Synthesis and Structure of $[Cr\{(\eta^6\text{-}C_6H_5)_2B\{NtBu(SiMe_3)\}\}]$ and $[Cr\{(\eta^6\text{-}C_6H_5)_2(BNMe_2)_2\}]$, the First Boron-Bridged Metalloarenophanes

Holger Braunschweig,*,† Melanie Homberger,‡ Chunhuas Hu,‡ Xiaolai Zheng,‡
Emanuel Gullo,† Guy Clentsmith,† and Matthias Lutz†

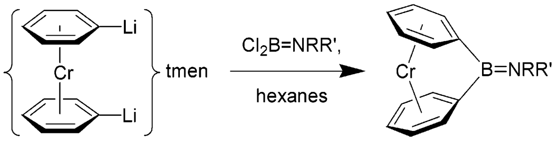
Institut für Anorganische Chemie, Universität Würzburg, Am Hubland,
D-97074 Würzburg, Germany, and Institut für Anorganische Chemie der
Technischen Hochschule, D-52056 Aachen, Germany

Received February 23, 2004

*Summary: Reaction of $[Cr(\eta^6\text{-}C_6H_5Li)_2]\cdot$tmen with (RR′)-$NBCl_2$ (R = R′ = $SiMe_3$; R = R′ = iPr; R = $SiMe_3$, R′ = tBu) and $B_2Br_2(NMe_2)_2$, respectively, in hexane yielded the strained [1]borachromoarenophanes $[Cr\{(\eta^6\text{-}C_6H_5)_2\text{-}BNRR'\}]$ (**4a**−**c**; R = R′ = $SiMe_3$; R = R′ = iPr; R = $SiMe_3$, R′ = tBu) and [2]borachromoarenophanes $[Cr\{(\eta^6\text{-}C_6H_5)_2(BNMe_2)_2\}]$ (**5**), respectively, in moderate yields as dark red solids; compounds **4c** and **5** were structurally characterized. **4c** exhibits the largest arene−arene tilt angle (26.6(3)°) reported for any [n]metalloarenophane.*

Our recent investigations on both strained[1] and unstrained[2a−e] [1]borametallocenophanes led to compounds of the type $[Fe\{(\eta^5\text{-}C_5H_4)_2BNR_2\}]$ (**1**; R = various ligands), which represent the first examples of [1]-ferrocenophanes with a bridging first-row element. Such strained *ansa*-ferrocenes are well-known with various bridging main-group elements as well as transition metals and have attracted considerable interest, due to their possible use as precursor molecules for the synthesis of novel organometallic polymers via ring-opening polymerization (ROP).[3] In contrast to the well-documented chemistry of [1]ferrocenophanes, related [1]-metalloarenophanes have been scarcely investigated and are restricted to a very few silicon- and germanium-bridged chromium and vanadium complexes of the type $[M\{(\eta^6\text{-}C_6H_5)_2ER_2\}]$ (**2a**,**b**, M = Cr, E = Si, R = Me, Ph; **3**, M = V, E = Si, R = various ligands).[4]

The present paper reports on the syntheses and full characterizations of the complexes $[Cr\{(\eta^6\text{-}C_6H_5)_2\text{-}BNRR'\}]$ (**4a**−**c**: R = R′ = $SiMe_3$; R = R′ = *i*Pr; R = $SiMe_3$, R′ = *t*Bu) and $[Cr\{(\eta^6\text{-}C_6H_5)_2(BNMe_2)_2\}]$ (**5**) as the first examples of [1]- and [2]metalloarenophanes with a bridging first-row element. Compounds **4a**−**c** were obtained from reactions of the corresponding aminodihaloboranes with a suspension of $[Cr(\eta^6\text{-}C_6H_5\text{-}Li)_2]\cdot$tmen according to eq 1 and isolated as dark red crystalline solids in yields ranging from 42% to 48%.[5] All complexes are extremely sensitive toward air and moisture and decompose readily in polar solvents such as MeOH, CH_2Cl_2, DMF, and DME at ambient temperature with formation of $[Cr\{(\eta^6\text{-}C_6H_6)_2]$ and various phenylborane species. This enhanced sensitivity in solvents commonly used as electrochemical standard mediums prevented collection of CV data: similar behavior was reported for the silicon analogues **2a**,**b**.[4]



4a; R, R′ = $SiMe_3$
4b; R, R′ = *i*Pr
4c; R = $SiMe_3$, R′ = *i*Pr

The NMR spectroscopic data, which closely resemble those of **2a**,**b**, indicate a significantly tilted structure

---

* To whom correspondence should be addressed. Tel: +49 (0)931 888 5260. Fax: +49 (0)931 888 4623. E-mail: holger.braunschweig@mail.uni-wuerzburg.de.

