

# Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)<sub>2</sub>Cr: Synthesis and Crystal Structure of a Ligand-Free *ansa*-Chromocene

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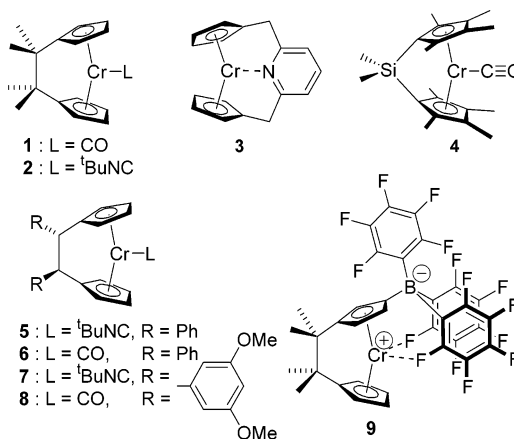
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**Summary:** Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)<sub>2</sub>Cr, the first example of an *ansa*-chromocene containing no additional ligands at chromium, was synthesized from Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)<sub>2</sub>Li<sub>2</sub> and CrCl<sub>2</sub>(THF)<sub>x</sub> in the presence of 2,6-xylyl isocyanide. The crystal structure of the complex was determined. The complex is paramagnetic and does not coordinate phosphines, phosphites, nitriles, amines, or acetylenes, but it reacts readily with 2,6-xylyl isocyanide to give mono- and diisocyanide complexes.

## Introduction

Although chromocene has been known for just over 50 years,<sup>1</sup> only a few examples of bridged *ansa*-chromocenes have been reported in the literature, mostly originating from the groups of Shapiro and Brintzinger (Chart 1).<sup>2</sup> A consistent characteristic of these complexes is their increased tendency, in comparison to unbridged chromocenes, to complete their 18-electron shell by coordinating an additional ligand, such as CO or isocyanide, to the metal center. While Cp<sub>2</sub>CrCO is only stable under an atmosphere of CO, the bridged complexes **1**, **4**, **6**, and **8** are stable in the absence of CO; complex **4** is stable even under sublimation conditions.<sup>3</sup> The preformed bending of the cyclopentadienyl rings by the *ansa* bridge seems to be mainly responsible for this behavior.<sup>4</sup> Coordination of an additional ligand to the metal center appears to be, in fact, an essential requirement for the synthesis of *ansa*-chromocene complexes: Reactions of lithium or magnesium salts of cyclopentadienyl ligands with CrCl<sub>2</sub>(THF)<sub>x</sub> in the absence of CO or isocyanide gave insoluble, uncharacterized, and probably polymeric products.<sup>2a,d</sup> Consequently, simple, bridged *ansa*-chromocenes of the general formula X(C<sub>5</sub>R<sub>4</sub>)<sub>2</sub>Cr (X

Chart 1



= bridging group) are absent from the chemical literature.<sup>5</sup> In one case, oxidation of an *ansa*-chromocene carbonyl complex to Cr(III) led to dissociation of the carbonyl ligand and formation of the CO-free complex **9**.<sup>2f</sup> In this complex, however, coordination of the anion obviously replaces the interaction with CO, as documented by the short Cr–F distances (Chart 1).<sup>2f</sup> Here, we report the surprising synthesis of Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)<sub>2</sub>Cr (**10**), the first *ansa*-chromocene without additional ligands at the chromium center, under conditions where the formation of the corresponding isocyanide adduct Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)<sub>2</sub>Cr(CNC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>) would have been expected.

