Synthesis of the first Metallasila-*closo*-dodecaborates(1−). Silaborate Complexes of Cobalt, Rhodium, and Iridium

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Complexation of the silaborate ligand $[MeSiB_{10}H_{10}]^{3-}$ is described for the first time. The syntheses of the sandwich anions $[(\eta^5\text{-}C_5Me_5)M(MeSiB_{10}H_{10})]^-$ (M = Co, Rh, Ir) are realized by reaction of the monodeprotonated silaborate with the respective pentamethylcyclopentadienyl transition metal chloride. The reaction products are characterized by mass spectrometry, elemental analyses, and multinuclear and two-dimensional NMR spectroscopy. Because of an unresolvable disorder in the solid state structure of $[NEt_4][(\eta^5\text{-}C_5Me_5)Rh(MeSiB_{10}H_{10})]$, the isobutyl-substituted derivative $[Ph_3PMe][(\eta^5\text{-}C_5Bu^iMe_4)Rh(MeSiB_{10}H_{10})]$, $[Ph_3PMe]$[**4**], was analyzed by an X-ray structure determination. The salt $[Ph_3PMe]$[**4**]·THF, $C_{37}H_{60}OPSiB_{10}Rh$, crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a = 9.838(4)$ Å, $b = 11.312(3)$ Å, $c = 18.858(5)$ Å, $\alpha = 92.68(2)°$, $\beta = 90.22(3)°$, $\gamma = 96.77(3)°$, and $Z = 2$.

Introduction

Most of the silicon coordination chemistry (showing a transition metal−silicon interaction) is based on silyl ($M-SiR_3$), silylene ($M{=}SiR_2$), silene $[M(\eta^2\text{-}CR_2SiR'_2)]$, and disilene $[M(\eta^2\text{-}Si_2R_4)]$ complexes.[1] Despite considerable effort concerning the preparation and coordination of the silacylopentadienide anion (Figure 1),[2,3] the homologue of the aromatic cyclopentadienide anion, only one example of a stable silacyclopentadienyl complex has been reported.[4] The electronic and steric analogies between carbocyclic ligands and borane cluster ligands are best demonstrated by comparison of the $[\eta^5\text{-}C_5Me_5]^-$ and the dicarbollide ligand $[C_2B_9H_{11}]^{2-}$ properties.[5] In view of current interest in silacyclopentadienyl coordination chemistry, we are interested in the coordination abilities of the so far unknown 7-methyl-7-sila-*nido*-undecaborate(3−) ligand $[MeSiB_{10}H_{10}]^{3-}$.

The key reaction for our investigations is the nucleophilic degradation of 1,2-dimethyl-1,2-disila-*closo*-dodecaborane ($Me_2Si_2B_{10}H_{10}$)[6] providing 7-methyl-7-sila-*nido*-undecaborate(1−) (**1**) as the tetraalkylammonium salt in yields up to 90%.[7] Recently, an alternative synthesis for sila-*nido*-undecaborate(1−) starting from deprotonated decaborane(14) was published by Gaines.[8] We previously reported that the sila-*nido*-undecaborate $[MeSiB_{10}H_{12}]^-$ (**1**) reacts with $K[BHEt_3]$ and iron(II) bromide to give the first transition metal complex of a silaborate cluster in 66% yield.[9] The surprising structure of the ferrasilaborate (Figure 2) reveals a dinuclear iron unit with two silaborate ligands η^5-coordinated to the iron centers.

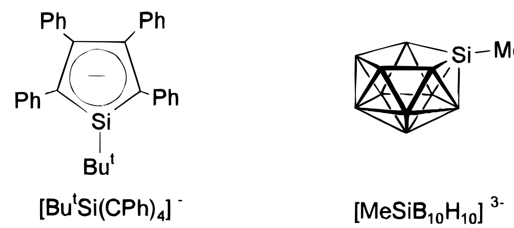

Figure 1. The silacyclopentadienide anion and the silaborate ligand.

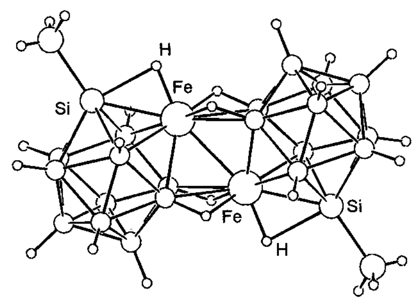

Figure 2. Anion structure of $[Bu_4N]_2[\{HFe(MeSiB_{10}H_{10})\}_2]$.

The short Fe−Si distance and the Fe−Si−H two-electron three-center bond are interesting features of this metallasilaborate. In order to extend the scope of the coordination chemistry of the silaborate ligand, we have investigated the reaction between the pentamethylcyclopentadienyl chlorides of cobalt, rhodium, and iridium and the silaborate anion **1**. Sandwich type complexes with fragments such as $M(\eta^5\text{-}C_5R_5)$ (M = Co, Rh, Ir) are known from a variety of icosahedral carbaboranes and heteroboranes.[10] Almost 30 years ago the synthesis of the cyclopentadienyl dicarbollide cobalt sandwich was published

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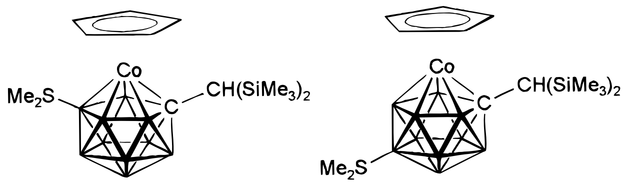

