Reactions of Cyclic Bis(amino)germylenes and -stannylenes with [CpFe(CO)₂]₂ and CpFe(CO)₂Me (Cp = η^5-C₅H₅). Syntheses and Single-Crystal X-ray Structures of Four New Insertion Compounds[1]

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The interaction of El(N^{t}Bu)₂SiMe₂, El = Ge, Sn with CpFe(CO)₂Me in toluene has yielded CpFe(CO)₂[El(N^{t}Bu)₂SiMe₂]Me, El = Ge (2) and El = Sn (3), respectively. Both compounds have been characterized by NMR, IR, MS, elemental analysis, and single crystal X-ray methods. Compound 2 crystallizes in the monoclinic system, space group $P2_1/m$, $Z = 2$, $a = 9.330(6)$ Å, $b = 12.552(9)$ Å, $c = 9.939(7)$ Å, $\beta = 105.01(2)°$, $V = 1124(1)$ Å³. The isostructural 3 forms orthorhombic crystals of space group $Pnma$, $Z = 4$, $a = 17.871(9)$ Å, $b = 12.998(7)$ Å, $c = 9.838(5)$ Å, $V = 2285(2)$ Å³. The refinement of 2 with 1431 unique, observed ($I > 2\sigma(I)$) reflections led to final agreement indices of $R = 0.043$, $R_w = 0.048$. The structure of 3 was refined to $R = 0.027$ ($R_w = 0.027$) by using 1397 unique and observed ($I > 2\sigma(I)$) reflections. Treatment of [CpFe(CO)₂]₂ with 2 equiv. of El(N^{t}Bu)₂SiMe₂ under identical reaction conditions afforded [CpFe(CO)₂]₂Ge(N^{t}Bu)₂SiMe₂, 4, for the cyclic germylene, whereas in the case of the tin homolog the tetranuclear complex {[CpFe(CO)₂Sn(N^{t}Bu)₂SiMe₂]₂·C₇H₈}, 5, was isolated. Complete characterizations (NMR, IR, MS, EA, single crystal X-ray determination) were carried out on both compounds. The solid state structure of 5 contains one of the longest (2.992(2) Å) unbridged tin–tin bonds known to date. The trinuclear compound 4 is triclinic, space group $P\bar{1}$, $Z = 2$. Its lattice parameters are: $a = 9.549(5)$ Å, $b = 10.102(5)$ Å, $c = 16.438(8)$ Å, $\alpha = 81.98(4)°$, $\beta = 74.00(3)°$, $\gamma = 62.80(3)°$, $V = 1355(1)$ Å³. Refinement of this structure using 3100 unique, observed ($I > 2\sigma(I)$) data led to agreement indices of $R = 0.023$ and $R_w = 0.023$. The tetranuclear 5 crystallizes as a toluene solvate. Crystal data: monoclinic, space group $P2_1/n$, $Z = 2$, $a = 10.547(7)$ Å, $b = 19.944(11)$ Å, $c = 11.366(7)$ Å, $\beta = 92.36(5)°$. Of 3024 collected data 2724 were considered unique and observed ($I > 3\sigma(I)$) and used in the refinement. Final agreement indices are $R = 0.031$, $R_w = 0.033$.

Introduction

We have recently begun a systematic investigation on the reaction of the cyclic group 14 amides, 1, with transition-metal compounds for the purpose of constructing clusterlike molecules.[2]
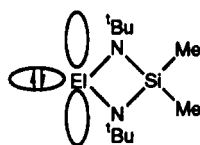
El = Ge, Sn   1

Preliminary findings have suggested that multi-metal-centered molecules obtained from these reactions have interesting catalytic properties and may be useful precursors for large-metal-core oxides.[3] To further our understanding of the crucial step in cluster synthesis, the formation of a metal–metal bond, we have studied the chemistry of the highly reactive carbene homologs 1 with transition metal organometallic compounds which are known to react with such group 14 species under metal-

metal bond formation, viz. [CpFe(CO)₂]₂ and CpFe-(CO)₂Me.[4,5]

Despite the ubiquity of group 14 derivatives of these Fp[6] compounds, we thought that the superior reactivity of 1 might lead to some unprecedented results.

Experimental Section

All operations were carried out in a modified Schlenk-type vacuum line. The reactions were done under an atmosphere of prepurified nitrogen. Liquids were transferred either by vacuum techniques or nitrogen-flushed pipettes. The solvents were scrupulously dried in a manner appropriate to each. The ^{1}H-NMR spectra were acquired on a Bruker WP 80 NMR spectrometer using benzene-d_6 as lock solvent. All chemical shifts are relative to TMS at 0.00 ppm. Infrared spectra were obtained in the solution phase on a Perkin-Elmer Spectrophotometer 883 instrument. Mass spectral data were acquired on Finnigan MAT

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(2) a) Veith, M.; Stahl, L.; Huch, V. *Inorg. Chem.* 1989, 28, 3278. b) Veith, M.; Stahl, L.; Huch, V. *J. Chem. Soc., Chem. Commun.* 1990, 359.

(3) Brunner, H.; Veith, M. Unpublished results.

(4) For a representative survey of CpFe(CO)₂ group 14 compounds, see: *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Krüerke, U., Ed.; Springer Verlag: New York, 1984; Part B 12. For [CpFe(CO)₂]₂ group 14 compounds, see: *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Krüerke, U.; Petz, W., Eds.; Springer Verlag: New York, 1980; Part C 3. More recent, related papers are: (a) Lappert, M. F.; McGeary, M. J. Parish, R. V. *J. Organomet. Chem.* 1989, 373, 107. (b) Barsuaskas, G.; Lei, D.; Hampden-Smith, M. J.; Duesler, E. N. *Polyhedron*, 1990, 9, 773.

(5) For a review on the role of germylenes and stannylenes in transition metal chemistry, see: Lappert, M. F.; Rowe, R. S. *Coord. Chem. Rev.* 1990, 100, 267.

(6) In keeping with common practice the CpFe(CO)₂ and [CpFe(CO)₂]₂ moieties will be abbreviated Fp und Fp₂, respectively, in this manuscript.

