A Planar Skeleton Heterocyclyne, 1,1-Diphenyl-4,5:8,9-dibenzo-1-silacycloundeca-4,8-diene-2,6,10-triyne, and Its Nickel(0) Complex

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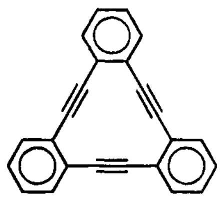
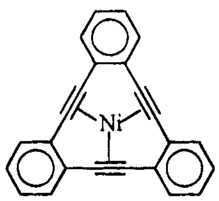
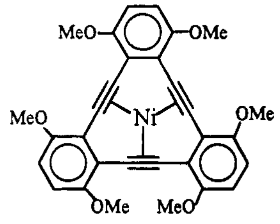
*Summary: A silicon-containing heterocyclyne (**2**) has been synthesized and characterized. Reaction of Ni-$(COD)_2$ with **2** affords a planar complex (**3**) in very high yield. The X-ray crystal structure shows that Ni(0) resides in the pocket of **2** and coordinates with unusual "trans" geometry alkynes.*

During the study of the synthesis and reaction chemistry of nickel(0) cyclotriyne complexes, significant reactivity differences have been observed that appear to be primarily correlated with the sizes of the central pockets.[1] The Ni(0)−C(alkyne) distances in Ni(TBC) and Ni(TPC) average about 1.96 Å, whereas other Ni(0)−C(alkyne) distances as short as 1.88 Å have been reported.[2] This suggests that the pocket of TBC is slightly larger than the optimum size for maximizing the bond strength between the alkynes and a centrally bound nickel(0). The bonding interaction can affect the reactivities of the nickel(0) complexes toward small molecules such as CO and O_2, a crucial point in our exploration for CO sensors.[3] To decrease the size of the cyclotriyne pocket, an analog of TBC in which one of the benzo rings is replaced with an $SiPh_2$ moiety has been prepared and its nickel(0) complex has been investigated.


TBC

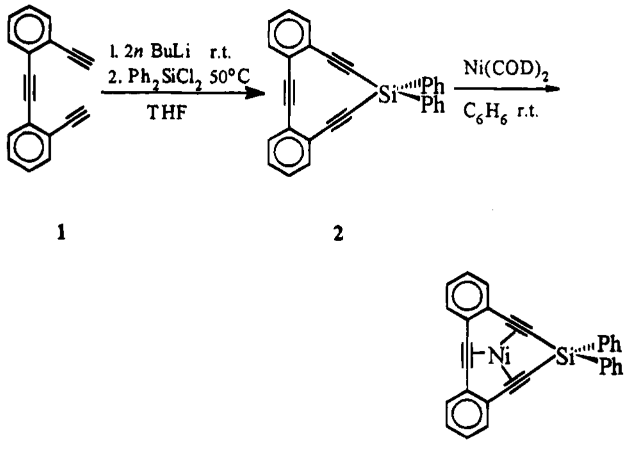


Ni(TBC)



Ni(TPC)

The reaction of 2,2′-diethynyltolane (**1**)[4] with *n*-butyllithium in THF at room temperature, followed by addition of dichlorodiphenylsilane, heating to 50 °C, and workup, results in the formation of the colorless heterocyclyne **2** in 53% isolated yield. The reaction of **2** with $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) gives the red complex **3** in very high yield.[5] Complex **3** is air stable in the solid state.



1 **2** **3**

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(5) All manipulations were carried out under an inert atmosphere using standard Schlenk techniques unless specified otherwise. **2**: To a solution of **1** (250 mg, 1.11 mmol) in 60 mL of THF was added 1.33 mL of freshly standardized *n*-BuLi (Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879−1880) in hexane (1.66 M, 2.21 mmol) at room temperature. After 4 h the resulting dilithio-2,2′-diethynyltolane was transferred via cannula to a solution of dichlorodiphenylsilane (0.23 mL, 1.11 mmol, HCl contaminate removed in vacuo prior to use) in 440 mL of THF. The mixture was stirred at 50 °C for 10 h. Water and methylene chloride were added in air to the mixture, and the organic phase was washed with water. The crude product was purified by chromatography on silica gel with 1:9 CH_2Cl_2−hexanes as the eluent to give 240 mg of colorless **2**. Crystallization of **2** from methylene chloride gave crystals suitable for X-ray structure determination. $C_{30}H_{18}Si$ (M_r 406.56): Anal. Calcd C, 88.63; H, 4.46. Found: C, 88.54; H, 4.82. ^1H NMR (300 MHz, C_6D_6) 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); ^{13}C NMR (300 MHz, $[D]_8$-THF) 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; $^1H\{^{29}Si\}$-HMBC NMR (600 MHz, $[D]_8$-THF) δ −45.00; EI MS *m/z* 406. **3**: To a colorless solution of **2** (90 mg, 0.22 mmol) in 10 mL of benzene was added $Ni(COD)_2$ (60.5 mg, 0.22 mmol). The solution immediately turned deep red. The reaction mixture was stirred at room temperature for 8 h. After removal of the solvent and COD in vacuo, a deep red powder was isolated (quantitative yield by NMR). Crystals suitable for X-ray structure analysis were obtained from benzene. $C_{30}H_{18}NiSi$ (M_r 465.24): ^1H NMR (300 MHz, C_6D_6) δ 8.05 (m, 4H), 7.85 (d, 2H), 7.72 (d, 2H), 7.15 (m, overlap with solvent), 6.93 (m, 4H); ^{13}C NMR (300 MHz, $[D]_8$-THF) 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; $^1H\{^{29}Si\}$-HMBC NMR (600 MHz, $[D]_8$-THF) δ −52.39; MS: *m/z* 464 (^{58}Ni).

