Carbonyl Transition Metal Complexes of a Silaborate Ligand☆

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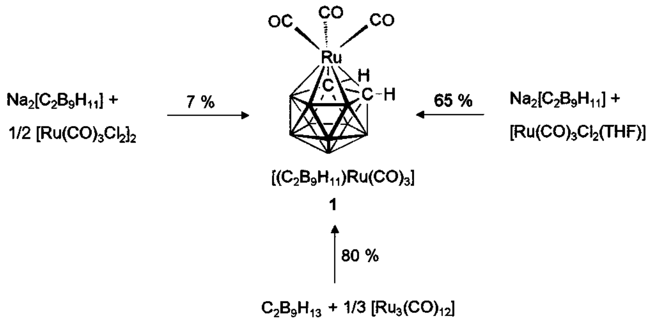
Reaction between three equivalents of the silaborate $[NEt_4][MeSiB_{10}H_{12}]$ (**2**) and one equivalent of $[Ru_3(CO)_{12}]$ resulted in almost quantitative formation of the mononuclear transition metal complex $[NEt_4][Ru(CO)_3(\eta^5\text{-}MeSiB_{10}H_{10})]$ (**5**), which was characterized by X-ray structure analysis. The trinuclear ruthenium complex $[NEt_4][Ru_3(CO)_8(\eta^5\text{-}MeSiB_{10}H_{10})]$ (**7**) was synthesized in high yield from the reaction of one equivalent of **2** and $[Ru_3(CO)_{12}]$. The cluster **7** reacts with two equivalents of PMe_2Ph with substitution of two carbonyl groups to give the substitution product $[NEt_4][Ru_3(CO)_6(PMe_2Ph)_2(\eta^5\text{-}MeSiB_{10}H_{10})]$ (**8**).

The coordination chemistry of the dicarbollide ligand $[C_2B_9H_{11}]^{2-}$ has been investigated for almost 35 years. Metallocene-like complexes, mixed cyclopentadienyl dicarbollide sandwich species, and carbonyl dicarbollide transition metal complexes are described in the literature[1]. Many of these metallacarboranes have compositions and structures which are related to their cyclopentadienyl counterparts. One of the most surprising properties of the dicarbollide coordination products is their remarkable stability towards air oxidation and hydrolysis. After 35 years of research in the field of metallacarborane chemistry a dicarbollide coordination product of almost every transition metal is known. In 1969 Hawthorne described for the first time the synthesis of a carbonyliron dicarbollide complex[2] and 20 years later he developed an organometallic chemistry based on the dimeric dicarbonyliron carborane [*closo*-3-CO-3,3′-(μ-CO)-3,1,2-$FeC_2B_9H_{11}]_2^{2-}$[3]. In the case of ruthenium Siedle[4] reported for the first time on the successful preparation of *closo*-3,3,3-$(CO)_3$-3,1,2-$RuC_2B_9H_{11}$ (**1**) (Figure 1). From the reaction between $[Ru(CO)_3Cl_2]_2$ and $[7,8\text{-}C_2B_9H_{11}]^{2-}$ in refluxing THF 7% of **1** has been isolated.

Figure 1. Syntheses of the tricarbonylruthenium dicarbollide complex



The yield of dicarbaruthena-*closo*-dodecaborane was improved nine years later by Hawthorne[5] to 65% by treating $[7,8\text{-}C_2B_9H_{11}]^{2-}$ with $[Ru(CO)_3Cl_2(THF)]$ in THF at 0°C. In 1995 Stone[6] published a further improvement of the yield to 80% with $[Ru_3(CO)_{12}]$ as a starting material. Reaction between $[C_2B_9H_{13}]$ and $[Ru_3(CO)_{12}]$ results exclusively in the formation of the mononuclear complex **1**. Whereas the carborane with methyl groups attached to the carbon atoms produces in the corresponding reaction a 1:2 mixture of mononuclear complex $[Ru(CO)_3(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_{11})]$ and trinuclear cluster $[Ru_3(CO)_8(\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_{11})]$.[7] The trinuclear ruthenium and osmium clusters $[M_3(CO)_8(\eta^5\text{-}7\text{-}NMe_3\text{-}7\text{-}CB_{10}H_{10}]$ (M = Os[8] and Ru[9]) were synthesized from the reaction of the zwitterionic monocarborane 7-NR_3-7-$CB_{10}H_{10}$ and the respective carbonylmetal complexes. In both cases no mononuclear transition metal complex is known.

