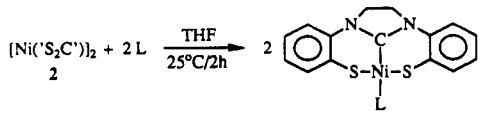

(2)

3 **3a**: L = PMe_3
3b: L = PPh_3 (T = 65°C)
3c: L = CN^-

The retention of the [Ni(S_2C)] core in the course of cleavage reactions according to eq 2 demonstrates the high stability of the Ni–C(carbene) bond. It can be attributed to several facts. The carbene C atom carries two N substituents, as in the case of "Wanzlick"[10] and "Arduengo" carbenes[11] or in Lappert-type carbene complexes.[12] Furthermore, the carbene donor is part of a tridentate ligand, and the Ni center in the [Ni(S_2C)] fragment is coordinated by two thiolate donors. These donors can act, via their lone pairs, as π-donors to the nickel center, increasing the electron density at the nickel and as a consequence thereof also the π-back-bonding from nickel to the carbene ligand. The π-donor bonds from thiolate donors to nickel and the resulting double-bond character of the Ni–S bonds are indicated by the Ni–S distances within the [Ni(S_2C)] fragments, which are relatively short when compared with the Ni–S distances in the thiolate bridges.

Formation of S→Ni π-donor bonds is expected to reduce the Lewis basicity of the thiolate S atoms, and this explains, at least partly, the complete inertness of **2** toward protonic acids. While metal thiolate complexes usually react with protonic acids to decoordinate the thiolate ligands,[13] **2** is stable even toward concentrated H_2SO_4, aqueous HCl, or solutions of gaseous HCl in boiling THF.

The present work has shown that highly stable Ni(II) carbene complexes can formed by reaction of C_1 sources, thiolate amine ligands, and Ni(II) salts. The question as to whether analogous reactions occur in the course of CO_2/CO conversion or CH_4 formation in CO dehydrogenases still remains open. Further investigations have shown that palladium and platinum form analogous complexes.

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Supplementary Material Available: Tables of crystal data and details of the structure solution and refinement, positional and thermal parameters, and bond distances and angles (6 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactivity of the First Diazagermocines

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Summary: New 1,3,2-diazagermines **2**, formed by reaction of 4-amino-1-azabutadienes **1** and diethyl- or diphenylgermanium dichloride, react with dimethyl acetylenedicarboxylate to yield novel 1,5,2-diazagermocines **3** in quantitative yield; the crystal structure of **3a** has been determined. The behavior of **3** toward hydrolysis and heating is also reported.

The chemistry of organosilicon compounds has been widely developed over the last few decades,[1] and the silicon amides in particular represent very useful species in organic synthesis.[2] For instance, we have been able to successfully exploit the reactivity of the nitrogen–silicon bond of 1,3,2-diazasilines toward esters of acetylenedi-

Table I. 1,5,2-Diazagermocines 3 Prepared from 1

compd[a]	R^1	R^2	R^3	R^4	R^5	mp, °C
3a	4-MeC_6H_4	Ph	Me	Ph	Et	126–128[b]
3b	4-MeC_6H_4	Ph	Me	Ph	Ph	158–160[b]
3c	Ph	Ph	Me	c-C_6H_{11}	Et	125–127[b]
3d	4-MeC_6H_4	Ph	Cl	Ph	Et	oil
3e	c-C_6H_{11}	H	H	4-$MeOC_6H_4$	Ph	*c*
3f	Bu	H	H	4-MeC_6H_4	Ph	*c*

[a] For isolated compounds **3a–d** yields from **1** >95% according to NMR spectra of the crude reaction mixtures. [b] Recrystallized from hexane–dichloromethane. [c] Not isolated (see text).

