Synthesis, structure, and reactivity of siloxides and germyloxides of iron(II) and cobalt(II)

Ya. V. Fedotova, E. V. Zhezlova, T. G. Mushtina, A. N. Kornev, T. A. Chesnokova, G. K. Fukin, L. N. Zakharov, and G. A. Domrachev*

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603950 Nizhny Novgorod, Russian Federation.
Fax: +7 (831 2) 66 1497. E-mail: akornev@imoc.sinn.ru

Iron and cobalt siloxides and germyloxides $[(Me_3Si)_3SiO]_2M$ (M = Fe (**1**), Co (**2**)), $(Me_5Si_2O)_2Fe$ (**3**), $(Pr^i{}_3SiO)_2M$ (M = Fe (**4**), Co (**5**)), $(Pr^i{}_3GeO)_2Fe$ (**6**), $(Ph_3SiO)_2Fe$ (**7**), $(Me_3SiO)_2Fe$ (**8**), $(Pr^i{}_3GeO)_2Fe(bpy)$ (**9**), and $[(Me_3Si)_2NFe(\mu\text{-}OSi_2Me_5)_2]_2Fe \cdot C_6H_6$ (**10**) were synthesized by the reactions of metal silylamides $[(Me_3Si)_2N]_2M$ (M = Fe, Co) with the corresponding silanols or triisopropylgermanol. The reaction of pentamethyldisilanol with iron(II) silylamide affords either polymeric complex **3** or coordination oligomer **10**, depending on the ratio of the reactants. The structures of complexes **9** and **10** were established by X-ray diffraction analysis. The interaction of the prepared compounds with carbon oxides was studied. Low-coordination cobalt siloxide is the only among all prepared compounds that absorbs CO (2 mol) at room temperature and under 1 atm to form an unstable cluster. Compounds **1**, **2**, and **4—8** react with CO_2 to form carbonate complexes, and their reactivity decreases with a decrease in the electron-donating ability of the substituents at the central atom: $(Me_3Si)_3SiO > Pr^i{}_3GeO \approx Pr^i{}_3SiO > Me_3SiO \gg Ph_3SiO$.

Key words: transition metals, silicon- and germanium-containing organic compounds, siloxides, X-ray diffraction analysis, coordination polymers.

Progress in the chemistry of individual metallosiloxanes[1] is due to their potentialities as models of heterogeneous oxide catalysts[2] or co-catalysts and their precursors. The structural and magnetic properties of these compounds are of special interest.[3] In this work, we continue our studies of transition metal siloxides[4] and present the data on the metal siloxides and germyloxides $(R_3EO)_2M$ (M = Fe, Co; E = Si, Ge; R = Me, Pr^i, Ph, Me_3Si; $R_3Si = Me_2(Me_3Si)Si$).

Results and Discussion

Synthesis and structure

Previously described iron and cobalt siloxides $[(Me_3Si)_3SiO]_2Fe$ (**1**) and $[(Me_3Si)_3SiO]_2Co$ (**2**)[4] and newly synthesized homoleptic siloxides and germyloxides of these metals $(Me_5Si_2O)_2Fe$ (**3**), $(Pr^i{}_3SiO)_2Fe$ (**4**), $(Pr^i{}_3SiO)_2Co$ (**5**)), $(Pr^i{}_3GeO)_2Fe$ (**6**), $(Ph_3SiO)_2Fe$ (**7**), and $(Me_3SiO)_2Fe$ (**8**) (Table 1) were prepared by the treatment of iron and cobalt silylamides with the corresponding silanols or triisopropylgermanol in aromatic or saturated hydrocarbons.

$$[(Me_3Si)_2N]_2M + 2\,R_3EOH \longrightarrow$$
$$\longrightarrow (R_3EO)_2M + 2\,(Me_3Si)_2NH \qquad (1)$$
$$\mathbf{1{-}8}$$

M = Fe, Co; $R_3E = (Me_3Si)_3Si$, Me_5Si_2, Me_3Si, $Pr^i{}_3Si$, $Pr^i{}_3Ge$, Ph_3Si

Table 1. Characteristics of compounds **1—10**

Compound	ν(MOE) /cm^{-1}	Appearance
1	960 s	Yellow crystals
2	935 s	Green crystals
3	940 w	Blue powder
4	950 s	Dark green oil
5	980 s	Violet oil
6	830 s	Dark green oil
7	950 s	Gray powder (form hexane), crystals (from toluene)
8	950 w	White powder
9	830 s	Dark green crystals
10	970 s	Light green crystals

The reaction of iron silylamide with triisopropylgermanol in the presence of an equivalent amount of 2,2´-bipyridyl (bpy) produced the adduct of siloxide **6** with 2,2´-bipyridyl, *viz.*, $(Pr^i{}_3GeO)_2Fe(bpy)$ complex (**9**). Compounds **1**, **2**, and **9** were isolated in the crystalline form; compounds **3**, **7**, and **8** are powders; and compounds **4**, **5**, and **6** are oily liquids.

The degree of association of siloxides $[R_3SiO]_2M$ depends substantially on the size of the R_3Si group. Previously described isostructural iron and cobalt tris(trimethylsilyl)siloxides **1** and **2** in the crystalline state are

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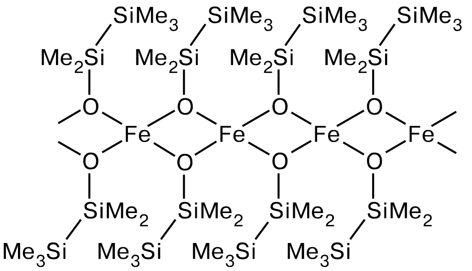
dimers.[4] However, judging from the molecular weight determined in benzene by cryoscopy, in a solution these compounds are monomeric. For example, for siloxide **1** $M_{calc} = 583$, $M_{cryosc} = 556$.

