Carbon atoms of the THF molecules as well as the symmetry-generated methyl hydrogens have been omitted for clarity. For additional information see the supplementary material. Selected bond distances (Å) and angles (deg): Cr1′–Cr1a = 1.968(2), Cr1–C1 = 2.22(1), Cr1–C2 = 2.15(2), C1–Li1 = 2.41(2), C2–Li1 = 2.40(2), Li1–O1 = 1.967(7), C1–Cr1–C2 = 83.0(6), Li1–C1–Cr1 = 67.4(4), Li1···H4 = 2.03, Li···H6 = 2.05, Li1–H2–C2 = 85.1.

The steric hindrance of **7** and **10** does not appear a sufficient reason alone to justify a rotameric phenomenon, since the two complexes crystallize in different crystal systems (monoclinic and orthorhombic) with remarkably different colors, magnetic properties, and coordination geometries of the metal atom. The possibility that either **7** or **10** might be a terminal hydrido species (TMEDA)-$Cr(H)(CH_2Ph)_2$ cannot be excluded by the absence of hydrogen observed during chemical degradation experiments carried out with 2 equiv of dry HCl in a closed vessel connected to a Toepler pump. The cyclic voltammograms of the two compounds, obtained under identical conditions, show two completely different patterns. Complex **10** displays a reversible one-electron reduction wave at −2.37 V ($E_{pa} - E_{pc}$ = 63 mV) and an additional irreversible reduction at −3.50 V (200 mV/s, V vs ferrocenium/ferrocene) (Figure 8). Unfortunately, comparison with data available for other Cr(III) complexes[20] is not appropriate due to the diversity of the substrates. Nevertheless, the $E_{2nd\ red} - E_{1st\ red}$ = 1.13 V is in good agreement with that determined in the case of some (monocyclopentadienyl)Cr(III) complexes,[20a] thus giving some indication that **10** might be a Cr(III) species. The voltammogram also shows two irreversible features at +0.42 and +0.97 V. Conversely, the cyclic voltammogram of complex **7** only shows an electrochemically irreversible reduction at −1.90 with a return peak wave at −1.20 V. Although these data are not conclusive for the assignment of the metal oxidation state, they clearly indicate that complexes **7** and **10** *are chemically different species* in spite of the remarkably similar ligand environments.

A further indication of the different natures of the two complexes is offered by EPR spectroscopy. While the intensely blue-green toluene solutions of the two complexes are EPR silent, probably due to signal saturation, the solid state spectra are totally different. Complex **7** shows the same intense and nonresolved band commonly observed for Cr(II) complexes, while **10** displays a complicated spectrum reminiscent of those observed for the Cr(III) Cp′CrMeCl derivatives.[21]

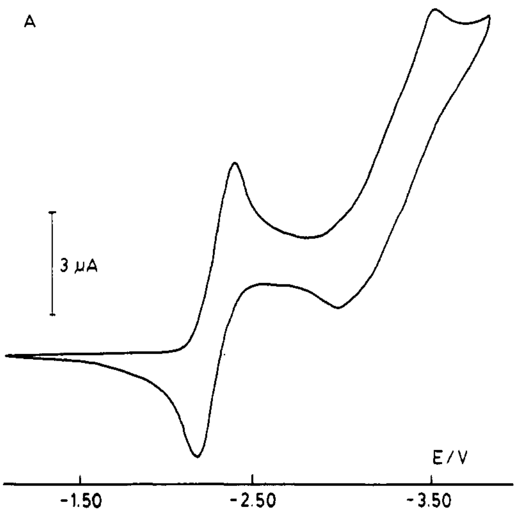
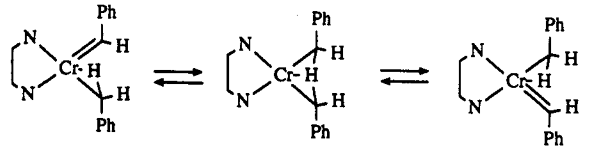


Figure 8. Cyclic voltammogram of **10** in THF at room temperature (supporting electrolyte Bu_4NBF_4 0.2 M, scan rate 200 mV/s, potential relative to Cp_2Fe).

