by-products of unknown structure were obtained from the ether layer.

Experimental Procedure

9: To a solution of bis(trimethylstannyl)methane (5.46 g, 16 mmol) in THF (32 mL) was added *n*BuLi (1.62 *M* hexane solution, 9.9 mL, 16 mmol) at −78 °C. After the mixture had been stirred for 15 min, a solution of **8** [9] (1.43 g, 8 mmol) in THF (8 mL) was added, and the mixture stirred for a further 20 min at this temperature. Methyl formate (3 mL, 49 mmol) was added, and then the reaction mixture was warmed up gradually and stirred for 4 h at 0 °C. The reaction mixture was quenched with aqueous NaHCO₃ solution and washed with diethyl ether. The aqueous solution was acidified with 4 *M* HCl and extracted with CHCl₃. After evaporation of the solvent pure **9** (981 mg, 66%) was obtained. ¹H NMR (60 MHz, CCl₄): δ = 1.15 (d, *J* = 7 Hz, 3H), 1.32 (s, 3H), 1.50 (s, 3H), 4.23–4.58 (m, 2H), 5.88 (d, *J* = 5 Hz, 1H), 7.91 (d, *J* = 5 Hz, 1H), 12.5 (br, 1H).

D-**10**: Compound **9** (365 mg, 2 mmol) was hydrolyzed by adding H₂SO₄ (3 drops) and refluxing in THF (20 mL) for 5 h. The reaction mixture was neutralized with NaHCO₃, concentrated in vacuo, and extracted with CHCl₃. Purification by sublimation afforded a pure sample of D-**10** (188 mg, 75%). M.p. 87–88 °C (sublimation); [α]D²³ = +218 (c =1.27, MeOH). ¹H NMR (400 MHz, CDCl₃): δ =1.57 (d, *J* =7.6 Hz, 3H), 3.58 (s, 1H), 3.97 (d, *J* =13.8 Hz, 1H), 4.20 (dq, *J* =13.8, 7.6 Hz, 1H), 5.46 (d, *J* =7.1 Hz, 1H), 7.38 (d, *J* =7.1 Hz, 1H). ¹³C NMR (CDCl₃): δ = 17.91, 72.69, 79.93, 103.4, 164.7, 194.2.

rac-**10**: m.p. 66 °C. Published value for L-**10** [8]: m.p. 86 °C (sublimation); [α]D²⁸ = −227 (c =1.3, MeOH).

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Novel Insertions of Carbene Homologues into Metal-η⁵–Cp Bonds: Sandwich Complexes with Ge₂Ni and Sn₂Ni Cores**

By *Michael Veith** and *Lothar Stahl*

The carbene homologues E(N*t*Bu)₂SiMe₂, E = Ge (**1**), Sn (**2**), are useful ligands for transition metal complexes because of their amphoteric Lewis acidic and Lewis basic properties.[1] It seemed promising to us to investigate their reaction behavior with the paramagnetic 20-electron complex nickelocene [Cp₂Ni]. When electrophiles react with [Cp₂Ni] they should attack the Cp rings, in contrast nucleophiles should attack the Ni atom (Scheme 1).[2]
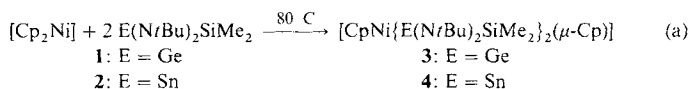
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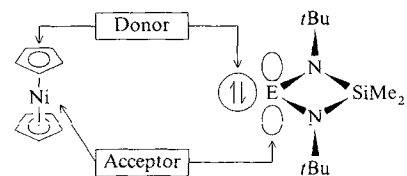
Scheme 1. E = element of Group 14.

If a green solution of [Cp₂Ni] and **1** or **2** in toluene is heated to approximately 80 °C [Eq. (a)], this solution turns black-brown with the formation of the products **3** or **4**.

$$[Cp_2Ni] + 2\,E(NtBu)_2SiMe_2 \xrightarrow{80\,°C} [CpNi\{E(NtBu)_2SiMe_2\}_2(\mu\text{-}Cp)] \quad (a)$$

1: E = Ge **3**: E = Ge
2: E = Sn **4**: E = Sn

The NMR spectra (¹H, ¹³C, ¹¹⁹Sn) of **3** and **4**[3] have sharp signals, which indicate that these complexes are diamagnetic. Particularly striking is the occurence of two resonance signals for the Cp ligands with markedly different chemical shifts. The ¹H NMR spectrum of **4** shows a singlet at δ = 5.07 typical for η⁵-bound Cp ligands, and a signal strongly shifted to low field at δ = 6.54 with tin satellites (*J* = 8.8 Hz, 27%). Coupling constants and intensities of the satellites indicate that the Cp ligand to which the signal at δ = 6.54 is assigned, is symmetrically π bound to two Sn atoms. As a result of the diastereotopic geminal SiMe₂ groups, the hydrogen atoms of the substituents of the SnN₂Si rings appear as three singlets. The NMR spectra hardly change on cooling the NMR samples to −80 °C; also the (cross-polarization magic angle spinning) CP-MAS ¹³C NMR spectrum of solid **4** is almost identical with the spectrum recorded in solution. The presence of only one sharp signal at δ ≈ 117 in the ¹³C NMR spectrum shows that the bridging Cp ligand rapidly rearranges haptotropically in solution and in the solid state. The IR spectra, which are almost identical for **3** and **4**, also indicate π-bound Cp units because of the small number of bands for the Cp ligands.

