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Reactions of 1,1,3,3-tetramethyldisilazane with dicobalt octacarbonyl and iron pentacarbonyl. Thermal decomposition of the cobalt and iron carbonyl silazane complexes

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The reaction of $(HMe_2Si)_2NH$ with $Co_2(CO)_8$ gives the complex $[Co_2(CO)_7(SiMe_2)_2NH_2]^+[Co(CO)_4]^-$. Its thermal decomposition starts with dissociation into the "acid" $HCo(CO)_4$ and the "base" $Co_2(CO)_7(SiMe_2)_2NH$. After that, the base and the initial complex decompose further under the action of $HCo(CO)_4$. The final products of this reaction are CO, NH_3, Co, volatile dimethylcyclosilazane, and a solid residue consisting of cobalt particles encapsulated into a polymethylsiloxane matrix and possessing properties of mixed para- and ferromagnetics with an ultimate specific magnetization of 64—74 G g^{-1}. Tetramethyldisilazane reacts with iron pentacarbonyl under UV irradiation to give relatively stable 1,3-bis(tetracarbonylhydrideiron)-1,1,3,3-tetramethyldisilazane. This product contains Fe—H...N hydrogen bonds, which stabilize it against dehydrogenation and cyclization to diironcyclodisilazane. Thermal decomposition of this product was investigated.

Key words: cobalt and iron complexes, tetramethyldisilasane, dicobalt octacarbonyl, iron pentacarbonyl, tetracarbonyl cobalt hydride, cobalt carbonyl silazane complex, iron carbonylhydride silazane complex, acid-base interaction, thermal decomposition of organometallic compounds, ferromagnetic properties.

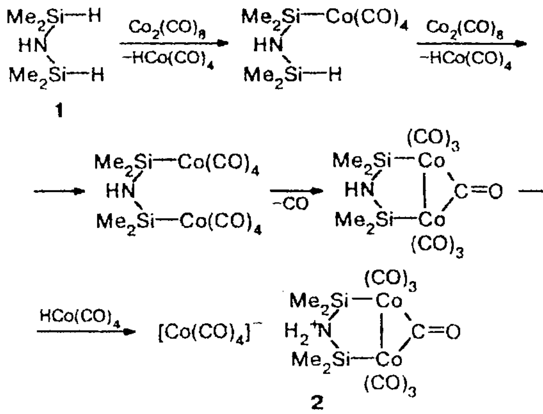
Transition metal complexes containing organosilicon ligands can be used as the initial compounds in the manufacture of ceramic[1] and ferromagnetic[2] materials and catalysts[3] and in the polymerization of hydrodisilazanes.[4] One of the most convenient methods for the synthesis of compounds of this type is oxidative addition of silicon organohydrides to metal carbonyls.[5] In this work, we studied the reaction of 1,1,3,3-tetramethyldisilazane (**1**) with dicobalt octacarbonyl and iron pentacarbonyl and thermal decomposition of the resulting cobalt and iron carbonyl disilazane complexes.

Results and Discussion

Reactions of compound 1 with $Co_2(CO)_8$. 1,1,3,3-Tetramethyldisiloxane, the oxygen analog of compound **1**, is known to readily react with dicobalt octacarbonyl to give thermally unstable 1,3-bis(tetracarbonylcobalt)tetramethyldisiloxane.[6] We showed that the N atom present in molecule **1** critically changes the reaction route compared to that of hydrodisiloxanes.

The reaction of **1** with $Co_2(CO)_8$ in benzene proceeds slowly at room temperature and rapidly at 60 °C and is accompanied by evolution of equal volumes of CO and H_2. A complex of 3,3,3,4,4,4-(μ-3,4)-heptacarbonyl-2,2,5,5-tetramethyl-1-aza-2,5-disila-3,4-dicobaltacyclopentane with tetracarbonylcobalt hydride (**2**) is formed as the major product. Several pathways to this compound can be conceived. One of them is shown in Scheme 1 and includes successive addition of two

Scheme 1



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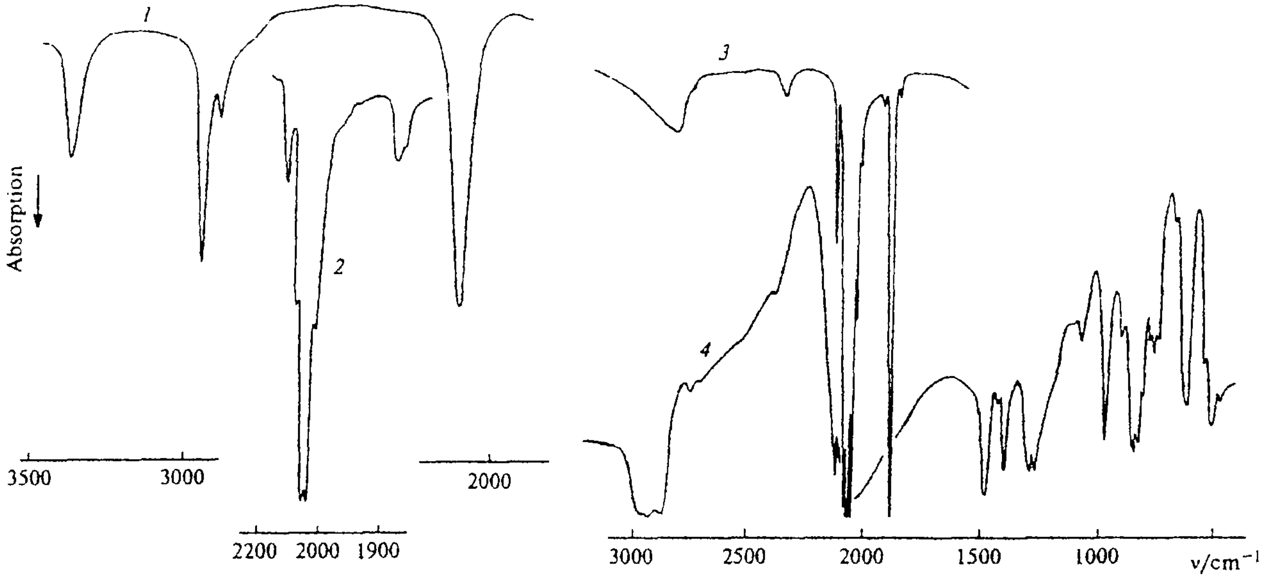