The reaction of pentamethyldisilanol with iron silylamide affords different products, depending on the ratio of reactants. When an excess (2.1 : 1) of pentamethyldisilanol is used, a solution is formed, whose concentrating results in a finely crystalline siloxide $(Me_5Si_2O)_2Fe$ (**3**) (reaction (1)), which is a poorly soluble coordination polymer



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The precipitate of **3** can again be dissolved only by refluxing for 3 h in THF. However, this results, most likely, in the complex with THF.

The same compounds taken in the 4 : 3 molar ratio afford the crystalline trinuclear complex $[(Me_3Si)_2NFe(\mu\text{-}OSi_2Me_5)_2]_2Fe \cdot C_6H_6$ (**10**) with a rather unusual structure (Fig. 1). As a rule, bonding of the R_3SiO groups (R is alkyl or aryl) with the metal atom results in the formation of either dimers (in the case of bulky groups, for example, $[(Ph_3SiO)_2Co(THF)]_2)$[5] or insoluble coordination polymers if the size of the substituents does not prevent association (for example, $[(Me_3SiO)_2M]_n$, M = Ni, Co).[1a] In the latter case, single crystals cannot be prepared, and the molecular structure of the compounds cannot be studied. Thus, complex **10** is a unique structurally characterized example of coordination of the molecular fragments of silylamide and siloxide at the first steps of formation of coordination polymer **3**.

The crystallographic data for compound **10** are presented in Table 2. The main angles and bond lengths are presented in Table 3. Three iron atoms in molecule **10** are in the same line, and the Fe_2O_2 cycles lie in the relatively perpendicular planes. The internal O—Fe—O angles at the central pseudotetrahedral iron atom are 83.74(13)°, whereas the external angles are 123.68(8)°. The internal angles at the terminal iron atoms (O—Fe—O) and at the bridging oxygen atoms (Fe—O—Fe) are closer to orthogonal and equal to 87.06(13)° and 94.60(10)°, respectively.

Among a variety of the known structures of metallosiloxanes, the trinuclear manganese(II) (siloxy)silylamide complex $[O(Ph_2SiO)_2]_2Mn_3[N(SiMe_3)_2]_2(THF)_2 \cdot 1/2THF$ can be somewhat analogous to compound **10**.[7] However, in this complex the metal atoms are arranged at an angle of 139.5°, which is caused, most likely, by spatial restrictions for the coordination of the bidentate tetraphenyldisiloxide ligand simultaneously with three manganese atoms.

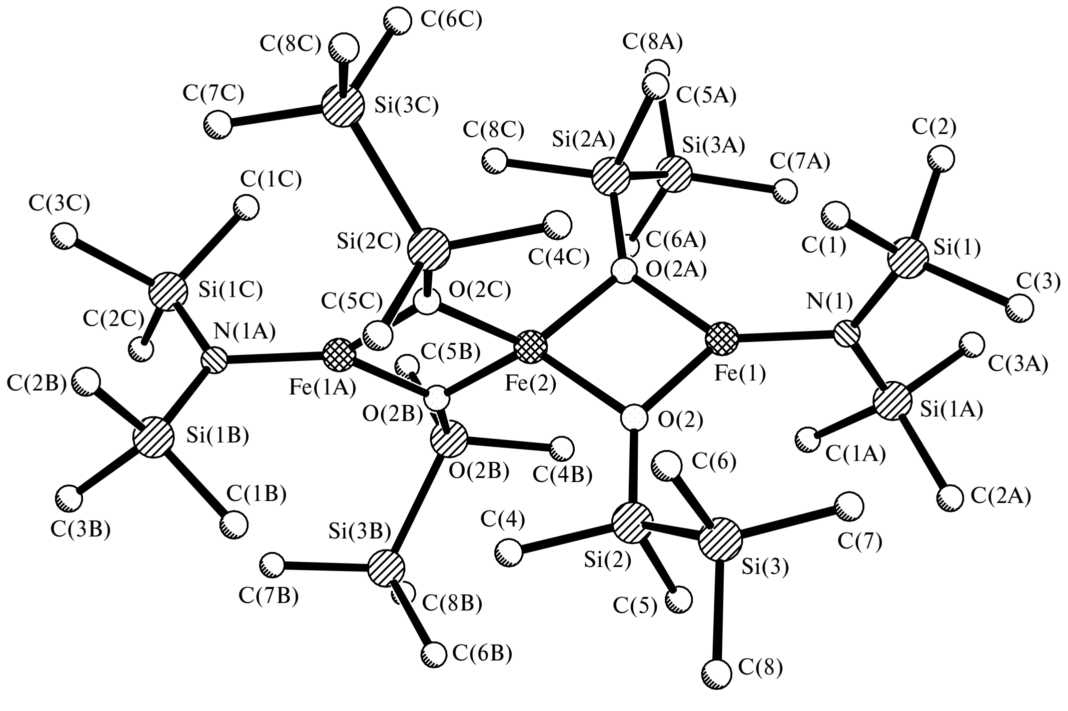

Fig. 1. Molecular structure of $[(Me_3Si)_2NFe(\mu\text{-}OSi_2Me_5)_2]_2Fe$ (**10**).

