Synthesis of 4:5-Benzo-1-cobalta-2-silacyclopentenes and their Reactions with Alkynes and Alkenes: An Expedient Route to Silicon-Containing Polycyclic Frameworks

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A convenient route to polycyclic compounds incorporating a silicon atom at a ring junction has been developed. Benzosilacyclobutenes tethered to alkynes or alkenes undergo intramolecular cycloadditions in the presence of $CpCo(CO)_2$. The incorporation of the CpCo(CO) moiety into the benzosilacyclobutene framework occurs regioselectively at the Ar−Si bond of the silacycle to give 1-cobalta-2-silacyclopentenes. On the basis of DFT/B3LYP calculations, a nonadiabatic mechanism involving changes in the spin state is proposed.

Introduction

Silacyclobutanes have a rich diversity of chemical applications due to their ring strain and Lewis acidity. A variety of group 10 transition-metal-catalyzed transformations of silacyclobutanes has been reported, including ring-opening dimerization and polymerization (ROP),[1] coupling reactions,[2] and ring opening and ring expansion with aldehydes.[3] 1-Metalla-2-silacyclopentanes have been postulated as likely intermediates in both ROP and cycloadditions to silacyclobutanes.[1,4,5] In analogy with transition-metal-catalyzed cyclotrimerizations of alkynes,[6] or cocyclizations of alkynes with alkenes,[7] which usually proceed via five-membered metallacycles, one could think of trapping these intermediates with double or triple C−C bonds (Figure 1). In an intramolecular version, this strategy would provide an expedient access to (rare[8]) polycyclic compounds displaying a silicon atom at the ring junction. This seems particularly relevant since the incorporation of a silicon atom into the framework of natural products can have a dramatic influence on the biological activities.[9] Intermolecular cycloadditions of alkynes and allenes to silacyclobutanes have already been successfully achieved under palladium catalysis.[4,10] However, this reaction is not regioselective and, at least in our hands, not compatible with alkenes. To address these critical issues, we have explored the reactivity of silacyclobutanes toward cobalt complexes. The scope and the limitations of the title reaction, as well as a mechanistic study based on DFT computations, are reported herein.

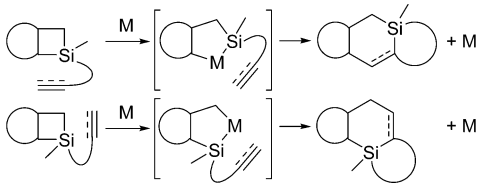

Figure 1. Prototypical metal-mediated intramolecular cycloadditions of silacyclobutanes to double or triple C−C bonds via C−Si activation.

Results and Discussion

Reactions of Cobalt Complexes with Benzosilacyclobutenes. We started our investigations using $CpCo(C_2H_4)_2$,[11] which has been exploited previously as an active source of CpCo in cooligomerizations of alkynes with alkenes.[12] The reaction of 1,1-diphenylbenzosilacyclobutene (**1a**) with stoichiometric or catalytic amounts of $CpCo(C_2H_4)_2$ gave rise to dimerization and higher oligomerization products (Scheme 1). The structure of the dimer **2** could be confirmed by its mass spectral characteristics, including a molecular ion at $m/z = 562$ (MNH_4^+). In the

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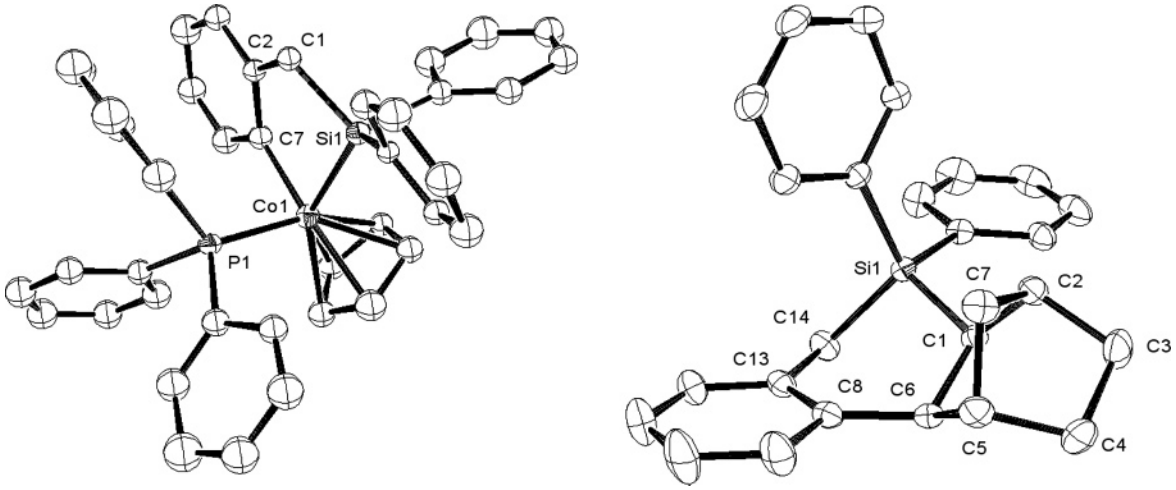
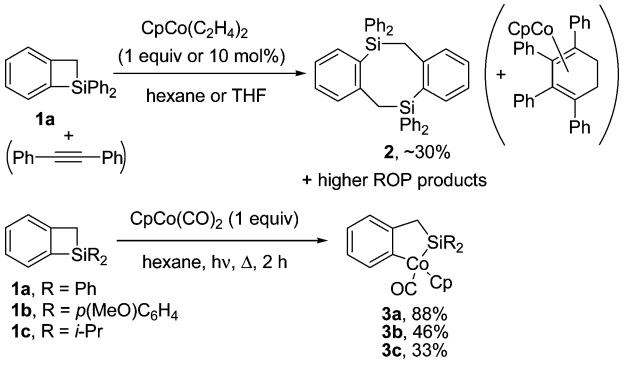


Figure 2. ORTEP of **4** (left) and **9** (right) with hydrogen atoms omitted for clarity (30% thermal ellipsoids).

Scheme 1. Divergent Behaviors of Benzosilacyclobutenes toward Cobalt Complexes



presence of an alkyne such as diphenylacetylene, the [2+2+2] cocyclization with a cobalt ethene ligand prevailed. To circumvent this problem, we decided to carry out a stepwise approach, acting first on the benzosilacyclobutene. In order to avoid the dimerization of the substrate, a cobalt complex with less labile ligands was chosen. Whereas $CpCo(C_2H_4)_2$ turns over already at room or lower temperatures, $CpCo(CO)_2$ requires light and/or heat to be active.[6] In sharp contrast with $CpCo(C_2H_4)_2$, the reactions of **1a**−**c** with $CpCo(CO)_2$ in refluxing hexane under visible light irradiation gave no ROP products. Instead, 1-cobalta-2-silacyclobutenes **3a**−**c** were isolated in 88, 48, and 33% yield, respectively, as deep yellow solids showing unexpected air stability for Co^{III} organometallic species. They were purified by flash chromatography on silica gel without special precautions. The carbonyl functionality was evident from ^{13}C NMR (**3a**: δ 203.8 ppm) and IR (**3a**: $\tilde{\nu}_{CO} = 1972\ cm^{-1}$) spectroscopy. The formation of a Co−Si bond was suggested by the strong downfield shift of the ^{29}Si nucleus compared to the starting material (^{29}Si NMR ($CDCl_3$): δ (ppm) = 48.1 (**3a**); −4.2 (**1a**)). Since ^1H and ^{13}C chemical shifts of the CH_2 group did not show any significant alteration compared to the starting material, we supposed that the Co insertion occurred regioselectively into the Ar−Si bond.[13]

Although crystals of **3a** were not suitable for single-crystal X-ray analysis, its structure was unambiguously confirmed after CO/PPh_3 exchange (Figure 2 and Table 1). An equimolar solution of **3a** and PPh_3 in CH_2Cl_2 was allowed to stand at room temperature for one week, and the slow evaporation produced X-ray-quality crystals. The diffraction study of complex **4** showed that the insertion of cobalt occurred into the most electrophilic C−Si bond of the four-membered ring, i.e., the Csp^2−Si one. The metallacycle adopts an envelope conformation with a fold angle of 136.2° in which the cobalt and the three carbon atoms are almost coplanar (Co−C7−C2−C1 3.7°). The Co−P bond length equals those reported for ((cyclopentadienylalkyl)phosphane)cobalt(III) chelate complexes with silyl ligands (2.17 Å).[14] The Co−Si bond is just slightly longer (2.27 vs 2.23−2.25 Å). Interestingly, the quite small Si−Co−C7 angle of 79.6° is indicative of some strain in the five-membered ring.[15]

Bimolecular Reactions of the Cobaltasilacyclopentenes with Alkynes or Alkenes. The site chosen for Co insertion into benzosilacyclobutenes is the more sterically hindered, but involves phenyl- rather than benzyl−silicon cleavage. The same

(7) For reviews, see: (a) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, pp 1129−1162. (b) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49−92. (c) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. *J. Chem. Rev.* **1996**, *96*, 635−662. (d) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901−2915. (e) Malacria, M.; Aubert, C.; Renaud, J.-L. In *Science of Synthesis: Houben-Weyl Methods of Molecular Transformations*; Lautens, M., Trost, B. M., Eds.; Georg Thieme Verlag: Stuttgart, 2001; Vol. 1, pp 439−530. (f) Gevorgyan, V.; Radhakrishnan, U.; Takeda, A.; Rubina, M.; Rubin, M.; Yamamoto, Y. *J. Org. Chem.* **2001**, *66*, 2835−2841. (g) Yamamoto, Y. *Curr. Org. Chem.* **2005**, *9*, 1699−1712.

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(12) For a recent example, see: Gandon, V.; Lebœuf, D.; Amslinger, S.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *Angew. Chem.* **2005**, *117*, 7276−7280; *Angew. Chem., Int. Ed.* **2005**, *44*, 7114−7118, and references therein.

(13) For a related Si−Si bond activation by $CpCo(CO)_2$, see: Jzang, T.-t.; Liu, C.-s. *Organometallics* **1988**, *7*, 1271−1277.

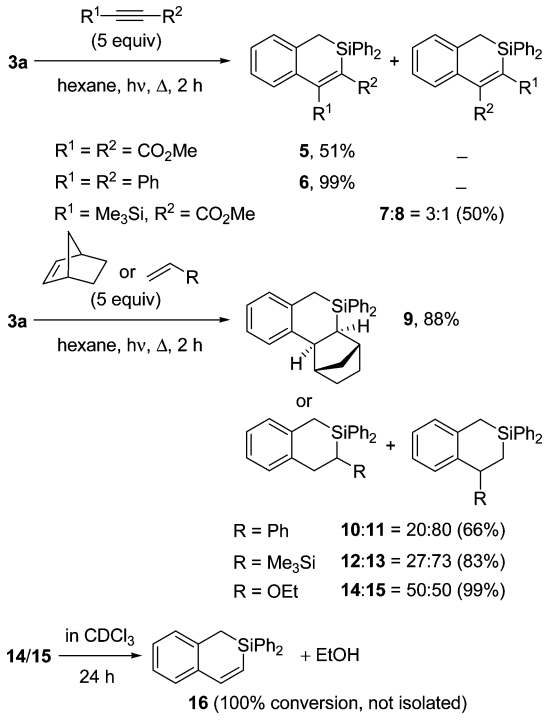
(14) Yong, L.; Hofer, E.; Wartchow, R.; Butenschön, H. *Organometallics* **2003**, *22*, 5463−5467.