## Results

**Synthesis of the Complexes.** When THF is added to a mixture of Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)<sub>2</sub>Li<sub>2</sub> and 2,6-xylyl isocyanide at 0 °C, the resulting solution turns deep blue immediately. Addition of a CrCl<sub>2</sub>(THF)<sub>x</sub> suspension in THF at 0 °C and stirring at ambient temperatures for several hours yielded, after removal of THF and extraction with pentane, Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)<sub>2</sub>Cr (**10**) in 46% yield as deep red crystals (Scheme 1). Complex **10** is paramagnetic, and in its <sup>1</sup>H NMR spectrum only one, very broad signal is observed. If a THF solution of Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)<sub>2</sub>Li<sub>2</sub> is added at 0 °C slowly to a suspension of CrCl<sub>2</sub>(THF)<sub>x</sub> and 2,6-xylyl isocyanide in THF, however, a mixture of Cr(CNC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>)<sub>6</sub> (**11**)<sup>7</sup> and the isocyanide adduct Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)<sub>2</sub>Cr(CNC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>) (**12**) was ob-

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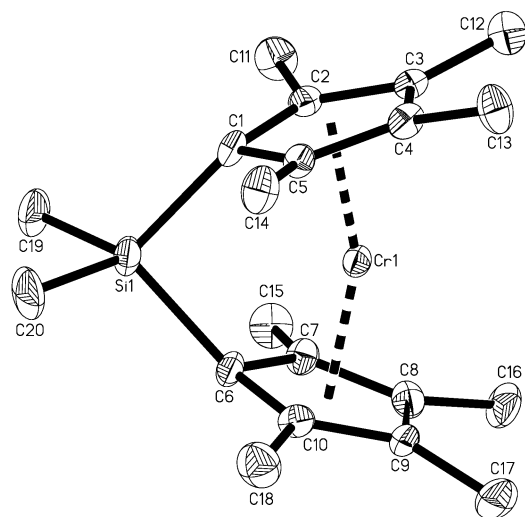
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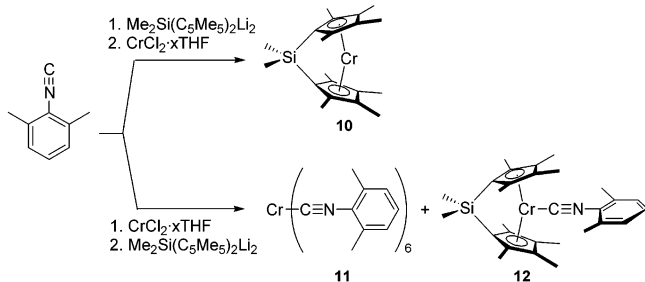
(5) A special case is **3**, where the additional ligand is incorporated in the bridge.<sup>2c</sup>

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**Figure 1.** Crystal structure of **10**. Hydrogen atoms and the second independent molecule are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

**Scheme 1**



tained, from which **12** was isolated by repeated crystallization (Scheme 1). Complex **12** is diamagnetic and its  $^1\text{H}$  NMR spectrum is in accord with  $C_{2v}$ -symmetry in solution (see the Experimental Section).

**Crystal Structures of 10 and 12.** Complex **10** crystallizes from pentane solutions in the triclinic space group  $P\bar{1}$  with two independent molecules per asymmetric unit. The crystal structure clearly displays that the steric strain resulting from the introduction of the  $\text{Me}_2\text{Si}$  bridge overrides the preference of chromocene for coplanar coordination of the cyclopentadienyl rings (Figure 1 and Table 1; details of the crystal structure determinations of **10** and **12** are given in Table 2).<sup>4b,8</sup> The  $\text{Cr}-\text{Z}(\text{Cp})$  distance ( $\text{Z}(\text{Cp})$  = centroid of the cyclopentadienyl rings) is the same as that found in  $(\text{C}_5\text{Me}_5)_2\text{Cr}$ .<sup>8</sup> While coplanar coordination of the cyclopentadienyl rings is prohibited by the silyl bridge, the  $\text{Z}(\text{Cp})-\text{Cr}-\text{Z}(\text{Cp})$  angle of  $158^\circ$  in **10** is considerably larger than corresponding values of  $143$ – $149^\circ$ , observed in *ansa*-chromocenes with CO or isocyanide coordinated