Table 2. Crystallographic data and X-ray diffraction parameters for compounds **9** and **10**

Parameter	**9**	**10**
Diffractometer	Siemens P3/PC	Smart
Molecular formula	$C_{28}H_{50}Ge_2O_2N_2Fe$	$C_{38}H_{102}Fe_3N_2O_4Si_{12}$
Molecular weight	647.73	1155.83
T/K	110(2)	
λ/Å	0.71073	
Crystal system	Triclinic	Tetragonal
Space group	$P\bar{1}$	$I4_{1/a}cd$
a/Å	11.49(2)	17.409(3)
b/Å	12.27(2)	17.409(3)
c/Å	12.49(2)	45.477(10)
α/deg	99.85(3)	90
β/deg	91.11(3)	90
γ/deg	116.39(3)	90
V/Å^3	1544(5)	13783(4)
Z	2	8
d_{calc}/g cm^{-3}	1.392	1.069
μ/mm^{-1}	2.42	0.860
Total number of measured reflections	16795	75177
Number of independent reflections (R_{int})	8488 0.0523	4963 0.052
Number of reflections with $I > 2\sigma(I)$	5805	4963
Number of refined parameters	316	135
R_1 ($I > 2\sigma(I)$)	0.0608	0.0664
wR_2	0.1103	0.1048

Triisopropylsiloxide derivatives of iron **4** and cobalt **5** and homoleptic iron triisopropylgermyloxide **6** are oily substances, which are infinitely soluble in any organic solvents. Complex **4** is monomeric in a solution: $M_{calc} = 402$, $M_{cryosc} = 406$.

Table 3. Main bond lengths and bond angles in compound **10**

Bond	d/Å	Angle	ω/deg
Fe(1)—N(1)	1.892(4)	N(1)—Fe(1)—O(2)	136.47(7)
Fe(1)—O(2)	1.944(2)	O(2)—Fe(1)—O(2A)^a	87.06(13)
Fe(1)—Fe(2)	2.9039(8)	N(1)—Fe(1)—Fe(2)	180.0
Fe(2)—O(2)	2.007(2)	O(2)—Fe(1)—Fe(2)	43.53(7)
Fe(2)—Fe(1A)^c	2.9039(8)	O(2A)^a—Fe(2)—O(2)	83.74(13)
Si(1)—N(1)	1.7366(19)	O(2A)^a—Fe(2)—O(2B)^b	123.68(8)
Si(2)—O(2)	1.662(3)	Fe(1A)^c—Fe(2)—Fe(1)	180.0
Si(2)—Si(3)	2.3524(15)	O(2)—Si(2)—Si(3)	112.66(12)
N(1)—Si(1A)^a	1.7366(19)	Si(1A)^a—N(1)—Si(1)	124.4(2)
		Si(1)—N(1)—Fe(1)	117.80(11)
		Si(2)—O(2)—Fe(1)	136.91(13)
		Si(2)—O(2)—Fe(2)	127.26(13)
		Fe(1)—O(2)—Fe(2)	94.60(10)

$^{a-c}$ Atoms found from the basic atoms by the symmetric transform: ^{a} $(-x, -y + 3/2, z)$, ^{b} $(-x + 3/4, -z + 1/4)$, ^{c} $(x - 3/4, -x + 3/4, -z + 1/4)$.

Although the structure of iron triphenylsiloxide **7** was not studied, it can be assumed that compound **7**, which is crystallized from toluene, is a structural analog of dinuclear cobalt triphenylsiloxide described previously[5] because the atomic radii of cobalt and iron are close.[6]

Iron trimethylsiloxide **8** is formed on mixing of the initial reactants as a white powder, whose solubility is very low even in high-polarity solvents, which is probably caused by the cross-linked structure of the coordination polymer that formed.

Attempts to isolate compounds **4—6** in the crystalline state were unsuccessful likely due to the disordered isopropyl fragments and association of the complexes in concentrated solutions. However, we prepared single crystals of compound **9**, the adduct of iron triisopropylgermyloxide with 2,2´-bipyridyl. Compound **9** is the first structurally characterized molecular complex containing the Fe—O—Ge fragment (Fig. 2). The Fe—O—Ge bond angles in complex **9** are 133.9(2)° and 144.6(2)° for the Ge(1)—O(1)—Fe(1) and Ge(2)—O(2)—Fe(1) fragments, respectively. The main bond lengths and bond angles in molecule **9** are presented in Table 4.

Reactivity

All studied compounds are oxygen- and moisture-sensitive. The absorption band corresponding to vibrations of the M—O—Si fragment[1] (see Table 1) and observed in the 900—1000 cm^{-1} interval disappears because of hydrolysis on storage of the compounds for several minutes in humid air. For individual compounds with a low degree of association (in particular, for dimers and trimers), this band is rather intense, whereas a low-intensity absorption is observed for coordination polymers **3** and **8**. In addition, hydrolysis of the soluble compounds, which oc-

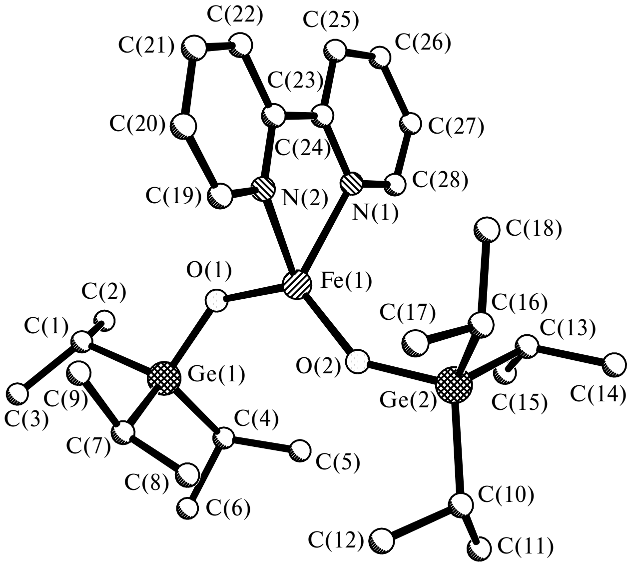

Fig. 2. Molecular structure of $(Pr^i{}_3GeO)_2Fe(bpy)$ (**9**).