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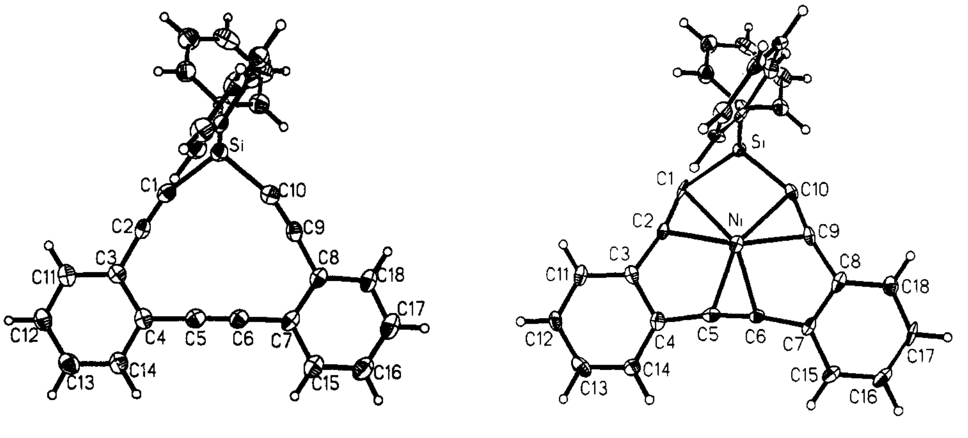

2 **3**

Figure 1. Molecular structures of compounds **2** and **3** with thermal ellipsoids drawn at 50% probability.

The ^{1}H NMR spectra of compounds **2** and **3** exhibit very similar patterns. Signals in the spectra of complex **3** are shifted downfield from the resonances in the spectra of the free ligand **2**. Similar results were observed for Ni(TBC) in the ^{1}H NMR spectra relative to that of TBC.[1] All signals in the ^{13}C NMR spectra of **3** shift down field except for the signal for C1/C10 (see the labeling diagram in Figure 1), assigned by using a ^{1}H coupled ^{13}C NMR experiment. Unexpectedly this resonance shifts upfield from 96.9 ppm in **2** to 73.8 ppm in **3**, indicating that the coordination of Ni(0) shields the alkyne carbons adjacent to the silicon exclusively. A $^{1}H\{^{29}Si\}$-HMBC NMR experiment[6] showed that complexing **2** with nickel(0) also shifts the Si signal upfield from −45.0 ppm for **2** to −52.4 ppm for **3**. The IR spectrum of **2** exhibits one strong band at 2153 cm^{-1} for the $\nu_{C\equiv C}$ stretch. Complex **3** shows two strong $\nu_{C\equiv C}$ stretching bands at 1996 and 1922 cm^{-1}.

The X-ray structures of compounds **2** and **3** are shown in Figure 1,[7,8] and selected bond distances and angles are given in Table 1. Compounds **2** and **3** crystallize in the space group $P2_1/n$ with nearly equivalent unit cell dimensions. For **2** the average distance from each alkyne carbon to the centroid of the six alkyne carbons is 2.069 Å, 0.02 Å less than the comparable distance in TBC.[9] Contrary to our expectations, the average Ni to alkyne distance in **3** is longer than in Ni(TBC). The Ni to C(alkyne) distances average 1.958 Å in Ni(TBC) and 2.015 Å in complex **3**, where they range from 1.989(4) (Ni−C6) to 2.052(4) Å (Ni−C1). The nickel is bound to the three alkynes as in Ni(TBC) but also shows a short contact to the silicon in the ring.

