123291-01-0; **14c** (silane entry), 123291-03-2; **14c** (coordination compound entry), 123330-17-6; **14d** (silane entry), 123291-02-1; **14e** (silane entry), 123291-06-5; **14e** (coordination compound entry), 123308-20-3; $Si(NMe_2)_4$, 1624-01-7; phenol, 108-95-2; 1-ethoxy-*N,N'*-bis(dimethylsilyl)azasilatrane (silane entry), 123291-04-3; 1-ethoxy-*N,N'*-bis(dimethylsilyl)azasilatrane (coordination compound entry), 123308-16-7; 1-hydro-*N,N'*-bis(trimethylsilyl)azasilatrane (silane entry), 123291-05-4; 1-hydro-*N,N'*-bis(trimethylsilyl)azasilatrane (coordination compound entry), 123308-19-0.

Supplementary Material Available: Tables of positional and anisotropic thermal parameters, bond lengths, least-squares planes, and bond angles (10 pages); a table of calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

Cobalt Carbonyl Complexes of Functional Ethynylsilanes. Reactivity at the Silicon Atom

Robert J. P. Corriu, Joël J. E. Moreau,* and Hervé Praet

CNRS, Unité Associée 1097, Institut de Chimie Fine, Université des Sciences et Techniques du Languedoc,
34060 Montpellier Cédex 1, France

Received May 9, 1989

The reaction of various functional ethynylsilanes with dicobalt octacarbonyl was found to give the corresponding acetylene–cobalt carbonyl complexes. The reaction of $Co_2(CO)_8$ proceeded selectively at the triple bond of most ethynylhydrosilanes. Cobalt complexes of ethynylsilanes having Si–H, Si–OR, Si–Cl, and Si–$Co(CO)_4$ bonds were obtained. The reactivity at the silicon atom in some of these complexes was studied. Reduction, alcoholysis, and aminolysis reactions were performed successfully. The reactions of strong nucleophiles such as organolithium or Grignard reagents led mainly to decomposition products. Some reactions of complexes of bis(silyl)acetylenes also were examined, and a few coordinated silacycloalkynes were isolated.

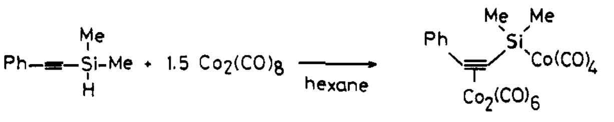
Introduction

As part of our objective to study organopolymetallic compounds, we became interested in examining the preparation and the reactivity of cobalt carbonyl complexes of ethynylsilanes. Whereas ethynyltrialkyl- or ethnyltriarylsilanes are known to react with dicobalt octacarbonyl, yielding the expected acetylene–cobalt complexes,[1-3] very few reports have dealt with complexes containing functional groups attached to the silicon atom.[4] Because of our interest in organopolymetallic compounds and polymers, we decided to prepare such functional cobalt carbonyl complexes of ethynylsilanes and to study the reactivity at the silicon center. The reactivity at a carbon atom adjacent to an organometallic moiety can be greatly affected by the metal atom. It is well established that carbenium ions are stabilized when attached α to ferrocenyl–, benchrotrenyl–, methylidyne–, or ethyne–cobalt carbonyl units.[5] The reactivity at the silicon atom in ethynylsilane–cobalt carbonyl complexes might therefore be affected by the organometallic moiety.

We wish to report here the preparation and some aspects of the reactivity at a functional silicon atom α to an acetylenic moiety complexed with a $Co_2(CO)_6$ unit. We found that various mono- and polyfunctional ethynylsilane–cobalt carbonyl complexes are accessible. Moreover, we observed that the dicobalt hexacarbonyl unit in these complexes can withstand a variety of reaction conditions, allowing various chemical transformations at the silicon center.

Results and Discussion

Reaction of Functional Ethynylsilanes with Dicobalt Octacarbonyl. In order to prepare various cobalt carbonyl complexes of ethynylsilanes having a functional group attached to silicon, we studied the reaction of functional ethynylsilanes with dicobalt octacarbonyl. We first examined the reactions of dimethyl(phenylethynyl)silane (**1**), which was easily prepared from dimethylchlorosilane and lithium phenylacetylide. Upon treatment with 1.5 mol of $Co_2(CO)_8$ in hexane, vigorous gas evolution occurred. The cobalt carbonyl complex **2** then was crystallized out of the crude reaction mixture in 84% yield (eq 1).



(1)

1

2, 84 %

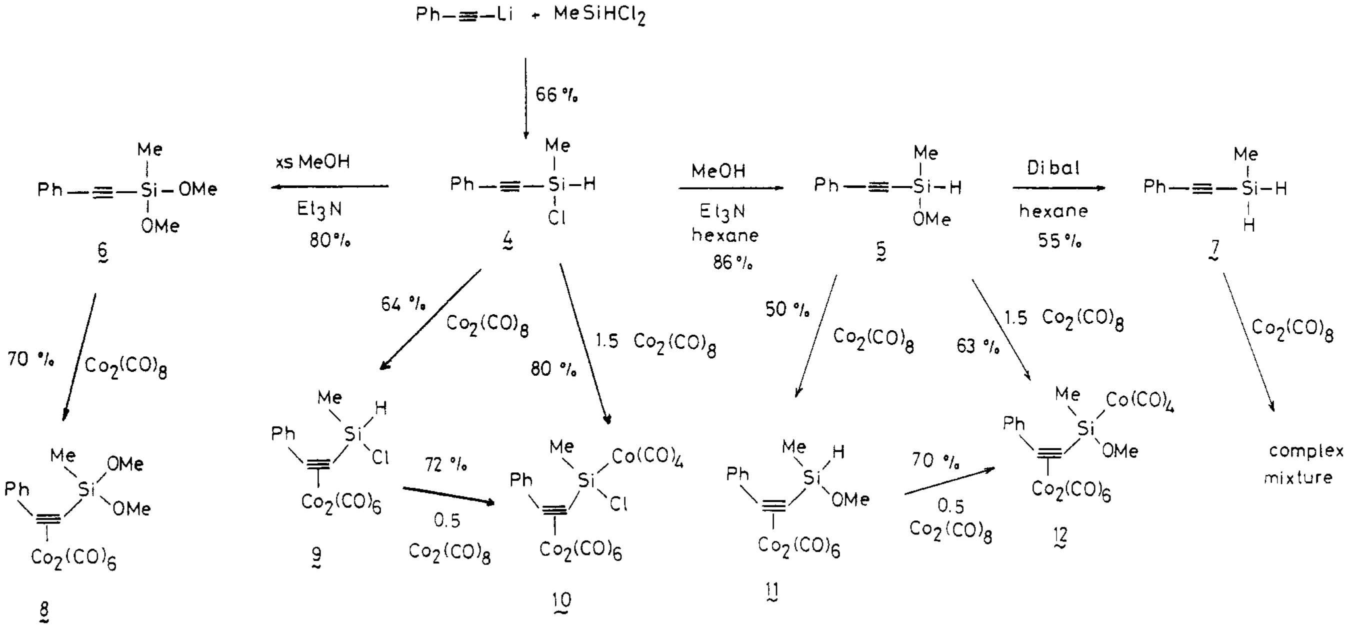
The infrared spectrum of **1** exhibited absorptions at frequencies both characteristic for acetylene–cobalt carbonyl complexes[6] and for silyl–cobalt tetracarbonyl complexes.[7,8] The reaction of $Co_2(CO)_8$ occurred both at the silicon center and at the triple bond, leading to an acetylenic complex having a silicon–cobalt bond. However, upon slow addition of a dilute solution of $Co_2(CO)_8$ to a

---

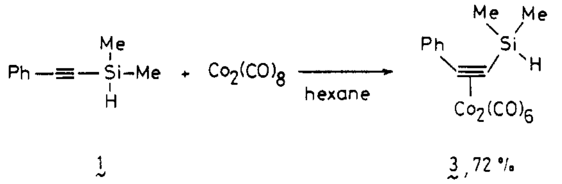
[1] Kruerke, U.; Hübel, W. *Chem. Ber.* **1961**, *94*, 2829.
[2] Seyferth, D.; White, D. L. *J. Organomet. Chem.* **1971**, *32*, 317.
[3] Pannell, K. H.; Crawford, G. M. *J. Coord. Chem.* **1973**, *2*, 251.
[4] Pannell, K. H.; Bassindale, A. R.; Fitch, J. W. *J. Organomet. Chem.* **1981**, *209*, C65.
[5] (a) Pettit, R.; Haynes, L. W. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1976; Vol. 5, p 2263 and references therein. (b) Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97. (c) Nicolas, K. M.; Nestle, M. O.; Seyferth, D. In *Transition Metal Organometallics*, Alper, H., Ed.; Academic Press: New York, 1978, Vol. 2, p 1 and references therein. (d) Seyferth, D.; Williams, G. H.; Eschbach, C. S.; Nestle, M. O., Merola, J. S.; Hallgren, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 4867.
[6] Dickson, R. S.; Fraser, P. S. *Adv. Organomet. Chem.* **1974**, *12*, 323.
[7] (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 1133. (b) Hagen, A. P.; MacDiarmid, A. G. *Inorg. Chem.* **1966**, *6*, 686; (c) Aylett, B. J.; Campbell, J. M. *Chem. Commun.* **1967**, 159.
[8] Ang, H. G.; Lau, P. T. *Organomet. Chem. Rev.* **1972**, *A8*, 135.