Fig. 1. IR spectrum of compounds **1** (*1*) and **2** (*2—4*): *1*, liquid film; *2*, CCl_4 solution; *3*, hexane solution; *4*, mineral oil mull.

tetracarbonylcobalt groups to the two Si—H bonds and ring closure in the intermediate 1,2-bis(tetracarbonylcobalt)tetramethyldisilazane. The carbonyl $HCo(CO)_4$ generated in the first two steps is known[7] to be a strong protic acid; hence, it protonates the N atom of the dicobaltadisilazane ring to give an ionic compound. Complex **2** is poorly soluble in aromatic, saturated, and chlorinated hydrocarbons, whereas nonionic compounds, like $Et_3SiCo(CO)_4$ [8] and $[OSiMeCo(CO)_4]_3$,[9] are readily soluble in these solvents.

The structure of complex **2** follows from the data of IR and ^1H and ^{13}C NMR spectroscopy. Figure 1 presents the IR spectra of the initial disilazane **1** and complex **2**. The IR spectrum of **2** contains a number of very intense absorption bands at 2100—1800 cm^{-1} and 530—450 cm^{-1} corresponding to stretching and deformation vibrations of the carbonyl groups, respectively. The absorption band for the Si—Me fragments is split into a doublet with frequencies of 1280, 1260 and 830, 805 cm^{-1}, indicating that the methyl groups in the molecule are nonequivalent.

The disilazane group accounts for two bands, at 950 and 603 cm^{-1}. The spectrum exhibits no absorption in the region of 3400 cm^{-1} (stretching vibrations of the disilazane N—H group) but exhibits a broad band with complex structure at 2800—2300 cm^{-1} (see Fig. 1, curve *4*, a mineral oil mull) or two bands, 2800 and 2325 cm^{-1} (see Fig. 1, curve *3*, a hexane solution), which can be assigned to the NH_2^+ fragment, formed upon the transfer of a proton from $HCo(CO)_4$ to the N atom in the disilazane fragment.[10] The 2100—1800 cm^{-1} range of the IR spectrum numbers nine absorption bands (see Fig. 1, curve *2*); this confirms the presence of two types of cobalt carbonyl fragments in molecule **2**: the band at 1880 cm^{-1} corresponds to $Co(CO)_4^-$ (see Fig. 1, curves *2*, *3*), while $Co_2(CO)_7$ accounts for the group of bands at 2000—2100 cm^{-1} (see Fig. 1, curves *2*, *3*) and the shoulder at 1842 cm^{-1} (μ-CO) (see Fig. 1, curve *2*).

The ^1H NMR spectrum recorded at room temperature contains only a signal for the methyl protons of the MeSi groups, whereas resonance absorption of the Si_2NH_2 group is not manifested. The absence of signals for the H atoms attached to nitrogen is a general property of ionic compounds of this type and is due to fast intermolecular exchange.[11,12] The ^{13}C NMR spectrum exhibits two signals, which points to nonequivalence of the methyl groups in cyclic compound **2**.

Analysis of the gases evolved during the reaction allows drawing some conclusions concerning the reaction mechanism. The reaction of compound **1** with 1 equiv. of $Co_2(CO)_8$ gives 1 equiv. each of H_2 and CO after 1.5 h at 60 °C or after 24 h at 25 °C. The composition of the gas phase changes during the reaction. Figure 2 presents the gas evolution curves recorded for **1** : $Co_2(CO)_8$ ratios of 1 : 1 and 2 : 1. It can be seen that immediately after mixing of the reactants, the gas phase consists mostly of CO but gradually it becomes enriched in hydrogen. Judging by the volume of the gases evolved, the reaction at 25 °C efficiently proceeds during the first 3 h and then slows down. The fast appearance of carbon monoxide confirms the scheme proposed for the formation of compound **2**. The gradual accumulation of hydrogen during the reaction is apparently[13] due to condensation of two molecules of $HCo(CO)_4$ to give $Co_2(CO)_8$ and H_2. The possibility of formation of H_2 upon the reaction of tetracarbonylcobalt hydride with **1** or with intermediate (tetracarbonylcobalt)-1,1,3,3-tetramethyldisilazane[14,15] also cannot be ruled out, although $HCo(CO)_4$ has been reported to be relatively inert with respect to silicon organohydrides.[16] The