311 or MAT 90 instruments, operating in the electron impact mode at 17 or 70 eV. The metallacycles $El(N^tBu)_2SiMe_2$, El = Ge, Sn, were prepared according to previously published procedures.[7] $[CpFe(CO)_2]_2$ was purchased from Alfa and used as received, and the $CpFe(CO)_2Me$ was synthesized by an established preparative route.[8]

$CpFe(CO)_2[Ge(N^tBu)_2SiMe_2]Me$, 2. Exactly 0.245 g (1.29 mmol) of $CpFe(CO)_2Me$ was dissolved in 20 mL of toluene in a 50-mL round-bottom flask. An equimolar amount of $Ge(N^t-Bu)_2SiMe_2$, diluted in 10 mL of toluene, was then added dropwise by pipette. Under magnetic stirring the reaction mixture was kept at 60 °C for 20 h. During this time the initially yellow solution turned orange-red. After the reaction had been judged complete by NMR techniques, the solvent was removed under a vacuum, leaving behind a yellow oil. The residue was dissolved in a small amount of hexanes and then cooled to –20 °C. This procedure yielded 0.554 g (92.2%) of lemon-yellow crystals. The compound is reasonably air-stable in the solid state and extremely soluble in all organic solvents. Melting point: 134 °C. Anal. Calcd for $C_{18}H_{32}N_2O_2SiFeGe$: C, 46.49%; H, 6.94%; N, 6.03%. Found: C, 46.82%; H, 7.15%; N, 5.91%. Mass spectrum, m/e (rel inten): 41 (42), 43 (28), 56 (14), 57 (35), 58 (13), 73 (40), 114 (25), 121 (33), 142 (12), 144 (20), 145 (11), 146 (28), 255 (18), 257 (21) 257 (11), 259 (35), 285 (51), 287 (74), 288 (36), 289 (100), 298 (18), 291 (27), 395 (16), 465 (0.4) = M^+.

$CpFe(CO)_2[Sn(N^tBu)_2SiMe_2]Me$, 3. This compound was prepared in a manner analogous to that of 2. A toluene solution containing 0.210 g (1.10 mmol) of $CpFe(CO)_2Me$ and 1.20 mmol of $Sn(N^tBu)_2SiMe_2$ was stirred at 60 °C for 24 h. Following a similar workup as for 2, 0.492 g (0.963 mmol) of lemon-yellow crystals were obtained. Yield: 87.5%. The compound is air-stable for hours in the solid state and very soluble in all organic solvents. Melting point: 119 °C. Anal. Calcd for $C_{18}H_{32}N_2O_2SiFeSn$: C, 42.30; H, 6.31; N, 5.48. Found: C, 42.43; H, 6.35; N, 5.48. Mass spectrum, m/e (rel inten): 39 (24), 41 (52), 42 (16), 43 (36), 55 (13), 56 (17), 57 (21), 58 (18), 59 (11), 69 (54), 73 (54), 74 (20), 81 (12), 100 (11), 114 (48), 119 (14), 121 (36), 130 (18), 131 (52), 149 (17), 169 (10), 177 (14), 181 (18), 185 (13), 187 (14), 192 (20), 288 (13), 290 (18), 301 (38), 302 (25), 303 (73), 304 (27), 305 (100), 306 (17), 307 (12), 309 (15), 437 (12), 438 (10), 439 (18), 441 (31), 493 (15), 495 (25), 496 (11), 497 (24), 499 (1), 511 (0.2) = M^+.

$[CpFe(CO)_2]_2Ge(N^tBu)_2SiMe_2$, 4. To a stirred solution of 0.344 g (1.00 mmol) of $[CpFe(CO)_2]_2$ in 40 mL of toluene was added by pipette 7 mL of a 0.30 M toluene solution of $Ge(N^t-Bu)SiMe_2$. The reaction mixture was kept at 60 °C for 20 h. During this time a gradual color change from maroon to orange-brown was observed. After it had been allowed to cool, the solution was filtered through a coarse frit to remove insolubles and then reduced in volume to 20 mL. A large crop of dark orange crystals (0.545 g, 0.850 mmol) was isolated from a cooled (–20 °C) solution after 3 days. This corresponds to a yield of 85.0%, based on the iron starting material. The crystals can be manipulated in the atmosphere for short period of time without noticeable decomposition. Melting point: 215 °C. Anal. Calcd for $C_{24}H_{34}N_2O_4SiFeGe$: C, 45.98; H, 5.47; N, 4.47. Found: C, 46.50; H, 5.64; N, 4.53. Mass spectrum, m/e (rel inten): 39 (40), 41 (23), 56 (67), 57 (67), 57 (11), 73 (35), 95 (16), 114 (21), 121 (100), 122 (13), 142 (16), 144 (23), 146 (29), 149 (17), 177 (15), 186 (26), 203 (11), 255 (38), 257 (50), 258 (21), 259 (72), 260 (12), 261 (16), 599 (0.01) = M^+ – CO.

$\{[CpFe(CO)_2Sn(N^tBu)_2SiMe_2]_2 \cdot C_7H_8\}$, 5. To a magnetically stirred toluene solution of $[CpFe(CO)_2]_2$ (0.278 g, 0.780 mmol) was added a 0.36 M solution (4.5 ml) of $Sn(N^tBu)SiMe_2$ by pipette. Within minutes of the addition the reaction mixture became intensely purple. The solution temperature was maintained at 60 °C for 18 h, during which the color reverted back to a dark red. Following filtration through a coarse frit, the solution volume

was reduced to 15 mL in vacuo. After 5 days at 0 °C, 0.743 g (0.749 mmol) of well-formed, dark-red needle crystals were isolated. Yield: 96.0%. Melting point: 148 °C. Anal. Calcd for $C_{41}H_{66}N_4O_4Si_2Fe_2Sn_2$: C, 42.30; H, 6.31; N, 5.48. Found: C, 42.43; H, 6.35; N, 5.48. Mass spectrum, m/e (rel inten): 437 (13), 439 (22), 440 (12), 441 (28), 493 (45), 494 (35), 495 (79), 496 (45), 497 (100) = 0,5 (M^+-C_7H_8), 498 (27), 499 (20) 501 (16), 655 (24), 656 (20), 657 (43), 658 (28), 659 (52), 660 (17), 661 (12), 992 (0.50) = M^+ – C_7H_8.

X-ray Crystallography

Suitable single crystals of 2–5 were inspected visually with a polarizing microscope and then sealed under a nitrogen atmosphere inside glass capillaries. Preliminary cell constants and possible space groups were determined from Weissenberg oscillation, zeroth- and first-layer photographs. The crystals were then transferred to a Siemens–Stoe four-circle diffractometer where accurate cell dimensions were obtained from 20 reflections in the 18–23° 2θ range. Intensities were measured at 291 K with the ω–θ scan technique, using monochromated Mo K_α radiation. The peaks were scanned at a variable rate (1.20–3.60°/min). Exactly 10.0° of background was collected on each side of the peak. Three standard reflections were checked every 60 min; they showed negligible decay. The data sets were subjected to LP and empirical absorption corrections.

