Synthesis of New Silicon−Cobalt Clusters

Stéphane Bourg, Bruno Boury,* Francis H. Carré, and Robert J. P. Corriu

UMR 5637, CC 007, Université Montpellier II, Place E. Bataillon,
34095 Montpellier Cedex 5, France

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Four complexes of general formula (μ-(RSi−Y−SiR))$Co_2(CO)_6$ (Y = CH_2CH_2, C_6H_4, $CH_2CH_2CH_2$) were formed in the reaction of $RSiH_2Y-H_2SiR$ with dicobalt octacarbonyl. The complexes were fully characterized, and the x-ray crystal structure analyses indicate a short Si···Si transannular distance which depends on the nature and the length of the bridge Y.

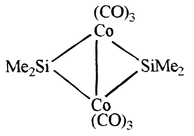
Introduction

Silicon-transition metal chemistry is involved in the catalyzed reactions of hydrosilanes or disilanes as well as in the preparation of organometallic precursors of materials.[1] Of interest are the dimeric binuclear clusters, with a four membered ring structure, M_2Si_2. Most of these structurally characterized rings have a planar geometry (for M = Pt,[2−5] Ru,[6] Mn,[7] Re,[7−9] W[10] or Ti[11]) but some of them have a butterfly geometry (for M = Pt,[12] Rh[13,14] or Co[15,16]). Various methods serve in the preparation of such clusters, but the most convenient route is the oxidative addition of an Si−H bond to the metal center followed by reductive elimination of a small molecule.[1] This is especially efficient for the synthesis of Si−Co bonded complexes which can be easily formed by reactions of a silicon hydride with dicobalt octacarbonyl (eq 1).[17]

$$Co_2(CO)_8 + 2R_3SiH \rightarrow 2R_3SiHCo(CO)_4 + H_2 \quad (1)$$

However, there are very few structurally characterized silicon−cobalt clusters. Numerous Si−Co-containing compounds have been prepared using as starting materials silanes of type $R^1R^2R^3SiH$ or $R^1R^2Si(H)-Y-Si(H)R^3R^4$ in reactions with $Co_2(CO)_8$.[18−23] Such reactions are known for germanium and tin hydrides as well. With these group 14 elements, reaction of R_2EH_2 (E = Ge or Sn) with $Co_2(CO)_8$ gave dimeric cyclic complexes of type $(OC)_3Co(\mu\text{-}ER_2)_2Co(CO)_3$.[24,25] With E = Si, this reaction is more complex. The expected $R_2HSiCo(CO)_4$ is formed, along with other polynuclear clusters, but no dimeric cyclic complex like $(OC)_3Co(\mu\text{-}ER_2)_2Co(CO)_3$ was isolated.[26,27]

However, complex **1** was prepared by reaction of $(CH_3)_2HSi-SiH(CH_3)_2$ with $Co_2(CO)_8$. The indicated structure was based on IR and NMR spectroscopic data.[28] The complexes **2** and **3** were isolated from the reaction of, respectively, $H_3Si-SiH_3$ and $H_3Si-S-SiH_3$ with $Co_2(CO)_8$ and characterized by X-ray crystal structure analysis.[16]



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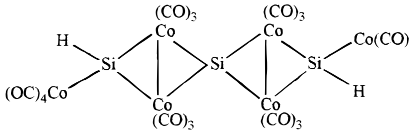

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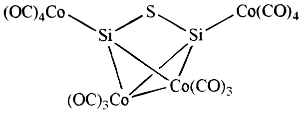

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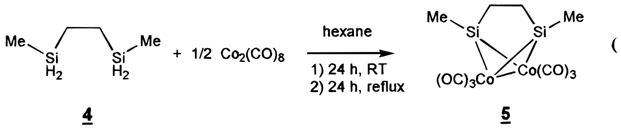
Table 1. Reaction Conditions

complex	silane[a] (mmol)	reaction conditions	yield[b] (%)
5	**4** (30)	24 h/RT and 24 h/60 °C	70
10	**6** (5)	24 h/RT and 36 h/60 °C	40
11	**7** (5)	24 h/RT	55
12	**8** (5)	24 h/RT and 120 h/60 °C	45

[a] Molar ratio silane/$Co_2(CO)_8$ = 2. [b] Yield of the crystalline, isolated complex.

