

Fig. 1. Molecular structure of **3a** (ORTEP, 50% probability thermal motion ellipsoids). Selected bond lengths [Å] and angles [°]: Ru-C1 1.99(2), C1-C2 1.36(3), C2-C3 1.38(2), C3-O3 1.30(2), Ru-O3 2.09(1), Ru-P 2.32(1), C3-C4 (1.49(2), C4-C5 1.35(2); Ru-C1-C2 116(1), C2-C3-O3 119(2), C3-O3-Ru 112(1), O3-Ru-C1 78.0(6).

109.79 ($^1J_{C,H} = 172$ Hz) can be assigned to the HC=C= group, and three singlets at $\delta = 166.88$, 148.83 and 148.42 stem from the (C=)₃ skeleton.

Compound **6a** reacts with water at room temperature to give **3a** quantitatively after 3 h. This demonstrates that complexes of type **3** and **4** are formed on addition of water to the C(3) carbon of the butatrienyl group of intermediate **6**.

Since the addition of methanol to the Ru=(C=)₂CR₂ moieties leads to 2-propenylidene-ruthenium complexes,¹⁶ the metallacumulene Ru=(C=)₄CPh₂ is likely to be the key intermediate in the reaction of the diynes **2** or **5** with the complexes **1** to afford complex **6** by addition of methanol.

Experimental

3a: **2a** (0.24 g, 1 mmol) was added to a solution of **1a** (0.41 g, 1 mmol) and NaPF₆ (0.18 g, 1 mmol) in 20 mL of dry methanol. The solution turned violet after a few minutes and then progressively dark red. The mixture was stirred for 20 h at room temperature. The solvent was removed in vacuo and the red solid was dissolved in 20 mL of THF. The solution was filtered, and crystallization from a THF/*n*-hexane (2/1) solution afforded 0.36 g (48%) of **3a** as orange crystals.

3a: IR (KBr): $\bar{\nu} = 1615$ [s, $\nu(C=O)$], 855 [s, $\nu(P-F)$] cm⁻¹; ¹H NMR (300.13 MHz, CDCl₃): $\delta = 6.77$ (s, 1H; HC=C), 5.57 (d, 1H, $^4J(P, H) = 0.8$ Hz; HC=C), 3.76 (s, 3H; OMe), 1.99 (s, 18H; C₆Me₆), 1.15 (d, 9H, $^2J(P, H) = 10.1$ Hz; PMe₃). ³¹P NMR: $\delta = 3.55$ (s, PMe₃), -144.39 (sept; PF₆[⊖]). ¹³C NMR: $\delta = 254.82$ (d, $^2J(P, C) = 20.4$ Hz; RuCOMe), 199.60 (s; C=O), 153.48 (s; =CPh₂), 121.92 ($^1J(C, H) = 156.6$ Hz, HC=CPh₂), 111.09 ($^1J(C, H) = 162.4$ Hz; HC=C(OMe)). Correct elemental analysis (C, H).

3b and **4a, b** were prepared analogously to **3a** and isolated in 52%, 56% and 58%, respectively. ¹³C-NMR data for Ru-COMe (75.469 MHz, CDCl₃): $\delta = (^2J(C, P) = 255.29/18.9$ Hz (**3b**), 253.11/20.2 Hz (**4a**), 253.76/20.3 Hz (**4b**): $\delta = ^1J(C, H) = 112.25/162.4$ Hz (**3b**), 110.79/161 Hz (**4a**), 111.38/161 Hz (**4b**).

6a: **1a** (0.30 g, 0.73 mmol) and NaPF₆ (0.13 g, 0.77 mmol) were dissolved in 20 mL of dry methanol and treated with 0.225 g, 0.73 mmol of 5,5-diphenyl-5-(trimethylsilyloxy)penta-1,3-diyne **5**. The mixture was stirred at room temperature for 1 h. Half of the solvent was removed in vacuo. The red-violet product was filtered and crystallized from dichloromethane/ether (20 mL/10 mL); Yield: 0.22 g (40%) of a violet powder of **6a**. Correct elemental analysis (C, H).

