

A Homoleptic [(Dimethylamino)methyl]chromium Complex with an Extremely Short Cr–Cr Bond, $[\{\text{Li}(\text{THF})\}_2\text{Cr}_2(\text{CH}_2\text{NMe}_2)_6]$

Frank Becke,[†] Peter Wiegeleben,[†] Tobias Rüffer,[†] Christoph Wagner,[†]
Roland Boese,[‡] Dieter Bläser,[‡] and Dirk Steinborn^{*,†}

*Institut für Anorganische Chemie, Martin-Luther-Universität Halle-Wittenberg,
Kurt-Mothes-Strasse 2, D-06120 Halle (Saale), Germany, and Institut für Anorganische
Chemie, Universität-Gesamthochschule Essen, Universitätsstrasse 5-7,
D-45117 Essen, Germany*

Received September 17, 1997

The homoleptic [(dimethylamino)methyl]chromate(II) complex $[\{\text{Li}(\text{THF})\}_2\text{Cr}_2(\text{CH}_2\text{NMe}_2)_6]$ (**1**) has been prepared by the reaction of $[\text{CrCl}_2(\text{THF})_2]$ with $\text{LiCH}_2\text{NMe}_2$ in a 1:3 molar ratio. The thermally stable complex **1** ($T_{\text{dec}} = 94\text{--}98\text{ }^\circ\text{C}$) is diamagnetic ($\chi_{\text{g}} = -1.19 \times 10^{-7} \text{ cm}^3 \text{ g}^{-1}$ (295 K); $\mu_{\text{eff}} = 0.67 \mu_{\text{B}}/\text{Cr}$), consistent with a Cr–Cr quadruple bond. The reaction of **1** with 1-bromopentane led to formation of the paramagnetic ($\mu_{\text{eff}} = 2.97 \mu_{\text{B}}/\text{Cr}$) Cr(III) derivative $[\{\text{Cr}(\eta^2\text{-CH}_2\text{NMe}_2)_2(\mu\text{-Br})\}_2]$ (**2**) with cleavage of the Cr–Cr quadruple bond. The structures of the dinuclear complexes **1** and **2** have been determined by X-ray crystallography. **1** (C_i symmetry) exhibits a supershort Cr–Cr quadruple bond (1.884(1) Å) that is not supported by bridging aminomethyl ligands. At each chromium, two CH_2NMe_2 ligands adopt an η^1 -coordination and one adopts an η^2 -coordination ($d(\text{Cr}–\text{C}) = 2.124(4)\text{--}2.139(4)$ Å). The primary donor set of lithium is made up of two nitrogen atoms, one oxygen atom (THF), and one methylene carbon atom. Complex **2** (C_i symmetry) has a planar central $\text{Cr}(\mu\text{-Br})_2\text{Cr}$ unit. All aminomethyl ligands are η^2 -coordinated ($d(\text{Cr}–\text{C}) = 2.030(5)$ and $2.043(5)$ Å) to complete a distorted-octahedral coordination sphere at chromium.

Introduction

The syntheses of thermally relatively stable, homoleptic (trimethylsilyl)methyl complexes of a great number of transition metals¹ inspired investigations of other types of homoleptic σ -alkyl transition-metal complexes. To date, there have been only a few examples of homoleptic functionalized methyl complexes of the type $[\text{M}(\text{CH}_2\text{YR}_n)_m]^{x-}$ ($x = 0, 1, 2, \dots$) with Lewis-basic heteroatom centers YR_n ($\text{YR}_n = \text{NR}_2, \text{PR}_2, \text{OR}, \text{SR}, \text{Cl}, \dots$; $\text{R} = \text{alkyl, aryl}$). Reported to date have been a complete series of (piperidino)methyl complexes ($\text{YR}_n = \text{NC}_5\text{H}_{10}$) of 3d metals (Ti–Ni),^{2,3} as well as $[\{\text{Li}(\text{Et}_2\text{O})\}_2\text{Ni}(\text{CH}_2\text{NMe}_2)_4]$,⁴ $[\{\text{Pd}(\mu\text{-}\eta^2\text{-CH}_2\text{SPh})_2\}_4]$,⁵ and $[\{\text{Li}(\text{Et}_2\text{O})\}_2\text{Ni}(\text{CH}_2\text{S}^t\text{Bu})_4]$.⁶ The nickelate complexes $[\{\text{Li}(\text{Et}_2\text{O})\}_2\text{Ni}(\text{CH}_2\text{YR}_n)_4]$ ($\text{YR}_n = \text{NC}_5\text{H}_{10}$,⁴ NMe_2 ,⁷