(15) For a related structure in the rhodium series, see: Mitchell, G. P.; Tilley, T. D. *Organometallics* **1998**, *17*, 2912−2916.

Table 1. Crystal Data and Structure Refinement for Compounds 4 and 9

	4	9
formula	$C_{42}H_{36}CoPSi$	$C_{26}H_{26}Si$
M (g·mol^{-1})	658.74	366.58
cryst class	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a (Å)	17.742(5)	9.652(4)
b (Å)	18.117(9)	10.6303(8)
c (Å)	20.848(12)	11.3573(7)
α (deg)	90	100.878(5)
β (deg)	99.46(4)	96.738(5)
γ (deg)	90	113.755(4)
volume (Å^3)	6610(5)	1022.95(9)
Z	8	2
μ (mm^{-1})	0.63	1.22
T (K)	295	250
diffractometer type	Enraf-Nonius-Mach3	KappaCCD-Enraf-Nonius
θ min, max	1, 25	2, 30
octants collected	0, 21; 0, 21; −24, 24	−13, 13; −14, 14; −15, 15
total and unique no. of data, R_{int}	12 435, 11 597, 0.03	18 799, 5897, 0.032
no. of reflns used	3791	3938
no. of reflns, no. of params	11 597, 392	5897, 245
R, R_w, GOF	0.0832, 0.0795, 1.178	0.037, 0.043, 1.069

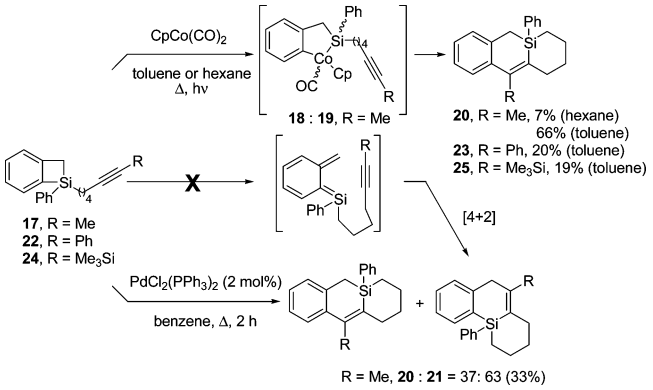
Scheme 2. Reactions of Complex 3a with Alkynes and Alkenes



regioselectivity was reported with $Fe_2(CO)_9$; however the resulting iron complexes proved unreactive toward alkynes and alkenes.[16] In contrast, under visible light irradiation, complex **3a** was actually transformed into benzosilacyclohexene **5** or **6** when mixed with an excess of DMAD or diphenylacetylene in refluxing hexane (Scheme 2). These products were obtained in 51 and 99% isolated yield, respectively. The incorporation of π systems into the starting benzosilacyclobutenes resulted in upfield shifts of the ^{29}Si signals (δ (ppm) = −4.2 (**1a**), −18.7 (**5**), −21.5 (**6**)).[1c] Methyl 3-(trimethylsilyl)propiolate gave a 3:1 regioisomeric mixture of compounds **7** and **8** in favor of the β-disilylated one, as indicated by NOE, DEPT, and 2D-NMR analyses.

(16) (a) Cundy, C. S.; Lappert, M. F.; Dubac, J.; Mazerolles, P. *J. Chem. Soc., Dalton Trans.* **1976**, 910−914. (b) Cundy, C. S.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1978**, 665−673.

Scheme 3. One-Pot Intramolecular Cycloadditions of Four-Carbon Alkyne-Tethered Benzosilacyclobutenes



Good yields were also obtained from alkenes. For instance, the reaction of **3a** with norbornene gave the polycyclic compound **9** in 88% yield as a single diastereomer whose stereochemical arrangement was unambiguously assigned after single-crystal X-ray analysis (see Table 1 and Supporting Information). Monosubstituted alkenes such as styrene or vinyltrimethylsilane gave mixtures of regioisomers in favor of the less crowded ones in good to excellent yields. Although not regioselective, the incorporation of ethyl vinyl ether proved very efficient (99% yield). Compounds **14** and **15** slowly eliminate ethyl alcohol after prolonged time in $CDCl_3$ to give silacyclohexene **16**. We suspect that this elimination is catalyzed by adventitious acid.

Intramolecular Version. When applying the conditions described above to alkyne-tethered benzosilacyclobutenes including a 4-methylene spacer, yields and conversion to the desired products were scarce. For instance, benzosilacyclobutene **17** afforded the linear tricyclic compound **20** in a low 7% isolated yield (Scheme 3). However, when boiling toluene was used instead of hexane, the isolated yield was improved to 66%. The regioselectivity observed during this cyclization rules out a [4+2] cyclization via a transient ortho(sila)quinodimethane, as described in the all-carbon series.[6d] Such a mechanism would provide only the angular isomer **21**, which is not obtained here. On the other hand, the intermediacy of 1-cobalta-2-silacyclobutenes could be confirmed by interrupting the irradiation after 1 h. In this case, diastereoisomeric complexes **18** and **19** could be isolated from the reaction mixture. Execution of the previously described palladium-based protocol[4] with **17** also led to cycloaddition products, albeit less efficiently and regioselectively, furnishing the two isomers **20** and **21** (1:1.7), in 33% combined yield.

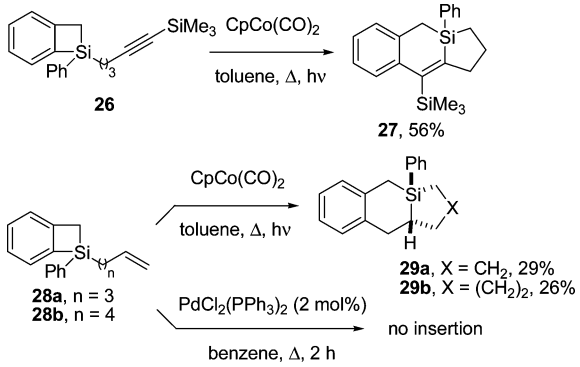
Benzosilacyclobutenes **22** and **24** were also rapidly converted into the corresponding vinyl silanes **23** and **25**. The transformation of the alkynyl-SiMe$_3$ moiety of **24** into a vinylsilane framework could be evidenced by the downfield shift of the ^{29}Si NMR signals (δ (ppm) −19.4 (**24**); −8.6 (**25**)). On the other hand, the resonance peak of the four-membered ring silicon was shifted upfield after subsequent vinylation (δ (ppm) 3.6 (**24**); −28.4 (**25**)). Disappointingly, the isolated yields corresponding to these two transformations were low (20 and 19%, respectively). However, reducing the tether length by one carbon as in **26** provided the linear 6/6/5 fused heterocycle **27** in an improved 56% isolated yield (Scheme 4). Intramolecular cy-

Table 2. Electronic Energies, Enthalpies, Free Energies, and Single-Point Energies

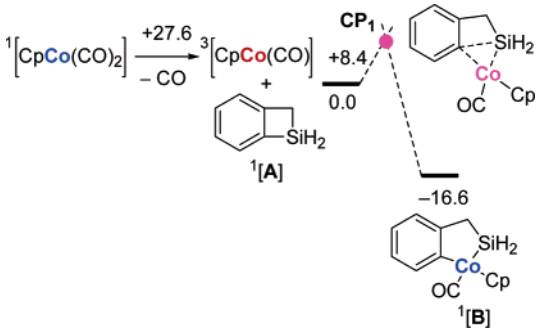
	LACVP(d,p)				6-311+G(2d,2p)
	E_{298} (au)[a]	H_{298} (au)[b]	G_{298} (au)[b]	imaginary frequency (cm^{-1})	E_{298} (au)[c]
CO	−113.304423	−113.301118	−113.323561		−113.351680632
C_2H_2	−77.302842	−77.299001	−77.321849		−77.3591391899
^{1}[CpCo(CO)$_2$]	−565.199077	−565.189503	−565.233265		−1803.13359318
^{1}[CpCo(CO)]	−451.814714	−451.807017	−451.846229		−1689.69812392
^{3}[CpCo(CO)]	−451.860227	−451.851449	−451.895024		−1689.73800388
^{3}[CpCo]	−338.483560	−338.477297	−338.512298		−1576.31379994
^{1}[**A**]	−560.919437	−560.911648	−560.950494		−561.139267695
CP$_1$					−2250.86388551
^{1}[**B**]	−1012.792175	−1012.776082	−1012.834751		−2250.90358583
^{3}[**C**]	−899.450007	−899.435319	−899.492715		−2137.50656881
CP$_2$					−2214.85132367
^{1}[**D**]	−976.758312	−976.741586	−976.800792		−2214.87588468
TS$_1$	−976.754843	−976.739036	−976.795993	−168	−2214.87042808
^{1}[**E**]	−976.776122	−976.759744	−976.819191		−2214.88914073
CP$_3$					−2214.88913481
^{3}[**E**]	−976.801837	−976.785151	−976.846704		−2214.91325369
TS$_2$	−976.794620	−976.778553	−976.838495	−180	−2214.90136677
^{3}[**F**]	−976.861188	−976.845063	−976.906026		−2214.96734703
^{1}[**G**]	−638.324558	−638.315123	−976.906026		−638.598563997

[a] Includes ZPE correction. [b]Includes thermal correction at 298 K. [c]Uncorrected.

Scheme 4. One-Pot Intramolecular Cycloadditions of Three-Carbon Alkene- and Alkyne-Tethered Benzosilacyclobutenes



Scheme 5. Computed Pathway for the Formation of 1-Cobalta-2-silacyclopentene B at the DFT/B3LYP Level (energies in kcal/mol)



cloaddition of C−C double bonds could also be accomplished, albeit less efficiently. Compounds **29a** and **29b** were obtained as single diastereomers in 29 and 26% yield, respectively. Comparatively, under palladium catalysis, the insertion of the C−C double bonds did not take place. Contrary to alkyne insertion, the incorporation of an alkene into the Ar−Si bond of the benzosilacyclobutene framework resulted in a downfield shift of the ^{29}Si signals as a result of the partial deconjugation, the silicon atom bearing two aryl groups in the starting material and only one in the product (δ (ppm) = 3.7 (**28a**); 13.6 (**29a**)).

