

Cobalt Complexes of Silicon and Germanium Heterocyclotriynes with One or Two Cyclyne Rings

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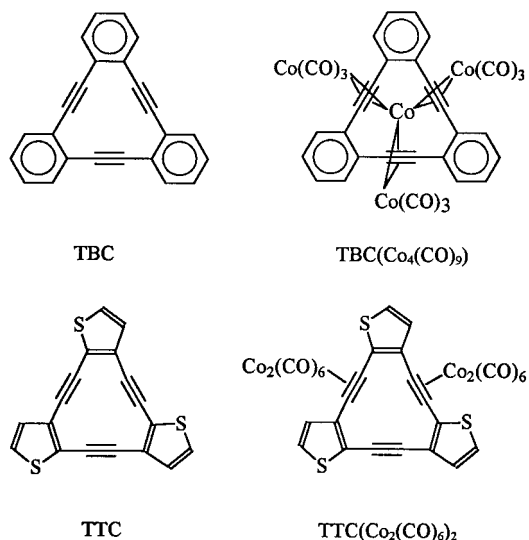
The synthesis and structural characterization of $\text{Ge}(\text{OBET})_2$, $\text{SiPh}_2(\text{OBET})(\text{Co}_2(\text{CO})_6)_2$, and $\text{Ge}(\text{OBET})_2(\text{Co}_2(\text{CO})_6)_2$ are reported. Reaction of $\text{Li}_2(\text{OBET})$, generated in situ from the reaction of $n\text{BuLi}$ and o -(bisethynyl)tolane ($\text{OBET})\text{H}_2$, with GeCl_4 in a 2:1 molar ratio gave $\text{Ge}(\text{OBET})_2$ in 64% yield. $\text{Ge}(\text{OBET})_2$ was characterized by ^1H NMR, ^{13}C NMR, elemental analysis, FDMS, and X-ray crystallography. $\text{Co}_2(\text{CO})_8$ selectively complexes to the bent alkynes adjacent to Ge or Si of $\text{Ge}(\text{OBET})_2$ and $\text{SiPh}_2(\text{OBET})$ and severely distorts the ligands. Comparisons are made to related complexes.

Introduction

Tribenzocyclotriyne (TBC) and its analogues have demonstrated intriguing and diverse reactivities toward transition metals.¹ The important feature of this ligand system is that three soft, polarizable alkynes are fixed in a trigonal plane. It has been shown that the size of the transition metal is extremely important in determining its coordination pattern toward TBC and the structure of mono metal complexes. The smaller transition metals, cobalt,² nickel,³ and copper,⁴ reside in the pocket of TBC; whereas larger transition metals such as silver⁵ form sandwich complexes.⁶ The size of the central pocket of TBC can be altered by using thieno groups instead of benzene rings in the system (TTC).⁷ This change results in dramatically different coordination chemistry, demonstrated by the differences between the two cobalt complexes of TBC² and TTC⁸ (see below for structures). In the TBC tetracobalt complex, one cobalt atom resides in the cavity of TBC. The other three cobalt atoms, one above each of the three alkynes, form a total of three Co–Co bonds with the cobalt atom at the center. In the TTC cobalt complex two dicobalt-hexacarbonyl moieties are bound to two alkynes, in the typical way that dicobalthexacarbonyl forms complexes

with alkynes,⁹ whereas the third alkyne remains uncomplexed even if excess dicobalt octacarbonyl is used.

Another way to alter the size of the central pocket is to substitute a heteroatom such as silicon or germanium for one of the benzene rings in TBC. We have previously described one such compound, $\text{SiPh}_2(\text{OBET})$.¹⁰ Here we report the synthesis and crystallographic characterization of the dipocket heterocyclotriyne $\text{Ge}(\text{OBET})_2$ and the selective complexation of $\text{Co}_2(\text{CO})_8$ with $\text{SiPh}_2(\text{OBET})$ and $\text{Ge}(\text{OBET})_2$.



Experimental Procedures

Materials. All chemicals were purchased from Aldrich and used as received unless otherwise stated. Solvents for reactions were dried and distilled before use. Tetrahydrofuran (THF) (Fisher), diethyl ether, and hexane were predried over sodium hydroxide and distilled from sodium benzophenone ketyl to which a small amount of tetraethylene glycol dimethyl ether was added. Germanium tetrachloride was purchased from Gelest and was distilled from anhydrous potassium carbonate

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Table 1. Crystal and Data Collection Parameters for Compounds SiPh₂(OBET)(Co₂(CO)₆)₂, Ge(OBET)₂, and Ge(OBET)₂(Co₂(CO)₆)₂

	SiPh ₂ (OBET)(Co ₂ (CO) ₆) ₂	Ge(OBET) ₂	Ge(OBET) ₂ (Co ₂ (CO) ₆) ₂
formula	Co ₄ SiO ₁₂ C ₄₂ H ₁₈	GeC ₃₆ H ₁₆ C ₄ H ₈ O	Co ₄ GeO ₁₂ C ₄₈ H ₁₆
mw	978.37	593.18	1092.92
cryst color	deep red	colorless	deep red
cryst size [mm]	0.40 × 0.50 × 0.60	0.16 × 0.26 × 0.38	0.25 × 0.50 × 0.55
space group	<i>P2</i> ₁ / <i>n</i>	<i>P</i> ₁	<i>P2</i> ₁ / <i>n</i>
<i>a</i> [Å]	12.099(7)	10.443(2)	11.540(7)
<i>b</i> [Å]	15.627(8)	11.400(2)	20.99(2)
<i>c</i> [Å]	21.699(10)	13.459(3)	18.60(2)
α [deg]	90	104.61(3)	90
β [deg]	90.32(4)	111.46(3)	90.48(6)
γ [deg]	90	94.28(3)	90
<i>V</i> [Å ³]	4102(4)	1418.0(5)	4503(7)
ρ _{calcd} [g cm ⁻³]	1.584	1.389	1.621
<i>Z</i>	4	2	4
<i>T</i> [K]	137	131	103
no. of reflex [indep]	7209	4725	7278
no. of reflex [obs, <i>I</i> > 2.0σ(<i>I</i>)]	5219	3443	2732
no. of params refined	532	379	571
R1 [%] (obs data on <i>F</i>)	6.33	5.95	9.64
R2 [%] (all data on <i>F</i> ²)	9.54	9.61	24.92