We have recently presented the first examples of transition metal complexes of the 7-sila-*nido*-undecaborate(1−) (**2**) cluster.[10] In the reaction of the deprotonated silaborate with iron(II) bromide we found with **3** (Figure 2) an unprecedented structural motif for cluster coordination chemistry.[11] The coordination of the silaborate cluster trianion is realized in the series of the cyclopentadienyl complexes of cobalt, rhodium **4** (Figure 2) and iridium.[12]

In this paper we report on the formation of silaborate ruthenium complexes. These complexes can be either mononuclear or trinuclear in dependency of the chosen stoichiometry between $[Ru_3(CO)_{12}]$ and $[MeSiB_{10}H_{12}]^-$.

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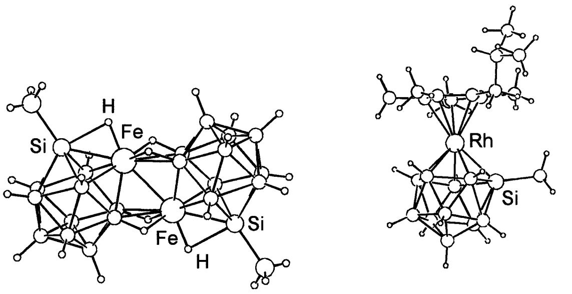
Figure 2. Transition metal silaborate complexes



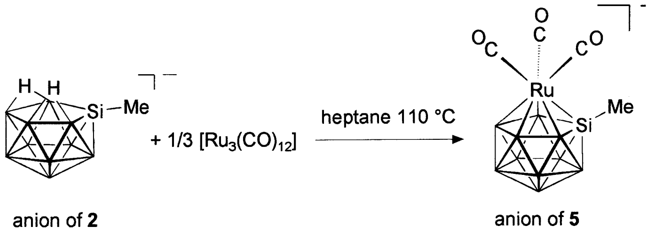
3 **4**

Results

Mononuclear Complexes

The mononuclear tricarbonylruthenium complex is readily formed by heating a suspension of three equivalents of $[NEt_4][MeSiB_{10}H_{12}]$ with one equivalent of $[Ru_3(CO)_{12}]$ in heptane for 15 h at 110°C (Scheme 1). The resulting dark brown oil was recrystallized by slow diffusion of Et_2O into a CH_2Cl_2 solution of the reaction mixture to give colourless crystals of $[NEt_4][Ru(CO)_3(MeSiB_{10}H_{10})]$ (**5**) in 92% yield.

Scheme 1. Synthesis of **5**



The metallasilaborate **5** was characterized by elemental analyses, NMR spectroscopy, mass spectrometry, and single crystal X-ray structure analysis. Six signals in the ^{11}B-NMR spectrum for ten boron atoms with an intensity ratio of 1:2:2:1:2:2 are consistent with C_s symmetry of the cluster anion of **5** in solution. In the two-dimensional $^{11}B\{^1H\}$-$^{11}B\{^1H\}$ COSY-NMR spectrum the cross peak between B3/6 and B4/5 is missing due to bridging by the silicon atom. The effect, that connections between boron atoms, which are bridged by hetero atoms, are not visible in the two-dimensional COSY ^{11}B-NMR spectrum, is known from other heteroboranes like carboranes[13].

The ^{11}B-NMR chemical shifts in heteroborane clusters are governed by the antipodal effect[14]. Substitution of a heteroatom in a borane cluster is equivalent to changes of the electronic structure of the cage compound, with the strongest variations at the antipodal atom. In the anion of **5** the two heteroatoms Ru and Si are opposite to the boron atoms B9 and B12. As expected the chemical shift for B12 opposite to the silicon atom appears at high field (δ = −9.7) in the range of values which are known from other metallasilaboranes (δ = −5.3 to −19.4)[11][12] (Figure 3). In comparison to B12 the resonance for B9, the boron atom opposite to the transition metal center, appears at lower field (δ = +4.1 to −0.1; M = Fe, Co, Rh, Ir)[12]. In the presented complex for B9 a value of δ = 12.2 was determined. This chemical shift represents the resonance at lowest field in the series of the so far known metallasilaboranes. It can be interpreted as an indicator for the electron-withdrawing ability of the tricarbonylruthenium group.

The stretching frequencies for the terminal carbonyl substituents of 2075 and 2002 cm^{-1} are smaller than the comparable values in **1** (2114, 2058 cm^{-1}). Obviously, π-back bonding in MCO is not as much reduced in **5** as in **1**, which could be attributed to stronger σ-donation by the silaborate ligand.

A perspective view of the anion of **5** is presented as the result of the X-ray crystal structure analysis in Figure 4 and selected interatomic distances are listed in the Table. The structural study confirms the prediction of the spectroscopic analyses, a *closo* structure for the ruthenasilaborate. The $Ru(CO)_3$ fragment is η^5-coordinated at the silaborate ligand. As a common structural motif for transition metal coordination on the silaborate ligand the distances to B7/11 [2.292(6), 2.300(6) Å] are shorter than to B3/6 [2.372(6), 2.377(6) Å][11][12].

