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Cobalt-Assisted Silicon−Silicon Bond Activation

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A number of oligosilylalkynes were converted to the respective dicobalt hexacarbonyl complexes. These compounds were found to be surprisingly reactive, indicating Si−Si bond activation in the coordination sphere of the cobalt atoms. The presence of more than one silicon−silicon bond restricted clean conversions, and therefore the pentamethyldisilanylphenylacetylene complex was prepared, which engaged in defined reactions. The rearrangement of an oligosilylalkyne dicobalt hexacarbonyl complex to a dicobalt hexacarbonyl bis(dialkylsilylene) complex was observed. The reaction of tris(trimethylsilyl)silane with dicobalt octacarbonyl yielded the product of formal replacement of two carbonyl ligands with dimethylsilylene groups.

Introduction

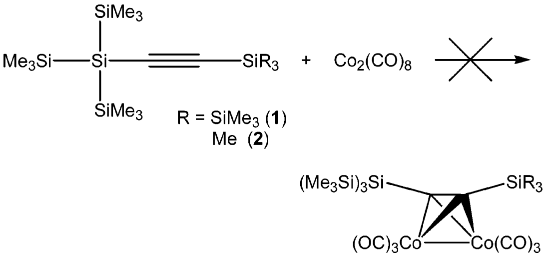
Over the last decades organocobalt chemistry has developed into a very vital field of organic and inorganic synthesis.[1] The fact that two carbonyl ligands in dicobalt octacarbonyl can be replaced by an alkyne was recognized in the early 1950s.[2] Since then, numerous complexes of this and related types have been prepared.[3]

One reason for the huge interest in this class of compounds is the stabilization of a positive charge in the α-position of an alkyne upon complexation. The Nicholas reaction, which is the reaction of a cobalt-coordinated propargyl alcohol with a nucleophile, depends on this effect.[4]

Also silyl-substituted alkynes have been subjected successfully to complexation conditions with dicobalt octacarbonyl.[5] To assess the enhanced chemical reactivity of silyl groups in the α-position of a complexed alkyne, Corriu et al. have investigated the reactivity of methoxy- and halosilyl alkynes.[6] Reactions such as alkylation, reduction, hydrolysis, and halogenation could be carried out at the coordinated compounds.[6] In a subsequent study the enhanced reactivity of the Si−H bond of a coordinated hydrosilylalkyne was found and investigated.[7] In another report Brook and co-workers have studied the prospects of generating transition metal-stabilized silylium cations.[8] It is interesting to notice that among all the reported examples of silylalkynes coordinated to the dicobalt hexacarbonyl fragment there are only three containing an oligosilyl unit.[9] Also the number of compounds with a cobalt-oligosilyl substructure is still very small.[10,11] As we have recently started to investigate the chemistry of oligosilylalkynes,[12] we also became interested in the possibility of studying cobalt complexes of these compounds.

Results and Discussion

Our first attempts to obtain a cobalt carbonyl oligosilylalkyne complex concentrated on bis[tris(trimethylsilyl)silyl]acetylene (**1**), which is easily available from tris(trimethylsilyl)silyl chloride and dilithium acetylide. However, while the reaction of bis(trimethylsilyl)acetylene with dicobalt octacarbonyl has been reported,[5] we were not able to obtain the bis[tris(trimethylsilyl)silyl]acetylene complex. As it is likely that steric reasons are responsible for this failure, we replaced one of the bulky tris(trimethylsilyl)silyl groups with trimethylsilyl. Nonetheless, also [tris(trimethylsilyl)silyl]trimethylsilylacetylene (**2**) did not react with dicobalt octacarbonyl.



Complete removal of the silyl substituent on one side of the alkyne (**3**) eventually led to success, and we were able to obtain the first oligosilylacetylene dicobalt hexacarbonyl complex (**3a**).

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(1) (a) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081−1119. (b) Welker, M. E. *Curr. Org. Chem.* **2001**, *5*, 785−807.

(2) Sternberg, H. W.; Greenfield, H.; Friedel, R. A.; Wotjz, J.; Markby, R. Wender, I. *J. Am. Chem. Soc*. **1954**, *76*, 1457−1458.

(3) (a) Dickson. R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323−377. (b) Went, M. J. *Adv. Organomet. Chem.* **1997**, *41*, 69−125.

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(5) (a) Krüerke, U.; Hübel, W. *Chem. Ber*. **1961**, *94*, 2829−2856. (b) Seyferth, D.; White, D. L. *J. Organomet. Chem.* **1971**, *32*, 317−322. (c) Pannell, K. H.; Crawford, G. M. *J. Coord. Chem.* **1973**, *2*, 251−255.

(6) Corriu, R. J. P.; Moreau, J. J. E.; Praet, H. *Organometallics* **1989**, *8*, 2779−2786.

(7) Corriu, R. J. P.; Moreau, J. J. E.; Praet, H. *Organometallics* **1990**, *9*, 2086−2091.

(8) (a) Ruffolo, R.; Decken, A.; Girard, L.; Gupta, H. K.; Brook, M. A.; McClinchey, M. J. *Organometallics* **1994**, *13*, 4328−4335. (b) Ruffolo, R.; Kainz, S.; Gupta, H. K.; Brook, M. A.; McGlinchey, M. J. *J. Organomet. Chem.* **1997**, *547*, 217−226.

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(10) (a) Hengge, E.; Siegl, H.; Stadelmann, B. *J. Organomet. Chem.* **1994**, *479*, 187−192. (b) Hengge, E.; Eibl, M.; Stadelmann, B. *Monatsh. Chem.* **1993**, *124*, 523−528. (c) Hengge, E.; Eibl, M. *Organometallics* **1991**, *10*, 3185−3189.

(11) (a) Pakkanen, T.; Kerber, R. C. *Inorg. Chim. Acta* **1981**, *49*, 47−52. (b) Kerber, R. C.; Pakkanen, T. *Inorg. Chim. Acta* **1979**, *37*, 61−65.

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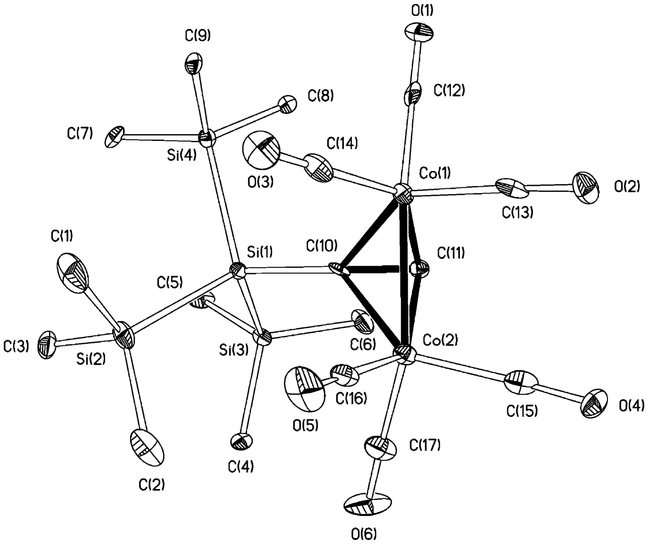
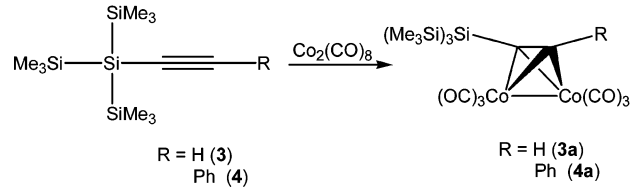


Figure 1. Molecular structure and numbering of **3a**. Selected bond lengths [Å] and bond angles [deg] with SDs: Co(1)−C(11) 1.957(10), Co(1)−C(10) 2.013(9), Co(1)−Co(2) 2.469(2), O(2)−C(13) 1.127(13), Si(1)−C(10) 1.878(10), Si(1)−Si(2) 2.348(4), Si(1)−Si(4) 2.362(4), Si(1)−Si(3) 2.367(4), C(10)−C(11) 1.310(15), C(11)−Co(1)−C(10) 38.5(4), C(11)−Co(1)−Co(2) 50.3(3), C(10)−Co(1)−Co(2) 52.4(3), C(10)−Si(1)−Si(2) 115.8(3), C(10)−Si(1)−Si(4) 108.0(3), Si(2)−Si(1)−Si(4) 111.06(15), C(10)−Si(1)−Si(3) 106.4(3), Si(2)−Si(1)−Si(3) 108.39(15), Si(4)−Si(1)−Si(3) 106.67(14), C(11)−C(10)−Si(1) 142.7(8), C(11)−C(10)−Co(1) 68.4(6), Si(1)−C(10)−Co(1) 137.6(5), C(11)−C(10)−Co(2) 67.3(6), Si(1)−C(10)−Co(2) 134.6(5), Co(1)−C(10)−Co(2) 75.5(3), C(10)−C(11)−Co(2) 74.2(6), C(10)−C(11)−Co(1) 73.1(6).

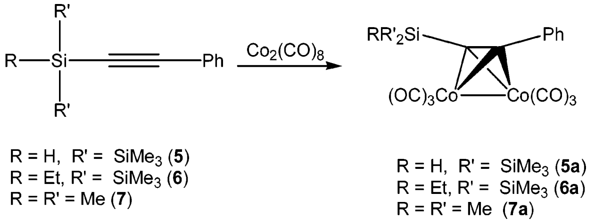
Also phenyl[tris(trimethylsilyl)silyl]acetylene (**4**) reacted smoothly to complex **4a**.



R = H (**3**)
Ph (**4**)

R = H (**3a**)
Ph (**4a**)

Both compounds were subjected to crystal structural analysis (Figures 1 and 2). In a similar way, also other compounds containing the silylated phenyl acetylene unit, including the known compound **7a**,[5] could be obtained.



R = H, R' = SiMe3 (**5**)
R = Et, R' = SiMe3 (**6**)
R = R' = Me (**7**)

R = H, R' = SiMe3 (**5a**)
R = Et, R' = SiMe3 (**6a**)
R = R' = Me (**7a**)

Chromatographic purification of dicobalt carbonyl alkyne complexes is a common practice.[3] It is also known that these complexes are fairly air stable. However, this was not the case with our compounds containing the oligosilyl unit (**3a**−**6a**), which rapidly decomposed when exposed to ambient conditions.

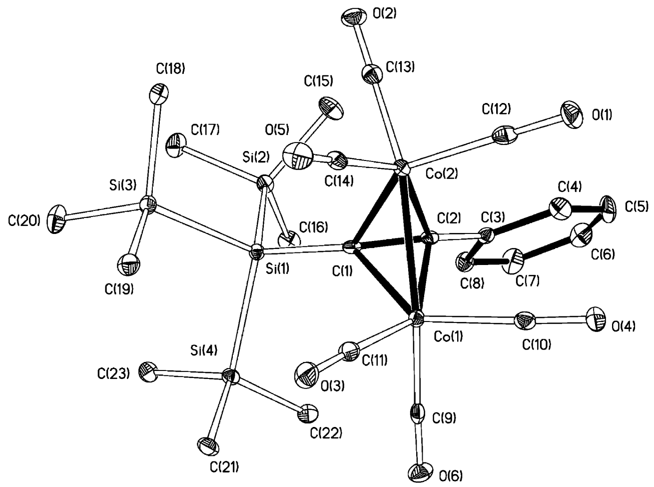
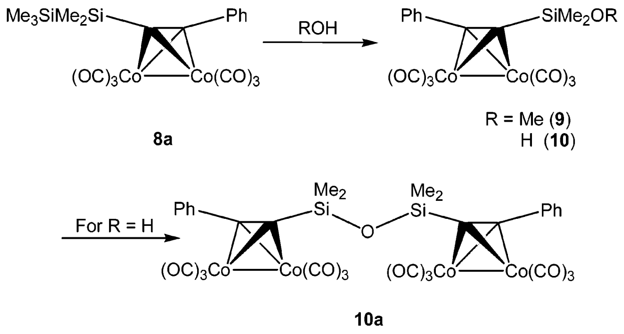


Figure 2. Molecular structure and numbering of **4a**. Selected bond lengths [Å] and bond angles [deg] with SDs: Co(1)−C(2) 1.981(3), Co(1)−C(1) 2.020(3), Co(1)−Co(2) 2.4574(7), Co(2)−C(13) 1.813(4), Si(1)−C(1) 1.876(3), Si(1)−Si(4) 2.3601(14), Si(1)−Si(3) 2.3683(14), Si(1)−Si(2) 2.3820(15), O(1)−C(12) 1.138(4), C(1)−C(2) 1.346(5), C(2)−Co(1)−C(1) 39.31(13), C(2)−Co(1)−Co(2) 51.11(9), C(2)−Co(2)−C(1) 39.38(13), C(1)−Si(1)−Si(4) 110.41(11), C(1)−Si(1)−Si(3) 111.55(11), Si(4)−Si(1)−Si(3) 108.06(5), Si(4)−Si(1)−Si(2) 106.80(5), Si(3)−Si(1)−Si(2) 109.66(5), Si(1)−C(1)−Co(2) 133.46(18), C(1)−C(2)−C(3) 142.2(3).

