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ORGANOMETALLOIDAL DERIVATIVES OF THE TRANSITION METALS

XI *. SYNTHESIS AND CRYSTAL STRUCTURES OF $Ph_3GeSiMe_3$ AND $Ph_3GeSiMe_2Fe(CO)_2(\eta^5\text{-}C_5H_5)$

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Summary

$Ph_3GeSiMe_3$ and $Ph_3GeSiMe_2Fe(CO)_2(\eta^5\text{-}C_5H_5)$ have been synthesized and their crystal structures determined. The Ge–Si bond in iron (2.405(2) Å) is longer by 0.021 Å than in the simple germylsilane (2.384(1) Å). The significant shortening of the Si–Fe bond (2.328(1) Å) in the iron complex compared to that in the analogous $Ph_3SiSiMe_2Fe(CO)_2(\eta^5\text{-}C_5H_5)$ (2.346(1) Å) and spectroscopic data indicate an enhanced Si–Fe interaction.

Introduction

Earlier studies involving Mössbauer, IR [1] and ^{29}Si NMR [2] spectra have shown that the reduced reactivity of the Si–M or Si–C–M linkages in complexes of the general type $(\eta^5\text{-}C_5H_5)M(CO)_2R$ (M = transition metal, R = silyl, polysilyl, silylmethyl and alkyl) is attributable to the pronounced σ inductive effect of the silicon atom rather than to iron–silicon retrodative π-bonding.

Comparison of the ^{29}Si NMR data for Ia and IIa prompted us to determine the crystal structure of IIa in order to throw light on the effect of σ donation on the molecular geometry [3]. In agreement with the results of the spectroscopic investigations the Si–Si bond (2.373(1) Å) in complex IIa was found to be longer by 0.018 Å

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* For part X see ref. 9.

than in the 'free ligand' Ia (2.355(1) Å [4]). This paper reports the synthesis and the crystal structures of the Ib and IIb germanium derivatives.

$Ph_3X{-}SiMe_3$	$Ph_3X{-}SiMe_2Fe(CO)_2(\eta^5{-}C_5H_5)$
(Ia: X = Si;	(IIa: X = Si;
Ib: X = Ge)	IIb: X = Ge)

Experimental

Synthesis

$Ph_3GeSiMe_2H$. To 100 ml of a THF/sodium (0.2 g-atom) dispersion was added 10 ml of a THF solution of triphenylbromogermane (0.05 mol) and naphthalene (0.005 mol). After 20 h stirring the solution was dark green. It was filtered into a pressure equilibrated dropping funnel and then added dropwise to a cooled (0°C) solution of Me_2SiHCl, (0.07 mol in THF). Upon mixing, the green colour of $Ph_3Ge^-Na^+$ disappeared. After one hour stirring the solvent was removed in vacuo. The gummy residue was extracted twice with 50 ml of hexane/methylene chloride (70/30) and the solvent was again removed in vacuo. Final recrystallization from hexane/methylene chloride (90/10) yielded 60% of the title product, m.p. 93°C. Anal. Found: C, 66.4; H, 6.01. $C_{20}H_{22}GeSi$ calcd.: C, 66.2; H, 6.11%. NMR: ^{29}Si -33.6 ppm; ^{13}C -5.18(Me), 137.87, 135.29, 128.45, 126.22 (Ph) ppm; ^1H 4.54 (SiH), 0.43, 0.54(Me), 7.57(Ph) ppm.