The short Ru−Si distance of 2.396(2) Å can be compared with distances in silyl complexes[15]. The short Ru−B7/11 and Ru−Si distances indicate a major contribution to these atoms of the pentagonal open face of the ligand for transition metal coordination. Tilley described in 1994 the synthesis of $(\eta^5\text{-}C_5Me_5)Ru[\eta^5\text{-}Me_4C_4SiSi(SiMe_3)_3]$ a stable silacyclopentadienyl complex of ruthenium[16]. In the case of the protonated derivative $[Cp^*Ru(H)\{\eta^5\text{-}Me_4C_4SiSi(SiMe_3)_3\}][BPh_4]$ a Ru−Si distance of 2.441(3) Å was determined by X-ray structure analysis.

Based on the isolobal analogy the $Ru(CO)_3$ fragment donates two electrons to the cluster electron count. Summation over the complete skeleton gives a total of 26 electrons, which corresponds to $2n+2$ electrons for a *closo* cluster with 12 edges.

The degradation product of *o*-silaborane **2** reacts with the trinuclear dodecacarbonyltriiron to give the tricarbonyliron silaborate cluster **6** in quantitative yield based on the ^{11}B-NMR spectra. The pattern in the two-dimensional $^{11}B\{^1H\}$-$^{11}B\{^1H\}$ COSY-NMR spectrum (Figure 5) and the ^{11}B chemical shifts of the iron derivative are strongly related to the ruthenium complex **5**.

6 was also characterized by mass spectrometry and IR spectroscopy. Unfortunately, the elemental analyses failed due to carbonyliron impurities.

Trinuclear Metallasilaborates

The *nido*-silaborate **2** reacts with $[Ru_3(CO)_{12}]$ in heptane at reflux temperatures to give the trinuclear rutheniumsilaborate cluster **7** (Scheme 2). The cluster was obtained in almost quantitative yield as yellow crystals by slow diffusion of Et_2O into a CH_2Cl_2 solution of the reaction mixture.

As with **5**, **7** was characterized by elemental analyses, mass spectrometry, IR spectroscopy, and NMR spec-

