Synthesis and Structure of Trinuclear Boryloxycarbyne Complexes

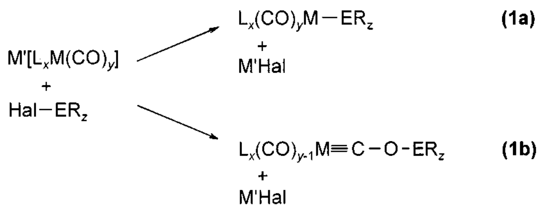
Holger Braunschweig,*[a] Carsten Kollann,[a] Margot Koster,[a] Ulli Englert,[a]
and Matthias Müller[b]

Keywords: Boron / Iron / Nickel / Carbyne complexes

The μ^3-boryloxycarbyne complexes $[\{Fe(CO)_3\}_3\{\mu^3\text{-}COBCl\{N\mathit{t}Bu(SiMe_3)\}\}_2]$ (**1**) and $[\{(\eta^5\text{-}C_5H_5)Ni\}_3\{\mu^3\text{-}COBX(NR_2)\}\mu^3\text{-}CO]$ (**2a**: NR_2 = $N\mathit{t}Bu(SiMe_3)$, X = Cl; **2b**: NR_2 = $N(SiMe_3)_2$, X = Cl; **2c**: NR_2 = NMe_2, X = $BNMe_2Cl$) were obtained by reaction of the anionic complexes $K_2[\{Fe(CO)_3\}_3\{\mu^3\text{-}CO\}_2]$ and $K[\{(\eta^5\text{-}C_5H_5)Ni(CO)]$ with the corresponding chloroboranes Cl_2BNR_2 {NR_2 = $N\mathit{t}Bu(SiMe_3)$, $N(SiMe_3)_2$}, or 1,2-dichlorodiboranes(4) $B_2(NMe_2)_2Cl_2$, respectively. The products are formed by a nucleophilic attack of the CO oxygen atom at the boron centres with subsequent salt elimination. All compounds were characterized by IR and multinuclear NMR spectroscopy, and the structures of **1** and **2c** in the solid state were determined by single-crystal X-ray diffraction studies.

Introduction

A large number of complexes $[L_x(CO)_yM-ER_z]$ with transition metal element bonds have been obtained over the last decades by salt elimination reactions between anionic complexes of the type $M'[L_xM(CO)_y]$ and element halides $HalER_z$ according to Equation 1a.[1a,b] More recently, this fundamental reaction has also been very successfully employed for the synthesis of transition metal complexes of boron, especially for boryl and borylene complexes.[2a,b] In the course of our investigations in this field we found that the mononuclear anionic complexes $K[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Mo, W) undergo salt elimination reactions with 1,2-diiododiboranes(4) by nucleophilic attack of the CO oxygen atom at the boron centre with formation of oxycarbyne complexes of the type $[1,2\text{-}\{(\eta^5\text{-}C_5H_5)M(CO)_2CO\}_2B_2(NMe_2)_2]$.[3] Despite the spectroscopic and experimental evidence for the nucleophilic character of the CO atom in anionic carbonyl complexes,[4a–d] this alternative pathway, with formation of the corresponding oxycarbyne complexes of the type $[L_x(CO)_{y-1}M{\equiv}C-O-ER_z]$ according to Equation 1b, has only been observed once before.[5] In the present paper we describe the syntheses of some trinuclear μ^3-boryloxycarbyne complexes, which were obtained from anionic carbonyl complexes and suitable haloboranes; these compounds are also formed by nucleophilic attack of CO oxygen atoms at boron and salt elimination.