S^tBu^6) and the palladium (phenylthio)methyl complex⁵ were structurally characterized. In the nickelate complexes, strong interactions between the Lewis-basic heteroatoms and the cationic lithium centers seem to be essential for high thermal stability ($T_{\text{dec}} = 60\text{--}115\text{ }^\circ\text{C}$).

It has been found that the reaction of $[\text{CrBr}_2(\text{THF})_2]$ with [(piperidino)methyl]lithium is strongly dependent on the solvent used: in THF the monomeric (high-spin) complex $[\{\text{Li}(\text{THF})\}_2\text{Cr}(\text{CH}_2\text{NC}_5\text{H}_{10})_4]$ ($\mu_{\text{eff}} = 4.93 \mu_{\text{B}}$) and in diethyl ether the dinuclear complex $[\text{Li}_2\text{Cr}_2(\text{CH}_2\text{NC}_5\text{H}_{10})_6]$ ($\mu_{\text{eff}} = 0.96 \mu_{\text{B}}/\text{Cr}$) are formed.² Due to very low solubility in common organic solvents, the latter complex is not suitable for further reactions, nor were we able to grow crystals of it. For this reason, we decided to investigate the analogous [(dimethylamino)methyl]chromium(II) complex. We report here the synthesis and molecular structure of the homoleptic complex $[\{\text{Li}(\text{THF})\}_2\text{Cr}_2(\text{CH}_2\text{NMe}_2)_6]$ (**1**) as well as the reaction of **1** with 1-bromopentane to give $[\{\text{Cr}(\eta^2\text{-CH}_2\text{NMe}_2)_2(\mu\text{-Br})\}_2]$ (**2**).

Results and Discussion

The reaction of $[\text{CrCl}_2(\text{THF})_2]$ with $\text{LiCH}_2\text{NMe}_2$ in a 1:3 molar ratio in diethyl ether affords the homoleptic [(dimethylamino)methyl]chromate(II) complex **1** in 53% yield (eq 1). The product is pyrophoric and moisture-sensitive and melts between 94 and 98 °C with decomposition, whereas the solvate-free (piperidino)methyl derivative $[\text{Li}_2\text{Cr}_2(\text{CH}_2\text{NC}_5\text{H}_{10})_6]$ exhibits a higher ther-

* To whom correspondence should be addressed.

[†] Universität Halle-Wittenberg.

[‡] Universität-GH Essen.

(1) (a) Wilkinson, G. *Chemia* **1973**, *27*, 165. (b) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Acc. Chem. Res.* **1974**, *7*, 209. (c) Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474. (d) Morris, R. J.; Girolami, G. S. *Organometallics* **1989**, *8*, 1478. (e) Hay-Motherwell, R. S.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Polyhedron* **1990**, *9*, 931.

(2) (a) Steinborn, D. *Z. Chem.* **1976**, *16*, 328. (b) Steinborn, D. *Z. Chem.* **1977**, *17*, 347.

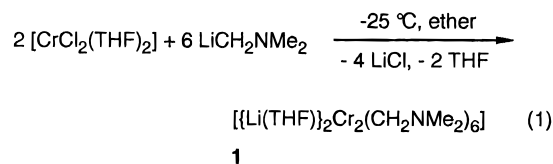
(3) Steinborn, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 401.

(4) Steinborn, D.; Becke, F.; Boese, R. *Inorg. Chem.* **1995**, *34*, 2625.

(5) Miki, K.; Yoshida, G.; Kai, Y.; Yasuoka, N.; Kasai, N. *J. Organomet. Chem.* **1978**, *149*, 195.

(6) Becke, F.; Rüffer, T.; Boese, R.; Bläser, D.; Steinborn, D. *J. Organomet. Chem.*, in press.