to remove dissolved HCl. *n*-Butyllithium (1.6 M) in hexane was purchased from Aldrich and was standardized with diphenylacetic acid.¹¹ Dicobalt octacarbonyl was purchased from Strem and used as received. *o*-(Bisethynyl)tolane ((OBET)H₂)¹² and 3,4:7,8-dibenzocyclo-3,7-diene-1,5,9-triyn-diphenylsilane (SiPh₂(OBET))^{10,12b} were prepared as described previously. All reactions were carried out under nitrogen using standard Schlenk, vacuum line, and glassware techniques unless otherwise noted.¹³

Bis(3,4:7,8-dibenzocyclo-3,7-diene-1,5,9-triyn)germane (Ge(OBET)₂). To a 100 mL flask charged with (OBET)H₂ (226.3 mg, 1.0 mmol) in 40 mL of THF was added *n*-butyllithium (1.32 mL, 1.51 M, 2.0 mmol) in a drybox. The solution turned deep red immediately. After 5 h of stirring at room temperature, the mixture was added via cannula to germanium tetrachloride (107 mg, 0.057 mL, 0.5 mmol) in 460 mL of THF at room temperature. The reaction mixture was brownish after adding half of the dilithium acetylide. The reaction mixture was stirred at room temperature for 12 h. It was opened to air, the THF was removed under vacuum, the solid residue was dissolved in CH₂Cl₂ and washed with H₂O, and the organic phase was dried over magnesium sulfate. The volatiles were evaporated under vacuum. The crude products were purified by chromatography on silica gel. Eluting with hexanes that were gradually changed to hexane/CH₂Cl₂ (3:1) gave 46% (121 mg) of the white solid product Ge(OBET)₂. Ge(OBET)₂ has relatively poor solubility in hydrocarbon solvents, but is soluble in THF at 40–50 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.65 (dd, 4H), 7.51 (dd, 4H), 7.40 (td, 4H), 7.32 (td, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 132.8, 131.4, 129.4, 128.5, 128.4, 124.0, 107.4, 92.5, 91.9. IR (C≡C): 2161 cm⁻¹. FDMS: *m/z* 522 (M⁺), 261 (M²⁺), molecular ion peaks are observed at 518, 519, 520, 521, 522, 523, and 524 due to the isotopes of germanium and carbon. Anal. Calcd for GeC₃₆H₁₆: C 82.98, H 3.18. Found: C 82.13; H 3.24.

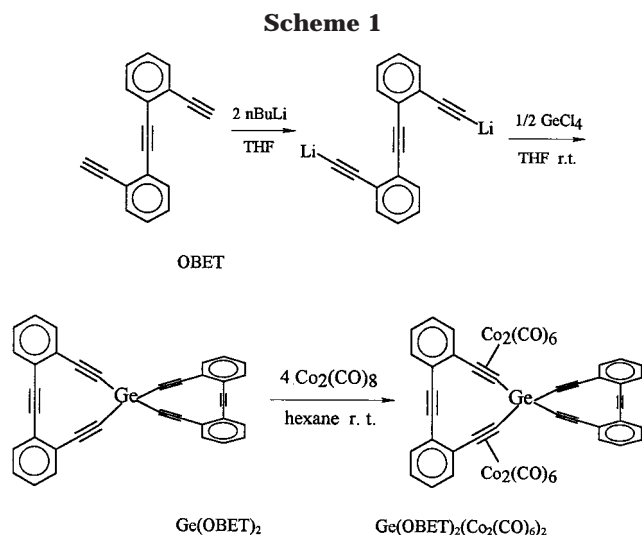
Cobalt Complex of 3,4:7,8-Dibenzocyclo-3,7-diene-1,5,9-triyn-diphenylsilane (SiPh₂(OBET)(Co₂(CO)₆)₂). To a solution of SiPh₂(OBET) (102 mg, 0.25 mmol) in 20 mL of diethyl ether was added Co₂(CO)₈ (185 mg, 0.5 mmol) with 8%

of hexane in an inert atmosphere box. The brown mixture was stirred at room temperature for 22 h. The solvent and any unreacted dicobalt octacarbonyl were pumped off under vacuum for 1.5 h. The residue was dissolved in diethyl ether and hexane, filtered, and crystallized. The NMR results indicated the reaction was quantitative. With a large excess of Co₂(CO)₈ the same product is obtained in quantitative yield based on SiPh₂(OBET). ¹H NMR (300 MHz, C₆D₆): δ 8.07 (d, 4H), 7.64 (d, 2H), 7.44 (d, 2H), 7.19 (m, overlap with solvent peak), 6.95 (sextet, 4H). ¹³C NMR (75 MHz, C₆D₆): δ 200.4, 141.1, 137.2, 136.7, 133.8, 131.0, 130.2, 128.6, 128.5, 128.2. IR: 2082, 2061, 2052, 2021, 1865, 1606 cm⁻¹. Several attempts to get elemental analysis of the cobalt complex, Co₄SiO₁₂C₄₂H₁₈, which was shown to be clean by NMR, were unsatisfactory. Spectra of the complex have been included in the Supporting Information.