**Table 1.** Selected Bond Distances (Å) and Bond Angles ( $^\circ$ ) for **10**, **12**, and **4**

|                                          | <b>10</b>                               | <b>12</b>             | <b>4</b> <sup>a</sup> |
|------------------------------------------|-----------------------------------------|-----------------------|-----------------------|
| $\text{Cr}(1)-\text{Z}(1)^b$             | 1.785; 1.781                            | 1.818                 | 1.808                 |
| $\text{Cr}(1)-\text{Z}(2)^b$             | 1.785; 1.787                            | 1.817                 | 1.809                 |
| $\text{Cr}(1)-\text{C}(\text{Cp})^b$     | 2.077(5)–2.243(5);<br>2.073(5)–2.246(5) | 2.155(3)–<br>2.223(3) | 2.145(5)–<br>2.220(5) |
| $\text{Cr}(1)-\text{C}(21)$              |                                         | 1.876(4)              | 1.844(6)              |
| $\text{Z}(1)-\text{Cr}(1)-\text{Z}(2)^b$ | 158.3; 158.3                            | 146.1                 | 147.4                 |
| $\text{Si}(1)-\text{C}(1)-\text{Z}(1)^b$ | 148.4; 148.4                            | 153.0                 | 152.9                 |
| $\text{Si}(1)-\text{C}(6)-\text{Z}(2)^b$ | 147.6; 148.2                            | 153.7                 | 151.9                 |
| $\text{C}(1)-\text{Si}(1)-\text{C}(6)$   | 96.3(2); 96.0(2)                        | 91.15(14)             | 91.7(2)               |
| $\text{Cr}(1)-\text{C}(21)-\text{N}(1)$  |                                         | 172.0(3)              | 178.5(6) <sup>c</sup> |
| $\text{C}(21)-\text{N}(1)-\text{C}(22)$  |                                         | 153.2(3)              |                       |

<sup>a</sup> Taken from ref 2d. <sup>b</sup>  $\text{Z}(1)$  = centroid  $\text{C}(1)-\text{C}(5)$ ,  $\text{Z}(2)$  = centroid  $\text{C}(6)-\text{C}(10)$ ,  $\text{C}(\text{Cp}) = \text{C}(1)-\text{C}(10)$ . <sup>c</sup>  $\text{Cr}(1)-\text{C}(21)-\text{O}(1)$ .

to chromium (**1**, **4**, **8**, **9**, **12**).<sup>2</sup> The bending of the  $\text{C}(\text{Cp})-\text{Si}$  bond out of the mean plane of the cyclopentadienyl ring, i.e., the complementary angle to  $\angle\text{Z}(\text{Cp})-\text{C}(\text{Cp})-\text{Si}$ , which can be considered as a measure of the steric strain introduced by the bridging group, has a rather large value of  $32^\circ$  for **10**, compared to values of  $26$ – $28^\circ$  for  $\text{Me}_2\text{Si}$ -bridged complexes (**4**,<sup>2d</sup> **12**) and  $2$ – $8^\circ$  for  $\text{R}_4\text{C}_2$ -bridged (**1**, **8**, **9**)<sup>2</sup> complexes with CO or isocyanide coordinated to chromium.

Complex **12** crystallizes from pentane solution in the orthorhombic space group  $P2_12_12_1$ . Within error margins, the coordination geometry around the chromium center is identical with that observed in the CO-coordinated complex **4** (Table 1, Figure 2).  $\text{Cr}-\text{Z}(\text{Cp})$  distances are slightly longer, by  $0.02$  Å, in **12** than in **10**. This might be due either to steric interactions between the isocyanide ligand and the methyl groups at the cyclopentadienyl rings or to the antibonding nature of the HOMO in bent chromocene complexes,<sup>4b</sup> which is only singly occupied in paramagnetic **10**. The  $\text{C}(21)-\text{N}(1)-\text{C}(22)$  angle of  $153^\circ$  is significantly smaller than  $180^\circ$ , in accord with substantial back-bonding to the isocyanide ligand. There are several indications that coordination of isocyanide reduces the steric strain introduced by the silyl bridge: (i) the deviation of the  $\text{C}(\text{Cp})-\text{Si}$  bond from the mean plane of the cyclopentadienyl rings is reduced from  $32$  to  $27^\circ$ , (ii) the  $\eta^5$  coordination of chromium is more symmetric and deviations in  $\text{Cr}-\text{C}(\text{Cp})$  distances are reduced from  $\pm 0.09$  to  $\pm 0.03$  Å, and (iii) the  $\text{Z}(\text{Cp})-\text{Cr}-\text{Z}(\text{Cp})$  angle is smaller by  $12^\circ$  in **12** than in **10**.