The structures were solved and refined with the SHELXTL-PLUS[9] program package. Molecular structures were drawn by using the XP routine of the same program.

$CpFe(CO)_2[Ge(N^tBu)_2SiMe_2]Me$, 2. The Weissenberg photographs revealed the presence of a 2_1 screw axis as the only systematic absences, indicating space groups $P2_1$ or $P2_1/m$. The structure was solved in the centrosymmetric space group with the heavy atom method. The Patterson synthesis revealed the positions of the metal atoms. All remaining carbon atoms and some of the hydrogens were located on subsequent difference Fourier syntheses. All non-hydrogen atoms were initially refined isotropically, but were given anisotropic thermal parameters in the latter stages of the refinement. Methyl groups, with the exception of those lying on the mirror plane, were treated as rigid entities with a common isotropic thermal parameter assigned to the hydrogens. The cyclopentadienyl hydrogen atoms were not included in the refinement.

$CpFe(CO)_2[Sn(N^tBu)_2SiMe_2]Me$, 3. The presence of diagonal- and a-glide planes were indicated by systematic absences. The structure was solved and refined successfully in space group $Pnma$.

$[CpFe(CO)_2]_2Ge(N^tBu)_2SiMe_2$, 4. The structure was solved by Patterson methods and refined successfully in space group $P\bar{1}$. After a series of difference Fourier syntheses the positions of all non-hydrogen atoms and most of the hydrogen atoms were located. The non-hydrogens were refined anisotropically. All methyl groups were treated as rigid bodies in the refinement. The cyclopentadienyl moieties were only initially treated as idealized pentagons with their attached hydrogen atoms. This procedure allowed the location of all cyclopentadienyl hydrogen atoms. The rigid group constraints were lifted in the final refinement cycles.

$\{[CpFe(CO)_2Sn(N^tBu)SiMe_2]_2 \cdot C_7H_8\}$, 5. Space group $P2_1/n$ was indicated unambiguously by the systematic

(7) a) Veith, M. *Angew. Chem. Int. Ed. Engl.* 1975, *14*, 263. b) Veith, M., Grosser, M. *Z. Naturforsch.* 1982, *37b*, 1975.

(8) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* 1956, *3*, 104.

(9) SHELXTL-PLUS (G. M. Sheldrick, A Program For Crystal Structure Determination, Version 4.0, 1989, Siemens Analytical X-ray Instruments, Madison, WI).

absences and the structure was solved and refined in this space group. The positions of the metal atoms and some of the other heavy atoms were taken from the initial Patterson map. Subsequent difference Fourier syntheses revealed the positions of the remaining non-hydrogens and of some of the hydrogens. The refinement was carried out in a manner similar to that of **4**. The compound crystallizes with one molecule of toluene per dimer. The toluene molecule is situated around the inversion center at 0, 1/2, 0. During the course of the refinement it became evident that the toluene moiety was severely disordered with at least two different orientations. Carbon atoms with a SOF of 0.5 were assigned to eight peaks of reasonable electron density and refined isotropically. A satisfying geometric model, however, could not be found for the toluene molecule.
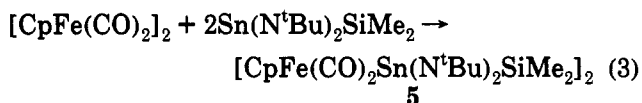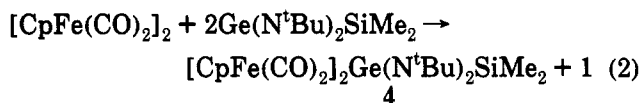
Results and Discussion

Synthesis. The newly reported compounds **2–5** were prepared using convenient methods and mild conditions, i.e. direct interaction of the reactants in toluene at temperatures slightly above ambient.

The combination of 1 equiv. each of $CpFe(CO)_2Me$ and $El(N^tBu)_2SiMe_2$ (El = Ge, Sn) in toluene according to eq 1 afforded $CpFe(CO)_2[El(N^tBu)_2SiMe_2]Me$ in nearly

$$CpFe(CO)_2Me + El(N^tBu)_2SiMe_2 \rightarrow$$

$$CpFe(CO)_2[El(N^tBu)_2SiMe_2]Me \quad (1)$$
$$El = Ge, \mathbf{2}; Sn, \mathbf{3}$$
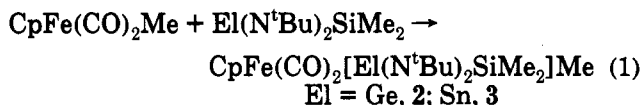
quantitative yields. Both compounds were isolated as lemon-yellow crystals of reasonable air stability.

The reactions of $[CpFe(CO)_2]_2$ with germylene and stannylene were carried out according to eqs 2 and 3, respectively. Despite identical stoichiometries and reac-

$$[CpFe(CO)_2]_2 + 2Ge(N^tBu)_2SiMe_2 \rightarrow$$

$$[CpFe(CO)_2]_2Ge(N^tBu)_2SiMe_2 + \mathbf{1} \quad (2)$$
$$\mathbf{4}$$

$$[CpFe(CO)_2]_2 + 2Sn(N^tBu)_2SiMe_2 \rightarrow$$

$$[CpFe(CO)_2Sn(N^tBu)_2SiMe_2]_2 \quad (3)$$
$$\mathbf{5}$$

tion conditions, nonhomologous compounds were isolated. Thus eq 2 gave the monoinsertion product **4**, while eq 3 yielded a compound which is the product of a formal double-insertion of $Sn(N^tBu)_2SiMe_2$ into the iron–iron bond of Fp_2.

The addition of the stannylene to the $[CpFe(CO)_2]_2$ solution initially produced an intensely purple reaction mixture which became dark red on heating. The purple color is likely due to a radical species, although NMR spectra of this solution showed no line broadening.

Both products, **4** and **5**, were crystallized directly from toluene solutions, following filtration. The iron–germanium compound is dark orange and air-stable for short periods of time, whereas the dark red ditin species decomposes readily upon short exposure to the atmosphere or long term exposure to sunlight.