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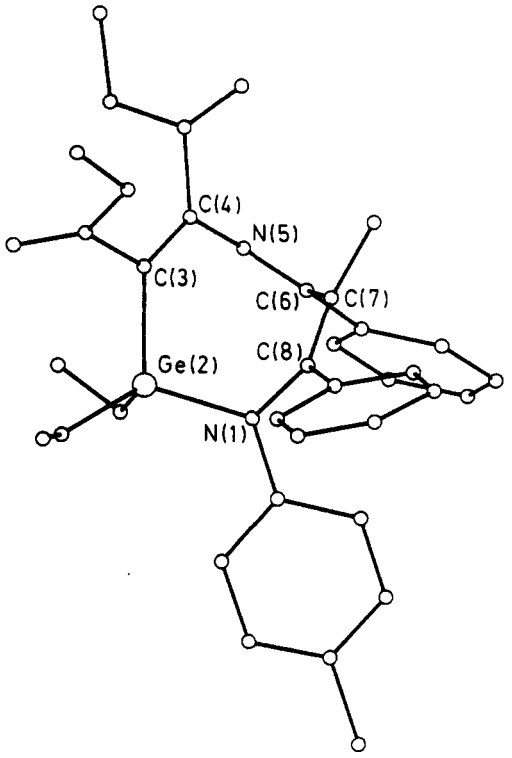
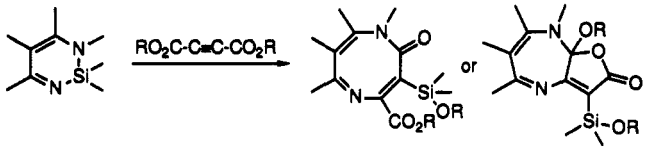


Figure 1. PLUTO plot of the structure of **3a**, showing the atomic numbering of the eight-membered ring.

carboxylic acid in the synthesis of silicon-substituted 1,5-diazocines and furo[1,4-*b*]diazepines (eq 1).[3] In sharp

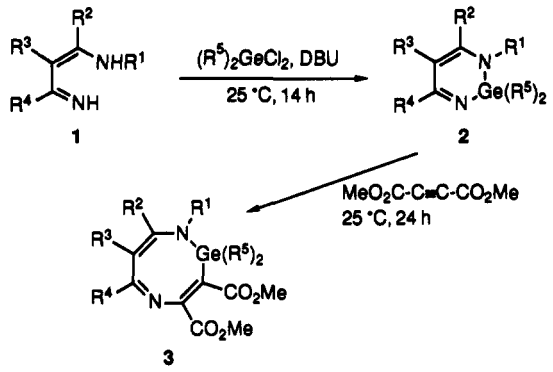


(1)

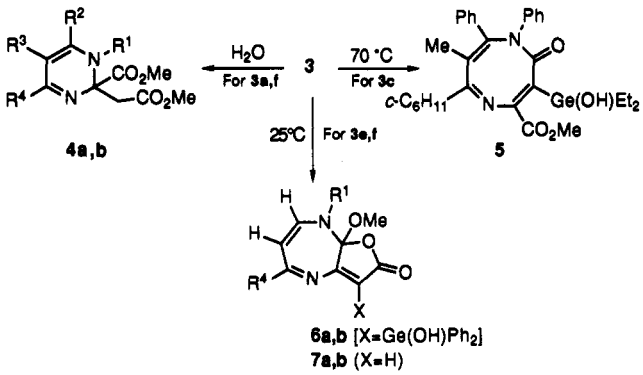
contrast to silicon, much less attention has been paid to the synthesis and reactivity of organogermanium compounds.[4,5] Continuing our interest in the chemistry of metal amides, we describe herein the first synthesis of 1,5,2-diazagermocines **3** from diazagermines **2**, as well as their characterization and chemical reactivity.

First, 1,3,2-diazagermines **2**, a new type of germanium-containing heterocycle,[6] were prepared from 4-amino-1-azabutadienes **1** and diethyl- or diphenylgermanium dichloride in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU); although compounds **2** can be characterized by NMR spectroscopy, they were formed in situ and allowed to react at 25 °C with dimethyl acetylenedicarboxylate (DMAD). Interestingly, insertion of the activated acetylene into the reactive germanium–nitrogen bond[7,8] occurred and novel 1,5,2-diazagermocines **3a–d**

Scheme I



Scheme II



were produced as yellow solids in apparently quantitative yield and high purity (>95% according to NMR; Scheme I, Table I).[9] The structure of **3** was assigned on the basis of spectral evidence and confirmed by the single-crystal X-ray diffraction study of **3a** (Figure 1).[10]

Because of the ease with which diazagermocines **3e,f** ($R^2 = R^3 = H$) undergo further rearrangement even at room

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(7) For insertion of DMAD in germylamines, see: Rivière-Baudet, M.; Satgé, J. *J. Organomet. Chem.* **1973**, *56*, 159.

