Planar Silicon and Germanium Heterocyclotriynes and Their Isomorphous Nickel(0) Complexes

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Received October 14, 1996[®]

The syntheses of three strained silicon or germanium heterocyclotriynes, from the dilithium dianion of 2,2'-diethynyltolane (Li₂(OBET)) and the dialkyldichlorosilanes or dialkyldichlorogermane, are described. Reactions of the heterocyclynes with Ni(COD)₂ give the nickel(0) complexes in very high yield. The heterocyclynes and their nickel complexes have been characterized by a variety of spectral techniques, and the X-ray crystal structures of compounds Si(*i*-Pr)₂(OBET), Ni[Si(*i*-Pr)₂(OBET)], SiPh₂(OBET), Ni[SiPh₂(OBET)], GePh₂-(OBET), and Ni[GePh₂(OBET)] are reported. The heterocyclynes and their nickel complexes possess isomorphous structures.

Introduction

Polyalkynylsilanes have attracted considerable attention recently because of the possibility of $\sigma - \pi$ interactions between the silicon atom and the alkyne triple bond.¹ There has also been a surge of activity in construction of strained cyclic organoethynylsilanes.² Some rigid cyclic ethynylsilanes can undergo ringopening polymerization.^{2f,3}

The interaction of TBC and related cyclotriynes with metal moities has resulted in the synthesis of a wide variety of novel metallic derivatives, including Ag(I) sandwich compounds,⁴ copper(I) aggregates,⁵ cobalt clusters,⁶ and, most relevant to the current paper, planar metallocyclynes of $Ni(0)^7$ and Cu(I),⁸ Figure 1. In this paper we report the synthesis and characterization of three strained silicon and germanium containing heterocyclynes in which one of the benzo rings is replaced with an SiR₂ or GeR₂ moiety. Nickel(0)

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Figure 1. Structures of TBC and Ni(TBC).

complexes of these heterocyclynes are also described. Portions of this work have appeared as a preliminary communication.9

Experimental Procedures

Materials: All chemicals were purchased from Aldrich Chemical, Co., and used as received unless otherwise stated. Solvents used for reactions were dried and distilled before use. THF was predried over sodium hydroxide and distilled from sodium benzophenone ketyl, to which a small amount of tetraethylene glycol dimethyl ether was added. Diisopropylamine and piperidine were distilled from sodium hydroxide. Trimethylsilylacetylene (Farchan) was dried over 4 Å molecular sieves and degassed using freeze-pump-thaw cycles. PdCl₂(NCPh)₂ was prepared by a literature method.¹⁰ The dichlorosilanes and diphenyldichlorogermane (Gelest) were distilled from anhydrous potassium carbonate. *n*-Butyllithium (1.6 M) in hexane was freshly standardized with diphenylacetic acid before use.¹¹ o-2,2'-diethynyltolanetolane, (OBET)H₂, was synthesized by modifications of published procedures.12 $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) was purchased from Strem and used as received. All reactions were carried out under nitrogen using standard Schlenk and vacuum-line

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procedures unless otherwise noted.¹³ Evaporation and concentration in vacuo were done at water aspirator pressure.

o-Iodo((trimethylsilyl)ethynyl)benzene (1). *o*-Bromoiodobenzene (50 g, 0.177 mol) and trimethylsilylacetylene (26.98 mL, 0.191 mol) were added to a stirred mixture of PdCl₂-(NCPh)₂ (1.695 g, 4.42 mmol), CuI (0.842 g, 4.42 mmol), and triphenylphosphine (2.32 g, 8.84 mmol) in 1300 mL of diisopropylamine at 0 °C. The orange solution became lighter, and a white precipitate formed at the end of addition of trimethylsilylacetylene. The solution turned gray to black after a half hour. The mixture was warmed to room temperature and was stirred overnight. The white salt was removed by filtration, and the solvent was removed under reduced pressure. The residue was purified by flash-chromatography on silica gel. Elution with hexane gave 41.7 g (93% yield) of **1** as a yellowish oil. ¹H-NMR (300 MHz, CDCl₃): δ 7.55 (d, 1H), 7.47 (d, H), 7.22 (t, overlap with solvent peak), 7.13 (t, 1H), 0.26 (s, 9H).

o-Bromoethynylbenzene (2). A solution of **1** (41.71 g, 0.165 mol), KF (9.59 g, 0.165 mol), and water (5.94 mL, 0.33 mol) in methanol (250 mL) was stirred at room temperature in air for 12 h. Water, hexane, and methylene chloride were added at 0 °C. The solution was washed with water and dried over magnesium sulfate. After evaporation of the solvent in vacuo, the product was purified by chromatography on silica gel. Elution with hexane gave 27.7 g (93% yield) of **2**. ¹H-NMR (300 MHz, CDCl₃): δ 7.57 (d, 1H), 7.51 (d, 1H), 7.26 (t, 1H), 7.18 (t, 1H), 3.36 (s, 1H).

Di-*o***-bromotolane (3).** Diisopropylamine (1150 mL) was added to a flask charged with $PdCl_2(NCPh)_2$ (1.017 g, 2.65 mmol), CuI (0.505 g, 2.65 mmol), and triphenylphosphine (1.390 g, 5.30 mmol). *o*-Bromoiodobenzene (42.846 g, 0.151 mol) and compound **2** (27.7 g, 0.153 mol) were introduced by cannula to the reaction mixture. The reaction was stirred for 12 h, with the formation of a heavy precipitate. The solution was filtered, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel with hexane, which was gradually changed to hexane and methylene chloride (6:1) to afford 3 in 92% yield (45.2 g) as a white solid. ¹H-NMR (300 MHz, CDCl₃): δ 7.62 (q, 2H), 7.59 (q, 2H), 7.29 (t, 2H), 7.19 (t, 2H). ¹³C-NMR (75 MHz, CDCl₃): δ 133.6, 132.5, 129.7, 127.0, 125.5, 125.1, 92.2.

