

## Notes

## In Search of a Versatile Pathway to *ansa*-Chromocene Complexes. Synthesis and Characterization of the Highly Unstable *ansa*-Chromocene Carbonyl Complex $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{CrCO}$

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**Summary:** In an effort to develop a general synthetic route to *ansa*-chromocene complexes with diverse ligand frameworks, we investigated *ansa*-magnosocene compounds as an alternative, potentially more versatile ligand source than *ansa*-calcoscene compounds. The first single-carbon-bridged *ansa*-chromocene compound,  $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{CrCO}$ , was isolated from the reaction between  $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{Mg}$  and  $\text{CrCl}_2$  in THF under an atmosphere of carbon monoxide. This new *ansa*-chromocene compound is considerably more air-sensitive and less chemically stable than its ethanediyl-bridged counterparts.

### Introduction

Despite the fact that bent-metallocene complexes of the early transition metals (groups 3–6) have been central to major advancements in organometallic chemistry over the past half-century,<sup>1</sup> the chemistry of bent-sandwich chromocene is poorly developed, primarily due to the tendency of dicyclopentadienylchromium complexes to lose one or both cyclopentadienyl rings upon participation in a chemical reaction.<sup>2</sup> In 1983, Brintzinger and co-workers reported the first bent-sandwich *ansa*-chromocene complex,  $\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{CrCO}$ ,<sup>3</sup> which is

stable to CO loss, unlike its unbridged counterpart,  $(\text{C}_5\text{H}_5)_2\text{CrCO}$ .<sup>4</sup> Our group discovered a more facile route to  $\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{CrCO}$  and other ethanediyl-bridged chromocene carbonyl and isocyanide complexes that employs *ansa*-calcoscene compounds as a ligand source (Scheme 1).<sup>5</sup> We have used these *ansa*-metallocene complexes of Cr(II) as an entry point to novel bent-metallocene complexes of Cr(III) and Cr(IV).<sup>6</sup> This method is versatile from the standpoint that it allows the introduction of differently substituted ethanediyl bridges within the *ansa*-metallocene ligand framework. However, the exclusive preparation of *ansa*-calcoscene compounds via the reductive coupling of fulvenes with  $\text{Ca}^0$  brings a limitation; it only allows *ansa*-metallocenes with two-carbon bridges to be prepared.<sup>7</sup> Since the reactivity of *ansa*-metallocene complexes of group 3–6 transition metals can be influenced dramatically by the constraints of the bridge on the metallocene geometry,<sup>8</sup> we sought a more general synthetic approach that would allow the preparation of single-atom-bridged complexes.

The silicon-bridged octamethylated *ansa*-chromocene complexes  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{CrCO}]$ ,<sup>9a</sup>  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{Cr}]$ ,<sup>9b</sup> and  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{CrCN-xylyl}]$ <sup>9b</sup> were prepared by Schaper et al. by reacting the dilithium salt of the ligand with  $\text{CrCl}_2(\text{THF})_2$ ; however, our repeated efforts to prepare *ansa*-chromocene

(1) (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley: New York, 2005; Chapter 5. (b) *Metallocenes: Synthesis, Reactivity, Applications*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, Germany, 1998.