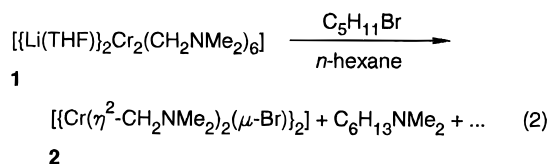
(7) Heinemann, F. W.; Becke, F.; Steinborn, D. *Z. Kristallogr.* **1997**, *212*, 679.



mal stability ($T_{\text{dec}} = 150\text{--}165^\circ\text{C}$).² The deep red crystals of **1** are soluble in ethers and aromatic hydrocarbons and even in aliphatic hydrocarbons such as *n*-hexane. Complex **1** is diamagnetic ($\chi_g = -1.19 \times 10^{-7} \text{ cm}^3 \text{ g}^{-1}$ (295 K), $\mu_{\text{eff}} = 0.67 \mu_{\text{B}}/\text{Cr}$) with a magnetic moment consistent with a dinuclear d^4 Cr(II) complex containing a Cr–Cr quadruple bond. Similar values of the residual paramagnetism were found in other Cr(II) complexes (e.g., $[\text{Li}_2\text{Cr}_2(\text{CH}_2\text{NC}_5\text{H}_{10})_6]$ ($0.96 \mu_{\text{B}}/\text{Cr}$),² $[\text{Cr}_2(\text{CH}_2\text{SiMe}_3)_4(\text{PMe}_3)_2]$ ($0.9 \mu_{\text{B}}/\text{Cr}$),⁸ $[\text{Cr}_2(\text{O}_2\text{CMe})_4(\text{NH}_3)_2]$ ($0.56 \mu_{\text{B}}/\text{Cr}$)⁹) and may be explained in terms of a temperature-independent paramagnetism (TIP).^{9,10} The ^1H NMR spectrum of **1** at ambient temperature in benzene- d_6 shows sharp signals for the THF solvate molecules (δ 1.40, 3.56 ppm) and a broad signal (δ 1.80–2.60 ppm) for the ligand protons in the expected intensity ratio.

1 reacts with LiAlD_4 in diethyl ether to give DCH_2NMe_2 (degree of deuteration 85% (MS)). THF is strongly coordinated in complex **1**. Thus, treating a solution of **1** in THF with TMEDA (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) at ambient temperature results neither in substitution of THF nor in any decomposition. In contrast, treatment of chromium(II) alkyl complexes $[\{\text{Li}(\text{THF})\}_4\text{Cr}_2\text{R}_8]$ ($\text{R} = \text{Me}, \text{CH}_2\text{Ph}, \text{CH}_2\text{CMe}_3, \text{CH}_2\text{CMe}_2\text{Ph}$)¹¹ and $[\{\text{Li}(\text{THF})\}_2\text{Cr}_2(\text{CH}_2\text{SiMe}_3)_6]$ ¹⁰ results in cleavage of the Cr–Cr quadruple bond.

Principally, aminomethyl complexes can add electrophiles to give nitrogen ylide complexes, as was shown in the reaction of $[\text{NiCp}(\text{CH}_2\text{NMe}_2)\text{PPh}_3]$ with MeI to give $[\text{NiCp}(\text{CH}_2\text{NMe}_3)\text{PPh}_3]\text{I}$.¹² Complex **1** reacts differently: with 1-bromopentane a dinuclear chromium(III) complex (**2**) was formed in 67% yield (eq 2).



Another product, *n*-hexyldimethylamine, was found, indicating that an oxidative addition of 1-bromopentane at the chromium atoms of **1** had occurred, followed by a reductive elimination of $\text{C}_6\text{H}_{13}\text{NMe}_2$.

The deep red crystals of **2** are very sensitive toward oxygen and moisture and are soluble in all common solvents. Like the chloro-bridged organo-Cr(III) com-

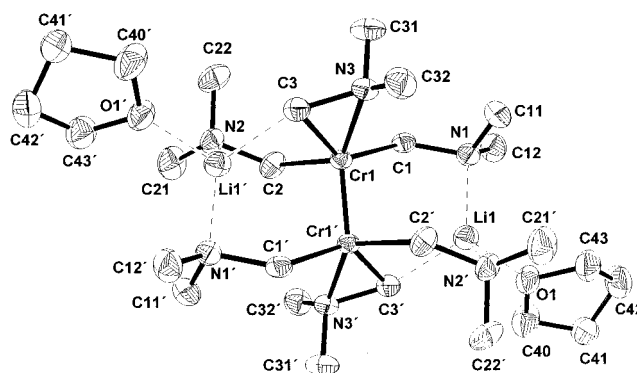


Figure 1. ORTEP drawing of the molecular structure of **1** (thermal ellipsoids at 50% probability). Hydrogen atoms are omitted for clarity.