Table 4. Main bond lengths and bond angles in compound **9**

Bond	d/Å	Angle	ω/deg
Fe(1)—O(2)	1.854(4)	O(2)—Fe(1)—O(1)	126.84(14)
Fe(1)—O(1)	1.887(5)	Ge(1)—O(1)—Fe(1)	133.9(2)
Ge(2)—O(2)	1.741(4)	Ge(2)—O(2)—Fe(1)	144.6(2)
Ge(1)—O(1)	1.774(4)	N(2)—Fe(1)—N(1)	74.70(15)
Ge(2)—C(10)	1.983(5)	C(13)—Ge(2)—C(16)	106.9(2)
Ge(1)—C(4)	1.966(6)	C(4)—Ge(1)—C(7)	114.0(2)
C(23)—C(24)	1.478(7)	O(2)—Fe(1)—N(2)	111.91(18)
C(21)—C(22)	1.385(7)	O(1)—Fe(1)—N(2)	107.72(17)
Fe(1)—N(2)	2.168(5)	O(2)—Ge(2)—C(16)	109.6(2)
Fe(1)—N(1)	2.177(5)	O(1)—Ge(1)—C(7)	107.71(19)

curs readily in a polar medium, produces the initial silanol (germanol) in ~100% yield and bivalent metal hydroxide. Complexes **1—3** and **10** containing the polysilyl fragments are pyrophoric in air.

When the size of substituents at the central atom increases, the ability of the compounds to self-association decreases and a possibility of coordination of small molecules appears.

Interaction of $[(Me_3Si)_3SiO]_2Co$ (2) with CO. We found that cobalt tris(trimethylsilyl)siloxide (**2**) in a toluene solution absorbs ~2 moles of CO per cobalt atom at room temperature and atmospheric pressure to form a dark brown solution. It is of interest that a solution of **2** in THF does not absorb CO under these conditions. This is probably related to the fact that the coordination sphere of cobalt is saturated with the donating THF molecules.

After concentrating a toluene solution and storage of the residue at 0 °C, a minor amount of dark brown crystals is precipitated. The IR spectrum of the new complex contains intense absorption bands at 840 and 1240 cm^{-1} corresponding to the SiMe fragments and a set of bands (2040, 2030, 2000, and 1870 cm^{-1}), which can be assigned to the cobalt-carbonyl fragments and bridging CO groups.[8,9] In addition, a new intense siloxane absorption band is observed at 1050 cm^{-1}, while the absorption at 935 cm^{-1} (Si—O—Co) disappears, as we suppose, due to migration of the oxygen atom with insertion to the silicon—silicon bond of the polysilanyl fragment.

It is known that the reaction of cobalt(I) tris(trimethylsilyl)silyltellurolate $Co[TeSi(SiMe_3)_3](PMe_3)_3$ with CO affords the dicarbonyl complex $Co(CO)_2[TeSi(SiMe_3)_3](PMe_3)_3$.[10] Thus, CO stabilizes the low-valent state of the metal favoring, in our case, the rearrangement of the more electronegative tris(trimethylsilyl)siloxide substituent to form the cobalt-silyl complex. Hydrolysis of the isolated carbonyl complex does not recover the initial tri(trimethylsilyl)silanol. Therefore, we propose the structure of the silylcobaltcarbonyl cluster $(Me_3Si)_2(Me_3SiO)SiCo_x(CO)_y$ for the isolated compound. It was difficult to completely characterize the complex because of its decomposion already at room temperature.

The other complexes synthesized by us do not react with CO at standard temperature and pressure.

*Interaction of homoleptic complexes **1**, **2**, and **4—8** with CO_2.* The interaction of CO_2 with metal alkoxides occurs, as a rule, as insertion at the metal—carbon bond to form the corresponding carbonate complexes.[11]

It was assumed[4] that the reaction of compound **1** with CO_2 affords the product of insertion of the oxygen atoms (from CO_2) at the silicon—silicon bonds of the polysilyl fragment, and the Fe—C bond forms. Our experiments show that the formation of the previously observed siloxane products is due to an oxygen admixture in CO_2. The reaction of compounds **1**, **2**, and **4—8** with CO_2 results in the insertion of the latter at the M—O bond and formation of the corresponding carbonates. The reactions occur in a solution of hydrocarbons at room temperature and under an atmospheric pressure. The appearance of absorption bands at 1550 and 1380 cm^{-1} in the IR spectra indicates the formation of the —OC(O)O— groups. Two moles of CO_2 are readily inserted only in the case of iron siloxide **1** and cobalt germyloxide **6**

$$\underset{\mathbf{1}}{[(Me_3Si)_3SiO]_2Fe} + 2\,CO_2 \xrightarrow{i} [(Me_3Si)_3SiOC(O)O]_2Fe, \qquad (2)$$

$$\underset{\mathbf{6}}{(Pr^i{}_3GeO)_2Co} + 2\,CO_2 \xrightarrow{ii} [Pr^i{}_3GeOC(O)O]_2Co. \qquad (3)$$

Conditions: *i*. 20 °C, 20 min; *ii*. 20 °C, 30 min.

The resulting carbonates are easily hydrolyzed to form the initial silanol (germanol), CO_2, and bivalent metal hydroxide. We failed to isolate possible intermediates, carbonic acid derivatives $(Me_3Si)_3SiOC(O)OH$ and $Pr^i{}_3GeOC(O)OH$, probably because of their instability.

The reactions of cobalt tris(trimethylsilyl)siloxide **2** and triisopropylsiloxides **4** and **5** with carbon dioxide are sharply slowed down after insertion of one mole of CO_2.

$$\underset{\mathbf{2}}{[(Me_3Si)_3SiO]_2Co} + CO_2 \longrightarrow (Me_3Si)_3SiOC(O)OCoOSi(SiMe_3)_3, \qquad (4)$$

$$\underset{\mathbf{4,\,5}}{(Pr^i{}_3SiO)_2M} + CO_2 \longrightarrow Pr^i{}_3SiOC(O)OMOSiPr^i{}_3. \qquad (5)$$

M = Fe (**4**), Co (**5**)

The IR spectrum of the product contains simultaneously absorption bands corresponding to the FeOSi and —OC(O)O— fragments. However, the products of insertion of one mole of CO_2 were not isolated in the pure state.