(2) (a) Sneeden, R. P. A. *Organochromium Compounds*; Academic Press: New York, 1975. (b) Abernethy, C. D.; Clyburne, J. A. C.; Cowley, A. H.; Jones, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 2329–2330. (c) Cotton, F. A.; Rice, G. W. *Inorg. Chim. Acta* **1978**, *27*, 75–78. (d) Cotton, F. A.; Daniels, L. M.; Kibala, P. A. *Inorg. Chem.* **1992**, *21*, 1865–1869. (e) Cotton, F. A.; Wang, W. *Polyhedron* **1985**, *4*, 1735–1739. (f) Kalousova, J.; Benes, L.; Votinsky, J.; Nadvornik, M. *Collect. Czech. Chem. Commun.* **1985**, *50*, 828–833. (g) Benes, L.; Kalousova, J.; Votinsky, J. *J. Organomet. Chem.* **1985**, *290*, 147–151. (h) Benes, L.; Votinsky, J.; Kalousova, J.; Nadvornik, M.; Klikorka, J. *Collect. Czech. Chem. Commun.* **1982**, *47*, 3381–3383. (i) Votinsky, J.; Kalousova, J.; Benes, L.; Nadvornik, M. *Z. Chem.* **1981**, *21*, 445–446. (j) Eremenko, I. L.; Pasynskii, A. A.; Volkov, O. G.; Ellert, O. G.; Kalinnikov, V. T. *J. Organomet. Chem.* **1981**, *222*, 235–240. (k) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Rideout, D. C. *Inorg. Chem.* **1979**, *18*, 120–125. (l) Pasynskii, A. A.; Eremenko, I. L.; Kalinnikov, V. T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 2843–2844. (m) Karol, F. J.; Wu, C.; Reichle, W. T.; Maraschin, N. J. *J. Catal.* **1979**, *60*, 68–76. (n) Wiberg, N.; Haering, H. W.; Huttner, G.; Friedrich, P. *Chem. Ber.* **1978**, *111*, 2708–2715. (o) Eremenko, I. L.; Pasynskii, A. A.; Gasanov, G. S.; Bagirov, S. A.; Ellert, O. G.; Novotortsev, V. M.; Kalinnikov, V. T.; Struchkov, Y. T.; Shklover, V. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, 1445–1446. (p) Bottomley, F.; Paez, D. E.; Sutin, L.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1985**, 597–598. (q) Bottomley, F.; Paez, D. E.; White, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 5651–5657.

(3) Schwemlein, H.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1983**, *256*, 285–289.

(4) (a) van Raaij, E. U.; Brintzinger, H. H. *J. Organomet. Chem.* **1988**, *356*, 315–323. (b) Wong, K. L. T.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1975**, *97*, 5143–5146.

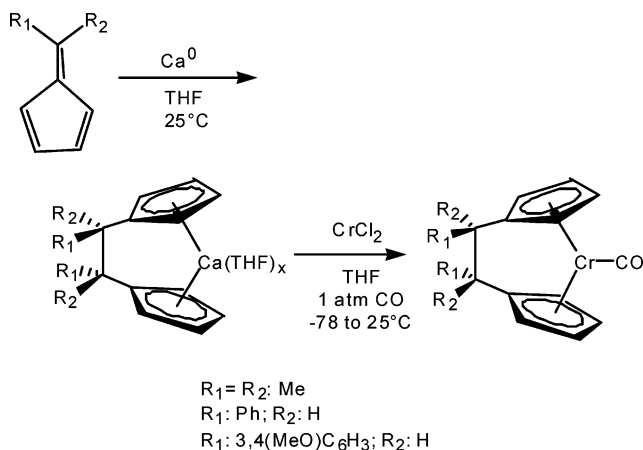
(5) (a) Foo, D. M. J.; Shapiro, P. J. *Organometallics* **1995**, *14*, 4957–4959. (b) Matare, G.; Foo, D. M. J.; Kane, K. M.; Zehnder, R.; Wagener, M.; Shapiro, P. J. *Organometallics* **2000**, *19*, 1534–1539. (c) Shapiro, P. J.; Zehnder, R.; Foo, D. M.; Perrotin, P.; Budzelaar, P. H. M.; Leitch, S.; Twamley, B. *Organometallics* **2006**, *25*, 719–732.

(6) (a) Foo, D. M. J.; Sinnema, P. J.; Twamley, B.; Shapiro, P. J. *Organometallics* **2002**, *21*, 1005–1007. (b) Sinnema, P. J.; Shapiro, P. J.; Foo, D. M. J.; Twamley, B. *J. Am. Chem. Soc.* **2002**, *124*, 10996–10997. (c) Sinnema, P. J.; Nairn, J.; Zehnder, R.; Shapiro, P. J.; Twamley, B.; Blumenfeld, A. *Chem. Commun.* **2004**, 110–111.

