H. Era, T. Tsuno, O. Manabe, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1435–1436; e) S. Shinkai, H. Hamada, H. Kuroda, O. Manabe, *Chem. Lett.* **1980**, 1235–1238; f) Y. Ohnishi, M. Kitami, *Tetrahedron Lett.* **1978**, 4035–4036.

[5] The following papers report oxidation of alcohols without confirming the formation of 1,4-dihydropyridines: a) K. Wallenfels, W. Hanstein, *Angew. Chem.* **1965**, *77*, 861–862; *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 869–870; b) A. Shirra, C. J. Suckling, *Tetrahedron Lett.* **1975**, 3323–3324; *J. Chem. Soc. Perkin Trans. 2* **1977**, 759–765.

[6] Y. Ohnishi, S. Tanimoto, *Tetrahedron Lett.* **1977**, 1909–1912.

[7] Ohno et al. attempted GAPDH-type model reactions of glyceraldehyde and its analogues with an NAD^+ model compound in aqueous media. Although an NADH anologue was obtained in 8–45% yield, the corresponding carboxylic acids, the oxidized form of substrates, could not be detected, in spite of the authors' best effort. The mechanism of the reduction has already been proven to be different from that suggested for the enzymatic reaction: A. Ohno, S. Ushida, S. Oka, *Tetrahedron Lett.* **1982**, *23*, 2487–2490; *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1822–1825.

[8] J. H. Babler, B. J. Invergo, *Tetrahedron Lett.* **1981**, *22*, 621–622.

[9] P. J. Harrigan, D. R. Trentham, *Biochem. J.* **1973**, *135*, 695–703.

[10] A. J. Kirby, D. R. Walwyn, *Gazz. Chim. Ital.* **1987**, *117*, 667–680.

[11] Reduction of **2a–d** with $NaBH_4$ in ethanol also afforded a significant amount of 1,6-dihydronicotinamides, the ^1H NMR spectra of which are identical to those of **4a–d**. All the signals (5H) of their dihydronicotinoyl rings were well separated from those of the other products such as **3a–d.**

[12] U. Berg, N. Åström, *Acta Chem. Scand.* **1995**, *49*, 599–608.

[13] a) D. C. Dittmer, A. Lombardo, F. H. Batzold, C. S. Greene, *J. Org. Chem.* **1976**, *41*, 2976–2981. b) J. W. Bunting, V. S. F. Chew, G. Chu, *ibid.* **1982**, *47*, 2303–2307.

[14] H. Minato, T. Ito, M. Kobayashi, *Chem. Lett.* **1977**, 13–16.

[15] P. van Eikeren, D. L. Grier, *J. Am. Chem. Soc.* **1977**, *99*, 8057–8060.

[16] W. S. Allison, H. B. White III, M. J. Connors, *Biochemistry* **1971**, *10*, 2290–2296.

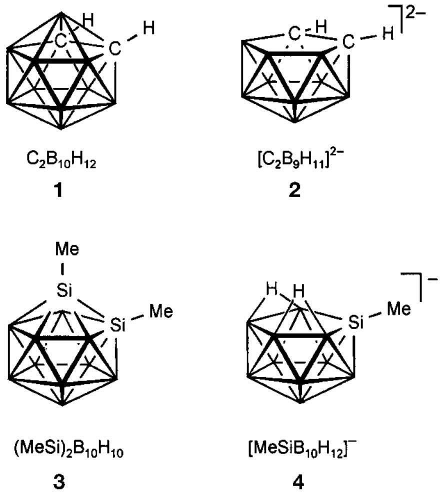
[17] The reaction of **2a** with **1** is expected to generate one equivalent of $MgBr_2$.

[18] The NADH model compound **3a** did not reduce **5** to **6** in the absence of magnesium ions. Therefore, the preceding GAPDH-type model reaction must provide an activator such as $MgBr_2$ for the following LDH-type model reaction.