Compounds **3** and **4** crystallize in monoclinic space groups with two molecules in the unit cell; their structures are not isotypic. The molecules lie on inversion centers of the space group *P*2₁/c (different choice of cell for **3**: *P*2₁/n) which, however, is not in agreement with the NMR spectroscopic data. It became clear during the structure determination that a statistical disorder of a part of the molecules (Cp ligands and the nickel atom) was present as regards the inversion center of the space group; despite this shortcoming, resulting from the packing of the molecules (cf., e.g., ref. [4]), the structures could be refined accurately, and all hydrogen atom positions could be determined from difference Fourier analyses.[5]

The molecular structure of **4**, in which two Cp ligands are bound in different ways, is depicted in Figure 1. The Cp ligands are coordinated sandwichlike to the three metal atoms; Cp¹ (C31–C35) is bound η⁵ to the Ni atom. The average Ni–C distance (2.097(9) Å) is shorter than that in [Cp₂Ni] (2.18 Å),[6] indicating a strong Ni–Cp bond (the Ni centers in **3** and **4** each achieve 18-electron configurations). The two Ni–Sn bonds are likewise very short and both almost identical in length (Ni–Sn 2.326(2), Ni–Snᴬ 2.369(2) Å); in the compound [(C₂H₄)₂NiSn{CH(SiMe₃)₂}₂], in which double bond contributions for the Ni–Sn bond are
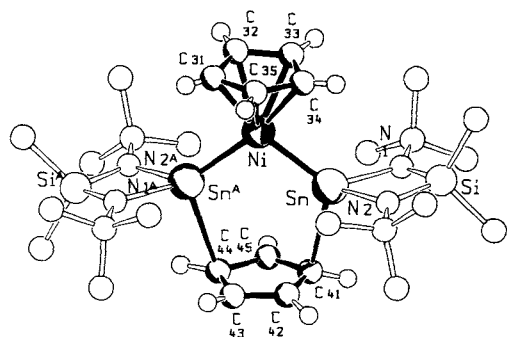
Fig. 1. Molecular structure of **4** (SCHAKAL [11b]). (The atoms labeled with the superscript A are symmetry equivalent [5].) Selected distances [Å] and angles [ ] (See also the text): Sn-Ni1,2 2.083(8), Si-N1,2 1.749(5), Sn ⋯ Sn^A 3.648(4); Sn-Ni-Sn^A 102.0(1), Ni-Sn-C41 116.7(2), Ni-Sn^A-C44 112.5(2), N1-Sn-N2 75.5(1).

discussed, the Ni–Sn distance is 2.387(1) Å.[7] The center of the Cp^1 ligand, the two tin atoms, and the Ni atom lie almost in one plane. The most unusual structural element in **4** is without doubt the coordination of the second Cp ligand, which symmetrically bridges the two stannylene units via the tin atoms in a π bound manner. One C atom of the Cp^2 ligand (C41 – C45) is coordinated to one of the Sn atoms and another C atom of the Cp^2 ligand (C41 – C45) is coordinated to the other Sn atom. The distances vary slightly (2.702(12) Å (Sn–C41) and 2.608(11) Å (Sn^A–C44)). The bond lengths correspond to the average Sn–C distance in stannocene (2.71 Å);[8] σ-bound Cp ligands have significantly shorter Sn–C distances (2.15–2.20 Å).[9] To our knowledge this is the first structure in which a Cp ligand bridges μ-η^1:η^1 two main group elements. Both Cp rings are planar and arranged almost parallel (deviation 3.1°); they form dihedral angles of 9.4° (Cp^1) and 6.3° (Cp^2) with the SiN$_2$Sn metallacycles. The C atoms of Cp^2 bound to the Sn atoms lie, as expected, approximately 0.01 Å above the best plane, the corresponding H atoms (H41, H44) lie relatively far below (approximately 0.38 Å) this plane. The C–C bond lengths of the Cp ligands vary from 1.389(15) to 1.486(17) Å and are typical for Cp ligands with a delocalized π system.