Cobalt Complex of Bis(3,4:7,8-dibenzocyclo-3,7-diene-1,5,9-triyn)germane (Ge(OBET)₂(Co₂(CO)₆)₂). A Schlenk flask was charged with Ge(OBET)₂ (52.1 mg, 0.1 mmol) and 50 mL of hexane. Dicobalt octacarbonyl (144 mg, 0.4 mmol) with 5% of hexane was added to the suspension of Ge(OBET)₂ in hexane in a drybox. The mixture was stirred at room temperature. After 18 h the white solid Ge(OBET)₂ was gone. After an additional 24 h the solvent and any unreacted dicobalt octacarbonyl were pumped off under vacuum for 5 h. The residue was dissolved in hexane and filtered. X-ray quality deep red crystals were successfully grown from a mixture of hexane and diethyl ether. The NMR results indicated an 80% yield. ¹H NMR (300 MHz, C₆D₆): δ 7.76 (d, 2H), 7.44 (q, 4H), 7.25 (d, 2H), 6.88 (m, 2H) 6.74 (m, 2H). ¹³C NMR (75 MHz, C₆D₆): δ 199.4, 138.9, 134.4, 133.1, 132.6, 131.0, 129.7, 128.7, 128.5, 128.2, 125.1, 122.8, 108.3, 99.3, 98.2, 97.9, 92.7, 79.0. IR 2086, 2061, 2054, 2029, 1865 cm⁻¹. Several attempts to get elemental analysis of the cobalt complex, which was shown to be clean by NMR, were unsatisfactory. Spectra of the complex have been included in the Supporting Information.

Crystal Structure Determinations. X-ray crystallographic data were collected using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) on a Syntex P2₁ diffractometer updated to a Siemens R3m/v and equipped with a Molecular Structure Corp. low-temperature device. X-ray data were collected using ω scans. Crystals of complexes suitable for X-ray diffraction were grown from a mixture of hexane and diethyl ether by slow evaporation of solvents. Crystals of Ge(OBET)₂ were obtained from THF. Cell dimensions were refined using 20–30 reflections with 20° ≤ 2θ ≤ 30°. Three check reflections were monitored every 97 reflections during

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data collection. The structures were solved by direct methods.¹⁴ Hydrogens were calculated, and further refinements¹⁵ were done using a riding model for the hydrogen atoms. Further details, refinement parameters, and results are listed in Table 1.

Results and Discussion:

Scheme 1 outlines the synthetic route for Ge(OBET)₂. The precursor *o*-(bisethynyl)tolane (OBET)H₂ was prepared by literature methods.¹² Deprotonation of (OBET)H₂ with 2 equiv of *n*-butyllithium produced Li₂(OBET). Addition of 0.5 mol of germanium tetrachloride per mole of Li₂(OBET) at room temperature resulted in the formation of Ge(OBET)₂ with a 46% yield. Ge(OBET)₂ was characterized by ¹H NMR, ¹³C NMR, elemental analysis, FDMS, and X-ray crystallography. Ge(OBET)₂ is an air stable white solid with relatively poor solubility compared to SiPh₂(OBET)₂. The UV spectra for Ge(OBET)₂ and SiPh₂(OBET)₂ are similar with absorption maxima at 334 nm ($\epsilon = 8.1 \times 10^4$) and 332 nm ($\epsilon = 2.4 \times 10^4$), respectively.

A crystal of Ge(OBET)₂ suitable for crystallographic characterization was obtained by slow evaporation of THF from a Ge(OBET)₂/THF solution. Ge(OBET)₂ crystallized in the triclinic space group $P\bar{1}$ with one molecule per asymmetric unit. The thermal ellipsoid labeling diagram of Ge(OBET)₂ is shown in Figure 1, and the packing diagram is shown in Figure 2. Selected bond lengths and angles are listed in Table 2. Each heterocyclene ring in the molecule of Ge(OBET)₂ is planar. The principal plane composed of atoms Ge and C1–C10 deviates from planarity by a mean deviation of 0.0510 Å, with individual deviations ranging from –0.1159 Å at C1 to –0.0046 Å at C9. The other principal plane composed of Ge and C11–C20 deviates from planarity by a mean deviation of 0.0552 Å, with deviations ranging from –0.1343 Å at Ge to –0.0002 Å at C14. Due to the tetrahedral geometry of the germanium atom, the two pockets are nearly perpendicular to each other with a dihedral angle of 96.8°. The bond lengths of the two alkynes located between two phenyl rings, C(5)–C(6)

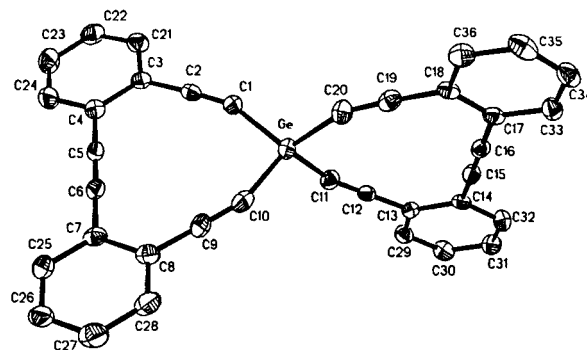


Figure 1. Molecular structure of Ge(OBET)₂ with thermal ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.