Iron(II) trimethylsiloxide **8** also absorbs CO_2 to form a carbonate complex (according to the IR spectroscopic data). However, the reaction rate decreases substantially likely due to a poor solubility of compound **8**. Only 0.5 moles of CO_2 are absorbed for 3 days.

Unlike other studied compounds, triphenylsiloxide **7** does not react with CO_2. The prolonged storage (5 days) of its toluene solution under CO_2 did not show a noticeable absorption of the latter.

The kinetics of this reaction in detail is difficult to study because the system is heterogeneous (gas—solution) and the oxygen traces exert a substantial effect. However, we can conclude at the qualitative level that the relative reactivity of the iron and cobalt siloxides and germyloxides decreases with a decrease in the electron-donating ability of the substituents at the silicon or germanium atom in the series: $(\mathrm{Me_3Si})_3\mathrm{Si} > \mathrm{Pr^i{}_3Ge} \approx \mathrm{Pr^i{}_3Si} > > \mathrm{Me_3Si} \gg \mathrm{Ph_3Si}$.* The iron compounds manifest somewhat higher reactivity compared to that of analogous cobalt derivatives. This agrees with the lower redox potential of iron $\varphi°(\mathrm{Fe^{2+}/Fe^0}) = -0.44$ V; $\varphi°(\mathrm{Co^{2+}/Co^0}) = -0.28$ V. It should be noted for comparison that iron(III) siloxide $[(\mathrm{Me_3Si})_3\mathrm{SiO}]_3\mathrm{Fe}$ synthesized previously[13] reacts with CO_2 rather slowly and does not react with oxygen. Accepting that the polarities of the M—O bonds in the considered iron and cobalt compounds are approximately the same, we can assert that the regularities found by us agree with the earlier[11] data on the decisive influence of the electron-donating ability of the central metal atom on the CO_2 binding.

Experimental

All procedures on synthesis, isolation, and purification of compounds were carried out *in vacuo* or under argon. Solvents were purified using standard methods[14]: hexane was distilled over sodium, and benzene and toluene were dehydrated and distilled with P_2O_5. Diethyl ether and THF were refluxed with NaOH and distilled over Na with addition of benzophenone. Compounds **1** and **2** [4] and silylamides $[(\mathrm{Me_3Si})_2\mathrm{N}]_2\mathrm{M}$ (M = Co and Fe)[15,16] were synthesized according to previously described procedures. Triphenylsilanol (98%, Aldrich) was used without additional purification.

NMR spectra were recorded on a Bruker DPX-200 instrument (200 MHz) using $\mathrm{Me_4Si}$ as internal standard.

IR spectra were recorded on a Perkin—Elmer-577 spectrophotometer in the region from 4000 to 400 cm^{-1}.

The content of cobalt and iron was determined by photometric titration; 1-nitrosonaphthol was used for cobalt, and 1,10-phenanthroline was applied for iron.[17]

The products of hydrolysis of the obtained compounds were analyzed on a Tsvet-530 gas chromatograph (column 0.3×200 cm, Inerton AW with 5% SE-30, thermal-conductivity detector, helium as carrier gas).

X-ray diffraction studies of compounds 9 and 10. Single crystals of complex **9** were prepared by crystallization from hexane, and those of complex **10** were obtained by crystallization from a hexane—benzene (1 : 1) mixture. A solvate benzene molecule was revealed in the crystal structure of compound **10**.

The crystallographic data for compounds **9** and **10** and the main details of X-ray diffraction experiment and refinement of the structures are presented in Table 2. Positions of H atoms were calculated from the geometric conditions and refined in the rider model. Absorption was applied by the SADABS program.

Iron(II) pentamethyldisiloxide $(\mathbf{Me_3SiSiMe_2O})_2\mathbf{Fe}$ (3). Pentamethyldisilanol[18] (1.93 g, 13.0 mmol) in hexane (15 mL) was added to a solution of $[(\mathrm{Me_3Si})_2\mathrm{N}]_2\mathrm{Fe}$ (2.35 g, 6.25 mmol) in hexane (25 mL). The mixture was heated for 3 h at 50 °C. A polycrystalline blue precipitate was formed upon concentrating the solution *in vacuo*. The mother liquor was decanted, and the precipitate was washed with hexane (the substance lost its solubility on crystallization). Solvent residues were removed *in vacuo*. Compound **3** was obtained as a light blue powder in 92% yield (2.02 g). Found (%): C, 35.01; H, 8.69; Fe, 15.70. $\mathrm{C_{10}H_{30}Si_4O_2Fe}$. Calculated (%): C, 34.26; H, 8.63; Fe, 15.93. IR, ν/cm^{-1}: 1240 s, 1060 w, 940 w (SiOFe), 840 s ($\mathrm{SiMe_3}$), 810 s ($\mathrm{SiMe_2}$), 690 m, 620 s.

Iron(II) triisopropylsiloxide $(\mathbf{Pr^i{}_3SiO})_2\mathbf{Fe}$ (4). To a solution of $[(\mathrm{Me_3Si})_2\mathrm{N}]_2\mathrm{Fe}$ (3.33 g, 8.85 mmol) in hexane (25 mL) was added $\mathrm{Pr^i{}_3SiOH}$ [19] (3.08 g, 17.7 mmol) in hexane (20 mL). The mixture was heated at 50 °C for 6 h. The green color of the solution slowly changed to dark green. The solvent and hexamethyldisilazane were removed *in vacuo* at 80 °C. A dark green oil was obtained in the residue. The yield was 3.38 g (95%). Found (%): C, 52.94; H, 10.39; Fe, 13.50. $\mathrm{C_{18}H_{42}Si_2O_2Fe}$. Calculated (%): C, 53.70; H, 10.52; Fe, 13.87. IR (liquid film, KBr), ν/cm^{-1}: 1460 s, 1384 m, 1368 m, 1250 w, 1079 m, 1020 m, 1000 m, 889 w, 845 w, 950 s (Si—O—Fe).