Results and Discussion

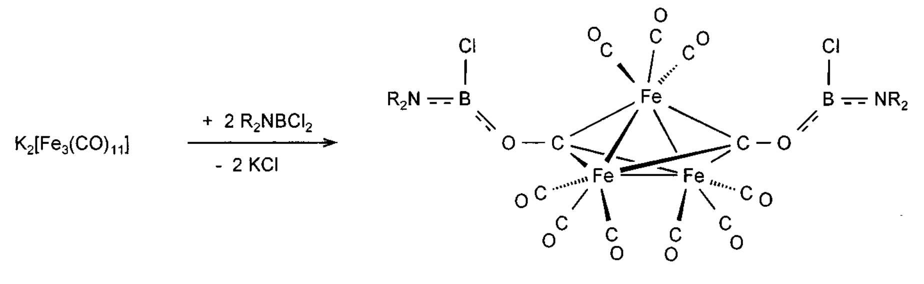
The reaction of the trimeric dianion $[Fe_3(CO)_{11}]^{2-}$, which was used as the corresponding dipotassium salt, with two equivalents of $Cl_2BN\mathit{t}Bu(SiMe_3)$ afforded the μ^3-oxycarbyne complex **1** according to Equation 2.

The product was isolated as red crystalline platelets in yields of about 62%. It is readily soluble in nonpolar solvents, extremely sensitive to air and moisture, and melts without decomposition at 124 °C. The structure of **1** in solution derives from IR and NMR spectroscopic data. A distinct high-field shift of the ^{11}B NMR signal at δ = 28.1 relative to that of the starting material $Cl_2BN\mathit{t}Bu(SiMe_3)$ (δ = 36.6)[6] indicates the formation of an oxoborane derivative, and all other spectroscopic findings, such as the CO stretching frequencies in the IR spectrum ($\tilde{\nu}$ = 2040, 2007 and 1942 cm^{-1}), confirmed our expectations.[7] An X-ray structure analysis was carried out on a single crystal of **1**, which was grown from a hexane solution at −30 °C. Although the quality of the structure refinement suffers from incorporated and disordered solvent molecules, the results unambigously prove the constitution of $[\{Fe(CO)_3\}_3\{\mu^3\text{-}COBCl\{N\mathit{t}Bu(SiMe_3)\}\}_2]$ (**1**) in the crystalline state (Figure 1).

The compound crystallizes in the space group $P\bar{1}$ (no. 2), and the molecule adopts C_1 symmetry. The three iron atoms form an almost regular triangle with iron-iron distances ranging between 250 and 253 pm. This $Fe_3(CO)_9$ moiety is capped by two μ^3-COBCl{$N\mathit{t}Bu(SiMe_3)$} carbyne ligands resulting in a central trigonal-bipyramidal Fe_3C_2 core with iron-carbon distances of about 195 pm. The boron-oxygen {B1−O1 = 138(1) pm, B2−O2 = 135(1) pm} and boron-nitrogen {B1−N1 = B2−N2 = 141(1) pm} bond lengths are in the expected range for B−O and B−N linkages with partial double bond character.[8]

---

[a] Institut für Anorganische Chemie der Technischen Hochschule,
Templergraben 55, D-52056 Aachen
E-mail: holger.braunschweig@ac.rwth-aachen.de
[b] Chemical Crystallography Laboratory University of Oxford,
9 Parks Road, Oxford OX1 3PD, UK



(2)

1; $NR_2 = NtBu(SiMe_3)$

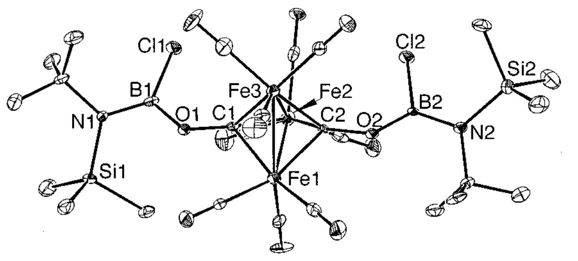


Figure 1. PLATON[21] representation of **1** in the crystal (displacement ellipsoids scaled to 30% probability, hydrogen atoms omitted); selected bond lengths (pm) and angles (deg): Fe1−Fe2 250.6(2), Fe1−Fe3 250.1(2), B2−O2 135(1), B1−O1 139(1), B1−N1 141(1), B2−N2 141(1); Fe2−Fe1−Fe3 60.80(5)