Figure 3. Structures of the two sandwich complexes 7-$(CH_3)_2S$-2-(η^5-C_5H_5)-1-[$((CH_3)_3Si)_2CH$]-2,1-$CoCB_{10}H_9$ and 12-$(CH_3)_2S$-2-(η^5-C_5H_5)-1-[$((CH_3)_3Si)_2CH$]-2,1-$CoCB_{10}H_9$.

by Hawthorne.[11] The analogous dicarbollide complexes of rhodium and iridium were synthesized by the reaction of Cs[*nido*-$C_2B_9H_{12}$] and the respective transition metal dichloride in moderate yield.[12] Another 11-vertex carbaborane, the carba-*nido*-undecaborane, was transformed into a cyclopentadienyl sandwich cobalt complex.[13] The thermal reaction between a substituted derivative of the carba-*nido*-undecaborane, derived from bis(trimethylsilyl)acetylene and decaborane(14), and Cp-$Co(CO)_2$ leads to a mixture of two sandwich complexes (Figure 3).

We report here the synthesis of the first sandwich type complexes containing a silaborate ligand.

Experimental Section

General Procedures and Materials. All reactions and manipulations were carried out in dry glassware under a nitrogen atmosphere using standard Schlenk tube techniques. $C_5Bu^iMe_4H$,[14] [(η^5-C_5Me_5)CoCl]$_2$,[15] [(η^5-C_5Me_5)$RhCl_2$]$_2$,[16] [(η^5-$C_5Bu^iMe_4$)$RhCl_2$]$_2$,[16] and [(η^5-C_5Me_5)$IrCl_2$]$_2$[16] were prepared by literature procedures. Solvents were freshly distilled from the appropriate drying agents under nitrogen before use.

^{29}Si NMR at 99.27 MHz, ^{11}B NMR at 164.364 MHz, ^{13}C NMR at 125.697 MHz, and ^{1}H NMR at 499.843 MHz were obtained at 25 °C on a Varian Unity 500 MHz spectrometer.

Mass spectra were obtained on a Varian MAT-CH-5, EI 70 eV. Elemental analyses were obtained from the Mikroanalytisches Labor Pascher, Remagen, Germany, and on a Carlo-Erba elemental analyzer.

[NEt$_4$][(C$_5$Me$_5$)Co(MeSiB$_{10}$H$_{10}$)] {[NEt$_4$][2]}. A solution of [NEt$_4$][MeSiB$_{10}$H$_{12}$] (0.250 g, 0.85 mmol) in THF (25 mL) was treated at −78 °C with 0.85 mL of a 1.0 M K[BHEt$_3$]−THF solution. After 2 h of stirring at room temperature, a white precipitate formed. The solvent and the BEt$_3$ were removed under vacuum, and the remaining white solid was suspended in 20 mL of THF. At −78 °C, [(η^5-C_5Me_5)CoCl]$_2$ (0.196 g, 0.43 mmol) was added as a powder to the suspension, resulting in an orange solution and hydrogen evolution (9.5 mL). The amount of hydrogen was measured with a gas buret. The reaction mixture was allowed to warm to room temperature and was stirred for an additional 2 h. The color turned brown-red. All volatiles were removed under vacuum. The resulting brown solid was recrystallized from a mixture of THF (80 mL) and Et_2O (20 mL). Yield: 0.323 g, 78.0%. ^{1}H{^{11}B} NMR ([D$_8$]THF): δ = 3.34 (q, $^3J_{HH}$ = 7.3 Hz, 8H, NCH_2CH$_3$), 2.45 (s, 1H, *H*9), 2.39 (s, 2H, *H*7/11), 1.75 (s, 15H, C$_5$(CH_3)$_5$), 1.42 (s, 2H, *H*3/6), 1.32 (t, $^3J_{HH}$ = 7.3 Hz, 12H, NCH$_2$CH_3), 1.22 (s, 2H, *H*4/5), 1.16 (s, 3H, *H*8/10/12), 0.76 (s, $^2J_{SiH}$ = 8.2 Hz, 3H, SiCH_3). ^{11}B NMR ([D$_8$]THF): δ = 8.7 (d, ^1J = 128 Hz, 2B, *B*7/11), −0.1 (d, ^1J = 134 Hz, 1B, *B*9), −6.2 (d, ^1J = 134 Hz, 2B, *B*3/6), −12.9 (d, ^1J = 122 Hz, 1B, *B*12), −14.4 (d, ^1J = 134 Hz, 2B, *B*8/10), −16.9 (d, ^1J = 134 Hz, 2B, *B*4/5). ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 93.0 (s, 5C, *C*$_5$(CH$_3$)$_5$), 53.9 (s, 4C, N*C*H$_2$CH$_3$), 9.8 (s, 5C, C$_5$(*C*H$_3$)$_5$), 8.6 (s, 4C, NCH$_2$*C*H$_3$), −8.7 (s, 1C, Si*C*H$_3$). ^{29}Si NMR ([D$_8$]THF): δ = 39.5 (s). CV (THF): −0.78 V. SIMS, *m/z* (I_{rel}, assignment): 130.3 (100, NEt$_4^+$) from cation spectrum; 355.1 (100, M$^-$) from anion spectrum. Anal. Calcd for $C_{19}H_{48}B_{10}CoNSi$: C, 46.98; H, 10.47; N, 2.88. Found: C, 47.02; H, 10.48; N, 2.70.

Alternative Synthesis of [NEt$_4$][2]. To a solution of [(η^5-C_5Me_5)CoCl]$_2$ (0.196 g, 0.43 mmol) in THF (25 mL) was added TlPF$_6$ (0.297 g, 0.85 mmol) as a powder. This solution was transferred at −78 °C to a solution of [NEt$_4$][MeSiB$_{10}$H$_{12}$] (0.250 g, 0.85 mmol) in THF (25 mL). The color of the reaction mixture turned dark blue, changing upon warming to dark green. After the reaction mixture was stirred for 2 h at room temperature, all volatiles were removed under vacuum. Crystals were grown from toluene at 4 °C. Yield: 0.270 g, 65.3%.