Bis-o-((trimethylsilyl)ethynyl)tolane (4). Trimethylsilylacetylene (27.8 mL, 196.5 mmol) was added by syringe to a mixture of compound **3** (22 g, 65.5 mmol), $PdCl_2(NCPh)_2$ (1.256 g, 3.28 mmol), CuI (0.624 g, 3.28 mmol), and triphenylphosphine (1.718 g, 6.55 mmol) in 500 mL of piperidine. The reaction was stirred at room temperature for 12 h, 50 °C for 10 h, and 80 °C for 2 h. The mixture was cooled, and the solvent was removed under vacuum. The residue was extracted with CH_2Cl_2 and water. The black residue was chromatographed on silica gel, with hexane gradually changed to a hexane and CH_2Cl_2 mixture (5:1) to afford **4** as a white solid in 86% yield (20.93 g). ¹H-NMR (300 MHz, C₆D₆): δ 7.60 (d, 2H), 7.42 (d, 2H), 6.84 (t, 2H), 6.75 (t, 2H).

Di-o-ethynyltolane (OBET)H₂. In air, compound **4** (6.5 g, 17.5 mmol), KF (2.036 g, 17.5 mmol), and water (1.2 mL, 70.1 mmol) were stirred in a THF/MeOH (50/40) mixture at room temperature overnight. The reaction mixture was then extracted with methylene chloride two times. The combined organic phase was then dried over magnesium sulfate. The pale yellow residue was chromatographed on silica gel, with hexane gradually changed to a hexane and methylene chloride mixture to afford (OBET)H₂ as a white solid product in 99% yield (3.92 g). ¹H-NMR (300 MHz, C₆D₆): δ 7.46 (d, 2H), 7.36 (d, 2H), 6.77 (m, 4H), 2.99 (s, 2H). ¹H-NMR (300 MHz, CDCl₃): δ 7.57 (d, 2H), 7.52 (d, 2H), 7.30 (m, 4H). FDMS: *m*/*z* 362 (M⁺). Anal. Calcd for C₁₈H₁₀: C, 95.55; H, 4.55. Found: C, 95.45; H, 4.59. IR (C=C stretch): 2326 cm⁻¹(w), 2106 cm⁻¹(s).

General Procedure for the Synthesis of Silacyclynes and Diphenylgermanecyclyne. (3,4:7,8-Dibenzodeca-3,7diene-1,5,9-triyne-1,10-diyl)diisopropylsilane (Si(i-Pr)2-(OBET)). n-Butyllithium (1.25 mL, 2.21 mmol) was added to (OBET)H₂ (250 mg, 1.105 mmol) in 50 mL of THF. The solution turned deep red immediately. After the solution was stirred for 7 h at room temperature, the mixture was added to diisopropyldichlorosilane (204.6 mg, 0.199 mL, 1.105 mmol) in 350 mL THF. After the reaction mixture was stirred at 55 °C for 24 h, the vellowish mixture was opened to air and worked up by removal of the volatiles at reduced pressure, extraction with CH₂Cl₂/H₂O, and drying of the organic phase over magnesium sulfate. The volatiles were removed under vacuum. Chromatography on silica gel, eluting with hexane, gave 177 mg (53% yield) of Si(i-Pr)2(OBET) as a white solid. Crystals suitable for X-ray diffraction were grown from a hexane and methylene chloride mixture by slow evaporation of solvents. ¹H-NMR (300 MHz, C₆D₆): δ 7.44 (d, 4H), 7.34 (d, 2H), 6.77 (m, 4H), 1.26 (d, 12H), 1.15 (m, 2H). ¹³C-NMR (75 MHz, C₆D₆): δ 133.0, 131.2, 129.2, 128.9, 128.5, 126.0, 110.3, 97.1, 93.6, 18.5, 12.7. FDMS: m/z 338 (M⁺). Anal. Calcd for SiC₂₄H₂₂: C, 85.15; H, 6.55. Found: C, 85.26; H, 6.60. IR (C≡C stretch): 2153 cm⁻¹(s).

(3,4:7,8-Dibenzodeca-3,7-diene-1,5,9-triyne-1,10-diyl)diphenylsilane (SiPh₂(OBET)). (OBET)H₂ (384.7 mg, 1.7 mmol) was deprotonated with *n*-butyllithium (1.99 mL, 3.4 mmol) in 50 mL THF for 3.5 h and added to Ph₂SiCl₂ (430 mg, 1.7 mmol) in 800 mL THF. After the mixture was stirred for 14 h at 60-65 °C, the mixture was worked up as above. Elution with hexane, changed gradually to hexane/methylene chloride (15:1), on silica gel gave a 64% yield of SiPh₂(OBET) (444.1 mg) as a white solid. Crystals suitable for X-ray diffraction were grown from a hexane and methylene chloride mixture by slow evaporation of solvents. ¹H-NMR (300 MHz, C₆D₆): δ 7.98 (m, 4H), 7.48 (d, 2H), 7.33 (d, 2H), 7.13 (m, overlap with solvent), 6.81 (t, 2H), 6.75 (t, 2H). ¹³C-NMR (75 MHz, CDCl₃): δ 135.1, 132.5, 131.9, 130.7, 130.5, 128.8, 128.2, 128.2, 128.1, 124.6, 110.0, 95.8, 92.5. ¹³C-NMR (75 MHz, THF d_8): δ 136.0, 133.5, 133.1, 131.7, 131.4, 130.0, 129.4, 129.3, 129.1, 125.7, 110.9, 96.9, 93.4. ¹H{²⁹Si}-HMBC NMR (600 MHz, THF- d_8): δ -45.00. EI MS: m/z 406. Anal. Calcd for C30H18Si (406.56): C, 88.63; H, 4.46. Found: C, 88.54; H, 4.82. IR (C=C stretch): 2153 cm⁻¹(s).