Spectroscopy. The ^1H NMR spectra of **2** and **3** (Table I) consist of essentially identical five-line patterns, the two Si–Me signals being due to diastereotopically different methyl groups. The metal-bound methyl groups of the

Table I. ^1H-NMR and Solution IR Data [$\nu(CO)$] of 2–5[a]

	chemical shift, ppm				
	Cp	N^tBu	$El–CH_3$	$Si–CH_3$	IR: $\nu(CO)$, cm^{-1}
2	4.32 (5)	1.26 (18)	1.17 (3)	0.49 (3) 0.39 (3)	2001 (s), 1994 (vs), 1945 (vs), 1914 (w), in hexane
3	4.28 (5)	1.28 (18)	0.90 (3)[b]	0.52 (3) 0.43 (3)	2001 (s), 1992 (vs), 1946 (vs), 1914 (w), in hexane
4	4.44 (10)	1.41 (18)	–	0.55 (6)	1992 (vs), 1968 (vs), 1940 (vs), 1919 (vs), in THF
5[c]	4.45 (10)	1.36 (36)	–	0.52 (12)	1985 (vs), 1968 (s), 1942 (vs), 1921 (s), in THF

[a] All spectra were recorded at 298 K; intensities are given in parentheses. NMR spectra were recorded in C_6D_6. [b] $J(^1H-^{117/119}Sn) = 42$ Hz. [c] Peaks for the toluene molecule are not reported.

starting material show a marked downfield shift compared to FpMe and, in the case of the tin compound, exhibit $^{117/119}Sn$ satellites. For the cyclopentadienyl group, one singlet resonance is observed at rather high field. In the related $FpGeMe_3$, $FpSnMe_3$ and FpMe the Cp signal is found at 4.7,[10] 4.68,[10] and 4.65 ppm, respectively.

The solution phase IR spectra of $CpFe(CO)_2[El(N^tBu)_2SiMe_2]Me$, El = Ge, Sn, are almost identical (Table I), with both compounds having two prominent bands of equal intensity in the terminal CO stretching region. Additional, weaker bands show the presence of one rotamer. The two major bands at 1946 and 1992 cm^{-1} can be assigned to the antisymmetric and symmetric stretching modes, respectively. They are at the low energy end of terminal CO stretches for such FpX compounds, attesting to the effect of **1** as electron-releasing groups.

In Table I there are listed the ^1H NMR and solution IR data of compounds **4** and **5**. Both species have rather simple three-line ^1H NMR spectra. In contrast to the NMR data of **2** and **3**, only one resonance is observed for the $SiMe_2$ groups, indicative of a symmetrical substitution at the group 14 metals. This observation is consistent with both the insertion of the metallacycles into the iron–iron bond of the Fp dimer and the replacement of one or both of the bridging carbonyl ligands by **1**. The integrated intensities for **4** show that one molecule of **1** has reacted with the iron dimer, whereas in **5** there is a 1 to 1 relationship between the signals for the stannylene and Fp moieties. The Cp protons appear to be highly shielded, similar to those in **2** and **3**. In the parent compound $[CpFe(CO)_2]_2$ the signal for the cyclopentadienyl ligands is observed at 4.84 ppm, whereas in the related Fp_2SnMe_2 and Fp_2GeMe_2 the Cp protons absorb at 4.76[11] and 4.77 ppm,[11] respectively.

The solution IR spectra of **4** and **5** have four bands in the CO stretching region for terminal carbonyls, thereby ruling out a CO substitution by **1**. Structural differences between **4** and **5** are confirmed by the relative intensities of these bands.

Single-Crystal X-ray Studies. For unambiguous structure identifications and to have available reliable bond parameters single crystal X-ray structure determinations were carried out on all four newly synthesized compounds. Data collection parameters for these structures are con-

(10) Bichler, R. E. J.; Booth, M. R.; Clark, H. C. *J. Organomet. Chem.* **1970**, *24*, 145.

(11) Flitcroft, N.; Harbourne, D. A.; Paul, I.; Tucker, P. M.; Stone, F. G. A. *J. Chem. Soc. A.* **1966**, 1130.

Table II. X-ray Data Collection Parameters for 2–5

	2	3	4	5
formula	$C_{18}H_{32}FeGeN_2O_2Si$	$C_{18}H_{32}FeN_2O_2SiSn$	$C_{24}H_{34}Fe_2GeN_2O_4Si$	$C_{41}H_{66}Fe_2N_4O_4Si_2Sn_2$
mol wt	464.9	511.1	626.9	1084.1
cryst system	monoclinic	orthorhombic	triclinic	monoclinic
space group	$P2_1/m$	$Pnma$	$P\bar{1}$	$P2_1/n$
a, Å	9.330(6)	17.871(9)	9.549(5)	10.547(7)
b, Å	12.552(9)	12.998(7)	10.102(5)	19.944(11)
c, Å	9.939(7)	9.838(5)	16.438(8)	11.366(7)
α, deg	90	90	81.98(4)	90
β, deg	105.01(2)	90	74.00(3)	92.36(5)
γ, deg	90	90	62.80(3)	90
V, Å^3	1124(1)	2285(2)	1355(1)	2395(1)
Z	2	4	2	2
d (calc), g/cm^3	1.359	1.471	1.536	1.509
2θ lin, deg	3–45	3–45	3–45	3–45
unique, obsd data	1431(2σ)	1397(2σ)	3100(2σ)	2724(3σ)
parameters	150	150	372	290
μ, cm^{-1}	20.47	17.92	22.33	17.16
R (F_0)	4.27	2.69	2.30	3.05
R_w (F_0)	4.79	2.68	2.27	3.30
max diff Fourier peak e/Å^3	0.94	0.28	0.33	0.73

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^3$) for CpFe(CO)$_2$[Ge(N^{t}Bu)$_2$SiMe$_2$]Me, 2

	x	y	z	$U_{eq}{}^a$
Fe	368(1)	2500	4155(1)	34(1)
Ge	2545(1)	2500	3310(1)	31(1)
Si	2804(3)	2500	724(3)	47(1)
N	2653(5)	1527(4)	1903(5)	37(2)
O	1678(6)	839(4)	6085(5)	75(2)
C(10)	1171(7)	1504(5)	5300(6)	45(3)
C(1)	2994(7)	392(5)	1952(7)	48(3)
C(11)	2183(11)	–185(6)	2883(10)	96(5)
C(12)	2443(9)	–97(6)	498(8)	83(4)
C(13)	4678(7)	205(6)	2474(9)	79(3)
C(3)	1250(15)	2500	–924(12)	80(6)
C(4)	4561(14)	2500	190(14)	85(6)
C(5)	4388(11)	2500	4837(12)	57(4)
C(51)	–837(9)	2500	2033(10)	65(5)
C(52)	–1209(7)	1591(6)	2712(7)	64(3)
C(53)	–1826(7)	1933(6)	3799(7)	66(3)