(7) (a) Rieckhoff, M.; Pieper, U.; Stalke, D.; Edelman, F. T. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1079–1081. (b) Kane, K. M.; Shapiro, P. J.; Vij, A.; Cubbon, R.; Rheingold, A. L. *Organometallics* **1997**, *16*, 4567–4571. (c) Sinnema, P.-J.; Shapiro, P. J.; Höhn, B.; Bitterwolf, T. E.; Twamley, B. *Organometallics* **2001**, *20*, 2883–2888. (d) Sinnema, P.-J.; Höhn, B.; Hubbard, R. L.; Shapiro, P. J.; Twamley, B.; Blumenfeld, A.; Vij, A. *Organometallics* **2002**, *21*, 182–191.

(8) (a) Zächmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Christopher, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525–9546. (b) Wang, B. *Coord. Chem. Rev.* **2006**, *250* (1–2), 242–258. (c) Shapiro, P. J. *Coord. Chem. Rev.* **2002**, *231* (1–2), 67–81.

(9) (a) Schaper, F.; Rentzsch, M.; Prosenc, M. H.; Rief, U.; Schmidt, K.; Brintzinger, H. H. *J. Organomet. Chem.* **1997**, *534*, 67–69. (b) Schaper, F.; Wrobel, O.; Schwoerer, R.; Brintzinger, H.-H. *Organometallics* **2004**, *23*, 3552–3555.

**Scheme 1. Synthetic Route to Ethanediyl-Bridged *ansa*-Chromocene(II) Complexes**


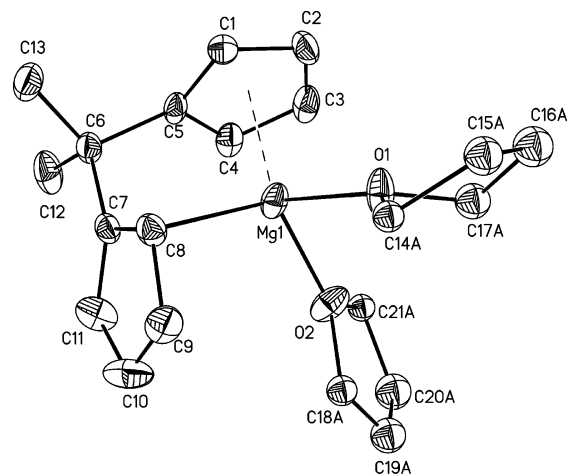
compounds from the lithium or sodium salts of  $\text{Y}(\text{C}_5\text{H}_5)_2$  ( $\text{Y} = \text{CMe}_2, \text{SiMe}_2$ ) or  $(\text{CH}_2)_2(\text{Indenyl})_2\text{K}_2$  appeared to afford only polymeric material.<sup>10</sup>

With an eye toward developing a simple, reliable, and general route to *ansa*-chromocene complexes with different types of bridges, we have investigated *ansa*-magnesocene compounds as an alternative ligand source, since diverse *ansa*-magnesocene compounds can be prepared by metalating the ligands with  $\text{Bu}_2\text{Mg}$ .<sup>11</sup> Herein we report our initial efforts using this approach, by which we prepared the highly strained, single-carbon-bridged *ansa*-chromocene complex  $[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{CrCO}]$  (**2**).