Attempts to carry out chromatographic purification resulted in a vigorous decomposition reaction on silica gel. These properties clearly suggested that in the cobalt-complexed oligosilylalkynes the Si−Si bonds are highly activated, similar to the Si−H bonds in Corriu's compounds.[7]

Experiments to react compound **4a** with oxygen, hydrogen, water, alcohols, phenylacetyene, and acetone gave complicated reaction mixtures in all cases, even at low temperatures. We assumed that the reason for this situation was the fact that there are three activated Si−Si bonds present in **4a**. Therefore, we decided to simplify the system and used pentamethydisilanylphenylacetylene (**8**) to prepare the dicobalt complex **8a**. This compound contains only one Si−Si bond, and it offers the additional advantage that, if related chemistry occurs as in Corriu's case,[7] the same products would be obtained. This was indeed the case, as we could see from the reaction of **8a** with methanol, which gave the known methoxy compound **9**.[6] Reaction of **8a** with water gave silanol **10**, which condensed further to the respective disiloxane (**10a**) under the reaction conditions.



8a

R = Me (**9**)
H (**10**)

10a

Corriu[7] and others[13] have shown that it is possible to add 2 equiv of dicobalt octacarbonyl to a dialkynylsilane.[7] We wanted

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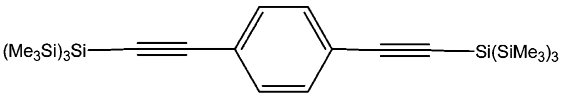
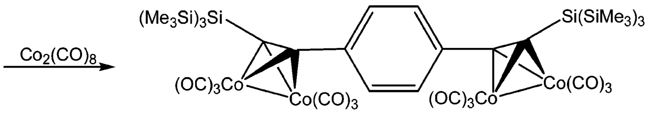
(12) (a) Fischer, R.; Frank, D.; Gaderbauer, W.; Kayser, C.; Mechtler, C.; Baumgartner, J.; Marschner, C. *Organometallics* **2003**, *22*, 3723−3731. (b) Mechtler, C.; Zirngast, M.; Baumgartner, J.; Marschner, C. *Eur. J. Inorg. Chem.* **2004**, 3254−3261. (c) Mechtler, C.; Zirngast, M.; Gaderbauer, W.; Wallner, A.; Baumgartner, J.; Marschner, C. *J. Organomet. Chem.* **2006**, *691*, 150−158.

(13) (a) Lang, H.; Weinmann, M.; Zsolnai, L. *J. Organomet. Chem.* **1996**, *522*, 277−289. (b) Gleiter, R.; Stahr, H. *Tetrahedron Lett.* **1996**, *37*, 1179−1182.

to find out if this is also possible for a dialkynyloligosilane. The double metalation of the 1,4-bis(oligosilyl)ethynylbenzene **11** to **11a** proceeded without any problem.

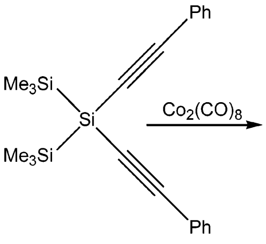


11

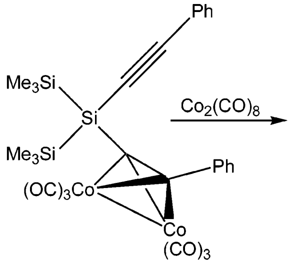


11a

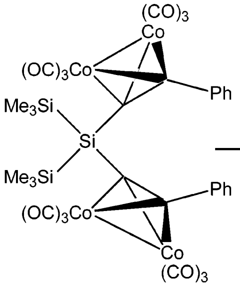
We also treated 2,2-bis(phenylethynyl)hexamethyltrisilane[38] (**12**) with dicobalt octacarbonyl. NMR spectroscopy of the reaction with 1 equiv indicated clean and complete formation of the expected monocomplexed product **12a**. Upon reaction with another equivalent of dicobalt octacarbonyl, **12b** was obtained. While we were able to obtain a crystal structure of **12a**, attempts to crystallize **12b** and to determine its crystal structure indicated that **12b** had suffered the formal loss of trimethysilylphenylacetylene and rearranged to the disilylene complex **13**.



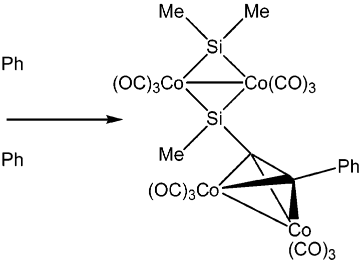
12



12a



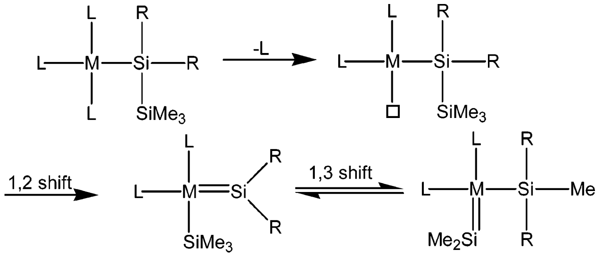
12b



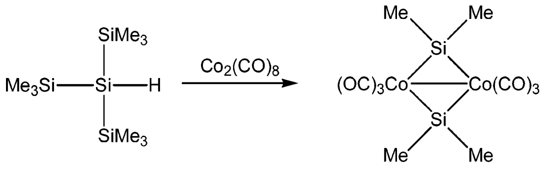
13

The structural motif of silylenes as bridging ligands for dicobalt complexes is not new. Similar complexes have been obtained by reaction of dicobalt octacarbonyl with hydro- and disilanes.[11,14] The reaction mechanism for the transformation of **12b** to **13** is not quite clear yet, but it should be noted that the cleavage of silyl acetylene bonds in the coordination sphere of cobalt is not without precedence.[15] The fact that the transformation involves methyl migration from a trimethylsilyl group to the central silicon atom seems to imply the involvement of a cobalt silyl−silylene complex as a reactive intermediate in a similar manner, as described in more detail below.

Scheme 1. Schematic Formation of Silyl−Silylene Transition Metal Complexes via 1,2 and 1,3 Shifts



From Chalk and Harrod's seminal studies on hydrosilation chemistry the reaction of hydrosilanes with dicobalt octacarbonyl is known to yield cobalt tetracarbonyl silyl complexes.[16] As we were not aware of an example where this reaction was carried out successfully with an oligohydrosilane, we reacted tris(trimethylsilyl)silane with dicobalt octacarbonyl in the expectation of obtaining the tris(trimethylsilyl)silyl cobalt tetracarbonyl complex. Much to our surprise we did not obtain this compound but complex **14**, where two of the carbonyl ligands of the starting material have been replaced by bridging dimethylsilylene groups. While **14** is already known from the reaction of dicobalt octacarbonyl with 1,1,2,2-tetramethyldisilane,[11] we have now determined its crystal structure and ^{29}Si NMR shifts.



14

The formation of **14** seems to be related to the formation of **13**. Similar Si−Si bond activation chemistry of oligosilanes[17] has been reported before for several other metals such as iron,[18] rhodium, and iridium,[19] but almost exclusively under irradiation conditions. Especially the groups of Pannell, Ogino, and Tilley have studied this field thoroughly. For many rearrangements and redistribution reactions of oligosilyl transition metal complexes silyl−silylene complexes are essential intermediates.[20] A 1,2 silyl shift allows oligosilyl transition metal complexes to avoid coordinative unsaturation, which may occur in the event of ligand dissociation. A further 1,3 shift usually of an alkyl group can establish an equilibrium between the silyl−silylene complex and a related silylene−silyl complex (Scheme 1).

As for the reaction mechanism leading to the formation of **14**, we also assume the involvement of silyl−silylene intermediates. We still believe that the initial step of the reaction sequence is the expected bimolecular oxidative addition, which leads to

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[14] (a) Borgdorff, J.; Duffy, N. W.; Robinson, B. H.; Simpson, J. *Inorg. Chim. Acta* **1994**, *224*, 73−79. (b) Bourg, S.; Boury, B.; Carré, F.; Corriu, R. J. P. *Organometallics* **1997**, *16*, 3097−3099. (c) Bourg, S.; Boury, B.; Carré, F. H.; Corriu, R. J. P. *Organometallics* **1998**, *17*, 167−172.

[15] Fritch, J. R.; Vollhardt, K. P. C.; Thompson, M. R.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 2768−2770.

[16] (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 1133−1135. (b) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1967**, *89*, 1640−1647.

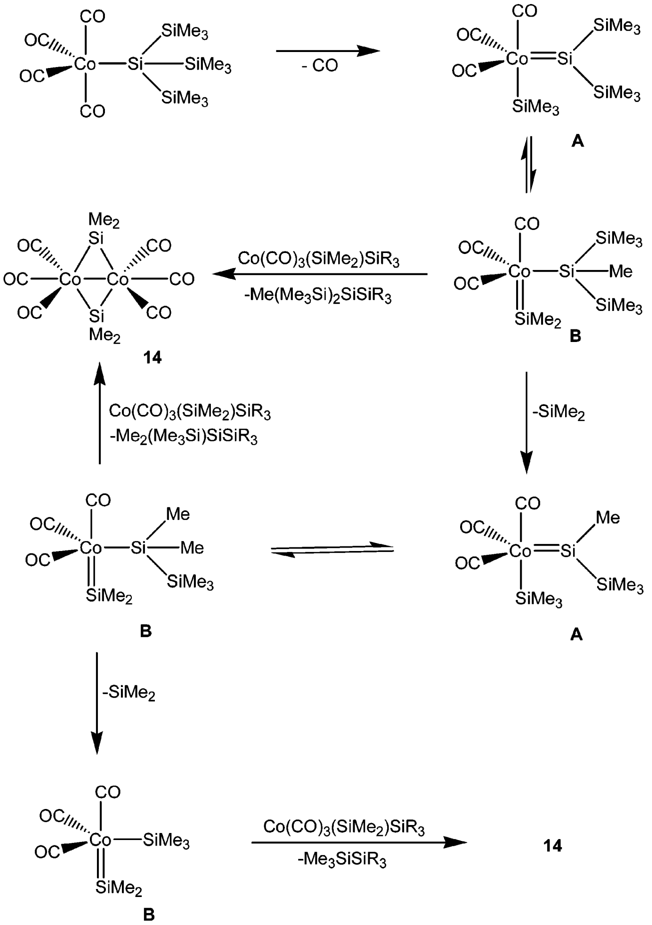
[17] For a review on the topic of Si−Si bond activation by transition metals see: Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351−1374.