Recently, we briefly reported the study of the reaction of 2,5-disilahexane, **4**, with dicobalt octacarbonyl. *A priori*, a mixture of products was expected because of the four reactive Si−H functions, but the dimeric cyclic complex **5** was isolated in 70% yield and fully characterized by X-ray crystal structure analysis (Eq 2).[29]

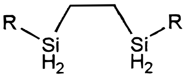


(2)

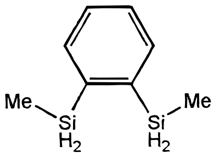
We have extended our studies of this reaction to other bis(dihydrosilyl)hydrocarbons and we report here the synthesis and structural characterization of three new silyl−cobalt complexes. These complexes are easily prepared by reaction of the corresponding bis(silyl)-hydrocarbon with dicobalt octacarbonyl. The structures of the resulting complexes were determined and the Si···Si distances are discussed along with the other geometrical parameters of the structures.

Results and Discussion

Synthesis of the Silanes. Bis(dihydrosilyl)hydrocarbons **4**, **6**, and **8** were prepared by hydrosilylation of the corresponding chlorosilanes using Speier's catalyst, leading only to the β-product of hydrosilylation, followed by reduction of the Si−Cl bonds. Compound **7** was obtained by Grignard−Wurtz coupling of methyldichlorosilane with 1,2-dibromobenzene by magnesium in THF. Compound **9** was synthesized following a procedure described by Dunoguès et al.,[30] the reaction of methyldichlorosilane and dichloromethane with magnesium and zinc in THF, followed by reduction of the Si−Cl bonds with $LiAlH_4$.



4 R = Me
6 R = Ph



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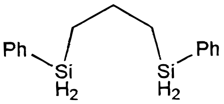

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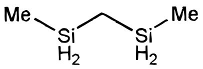

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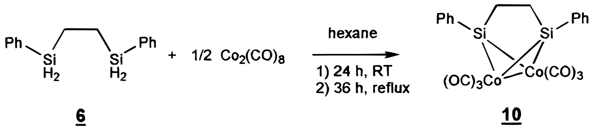
Synthesis of the Complexes. The reactions of these silanes with $Co_2(CO)_8$ were carried out in hexane using an excess of the silane. The formation of the respective products was monitored by infrared spectroscopy since the $Co_2(CO)_6$ part of the complexes resulted in a limited and characteristic number of ν_{CO} bands (eqs 3−5).[25] Reaction conditions are summarized in Table 1. All of these complexes are unstable at room temperature but can be stored for a few weeks in the crystallization solvent, at −20 °C. With silane **9**, a reaction occurred but no complex was isolated, nor could one be clearly identified since the infrared spectrum presents numerous and unidentified ν_{CO} bands.



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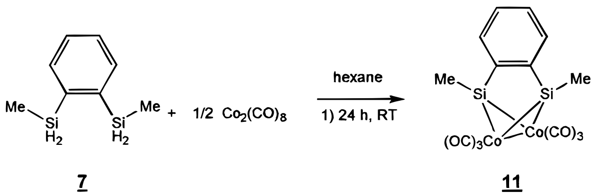

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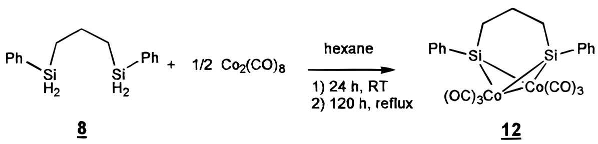
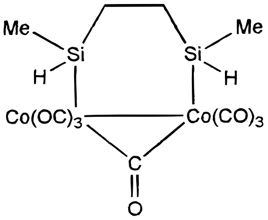


(5)

In the case of **4**, complex **13**, which may be considered as an intermediate on the way to complex **5**, was identified in the crude mixture after 24 h at room temperature. It was characterized by NMR and infrared spectroscopy (eq 2).[29] The ^1H NMR spectrum showed an Si−H signal (multiplet at 3.36 ppm) and no Si−Co−H signal, expected in the range 0 to −15 ppm. In the ^{29}Si NMR spectrum, the major signal at 60.5 ppm is attributed to **13**. The small signal at 45.8 ppm is believed to be due to $(OC)_4CoSiH(CH_3)CH_2CH_2SiH(CH_3)Co(CO)_4$ by reference to $(OC)_4CoSi(CH_3)_2CH_2CH_2Si(CH_3)_2Co(CO)_4$ (47.1 ppm).[21] A tiny signal at 57.2 ppm is unassigned. The FT-IR spectrum showed the presence of Si−H (2120 cm^{-1}) and bridging CO ligands (1835 cm^{-1}), in agreement with structure **13**. The possible presence of **14** was excluded because signals expected around −29 ppm for the remaining $SiH_2(CH_3)$ group and above 100 ppm for a silicon atom bonded to two cobalt atoms were not observed.



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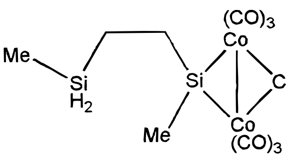

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The effect of the use of an excess of the silanes is not understood, but it clearly improves the selectivity for and the yield of the dimeric cyclic complexes.