Theoretical Calculations. We next attempted to answer some questions about the mechanism, e.g., (i) does the reaction between 1-cobalta-2-silacyclobutene and alkynes (alkenes) proceed associatively or does it require dissociation of CO? (ii) if CO is lost, does the next step correspond to a [4+2] cycloaddition between the unsaturated metallacycle and the alkyne (alkene) or does it correspond to an insertion? (iii) if insertion prevails, does it occur into the Co−C or the Co−Si bond of the metallacycle? In order to gain deeper insight, we studied the mechanism of the reaction of benzosilacyclobutene **A** with CpCo(CO)$_2$ and acetylene by means of DFT computations at the B3LYP/LACVP(d,p) level (Schemes 4 and 5). The choice of this level of theory was validated by a very good agreement between the structural parameters of complex **4** and the computed ones for its parent compound (see Supporting Information). Energies were then reevaluated at the 6-311+G(2d,2p) level for all atoms, as suggested by Poli and Smith.[17]

No associative pathway between CpCo(CO)$_2$ and benzosilacyclobutene **A** leading to **B** could be found. Therefore, we envisaged the dissociation of CpCo(CO)$_2$ into CpCo(CO) and CO (Scheme 5). It is now well-established that unsaturated d^8 CpML species usually exhibit a triplet ground state, whereas the 18-electron ones (CpMLL′) exhibit a singlet ground state.[18] A spin change is therefore required when ^{1}[CpCo(CO)$_2$] eliminates CO (under irradiation or heat) to give ^{3}[CpCo(CO)]. Reactions that require a spin change are likely to occur if a minimum energy crossing point (MECP) of the singlet and triplet energy surfaces can be found close to the reagents (two-state mechanism).[18,19] This was actually the case for the dissociation of ^{1}[CpCo(CO)$_2$] into ^{3}[CpCo(CO)] and CO, as shown by Harvey and co-workers.[18d] In order to connect ^{3}[CpCo(CO)] and benzosilacyclobutene **A** with complex **B** of singlet ground state, we sought a nearby MECP. **CP$_1$** was actually located 8.4 kcal/mol above the reactants (Table 2). At this point, the Co−C and Co−Si bonds are essentially formed (Figure 3, **CP$_1$**: Co−C = 2.04 Å, Co−Si = 2.37 Å; **B**: Co−C

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(18) See: (a) Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1996**, *118*, 1487−1496. (b) Su, M.-D.; Chu, S.-Y. *Chem.−Eur. J.* **1999**, *5*, 198−207. (c) Smith, K. M.; Poli, R.; Harvey, J. N. *Chem.−Eur. J.* **2001**, *7*, 1679−1690. (d) Carreón-Macedo, J.-L.; Harvey, J. N. *J. Am. Chem. Soc.* **2004**, *126*, 5789−5797. (e) Petit, A.; Richard, P.; Cacelli, I.; Poli, R. *Chem.−Eur. J.* **2006**, *12*, 813−823. (f) Gandon, V.; Agenet, N.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *J. Am. Chem. Soc.* **2006**, *128*, 8509−8520, and pertinent references therein.

(19) (a) Yarkony, D. R. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; p 642. (b) Yarkony, D. R. *J. Phys. Chem.* **1996**, *100*, 18612−18628. (c) Schröder, D.; Shaik, S.; Schwartz, H. *Acc. Chem. Res.* **2000**, *33*, 139−145.

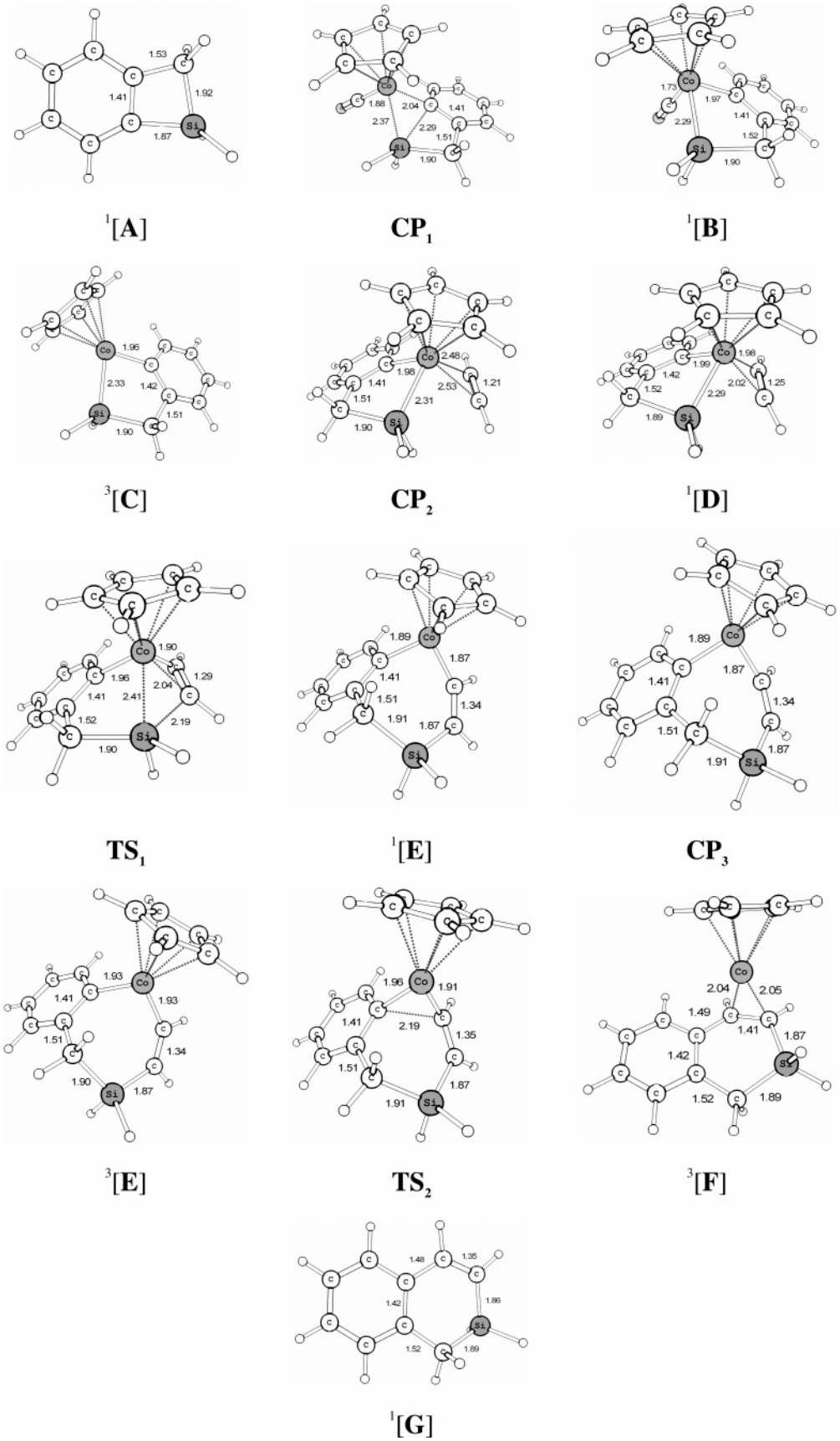
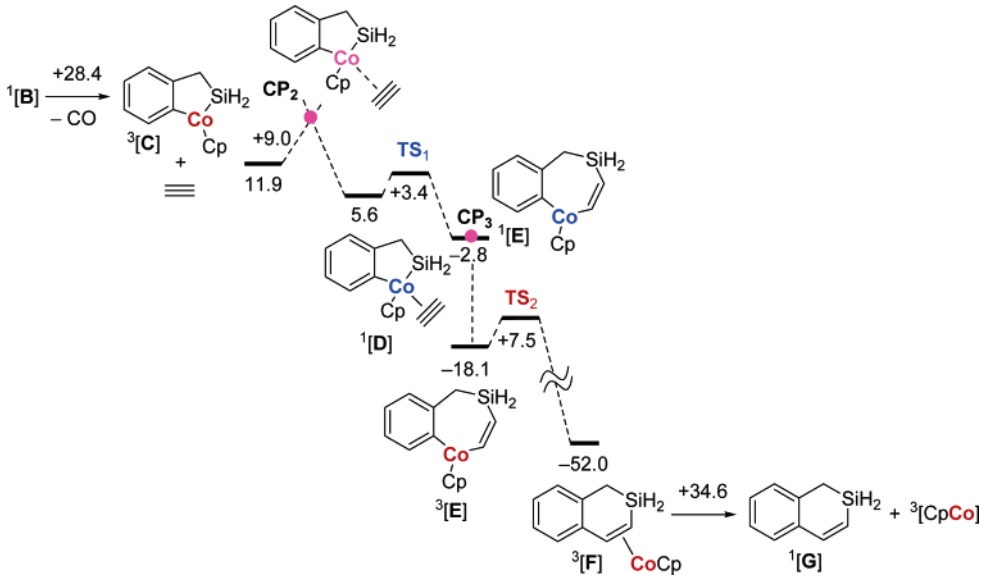


Figure 3. Structures of various species depicted in Schemes 4 and 5, with selected bond distances (Å).

= 1.97 Å, Co−Si = 2.29 Å). The distance corresponding to the breaking Csp^2−Si bond is already long (Csp^2−Si in **A**: = 1.87 Å; **CP$_1$**: 2.29 Å; **B**: 2.80 Å). The main difference between **CP$_1$** and **B** is the Co−C−C−C fold angle of the five-membered ring (**CP$_1$**: 29.0°; **B**: 4.2°). This step is appreciably exothermic by 16.5 kcal/mol.

Again, no favorable associative pathway could be modeled for the transformation of **B** into **D** (Scheme 6). The energy

Scheme 6. Computed Pathway for the Formation of Silacyclohexene G at the DFT/B3LYP Level (energies in kcal/mol, relative to the {^{3}[CpCo(CO)] + A} system)

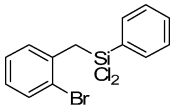


required for the dissociation of CO was evaluated to be 28.4 kcal/mol. The triplet species **C** then reacts with acetylene to give singlet complex **D**. The crossing point corresponding to this reaction lies 9.0 kcal/mol above **C**. The geometry at **CP$_2$** is close to that of **D** except for the distance between Co and the center of the C−C triple bond (**CP$_2$**: 2.43 Å; **D**: 1.90 Å). This transformation is exothermic by 6.3 kcal/mol. From complex **D**, insertion of the complexed alkyne into the Co−Si bond is found to be kinetically twice as easy as the insertion into the Co−C bond (3.4 kcal/mol vs 7.5 kcal/mol). The formation of the resulting 16-electron complex **E** in the singlet state is exothermic by 8.4 kcal/mol. The relaxation of this complex to its triplet ground state (ΔE_{S-T} = 15.3 kcal/mol) is made straightforward by the existence of **CP$_3$**, virtually superimposed with singlet **E** (ΔE < 0.1 kcal/mol, rmsd 0.0007). Finally, a transition state connecting the two triplet species **E** and **F** was found 7.5 kcal/mol above triplet **E**. This transformation is strongly exothermic by 33.9 kcal/mol. The dissociation of **F** into the final product **G** and CpCo requires 34.6 kcal/mol. The latter fragment has a triplet ground state ($\Delta E_{Singlet-Triplet}$ = 38.0 kcal/mol, $\Delta E_{Singlet-Quintet}$ = 29.3 kcal/mol). Manifold effort failed to locate a transition state connecting ^{3}[CpCo] and **A** to ^{3}[**C**]. This might explain why the reaction requires a stoichiometric amount of CpCo(CO)$_2$. One way to address this issue could be the use of an external source of CO to regenerate CpCo(CO).