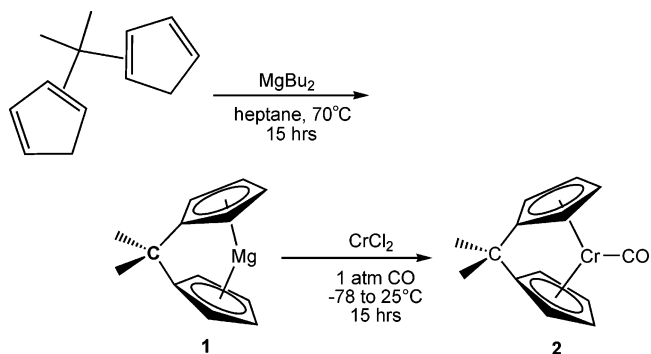
**Results and Discussion**

**Synthesis and X-ray Crystal Structure of  $[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{Mg}(\text{THF})_2]$  (**1**·2THF).** The synthesis of the *ansa*-magnesocene compound  $[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{Mg}(\text{THF})_2]$  (**1**·2THF) and its molecular structure were reported briefly in an article by Cremer et al. in 1997.<sup>11a</sup> **1**·2THF was prepared by reacting  $\text{Me}_2\text{C}(\text{C}_5\text{H}_5)_2$  with  $\text{Bu}_2\text{Mg}$  in pentane followed by crystallization of the compound from THF. We modified the synthesis slightly by heating the reagents in heptane at 70 °C and isolated  $[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{Mg}]$  (**1**) in nearly quantitative yield (87%) as a white precipitate. X-ray-quality crystals of **1**·2THF were obtained by slowly cooling a hot (ca. 70 °C) saturated solution of **1** in a THF–toluene mixture (1:7) to room temperature. The molecular structure of the compound is shown in Figure 1. The magnesium adopts a highly distorted tetrahedral geometry. Ring C1–C5 is  $\eta^5$ -coordinated. The arrangement of single and double C–C bonds within the ring C6–C10 indicates  $\eta^1$  coordination of that ring at C7, with the close proximity of C8 to Mg1 being due to the geometric constraints of the *ansa* bridge rather than a bonding interaction between the atoms. For comparison, molecular structures of related *ansa*-magnesocene compounds containing *tert*-butyl-substituted cyclopentadienyl rings that were bridged by  $\text{MeSi} <$  and  $-\text{H}_2\text{CCH}_2-$  groups exhibited  $\eta^5:\eta^1$  and  $\eta^5:\eta^5$  ring coordination, respectively.<sup>11b</sup>

**Synthesis and X-ray Crystal Structure of  $[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{CrCO}]$  (**2**).** The title compound was prepared by applying an atmosphere of carbon monoxide to an unstirred equimolar mixture of **1** and chromium(II) chloride in THF at  $-78$  °C and



**Figure 1.** Thermal ellipsoid (30%) drawing of **1**·2THF. Hydrogen atoms are omitted for clarity. The dotted line represents the  $\eta^5$  bonding of the Mg to the Cp. Selected bond lengths (Å) and angles (deg): Mg–O(av) = 2.026; Mg–centroid = 2.154; Mg1–C7 = 2.578(4); Mg1–C8 = 2.314(4); O1–Mg1–O2 = 88.81(12); C5–C6–C7 = 105.8(3); C12–C6–C13 = 108.8(3).

**Scheme 2. Synthetic Route to  $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{CrCO}$  (**2**)**


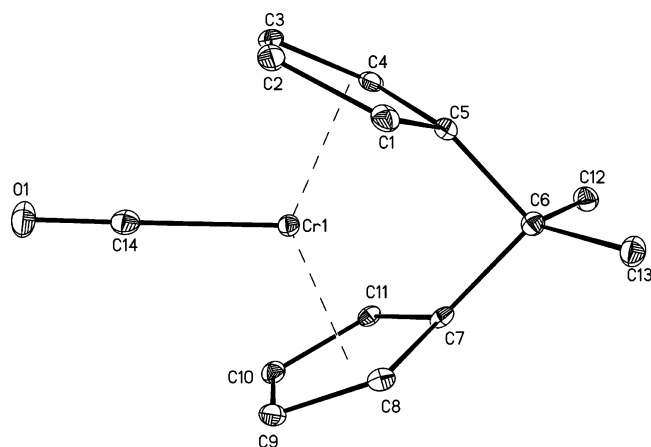
warming the reaction mixture gradually to room temperature with stirring to afford a deep red-brown solution (see Scheme 2). Subsequent removal of the volatiles followed by extraction and crystallization of the product with pentane afforded  $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{CrCO}$  (**2**) in 14% yield as red-orange needles. Although thermally stable, complex **2** is *extremely* air sensitive and decomposes readily even under an  $\text{N}_2$  atmosphere that is not rigorously oxygen free. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra exhibit two cyclopentadienyl resonances, consistent with the  $\text{C}_{2v}$  symmetry of the complex. All proton and carbon signals assignments are based on a combination of HMBC and HSQC experiments (see the Supporting Information). The  $^{13}\text{C}$  NMR chemical shift of the carbonyl ligand (256 ppm) of **2** is similar to that of  $\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{CrCO}$  (261 ppm).<sup>12</sup>