Table 1. Selected Distances (Å) and Angles (deg) for $[\{\text{Li}(\text{THF})\}_2\text{Cr}_2(\text{CH}_2\text{NMe}_2)_6]$ (**1**)^a

Cr1–Cr1'	1.884(1)	Cr1–C1	2.137(4)
Cr1–C2	2.124(4)	Cr1–C3	2.139(4)
Cr1–N3	2.185(4)	Cr1–Li1'	2.762(6)
C1–N1	1.502(4)	N1–C11	1.444(6)
N1–C12	1.456(6)	C2–N2	1.501(4)
N2–C21	1.456(6)	N2–C22	1.453(6)
C3–N3	1.478(5)	N3–C31	1.475(6)
N3–C32	1.458(6)	Li1–O1	2.044(7)
Li1–N1	2.056(8)	Li1–N2'	2.071(9)
Li1–C3'	2.197(8)	Li1–C2'	2.536(9)
Li1–C1	2.724(7)		
Cr1–C1–N1	123.4(3)	Cr1–C2–N2	119.7(3)
Cr1–C3–N3	71.7(2)	Cr1'–Cr1–C1	103.7(1)
Cr1'–Cr1–C2	96.3(1)	Cr1'–Cr1–C3	114.0(1)
Cr1'–Cr1–N3	123.0(1)	C1–Cr1–C2	90.8(2)
C1–Cr1–N3	102.7(1)	C3–Cr1–N3	40.0(1)
C2–Cr1–C3	103.2(2)	N1–Li1–O1	103.7(4)
O1–Li1–N2'	101.8(3)	N1–Li1–C3'	112.8(3)
N2'–Li1–C3'	107.7(4)	N1–Li1–N2'	127.4(4)
O1–Li1–C3'	98.7(3)		

^a Symmetry transformations used to generate equivalent atoms: (') $1 - x, 1 - y, 1 - z$.

plex $[\{\text{Cr}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2\text{Ph})(\mu\text{-Cl})_2\}]$ ($T_{\text{dec}} = 166^\circ\text{C}$),¹³ complex **2** is thermally very stable and decomposes only at temperatures between 163 and 178°C . Complex **2** is paramagnetic ($\mu_{\text{eff}} = 2.97 \mu_{\text{B}}/\text{Cr}$), but its magnetic moment is exceedingly reduced in comparison with the expected spin-only value for a mononuclear Cr(III) complex ($\mu_{\text{eff}} = 3.87 \mu_{\text{B}}$). This may be the result of antiferromagnetic coupling between the chromium atoms which was assumed for other dinuclear Cr(III) complexes with chloro bridges such as $[\{\text{Cr}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2\text{Ph})(\mu\text{-Cl})_2\}]$ ($\mu_{\text{eff}} = 3.0 \mu_{\text{B}}/\text{Cr}$ (295 K))¹³ and $[\{\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CH}_3)(\mu\text{-Cl})_2\}]$ ($\mu_{\text{eff}} = 3.55 \mu_{\text{B}}/\text{Cr}$ (300 K)).¹⁴

Structure of $[\{\text{Li}(\text{THF})\}_2\text{Cr}_2(\text{CH}_2\text{NMe}_2)_6]$ (1**).** An ORTEP¹⁵ drawing giving the atom-numbering scheme is shown in Figure 1, and selected structural parameters are listed in Table 1. Complex **1** crystallizes as discrete molecules. No unusually short contacts between adjacent molecules are observed. The molecule shows C_i symmetry with a crystallographic inversion center in the midpoint of the Cr–Cr quadruple bond. The main feature of the structure is the supershort ($<1.9 \text{ Å}$)¹⁶

(8) Andersen, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446.

(9) Larkworthy, L. F.; Tabatabai, J. M. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 427.

(10) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646.