Comparison of the Structures. The complexes **5** and **10**−**12** were fully characterized by X-ray diffraction crystal structure analysis. The ORTEP drawings of the

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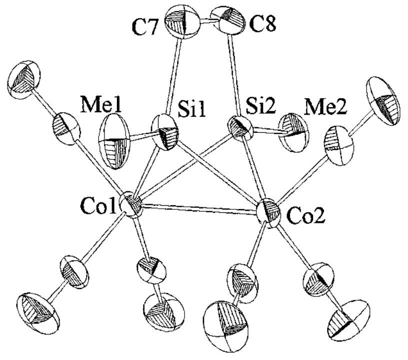

Figure 1. ORTEP drawing of complex **5**. The thermal ellipsoids are at the 30% probability level.

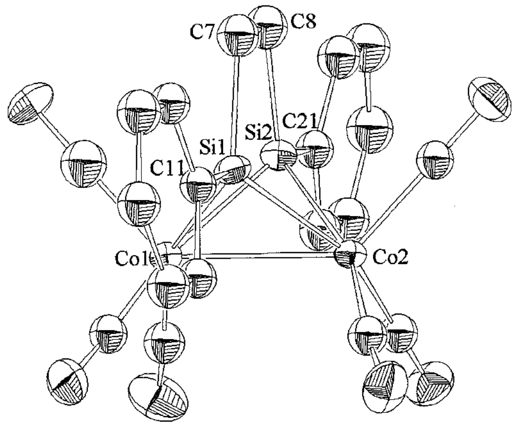

Figure 2. ORTEP drawing of complex **10**. The thermal ellipsoids are at the 30% probability level.

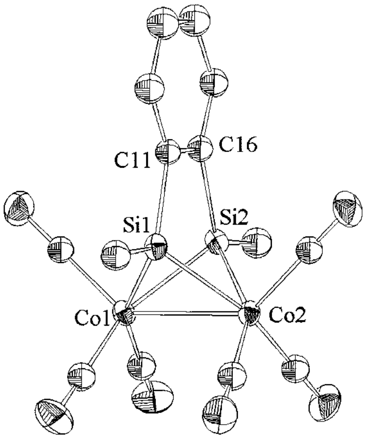

Figure 3. ORTEP drawing of complex **11**. The thermal ellipsoids are at the 30% probability level.

four structures are shown in Figures 1−4, and crystal data are summarized in Table 2. The crystal system of complex **5** is monoclinic, whereas the three other complexes crystallize in the triclinic crystal system. Selected bond angles and distances of complexes **5** and **10**−**12** are listed in Tables 3−6, respectively.

The cyclic structures of all the complexes have a butterfly geometry, and they differ from each other by the nature of the wing tip−wing tip bridge. The ORTEP drawings along the Si⋯Si axis show that the structures of complexes **5**, **10**, and **11** are very close to C_{2v} symmetry (Figure 5). In complex **12**, the structure is more distorted, due to the $-(-CH_2-)_3-$ bridge. The central carbon atom, C8, is out of the plane defined by the two silicon atoms and the two other carbon atoms of the bridge, C7 and C9. Therefore, the steric hindrance of the methylene group, C8, induces a staggered conformation of the $Co_2(CO)_6$ moiety. (Figure 6).

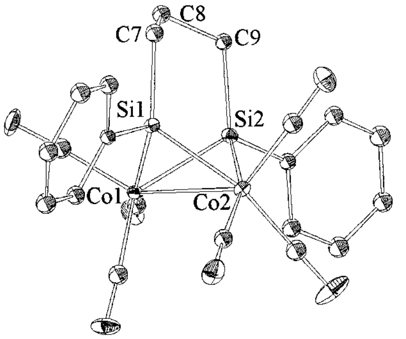

Figure 4. ORTEP drawing of complex **12**. The thermal ellipsoids are at the 30% probability level.

The value of the dihedral angle Si−C−C−Si is 2.4° in complex **5**, 1.8° in complex **10**, and 0.6° in complex **11**. The very low value of this angle in **11** is explained by the fact that the two carbon atoms of the bridge belong to the aromatic ring.

In complex **11**, the Si1−C11−C16 angle is 110.9(3)°, that is, a constraint of −9.1° compared with the normal angle of 120 °C, whereas the Si1−C7−C8 angle in complex **5** or **10** is much less constrained (108.1(4)° in **5**, 108.4(4)° in **10** instead of 109.5°). In complex **12**, Si1−C7−C8, C7−C8−C9, and C8−C9−Si2 are ∼114°, that is, a constraint of +4 to +5°.