† Universität Würzburg.

‡ Technische Hochschule Aachen.

(1) (a) Braunschweig, H.; Dirk, R.; Müller, M.; Nguyen, P.; Gates, D. P.; Manners, I. *Angew. Chem.* **1997**, *109*, 2433; *Angew. Chem., Int. Ed.* **1997**, *36*, 2338. (b) Braunschweig, H.; Dirk, R.; Englert, U.; Berenbaum, A.; Jäkle, F.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 5765.

(2) (a) Braunschweig, H.; von Koblinski, C.; Wang, R. *Eur. J. Inorg. Chem.* **1999**, 69. (b) Braunschweig, H.; von Koblinski, C.; Mamuti, M.; Englert, U.; Wang, R. *Eur. J. Inorg. Chem.* **1999**, 1899. (c) Braunschweig, H.; von Koblinski, C.; Englert, U. *Chem. Commun.* **2000**, 1049. (d) For other structurally authentic [1]borazirconocenophanes with three-coordinate boron see: Ashe, A. J.; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 2288. (e) For a recent review on boron-bridged group 4 *ansa*-metallocenes see: Shapiro, P. J. *Eur. J. Inorg. Chem.* **2001**, 321. (f) Braunschweig, H.; Breitling, F. M.; Gullo, E.; Kraft, M. *J. Organomet. Chem.* **2003**, *680*, 31.

(3) (a) Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1980**, *194*, 91. (b) Seyferth, D.; Withers, H. P. *Organometallics* **1982**, *1*, 1275. (c) Broussier, R.; Da Rold, A.; Gautheron, B.; Dromzee, Y.; Jeannin, Y. *Inorg. Chem.* **1990**, *29*, 1817. (d) Broussier, R.; Da Rold, A.; Gautheron, B.; Dromzee, Y.; Jeannin, Y. *J. Organomet. Chem.* **1992**, *427*, 231. (e) Pudelski, J. K.; Gates, D. P.; Rulkens, R.; Lough, A. J.; Manners, I. *Angew. Chem.* **1995**, *107*, 1633; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1506. (f) Herberhold, M. *Angew. Chem.* **1995**, *107*, 1985; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1837. (g) Rulkens, R.; Lough, A. J.; Manners, I. *Angew. Chem.* **1996**, *108*, 1929; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1805. (h) Manners, I. *Angew. Chem.* **1996**, *108*, 1712; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602 and references therein.

(4) For chromium species see: (a) Elschenbroich, C.; Hurley, J.; Metz, B.; Massa, W.; Baum, G. *Organometallics* **1990**, *9*, 889. (b) Hultzsch, K. C.; Nelson, J. M.; Lough, A. J.; Manners, I. *Organometallics* **1995**, *14*, 5496. (c) Elschenbroich, C.; Schmidt, E.; Gondrum, R.; Metz, B.; Burghaus, O.; Massa, W.; Wocadlo, S. *Organometallics* **1997**, *16*, 4589. For vanadium species see: (d) Elschenbroich, C.; Bretschneider-Hurley, A.; Hurley, J.; Massa, W.; Wocadlo, S.; Pebler, J.; Reijerse, E. *Inorg. Chem.* **1993**, *32*, 5421. (e) Elschenbroich, C.; Bretschneider-Hurley, A.; Hurley, J.; Behrendt, A.; Massa, W.; Wocadlo, S.; Reijerse, E. *Inorg. Chem.* **1995**, *34*, 743.