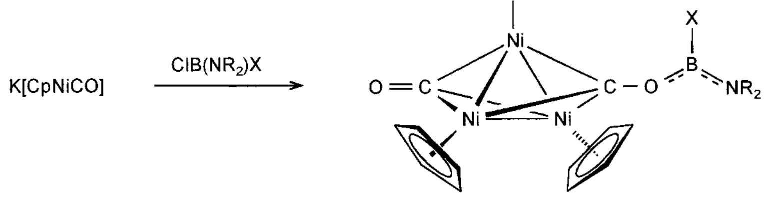
Related trinuclear nickel carbyne complexes were obtained from the reaction of mononuclear $K[\{(\eta^5\text{-}C_5H_5)NiCO]$ with monoborane- or diborane(4)chlorides, respectively (Equation 3).

The formation of $[\{(\eta^5\text{-}C_5H_5)Ni\}_3\{\mu^3\text{-}COBX(NR_2)\}\mu^3\text{-}CO]$ (**2a**, $NR_2 = NtBu(SiMe_3)$, X = Cl; **2b**, $NR_2 = N(SiMe_3)_2$, X = Cl; **2c**, $NR_2 = NMe_2$, $X = BNMe_2Cl$) was again achieved from nucleophilic attack of a CO oxygen atom at the boron centre. All three boryloxycarbyne complexes were isolated in 12%−15% yields as black, crystalline solids that dissolve readily in nonpolar solvents such as hexane. Solutions of **2a−c** are stable for several days at ambient temperature under an inert gas atmosphere, but exposure to air immediately leads to decomposition.

The compounds $[\{(\eta^5\text{-}C_5H_5)Ni\}_3\{\mu^3\text{-}COBX(NR_2)\}\mu^3\text{-}CO]$ (**2a**, $NR_2 = NtBu(SiMe_3)$, X = Cl; **2b**, $NR_2 = N(SiMe_3)_2$, X = Cl; **2c**, $NR_2 = NMe_2$, $X = BNMe_2Cl$) are obviously the products of a complex, nonstoichiometric reaction, and hence, attempts were made to obtain the nickel complexes directly from the corresponding trinuclear monoanion $[\{(\eta^5\text{-}C_5H_5)Ni\}_3\{\mu^3\text{-}CO\}_2]^-$.[9] Interestingly, these reactions always resulted in mixtures of several boron-containing species and the formation of compounds **2a−c** could not be observed.

The molecular structure of the trinuclear nickel complexes in solution was deduced from IR and multinuclear NMR spectroscopic measurements. The boryl compounds **2a,b** show the expected shift to higher field for the ^{11}B NMR signals [$\delta = 26.0$ (**2a**) and $\delta = 25.9$ (**2b**)], whereas the diboran(4)yl derivative **2c** is characterized by two signals at $\delta = 30.9$ and 38.0. The position of the latter signal is almost unaltered with respect to that of the starting diborane(4) $B_2(NMe_2)_2Cl_2$,[10] and is assigned to the chloride-substituted boron atom, while the distinct high-field shift of the other signal clearly indicates the boron-oxygen linkage. Due to a restricted rotation around the boron-nitrogen double bonds the four methyl groups exhibit four signals in the ^1H and ^{13}C NMR spectra. The CO stretching frequencies in the IR spectra at $\tilde{\nu} = 1719$ (**2a**), 1716 (**2b**) and 1734 cm^{-1} (**2c**) are in the expected range for μ^3-CO ligands. An X-ray structure analysis was carried out for the diborane(4) derivative **2c** (Figure 2).