For all the complexes, each silicon atom is bonded to two cobalt atoms with a mean Si−Co bond length of 2.29 Å, in the range of a Si−Co single bond[31,32] and near the values observed in the similar complexes **2** and **3**.[16] The Co−Co bond length is almost the same for all the complexes, between 2.61 and 2.65 Å. This value is similar to those reported for complexes **2** and **3**. This Co−Co bond length in the $Co_2(CO)_6$ moiety of these complexes is longer than those in disubstituted acetylene complexes, $(R_2C_2)Co_2(CO)_6$, described by Cotton[33] (R = *t*-Bu) or Sly[34] (R = Ph).

For compounds **5**, **10**, and **11**, with a Si−C−C−Si bridge, the Si⋯Si distance is between 2.69 and 2.73 Å. For **12**, with a $-(-CH_2-)_3-$ bridge, this distance is 2.87 Å. These transannular distances are shorter than the sum of the van der Waals radii (3.4 Å) and even in the range of the longest known Si−Si bonds.[35] In these complexes as well as in complex **3**, with a sulfur bridge (2.498(2) Å), the shortness of the Si⋯Si distance could be explained by the presence of a bonding interaction between the two silicon atoms. However, a similar distance is observed in complex **2**, with no Si−Si bond.

The Co−Si−Co angle remain almost unchanged in the different complexes but the Si−Co−Si angles vary from 65.8° in complex **3** (in which the Si⋯Si distance is the shortest) to 78° in complex **12** (in which the Si⋯Si distance is the longest) (Table 7).

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Table 2. Crystal Data, Intensity Measurements, and Refinements of Complexes 5 and 10−12

	5	**10**	**11**	**12**
formula	$C_{10}H_{10}Co_2O_6Si_2$	$C_{20}H_{14}Co_2O_6Si_2$	$C_{14}H_{10}Co_2O_6Si_2$	$C_{21}H_{16}Co_2O_6Si_2$
cryst system	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	7.683(2)	7.604(3)	7.514(2)	8.395(5)
b, Å	23.717(3)	10.263(2)	9.314(1)	9.976(6)
c, Å	8.910(2)	15.221(4)	13.367(2)	13.574(8)
α		103.43(2)	95.64(1)	89.01(5)
β	108.76(2)	95.40(3)	93.12(2)	76.13(5)
γ		109.89(2)	108.82(1)	82.11(5)
vol, $Å^3$	1537.3(5)	1066.7	877.5	1093.1
mol wt	400.1	524.37	448.27	538.4
Z	4	2	2	2
d_{calc}, g cm^{-3}	1.729	1.633	1.696	1.636
cryst size	0.2 × 012 × 0.12	0.30 × 0.10 × 0.10	0.4 × 0.08 × 0.08	0.25 × 0.12 × 0.10
cryst color	yellow	beige	beige	light yellow
recryst solvent	hexane	hexane	hexane	hexane
mp, °C	110 °C (dec)	110 °C (dec)	110 °C (dec)	110 °C (dec)
temp of data collctn	163 K	165 K	165 K	165 K
method of data collctn	ω/θ	ω/θ	ω/θ	ω/θ
radiation (graphite monochrom)	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ, cm^{-1}	23.3	16.95	20.46	16.5
2θ limits, deg	4−52	4−50	4−46	4−50
no. of unique reflns	2667	3430	2314	2723
no. of obsd reflns	2046	2662	1971	1798
final no. of variables	189	173	155	177
R	0.0386	0.0445	0.036	0.036
Rw	0.0421	0.0487	0.040	0.037
residual electron. density	0.67	0.91	0.84	0.48

Table 3. Main Interatomic Distances (Å) and Main Bond Angles (deg) of Complex 5

Co1−Co2	2.612(1)	Si1−Me1	1.855(5)
Co1−Si1	2.284(1)	Si2−Me2	1.869(7)
Co1−Si2	2.278(2)	Si1−C7	1.882(6)
Co2−Si1	2.281(1)	Si2−C8	1.889(6)
Co2−Si2	2.275(2)	Co−C	1.77 (mean)
Si1···Si2	2.691(2)	C−O	1.137 (mean)
C7−C8	1.534(8)		
Si1−Co1−Si2	72.29(5)	Co1−Si1−Me1	124.2(2)
Si1−Co2−Si2	72.39(5)	Co1−Si1−C7	111.0(2)
Co1−Si1−Co2	69.80(4)	Co2−Si1−C7	111.1(2)
Co1−Si2−Co1	70.01(5)	C7−Si1−Me1	111.3(2)
Si1−C7−C8	108.1(4)	Me1−Si1−Co2	123.4(2)
C7−C8−Si2	107.6(4)	Me1−Si1···Si2	176.5(2)
Si−Co−Co	55 (mean)	Co−C−O	178.6 (mean)