The C–O stretch of **2**, at  $1918\text{ cm}^{-1}$ , is slightly higher in energy than those of  $\text{Cp}_2\text{CrCO}$  ( $1900\text{ cm}^{-1}$ ),  $\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{CrCO}$  ( $1905\text{ cm}^{-1}$ ),<sup>3</sup> and *rac*- $\text{Ph}_2\text{C}_2\text{H}_2(\text{C}_5\text{H}_5)_2\text{CrCO}$  ( $1882\text{ cm}^{-1}$ ),<sup>5b</sup> indicative of less  $\pi$ -back-bonding between the chromium and the carbonyl ligand. X-ray-quality crystals of **2** were grown from a pentane solution at  $-20$  °C. The molecular structure of the complex is shown in Figure 2. Selected structural parameters for **2** are compared with those of  $\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{CrCO}$  and *rac*- $\text{Ar}_2\text{C}_2\text{H}_2(\text{C}_5\text{H}_5)_2\text{CrCO}$  (Ar = 3,4-(MeO) $_2\text{C}_6\text{H}_3$ ) in Table 2. The data indicate that the Cr–CO bond length in **2**

(10) Kane, K.; Matare, G.; Zehnder, R.; Sinnema, P. J.; Foo, D. M. J.; Shapiro, P. J. Unpublished results.

(11) (a) Cremer, C.; Jacobsen, H.; Burger, P. *Chimia* **1997**, *51*, 650–653. (b) Damrau, H.-R.; Geyer, H. A.; Proscenc, M.-H.; Weeber, A.; Schaper, F.; Brintzinger, H. H. *J. Organomet. Chem.* **1998**, *553*, 331–343.

(12) Gutmann, S.; Burger, P.; Proscenc, M. H.; Brintzinger, H. H. *J. Organomet. Chem.* **1990**, *397*, 21–28.



**Figure 2.** Thermal ellipsoid (30%) drawing of **2**. Hydrogen atoms are omitted for clarity. Selected bond angles (deg): C5–C6–C7 = 94.71(15); C12–C6–C13 = 109.95(16).