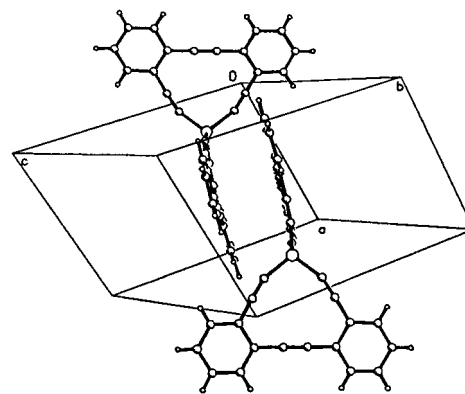


Figure 2. Packing diagram of Ge(OBET)₂.

and C(15)–C(16), are 1.208(7) and 1.197(7) Å, respectively, while the bond lengths of the four alkynes next to germanium range from 1.191(7) to 1.207(7) Å. The four Ge–alkyne bond lengths range from 1.884(5) to 1.889(6) Å. The inner germanium alkyne angles of C1–Ge–C10 and C11–Ge–C20 are 100.9(2)° and 100.6(2)°, respectively. These angles are approximately 8° smaller than a normal tetrahedral angle. The comparable angle in SiPh₂(OBET)₂ is 101.6(1)°. A THF solvent molecule cocrystallized with Ge(OBET)₂. The packing diagram of Ge(OBET)₂ is shown in Figure 2. The principal feature is that one of the cyclene rings in the first molecule is parallel to another in the second molecule.

Synthesis of Cobalt Complexes of SiPh₂(OBET) and Ge(OBET)₂ and Their Crystal Structures. In the hope that an analogue of the TBC cobalt complex, TBC(Co₄(CO)₉), might be obtained, we combined 2 molar equiv of Co₂(CO)₈ with SiPh₂(OBET) in diethyl ether at room temperature. The synthetic route is outlined in Scheme 2. Both the starting material and the product were soluble. ¹H and ¹³C NMR results indicated that SiPh₂(OBET) reacted completely with the formation of only one product. Crystals suitable for X-ray crystallographic analysis were obtained from a solvent mixture of diethyl ether and hexane. We have found that this is a very effective solvent mixture for crystallization for these and related molecules. The more volatile and polar solvent, diethyl ether, evaporates first. Thus the polarity of the mixture decreases gradually, solubility of the solute decreases, and crystals form. The complex SiPh₂(OBET)(Co₂(CO)₆)₂ has a deep red color.

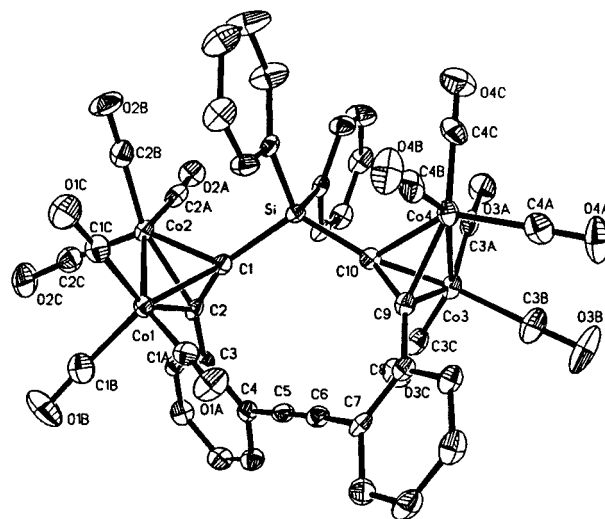
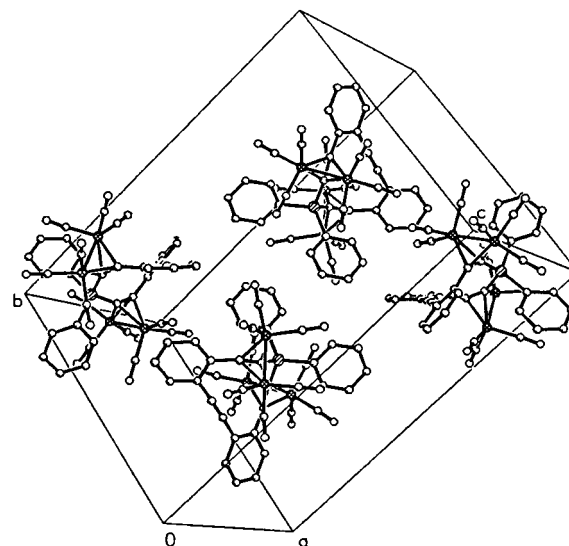
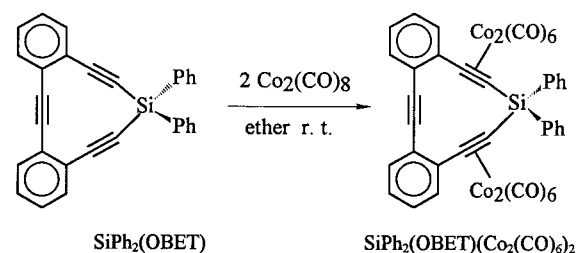
SiPh₂(OBET)(Co₂(CO)₆)₂ crystallized in the monoclinic space group $P2_1/n$ with one molecule per asymmetric unit. The thermal ellipsoid labeling diagram for SiPh₂

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Ge(OBET)₂ and Ge(OBET)₂(Co₂(CO)₆)₂

