The liquified gasses (ethene, propene, 1-butene) were first condensed into a steel cylinder and then introduced into the autoclave under pressure.

All products were unambiguously identified by GC/MS. After distillation of the products NMR spectra consistent with literature information were obtained.

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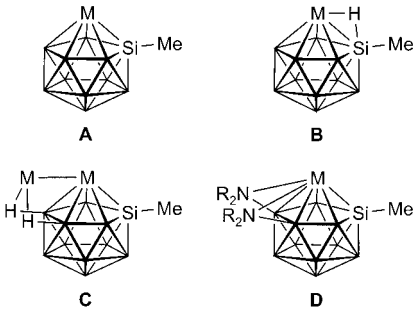
A Novel Coordination Mode of 7-Methyl-7-sila-*nido*-undecaborate(1 –)**

Lars Wesemann,* Michael Trinkaus, and Michael Ruck

The first transition metal complex of a silaborate, 7-methyl-7-sila-*nido*-undecaborate(1 –) ($MeSiB_{10}H_{12}^-$), a derivative of the higher homologue of the carbollide ligand, was described only two years ago.[1] In analogy to the carbon-containing cluster, the silaborate ligand will be referred to as a silollide ligand in the following. The known coordination modes of various complexes of this type that have been characterized by single-crystal structure analyses are depicted in Scheme 1.



Scheme 1. Coordination modes of 7-methyl-7-sila-*nido*-undecaborate(1 –).

Type **A** resembles the typical η^5 coordination mode, as known for many complexes of the dicarbollide (*nido*-$C_2B_9H_{12}^-$)[2] and carbollide (*nido*-$CB_{10}H_{13}^-$)[3, 4] ligands and as is found in the mixed sandwich anions $[Cp^*M(MeSiB_{10}H_{10})]^-$ (M = Co, Rh, Ir)[5] and the carbonyl complexes $[(CO)_3M(MeSiB_{10}H_{10})]^-$ (M = Ru, Fe).[6] Both coordination types **B** and **C** are observed in the dinuclear complex $[NBu_4]_2[\{HFe(MeSiB_{10}H_{10})\}_2]$.[1] Herein we will describe compounds of type **D** which display a hitherto unknown coordination pattern in borane and heteroborane chemistry that results from an unexpected B,H activation.

Jordan[7] and co-workers adapted a method of Chandra and Lappert[8] for the synthesis of dicarbollide complexes from transition metal amides. Application of the same reaction to the silollide ligand yields the highly air- and moisture-sensitive metallasilaborates $[NEt_4][Nb(MeSiB_{10}H_{10})(NMe_2)_3]$ (**1**) and $[NEt_4][Ta(MeSiB_{10}H_{10})(NMe_2)_3]$ (**2**) from [*nido*-$MeSiB_{10}H_{12}]^-$ and $[Nb(NMe_2)_5]$ or $[Ta(NMe_2)_5]$ [Eq. (1)]. The reaction is almost quantitative according to NMR spectroscopy.

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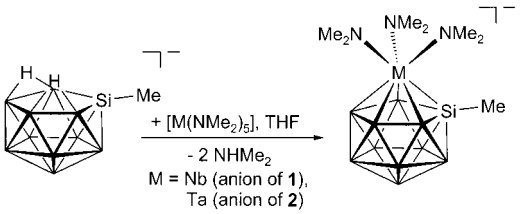
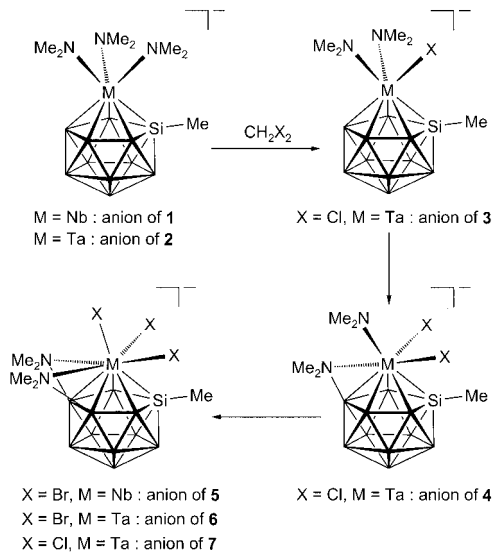