Scheme 3



The values of the magnetic moments of **7** and **10** [μ_{eff} = 4.68 μ_B and μ_{eff} = 3.96 μB respectively] are consistent with d^4 and d^3 electronic configurations and support the proposed assignment of the oxidation states. Since chemical degradation experiments do not provide evidence that complex **10** might be a terminal hydride, we tentatively propose a Cr(III) carbene formulation (TMEDA)Cr(=CHPh)(CH_2Ph).

The similarity of the Cr–C distances formed by the benzyl and benzylidene groups in complex **10** suggests that the two groups might interconvert via simple hydrogen transfer (Scheme 3). Unfortunately, the crystal structure was not of sufficient quality to conclusively substantiate the positions of all the hydrogen atoms as determined from the difference Fourier maps. However, one peak, which was successfully refined as hydrogen, was located in the region intermediate between the benzylic carbon and chromium [Cr1–H26 = 1.31 Å, C6–H26 = 1.14 Å] and was rather close to the other aliphatic carbon of the benzylidene group [C13···H26 = 2.10 Å].

There is an interesting parallel between the chemical behavior and structural features of Cr(II) alkylchromates[9f,12] and that observed in the chemistry of anionic Cr(II) alkoxides (Scheme 4),[19,22,23] thus reinforcing the idea that the Lewis acidity of the alkali-metal cation is indeed a crucial factor for assembling the di- and polymetallic frames of these species.[12,22] However, while in the case of the dinuclear alkoxides it is rather straightforward to imagine how Cr–(OR)–M–(OR)–Cr bridges may hold together dimetallic structures of $(RO)_8Cr_2[M(L)]_4$ [R = Ph, *i*-Pr; M = Na; L = THF, pyridine][22,23] in the absence

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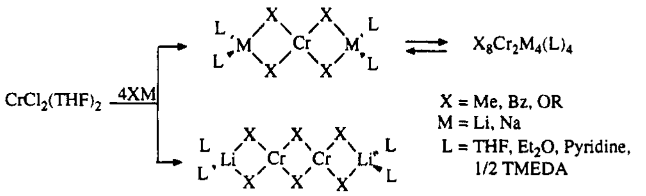
[20] (a) Thomas, B. J.; Noh, S. K.; Schulte, G. K.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 893. (b) Theopold, K. H. *Acc. Chem. Res.* **1990**, *23*, 263.

[21] Barrera, J. A.; Wilcox, D. E. *Inorg. Chem.* **1992**, *31*, 1745.

[22] Edema, J. J. H.; Gambarotta, S.; van Bolhuis, F.; Spek, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 2142.

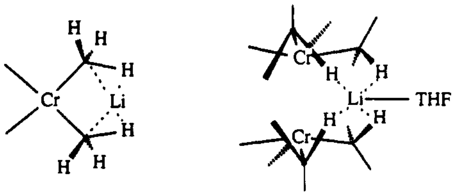
[23] Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; van Bolhuis, F.; Spek, A. L.; Smeets, W. J. J. *Inorg. Chem.* **1990**, *29*, 2147.