Table 4. Main Interatomic Distances (Å) and Main Bond Angles (deg) of Complex 10

Co1−Co2	2.650(1)	Si1−C11	1.867(6)
Co1−Si1	2.292(2)	Si2−C21	1.869(6)
Co1−Si2	2.295(2)	Si1−C7	1.892(6)
Co2−Si1	2.289(2)	Si2−C8	1.886(6)
Co2−Si2	2.286(2)	Co−C	1.77 (mean)
Si1···Si2	2.734(2)	C−O	1.135 (mean)
C7−C8	1.539(8)		
Si1−Co1−Si2	73.2(1)	Co1−Si1−C11	126.5(2)
Si1−Co2−Si2	73.4(1)	Co1−Si1−C7	109.9(2)
Co1−Si1−Co2	70.7(1)	Co2−Si1−C7	109.4(2)
Co1−Si2−Co1	70.7(1)	C7−Si1−C11	110.4(3)
Si1−C7−C8	108.4(4)	C11−Si1−Co2	124.2(2)
C7−C8−Si2	108.4(4)	C11−Si1···Si2	177.4(2)
Si−Co−Co	54.6 (mean)	Co−C−O	177.5 (mean)

Table 5. Main Interatomic Distances (Å) and Main Bond Angles (deg) of Complex 11

Co1−Co2	2.616(1)	Si1−Me1	1.867(5)
Co1−Si1	2.288(1)	Si2−Me2	1.859(5)
Co1−Si2	2.281(1)	Si1−C11	1.876(4)
Co2−Si1	2.290(1)	Si2−C16	1.880(4)
Co2−Si2	2.293(1)	Co−C	1.782 (mean)
Si1···Si2	2.718(1)	C−O	1.136 (mean)
C11−C16	1.416(6)		
Si1−Co1−Si2	73.0(04)	Co1−Si1−Me1	123.9(2)
Si1−Co2−Si2	72.8(04)	Co1−Si1−C11	109.3(1)
Co1−Si1−Co2	69.7(04)	Co2−Si1−C11	108.2(1)
Co1−Si2−Co1	69.8(04)	C11−Si1−Me1	113.3(2)
Si1−C11−C16	110.9(3)	Me1−Si1−Co2	125.1(1)
C11−C16−Si2	109.7(3)	Me1−Si1···Si2	177.1(2)
Si−Co−Co	55.13 (mean)	Co−C−O	178.9 (mean)

Table 6. Main Interatomic Distances (Å) and Main Bond Angles (deg) of Complex 12

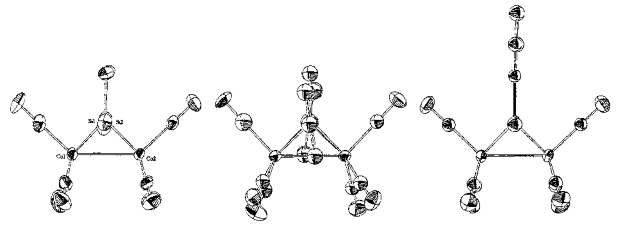
Co1−Co2	2.641(1)	Si1−C11	1.862(6)
Co1−Si1	2.268(2)	Si2−C21	1.865(6)
Co1−Si2	2.290(2)	Si1−C7	1.877(6)
Co2−Si1	2.310(2)	Si2−C9	1.883(6)
Co2−Si2	2.302(2)	C8−C9	1.532(9)
Si1···Si2	2.874(2)	Co−C	1.779 (mean)
C7−C8	1.534(9)	C−O	1.138 (mean)
Si1−Co1−Si2	78.2(1)	Co1−Si1−C11	118.2(2)
Si1−Co2−Si2	77.1(1)	Co1−Si1−C7	120.0(2)
Co1−Si1−Co2	70.5(1)	Co2−Si1−C7	115.9(2)
Co1−Si2−Co1	70.2(1)	C7−Si1−C11	106.3(3)
Si1−C7−C8	114.6(4)	C11−Si1−Co2	123.3(2)
C7−C8−C9	113.3(5)	C11−Si1···Si2	168.2(2)
C8−C9−Si2	114.0(5)	Co−C−O	176.5 (mean)
Si−Co−Co	54.8 (mean)		

Interestingly, for all the complexes of the Si_2Co_2 type that we report, the Si···Si distance is related to the nature of the bridge (Table 8).

Spectroscopic Characterizations of the Complexes. The crystalline clusters, **5** and **10**−**12**, were also characterized by NMR and infrared spectroscopies (Table 9).