(1)

Compounds **1** and **2** react with any solvent able to dissolve them, making it impossible to gain crystals. Nevertheless they can be isolated from THF in good yields, and characterized by NMR spectroscopy and by C,H elemental analysis if worked up quickly. Both products show six ^{11}B NMR signals in the ratios 2:2:2:1:2:1 as expected for C_s symmetry. The spectrum is shifted to lower field in comparison with that of the precursor [*nido*-$MeSiB_{10}H_{12}]^-$. Interestingly, the coupling constant $^1J_{B,H}$ for the boron atoms B7 and B11 in the vicinity of the metal center (110 Hz) is reduced significantly [$^1J_{B,H}$(B12) = 134 Hz].

Reaction of **1** or **2** with THF over more than 24 h leads to insoluble products, whereas reaction with dichloromethane or dibromomethane at room temperature selectively gives a series of new compounds (Scheme 2), depending on the reaction time. The rate of these reactions allows the course of the reaction to be monitored by ^{11}B NMR spectroscopy.



Scheme 2. Reactions of **1** and **2** with dichloromethane and dibromomethane.

Reaction of the trisamido complex **2** with dichloromethane at room temperature gives [NEt_4][Ta($MeSiB_{10}H_{10}$)(NMe_2)$_2$Cl] (**3**) within two days, as deduced from NMR evidence. The monochloro complex **3** also evolves from a mixture of **2** in THF with an excess of zirconium tetrachloride $(ZrCl_4)_x$ as a chloride-amide exchanger. Astonishingly, after six days **3** is almost quantitatively transformed to [NEt_4][Ta($MeSiB_{10}H_9$)(μ-NMe_2)(NMe_2)Cl$_2$] (**4**), which contains the above-mentioned unusual amido bridge between B7 and the tantalum atom. The μ-amido complex **4** can be isolated as brownish crystals by slow diffusion of hexane into the reaction mixture. In agreement with the loss of symmetry from C_s to C_1 the ^{11}B NMR spectrum of **4** shows ten signals (one for each B atom). The signal of the boron atom carrying the nitrogen bridge (B7) experiences the strongest downfield shift in comparison with that of **3**. The most conspicuous change is the disappearance of the B,H coupling of the signal of atom B7 in the proton-coupled ^{11}B NMR spectrum, confirming the removal of the hydrogen atom from the bridging position.

Whereas B,H activation is a relatively common phenomenon in borane and heteroborane chemistry, the formation of a nonmetal bridge between a cage boron atom and a metal center is rarely observed. Examples of M-C-B bridges have been reported by Stone and co-workers.[9, 10] Another example is the so-called orthoboronation reaction in which the phenyl group of a phosphane ligand binds to a cage boron atom.[11]

In dibromomethane the reaction of the trisamido complexes **1** or **2** goes one step further to produce [NEt_4]-[Nb($MeSiB_{10}H_8$)(μ-NMe_2)$_2$Br$_3$] (**5**) and [NEt_4][Ta($MeSiB_{10}H_8$)-(μ-NMe_2)$_2$Br$_3$] (**6**), respectively, which contain two B-N-M bridges (Scheme 2). In contrast to **4**, compounds **5** and **6** show, according to C_s symmetry, six signals in the ratios 2:2:2:1:2:1 in the ^{11}B NMR spectrum. The NMR data reveal that refluxing **2** in CH_2Cl_2 for two days gives [NEt_4]-[Ta($MeSiB_{10}H_8$)(μ-NMe_2)$_2$Cl$_3$](**7**). Crystals of the tribromide complexes **5** and **6** can be obtained in good yields by slow diffusion of hexane into the reaction mixture at $-30\,^\circ$C. The constitution of [NBu_4][Nb($MeSiB_{10}H_8$)(μ-NMe_2)$_2$Br$_3$](**5′**) was verified by a single-crystal structure analysis; the molecular structure of the anion is depicted in Figure 1.[12]