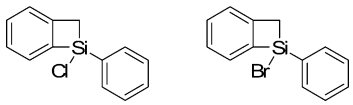
In conclusion, we have found that the reaction of CpCo(CO)$_2$ with benzosilacyclobutenes gives the corresponding unprecedented 1-cobalta-2-silacylobutenes after regioselective insertion of cobalt into the phenyl−silicon bond of the silacycle. Unlike their iron counterparts, these complexes are reactive with alkynes and alkenes (electron-rich or electron-poor) to give benzosilacyclohexenes. The one-pot intramolecular version of this reaction provides access to polycyclic compounds incorporating a silicon atom at the ring junction. A two-state mechanism is proposed on the basis of DFT computations. It shows that the dissociation of CO opens a vacant site for the alkyne, which inserts preferably into the Co−Si σ-bond. We are now applying this new reaction to the synthesis of silicon containing bioisosters of natural products.

Experimental Section

General Methods. Reactions were carried out under argon using standard Schlenk techniques. Dichloromethane was distilled over calcium hydride. *n*-Hexane, benzene, and toluene were distilled from $NaK_{2.8}$. THF was distilled from sodium benzophenone ketyl. The reactions were irradiated (visible light) using a quartz (non-UV block) 300 W ELW AX2275.GY5.3 120V halogen lamp (color temperature 3350 K) at 50% of its power (using a potentiometer). Thin-layer chromatography (TLC) was performed on Merck 60 F_{254} silica gel. Merk Gerudan SI 60 Å silica gel (35−70 μm) was used for column chromatography. CpCo(CO)$_2$ was purchased from Aldrich and used as received. CpCo(C_2H_4)$_2$ was prepared according to a known procedure.[11a] ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 20 °C at 400, 100, and 162 MHz, respectively, on a Bruker AVANCE400 spectrometer. ^{29}Si spectra were recorded at 20 °C at 60 MHz on a Bruker AVANCE300 spectrometer (SiH INEPT). Chemical shifts (δ) are given in ppm, referenced to the residual proton resonance of the solvents (7.26 for $CDCl_3$; 7.16 for C_6D_6), to the residual carbon resonance of the solvent (77.16 for $CDCl_3$; 128.06 for C_6D_6), or using a coaxial tube of H_3PO_4 80% in H_2O as a reference for ^{31}P or external reference (TMS) for ^{29}Si. Coupling constants (*J*) are given in hertz (Hz). The terms m, s, d, t, q, and quint refer to multiplet, singlet, doublet, triplet, quartet, and quintet; br means that the signal is broad. When possible, NMR signals were assigned on the basis of NOE, DEPT, and 2D-NMR (COSY, HMBC) experiments. Elemental analyses, low-resolution mass spectra (MS), and high-resolution mass spectra (HRMS) were performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie or by the Service de Spectrométrie de Masse de l'ICSN-CNRS, Gif-sur-Yvette. Infrared spectra (IR) were recorded on a Bruker Tensor 27 spectrometer. Melting points were obtained on a Büchi capillary apparatus and were not corrected. Copies of the ^{1}H and ^{13}C NMR spectra of all new compounds have been deposited with the Supporting Information as evidence of their purity.



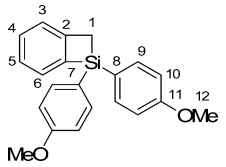
(2-Bromobenzyl)dichloro(phenyl)silane.[20] The Grignard reagent of 2-bromobenzyl bromide (25 g, 100 mmol) was prepared at 0 °C in 100 mL of diethyl ether: the bromide, in 90 mL of diethyl ether, was added over 2 h on magnesium turnings (2.43 g, 100 mmol) covered by 10 mL of diethyl ether. Then, the reaction mixture was allowed to stir for 1 h at rt. The Grignard reagent was transferred via cannula into a solution of phenyltrichlorosilane (40 mL, 250 mmol) in 80 mL of diethyl ether at 0 °C. The solution was refluxed for 17 h, the salts were eliminated by filtration, and the solvent removed *in vacuo*. Fraction distillation gave 25.9 g of excess phenyltrichlorosilane (35 °C, 0.04 mmHg) and 24.7 g (71%) of (2-bromobenzyl)dichloro(phenyl)silane (110 °C, 0.04 mmHg) as a colorless oil. ^{1}H NMR (C_6D_6): δ 7.54−7.52 (m, 2 H), 7.26 (dd, J = 8.1 Hz, J = 1.2 Hz, 1 H), 7.10−7.06 (m, 1 H), 7.03−6.99 (m, 2 H), 6.95 (dd, J = 7.7 Hz, J = 1.6 Hz, 1 H), 6.80 (td, J = 7.6 Hz, J = 1.3 Hz, 1 H), 6.57 (td, J = 7.7 Hz, J = 1.7 Hz, 1 H), 2.89 (s, 2 H). ^{13}C NMR (C_6D_6): δ 133.7 (C_{arom}), 133.0 (2 CH_{arom}), 132.2 (CH_{arom}), 130.8 (CH_{arom}), 129.9 (CH_{arom}), 127.4 (2 CH_{arom}), 126.6 (CH_{arom}), 126.6 (CH_{arom}), 123.9 (C_{arom}), 29.4 (CH_2), one C_{arom} overlapped with solvent residual peak. ^{29}Si NMR (C_6D_6): δ 13.4.



1-Chloro- and 1-Bromo-1-phenyl-2:3-benzo-1-silacyclobut-2-ene.[21] (2-Bromobenzyl)dichloro(phenyl)silane (24.7 g, 71 mmol) and 1,2-dibromoethane (0.6 mL, 7 mmol) in diethyl ether (80 mL) were added within 6 h, maintaining a gentle reflux, over magnesium turnings (3.45 g, 142 mmol). The reaction mixture was allowed to stir for 1 h at rt. The solution was refluxed for 24 h, and then the salts were removed by filtration and the solvent was removed *in vacuo*. Fraction distillation yielded 13.7 g of 1-chloro- and 1-bromo-1-phenyl-2:3-benzo-1-silacyclobut-2-ene (65−73 °C, 0.04 mmHg) as a 3:1 mixture (colorless oil). ^{1}H NMR (C_6D_6): δ 7.63−7.60 (m, 2 H), 7.21−7.19 (m, 1 H), 7.17−6.97 (m, 6 H), 2.60 (d, J_{AB} = 17.2 Hz, 1 H), 2.48 (d, J_{AB} = 17.2 Hz, 1 H); Si−Br compound: 2.67 (d, J_{AB} = 17.2 Hz, 1 H), 2.51 (d, J_{AB} = 17.2 Hz, 1 H). ^{13}C NMR (C_6D_6): δ 150.2 (C_{arom}), 143.2 (C_{arom}), 134.4 (CH_{arom}), 134.3 (CH_{arom}), 133.1 (CH_{arom}), 132.9 (CH_{arom}), 131.4 (CH_{arom}), 130.9 (CH_{arom}), 128.6 (CH_{arom}), 128.0 (CH_{arom}), 127.4 (CH_{arom}), 127.2 (CH_{arom}), 26.4 (CH_2, Si−Br), 26.2 (CH_2, Si−Cl). ^{29}Si NMR (C_6D_6): δ 2.6 (Si−Cl), −1.1 (Si−Br).

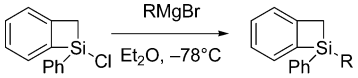
Benzosilacyclobutenes. Compounds **1a** and **1c** were prepared according to a literature procedure.[22]

Compound 1b. The Grignard reagent of 4-bromoanisole (1.75 M, 9 mL, 15.7 mmol, prepared as above at gentle reflux instead of 0 °C) was added to a solution of 1,1-dichloro-2:3-benzo-1-silacyclobut-2-ene[23] (1.49 g, 7.9 mmol) in 20 mL of diethyl ether at −78 °C. The solution was allowed to warm to rt overnight. The reaction was quenched with saturated NH_4Cl, and the organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed by rotary evaporation. Flash chromatography over silica gel using petroleum ether/diethyl ether (9:1) as eluent yielded **1b** as a colorless oil (1.53 g, 58%).



Compound **1b**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.57 (d, J = 7.6 Hz, 4 H), 7.47 (br s, 1 H), 7.38−7.35 (m, 1 H), 7.28−7.26 (m, overlap with solvent residual peak, 2 H), 3.81 (s, 6 H, H_{12}), 2.56 (d, 2 H, H_1). ^{13}C NMR ($CDCl_3$): δ 161.9 (2 C, C^{IV}), 152.2 (C^{IV}), 144.8 (C^{IV}), 137.1 (2 C, C^{III}), 131.3 (C^{III}), 128.3 (C^{III}), 127.5 (C^{III}), 127.2 (C^{III}), 125.6 (2 C, C^{IV}), 114.3 (2 C, C^{III}), 54.5 (2 C, C_{12}), 21.1 (C_1). ^{29}Si NMR ($CDCl_3$): δ −4.6. IR (neat): $\tilde{\nu}_{max}$ 3439, 3023, 2836, 1593, 1503, 1278, 1248, 1208, 1116, 1029 cm^{-1}.

The following compounds were prepared from 1-chloro- and 1-bromo-1-phenyl-2:3-benzo-1-silacyclobut-2-ene (using the procedure described in the literature)[24] followed by condensation of the corresponding Grignard or lithium reagent (according to the procedure reported in the literature).[23]

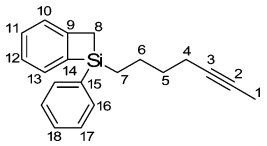


	R	Yield
17	$(CH_2)_4$–C≡C–CH_3	33%
22	$(CH_2)_4$–C≡C–$SiMe_3$	30%
24	$(CH_2)_4$–C≡C–Ph	20%[a]
26	$(CH_2)_3$–C≡C–$SiMe_3$	7%
28a	$(CH_2)_3$–CH=CH_2	61%
28b	$(CH_2)_4$–CH=CH_2	68%

[a] Grignard reagent is unstable,[25] lithium derivative was used instead.

Representative Procedure. The Grignard reagent of 1-bromopent-4-ene (1.18 mL, 10 mmol) was prepared at room temperature in 15 mL of diethyl ether. The bromide was added over 2 h on magnesium turnings (272 mg, 11.2 mmol), then the reaction mixture was allowed to stir for 2 h at room temperature. It was then canulated into a solution of 1-chloro- and 1-bromo-1-phenyl-2:3-benzo-1-silacyclobut-2-ene (7.5 mmol) in 15 mL of diethyl ether at −78 °C. The solution was allowed to warm to room temperature overnight. The reaction was quenched with saturated NH_4Cl, and the organic layer was washed with brine and dried with $MgSO_4$. The solvent was removed by rotary evaporation. Flash chromatography over silica gel using petroleum ether as eluent yields compound **28a** as a transparent oil (1.92 g, 61%).

Due to 4- and 5-*exo*-dig autocyclization of the Grignard reagent,[25] or the lithium derivative,[26] the yields corresponding to compounds **17**, **22**, **24**, and **26** are irremediably low.