(8) In contrast, insertion of DMAD into the nitrogen–germanium bond of 4,5-unsubstituted 1,3-diazagermacyclopent-4-enes does not take place, but rather a [2 + 2] cycloaddition (enamine-like reactivity) followed by electrocyclic ring opening leading to 1,3-diaza-2-germacyclohepta-4,6-dienes occurs.[6]

(9) To a solution of **1** (5 mmol) and DBU (1.5 mL, 10 mmol) in toluene (40 mL) was slowly added a solution of substituted dichlorogermanium (10 mmol) in toluene (20 mL); the mixture was stirred overnight at room temperature. The hydrochloride salt formed was filtered off and the filtrate treated with dimethyl acetylenedicarboxylate (0.85 g, 6 mmol) at 25 °C for 24 h. The mixture was evaporated under reduced pressure to furnish pure, air-sensitive compounds **3a–d**. For analytical purposes **3a–c** were recrystallized from hexane–dichloromethane (4:1 v/v). Spectral data for **3c**: IR (KBr) ν(C=O) 1726 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.1–1.9 (m, 20 H), 1.8 (s, 3 H), 2.2–2.4 (m, 1 H), 3.8 (s, 6 H), 6.6–6.7 (m, 2 H), 7.0–7.25 (m, 6 H), 7.35–7.45 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.5 (s), 169.5 (s), 163.2 (s), 152.2 (s), 148.0 (s), 140.1 (s), 137.0 (s), 129.5 (d), 128.5 (d), 128.2 (s), 127.6 (d), 127.4 (d), 123.2 (s), 117.7 (d), 116.6 (d), 52.4 (q), 51.8 (q), 46.3 (d), 30.9 (t), 28.5 (t), 26.2 (t), 25.8 (t), 25.3 (t), 17.2 (q), 10.2 (t), 9.0 (q), 8.5 (q), 8.5 (t); EIMS *m/z* (70 eV) 590 (M^+). Anal. Calcd: C, 65.22; H, 6.84; N, 4.75. Found: C, 65.60; H, 7.05; N, 4.80.

(10) Crystal data for compound **3a**: M_r = 597.25, monoclinic, $P2_1/c$, a = 14.613 (9) Å, b = 11.663 (3) Å, c = 18.760 (9) Å, β = 98.06 (7)°, V = 3165 (6) Å^3, Z = 4, D_{expl} = 1.25 g/cm^3, μ(Mo Kα) = 9.88 cm^{-1}, T = 293 K, yellow crystal, size 0.26 × 0.20 × 0.13 mm, Mo Kα radiation (λ = 0.710 73 Å), graphite monochromator. A total of 6012 reflections were measured on an Enraf-Nonius CAD4 diffractometer (ω–2Θ scan technique), range 0° < Θ < 25° and *hkl* −17,0,0 to 17,13,22; there were 5516 unique reflections (R_{int} = 0.032, averaging of some doubly measured reflections) and 1569 observed reflections ($I > 3\sigma(I)$). Semiempirical and empirical absorption corrections were applied. The structure was solved by direct methods (SHELXS86) and anisotropically refined, except C32 (see supplementary material), which was isotropically refined (SHELX76) to a final R = 0.056 (354 parameters, R_w = 0.057, $w = 1/(\sigma^2(F_o) + 0.0009F_o^2)$. The maximum shift/error was 0.3, and the maximum residual electron density was 0.43 e/Å^3. Because of the disorder found, one of the ethyl groups was refined as a rigid group riding on the Ge atom.