10.1021/om049872q CCC: \$27.50

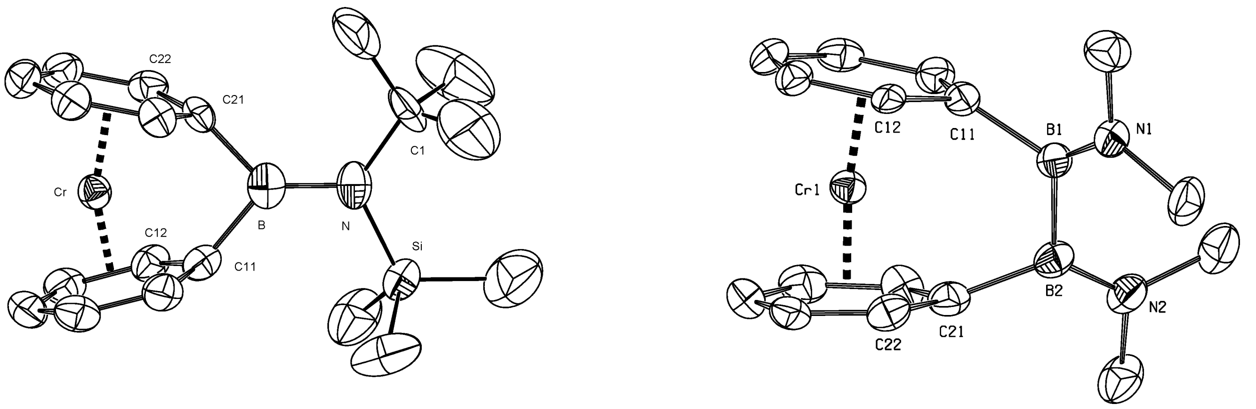
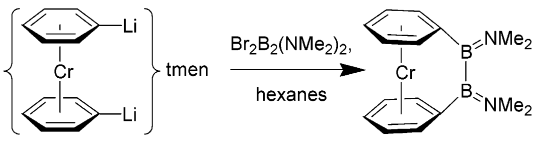


Figure 1. Molecular structures of **4c** (left) and **5** (right).[9] Selected distances (Å) and angles (deg) for **4c**: B−N = 1.398(6), B−C21 = 1.601(7), B−C11 = 1.617(7), C11−C12 = 1.410(6), C14−C15 = 1.385(7), Cr−C11 = 2.084(5), Cr−C14 = 2.182(5); C11−B−N1 = 129.3(5). Selected distances (Å) and angles (deg) for **5**: B1−N1 = 1.390(9), B1−B2 = 1.718(12), B2−N2 = 1.376(9), B2−C21 = 1.590(10), C21−C22 = 1.432(8), C14−C15 = 1.396(8), Cr−C11 = 2.142(6), Cr−C14 = 2.159(6),; C11−B1−N1 = 120.3(5), N1−B1−B2 = 129.4(6), N2−B2−B1 = 127.3(6).

for **4a**−**c** in solution.[4a−c] In particular, the high-field-shifted and separated ^{1}H NMR signals for the ortho, meta, and para hydrogen atoms of the aryl ligands ranging from δ 3.63 to 4.77 ppm corroborate the presence of strained molecules.[4b] The ^{11}B NMR resonances between δ 43.2 and 50.4 ppm match those of **1**, thus being in the expected range for aminodiarylboranes.

According to the aforementioned synthesis the related [2]borachromoarenophane [Cr{(η^6-C_6H_5)$_2$($BNMe_2$)$_2$}] (**5**) was obtained in 39% yield as a crystalline solid from reaction of the diborane(4) $B_2Br_2(NMe_2)_2$ (eq 2).[6] Although showing a similar appearance with respect to color and sensitivity, the diboron-bridged species **5** represents a significantly less strained molecule. For example, this becomes evident from the less shielded resonances (δ 4.46−4.69 ppm) of the aryl protons in the ^{1}H NMR spectrum. Those signals are also less separated, thus showing only one broad resonance for the meta and para hydrogen atoms. Further spectroscopic data such as the ^{11}B NMR signal at δ 46.3 ppm meet the expectations.