**Table 1. Crystallographic Data for 1 and 2**

	1	2
empirical formula	C <sub>21</sub> H <sub>30</sub> MgO <sub>2</sub>	C <sub>14</sub> H <sub>14</sub> CrO
formula wt	338.76	250.25
temp, K	185(2)	87(2)
wavelength, Å	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , Å	14.3948(8)	12.8735(6)
<i>b</i> , Å	8.3443(5)	8.3211(4)
<i>c</i> , Å	15.8022(9)	11.1528(5)
$\alpha$ , deg	90	90
$\beta$ , deg	90.894(1)	115.549(1)
$\gamma$ , deg	90	90
<i>V</i> , Å <sup>3</sup>	1897.84(19)	1077.88(9)
<i>Z</i>	4	4
$\rho_{\text{calcd}}$ , Mg/m <sup>3</sup>	1.186	1.542
abs coeff, mm <sup>-1</sup>	0.103	1.032
<i>F</i> (000)	736	520
cryst size, mm <sup>3</sup>	0.37 × 0.13 × 0.05	0.35 × 0.22 × 0.05
cryst color, habit	colorless, plate	orange, plate
$\theta$ range for data collectn, deg	2.58–25.27	1.75–25.25
<i>hkl</i> ranges	–17 to +17, –10 to +10, –18 to +18	–15 to +15, –9 to +9, –13 to +13
no. of rflns collected	21 376	16 506
no. of indep rflns	3440 ( <i>R</i> (int) = 0.1011)	1958 ( <i>R</i> (int) = 0.0302)
max, min transmissn	0.9949, 0.9628	0.9502, 0.7139
no. of data/restraints/params	3440/24/212	1958/0/147
goodness of fit on <i>F</i> <sup>2</sup>	1.003	1.066
final <i>R</i> indices ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> 1 = 0.0673, w <i>R</i> 2 = 0.1385	<i>R</i> 1 = 0.0303, w <i>R</i> 2 = 0.0755
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1289, w <i>R</i> 2 = 0.1652	<i>R</i> 1 = 0.0337, w <i>R</i> 2 = 0.0773
largest diff peak, hole, e Å <sup>-3</sup>	0.286, –0.249	0.365, –0.252

is shorter than in the other two complexes; however, differences among the CrC–O bond lengths are negligible. Although the centroid–Cr–centroid angles are comparable among the three different complexes, the significantly larger angle between cyclopentadienyl ring planes of **2** and significantly shorter distance between the ipso cyclopentadienyl ring carbons relative to the ethanediyl-bridged complexes highlight the greater strain imposed on the metallocene geometry by the single-carbon bridge. The difficulty with which the chromocene accommodates the single-carbon bridge is also reflected in the greater deviation of the centroid–C<sub>ipso</sub>–C6 bond angle from 180° in **2** relative to the angles in the ethanediyl-bridged complexes (final entry, Table 2). This distortion is not as great as that observed in single-

**Table 2. Comparison of Selected Bond Distances (Å) and Angles (deg) among *ansa*-Chromocene Carbonyl Complexes**

	<b>2</b>	Me <sub>4</sub> C <sub>2</sub> (C <sub>5</sub> -H <sub>4</sub> ) <sub>2</sub> CrCO <sup>a</sup>	<i>rac</i> -Ar <sub>2</sub> C <sub>2</sub> H <sub>2</sub> -(C <sub>5</sub> H <sub>4</sub> ) <sub>2</sub> CrCO <sup>b</sup>
centroid–Cr–centroid	143.5	143.3	143.4
Cr–CO	1.876(2)	1.85(1)	1.848(6)
CrC–O	1.159(3)	1.16(1)	1.171(7)
$\angle$ (ring planes)	50.5	38.5	39.8
nonbonded ipso	2.25	2.61	2.61
C(Cp1)–C(Cp2)			
Cr–centroid(av)	1.774	1.78	1.792
centroid–C <sub>ipso</sub> –C <sub>bridge</sub> (av)	157.4	177.6	173.2

<sup>a</sup> Data from ref 3. <sup>b</sup> Ar = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>. Data from ref 5b.

atom-bridged ferrocene complexes;<sup>13</sup> however, it is slightly greater than that of a single-carbon-bridged titanocene complex.<sup>14</sup>

Preliminary experiments show that the strain of the bridge has a noticeable effect on the reactivity of the *ansa*-chromocene system. For example, whereas ethanediyl-bridged *ansa*-chromocene carbonyl complexes readily undergo CO ligand substitution by isocyanide ligands,<sup>6c</sup> **2** reacts very slowly (days) with 1 molar equiv of xylyl isocyanide to form an insoluble, presumably polymeric, product.