(3,4:7,8-Dibenzodeca-3,7-diene-1,5,9-triyne-1,10-diyl)diphenylgermane (GePh₂(OBET)). (OBET)H₂ (0.1743 g, 0.77 mmol) was combined with *n*-butyllithium (0.885 mL, 1.54 mmol) in 25 mL of THF. After the mixture was stirred for 4.5 h, the dilithium dianion was transferred to a flask charged with 500 mL THF. Diphenyldichlorogermane (0.229 mg, 0.77 mmol) in 20 mL of THF was added via cannula. The reaction mixture turned to green/brown. The mixture was stirred for 14 h at room temperature and worked up in air as described above. Elution with a hexane and methylene chloride mixture (8:1) on silica gel gave 86.3% of GePh₂(OBET) (0.426 g) as a white solid. ¹H-NMR (300 MHz, CDCl₃): δ 7.72–7.76 (m, 4H), 7.63 (d, 2H), 7.51 (d, 2H), 7.39-7.43 (m, 6H), 7.32 (m, 4H). ¹³C-NMR (75 MHz, CDCl₃): δ 134.2, 133.1, 132.5, 130.8, 130.1, 128.6, 128.5, 128.1, 128.0, 124.7, 107.8, 95.7, 92.4. ¹³C{¹H}-NMR (75 MHz, CDCl₃): δ 107.8 (d, J = 5.4 Hz), 95.7 (s), 92.4 (d, J = 5.0 Hz).

Preparation of (Ni[Si(*i***-Pr)₂(OBET)]).** To a colorless solution of Si(*i*-Pr)₂(OBET) (75 mg, 0.22 mmol) in 30 mL benzene was added Ni(COD)₂ (68 mg, 0.247 mmol). The solution immediately turned deep red. The reaction mixture was stirred at room temperature for 12 h. After removal of the volatile components in vacuo, the deep red powder Ni[Si(*i*-Pr)₂(OBET)] was isolated (85% yield by NMR). Crystals suitable for X-ray structure analysis were obtained from benzene. ¹H-NMR (300 MHz, C₆D₆): δ 7.86 (d, 2H), 7.72 (d, 2H), 6.91 (m, 4H), 1.40 (m, 2H), 1.17 (d, 12H). ¹³C-NMR (75 MHz, C₆D₆): δ 140.7, 137.7, 132.7, 130.8, 130.0, 129.7, 127.6, 108.2, 75.0, 17.6, 13.6.

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Preparation of Ni[SiPh₂(OBET)]. To a colorless solution of SiPh₂(OBET) (90 mg, 0.22 mmol) in 10 mL benzene was added Ni(COD)₂ (60.5 mg, 0.22 mmol). The solution immediately turned to a deep red color. The reaction mixture was stirred at room temperature for 8 h. Removal of the volatile components in vacuo led to the isolation of the deep red powder Ni[SiPh₂(OBET)] (quantitative yield by NMR). Crystals suitable for X-ray structure analysis were obtained from benzene. ¹H-NMR (300 MHz, C₆D₆): δ 8.05 (m, 4H), 7.85 (d, 2H), 7.72 (d, 2H), 7.15 (m, overlap with solvent), 6.93 (m, 4H). ¹³C-NMR (75 MHz, THF-d₈): δ 141.1, 138.0, 135.5, 135.3, 131.3, 131.1, 130.5, 129.2, 2 signals at 129.0, 128.2, 107.1, 73.8. ¹H{²⁹Si}-HMBC NMR (600 MHz, THF-d₈): δ -52.39. MS: *m/z* 464 (⁵⁸Ni). IR (C=C stretch): 1996 cm⁻¹(s), 1929 cm⁻¹(w).

Preparation of Ni[GePh₂(OBET)]. To a colorless solution of GePh₂(OBET) (73.8 mg, 0.16 mmol) in 30 mL benzene was added Ni(COD)₂ (45 mg, 0.16 mmol). The solution immediately turned red and gradually grew darker. The reaction mixture was stirred at room temperature for 24 h. After removal of the volatile components in vacuo, the deep red powder Ni[GePh₂(OBET)] was isolated (1:3 ratio of starting material to the complex by NMR). Crystals suitable for X-ray structure analysis were obtained from benzene. ¹H-NMR (300 MHz, C₆D₆): δ 7.95 (d, J = 7.9 Hz, 2H), 7.87–7.91 (m, 4H), 7.76 (d, J = 7.0 Hz, 2H), 7.10 (td, 6H), 6.95 (m, 4H). ¹³C-NMR (75 MHz, C₆D₆): δ 140.6, 138.4, 135.7, 135.0, 134.4, 130.8, 130.3, 130.2, 127.9, 126.0, 108.5, 68.3.

Reactions of Ni[SiPh₂(OBET)] with Carbon Monoxide in THF Solution. Ni[SiPh₂(OBET)] (10 mg) was added to 8 mL of THF under inert atmosphere. The red solution was frozen with liquid N₂, and the flask was evacuated. The system was warmed to room temperature, and carbon monoxide was added. The red color of the initial solution was totally gone after 2.5 minutes. The volatile components were removed under vacuum. The ¹H-NMR spectrum showed that Ni[SiPh₂(OBET)] was completely converted to its free ligand SiPh₂(OBET).