(11) (a) Hao, S.; Song, J.-I.; Berno, P.; Gambarotta, S. *Organometallics* **1994**, *13*, 1326. (b) Hao, S.; Gambarotta, S.; Bensimon, C. *J. Am. Chem. Soc.* **1992**, *114*, 3556.

(12) (a) Sepelak, D. J.; Pierpont, C. G.; Barefield, E. K.; Budz, J. T.; Poffenberger, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 6178. (b) Barefield, E. K.; Sepelak, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 6542.

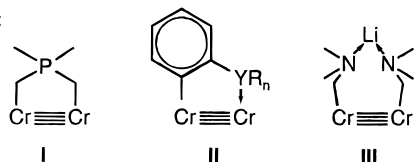
(13) Bhandari, G.; Kim, Y.; McFarland, J. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1995**, *14*, 738.

(14) Richeson, D. S.; Hsu, S.-W.; Fredd, N. H.; van Duyne, G.; Theopold, K. H. *J. Am. Chem. Soc.* **1986**, *108*, 8273.

(15) Johnson, C. K. ORTEP-II; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

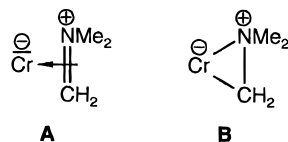
Table 2. Homoleptic Organochromium(II) Complexes with Supershort Cr–Cr Quadruple Bonds^a

	bridge type	<i>d</i> (Cr–Cr) (Å)	<i>d</i> (Cr–C) (Å)	lit.
[Cr ₂ {(CH ₂) ₂ PMe ₂ }] ₄	I	1.895(3)	2.21(1)–2.23(1)	17
[Cr ₂ (<i>o</i> -Me ₂ NC ₆ H ₄) ₄]	II (YR _n = NMe ₂)	1.877(1)	2.037(5)	18
[Cr ₂ (TMP) ₄] ^b	II (YR _n = OMe)	1.849(2)	2.055(6), 2.067(5)	19
[Cr ₂ (DMP) ₄] ^c	II (YR _n = OMe)	1.847(1)	2.049(7)–2.086	19
[Cr ₂ (2-MeO-5-MeC ₆ H ₃) ₄]	II (YR _n = OMe)	1.828(2)	2.058(8), 2.061(7)	20
[{Li(THF)} ₂ Cr ₂ (CH ₂ NMe ₂) ₆]	III	1.884(1)	2.124(4)–2.139(4)	<i>d</i>

^a Bridge types:^b TMP = 2,4,6-trimethoxyphenyl. ^c DMP = 2,6-dimethoxyphenyl. ^d This work.

Cr–Cr bond length of 1.884(1) Å in spite of the absence of ligand bridges between the chromium atoms. To date, such exceedingly short Cr–Cr bonds were observed in homoleptic organochromates only with ring-substituted bridging phenyl ligands and phosphorus ylide ligands (see Table 2).

The coordination behavior of the aminomethyl ligands is quite different. Four (dimethylamino)methyl ligands adopt an η^1 - and two an η^2 -coordination mode. The η^2 -CH₂NMe₂ ligands are characterized by a small Cr–C–N bond angle (71.7(2)°) and a slightly shorter CH₂–N bond length (*d*(C3–N3) = 1.478(5) Å vs *d*(C1–N1) = 1.502(4) Å and *d*(C2–N2) = 1.501(4) Å). Nevertheless, the C3–N3 bond is in the range of typical C–N single bonds and is much longer than the corresponding bond in [Ni(η^2 -CH₂NMe₂)Cl(PPh₃)] (*d*(CH₂–N) = 1.392(6) Å)¹² that was characterized as a cationic heteroolefin complex (iminium cation as ligand) (see type A). In contrast,



the η^2 -coordinated ligands in **1** are arranged in a chromaazacyclopropane fashion (type B). In spite of different coordination, the Cr–C bond lengths do not differ significantly (*d*(Cr–C) = 2.124(4)–2.139(4) Å).