Compound **17**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.61−7.58 (m, 2 H, H_{16}), 7.42−7.35 (m, 5 H), 7.26−7.20 (m, 2 H), 2.39 (d, J_{AB} = 16.7 Hz, 1 H, H_8), 2.32 (d, J_{AB} = 16.7 Hz, 1 H, H_8), 2.14−2.09 (m, 2 H, H_4), 1.75 (t, J = 2.5 Hz, 3 H, H_1), 1.60−1.54 (m, 4 H, H_5−6), 1.30−1.20 (m, 2 H, H_7). ^{13}C NMR ($CDCl_3$): δ 151.7 (C_9), 143.7 (C_{14}), 135.7 (C_{15}), 134.2 (2 C, C_{16}), 131.0 (C^{III}), 130.7 (C^{III}), 129.8 (C^{III}), 128.0 (2 C, C_{17}), 126.9 (C^{III}), 126.5 (C^{III}), 79.0 (C_3), 75.6 (C_2), 32.2 (C^{II}), 23.0 (C^{II}), 19.3 (C_8), 18.2 (C_4), 13.3

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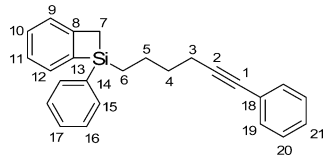
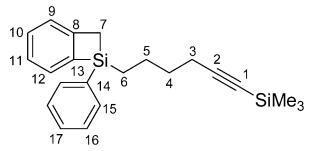
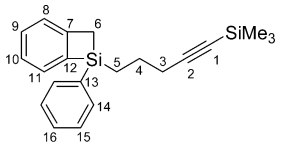
(C_7), 3.4 (C_1). ^{29}Si NMR ($CDCl_3$): δ 3.6. IR (neat): $\tilde{\nu}_{max}$ 3050, 2918, 2855, 1959, 1584, 1428, 1100, 1041, 780, 734, 697 cm^{-1}. Anal. Calcd for $C_{21}H_{28}Si$: C, 82.70; H, 7.63. Found: C, 82.51; H, 7.88.



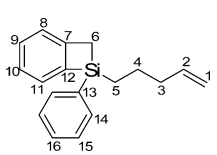
Compound **22**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.61−7.59 (m, 2 H, H_{15}), 7.42−7.31 (m, 7 H), 7.26−7.19 (m, 5 H), 2.41 (t, overlap, 2 H, H_3), 2..41 (d, overlap, 1 H, H_7), 2.33 (d, J_{AB} = 16.9 Hz, 1 H, H_7), 1.70−1.67 (m, 4 H, $H_{4,5}$), 1.33−1.25 (m, 2 H, H_6). ^{13}C NMR ($CDCl_3$): δ 151.7 (C_8), 143.6 (C_{13}), 135.6 (C_{14}), 134.2 (2 C, C_{15}), 131.5 (2 C, C_{19}), 131.0 (C^{III}), 130.8 (C^{III}), 129.8 (C^{III}), 128.1 (2 C^{III}), 128.0 (2 C^{III}), 127.5 (C_{21}), 126.9 (C^{III}), 126.6 (C^{III}), 124.0 (C_{18}), 90.0 (C_2), 80.8 (C_1), 31.8 (C^{II}), 23.1 (C^{II}), 19.3 (C_7), 18.9 (C^{II}), 13.4 (C_6). IR (neat): $\tilde{\nu}_{max}$ 3052, 2929, 2857, 2227, 1598, 1489, 1428, 1110, 1041 cm^{-1}. MS (CI): 388 ($M(H_2O)NH_4^+$, 100), 370 (MNH_4^+, 4), 335 (MH^+, 2), 279 (10), 230 (8). HRMS(ES^+): calcd for $C_{25}H_{25}Si$ (MH^+) 353.1720; found 353.1725.



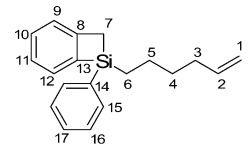
Compound **24**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.59−7.57 (m, 2 H, H_{15}), 7.42−7.33 (m, 7 H), 7.26−7.19 (m, 2 H), 2.38 (d, J_{AB} = 16.7 Hz, 1 H, H_7), 2.31 (d, J_{AB} = 16.7 Hz, 1 H, H_7), 2.20 (t, J = 6.7 Hz, 2 H, H_3), 1.60−1.57 (m, 4 H, $H_{4,5}$), 1.27−1.24 (m, 2 H, H_6), 0.11 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 151.7 (C_8), 143.6 (C_{13}), 135.6 (C_{14}), 134.1 (2 C, C_{15}), 131.0 (C^{III}), 130.8 (C^{III}), 129.8 (C^{III}), 128.0 (2 C^{III}, C_{16}), 126.9 (C^{III}), 126.6 (C^{III}), 107.2 (C_2), 84.6 (C_1), 31.8 (C^{II}), 23.0 (C^{II}), 19.4 (C_7), 19.2 (C^{II}), 13.4 (C_5), 0.13 (3 C, $SiMe_3$). ^{29}Si NMR (C_6D_6): δ 3.6, −19.4 ($SiMe_3$), due to poor spin relaxation, the silicon atom of the silacycle is hardly observed. IR (neat): $\tilde{\nu}_{max}$ 3053, 2930, 2173, 1429, 1111, 1041 cm^{-1}. MS (CI): 384 ($M(H_2O)NH_4^+$, 100), 367 ($M(H_2O)H^+$, 12), 365 (16), 349 (MH^+, 9), 324 (23), 307 (15), 230 (7), 90 (18). HRMS(ES^+): calcd for $C_{22}H_{29}Si_2$ (MH^+) 349.1802; found 349.1804.



Compound **26**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.60−7.58 (m, 2 H, H_{14}), 7.41−7.34 (m, 5 H), 7.23−7.19 (m, 2 H), 2.39 (d, J_{AB} = 17.8 Hz, 1 H, H_6), 2.32 (d, J_{AB} = 17.8 Hz, 1 H, H_6), 2.28 (t, J = 6.9 Hz, 2 H, H_3), 1.77−1.66 (m, 2 H, H_4), 1.44−1.32 (m, 2 H, H_5), 0.11 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 151.7 (C_7), 143.4 (C_{12}), 135.4 (C_{13}), 134.2 (2 C, C_{14}), 131.0 (C^{III}), 130.9 (C^{III}), 129.9 (C^{III}), 128.0 (2 C, C_{15}), 126.9 (C^{III}), 126.6 (C^{III}), 107.1 (C_2), 85.0 (C_1), 23.3 (C_3), 23.1 (C_4), 19.3 (C_6), 13.3 (C_5), 0.2 (3 C, $SiMe_3$). IR (neat): $\tilde{\nu}_{max}$ 3053, 2933, 2173, 1428, 1248, 1111, 1041, 841 cm^{-1}. MS (CI): 380 ($M(H_2O)NH_4^+$, 100), 353 ($M(H_2O)H^+$, 20), 335 (MH^+, 3). HRMS(ES^+): calcd for $C_{21}H_{27}Si_2$ (MH^+) 335.1646; found 335.1650.

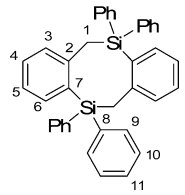


Compound **28a**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.59−7.57 (m, 2 H, H_{14}), 7.41−7.34 (m, 5 H), 7.23−7.19 (m, 2 H), 5.76 (ddt, J = 17.0 Hz, J = 10.2 Hz, J = 6.7 Hz, 1 H, H_2), 4.99−4.93 (m, 2 H, H_1), 2.38 (d, J_{AB} = 16.8 Hz, 1 H, H_6), 2.31 (d, J_{AB} = 16.8 Hz, 1 H, H_6), 2.17−2.09 (m, 2 H, H_3), 1.65−1.53 (m, 2 H, H_4), 1.33−1.20 (m, 2 H, H_5). ^{13}C NMR ($CDCl_3$): δ 151.7 (C_7), 143.7 (C_{12}), 138.5 (C_1), 135.7 (C_{13}), 134.1 (2 C, C_{14}), 131.0 (C^{III}), 130.8 (C^{III}), 129.8 (C^{III}), 128.0 (2 C, C_{15}), 126.9 (C^{III}), 126.6 (C^{III}), 114.9 (C_2), 37.1 (C_3), 23.3 (C_4), 19.3 (C_6), 13.4 (C_5). ^{29}Si NMR ($CDCl_3$): δ 3.7. IR (neat): $\tilde{\nu}_{max}$ 3052, 2923, 1640, 1585, 1429, 1111 cm^{-1}. Anal. Calcd for $C_{18}H_{20}Si$: C, 81.76; H, 7.62. Found: C, 81.33; H, 7.89.



Compound **28b**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.60−7.58 (m, 2 H, H_{15}), 7.42−7.34 (m, 5 H), 7.26−7.19 (m, 2 H), 5.78 (ddt, J = 17.1 Hz, J = 10.1 Hz, J = 6.8 Hz, 1 H, H_2), 4.99−4.90 (m, 2 H, H_1), 2.38 (d, J_{AB} = 16.7 Hz, 1 H, H_7), 2.34 (d, J_{AB} = 16.7 Hz, 1 H, H_7), 2.06−2.01 (m, 2 H, H_3), 1.57−1.44 (m, 4 H, H_{4-5}), 1.29−1.24 (m, 2 H, H_6). ^{13}C NMR ($CDCl_3$): δ 151.7 (C_8), 143.8 (C_{13}), 138.8 (C_1), 135.8 (C_{14}), 134.1 (2 C, C_{15}), 131.0 (C^{III}), 130.7 (C^{III}), 129.8 (C^{III}), 128.0 (2 C, C_{16}), 126.9 (C^{III}), 126.5 (C^{III}), 114.3 (C_2), 33.4 (C_3), 32.3 (C^{II}), 23.3 (C^{II}), 19.3 (C_7), 13.7 (C_6). IR (neat): $\tilde{\nu}_{max}$ 3052, 2922, 1640, 1585, 1428, 1111 cm^{-1}. Anal. Calcd for $C_{18}H_{20}Si$: C, 81.95; H, 7.96. Found: C, 81.95; H, 7.96.

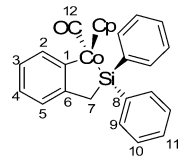
Reaction of 1 with $CpCo(C_2H_4)_2$. $CpCo(C_2H_4)_2$ (181 mg, 1 mmol or 18 mg, 0.1 mmol) was added at −20 °C to a solution of benzosilacyclobutene **1** (274 mg, 1 mmol) in *n*-hexane or THF (10 mL). The solution was allowed to warm to room temperature and to stir overnight. Silica was added and the solvent was removed by rotary evaporation. The solid residue was submitted to flash chromatography over silica gel using a pentane/diethyl ether (9:1) mixture to afford ∼80 mg (∼30%) of **2**.