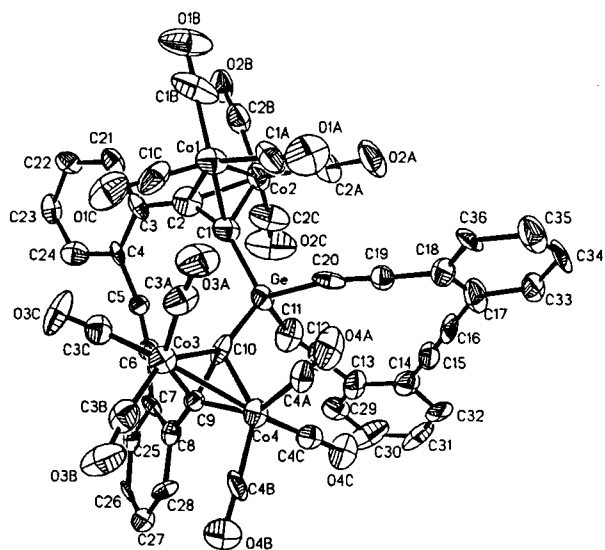
	Ge(OBET) ₂	Ge(OBET) ₂ -(Co ₂ (CO) ₆) ₂
Ge-C(1)	1.884(5)	1.96(2)
Ge-C(10)	1.889(6)	1.92(2)
Ge-C(11)	1.889(5)	1.95(2)
Ge-C(20)	1.884(5)	1.86(2)
C(1)-C(2)	1.196(7)	1.34(2)
C(2)-C(3)	1.440(7)	1.42(2)
C(3)-C(4)	1.410(7)	1.40(2)
C(4)-C(5)	1.429(7)	1.48(2)
C(5)-C(6)	1.208(7)	1.18(2)
C(6)-C(7)	1.442(7)	1.42(2)
C(7)-C(8)	1.410(7)	1.45(2)
C(8)-C(9)	1.425(7)	1.42(2)
C(9)-C(10)	1.202(7)	1.39(2)
C(11)-C(12)	1.191(7)	1.17(2)
C(12)-C(13)	1.436(7)	1.49(2)
C(13)-C(14)	1.415(7)	1.37(2)
C(14)-C(15)	1.441(7)	1.38(2)
C(15)-C(16)	1.197(7)	1.22(2)
C(16)-C(17)	1.426(7)	1.47(2)
C(17)-C(18)	1.409(7)	1.44(2)
C(18)-C(19)	1.430(7)	1.43(2)
C(19)-C(20)	1.207(7)	1.28(2)
C(1)-Ge-C(10)	100.9(2)	116.4(6)
C(1)-Ge-C(11)	111.4(2)	114.8(7)
C(1)-Ge-C(20)	117.2(2)	106.9(6)
C(10)-Ge-C(11)	113.8(2)	107.7(7)
C(10)-Ge-C(20)	113.7(2)	108.2(6)
C(11)-Ge-C(20)	100.6(2)	101.7(7)
C(2)-C(1)-Ge	159.7(5)	152.2(12)
C(1)-C(2)-C(3)	177.4(5)	144(2)
C(2)-C(3)-C(4)	119.4(4)	124(2)
C(3)-C(4)-C(5)	121.0(5)	123.4(13)
C(4)-C(5)-C(6)	178.8(6)	170(2)
C(5)-C(6)-C(7)	179.6(6)	171(2)
C(6)-C(7)-C(8)	120.2(5)	123.6(13)
C(7)-C(8)-C(9)	120.1(5)	120.3(13)
C(8)-C(9)-C(10)	177.9(6)	142.6(14)
C(9)-C(10)-Ge	159.7(5)	138.1(11)
C(12)-C(11)-Ge	161.1(5)	159(2)
C(11)-C(12)-C(13)	177.3(5)	177(2)
C(12)-C(13)-C(14)	119.1(4)	118(2)
C(13)-C(14)-C(15)	120.7(4)	124(2)
C(14)-C(15)-C(16)	178.9(5)	177(2)
C(15)-C(16)-C(17)	178.8(5)	178(2)
C(16)-C(17)-C(18)	121.0(4)	121(2)
C(17)-C(18)-C(19)	119.3(4)	119(2)
C(18)-C(19)-C(20)	176.8(6)	176(2)
C(19)-C(20)-Ge	159.3(5)	158.9(13)
Co(1)-C(1)		1.95(2)
Co(1)-C(2)		1.969(14)
Co(1)-Co(2)		2.491(4)
Co(2)-C(1)		1.96(2)
Co(2)-C(2)		1.97(2)
Co(3)-C(9)		2.001(14)
Co(3)-C(10)		1.936(14)
Co(3)-Co(4)		2.486(4)
Co(4)-C(9)		1.967(14)
Co(4)-C(10)		1.993(14)
C(2)-C(1)-Co(1)		70.6(10)
C(2)-C(1)-Co(2)		70.4(10)
Co(1)-C(1)-Ge		132.5(8)
Co(2)-C(1)-Ge		123.2(9)
C(1)-C(2)-Co(1)		69.4(9)
C(3)-C(2)-Co(1)		134.2(12)
C(1)-C(2)-Co(2)		69.7(10)
C(3)-C(2)-Co(2)		133.1(12)
C(10)-C(9)-Co(4)		70.5(8)
C(8)-C(9)-Co(4)		134.9(11)
C(10)-C(9)-Co(3)		66.8(8)
C(8)-C(9)-Co(3)		135.2(11)
C(9)-C(10)-Co(3)		71.9(9)
Ge-C(10)-Co(3)		144.8(8)
C(9)-C(10)-Co(4)		68.4(8)
Ge-C(10)-Co(4)		124.7(7)

**Figure 3.** Molecular structure of SiPh₂(OBET)(Co₂(CO)₆)₂ with thermal ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.**Figure 4.** Packing diagram of SiPh₂(OBET)(Co₂(CO)₆)₂.**Scheme 2**