0276-7333/89/2308-2779$01.50/0

Scheme I. Reactions of Functional Ethynylsilanes with Dicobalt Octacarbonyl

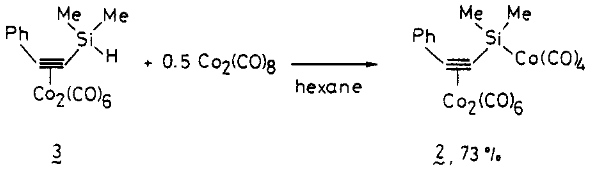


hexane solution of ethynylsilane **1**, selective complexation of the carbon–carbon triple bond (eq 2) occurred. The



(2)

hydroethynylsilane–cobalt carbonyl complex **3** was obtained as a crystalline solid in 72% yield. Complex **3** can further react with 0.5 mol of $Co_2(CO)_8$ to yield the tricobalt complex **2** (eq 3). The high selectivity observed in the



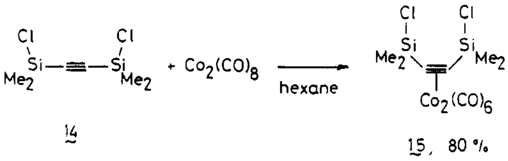
(3)

cobalt carbonyl reaction led us to examine the case of difunctional ethynylsilanes. The reactions that we performed are shown in Scheme I.

The reaction of lithium phenylacetylide with methyldichlorosilane gave the hydrochlorosilane **4** in 66% yield. From compound **4**, the reaction of 1 mol of methanol in the presence of triethylamine led to methoxysilane **5** in 86% yield. Similarly, reaction with an excess of methanol/triethylamine gave an 80% yield of the dimethoxysilane **6**. The formation of **6** resulted from the methanolysis of the silicon–chlorine bond in the first step and then from the dehydrogenative methanolysis of the silicon–hydrogen bond catalyzed by an excess of triethylamine.[9,10] Also, the dihydrosilane **7** was isolated upon *i*-Bu_2AlH reduction of methoxysilane **5**.

We then treated the various ethynylsilane **4–7** with dicobalt octacarbonyl in hexane. The reaction of the dimethoxysilane **6** gave the expected complex **8** in good yield. The reaction of the hydrochlorosilane **4** also was performed. Complex **9** was obtained in 64% yield by selective complexation of the triple bond. On the other hand, the reaction with 1.5 mol of dicobalt octacarbonyl gave an 80% yield of complex **10** having a silicon–cobalt bond. Similarly, the reaction of the methoxyhydrosilane **5** with 1 or 1.5 mol of dicobalt octacarbonyl led, respectively, to complexes **11** and **12** with good selectivities. Complexes **10** and **12** also have been obtained in high yields from the hydrosilanes **9** and **11** upon reaction of 0.5 mol of $Co_2(CO)_8$ in hexane. However, the reaction of the dihydrosilane **7** was not selective and gave a complex mixture of products from which no pure compound could be isolated. Polynuclear complexes arising from both reactions at the triple bond and at the silicon–hydrogen bond probably are formed owing to the high reactivity of the dihydride species.[11,12]

We also were interested in synthesizing acetylenic complexes containing two functional silicon atoms; hence, the known bis(dimethylsilyl)acetylenes **13**[2,13] and **14**[14] were treated with dicobalt octacarbonyl. Chlorosilane **14** in hexane gave an 80% yield of the previously mentioned[4] cobalt complex **15** (eq 4).



(4)

As in the previous case, the reaction of the acetylenic hydrosilane **13** was found to proceed selectively with $Co_2(CO)_8$, leading to complexes **16** and **17** (eq 5 and 6). Complex **16** crystallized from the reaction mixture in high yield. Crystallization of the tricobalt complex **17** was more difficult, and pure material was isolated in lower yield.

It appeared that the reactions of $Co_2(CO)_8$ with various functional ethynylsilanes allowed isolation of a variety of silylacetylene–cobalt complexes with Si–H, Si–OR, and

---

[9] Gilman, H.; Dunn, G. E.; Hartzfeld, H.; Smith, A. G. *J. Am. Chem. Soc.* **1955**, *77*, 1287.

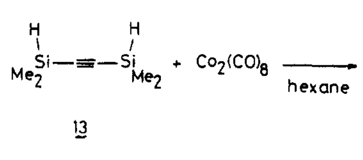
[10] Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1976**, *114*, 135.

[11] Gosbeth, P.; Vahrenkamp, H. *Chem. Ber.* **1985**, *118*, 1143.

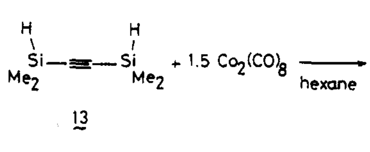
[12] Corriu, R. J. P., Moreau, J. J. E., unpublished work.

[13] (a) Seyferth, D.; White, D. L. *J. Organomet. Chem.* **1971**, *32*, 317. (b) Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem.* **1973**, *63*, 107.

[14] Frisch, K. C.; Young, R. B. *J. Am. Chem. Soc.* **1952**, *7*, 4853.



(5)



(6)

Si–Cl bonds. The formation of a Si–Co bond also is of interest since this bond is a reactive one. Substitution reactions can be performed at the silicon atom in organosilylcobalt complexes.[15,16]

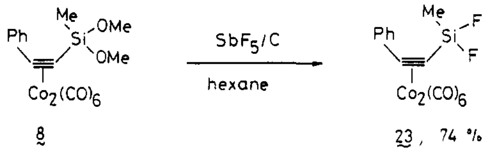
Reactivity at the Functional Silicon Atom. Having obtained various functional compounds, we then examined the chemical reactivity of these complexes in order to achieve some chemical transformations by attaching a new functional group at silicon and to explore some possible uses in organometallic synthesis.

Reactivity of the Silicon–Cobalt Bond. The silicon–cobalt bond in silyl–transition-metal complexes reacts with nucleophilic reagents. Nucleophilic substitution at the silicon atom with cleavage of the Si–Co bond occurred with various reagents.[15-19] Some of the reactions that we performed are shown in Scheme II.

The methanolysis of the silicon–cobalt bond[17] in **2** was carried out in dichloromethane solution and led to the methoxysilane **18** in high yield. The same reaction performed with the bis(silyl) complex **17** also yielded the disubstituted product **19**. In the case of the *p*-methoxyphenol reaction, however, a lower yield was obtained. The phenoxysilane **20** was formed in good yield, but we could isolate the pure product only in lower yield. The attempted reaction of **2** with aniline failed at 25 °C and led to decomposition when the mixture was heated above 50 °C. Complex **2** thus is less reactive toward aniline than $(EtO)_3Si–Co(CO)_4$.[18] The reported cleavage of the Si–Co bond by lithium aluminum hydride[19] led to decomposition in complex **2**. Similar behavior was found in the reduction of silicon derivatives of methylidyne–tricobalt nonacarbonyl clusters.[20] However, we found that upon treatment with diisobutylaluminum hydride (Dibal) in hexane, the hydrosilane **3** was formed and isolated in 47% yield.

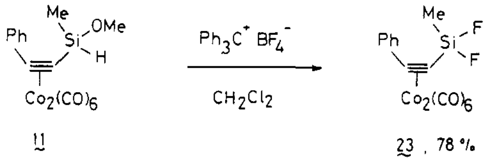
Reactivity of the Silicon–Oxygen Bond. The complexed methoxysilane **18** also represents an interesting substrate. Some reactions are represented in Scheme III.

As in the case of the silyl–cobalt complex, reduction afforded the hydrosilane **21** although it was isolated only in moderate yield. However, attempted reduction of the dimethoxy complex **8** using AlH_3 or Dibal failed. The partial formation of the expected dihydrosilane was monitored by NMR analysis of the crude mixture, but the product decomposed before it could be isolated. Methoxysilanes are also good precursors of halosilanes. The reaction of complex **18** with boron tribromide in dichloromethane allowed isolation of the bromosilane **21** in good yield. The fluorosilane **22** also was obtained in high yield from the methoxy compound **18** upon treatment with boron trifluoride etherate or antimony pentafluoride. Difluorosilanes have also been obtained from difunctional complexes. The dimethoxysilane **8** reacted with SbF_5/C in hexane to give the difluoro complex **23** (eq 7).