**Reactivity of 10.** NMR-scale reactions of **10** with  $\text{P}(\text{O}^i\text{Pr})_3$ ,  $\text{P}(\text{OMe})_3$ ,  $\text{PMe}_3$ ,  $\text{CH}_3\text{CN}$ ,  $\text{NMe}_3$ ,  $\text{NEt}_3$ , 1-hexene,  $\text{PhCCPh}$  and  $\text{Me}_3\text{SiCCSiMe}_3$  did not lead to any coordination products detectable by NMR.<sup>9</sup> Reaction of **10** with 2,6-xylyl isocyanide, however, immediately yielded the isocyanide complex **12**.<sup>10</sup> Under otherwise identical conditions, no coordination of 2,6-xylyl isocyanide to  $\text{Cp}_2\text{Cr}$  or  $\text{Cp}^*_2\text{Cr}$  was observed in NMR control experiments.

(7) (a) Single crystals of **11** were obtained in small amounts during the recrystallization of the crude reaction mixture containing **11** and **12** (Table 2). The values  $d_{\text{Cr}-\text{C}} = 1.92$  Å,  $\angle\text{Cr}-\text{C}-\text{N} = 177$ – $178^\circ$ , and  $\angle\text{C}-\text{N}-\text{C} = 165$ – $170^\circ$  are in the range expected for hexakis(isocyanide)chromium(0) complexes ( $d_{\text{Cr}-\text{C}} = 1.87$ – $1.96$  Å,  $\angle\text{Cr}-\text{C}-\text{N} = 174$ – $178^\circ$ , and  $\angle\text{C}-\text{N}-\text{C} = 150$ – $173^\circ$ ). (b) Ljungstrom, E. *Acta Chem. Scand. A* **1978**, 32, 47. (c) Lentz, D. J. *Organomet. Chem.* **1990**, 381, 205. (d) Anderson, K. A.; Scott, B.; Wherland, S.; Willett, R. D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, 47, 2337. (e) Acho, J. A.; Lippard, S. J. *Organometallics* **1994**, 12, 1294. (f) Barybin, M.; Holovics, T. C.; Deplazes, S. F.; Lushington, G. H.; Powell, D. R.; Toriyama, M. *J. Am. Chem. Soc.* **2002**, 124, 13668.

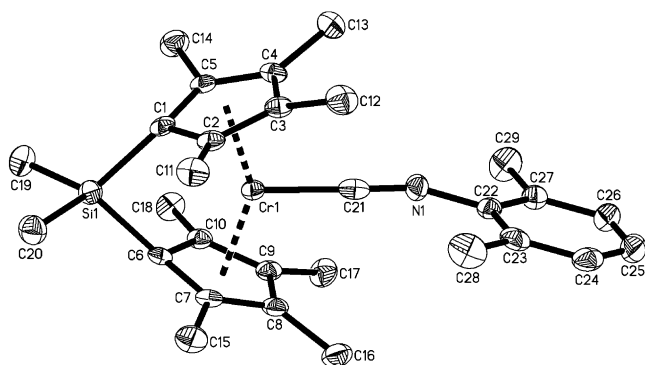
(8) Blümel, J.; Herker, M.; Hiller, W.; Köhler, F. H. *Organometallics* **1996**, 15, 3474.