[18] (a) Jones, K. L.; Pannell, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 11336−11340. (b) Pannell, K. H.; Rozell, J. M., Jr.; Hernandez, C. *J. Am. Chem. Soc.* **1989**, *111*, 4482−4485.

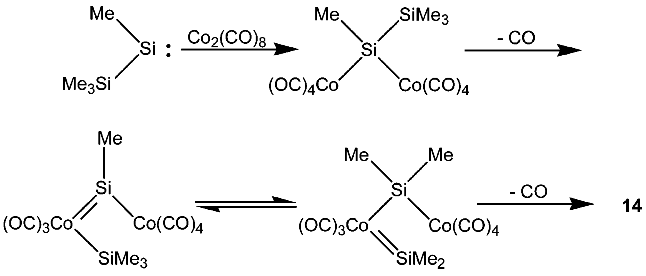
[19] (a) Mitchell, G. P.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 5472−5474. (b) Mitchell, G. P.; Tilley, T. D. *Organometallics* **1996**, *15*, 3477−3479.

[20] For reviews covering silyl−silylene transition metal complexes see: ref 17 and: (a) Okazaki, M.; Tobita, H.; Ogino, H. *Dalton Trans.* **2003**, 493−506. (b) Ogino, H. *Chem Rec.* **2002**, *2*, 291−306.

Scheme 2. Tentative Mechanism for the Formation of 14



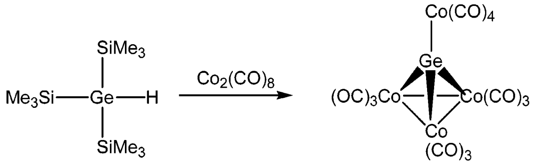
Scheme 3. Formation of 14 via the Rearrangement of a Dicobalt Complex



the formation of tris(trimethylsilyl)silyl cobalt tetracarbonyl. Loss of a carbonyl ligand then initiates the formation of a bis(trimethylsilyl)silylene(trimethylsilyl) cobalt tricarbonyl complex (type A) via an intramolecular 1,2 silyl migration (Scheme 2). The formed compound is in equilibrium with a [methylbis(trimethylsilyl)silyl](dimethylsilylene) cobalt tricarbonyl isomer (type B) (Scheme 2). Bimolecular reductive elimination of two silyl(dimethylsilylene)cobalt tricarbonyl (type B) complexes can give rise to the formation of **14** and a disilane.[21] Alternatively, the silyl−silylene complexes can also extrude a silylene fragment such as dimethylsilylene, which can be trapped by either tris(trimethylsilyl)silane[22] or dicobalt octacarbonyl. The resulting coordinatively unsaturated fragment would stabilize itself by another 1,2 shift and the formation of another silyl−silylene complex (Scheme 2). The trapping product with the dicobalt complex could also undergo silyl−silylene rearrangement processes, which lead to the formation of **14** (Scheme 3), as has been shown for a related diiron complex.[23]

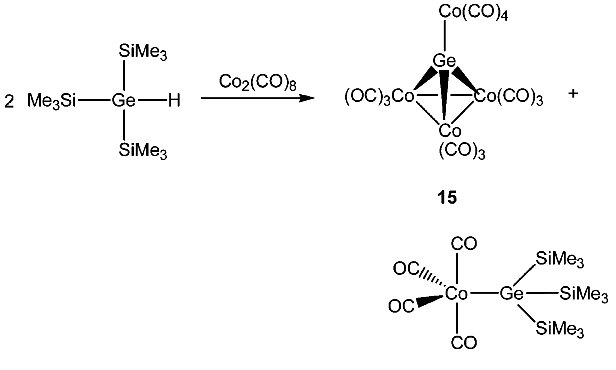
The possibility for different silyl−silylene complexes to undergo bimolecular reductive elimination allows for the formation of several different disilanes. The additional involvement of silylene trapping chemistry, which can also lead to follow-up chemistry with cobalt carbonyls, further complicates the course of the reaction. This situation is reflected by the ^{29}Si NMR spectra of the reaction. Besides the resonance for **14**, other signals indicate the presence of $(CO)_4CoSiMe_3$ and a number of methylated oligosilanes including resonances for double- and triple-silylated silicon atoms.

To find out if similar chemistry occurs also with germanium, the reaction of dicobalt octacarbonyl was repeated with tris(trimethylsilyl)germane. Given the chemical similarity between silicon and germanium, we expected to observe similar chemistry that probably would feature a dimethylgermylene ligand. However, we could isolate neither the tris(trimethylsilyl)germyl cobalt tetracarbonyl complex (**16**) nor a silylene or germylene complex related to **14** but rather the tetracobalt germanium complex **15**,[24] which was already known from the reaction of germanium tetrabromide with sodium tetracarbonylcobaltate or alternatively from the reaction of dicobalt octacarbonyl with germane (GeH_4).[24]



15

Changing the stoichiometry of the reaction to 2 equiv of tris(trimethylsilyl)germane eventually allowed us to isolate the tris(trimethylsilyl)germyl cobalt tetracarbonyl complex **16** besides a substantial amount of **15**. Again the ^{29}Si NMR spectrum of the reaction mixture indicated the presence of $(CO)_4CoSiMe_3$.



15

16

On the basis of these observations we can postulate a possible mechanism for the formation of **15** (Scheme 4). Starting from the initial formation of **16**, a 1,2 shift related to the chemistry described above seems reasonable. However, at this point the

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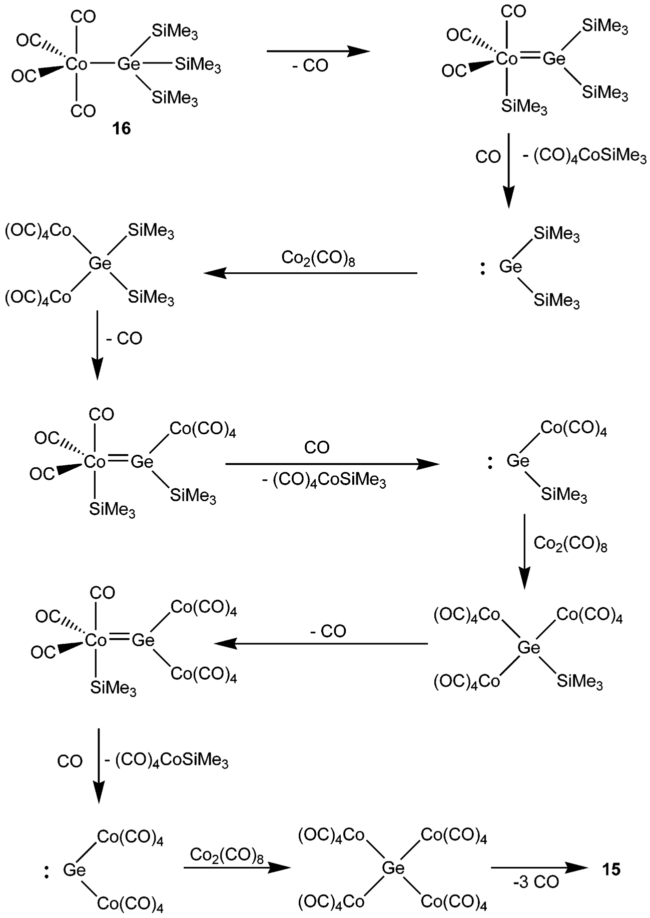
[21] Brookes, A.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 3469−3471.

[22] Pannell, K. H.; Brun, M.-C.; Sharma, H.; Jones K.; Sharma, S. *Organometallics* **1994**, *13*, 1075−1077.

[23] Ueno, K.; Hamashima, N.; Shimoi, M.; Ogino, H. *Organometallics* **1991**, *10*, 959−962.

[24] (a) Schmid, G.; Etzrodt, G. *J. Organomet. Chem.* **1977**, *107*, 367−371. (b) Boese, R.; Schmid, G. *J. Chem. Soc., Chem. Commun.* **1979**, 349−350. (c) Gerlach, R. F.; Mackay, K. M.; Nicholson, B. K. *J. Organomet. Chem.* **1979**, *178*, C30−C32.

Scheme 4. Possible Mechanism for the Formation of 14



dissociation of the more stable germylene, instead of the silylene, is more likely.[25,26] Insertion of the germylene into the cobalt−cobalt bond of dicobalt octacarbonyl, which is a known process,[26] concludes the sequence, which replaces one trimethylsilyl group by a cobalt tetracarbonyl unit. Repetition of the sequence—dissociation of CO, 1,2 shift, dissociation of germylene, insertion into the Co−Co bond—occurs until all silyl groups are replaced by cobalt tetracarbonyl moieties. Loss of three carbonyl ligands, which is probably favored for steric reasons, finally leads to the formation of **15** (Scheme 4).

Attempts to react other silicon−silicon containing compounds such as tetrakis(trimethylsilyl)silane or dodecamethylcyclohexasilane with dicobalt octacarbonyl were not successful. We therefore assume that the reaction of the cobalt complex with Si−Si bonds does not take place in an intermolecular fashion but requires either previous coordination via the alkynyl unit or the oxidative addition into the Si−H bond to occur within the coordination sphere of the complex.

X-ray Crystallography. Compounds **3a**, **4a**, **5**, **7a**, **8a**, **9**, **10a**, **12a**, **13**, **14**, **15**, and **16** were subjected to single-crystal X-ray diffraction analysis. Except for **5** all of these are cobalt complexes. Interestingly the structural features of **5** (Figure 3) are somewhat different compared to the recently obtained structure of **4**.[38] The acetylenic bond distance is relatively long (1.21 Å) compared to 1.19 Å in **4**. Also the Si−Si bond lengths are somewhat longer. The fact that the hydride substituent does not require much space causes an expansion of the Si−Si−Si angle to almost 121°. While the connection between the phenyl and the alkyne moiety is almost perfectly linear, a slight bending was observed for the C−C−Si angle (174°). The hydrogen atom on silicon was found and not calculated.

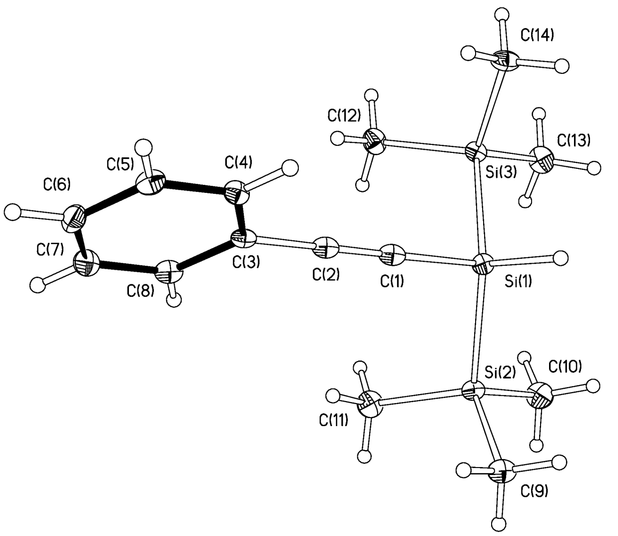


Figure 3. Molecular structure and numbering of **5**. Selected bond lengths [Å] and bond angles [deg] with SDs: Si(1)−C(1) 1.858(3), Si(1)−Si(2) 2.3569(13), Si(1)−Si(3) 2.3581(13), C(1)−C(2) 1.214(4), C(2)−C(3) 1.440(4), C(1)−Si(1)−Si(2) 105.49(10), C(1)−Si(1)−Si(3) 104.37(10), Si(2)−Si(1)−Si(3) 120.92(5), C(2)−C(1)−Si(1) 174.4(3), C(1)−C(2)−C(3) 179.4(4).