Figure 3. ^{11}B-NMR chemical shifts

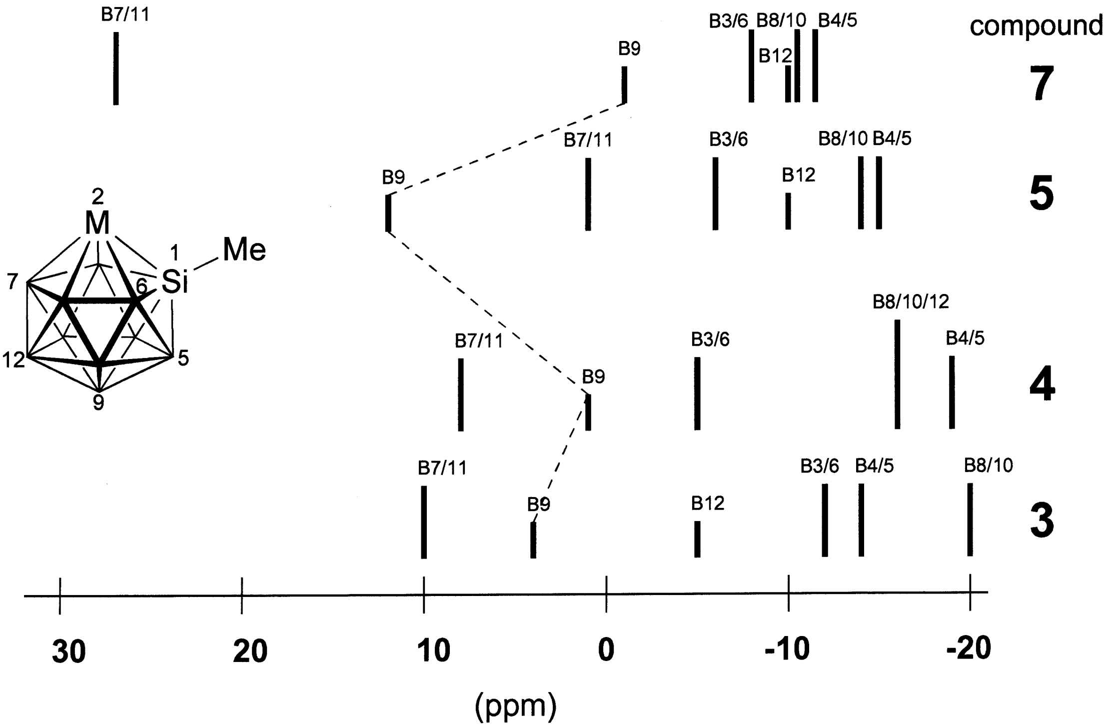


Figure 4. Molecular structure for the anion of **5**

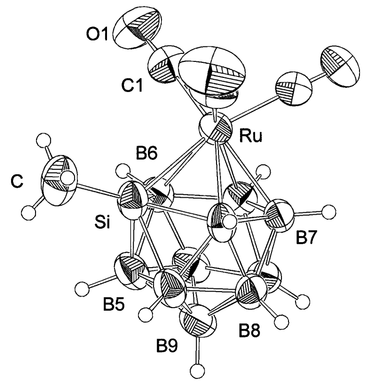
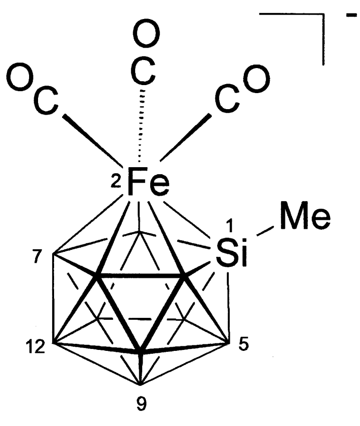


Table 1. Selected interatomic distances [Å] in **5**

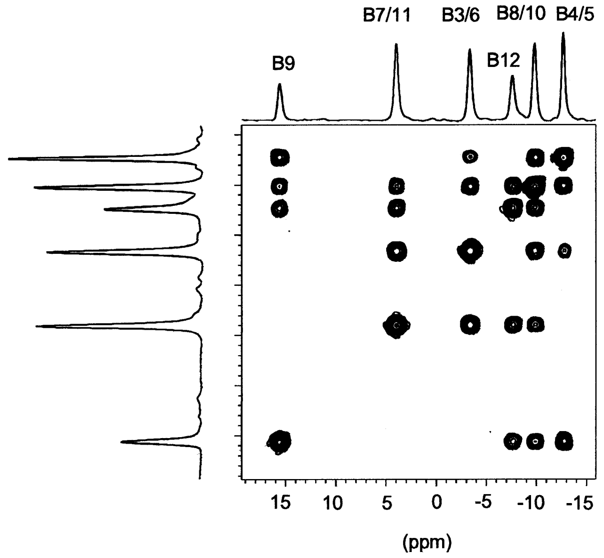
Ru−C1	1.919(7)	B3−B4	1.834(9)
Ru−C2	1.937(6)	B3−B7	1.815(8)
Ru−C3	1.901(7)	B3−B8	1.764(9)
Ru−Si	2.396(2)	B4−B5	1.854(9)
Ru−B3	2.372(6)	B4−B8	1.765(9)
Ru−B6	2.377(6)	B4−B9	1.766(11)
Ru−B7	2.292(6)	B5−B6	1.822(10)
Ru−B11	2.300(6)	B5−B9	1.763(10)
Si−C4	1.859(6)	B5−B10	1.750(10)
Si−B3	2.091(6)	B6−B10	1.751(10)
Si−B4	2.027(7)	B6−B11	1.793(9)
Si−B5	2.033(7)	B7−B8	1.791(9)
B7−B12	1.781(9)	B10−B11	1.779(9)
B8−B9	1.775(9)	B10−B12	1.765(9)
B8−B12	1.781(9)	B11−B12	1.782(9)
B9−B10	1.758(10)	B7−B11	1.865(8)
B9−B12	1.764(9)	Si−B6	2.104(7)

troscopy. On the basis of these spectroscopical data the constitution of **7** was unequivocally determined. The silaborate ligand is η^5-coordinated at one ruthenium atom replacing two carbonyl substituents. Two BH units coordinate at the other two ruthenium atoms of the Ru_3 cluster, replacing each one carbonyl substituent. Coordination of the BH units of B7/11 is proven by the reduced coupling constant of $^1J_{BH}$ = 67 Hz, the shift to low field in the ^{11}B-NMR spectrum for the resonances of B7/11 (Figure 3), and the cross peak in the two dimensional HMQC $^1H\{^{11}B\}$-$^{11}B\{^1H\}$ NMR spectrum between the resonances for B7/11 and a broad quadruplet in the ^{1}H-NMR spectrum at $\delta = -10$. Longer reaction times resulted in the decomposition of **7** and the isolation of the mononuclear cluster **5** together with the formation of a tetranuclear ruthenium cluster anion $[NEt_4][(\mu\text{-}H)_3Ru_4(CO)_{12}]$[17]. In contrast to the inertness of **5** towards nucleophiles **7** reacts readily with phosphanes (Scheme 2) to give the disubstituted derivative **8**. Carbonyl substitution at the ruthenium cluster skeleton is known from the dicarbollide analogues. **7** reacts with two equivalents of PMe_2Ph under substitution of one carbonyl group at each $Ru(CO)_3$ unit. In contrast to the analogue reaction of $[Ru_3(CO)_8(C_2B_9H_{11})]$ leading to oxidative addition of one coordinated BH unit at a ruthenium centre in the silaborane case the coordinated BH units of B7/11 remain unchanged. The constitution of **8** was deduced from the spectroscopical data together with elemental analysis and mass spectrometry. As in **7** a reduced coupling constant ($^1J_{BH}$ = 83 Hz) for the BH units of B7/11, a low-field chemical shift in the ^{11}B NMR for B7/11 and a cross peak in the HMQC $^1H\{^{11}B\}$-$^{11}B\{^1H\}$ between the resonances for B7/11 and a signal at $\delta = -10.6$ indicates the coordination