Reactions of Solid Ni[SiPh₂(OBET)] with Carbon Monoxide. A 100 mL flask was charged with the deep red complex Ni[SiPh₂(OBET)] (10 mg). The flask was evacuated, and carbon monoxide added. No color change was observed, even after 1 year.

Reactions of Ni[SiPh₂(OBET)] with O₂. In solution, Ni[SiPh₂(OBET)] rapidly reacts with O₂, as do the other nickel complexes reported here. In the solid state, these complexes are very stable to O₂. The crystal used for the Ni[SiPh₂-(OBET)] crystal structure was mounted in air on a glass fiber. After 1 year of exposure to air, this crystal showed no decomposition by X-ray diffraction.

Crystal Structure Determinations. X-ray crystallographic data were collected using Mo K α radiation ($\lambda = 0.710$ 73 Å) on a Syntex P2₁ diffractometer updated to a Siemens R3m/v and equipped with a Molecular Structure Corp. lowtemperature device. X-ray data were collected using ω scans. Laue group symmetry was determined by photographs. Cell dimensions were refined using selected reflections from $20^\circ \leq$ $2\theta \leq 30^{\circ}$. Three check reflections were monitored every 97 reflections during the data collection. Systematic absences agree with the space groups. Structures were solved by direct methods,14 and models were completed by assigning reasonable Fourier difference electron densities.¹⁵ Hydrogen positions were calculated using a riding model and returned before each cycle of least-squares refinement.¹⁶ Final results are listed in Table 1 for Si(i-Pr)2(OBET) and Ni[Si(i-Pr)2(OBET)] and Table 2 for SiPh₂(OBET), GePh₂(OBET), Ni[SiPh₂(OBET)], and Ni[GePh₂(OBET)].

Table	1.	Crystal and Data Collection Parameters
	fo	r Compounds Si(<i>i</i> -Pr) ₂ (OBET) and
		Ni[Si(<i>i</i> -Pr) ₂ (OBET)]

Si(<i>i</i> -Pr) ₂ (OBET)	Ni[Si(<i>i</i> -Pr) ₂ (OBET)]
C24H22Si	NiC24H22Si
338.51	397.2
colorless	red
$0.21\times0.30\times0.42$	$0.30 \times 0.40 \times 0.40$
$P\overline{1}$	$P\bar{1}$
8.201(2)	8.177(2)
10.966(2)	10.977(2)
11.451(2)	11.386(2)
94.44(3)	94.12(3)
90.79(3)	90.45(11)
111.39(3)	111.31(3)
955.0(3)	949.0(3)
1.177	1.390
2	2
123	97
2494	3330
1972 ($I > 2.0\sigma(I)$)	2995 ($F > 2\sigma(F)$)
230	239
9.03	3.73
10.8	4.29
	$\begin{array}{c} {\rm Si}(i\mbox{-}{\rm Pr})_2(\mbox{OBET}) \\ {\rm C}_{24}{\rm H}_{22}{\rm Si} \\ {\rm 338.51} \\ {\rm colorless} \\ 0.21 \times 0.30 \times 0.42 \\ P\mbox{I} \\ {\rm 8.201(2)} \\ 10.966(2) \\ 11.451(2) \\ 94.44(3) \\ 90.79(3) \\ 111.39(3) \\ 955.0(3) \\ 1.177 \\ 2 \\ 123 \\ 2494 \\ 1972 \ (I \geq 2.0\sigma(I)) \\ 230 \\ 9.03 \\ 10.8 \\ \end{array}$

Results and Discussion

Scheme 1 presents the synthetic route to the target ligands. Reaction of 2,2'-diethynyltolane, (OBET)H₂,15 with *n*-butyllithium in THF at room temperature resulted in immediate formation of the deep red dilithium dianion (OBET)Li₂. The heterocyclynes were obtained by adding dialkyldichlorosilanes or dialkyldichlorogermanes to (OBET)Li2 in highly dilute solutions (0.002 M) to avoid the formation of oligomers and polymers.¹⁷ The conditions for the formation of silicon cyclynes included heating to 60-70 °C. The formation of the germanium cyclyne (GePh₂(OBET)) was carried out at room temperature. Workup results in formation of the colorless air-stable heterocyclynes. The germanium cyclyne was prepared in a higher yield (86% for GePh₂-(OBET)) than were the silicon cyclynes (64% for SiPh₂-(OBET) and 53% for Si(*i*-Pr)₂(OBET)). The higher yield and milder reaction conditions for synthesizing the germanium cyclynes than those required for silicon cyclynes indicates that the dialkyldichlorogermanes are more reactive toward the intermediate dilithium dianion than the dialkyldichlorosilanes. Reactions of the three heterocyclynes with Ni(COD)₂ gave red complexes in very high yields. The complexes are less soluble than their ligands.