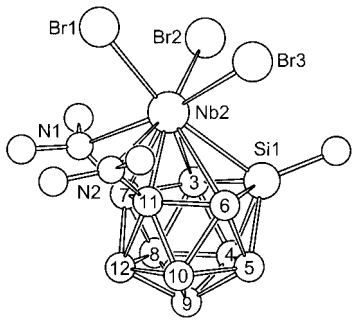


Figure 1. Molecular structure of the [Nb($MeSiB_{10}H_8$)(μ-NMe_2)$_2$Br$_3$]$^-$ anion in the crystal structure of **5′**.

The niobium atom is coordinated to the silaborate moiety and exhibits two long interatomic distances (2.576(7), 2.610(8) Å) to the boron atoms, B3 and B6, neighboring the silicon atom and two short distances (2.138(8), 2.342(7) Å) to B7 and B11. This structural motif has also been observed in the other metallasilaborates.[1, 5, 6] One example for the coordination of a carborane ligand at a $CpNbMe_2$ fragment is known: the Nb–B distances are 2.456(4), 2.410(4), and 2.414(4) Å.[15] The Nb–Si distance of 2.670(3) Å is comparable with the distances reported for Nb–Si single bonds in [$Cp_2Nb(C_2H_4)SiMe_3$] (2.669(1) Å)[16] and [$Cp_2NbH(SiMe_3)_2$] (2.584(2), 2.611(2) Å).[17] The Nb–N distances (2.488(6), 2.506(6) Å) are much longer than the single bond value in the amine adduct [Nb(OAr-2,6-Ph_2)$_3$NMe($HNMe_2$)] (2.326(6) Å).[18] The B–N distances (1.509(8), 1.492(8) Å) lie

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in the range between a typical single (B–N: 1.58 Å) and a double (B=N: 1.41 Å) bond.[19]

The new metallasilaborates presented obey Wade's rules.[20]

Experimental Section

5: $[NEt_4][MeSiB_{10}H_{12}]$ (197.7 mg, 0.67 mmol) was dissolved in CH_2Br_2 (10 mL), cooled to the freezing point of the solvent, and added to a similarly cold solution of $Nb(NMe_2)_5$ (265.9 mg, 1.26 equiv) in dibromomethane (10 mL). The solution was allowed to warm to room temperature and stirred for four days. The resulting dark brown solution was filtered and then layered with hexane to give green-black crystals at $-30\,^{\circ}C$ that contained one equivalent of CH_2Br_2. Recrystallization from dichloromethane gave crystals containing one equivalent of CH_2Cl_2. Crystals for X-ray structure analysis were obtained by an analogous procedure using $[NBu_4]^+$ as counterion. Yield: 0.392 g (73 %). $^1H\{^{11}B\}$ NMR (CD_2Cl_2, 500 MHz, TMS): $\delta = 0.98$ (s, 3H, SiMe), 2.15 (s, 1H, H12), 2.21 (s, 1H, H9), 2.63 (s, 2H, H8/10), 2.67 (s, 6H, μ-NMe_2), 2.79 (s, 2H, H4/5), 3.00 (s, 6H, μ-NMe_2), 3.47 (s, 2H, H3/6), 4.97 (s, 2H, CH_2Br_2); ^{11}B NMR (CD_2Cl_2, 160 MHz, $Et_2O \cdot BF_3$): $\delta = 32.1$ (s, B7/11), 13.8 (d, $^1J = 134$ Hz, B 3/6), -2.2 (d, $^1J = 134$ Hz, B9/4/5), -9.0 (d, $^1J = 134$ Hz, B8/10), -11.7 (d, $^1J = 134$ Hz, B12); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): $\delta = -4.6$ (s, MeSi), 51.5 (s, μ-NMe_2), 56.9 (s, μ-NMe_2); ^{29}Si NMR (CD_2Cl_2, 100 MHz, TMS): $\delta = 36.22$; C, H, N analysis (%): calcd: C 21.09, H 5.94, N 5.27; found: C 20.92; H 6.15, N 5.77.