temperature (see below), they were not isolated, but their structure was supported by hydrolysis. Thus, evidence for the presence of **3f** came from the fact that the dihydropyrimidine **4b** (R^1 = Bu, R^2 = R^3 = H, R^4 = 4-MeC_6H_4) was obtained (oil, 93% yield from 1) when the reaction of the corresponding diazagermine **2** with DMAD was conducted at −20 °C followed by addition of water;[11] in the same way, the isolated diazagermocine **3a** furnished **4a** (R^1 = 4-MeC_6H_4, R^2 = R^4 = Ph, R^3 = Me; oil, 95% yield) on treatment at room temperature for 2 h with tetrahydrofuran–water (Scheme II).[12]

Finally, the behavior of **3** toward heating was tested. First, diazagermocine **3c** (R^1 = R^2 = Ph, R^3 = Me, R^4 = *c*-C_6H_{11}) at 70 °C underwent nitrogen–germanium bond cleavage and rearrangement to yield, after acidic aqueous workup, the new germanium-substituted diazocine **5** (mp 150–152 °C) in 84% yield[13] along with an unidentified minor compound (ca. 10%). On the other hand, when the intermediates **3e,f** were formed at 25 °C, they rearranged under the reaction conditions to afford in high yield new germanium-substituted furo[1,4-*b*]diazepines **6a** (mp 151–153 °C, 93% yield) and **6b** (mp 65–67 °C, 88% yield), which were degermylated with trifluoroacetic acid to form the previously reported heterocycles[3c] **7a** (90% yield from 1) and **7b** (82% yield from 1), respectively.[14] From a synthetic point of view, the preparation of seven-membered heterocycles **7** from azadienes **1** is best accomplished in terms of yield and reaction conditions by using germanium derivatives instead of the silicon analogues (e.g., for compound **7a** 25 °C, 90% yield vs 60 °C, 72% yield).

In summary, we have developed a simple and quantitative entry to 1,5,2-diazagermocines **3**, a new class of germanium-containing heterocycles, based on the reactivity of the nitrogen–germanium bond toward dimethyl acetylenedicarboxylate. On the other hand, the thermal behavior of **3** enabled us to cleanly obtain important medium-ring heterocycles with a germanium appendage.[15] Finally, we have found that the reactivity of the nitrogen–germanium bond toward insertion into activated triple bonds, e.g. DMAD, is higher than that of the nitrogen–silicon bond.

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Supplementary Material Available: Crystal structure data for **3a**, including tables of positional and thermal parameters, bond lengths and angles, least-squares planes, and torsion angles, an additional view of the structure of **3a**, text giving details of the syntheses of **2–7**, and tables of spectral and analytical data for **3–6** (16 pages). Ordering information is given on any current masthead page.

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(11) A solution of **2** (1 mmol), prepared as above[9] from **1** (R^1 = Bu, R^2 = R^3 = H, R^4 = 4-MeC_6H_5) and Ph_2GeCl_2, was treated with DMAD at −20 °C for 18 h. Then, cold water (10 mL) was added; the mixture was extracted with ether (2 × 10 mL) and dried over sodium sulfate. The solvents were evaporated at reduced pressure, and the residue was chromatographed (silica gel, hexane–ether 1:1 v/v) to give **4b** as a yellow oil (0.33 g, 93% yield). Spectral data for **4b**: IR (neat) ν(C=O) = 1735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, 3 H, J = 7.1 Hz), 1.25–1.4 (m, 2 H), 1.55–1.7 (m, 2 H), 2.35 (s, 3 H), 3.1–3.3 (m, 4 H), 3.7 (s, 3 H), 3.8 (s, 3 H), 5.5 (d, 1 H, J = 7.6 Hz), 6.7 (d, 1 H, J = 7.6 Hz), 7.15 (d, 2 H, J = 8.2 Hz), 7.7 (d, 2 H, J = 8.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0 (s), 170.4 (s), 162.2 (s), 144.1 (d), 139.7 (s), 135.0 (s), 128.7 (d), 126.8 (d), 91.7 (d), 80.0 (s), 52.6 (q), 51.7 (q), 50.3 (t), 40.8 (t), 32.3 (t), 21.2 (q), 19.8 (t), 13.7 (q); EIMS m/z (70 eV) 358 (M^+). Anal. Calcd: C, 67.02; H, 7.31; N, 7.81. Found: C, 67.11; H, 7.39; N, 7.89.