5

The different geometries for the monoboron- and diboron-bridged complexes in solution, as already indicated by the NMR spectroscopic data, were proven by X-ray structure determinations (Figure 1).[7] Suitable single crystals of **4c** and **5** were obtained from hexane at −30 °C. [Cr{(η^6-C_6H_5)$_2$B{N*t*Bu($SiMe_3$)}}] (**4c**) crystallizes in the monoclinic space group $P2_1/c$, and the molecule adopts approximate C_s symmetry in the crystal. The much greater tilt angle of 26.6(3)° with respect to 14.4° for the silylene-bridged analogue [Cr{(η^6-C_6H_5)$_2$-$SiMe_2$}] (**2b**)[4b] proves the expected effect of the small bridging boron atom, which affords a molecule with a significantly greater intrinsic strain. As a consequence, the Cr−C_{ipso} distances are smaller while the Cr−C_{para} distances are larger in **4c** than in **2b**. The two benzene rings adopt an almost eclipsed position, indicated by the torsion angle cg1−C11−C21−cg2 = 2.0(5)°. The diboron-bridged complex [Cr{(η^6-C_6H_5)$_2$($BNMe_2$)$_2$}] (**5**) crystallizes in the orthorhombic space group $Pna2_1$, and the molecule adopts C_2 symmetry in the crystal. The significantly decreased strain of **5** in comparison with **4c** is reflected in a smaller tilt angle of only 10.1(3)°. The benzene rings adopt now a staggered geometry, as

---

(5) Spectroscopic data for **4a**: ^{1}H NMR δ 0.43 (s, 18 H; $SiMe_3$), 3.63 (m, 4 H; *o*-C_6H_5), 4.53 (m, 4 H; *m*-C_6H_5), 4.73 (m, 2 H; *p*-C_6H_5); ^{11}B{^{1}H} NMR: δ 50.4; ^{13}C{^{1}H} NMR δ 5.39 ($SiMe_3$), 74.84, 79.52, 82.32 (C_6H_5); MS (70 eV) *m*/*z* (%) 377 (12) [M^+], 325 (15) [M^+ − Cr], 310 (53) [M^+ − Cr − CH_3], 299 (19) [M^+ − C_6H_5], 248 (19) [M^+ − C_6H_5 − Cr], 160 (14) [(Me_3Si)$_2$N], 78 (6) [C_6H_5], 73 (38) [$SiMe_3$], 52 (2) [Cr]. Anal. Calcd for $C_{18}H_{28}BCrNSi_2$: C, 57.27; H, 7.48; N, 3.71. Found: C, 57.00; H, 7.28; N, 3.83. Spectroscopic data for **4b**: ^{1}H NMR δ 1.25 (d, ^3J(H,H) = 7.02 Hz, 12 H; Me), 3.63 (sept, ^3J(H,H) = 7.02 Hz, 2 H; $CHMe_2$), 3.82 (m, 4 H; *o*-C_6H_5), 4.59 (m, 4 H; *m*-C_6H_5), 4.77 (m, 2 H; *p*-C_6H_5); ^{11}B{^{1}H} NMR δ 43.2; ^{13}C{^{1}H} NMR δ 24.44 (Me), 48.68 ($CHMe_2$), 74.69, 79.83, 82.31 (C_6H_5); MS (70 eV) *m*/*z* (%) 265 (18) [M^+ − Cr], 250 (100) [M^+ − Cr − CH_3], 165 (15) [M^+ − *i*Pr_2N − Cr], 100 (2) [*i*Pr_2N], 78 (6) [C_6H_5], 58 (6) [*i*PrN], 52 (4) [Cr]. Anal. Calcd for $C_{18}H_{24}BCrN$: C, 68.14; H, 7.63; N, 4.42. Found: C, 67.98; H, 7.51; N, 4.39. Spectroscopic data for **4c**: ^{1}H NMR δ 0.49 (s, 9 H; $SiMe_3$), 1.54 (s, 9 H; *t*Bu), 3.66 (m, 4 H; *o*-C_6H_5), 4.55 (m, 4 H; *m*-C_6H_5), 4.72 (m, 2 H; *p*-C_6H_5); ^{11}B{^{1}H} NMR δ 47.41; ^{13}C{^{1}H} NMR δ 6.47 ($SiMe_3$), 34.70 (*t*Bu), 73.12, 73.93, 79.18, 79.23, 82.18 (C_6H_5); MS (70 eV) *m*/*z* (%) 361 (3) [M^+], 309 (2) [M^+ − Cr], 294 (100) [M^+ − Cr − CH_3], 238 (10) [M^+ − Cr − $SiMe_3$], 222 (8) [M^+ − Cr − $SiMe_3$ − CH_3], 165 (9) [M^+ − Cr − *t*BuN$SiMe_3$], 144 (79) [*t*BuN$SiMe_3$], 73 (72) [$SiMe_3$], 57 (56) [*t*Bu], 52 (12) [Cr]. Anal. Calcd for $C_{19}H_{24}BCrNSi$: C, 63.14; H, 7.81; N, 3.88. Found: C, 62.84; H, 7.24; N, 3.61.