^{a} Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^3$) for CpFe(CO)$_2$[Sn(N^{t}Bu)$_2$SiMe$_2$]Me, 3

	x	y	z	$U_{eq}{}^a$
Sn	6337(1)	2500	2280(1)	35(1)
Fe	5211(1)	2500	719(1)	38(1)
Si	6294(1)	2500	5135(2)	47(1)
N	6307(2)	3468(3)	3943(4)	41(1)
C(10)	5642(3)	3480(4)	–185(5)	50(2)
O	5911(2)	4139(3)	–798(4)	81(2)
C(1)	6490(3)	444(3)	4015(5)	47(2)
C(11)	6135(4)	5110(4)	2830(6)	91(3)
C(12)	6165(3)	5028(5)	5307(6)	77(3)
C(13)	7332(3)	4732(5)	4005(7)	84(3)
C(3)	5428(6)	2500	6179(11)	68(4)
C(4)	7095(7)	2500	6357(11)	79(5)
C(5)	7396(5)	2500	1247(11)	67(4)
C(51)	4578(4)	2500	2512(9)	77(4)
C(52)	4403(3)	1633(5)	1727(7)	81(3)
C(53)	4121(3)	1963(5)	463(7)	90(3)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Selected Bond Lengths and Angles for CpFe(CO)$_2$[Ge(N^{t}Bu)$_2$SiMe$_2$]Me, 2

Bond Lengths (Å)			
Fe–Ge	2.390(2)	Fe–C(10)	1.726(6)
Fe–C(51)	2.117(9)	Fe–C(52)	2.105(7)
Fe–C(53)	2.108(7)	Ge–N	1.879(5)
Ge–C(5)	1.977(9)	Si–N	1.724(5)
Si–C(3)	1.885(11)	Si–C(4)	1.849(15)
N–C(1)	1.457(8)	O–C(10)	1.157(8)
C–C(*tert*-butyl)	1.531(9)^a	C–C(Cp)	1.417(7)^a

Bond Angles (deg)			
Ge–Fe–C(10)	88.2(2)	Ge–Fe–C(10A)	88.2(2)
C(10)–Fe–C(10A)	92.9(4)	Fe–Ge–N	118.4(2)
Fe–Ge–C(5)	112.3(4)	N–Ge–C(5)	111.6(3)
N–Ge–NA	81.1(3)	N–Si–C(3)	114.3(3)
N–Si–C(4)	115.5(3)	C(3)–Si–C(4)	106.9(6)
N–Si–NA	90.2(3)	Ge–N–Si	94.3(2)
Ge–N–C(1)	131.6(4)	Si–N–C(1)	131.2(4)
Fe–C(10)–O	178.1(7)	N–C(1)–C(11)	110.3(6)
N–C(1)–C(12)	110.1(5)	N–C(1)–C(13)	110.8(5)
C–C–C(*tert*-butyl)	108.5(20)^a	C–C–C(Cp)	107.9(9)^a

^{a} Denotes average value.

Table VI. Selected Bond Lengths and Angles for CpFe(CO)$_2$[Ge(N^{t}Bu)$_2$SiMe$_2$]Me, 3

Bond Lengths (Å)			
Sn–Fe	2.532(2)	Sn–N	2.065(4)
Sn–C(5)	2.148(9)	Fe–C(10)	1.734(5)
Fe–C(51)	2.095(9)	Fe–C(52)	2.082(6)
Fe–C(53)	2.085(6)	Si–N	1.719(4)
Si–C(3)	1.857(12)	Si–C(4)	1.870(11)
N–C(1)	1.453(6)	C(10)–O	1.153(7)
C–C(*tert*-butyl)	1.519(8)^a	C–C(Cp)	1.402(7)^a

Bond Angles (deg)			
Fe–Sn–N	117.4(1)	Fe–Sn–C(5)	114.4(3)
N–Sn–C(5)	113.5(2)	N–Sn–NA	75.1(2)
Sn–Fe–C(10)	87.6(2)	C(10)–Fe–C(10A)	94.5(4)
N–Si–C(3)	112.9(3)	N–Si–C(4)	115.3(2)
C(3)–Si–C(4)	106.4(5)	N–Si–NA	94.0(3)
Sn–N–Si	95.4(2)	Sn–N–C(1)	128.7(3)
Si–N–C(1)	133.0(3)	Fe–C(10)–O	178.3(5)
N–C(1)–C(11)	109.4(4)	N–C(1)–C(12)	110.3(4)
N–C(1)–C(13)	111.5(4)	C–C–C(*tert*-butyl)	108.5(15)^a
C–C–C(Cp)	107.8(9)^a		

^{a} Denotes average value.

tained in Table II. The results of these studies are shown in Figures 1–3. All pertinent atomic coordinates and bond parameters are listed in Tables III–X.

Compounds 2–5 crystallize in lattices which show no intramolecular contacts other than those of the van der Waals type. The dinuclear 2 and 3 are isostructural; for the sake of brevity only the structural details of 2 are discussed below, with the corresponding values for 3 given in parentheses.

Molecular Structure of CpFe(CO)$_2$[Ge-(N^{t}Bu)$_2$SiMe$_2$]Me, 2, and CpFe(CO)$_2$[Sn(N^{t}Bu)$_2$-SiMe$_2$]Me, 3. Complex 2 (Figure 1) is a typical example

Table VII. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for CpFe(CO)₂Ge(NᵗBu)₂SiMe₂, 4