A Surprising Adduct of a *closo* Cluster[**]

Lars Wesemann,[*] Yves Ramjoie, Michael Trinkaus, Beate Ganter, and Jens Müller[*]

In 1968 Hawthorne et al. published the preparation and characterization of 7,8-dicarba-*nido*-undecaborate(1–) (**2**), the product of the nucleophilic degradation of *o*-carborane (**1**) (Scheme 1).[1] The reaction of dicarba-*closo*-dodecaborane(12) with potassium hydroxide in ethanol gave the eleven-vertex cluster anion **2**. An adduct formed from the attacking ethoxide anion and the neutral *closo* cluster was formulated as a possible reaction intermediate. In *o*-silaborane[2] (**3**), the silicon atoms are unique in that they are incorporated in the skeleton of a borane cluster framework. We are interested in the reactivity patterns of this icosahedral cluster and especially in the silicon centers. The first reaction of *o*-silaborane to be explained was the nucleophilic degradation.[3] Removal of a silicon vertex from the icosahedral cluster results in almost quantitative isolation of the sila-*nido*-undecaborate(1–) (**4**). This eleven-vertex cluster is a versatile starting material for the synthesis of transition metal complexes with interactions between the silicon and the metal.[4, 5]



Scheme 1. *o*-Carborane and *o*-silaborane and their degradation products.

In this paper we present first insights into the nucleophilic degradation of *o*-silaborane. Attack of one equivalent OH^- in H_2O, MeO^- in MeOH, or pure NH_3, results in the removal of a silicon vertex from the *closo* cluster **3**.[3] According to a plausible mechanism for the degradation, in the first step an adduct is formed comprising the nucleophile and the *closo* cluster (Scheme 2). This adduct should then react with a protic solvent to form the isolated reaction product.

$$\underset{\mathbf{3}}{(MeSi)_2B_{10}H_{10}} + [OMe]^- \longrightarrow [(MeO)(MeSi)_2B_{10}H_{10}]^-$$

$$[(MeO)(MeSi)_2B_{10}H_{10}]^- + 2\,MeOH \longrightarrow \underset{\mathbf{4}}{[MeSiB_{10}H_{12}]^-} + MeSi(OMe)_3$$

Scheme 2. Nucelophilic degradation of o-silaborane **3** to sila-*nido*-undecaborate(1–) **4**.

In order to verify the existence of the adduct, we studied nucleophilic attack on **3** in an aprotic solvent by NMR spectroscopy. The cluster **3** was treated with one equivalent of $LiNEt_2$ in THF, and the ^{11}B NMR spectrum (Figure 1) of the reaction mixture shows the quantitative formation of a new compound. Four signals in the ^{11}B NMR spectrum corresponding to ten boron atoms indicate that the product still has C_{2v} symmetry. A shift of the ^{29}Si signal from –38 to –76 ppm

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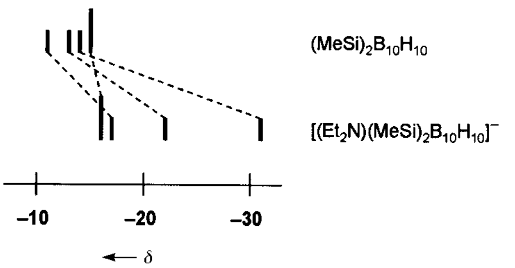
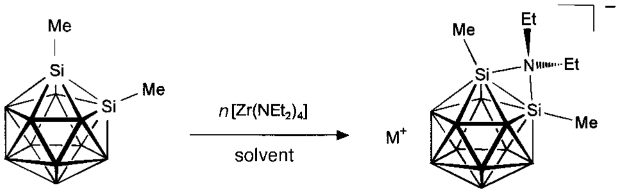