[NEt$_4$][(C$_5$Me$_5$)Rh(MeSiB$_{10}$H$_{10}$)] {[NEt$_4$][3]}. A solution of [NEt$_4$][MeSiB$_{10}$H$_{12}$] (0.250 g, 0.85 mmol) in THF (25 mL) was treated at −78 °C with 0.85 mL of a 1.0 M K[BHEt$_3$]−THF solution. After 2 h of stirring at room temperature, a white precipitate formed. The solvent and the BEt$_3$ were removed under vacuum, and the remaining white solid was suspended in 20 mL of THF. At −78 °C, [(η^5-C_5Me_5)$RhCl_2$]$_2$ (0.263 g, 0.43 mmol) was added as a powder to the suspension, resulting in an orange solution. The reaction mixture was allowed to warm to room temperature and was stirred for an additional 2 h. The color turned brown-red. All volatiles were removed under vacuum. The resulting brown solid was recrystallized from a mixture of THF (80 mL) and Et_2O (20 mL). Yield: 0.401 g, 89.0%. ^{1}H{^{11}B} NMR ([D$_8$]THF): δ = 3.30 (q, $^3J_{HH}$ = 7.3 Hz, 8H, NCH_2CH$_3$), 2.95 (s, 1H, *H*9), 2.38 (s, 2H, *H*7/11), 1.87 (s, 15H, C$_5$(CH_3)$_5$), 1.68 (s, 2H, *H*3/6), 1.52 (s, 5H, *H*4/5/8/10/12), 1.32 (t, $^3J_{HH}$ = 7.3 Hz, 12H, NCH$_2$CH_3), 0.67 (s, $^2J_{SiH}$ = 8.5 Hz, 3H, SiCH_3). ^{11}B NMR ([D$_8$]THF): δ = 8.9 (d, ^1J = 134 Hz, 2B, *B*7/11), 1.6 (d, ^1J = 134 Hz, 1B, *B*9), −6.1 (d, ^1J = 134 Hz, 2B, *B*3/6), −14.8 (d, ^1J = 134 Hz, 1B, *B*12), −15.7 (d, ^1J = 134 Hz, 2B, *B*8/10), −19.0 (d, ^1J = 134 Hz, 2B, *B*4/5). ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 98.8 (d, J_{RhC} = 4.4 Hz, 5C, *C*$_5$(CH$_3$)$_5$), 54.2 (s, 4C, N*C*H$_2$CH$_3$), 8.8 (s, 4C, NCH$_2$*C*H$_3$), 8.4 (s, 5C, C$_5$(*C*H$_3$)$_5$), −9.0 (s, 1C, Si*C*H$_3$). ^{29}Si NMR ([D$_8$]THF): δ = 33.1 (s). SIMS, *m/z* (I_{rel}, assignment): 130.2 (NEt$_4^+$) from cation spectrum; 399.2 (100, M$^-$) from anion spectrum. Anal. Calcd for $C_{19}H_{48}B_{10}NRhSi$: C, 43.08; H, 9.13. Found: C, 40.71; H, 8.83.

Alternative Syntheses of [NEt$_4$][3]. (a) To a solution of [NEt$_4$][MeSiB$_{10}$H$_{12}$] (0.250 g, 0.85 mmol) in THF (25 mL), were added 1,8-bis(dimethylamino)naphthalene (Proton Sponge) (0.365 g, 1.70 mmol) and [Cp*RhCl$_2$]$_2$ (0.263 g, 0.43 mmol) at −78 °C as powders. The reaction mixture was allowed to stir at room temperature for 24 h, during which the color of the solution became dark red. All volatiles were removed in vacuum. The resulting dark red-brown solid was recrystallized from toluene (30 mL) at 4 °C. Yield: 0.189, 41.9%.

(b) To a solution of [(η^5-C_5Me_5)$RhCl_2$]$_2$ (0.263 g, 0.43 mmol) in THF (25 mL) was added TlPF$_6$ (0.595 g, 1.70 mmol) as a powder. This solution was transferred at −78 °C to a solution of [NEt$_4$][MeSiB$_{10}$H$_{12}$] (0.250 g, 0.85 mmol) in THF (25 mL). The color of the reaction mixture turned orange, changing upon warming to dark red. After the reaction mixture was stirred for 2 h at room temperature, all volatiles were removed under vacuum. Crystals were grown from a mixture of THF (80 mL) and Et_2O (20 mL) at 4 °C. Yield: 0.241 g, 53.4%.