	x	y	z	$U_{eq}{}^a$
Ge	1073(1)	2493(1)	2411(1)	25(1)
Fe(1)	2753(1)	3482(1)	1304(1)	35(1)
Fe(2)	-1726(1)	4300(1)	3097(1)	33(1)
Si	2266(1)	-411(1)	2824(1)	30(1)
C(10)	1015(5)	4955(5)	1062(2)	45(2)
O(1)	-67(4)	5947(3)	867(2)	72(2)
C(20)	2823(5)	4430(4)	2098(3)	48(2)
O(2)	2969(4)	5048(3)	2578(2)	79(2)
C(30)	-2209(5)	4522(4)	2118(3)	42(2)
O(3)	-2639(3)	4702(3)	1507(2)	65(2)
C(40)	-1147(5)	5760(5)	2933(3)	51(2)
O(4)	-866(4)	6752(3)	2864(2)	90(2)
N(1)	2220(3)	1129(3)	3193(2)	28(1)
N(2)	1190(3)	685(3)	2103(2)	26(1)
C(1)	3062(4)	1230(4)	3793(2)	37(2)
C(11)	4783(5)	1005(5)	3351(3)	57(3)
C(12)	3158(5)	15(5)	4474(2)	57(3)
C(13)	2140(5)	2740(5)	4233(3)	62(3)
C(2)	462(4)	323(4)	1534(2)	34(2)
C(21)	-1250(5)	513(5)	1970(3)	53(2)
C(22)	391(5)	1302(4)	729(2)	50(2)
C(23)	1507(5)	-1311(4)	1276(3)	53(2)
C(3)	1233(5)	-1404(4)	3617(2)	49(2)
C(4)	4348(4)	-1869(4)	2367(3)	50(2)
C(51)	3548(5)	2522(5)	111(3)	48(2)
C(52)	3969(5)	1382(5)	729(3)	44(2)
C(53)	4997(5)	1575(5)	1117(3)	48(2)
C(54)	5236(5)	2832(5)	721(3)	55(3)
C(55)	4344(5)	3400(5)	107(3)	54(3)
C(51A)	-1618(5)	2870(5)	4165(3)	46(2)
C(52A)	-2163(6)	4317(5)	4424(3)	52(3)
C(53A)	-3623(6)	5217(6)	4177(3)	65(3)
C(54A)	-3980(6)	4349(7)	3763(3)	68(3)
C(55A)	-2720(7)	2880(6)	3749(3)	58(3)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VIII. Selected Bond Lengths and Angles for [CpFe(CO)₂]₂Ge(NᵗBu)₂SiMe₂, 4

Bond Lengths (Å)			
Ge-Fe(1)	2.497(1)	Ge-Fe(2)	2.490(1)
Ge-N(1)	1.911(3)	Ge-N(2)	1.909(3)
Fe(1)-C(10)	1.752(4)	Fe(1)-C(20)	1.755(5)
Fe(1)-C(51)	2.097(5)	Fe(1)-C(52)	2.108(4)
Fe(1)-C(53)	2.104(4)	Fe(1)-C(54)	2.114(5)
Fe(1)-C(55)	2.114(4)	Fe(2)-C(30)	1.751(5)
Fe(2)-C(40)	1.762(6)	Fe(2)-C(51A)	2.107(4)
Fe(2)-C(52A)	2.106(4)	Fe(2)-C(53A)	2.108(4)
Fe(2)-C(54A)	2.111(6)	Fe(2)-C(55A)	2.089(7)
Si-N(1)	1.725(4)	Si-N(2)	1.718(3)
Si-C(3)	1.873(5)	Si-C(4)	1.869(3)
C(10)-O(1)	1.149(5)	C(20)-O(2)	1.144(7)
C(30)-O(3)	1.149(6)	C(40)-O(4)	1.134(7)
N(1)-C(1)	1.473(6)	N(2)-C(2)	1.475(6)
C-C(tert-butyl 1)	1.530(5)^a	C-C(tert-butyl 2)	1.532(5)^a
C-C(Cp)	1.408(12)^a	C-C(CpA)	1.402(12)^a

Bond Angles (deg)			
Fe(1)-Ge-Fe(2)	117.4(1)	Fe(1)-Ge-N(1)	113.8(1)
Fe(2)-Ge-N(1)	113.4(1)	Fe(1)-Ge-N(2)	113.5(1)
Fe(2)-Ge-N(2)	113.4(1)	N(1)-Ge-N(2)	79.6(1)
Ge-Fe(1)-C(10)	91.4(2)	Ge-Fe(1)-C(20)	88.7(2)
C(10)-Fe(1)-C(20)	95.1(2)	Ge-Fe(2)-C(30)	87.9(1)
Ge-Fe(2)-C(40)	91.4(1)	C(30)-Fe(2)-C(40)	95.5(2)
N(1)-Si-N(2)	90.5(2)	N(1)-Si-C(3)	115.5(2)
N(2)-Si-C(3)	114.8(2)	N(1)-Si-C(4)	114.5(2)
N(2)-Si-C(4)	115.7(2)	C(3)-Si-C(4)	105.8(2)
Fe(1)-C(10)-O(1)	176.0(4)	Fe(1)-C(20)-O(2)	175.0(4)
Fe(2)-C(30)-O(3)	175.2(3)	Fe(2)-C(40)-O(4)	175.6(3)
Ge-N(1)-Si	94.8(2)	Ge-N(1)-C(1)	134.2(3)
Si-N(1)-C(1)	130.1(2)	Ge-N(2)-Si	95.1(2)
Ge-N(2)-C(2)	134.0(2)	Si-N(2)-C(2)	130.5(2)
N(1)-C(1)-C(11)	111.4(3)	N(1)-C(1)-C(12)	108.8(4)
N(1)-C(1)-C(13)	111.3(3)	N(2)-C(2)-C(21)	111.7(3)
N(2)-C(2)-C(22)	111.5(4)	N(2)-C(2)-C(23)	108.7(3)
C-C-C(tert-butyl 1)	108.4(4)^a	C-C-C(tert-butyl 2)	108.3(5)^a
C-C-C(Cp)	108.0(6)^a	C-C-C(CpA)	108.0(7)^a

^{a} Denotes average value.

of a "piano-stool" compound, so commonly found for mono-Cp species, albeit one with a rather large leg. Alternatively the molecule may be described as a Fp- and methyl-substituted germanium metallacycle, not an unreasonable description given the relative sizes of the molecular moieties. The solid state structure of 2 possesses crystallographically imposed mirror symmetry which relates the molecular halves via a plane passing through the metal atoms. A central iron–germanium bond of 2.390(2) Å (Fe-Sn = 2.532(2) Å), exactly the sum of the metals' covalent radii, links the group 14 atom of distorted tetrahedral geometry with a pseudotetrahedrally coordinated iron atom. Thus, the angle between the centroid of the Cp ligand (centr), the iron, and the germanium atoms is 121.3° (centr-Fe-Sn = 120.1°), the angle centr-Fe-CO being 127.3° (127.1°). The carbonyl ligands enclose an angle of 92.9(4)° (94.5(4)°). The major deviation from ideal tetrahedral geometry about germanium is due to the very acute N-Ge-N angle of 81.1(3)° (N-Sn-N = 75.1(2)°). In contrast, the C(5)-Ge-Fe angle has an almost ideal tetrahedral value, being 112.3(4)° (114.4(3)°). The Ge-CH₃ distance of 1.977(9) Å (Sn-CH₃ = 2.148(9) Å) is typical of Ge(IV)-methyl bonds.[1,12]

Bond parameters within the essentially planar metallacycle (none of the four atoms deviates from the best least-squares plane by more than 0.04 Å (0.04 Å)) do not differ significantly from those in other compounds of this molecular moiety.