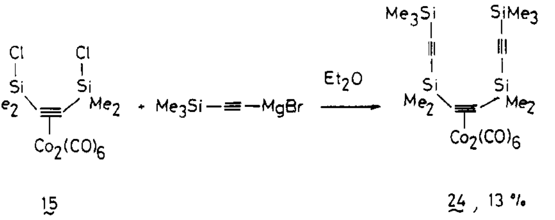
(7)

In the case of the hydromethoxysilane complex **11**, reaction with triphenylmethyl tetrafluoroborate in CH_2Cl_2 also led to the formation of the difluoro complex **24** (eq 8). First fluorination of the Si–H bond occurred with formation of Ph_3CH and BF_3. The intermediate fluoromethoxy complex thus formed could not be isolated and was converted to the difluoro complex **23** upon reaction with BF_3.



(8)

Reactions of the Silicon–Chlorine Bond. The Si–Cl bond is one of the most reactive silicon–heteroatom bonds. We looked at the reactivity of the bis(chlorosilyl) complex **15** toward nucleophiles. It turned out that the reaction of organolithium reagents (MeLi, PhLi) even at low temperature led to decomposition of the starting cobalt carbonyl complex **15**. The same decomposition occurred upon treatment with phenyl Grignard reagent. Nucleophilic attack at carbonyl ligands probably is responsible for the observed results. Such nucleophilic attack was observed on a CO ligand in a tricarbonyl(silacyclopentadiene)iron complex and took place faster than nucleophilic attack at Si. The oxycarbene intermediate underwent an intramolecular trapping reaction, allowing isolation of a (silyloxy)carbene complex.[21] Earlier reports also showed an electrophilic attack by silicon at a coordinated carbonyl group.[22] In the case of complex **15**, no intramolecular trapping occurred and decomposition was observed.



(9)

A partial substitution reaction at the silicon atom was, however, observed upon treatment of complex **15** with magnesium (trimethylsilyl)acetylide (eq 9). Complex **24** was isolated in low yield. In the case of the difunctional

---

[15] Colomer, E.; Corriu, R. J. P. *Top. Curr. Chem.* **1981**, *96*, 79 and references therein.

[16] Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. *Top. Stereochem.* **1984**, *15*, 42 and references therein.

[17] (a) Baay, Y. L.; MacDiarmid, A. G. *Inorg. Chem.* **1969**, *8*, 986; *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 159. (b) Sommer, L. H.; Lyons, J. E.; Fujimoto, H. *J. Am. Chem. Soc.* **1969**, *91*, 705.

[18] Magomedov, G. K. I.; Shkol'nik, O. V.; Syrkin, V. G.; Sigachev, S. A. *Zh. Obsch. Khim. Engl. Transl.* **1979**, 2050.

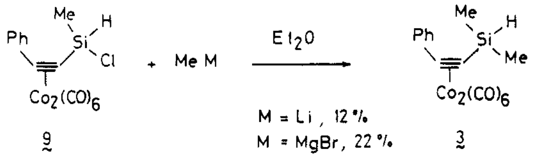
[19] Colomer, E.; Corriu, R. J. P. *J. Organomet. Chem.* **1977**, *133*, 159; *J. Chem. Soc., Chem. Commun.* **1977**, 73.

[20] Combes, C.; Corriu, R. J. P.; Henner, B. *J. Organomet. Chem.* **1981**, *221*, 257.

[21] (a) Corriu, R. J. P.; Guerin, C.; Henner, B.; Wong Chi Man, W. W. C. *J. Organomet. Chem.* **1987**, *320*, C1. (b) Carre, F. H.; Corriu, R. J. P.; Guerin, C.; Henner, B.; Wong Chi Man, W. W. C. *Ibid.* **1987**, *336*, C1.

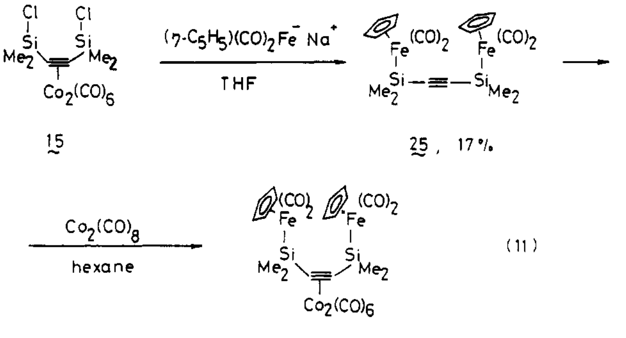
[22] (a) Curtis, D. *Inorg. Chem.* **1972**, *11*, 802. (b) Nicholson, B. K.; Simpson, J. *J. Organomet. Chem.* **1978**, *155*, 237.

complex **9**, which has a more electrophilic silicon center, a competitive reaction between the two electrophilic Si and CO centers is possible. Substitution took place at silicon although only to a moderate extent (eq 10). Reaction of



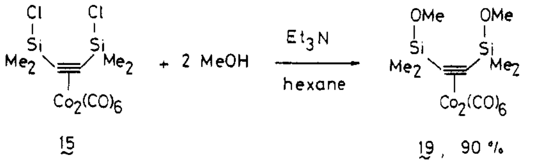
(10)

methyllithium led to the recovery of only 12% of the substitution product. The yield was improved to 22% by use of methyl Grignard reagent. Reactions at the $Co_2(CO)_6$ unit take place in most cases. Even upon reaction of the cyclopentadienyldicarbonylferrate anion, the decomplexation of the triple bond occurred. The reaction of $(\eta\text{-}C_5H_5)(CO)_2Fe^-Na^+$ was carried out in THF at -30 °C (eq 11). Complex **25** was crystallized out of the reaction mixture in 17% yield. The infrared spectrum of **26** clearly shows the absence of the $Co_2(CO)_6$ unit. Coordination of the free triple bond then was achieved by treatment with $Co_2(CO)_8$ leading to complex **26** in 77% yield. It appears that the reaction of strong nucleophiles is not selective at silicon and causes the displacement of the $Co_2(CO)_6$ unit or results in an attack at the carbonyl ligand.

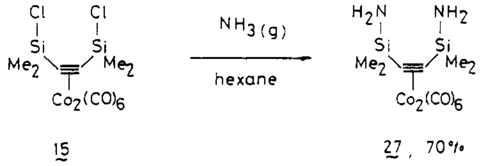


(11)

The reaction of weak nucleophiles such as methanol or ammonia, however, took place selectively at silicon. The methoxysilane complex **19** was obtained in high yield (eq 12). Interestingly, the reaction of ammonia proceeded also in high yield (eq 13). The diamino silane complex **27** is a stable red-black solid and did not spontaneously lead to the formation of macrocyclic or oligomeric silazanes.



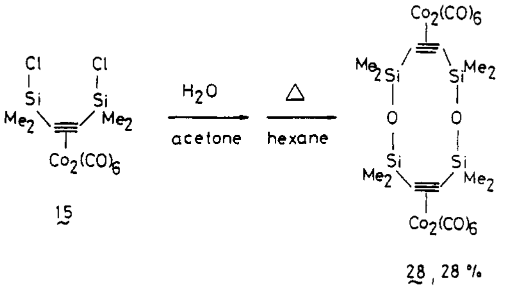
(12)



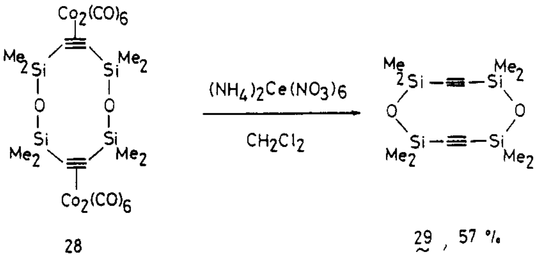
(13)

Formation of Cyclosiloxanes and Silazanes. The reactions of bis(silyl)acetylene complexes were of interest for the formation of coordinated silacycloalkynes. Cobalt and platinum complexes of organic cycloalkynes have been reported.[5c,23] The bent geometry of the silylacetylene molecule upon coordination might favor a cyclization reaction.[5c] We therefore examined a few reaction of functional bis(silyl)ethyne complexes.

The hydrolysis of the chlorosilane complex **15** was carried out in acetone giving mainly hydroxy compounds that were not isolated and upon heating led to a cyclosiloxane complex, **28** (eq 14). The analytical data are in agreement with the proposed structure. The mass spectra, however, did not show the molecular ion M^+ for m/e = 884 but rather a peak at m/e = 740 that corresponds to loss of five carbon monoxide molecules. The mass spectra then exhibited peaks corresponding to elimination of other carbonyl ligands and successive loss of four cobalt atoms. The 10-membered structure of complex **28** was confirmed by cerium(IV) oxidation that allowed recovery of the free cycloalkanediyne **29** (eq 15).