(9) Some evidence for an interaction between diphenylacetylene and **10** might be derived from a series of  $m/z = m(\text{10}) + n \times m(\text{PhCCPh})$  ( $n = 1$ – $4$ ) in EI or FAB mass spectra of mixtures of **10** and diphenylacetylene after evaporation of the volatiles. This series was not observed when the residue was exposed to air. No analogous series of  $m/z = x + n \times m(\text{PhCCPh})$  were observed in mass spectra of **10**, diphenylacetylene,  $\text{Cp}_2\text{Cr}$ /diphenylacetylene mixtures, or  $\text{Cp}^*_2\text{Cr}$ /diphenylacetylene mixtures.

Table 2. Details of the Crystal Structure Determinations<sup>a</sup>

|                                                    | 10                                   | 12                                            | 11                                               |
|----------------------------------------------------|--------------------------------------|-----------------------------------------------|--------------------------------------------------|
| formula                                            | C <sub>20</sub> H <sub>30</sub> CrSi | C <sub>29</sub> H <sub>39</sub> CrNSi         | C <sub>54</sub> H <sub>54</sub> CrN <sub>6</sub> |
| CCSD no. <sup>b</sup>                              | 230672                               | 230673                                        | 230674                                           |
| diffractometer used                                | Enraf-Nonius CAD4                    | Enraf-Nonius CAD4                             | Bruker P4                                        |
| M <sub>w</sub> ; F(000)                            | 350.53; 752                          | 481.70; 1032                                  | 839.03; 444                                      |
| cryst color and form                               | deep red plates                      | deep blue cubes                               | red plates                                       |
| cryst size (mm)                                    | 0.3 × 0.2 × 0.1                      | 0.4 × 0.4 × 0.4                               | 0.2 × 0.2 × 0.1                                  |
| T (K); d <sub>calcd</sub> (g/cm <sup>3</sup> )     | 153; 1.277                           | 173; 1.250                                    | 233; 1.180                                       |
| cryst syst                                         | triclinic                            | orthorhombic                                  | triclinic                                        |
| space group                                        | P $\bar{1}$                          | P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> | P $\bar{1}$                                      |
| unit cell                                          |                                      |                                               |                                                  |
| a (Å)                                              | 10.068(2)                            | 10.002(2)                                     | 10.761(6)                                        |
| b (Å)                                              | 12.804(3)                            | 12.855(3)                                     | 11.709(6)                                        |
| c (Å)                                              | 15.302(3)                            | 19.902(4)                                     | 11.885(5)                                        |
| α (deg)                                            | 100.87(4)                            | 90                                            | 108.78(4)                                        |
| β (deg)                                            | 105.80(6)                            | 90                                            | 102.63(5)                                        |
| γ (deg)                                            | 98.45(2)                             | 90                                            | 114.25(4)                                        |
| V (Å <sup>3</sup> ); Z                             | 1822.6(6); 4                         | 2558.9(9); 4                                  | 1181.1(10); 1                                    |
| θ range (deg); completeness (%)                    | 2.2–25.0; 99.9                       | 2.1–23.0; 99.5                                | 2.2–24.0; 83.7                                   |
| no. of collected/indep rflns; R <sub>int</sub> (%) | 6788/6382; 4.09                      | 4046/3522; 2.05                               | 3313/3108; 6.23                                  |
| μ (mm <sup>-1</sup> ); abs cor                     | 0.689; none                          | 0.511; none                                   | 0.284; none                                      |
| R1(F); wR2(F <sup>2</sup> ) (I > 2σ(I)) (%)        | 5.63; 12.62                          | 3.19; 7.16                                    | 7.28; 12.18                                      |
| R1(F); wR2(F <sup>2</sup> ) (all data) (%)         | 13.08; 15.06                         | 4.45; 7.67                                    | 17.33; 15.83                                     |
| GO(F <sup>2</sup> ); Flack X                       | 0.996                                | 0.981; 0.00(2)                                | 1.020                                            |
| resid electron dens (e Å <sup>-3</sup> )           | 0.814                                | 0.172                                         | 0.215                                            |

<sup>a</sup> Conditions: Mo Kα radiation (71.073 pm); graphite monochromator. Crystal decay was monitored by measuring 3 standard reflections every 100 reflections or every 1 h. Structures were solved using direct methods.<sup>16</sup> All non-hydrogen atoms were refined anisotropically by least-squares procedures based on  $F^2$ . Hydrogens were refined on calculated positions with fixed isotropic  $U$  values, using riding model techniques.<sup>16</sup> <sup>b</sup> Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033.