Figure 5. $^{11}B\{^{1}H\}$-$^{11}B\{^{1}H\}$ COSY-NMR spectrum of the anion of **6**



anion of 6

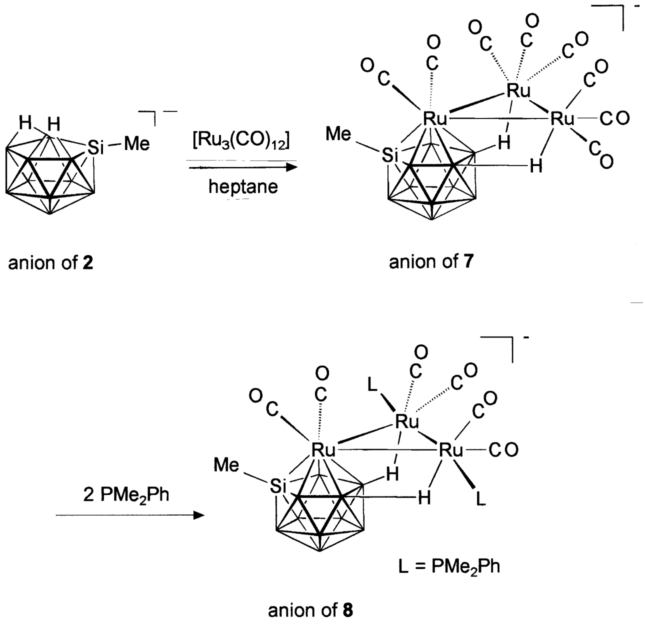


of these BH units at the ruthenium centres. The C_s symmetry of the cluster anion in solution is proven by five signals in the ^{11}B NMR for ten boron atoms, the resonances for B3/6 and B9 are accidentily isochronic, and one ^{31}P-NMR resonance for the two phosphane ligands. **8** crystallizes with one equivalent of dichloromethane in the space group $P2_1/a$ with a = 13.881(3), b = 12.773(7), c = 27.2800(9) Å, and β = 97.99(2)°. Due to an immediate loss of cocrystallized CH_2Cl_2 after isolation from the solution, no crystals of good quality could be obtained. Reflections were broad and of relative low intensity. In addition the atoms of the CH_2Cl_2 show large displacement parameters. Therefore no geometric details of the structure will be discussed but the constitution of **8** was confirmed.

Conclusion

The anionic degradation product of *o*-silaborane reacts with dodecacarbonyltriruthenium to give the first carbonyl transition metal complexes with a silaborate ligand. In contrast to the syntheses of the carbonylruthenium dicarbollide and monocarbollide complexes the formation of the mononuclear or trinuclear ruthenium complex is determined by the stoichiometry of silaborate and carbonylruthenium.

Scheme 2. Syntheses of **7** and **8**



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Experimental Section

General: All manipulations were carried out under dry N_2 in Schlenk glassware. Solvents were dried and purified by standard methods and were stored under N_2. − NMR: Varian Unity 500 (500 MHz, ^{1}H, int. TMS; 126 MHz, $^{13}C\{^{1}H\}$, int. TMS; 202 MHz, ^{31}P, ext. H_3PO_4; 160 MHz, ^{11}B, ext. BF_3OEt_2; 100 MHz, ^{29}Si, ext. TMS). − MS: Finnigan MAT 95. − Elemental analysis: Institut für Anorganische Chemie RWTH Aachen, Carlo-Erba elemental analyzer, Modell 1106; Mikroanalytisches Labor Pascher, Remagen.