Lithium is distorted tetrahedrally, coordinated (ignoring the weak contact *d*(Li1–C2') = 2.536(9) Å) by two nitrogen atoms, one oxygen atom (THF), and one methylene carbon atom (*d*(Li1–C3') = 2.197(8) Å). Thus, the Cr–Cr bond in **1** is supported solely by the two bridging lithium centers. The Li–Cr distance (*d*(Li1'–Cr1) = 2.762(6) Å) is in the range found for the two other structurally investigated dinuclear organochromate(II) complexes [{Li(THF)}₄Cr₂Me₈] (2.56(3) Å)²¹ and [{Li(THF)}₄Cr₂(C₄H₈)₄] (C₄H₈ = 1,4-butanediyl, 2.54(5)–2.71(6) Å).²²

(16) Cotton, F. A.; Walton, R. A., *Multiple Bonds Between Metal Atoms*; Clarendon Press: Oxford, U.K., 1993.

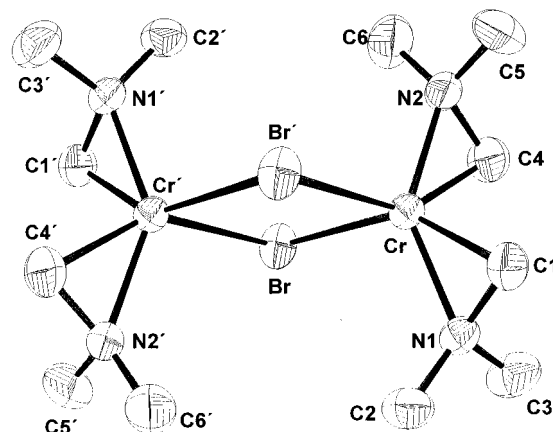
(17) Cotton, F. A.; Hanson, B. E.; Ilsley, W. H.; Rice, G. W. *Inorg. Chem.* **1979**, *18*, 2713.

(18) Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; Spek, A. L. *Organometallics* **1992**, *11*, 2452.

(19) Cotton, F. A.; Koch, S. A.; Millar, M. *Inorg. Chem.* **1978**, *17*, 2087.

(20) Cotton, F. A.; Koch, S. A.; Millar, M. *Inorg. Chem.* **1978**, *17*, 2084.

(21) Krausse, J.; Marx, G.; Schödl, G. *J. Organomet. Chem.* **1970**, *21*, 159.

**Figure 2.** ORTEP drawing of the molecular structure of **2** (thermal ellipsoids at 50% probability). Hydrogen atoms are omitted for clarity.**Table 3. Selected Distances (Å) and Angles (deg) for [{Cr(η^2 -CH₂NMe₂)₂(μ -Br)}₂] (**2**)^a**

Cr...Cr'	3.823(1)	Cr–Br	2.625(1)
Cr–Br'	2.631(1)	Br...Br'	3.607(1)
Cr–C1	2.043(5)	Cr–N1	2.055(4)
Cr–C4	2.030(5)	Cr–N2	2.057(4)
C1–N1	1.461(6)	C4–N2	1.444(7)
N1–C2	1.463(6)	N1–C3	1.470(6)
N2–C5	1.477(8)	N2–C6	1.450(8)
Cr–Br–Cr'	93.3(1)	Br–Cr–Br'	86.7(1)
Cr–C1–N1	69.6(3)	Cr–C4–N2	70.3(3)
C1–Cr–N1	41.8(2)	C4–Cr–N2	41.4(2)

^a Symmetry transformation used to generate equivalent atoms: (') $-x, -y + 1, -z$.

Structure of [{Cr(η^2 -CH₂NMe₂)₂(μ -Br)}₂] (2**).** The molecular structure is shown in Figure 2. Selected bond lengths and bond angles are listed in Table 3. Complex **2** exhibits *C_i* symmetry with a planar Cr(μ -Br)₂Cr unit. The Cr...Cr' distance in **2** (3.823(1) Å) excludes a metal–metal interaction and is considerably longer than those in chloro-bridged organochromium complexes such as [{Cr(η^5 -C₅Me₅)(CH₃)(μ -Cl)}₂] (3.278(1) Å),²³ [{Cr(η^5 -C₅H₅)(CH₃)(μ -Cl)}₂] (3.287(1) Å),¹⁴ and [{Cr(η^5 -C₅Me₅)(CH₂Ph)(μ -Cl)}₂] (3.343(1) Å).¹³ The aminomethyl ligands in **2** are η^2 -coordinated at chromium to complete the strongly distorted octahedral coordination sphere of chromium. There are no significant differences in bond lengths (*d*(Cr–C) = 2.043(5)/2.030(5) Å; *d*(C–N) =

(22) Krausse, J.; Schödl, G. *J. Organomet. Chem.* **1971**, *27*, 59.(23) Herrmann, W. A.; Thiel, W. R.; Herdtweck, E. *J. Organomet. Chem.* **1988**, *353*, 323.