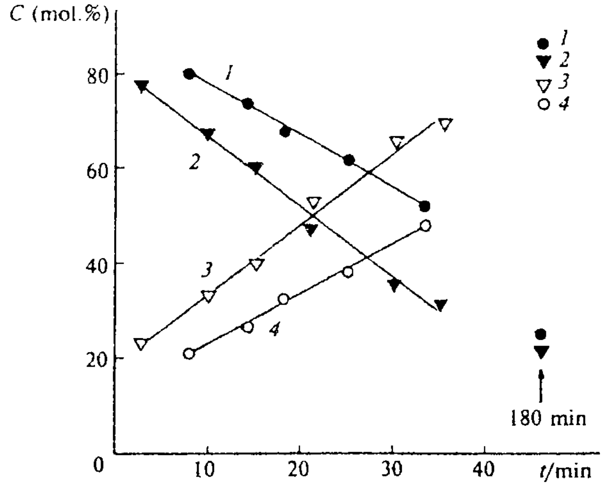

Fig. 2. Time dependence of the CO concentration (*1*, *2*) and H_2 (*3*, *4*) in the gas phase during the reaction of **1** with $Co_2(CO)_8$ at 2 : 1 (*1*, *4*) or 1 : 1 (*2*, *3*) molar ratio of the reactants.

question in what particular step the acid $HCo(CO)_4$ adds to bases, *i.e.*, to the initial silazane **1** and to the three intermediate cobalt carbonyl disilazane derivatives, shown in Scheme 1, remains open. In all probability, this interaction starts with compound **1**, because even in the first papers dealing with the synthesis of the complexes $R_3NH^+Co(CO)_4^-$ and $R_3SiNR_2H^+Co(CO)_4^-$ by the reaction of $HCo(CO)_4$ with R_3N and R_3SiNR_2, respectively, it was noted[11,17] that reactions of this type occur very rapidly.

It is known[18] that organic bases B (amines, alcohols) easily displace the carbonyl groups from $Co_2(CO)_8$. This gives an ionic compound in which the doubly charged cobalt cation is counterbalanced by two cobalt-carbonyl anions (Scheme 2).

Scheme 2

$$3\,[Co(CO)_4]_2 + 12\,B \longrightarrow 2\,[CoB_6]^{2+}[Co(CO)_4^-]_2 + 8\,CO$$

A similar transformation can also be induced by organosilicon amine **1**. To verify the possibility of this reaction, we studied the behavior of $Co_2(CO)_8$ in the presence of hexamethyldisilazane. It was found that the latter compound does not react with $Co_2(CO)_8$ according to Scheme 2 but causes its disproportionation to give $Co_4(CO)_{12}$ (Scheme 3).

Scheme 3

$$2\,Co_2(CO)_8 \xrightarrow{(Me_3Si)_2NH,\ C_6H_6} Co_4(CO)_{12} + 4\,CO$$

At room temperature, this reaction is slow. The degree of conversion of $Co_2(CO)_8$ is 35% over a period of 24 h and 50% over a period of 72 h. The process resembles the transformation of $Co_2(CO)_8$ in the presence of *tert*-butyl alcohol. Whereas methanol and ethanol react with it according to Scheme 2, more bulky *tert*-butyl alcohol does not replace the carbonyl groups but induces[18] the transformation of $Co_2(CO)_8$ into $Co_4(CO)_{12}$.

Since $Co_2(CO)_8$ disproportionates to give $Co_4(CO)_{12}$ on treatment with hexamethyldisilazane, hydrodisilazane **1** can also induce a similar transformation under the conditions of our experiments; this occurs in parallel with the main reaction. The resulting poorly soluble $Co_4(CO)_{12}$ can react with **1** or be simply accumulated in the reaction mixture. To study the behavior of dodecacarbonyltetracobalt, we introduced it in the reaction with 1,1,2,2-tetramethyldisilazane in benzene at 25 °C. HPLC analysis of the reaction mixture showed that cobaltsilazane **2** is formed as the main reaction product. Judging by the volume of the gases evolved and the amount of compound **1** consumed, $Co_4(CO)_{12}$ reacts with **1** much more slowly than $Co_2(CO)_8$. Thus after 24 h, the degree of conversion of **1** was only 33%. As in the reaction with $Co_2(CO)_8$, the gas phase consisted of H_2 and CO. These results indicate that accumulation of compound **2** is mainly due to the reaction of **1** with $Co_2(CO)_8$ (see Scheme 1) rather than with $Co_4(CO)_{12}$ formed during the reaction. When an excess of **1** is used, the gas phase is enriched in carbon monoxide to a somewhat greater extent than in the case where equimolar amounts of the reactants are used (see Fig. 2). Evidently, this is due to the fact that at higher concentrations of disilazane, which is responsible for the disproportionation of dicobalt octacarbonyl, the contribution of this transformation increases. HPLC analysis confirms the presence of dodecacarbonyltetracobalt in the $[\mathbf{1} + Co_2(CO)_8]$ reaction mixture. This carbonyl is the main impurity, which can be removed from compound **2** by repeated recrystallization.