[Ph$_3$PMe][(C$_5$Bu^{i}Me$_4$)Rh(MeSiB$_{10}$H$_{10}$)] {[Ph$_3$PMe][4]}. A solution of [Ph$_3$PMe][MeSiB$_{10}$H$_{12}$] (0.250 g, 0.56 mmol) in THF (25 mL) was treated at −78 °C with 0.56 mL of a 1.0 M K[BHEt$_3$]−THF solution. After 2 h of stirring at room temperature, a white precipitate formed. The solvent and the BEt$_3$ were removed under vacuum, and

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the remaining white solid was suspended in 20 mL of THF. At −78 °C, $[(\eta^5\text{-}C_5Bu^iMe_4RhCl_2]_2$ (0.199 g, 0.28 mmol) was added as a powder to the suspension, resulting in an orange solution. The reaction mixture was allowed to warm to room temperature and was stirred for an additional 2 h. The color turned brown-red. All volatiles were removed under vacuum. The resulting brown solid was recrystallized from a mixture of THF (80 mL) and Et_2O (20 mL). Yield: 0.383 g, 91.7%. $^1H\{^{11}B\}$ NMR ($[D_8]$THF): δ = 7.78 (m, 18H, $(C_6H_5)_3P$), 3.06 (d, J_{PH} = 14.0 Hz, 3H, PCH_3), 2.95 (s, 1H, *H*9), 2.38 (s, 2H, *H*7/11), 2.23 (d, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2CHMe_2), 1.85 and 1.84 (s, 12H, $C_5(CH_3)_4$), 1.70 (s, 2H, *H*3/6), 1.67 (m, 1H, CH_2CHMe_2), 1.52 (s, 5H, *H*4/5/8/10/12), 0.86 (d, $^3J_{HH}$ = 7.0 Hz, 6H, $CH(CH_3)_2$), 0.63 (s, $^2J_{SiH}$ = 7.9 Hz, 3H, $SiCH_3$). ^{11}B NMR ($[D_8]$THF): δ = 9.2 (d, ^1J = 134 Hz, 2B, *B*7/11), 2.2 (d, ^1J = 134 Hz, 1B, *B*9), −6.0 (d, ^1J = 134 Hz, 2B, *B*3/6), −14.5 (d, ^1J = 134 Hz, 2B, *B*12), −15.4 (d, ^1J = 134 Hz, 2B, *B*8/10), −18.9 (d, ^1J = 134 Hz, 2B, *B*4/5). $^{13}C\{^1H\}$ NMR ($[D_8]$THF): δ = 134.6 (s, 3C, $(C_6H_5)_3P$), 133.0 (d, $^2J_{PC}$ = 10 Hz, 6C, $(C_6H_5)_3P$), 129.9 0 (d, $^3J_{PC}$ = 13 Hz, 6C, $(C_6H_5)_3P$), 119.7 0 (d, $^1J_{PC}$ = 89 Hz, 3C, $(C_6H_5)_3P$), 104.2 (d, 1C, J_{RhC} = 4.9 Hz, $RhCCH_2$), 101.4 and 100.3 (d, J_{RhC} = 4.9 Hz, 4C, RhC_4), 36.0 (s, 1C, CH_2CHMe_2), 31.7 (s, 1C, $CHMe_2$), 23.9 (s, 2C, $CH(CH_3)_2$), 11.4 and 10.8 (s, 4C, $C_5(CH_3)_4$), 7.4 (d, $^1J_{PC}$ = 56 Hz, 3C, PCH_3), −6.5 (s, 1C, $SiCH_3$). ^{29}Si NMR ($[D_8]$-THF): δ = 34.2 (s). SIMS, *m/z* (I_{rel}, assignment): 277.33 (100, Ph_3PMe^+) from cation spectrum; 441.52 (100, M^-) from anion spectrum. Anal. Calcd for $C_{33}H_{52}B_{10}PRhSi$: C, 55.14; H, 7.29. Found: C, 54.99; H, 8.14.

$[NEt_4][(C_5Me_5)Ir(MeSiB_{10}H_{10})]$ {$[NEt_4][5]$}. A solution of $[NEt_4]$-$[MeSiB_{10}H_{12}]$ (0.250 g, 0.85 mmol) in THF (25 mL) was treated at −78 °C with 0.85 mL of a 1.0 M $K[BHEt_3]$−THF solution. After 2 h of stirring at room temperature, a white precipitate formed. The solvent and the BEt_3 were removed under vacuum, and the remaining white solid was suspended in 20 mL of THF. At −78 °C $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ (0.331 g, 0.43 mmol) was added as a powder to the suspension, resulting in an orange solution. The reaction mixture was allowed to warm to room temperature and was stirred for an additional 2 h. The color turned brown-red. All volatiles were removed under vacuum. The resulting brown solid was recrystallized from a mixture of THF (80 mL) and Et_2O (20 mL). Yield: 0.354 g, 67.2%. $^1H\{^{11}B\}$ NMR ($[D_8]$THF): δ = 3.34 (q, $^3J_{HH}$ = 7.3 Hz, 8H, NCH_2CH_3), 2.02 (s, 3H, *H*7/9/11), 1.96 (s, 15H, $C_5(CH_3)_5$), 1.62 (s, 2H, *H*3/6), 1.52 (s, 5H, *H*4/5/8/10/12), 1.32 (t, $^3J_{HH}$ = 7.3 Hz, 12H, NCH_2CH_3), 0.66 (s, $^2J_{SiH}$ = 8.1 Hz, 3H, $SiCH_3$). ^{11}B NMR ($[D_8]$THF): δ = 0.1 (d, ^1J = 128 Hz, 1B, *B*9), −1.7 (d, ^1J = 134 Hz, 2B, *B*7/11), −14.6 (d, ^1J = 140 Hz, 2B, *B*3/6), −18.6 (d, ^1J = 140 Hz, 2B, *B*8/10), −19.4 (d, ^1J = 152 Hz, 1B, *B*12), −22.5 (d, ^1J = 140 Hz, 2B, *B*4/5). $^{13}C\{^1H\}$ NMR ($[D_8]$THF): δ = 94.1 (s, 5C, $C_5(CH_3)_5$), 54.1 (s, 4C, NCH_2CH_3), 8.6 (s, 4C, NCH_2CH_3), 7.9 (s, 5C, $C_5(CH_3)_5$), −11.6 (s, 1C, $SiCH_3$). ^{29}Si NMR ($[D_8]$THF): δ = 2.8 (s). SIMS, *m/z* (I_{rel}, assignment): 130.18 (100, NEt_4^+) from cation spectrum; 489.0 (100, M^-) from anion spectrum. Anal. Calcd for $C_{19}H_{48}B_{10}IrNSi$: C, 36.87; H, 7.82; N, 2.26. Found: C, 35.96; H, 7.82; N, 2.13.