The ¹H-NMR spectra of compounds Si(*i*-Pr)₂(OBET), SiPh₂(OBET), GePh₂(OBET), and their corresponding nickel complexes exhibit very similar patterns for the protons on the tolane moieties. Signals in the ¹H-NMR spectra of Ni[Si(i-Pr)2(OBET)], Ni[SiPh2(OBET)], and Ni[GePh₂(OBET)] are shifted downfield from the resonances in the spectra of the free ligands. Similar results were observed for Ni(TBC) relative to TBC.⁷ The ¹³C-NMR spectra of the representative ligand SiPh₂(OBET) and its nickel complex show that all of the signals of SiPh₂(OBET) are shifted downfield except the signal for the alkyne carbons α to the silicon atom, C1 and C10 (see the labeling diagram in Figure 2), which was assigned by using a ¹H-coupled ¹³C-NMR experiment. This resonance shifts upfield from 96.9 ppm in the free ligand SiPh₂(OBET) to 73.8 ppm in Ni[SiPh₂(OBET)],

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Table 2. Crystal and Data Collection Parameters for SiPh₂(OBET), GePh₂(OBET), Ni[SiPh₂(OBET)], and Ni[GePh₂(OBET)]

	SiPh ₂ (OBET)	GePh ₂ (OBET)	Ni[SiPh ₂ (OBET)]	Ni[GePh ₂ (OBET)]
formula	C ₃₀ H ₁₈ Si	C ₃₀ H ₁₈ Ge	C ₃₀ H ₁₈ SiNi	C ₃₀ H ₁₈ GeNi
mol wt	406.53	451.03	465.24	509.74
cryst color	colorless	colorless	red	red(darker)
cryst size (mm)	$0.20\times0.40\times0.60$	0.30 imes 0.50 imes 0.60	0.15 imes 0.20 imes 0.40	0.25 imes 0.30 imes 0.50
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	12.321(2)	12.376(2)	12.231(2)	12.292(2)
b (Å)	10.034(2)	10.012(2)	10.028(2)	10.033(2)
<i>c</i> (Å)	18.736(4)	18.858(4)	18.718(4)	18.865(4)
β (deg)	108.08(3)	107.97(3)	107.62(3)	107.45(3)
$V(Å^3)$	2201.9(7)	2222.9(7)	2188.1(7)	2219.5(7)
$ ho_{ m calcd}$ (g cm ⁻³)	1.226	1.348	1.412	1.526
Z	4	4	4	4
T (K)	130	95	130	109
no. reflns (indep)	2875	3883	2860	3909
no. reflns (obs)	2133 ($I > 2\sigma(I)$)	$3277 (I > 2\sigma(I))$	2148 ($I > 2\sigma(I)$)	3020 ($I > 2\sigma(I)$)
no. params refined	283	283	291	291
R1 (%)	4.18	3.51	4.59	4.13
R2 (%, all data)	7.01	4.71	7.53	6.46





indicating the coordination of Ni(0) strongly shields the alkyne carbons adjacent to the silicon. In TBC, the alkyne carbon resonance shifts downfield upon coordination with nickel(0). Measurement of the ²⁹Si NMR of Ni[SiPh₂(OBET)] was not possible using Cr(acac)₃ as a relaxation agent or by use of polarization transfer

techniques (DEPT and INEPT). A ¹H{²⁹Si}-HMBC NMR experiment¹⁸ showed that complexing SiPh₂-(OBET) with nickel(0) also shifts the Si signal upfield from -45.00 ppm for SiPh₂(OBET) to -52.39 ppm for Ni[SiPh₂(OBET)]. HMBC is particularly useful for observing long-range (two- or three-bond) connectivities and can be applied to the detection of nuclei bound to phenyl rings. The IR spectra of the ligands exhibit one strong band at 2153 cm⁻¹ for the $\nu_{C=C}$ stretch. The complexation of the nickel atom to the alkynes distorts the symmetry of the alkynes so that the complexes show two strong $\nu_{C=C}$ stretching bands at 1996 and 1922 cm⁻¹.

The electronic absorption spectrum shows that the maximum absorption occurs at 332, 334, 332, 332, and 290 nm for (OBET)H₂, Si(*i*-Pr)₂(OBET), SiPh₂(OBET), GePh₂(OBET), and TBC, respectively. Among these compounds, TBC has the lowest absorption maximum. The rest of the compounds have similar values. Their molar absorption coefficients are 1.90×10^4 , 1.97×10^4 , 2.37×10^4 , 2.35×10^4 , and 2.24×10^5 for OBET, Si(*i*-Pr)₂(OBET), SiPh₂(OBET), GePh₂(OBET), and TBC, respectively.

We have examined the reactivities of Ni[SiPh₂-(OBET)] with air and CO in solution and in the solid state. The complex Ni[SiPh₂(OBET)] dissolved in THF reacts with air to form the free ligand within 5 min. It also decomposes to its free ligand within 2 min when CO is bubbled into an air-free THF solution of Ni[SiPh₂-(OBET)]. These reactions are more rapid than those of Ni(TBC). Ni[SiPh₂(OBET)] as a solid does not react with CO or air, even after being exposed to either for 1 year.

We have obtained the X-ray structures of Si(*i*-Pr)₂-(OBET), Ni[Si(*i*-Pr)₂(OBET)], SiPh₂(OBET), Ni[SiPh₂-(OBET)], GePh₂(OBET), and Ni[GePh₂(OBET)]. One of the interesting features of these crystal structures is that the ligands and their nickel complexes possess isomorphous structures. Isomorphous crystals are those in which the atomic positions are the same but differ in the identity of the atoms; inclusion of additional atoms also conforms with the definition.¹⁹ Both the ligand of Si(*i*-Pr)₂(OBET) and its nickel(0) complex Ni[Si(*i*-Pr)₂(OBET)] crystallize in the space group $P\overline{1}$

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Figure 2. Thermal ellipsoid plots of Si(*i*-Pr)₂(OBET), Ni[Si(*i*-Pr)₂(OBET)], SiPh₂(OBET), Ni[SiPh₂(OBET)], GePh₂(OBET)], and Ni[GePh₂(OBET)], with thermal ellipsoids drawn at the 50% probability level.

with nearly equivalent unit cell dimensions and atom positions (Table 1). Compounds SiPh₂(OBET), Ni[SiPh₂-(OBET)], GePh₂(OBET), and Ni[GePh₂(OBET)] crystallize in the space group P_{2_1}/n with again nearly equivalent unit cell dimensions and atom positions among the four compounds (Table 2). This is not the case with TBC and NiTBC nor TPC and NiTPC, which posses a similar coordination pattern to that of the heterocyclynes discussed here.⁷ The molecular structures of Si(*i*-Pr)₂-(OBET), Ni[Si(*i*-Pr)₂(OBET)], SiPh₂(OBET), Ni[SiPh₂-(OBET)], GePh₂(OBET), and Ni[GePh₂(OBET)] are shown in Figure 2. Selected bond lengths and angles are listed in Table 3.