Reaction of compound 1 with $Fe(CO)_5$. Thermal and photolytic reactions of silicon organohydrides with iron carbonyls $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ are used to prepare iron carbonyl silyl complexes. Depending on the conditions of the reaction of silicon hydride with iron carbonyl, complexes of various structures can be obtained: three- and four-membered iron-and-silicon rings, compounds with an Fe—Fe bond and bridging CO and SiR_2 groups,[5,19,20] and compounds with agostic hydrogen atoms.[21] It was found[6] that silicon hydrides $HR_2SiXSiR_2H$ (R = Me, X = O, CH_2) react with $Fe(CO)_5$ in pentane on exposure to UV light to give five-membered rings $SiR_2XSiR_2Fe(CO)_4Fe(CO)_4$. A similar derivative (R = Ph, X = O) is formed in the reaction of $HPh_2SiOSiPh_2H$ with $Fe(CO)_5$ ($h\nu$) or $Fe_2(CO)_9$ (25 °C).[21] Our study of the reaction of **1** with $Fe(CO)_5$ showed that the N atom stops the reaction in the step of formation of the iron carbonyl hydride complex and prevents the formation of a cyclic analog of O- and CH_2-containing derivatives.

At room temperature, $Fe(CO)_5$ does not react with **1** without UV irradiation. Irradiation of a solution of **1** and $Fe(CO)_5$ in hexane results in gradual accumulation of a white precipitate of 1,3-bis(tetracarbonylhydride-iron)-1,1,3,3-tetramethyldisilazane (**3**) (Scheme 4).

Scheme 4

$$\underset{\mathbf{1}}{(HMe_2Si)_2NH} + Fe(CO)_5 \xrightarrow[25\ ^\circ C,\ 10\ h]{h\nu,\ hexane}$$

$$\longrightarrow \underset{\mathbf{3}}{[(CO)_4(H)FeSiMe_2]_2NH} + 2\ CO$$

Analysis of the gas phase shows the presence of CO (86%) and H_2 (14%). The yield of **3** is only 18%. In addition to **3**, the reaction affords other silyl iron carbonyl compounds, which, unlike **3**, are readily soluble in hexane. The attempt to separate these compounds by column chromatography (Al_2O_3) failed, apparently, due to the high reactivity of iron hyride and disilazane groups. Compound **3** can be easily separated from impurities by filtration and washing with hexane. It is a white pyrophoric powder. During storage in a sealed evacuated tube at 25 °C, its color gradually (within 2 days) changes from white to pink and then to brown. On cooling, the color change slows down (only up to light pink). At −10 °C, the compound can be kept virtually unchanged for 1 month.

The IR spectrum of **3** (Fig. 3) contains absorption bands typical of the $Fe(CO)_4$ fragment at 2000 and 600 cm^{-1}, the Si—Me bond at 1245 and 830 cm^{-1}, and the Fe—H bond at 1840 cm^{-1}. The half-width of the ν(Fe—H) band is ~150 cm^{-1}, *i.e.*, it is 3—4 times larger than the half-width of the ν(M—H) bond with terminal hydrogen atoms. This implies that the hydrogen atom of the Fe—H bond occupies a bridging position of the μ_2 or μ_3 type.[22—25] The 2500—3400 cm^{-1} range of the IR spectrum contains two absorption bands, a band at 3270 cm^{-1} ($\nu(N—H)_{assoc}$) and a broad nonresolved band at 2500—2750 cm^{-1} ($\nu(N^+H_2)$).[10] These data indicate that product **3** contains not only associated H...N fragments but also species with complete transfer of the proton from the "acid" FeH to the "base" N (Scheme 5).

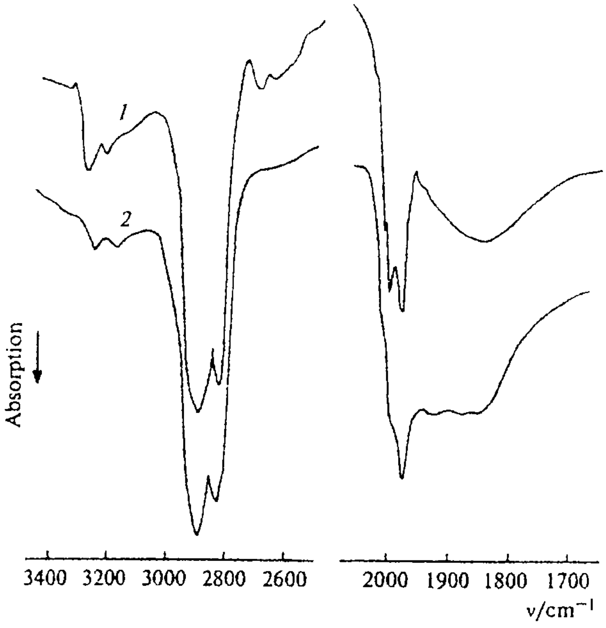

Fig. 3. IR spectrum of mineral oil mulls of compound **3** (*1*) and the product of its thermolysis (85 °C, 2 h) (*2*).