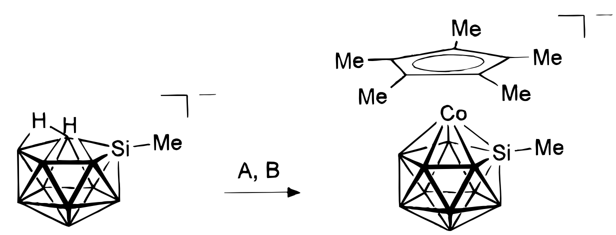
X-ray Crystallographic Analysis of $[Ph_3PMe][(C_5Bu^iMe_4)Rh(MeSiB_{10}H_{10})]\cdot THF$ {$[Ph_3PMe][4]\cdot THF$}. A yellow single crystal was grown by diffusion of Et_2O into a THF solution of the complex. A crystal of approximate dimensions 0.50 × 0.30 × 0.25 mm was studied on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). Crystal data and the parameters for data collection and structure refinement are compiled in Table 1. The structure of $[Ph_3PMe][\mathbf{4}]\cdot THF$ was solved by the Patterson method. The remaining atom positions resulted from subsequent refinement cycles and Fourier-difference syntheses.[17] An empirical absorption correction based on ψ-scans[18] was applied (maximum/minimum transmission: 99.34/93.98%). In the final least-squares full-matrix refinement (based on F_o) all non-hydrogen atoms were refined with anisotropic thermal displacement parameters, hydrogen atoms bonded to boron atoms were refined isotropically, and all other hydrogen atoms were treated as riding atoms (C−H = 0.98 Å, B_H = 1.3 B_C). No hydrogen atoms were calculated for the THF molecule because of large anisotropic displacement parameters.

Table 1. Summary of Crystallographic Data for $[Ph_3PMe][(\eta^5\text{-}C_5Bu^iMe_4)Rh(MeSiB_{10}H_{10})]\cdot THF$ {$[Ph_3PMe][\mathbf{4}]\cdot THF$}

empirical formula	$RhPSiOC_{37}B_{10}H_{60}$
M_r	790.97
T/°C	−70
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
a/Å	9.838(4)
b/Å	11.312(3)
c/Å	18.858(5)
α/deg	92.68(2)
β/deg	90.22(3)
γ/deg	96.77(3)
V/Å^3	2082(2)
Z	2
d_{calcd}/g cm^{-3}	1.262
μ(Mo Kα)/cm^{-1}	4.97
λ(Mo Kα)/Å	0.717 03
F(000)/e	828
crystal dimensions/mm	0.5 × 0.3 × 0.25
no. of reflcns measd	7983
no. of independent reflcns	4612
2θ range/deg	6−51
final residuals	R = 0.063,[a] R_w = 0.062[b]
goodness of fit	1.355
res el density/(e/Å^3)	0.85

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$; $w^{-1} = \sigma^2(F_o)$.

Scheme 1



$[NEt_4]\cdot\mathbf{1}$ $[NEt_4]\cdot\mathbf{2}$

A: $K[BHEt_3]$ - H_2,

0.5 $[Cp^*CoCl]_2$, - KCl, -0.5 H_2

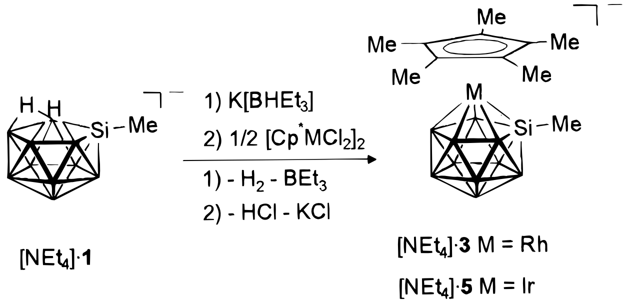
B: $TlPF_6$ + 0.5 $[Cp^*CoCl]_2$, -TlCl, -0.5 H_2

Results and Discussion

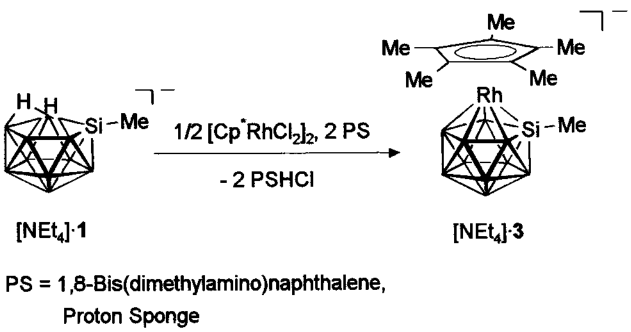
Syntheses of the Sandwich Complexes $[NEt_4][2]$, $[NEt_4]$-$[3]$, $[Ph_3PMe][4]$, and $[NEt_4][5]$. The cobaltasilaborate cluster anion **2** can be prepared by two possible procedures. Yields of 78% of crystalline $[NEt_4][\mathbf{2}]$ can be isolated from the reaction of the half-sandwich cobalt complex $\{[Co(\eta^5\text{-}C_5Me_5)Cl]_2\}$ with 2 equiv of monodeprotonated silaborate ligand $[MeSiB_{10}H_{11}]^{2-}$ in tetrahydrofuran. The silaborate ligand is deprotonated with 1 equiv of $K[BHEt_3]$ in tetrahydrofuran before adding the cobalt chloride at −78 °C (Scheme 1). After several hours of stirring at room temperature, the solvent is removed in vacuum to yield a dark brown powder. On the basis of the ^1H and ^{11}B NMR spectroscopic investigations, this reaction product is identified as the pure cobalt complex $[NEt_4][\mathbf{2}]$. Recrystallization of the dark brown powder from a mixture of tetrahydrofuran and diethyl ether affords the sandwich complex $[NEt_4][2\text{-}(\eta^5\text{-}C_5Me_5)\text{-}closo\text{-}2,1\text{-}Co(MeSiB_{10}H_{10})]$ {$[NEt_4][\mathbf{2}]$} in 78% yield as air-stable dark yellow crystals.