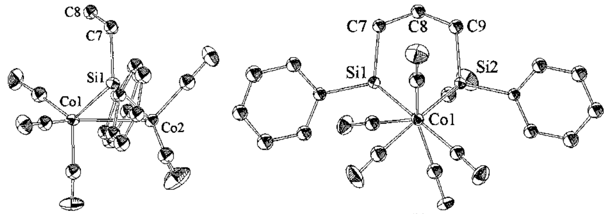
The limited number of the ν_{CO} stretching vibrations is related to the symmetrical arrangement of these ligands. With an overall molecular symmetry close to C_{2v}, five stretching modes are expected[25] and are effectively observed. Qualitatively, the spectra of all the complexes are the same, but the positions of the bands are different.

The ^{29}Si NMR spectra of the complexes exhibit signals at a chemical shift near or greater than 180 ppm. These values are some of the highest reported for a silicon



(a) complex 5 (b) complex 10 (c) complex 11

Figure 5. View of the complexes **5**, **10**, and **11** along the Si···Si axis.



(a) Si...Si axis (b) Co-Co axis. The $Co_2(CO)_6$ moiety is in a staggered conformation

Figure 6. View of complex **12** along the (a) Si···Si and (b) Co−Co axes.

Table 7. Comparison of the Main Geometrical Parameters of the Structures

cpd	Co−Si (Å av)	Co-Co (Å)	Si···Si (Å)	Co−Si−Co (deg, av)	Si−Co−Si (deg, av)
5	2.28	2.612(1)	2.691(2)	69.9	72.3
10	2.29	2.650(1)	2.734(2)	70.7	73.3
11	2.29	2.616(1)	2.718(1)	69.8	72.9
12	2.29	2.641(1)	2.874(2)	70.3	78.0
2[a]	2.29	2.615	2.85	69.5	77.1
3[a]	2.30	2.623(1)	2.498(2)	69.9	65.8

[a] Reference 16.

Table 8. Change of the Si···Si Distance as a Function of the Bridge between Si Atoms

cpd	bridge	Si···Si distance (Å)	Si−Co−Si angle (deg)
3[a]	−S−	2.498(2)	65.8
5, **11**, **10**	−C−C−	2.691(2), 2.718(2), 2.734(2)	72.3, 72.9, 73.3
2[a]	no bridge	2.85	77.1
12	−C−C−C−	2.87	78

[a] Reference 16.

chemical shift and they are related to the presence of two Si−Co bonds at each silicon atom. To our knowledge, higher values have been reported only for some silylene−ruthenium species.[37]

For all compounds, the ^{1}H NMR spectrum was recorded between 15 and −20 ppm. The absence of a resonance around −5 or −10 ppm confirms the absence of Si−H···Co or Si···H−Co links (which have been reported for some transition metal−silyl complexes[2,9,10,38,39]). The ^{1}H and ^{13}C NMR spectra, as expected, are close to those of the starting organosilicon compounds.

Conclusion

For the first time, bis(dihydrosilyl)hydrocarbons have been used successfully to prepare dimeric cyclic clusters containing a Si_2Co_2 ring. The X-ray crystal structure indicated short Si···Si distances. They will also provide useful data for Mulliken overlap calculations, leading to a better understanding of Si···Si interaction.[36]

Experimental Section

General Comments. All reactions were carried out under an atmosphere of dry nitrogen. Solvents were dried using standard techniques. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer. NMR spectra were obtained with a Bruker Advance DPX 200 (^{1}H, ^{13}C) or a Bruker WP 200 SY (^{29}Si), solvent $CDCl_3$ or C_6D_6, and TMS as an internal standard.

Mass spectra were mesured on a JEOL DX 300 by EI ionization at 30 eV.

Synthesis of (2,5-disilahexane)hexacarbonyldicobalt (**5**) was detailed in our previous communication[29] as was the intermediary compound **13**. Compound **9** was synthesized following the method described in the literature.[30]

Spectroscopic data of complexes **5** and **10**−**12** are given Table 9

1,4-Diphenyl-1,4-disilabutane (6). The 1,2-bis(phenyldichlorosilyl)ethane was prepared using the procedure described in the literature.[40] Phenyldichlorosilane (42.5 g, 0.24 mol), phenylvinyldichlorosilane (48.7 g, 0.24 mol) and $H_2PtCl_6\cdot 6H_2O$ (50 mg, 0.5 mol ‰) were mixed (without solvent) and heated for 5 h at 130 °C. By distillation (60 °C, 0.2 mmHg), 43 g (yield 47%) of the 1,1,4,4-tetrachloro-1,4-diphenyl-1,4-disilabutane was obtained.