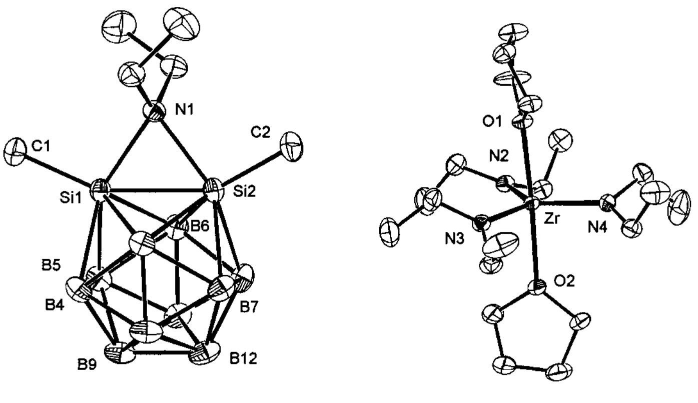
Figure 1. ^{11}B NMR spectra of *o*-silaborane (from left to right: B8/10, B9/12, B3/6, B4/5/7/11) and the anionic adduct with diethylamide (from left to right: B4/5/7/11, B8/10, B9/12, B3/6).

can be interpreted as an increase of the coordination number for the silicon atoms in the cluster. The silicon resonance signal was detected indirectly with the HMQC $^1H/^{29}Si$ NMR pulse sequence. As expected, the two-dimensional NMR spectrum shows a correlation between the silicon signal and the signal for the methyl groups attached to the silicon atoms. Interestingly, a second correlation with the CH_2 signal of the diethylamido group is also observed. From these spectroscopic features, it can be concluded that the diethylamido group is connected to both silicon atoms. The solid-state structure of the anionic adduct was determined by investigation of the $[Zr(NEt_2)_3(thf)_2][(Et_2N)(MeSi)_2B_{10}H_{10}]$ salt (**5**).[6] This adduct was obtained quantitatively from the reaction of **3** with an excess of $[Zr(NEt_2)_4]$ (Scheme 3a). The stoichiometric reaction, in contrast, resulted in an equilibrium between starting materials and product (Scheme 3b). The same ratio was observed after dissolution of the crystalline adduct **5**, which had been previously characterized by elemental analysis. Use of a stronger donor ligand such as 4-*tert*-butylpyridine in a stoichiometric reaction results in almost complete formation of the adduct (Scheme 3c). In all cases, the initial *closo* cluster **3** was recovered by the reaction of the adduct **5** with methyl iodide.



3 **5, 6**

Scheme 3. Reaction conditions and products: a) THF, $n>1$ (excess), $M^+ = [Zr(NEt_2)_3(thf)_2]^+$, **5**; b) THF, $n=1$, equilibrium mixture of **3** and **5**; c) CH_2Cl_2, $n=1$, 2py′, $M^+ = [Zr(NEt_2)_3(py')_2]^+$, **6** (py′ = 4-*tert*-butylpyridine).



$[(Et_2N)(MeSi)_2B_{10}H_{10}]^-$ $[Zr(NEt_2)_3(thf)_2]^+$

Figure 2. Structures of the anion (left) and the cation (right) of **5** in the crystal (PLATON representation,[8] ellipsoids at 30% probability level). Selected distances [Å] and angles [°]: Si1–Si2 2.332(1), Si1–N1 1.999(2), Si2–N1 1.967(2), Si1–B3 2.091(3), Si1–B4 2.082(3), Si1–B5 2.091(3), Si1–B6 2.103(3), Si2–B3 2.108(3), Si2–B6 2.114(3), Si2–B7 2.089(3), Si2–B11 2.079(3), B3–B4 1.866(5), B3–B7 1.869(4), B3–B8 1.777(4), B4–B5 1.777(4), B4–B8 1.757(5), B4–B9 1.769(5), B5–B6 1.866(4), B5–B9 1.770(5), B5–B10 1.774(5), B6–B10 1.764(4), B6–B11 1.860(4), B7–B8 1.772(5), B7–B11 1.768(4), B7–B12 1.759(5), B8–B9 1.765(5), B8–B12 1.786(4), B9–B10, 1.786(4), B9–B12 1.738(5), B10–B11 1.765(4), B10–B12 1.780(5), B11–B12 1.766(4), Zr–O2 2.246(2), Zr–N2 2.024(2), Zr–N3 2.028(2), Zr–N4 2.027(2); C1-Si1-Si2 152.3(1), C2-Si2-Si1 154.3(1); Zr-O1 2.245(2).