(12) The formation of heterocycles **4** does not take place by reaction of **1** with DMAD; see: (a) Barluenga, J.; Fustero, S.; Gotor, V. *Synthesis* **1975**, 191. (b) Barluenga, J.; Tomas, M.; Fustero, S.; Gotor, V. *Synthesis* **1979**, 345.

(13) A solution of **3c** (0.29 g, 0.5 mmol) in toluene (15 mL) was heated at 70 °C for 24 h. Then, the mixture was poured into ice-cooled 1 M H_2SO_4 (10 mL), extracted with ether (2 × 10 mL) washed with water, and dried over sodium sulfate. Removal of solvents followed by column chromatography furnished **5** (0.24 g, 84% yield). Further recrystallization from hexane–ether (2:1 v/v) gave a pure analytical sample. Spectral data for **5**: IR (KBr) ν(C=O) = 1730, 1710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.7 (t, 3 H, J = 7.1 Hz), 1.0–1.2 (m, 7 H), 1.25–1.35 (m, 4 H), 1.6–1.9 (m, 7 H), 2.1 (s, 3 H), 2.8–2.95 (m, 1 H), 3.8 (s, 3 H), 6.9–7.4 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4 (s), 165.4 (s), 165.3 (s), 147.9 (s), 143.2 (s), 137.1 (s), 136.3 (s), 131.5 (s), 131.0 (s), 128.7 (d), 128.6 (d), 128.4 (d), 128.2 (d), 124.6 (d), 120.6 (d), 52.8 (q), 42.6 (d), 31.5 (t), 26.5 (t), 25.8 (t), 15.8 (q), 12.6 (t), 9.5 (t), 7.1 (2 q); EIMS m/z (70 eV) 576 (M^+). Anal. Calcd: C, 64.73; H, 6.66; N, 4.87. Found: C, 64.86; H, 6.75; N, 4.70.

(14) To a solution of **2** (R^2 = R^3 = H) (1 mmol) in toluene (20 mL), prepared as described above,[9] was added DMAD (0.16 g, 1.1 mmol), and the mixture was stirred at room temperature for 24 h. The resulting mixture was poured into ice-cooled 1 M H_2SO_4 (15 mL), extracted with ether (3 × 15 mL), washed with water, and dried over sodium sulfate. The solvents were evaporated at reduced pressure, and the crude mixture was chromatographed (silica gel; hexane–ether 2:1 v/v) to give **6a,b** (88–93% yield). Compounds **6** (0.5 mmol) were then treated with trifluoroacetic acid (0.38 mL, 5 mmol) in dichloromethane at room temperature for 12 h. The resulting mixture was diluted with water (15 mL), extracted with dichloromethane (2 × 15 mL), and dried (Na_2SO_4). The organic layer was evaporated under reduced pressure and the residue subjected to chromatography on silica gel (hexane–ether 3:1 v/v) to yield compounds **7**.[3c] Spectral data for **6a**: IR (neat) ν(C=O) = 1730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.1–1.9 (m, 10 H), 3.2 (s, 3 H), 3.8 (s, 3 H), 4.1–4.2 (m, 1 H), 5.8 (d, 1 H, J = 9.7 Hz), 6.85 (d, 2 H, J = 8.9 Hz), 6.9 (d, 1 H, J = 9.7 Hz), 7.3–7.5 (m, 6 H), 7.7–7.85 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5 (s), 167.2 (s), 165.5 (s), 162.1 (s), 141.2 (d), 136.2 (s), 135.1 (d), 133.7 (d), 133.6 (d), 131.4 (s), 130.0 (d), 129.8 (d), 128.2 (d), 127.2 (d), 113.7 (d), 108.3 (s), 103.9 (s), 95.6 (d), 60.6 (d), 55.3 (q), 49.7 (q), 34.1 (t), 33.3 (t), 25.9 (t), 25.5 (t), 25.1 (t); EIMS m/z (70 eV) 612 (M^+). Anal. Calcd: C, 64.85; H, 5.61; N, 4.58. Found: C, 64.69; H, 5.90; N, 4.50.

(15) Heterocyclic compounds containing trialkylgermanium substituents have been reported to show antitumor activity.[5a]