(6) Spectroscopic data for **5**: ^{1}H NMR δ 2.80 (s, 6H; Me_2N), 2.84 (s, 6H; Me_2N), 4.46 (br, 6 H; *m*-/*p*-C_6H_5), 4.69 (br s, 4 H, *o*-C_6H_5); ^{11}B{^{1}H} NMR δ 46.3; ^{13}C{^{1}H} NMR δ 0.59 (Me_2N), 43.68 (Me_2N), 77.22, 78.22, 80.36 (C_6H_5); MS (70 eV) *m*/*z* (%) 316 (100) [M^+], 273 (22) [M^+ − NMe_2], 263 (16) [M^+ − Cr], 211 (2) [M^+ − (Me_2N)$_2B_2$], 132 (14) [M^+ − Cr − $Me_2NBC_6H_5$], 51 (30) [Cr]. Anal. Calcd for $C_{16}H_{22}B_2CrN_2$: C, 60.80; H, 7.02; N, 8.87. Found: C, 60.95; H, 6.82; N, 8.54.

(7) Crystal data for **4c**: $C_{19}H_{28}BCrNSi$, M_r = 361.33, monoclinic, space group $P2_1/c$ (No. 14), a = 6.391(4) Å, b = 11.612(2) Å, c = 25.490(3) Å, β = 97.13(2)°, V = 1877(1) Å^3, Z = 4, ρ_{calcd} = 1.28 cm^{-3}, μ(Mo Kα) = 0.66 mm^{-1}, T = 223(2) K. 8109 reflections measured, of which 4075 were unique (R_{int} = 0.070), solution by direct methods,[8a] refinement[8b] on F^2 to R1 = 0.069 for observed data and wR2 = 0.169 for all data. Crystal data for **5**: $C_{16}H_{22}B_2CrN_2$, M_r = 315.98, orthorhombic, space group $Pna2_1$ (No. 33), a = 18.989(4) Å, b = 8.7368(8) Å, c = 9.422(3) Å, V = 1563.2(5) Å^3, Z = 4, ρ_{calcd} = 1.34 Mg m^{-3}, μ(Mo Kα) = 0.72 mm^{-1}, T = 203(2) K, 3367 reflections measured, of which 3054 were unique (R_{int} = 0.045), solution by direct methods,[8a] refinement[8b] on F^2 to R1 = 0.062 for observed data and wR2 = 0.161 for all data.

(8) (a) Sheldrick, G. M. SHELXS-97, Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, 1997. (b) Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

(9) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

indicated by the torsion angle cg1−C11−C21−cg2 = 11.4(5)°. Besides, the boron−nitrogen (1.390(9) and 1.376(9) Å) and boron−boron distances (1.718(12) Å) are in the expected range for B−N double and B−B single bonds, respectively. Currently, investigations on utilizing the aforementioned borachromoarenophanes as precursors for the buildup of polymeric materials are in progress. Preliminary polymerization studies show that **4a** undergoes ring opening upon treatment with BuLi with formation of dimers, as indicated by mass spectrometry. Thermally induced ROP, however, appears to be less suitable, since heating of the [1]-borachromoarenophanes to temperatures above 200 °C is accompanied by decomposition and deposition of chromium metal.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Text detailing the synthetic procedures and the structure determination details for **4c** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-157467 (**4c**) and CCDC-157467 (**5**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, (+44)1223-336-033; E-mail, deposit@ccdc.cam.ac.uk).

OM049872Q