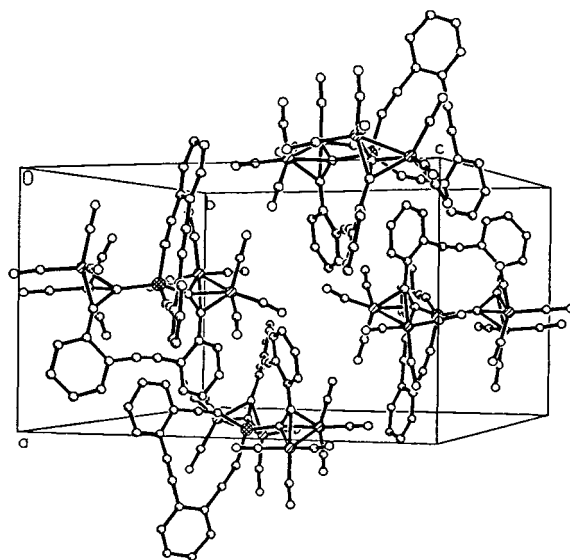
(OBET)(Co₂(CO)₆)₂ is shown in Figure 3, and the packing diagram is shown in Figure 4. Selected bond lengths and angles are listed in Table 3. For reference and comparison with SiPh₂(OBET)(Co₂(CO)₆)₂, the corresponding bond lengths and angles of its free ligand SiPh₂(OBET) are also included in Table 3. The cobalt carbonyls selectively coordinate to the strained alkynes adjacent to the silicon heteroatom, even though there are two bulky phenyl groups on this atom. The third alkyne remains uncomplexed, as is the case with the cobalt complex of TTC. The fact that the alkynes are bent appears to be responsible for the selectivity of the

Table 3. Selected Bond Lengths [Å] and Angles [deg] for SiPh₂(OBET)(Co₂(CO)₆)₂ and SiPh₂(OBET)

	SiPh ₂ (OBET)- (Co ₂ (CO) ₆) ₂	SiPh ₂ (OBET)	SiPh ₂ (OBET)- (Co ₂ (CO) ₆) ₂	SiPh ₂ (OBET)	
Co(1)–C(1)	2.007(7)		C(19)–Si–C(25)	117.0(3)	112.1(1)
Co(1)–C(2)	1.993(7)		Si–C(1)–C(2)	148.4(6)	162.5(2)
Co(1)–Co(2)	2.458(2)		Co(1)–C(1)–C(2)	69.8(4)	
Co(2)–C(1)	2.007(7)		Co(1)–C(1)–Si	139.0(4)	
Co(2)–C(2)	1.972(7)		Co(2)–C(1)–C(2)	68.9(4)	
Co(3)–C(9)	1.989(7)		Co(2)–C(1)–Si	122.8(4)	
Co(3)–C(10)	1.997(7)		C(1)–C(2)–C(3)	146.5(7)	174.7(3)
Co(3)–Co(4)	2.473(2)		C(1)–C(2)–Co(2)	71.6(4)	
Co(4)–C(9)	1.977(8)		C(3)–C(2)–Co(2)	133.8(5)	
Co(4)–C(10)	2.005(7)		C(1)–C(2)–Co(1)	70.9(4)	
Si–C(1)	1.860(8)	1.818(3)	C(3)–C(2)–Co(1)	129.1(5)	
Si–C(10)	1.870(7)	1.826(3)	C(4)–C(3)–C(2)	120.0(6)	119.0(2)
Si–C(19)	1.880(7)	1.854(3)	C(3)–C(4)–C(5)	121.3(7)	120.7(2)
Si–C(25)	1.882(7)	1.863(3)	C(6)–C(5)–C(4)	176.7(8)	177.5(3)
C(1)–C(2)	1.345(10)	1.208(4)	C(5)–C(6)–C(7)	177.2(8)	178.3(3)
C(2)–C(3)	1.465(10)	1.430(4)	C(8)–C(7)–C(15)	119.8(7)	118.9(2)
C(3)–C(4)	1.423(10)	1.412(3)	C(8)–C(7)–C(6)	121.8(7)	121.1(2)
C(4)–C(5)	1.436(11)	1.435(4)	C(7)–C(8)–C(9)	121.7(7)	118.4(2)
C(5)–C(6)	1.208(11)	1.194(4)	C(10)–C(9)–C(8)	147.5(7)	174.4(3)
C(6)–C(7)	1.448(10)	1.429(4)	C(10)–C(9)–Co(4)	71.6(4)	
C(7)–C(8)	1.417(11)	1.411(4)	C(8)–C(9)–Co(4)	133.4(5)	
C(7)–C(15)	1.418(11)	1.396(4)	C(10)–C(9)–Co(3)	70.8(4)	
C(8)–C(18)	1.405(10)	1.389(4)	C(8)–C(9)–Co(3)	128.2(5)	
C(8)–C(9)	1.458(10)	1.434(4)	Co(4)–C(9)–Co(3)	77.2(3)	
C(9)–C(10)	1.334(10)	1.205(3)	C(9)–C(10)–Si	156.3(6)	163.5(3)
C(1)–Si–C(10)	114.9(3)	101.6(1)	C(9)–C(10)–Co(3)	70.1(4)	
C(1)–Si–C(19)	106.3(3)	113.8(1)	Si–C(10)–Co(3)	130.2(4)	
C(10)–Si–C(19)	107.9(3)	110.7(1)	C(9)–C(10)–Co(4)	69.3(4)	
C(1)–Si–C(25)	105.4(3)	109.1(1)	Si–C(10)–Co(4)	122.9(4)	
C(10)–Si–C(25)	105.7(3)	108.9(1)			