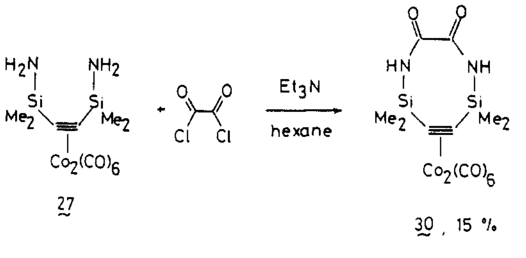


(14)

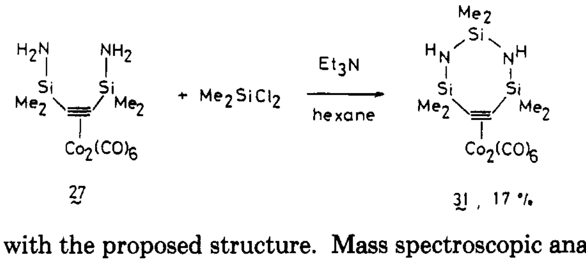


(15)

The preparation of cyclic compounds also was considered by using the diamino complex **27** as starting material. The reaction of oxalyl chloride in the presence of triethylamine gave black crystals of complex **31** in low yield (eq 16). Analytical data are consistent with the proposed 8-membered cyclic structure. However, we could not obtain a mass spectral analysis of complex **30** and an attempted decomplexation led to decomposition of the material. Therefore, we cannot exclude the formation of a larger macrocycle in eq 15. Under similar reaction conditions, we treated Me_2SiCl_2 with the diamino complex **29** to give the coordinated 7-membered disilacycloalkyne **31** in 17% yield (eq 17). All analytical data are consistent with the proposed structure. Mass spectroscopic analysis



(16)

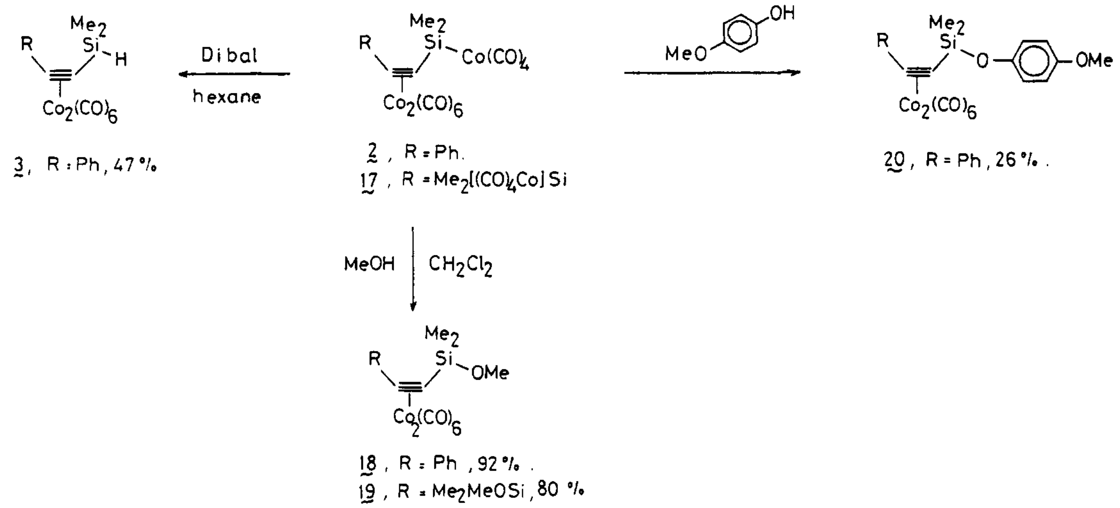


(17)

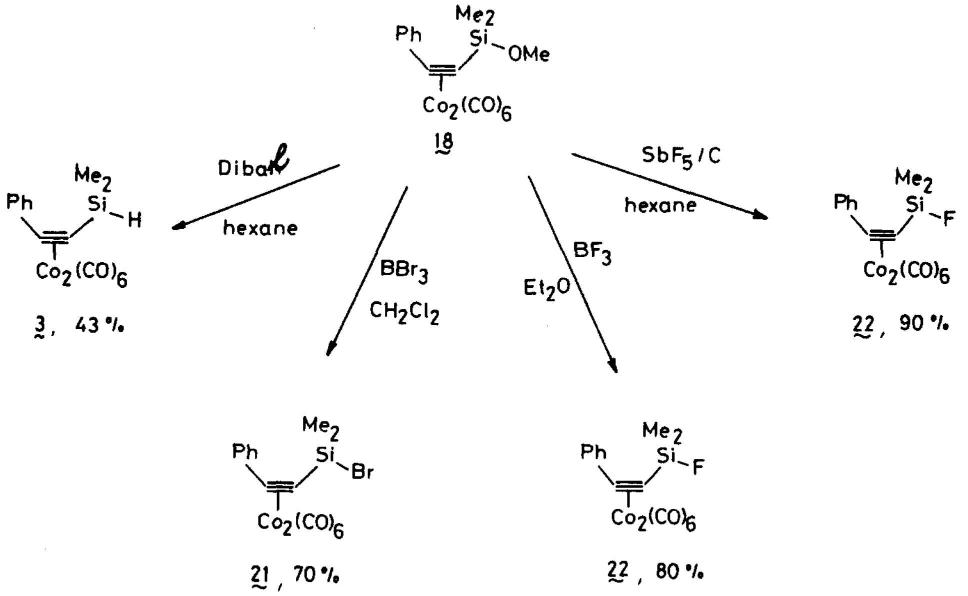
---

(23) (a) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750; (b) Petersen, H.; Meier, H. *Nouv. J. Chim.* **1980**, *4*, 687.

Scheme II. Reactions of Silyl-Cobalt Complexes 2 and 17



Scheme III. Reactions of Methoxysilane Complex 18



showed the molecular ion M^+ (m/e = 514) and successive loss of six carbon monoxide molecules and two cobalt atoms.

In conclusion, we have been able to prepare various cobalt carbonyl complexes of ethynylsilanes with functional groups at silicon. These compounds were obtained by selective complexation of functional ethynylsilanes or by reacting their cobalt carbonyl complexes. No peculiar reactivity of the Si–X bond α to an acetylene–cobalt carbonyl unit was noted.

Experimental Section

All reactions were carried out under nitrogen by use of a vacuum line and Schlenk tube techniques. Solvent were dried and distilled before use. Melting points were measured by using an oil circulating apparatus under vacuum and are uncorrected. IR spectra were recorded with a Perkin-Elmer 298 spectrophotometer in the form indicated. ^1H NMR spectra were recorded on a Varian EM 360 or EM 390 spectrometer, ^{13}C NMR spectra with a Bruker WP 80 spectrometer, and ^{29}Si NMR spectra on a Brucker WP 200 SY apparatus. (Solvents and chemical shifts (δ relative to Me_4Si) are indicated). Mass spectra were measured on a JEOL JMS-D 100 or JMS-DX 300 mass spectrometer (ionization energy 70 eV). Elemental analysis were performed by the Service Central de Micro-analyse du Centre National de la Recherche Scientifique.

Organosilane Starting Materials. Dimethyl(phenylethynyl)silane (1). A 2.5 M hexane solution of n-butyllithium (0.1 mol, 40 mL) at 0 °C was added slowly to 100 mL of a hexane solution of phenylacetylene (10.2 g, 0.1 mol) and then stirred for 1 h at room temperature. The mixture then was cooled to 0 °C and 9.45 g (0.1 mol) of dimethylchlorosilane in 100 mL of hexane slowly added. The mixture then was stirred for 12 h at room temperature, and the crude reaction mixture was poured into a 2 N aqueous HCl solution at 0 °C. After extraction with ether, the organic solution was collected and dried over Na_2SO_4 and the ether was evaporated. The residue upon distillation allowed isolation of 9.9 g of compound 1 (62%): bp^{20} 92 °C; IR (CCl_4, cm^{-1}) $\nu(C{\equiv}C)$ 2160, ν(Si–H) 2140; ^1H NMR (CCl_4, δ), 0 (6 H, d, J = 5 Hz), 3.9 (1 H, m), 6.8 (5 H, m); ^{29}Si NMR ($CDCl_3$, δ) −21.37; mass spectrum, m/e (rel int, assignment) 160 (34, M^+), 145 (100, $M^+ - CH_3$). Anal. Calcd for $C_{10}H_{12}Si$: C, 74.93; H, 7.50. Found: C, 74.72; H, 7.46.

Chloromethyl(phenylethynyl)silane (4). A solution of lithium phenylacetylide (prepared as above from 0.2 mole of phenylacetylene) was added dropwise to a solution (23 g) of methyldichlorosilane (0.2 mol) in 200 mL of hexane at −80 °C. The mixture was warmed slowly to room temperature and stirred for 12 h. The solvent then was pumped to dryness and the residue extracted several times with hexane. After evaporation of hexane, the residual oil was distilled to give 23.8 g of compound 4 (66%) with characteristics similar to those reported:[24] bp^{20} 107–108 °C;

---

[24] Florensova, D. N.; Sokolov, B. A.; Volkova, L. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* (*Engl. Transl.*) **1973**, 1390.