6a: IR (KBr): $\bar{\nu} = 2080$ [s, $\nu(C=C=C=C)$]; 855 [vs, $\nu(P-F)$] cm⁻¹, ³¹P NMR (121.49 MHz, CD₂Cl₂): $\delta = 10.54$ (s; PMe₃), -143.45 (sept., PF₆[⊖]); ¹H NMR (300.13 MHz, CD₂Cl₂): $\delta = 7.69$ –7.47 (m, 10H; Ph), 7.29 (s, 1H; =C=CH), 4.51 (s, 3H; OMe); 2.06 (d, 18H; $^4J(P, H) = 0.7$ Hz; C₆-Me₆), 1.40 (d, 9H; $^2J(P, H) = 10.6$ Hz; PMe₃). ¹³C NMR (75.469 MHz, CD₂Cl₂): $\delta = 295.13$ ($^2J(C, P) = 21.2$ Hz; Ru-C-OMe), 166.88, 148.83 and 148.42 (=C=C=CPh₂), 109.79 ($^1J(C, H) = 172$ Hz; HC=C=), 106.47 (C₆Me₆),

67.43 (OMe), 16.41 (C₆Me₆), 16.05 ($^1J(C, P) = 34.6$ Hz; PMe₃). The conformation of the carbene ligand is based on an NOE experiment.

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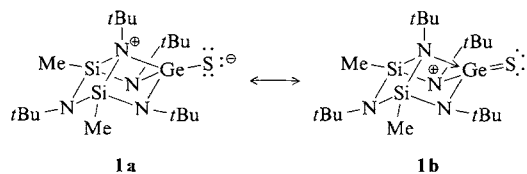
1a, 80298-82-4; **1b**, 110800-51-6; **2a**, 4945-70-4; **2b**, 763-12-2; **3a**, 124686-52-8; **3b**, 124686-54-0; **4a**, 124686-56-2; **4b**, 124686-58-4; **5**, 124686-50-6; **6a**, 124686-60-8.

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[7] Presented at the international symposium "Interfaces in Metal Complex Chemistry", July 10–14, 1989, Rennes, France.
[8] Crystals for X-ray analysis were obtained from a THF/ether (1/2) solution. **3a** crystallizes in the space group P2₁/n with $a = 13.788(5)$, $b = 13.328(5)$, $c = 18.457(6)$ Å, $\beta = 100.21(3)^\circ$, $Z = 4$, $V = 3338$ Å³, $\rho_{\text{calcd}} = 1.488$ g cm⁻³, crystal dimensions 0.50 × 0.20 × 0.10 mm. The diffraction data were collected with a single-crystal diffractometer CAD-4 (graphite monochromator, MoK α -radiation, ($\theta - 2\theta$ scan) at 293 K. 5855 reflections were obtained in the range $3^\circ < 2\theta < 50^\circ$, 1831 with $I > 3\sigma(I)$ considered as observed. The structure was solved by the heavy atom method and refined by full-matrix least-squares calculations and unit weights, using absorption correction data; all calculations were carried out with the program system 'X RAY-70'. The fluorides of the hexafluorophosphate ion showed extremely high temperature factors and some unresolved disorder and they were fixed at the position of the maxima in the Fourier map. Anisotropic treatment of the non-hydrogen atoms, except the [PF₆][⊖] ion, gave $R = 0.064$ for the observed reflections. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-54350, the names of the authors, and the journal citation.
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An Intramolecularly Lewis-Base-Stabilized Ge=N-Compound and a Related Ge-Fe Complex

By Michael Veith,* Sabine Becker, and Volker Huch

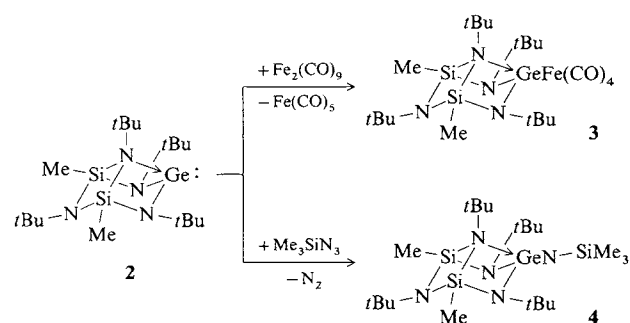
We have recently demonstrated that a germanium-sulfur double bond can be stabilized by intramolecular addition of bases to the germanium atom. The bonds in the polycyclic azasilagermane **1** can be formally described in terms of the resonance structures **1a** and **1b**.¹¹



[*] Prof. Dr. M. Veith, Dipl.-Chem. S. Becker, Dr. V. Huch
Institut für Anorganische Chemie der Universität
D-6600 Saarbrücken 11 (FRG)

We have now considered the question of whether germanediylamines (germanimines) and germanediyl-transition-metal complexes analogous to **1** can also be prepared, i.e. whether the sulfur in **1** can be replaced by a nitrene, e.g. $\text{Me}_3\text{Si}-\dot{\text{N}}$, or an isolobal complex fragment such as $\text{Fe}(\text{CO})_4$. Stable germanediylamines have only recently been isolated and spectroscopically characterized,^[2] while germanediyl complexes of the transition metals have been known for some time.^[3] Some X-ray structure analyses of silanediylamines (silanimines) and base-stabilized silanediylamines have been carried out independently by others.^[4]

The target compounds **3** and **4** are obtained in high yields upon reaction of the germanediyl **2** with nonacarbonyliron and trimethylsilylazide respectively at room temperature. The reactions proceed in accord with Scheme 1, with elimination of pentacarbonyliron and dinitrogen, respectively.