(17) *MolEN*: *An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.
(18) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

Scheme 2



Scheme 3



The other possible synthesis starts with a dehalogenation of [{Co(η^5-C_5Me_5)Cl}$_2$] with $TlPF_6$ in tetrahydrofuran. After removal of the TlCl by filtration, the silaborate ligand is added at −78 °C. [NEt_4][**2**] is isolated after crystallization in a yield of 65% (Scheme 1). In both cases, the cobalt atom is oxidized on complexation with the silaborate ligand. Therefore evolution of a 0.5 equiv of hydrogen can be measured during the reaction.

The rhodium and iridium silaborate complexes are synthesized by reaction of the monodeprotonated silaborate and the respective pentamethylcyclopentadienyl transition metal dichloride {[M(η^5-C_5Me_5)Cl_2]$_2$, M = Rh, Ir}. In both cases, the sandwich complexes are isolated as yellow air-stable crystals in yields of 89% [NEt_4][**3**] and 67% [NEt_4][**5**] (Scheme 2).

Two alternative syntheses were developed for the rhodium silaborate complex. The reaction of **1**, {[Rh(η^5-C_5Me_5)Cl_2]$_2$}, and Proton Sponge [1,8-bis(dimethylamino)naphthalene] as the deprotonating agent affords [NEt_4][**3**] in 42% yield (Scheme 3).

In analogy to [NEt_4][**2**] the dehalogenated (pentamethylcyclopentadienyl)rhodium fragment reacts with the silaborate **1** to give [NEt_4][**3**] as yellow crystals after recrystallization from THF−Et_2O in 53% yield. [Ph_3PMe][**4**] can be obtained in analogy to [NEt_4][**3**] from the reaction between the deprotonated silaborate [$MeSiB_{10}H_{11}$]$^{2-}$ and {[Rh(η^5-$C_5Bu^iMe_4$)Cl_2]$_2$} in a yield of 92%.

On the basis of ^{11}B NMR spectroscopic investigations, the formation of the sandwich complexes was not observed from the reaction between the completely deprotonated ligand [$MeSiB_{10}H_{10}$]$^{3-}$ and the respective transition metal chloride.

X-ray Structural Analysis of [Ph$_3$PMe][4]·THF. In order to establish firmly the structure of the sandwich salts, a single-crystal X-ray investigation was carried out on [Ph_3PMe][(η^5-$C_5Bu^iMe_4$)Rh($MeSiB_{10}H_{10}$)] (Tables 1 and 2). A suitable crystal was obtained from slow diffusion of diethyl ether into a tetrahydrofuran solution of [Ph_3PMe][**4**] at +4°C. The salt [Ph_3PMe][**4**]·crystallizes with 1 equiv of THF. Under vacuum, these crystals lost the THF and were afterward found to be useless for crystal structure analysis. Selected interatomic distances of the sandwich anion **4** are listed in Table 3, and the structure is shown in Figure 4. The rhodasilaborate anion adopts a *closo* structure composed of the polyhedral $RhSiB_{10}$ unit. The

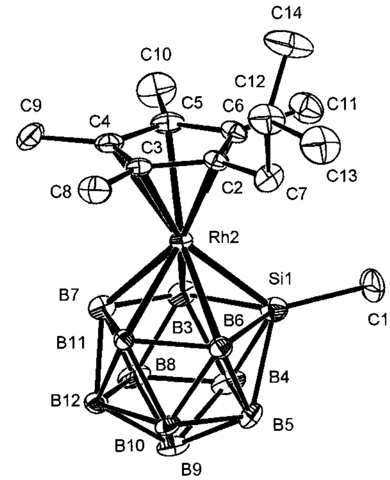


Figure 4. PLATON[19] drawing of [2-(η^5-$C_5Bu^iMe_4$)-*closo*-2,1-Rh-($MeSiB_{10}H_{10}$)]$^-$ (**4**).

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for [2-(η^5-$C_5Bu^iMe_4$)-*closo*-2,1-Rh($MeSiB_{10}H_{10}$)]$^-$ (**4**)

atom	*x/a*	*y/b*	*z/c*	*U*(eq)[a]
Rh2	0.21950(6)	0.45511(5)	0.20762(3)	0.0239(1)
Si1	−0.0006(2)	0.4116(2)	0.1668(1)	0.0372(6)
C1	−0.0633(9)	0.3554(9)	0.0776(5)	0.062(3)
B3	0.0609(9)	0.5835(8)	0.2101(5)	0.038(3)
B4	−0.1154(9)	0.5150(8)	0.2259(5)	0.040(3)
B5	−0.1183(9)	0.3595(8)	0.2516(5)	0.034(2)
B6	0.0593(9)	0.3187(7)	0.2518(5)	0.030(2)
B7	0.1529(9)	0.5741(7)	0.2914(5)	0.033(2)
B8	−0.0223(9)	0.6055(8)	0.2919(6)	0.040(3)
B9	−0.1252(9)	0.4759(8)	0.3158(5)	0.036(2)
B10	−0.0209(8)	0.3637(8)	0.3312(5)	0.029(2)
B11	0.1512(8)	0.4210(7)	0.3164(4)	0.024(2)
B12	0.0347(9)	0.5135(8)	0.3569(5)	0.032(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