Cobalt(II) triisopropylsiloxide $(\mathbf{Pr^i{}_3SiO})_2\mathbf{Co}$ (5). To a solution of $[(\mathrm{Me_3Si})_2\mathrm{N}]_2\mathrm{Co}$ (2.35 g, 6.2 mmol) in benzene (25 mL) was added a solution of $\mathrm{Pr^i{}_3SiOH}$ [19] (2.16 g, 12.4 mmol) in benzene (20 mL). The solution changed its color from green to violet with pouring together the reactants. The reaction mixture was stored for 10 h at ~20 °C. The solvent and hexamethyldisilazane were removed *in vacuo* at 80 °C. A dark violet oil was obtained in the residue. The yield was 2.41 g (96%). Found (%): C, 51.92; H, 10.19; Co, 13.80. $\mathrm{C_{18}H_{42}Si_2O_2Co}$. Calculated (%): C, 53.30; H, 10.44; Co, 14.53. IR (liquid film, KBr), ν/cm^{-1}: 1465 s, 1384 m, 1368 m, 1250 w, 1080 m, 1015 m, 1000 m, 889 w, 845 w, 980 s (Si—O—Co).

Iron(II) triisopropylgermyloxide $(\mathbf{Pr^i{}_3GeO})_2\mathbf{Fe}$ (6). Triisopropylgermanol[20] (0.48 g, 2.2 mmol) in hexane (10 mL) was added to a solution of $[(\mathrm{Me_3Si})_2\mathrm{N}]_2\mathrm{Fe}$ (0.41 g, 1.1 mmol) in hexane (10 mL). During mixing of the reactants the green color of the solution gained a brown tint. The reaction mixture was stored for 10 h at ~20 °C. The solvent and hexamethyldisilazane were removed *in vacuo* at 80 °C. A green-brown oil was obtained in the residue. The yield was 0.52 g (97%). Found (%): C, 49.35; H, 8.80; Fe, 10.94. $\mathrm{C_{18}H_{42}Ge_2O_2Fe}$. Calculated (%): C, 49.98; H, 8.61; Fe, 11.36. IR (liquid film, KBr), ν/cm^{-1}: 2900 v.s, 2840 m, 1445 s, 1370 m, 1355 m, 1235 m, 1010 m, 980 m, 870 m; 830 s (Ge—O—Fe); 740 w, 640 m; 565 s, ν_{as}(Ge—C); 520 w, ν_s(Ge—C).

Iron(II) triphenylsiloxide $(\mathbf{Ph_3SiO})_2\mathbf{Fe}$ (7). Triphenylsilanol (0.55 g, 2 mmol) in hexane (10 mL) was added to a solution of $[(\mathrm{Me_3Si})_2\mathrm{N}]_2\mathrm{Fe}$ (0.37 g, 1.0 mmol) in hexane (10 mL). The

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* This series was chosen based on the additive contribution of the substituents and analysis of the available inductive constants of the silicon- and germanium-containing organic substituents.[12]

mixture was heated for 20 min at 80 °C. During this time, a green crystalline precipitate formed on the tube walls. The solvent and hexamethyldisilazane were removed *in vacuo* at 80 °C. The solid residue was recrystallized from hexane. Light green crystals sensitive to oxygen were obtained in 95% yield (0.57 g). Found (%): C, 71,75; H, 4.63; Fe, 9.50. $C_{36}H_{30}Si_2O_2Fe$. Calculated (%): C, 71.27; H, 4.98; Fe, 9.21. IR (Nujol, KBr), ν/cm^{-1}: 1950 w, 1880 w, 1810 w, 1760 w, 1580 m, 1420 m, 1100 s (Ph), 1010 s, 950 s (Si—O—Fe), 870 s, 730 w, 700 s, 500 s (SiC_3). $\mu_{eff} = 3.8\mu_B$.

Iron(II) trimethylsiloxide ($(Me_3SiO)_2Fe$) (8). To a solution of $[(Me_3Si)_2N]_2Fe$ (3.02 g, 8.0 mmol) in hexane (15 mL) was added Me_3SiOH [21] (1.44 g, 16.0 mmol) in hexane (10 mL). A white powder precipitated with pouring together the reactants was filtered off and washed with hexane. The solvent was removed *in vacuo* at 50 °C. The yield was 1.83 g (98%). Found (%): C, 30.31; H, 7.71; Fe 23.59. $C_6H_{18}Si_2O_2Fe$. Calculated (%): C, 30.76; H, 7.75; Fe 23.84. IR (Nujol, KBr), ν/cm^{-1}: 1240 s ($SiMe_3$), 1030 w, 950 w (Fe—O—Si), 870 m, 840 (s) ($SiMe_3$), 750 s, 690 m, 680 m ($SiMe_3$); $\mu_{eff} = 3.5\mu_B$.

Iron triisopropylgermyloxide 2,2´-bipyridyl ($(Pr^i_3GeO)_2Fe(bpy)$) (9) was synthesized similarly to compound **6** by addition of an equivalent amount (1.1 mmol) of 2,2´-bipyridyl. Dark green crystals were recrystallized from hexane and obtained in 94% yield (0.67 g). Found (%): C, 51.23; H, 7.95; Fe, 8.93. $C_{28}H_{50}Ge_2O_2N_2Fe$. Calculated (%): C, 51.92; H, 7.78; Fe, 8.62. IR (Nujol, KBr), ν/cm^{-1}: 1580 m, 1300 w, 1145 w, 980 m, 870 m, 830 s, 760 m, 745 m, 635 m, 550 s.