Compound **2**: white solid, mp 198−201 °C. ^{1}H NMR ($CDCl_3$): δ 7.57−7.55 (m, 4 H), 7.42−7.32 (m, 10 H), 7.23−7.12 (m, 4 H), 7.16−7.14 (m, 4 H), 6.98−6.94 (m, 4 H), 6.51−6.49 (m, 2 H), 3.05 (d, J_{AB} = 13.4 Hz, 2 H, H_1), 2.37 (d, J_{AB} = 13.4 Hz, 2 H, H_1). ^{13}C NMR ($CDCl_3$): δ 145.1 (2 C, C^{IV}), 137.3 (2 C, C^{III}), 136.4 (4 C, C_9), 135.9 (2 C, C^{IV}), 135.3 (4 C, C_9), 133.6 (2 C, C_8), 133.5 (2 C, C_8), 130.3 (2 C, C^{III}), 129.5 (2 C, C^{III}), 129.3 (2 C, C^{III}), 129.2 (2 C, C^{III}), 127.8 (4 C, C_{10}), 127.5 (4 C, C_{10}), 123.5 (2 C, C^{III}), 22.0 (2 C, C_1). ^{29}Si NMR ($CDCl_3$): δ −6.2. IR (neat): $\tilde{\nu}_{max}$ 3048, 1584, 1407, 1197, 1107 cm^{-1}. MS (CI): 562 (MNH_4^+, 100), 545 (MH^+, 98), 467 ($(M - Ph)^+$, 17).

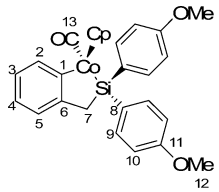
Preparation of Cobalt Complexes. An *n*-hexane solution (10 mL) of benzosilacyclobutene **1a** (274 mg, 1 mmol) and $CpCo(CO)_2$ (140 μL, 1 mmol) was refluxed for 2 h under irradition. The mixture was concentrated under reduced pressure and purified over silica gel using a pentane/diethyl ether (95:5) mixture to afford 373 mg (88%) of **3a**.

Complex **3a**: yellow solid, mp 47 °C dec. ^{1}H NMR ($CDCl_3$): δ 7.48−7.28 (m, 11 H), 7.20 (d, J = 7.1 Hz, 1 H), 6.95 (td, J = 7.3 Hz, J' = 1.3 Hz, 1 H), 6.86 (td, J = 7.6 Hz, J' = 1.8 Hz, 1 H),

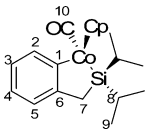


4.92 (s, 5 H, Cp), 2.89 (s, 2 H, H_7). ^{13}C NMR ($CDCl_3$): δ 203.8 (C_{12}), 152.7 (C_6), 144.5 (C^{III}), 143.6 (C^{IV}), 143.4 (C^{IV}), 140.4 (C^{IV}), 134.6 (2 C, C_9), 133.9 (2 C, C_9), 128.9 (C_{11}), 128.7 (C_{11}), 127.8 (2 C, C_{10}), 127.7 (2 C, C_{10}), 127.2 (C^{III}), 124.8 (C^{III}), 124.2 (C^{III}), 89.5 (5 C, Cp), 32.2 (C_7). IR (neat): $\tilde{\nu}_{max}$ 3043, 1987 (CO), 1426, 1098, 1006 cm^{-1}. ^{29}Si NMR ($CDCl_3$): δ 48.1. MS (CI): 443 (18), 442 (MNH_4^+, 43), 425 (MH^+, 6), 399 (12), 398 (45), 397 ((MH $-$CO)$^+$, 100), 396 (12), 290 (15). Anal. Calcd for $C_{25}H_{21}CoOSi$: C, 70.74; H, 4.99. Found: C, 70.74; H, 5.16.

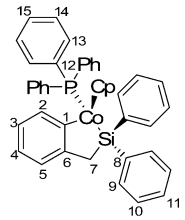
The same procedure was used to prepare **3b** (106 mg, 46%) and **3c** (52 mg, 33%) from benzosilacyclobutene **1b** (183 mg, 0.55 mmol) and **1c** (92 mg, 0.45 mmol) using 63 μL of $CpCo(CO)_2$.



Compound **3b**: yellow solid, mp 45 °C dec. ^{1}H NMR (C_6D_6): δ 7.53 (d, J = 7.6 Hz, 1 H), 7.45$-$7.38 (m, 4 H), 7.23 (d, J = 7.4 Hz, 1 H), 7.01$-$6.88 (m, 6 H), 4.95 (s, 5 H, Cp), 3.83 (s, 6 H, H_{12}), 2.89 (s, 2 H, H_7). ^{13}C NMR (C_6D_6): δ 203.9 (CO), 160.2 (C^{IV}), 160.0 (C^{IV}), 152.7 (C^{IV}), 144.4 (C^{III}), 143.8 (C^{IV}), 136.0 (C^{III}), 135.3 (C^{III}), 134.4 (C^{IV}), 131.6 (C^{IV}), 127.1 (C^{III}), 124.7 (C^{III}), 124.1 (C^{III}), 113.4 (C^{III}), 113.3 (C^{III}), 89.5 (5 C, Cp), 55.0 (2 C, C_{12}), 32.9 (C_7). ^{29}Si NMR ($CDCl_3$): δ 47.0. IR (neat): $\tilde{\nu}_{max}$ 2926, 1989, 1591, 1441, 1275, 1245, 1181, 1099, 1030 cm^{-1}. Anal. Calcd for $C_{27}H_{25}CoO_3Si$: C, 66.93; H, 5.20. Found: C, 66.96; H, 5.57.

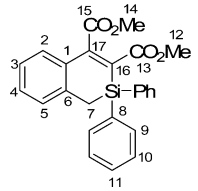


Complex **3c**: yellow solid. ^{1}H NMR (C_6D_6): δ 7.36 (d, J = 6.6 Hz, 1 H), 7.19$-$7.16 (m, 1 H), 6.99 (td, J = 7.3 Hz, J' = 1.3 Hz, 1 H), 6.90 (t, J = 7.6 Hz, 1 H), 4.59 (s, 5 H, Cp), 2.53 (d, J_{AB} = 16.0 Hz, 1 H, H_7), 2.23 (d, J_{AB} = 16.0 Hz, 1 H, H_7), 1.18$-$1.04 (m, 11 H), 0.78 (d, J = 7.3 Hz, 3 H, H_9). ^{13}C NMR ($CDCl_3$): δ 203.7 (C_{10}), 152.9 (C_6), 144.5 (C^{III}), 127.8 (C^{III}), 125.0 (C^{III}), 124.4 (C^{III}), 87.9 (5 C, Cp), 28.0 (C_7), 20.1 (2 C, C_9), 19.9 (C_8), 19.8 (C_8), 19.6 (C_9), 19.4 (C_9). IR (neat): $\tilde{\nu}_{max}$ 3054, 2942, 2863, 1972 (CO), 1460 cm^{-1}.

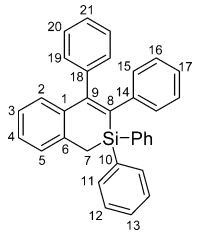


Complex **4**: red solid. ^{1}H NMR ($CDCl_3$): δ 8.02$-$8.00 (m, 1 H), 7.61$-$7.51 (m, 5 H), 7.31$-$6.74 (m, 23 H), 4.54 (s, 5 H, H_{16}), 1.86 (d, J_{AB} = 16.2 Hz, 1 H, H_7), 1.16 (d, J_{AB} = 16.2 Hz, 1 H, H_7). ^{13}C NMR ($CDCl_3$): δ 156.2 (C_6), 148.7 (C^{IV}), 147.2 (C^{III}), 142.8 (C^{IV}), 135.8 (C^{IV}), 135.4 (C^{IV}), 135.3 (C^{III}), 134.2 (2 C, C_9), 134.1 (2 C, C_9), 133.5 (C^{III}), 129.3 (C^{III}), 128.4 (C^{III}), 127.7 (C^{III}), 127.3$-$127.2 (m, 13 C, C^{III}), 122.6 (C^{III}), 122.3 (C^{III}), 87.6 (5 C, C_{16}), 28.8 (C_7). ^{31}P NMR ($CDCl_3$): δ 56.3.

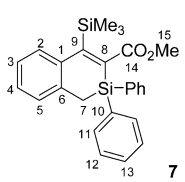
Bimolecular Insertions of Alkynes or Alkenes. General procedure: complex **3** (1 mmol) and the desired alkyne or alkene (5 mmol) were dissolved in *n*-hexane (10 mL). The mixture was refluxed under irradiation until completion (ca. 1$-$2 h). Silica was added, and the solvent was removed by rotary evaporation. The solid residue was submitted to flash chromatography over silica gel using a gradient mixture of pentane and diethyl ether.



Compound **5**: white solid, mp 113 °C. ^{1}H NMR ($CDCl_3$): δ 7.58$-$7.55 (m, 4 H, H_9), 7.41$-$7.37 (m, 2 H), 7.34$-$7.31 (m, 4 H), 7.23$-$7.14 (m, 4 H), 3.93 (s, 3 H, H_{14}), 3.51 (s, 3 H, H_{12}), 2.73 (s, 2 H, H_7). ^{13}C NMR ($CDCl_3$): δ 169.6 ($C_{13|15}$), 169.2 ($C_{13|15}$), 155.0 (C_{17}), 136.7 (2 C, C_8), 135.2 (4 C, C_9), 131.9 (C^{III}), 131.8 (C^{IV}), 131.4 (C^{IV}), 130.3 (C^{III}), 130.1 (2 C, C_{11}), 129.5 (C^{III}), 127.9 (4 C, C_{10}), 127.8 (C^{IV}), 126.3 (C^{III}), 52.6 ($C_{12|14}$), 51.7 ($C_{12|14}$), 19.5 (C_7). ^{29}Si NMR ($CDCl_3$): δ $-$18.7. IR (neat): $\tilde{\nu}_{max}$ 1734, 1713, 1430, 1236 cm^{-1}. Anal. Calcd for $C_{25}H_{22}O_4Si$: C, 72.44; H, 5.35. Found: C, 72.10; H, 5.53.



Compound **6**: yellow solid, mp 58 °C. ^{1}H NMR (C_6D_6): δ 7.59$-$7.57 (m, 4 H, H_{11}), 7.13$-$6.70 (m, 20 H), 2.81 (s, 2 H, H_7). ^{13}C NMR ($CDCl_3$): δ 153.4 (C_9), 142.5 ($C_{14|18}$), 141.7 ($C_{14|18}$), 138.7 (C^{IV}), 137.3 (C^{IV}), 135.4 (4 C, C_{11}), 135.3 (C^{IV}), 133.4 (2 C, C_{10}), 131.4 (C^{III}), 130.6 (2 C, C_{13}), 130.4 (C^{III}), 129.6 (2 C, C_{15}), 128.6 (2 C, C_{19}), 127.7 (4 C, C_{12}), 127.6 (2 C, C_{16}), 127.5 (C^{III}), 127.4 (2 C, C_{20}), 126.3 (C^{III}), 125.4 (C^{III}), 124.8 (C^{III}), 20.3 (C_7). ^{29}Si NMR ($CDCl_3$): δ $-$21.5. IR (neat): $\tilde{\nu}_{max}$ 1427, 1108, 764, 733 cm^{-1}. MS (FAB): 469 (38), 468 (MNH_4^+, 80), 452 (45), 451 (MH^+, 100). HRMS(ES$^+$): calcd for $C_{33}H_{26}Si$ 450.1804; found 450.1795.