This compound crystallizes in the monoclinic space group $P2_1/n$, and the molecule adopts C_1 symmetry. The three nickel atoms form a regular triangle, with Ni−Ni bond lengths of about 243 pm, which is capped on one side by a μ^3-CO ligand and on the other side by a μ^3-oxycarbyne



(3)

2a, $NR_2 = N\,tBu(SiMe_3)$, X = Cl

2b, $NR_2 = N(SiMe_3)_2$, X = Cl

2c, $NR_2 = NMe_2$, $X = BNMe_2Cl$

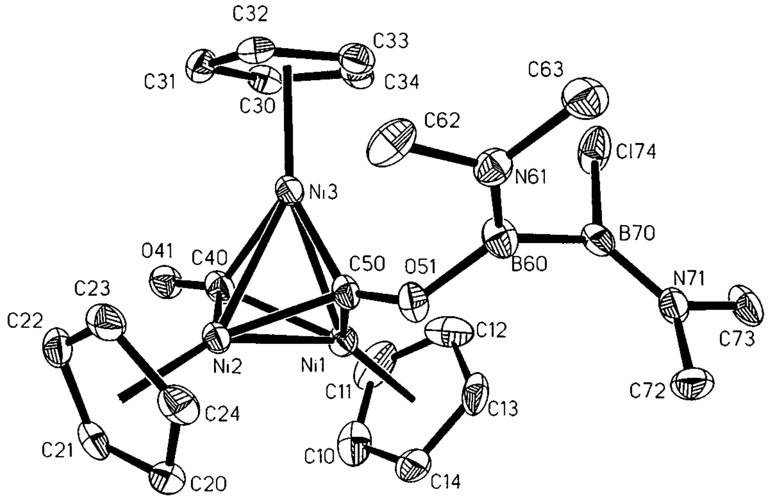


Figure 2. CAMERON[22] representation of **2c** in the crystal (displacement ellipsoids scaled to 30% probability, hydrogen atoms omitted); selected bond lengths (pm) and angles (deg): Ni1−Ni2 243.19(9), Ni1−Ni3 243.33(9), B60−B70 172.2(7), B70−N71 135.3(7), B60−N61, 137.7(8), B60−O51 143.4(7); Ni2−Ni1−Ni3 59.98(3)

moiety. The structural parameters of the central Ni_3C_2 core resemble those of the trimeric monoanion $[\{(\eta^5\text{-}C_5H_5)Ni\}_3\{\mu^3\text{-}CO\}_2]^-$,[9] and the geometry of the boryloxycarbyne moiety $C-O-B(NMe_2)-B(NMe_2)Cl$ is similar to that of the related mononuclear complex $[1,2\text{-}\{(\eta^5\text{-}C_5H_5)Mo(CO)_2CO\}_2B_2(NMe_2)_2]$.[3] In both cases the boron-nitrogen bond lengths range from 135 to 137 pm, thus indicating double bonds, whereas the boron-oxygen bond lengths of about 144 pm are evidence for B−O linkages without significant π-interactions. These observations with respect to the bonding situation of the boron atom to the neighbouring RO- and R_2N groups of **2c** are in contrast to the results described for $[\{Fe(CO)_3\}_3\{\mu^3\text{-}COBCl\text{-}\{NtBu(SiMe_3)\}\}_2]$ (**1**). The hindered rotation of the Me_2N groups in **2c**, which was not observed for the monoborane derivatives **1** and **2a**,**b**, gives further evidence for less effective boron-nitrogen π-interaction bond in the latter complexes, which may be due to the electron-withdrawing effect of the $SiMe_3$ groups.