IR (CCl_4, cm^{-1}) ν(Si–H) 2158; ^{1}H NMR (C_6D_6, δ), 0.4 (3 H, d, *J* = 5 Hz), 5.0 (1 H, q, *J* = 5 Hz), 7.1 (5 H, m); ^{29}Si NMR ($CDCl_3$, δ) +48.38.

Methoxymethyl(phenylethynyl)silane (5). To a 500-mL hexane solution of 6.4 g (0.2 mol) of anhydrous methanol and of 25.2 g (0.25 mol) of triethylamine was added slowly, at −20 °C, 36 g (0.2 mol) of chlorosilane **4** in 200 mL of dry hexane. After the addition was completed, the mixture was stirred for an additional 4 h. The reaction mixture then was filtered to eliminate the ammonium salt. The solvent was removed by evaporation under vacuum and distillation of the residue gave 30 g (86%) of a colorless liquid: bp^{15} 105–108 °C. IR (neat, cm^{-1}) ν(Si–H,C≡C) 2160, ν(Si–O) 1060; ^{1}H NMR ($CDCl_3$, δ), 0.35 (3 H, d, *J* = 5 Hz), 3.5 (3 H, s), 4.7 (1 H, q, *J* = 5 Hz), 7.35 (5 H, m); ^{13}C NMR ($CDCl_3$, δ) 1.73, 51.92, 89.52, 106.8, 122.46, 128.44, 129.31, 132.36; ^{29}Si NMR ($CDCl_3$, δ) −22.24; mass spectrum, *m/e* (rel int, assignment) 176 (30, M^+), 175 (32, $M^+ - H$), 161 (66, $M^+ - CH_3$), 145 (40, $M^+ -$ OMe). Anal. Calcd for $C_{10}H_{12}OSi$: C, 68.13; H, 6.86. Found: C, 68.26; H, 6.72.

Dimethoxymethyl(phenylethynyl)silane (6). To a solution of chlorosilane **2** (36 g, 0.2 mol) in 400 mL of dry hexane at −20 °C was added dropwise 300 mL of an hexane solution containing 16 g (0.5 mol) of methanol and 60.6 g (0.6 mol) of triethylamine. After the addition was completed, the reaction was warmed to room temperature and stirred for an additional 6 h. The ammonium salts were eliminated by filtration and the solvents removed from the filtrate. The residue then was distilled to give 32 g (80% yield) of the dimethoxysilane **6**: bp^{15} 129–130 °C; IR (neat, cm^{-1}) ν(C≡C) 2160, ν(Si–O) 1080; ^{1}H NMR ($CDCl_3$, δ) 0.35 (3 H, s), 3.65 (6 H, s), 7.4 (5 H, m); ^{13}C NMR ($CDCl_3$, δ) −3.14, 50.92, 87.74, 122.37, 128.49, 129.35, 132.5.

Methyl(phenylethynyl)silane (7). A solution containing 5.45 g (31 mM) of **5** in 30 mL of hexane was cooled at −20 °C. Then was added dropwise 31 mL of a 1 M solution of diisobutylaluminum hydride in hexane (31 mM). The mixture was warmed to room temperature and stirred for 12 h. Hydrolysis was carried out at 0 °C with 2 N aqueous HCl. The mixture was extracted with ether and dried over Na_2SO_4, and the solvent was evaporated. Distillation of the residue afforded 2.5 g (55% yield) of methyl(phenylethynyl)silane (**7**): bp^{15} 80–82 °C; IR (neat, cm^{-1}) ν(Si–H, C≡C) 2159. ^{1}H NMR (C_6D_6, δ) 0.15 (3 H, t, *J* = 5 Hz), 4.25 (2 H, q, *J* = 5 Hz), 7.2 (5 H, m); ^{13}C NMR ($CDCl_3$, δ) −7.07, 87.05, 107.95, 122.40, 128.41, 129.10, 132.10. Anal. Calcd for $C_9H_{10}Si$: C, 73.92; H, 6.89. Found: C, 73.67; H, 6.93.

Bis(dimethylsilyl)ethyne (13). This compound was obtained according to the method described.[13]

Bis(chlorodimethylsilyl)ethyne (14). A solution of 2.8 g of the dihydrosilane **13** in 50 mL of CCl_4 was placed at 0 °C. Then was added dropwise a saturated solution of chlorine in CCl_4 under a stream of dinitrogen until a yellow color persisted. The mixture was warmed to room temperature and the solvent removed in vacuo. Distillation of the residue afforded 3.08 g (73%) of the chlorosilane **14**, bp^{20} 80 °C. The isolated compound exhibits physical characteristics similar to those reported:[14] bp^{20} 80 °C; ^{1}H NMR (CCl_4, δ) 0.56 (s).

Reactions of Ethynylsilanes with $Co_2(CO)_8$. Synthesis of Complex 2. A 100-mL pentane solution containing 14 g (87 mM) of **1** was added slowly at 25 °C to 44 g (130 mM) of $Co_2(CO)_8$ dissolved in 100 mL of pentane. The solution then was stirred for 12 h at room temperature, filtered, and pumped to dryness. The residue was dissolved in a minimum quantity of pentane, filtered, and cooled. A first crop of black crystals (45 g) were collected followed by an additional 6.7 g of compound **2** (total yield 84%): mp 88–89 °C; IR (CCl_4, cm^{-1}) ν(CO) 2096, 2088, 2056, 2033, 1998; ^{1}H NMR (C_6D_6, δ) 0.9 (6 H, s), 7.3 (5 H, br s); ^{13}C NMR ($CDCl_3$, δ) 9.9, 82.8, 107.9, 127.8, 128.5, 129.7, 137.9, 200; ^{29}Si NMR ($CDCl_3$, δ) 32.78 ($^2J_{Si-H}$ = 21 Hz); mass spectrum, *m/e* (rel int, assignment) 616 (0.7, M^+), 588 (6, $M^+ - CO$), 560 (7, $M^+ - 2\ CO$), 532 (9, $M^+ - 3\ CO$), 504 (8, $M^+ - 4\ CO$), 476 (16, $M^+ - 5\ CO$), 448 (12, $M^+ - 6\ CO$), 420 (15, $M^+ - 7\ CO$), 392 (12, $M^+ - 8\ CO$), 364 (7, $M^+ - 9\ CO$), 218 (5, $M^+ - Co_2(CO)_{10}$), 159 (18, $M^+ - Co_3(CO)_{10}$). Anal. Calcd for $C_{20}H_{11}O_{10}SiCo_3$: C, 38.98; H, 1.79. Found: C, 38.65; H, 1.60.

Synthesis of Complex 3. A solution of 8.55 g (25 mM) of $Co_2(CO)_8$ in 250 mL of hexane was added slowly to a solution of hydrosilane **1**, 4 g (25 mM) in 250 mL of hexane. The mixture was stirred for 12 h at 25 °C and then filtered. The clear filtrate was pumped to dryness and the residue dissolved in the minimum amount of hexane. After filtration, the filtrate was cooled to −20 °C for several hours. The red-black crystals that deposited [8.0 g (72%)] were collected: mp 63–64 °C; IR (CCl_4, cm^{-1}) ν(C≡O) 2090, 2054, 2024; ^{1}H NMR (C_6D_6, δ) 0.3 (6 H, d, *J* = 4 Hz), 4.85 (1 H, hept), 7.25 (5 H, m); ^{13}C NMR ($CDCl_3$, δ) −1.71, 128.1, 130.0, 138.1, 199.7; ^{29}Si NMR ($CDCl_3$, δ) +32.73. Anal. Calcd for $C_{16}H_{12}O_6SiCo_2$: C, 43.07; H, 2.72. Found: C, 43.27; H, 3.06.

Reaction of Complex 3 with $Co_2(CO)_8$. A solution containing 0.89 g (2 mM) of complex **3** and 0.34 g (1 mM) of $Co_2(CO)_8$ in 5 mL of hexane was stirred at 50 °C for 6 h. The solvent then was evaporated and the black residue extracted with pentane. Crystallization afforded 0.90 g (73%) of complex **2** as black crystals having the same characteristics as previously reported.

Synthesis of Complex 9. The reaction of the hydroethynylsilane **4** (4.8 g, 14 mM) with 2.6 g (14 mM) of $Co_2(CO)_8$ in 300 mL of hexane was conducted as for the preparation of complex **3**. Crystallization afforded 4.0 g (64%) of red-black crystals: mp 79–81 °C; IR (CCl_4, cm^{-1}) ν(Si–H) 2158, ν(C≡O) 2093, 2060, 2030; ^{1}H NMR (C_6D_6, δ) 0.5 (3 H, d, *J* = 4 Hz), 5.6 (1 H, q), 7.4 (5 H, m); ^{13}C NMR ($CDCl_3$, δ) 2.13, 128.7, 129.2, 130.2, 137.5, 200.0; Mass spectrum, *m/e* (rel int, assignment) 438 (3, $M^+ - CO$), 410 (7, $M^+ - 2\ CO$), 382 (5, $M^+ - 3\ CO$), 354 (26, $M^+ - 4\ CO$), 326 (15, $M^+ - 5\ CO$), 298 (57, $M^+ - 6\ CO$), 239 (12, $M^+ - Co(CO)_6$), 180 (60, $M^+ - Co_2(CO)_6$), 165 (100, $M^+ - CH_3Co_2(CO)_6$). Anal. Calcd for $C_{15}H_9O_6SiClCo_2$: C, 38.61; H, 1.94. Found: C, 38.91; H, 2.07.