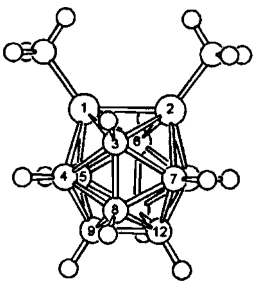
The solid-state structure of the anion in **5** is shown in Figure 2.[6] As indicated by NMR spectroscopy, the Si–Si cluster edge is bridged by a diethylamido group. The Si–N distances of 1.999(2) and 1.967(2) Å are slightly longer than the sum of the covalent radii and can be compared with the Si–N distance of 1.95 Å in cyclic $[(Me_2N)SiH_3]_5$.[9] To our surprise, the B–B, Si–B, and Si–Si distances show only small differences from those in **3**. Thus the Si–Si distance in the adduct (2.332(1) Å) is only 0.024 Å longer than in the unbridged *o*-silaborane (2.308(2) Å). The biggest structural change is the enlargement of the C-Si-Si angle by 28°. The structure of the cation is related to the published structure of the $[Ti(NMe_2)_3py_2]^+$ cation (py = pyridine).[10]

In order to understand the properties of silaboranes better, we performed ab initio calculations.[11] There are two equivalent solutions for the $^{11}B/^{11}B$ COSY NMR spectra for the starting compound **3** and the anion in **5**. In order to make an unambiguous assignment, we calculated the chemical shifts with the GIAO method[12] at the B3LYP/6-311+G(d, p) level[13] based on B3LYP/6-31G(d) geometries.[14] Table 1 summarizes the observed and calculated bond lengths and angles, and Figure 3 depicts the ab initio geometries and the ^{11}B and ^{29}Si NMR chemical shifts. The calculated structural

Table 1. Selected bond lengths [Å] and angles [°] for **3** and the anion in **5**. Calculated (B3LYP/6-31G(d)) and mean observed values (figures in parentheses).

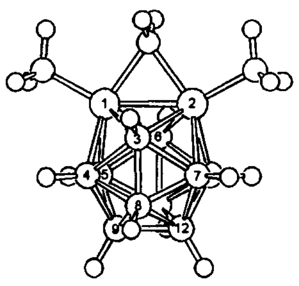
	3[a]	Anion in **5**[b]
Si–N		2.03 (1.98)
Si–C	1.87 (1.83)	1.91 (1.87)
Si–Si	2.32 (2.31)	2.38 (2.33)
Si–B3, 6	2.14 (2.11)	2.11 (2.10)
Si–B4, 5	2.03 (2.02)	2.08 (2.09)
B3–B4, 7	1.86 (1.85)	1.89 (1.87)
B3–B8	1.78 (1.77)	1.79 (1.77)
B4–B5	1.88 (1.86)	1.79 (1.77)
B4–B8	1.77 (1.77)	1.78 (1.77)
B4–B9	1.77 (1.77)	1.77 (1.77)
B8–B9	1.79 (1.78)	1.79 (1.78)
B9–B12	1.79 (1.78)	1.75 (1.74)
C-Si-Si	126 (124)	152 (153)

[a] Values in parentheses were taken from ref. [2]. [b] Calculations were performed on a μ-NH_2 group (see Figure 3).