The central pockets consisting of the group 14 atom and C1–C10 in the free ligand are nearly planar. In the complexes, this pocket and the nickel atom are likewise nearly planar. In the four phenyl-substituted silicon and germanium cyclynes and their complexes, the maximum deviations from planarity for the atoms forming the central pocket always occur at the heteroatoms (0.112(1) Å for Ge and 0.098(1) Å for Si) and minima at C1 (0.001(2)–0.007(2) Å) or Ni (0.001(1)– 0.002(1) Å), indicating similar packing forces in each of the crystals as would be expected for ismorphous structures. Si(*i*-Pr)₂(OBET) and Ni[Si(*i*-Pr)₂(OBET)] show slightly greater deviations from planarity with maxima at C8 (0.088(2) and 0.086(2) Å) and minima at C1 (0.007(2) and 0.005(2) Å).

For the free ligands, the pocket size is estimated by calculating the distance from each alkyne carbon to the centroid of the six alkyne carbons (C1, C2, C5, C6, C9, and C10), whereas for their complexes, pocket size is determined by calculating the distance from each alkyne carbon to the nickel atom (Table 3). The Ni to alkyne carbon distances are largest for the alkyne carbons α to the silicon or germanium with Ni-C1 and Ni-C10 distances ranging from 2.047(5) to 2.094(4) Å. The corresponding centroid to alkyne carbon distances in the free ligands are not significantly different and range from 2.027 to 2.087 Å. The bond lengths for the nickel to alkyne carbons β to the Si or Ge (Ni–C2, Ni–C9) are significantly shorter and range from 1.999(3) to 2.014(4) Å. For the free ligands, the distances from the centroid to alkyne carbons β to the Si or Ge, C2 and C9, range

Table 3. Selected Interatomic Distances (Å) and Angles (deg)^a

				Ŭ	0	
	Si(<i>i</i> -Pr) ₂ (OBET)	Ni[Si(<i>i</i> -Pr) ₂ (OBET)]	SiPh ₂ (OBET)	Ni[SiPh ₂ (OBET)]	GePh ₂ (OBET)	Ni[GePh ₂ (OBET)]
Si(Ge)-C1	1.818(5)	1.852(3)	1.818(3)	1.840(5)	1.895(3)	1.931(5)
Si(Ge)-C10	1.827(5)	1.842(3)	1.826(3)	1.840(5)	1.903(3)	1.931(4)
C1-C2	1.215(7)	1.248(4)	1.208(4)	1.250(6)	1.204(4)	1.237(6)
C9-C10	1.206(7)	1.260(5)	1.205(3)	1.253(6)	1.205(4)	1.250(6)
C5-C6	1.197(7)	1.243(4)	1.194(4)	1.237(6)	1.205(4)	1.239(6)
C2-C3	1.435(7)	1.443(4)	1.430(4)	1.437(7)	1.431(4)	1.443(6)
C4-C5	1.421(7)	1.435(4)	1.435(4)	1.447(7)	1.428(4)	1.439(6)
C6-C7	1.428(7)	1.446(4)	1.429(4)	1.439(7)	1.431(4)	1.437(6)
C8-C9	1.434(7)	1.435(5)	1.434(4)	1.450(7)	1.440(4)	1.444(6)
Ni-Si(Ge)	2.655*	2.548(1)	2.615	2.509(2)	2.684	2.592(1)
Ni-C1	2.047*	2.049(3)	2.041	2.052(4)	2.087	2.092(4)
Ni-C10	2.029*	2.049(3)	2.027	2.047(5)	2.067	2.094(4)
Ni-C2	2.116*	1.999(3)	2.140	1.999(5)	2.160	2.002(4)
Ni-C9	2.115*	2.001(3)	2.143	2.005(5)	2.166	2.014(4)
Ni-C5	2.042*	2.002(3)	2.029	1.990(5)	2.031	1.991(4)
Ni-C6	2.055*	1.999(3)	2.028	1.989(4)	2.031	1.997(4)
C1-Si(Ge)-C10	100.1(2)	105.4(1)	101.6(1)	107.0(2)	100.6(1)	105.1(2)
Si(Ge)-C1-C2	162.7(4)	151.2(3)	162.5(2)	149.8(4)	161.5(2)	148.6(4)
Si(Ge)-C10-C9	163.6(4)	151.3(2)	163.5(3)	150.0(4)	162.6(3)	148.5(4)
C1-C2-C3	175.6(5)	169.4(3)	174.7(3)	168.5(5)	176.0(3)	167.0(4)
C10-C9-C8	175.1(5)	169.6(3)	174.4(3)	169.7(5)	175.2(3)	167.7(5)
C4-C5-C6	177.1(5)	172.1(3)	177.5(3)	171.6(5)	177.2(3)	170.7(4)
C7-C6-C5	177.2(5)	171.5(3)	178.3(3)	171.3(5)	178.1(3)	171.7(5)

^a Distances indicated by * are from the calculated centroid of the alkyne carbons to each alkyne carbon for the free ligands.

from 2.115 to 2.166 Å. The nickel to alkyne carbon distances for the alkyne carbons bridging two phenyl groups range from 1.989(4) to 2.002(3) and are significantly shorter than the centroid to alkyne carbon distances in the free ligands (2.028–2.055 Å) but are not significantly different from those for the nickel to alkyne carbons β to the Si(Ge). The nickel to alkyne carbon distance in Ni(TBC) is 1.958(5) Å. The Si(*i*-Pr)₂-(OBET), SiPh₂(OBET), and GePh₂(OBET) free ligands appear to have pockets slightly smaller than TBC, whereas their corresponding nickel complexes, Ni[Si(*i*-Pr)₂(OBET)], Ni[SiPh₂(OBET)], and Ni[GePh₂(OBET)], have significantly larger pockets than Ni(TBC).