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere with common Schlenk techniques. Solvents and reagents were dried by standard procedures, distilled, and stored under nitrogen over molecular sieves. $B_2(NMe_2)_2Cl_2$,[10] $Cl_2BN(SiMe_3)_2$,[11] $Cl_2BNtBu(SiMe_3)$,[6] $K_2[Fe_3(CO)_{11}]$,[12] and $K[(\eta^5\text{-}C_5H_5)Ni(CO)]$[13] were synthesised according to literature procedures. − NMR: Varian Unity 500 at 499.843 MHz (^1H, internal standard TMS), 150.364 MHz (^{11}B, BF3·OEt2 in C_6D_6 as external standard), 125.639 MHz ($^{13}C\{^1H\}$, APT, internal standard TMS); all NMR spectra were recorded in C_6D_6 as solvent unless otherwise stated. − Elemental analyses (C, H, N): Carlo−Erba elemental analyzer, model 1106. − IR: Perkin−Elmer FT-IR 1720x

$[\{Fe(CO)_3\}_3\{\mu^3\text{-}COBCl\{NtBu(SiMe_3)\}\}_2]$ (1): Neat $Cl_2BN(tBu)\text{-}SiMe_3$ (1.70 g, 7.52 mmol) was added to a dark red suspension of $K_2[Fe_3(CO)_{11}]$ (2.08 g, 3.76 mmol) in 30 mL benzene at ambient temperature. The reaction mixture was stirred for 15 min and the solvent was subsequently removed under high vacuum. The orange-red residue was extractet with 30 mL of hexane, and after filtration and cooling to −30°C, compound **1** (1.99 g, 61.7%) was obtained as an extremely air-sensitive red solid. Recrystallisation from hexane at −30°C yielded dark red platelets of **1**, m.p. 124°C (sealed tube). − ^1H NMR: δ = 0.46 (s, 18 H, $SiMe_3$), 1.53 (s, 18 H, CMe_3). − ^{11}B NMR: δ = 28.1 (s). − ^{13}C NMR: δ = 5.4 ($SiMe_3$), 32.8 (C*Me*$_3$), 56.6 (*C*Me$_3$), 209.8 (CO), no signals for μ^3-carbyne were found. − IR (toluene): ṽ = 2040, 2007, 1942 cm^{-1} (CO). − $C_{25}H_{36}B_2Cl_2Fe_3N_2O_{11}Si_2$ (856.78): calcd. C 35.04, H 4.24, N 3.27; found C 34.55, H 4.36, N 3.02.

$[\{(\eta^5\text{-}C_5H_5)Ni\}_3\{\mu^3\text{-}COBCl\{NtBu(SiMe_3)\}\}\mu^3\text{-}CO]$ (2a): Neat $Cl_2BNtBu(SiMe_3)$ (1.01 g, 4.45 mmol) was added to a suspension of $K[(\eta^5\text{-}C_5H_5)Ni(CO)]$ (0.85 g, 4.45 mmol) in 20 mL of toluene at 0°C. The black reaction mixture was stirred for 20 min, warmed to ambient temperature and all volatiles were removed under high vacuum. The remaining solid was extracted with 20 mL of hexane and the resulting black suspension was filtered. The residue was discarded after rinsing with two portions of 5 mL of hexane. After evaporating the dark red filtrate to ca. 20 mL and cooling to −30°C, compound **2a** (0.38 g, 14%) was obtained as a black microcrystalline solid, no m.p. observed, decomposition above 200°C (sealed tube). − ^1H NMR: δ = 0.47 (s, 9 H, $SiMe_3$), 1.51 (s, 9 H, CMe_3), 5.11 (s, 15 H, C_5H_5). − ^{11}B NMR: δ = 26.0 (s). − ^{13}C NMR: δ = 5.4 ($SiMe_3$), 32.8 (C*Me*$_3$), 56.1 (*C*Me$_3$), 92.6 (C_5H_5), no signals for μ^3-CO and μ^3-carbyne observed. − IR (toluene): ṽ = 1719 cm^{-1} (s, μ^3-CO). − $C_{24}H_{33}BClNNi_3O_2Si$ (617.69): calcd. C 46.64, H 5.38, N 2.27; found C 45.97, H 5.45, N 2.36.