Scheme 1. Synthesis of **3** and **4**.

The $^1\text{H-NMR}$ spectra of **3** and **4** in solution^[5] differ primarily in that three signals are observed for the *tert*-butyl groups in the case of **3**, whereas only two signals are observed in the case of **4**. Thus, in **3** the donor bond from the nitrogen to the germanium atom is closed on the $^1\text{H-NMR}$ time scale, whereas in the case of **4** (like in **1**^[1]) a bond fluctuation occurs (see also the $^{13}\text{C-NMR}$ spectrum of **4**^[5]). The ΔG^\ddagger value of **4** derived from the temperature dependence of the $^1\text{H-NMR}$ spectra is $56(9) \text{ kJ mol}^{-1}$ at 298 K and is thus 8 kJ mol^{-1} smaller than that of **1**. The marked difference in the activation entropies of **1** and **4** ($\Delta S^\ddagger(\mathbf{1}) = -51(5)$, $\Delta S^\ddagger(\mathbf{4}) = -95(9) \text{ J mol}^{-1} \text{ K}^{-1}$) is apparently associated with the additional trimethylsilyl groups in **4**.

The results of the X-ray structure analyses of **3** and **4** are collected in Figure 1.^[6] In the solid state, both compounds are present as isolated molecules with only van-der-Waals contacts. **3** contains a crystallographic mirror plane, whereas **4** loses its point symmetry $C_s(m)$ in the crystal. In both molecules the germanium atom is incorporated in a second-order cubane-like $\text{Si}_2\text{N}_4\text{Ge}$ cage by bonding to three nitrogen atoms. The fourth coordination site of the germanium atom is taken up in an $\text{Fe}(\text{CO})_4$ and $\text{N}(\text{SiMe}_3)$ group, respectively. The nitrogen atom N5 in **4** is only twofold coordinated; the Ge-N5-Si3 angle is $151.2(7)^\circ$.

The germanium atoms in **3** and **4** are *not* in a tetrahedral environment but lie almost in a plane together with the bond partners N1, N1' and Fe or N2, N3 and N5 (sum of angles at Ge in **3**: 354.7° , in **4**: 357.7°). The fourth bond to a further nitrogen atom of the polycycle forms an angle of 49 and 57° , respectively, to this plane. From a comparison of the Ge-N bond lengths it follows that this fourth interaction is the weakest (**3**: $\Delta(\text{N3-Ge/N1-Ge}) = 0.144 \text{ \AA}$; **4**: $\Delta(\text{N1-Ge/N(2,3)-Ge}) = 0.156 \text{ \AA}$).