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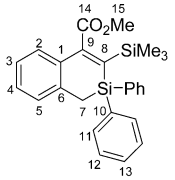

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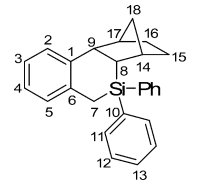
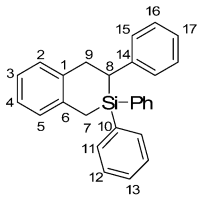
7:8 mixture: colorless oil. ^{1}H NMR (C_6D_6): δ 7.57$-$7.55 (m, 8 H, H_{11}, **7** and **8**), 7.35$-$7.33 (m, 2 H, **7** and **8**), 7.10$-$7.07 (m, 12 H, **7** and **8**), 6.94$-$6.82 (m, 6 H, **7** and **8**), 3.49 (s, 3 H, H_{15}, **8**), 3.15 (s, 3 H, H_{15}, **7**), 2.52 (s, 2 H, H_7, **7**), 2.41 (s, 2 H, H_7, **8**), 0.45 (s, 9 H, $SiMe_3$, **7**), 0.16 (s, 9 H, $SiMe_3$, **8**).



Compound **9**: white solid, mp 112 °C. ^{1}H NMR ($CDCl_3$): δ 7.54−7.10 (m, 14 H), 3.36 (d, J = 9.4 Hz, 1 H, H_9), 2.73 (d, J_{AB} = 15.7 Hz, 1 H, H_7), 2.66 (d, J = 4.0 Hz, 1 H, H_{17}), 2.50 (d, J_{AB} = 15.7 Hz, 1 H, H_7), 2.42 (br s, 1 H, H_{14}), 1.90−1.59 (m, 5 H, $H_{15,16,8}$), 1.46 (br d, J_{AB} = 9.8 Hz, 1 H, H_{18}), 1.11 (br d, J_{AB} = 10.1 Hz, 1 H, H_{18}).^{13}C NMR ($CDCl_3$): δ 142.6 (C^{IV}), 136.3 (C^{IV}), 135.6 (C^{IV}), 135.4 (2 C, C_{11}), 135.0 (C^{IV}), 134.8 (2 C, C_{11}), 132.6 (C_{13}), 130.2 (C_{13}), 129.5 (C^{III}), 129.2 (C^{III}), 127.9 (2 C, C_{12}), 127.8 (2 C, C_{12}), 126.0 (C^{III}), 125.8 (C^{III}), 51.4 (C_9), 47.2 (C_{17}), 39.1 (C_{14}), 36.2 (C_{18}), 34.1 (C_{16}), 29.6 (C_{15}), 29.0 (C_8), 17.9 (C_7). ^{29}Si NMR ($CDCl_3$): δ −13.7. IR (neat): $\tilde{\nu}_{max}$ 3047, 2943, 2857, 1482, 1425, 1260, 1104, 1025 cm^{-1}. Anal. Calcd for $C_{26}H_{26}Si$: C, 85.19; H, 7.15. Found: C, 84.95; H, 7.28.



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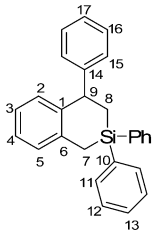
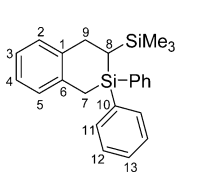


11

10:**11** mixture: colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.55−6.62 (m, 38 H, **10** and **11**), 4.98 (t, J = 3.6 Hz, 1 H, H_9, **11**), 3.15−3.10 (m, 2 H, H_9, **10**), 2.89−2.85 (m, 1 H, H_8, **10**), 2.83 (d, J = 3.6 Hz, 2 H, H_8, **11**), 2.80 (s, 2 H, H_7, **11**), 2.69 (d, J_{AB} = 17.4 Hz, 1 H, H_7, **10**), 2.52 (d, J_{AB} = 17.4 Hz, 1 H, H_7, **10**). The aromatic region of the spectrum presents too many peaks to be unambiguously assigned. ^{13}C NMR ($CDCl_3$): δ 37.5 (C_8, **11**), 34.1 (C_9, **11**), 31.2 (C_8, **10**), 29.7 (C_9, **10**), 23.8 (C_7, **11**), 20.2 (C_7, **10**). ^{29}Si NMR ($CDCl_3$): δ −15,1, −14.6. MS (CI): 394 (MNH_4^+, 100), 377 (MH^+, 19), 316 (5), 302 (8), 290 (70). HRMS(ES^+): calcd for $C_{27}H_{25}Si$ (MH^+) 377.1720; found 377.1728.



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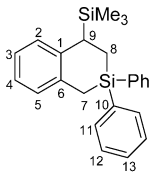
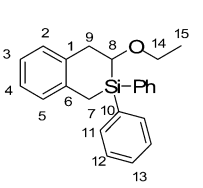


13

12:**13** mixture: colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.65−7.00 (m, 28 H, **12** and **13**), 2.91 (t, J = 6.7 Hz, 1 H, H_9, **13**), 2.80 (d, J_{AB} = 16.9 Hz, 1 H, H_7, **13**), 2.58 (s, 2 H, H_7, **12**), 2.56−2.52 (m of ABX, 1 H, H_8, **12**), 2.53 (d, J_{AB} = 17.2 Hz, 1 H, H_7, **13**), 1.69 (dd, A of ABX, J_{AB} = 15.3 Hz, J_{AX} = 7.6 Hz, 1 H, H_9, **12**), 1.39 (dd, B of ABX, J_{AB} = 15.3 Hz, J_{AX} = 6.8 Hz, 1 H, H_9, **12**), 1.17 (dd, J_{AB} = 15.4 Hz, J' = 7.6 Hz, 1 H, H_9, **13**), 1.01 (dd, J_{AB} = 15.3 Hz, J' = 5.8 Hz, 1 H, H_9, **13**), 0.13 (s, 9 H, $SiMe_3$, **12**), 0.00 (s, 9 H, $SiMe_3$, **13**).



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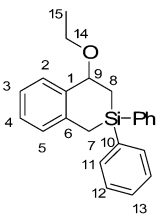
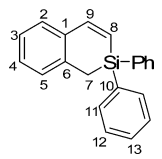


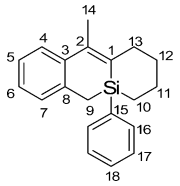
15

14:**15** mixture: colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.92−7.00 (m, 28 H, **14** and **15**), 4.75 (dd, J = 6.1 Hz, J' = 3.5 Hz, 1 H, H_9, **15**), 3.93 (t, J = 7.8 Hz, 1 H), 3.55 (t, J = 8.5 Hz, 1 H), 3.37−3.27 (m, 3 H, H_8, **14**, H_{14}), 3.22−3.18 (m, 1 H, H_{14}), 3.07−3.03 (m, 1 H, H_{14}), 2.94 (d, J_{AB} = 14.4 Hz, 1 H, H_7), 2.75 (d, J_{AB} = 17.4 Hz, 1 H, H_7), 2.56 (d, J_{AB} = 14.4 Hz, 1 H, H_7), 2.50 (d, J_{AB} = 17.4 Hz, 1 H, H_7), 1.96 (dd, J_{AB} = 14.6 Hz, J' = 6.1 Hz, 1 H, H_9, **14**), 1.54 (dd, J_{AB} = 14.6 Hz, J' = 3.5 Hz, 1 H, H_9, **14**), 1.15 (t, J = 7.1 Hz, 3 H, H_{15}), 1.06 (t, J = 7.1 Hz, 3 H, H_{15}).

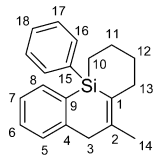


Compound **16**: the **14**:**15** mixture decomposes in $CDCl_3$ to give **16** within 24 h (100% conversion). ^{1}H NMR ($CDCl_3$): δ 7.66−6.98 (m, 14 H), 6.33 (d, J = 14.9 Hz, 1 H, H_9), 4.73 (d, J = 15.1 Hz, 1 H, H_8), 2.75 (s, 2 H, H_7).

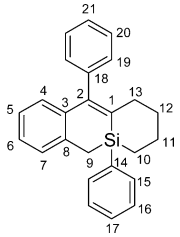
Intramolecular Insertion of Alkynes or Alkenes. General procedure: the benzosilacyclobutene (0.5 mmol) was dissolved in toluene (5 mL). $CpCo(CO)_2$ (70 μL, 0.5 mmol) was added. The mixture was refluxed under irradiation until completion (1−2 h). Silica was added, and the solvent was removed by rotary evaporation. The solid residue was submitted to flash chromatography over silica gel using a gradient mixture of pentane and diethyl ether.



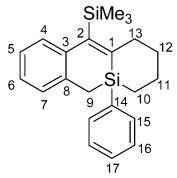
Compound **20**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.38−7.35 (m, 1 H), 7.27−7.12 (m, 6 H), 7.06−6.99 (m, 2 H), 3.01 (dt, J = 15.4 Hz, J' = 3.8 Hz, 1 H, H_{13}), 2.26 (s, 2 H, H_9), 2.20 (d, J = 1.2 Hz, 3 H, H_{14}), 2.10−2.03 (m, 2 H, $H_{11,13}$), 1.95−1.92 (m, 1 H, H_{12}), 1.64−1.56 (m, 1 H, H_{11}), 1.49−1.37 (m, 2 H, $H_{10,12}$), 0.82 (td, J = 5.3 Hz, J' = 12.9 Hz, 1 H, H_{10}). ^{13}C NMR ($CDCl_3$): δ 141.9 (C^{IV}), 140.3 (C^{IV}), 135.6 (C^{IV}), 134.7 (C^{IV}), 134.6 (C^{IV}), 134.2 (2 C, C_{16}), 131.2 (C^{III}), 129.2 (C^{III}), 127.7 (2 C, C_{17}), 126.3 (C^{III}), 126.1 (C^{III}), 125.5 (C^{III}), 32.4 (C_{13}), 29.7 (C_{12}), 23.7 (C_{11}), 20.7 (C_9), 16.5 (C_{14}), 12.0 (C_{10}). IR (neat): $\tilde{\nu}_{max}$ 3066, 3013, 2923, 2851, 2360 (C═C), 2342 (C═C), 1587, 1479, 1427, 1113, 1080 cm^{-1}.



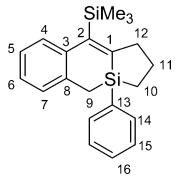
Compound **21** (contaminated by 37% of compound **20**): this compound was obtained under palladium catalysis (colorless oil).[4] ^{1}H NMR ($CDCl_3$): δ 7.54−7.50 (m, 3 H), 7.30−7.23 (m, 5 H), 7.21−712 (m, 1 H), 3.72 (dd, A of ABX, J = 20.1 Hz, J_{AB} = 3.1 Hz, 1 H, H_3), 3.44 (d, J_{AB} = 20.1 Hz, 1 H, H_3), 2.88 (dt, J = 14.6 Hz, J = 3.5 Hz, 1 H, H_{13}), 2.16−2.05 (m, 2 H, $H_{12,13}$), 1.94 (s, 3 H, H_{14}), 1.79−1.21 (m, 4 H, $H_{10,11,12}$), 0.97−0.90 (m, 1 H, H_{10}). ^{13}C NMR ($CDCl_3$): δ 145.9 (C^{IV}), 143.5 (C^{IV}), 137.1 (C^{IV}), 134.5 (2 C, C_{16}), 133.1 (C^{III}), 133.0 (C^{IV}), 129.2 (C^{IV}), 129.0 (C^{III}), 128.8 (C^{III}), 128.1 (C^{III}), 127.9 (2C, C_{17}), 125.5 (C^{III}), 42.7(C_3), 31.6 (C_{13}), 29.9 (C_{12}), 24.3 (C_{11}), 19.8 (C_{14}), 11.6 (C_{10}).