$[\{(\eta^5\text{-}C_5H_5)Ni\}_3\{\mu^3\text{-}COBCl\{N(SiMe_3)_2\}\}\mu^3\text{-}CO]$ (2b): As described above for **2a** neat $Cl_2BN(SiMe_3)_2$ (1.48 g, 6.13 mmol) was treated with $K[(\eta^5\text{-}C_5H_5)Ni(CO)]$ (1.17 g, 6.13 mmol). to give **2b** (0.47 g, 12%) as a black microcrystalline solid, no m.p. observed, decomposition above 200°C (sealed tube). − ^1H NMR: δ = 0.42 (s, 18 H, $SiMe_3$), 5.10 (s, 15 H, C_5H_5). − ^{11}B NMR: δ = 25.9 (s). − ^{13}C NMR: δ = 3.5 (s, $SiMe_3$), 92.7 (C_5H_5), no signals for μ^3-CO and μ^3-carbyne observed. − IR (toluene): ṽ = 1716 cm^{-1} (s, μ^3-CO). − $C_{23}H_{33}BClNNi_3O_2Si_2$ (634.10): calcd. C 43.56, H 5.24, N 2.21; found C 43.01, H 5. 38, N 2.32.

$[\{(\eta^5\text{-}C_5H_5)Ni\}_3\{\mu^3\text{-}COBNMe_2\{BNMe_2Cl\}\}\mu^3\text{-}CO]$ (2c): As described above for **2a** neat $B_2(NMe_2)_2Cl_2$ (1.07 g, 5.92 mmol) was treated with $K[(\eta^5\text{-}C_5H_5)Ni(CO)]$ (1.13 g, 5.92 mmol). to give **2c** (0.44 g, 13%) as a black microcrystalline solid, m.p. 87°C (sealed tube). − ^{1}H NMR: δ = 2.48, 2.62, 2.65, 2.73 (s, 6 H, NMe), 5.18 (s, 15 H, C_5H_5). − ^{11}B NMR: δ = 30.9 (s, BO), 38.0 (s, BCl). − ^{13}C NMR: δ = 36.3, 37.9, 38.7, 42.4 (NMe), 92.2 (C_5H_5), no signals for μ^3-CO and μ^3-carbyne observed. − IR (toluene): $\tilde{\nu}$ = 1734 cm^{-1} (m, μ^3-CO). − $C_{21}H_{27}B_2ClN_2Ni_3O_2$ (572.63): calcd. C 44.01, H 4.75, N 4.89; found C 43.39, H 5.10, N 4.74.

X-ray Crystal Structure Determination of Compound 1·0.5 hexane

Experimental: Crystals of **1**·0.5 hexane were grown from a hexane solution at −30°C. A dark red rod of approximate dimensions $0.60 \times 0.32 \times 0.24$ mm^3 was selected and mounted on a glass fibre in a cold (203 K) stream of nitrogen.

Crystal Data: $C_{28}H_{43}B_2ClFe_3N_2O_{11}Si_2$, M = 899.90 g mol^{-1}, triclinic, a = 8.432(2) Å, b = 12.591(4) Å, c = 19.067(2) Å, α = 78.68(2)°, β = 85.00(2)°, γ = 88.32(3)°, V = 1977(1) Å^3, space group P1bar (no. 2), Z = 4, D_X = 1.51 g cm^{-3}, μ = 13.34 cm^{-1}.

Data Collection and Processing: Intensity data were collected at 203 K on an Enraf−Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). 8318 reflections were measured in the scan range $3° < \theta < 26°$ and corrected for Lorentz and polarization effects. An empirical absorption correction based on azimuthal scans[14] was applied before averaging over symmetry related reflections. Of 7763 independent reflections 4741 data with $I > 1.0\ \sigma(I)$ were considered observed.