So far we have been unable to obtain reproducible cyclic voltammetry data on complex **2**. Interestingly, theoretical calculations indicate that the Cr<sup>II/III</sup> redox potential is not significantly influenced by the degree of bending between the cyclopentadienyl rings.<sup>15</sup>

In contrast to the ethanediyl-bridged chromocene carbonyl compounds, oxidation of **2** with 1 molar equiv of [Cp<sub>2</sub>Fe][B(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>] did not afford an isolable 17e chromocenium carbonyl salt, although Cp<sub>2</sub>Fe was formed in the reaction. The ESR spectrum of the reaction product was more complex than what is expected for a single, low-spin 17e species.<sup>6a</sup> The identity of this product has yet to be determined.

Curiously, our efforts to prepare the analogous Me<sub>2</sub>Si-bridged chromocene carbonyl complex using Me<sub>2</sub>Si(C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>Mg(THF)<sub>2</sub> has yielded only insoluble, presumably polymeric, materials.

In conclusion, we have demonstrated the synthesis of Me<sub>2</sub>C-(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>CrCO using a *ansa*-magnesocene ligand source. The single-carbon-bridged complex is less stable and reacts less predictably than related ethanediyl-bridged complexes. The generality of this synthetic approach to *ansa*-chromocene complexes is still in doubt, given the poor results with Me<sub>2</sub>Si-(C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>Mg(THF)<sub>2</sub>. Nevertheless, it is an attractive approach that warrants further investigation, due to the broad variety of *ansa*-magnesocene compounds that are available through simple metalation of the metallocene ligand framework with Bu<sub>2</sub>Mg.<sup>11</sup>

## Experimental Section

**General Considerations.** Me<sub>2</sub>C(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> was prepared as described in the literature.<sup>16</sup> Di-*n*-butylmagnesium (1 M solution in heptane) and CrCl<sub>2</sub> were purchased from Aldrich and used as received. THF, pentane, and heptane were dried over and distilled from sodium/benzophenone immediately prior to use. C<sub>6</sub>D<sub>6</sub> (99.5%

(13) Shapiro, P. J. *Coord. Chem. Rev.* **2002**, *231*, 67–81 and references therein.

(14) Shaltout, R. M.; Corey, J. Y.; Rath, N. P. *J. Organomet. Chem.* **1995**, *503*, 205–212.

(15) Shapiro, P. J.; Sinnema, P.-J.; Perrotin, P.; Budzelaar, P. H. M.; Weihe, H.; Twamley, B.; Zehnder, R. A.; Nairn, J. J. Submitted for publication.

(16) Nifant'ev, I. E.; Yarnykh, V. L.; Borzov, M. V.; Mazurchik, B. A.; Mstyslavsky, V. I.; Roznyatovsky, V. A.; Ustynuk, Y. A. *Organometallics* **1991**, *10*, 3739–3745.



D) was purchased from Cambridge Isotope laboratories and stored over 4A molecular sieves. All compounds were handled and stored in a nitrogen-filled glovebox and were manipulated using argon and vacuum Schlenk techniques. IR spectra of the compounds were recorded on an Avatar 370 FT-IR Thermo Nicolet instrument. NMR spectra were run on a Bruker AMX 300 NMR spectrometer (300 MHz  $^1\text{H}$ ).

**Synthesis of  $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{Mg}$  (1).** A 1 M solution of  $\text{Bu}_2\text{Mg}$  (13.2 mL) was added all at once via syringe to a solution of  $\text{Me}_2\text{C}(\text{C}_5\text{H}_5)_2$  (2.28 g, 13.2 mmol) in 45 mL of heptane under a blanket of argon cooled to 0 °C with an ice–water bath. The reaction mixture was warmed to 70 °C. Gas evolution was observed when the reaction mixture reached ca. 60 °C, and a white precipitate formed. The reaction mixture was stirred at 70 °C overnight under argon. The product was isolated by filtration and washed twice with pentane (20 mL) to yield 2.28 g (89%) of  $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{Mg}$  as a white powder.

$^1\text{H}$  NMR ( $\text{THF}/\text{C}_6\text{D}_6$ , 300 MHz, 303 K):  $\delta$  6.06, 5.95 (m, 8 H,  $\text{C}_5\text{H}_4$ ,  $J = 2.4$  Hz), 2.15 (s, 6 H,  $\text{C}(\text{CH}_3)_2$ ).