1.461(6)/1.444(7) Å) and Cr–C–N angles (69.6(3)/70.3(3)°) between them. All these values are only slightly smaller than those in the chromaazacyclopropane ring of complex **1**.

The homoleptic dinuclear chromium complex **1** is the first structurally characterized complex of the type [Li₂Cr₂R₆]. Its supershort Cr–Cr distance is of special interest because of the unique ligand sphere and also with respect to the discussion of the strength of Cr–Cr quadruple bonds and their existence at all.¹¹ The heteroleptic dinuclear complex **2** is the first organochromate(III) with a central Cr(μ-Br)₂Cr unit.

Experimental Section

General Comments. All reactions and manipulations were carried out under purified argon using standard Schlenk techniques. (*Warning:* compound **1** is pyrophoric. Appropriate precautions should be taken for its safe manipulation.) Diethyl ether and THF were distilled from sodium benzophenone ketyl. *n*-Hexane and benzene-*d*₆ were dried with LiAlH₄. NMR spectra were recorded on a JEOL JNM-FX 200 NMR spectrometer using the protio impurities of the deuterated solvents as references for ¹H spectroscopy. Mass spectra (EI, 70 eV) were obtained by using an AMD 402 instrument. The lithium and chromium contents were determined by ICP-AES (Unicam, PU 7000). Room-temperature magnetic susceptibilities were determined using a self-constructed balance which utilizes the Gouy method. GC–MS investigations were carried out on an HP 5890 Series II/HP 5972 (Hewlett-Packard). LiCH₂NMe₂ was prepared according to a published procedure.⁴ C₆H₁₃NMe₂ (reference substance for GC–MS) was synthesized from HNMe₂ and C₆H₁₃Br.

Synthesis of [(Li(THF))₂Cr₂(CH₂NMe₂)₆] (1**).** To a stirred suspension of LiCH₂NMe₂ (2.3 g, 35.4 mmol) in diethyl ether (50 mL) was added slowly 3.1 g (11.7 mmol) of [CrCl₂(THF)₂] at –25 °C. After the reaction mixture had been stirred for 2 h at room temperature, the formed LiCl was filtered. The red filtrate was concentrated to 35 mL under oil-pump vacuum. At –78 °C, the precipitated deep red crystals of **1** were filtered, recrystallized from diethyl ether (25 mL), and dried *in vacuo*. Yield: 1.9 g (53%). Anal. Calcd for C₂₆H₆₄Cr₂Li₂N₆O₂: Li, 2.27; Cr, 17.03. Found: Li, 2.34; Cr, 17.41. ¹H NMR (199.50 MHz, benzene-*d*₆): δ 1.40 (m, 8H, THF), 1.80–2.60 (br, not resolved, 48H, CH₂N(CH₃)₂), 3.56 (t, 8H, THF). χ_g = –1.19 × 10^{–7} cm³ g^{–1} (295 K); μ_{eff} = 0.67 μ_B/Cr. T_{dec} = 94–98 °C.

Reaction of **1 with 1-Bromopentane.** To a stirred suspension of **1** (0.9 g, 1.5 mmol) in *n*-hexane (30 mL) was added 1.1 mL (9.0 mmol) of 1-bromopentane at –78 °C. After the reaction mixture had been stirred for 2 h at room temperature, the white precipitate which had formed was filtered. The red filtrate was concentrated to 20 mL under oil-pump vacuum. At –78 °C, the deep red crystals of [(Cr(η²-CH₂NMe₂)₂(μ-Br))₂] (**2**) were filtered and dried *in vacuo*. Yield: 0.5 g (67%). Anal. Calcd for C₁₂H₃₂Br₂Cr₂N₄: Cr, 20.96. Found: Cr, 20.39. χ_g = 14.28 × 10^{–6} cm³ g^{–1} (295 K); μ_{eff} = 2.97 μ_B/Cr. T_{dec} = 163–178 °C.