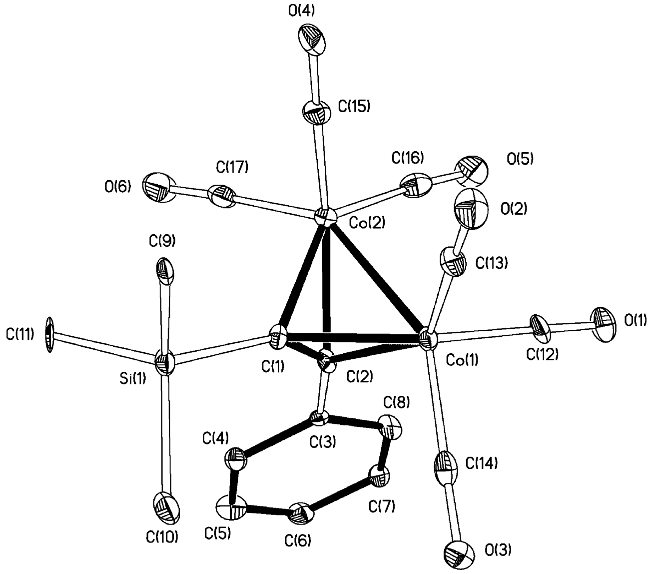


Figure 4. Molecular structure and numbering of **7a**. Of two crystallographically independent molecules in the asymmetric unit, only one is shown. Selected bond lengths [Å] and bond angles [deg] with SDs: Co(1)−C(2) 1.965(7), Co(1)−C(1) 1.998(7), Co(1)−Co(2) 2.4717(14), Si(1)−C(1) 1.856(7), Si(1)−C(9) 1.861(7), O(1)−C(12) 1.114(9), C(1)−C(2) 1.333(10), C(2)−Co(1)−C(1) 39.3(3), C(2)−Co(1)−Co(2) 51.8(2), C(2)−Co(2)−Co(1) 50.9(2), C(1)−Co(2)−Co(1) 51.8(2), C(1)−Si(1)−C(9) 110.5(3), C(1)−Si(1)−C(11) 107.8(4), Si(1)−C(1)−Co(2) 132.4(4), Si(1)−C(1)−Co(1) 130.9(4), C(1)−C(2)−C(3) 142.3(7).

The structural features of the silylated alkynyl dicobalt hexacarbonyl complexes (Figures 1, 2, 4−9) are listed in Table 2. Compared to the already substantial number of structurally characterized alkynyl dicobalt hexacarbonyl complexes,[3b] the silylated complexes do not exhibit extraordinary structural

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[25] (a) Pannell, K. H.; Sharma, S. *Organometallics* **1991**, *10*, 1655−1656. (b) Sharma, S.; Pannell, K. H. *Organometallics* **2000**, *19*, 1225−1231.

[26] McIndoe, J. S.; Nicholson, B. K. *J. Organomet. Chem.* **1999**, *577*, 181−188.

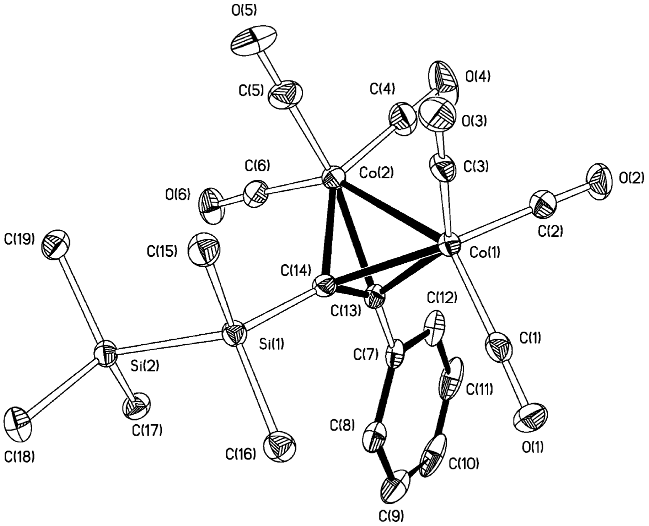

Figure 5. Molecular structure and numbering of **8a**. Selected bond lengths [Å] and bond angles [deg] with SDs: Co(1)−C(13) 1.984(3), Co(1)−C(14) 1.996(3), Co(1)−Co(2) 2.4798(9), Co(2)−C(13) 1.970(3), Co(2)−C(14) 1.992(3), Si(1)−C(14) 1.856(3), Si(1)−Si(2) 2.3503(13), C(13)−Co(1)−C(14) 39.50(12), C(13)−Co(1)−Co(2) 50.90(9), C(14)−Co(1)−Co(2) 51.49(8), C(14)−Si(1)−Si(2) 110.72(10).

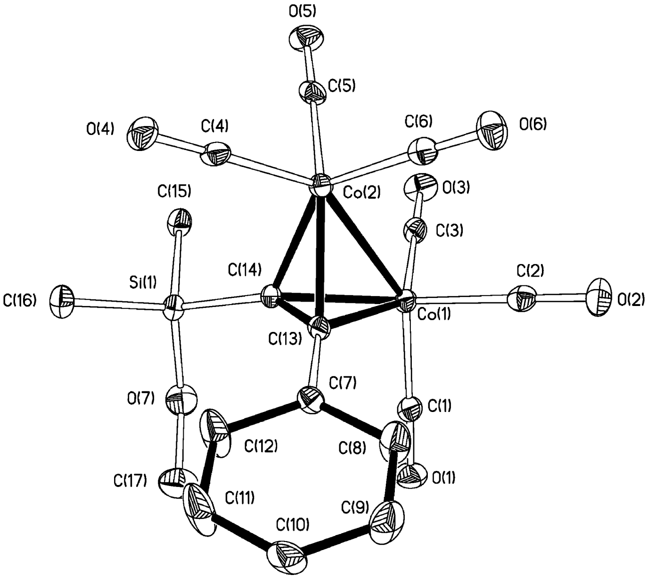

Figure 6. Molecular structure and numbering of **9**. Of two crystallographically independent molecules in the asymmetric unit, only one is shown. Selected bond lengths [Å] and bond angles [deg] with SDs: Co(1)−C(1) 1.801(4), Co(1)−C(2) 1.812(4), Co(1)−Co(2) 2.4705(9), O(1)−C(1) 1.132(4), O(7)−C(17) 1.385(5), C(1)−Co(1)−C(2) 99.37(17), C(1)−Co(1)−Co(2) 149.08(11), C(2)−Co(1)−Co(2) 100.45(11), O(7)−Si(1)−C(15) 105.91(16).

characteristics. Co−Co distances are close to the average of 2.47 Å. Also the elongation of the acetylenic bond to values between 1.31 and 1.35 Å groups nicely around the average of 1.34 Å. The Si−C bond lengths of 1.87 Å (**3a**, **4a**) and 1.85 Å (**7a**−**13**) still reflect the slightly shortened Si−C_{sp} connection compared to typical Si−C_{sp3} bonds. The angles around the alkyne carbon atoms are perfectly within the range of what would be expected for the phenyl-substituted carbon (140−143°) but are somewhat less expanded for the silicon-substituted carbon (145−148°). Again the hydrogen atom on silicon was found and not calculated. Only compound **13** (Figure 9), with the rearranged cobalt cluster sidearm, exhibits a coordinated unit with a higher sp-character (angles of 146° and 153°).

Compound **13** (Figure 9) contains two dicobalt cluster units. One unit is a conventional dicobalt hexacarbonyl acetylene complex, but the other one can be interpreted as a dicobalt octacarbonyl in which the two bridging carbonyl groups have been replaced by dialkylsilylene groups. Structures of similar compounds have been studied previously by Corriu.[14b,c] The Co−Co bond length in this unit is elongated to 2.67 Å. The Si−Co distances are in the range between 2.27 and 2.30 Å. The Co−Si−Co angles are, at 72°, rather small, as expected for a three-membered ring. However, also the C−Si−C angles are, at 103° and 105°, rather small, indicating a high p-orbital character. The situation for the structure of the more prototypic compound **14** (Figure 10) is very similar to what was found for **13**. Two virtually identical, but crystallographically independent molecules are present in the asymmetric unit. The Co−Co bond length is 2.66 Å, and the Si−Co distances are close to 2.28 Å. The Co−Si−Co angles are at 71°, and the C−Si−C angles are,

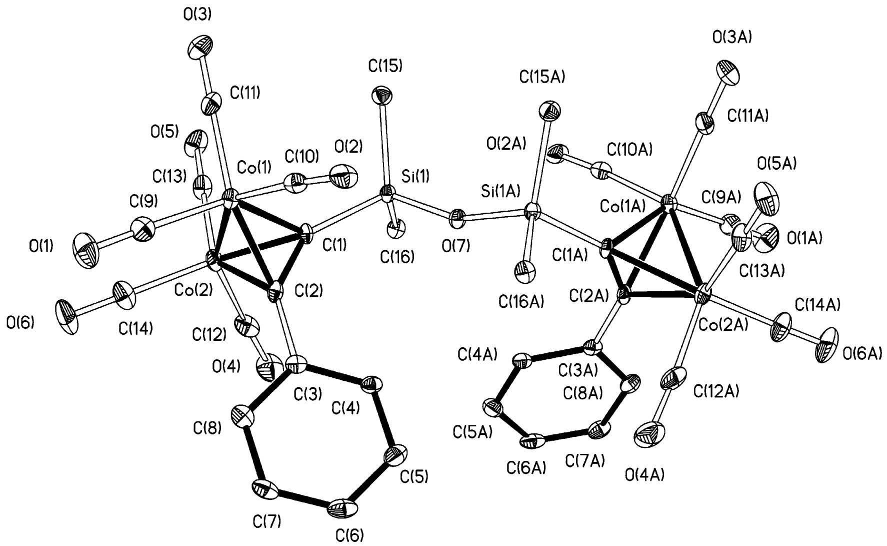

Figure 7. Molecular structure and numbering of **10a**. Selected bond lengths [Å] and bond angles [deg] with SDs: Co(1)−C(9) 1.817(7), Co(1)−C(1) 1.992(5), Co(1)−Co(2) 2.4810(12), Co(2)−C(2) 1.966(5), Co(2)−C(1) 1.986(5), Si(1)−O(7) 1.6398(19), Si(1)−C(15) 1.852(6), O(1)−C(9) 1.132(8), C(2)−Co(1)−C(1) 40.0(2), C(2)−Co(1)−Co(2) 50.86(15), C(1)−Co(1)−Co(2) 51.32(15), C(2)−Co(2)−C(1) 40.1(2), O(7)−Si(1)−C(1) 107.2(2), Si(1)−O(7)−Si(1)#1 158.4(4).