The compound (43 g, 0.11 mol) was reduced with $LiAlH_4$ (9.5 g, 0.25 mol) in Et_2O. The mixture was hydrolyzed in HCl/ice. The separated organic layer was dried and filtered. The solvent was removed, and the product was purified by distillation (81 °C, 5 mmHg) to give 21.1 g (84 mmol, yield 75%). ^{1}H NMR ($CDCl_3$, δ, ppm) 7.65 (4H, m, Ar); 7.46 (6H, m, Ar); 4.42 (4H, m, SiH_2); 1.11 (4H, m, CH_2). ^{13}C NMR ($CDCl_3$, δ, ppm) 136.0; 132.9; 130.4; 128.8; 5.2. ^{29}Si NMR ($CDCl_3$, δ, ppm) −27.37. IR (hexane, cm^{-1}) Si−H 2137. Anal. Calcd for $C_{14}H_{18}Si_2$: C, 69.42; H, 7.44. Found: C, 69.38; H, 7.78.

1,2-Bis(methylsilyl)benzene (7). *o*-Dibromobenzene (23.6 g, 0.1 mol) in 100 mL of THF was slowly added to methyldichlorosilane (28.7 g, 0.25 mol) in 25 mL of THF and 6 g of Mg (0.25 g atom). The mixture was stirred overnight after the end of the addition. Then 100 mL of ether was added, and the mixture was filtered. The solvents were removed *in vacuo*. The residue was dissolved in pentane and filtered. Pentane was removed *in vacuo*, and the residue was treated with $LiAlH_4$ (4 g, 0.1 mol) in 200 mL of ether. After an additional hour of stirring, the mixture was poured into an aqueous solution of hydrochloric acid (pH <1). The organic layer was separed and dried. The solvent was removed by distillation at atmospheric pressure. Compound **6** was purified by distillation (125 °C, 20 mmHg). Yield 3.2 g (19%). ^{1}H NMR ($CDCl_3$, δ, ppm) 7.72 (2H, m, Ar); 7.48 (2H, m, Ar); 4.57 (4H, q, SiH_2); 1.54 (6H, t, CH_3). ^{13}C NMR ($CDCl_3$, δ, ppm) 141.3; 136.3; 129.4; −6.3. ^{29}Si NMR ($CDCl_3$, δ, ppm) −37.84. IR (hexane, cm^{-1}) Si−H 2143. Anal. Calcd for $C_8H_{14}Si_2$: C, 57.83; H, 8.43. Found: C, 57.78; H, 7.95.

1,5-Diphenyl-1,5-disilapentane (8). This compound was synthesized by hydrosilylation of 8.7 g (0.04 mol) of allylphenyldichlorosilane with 7 g (0.04 mol) of phenyldichlorosilane in hexane in the presence of ($H_2PtCl_6\cdot 6H_2O$, *i*-PrOH) . After 3 h of stirring at reflux, the solution was cooled to room

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Table 9. Spectroscopic Data of Complexes 5 and 10−12

cpd	NMR (δ, ppm)			IR (cm^{-1}) (hexane)
	^{1}H	^{13}C	^{29}Si	
5	1.36 (CH_2); 1.14 (CH_3)^a	201.5 (CO); 199.9 (CO); 16.98 (CH_3); 6.49 (CH_2)^b	210.3^b	2072.6; 2031.9; 2017.7; 1993.5; 1983.2 sh
10	7.88 (Ar); 7.54 (Ar); 1.72 (CH_2)^a	204.0 (CO); 196.8 (CO); 138.9 (Ar); 134.7 (Ar); 131.5 (Ar); 128.7 (Ar); 13.9 (CH_2)^a	196.3^b	2073.5; 2033.2; 2017.9; 1993.9; 1984.2
11	7.33 (Ar); 6.98 (Ar); 1.01 (CH_3)^a	203.9 (CO); 196.7 (CO); 131.2 (Ar); 129.5 (Ar); 128.35 (Ar); 1.35 (CH_3)^a	190.2^b	2072.7; 2034.1; 2015.7; 2003.4; 1994.0
12	7.61 (Ar); 7.40 (Ar); 2.21 (CCH_2C); 1.30 ($SiCH_2C$)^a	202.8 (CO); 198.6 (CO); 142.2 (Ar); 133.6 (Ar); 130.2 (Ar); 128.2 (Ar); 22.9 ($C\mathit{C}H_2C$); 17.9 ($Si\mathit{C}H_2C$)^a	178.0 ^{a}	2076.6; 2037.7; 2027.1; 1995.8; 1986.2 sh

^{a} $CDCl_3$. ^{b} C_6D_6.

temperature. The solvent was removed, and the residue was directly reduced with $LiAlH_4$ as described above. The compound was purified by distillation (94 °C, 5 mmHg) to give 5.25 g (50%) of 1,5-diphenyl-1,5-disilapentane. ^{1}H NMR ($CDCl_3$, δ, ppm) 7.72 (4H, m, Ar); 7.53 (6H, m, Ar); 4.50 (4H, t, SiH_2); 1.85 (2H, m, CCH_2C); 1.24 (4H, $SiCH_2C$). ^{13}C NMR ($CDCl_3$, δ, ppm) 135.8; 133.0; 130.1; 128.6; 21.5 (CCH_2C); 14.2 ($SiCH_2C$). ^{29}Si NMR ($CDCl_3$, δ, ppm) −31.47. IR (hexane, cm^{-1}) Si−H 2137. Anal. Calcd for $C_{15}H_{20}Si_2$: C, 70.31; H, 7.81. Found: C, 70.41; H, 8.52.