Synthesis of Complex 10. The reaction of 2.7 g (15 mM) of hydrogenoethynylsilane **4** with 7.7 g (22.5 mM) of $Co_2(CO)_8$ in hexane similarly allowed isolation of 7.6 g (80% yield) of black crystals: mp 70–72 °C; IR (hexane, cm^{-1}) ν(C≡O) 2105, 2092, 2062, 2047, 2036, 2023, 2006; ^{1}H NMR (C_6D_6, δ) 1.2 (3 H, s), 7.4 (5 H, m); ^{13}C NMR ($CDCl_3$, δ) 14.4, 128.3, 128.9, 130.0, 137.5, 197.0, 199.3. Anal. Calcd for $C_{19}H_8O_{10}SiClCo_3$: C, 35.84; H, 1.26. Found: C, 35.63; H, 1.25.

Reaction of Complex 9 with $Co_2(CO)_8$. To a solution of 0.51 g (1.5 mM) of $Co_2(CO)_8$ in 3 mL of heptane was added a solution of 1.40 g (3 mM) of complex **9** in 3 mL of heptane. The mixture was stirred for 8 h and pumped to dryness. Extraction of the residue with hexane and cooling at −20 °C gave 1.37 g (72%) of black crystals having characteristics identical with those of complex **10** reported above.

Synthesis of Complex 11. The reactions was performed under the conditions described for the preparation of complex **9** starting from 1.5 g (8.5 mM) of the methoxysilane **5** and 2.9 g (8.5 mM) of $Co_2(CO)_8$ in 200 mL of hexane. Complex **11** (2.25 g, 50%) was isolated as black crystals: mp 42–44 °C; IR (CCl_4, cm^{-1}) ν(Si–H) 2140, ν(C≡O) 2092, 2057, 2029), ν(Si–O) 1080; ^{1}H NMR (toluene-d_8, δ) 0.4 (3 H, d, *J* = 4 Hz), 3.45 (3 H, s), 5.35 (1 H, q), 7.4 (5 H, m); ^{13}C NMR ($CDCl_3$, δ) −1.45, 52.3, 128.7, 129.1, 130.2, 138.0, 200.0. Anal. Calcd for $C_{16}H_{12}O_7SiCo_2$: C, 41.57; H, 2.61. Found: C, 41.47; H, 2.56.

Synthesis of Complex 12. The reaction was performed as for the preparation of complex **10** using 3.0 g (17 mM) of the methoxysilane **5** and 8.7 g (25 mM) of $Co_2(CO)_8$ in 150 mL of hexane. Complex **12** (6.7 g, 63%) was isolated as black crystals: mp 49–51 °C; IR (CCl_4, cm^{-1}) ν(C≡O) 2099, 2089, 2057, 2033, 1996, ν(Si–O) 1090; ^{1}H NMR (C_6D_6, δ) 0.95 (3 H, s), 3.43 (3 H, s), 7.4 (5 H, m); ^{13}C NMR ($CDCl_3$, δ), 9.45, 51.9, 81.0, 106.2, 128.0, 128.6, 130.1, 138.1, 195–200 (br); mass spectrum, *m/e* (rel int, assignment) 604 (2, $M^+ - CO$), 576 (2, $M^+ - 2\ CO$), 548 (2, $M^+ - 3\ CO$), 520 (3, $M^+ - 4\ CO$), 492 (2, $M^+ - 5\ CO$), 464 (3, $M^+ - 6\ CO$), 436 (6, $M^+ - 7\ CO$), 408 (5, $M^+ - 8\ CO$), 380 (3, $M^+ - 9\ CO$), 352 (4, $M^+ - 10\ CO$), 175 (16, $M^+ - Co_3(CO)_{10}$). Anal. Calcd for $C_{20}H_{11}O_{11}SiCo_3$: C, 38.00; H, 1.75. Found: C, 38.02; H, 1.72.

Reaction of Complex 11 with $Co_2(CO)_8$. The reaction of complex **11** was performed as for complex **9** using 0.92 g (2 mM) of complex **11** and 0.34 g (1 mM) of $Co_2(CO)_8$. Crystallization gave 0.88 g of black solid having characteristics identical with those of complex **12**.

Reactions of Silyl–Cobalt Tetracarbonyl Complexes. Methanolysis of Complex 2. To a solution of 18.5 g of complex **2** (30 mM) in 50 mL of CH_2Cl_2 was added slowly a solution of 1.00 g (30 mM) of methanol in 30 mL of CH_2Cl_2. The mixture was stirred at room temperature for 4 h and filtered. The filtrate was then pumped to dryness and the residue extracted several times with hexane. The hexane solution was concentrated in vacuo and cooled to −20 °C. The black crystals which deposited were collected and washed with cold hexane; 13.1 g (92% of complex **18** was obtained: mp 55–56 °C; IR (CCl_4, cm^{-1}) ν(C≡O) 2089, 2055, 2026; ^1H NMR (CCl_4, δ), 0.45 (6 H, s), 3.45 (3 H, s), 7.4 (5 H, m); ^{13}C NMR ($CDCl_3$, δ) −0.43, 51.04, 128.09, 128.97, 130.12, 138.33, 199.9. ^{29}Si NMR ($CDCl_3$, δ) 7.56 ($^2J_{Si-H}$ = 20 Hz); mass spectrum, *m/e* (rel int, assignment) 448 (1, $M^+ - CO$), 420 (2, $M^+ - 2\ CO$), 392 (2, $M^+ - 3\ CO$), 364 (2, $M^+ - 4\ CO$), 336 (8, $M^+ - 5\ CO$), 308 (3, $M^+ - 6\ CO$), 190 (10, $M^+ - Co_2(CO)_6$), 175 (100, $M^+ - CH_3Co_2(CO)_6$). Anal. Calcd for $C_{17}H_{14}O_7SiCo_2$: C, 42.87; H, 2.96. Found: C, 43.03; H, 2.86.

Methanolysis of Complex 17. The above reaction performed in hexane starting with 15.4 g (20 mM) of complex **17** allowed isolation of 7.8 g (80% yield) of the dimethoxy complex **19** as black crystals: mp 186–188 °C; IR (CCl_4, cm^{-1}) ν(C≡O), 2090, 2055, 2028, ν(Si–O) 1090; ^1H NMR (CCl_4, δ) 0.35 (12 H, s), 3.5 (6 H, s). Anal. Calcd for $C_{14}H_{18}O_8Si_2Co_2$: C, 34.61; H, 3.81. Found: C, 34.43; H, 3.70.

Reaction of Complex 2 with *p*-Methoxyphenol. To a solution of 2.2 g (3.5 mM) of complex **2** in 10 mL of THF was added 5 mL of a THF solution containing 0.44 g of *p*-methoxyphenol. The mixture was stirred for 3 h at 40 °C. An infrared spectrum of the crude reaction mixture showed the disappearance of absorptions at 2096 and 1998 cm^{-1} of the starting material. The solvent was removed in vacuo, and the black residue was chromatographed on a Florisil column (30–60 mesh, Fluka). Elution first with pentane and then with a pentane/ether (7/3) mixture gave 0.52 g of complex **20** as a black viscous oil (26% yield): IR (CCl_4, cm^{-1}) ν(C≡O) 2089, 2050, 2019; ^1H NMR (CCl_4, δ) 0.3 (6 H, s), 3.4 (3 H, s), 6.4 (4 H, s), 7.5 (5 H, m); ^{13}C NMR ($CDCl_3$, δ), 0.8, 55.7, 114.8, 120.3, 128.1, 128.9, 130.2, 138.0, 200.0. Anal. Calcd for $C_{23}H_{18}O_8SiCo_2$: C, 48.61; H, 3.19. Found: C, 48.36; H, 3.14.

Reaction of Complex 2 with Dibal. To a 10-mL hexane solution containing 2.3 g (3.6 mM) of complex **2** at −20 °C was added slowly 3.6 mL of a 1 M hexane solution diisobutylaluminum hydride. The mixture was warmed to room temperature, stirred for 12 h, and then hydrolyzed with a 2 N aqueous HCl solution. After extraction with ether, the organic solution was dried over Na_2SO_4 and the solvent was evaporated. The residue was chromatographed on an acid alumina column. Elution with pentane allowed recovery of 0.75 g (47%) of complex **3** having characteristics identical with those reported previously.