$[NEt_4][Ru(CO)_3(\eta^5\text{-}MeSiB_{10}H_{10})]$ (**5**): Tetraethylammonium dodecahydro-7-methyl-7-sila-*nido*-undecaborate(1−) (**2**; 250 mg, 0.85 mmol) was suspended with 25 ml of heptane and dodecacarbonyltriruthenium (181 mg, 639.3 g/mol, 0.28 mmol). The mixture was refluxed for 15 h and the solvent was evaporated in vacuum to give a red oily residue. Recrystallization was carried out by slow diffusion of diethyl ether into a solution of dichloromethane at −30°C to give 376 mg (93% yield) of **5** as colourless crystals. − IR (KBr) $\tilde{\nu}$ = 2075 cm^{-1} (CO), 2002 (CO). − $^{1}H\{^{11}B\}$ NMR (CD_2Cl_2): δ = 3.67 (s, 1 H, H9), 2.14 (s, 2 H, H7/11), 2.00 (s, 2 H, H3/6), 1.92 (s, 1 H, H12), 1.84 (s, 2 H, H4/5), 1.37 (s, 2 H, H8/10), 0.84 (s, 3 H, $SiCH_3$). − $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ = 196.4 (s, 3 C, CO), −4.8 (s, 1 C, $SiCH_3$). − ^{11}B NMR (CD_2Cl_2): δ = 12.2 (d, ^{1}J = 134 Hz, 1 B, B9), 0.7 (d, ^{1}J = 134 Hz, 2 B, B7/11), −6.2 (d,

^1J = 134 Hz, 2 B, B3/6), −9.7 (d, ^1J = 134 Hz, 1 B, B12), −13.8 (d, ^1J = 158 Hz, 2 B, B8/10), −15.1 (d, ^1J = 146 Hz, 2 B, B4/5). – ^{29}Si NMR (CD_2Cl_2): δ = 28.2 (s, MeSi). – MS (70 eV) SIMS; *m/z* (%): 347.2 (100) [M^-]. – $C_{12}H_{33}B_{10}NO_3RuSi$ (476.66): calcd. C 30.24, H 6.98; found C 29.41, H 5.90.

X-ray Crystallographic Study of **5**: $C_{12}H_{33}B_{10}NO_3RuSi$; formula mass 476.66 g mol^{-1}; monoclinic space group *C*2/*c* (no. 15); *a* = 32.641(5), *b* = 8.451(3), *c* = 21.489(3) Å, β = 125.73(2)°, *V* = 4812(2), *Z* = 8, $d_{\text{calcd.}}$ = 1.316 g cm^{-3}; $\mu_{lin.}$ = 0.714 mm^{-1}. Enraf-Nonius CAD4 diffractometer; Mo-K_α radiation (λ = 0.71070 Å); graphite monochromator. Data collection at room temperature on a crystal of about 1.1 × 0.2 × 0.2 mm using ω-scans ($6° \leq 2\theta \leq 60°$) yielded 7093 reflections, which after merging the symmetry equivalents gave 6983 independent reflections with 3888 observations [$I > 2\sigma(I)$]. Intensity data were corrected for Lorentz and polarization effects, and a semi-empirical absorption correction (using ψ-scans)[18] was applied with the program system MolEN.[19] After solving the structure by direct and Difference Fourier methods[20], the structure was refined against F^2 using SHELXL-93[21] with anisotropic parameters for the non hydrogen atoms. This resulted in *wR*2 = 0.134 and *R* = 0.061 (observed reflections only) for 289 variables (GOF = 1.169). The hydrogen atoms attached to boron atoms were refined in their positions; the remaining hydrogen atoms were included into calculated positions. A final difference Fourier map gave min./max. residual electron densities of 0.940/ −1.361 eA^{-3}[22].

[NEt$_4$][Fe(CO)$_3$(η^5-MeSiB$_{10}$H$_{10}$)] (**6**): Tetraethylammonium dodecahydro-7-methyl-7-sila-*nido*-undecaborate(1−) (**2**; 250 mg 0.85 mmol) was suspended with 25 ml of heptane and dodecacarbonyltriruthenium (429 mg, 503.7 g/mol, 0.85 mmol). The mixture was refluxed for 15 h and the solvent was evaporated in vacuum to give a red oily residue, which could not be purified by recrystallization. – IR (KBr) ṽ = 2081 cm^{-1} (CO), 2009 (CO). – ^{1}H{^{11}B} NMR (CD_2Cl_2): δ = 3.57 (s, 1 H, H9), 2.35 (s, 2 H, H7/11), 2.11 (s, 1 H, H12), 1.94 (s, 4 H, H3/6, 4/5), 1.91 (s, 2 H, H8/10), 0.81 (s, 3 H, $SiCH_3$). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 208.6 (s, 3 C, CO), −7.1 (s, 1 C, $SiCH_3$). – ^{11}B NMR (CD_2Cl_2): δ = 13.9 (d, ^1J = 134 Hz, 1 B, B9), 3.1 (d, ^1J = 122 Hz, 2 B, B7/11), −3.8 (d, ^1J = 134 Hz, 2 B, B3/6), −8.4 (d, ^1J = 134 Hz, 1 B, B12), −10.6 (d, ^1J = 134 Hz, 2 B, B8/10), −12.9 (d, ^1J = 146 Hz, 2B, B4/5). – ^{29}Si NMR (CD_2Cl_2): δ = 38.9 (s, MeSi). – MS (70 eV) SIMS; *m/z* (%): 301.2 (100) [M^-], 272.3 (23, M^- − CO), 245.1 (22, M^- − 2CO).