TABLE 1

CRYSTAL DATA, DATA COLLECTION AND LEAST-SQUARES PARAMETERS

Empirical formula	Ib $C_{21}H_{24}GeSi$	IIb $C_{27}H_{25}O_2GeSiFe$
M(a.m.u.)	377.1	538.0
a(Å)	11.344(1)	8.684(2)
b(Å)		35.297(10)
c(Å)	8.861(1)	8.173(2)
β (deg.)		96.1(2)
V(Å^3)	987.5(3)	2491(2)
Space group	$P\bar{3}$	$P2_1/c$
Z	2	4
$F(000)$	392	1100
D_c(g cm^{-3})	1.268	1.435
λ (Mo-K_α) (Å)	0.71073	
μ (Mo-K_α) (cm^{-1})	15.9	18.4
2θ limits	3–60	3–50
Scan technique	θ–2θ	
Reflexions with non-zero intensity	1841	3288
Reflexions used in least-squares, NO	1445	2792
Number of variables, NV	71	289
Weighting scheme	$w = 4IL/(\sigma(I)^2 + (0.01I^2))$ [a]	
R_o	0.028	0.048
R_w	0.034	0.067
$(\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(NO - NV))^{1/2}$	1.856	1.881
Approx. crystal size (mm)	0.15 × 0.35 × 0.50	0.25 × 0.25 × 0.06

[a] Where I is the net intensity and L the Lorenz-polarization factor.

$Ph_3GeSiMe_2Cl$. Chlorine was bubbled into a carbon tetrachloride solution of $Ph_3GeSiMe_2H$ until the Si–H stretching frequency as monitored by infrared spectroscopy had disappeared. Immediate removal of the solvent followed by recrystallization from hexane gave a 95% yield of the title product. Anal. Found: C, 61.3; H, 5.47. $C_{20}H_{21}ClGeSi$ calcd.: C, 60.4; H, 5.32%. NMR: ^{29}Si 25.56 ppm; ^{13}C 4.01(Me), 136.03, 135.27, 128.83, 128.34(Ph) ppm; ^{1}H 0.80(Me), 7.53(Ph) ppm.

$Ph_3GeSiMe_2Fe(CO)_2(\eta^5\text{-}C_5H_5)$ (IIb). A THF solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-Na^+$ was added dropwise to a cooled (0°C) and stirred solution of $Ph_3GeSiMe_2Cl$. The mixture was stirred for 1 h and the solvent then removed in vacuo. The resulting oil and wax was dissolved in the minimum of hexane/methylene chloride (80/20) and the solution was poured onto an alumina column. Elution with the same solvent mixture and collection of the first yellow band, removal of the solvent in vacuo, and recrystallization of the residue from hexane, gave the yellow crystalline product in 65% yield, m.p. 142°C. NMR: ^{29}Si −10.43 ppm; ^{13}C 6.05($SiMe_2$), 215.1[$(CO)_2$], 83.3(C_5H_5), 140.1, 135.5($GePh_3$) (in C_6D_6) ppm. IR: $\nu(C{\equiv}O)$ 2001, 1949 (hexane).

X-ray structure determinations

The determination of the unit cell dimensions and the collection of intensities were performed on a computer-controlled four-circle Enraf–Nonius CAD-4 diffractometer at room temperature. Crystal data, data collection and least-squares parameters are summarized in Table 1.

Compounds Ib and IIb are isomorphous with Ia and IIa, respectively.

The structure determination of Ib

Equivalent relfexions were collected by measuring all intensities available in the hemisphere of the molybdenum limiting sphere. A set of 3142 reflexions were thus

TABLE 2

FINAL POSITIONAL PARAMETERS×10^4 (×10^3 FOR THE HYDROGEN ATOMS) AND B_{eq} [a] ($Å^2$) VALUES (B FOR THE HYDROGEN ATOMS) FOR COMPOUND Ib

Atom	x/a	y/b	z/c	B_{eq}/B
Ge	2/3	1/3	3474.6(3)	2.760(5)
Si	2/3	1/3	6164.9(9)	3.75(2)
C(1)	7247(1)	2092(1)	2684(2)	2.54(3)
C(2)	8204(2)	1901(2)	3448(2)	3.12(4)
C(3)	8583(2)	985(2)	2947(3)	3.39(5)
C(4)	8013(2)	243(2)	1660(3)	3.53(5)
C(5)	7083(2)	430(2)	860(2)	3.87(4)
C(6)	6699(2)	1338(2)	1377(2)	3.06(4)
C(7)	8398(3)	4607(3)	6845(3)	6.98(6)
H(2)	862(1)	244(2)	429(2)	4.7(4)
H(3)	924(2)	87(2)	358(2)	5.8(5)
H(4)	827(2)	−40(2)	135(2)	5.8(5)
H(5)	665(2)	−8(2)	−8(3)	5.4(1)
H(6)	608(2)	148(2)	82(2)	4.7(4)
H(7a)	843(2)	459(2)	786(3)	8.5(6)
H(7b)	913(2)	443(3)	642(4)	14.6(8)
H(7c)	865(2)	551(2)	647(3)	11.3(8)