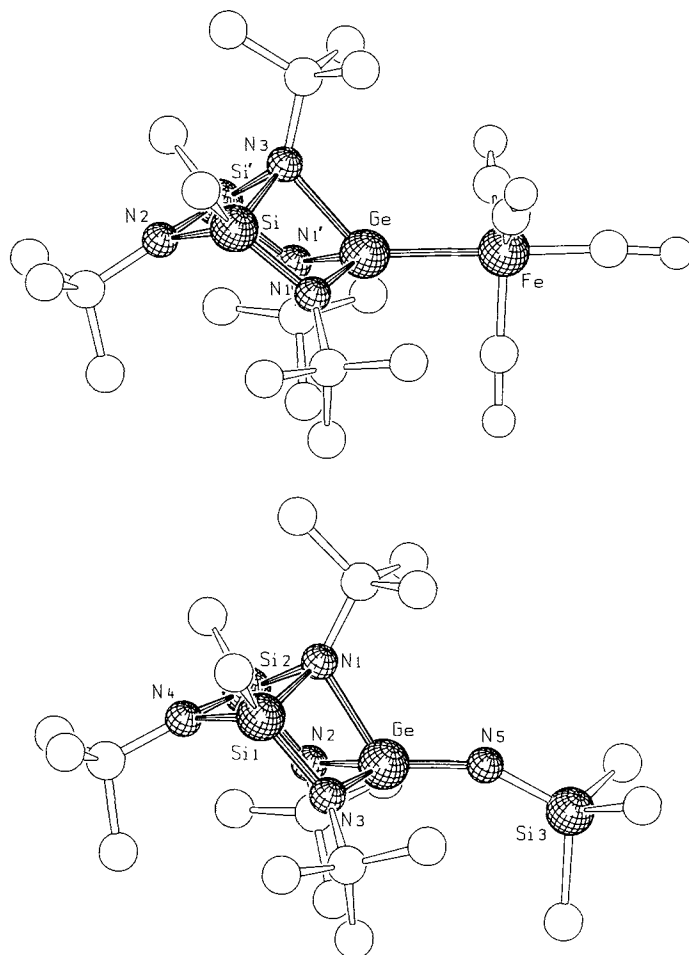


Fig. 1. The crystal structures of **3** (top) and **4** (bottom) (Schakal drawings, the carbon atoms are not shown). Some important bond lengths [\AA] and angles [$^\circ$]: **3**: Ge-Fe 2.348(1), Ge-N1 1.916(3), Ge-N3 2.060(4), Si-N1 1.718(3), Si-N2 1.735(3), Si-N3 1.821(3); N3-Ge-Fe 130.6(1), N1-Ge-Fe 122.8(1), N1-Ge-N1' 109.1(1), N1-Ge-N3 78.8(1), **4**: Ge-N1 2.045(7), Ge-N2 1.896(7), Ge-N3 1.882(7), Ge-N5 1.688(9), Si1-N1 1.819(7), Si1-N3 1.710(7), Si2-N1 1.803(7), Si2-N2 1.697(8), Si3-N5 1.648(9); N1-Ge-N5 122.6(4), N2-Ge-N3 108.3(3), N2-Ge-N5 125.8(4), N3-Ge-N5 123.6(4), N2-Ge-N1 78.5(3), N3-Ge-N1 79.5(3), Ge-N5-Si3 151.2(7).

The Ge-N bond lengths for the three different nitrogen atoms in **4** (N1 quadruply, N2 and N3 each triply, and N5 only doubly coordinated) correlate as usual with the coordination numbers.

Of special interest are the Ge-Fe and the $\text{Ge-}\lambda^2\text{-N}$ bond lengths. They have to be assessed differently! The value found for Ge-Fe corresponds approximately to the sum of the single bond radii of the two elements (2.39 \AA ,^[7a] 2.37 \AA ^[7b]). The Ge-N5 distance is very much smaller than expected for a single bond (1.86 \AA ^[7b]) and on taking into account the larger atomic radius of germanium is comparable with the $\text{Si-}\lambda^2\text{-N}$ distances ($1.57\text{--}1.60 \text{ \AA}$) in free and base-stabilized silanediylamines.^[4] The bond shortening relative to the standard single bond is 9% in the case of $\text{Ge-}\lambda^2\text{-N}$ in **4**, whereas it is noticeably smaller (7%) in the case of Ge-S in **1** ($\text{Ge-}\lambda^1\text{-S} = 2.063(3)$,^[1] $\text{Ge-}\lambda^2\text{-S} = 2.21$ ^[7b]). The Si3-N5 bond length and the Ge-N5-Si3 angle in **4** resemble the corresponding bond length and bond angle in (thf) $\text{Me}_2\text{Si}=\text{N-Si}t\text{Bu}_3$ ($\text{N-Si} 1.66 \text{ \AA}$, $\text{Si}=\text{N-Si} 161.3^\circ$ ^[4]).

As quittance for the description of the bonding in **3** and **4**, it follows from the experimental data that:

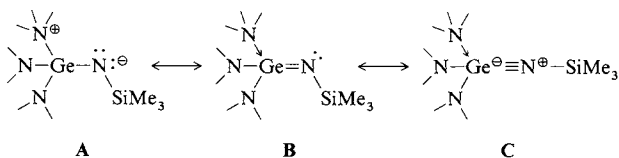
1) The germanium-iron bond in **3** is analogous to the bonding of a classical two-electron donor to a transition

metal. A back-bonding of the metal to the germanium cannot be ruled out, but if present does not lead to a drastic bond shortening. The addition of the $\text{Fe}(\text{CO})_4$ fragment to **2** leads to a strengthening of the donor bond $\text{N3} \rightarrow \text{Ge}$, as can be deduced from the different $^1\text{H-NMR}$ spectra^[1] (in the case of **3** no coalescence of the nonequivalent *tert*-butyl groups is observed up to 90°C).

2) In **4**, the plane in which the $\text{N2}, \text{N3}$ and N5 atoms lie and the plane through the atoms $\text{Ge}, \text{N5}$ and Si3 are orthogonal. Hence, a $p_\pi-p_\pi$ bond between Ge and N5 can be ruled out on geometric grounds, independently of the coordination number of Ge .