3

-36.3 (-37.8)	Si 1, 2	-98.0 (-76.2)
-16.7 (-13.6)	B 3, 6	-33.4 (-30.7)
-16.6 (-14.7)	B 4, 5, 7, 11	-17.8 (-16.5)
-11.8 (-11.3)	B 8, 10	-17.7 (-17.1)
-12.8 (-12.8)	B 9, 12	-23.2 (-21.7)



anion of **5**

Figure 3. Calculated (B3LYP-GIAO/6-311 + G(d, p)//B3LYP/6-31G(d))[12–14] and observed ^{29}Si and ^{11}B NMR chemical shifts (figures in parentheses).[18]

data matches the measured data well (Table 1), and there is also good agreement between the theoretical and experimental NMR data.

The greatest differences are found for ^{11}B NMR shifts for the vertices B3 and B6: $\delta = 3.1$ for **3** and 2.7 for the anionic cluster in **5**. The calculated value of $\delta(^{29}\text{Si}) = -36.3$ for the *o*-silaborane deviates by only 1.5 ppm from the experimental shift. In contrast, the predicted $\delta(^{29}\text{Si})$ value for the amino-bridged species is shifted 21.8 ppm upfield in comparison with the measured value of −76.2. Evidently, this difference must be mainly due to the alkyl groups of the bridging N atom since the ab initio calculation was performed on a μ-NH$_2$ instead of a μ-NEt$_2$ group.

The relationship between the empirical formula, the electron count, and geometry of an electron-deficient cluster has been reported by Williams and Wade.[15] As expected from these cluster rules, aza-*closo*-dodecaborane reacts with nucleophiles to form twelve-vertex *nido* compounds.[16] A Et_2N^- group in a bridging position donates four electrons to a cluster framework. Therefore, the *closo*-silaborane **3** should form an *arachno* compound after reaction with $[\text{Zr(NEt}_2)_4]$. Surprisingly, the twelve-vertex cage of **3** is almost unchanged by addition of Et_2N^-. Although the structural effects are small, the NMR properties of the anion in **5** are distinctively different from the starting borane **3**; the upfield shift and the enlargement of the range of the ^{11}B resonances (see Figures 1 and 3) are a result of electron donation to the cluster. In short, the anion of **5** exhibits a *closo* cluster framework with an *arachno* electron count. Evidently the disila unit has acceptor properties reminiscent of silicon compounds that can act as inverse chelate ligands.[17]

Experimental Section

5: $[\text{Zr(NEt}_2)_4]$ (1.876 g, 4.94 mmol) was added to **3** (0.460 g, 2.25 mmol) in THF (25 mL) at room temperature. The solution turned slightly yellow and was stirred overnight. The yield of **5** was quantitative relative to **3,** as shown by NMR spectroscopy. Crystals suitable for elemental analysis and X-ray crystallography were obtained from a mixture of THF and toluene at room temperature in a yield of 85.0 % (1.393 g, 1.91 mmol).[19] NMR spectra were recorded in [D$_8$]THF at 25 °C with an excess of $[\text{Zr(NEt}_2)_4]$, which has been omitted from the spectra. ^{1}H{^{11}B} NMR (500 MHz, TMS): $\delta = 0.66$ (s, 2H, H3/6), 0.70 (s, 6H, SiMe), 1.01 (t, 6H, μ-NCH$_2$CH$_3$), 1.04 (s, 2H, H8/10), 1.13 (tr, 18H, ZrNCH$_2$CH$_3$), 1.27 (s, 4H, H4/5/7/11), 1.31 (s, 2H, H9/12), 1.77 (m, 8H, coord. THF, O(CH$_2$CH$_2$)$_2$), 3.08 (q, 4H, μ-NCH$_2$CH$_3$), 3.49 (q, 12H, ZrNCH$_2$CH$_3$), 3.62 (m, 8H, coord. THF, O(CH$_2$CH$_2$)$_2$); ^{11}B NMR (160 MHz, Et$_2$O·BF$_3$): $\delta = -16.5$ (d, $^1J = 122$ Hz, B4/5/7/11), −17.1 (d, $^1J = 147$ Hz, B8/10), −21.7 (d, $^1J = 134$ Hz, B9/12), −30.7 (d, $^1J = 122$ Hz, B3/6); ^{13}C{^{1}H} NMR (125 MHz, TMS): $\delta = 8.1$ (MeSi), 12.4 (μ-NCH$_2$CH$_3$), 14.9 (ZrNCH$_2$CH$_3$), 26.2 (coord. THF, O(CH$_2$CH$_2$)$_2$), 37.8 (μ-NCH$_2$CH$_3$), 41.8 (ZrCH$_2$CH$_3$), 68.0 (coord. THF, O(CH$_2$CH$_2$)$_2$); ^{29}Si NMR (100 MHz,TMS): $\delta = -76.2$.