An unusual mode of an alkyne bonding to a metal is observed in the three nickel complexes. The alkyne moieties next to the heteroatoms of the nickel complexes adopt a trans geometry rather than a cis geometry, as expected from the Dewar-Chatt-Duncanson bonding model.²⁰ The *trans* geometry is all the more surprising if one considers that planarity of the central pocket is preserved in the nickel complexes. The silicon or germanium atoms do not deviate any more from the plane of the ligand in the nickel complexes toward what would be a *cis* configuration than they do in the corresponding free ligands (see Table 3). In all three nickel complexes, C1 and C10 are displaced away from the nickel(0) slightly. In comparison with their corresponding ligands, the E-C1-C2 and E-C10-C9 angles (E = Si or Ge) are shifted by averages of 11.95° , 13.10° , and 13.45° for Ni[Si(i-Pr)2(OBET)], Ni[SiPh2(OBET)], and Ni[GePh₂(OBET)], respectively. Carbons 2 and 9 are displaced toward the nickel atom causing the C1-C2–C3 and C8–C9–C10 angles to shift upon complexation by averages of 15.15°, 16.35°, and 17.05° for Ni[Si(i-Pr)2(OBET)], Ni[SiPh2(OBET)], and Ni[GePh2-(OBET)], respectively. The $E-C \equiv C$ angles range from 148.5(4)° to 151.3(2)°, and the C=C-Ph angles adjacent to the heteroatoms range from 167.0(4)° to 169.7(5)° in the three nickel(0) complexes.

The alkynes next to the heteroatom, C1≡C2 and C9=C10, have average bond distances of 1.254(5), 1.252(6), and 1.244(6) Å for Ni[Si(*i*-Pr)₂(OBET)], Ni[SiPh₂(OBET)], and Ni[GePh₂(OBET)], respectively, which is an increase of approximately 0.05 Å from the free ligands. These are longer, but not significantly so, than the alkynes, C5=C6, bridging the two phenyl rings, which have bond distances of 1.243(4), 1.237(6), and 1.239(6) Å for Ni[Si(*i*-Pr)₂(OBET)], Ni[SiPh₂(OBET)], and Ni[GePh₂(OBET)], respectively. This indicates that complexation of C1=C2 and C9=C10 to nickel may be slightly stronger than that of C5=C6. The average alkyne bond lengths in Ni(TBC) and Ni(TPC) are 1.240(10) and 1.244(5) Å, respectively. The reported C=C length in $L_2Ni(XC=CY)$ type complexes is ca. 1.27 -1.28 Å.²¹

The coordination of the nickel into the trialkyne pockets enlarges the C1–E–C10 (E = Si or Ge) angles from 100.1(2)°, 101.6(1)°, and 100.6(1)° for Si(*i*-Pr)₂-(OBET), SiPh₂(OBET), and GePh₂(OBET), respectively, to 105.4(1)°, 107.0(2)°, and 105.1(2)° for the corresponding complexes (Table 3). Incremental release of the strain on the heteroatoms toward the normal tetrahedral angle is observed in the series. The silicon and germanium alkyne carbon bond lengths are increased significantly upon complexation. However, in both the complexes and in the free ligands, E–C distances show the shortening expected for E–C(sp) as compared to $E-C(sp^3)$.²²

In Ni[Si(*i*-Pr)₂(OBET)], Ni[SiPh₂(OBET)], and Ni-[GePh₂(OBET)], relatively short Ni–E separations are observed of 2.548(1), 2.509(2), and 2.592(4) Å, respectively. The question arises whether these short Ni–E contacts represent a bonding interaction. The sum of

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Planar Silicon and Germanium Heterocyclotriynes

the covalent radii of nickel and silicon or germanium are in the range 2.32-2.41 Å and 2.37-2.43 Å.²³⁻²⁵ Using Pauling's equation to estimate bond order,²⁶ the observed Ni-E separations correspond to bond orders of 0.48-0.89 for the silicon complexes and 0.49-0.59 for the germanium complex, when compared to the sum of covalent radii. Ni-Si single-bond lengths are found to be at or below the sum of the covalent radii for the halide-substituted compounds Ni(SiCl₃)₂(CO)₃ (2.383(3) and 2.289(3) Å)²⁷ and Ni(SiF₃)₂(PMe₃)₃ (2.182(4) Å)²⁸ and for the theoretical compounds Ni(SiH₂)₅ (2.20 Å) and Ni(SiH₂)₆ (2.41 Å).²⁹ Actual Ni-Ge single-bond distances range from smaller to larger than the sum of covalent radii in [Ni(GePh₃)(Cp)(CdGePh₃)]₂Cd (2.308 Å),³⁰ $[N(PPh_3)_2]_2[Ni_{10}(\mu^{10}-Ge)(CO)_{20}]$ (2.470(1) Å), and $[N(PPh_3)_2]_2[Ni_{12}(\mu^{12}-Ge)(CO)_{22}]$ (2.493(1) and 2.691(1) Å).³¹ The distance of the E atom from the calculated centroid (determined from C1, C2, C5, C6, C9, and C10) is 2.655, 2.615, and 2.648 Å for the free ligands Si(i-Pr)₂(OBET), SiPh₂(OBET), and GePh₂(OBET), respectively, a distance which is considerably larger than the Ni-E distance observed in the complexes. This suggests a Ni-E bonding interaction because it appears the E atom has been pulled in by complex formation. The significantly longer Ni-Si distance (by 0.039 Å) in Ni[Si(*i*-Pr)₂(OBET)] than that in Ni[SiPh₂(OBET)] is consistent with a Ni \rightarrow Si dative interaction because a SiPh₂ moiety would be a better acceptor of electron density than a Si(*i*-Pr)₂ moiety. A Ni \rightarrow E dative interaction rather than a normal Ni-E covalent bond is consistent with the observed long distances and calculated weak bond orders. As discussed below, a Ni \rightarrow E is not the only possible explanation for the Ni–E distances.