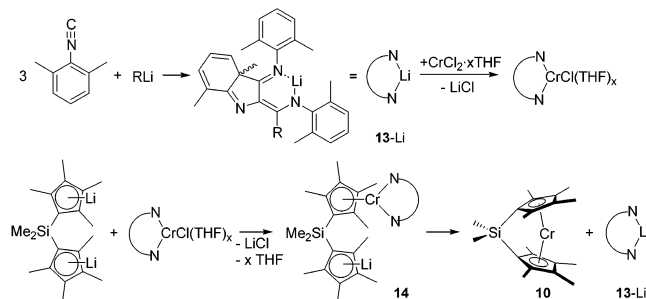
**Figure 2.** Crystal structure of **12**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

## Discussion

The crystal structure of **10** confirms not only that coordination of an additional ligand to the chromium center is stabilized by the bridging of the cyclopentadienyl rings but also that the absence of such a ligand enhances the steric strain in the complex introduced by the bridge. The question thus arises as to why **10** is obtained from 2,6-xylyl isocyanide/ligand lithium salt mixtures but not by direct reaction of the ligand lithium

(10) In the presence of excess isocyanide **12** is converted slowly over hours to a  $C_1$ -symmetric diisocyanide complex. Due to the strong similarity of its NMR spectrum with that of  $\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)[\eta^2\text{-C}_5\text{Me}_3(\text{H})(\eta^1\text{-CH}_2)]\text{Cr}(\text{CO})_2$ , which was obtained by reaction of  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)\text{Cr}(\text{CO})$  with excess  $\text{CO}$ ,<sup>2d</sup> the diisocyanide adduct is most probably  $\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)[\eta^2\text{-C}_5\text{Me}_3(\text{H})(\eta^1\text{-CH}_2)]\text{Cr}(\text{CNC}_6\text{Me}_2\text{H}_3)_2$ . If **10** is obtained as a powder instead of crystalline material from the pentane solutions, reaction with 2,6-xylyl isocyanide yields a mixture of mono- and diisocyanide adducts immediately. The presence of  $\text{Cr}^{\text{III}}$  impurities might catalyze the isocyanide addition to **12** by way of an electron-transfer mechanism, as observed for the CO addition to  $\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{-CrCO}$  (Van Raaij, E. U.; Brintzinger, H.-H. *J. Organomet. Chem.* **1988**, 356, 315).

## Scheme 2



salt with  $\text{CrCl}_2(\text{THF})_x$ . The fast reaction of **10** with 2,6-xylyl isocyanide clearly indicates that major amounts of isocyanide cannot be present in reaction mixtures from which **10** was isolated. A probable fate of the isocyanide might be the trimerization to **13-Li**, which was reported for the reaction of 2,6-xylyl isocyanide with  $\text{MeLi}$  or  $n\text{BuLi}$  (Scheme 2).<sup>11</sup> The anionic ligand **13** is structurally analogous to diphenyl-“nacnac” ligands, which have been shown to react with  $\text{CrCl}_2$  salts with substitution of chloride.<sup>12</sup> Diphenyl-“nacnac” or -diimine ligands with substituents in the ortho position of the phenyl groups are employed as ligands for olefin polymerization catalysts and are to be considered as sterically bulky ligands, due to the perpendicular orientation of the phenyl rings.<sup>13</sup> We thus propose the reaction mechanism outlined in Scheme 2 for the formation of **10**: reaction of 2,6-xylyl isocyanide with

(11) (a) The color of a THF solution of the reaction product was reported to be deep blue. (b) Murakami, M.; Ito, H.; Ito, Y. *Chem. Lett.* **1996**, 7.