[a] B_{eq} is defined as 4/3trace(BG) where B is the thermal motion tensor and G is the direct metric tensor.

recorded. A structure factor calculation was performed for the unaveraged data with the final atomic coordinates of Ia (Si(1) atom taken as germanium) with isotropic temperature factors ($R = 0.06$). An empirical absorption correction [5] was then calculated, which lowered R to 0.05. The minimum and maximum corrections were 0.914 and 1.127. The corrected set of reflexions were then averaged giving a final set of 1841 data (the agreement factors of averaging for all reflexions were 0.026 on intensity and 0.021 on F). Anisotropic thermal parameters were refined for the non-hydrogen atoms and hydrogen atoms with isotropic temperature factors were refined in three final cycles. Final atomic coordinates are given in Table 2.

The structure determination of IIb

A total of 4375 unique intensity data were collected, of which 1087 had zero intensity and they were excluded from the final data set. Because of the unfavourable crystal shape (thin blade) a psi-scan [6] absorption correction was applied. Six

TABLE 3

FINAL POSITIONAL ($\times 10^4$) PARAMETERS AND B_{eq} (Å^2) VALUES FOR THE NON-HYDROGEN ATOMS FOR COMPOUND IIb

Atom	x/a	y/b	z/c	B_{eq}
Fe	7567.0(8)	500.1(2)	2347.7(9)	3.30(3)
Ge	10293.5(6)	1435.1(2)	2926.5(7)	3.12(2)
Si	9091(2)	946.7(5)	1179(2)	3.26(6)
O(1)	6395(5)	223(1)	−975(5)	7.2(2)
O(2)	10282(5)	33(1)	3048(5)	6.0(2)
C(1)	8840(6)	1749(1)	4006(6)	3.2(2)
C(2)	7498(6)	1890(2)	3128(7)	4.1(2)
C(3)	6442(7)	2105(2)	3886(8)	5.1(3)
C(4)	6704(7)	2183(2)	5536(8)	5.1(3)
C(5)	7999(7)	2051(2)	6419(7)	5.1(3)
C(6)	9052(6)	1833(2)	5675(7)	4.4(2)
C(7)	11354(6)	1772(1)	1503(6)	3.3(2)
C(8)	10708(7)	2104(2)	874(7)	4.6(3)
C(9)	11408(8)	2319(2)	−212(8)	5.7(3)
C(10)	12800(8)	2216(2)	−725(8)	5.8(3)
C(11)	13493(7)	1893(2)	−110(8)	6.1(3)
C(12)	12780(7)	1670(2)	987(8)	5.0(3)
C(13)	11861(6)	1239(2)	4628(6)	3.2(3)
C(14)	13151(6)	1449(2)	5187(7)	4.6(3)
C(15)	14249(6)	1306(2)	6393(7)	5.1(3)
C(16)	14074(6)	960(2)	7021(7)	4.7(2)
C(17)	12819(7)	745(2)	6478(7)	4.5(2)
C(18)	11711(6)	884(2)	5288(7)	3.9(2)
C(19)	10773(7)	732(2)	247(8)	5.4(3)
C(20)	7957(8)	1215(2)	−544(7)	6.5(3)
C(21)	6247(7)	937(2)	3212(9)	6.2(3)
C(22)	5289(7)	668(2)	2532(8)	5.7(3)
C(23)	5564(7)	329(2)	3362(8)	5.2(3)
C(24)	6765(7)	399(2)	4635(7)	6.5(3)
C(25)	7185(7)	778(2)	4497(8)	6.6(3)
C(26)	7211(6)	331(2)	346(7)	4.6(3)
C(27)	9219(6)	220(2)	2766(6)	3.9(2)