Bis[bis(trimethylsilylamino)]tetrakis(μ_2-pentamethyldisiloxy)]triiron benzenemonosolvate, $[(Me_3Si)_2NFe(\mu\text{-}OSi_2Me_5)_2]_2Fe \cdot C_6H_6$ (10). Pentamethyldisilanol[18] (0.59 g, 4.0 mmol) in hexane (5 mL) was added to a solution of $[(Me_3Si)_2N]_2Fe$ (1.13 g, 3.0 mmol) in hexane (15 mL). The mixture was heated for 3 h at 50 °C. Compound **10** as a solvate with a benzene molecule was crystallized from a benzene—hexane (1 : 1) mixture by slow cooling of the warm solution to ~20 °C. The mother liquor was decanted. Solvent residues were removed in an argon flow. Compound **10** (0.88 g, 85%) was obtained as light green crystals. Found (%): C, 38.87; H, 9.06; Fe, 14.11. $C_{38}H_{102}Si_{12}O_4N_2Fe_3$. Calculated (%): C, 39.48; H, 8.90; Fe, 14.50. IR, ν/cm^{-1}: 1400 w, 1250 v.s ($SiMe_3$), 970 s, 890 w, 850 s ($SiMe_3$), 800 m ($SiMe_2$), 770 m, 700 m, 680 m, 620 s, 460 s.

Interaction of complex 2 with CO. An ampule containing complex **2** (0.59 g, 1.0 mmol) in toluene (5 mL) was connected to a mercury burette filled with CO and stored for 24 h at 20 °C. The green color of the solution slowly changed to brown. The total volume of the absorbed gas was 40 mL (1.8 mmol). The solution was concentrated *in vacuo*, and the liquid residue was stored for 1 h at 0 °C. The mother liquor was decanted, and black-brown crystals were analyzed by IR spectroscopy. IR, ν/cm^{-1}: 2040 s, 2030 s, 2000 s, 1870 m (CO), 1240 s ($SiMe_3$), 1050 s (Si—O—Si), 840 v.s ($SiMe_3$). An attempt to recrystallize the crystals resulted in resin-like products.

Interaction of compounds 1, 2, and 4—7 with CO_2. The reactions were carried out under similar conditions (1 atm, 20 °C), and the blank experiment was conducted without the complexes. Before use, carbon dioxide was purified by twice freezing in liquid nitrogen followed by passing through P_2O_5.

Interaction of complex $[(Me_3Si)_3SiO]_2Fe$ (1) with CO_2. An evacuated ampule containing compound **1** (0.58 g, 1.0 mmol) in hexane (15 mL) was connected to a mercury burette filled with CO_2. During 3 min at 20 °C, 22 mL (1 mmol) of CO_2 were absorbed. The second mmole of CO_2 reacted within 17 min, after which gas absorption stopped. The solution changed its yellow-green color to brown. Hexane was removed to give a viscous oil, which solidified with time to afford a fine-crystalline product. Recrystallization of the latter is difficult due to its high solubility in hexane. The yield was 0.63 g (95%). Found (%): C, 36.45; H, 8.20; Fe, 8.07. $[(Me_3Si)_3SiOC(O)O]_2Fe$ ($C_{20}H_{54}Si_8O_6Fe$). Calculated (%): C, 35.79; H, 8.11; Fe, 8.32. IR (Nujol, KBr), ν/cm^{-1}: 1530 m, 1380 m (—OC(O)O—), 1240 s (SiMe), 1050 w, 935 m, 840 s (SiMe), 750 m, 700 w, 620 m (SiC_3).

Interaction of complex $[(Me_3Si)_3SiO]_2Co$ (2) with CO_2. An evacuated ampule containing complex **2** (0.59 g, 1.0 mmol) in hexane (15 mL) was connected to a mercury burette filled with CO_2. The first mmole of CO_2 was absorbed rapidly (30 min), then absorption slowed down, and 0.6 mmoles of CO_2 were additionally absorbed during the next day. The dark green color of the solution changed to dark blue. The solvent was removed *in vacuo* from the reaction mixture, and a dark blue oil remained in the residue. IR (liquid film, KBr), ν/cm^{-1}: 1240 m, 840 s (SiMe); 1550 m, 1370 m (—OC(O)O—), 750 m, 680 w, 620 w (SiC_3).

Interaction of complex $(Pr^i_3SiO)_2Fe$ (4) with CO_2. An evacuated ampule containing siloxide **4** (0.40 g, 1.0 mmol) in hexane (15 mL) was connected to a mercury burette filled with CO_2. During 30 min at 20 °C, 1 mmole of CO_2 was absorbed, and then absorption ceased. The gray-green color of the solution deepened during the reaction. Hexane was removed to give a viscous oil. IR (liquid film, KBr), ν/cm^{-1}: 1550 m, 1385 m (—OC(O)O—), 1370 m, 1250 w, 1080 m, 1020 m, 1000 m, 925 w, 889 w, 845 w (Pr^i_3Si), 940 m (Si—O—Fe).

Interaction of complex $(Pr^i_3SiO)_2Co$ (5) with CO_2. An evacuated ampule containing siloxide **5** (0.41 g, 1.0 mmol) in hexane (15 mL) was connected to a mercury burette filled with CO_2. Under standard conditions, the solution absorbed 22 mL (1 mmol) of CO_2 for 50 min, after which gas absorption slowed down. Next 24 h resulted in the additional absorption of 0.1 mmoles of CO_2. The color of the solution became dark violet during the reaction. After the solvent was removed, a viscous oil was obtained. IR (liquid film, KBr), ν/cm^{-1}: 1560 s, 1390 s (—OC(O)O—), 1385 m, 1365 m, 1250 w, 1080 m, 1020 m, 1000 m, 925 w, 890 w, 845 w (Pr^i_3Si).