**Synthesis of  $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{CrCO}$  (2).** THF (150 mL) was transferred under vacuum to a 500 mL Schlenk flask charged with  $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\text{Mg}$  (1.50 g, 7.70 mmol) and  $\text{CrCl}_2$  (0.95 g, 7.70 mmol) and cooled to –78 °C. An atmosphere of CO was admitted to the vessel, and the reaction mixture was gradually warmed to room temperature with stirring. After 15 h, the volatiles were removed under vacuum. Pentane-soluble product was extracted from the solid residue containing  $\text{MgCl}_2$  until the filtrate turned colorless. The combined filtrates were concentrated to 50 mL and cooled to –78 °C, affording **2** as a red-brown powder (2 crops: 0.264 g, 14%).

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  4.05 (m, 4H,  $\alpha\text{-C}_5\text{H}_4$ ,  $J = 1.8$ , 2.1 Hz), 3.75 (m, 8H,  $\beta\text{-C}_5\text{H}_4$ ,  $J = 2.1$  Hz), 0.74 (s, 6H,  $\text{C}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  256.0 (CO), 81.9 ( $\alpha\text{-C}_5\text{H}_4$ ), 76.0 ( $\beta\text{-C}_5\text{H}_4$ ), 52.7 (quat  $\text{C}_5\text{H}_4$ ), 36.8 ( $\text{C}(\text{CH}_3)_2$ ), 21.6 ( $\text{C}(\text{CH}_3)_2$ ). IR (Nujol mull, NaCl): 1916  $\text{cm}^{-1}$  (CO). Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{CrO}$ : C, 61.19; H, 5.64. Found: C, 68.38; H, 5.57. We attribute the error in the measured carbon value to the extreme air sensitivity of the complex.

Orange plate-shaped single crystals were obtained from a saturated pentane solution at –20 °C over 4 days.

**X-ray Crystal Structure Determinations of 1·2THF and 2.** Crystals of the compounds were removed from the flask and covered with a layer of hydrocarbon oil. Suitable crystals were selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream.<sup>17</sup> Data for **1**·2THF and **2** were collected at 185(2) and 87(2) K, respectively, using a Bruker/Siemens SMART APEX

instrument (Mo  $\text{K}\alpha$  radiation,  $\lambda = 0.71073$  Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using  $\omega$  scans of 0.3° per frame for 10 s, and full spheres of data were collected. A total of 2450 frames were collected with a final resolution of 0.83 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART<sup>18</sup> software and refined using SAINTPlus<sup>19</sup> on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.<sup>20</sup> The structures were solved by direct methods and refined by least-squares methods on  $F^2$  using the SHELXTL program package.<sup>21</sup> Both structures were solved in the space group  $P2_1/n$  (No. 14) by analysis of systematic absences. The coordinated THF molecules in **1**·2THF were disordered (55:45 occupancy) and held isotropic, and restraints were applied to optimize the geometry and thermal displacement. All other non-hydrogen atoms were refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

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**Supporting Information Available:** CIF files giving X-ray crystallographic information for compounds **1** and **2** and  $^1\text{H}$ ,  $^{13}\text{C}$ , HMBC, and HSQC NMR spectra for compound **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) Hope, H. *Prog. Inorg. Chem.* **1994**, *41*, 1–19.

(18) SMART version 5.626, Bruker Molecular Analysis Research Tool; Bruker AXS, Madison, WI, 2002.

(19) SAINTPlus version 6.45a, Data Reduction and Correction Program; Bruker AXS, Madison, WI, 2003.

(20) SADABS version 2.01, Empirical Absorption Correction Program; Bruker AXS, Madison, WI, 2004.

(21) Sheldrick, G. M. SHELXTL version 6.10, Structure Determination Software Suite; Bruker AXS, Madison, WI, 2001.