Table 3. Selected Interatomic Distances (Å) for [2-(η^5-$C_5Bu^iMe_4$)-*closo*-2,1-Rh($MeSiB_{10}H_{10}$)]$^-$ (**4**)

Rh2−Si1	2.285(2)	Rh2−C2	2.209(7)
Rh2−B3	2.253(9)	Rh2−C3	2.217(7)
Rh2−B6	2.262(9)	Rh2−C4	2.239(8)
Rh2−B7	2.18(1)	Rh2−C5	2.227(8)
Rh2−B11	2.198(9)	Rh2−C6	2.229(7)
Si1−C1	1.846(9)	Si1−B3	2.09(1)
Si1−B4	2.02(1)	Si1−B5	2.05(1)
Si1−B6	2.079(9)		
B3−B4	1.85(1)	B3−B7	1.79(1)
B3−B8	1.77(1)	B4−B5	1.84(1)
B4−B8	1.76(2)	B4−B9	1.77(1)
B5−B6	1.86(1)	B5−B9	1.75(1)
B5−B10	1.77(1)	B6−B10	1.78(1)
B6−B11	1.80(1)	B7−B8	1.80(1)
B7−B11	1.81(1)	B7−B12	1.80(1)
B8−B9	1.76(1)	B8−B12	1.77(1)
B9−B10	1.76(1)	B9−B12	1.75(1)
B10−B11	1.77(1)	B10−B12	1.76(1)
B11−B12	1.79(1)	C2−C3	1.42(1)
C2−C6	1.44(1)	C2−C7	1.49(1)
C3−C4	1.43(1)	C3−C8	1.49(1)
C4−C5	1.41(1)	C4−C9	1.48(1)
C5−C6	1.42(1)	C5−C10	1.49(1)
C6−C11	1.49(1)	C7−C12	1.52(1)
C12−C13	1.54(1)	C12−C14	1.53(1)

(19) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.

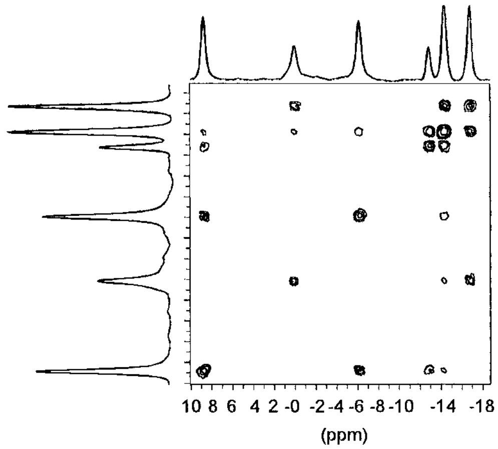


Figure 5. $^{11}B\{^{1}H\}-^{11}B\{^{1}H\}$ COSY NMR spectrum of [2-(η^5-C_5Me_5)-*closo*-2,1-Co($MeSiB_{10}H_{10}$)]$^-$ (**2**). From right to left: B4/5, B8/10, B12, B3/6, B9, B7/11.

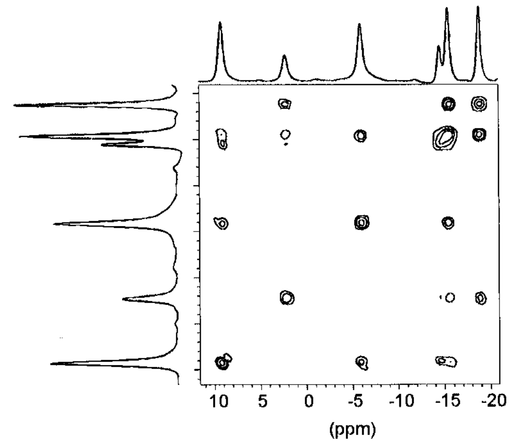


Figure 6. $^{11}B\{^{1}H\}-^{11}B\{^{1}H\}$ COSY NMR spectrum of [2-(η^5-C_5Me_5)-*closo*-2,1-Rh($MeSiB_{10}H_{10}$)]$^-$ (**3**). From right to left: B4/5, B8/10, B12, B3/6, B9, B7/11.

rhodium atom is approximately centered over the silaborate open face, giving rise to a distance between the rhodium atom and the plane through Si, B3, B6, B7, B11 of 1.532(1) Å. The Rh−Si distance of 2.286(2) Å is in the range of Rh−Si bond lengths found for rhodium silyl derivatives [RhHCl($SiCl_3$)(PPh_3)$_2$ 2.203(4) Å,[20] (η^5-C_5Me_5)Rh($SiEt_3$)$_2$$H_2$ 2.379(2) Å[21]]. Due to geometric constraints the Rh−B distances of the two boron atoms neighboring the silicon atom are longer [Rh−B3 2.251-(9), Rh−B6 2.262(8) Å] than the other Rh−B distances [Rh−B7 2.179(9), Rh−B11 2.196(8) Å]. This situation is known from the X-ray structure investigations of the stannasila-*closo*-dodecaborate(1−)[22] and the ferrasila-*closo*-dodecaborate.[9] The Rh−B distances are known from the dicarbollide ligand coordinated via the pentagonal open face.[12] The small slip distortion of 0.02 Å from the rhodium atom concerning the best plane through Si, B3, B6, B7, B11 and the small angle [4(2)°] between this plane and the cyclopentadienyl ligand confirm the *closo* geometry of the rhodasila-*closo*-dodecaborate.