The structure of **3** (Fig. 2) is similar to that of **4**. However, the Ni–Ge and Ge–Cp^2 distances differ considerably more than the corresponding Sn distances in **4**. The Ni–Ge bond
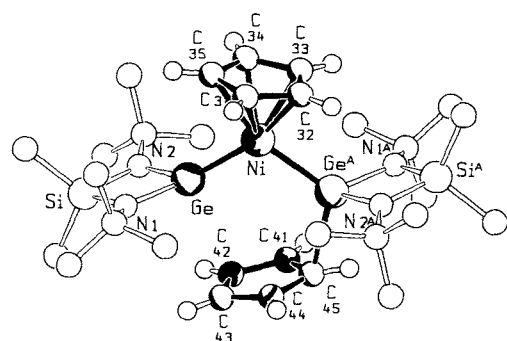

Fig. 2. Molecular structure of **3** (see also legend in Fig. 1). Other selected distances [Å] and angles [ ] not discussed in text: Ni-C31-35 2.057(20), Ge-C41 3.007(7), Ge-C44 3.016(8), Ge-N1,2 1.864(3), Si-N1,2 1.729(2), Ge ⋯ Ge^A 3.549(7); Ge-Ni-Ge^A 109.6(1), Ni-Ge^A-C45 113.9(2), N1-Ge-N2 81.2(2).

lengths 2.085(3) and 2.258(3) Å differ significantly; the former distance is extremely short. The coordination of the "bridging" Cp^2 ligand (C41 – C45) must be described as η^1-

π in **3**, since all the Ge–C distances of this ligand are greater than 3.0 Å with the exception of the Ge^A–C45 bond (2.329(8) Å). The Ge–Ni distance is short, but the Ge–Cp^2 distance is long; exactly the opposite is true for the distances to the Ge^A atom. The asymmetry of **3** compared to **4** in the solid state reflects the formation process of the compounds by insertion of the carbene homologue into the Ni–Cp bond far better than the structure of **4**. As for the Sn–Cp^2 bond in **4**, the Ge–Cp^2 interaction in **3**, however, is clearly to be considered as a π bond, which is revealed both by the long Ge–C45 distance compared to usual σ bonds and also the C–H coupling constants.[3]

The structures of **3** and **4** are also interesting in view of the elucidation of the reaction mechanism of a Lewis base attack on [Cp$_2$Ni].[12] Compounds **3** and **4** can be considered as intermediates of such reactions, which cannot be isolated for usual Lewis bases (CO, PR$_3$).

Experimental Procedure

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[3] NMR spectra (200 MHz, C$_6$D$_6$, 292K, TMS): **3**: ^{1}H NMR: δ = 0.46 (6H; SiMe), 0.48 (6H; SiMe), 1.29 (36H; tBu), 5.07 (5H; NiCp), 6.35 (5H; (μ-Cp)Ge$_2$); ^{13}C NMR: δ = 6.0 (q, ^1J(C, H) = 117 Hz, 2C; SiMe), 7.4 (q, ^1J(C, H) = 117 Hz, 2C; SiMe), 34.6 (q, ^1J(C, H) = 123 Hz, 12C; C-CH$_3$), 52.7 (s, 4C; C-CH$_3$), 91.8 (d, ^1J(C, H) = 175 Hz, 5C; NiCp), 120.4 (d, ^1J(C, H) = 163 Hz, 5C; (μ-Cp)Ge$_2$).

4: ^{1}H NMR: δ = 0.48 (6H; SioMe), 0.55 (6H; SiMe), 1.27 (36H; tBu), 5.07 (5H; NiCp), 6.54 (^2J (H, $^{117/119}$Sn) = 8.8 Hz (27%), 5H; (μ-Cp)Sn$_2$); ^{13}C NMR: δ = 7.9 (q, ^1J(C, H) = 117 Hz, 2C; SiMe), 8.6 (q, ^1J(C, H) = 117 Hz, 2C; SiMe), 35.8 (q, ^1J(C, H) = 132 Hz, 12C; C-CH$_3$), 53.0 (s, 4C; C-CH$_3$), 89.1 (d, ^1J(C, H) = 176 Hz, ^1J (C, $^{117-119}$Sn) = 15.2 Hz, 5C; NiCp), 117.4 (d, ^1J(C, H) = 165 Hz, ^2J(C, $^{117-119}$Sn) = 13.2 Hz, 5C; (μ-Cp)Sn$_2$); ^{119}Sn{^{1}H} NMR: δ = 313.3; ^{13}C Cp-MAS NMR: δ = 9.9 (br. s, 4C; SiMe), 36.2 (12C; C-CH$_3$), 53.6 (d, asymmetric quadrupolar splitting ^{14}N: 100.3 Hz, 4C; C-CH$_3$), 89.4 (5C; NiCp), 116.9 (5C; (μ-Cp)Sn$_2$).

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[5] Structure determination with Siemens AED2; Mo$_{K_\alpha}$ radiation, SHELXTL program [11]. **3**: monoclinic, P2$_1$/n, a = 9.484(12), b = 11.455(11), c = 16.661(14) Å, β = 91.20(9)°, Z = 2; 1650 reflections with 77 F$_0$ < 2σ, 183 parameters, R = 0.0309, R$_w$ = 0.0314. **4**: monoclinic, P2$_1$/c, a = 11.749(8), b = 9.886(4), c = 16.567(19) Å, β = 93.64(2)°, Z = 2; 1679 reflections with 39 F$_0$ < 1σ, 229 parameters, R = 0.0231, R$_w$ = 0.0196. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2 (FRG) on quoting the depository number CSD-56681, the names of the authors, and the journal citation.

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