reflections were used to calculate an average transmission curve. The minimum and maximum transmission factors were 0.88 and 1.00. The final atomic coordinates of IIa (Si(1) atom taken as germanium) were used as a trial model ($R = 0.085$). Non-hydrogen atoms were refined by anisotropic least-squares. No hydrogen atoms were refined. Final atomic coordinates for non-hydrogen atoms are given in Table 3 *. For the source of atomic scattering factors and anomalous dispersion coefficients see ref. 3. All calculations were performed on a PDP 11/34 (64k) minicomputer with the E.N. SDP program package and local programs.

Discussion

The molecular structures are shown in Fig. 1 and 2. To the best of our knowledge, the crystal structures of Ib and IIb are the first published for molecules containing Si–Ge bonds.

In view of the isomorphism the conformational features of both molecules are necessarily substantially the same as those of the corresponding disilyl compounds.

A comparison of the interatomic distances (Tables 4 and 5) involving Ge, Si and Fe atoms indicate that the σ-donor property of the silicon atom in IIb is more prominent than in IIa. The Ge–Si distance in IIb (2.405(2) Å) is longer by 0.021 Å than that in Ib (2.384(1) Å). The lengthening of the Ge–Si bond is accompanied by a significant shortening of the Si–Fe bond compared to that in IIa (2.328(1) and 2.346(1) Å), indicating a stronger iron–silicon interaction.

Additional evidence for such a strengthening of the Si–Fe bond in the germylsilyl complex comes from the infrared and ^{29}Si NMR spectral data for the complex.

The infrared spectrum in hexane exhibits two terminal CO stretching frequencies at 2001 and 1949 cm^{-1}. The related $Ph_3SiSiMe_2$ complex exhibits bands at 1999 and 1947 cm^{-1}. As we have previously shown, such variations, although small, are

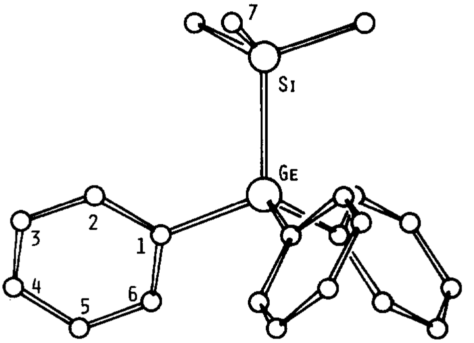

Fig. 1. The molecular diagram of Ib with the numbering of atoms. Numbers are for carbon atoms unless indicated otherwise. Hydrogen atoms are omitted.

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* Lists of observed and calculated structure factors and anisotropic thermal parameters may be obtained from L.P. (Budapest).

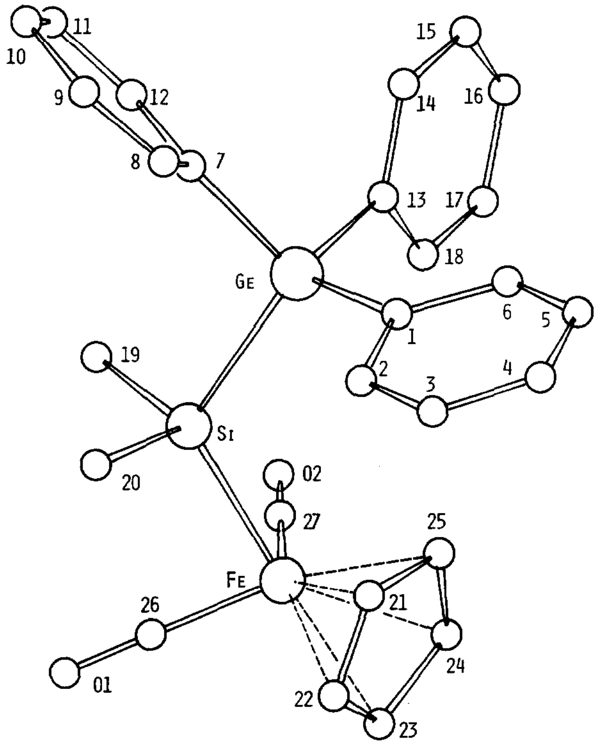

Fig. 2. The molecular diagram of IIb with the numbering of atoms. Numbers are for carbon atoms unless indicated otherwise. Hydrogen atoms are omitted.