The existence of strong hydrogen bonds[22—24] resulting in the appearance of an ionic structure is the main reason for the poor solubility of complex **3** and its stability with respect to dehydrogenation giving the diirondisilazane five-membered ring $(CO)_4\overline{FeSiMe_2NHSiMe_2Fe}(CO)_4$, as has been observed for oxygen analogs of hydrodisilazane **1**, *viz.*, 1,1,3,3-tetramethyldisiloxane[6] and 1,1,3,3-tetraphenyldisiloxane.[21] An alternative route for the transformation of compound **3** is migration of the H atom from Fe to N to give an amine-stabilized dimethylsilylene iron tetracarbonyl complex, $(CO)_4Fe{=}SiMe_2 \cdot NH_2SiMe_2Fe(CO)_4H$. Two steps of this reaction can give the complex $(CO)_4Fe{=}SiMe_2 \cdot NH_3$, which would decompose with evolution of ammonia. This rearrangement of silyltetracarbonylhydride iron complexes was discovered in a study of the photochemical reaction of diethylamino(dimethyl)silane[26] and tris(dimethylamino)silane[27] with iron pentacarbonyl. Compound **3** does not react selectively according to either of the above pathways, although reactions of this type apparently do occur. Thus GLC analysis of the gas resulting from partial decomposition of **3** for 48 h at 25 °C was found to contain a small amount of hydrogen, and in the case where decomposition was carried out with heating, the gas also contained ammonia. The addition of HMPA to a dispersion of **3** in hexane induces its fast decomposition accompanied by intense evolution of NH_3.

Compound **3** slowly reacts with CCl_4 to give $CHCl_3$, CH_2Cl_2, a precipitate, and an organosilicon iron carbonyl derivative soluble in CCl_4. Transition metal hydrides are known[25] to reduce CCl_4 to $CHCl_3$. The presence of dichloromethane among the reaction products points to high reactivity of hydride **3** toward chlorinated hydrocarbons.

Scheme 5

$$\mathbf{3} \rightleftharpoons 1/2\ [HFe(CO)_4SiMe_2]_2NH_2^+\ {}^-Fe(CO)_4SiMe_2NHSiMe_2Fe(CO)_4H$$

Thermal decomposition of compounds 2 and 3. Compound **2** in the solid state is relatively stable in air. Its color changes only after 5—7 h. Solutions are more sensitive to atmospheric oxygen and moisture. Compound **2** can be sublimed *in vacuo* (0.05 Torr) but the process is accompanied by decomposition of the main bulk of the substance. Apparently, sublimation occurs *via* dissociation of **2** to an acid and a base followed by recombination of separate fragments of the molecule on a cooled surface. Decomposition starts at 90 °C and efficiently proceeds at 100—110 °C. Heating of compound **2** in sealed evacuated tubes at 150 and 250 °C results in deposition of a semitransparent mirror of metallic cobalt on the tube walls. The weight loss (63% at 250 °C) is somewhat lower than the proportion of the cobalt carbonyl part, $Co_3(CO)_{11}$, in molecule **2** (79%). During heating, the main bulk of cobalt (70%) present in compound **2** is deposited on the walls, whereas 30% remains in the solid residue.

The IR spectrum of the gases evolved at 250 °C exhibits two very intense absorption bands at 2175 and 2120 cm^{-1}, which correspond to carbon monoxide, and a series of medium-intensity bands, indicating the presence of associated ammonia molecules (3140 ($H_2NH\cdots NH_3$), 3040 ($H_2NH\cdots O{=}C$), 970, 920 cm^{-1}) and a volatile organosilicon compound (2985, 1405, 1260, and 820 cm^{-1} (Si—Me)) containing a four-membered silicon-and-nitrogen ring (1040 cm^{-1} (SiNSiN)).[28]

Analysis of the IR spectra of solid pyrolysis products shows that even at 120 °C most of the carbonyl and disilazane groups are removed from the solid phase. The spectrum still contains weak absorption bands at 2005 cm^{-1} (CO) and 930, 605 cm^{-1} (Si—N). When the temperature is increased to 150 °C, the band at 2005 cm^{-1} completely disappears, while the bands at 930 and 605 cm^{-1} disappear at 250 °C.

According to IR spectroscopic data, the final product is a polymethylsiloxane matrix (1250, 800 (Si—Me), and 1065 cm^{-1} (SiOSi)) incorporating cobalt particles. The content of cobalt is 44% (w/w). The formation of the polysiloxane occurs with participation of the O atoms of the carbonyl groups.[29] The presence of a large amount of ammonia and the absence of disilazane groups in the solid residue attest to the fact that thermal decomposition starts with dissociation of compound **2** into the "acid" $HCo(CO)_4$ and the "base" $Co_2(CO)_7(SiMe_2)_2NH$; after that, tetracarbonylcobalt hydride cleaves the Si—N and Si—Co bonds in molecule **2** to give ammonia and intermediates containing $=Co(CO)_3H$ and $-NH-SiMe_2Co(CO)_4$ fragments. Subsequent decomposition of the latter intermediate can give volatile cyclosilazanes, which are detected in the gas phase by IR spectroscopy.

Figures 4 and 5 present magnetization curves for complex **2** and solid products of its decomposition at 150 °C (SPD 150) and 250 °C (SPD 250). The initial cobalt carbonyl disilazane **2** is a weak diamagnetic containing a ferromagnetic as a microimpurity (the magnetic effects for this compound are close to zero, see Fig. 4). However, the thermolysis products are mixtures of strong ferro- and paramagnetics (see Fig. 5). The maximum specific magnetizations of ferromagnetic components of **2**, SPD 150, and SPD 250 are 0.0056, 64, and 60 G g^{-1}, respectively. In the latter cases, hysteresis is observed (see Fig. 5). Mixed para- and ferromagnetic materials have been synthesized in our previous study[30] by heating cobalt carbonyl organosilicon compounds. The maximum magnetization values found in the present study are several times higher than those published previously[30] and are attained at lower temperatures. The dependence s = *f*(*T*) also passes through a maximum.