Reactions of Methoxysilane Complexes. Reaction of 18 with Dibal. To a 20-mL hexane solution of 2.8 g (5.9 mM) of complex **18** at −20 °C was added slowly 6 mL of a 1 M solution of diisobutylaluminum hydride in hexane. The solution was warmed to room temperature and stirred for 4 h. Treatment of the reaction mixture and isolation of the product were carried out as above to give 1.2 g (43%) of complex **3**.

Reaction of 18 with BBr_3. A 1 M solution (1.5 mL, 1.5 mM) of BBr_3 in Ch_2Cl_2 was added slowly at −78 °C to a solution containing 2.1 g (4.5 mM) of complex **18** in 10 mL of CH_2Cl_2. The mixture then was warmed to room temperature and stirred for 4 h. After evaporation of the solvent, the residue was extracted with pentane, filtered, concentrated, and cooled to −20 °C. The black crystals that deposited were recrystallized in CH_3CN to give 1.65 g (70%) of complex **21**: mp 90–92 °C; IR (CCl_4, cm^{-1}) ν(C≡O) 2090, 2054, 2023; ^1H NMR ($CDCl_3$, δ), 0.6 (6 H, s), 7.3 (5 H, m); ^{13}C NMR ($CDCl_3$, δ) 2.6, 128.1, 128.8, 130.1, 138.2, 199.8. Anal. Calcd for $C_{16}H_{11}O_6SiBrCo_2$: C, 36.59; H, 2.11. Found: C, 36.78; H, 2.13.

Reaction of 18 with $BF_3{\cdot}Et_2O$. To a solution of the methoxy complex **18** (2.1 g, 4.5 mM) in 10 mL of diethyl ether at −78 °C was added slowly 0.24 mL (2 mM) of $BF_3{\cdot}Et_2O$ diluted with 5 mL of ether. The mixture was warmed to room temperature, stirred for 4 h, and pumped to dryness, and the residue was extracted with pentane. After filtration, the solution was concentrated and cooled to −20 °C. Black crystals of fluoro complex **22** (1.67 g, 80%) were collected: mp 93–94 °C; IR (hexane, cm^{-1}) ν(C≡O) 2092, 2057, 2029; ^1H NMR ($CDCl_3$, δ) 0.6 (6 H, d, *J* = 8 Hz), 7.45 (5 H, m); ^{13}C NMR ($CDCl_3$, δ), 0.34 (d, *J* = 16.5 Hz), 128.3, 129.1, 130.0, 137.7, 199.4. Anal. Calcd for $C_{16}H_{11}O_6SiFCo_2$: C, 41.40; H, 2.38. Found: C, 41.34; H, 2.47.

Reaction of 18 with SbF_5/C. At −20 °C, a solution of 7.6 g (16 mM) of complex **18** in 40 mL of hexane was added to a suspension of 3.45 g of a 50% w/w SbF_5/graphite (Alfa) in 20 mL of hexane. The mixture was stirred for 10 h at room temperature, filtered, and pumped to dryness and the residue extracted with hexane. Crystallization as above gave 6.7 g (90%) of complex **22** with characteristics identical with those reported above.

Reaction of 8 with SbF_5/C. The reaction was carried out as above using 2.9 g (6 mM) of the dimethoxy complex **8** and 2.6 g of SbF_5/C in 30 mL of hexane. Crystallization from pentane gave 2.2 g (74%) of red-black crystals of the difluoro compound **23**: mp 76–78 °C; IR (hexane, cm^{-1}) ν(C≡C) 2098, 2065, 2035; ^1H NMR ($CDCl_3$, δ) 0.35 (3 H, t, *J* = 6 Hz), 7.4 (5 H, m); ^{13}C NMR ($CDCl_3$, δ) −3.64 (t, *J* = 20 Hz), 128.8, 129.3, 130.3, 137.4, 199.0; ^{19}F NMR (C_6D_6, δ (reference C_6F_6)) −199. Anal. Calcd for $C_{15}H_8O_6SiF_2Co_2$: C, 38.48; H, 1.72. Found: C, 38.75; H, 1.76.

Reaction of 11 with $Ph_3C^+BF_4^-$. A solution containing 0.7 g (2.2 mM) of triphenylmethyl tetrafluoroborate in 10 mL of CH_2Cl_2 was added at 0 °C to a solution of 1.0 g (2.2 mM) of complex **11** in 10 mL of CH_2Cl_2. The mixture was stirred at 0 °C for 10 h and the solvent evaporated. The residue was extracted with hexane and crystallized at −20 °C. After elimination of triphenylmethane, further crystallization gave 0.8 g (78%) of complex **23** having physical characteristics identical with those reported above.

Reactions of Chlorosilane Complexes. Reaction of Complex 9 with Methyllithium. At −78 °C, 5 mL of a 1 M ether solution of methyllithium was added slowly to a solution of 2.3 g (5 mM) of chlorosilane **9** in 20 mL of diethyl ether. The reaction mixture was warmed slowly to room temperature and stirred for 4 h. After hydrolysis with 2 N aqueous HCl, extraction with ether, and drying over Na_2SO_4, the solvent was evaporated in vacuo. The residue was purified by column chromatography (Florisil, pentane) to give 0.27 g (12%) of complex **3** identical with the compound previously obtained.

Reaction of Complex 9 with Methylmagnesium Bromide. The reaction was performed as above using 5 mL of methyl Grignard reagent (1 M solution in ether). Isolation of the product as above led to 0.48 g (22%) of the same complex **3**.

Reaction of Complex 15 with $Me_3SiC{\equiv}CMgBr$. At −20 °C, a solution of 2.5 g (5 mM) in 10 mL of THF was added to a THF solution of magnesium (trimethylsilyl)acetylide prepared from 1.0 g (10 mM) of (trimethylsilyl)acetylene in 10 mL of THF and 9 mL of a 1.1 M solution of ethylmagnesium bromide in THF. After the addition was completed, the mixture was stirred at room temperature for 10 h and at 50 °C for 2 h. After hydrolysis (2 N aqueous HCl), extraction, and drying, the solvent was evaporated. The black oily residue was purified by column chromatography (acid alumina) and eluted with a pentane/CH_2Cl_2 (9/1) mixture. The compound isolated was further purified by crystallization from methanol to give 0.4 g (13% yield) of black crystals: mp 63–64 °C; IR (CCl_4, cm^{-1}) ν(C≡O) 2083, 2046, 2020; ^1H NMR (CCl_4, δ) 0 (18 H, s), 0.35 (12 H, s); ^{13}C NMR ($CDCl_3$, δ)) −1.00, 1.08, 85.24, 89.29, 110.32, 116.00, 200.43; mass spectrum, *m/e* (rel int, assignment) 452 (1, $M^+ - 6\ CO$), 393 (4, $M^+ - Co(CO)_6$), 334 (10, $M^+ - Co_2(CO)_6$), 319 (9, $M^+ - CH_3Co_2(CO)_6$). Anal. Calcd for $C_{22}H_{30}O_6Si_4Co_2$: C, 42.57; H, 4.87. Found: C, 42.14; H, 4.80.

Reaction of 15 with $(\eta\text{-}C_5H_5)(CO)_2Fe^-Na^+$. A solution of cyclopentadienyldicarbonylferrate prepared from 3.5 g (12 mM) of $[Fe(\eta\text{-}C_5H_5)(CO)_2]_2$ and sodium amalgam in 30 mL of THF was added slowly to a hexane solution containing 3 g (6 mM) of the dichloro complex **15** at −30 °C. The mixture then was allowed to warm to room temperature and stirred for 10 h. The reaction mixture was pumped to dryness and the residue dissolved in hexane. Filtration, after cooling to −20 °C, yielded 0.50 g (17%) of yellow crystals of complex **25**: mp 68–70 °C. IR (CCl_4, cm^{-1}) ν(C≡O) 1998, 1943; ^1H NMR (CCl_4, δ) 0.5 (12 H, s), 4.7 (10 H, s); mass spectrum, *m/e* (rel int, assignment) 466 (2, $M^+ - CO$), 438 (34, $M^+ - 2\ CO$), 410 (23, $M^+ - 3\ CO$), 382 (100, $M^+ - 4\ CO$), 261 (22, $M^+ - (C_5H_5)(CO)_4Fe$). Complex **25** was further treated with 0.35 g (1 mM) of $Co_2(CO)_8$ in 30 mL of hexane. The mixture was stirred at room temperature for 12 h. After evaporation of the solvent, the residue was dissolved in hexane. Crystallization at −20 °C gave 0.60 g (77%) of black crystals of **26**: mp 90–92

°C; IR (hexane, cm^{-1}) ν(C$\equiv$O) 2081, 2047, 2020, 2000, 1950; ^{1}H NMR (CCl$_4$, δ) 0.7 (12 H, s), 4.8 (10 H, s). Anal. Calcd for $C_{26}H_{22}O_{10}Si_2Fe_2Co_2$: C, 40.03; H, 2.84. Found: C, 40.04; H, 2.67.