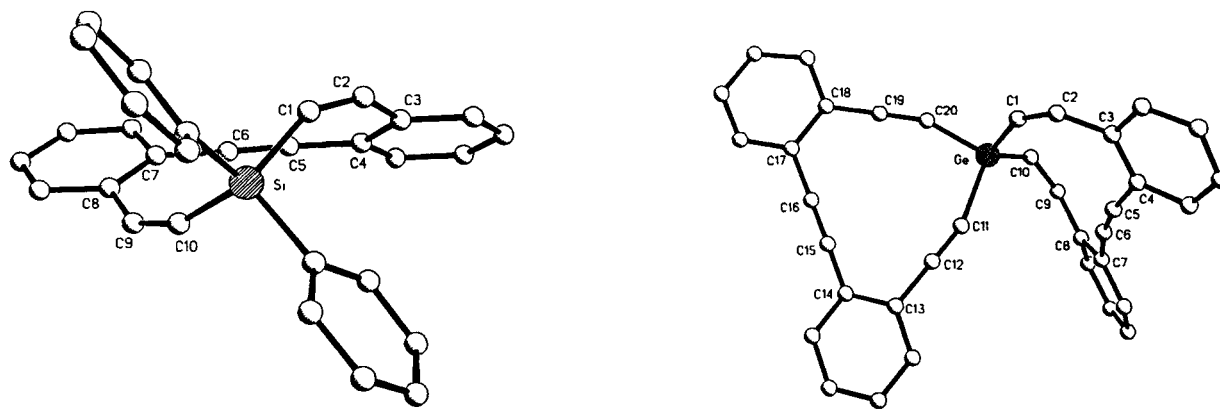
**Figure 5.** Molecular structure of Ge(OBET)₂(Co₂(CO)₆)₂ with thermal ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.

complexation with dicobalt octacarbonyl. The inner silicon alkyne C1–Si–C10 bond angles are expanded from 101.6(1)° in the free ligand to 114.9(3)° in the cobalt complex. The C≡C alkyne bonds adjacent to silicon are lengthened from 1.208(4) and 1.205(3) Å in the free ligand to 1.345(10) and 1.334(10) Å in its cobalt complex, which is comparable to the complexed C≡C alkyne bonds of 1.340(8) and 1.326(8) Å in TTC(Co₂(CO)₆)₂.⁹ The Si–C1–C2 and Si–C10–C9 angles in SiPh₂(OBET) of 162.5(2) and 163.5(3) are decreased to 148.4(6)° at Si–C1–C2 and 156.3(6)° at Si–C10–C9 in the complex. The angles at C1–C2–C3 and C10–C9–C8 of 174.5(2)° and 174.4(3)° in the free ligand are decreased to 146.5(7)° for C1–C2–C3 and 147.5(7)° for C10–C9–C8

**Figure 6.** Packing diagram of Ge(OBET)₂(Co₂(CO)₆)₂.

in its cobalt complex. The alkyne bonds of the free ligand TTC are also bent, though only slightly so, with C≡C–C bond angles ranging from 175.5(4)° to 176.4(3)°. The Co–Co bond lengths of 2.458(2) and 2.473(2) Å in SiPh₂(OBET)(Co₂(CO)₆)₂ are comparable to those of 2.446(1) and 2.450(1) Å in TTC(Co₂(CO)₆)₂. As will be described later, the planarity of the free ligand SiPh₂(OBET) is dramatically twisted in its complex. The ¹H NMR and ¹³C NMR spectral results are consistent with the crystal structure.

The high selectivity of the complexation of cobalt toward the bent alkynes observed in SiPh₂(OBET)(Co₂(CO)₆)₂ led us to examine the cobalt chemistry of the dipocket ligand Ge(OBET)₂ (see Scheme 1). With expectations of similar reactivity to that of SiPh₂-

SiPh₂(OBET) portion of SiPh₂(OBET)(Co₂(CO)₆)₂Ge(OBET)₂ portion of Ge(OBET)₂(Co₂(CO)₆)₂**Figure 7.** Geometries of the ligands in their cobalt complexes.

(OBET), i.e., dicobalthexacarbonyl moieties would complex with the four bent alkynes adjacent to the germanium atom in Ge(OBET)₂, 4 molar equiv of dicobalt octacarbonyl were used. The starting free ligand Ge(OBET)₂ was not immediately soluble in hexane. However, it was no longer present as a solid after stirring for 1 day. It has been observed that the solubility of cobalt alkyne complexes is considerably greater than the uncomplexed ligands.⁹ The reaction was completed in 80% yield based on the ¹H NMR spectra in C₆D₆, which showed only one final product and starting materials. The ¹³C NMR spectrum shows one sharp carbonyl signal at 199.4 ppm, which indicates the carbonyl carbons are equivalent on the NMR time scale, and 17 sharp signals from 79.0 to 138.9 ppm with one peak apparently buried in the solvent peaks. However, six alkyne signals are observed instead of three. The solution of the product in hexane is deep red in color as is SiPh₂(OBET)(Co₂(CO)₆)₂. A crystal suitable for X-ray determination was obtained from a mixture of diethyl ether and hexane solvents. Ge(OBET)₂(Co₂(CO)₆)₂ crystallizes in the monoclinic space group *P*2₁/*n* with one molecule per asymmetric unit. A thermal ellipsoid labeling diagram of this complex is displayed in Figure 5, and a packing diagram is shown in Figure 6. Selected bond lengths and angles are listed in Table 2 for ease of comparison with relevant distances and angles in Ge(OBET)₂. Surprisingly only two alkynes of one of the pockets are complexed. The three alkynes of the other pocket were left intact even though a large excess of dicobalt octacarbonyl was present. The two alkynes next to germanium in the other pocket (C11≡C12 and C19≡C20) apparently do not react with dicobaltoctacarbonyl because of the steric hindrance from the two dicobalthexacarbonyl moieties complexed to C1≡C2 and C9≡C10. The unreacted pocket is similar to the pockets in free Ge(OBET)₂ with a mean deviation from planarity of 0.0716 Å, ranging from -0.0045 Å at C18 to 0.1427 Å at C17 of the least-squares plane defined by Ge and C11–C20. The inner angle at germanium with the neighboring alkynes is widened 1° in the uncomplexed ring, whereas the complexed ring shows a 15.7° widening angle at germanium. The complexed pocket shows changes similar to those observed in SiPh₂(OBET)(Co₂(CO)₆)₂. The alkyne bonds adjacent to germanium lengthened from 1.199(6)