[NEt$_4$][Ru$_3$(CO)$_8$(η^5-MeSiB$_{10}$H$_{10}$)] (**7**): Tetraethylammonium dodecahydro-7-methyl-7-sila-*nido*-undecaborate(1−) (**2**, 250 mg 0.85 mmol) was suspended with 25 ml of heptane and dodecacarbonyltriruthenium (544.4 mg, 639.3 g/mol, 0.85 mmol). The mixture was refluxed for 15 h and the solvent was evaporated in vacuum to give a red oily residue. Recrystallization was carried out by slow diffusion of diethyl ether into a solution of dichloromethane at −30°C to give 697 mg (91% yield) of **7** as yellow crystals. – IR (KBr) ṽ = 2071 cm^{-1} (CO), 2029 (CO), 1994 (CO), 1972 (CO). – ^{1}H{^{11}B} NMR (CD_2Cl_2): δ = 2.83 (s, 1 H, H9), 2.18 (s, 1 H, H12), 1.97 (s, 4 H, H4/5/8/10), 1.86 (s, 2 H, H3/6), 0.83 (s, 3 H, $SiCH_3$), −10.25 (s, 2 H, H7/11). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 211.8 (s, 1 C, CO), 206.1 (s, 1 C, CO), 200.3 (s, 1 C, CO), 199.5 (s, 1 C, CO), 197.2 (s, 1 C, CO), 196.4 (s, 1 C, CO), 194.2 (s, 1 C, CO), 191.3 (s, 1 C, CO), 53.6 (s, 4 C, NCH_2CH_3), 8.0 (s, 4 C, NCH_2CH_3) −4.5 (s, 1 C, $SiCH_3$). – ^{11}B NMR (CD_2Cl_2): δ = 27.1 (d, ^1J = 67 Hz, 2 B, B7/11), −0.9 (d, ^1J = 140 Hz, 1 B, B9), −8.1 (d, ^1J = 134 Hz, 2 B, B3/6), −9.8 (d, ^1J = 153 Hz, 1 B, B12), −10.8 (d, ^1J = 116 Hz, 2 B, B8/10), −11.3 (d, ^1J = 104 Hz, 2 B, B4/5). – ^{29}Si NMR (CD_2Cl_2): δ = 6.7 (s, MeSi). – MS (70 eV) SIMS; *m/z* (%): 690.6 (18) [M^- − 2CO], 662.8 (64) [M^- − CO], 634.8 (100) [M^- − 2CO]. – $C_{17}H_{31}B_{10}NO_8Ru_3Si$ (816.83): calcd. C 25.00, H 3.83, N 1.72; found C 24.66, H 4.01, N 1.69.

[NEt$_4$][Ru$_3$(CO)$_6$(PMe$_2$Ph)$_2$(η^5-MeSiB$_{10}$H$_{10}$)] (**8**): 200 mg (*M* = 818.8 g/mol, 0.24 mmol) of **7**, dissolved in 20 ml of THF, was treated with 71 μl of PMe_2Ph (*M* = 138.2 g/mol, 0.50 mmol) at room temperature. After heating for 2 h under reflux, the solution was concentrated to dryness and the resulting orange solid was recrystallized from 20 ml of CH_2Cl_2 by slow diffusion of hexane at −30°C to give 233 mg (91% yield) of **8** as red crystals. – IR (dioxane) ṽ = 2050 cm^{-1} (CO), 1962 (CO). – ^{1}H{^{11}B} NMR ([D$_8$]THF): δ = 7.44−7.22 (m, 10 H, PPh), 2.62, 1.87, 1.78, 1.69 (s, br., BH), 1.71 (s, br., 12 H, PMe_2), 0.69 (s, 3 H, $SiCH_3$), −10.55 (q, br., 2 H, BHRu). – ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 211.1, 204.3, 201.2 (s, 2 C, CO), 142.4 (s, br., 2 C, PC), 129.2, 128.6, 128.3 (s, Ph), 52.9 (s, 4 C, N*C*H$_2$CH$_3$), 7.8 (s, 4 C, NCH$_2$*C*H$_3$), −4.0 (s, 1 C, $SiCH_3$). – ^{11}B NMR ([D$_8$]THF): δ = 26.0 (d, ^1J = 83 Hz, 2 B, B7/11), −3.0 (d, ^1J = 140 Hz, 3 B, B3/6/9), −10.2 (d, ^1J = 134 Hz, 2 B, B4/5), −11.7 (d, ^1J = 109 Hz, 1 B, B12), −12.5 (d, ^1J = 141 Hz, 2 B, B8/10). – ^{29}Si NMR ([D$_8$]THF): δ = −29.8 (s, MeSi). – ^{31}P NMR ([D$_8$]THF): δ = −4.3 (s, 2 P, PMe_2Ph). – MS (70 eV) SIMS; *m/z* (%): 910.2 (100) [M^- − 10]. – $C_{31}H_{55}B_{10}NO_6P_2Ru_3Si$-($CH_2Cl_2$) (1124.06): calcd. C 34.19, H 5.11; found C 33.85, H 4.93.