(12) (a) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Eur. J. Inorg. Chem.* **2001**, 1895. (b) MacAdams, L. A.; Kim, W.-K.; Liable-Sands, L. M.; Guzei, I. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **2002**, 21, 952.

(13) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, 103, 283.

$\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{Li}_2$  (or possibly also with  $n\text{BuLi}$  if present as an impurity) yields the trimerization product **13**-Li, which reacts with  $\text{CrCl}_2(\text{THF})_x$  by substitution of a chloride ligand to form **13**- $\text{CrCl}(\text{THF})_x$  (or its dimer  $\{\text{13-Cr}(\mu\text{-Cl})\}_2$ ).<sup>12b</sup> Reaction of **13**- $\text{CrCl}(\text{THF})_x$  with the remaining  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{Li}_2$  yields the monocyclopentadienyl complex **14**. Coordination of the second cyclopentadienyl ring then proceeds with elimination of **13**-Li and formation of **10**, since the 20-electron complex  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{Cr}(\text{13})]\text{Li}$  is disfavored by steric as well as by electronic effects.

Three reasons seem thus to be responsible for the unexpected formation of **10**:<sup>14</sup> (i) trimerization of 2,6-xylyl isocyanide to the bulky, chelating anion **13**, (ii) reaction of **13**-Li with  $\text{CrCl}_2(\text{THF})_x$ , which prevents the formation of polymeric products in the same way that CO or isocyanides do, and (iii) the steric demand and the anionic, chelating nature of **13**, which leads to its elimination from the complex upon coordination of the second cyclopentadienyl ring. Since **13**-Li is regenerated in the reaction sequence depicted in Scheme 3 and since **13**- $\text{CrCl}(\text{THF})_x$  is probably more soluble and thus more reactive than  $\text{CrCl}_2(\text{THF})_x$ , it might not be necessary that **13**-Li is present in stoichiometric amounts. In agreement with this proposal, the isolated yield of **10** is higher, even after crystallization, than the theoretical yield of **13**-Li.

To establish whether the presence of an anionic, chelating ligand of the type  $\text{N}^-\text{N}^-$  represents a general synthetic route to *ansa*-chromocene complexes, subsequent investigations will be aimed at the synthesis of defined  $(\text{N}^-\text{N})\text{CrCl}$  complexes and their use as precursors for *ansa*-chromocene syntheses.

### Experimental Section

All reactions were carried out under an argon or nitrogen atmosphere using Schlenk-line or glovebox techniques. THF and pentane were distilled from Na under an argon atmosphere and degassed at  $-78^\circ\text{C}$  under a dynamic vacuum.  $\text{C}_6\text{D}_6$  was dried over molecular sieves (4 Å).  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{Li}_2$ <sup>2d</sup> and  $\text{CrCl}_2(\text{THF})_x$ <sup>15</sup> were synthesized as described in the literature. All other chemicals were obtained from commercial suppliers and used as received.

**$\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)_2\text{Cr}$  (**10**).** A mixture of  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{Li}_2$  (200 mg, 0.64 mmol) and 2,6-xylyl isocyanide (105 mg, 0.80 mmol) was cooled to  $0^\circ\text{C}$ . THF (15 mL)

was cooled to  $0^\circ\text{C}$  and added to this mixture via syringe to yield a deep blue-violet solution.  $\text{CrCl}_2(\text{THF})_x$  (180 mg) was suspended in THF (15 mL) and added over a period of 45 min, while the temperature was kept at  $0^\circ\text{C}$ . The ice bath was removed and the reaction mixture was stirred overnight to yield a brown solution. The solvent was removed under vacuum and the residue extracted with pentane ( $6 \times 10$  mL) until the filtrate was nearly colorless. The brown filtrate was concentrated to ca. 20 mL and cooled to  $-80^\circ\text{C}$ . After 3 days, deep red crystals of **10** were isolated by filtration (104 mg, 46%). Anal. Calcd for  $\text{C}_{20}\text{H}_{30}\text{CrSi}$ : C, 68.53; H, 8.63. Found: C, 68.24; H, 8.78. EI-MS (70 eV,  $185^\circ\text{C}$ ): 350 (100%,  $\text{M}^+$ ), 335 (5%,  $\text{M}^+ - \text{Me}$ ), 320 (4%,  $\text{M}^+ - 2\text{Me}$ ), 175 (7%,  $\text{M}^{2+}$ ), 52 (40%,  $\text{Cr}^+$ ). UV/vis (methylcyclohexane, 296 K): 278 nm,  $\epsilon > 6000$  L/(mol cm); 348 nm,  $\epsilon = 3800$  L/(mol cm); 506 nm,  $\epsilon = 430$  L/(mol cm).