The bond distances and angles of the Fp rest are unremarkable and are quite typical of FpX species, with Fe-Cp (avg) = 2.109(7) Å (2.086(7) Å) and Fe-centr = 1.73 Å (1.72 Å).[13] It appears, however, that due to the shorter Fe-El distance and the resulting increased steric crowding, the Fe-Cp distance is slightly longer in 2.

Molecular Structure of [CpFe(CO)₂]₂Ge-(NᵗBu)₂SiMe₂, 4. An ORTEP drawing of the trinuclear metal cluster 4 is shown in Figure 2. The perspective view nicely demonstrates the origin of 4 as the product of a germylene insertion into the Fe-Fe bond of the Fp dimer. The geometries about the three metal atoms are distorted tetrahedral. Thus, the Fe(1)-Ge-Fe(2) angle is 117.4(1)°, whereas the value for Fe-Ge-N (avg) is 113.5(1)°. Only the intraannular N-Ge-N angle of 79.6(1)° deviates substantially from ideal geometry. The Fe(1)-Ge and Fe(2)-Ge bonds are of nearly equal length, being 2.497(1) and 2.490(1) Å, respectively. These distances are markedly longer (by about 0.10 Å) than the Fe-Ge bond in 2 and this is almost certainly due to the much greater steric repulsion in 4. Steric crowding is also reflected in increased Ge-N distances. For example, the average Ge-N distance in this trinuclear complex is 1.910(3) Å, compared to 1.879(5) Å in the dinuclear 2.

The relative orientation of the ligands is such as to minimize steric strain. The Cp rings are tilted toward the basket-shaped opening of the metallacycle, and the Fp

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(13) Miller, J. R.; Stephens, F. S. *J. Chem. Soc. Dalton Trans.* **1975**, 833.

Table IX. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for {[CpFe(CO)₂Sn(NᵗBu)₂SiMe₂]₂·C₇H₈}, 5

	x	y	z	$U_{eq}{}^a$
Sn	20(1)	729(1)	308(1)	35(1)
Fe	910(1)	1002(1)	2425(1)	46(1)
Si	−930(2)	1736(1)	−1286(1)	49(1)
N(1)	−1629(4)	1240(2)	−268(3)	45(2)
N(2)	546(4)	1356(2)	−1069(3)	44(2)
C(10)	386(6)	1816(4)	2125(5)	58(2)
O(1)	54(5)	2361(3)	1989(4)	89(2)
C(20)	2432(6)	1121(3)	1916(5)	59(2)
O(2)	3468(4)	1194(3)	1672(4)	90(2)
C(1)	−2955(5)	1150(3)	18(5)	51(2)
C(11)	−3528(6)	572(4)	−710(7)	83(3)
C(12)	−3052(6)	985(5)	1309(6)	92(3)
C(13)	−3709(6)	1786(3)	−255(6)	79(3)
C(2)	1781(5)	1579(3)	−1471(5)	52(2)
C(21)	2717(6)	1001(3)	−1362(6)	67(3)
C(22)	1654(7)	1790(4)	−2755(5)	90(3)
C(23)	2305(6)	2173(3)	−742(6)	76(3)
C(3)	−1633(6)	1678(4)	−2838(5)	72(3)
C(4)	−985(7)	2648(3)	−943(6)	75(3)
C(51)	330(12)	1013(5)	4169(7)	97(4)
C(52)	−463(7)	592(7)	3466(8)	100(5)
C(53)	226(10)	81(5)	3041(6)	82(4)
C(54)	1465(8)	176(4)	3450(8)	83(4)
C(55)	1490(10)	746(5)	4142(7)	93(4)
Cb	355(23)	5177(14)	8826(22)	104(7)
Cc	1218(27)	4019(14)	9610(25)	160(12)
Cd	425(25)	4198(15)	10497(27)	132(8)
Ce	92(22)	4089(12)	11134(20)	132(9)
Cf	−715(24)	5171(16)	11118(26)	125(9)
Cg	786(28)	4330(17)	9527(27)	124(9)
Ch	425(20)	4711(13)	9567(21)	102(7)
Cj	−109(17)	4625(11)	10675(19)	80(5)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table X. Selected Bond Lengths and Angles for {[CpFe(CO)₂Sn(NᵗBu)₂SiMe₂]₂·C₇H₈}, 5

Bond Lengths (Å)			
Sn–SnA	2.991(2)	Sn–Fe	2.605(2)
Sn–N(1)	2.101(4)	Sn–N(2)	2.097(4)
Fe–C(10)	1.744(7)	Fe–C(20)	1.749(7)
Fe–C(51)	2.100(9)	Fe–C(52)	2.079(10)
Fe–C(53)	2.105(9)	Fe–C(54)	2.088(9)
Fe–C(55)	2.085(8)	Si–N(1)	1.713(5)
Si–N(2)	1.743(5)	Si–C(3)	1.889(6)
Si–C(4)	1.861(6)	N(1)–C(1)	1.463(7)
N(2)–C(2)	1.469(7)	C(10)–O(1)	1.151(9)
C(20)–O(2)	1.150(8)	C–C(*tert*-butyl 1)	1.522(9)^a
C–C(*tert*-butyl 2)	1.525(9)^a	C–C(Cp)	1.377(29)^a

Bond Angles (deg)			
Fe–Sn–N(1)	116.7(1)	Fe–Sn–N(2)	117.9(1)
N(1)–Sn–N(2)	73.8(2)	Fe–Sn–SnA	114.9(1)
N(1)–Sn–SnA	113.2(1)	N(2)–Sn–SnA	114.0(1)
Sn–Fe–C(10)	85.1(2)	Sn–Fe–C(20)	91.4(2)
C(10)–Fe–C(20)	95.7(3)	N(1)–Si–N(2)	93.6(2)
N(1)–Si–C(3)	115.5(3)	N(2)–Si–C(3)	114.9(3)
N(1)–Si–C(4)	113.9(3)	N(2)–Si–C(4)	115.5(3)
C(3)–Si–C(4)	103.9(3)	Sn–N(1)–Si	96.6(2)
Sn–N(1)–C(1)	131.4(3)	Si–N(1)–C(1)	131.7(4)
Sn–N(2)–Si	95.8(2)	Sn–N(2)–C(2)	132.7(3)
Si–N(2)–C(2)	128.8(4)	Fe–C(10)–O(1)	176.3(5)
Fe–C(20)–O(2)	174.6(5)	N(1)–C(1)–C(11)	109.5(5)
N(1)–C(1)–C(12)	110.3(4)	N(1)–C(1)–C(13)	110.5(5)
N(2)–C(2)–C(21)	109.2(5)	N(2)–C(2)–C(22)	109.7(5)
N(2)–C(2)–C(23)	111.8(5)	C–C–C(*tert*-butyl 1)	108.8(2)^a
C–C–C(*tert*-butyl 2)	108.7(1)^a	C–C–C(Cp)	108.0(20)^a

^{a} Denotes average value.

moieties are twisted about the Fe–Ge bond to allow a staggered orientation of the carbonyl ligands.