Structure Solution and Refinement: The structure was solved by direct methods[15] and refined on structure factors with the SDP program suite.[16] The crystal structure exhibits a large void of ca 100 Å^3 close to the crystallographic inversion centre, which contains a disordered hexane molecule. All non-hydrogen atoms, except those of the disordered solvent were refined with anisotropic displacement parameters, and hydrogen atoms for the nondisordered part of the structure were included as riding with C−H = 0.98 Å, $U_{iso}(H) = 1.3\ U_{eq}(C)$. The C atoms of the hexane moiety were assigned isotropic displacement parameters. Convergence was obtained for 440 variables and 4741 observations at R = 0.10, R_w = 0.095 and GOF = 1.774. A final difference Fourier synthesis showed a local maximum of 3.5 e Å^{-3} close (0.9 Å) to Fe1; residual electron density was still located in the region of the disordered solvent.

X-ray Crystal Structure Determination of Compound 2c

Experimental: Crystals of **2c** were grown from a hexane solution at −30°C. A crystal was immersed in highly viscous perfluoropolyether under argon to exclude oxygen. It was mounted on a glass fibre and plunged into a cold (100 K) nitrogen stream.

Crystal Data: $C_{21}H_{27}B_2ClN_2Ni_3O_2$, M = 572.66 g mol^{-1}, monoclinic, a = 12.722(1) Å, b = 9.463(1) Å, c = 19.309(2) Å, β = 92.477(6)°, V = 2322 Å^3, space group $P\ 2_1/n$, Z = 4, D_X = 1.624 g cm^{-3}, μ = 25.35 cm^{-1}, black crystals, crystal dimensions $0.26 \times 0.21 \times 0.16$ mm^3.

Data Collection and Processing: The data were collected at 100 K on an Enraf−Nonius DIP2020 image plate diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). 32395 Reflections were measured ($1 < \theta < 26°$, $-15 \le h \le 15$, $-11 \le k \le 11$, $-24 \le l \le 24$). The 4646 unique reflections obtained gave 2618 reflections with $I > 3\sigma(I)$. The images were processed with the DENZO and SCALEPACK programs.[17] Corrections for Lorentz and polarisation effects were made. No corrections for anomalous scattering, absorption or extinction were performed.

Structure Solution and Refinement: The crystal structure was solved by direct methods and refined by the full-matrix least-squares method. Subsequent difference Fourier analysis revealed the terminal (Cl)(Me_2N)B fragment to be disordered over two sites. The refinement of the occupancies of the two disordered groups converged at a ratio of 0.17 to 0.83. The atoms B80 and N81 of the isomer with the smaller occupancy factor were refined with isotropic displacement parameters. All non-hydrogen atoms with the exception of B80, N81, C82 and C83 were refined anisotropically. The B−B bond lengths, the B−Cl bond lengths and the B−N bond lengths of the B−B(Cl)(NMe_2) fragment were restrained to have the same lengths in both isomers. The carbon atoms C82 and C83 of the isomer with minor occupancy could not be found in difference maps. Towards the final stage of the structure determination C82, C83 and all hydrogen atoms were added geometrically (N−C = 1.47 Å, C−H = 1.00 Å) after each refinement cycle. Their isotropic temperature factors were chosen to be equal to U[iso] of the heavy atom to which they are linked. During refinement the geometrically added atoms were treated with fixed thermal and positional parameters. They were included in the structure factor calculations. The 298 refined parameters and 2624 observations resulted in an observation/refined parameter ratio of 8.8. A Chebyshev weighting scheme[18] with parameters 2.27, 0.679 and 1.68 was applied. Refinement on F converged at R = 0.038, R_w = 0.048 and GOF = 0.84. A final difference Fourier synthesis showed minimum and maximum residual electron densities of −0.43 and 0.45 e Å^{-3}. All crystallographic calculations were carried out with the CRYSTALS program package.[19] Neutral atom scattering factors were taken from the International Tables for Crystallography.[20]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-121748 (**1**) and -121749 (**2c**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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

[1] [1a] D. A. Robertus, G. L. Geoffrey in *Comprehensive Organometallic Chemistry, Vol. 2* (Ed.: G. Wilkinson, F. G. A. Stone, E. W. Abel) Pergamon, Oxford, **1982**, p. 763−879. − [1b] R. B. King, *Acc. Chem. Research*, **1970**, *3*, 417−427.