☆ Dedicated to Prof. Dr. *Heinrich Nöth* on the occasion of his 70th birthday.

[1] [1a] M. F. Hawthorne, *Acc. Chem. Res.* **1968**, *1*, 281−288. – [1b] A. K. Saxena, N. S. Hosmane, *Chem. Rev.* **1993**, *93*, 1081−1124.

[2] M. F. Hawthorne, H. W. Ruhle, *Inorg. Chem.* **1969**, *8*, 176−178.

[3] [3a] S. S. Lee, C. B. Knobler, M. F. Hawthorne, *Organometallics* **1991**, *10*, 670−677. – [3b] S. S. Lee, C. B. Knobler, M. F. Hawthorne, *Organometallics* **1991**, *10*, 1054−1062.

[4] A. R. Siedle, *J. Organomet. Chem.* **1975**, *90*, 249−256.

[5] P. E. Behnken, M. F. Hawthorne, *Inorg. Chem.* **1984**, *23*, 3420−3423.

[6] S. Anderson, D. F. Mullica, E. L. Sappenfield, F. G. A. Stone, *Organometallics* **1995**, *14*, 3516−3526.

[7] Y.-H. Liao, D. F. Mullica, E. L. Sappenfield, F. G. A. Stone, *Organometallics* **1996**, *15*, 5102−5111.

[8] V. N. Lebedev, D. F. Mullica, E. L. Sappenfield, F. G. A. Stone, *J. Organomet. Chem.* **1997**, *536−537*, 537−539.

[9] V. N. Lebedev, D. F. Mullica, E. L. Sappenfield, F. G. A. Stone, *Organometallics* **1996**, *15*, 1669−1675.

[10] L. Wesemann, U. Englert, D. Seyferth, *Angew. Chem.* **1995**, *107*, 2435−2436; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2236−2238.

[11] L. Wesemann, Y. Ramjoie, B. Ganter, B. Wrackmeyer, *Angew. Chem.* **1997**, *109*, 902−904; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 888−890.

[12] L. Wesemann, Y. Ramjoie, M. Trinkaus, B. Ganter, *Inorg. Chem.* **1997**, *36*, 5192−5197.

[13] T. L. Venable, W. C. Hutton, R. N. Grimes, *J. Am. Chem. Soc.* **1984**, *106*, 29−37.

[14] [14a] M. Bühl, P. v. R. Schleyer, Z. Havlas, D. Hynk, S. Hermanek, *Inorg. Chem.* **1991**, *30*, 3107−3111. – [14b] S. Hermanek, *Chem. Rev.* **1992**, *92*, 325−362.

[15] D. A. Straus, T. D. Tilley, A. L. Rheingold, S. J. Geib, *J. Am. Chem. Soc.* **1987**, *109*, 5872−5873.

[16] W. P. Freeman, T. D. Tilley, A. L. Rheingold, *J. Am. Chem. Soc.* **1994**, *116*, 8428−8429.

[17] J. W. Koepke, J. R. Johnson, S. A. R. Knox, H. D. Kaesz, *J. Am. Chem. Soc.* **1975**, *97*, 3947−3952.

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

[19] C. K. Fair, *MolEN, An Interactive Structure Solution Procedure,*

Enraf-Nonius, Delft, The Netherlands, **1990**.
[20] G. M. Sheldrick, SHELXS-86, *Acta Crystallogr.* **1990**, *A46,* 467.
[21] G. M. Sheldrick, *Program for the refinement of Crystal Structures*, Universität Göttingen, **1993**.
[22] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-408509, the names of the authors, and the journal citation.

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