(1,4-Diphenyl-1,4-disilabutane)hexacarbonyldicobalt (10). To 20 mL of hexane was added 0.855 g (2.5 mmol) of dicobalt octacarbonyl and then 1.21 g (5 mmol) of 1,2-bis(phenylsilyl)ethane was added dropwise. The mixture was stirred for 24 h at room temperature and then heated at reflux for 36 h. The mixture was filtered quickly through Celite. The filtrate was concentrated and kept at −20 °C. Compound **10** crystallized as beige needles. Yield 0.71 g (55%). Mass spectrum (EI, 30 eV) parent ion M + 524. Elemental analyses were not reproductible due to the decomposition of the crystals at room temperature in sealed vials.

(1,2-Bis(methylsilyl)benzene)hexacarbonyldicobalt (11). To 20 mL of hexane was added 0.855 g (2.5 mmol) of dicobalt octacarbonyl, and then 0.83 g (5 mmol) of 1,2-bis(methylsilyl)benzene was added dropwise. The mixture was stirred for 24 h at room temperature and then was filtered quickly through Celite. The filtrate was concentrated and kept at −20 °C. Compound **11** crystallized as beige needles. Yield 0.45 g (40%). Mass spectrum (EI, 30 eV) ion M^+ 420 corresponding to the loss of one CO group. Elemental analyses were not reproductible due to the decomposition of the crystals at room temperature in sealed vials.

(1.5-Diphenyl-1,5-disilapentane)hexacarbonyldicobalt (12). To 20 mL of hexane was added 0.855 g (2.5 mmol) of dicobalt octacarbonyl, and then 1.28 g (5 mmol) of 1.5-diphenyl-1,5-disilapentane was added dropwise. The mixture was stirred for 24 h at room temperature and then heated at reflux for 120 h. The mixture was filtered quickly through Celite. The filtrate was concentrated and kept at −20 °C. Compound **12** crystallized as light yellow blocks. Yield 0.6 g (45%). Mass spectrum (EI, 30 eV) parent ion M + 538. Elemental analyses were not reproductible due to the decomposition of the crystals at room temperature in sealed vials.

Crystal Structure of Compounds 10, 11, and 12. (a) Crystal Preparation. All the crystals were grown by slowly cooling to −20 °C a hexane solution in nitrogen atmosphere. A beige needle (complexes **10**, 0.10 × 0.10 × 0.30, and **11**, 0.08x.0.8x.0.40) or a yellow block (complex **12**, 0.25 × 0.12 × 0.10 mm^3) was mounted on a Nonius CAD 4 automate diffractometer at 165 K.

(b) X-ray Data Collection. Data were collected with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Lattice constants come from a least-squares refinement of 25 reflections obtained in the range 8.4 < 2θ < 35.6 for **10**, 15.3 < 2θ < 24.1 for **11**, and 12.4 < 2θ < 30.6 for **12**. The intensities of three standard reflections were monitored at intervals of 60 min; no significant change in these intensities occurred during data collection. The structure amplitudes were obtained after the usual Lorentz and polarization reduction. Only the reflections having $F > 6\sigma(F)$ for the complexes **10** and **11** and $F > 2.5\sigma(F)$ for complex **12** were considered to be observed.

(c) Structures Determination and Refinement. The structures were solved by the direct methods (SHELXS-86 program[41]); most of the non-hydrogen atoms of each complex were positioned. A subsequent difference Fourier synthesis revealed all the remaining non-hydrogen atoms. After three least-squares refinement cycles for **10** and **11** or six for **12**, with anisotropic thermal parameters for all atoms (conventional R: 0.051 for **10**, 0.043 for **11**, and 0.045 for **12**) were performed, and then hydrogen atoms were positioned by calculation (SHELX-76 program[42]). The contribution of the hydrogen atoms made the refinement to converge to the final R (R_w) values: 0.045 (0.049) for **10**, 0.036 (0.040) for **11**, and 0.036 (0.037) for **12**.

Supporting Information Available: Full lists of atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and calculated hydrogen atom coordinates of complexes **10**−**12** (10 pages). Ordering information is given on any current masthead page.

OM970685K

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