Polycarbosilanes containing main-chain acetylenic units have electron delocalization through the silicon atoms via $\sigma^* - \pi$ hyperconjugation.³² By way of $\sigma^* - \pi$ hyperconjugation, it is generally accepted that silicon can stabilize partial β -positive and α -negative charges.³³ Asymmetrically substituted acetylenes, especially those substituted by SiR_3 (R = Me or Ph), show a significant increase in polarization on coordination to Ni(0) in the complexes $(Ph_3P)_2Ni(\mu^2-PhC \equiv CSiR_3)$.³⁴ Polarization of an alkyne $C \equiv C$ bond should give rise to different

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Figure 3. Packing diagram of Ni[Si(*i*-Pr)₂(OBET)].



Figure 4. Packing diagram of SiPh₂(OBET).

bonding distances for each of the acetylenic carbons to the complexed metal as in $(Ph_3P)_2Ni(\mu^2-PhC \equiv CSiMe_3)$ where the Ni-C(Ph) distance is 1.884(6) Å and the Ni-C(SiMe₃) distance is 1.926(6) Å. Consistent with this, in the three nickel complexes reported here, the Ni-C1 and Ni-C10 distances are significantly longer (ca. 0.06 Å) than the Ni-C2 and Ni-C9 distances. This may partially account for the expansion of the C1-E-C10 angle, the novel trans geometry of the complexed acetylenes directly adjacent to the silicon, and the short Ni-E contact. However, the nickel complexes reported herein show some differences from $(Ph_3P)_2Ni(\mu^2 -$ PhC=CSiR₃). In the ¹³C NMR spectra of $(Ph_3P)_2Ni(\mu^2 -$ PhC≡CSiR₃), both alkyne carbon resonances shift downfield from those of the free ligand. As discussed earlier, this is different from what is observed for Ni[Si(*i*-Pr)₂-(OBET)], Ni[SiPh₂(OBET)], and Ni[GePh₂(OBET)]. These differences may be due to the strain imposed by the cyclic system or may indicate some other difference in the bonding, such as a Ni-E interaction. It is unclear whether the upfield shift in the ²⁹Si NMR observed between SiPh₂(OBET) and Ni[SiPh₂(OBET)] is indicative of a Ni-Si bonding interaction. Unfortunately ²⁹Si NMR of $(Ph_3P)_2Ni(\mu^2-PhC \equiv CSiR_3)$, which could serve as reference molecules for an unstrained system, were not reported. More definitive answers with respect to any metal to group 14 bonding may be obtained if we

⁽²³⁾ The available values of covalent radii are for Ni(II) complexes. It would be expected that Ni(0) would be slightly larger than Ni(II).

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prepare the platinum complexes $Pt[SiR_2(OBET)]$. The magnitude of the couplings between ¹⁹⁵Pt and ²⁹Si and ¹³C may help us determine the types of bonding involved in such complexes.

For the purpose of predicting one-dimensional conductivity, it is important to compare Ni–Ni intermolecular distances and packing patterns among the nickel cyclyne complexes. There are two packing patterns among the six compounds due to their isomorphous crystal structures, depending on whether the group 14 atom has isopropyl or phenyl substituents. One pattern is of Si(*i*-Pr)₂(OBET) and its nickel complex (Figure 3). The other is that of the phenyl-substituted heterocyclynes of SiPh₂(OBET), Ni[SiPh₂(OBET)], and the germanium analogs (Figure 4). The central pockets of Si(*i*-Pr)₂(OBET) and Ni[Si(*i*-Pr)₂(OBET)] molecules are stacked parallel to each other. The interplanar distance of 3.463 Å in the free ligand decreases to 3.258 Å in the nickel complex. In contrast, Ni[SiPh₂(OBET)] and its isomorphs do not stack, but the interplanar distances between the two molecules related by an inversion center is 3.590, 3.567, 3.573, and 3.561 Å for SiPh₂-(OBET), Ni[SiPh₂(OBET)], GePh₂(OBET), and Ni[GePh₂-(OBET)], respectively. The interplanar distance in Ni(TBC) is 3.35(1) Å. The close interplanar stacking in Si(*i*-Pr)₂(OBET) and Ni[Si(*i*-Pr)₂(OBET)], if present in doped systems, would be expected to provide increased conductivity.

Acknowledgment. We thank the National Science Foundation for financial support and Dr. Robert Lattimer of BFGoodrich for providing the FD-MS data.

Supporting Information Available: Tables of anisotropic thermal parameters, bond lengths and angles, hydrogen parameters, and least squares planes (42 pages). Ordering information is given on any current masthead page.

OM960868R