indicative of a greater σ donation for the group with the higher stretching frequencies [1], in accord with the shorter Fe–Si bond lengths.

The ^{29}Si resonance for the germylsilyl complex appears at +27.5 ppm relative to TMS, whereas that for the corresponding $Ph_3GeSiMe_3$ compound is at −10.4 ppm. This corresponds to a shift of 37.9 ppm upon replacing a methyl group by the $C_5H_5Fe(CO)_2$ group. The corresponding shift for the disilyl compounds is +33.8. This difference is another indication that the replacement of a triphenylsilyl group by the triphenylgermyl group in the iron complexes permits a greater removal of electron density by the iron atom from the bonded silicon atom.

The Ge–C bonds are somewhat longer than that reported for Ph_4Ge [7]. The high thermal motion of C(7) in Ib accounts for the apparently rather short Si–C

TABLE 4

RELEVANT BOND DISTANCES AND ANGLES FOR COMPOUND Ib

Bond distances (Å)			
Ge–Si 2.384(1), Ge–C(1) 1.958(1), Si–C(7) 1.863(3)			
Bond angles (°)			
Si–Ge–C(1)	111.0(1)	C(1)–Ge–C(1)′	107.9(1)
Ge–Si–C(7)	108.9(1)	C(7)–Si–C(7)′	110.1(2)

TABLE 5

RELEVANT BOND DISTANCES AND ANGLES FOR COMPOUND IIb

Bond distances (Å)					
Fe–Si	2.328(2)	Fe–C(27)	1.746(6)	O(1)–C(26)	1.146(7)
Fe–C(21)	2.089(7)	Ge–Si	2.405(2)	O(2)–C(27)	1.138(7)
Fe–C(22)	2.086(6)	Ge–C(1)	1.959(5)	C(21)–C(22)	1.343(9)
Fe–C(23)	2.094(6)	Ge–C(7)	1.960(4)	C(21)–C(25)	1.378(9)
Fe–C(24)	2.094(5)	Ge–C(13)	1.966(5)	C(22)–C(23)	1.384(10)
Fe–C(25)	2.069(5)	Si–C(19)	1.877(6)	C(23)–C(24)	1.414(8)
Fe–C(26)	1.738(5)	Si–C(20)	1.885(6)	C(24)–C(25)	1.394(10)

Bond angles (°)			
Si–Fe–C(26)	84.2(3)	Fe–Si–C(20)	111.8(4)
Si–Fe–C(27)	88.4(3)	Ge–Si–C(19)	102.9(4)
C(26)–Fe–C(27)	92.9(5)	Ge–Si–C(20)	104.1(4)
Si–Ge–C(1)	114.4(2)	C(19)–Si–C(20)	105.5(5)
Si–Ge–C(7)	106.5(2)	C(22)–C(21)–C(25)	108.5(10)
Si–Ge–C(13)	113.1(3)	C(21)–C(22)–C(23)	110.0(10)
C(1)–Ge–C(7)	106.9(3)	C(22)–C(23)–C(24)	106.6(10)
C(1)–Ge–C(13)	108.2(4)	C(23)–C(24)–C(25)	106.7(9)
C(7)–Ge–C(13)	107.4(4)	C(21)–C(25)–C(24)	108.3(10)
Fe–Si–Ge	118.1(1)	Fe–C(26)–O(1)	178.3(9)
Fe–Si–C(19)	113.2(4)	Fe–C(27)–O(2)	178.9(9)

interatomic distance of 1.863 Å. A correction for riding motion [8] gives a value of 1.894.

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