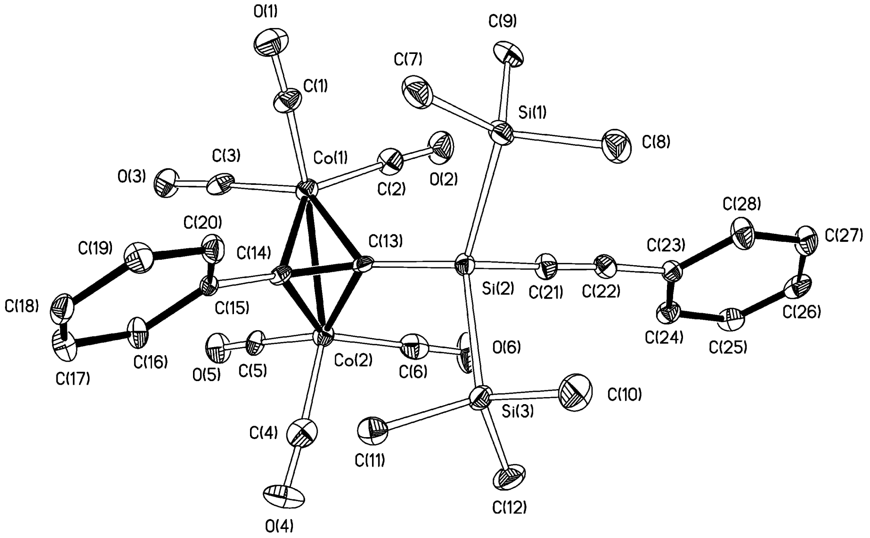

Figure 8. Molecular structure and numbering of **12a**. Of two crystallographically independent molecules in the asymmetric unit, only one is shown. Selected bond lengths [Å] and bond angles [deg] with SDs: Co(1)−C(1) 1.789(6), Co(1)−C(3) 1.814(6), Co(1)−C(14) 1.976(5), Co(1)−C(13) 1.996(5), Co(1)−Co(2) 2.4776(10), Si(1)−Si(2) 2.358(2), Si(2)−C(21) 1.838(5), Si(2)−C(13) 1.856(5), O(1)−C(1) 1.146(6), C(13)−C(14) 1.340(7), C(1)−Co(1)−C(3) 97.3(2), C(1)−Co(1)−C(2) 102.9(3), C(1)−Co(1)−C(14) 98.4(2), C(3)−Co(1)−C(14) 104.6(2), C(2)−Co(1)−C(14) 137.6(2), C(1)−Co(1)−C(13) 101.7(2), C(3)−Co(1)−C(13) 141.2(2), C(2)−Co(1)−C(13) 99.9(2), C(14)−Co(1)−C(13) 39.42(19).

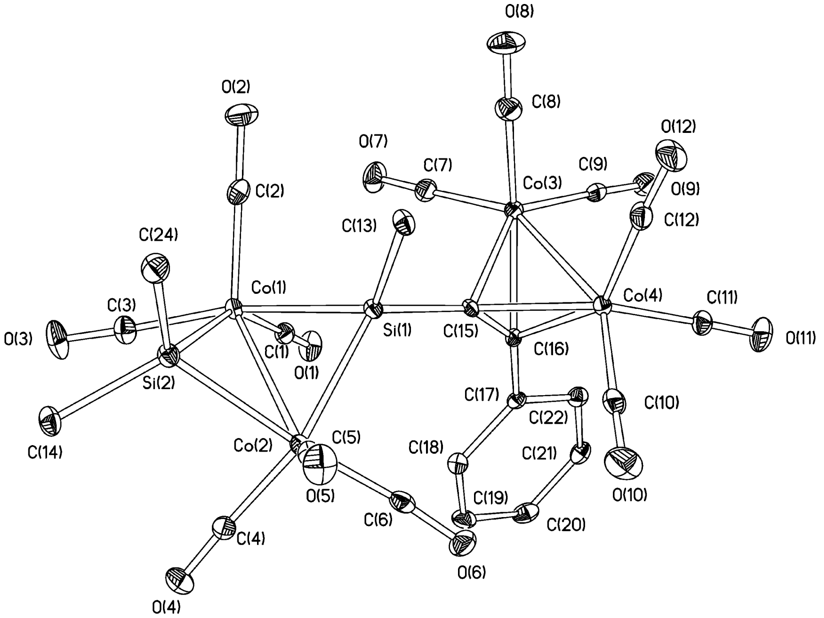

Figure 9. Molecular structure and numbering of **13**. Selected bond lengths [Å] and bond angles [deg] with SDs: Co(1)−C(2) 1.763(3), Co(1)−Si(2) 2.2775(12), Co(1)−Co(2) 2.6734(11), Co(2)−C(5) 1.760(3), Co(2)−Si(1) 2.2731(10), Co(3)−C(7) 1.805(4), Co(3)−C(15) 2.000(3), Co(3)−Co(4) 2.4602(11), Co(4)−C(10) 1.803(4), C(2)−Co(1)−C(3) 105.60(15), C(2)−Co(1)−C(1) 109.73(14), C(3)−Co(1)−C(1) 94.45(14), C(2)−Co(1)−Si(2) 98.96(11), C(1)−Co(1)−Si(2) 150.86(10), C(2)−Co(1)−Si(1) 83.63(10), C(3)−Co(1)−Si(1) 166.30(11), C(1)−Co(1)−Si(1) 91.79(10), Si(2)−Co(1)−Si(1) 86.31(4).

with values close to 102°, even smaller than in **13**. In Corriu's molecules[14] the silylene units are always connected by an alkyl chain tether. Therefore, the distances between the coordinating silicon (2.69−2.87 Å) atoms are within the range of the longest reported Si−Si bonds. For the cases of compounds **13** (Si···Si = 3.12 Å) and **14** (Si···Si = 3.05 Å) these distances are longer but still considerably shorter than the sum of their van der Waals radii.

The crystal structure of compound **15** was determined previously at ambient temperature.[24b] As our structure (Figure 11) was obtained at 100 K, it is slightly different but in essence confirms the data from the previous analysis. As a difference we observed a formal doubling of a cell constant and as a consequence two independent molecules in the asymmetric unit. The structure consists of a tetrahedron assembled from three cobalt and one germanium atom. The three cobalt atoms bear three carbonyl ligands and acquire a distorted octahedral geometry. The fourth valence of the germanium atom is saturated by a bond to a cobalt tetracarbonyl unit. The three cobalt atoms of the tetrahedron form an approximate equilateral triangle with bond angles close to 60°. The respective angles around germanium are extended to approximately 69°. The Ge−Co bond lengths within the tetrahedron are between 2.27 and 2.30 Å, while the exocyclic bond is, at 2.34 Å, somewhat longer. The

Table 1. Comparison of ^{29}Si and ^{13}C NMR Shifts of Alkynylsilanes and the Respective Dicobalt Hexacarbonyl Complexes[a]

alkynyl silane	$^{29}Si_{central}$ [ppm]	$^{13}C_{alkynyl}$ [ppm]	cobalt complex	$^{29}Si_{central}$ [ppm]	$^{13}C_{alkynyl}$ [ppm]
3	−100.7	96.8/83.4	**3a**	−67.7	90.5/82.9
4	−100.5	108.6/88.4	**4a**	−67.1	111.4/75.8
5	−90.2	110.2/86.2	**5a**	−55.3.	107.9/71.5
6	−57.7	109.9/90.2	**6a**	−33.8	109.1/77.9
7	−18.2	105.8/94.1	**7a**	0.7	106.0/79.8
8	−36.9	108.1/93.1	**8a**	−18.0	107.0/80.1
$MeOSiMe_2CCPh$[35]		105.3/91.1	**9**	6.9	105.9/79.8
11	−100.5	109.1/90.3	**11a**	−66.9	109.7/76.1
12	−80.8	110.2/86.9	**12a**	−53.3	107.9/72.5
			12b	−53.7	107.9/72.5

[a] ^{29}Si: the resonance for the Si atom attached to the alkynyl unit is shown. ^{13}C: the alkynyl carbon shifts: C(R)/C(Si).

Table 2. Selected Bond Lengths and Angles of Cobalt Complexes of Silyl Alkynes

compound	Co−Co [Å]	*C*≡*C* [Å]	C_{alkyne}−Si [Å]	C_{alkyne}−Co [Å]	R−C−C/C−C−Si [deg]
3a	2.469(2)	1.310(15)	1.878(10)	1.939−2.021	−/142.7
4a	2.4573(7)	1.349(5)	1.873(4)	1.966−2.033	142.6/145.1
7a	2.4717(13)	1.330(10)	1.858(7)	1.966−1.998	142.4/148.5
8a	2.4798(9)	1.345(4)	1.856(3)	1.970−1.996	143.3/148.1
9	2.4705(9)	1.344(5)	1.843(4)	1.951−1.994	140.5/148.1
10a	2.4810(12)	1.356(8)	1.852(6)	1.966−1.992	139.8/147.2
12a	2.4776(10)	1.340(7)	1.856(5)	1.966−2.010	140.6/145.9
13	2.4602(11)	1.332(4)	1.857(3)	1.989−2.000	146.4/153.2

Table 3. Crystallographic Data for Compounds 3a, 4a, 5, 7a, 8a, and 9

	3a	**4a**	**5**	**7a**	**8a**	**9**
empirical formula	$Co_2O_6Si_4C_{17}H_{28}$	$Co_2O_6Si_4C_{23}H_{32}$	$Si_3C_{14}H_{24}$	$Co_2O_6SiC_{17}H_{14}$	$Co_2O_6Si_2C_{19}H_{20}$	$Co_4O_{14}Si_2C_{34}H_{28}$
M_w	558.61	634.7	276.60	460.23	518.39	952.46
temperature [K]	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
size [mm]	0.20 × 0.20 × 0.20	0.40 × 0.20 × 0.20	0.35 × 0.35 × 0.20	0.30 × 0.28 × 0.19	0.36 × 0.30 × 0.26	0.40 × 0.28 × 0.18
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	*Pbca*	*P*2(1)	*P*2(1)/*n*	*Cc*	*P*2(1)/*n*	$P\bar{1}$
a [Å]	12.731(3)	9.601(2)	14.197(3)	8.396(2)	8.673(2)	7.983(2)
b [Å]	14.117(3)	9.874(2)	6.021(2)	14.220(3)	11.268(2)	15.895(3)
c [Å]	29.964(6)	15.963(3)	20.974(4)	32.546(7)	24.248(5)	16.094(3)
α [deg]	90	90	90	90	90	101.32(3)
β [deg]	90	91.95(3)	95.61(3)	94.61(3)	91.57(3)	98.75(3)
γ [deg]	90	90	90	90	90	97.44(3)
V [Å^3]	5385(2)	1512(5)	1784(2)	3873(2)	2369(2)	1952(2)
Z	8	2	4	8	4	2
ρ_{calc} [g cm^{-3}]	1.378	1.394	1.030	1.578	1.453	1.620
absorp coeff [mm^{-1}]	1.436	1.288	0.248	1.803	1.531	1.795
F(000)	2304	656	600	1856	1056	960
θ range	$2.10 < \theta < 22.00$	$2.12 < \theta < 24.00$	$1.66 < \theta < 25.00$	$2.51 < \theta < 26.37$	$1.68 < \theta < 26.36$	$1.31 < \theta < 26.37$
no. of reflns collected/unique	27 703/3298	9722/4668	12 008/3138	15 066/7654	18 272/4822	15 609/7837
completeness to *θ* [%]	99.9	99.5	99.9	99.6	99.7	98.5
no. of data/restraints/params	3298/12/275	4668/1/325	3138/0/164	7654/2/476	4822/0/267	7837/0/493
goodness of fit on F^2	1.40	1.08	1.15	1.08	0.92	0.93
final *R* indices [$I > 2\sigma(I)$]	R1=0.098, wR2=0.187	R1=0.033, wR2=0.067	R1=0.070, wR2=0.175	R1=0.061, wR2=0.123	R1=0.043, wR2=0.096	R1=0.043, wR2=0.089
R indices (all data)	R1=0.102, wR2=0.188	R1=0.035, wR2=0.068	R1=0.078, wR2=0.182	R1=0.073, wR2=0.129	R1=0.067, wR2=0.104	R1=0.072, wR2=0.096
largest diff peak/hole [e$^-$/ Å^3]	0.63/−0.58	0.50/−0.25	0.81/−0.43	1.26/−0.56	0.59/−0.36	0.74/−0.37

Co−Co bond lengths between 2.59 and 2.62 Å are within the range of what was observed for other tricobalt group 14 tetrahedral clusters.