Of all the cobalt carbonyl organosilicon compounds,[30] complex **2** is thermally the least stable. Its fast and

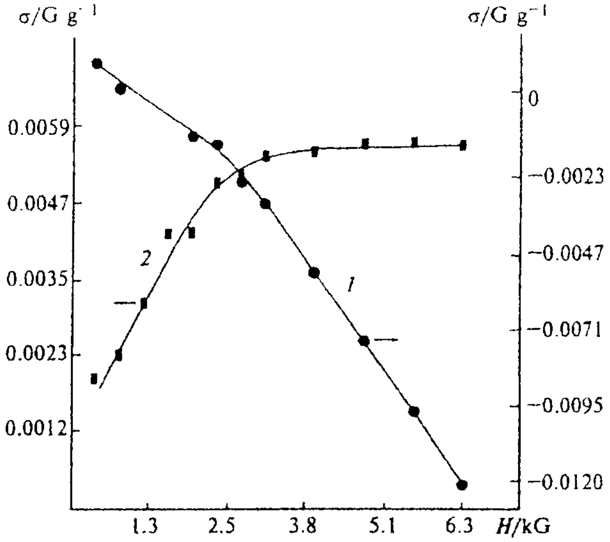

Fig. 4. Dependence of the specific magnetization (σ) on the magnetic field intensity (*H*) for compound **2**: *1*, overall curve; *2*, ferromagnetic component.

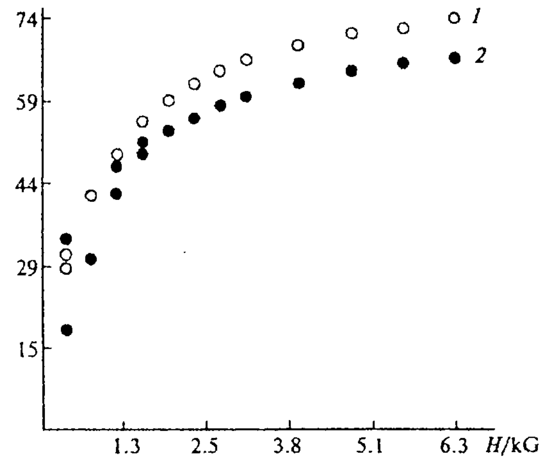

Fig. 5. Dependence of the specific magnetization (σ) on the magnetic field intensity (*H*) for the products of thermolysis of compound **2** at 150 °C (*1*) and 250 °C (*2*).

almost complete decomposition even at 150 °C is due to the presence of two components, an acid and a base, within the same molecule. Moreover, the latter is able to decompose further under the action of the former (the Si—N [31] and Si—Co [19] bonds are easily cleaved by acids). The carbonyl $HCo(CO)_4$ resulting from dissociation is also relatively thermally unstable.[13]

Heating of 3 at 85 °C for 2 h leads to evolution of carbon monoxide, ammonia, hydrogen, and iron pentacarbonyl and formation of a dark brown pyrophoric solid insoluble in $CDCl_3$. In the IR spectrum of this product (see Fig. 3), the absorption bands in the 3200 cm^{-1} region (νNH) are retained, whereas the bands in the 2500—2750 cm^{-1} range (N^+H_2) are missing. The intensity of the band at 1980 cm^{-1} (νCO) is approximately half that of the band at 1245 cm^{-1} (Si—Me) in the initial compound; this points to substantial decarbonylation of 3. A broad plateau overlapping the band at 1856 cm^{-1} (ν(Fe—H)) and caused by vibrations of the bridging CO group is observed on the low-frequency side of the band at 1980 cm^{-1}. In addition, the IR spectrum of the product exhibits two intense bands at 1015 and 790 cm^{-1} due to vibrations of the Si—O—Si fragment in cyclic siloxanes and a medium-intensity band at 925 cm^{-1} (Fe—O—Si). The intensity of the band at 850 cm^{-1} is much lower than the intensity of the band at 1245 cm^{-1}, and the band at 790 cm^{-1} has a shoulder on the high-frequency side. The reason for this intensity redistribution is elimination of one methyl group from the Me_2Si fragment. Therefore, the thermolysis product contains both Me_2Si and MeSi groups.

Thus, thermal treatment results in decarbonylation and demethylation of compound 3 and yields iron-siloxane-silazane rings and oligomers. Siloxanes are also formed in the reactions of transition metal silyl complexes containing CO groups, which serve as the source of oxygen.[29,32] Decarbonylation is accompanied by the formation of iron pentacarbonyl, carbon monoxide, and bridging CO groups. The final product contains a considerable number of iron hydride groups, whereas the content of disilazane fragments becomes very low. The N atoms are eliminated as ammonia, which results from the transfer of hydrogen from Fe to the N atom of the $H_2N^+(Si\equiv)_2$ group. Heating of 3 for 2 h at 250 °C in a sealed evacuated tube affords a ferromagnetic solid residue stable in air, whose maximum magnetization is $s = 21$ G g^{-1}. The relatively high s value indicates that the product contains a ferromagnetic phase of iron and/or its oxides.