3) The donor bond $\text{N1} \rightarrow \text{Ge}$ in **4** competes, similarly as in the case of **1**^[1] in solution, with the $\text{N4} \rightarrow \text{Ge}$ bond. This bond fluctuation has a highly negative activation entropy (ca. $-96 \text{ J mol}^{-1} \text{ K}^{-1}$), which could be explained in terms of a threefold and symmetrically coordinated germanium atom in the transition state.

4) Of the resonance structures **A–C**, **A** best reproduces the polar portions. Thus seen, **4** can in the broadest sense be



referred to as a neutral pendant to a germylsilylamide or disilylamide ion.^[8] The stabilization of negative partial charges on N by electropositive Si has already been pointed out on a number of occasions.^[9] However, the coordination geometry found at the germanium atom is not satisfactorily explained in terms of the resonance structure **A**.

The resonance structure **B** takes into account possible $d_\pi-p_\pi$ bonds between Ge and N5 and must, by all means, also be taken into consideration besides the structure **A**. The observed Ge-N-Si angle suggests a resonance between **B** and **C**, but details of the structure would indicate that the widening of the angle is largely of steric origin.

Experimental

A solution of **2** (217 mg, 0.49 mmol) **1** in benzene (5 mL) was treated at room temperature, either dropwise with a solution of trimethylsilylazide (59 mg, 0.49 mmol) in benzene (2 mL) or with 178.2 mg (0.49 mmol) of $\text{Fe}_2(\text{CO})_9$. The resulting solution, or suspension, was stirred for 12 h and the solvent removed by distillation. Subsequent sublimation at $80^\circ\text{C}/0.001$ torr or crystallization from toluene, afforded 185 mg (71%) of **4** and 291 mg (97%) of **3** (yellow crystals), respectively.

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2, 124686-70-0; **2** (salt), 124686-67-5; **3**, 124686-68-6; **4**, 124686-69-7; $\text{Fe}_2(\text{CO})_9$, 15321-51-4; Me_3SiN_3 , 4648-54-8.

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- [4] G. Reber, J. Riede, N. Wiberg, K. Schurz, G. Müller, *Z. Naturforsch. B* 44 (1989) 786.
- [5] $^1\text{H-NMR}$ (80 MHz, C_6D_6 , TMS as standard): **3** (307 K): $\delta = 0.48$ (s, 6H, SiCH_3), 1.07 (s, 9H, $\text{NC}(\text{CH}_3)_3$), 1.28 (s, 9H, $\text{NC}(\text{CH}_3)_3$), 1.43 (s, 18H, $\text{NC}(\text{CH}_3)_3$). No coalescence of the signals at $\delta = 1.07$ and 1.28 up to 363 K. **4** (307 K): $\delta = 0.50$ (s, 6H, SiCH_3), 0.61 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 1.22 (s, 18H, $\text{NC}(\text{CH}_3)_3$), 1.46 (s, 18H, $\text{NC}(\text{CH}_3)_3$). **4** (217 K): $\delta = 0.48$ (s, 6H, SiCH_3), 0.59 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 1.13 (s, 9H, $\text{NC}(\text{CH}_3)_3$), 1.31 (s, 9H, $\text{NC}(\text{CH}_3)_3$), 1.51 (s, 18H, $\text{NC}(\text{CH}_3)_3$). Coalescence temperature $T_c = 237$ K. $^{13}\text{C}\{^1\text{H}\}$ -NMR (20 MHz, 307 K): **4**: $\delta = 2.6$ (SiCH_3), 6.0 ($\text{Si}(\text{CH}_3)_3$), 31.8 ($\text{NC}(\text{CH}_3)_3$), 33.6 ($\text{NC}(\text{CH}_3)_3$), 52.5 ($\text{NC}(\text{CH}_3)_3$), 59.3 ($\text{NC}(\text{CH}_3)_3$).
- [6] Crystallographic data: **3**: orthorhombic, *Pnma*, $a = 19.07(1)$, $b = 14.629(7)$, $c = 10.611(7)$ Å, $V = 2961$ Å³, $Z = 4$; 1936 reflections, 217 as not observed ($F_0 \leq 2\sigma_F$), 197 parameters $R = 0.037$.—**4**: orthorhombic, *Pbca*, $a = 17.52(1)$, $b = 17.52(1)$, $c = 20.11(2)$, $V = 6170$ Å³, $Z = 8$; 3325 reflections, 1090 as not observed ($F_0 \leq \sigma_F$), 303 parameters, $R = 0.066$.—Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-54918, the names of the authors, and the journal citation.
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