6: $[\text{Zr(NEt}_2)_4]$ (0.522 g, 1.375 mmol) and a slight excess of 4-*tert*-butylpyridine (600 μL, ca. 3 equiv) were added to **3** (0.281 g, 1.375 mmol) in CH$_2$Cl$_2$ (30 mL) at room temperature. The reaction mixture was stirred for 14 h during which time the color changed to orange-brown. The solvent was changed to THF, 30 mL of toluene was added and the solution was slowly evaporated at 10^{-1} mbar. Yellow crystals were obtained which were filtered and washed several times with toluene. Recrystallization from THF/toluene gave **6** in 90.0 % yield (1.058 g, 1.24 mmol).[19] NMR spectra were recorded in [D$_8$]THF at 25 °C; ^{1}H{^{11}B} NMR (500 MHz, TMS): $\delta = 0.66$ (s, 2H, H3/6), 0.70 (s, 6H, SiMe), 0.99 (tr, $^3J = 7.3$ Hz, 6H, μ-NCH$_2$CH$_3$), 1.04 (s, 2H, H8/10), 1.10 (br., ZrNCH$_2$CH$_3$), 1.27 (s, 4H, H4/5/7/11), 1.31 (s, 2H, H9/12), 1.32 (s, 18H, *t*Bu), 3.08 (q, $^3J = 7.3$ Hz, 4H, μ-NCH$_2$CH$_3$), 3.47 (q, $^3J = 6.4$ Hz, 12H, ZrNCH$_2$CH$_3$), 7.30 (br., 4H, *p*py), 8.46 (br., 4H, *o*py); ^{11}B NMR (160 MHz, Et$_2$O·BF$_3$): $\delta = -16.4$ (d, $^1J = 122$ Hz, B4/5/7/11), −17.0 (d, $^1J = 147$ Hz, B8/10), −21.6 (d, $^1J = 134$ Hz, B9/12), −30.4 (d, $^1J = 122$ Hz, B3/6); ^{13}C{^{1}H} NMR (125 MHz, TMS): $\delta = 8.1$ (MeSi), 12.4 (μ-NCH$_2$CH$_3$), 14.7 (ZrNCH$_2$CH$_3$), 30.3, 30.5 (*t*Bu), 37.8 (μ-NCH$_2$CH$_3$), 42.0 (ZrNCH$_2$CH$_3$), 123.9, 150.5 (py), (the signal for C4 was not observed); ^{29}Si NMR (100 MHz,TMS): $\delta = -76.0$.

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[1] M. F. Hawthorne, D. C. Young, P. M. Garnett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, P. A. Wegner, *J. Am. Chem. Soc.* **1968**, *90*, 862 – 868.

[2] a) D. Seyferth, K. Büchner, W. S. Rees, Jr., W. M. Davis, *Angew. Chem.* **1990**, *102*, 911 – 913; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 918 – 920; b) D. Seyferth, K. D. Büchner, W. S. Rees, L. Wesemann, W. M. Davis, S. S. Bukalov, L. A. Leites, H. Bock, B. Solouki, *J. Am. Chem. Soc.* **1993**, *115,* 3586 – 3594.