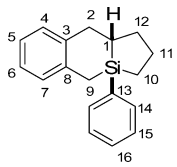
Compound **23**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.41−7.37 (m, 4 H), 7.33−7.23 (m, 4 H), 7.16−7.14 (m, 2 H), 7.09 (d, J_{AB} = 7.4 Hz, 1 H), 7.00−6.90 (m, 2 H), 6.66 (d, J_{AB} = 7.6 Hz, 1 H), 2.52−2.44 (m, 2 H, $H_{9,13}$), 2.38 (d, J_{AB} = 15.4 Hz, 1 H, H_9), 2.13−2.05 (m, 2 H, $H_{11,13}$), 1.80−1.77 (m, 1 H, H_{12}), 1.54−1.50 (m, 2 H, $H_{10,11}$), 1.22−1.15 (m, 1 H, H_{12}), 0.90−0.81 (m, 1 H, H_{10}). ^{13}C NMR ($CDCl_3$): δ 149.1 (C^{IV}), 141.4 (C^{IV}), 139.2 (C^{IV}), 135.6 (C^{IV}), 135.3 (C^{IV}), 134.9 (C^{IV}), 134.2 (2 C, C_{15}), 131.4 (C^{III}), 129.9 (C^{III}), 129.4 (C^{III}), 128.1 (2 C, C_{20}), 127.9 (2 C, C_{16}), 126.5 (C^{III}), 126.3 (C^{III}), 125.2 (C^{III}), 34.3 (C_{13}), 30.0 (C_{12}), 23.8 (C_{11}), 20.6 (C_9), 12.4 (C_{10}). IR (neat): $\tilde{\nu}_{max}$ 3013, 2922, 2850, 2246 (C═C), 1949, 1727, 1580, 1441, 1427, 1111, 1028, 906 cm^{-1}.



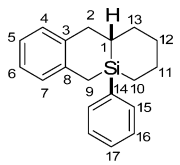
Compound **25**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.16−6.94 (m, 9 H), 2.52−2.44 (m, 1 H, H_{13}), 2.22−2.14 (m, 4 H, $H_{9,12,13}$), 2.00−1.96 (m, 1 H, H_{11}), 1.56−1.54 (m, 2 H, $H_{10,12}$), 1.39−1.35 (m, 1 H, H_{11}), 0.85−0.77 (m, 1 H, H_{10}), 0.3 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 157.1 (C^{IV}), 152.2 (C^{IV}), 141.7 (C^{IV}), 134.5 (C^{IV}), 134.3 (2 C, C_{15}), 134.1 (C^{IV}), 130.5 (C^{III}), 129.3 (C^{III}), 128.9 (C^{III}), 127.7 (2 C, C_{16}), 125.4 (C^{III}), 124.6 (C^{III}), 37.5 (C_{13}), 30.4 (C_{12}), 24.1 (C_{11}), 21.2 (C_9), 12.7 (C_{10}), 2.7 (3 C, $SiMe_3$). ^{29}Si NMR (C_6D_6): δ −8.6 ($SiMe_3$), −28.4. IR (neat): $\tilde{\nu}_{max}$ 3051, 2921, 2852, 1711, 1592, 1474, 1404, 1250, 1112 cm^{-1}. MS (CI): 366 (MNH_4^+, 17), 349 (MH^+, 100), 90 (34). HRMS(ES$^+$): calcd for $C_{22}H_{29}Si_2$ (MH^+) 349.1802; found 349.1806.



Compound **27**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.24−7.22 (m, 1 H), 7.17−7.05 (m, 7 H), 6.99−6.95 (m, 1 H), 2.76 (dt, J_{AB} = 15.5 Hz, J = 6.2 Hz, 1 H, H_{12}), 2.49 (dt, J_{AB} = 15.5 Hz, J = 7.5 Hz, 1 H, H_{12}), 2.31 (d, J_{AB} = 14.3 Hz, 1 H, H_9), 2.23 (d, J_{AB} = 14.3 Hz, 1 H, H_9), 2.11−189 (m, 2 H, H_{11}), 1.22 (dt, J_{AB} = 14.9 Hz, J = 7.4 Hz, 1 H, H_{12}), 0.97 (dt, J_{AB} = 14.9 Hz, J = 7.3 Hz, 1 H, H_{12}), 0.27 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 164.5 (C^{IV}), 149.5 (C^{IV}), 143.4 (C^{IV}), 134.5 (C^{IV}), 134.3 (2 C, C_{14}), 133.4 (C^{IV}), 131.4 (C^{III}), 129.3 (C^{III}), 128.9 (C^{III}), 127.7 (2 C, C_{15}), 125.7 (C^{III}), 125.1 (C^{III}), 35.1 (C_{12}), 26.8 (C_{11}), 20.5 (C_9), 9.8 (3 C, C_{10}), 2.0 ($SiMe_3$). IR (neat): $\tilde{\nu}_{max}$ 3051, 2925, 2856, 1469, 1447, 1248, 1142 cm^{-1}.



Compound **29a**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.38−7.36 (m, 2 H), 7.29−7.23 (m, 3 H), 7.06−6.99 (m, 4 H), 2.89 (dd, J_{AB} = 13.6 Hz, J = 5.8 Hz, 1 H, H_2), 2.61 (dd, J_{AB} = 13.4 Hz, J = 8.4 Hz, 1 H, H_2), 2.29 (d, J_{AB} = 14.7 Hz, 1 H, H_9), 2.19 (d, J_{AB} = 14.7 Hz, 1 H, H_9), 1.82−1.73 (m, 1 H, H_{12}), 1.70−1.63 (m, 1 H, H_{11}), 1.55−1.44 (m, 2 H, $H_{1,11}$), 1.40−1.33 (m, 1 H, H_{12}), 0.89−0.81 (m, 1 H, H_{10}), 0.76−0.69 (m, 1 H, H_{10}). ^{13}C NMR ($CDCl_3$): δ 140.7 (C^{IV}), 137.2 (C^{IV}), 136.4 (C^{IV}), 134.1 (2 C, C_{14}), 129.7 (C^{III}), 129.4 (C^{III}), 129.1 (C^{III}), 127.9 (2 C, C_{15}), 126.5 (C^{III}), 125.1 (C^{III}), 36.4 (C_2), 33.7 (C_{12}), 25.8 (C_{11}), 23.0 (C_1), 18.2 (C_9), 11.7 (C_{10}). ^{29}Si NMR ($CDCl_3$): δ 13.6. IR (neat): $\tilde{\nu}_{max}$ 3066, 3012, 2920, 2850, 1489, 1453, 1427, 1112, 1065 cm^{-1}. Anal. Calcd for $C_{18}H_{20}Si$: C, 81.76; H, 7.62. Found: C, 81.62; H, 7.82.



Compound **29b**: colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.47−7.44 (m, 2 H), 7.34−7.30 (m, 3 H), 7.14−7.07 (m, 4 H), 2.86 (dd, J_{AB} = 13.7 Hz, J = 11.0 Hz, 1 H, H_2), 2.76 (dd, J_{AB} = 13.7 Hz, J = 4.5 Hz, 1 H, H_2), 2.31 (d, J_{AB} = 15.4 Hz, 1 H, H_9), 2.13 (d, J_{AB} = 15.4 Hz, 1 H, H_9), 1.89−1.77 (m, 2 H), 1.70−1.67 (m, 1 H), 1.52−1.50 (m, 2 H), 1.44−1.37 (m, 1 H), 1.24−1.18 (m, 2 H), 0.88−0.81 (m, 1 H, H_{10}), 0.76−0.69 (m, 1 H, H_{10}). ^{13}C NMR ($CDCl_3$): δ 141.4 (C^{IV}), 137.6 (C^{IV}), 137.1 (C^{IV}), 133.9 (2 C, C_{15}), 130.0 (C^{III}), 129.2 (C^{III}), 128.8 (C^{III}), 127.8 (2 C, C_{16}), 126.4 (C^{III}), 125.0 (C^{III}), 37.6 (C_2), 31.7 (C^{II}), 25.7 (C^{II}), 23.7 (C^{II}), 20.7 (C_1), 19.4 (C_9), 10.3 (C^{II}). IR (neat): $\tilde{\nu}_{max}$ 2915, 1693, 1402, 1113 cm^{-1}. Anal. Calcd for $C_{18}H_{20}Si$: C, 81.95; H, 7.96. Found: C, 82.08; H, 8.01.

Crystal Structure Determinations. X-ray intensity data were recorded on a Enraf-Nonius Mach or Enraf-Nonius KappaCCD diffractometer with monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection strategies were assigned on the basis of the apparent Laue symmetry obtained from a preliminary examination of the unit cell (full sphere for a triclinic setting and an arbitrary hemisphere for higher symmetries). Data were integrated with the CRYSTALS software package[27] and corrected for Lorentz−polarization effects, and an empirical absorption correction was applied within DIFABS.[28] The space group for each compound was assigned on the basis of systematic absences observed within the data. Structures were solved by direct methods[29] and expanded using Fourier methods and refined routinely.[27] Hydrogen atoms were included in geometrically calculated positions with thermal parameters tied to the atom to which they are bonded. A summary of the crystal and structure refinement data can be found in Table 1. CCDC 600 441 and 600 442 contain the supplementary data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT Calculations. All geometries of intermediates and transition states were optimized fully without symmetry constraints using the Gaussian 03 program.[30] The DFT computations were carried out using the B3LYP functional as implemented in Gaussian. The computations were done using the LACVP(d,p) basis set: the cobalt atom was described by a double-ζ basis set with the effective core potential of Hay and Wadt (LANL2DZ),[31] and the 6-31G(d,p) basis set[32] was used for the other elements. Frequency calculations were performed to confirm the nature of the stationary points and to obtain zero-point energies (ZPE). The connectivity between stationary points was established by intrinsic reaction coordinate calcula-

(27) CRYSTALS: Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, *36*, 1487.

(28) DIFABS: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *39*, 158−166.

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(31) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299−310.

(32) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724−728. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−2261. (c) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (d) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209. (e) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163−168.

tions (IRC). Single-point calculations were carried out at the B3LYP/6-311+G(2d,2p) level; the energies given are uncorrected. The minimum energy crossing points (MECPs) were optimized using the code developed by Harvey and coworkers.[33a] The vibrational analyses at these points were executed within the $(3N-7)$-dimensional hypersurface of the seam of crossing.[33b] The Chemcraft program was used to draw the calculated structures.[34]

(33) (a) Harvey, J. N.; Aschi, M. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5555−5563. (b) Harvey, J. N.; Aschi, M.; Schwarz, H.; Koch, W. *Theor. Chem. Acc.* **1998**, *99*, 95−99.

(34) http://www.chemcraftprog.com.

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Supporting Information Available: NMR spectra of all new compounds. Coordinates of computed structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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