**$\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)_2\text{Cr}(\text{CNC}_6\text{Me}_2\text{H}_3)$  (**12**).** A mixture of  $\text{CrCl}_2(\text{THF})_x$  (357 mg) and 2,6-xylyl isocyanide (205 mg, 1.6 mmol) in THF (30 mL) was cooled to  $0^\circ\text{C}$ . A solution of  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{Li}_2$  (400 mg, 1.3 mmol) in THF (30 mL) was added over a period of 1 h. The ice bath was removed and the reaction mixture stirred for 3 h. The solvent was evaporated and the residue extracted with pentane ( $3 \times 30$  mL). The solution was concentrated to 20 mL and cooled to  $-80^\circ\text{C}$ . Filtration yielded a mixture of "black" crystals of **12** and red powder of  $\text{Cr}(\text{CNC}_6\text{Me}_2\text{H}_3)_6$  (**11**). Repeated crystallization from pentane yielded pure **12** (62 mg, 0.13 mmol, 9.9%). Anal. Calcd for  $\text{C}_{29}\text{H}_{39}\text{CrNSi}$ : C, 72.30; H, 8.16; N, 2.91. Found: C, 71.45; H, 8.29; N, 3.23.  $^1\text{H}$  NMR (296 K,  $\text{C}_6\text{D}_6$ ):  $\delta$  6.6–7.0 (m, 3H), 2.48 (s, 6H,  $\text{C}_6\text{Me}$ ), 1.79 (s, 12H,  $\beta\text{-C}_5\text{Me}$ ), 1.64 (s, 12H,  $\alpha\text{-C}_5\text{Me}$ ), 0.57 (s, 6H,  $\text{SiMe}$ ). IR (pentane):  $1950\text{ cm}^{-1}$  ( $\nu_{\text{CN}}$ ).

**$\text{Cr}(\text{CNC}_6\text{Me}_2\text{H}_3)_6$  (**11**).** Small quantities of crystalline **11** were obtained by slow evaporation of a solution containing a mixture of **11** and **12**, followed by hand-picking red crystals of **11**.  $^1\text{H}$  NMR (296 K,  $\text{C}_6\text{D}_6$ ):  $\delta$  n.r., 6.78 (m, 2H), 2.48 (s, 6H,  $\text{C}_6\text{Me}$ ).

**NMR-Scale Reactions.** Two to four equivalents of the desired ligand were added, by use of Eppendorf pipets in the case of liquids, in the glovebox to an NMR tube containing a red solution of **10** (10 mg, 0.03 mmol) in  $\text{C}_6\text{D}_6$  (0.6 mL). The tube was sealed with a rubber stopper. NMR spectra were recorded immediately after mixing and after storing the NMR tube for 24 h at ambient temperatures under an inert atmosphere. With the exception of 2,6-xylyl isocyanide, neither a color change nor NMR signals indicating the formation of an 18-electron complex were observed.

**Supporting Information Available:** Details of the crystal structure determinations for **10**–**12**; these data are also available as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(14) While it might be debatable whether complex **10** is a Cr(III) hydride, the absence of any extra electron density attributable to a hydride ligand in the vicinity of the Cr center in the crystal structure data and the clean and complete conversion of **10** to **12** without detectable side products provide evidence for the correct structural assignment of **10**.

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