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

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

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

[6] Crystal structure analysis of **5**: ENRAF-Nonius CAD4 diffractometer, Mo$_{K\alpha}$ radiation, graphite monchromator; intensity data with ω scans collected at 203 K. Colorless crystal, 0.60 × 0.60 × 0.15 mm, triclinic, space group $P\bar{1}$ (No. 2); $a = 10.443(2)$, $b = 13.864(3)$, $c = 14.869(2)$ Å, $\alpha = 83.94(1)$, $\beta = 85.78(1)$, $\gamma = 76.96(1)^\circ$, $V = 2083(1)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.161$ g cm^{-3}, $\mu(\text{Mo}_{K\alpha}) = 3.43$ cm^{-1}, $F(000) = 780$, 7799 reflections with $3 < \theta < 25^\circ$, 6055 independent reflections with $I > \sigma(I)$ in the structure solution and refinement[7] for 665 parameters; $R = 0.032$, $R_w = 0.039$, GOF = 1.271, $w^{-1} = \sigma^2(F_0)$; hydrogen atoms from the second THF molecule (bonded to C23 – C26) were treated as riding atoms, all other hydrogen atoms were refined isotropically. 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-100936. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[7] MolEN, *An interactive Structure Solution Procedure*, Enraf-Nonius, Delft (Netherlands) **1990**.

[8] A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34.

[9] T. M. Klapötke, I. C. Tornieporth-Oetting, *Nichtmetallchemie*, VCH, Weinheim, **1994**, pp 254–255.

[10] C. Boisson, J. C. Berthet, M. Ephritikhine, M. Lance, M. Nierlich, *J. Organomet. Chem.* **1997**, *531*, 115–119.

[11] See also: E. D. Jemmis, B. Kiran, *J. Am .Chem. Soc.* **1997**, *119*, 4076–4077 (B3LYP/6-31G(d) geometry of $Si_2B_{10}H_{12}$).

[12] For application to borane chemistry see: X. Y. Yang, H. Jiao, P. von R. Schleyer, *Inorg. Chem.* **1997**, *36*, 4897–4899, and references therein.

[13] a) A. D. Becke, *Phys. Rev.* **1988**, *A38*, 3098–3100; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; c) C. Lee, W. Yong, R. G. Parr, *Phys. Rev.* **1988**, *B37*, 785–789.

[14] All calculations were performed with Gaussian 94; M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1995**.

[15] K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1–66; R. E. Williams, *Advances in Boron Chemistry* (Ed.: W. Siebert), The Royal Society of Chemistry, Cambridge, **1997**.

[16] F. Meyer, J. Müller, P. Paetzold, R. Boese, *Angew. Chem.* **1992**, *104*, 1221–1222; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1227–1228.

[17] M. E. Jung, H. Xia, *Tetrahedron Lett.* **1988**, 297–300; K. Tamao, T. Hayashi, Y. Ito, *J. Am. Chem. Soc.* **1990**, *112*, 2422–2423.

[18] The ^{11}B and ^{29}Si NMR shifts are reported relative to $BF_3 \cdot OEt_2$ and TMS, respectively. It is inconvenient to compute the magnetic shielding of $BF_3 \cdot OEt_2$, and so B_2H_6 was calculated instead and set to 16.6 ppm (T. P. Onak, H. L. Landesman, R. E. Williams, I. Shapiro, *J. Phys. Chem.* **1959**, *63*, 1533–1535). The absolute chemical shieldings at the B3LYP-GIAO/6-311+G(d, p)//B3LYP/6-31G(d) level are: 84.11 ppm (^{11}B of B_2H_6) and 338.80 ppm (^{29}Si of TMS).

[19] Correct C,H analyses for **5** and **6** were obtained.