The crystal structure of **16** (Figure 12) again revealed two crystallographically independent molecules. Cobalt has a trigonal bipyramidal coordination sphere with the tris(trimethylsilyl)germyl group occupying an apical position. The bond to the carbonyl group in *trans* position to the germanium atom is slightly elongated (1.86 and 1.83 Å) compared to the carbonyls in equatorial position (1.79−1.80 Å). The equatorial carbonyl ligands on cobalt are oriented in a staggered conformation with respect to the trimethylsilyl groups on germanium. A search in the Cambridge Crystallographic Database (CCDC) for tetravalent germanium compounds with germanium connected to cobalt gave bond distances ranging from 2.29 to 2.48 Å. With measured values above 2.52 Å compound **16** falls out of this range. The reason for this is likely due to the fact that most of the compared structures contained triorganogermyl moieties. While there are a substantial number of crystal structures containing the tris(trimethylsilyl)germyl unit in the Cambridge Crystallographic Database, most of these compounds are variations of the tris(trimethylsilyl)germyl anion with different counterions. However, comparison of **16** with the few remaining structures reveals that Si−Ge bond distances of 2.40 Å are exactly within the range of what to expect.

NMR Spectroscopy. The cobalt complexes have been investigated for their ^{29}Si and ^{13}C NMR spectroscopic properties (Table 1). ^{29}Si NMR shifts are usually very sensitive to the electronic situation. A comparison of the chemical shifts of the central silicon atoms of tris(trimethylsilyl)silyl compounds substituted with sp-, sp^2-, and sp^3-hybridized carbon atoms shows resonances at ca. −100 ppm for $(Me_3Si)_3Si{-}C{\equiv}CR$,[38] ca. −82 ppm for $(Me_3Si)_3Si{-}CH{=}CHR$,[27] −76.8 ppm for $(Me_3Si)_3Si{-}Ph$,[28] and ca. −79 ppm for $(Me_3Si)_3Si{-}CH_2CH_3$.[29] For

Table 4. Crystallographic Data for Compounds 10a, 12a, 13, 14, 15, and 16

	10a	**12a**	**13**	**14**	**15**	**16**
empirical formula	$Co_4O_{13}Si_2C_{32}H_{22}$	$Co_2O_6Si_3C_{28}H_{28}$	$Co_4O_{12}Si_2C_{23}H_{14}$	$Co_4O_{12}Si_4C_{20}H_{24}$	$Co_4O_{13}GeC_{13}$	$Co_2O_8Ge_2Si_6C_{26}H_{54}$
M_w	906.40	662.63	774.24	804.47	672.44	926.27
temperature [K]	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
size [mm]	0.36 × 0.30 × 0.26	0.45 × 0.35 × 0.22	0.43 × 0.35 × 0.20	0.40 × 0.28 × 0.18	0.40 × 0.28 × 0.18	0.48 × 0.36 × 0.28
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic	triclinic	monoclinic
space group	$C2/c$	$Pna2(1)$	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$	$P2(1)$
a [Å]	28.608(6)	18.228(4)	9.054(2)	14.389(3)	7.978(2)	15.840(3)
b [Å]	9.055(2)	9.707(2)	10.563(2)	14.801(3)	16.020(3)	9.423(2)
c [Å]	15.553(3)	35.846(7)	15.355(3)	15.668(3)	16.653(3)	15.874(3)
α [deg]	90	90	79.76(3)	90	72.76(3)	90
β [deg]	113.67(3)	90	78.22(3)	110.96(3)	77.30(3)	111.46(3)
γ [deg]	90	90	83.52(3)	90	78.54(3)	90
V [Å ^{3}]	3690(2)	6343(2)	1410(5)	3116(2)	1953(6)	2205(8)
Z	4	8	2	4	4	2
ρ_{calc} [g cm^{-3}]	1.632	1.388	1.823	1.715	2.276	1.395
absorp coeff [mm^{-1}]	1.893	1.196	2.457	2.300	4.890	2.289
F(000)	1816	2720	768	1616	1288	952
θ range	$1.55 < \theta < 25.00$	$2.17 < \theta < 25.00$	$1.97 < \theta < 25.00$	$1.52 < \theta < 26.37$	$1.34 < \theta < 26.33$	$1.38 < \theta < 26.37$
no. of reflns collected/unique	12 832/3255	41 693/11 131	9951/4867	24434/6362	15 627/7836	17 048/8685
completeness to θ [%]	99.8	99.9	98.0	99.8	98.4	98.7
no. of data/restraints/params	3255/0/233	11131/1/716	4867/0/373	6362/0/369	7836/0/559	8685/1/416
goodness of fit on F^2	1.31	1.01	1.09	0.94	1.09	1.09
final R indices [$I > 2\sigma(I)$]	R1=0.071, wR2=0.141	R1=0.055, wR2=0.142	R1=0.032, wR2=0.077	R1=0.040, wR2=0.083	R1=0.043, wR2=0.089	R1=0.075, wR2=0.177
R indices (all data)	R1=0.079, wR2=0.145	R1=0.059, wR2=0.145	R1=0.037, wR2=0.080	R1=0.075, wR2=0.094	R1=0.072, wR2=0.096	R1=0.077, wR2=0.179
largest diff peak/hole [e$^-$/Å^3]	0.84/−0.68	3.81/−1.93	0.55/−0.36	0.75/−0.46	0.74/−0.37	1.51/−1.49

compounds **3** and **4** a downfield shift to −67 ppm is observed upon complexation. This value is in accordance with other π-organosilyl transition metal complexes.[30] It shows that the silicon interacts with the metal complex and hints at the electrophilicity observed. Similar downfield shifts are also observed for the other compounds in this series (Table 1). Resonances at +0.7 ppm for **7a** and at −18.0 ppm for **8a** are close to those for the methyl-substituted compounds tetramethylsilane (0.0 ppm) and hexamethyldisilane[31] (−19.4 ppm).

The ^{29}Si NMR resonances for the silylene units in compounds **13** and **14** are, as expected, observed at very low field. Shifts for **13** were found at +214.8 and +191.1 ppm and at +213.4 ppm for the bis(dimethylsilylene) compound **14**. These values are in accordance with data found by Corriu et al., whose shifts were in the range between +178 and +210 ppm.[14b,c] For dimethylsilylene units bridging to different dimetallic systems very similar resonances have been observed.[32,33]

^{13}C NMR spectroscopic investigations of alkynes coordinated to the dicobalt hexacarbonyl fragment have shown that silyl-substituted alkynes show a different behavior compared to alkyl- and aryl-substituted compounds.[34] While the latter usually experience a downfield shift upon complexation, the situation for the phenylsilylalkynes shows an upfield shift for the carbon attached to silicon while the carbon connected to phenyl is not affected much.

Conclusion

The synthesis of the first examples of tris(trimethylsilyl)-silylacetylene dicobalt hexacarbonyl complexes has revealed unusual reactivity of these compounds, which is likely due to silicon−silicon bond activation in the coordination sphere of cobalt. With a more simple system containing only one Si−Si bond, chemistry that is related to Corriu's Si−H bond activation examples[7] could be observed. Reaction of tris(trimethylsilyl)-

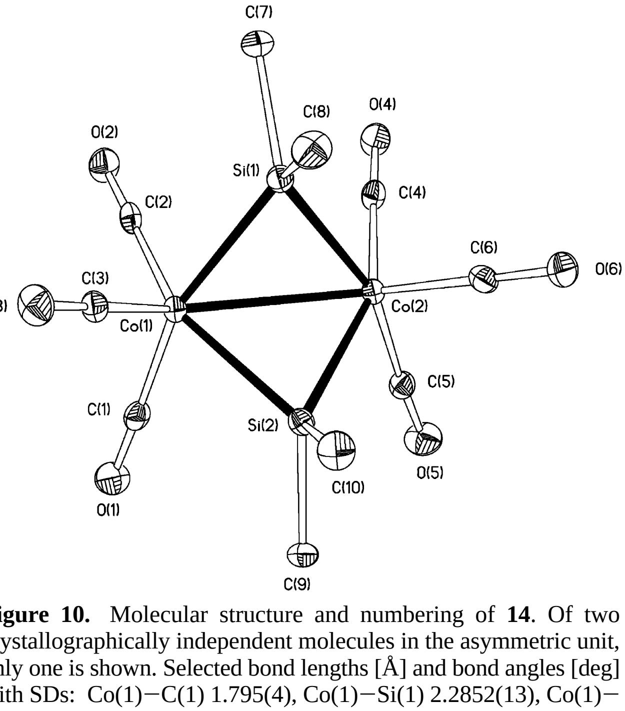

Figure 10. Molecular structure and numbering of **14**. Of two crystallographically independent molecules in the asymmetric unit, only one is shown. Selected bond lengths [Å] and bond angles [deg] with SDs: Co(1)−C(1) 1.795(4), Co(1)−Si(1) 2.2852(13), Co(1)−Si(2) 2.2875(12), Co(1)−Co(2) 2.6587(9), Co(2)−Si(2) 2.2839-(13), Co(2)−Si(1) 2.2841(12), Si(1)−C(7) 1.874(4), O(1)−C(1) 1.132(4), C(3)−Co(1)−C(1) 107.38(17), C(3)−Co(1)−C(2) 109.49-(16), C(1)−Co(1)−C(2) 96.63(17), C(3)−Co(1)−Si(1) 88.90(12), C(1)−Co(1)−Si(1) 160.80(12), C(2)−Co(1)−Si(1) 87.09(13), C(3)−Co(1)−Si(2) 95.27(12), C(1)−Co(1)−Si(2) 84.08(12), C(2)−Co-(1)−Si(2) 153.62(12),Si(1)−Co(1)−Si(2) 84.34(5).

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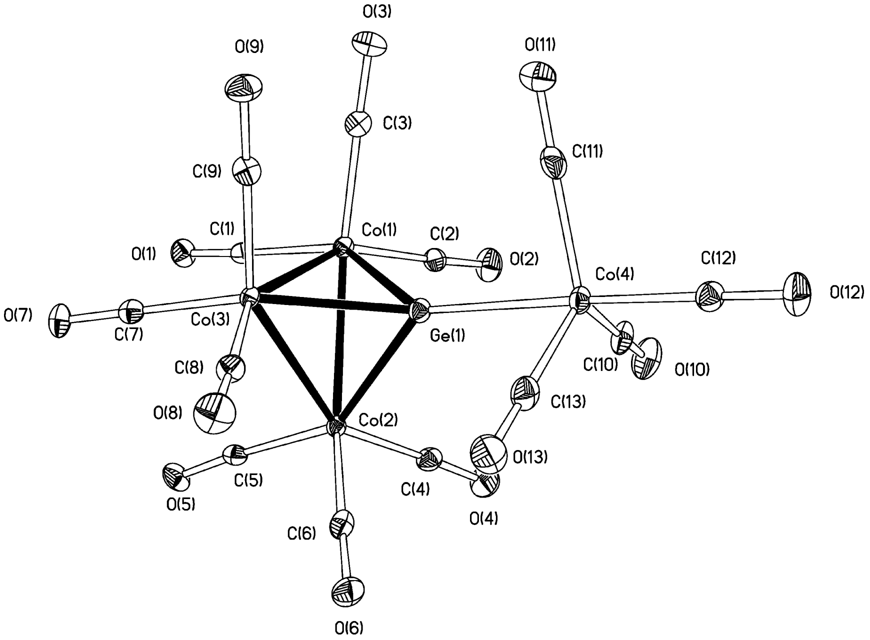

Figure 11. Molecular structure and numbering of **15** (only one of two independent molecules shown). Selected bond lengths [Å] and bond angles [deg] with SDs: Co(1)−C(1) 1.830(6), Co(1)−Ge(1) 2.2746(13), Co(1)−Co(3) 2.5945(13), Co(1)−Co(2) 2.6215(15), Co(2)−Ge(1) 2.2899(12), Co(2)−Co(3) 2.6014(12), Co(3)−Ge(1) 2.2999(11), Co(4)−Ge(1) 2.3438(13), O(1)−C(1) 1.126(8), Ge(1)−Co(1)−Co(3) 55.91(4), Ge(1)−Co(1)−Co(2) 55.22(4), Co(3)−Co(1)−Co(2) 59.83(4), Ge(1)−Co(2)−Co(3) 55.66(3), Ge(1)−Co(2)−Co(1) 54.67(4), Co(3)−Co(2)−Co(1) 59.57(4), Ge(1)−Co(3)−Co(1) 54.99(3), Ge(1)−Co(3)−Co(2) 55.29(4), Co(1)−Co(3)−Co(2) 60.60(4).