* * *

The reactions of 1 with $Co_2(CO)_8$ and $Fe(CO)_5$ give transition metal hydrides ($HCo(CO)_4$, $HFe(CO)_4SiMe_2$), which react with a base (the NH group) as protic acids giving rise to compounds with strong acid-base interactions resulting in the formation of stable ionic compounds. The strongest acid, $HCo(CO)_4$, is completely bound[25] with the base. In the case of $HFe(CO)_4SiMe_2$, which is a weaker acid, the reaction product contains both associated fragments, HN...HFe, and groups with complete proton transfer, $H_2N^+Fe^-$. The strong acid-base interactions in products 2 and 3 influence their thermal decomposition. Both compounds decompose with evolution of ammonia, resulting from the transfer of the H atom from the acidic center, M—H, to the N atom of the $H_2N^+(SiMe_2—)_2$ group. A distinctive feature of the thermal decomposition of 2 is liberation of a large amount of metallic cobalt, whereas decomposition of 3 on moderate heating is distinguished by the retention of a substantial amount of iron hydride groups. Due to the virtually complete loss of nitrogen, the ferromagnetic products of thermolysis of 2 become encapsulated into a polymethylsiloxane (but not silazane) matrix.

Experimental

IR spectra were recorded on Perkin—Elmer-577 (solution in hexane or CCl_4, mineral oil mulls) and UR-20 (gas phase) spectrophotometers; ^1H and ^{13}C NMR spectra were measured on a Tesla BS-567 A spectrometer (100 MHz) using $CDCl_3$ as the solvent and $CHCl_3$ (δ 7.25) and $(Me_3Si)_2O$ (δ 0.055) as the internal standards. UV spectra were obtained on a Specord M-40 spectrophotometer.

HPLC analysis was performed on a Tsvet-306 liquid chromatograph with a 150×3 mm column, packed with Separon-SGX with a particle diameter of 5 mm, and a UV detector (256 nm), using hexane as the eluent. Gases were analyzed as described previously[30] on a Tsvet-530 gas chromatograph with a 0.3×100 cm stainless-steel column (NaX molecular sieves, katharometer, and argon as the carrier gas).

Magnetochemical measurements were carried out at 25 °C on a Bruker B-E15 Faraday balance. The cobalt content was found by titration.[33] Prior to the analysis, a 0.1—0.2 g sample of compound 2 or a solid product of its pyrolysis was dissolved with heating in 5 mL of concentrated HCl. The iron content in compound 3 and in the products of its thermolysis was determined by titration[33] after the sample had been decomposed first with 20% KOH and then with concentrated HNO_3 on heating.

The reactions were carried out under argon or *in vacuo*. Thermal decomposition of compounds 2 and 3 was carried out in sealed evacuated tubes.

The reaction of silazane 1 with $Co_2(CO)_8$. *A.* A solution of silazane 1 (1.15 g, 8.6 mmol) in 10 mL of benzene was added dropwise with stirring to a solution of $Co_2(CO)_8$ (2.76 g, 8.1 mmol) in 10 mL of benzene. No warming-up of the reaction mixture was observed. When 170 mL of a gas had been collected in the gas meter, the evolution slowed down. On heating of the mixture for 1.5 h at 60 °C, an additional 230 mL of a gas evolved and a black solid precipitated. The mixture was cooled, the precipitate was separated, and the filtrate was concentrated *in vacuo*. The resulting precipitate was combined with the first portion and recrystallized from CH_2Cl_2—hexane (1 : 1). HPLC analysis of the product showed the presence of $Co_4(CO)_{12}$ as an impurity. Repeated crystallization from hexane gave 1.37 g (3.08 mmol, 38%) of pure compound 2 as red thin hexahedral plates. Found (%): C, 29.14; H, 2.50; Co, 26.71. $C_{15}H_{14}Co_3NO_{11}Si_2$. Calculated (%): C, 29.19; H, 2.89; Co, 28.64. ^1H NMR ($CDCl_3$), δ: 0.059 (s, 12 H, Me). ^{13}C NMR ($CDCl_3$), δ: 1.044 and 1.159 (both s, Me). UV (hexane), λ/nm: 254, 262, 270, 295, 307, 375.

B. A degassed benzene solution (20 mL) of silazane **1** (0.82 g, 6.2 mmol) was added *in vacuo* with cooling with liquid nitrogen to $Co_2(CO)_8$ (2.16 g, 6.3 mmol). The reaction mixture was heated to ~20 °C and shaken. Gas samples for GLC analysis were withdrawn from the reactor. The H_2 : CO ratios after 20, 45, 70, and 140 h were 52 : 48, 58 : 42, 55 : 45, and 56 : 44, respectively. The solution was decanted, and the precipitate was recrystallized first from CH_2Cl_2 (−20 °C) and then from CH_2Cl_2—hexane to give 1.04 g (37%) of compound **2**.

C. Solutions of $Co_2(CO)_8$ (0.42 g, 1.2 mmol) in 5 mL of benzene and silazane **1** (0.16 g, 1.2 mmol) in 5 mL of benzene were mixed *in vacuo* in a Chugaev—Tserevitinov setup, equipped with a fluoroplastic valve, at 25 °C. The evolved gas was analyzed by GLC. The volume of a sample taken for the analysis was 50% of the total gas volume over the reaction mixture; therefore, the gas phase became enriched in the gas evolved in the final reaction steps. The data on the variation of the gas composition are presented in Fig. 2.