Molecular Structure of {[CpFe(CO)₂Sn(NᵗBu)₂-SiMe₂]₂·C₇H₈}, 5. Figure 3 shows a perspective drawing
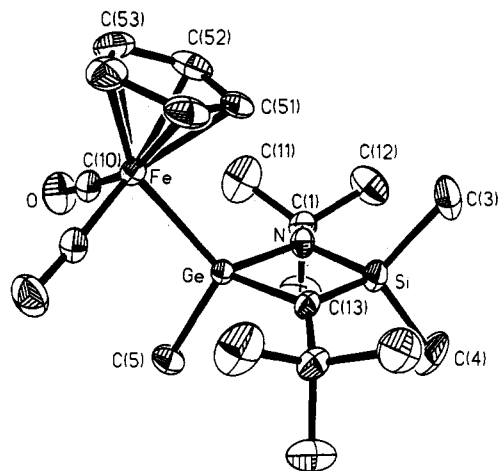
Figure 1. Perspective view and numbering scheme for CpFe(CO)₂[Ge(NᵗBu)₂SiMe₂]Me, 2.
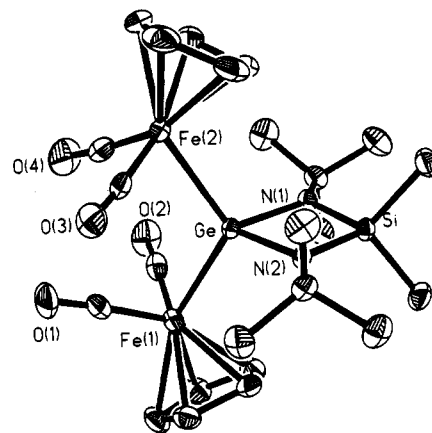
Figure 2. Perspective view and partial numbering scheme for [CpFe(CO)₂]₂Ge(NᵗBu)₂SiMe₂, 4.
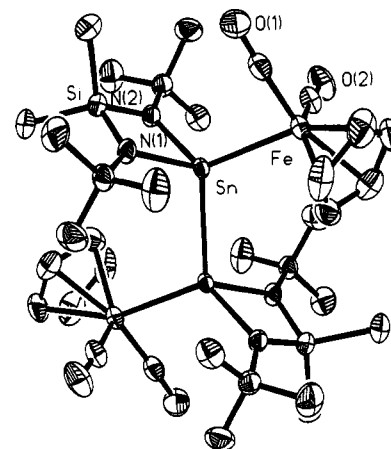
Figure 3. Perspective view and partial numbering scheme for {[CpFe(CO)₂Sn(NᵗBu)₂SiMe₂]₂·C₇H₈, 5. The solvent molecule has not been drawn.

of the solid state structure of 5. The centrosymmetric molecule consists of a zigzag chain of four pseudotetrahedrally coordinated metal atoms. The structure of this molecule is reminiscent of the tetrastannane [Ph₃-Sn(ᵗBu₂Sn)₂SnPh₃] which also has a tetrametallic chain.[14] In this homometallic compound the Sn–Sn bonds are somewhat shorter, however, being 2.83 Å (outer) and 2.87 Å (inner). This similarity suggests the formulation of 5

(14) Adams, S.; Dräger, M. *Angew. Chem.* **1987**, *99*, 1280.

as a Fp-substituted distannane with a very long tin–tin bond of 2.992(2) Å. To our knowledge this constitutes one of the longest known unbridged tin–tin bond in a molecular compound of this metal. The bond is considerably longer than the interatomic distances in α-tin (2.81 Å) and is of the same magnitude as the shortest contacts in β-tin (3.02 Å).[15] The extreme length of this bond reflects the steric crowding in the dimer. Steric factors are also responsible for the lengthening of other bonds in the molecule. Thus, the Fe–Sn bond is 2.605(2) Å long, compared to 2.532(2) Å in 3, and the average Sn–N distance in 5 is 2.099(4) Å., versus 2.065(4) Å in the iron–tin half-sandwich compound.

Conclusion

The cyclic bis(amido)germylenes and -stannylenes, 1, insert cleanly and in high yield into the iron–iron bond of [CpFe(CO)$_2$]$_2$ and the iron–carbon bond of CpFe(CO)$_2$Me. Possible competing reactions, such as the replacement of bridging or terminal carbonyl ligands were not observed.[16] The products for all but one reaction were the expected monoinsertion species. The treatment of [CpFe(CO)$_2$]$_2$ with Sn(N^{t}Bu)$_2$SiMe$_2$, however, yielded an unusual double-insertion product with an exceedingly long tin–tin bond.

Compounds 2–5 are unusual among group 14 amide-derived Fp insertion compounds in being the products of a direct insertion of the amidogermylenes and -stannylenes. The common route to such species is the halogen-exchange reaction of FpElCl$_3$ or FpElCl$_2$Fp with the appropriate anion.[4]

The reason for the different reaction behavior of Ge(N^{t}Bu)$_2$SiMe$_2$ towards Fp$_2$ is still unclear. A germylene analog of 5 would most likely not be stable;[17] due to the much shorter Fe–Ge and Ge–Ge bond the steric crowding in such a hypothetical molecule would undoubtedly be even greater than that in 5. It is also possible that kinetic factors are responsible and that reactions in eqs 2 and 3 proceed via entirely different mechanisms. The ditin species 5 may be regarded as the first step toward polystannanes. Such compounds are commonly made by the reduction of tin(IV) species.[18] In contrast, reaction in eq 3 has produced a tetrametallic chain as the result of an insertion into an existing metal–metal bond. The formation of the tin–tin bond is somewhat different from the autodimerization of [(Me$_3$Si)$_2$CH]$_2$Sn.[19] We are intrigued by the possibility of extending this method to the synthesis of even longer metal chains and ultimately "molecular metals".[14]

(15) Müller, U. *Anorganische Strukturchemie*; Teubner: Stuttgart, Germany, 1991.
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