[2] [2a] H. Braunschweig, *Angew. Chem.* **1998**, *110*, 1882−1898, *Angew. Chem. Int. Ed.* **1998**, *37*, 1786−1801. − [2b] G. I. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell, L. J. Wright, *Chem. Rev.* **1998**, *98*, 2685−2722.

[3] H. Braunschweig, M. Koster, K. W. Klinkhammer, *Angew. Chem.* **1999**, *111*, 2368−2370, *Angew. Chem. Int. Ed.* **1999**, *38*, 2229−2231.

[4] [4a] M. J. Bennet, W. A. G. Graham, R. A. Smith, R. P. Stewart, *J. Am. Chem. Soc.* **1973**, *95*, 1684−1686. − [4b] D. F. Shriver, *J. Organomet. Chem.* **1975**, *94*, 259−271. − [4c] A. A. Pasinskii, I. L. Eremenko, G. Z. Suleimanov, Y. A. Nuriev, I. P. Beletskaya, V. E. Shklover, Y. T. Struchkov, *J. Organomet. Chem.* **1984**, *266*, 45−52. − [4d] U. Schubert, E. Kunz, M. Knorr, J. Müller, *Chem. Ber.* **1987**, *120*, 1079−1085.

[5] R. N. Vrtis, C. P. Rao, S. Warner, S. J. Lippard, *J. Am. Chem. Soc.* **1988**, *110*, 2669−2670.

[6] R. H. Neilson, R. L. Wells, *Syn. React. Inorg. Metallorg. Chem.* **1977**, *7*, 151−155.

[7] E. Carbrera, J. C. Daran, Y. Jeannin, *J. Chem. Soc., Chem. Commun.* **1988**, 607−608.

[8] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1989**, S1 − S19.

[9] J. J. Maj, A. D. Rae, L. F. Dahl, *J. Am. Chem. Soc.* **1982**, *104*, 3054−3063.

[10] H. Nöth, W. Schick, H. Meister, *J. Organomet. Chem.* **1964**, *1*, 401−410.

[11] P. Geymayer, E. G. Rochow, U. Wannagat, *Angew. Chem.* **1964**, *76*, 499−501; *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 633−635.

[12] H. A. Hodali, D. F. Shriver, *Inorg. Synth.* **1980**, *20*, 222−223.

[13] R. A. Fischer, J. Behm, E. Herdtweck, C. Kronseder, *J. Organomet. Chem.* **1992**, *437*, C29 − C34.

[14] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr., A24*, **1968**, 351.

[15] G. M. Sheldrick, *SHELXS86, Program for Structure Solution*, University of Göttingen, **1986**.

[16] ENRAF-Nonius SDP Version 5.0, **1989**.

[17] D. Gewirth, *The HKL Manual*, written with the cooperation of the program authors Z. Otwinowski and W. Minor, Yale University, **1995**.

[18] E. Prince, Mathematical Techniques in Crystallography and Material Sciences, Springer-Verlag Inc., New York, **1982**.

[19] D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge, *CRYSTALS Issue 10*, Chemical Crystallography Laboratory, University of Oxford, **1996**.

[20] *International Tables for Crystallography*, Vol. C, Kluwer Academic Publishers, Dordrecht, **1992**.

[21] A. L. Spek, University of Utrecht, **1994**.

[22] L. J. Pearce, K. C. Prout, D. J. Watkin, *CAMERON*, Chemical Crystallography Laboratory, Oxford, **1996**.

Received May 19, 1999
[I99177]