Methanolysis of Complex 15. At 0 °C, a solution containing 1.3 g (40 mM) of methanol in 50 mL of hexane was added to a solution of 10.0 g (20 mM) of the chloro complex **15** in 50 mL of hexane. The solution then was stirred for 12 h at 25 °C. The mixture was pumped to dryness and the residue extracted with hexane. After the filtrate was cooled, 9.0 g of black crystals of complex **9** (90%), identical with the sample previously described, was obtained.

Ammonolysis of Complex 15. Gaseous ammonia, previously dried by passing though KOH pellets, was bubbled at −20 °C into a solution containing 5.0 g (10 mM) of complex **15** in 100 mL of pentane. After an hour, the reaction mixture was filtered and pumped to dryness. Extraction of the residue with hexane and crystallization at −20 °C afforded 3.2 g of red-black crystals of diamino complex **27** (70% yield): mp 163–165 °C; IR (CCl$_4$, cm^{-1}) νN–H) 3485, 3410, ν(C$\equiv$O) 2086, 2047, 2019; ^{1}H NMR (CCl$_4$, δ) 0.35 (12 H, s) 0.75 (2 H, s); mass spectrum, *m/e* (rel int, assignment), 430 (1, $M^+ - CO$), 402 (1, $M^+ - 2\,CO$), 374 (1, $M^+ - 3\,CO$), 346 (1, $M^+ - 4\,CO$), 318 (1, $M^+ - 5\,CO$), 290 (10, $M^+ - 6\,CO$), 231 (3, $M^+ - Co(CO)_6$), 171 (1, $M^+ - Co_2(CO)_6$). Anal. Calcd for $C_{12}H_{16}O_6N_2Si_2Co_2$: C, 31.45; H, 3.51. Found: C, 31.64; H, 3.40.

Formation of Cyclosiloxanes and Silazanes. Hydrolysis of Complex 15. A solution of 5 g (10 mM) of dichloro complex **15** and 10 mL of water in 50 mL of acetone was stirred for 10 h at room temperature. After solvents were removed in vacuo, the residue was dissolved in 100 mL of hexane and heated to 60 °C for 2 h. The mixture was filtered, concentrated, and cooled at −20 °C to give 1.25 g (28%) of complex **28** as black crystals: mp 137–138 °C; IR (CCl$_4$, cm^{-1}) ν(C$\equiv$O) 2096, 2058, 2028, ν(Si–O) 1075; ^{1}H NMR (CCl$_4$, δ) 0.4 (s); mass spectrum, *m/e* (rel int, assignment) 744 (0.5, $M^+ - 5\,CO$), 660 (2, $M^+ - 8\,CO$), 604 (1, $M^+ - 10\,CO$), 576 (1, $M^+ - 11\,CO$), 548 (1, $M^+ - 12\,CO$), 489 (1; $M^+ - Co(CO)_{12}$), 430 (3, $M^+ - Co_2(CO)_{12}$), 371 (4, $M^+ - Co_3(CO)_{12}$), 312 (16, $M^+ - Co_4(CO)_{12}$), 297 (100, $M^+ - CH_3Co_4(CO)_{12}$). Anal. Calcd for $C_{24}H_{24}O_{14}Si_4Co_4$: C, 32.59; H, 2.73. Found: C, 32.18; H, 3.03. Complex **28** was added to a solution containing 0.8 g (15 mM) of ceric ammonium nitrate in 10 mL of acetone and stirred until the black color disappeared. The solvent then was removed and the residue extracted with pentane. Crystallization afforded 0.24 g (57%) of colorless crystals of compound **29**: mp 110–112 °C; IR (CCl$_4$, cm^{-1}) ν(Si–C) 1258, ν(Si–O) 1060; ^{1}H NMR (CCl$_4$, δ) 0.02 (s); ^{13}C NMR (CDCl$_3$, δ) 1.87, 112.88; mass spectrum, *m/e* (rel int, assignment) 312 (50, M^+), 297 (100, $M^+ - CH_3$).

Reaction of Complex 27 with Oxalyl Chloride. A solution of 0.55 mL (6.5 mM) of oxalyl dichloride in 60 mL of pentane was added at −20 °C to a solution containing 3.0 g (6.5 mM) of diamino complex **27** and 1.6 mL (20 mM) of triethylamine in 60 mL of pentane. The mixture was stirred for 12 h at room temperature and filtered. Evaporation of the pentane, followed by extraction of the residue with hexane, led to the isolation of 0.5 g (15% yield) of black crystals of complex **30**: mp 150 °C dec; IR (CCl$_4$, cm^{-1}) ν(N–H) 3340, ν(C$\equiv$O) 2080, 2042, 2016, ν(C=O) 1680; ^{1}H NMR (CDCl$_3$, δ) 0.65 (12 H, s) 1.35 (2 H, s). Anal. Calcd for $C_{14}H_{14}O_8N_2Si_2Co_2$: C, 32.82; H, 2.75. Found: C, 32.85; H, 3.06.

Reaction of Complex 27 with Dimethyldichlorosilane. A solution of dimethyldichlorosilane (0.86 mL, 7.2 mM) in 70 mL of hexane was added at 0 °C to a solution containing 3.3 g (7.2 mM) of complex **27** and 1.6 mL (20 mM) of triethylamine in 70 mL of hexane. The mixture was stirred at room temperature for 12 h and filtered, and the solvent was evaporated. The residue was extracted with hexane and crystallization afforded 0.60 g (17%) of black crystals of complex **31**: mp 192.193 °C dec; IR (CCl$_4$, cm^{-1}) ν(N–H) 3320, ν(C$\equiv$O) 2080, 2040, 2019; ^{1}H NMR (CCl$_4$, δ) 0.3 (s); ^{13}C NMR (CDCl$_3$, δ) 1.56, 5.39; mass spectrum, *m/e* (rel int, assignment) 514 (4, M^+), 486 (6, $M^+ - CO$), 458 (8, $M^+ - 2\,CO$), 430 (13, $M^+ - 3\,CO$), 402 (1, $M^+ - 4\,CO$), 374 (4, $M^+ - 5\,CO$), 346 (4, $M^+ - 6\,CO$), 287 (1, $M^+ - Co(CO)_6$), 228 (1, $M^+ - Co_2(CO)_6$), 213 (2, $M^+ - CH_3Co_2(CO)_6$). Anal. Calcd for $C_{14}H_{20}O_6N_2Si_3Co_2$: C, 32.68; H, 3.91. Found: C, 32.45; H, 3.74.

Molybdenum Carbyne, Vinylidene, and Ketenyl Complexes with Hydrotris(3,5-dimethylpyrazolyl)borate Ligands

Douglas C. Brower, Michaela Stoll, and Joseph L. Templeton*

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

Received May 16, 1989

Treatment of Tp′(CO)$_2$Mo[η^2-C(O)R] η^2-acyl complexes with excess sodium ethoxide in refluxing ethanol affords carbyne complexes Tp′(CO)$_2$Mo(CR) (Tp′ = hydrotris(3,5-dimethylpyrazolyl)borate; R = methyl, ethyl). The carbyne complexes can be deprotonated at low temperature to form anionic vinylidene complexes that are susceptible to electrophilic attack by methyl iodide or ethyl iodide at the vinylidene β-carbon. Photochemical carbonyl substitution occurs in acetone or acetonitrile solvent for the methyl carbyne complex, but the known phenyl analogue undergoes photochemical carbonyl–carbyne coupling to form an η^2-ketenyl complex under these conditions.

Transition-metal carbyne complexes can be prepared by a number of routes,[1] including the classic Fischer preparation involving abstraction of alkoxide from alkoxycarbene complexes,[2] abstraction of α-hydrogen from Schrock-type alkylidene complexes,[3] and rearrangement of σ-vinyl complexes.[4] The formal abstraction of oxide, O^{2-}, from metal acyl precursors[5] with strong Lewis acids has been developed by Mayr[6] into an efficient approach to group VI carbynes (eq 1). Stone and co-workers[7] have applied this protocol to prepare a series of Cp(CO)$_2$M(CAr)

---

(1) Kim, H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51.

(2) Fischer, E. O.; Schubert, U. *J. Organomet. Chem.* **1975**, *100*, 59.

(3) (a) Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 2935. (b) Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932.

(4) Green, M. *J. Organomet. Chem.* **1986**, *300*, 93.

(5) (a) Fischer, H.; Fischer, E. O. *J. Organomet. Chem.* **1974**, *69*, C1. (b) Himmelreich, D.; Fischer, E. O. *Z. Naturforsch.* **1982**, *37B*, 1218.

(6) McDermott, G. A.; Dorries, A. M.; Mayr, A. *Organometallics* **1987**, *6*, 925.

(7) Dossett, S. J.; Hill, A. F.; Jeffery, J. C.; Marken, F.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1988**, 2443.

0276-7333/89/2308-2786$01.50/0 © 1989 American Chemical Society