Å in the free ligand to 1.365(3) Å on average for the alkynes coordinated to the cobalt atoms. The Ge–C≡C angles, such as Ge–C1–C2 and Ge–C10–C9, range from 159.7(5)° to 161.1(5)° in the Ge(OBET)₂ and are decreased to 138.1(11)° at Ge–C10–C9 and 152.2(12)° at Ge–C1–C2 for the complexed alkynes in Ge(OBET)₂(Co₂(CO)₆)₂. The C–C≡C angles adjacent to Ge range from 176.8(6) to 177.9(6) in the free ligand and are decreased to 144(2)° for C1–C2–C3 and 142.6(14)° for C10–C9–C8 in the complex. The Co–Co bond lengths are 2.486(4) and 2.491(4) Å.

A comparison of the two complexes SiPh₂(OBET)(Co₂(CO)₆)₂ and Ge(OBET)₂(Co₂(CO)₆)₂ is of interest. The ligands in both complexes are considerably distorted from planarity. Figure 7 shows the ligands SiPh₂(OBET) and Ge(OBET)₂ in their complexes with the dicobalthexacarbonyl moieties omitted. In SiPh₂(OBET)(Co₂(CO)₆)₂, the ligand is twisted in an “S” fashion with one alkyne going above the plane and the other going below the plane of the tolane moiety, whereas in Ge(OBET)₂(Co₂(CO)₆)₂, both alkynes bend in the same direction so that the whole plane is “hanging” down (see Figure 7). The uncoordinated alkyne in SiPh₂(OBET)(Co₂(CO)₆)₂ is relatively linear (176.7(8)° at C4–C5–C6 and 177.2(8)° at C5–C6–C7), but the uncoordinated alkyne in the coordinated cyclyne ring in Ge(OBET)₂(Co₂(CO)₆)₂ is bent (170(2)° at C4–C5–C6 and 171(2)° at C5–C6–C7). In their free ligands, C4–C5–C6 and C5–C6–C7 angles are 177.5(3)° and 178.3(3)°, respectively in SiPh₂(OBET), and range from 178.8(6)° to 179.6(6)° in Ge(OBET)₂. A distortion similar to that found in the SiPh₂(OBET) ligand in SiPh₂(OBET)(Co₂(CO)₆)₂ has been found in the cobalt complex of cyclooct-3-ene-7,8-diphenyl-1,5-diyne (Figure 8).¹⁶ In this molecule two cobalt atoms bind to one alkyne below the cyclic plane and the other two cobalt atoms bind to another alkyne above the cyclic plane. The distortion of the Ge(OBET)₂ ligand in Ge(OBET)₂(Co₂(CO)₆)₂ is similar to that of the TTC ligand in TTC(Co₂(CO)₆)₂. As mentioned above, in each complex the angles at C1 and C10, both of which are adjacent to the heteroatoms Si or Ge, are significantly different, which is not the case in their free ligands. The difference between angles of Ge–C1–C2

(16) Melikyan, G. G.; Khan, M. A.; Nicholas, K. M. *Organometallics* 1995, 14, 2170.

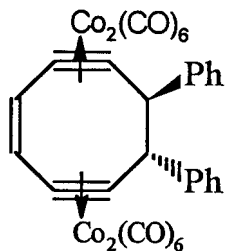


Figure 8. Cobalt complex of cyclooct-3-ene-7,8-diphenyl-1,5-diyne.

and Ge–C10–C9 in $\text{Ge}(\text{OBET})_2(\text{Co}_2(\text{CO})_6)_2$ is 14° , and the difference between Si–C1–C2 and Si–C10–C9 in $\text{SiPh}_2(\text{OBET})(\text{Co}_2(\text{CO})_6)_2$ is 8° .

To compare the size of the cavity in the $\text{SiPh}_2(\text{OBET})$ ring with the cavity size in TBC and TTC, the distance from each alkyne carbon to the centroid of the six alkyne carbons has been calculated. In the $\text{SiPh}_2(\text{OBET})$ ligand the average distance from the calculated centroid to each alkyne carbon is 2.069 \AA , ranging from 2.142 \AA for the alkyne carbons β to the silicon, 2.037 \AA for the alkyne carbons α to the silicon, and 2.029 \AA for the alkyne carbons between the two phenyl groups. Similar distances are observed in the $\text{Ge}(\text{OBET})_2$ ligand. The comparable values are 2.140 \AA for TTC and 2.08 \AA for TBC.

This work has led us to the hypothesis that $\text{Co}_2(\text{CO})_8$ will selectively complex to bent alkynes in the presence of linear alkynes in the same molecule. The selectivity is presumably due to the fact that $\text{Co}_2(\text{CO})_8$ usually forms complexes with an alkyne in such a way that the alkyl or aryl groups on the alkyne are bent away from the metal. An uncomplexed bent alkyne would be of higher energy due to strain than a linear alkyne and would therefore be more reactive. Complexation would give a decrease in strain in the bent alkyne because alkynes bound to $\text{Co}_2(\text{CO})_8$ are typically bent. It is probable that other metals and reagents will exhibit similar selectivity with bent versus linear alkynes. We are currently examining this possibility.

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Supporting Information Available: Tables of anisotropic thermal parameters, bond lengths and angles, and hydrogen parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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