Single-crystal cell measurements of [NEt_4][**2**], -[**3**], and -[**5**] have shown that these salts are isotypic, with measured unit cell dimensions and volumes differing by ≤2%. [NEt_4][**3**] crystallizes in the monoclinic space group $P2_1/a$ (No. 14) with cell dimensions $a = 17.87(1)$ Å, $b = 9.594(3)$ Å, $c = 18.912$-(7) Å, and $\beta = 115.71(5)°$. Due to a disorder of the silaborate ligand, the refinement of the structure did not yield precise parameters. In order to obtain a crystal structure analysis of a nondisordered sandwich complex, we varied the countercation and changed the C_5Me_5 ligand to the $C_5Bu^iMe_4$ ligand.

Spectroscopic Characterization of the Metallasila-*closo*-dodecaborates(1−). All sandwich complexes obtained in this study were characterized by multinuclear magnetic resonance spectroscopy, two-dimensional $^{11}B\{^{1}H\}-^{11}B\{^{1}H\}$ COSY NMR spectroscopy, $^{11}B\{^{1}H\}-^{1}H\{^{11}B\}$ HMQC NMR spectroscopy, and secondary-ion mass spectrometry.

In contrast to the phenomenon that cross-peaks between heteroatom-bridged boron atoms are not visible,[23] no cross-peaks are missing in the two-dimensional $^{11}B\{^{1}H\}-^{11}B\{^{1}H\}$ COSY NMR spectra of **2**, **3**, and **5** (Figures 5−7). Six signals in the ^{11}B NMR spectra for 10 boron atoms of the metallasila-*closo*-dodecaborates(1−) indicate C_s symmetry in solution. The ^{11}B NMR signals were related to the respective boron atoms in the cluster framework on the assumption that the transition metal is responsible for a much stronger antipodal shift to low field. For the Co, Rh, and Ir silaborate clusters, the difference between the antipodal shifts for the boron atoms opposite to the transition metal and the silicon atoms is larger than 10 ppm (SiCo, 12.8; SiRh, 16.4; SiIr, 19.5).

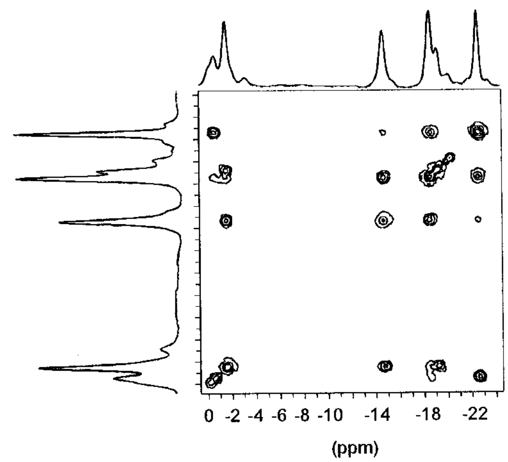


Figure 7. $^{11}B\{^{1}H\}-^{11}B\{^{1}H\}$ COSY NMR spectrum of [2-(η^5-C_5Me_5)-*closo*-2,1-Ir($MeSiB_{10}H_{10}$)]$^-$ (**5**). From right to left: B4/5, B12, B8/10, B3/6, B7/11, B9.

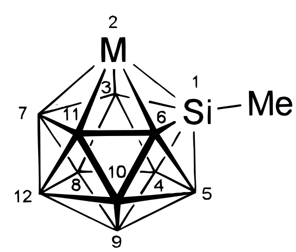


Figure 8. Numbering in [$MMeSiB_{10}H_{10}$]$^-$.

The $^{11}B\{^{1}H\}$ NMR signals for the boron atoms (B7/11, B3/6) (Figure 8) of the $CoSiB_{10}$ and $RhSiB_{10}$ skeleton exhibit a typical downfield shift whereas the resonances for B4/5 and B8/10 appear at slightly changed values in comparison to those of $Me_2Si_2B_{10}H_{10}$.[6] The respective resonances for B7/11 and B3/6 of the iridium derivative **5** appear at remarkably higher field. A slight shift of the ^{11}B NMR signals to higher field was also observed in the Co, Rh, Ir series of the [(C_5R_5)M-($C_2B_9H_{11}$)] complexes.

(20) Manojlovic-Muir, L.; Muir, K. W.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 447. Muir, K. W.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 440.
(21) Fernandez, M.-J.; Bailey, P. M.; Bentz, P. O.; Ricci, J. S.; Koetzle, T. F.; Maitlis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 5458.
(22) Wesemann, L.; Ramjoie, Y.; Ganter, B.; Maisch, H. *Chem. Ber.* **1996**, *129*, 837.
(23) Venable,T. L.; Hutton, W. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 29.

On complexation, the resonance in the ^{29}Si NMR spectrum appears at lower field with respect to the starting material $[MeSiB_{10}H_{12}]^-$ ($\delta = -36$).

Conclusion

The results reported above represent the second contribution to transition metal silaborate chemistry. Formally, the silaborate ligand is coordinated as the $[MeSiB_{10}H_{10}]^{3-}$ trianion to the transition metal which adopts an 18-electron configuration in the sandwich complexes.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm Polyeder).

Supporting Information Available: Tables listing atomic positional parameters, thermal parameters, and bond lengths and angles (8 pages). An X-ray crystallographic file, in CIF format is available on the Internet only. Ordering and access information is given on any current masthead page.

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