6: Same procedure as for **5** with $[NEt_4][MeSiB_{10}H_{12}]$ (273.0 mg, 0.93 mmol) and $Ta(NMe_2)_5$ (397.2 mg, 0.98 mmol, 1.06 equiv). Yield: 0.564 g (69 %). $^1H\{^{11}B\}$ NMR (CD_2Cl_2, 500 MHz, TMS): $\delta = 0.98$ (s, 3H, SiMe), 2.37 (s, 1H, H12), 2.73 (s, 1H, H9), 2.80 (s, 6H, μ-NMe_2), 2.85 (s, 2H, H8/10), 3.11 (s, 6H, μ-NMe_2), 3.07 (s, 2H, H4/5), 3.31 (s, 2H, H3/6); ^{11}B NMR (CD_2Cl_2, 160 MHz, $Et_2O \cdot BF_3$): $\delta = 28.5$ (s, B7/11), 8.3 (d, $^1J = 134$ Hz, B 3/6), -5.1 (d, $^1J = 134$ Hz, B4/5), -6.1 (d, $^1J = 134$ Hz, B9), -10.8 (d, $^1J = 134$ Hz, B8/10), -13.4 (d, $^1J = 134$ Hz, B12); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): $\delta = -5.0$ (s, MeSi), 51.6 (s, μ-NMe_2), 57.0 (s, μ-NMe_2); ^{29}Si-NMR (CD_2Cl_2, 100 MHz, TMS): $\delta = 30.25$; C, H analysis (%): calcd: C 19.04, H 5.13; found: C 19.27, H 5.33.

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[12] X-ray structure analysis of **5′**: $C_{21}H_{59}B_{10}Br_3N_3NbSi$; $M_r = 822.54$; triclinic space group $I\bar{1}$ (no. 2) non-standard setting; $a = 25.209(9)$, $b = 10.556(4)$, $c = 27.675(9)$ Å, $\alpha = 88.65(9)$, $\beta = 93.91(6)$, $\gamma = 91.00(9)^{\circ}$, $V = 7344(5)$, $Z = 8$, $\rho_{calcd} = 1.488\ g\,cm^{-3}$; $\mu_{lin.} = 3.64\ mm^{-1}$; Stoe IPDS diffractometer; $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å); graphite monochromator; data collection at 200(2) K on a single crystal $0.7 \times 0.5 \times 0.2\ mm^3$, $1.5^{\circ} \le \theta \le 22.7^{\circ}$, $0 \le \phi \le 200^{\circ}$; 15285 reflections measured, 8777 independent, 5071 observed with $I > 2\sigma(I)$; corrections for Lorentz and polarization factors; numerical absorption correction,[13] max./ min. transmission 0.48/0.15; structure solution with direct methods and difference Fourier synthesis;[14] F^2 refinement, isotropic displacement parameters, hydrogen atoms in calculated positions (C–H 0.98, B–H 1.12 Å), split positions for Nb and Br atoms; convergence was obtained for 271 variables with $wR2 = 0.064$, $R1$(observed) = 0.046, GOF = 1.003; max./ min. residual electron density $+0.76/-0.66\ e\,Å^{-3}$. The crystal structure is very close to monoclinic symmetry (pseudo symmetry *I*2/*a*), but neither the metric nor the reflection conditions for the higher symmetry are met. Although both independent anions might be connected by a twofold axis, the $[Bu_4N]^+$ ions differ in conformation. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115869. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-36-033; e-mail: deposit@chemcrys.cam.ac.uk).
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Supramolecular Sensors for the Detection of Alcohols**

Roberta Pinalli, Francine F. Nachtigall, Franco Ugozzoli, and Enrico Dalcanale*

In memory of Antonino Fava

The quest for selectivity is one of the key issues in developing new, efficient chemical sensors.[1] The use of supramolecular structures has proved to be one of the best approaches to

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