Reaction of silazane 1 with $Co_4(CO)_{12}$. A degassed solution of silazane **1** (0.39 g, 2.94 mmol) in 10 mL of benzene was added *in vacuo* with ice-water cooling to $Co_4(CO)_{12}$ (0.84 g, 1.46 mmol). The tube was heated to ~20 °C and periodically shaken. After 24 h, when 41 mL of a gas (H_2 : CO = 57 : 43) had been evolved, accumulation of the gas ceased. According to GLC, the degree of conversion of **1** was 33%. The benzene was removed *in vacuo*, and 10 mL of CH_2Cl_2 and 10 mL of hexane were added to the residue. The solution was decanted and analyzed by HPLC, which showed the presence of complex **2** and $Co_4(CO)_{12}$ in a ratio of ~1 : 1. We could not isolate a pure sample of compound **2** from this solution.

Thermal decomposition of compound 2. *A.* A sample of compound **2** (0.1—0.2 g) was heated in a sealed evacuated tube for 2 h at 120, 150, and 250 °C. The IR spectra of the residues, ν/cm^{-1}: 2005 (C≡O), 1245, 790 (Si—CH_3), 1205 (?), 1075, 1035 (SiOSi), 930 (Si—N) (120 °C); 1250, 800 (Si—Me), 1160 (?), 1060, 1020 (SiOSi), 930 (Si—N) (150 °C); 1250, 800 (Si—Me), 1150 (?), 1065, 1015 (SiOSi) (250 °C). GLC of the gas phase gave: CO : H_2 = 99 : 1 (150 °C); CO : CH_4 = 99.98 : 0.02 (250 °C).

B. A solution of compound **2** (0.19 g) was heated for 2 h at 250 °C to give 0.032 g of a black residue and 0.038 g of a mirror film on the tube walls. The content of Co in the residue was 44.3%, and that in the mirror film was 100%. The IR spectrum of the gas phase, ν/cm^{-1}: 3140 (N—H···NH_3); 3040 (N—H···OC); 2985, 1405, 1200, 820 (C—H); 2380 (C≡N); 1040, 970, 920 (Si—N).

1,2-Bis(tetracarbonylhydrideiron)-1,1,2,2-tetramethyldisilazane (3). $Fe(CO)_5$ (2.87 g, 14.6 mmol) was condensed into a degassed solution of silazane **1** (0.79 g, 5.95 mmol) in 20 mL of hexane. The reaction was carried out in a 55-mL quartz tube, equipped with a fluoroplastic valve, on exposure to the full radiation of a medium-pressure PRK-4 mercury lamp and with air cooling. The reaction mixture was stirred by rotation of the tube around a longitudinal axis. (The reaction performed in a quartz vessel cooled with water with stirring by an argon stream resulted in much lower degrees of conversion of the initial compounds and lower yields of compound **3** due to overgrowing of the reactor walls with a brown deposit consisting of iron carbonyl organosilicon compounds.) Gas samples were taken at definite intervals and analyzed by TLC. After each withdrawal of a sample, the reaction mixture was frozen, and the tube was evacuated. Gradually, a white precipitate accumulated and the solution turned brown. The CO : H_2 ratios after 40, 100, 160, and 240 min were 88 : 12, 89 : 11, 87 : 13, and 86 : 14, and the pressures in the tube were 360, 650, 550, and 880 Torr, respectively. The precipitate was filtered off and washed with hexane to give 0.5 g (18%) of compound **3** as a white powder, rapidly oxidized in air with evolution of a large amount of heat (samples of >0.1 g were oxidized with ignition). Found (%): C, 29.66; H, 3.66; Fe, 22.4. $C_{12}H_{15}Fe_2NSi_2$. Calculated (%): C, 30.72; H, 3.22; Fe, 23.8. IR, ν/cm^{-1}: 3270, 2700 (N—H); 2010, 2000, 1955, 630, 610, 510 (C≡O); 1840 (Fe—H); 1245, 840, 810, 750 (Si—Me); 870, 600 (Si—N).

Thermal decomposition of compound 3. *A.* A sample of compound **3** (0.13 g, 0.277 mmol) was heated for 6 h at 60 °C in a sealed evacuated tube. According to GLC, the gas phase contained H_2 and CO in 79 : 21 ratio, 0.02 mmol of hydrogen evolved, and the degree of conversion of **3** was 7.3%. The tube with the substance was evacuated, sealed, and heated again for 5 h at 60 °C. The degree of conversion of **3** was 23.2%, the overall degree of conversion was 30.5%. IR spectroscopy of the gas phase showed the presence of CO, NH_3, and $Fe(CO)_5$.

B. A sample of compound **3** (0.10 g, 0.213 mmol) was heated for 2 h at 85 °C, the volatile products being collected in a trap cooled with liquid nitrogen to give 0.062 g of a dark brown pyrophoric powder containing 18.3% iron. IR, ν/cm^{-1}: 3250, 3170 (N—H); 2010, 2000, 1980, 1930, 610 (Fe—C≡O); 1856 (Fe—H···N); 1245, 850, 790 (Si—Me); 1075, 1050, 1015 (Si—O—Si); 925 (Si—O—Fe); 970 (Si—N). The trapped material contained some $Fe(CO)_5$.

C. A sample of compound **3** (0.07 g) was heated for 2 h at 100 °C in a sealed evacuated tube. The IR spectrum of the gas phase, ν/cm^{-1}: 3340, 1630, 1035, 995, 967, 930, 890, 853 (NH_3); 2175, 2120 (CO); 2035, 2015 (Fe—C≡O). The content of iron in the solid residue was 27.2%.

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