Scheme 4



of direct Cr–Cr bonds, it turns out to be more difficult to understand how extremely short Cr–Cr contacts might be enforced by Cr–Me–Li–Me–Cr bridges, such as in the case of complexes 1, if no Cr–Cr bond is present in the complex.[12] The crystal structure of the monomeric $Me_4CrLi_2(TMEDA)_2$ has indicated that Li···H–CH$_2$–Cr interactions are folding $CrLiMe_2$ cores and are responsible for the occurrence of rather short Cr–Li nonbonding distances (2.5 Å). It is thus possible that a similar Li–CH$_3$ agostic interaction may be responsible also for holding together the dinuclear structures of $R_8Cr_2Li_4$ (1). In other words, the dissociation of TMEDA from $Me_4CrLi_2(TMEDA)_2$ during the formation of $Me_8Cr_2Li_4(THF)_4$ is making available an empty coordination site on the lithium atom which is then available to form another agostic interaction, thus assembling the dimer. The very short Cr–Cr contact may be nothing more than the optimization of C–H–Li bond distances and angles (Chart 1). Unfortunately, the crystal structure reported by Krausse more than 20 years ago[11] was not sufficiently accurate to allow the location and refinement of the hydrogen atom positions. Therefore, in order to clarify the important issue of the Cr–Cr bonding in $Me_8Cr_2Li_4$, we felt that it was worthwhile to attempt to improve upon this feature. A correct assignment of the space group combined with the employment of low temperature data collection gave better agreement factors and allowed us to locate and successfully refine the hydrogen atom position.[24] The crystal structure which has confirmed the overall chemical connectivity as described by Krausse (Figure 7), has also shown that indeed the same Li–H agostic-like interactions present in the monomeric $Me_4CrLi_2(TMEDA)_2$ are present in **1a**. The Li–H distances [Li–H4 = 2.03 Å, Li–H6 = 2.05 Å] and, even more strikingly, the Li–H–C angles [Li–H2–C2 = 85.12°] are very comparable to those of $Me_4CrLi_2(TMEDA)$, thus confirming that the very short Cr–Cr contact of $Me_8Cr_2Li_4(THF)_4$ [Cr–Cr = 1.968(2) Å] is just the result of favorable geometrical features. This idea is further corroborated by the fact that the same Li···H agostic interactions are also present in the neopentyl derivative **4** and, as in the case of **2**, they are capable of folding $CrLiR_2$ cores. The fact that these interactions have been determined so far in three different Cr(II) alkyls suggests that they are significant and that they may be characteristic of the chemistry of Cr(II) alkyls. In line with these observations, the aromatic analogues $Ph_4CrLi_2L_n$ [Ph = phenyl (n = 2, mesityl (n=1); L = THF, pyridine][9f] are monomeric and isostructural with **2**. The failure of these species to dimerize can likely be ascribed both to the absence of α-hydrogen atoms and the consequent inability to form agostic interactions with the alkali-metal cation and to the interaction of the alkali-metal cation with the π orbitals of the aromatic rings which probably quenches the Lewis acidity of the alkali-metal cation.

Chart 1



In conclusion, the synthesis, characterization, and stability properties of a novel series of Cr(II) alkylchromates have been described. While the structures were strongly dependent on the reagent stoichiometric ratio used during the preparation, the employment of a chelating diamine as ancillary ligand gave a surprising series of transformations, enabling the preparation and characterization of highly reactive functionalities such as alkylidene and chromacyclobutane. Since these findings may open new perspectives in the reactivity of divalent chromium, we are currently exploring the chemical reactivity of these species.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada (operating grant).

Supplementary Material Available: Tables listing crystal data, atomic positional parameters, temperature factors, torsion angles, bond angles and distances, and hydrogen atom positional parameters associated with complexes **1a**, **4**, **5**, **6**, **7**, **9**, and **10** and structural diagrams of **1a**, **5**, and **6** (175 pages). Ordering information is given on any current masthead page.

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[24] Crystal Data for **1a**: $C_{24}H_{56}Cr_2Li_4O_4$, $M = 540.46$, tetragonal, $I\bar{4}$, $a = 11.476(3)$ Å, $c = 11.856(4)$ Å, $V = 1562.5(8)$ Å^3, $Z = 2$, $T = -160$ °C, Mo Kα, $R = 0.030$, $R_w = 0.039$ for 559 reflections out of 621 unique. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located and refined isotropically. For more details see the supplementary material.