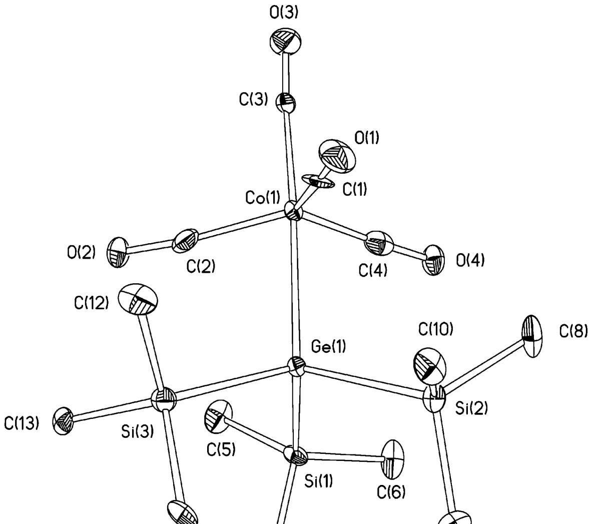

Figure 12. Molecular structure and numbering of **16** (only one of two independent molecules shown). Selected bond lengths [Å] and bond angles [deg] with SDs: Co(1)−C(1) 1.802(13), Co(1)−Ge(1) 2.5292(19), Ge(1)−Si(3) 2.401(3), Si(1)−C(6) 1.836(12), C(1)−O(1) 1.136(16), Si(1)−Ge(1)−Si(2) 109.04(11), Si(3)−Ge(1)−Co(1) 110.36(9), Si(1)−Ge(1)−Co(1) 108.44(9), Si(2)−Ge(1)−Co(1) 110.79(9).

silane with dicobalt octacarbonyl yielded a dicobalt hexacarbonyl complex with two bridging dimethylsilylene ligands. The formation of this compound can be rationalized by the occurrence of silyl−silylene metal complexes. Such complexes are well established in the chemistry of numerous metals and have been discussed also for cobalt.[25] The rather facile structural rearrangement and degradation of the coordinated oligosilyl residue seem to be responsible for the noticeable lack of examples of oligosilyl cobalt compounds. Further investigations in this direction are currently under way.

The reaction of tris(trimethylsilyl)germane with dicobalt octacarbonyl led to the cleavage of all germanium−silicon bonds and the formation of a naked germanium atom connected to four cobalt carbonyl units. A likely explanation for this reaction involves several silyl−germylene cobalt complex intermediates.

Experimental Section

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen or argon using either Schlenk techniques or a glovebox. All solvents besides $CDCl_3$ were dried over sodium/potassium alloy under nitrogen and were freshly distilled prior to use. Potassium *tert*-butoxide was purchased exclusively from Merck. Dicobalt octacarbonyl was freshly sublimed prior to use. All other chemicals were obtained from different suppliers and used without further purification.

^1H (300 MHz), ^{13}C (75.4 MHz), and ^{29}Si (59.3 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer. Samples for ^{29}Si spectra were either dissolved in a deuterated solvent or measured with a D_2O capillary in order to provide an external lock frequency signal. To compensate for the low isotopic abundance of ^{29}Si, the INEPT pulse sequence was used for the amplification of the signal.[36] Elemental analysis was carried out using a Heraeus Vario Elementar. GC analyses were carried out using a HP 5890 series II (capillary column DB-1HT; 15 m × 0.251 mm; 0.1 μm) with a flame ionization detector or a HP 5971A mass spectrometer.

The following starting materials were synthesized according to literature procedure: tris(trimethylsilyl)silylethyne (**3**),[37] tris(tri-

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methylsilyl)silylphenylacetylene (**4**),[38] $MgBr_2{\cdot}Et_2O$,[39] trimethylsilylphenylacetylene (**7**),[40] pentamethyldisilylphenylacetylene (**8**),[29,41] 1,4-bis[tris(trimethylsilyl)silylethynyl]benzene (**11**),[38] 2,2-bis(phenylalkynyl)octamethyltrisilane (**12**),[38] tris(trimethylsilyl)silane,[42] and tris(trimethylsilyl)germane.[43]

X-ray Structure Determination. For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, and data collection was performed with a Bruker-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The data were reduced to F_o^2 and corrected for absorption effects with SAINT[44] and SADABS,[45] respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97).[46] If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. All diagrams were drawn with 30% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity.

Crystallographic data (excluding structure factors) for the structures of compounds **3a**, **4a**, **5**, **7a**, **8a**, **9**, **10a**, **12a**, **13**, **14**, **15**, and **16** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-606613 (**3a**), CCDC-606606 (**4a**), CCDC-606610 (**5**), CCDC-606608 (**7a**), CCDC-606612 (**8a**), CCDC-606614 (**9**), CCDC-606616 (**10a**), CCDC-606609 (**12a**), CCDC-606607 (**13**), CCDC-606611 (**14**), CCDC-606615 (**15**), and CCDC-614323 (**16**). Copies of the data can be obtained free of charge on application via the Internet at: http://www.ccdc.cam.ac.uk/products/csd/request/.

General Procedure A. A pentane solution of the alkynyl silane was added dropwise at room temperature to $Co_2(CO)_8$ (1 or 1.02 equiv) dissolved in pentane. After stirring for 12 h the solvent was reduced in a vacuum and the residue recrystallized at −70 °C.

Bis(trimethylsilyl)silylphenylacetylene (5). To a solution of tris(trimethylsilyl)silylphenylacetylene (2.86 g, 8.20 mmol) in THF was added potassium *tert*-butoxide (0.966 g, 8.61 mmol). After an immediate color change to deep red the solution was stirred for 3 h and $MgBr_2{\cdot}Et_2O$ (2.12 g, 8.20 mmol) was added. After 2 h the mixture was poured onto 2 M H_2SO_4/Et_2O, extracted several times with diethyl ether, and dried over Na_2SO_4. The solvent was removed in a vacuum and the remaining oil distilled (140 °C, 1 mbar). Colorless crystals of **5** were obtained (2.17 g, 96%). ^{29}Si NMR (C_6D_6, δ ppm): −14.3, −90.2. ^{13}C NMR (C_6D_6, δ ppm): 138.4, 132.0, 128.4, 124.4, 110.2, 86.2, 0.5. ^1H NMR (C_6D_6, δ ppm): 7.42 (m, 2H), 6.91 (m, 3H), 4.00 (s, 1H), 0.29 (s, 18H). MS: *m*/*z* (%) 276(8) M^+, 261(37), 233(8), 217(100), 202(37), 187(81), 159(25), 129(18), 116(36), 102(4), 73(61). Anal. Calcd for $C_{14}H_{24}Si_3$ (276.60): C 60.79, H 8.75. Found: C 60.02, H 8.92.

Ethylbis(trimethylsilyl)silylphenylacetylene (6). Tris(trimethylsilyl)silylphenylacetylene (0.200 g, 0.573 mmol) was dissolved in THF, and potassium *tert*-butoxide (0.065 g, 0.583 mmol) was added. After 2 h a mixture of THF and ethyl bromide (1 mL each) was added dropwise to the deep red solution. The solution turned colorless, and cooled 2 M H_2SO_4 (10 mL) was added. The mixture was extracted several times with diethyl ether and dried over Na_2SO_4. The solvent was removed in a vacuum and the remaining oil subjected to distillation (130 °C, 1 mbar). **6** was obtained as a light yellow oil (0.131 g, 75%). ^{29}Si NMR (C_6D_6, δ ppm): −15.6, −57.7. ^{13}C NMR (C_6D_6, δ ppm): 132.1, 128.4, 128.1, 124.4, 109.9, 90.2, 10.7, 3.3, −0.8. ^1H NMR (C_6D_6, δ ppm): 7.42 (m, 2H), 6.92 (m, 3H), 1.21 (t, 3H, $J = 8$ Hz), 0.92 (q, 2H, $J = 8$ Hz), 0.28 (s, 18H). MS: *m*/*z* (%) 304(55) M^+, 275(20), 261(15), 231(20), 203(70), 187(23), 159(48), 130(69), 102(81), 73(100). Anal. Calcd for $C_{16}H_{28}Si_3$ (304.65): C 63.08, H 9.26. Found: C 62.87, H 9.21.

Pentamethyldisilanylphenylacetylene (8). The compound was prepared as described in ref 41 as a colorless liquid. ^{29}Si NMR (C_6D_6, δ ppm): −19.0, −36.9. ^{13}C NMR (C_6D_6, δ ppm): 138.4, 132.1, 128.4, 123.9, 108.1, 93.1, −2.5, −2.9. ^1H NMR (C_6D_6, δ ppm): 7.42 (m, 2H), 6.93 (m, 3H), 0.29 (s, 6H), 0.18 (s, 9H). MS: *m*/*z* (%) 232(23) M^+, 217(70), 181(5), 159(100), 129 (21), 105(12), 73(65).

Preparation of the Dicobalt Hexacarbonyl Complex of Tris(trimethylsilyl)silylacetylene (3a). Tris(trimethylsilyl)silylacetylene (**3**) (0.200 g, 0.733 mmol) and $Co_2(CO)_8$ (0.256 g, 0.748 mmol) were reacted according to procedure A. Deep red crystals were obtained after recrystallization (0.371 g, 90%). ^{29}Si NMR (C_6D_6, δ ppm): −12.3, −67.7. ^{13}C NMR (C_6D_6, δ ppm): 201.0, 90.5, 82.9, 1.4. ^1H NMR (C_6D_6, δ ppm): 6.25 (s, 1H), 0.27 (s, 27H). Anal. Calcd for $C_{17}H_{28}Co_2O_6Si_4$ (558.61): C 36.55, H 5.05. Found: C 36.71, H 5.12.

Preparation of the Dicobalt Hexacarbonyl Complex of Tris(trimethylsilyl)silylphenylacetylene (4a). Tris(trimethylsilyl)silylphenylacetylene (**4**) (0.100 g, 0.287 mmol) and $Co_2(CO)_8$ (0.098 g, 0.287 mmol) were reacted according to procedure A. Deep red crystals were obtained after recrystallization (0.171 g, 94%). ^{29}Si NMR (C_6D_6, δ ppm): −11.9, −67.1. ^{13}C NMR (C_6D_6, δ ppm): 200.6, 139.2, 129.9, 128.7, 127.9, 111.4, 75.8, 2.4. ^1H NMR (C_6D_6, δ ppm): 7.52 (m, 2H), 7.05 (m, 2H), 6.96 (m, 1H), 0.28 (s, 27H). Anal. Calcd for $C_{23}H_{32}Co_2O_6Si_4$ (634.70): C 43.52, H 5.08. Found: C 43.28, H 4.99.

Preparation of the Dicobalt Hexacarbonyl Complex of Bis(trimethylsilyl)silylphenylacetylene (5a). Bis(trimethylsilyl)silylphenylacetylene (**5**) (0.100 g, 0.362 mmol) and $Co_2(CO)_8$ (0.124 g, 0.362 mmol) were reacted according to procedure A. The reaction mixture was stirred for 5 h. A red oil was obtained (0.135 g, 95%). ^{29}Si NMR (C_6D_6, δ ppm): −13.9, −55.3. ^{13}C NMR (C_6D_6, δ ppm): 200.5, 138.4, 131.9, 129.9, 128.0, 107.9, 71.5, 0.3. ^1H NMR (C_6D_6, δ ppm): 7.64 (m, 2H), 7.04 (m, 3H), 4.29 (s, 1H), 0.24 (s, 18H). Anal. Calcd for $C_{20}H_{24}Co_2O_6Si_3$ (562.52): C 42.70, H 4.30. Found: C 42.71, H 4.42.