Reaction of **1 with LiAlD₄.** To a stirred suspension of **1** (0.2 g, 0.3 mmol) in diethyl ether (10 mL) was added about 0.1 g of LiAlD₄ at –78 °C. The reaction mixture was warmed slowly to room temperature and stirred for 2 h. After hydrolysis (H₂O, 0 °C), the formed Me₂NCH₂D was allowed to react with MeI in the gas phase. The [NMe₃(CH₂D)]I formed was thermolyzed; the methyl iodide formed was investigated by MS to determine its degree of deuteration.

X-ray Structure Determination of **1 and **2**.** Suitable deep red single crystals were obtained from a diethyl ether

Table 4. Crystal Data and Structure Refinement Details for **1 and **2****

	1	2
empirical formula	C ₂₆ H ₆₄ Cr ₂ Li ₂ N ₆ O ₂	C ₆ H ₁₆ BrCrN ₂
fw	610.7	248.12
T (K)	173	220(2)
cryst syst	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
<i>a</i> (Å)	9.258(4)	8.382(2)
<i>b</i> (Å)	9.680(5)	12.116(2)
<i>c</i> (Å)	10.974(5)	10.887(3)
α (deg)	111.01(4)	90
β (deg)	95.99(4)	108.23(2)
γ (deg)	103.19(4)	90
<i>V</i> (Å ³)	872.2(7)	1050.2(4)
<i>Z</i>	1	4
<i>D</i> _{calcd} (g cm ^{–3})	1.163	1.569
μ (Mo Kα) (mm ^{–1})	0.652	4.836
<i>F</i> (000)	332	500
scan range (deg)	3.0 < 2θ < 45.0	3.18 < θ < 28.15
index ranges	–9 ≤ <i>h</i> ≤ 9 –10 ≤ <i>k</i> ≤ 9 0 ≤ <i>l</i> ≤ 11	–10 ≤ <i>h</i> ≤ 9 –15 ≤ <i>k</i> ≤ 15 –12 ≤ <i>l</i> ≤ 14
no. of rflns coll'd	2421	5511
no. of indep rflns	2278	2369
no. of params refined	176	107
goodness of fit on <i>F</i> (<i>F</i> ²)	1.01	(1.149)
<i>R</i> (<i>R</i> ₁) [<i>I</i> > 2σ(<i>I</i>)]	0.0488	(0.0412)
<i>R</i> _w (<i>wR</i> ₂), all data	0.0564	(0.1162)
largest diff peak (e Å ^{–3})	0.63	0.562
largest diff hole (e Å ^{–3})	–0.60	–0.692

solution (**1**) and from a diethyl ether/*n*-hexane solution (**2**) at –78 °C. X-ray measurements were performed on a Nicolet R3m/V (**1**) and on a Stoe IPDS diffractometer (**2**) with Mo Kα radiation (0.710 73 Å, graphite monochromator). Crystal data and details of data collection, structure solution, and refinement are summarized in Table 4. The structure of **1** was solved by Patterson syntheses and refined by full-matrix least-squares methods on *F*, with the SHELXTL-Plus computer program.²⁴ The structure of **2** was solved by direct methods with SHELXS-86²⁵ and refined using full-matrix least-squares procedures on *F*² (SHELXL-93²⁶). All non-hydrogen atoms were refined with anisotropic thermal parameters. For compound **1**, hydrogen atoms were treated as riding groups in ideal positions with groupwise isotropic temperature factors. For compound **2**, hydrogen atoms were included with isotropic thermal parameters of 1.2 times the equivalent isotropic thermal parameters of the corresponding carbon atoms.

Acknowledgment. We wish to thank Prof. Helmut Drevs of the Fachhochschule Merseburg for the magnetic measurements. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Complete tables of atomic coordinates, H atom parameters, bond distances, bond angles, and anisotropic thermal parameters for **1** and **2** (12 pages). Ordering information is given on any current masthead page.

OM970821L

(24) SHELXTL-Plus, Version 4.2/Iris, a complete software package for solving, refining and displaying crystal structures; Siemens, Madison, WI, 1991.

(25) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(26) Sheldrick, G. M. SHELXL-93, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1993.