Interaction of complex $(Pr^i_3GeO)_2Fe$ (6) with CO_2. An evacuated ampule containing germyloxide **6** (0.49 g, 1.0 mmol) in hexane (15 mL) was connected to a mercury burette filled with CO_2. During 15 min at 20 °C, 22 mL (1 mmol) of CO_2 were absorbed. The second mmole of CO_2 reacted within 1 h, after which gas absorption ceased. The gray-green solution gained a violet color. Hexane was removed to produce a viscous oil. The yield was 0.55 g (95%). Found (%): C, 40.87; H, 7.55; Fe, 9.58. $[Pr^i_3GeOC(O)O]_2Fe$ ($C_{20}H_{42}Ge_2O_6Fe$). Calculated (%): C, 41.45; H, 7.30; Fe, 9.64. IR (Nujol, KBr), ν/cm^{-1}: 1540 v.s, 1350 s (—OC(O)O—), 1065 m, 1010 m, 630 m, 565 m (Pr^i_3Ge).

Hydrolysis of compounds 1—8. Tetrahydrofuran (3 mL) was condensed to a degassed weighted sample (~0.05—0.1 g) of the analyzed compound, and then a tenfold molar excess of water was added. The mixture was stored until metal hydroxide completely precipitated (~20—30 min) and then was centrifuged. The precipitate was dried *in vacuo* and dissolved in a minimal amount of 0.1 *N* HCl. The metal content was determined by photometric titration[17] and by burning of a weighted sample in an $HClO_4$—H_2SO_4 mixture followed by microanalysis.[17] The corresponding silanols and triisopropylgermanol were found in the centrifugate by GLC.

Hydrolysis of carbonates was performed similarly to the hydrolysis of compounds **1—8**, and CO_2 evolved was determined chromatographically using Silipor 600 GC as sorbent and volumetrically using a mercury burette. The corresponding silanols or triisopropylgermanol were found in the liquid phase by GLC.

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References

1. (a) M. G. Voronkov, E. A. Maletina, and V. K. Roman, *Geterosiloksany* [*Heterosiloxanes*], Nauka, Novosibirsk, 1984 (in Russian); (b) R. Murugavel, A. Voight, M. G. Walawalkar, and H. W. Roesky, *Chem. Rev.*, 1996, **96**, 2205.
2. F. J. Feher and R. L. Blanski, *J. Am. Chem. Soc.*, 1992, **114**, 5886.
3. (a) A. L. Buchachenko, *Usp. Khim.*, 1990, **59**, 529 [*Russ. Chem. Rev.*, 1990, **59** (Engl. Transl.)]; (b) A. Cornia, A. C. Fabretti, D. Gatteschi, G. Palyi, E. Rentschler, O. I. Shchegolikhina, and A. A. Zhdanov, *Inorg. Chem.*, 1995, **34**, 5383.
4. A. N. Kornev, T. A. Chesnokova, E. V. Zhezlova, G. K. Fukin, L. N. Zakharov, and G. A. Domrachev, *Dokl. Akad. Nauk*, 1999, **369**, 203 [*Dokl. Chem.*, 1999 (Engl. Transl.)].
5. G. A. Sigel, R. A. Bartlett, D. Decker, M. M. Olmstead, and P. P. Power, *Inorg. Chem.*, 1987, **26**, 1773.
6. S. S. Batsanov, *Zh. Neorg. Khim.*, 1991, **36**, 3015 [*J. Inorg. Chem. USSR*, 1991, **36** (Engl. Transl.)].
7. H.-G. Gosink, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, E. Irmer, and R. H. Irmer, *Organometallics*, 1994, **13**, 3420.
8. O. Vohler, *Chem. Ber.*, 1958, **91**, 1161.
9. K. M. Abraham and G. Urry, *Inorg. Chem.*, 1973, **12**, 2850.
10. D. E. Gindelberger and J. Arnold, *Inorg. Chem.*, 1993, **32**, 5813.
11. X. Yin and J. R. Moss, *Coord. Chem. Rev.*, 1999, **181**, 27.
12. A. N. Egorochkin and M. G. Voronkov, *Elektronnoe stroenie organicheskikh soedinenii kremniya, germaniya i olova* [*Electronic Structure of Organic Silicon, Germanium, and Tin Compounds*], Izd-vo SO RAN, Novosibirsk, 2000, 614 pp. (in Russian).
13. A. N. Kornev, T. A. Chesnokova, V. V. Semenov, E. V. Zhezlova, L. N. Zakharov, L. G. Klapshina, G. A. Domrachev, and V. S. Rusakov, *J. Organomet. Chem.*, 1997, **547**, 113.
14. C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, 1988.
15. R. A. Andersen, K. Faegri, J. C. Green, A. Haaland, M. F. Lappert, W.-P. Leung, and K. Rypdal, *Inorg. Chem.*, 1988, **27**, 1782.
16. H. Burger and U. Wannagat, *Monatsh. Chem.*, 1963, **94**, 1007.
17. Z. Marczenko, *Kolorymetryszne oznaczanie pierwiastkow*, Wydawnictwa Naukowo-Techniszne, Warszawa, 1968, 501 pp. (in Polish).
18. U. G. Stolberg, *Chem. Ber.*, 1963, **96**, 2798.
19. C. Eaborn, *J. Chem. Soc.*, 1952, 2840.
20. H. H. Anderson, *J. Am. Chem. Soc.*, 1953, **75**, 814.
21. M. F. Shostakovskii, I. A. Shikhiev, D. A. Kochkin, and V. I. Belyaev, *Zh. Obshch. Khim.*, 1954, **24**, 2202 [*J. Gen. Chem. USSR*, 1954, **24** (Engl. Transl.)].

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