Cationic Gold(I) Complexes: Highly Efficient Catalysts for the Addition of Alcohols to Alkynes[**]

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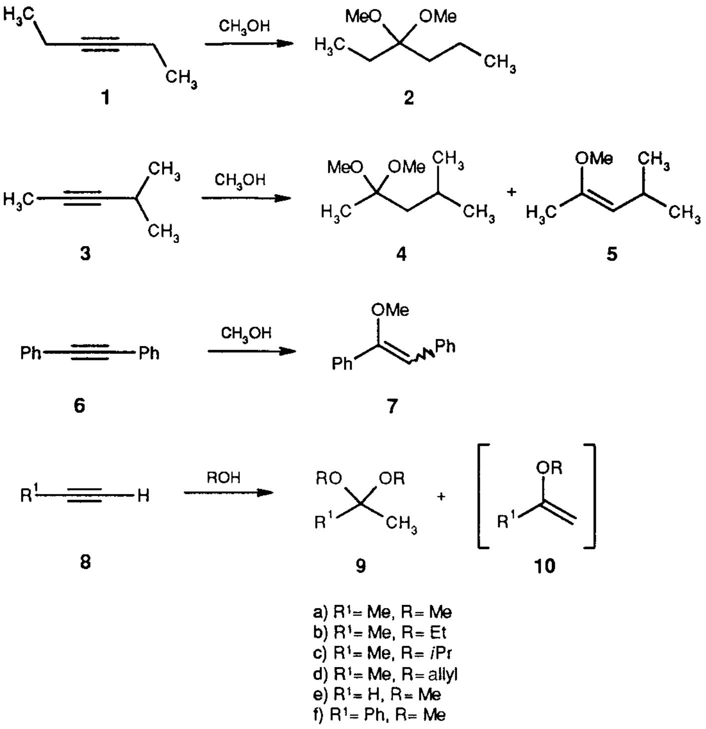
In memory of Dr. Marco Häser

The mercury(II)-catalyzed addition of alcohols to alkynes has been known for almost three-quarters of a century.[1] The original catalyst has been further developed,[2] but its preparation by the heating of red mercury(II) oxide with boron trifluoride etherate and trichloroacetic acid in methanol still retains a touch of alchemy, and very little is known about the reaction mechanism.[2g] This material catalyzes the addition of primary, secondary, and even some tertiary alcohols to acetylene[2a] as well as to mono-[2b] and disubstituted acetylenes.[2c] However, it has the serious drawback that under the reaction conditions the mercury(II) is quickly reduced to metallic mercury, which is catalytically inactive, so 100 moles of product at most can be produced per mole of mercury(II) salt introduced.

An alternative mercury-free catalyst for this reaction has long been sought, but with little success.[3] Two recent papers describe the use of gold(III) catalysts ($NaAuCl_4$) for the addition of water and methanol to nonactivated alkynes,[4] but this catalyst shows the same disadvantage: It is quickly reduced to inactive metallic gold, so no more than 50 moles of product can be synthesized per mole of gold. The fact that the literature on homogeneous catalysis with gold complexes is extremely sparse,[4, 5] and that until recently gold was thought to be "catalytically dead,"[6] made the quest for an efficient gold(I) catalyst all the more interesting.

Here we report a new, very efficient class of gold(I) catalysts for the addition of alcohols to alkynes under mild conditions ($T = 20-50\,^{\circ}C$, H^+ as cocatalyst).[7] In numerous studies carried out in our laboratory we have found that cationic gold(I) complexes of the general type $[L-Au^+]$ (where L is a phosphane, a phosphite, or an arsine)[8] are excellent catalysts for the addition of alcohols to alkynes. These catalysts achieve total turnover numbers of up to 10^5 moles of product per mole of catalyst, with turnover frequencies of up to $5400\ h^{-1}$. They are neither water nor air sensitive, and the reaction can usually be conducted without a solvent. Scheme 1 shows examples of the addition of alcohols to unsubstituted alkynes with methyl(triphenylphosphane)gold(I) and methanesulfonic acid as precursors for in situ generation of the catalyst.



Scheme 1. Addition of alcohols to unsubstituted alkynes in the presence of the catalyst prepared from methyl(triphenylphosphane)gold(I) and methanesulfonic acid.

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