Preparation of the Dicobalt Hexacarbonyl Complex of Ethylbis(trimethylsilyl)silylphenylacetylene (6a). Ethylbis(trimethylsilyl)silylphenylacetylene (**6**) (0.122 g, 0.400 mmol) and $Co_2(CO)_8$ (0.136 g, 0.400 mmol) were reacted according to procedure A. Black crystals were obtained after recrystallization (0.224 g, 95%). ^{29}Si NMR (C_6D_6, δ ppm): −14.9, −33.8. ^{13}C NMR (C_6D_6, δ ppm): 200.6, 138.4, 130.1, 128.8, 128.2, 109.1, 77.9, 10.5, 7.8, 0.7. ^1H NMR (C_6D_6, δ ppm): 7.59 (m, 2H), 7.01 (m, 2H), 6.97 (m, 1H), 1.17 (m, 5H), 0.23 (s, 18H). Anal. Calcd for $C_{22}H_{28}Co_2O_6Si_3$ (590.58): C 44.74, H 4.78. Found: C 44.17, H 4.88.

Preparation of the Dicobalt Hexacarbonyl Complex of Trimethylsilylacetylene (7a). Trimethylsilylphenylacetylene (**7**) (0.200 g, 1.147 mmol) and $Co_2(CO)_8$ (0.400 g, 1.170 mmol) were reacted according to procedure A. Deep red crystals were obtained after recrystallization (0.525 g, 98%). ^{29}Si NMR (C_6D_6, δ ppm): 0.7. ^{13}C NMR (C_6D_6, δ ppm): 200.2, 138.4, 129.9, 129.2, 128.3, 106.0, 79.8, 0.6. ^1H NMR (C_6D_6, δ ppm): 7.40 (m, 2H), 6.95 (m, 3H), 0.19 (s, 9H). Anal. Calcd for $C_{17}H_{14}Co_2O_6Si$ (460.24): C 44.36, H 3.07. Found: C 44.24, H 3.01.

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Preparation of the Dicobalt Hexacarbonyl Complex of Pentamethyldisilanylphenylacetylene (8a). 1,1,1,2,2-Pentamethyldisilanylphenylacetylene (**8**) (0.100 g, 0.430 mmol) and $Co_2(CO)_8$ (0.147 g, 0.430 mmol) were reacted according to procedure A. The reaction mixture was stirred for only 4 h. Red crystals were obtained after recrystallization (0.211 g, 95%). ^{29}Si NMR (C_6D_6, δ ppm): −15.8, −18.0. ^{13}C NMR (C_6D_6, δ ppm): 200.5, 138.3, 130.1, 129.9, 129.1, 107.0, 80.1, −0.6, −1.8. ^{1}H NMR (C_6D_6, δ ppm): 7.61 (m, 3H), 6.96 (m, 2H), 0.43 (s, 6H), 0.09 (s, 9H). Anal. Calcd for $C_{19}H_{20}Co_2O_6Si_2$ (518.40): C 44.02, H 3.89. Found: C 43.70, H 3.84.

Methanolysis of 8a (9). The same amount and procedure as for **8a** was used, but after stirring for 4 h methanol (0.017 mL, 0.430 mmol) was added. The conversation was complete after 3 days (NMR control). The solvent was removed and the remaining solid recrystallized from pentane at −30 °C. Red crystals (0.156 g, 76%) were obtained. ^{29}Si NMR (C_6D_6, δ ppm): 6.9. ^{13}C NMR (C_6D_6, δ ppm): 200.2, 138.3, 130.1, 129.9, 128.4, 105.9, 79.8, 50.7, −0.7. ^{1}H NMR (C_6D_6, δ ppm): 7.68 (m, 2H), 7.02 (m, 3H), 3.32 (s, 3H), 0.37 (s, 6H). Anal. Calcd for $C_{17}H_{14}Co_2O_7Si$ (476.24): C 42.87, H 2.96. Found: C 42.26, H 3.07.

Hydrolysis of 8a and Subsequent Condensation (10 and 10a). 1,1,1,2,2-Pentamethyldisilylphenylacetylene (**8**) (0.200 g, 0.860 mmol) and $Co_2(CO)_8$ (0.294 g, 0.860 mmol) were reacted according to procedure A. After complete conversion (2.5 h) water (0.031 mL, 1.72 mmol) was added. NMR spectra after 4 h indicated a mixture of **10** and **10a**. After cooling to −30 °C dark red crystals (0.110 g, 28%) precipitated. A crystal structure analysis showed the crystals to be compound **10a**. NMR analysis of the mother liquor indicated the presence of **10**, which slowly reacted to **10a**.

NMR Data. Silanol (**10**): ^{29}Si NMR (C_6D_6, δ ppm): 5.1. ^{13}C NMR (C_6D_6, δ ppm): 200.1, 138.1, 130.1, 129.2, 128.3, 104.7, 76.9, 1.4. ^{1}H NMR (C_6D_6, δ ppm): 7.65 (m, 5H), 1.70 (s, 1H), 0.32 (s, 6H).

Siloxane (**10a**): ^{29}Si NMR (C_6D_6, δ ppm): −1.5. ^{13}C NMR (C_6D_6, δ ppm): 200.1, 138.2, 130.2, 129.1, 128.5, 105.3, 77.6, 2.5. ^{1}H NMR (C_6D_6, δ ppm): 7.01 (m, 5H), 0.48 (s, 12H). Anal. Calcd for $C_{32}H_{22}Co_4O_{13}Si_2$ (906.41): C 42.40, H 2.45. Found: C 42.07, H 2.65.

Preparation of the Tetracobalt Dodecacarbonyl Complex of 1,4-Bis[tris(trimethylsilyl)silylethynyl]benzene (11a). 1,4-Bis[tris(trimethylsilyl)silylethynyl]benzene (**11**) (0.073 g, 0.118 mmol) and $Co_2(CO)_8$ (0.081 g, 0.236 mmol) were reacted according to procedure A. Black crystals were obtained after recrystallization (0.131 g, 94%). ^{29}Si NMR (C_6D_6, δ ppm): −11.9, −66.9. ^{13}C NMR (C_6D_6 δ ppm): 200.4, 139.3, 130.2, 109.7, 76.1, 2.3. ^{1}H NMR (C_6D_6 δ ppm): 7.65 (s 4H), 0.30 (s 54H). Anal. Calcd for $C_{40}H_{58}Co_4O_{12}Si_8$ (1191.30): C 40.33, H 4.91. Found: C 40.07, H 4.97.

Preparation of the Dicobalt Hexacarbonyl Complex of 2,2-Bis(phenylethynyl)octamethyltrisilane (12a). 2,2-Bis(phenylethynyl)octamethyltrisilane (**12**) (0.200 g, 0.531 mmol) and $Co_2(CO)_8$ (0.182 g, 0.531 mmol) were reacted according to procedure A for 2 h. Black crystals were obtained after recrystallization (0.324 g, 92%). ^{29}Si NMR (C_6D_6, δ ppm): −12.3, −53.3. ^{13}C NMR (C_6D_6, δ ppm): 200.3, 138.3, 135.7, 131.8, 130.3, 128.9, 128.6, 128.5, 123.8, 111.7, 107.9, 90.0, 72.5, −0.3. ^{1}H NMR (C_6D_6, δ ppm): 7.84 (m, 2H), 7.46 (m, 2H), 7.05 (m, 3H), 6.98 (m, 3H), 0.36 (s, 18H). Anal. Calcd for $C_{28}H_{28}Co_2O_6Si_3$ (662.64): C 50.75, H 4.26. Found: C 49.98, H 4.37.

Preparation of the Tetracobalt Dodecacarbonyl Complex of 2,2-Bis(phenylethynyl)octamethyltrisilane (12b) and Its Rearrangement Product (13). 2,2-Bis(phenylethynyl)octamethyltrisilane (**12**) (0.100 g, 0.265 mmol) and $Co_2(CO)_8$ (0.182 g, 0.531 mmol) were reacted according to procedure A for 16 h. NMR spectroscopic characterization indicated quantitative formation of **12b**. ^{29}Si NMR (C_6D_6, δ ppm): −13.0, −53.7. ^{13}C NMR (C_6D_6, δ ppm): 200.4, 138.3, 131.8, 130.3, 128.9, 107.9, 72.5, −0.4. ^{1}H NMR (C_6D_6, δ ppm): 7.70 (m, 2H), 7.33 (m, 4H), 7.07 (m, 4H), 0.27 (s, 18H).

After recrystallization from pentane black crystals (0.229 g) were obtained. Single-crystal structure analysis showed the formation of **13**. Subsequent spectroscopic characterization showed the complete conversion of **12b** to **13**. ^{29}Si NMR (C_6D_6, δ ppm): 214.8, 191.1 (HMBC). ^{13}C NMR (C_6D_6, δ ppm): 219.1, 200.3, 137.8, 130.7, 130.2, 128.4, 107.8, 88.6, 14.5, 12.5, 9.9. ^{1}H NMR (C_6D_6, δ ppm): 7.55 (m, 2H), 6.99 (m, 3H), 1.18 (s, 3H), 0.73 (s, 3H), 0.60 (s, 3H). Anal. Calcd for $C_{23}H_{14}Co_4O_{12}Si_2$ (774.25): C 35.68, H 1.82. Found: C 35.61, H 1.89.

Preparation of μ_2-$(Me_2Si)_2Co_2(CO)_6$ (14). To a solution of tris(trimethylsilyl)silane (0.586 g, 2.357 mmol) in heptane (3 mL) was added dropwise $Co_2(CO)_8$ (0.806 g, 2.357 mmol) in heptane (5 mL). After stirring at 50 °C for 8 days complete conversion was observed. Cooling the solution to −70 °C caused the precipitation of black crystals (0.210 g, 22%) of **14**. ^{29}Si NMR (C_6D_6, δ ppm): 213.4 (HMBC). ^{13}C NMR (C_6D_6, δ ppm): 221.1, 11.9. ^{1}H NMR (C_6D_6, δ ppm): 0.71 (s, 12H). Anal. Calcd for $C_{10}H_{12}Co_2O_6Si_2$ (402.24): C 29.86, H 3.01. Found: C 29.74, H 2.76.

Preparation of μ_3-(germylidyncobaltotetracarbonyl)cyclotris(cobalt tricarbonyl) (15). To a solution of tris(trimethylsilyl)germane (0.230 g, 0.784 mmol) in pentane (2 mL) was added dropwise $Co_2(CO)_8$ (0.268 g, 0.784 mmol) in pentane (4 mL). After stirring at room temperature for 16 h complete conversion was observed. Cooling the solution to −70 °C caused the precipitation of black crystals (0.152 g, 58%) of **15**. ^{13}C NMR (C_6D_6, δ ppm): 201.5, 201.0, 193.5. Anal. Calcd for $C_{13}Co_4GeO_{13}$ (672.47): C 23.22. Found: 23.57.

Preparation of Tris(trimethylsilyl)germyl Cobalt Tetracarbonyl (16). A solution of tris(trimethylsilyl)germane (0.200 g, 0.682 mmol) in pentane (3 mL) was added dropwise to $Co_2(CO)_8$ (0.117 g, 0.341 mmol) in pentane (3 mL). After stirring at room temperature for 3 days complete conversion of the germane was observed. Cooling the solution to −70 °C caused the precipitation of black (**15**) and yellow (**16**) crystals. ^{29}Si NMR (C_6D_6, δ ppm): 0.0. ^{13}C NMR (C_6D_6, δ ppm): 200.9, 2.5. ^{1}H NMR (C_6D_6, δ ppm): 0.34 (s, 27H). Anal. Calcd for $C_{13}H_{27}CoGeO_4Si_3$ (463.15): C 33.71, H 5.88. Found: C 33.37, H 5.98.

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