Table 1. Selected Interatomic Distances (Å) (Standard Deviations in Parentheses) and Angles (deg) for 2 and 3

	2	3
Si−C1	1.818(3)	1.840(5)
Si−C10	1.826(3)	1.840(5)
C1−C2	1.208(4)	1.250(6)
C2−C3	1.430(4)	1.437(7)
C4−C5	1.435(4)	1.447(7)
C5−C6	1.194(4)	1.237(6)
C6−C7	1.429(4)	1.439(7)
C8−C9	1.434(4)	1.450(7)
C9−C10	1.205(3)	1.253(6)
C1−Si−C10	101.6(1)	107.1(2)
Si−C1−C2	162.5(2)	149.5(5)
Si−C10−C9	163.5(3)	150.3(4)
C1−C2−C3	174.7(3)	168.4(6)
C8−C9−C10	174.4(3)	170.0(5)
C4−C5−C6	177.5(3)	172.0(6)
C5−C6−C7	178.3(3)	171.1(5)
Ni−Si		2.509(2)
Ni−C1		2.052(4)
Ni−C2		1.999(5)
Ni−C5		1.990(5)
Ni−C6		1.989(4)
Ni−C9		2.005(5)
Ni−C10		2.047(5)
Ni−C1−C2		69.7(3)
Ni−C2−C1		74.4(3)
Ni−C10−C9		70.1(3)
Ni−C9−C10		73.8(3)

An unusual mode of alkyne bonding to a metal is observed in which the alkyne substituents have a trans geometry rather than the cis geometry expected from the Dewar−Chatt−Duncanson bonding model.[10] The trans geometry is all the more surprising if one considers that planarity of the central pocket is preserved in **3**. The silicon does not deviate any more from the principal plane of the ligand[11] (0.118 Å, mean deviation

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(6) Bax, A.; Summers, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 2093−2094.

(7) Crystal structure for **2**: colorless parallelepiped, crystal size 0.20 × 0.40 × 0.60 mm^3, monoclinic space group $P2_1/n$ (No. 14), a = 12.321(2) Å, b = 10.034(2) Å, c = 18.736(4) Å, β = 108.08(3)°, V = 2201.9(7) Å^3, Z = 4, ϱ_{calcd} = 1.226 g cm^{-3}, T = 130 K, graphite monochromator, Mo Kα radiation, θ range 1.76−22.50°, 3768 reflections collected, 2875 independent and 2133 observed with $I > 2.0\sigma(I)$, R1 = 0.0418 (based on F), R2w = 0.0744 (based on F^2) using 283 parameters. Crystal structure for **3**: red parallelepiped, 0.15 × 0.20 × 0.40 mm^3, monoclinic space group $P2_1/n$, a = 12.231(2) Å, b = 10.028(2) Å, c = 18.718(4) Å, β = 107.62(3)°, V = 2188.1(7) Å^3, Z = 4, ϱ_{calcd} = 1.412 g cm^{-3}, T = 130 K, Mo Kα radiation, θ range 1.77−22.50°, 3755 reflections collected, 2860 independent and 2148 observed with $I > 2.0\sigma(I)$, semiempirical absorption correction (min/max transmission 0.692/0.800), structure solution using direct methods, R1 = 0.0459 (based on F), R2w = 0.0869 (based on F^2) using 291 parameters.

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(11) The principal plane of ligand **2** was calculated as the least-squares plane including Si and carbons C1−C18 inclusive.

0.055 Å) toward what would be a cis configuration than it does in the free ligand (0.120 Å, mean deviation 0.059 Å). In complex **3**, C1 and C10 are displaced away from the nickel(0); thus, the Si−C1−C2 and Si−C10−C9 angles are reduced by an average of 13.1° in comparison with those in ligand **2**. C2 and C9 are displaced toward the nickel atom, causing the C1−C2−C3 and C8−C9−C10 angles to change by an average of 16.3°. In complex **3**, the average C≡C bond distance of these two alkynes is 1.252 Å, which is 0.015 Å longer than that of the third alkyne C5−C6. A similar bonding geometry is found in the Co(CO) complex of $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(CCPh_2)_2$,[12] where the coordinated cobalt may interact with a nearly tetrahedral titanium and is bound to two unusual trans-geometry acetylides.

The coordination of the nickel into the trialkyne pocket expands the alkyne−silicon−alkyne angle from 101.6(1)° in **2** to 107.1(2)° in **3**. Other angles at silicon change by less than 1.5° in going from **2** to **3**. The nickel−silicon distance 2.509(2) Å can be compared with known Ni−Si distances of 2.283 and 2.182 Å in the compounds $Ni(SiCl_3)_2(CO)_3$ and $Ni(SiF_3)_2(PMe_3)_3$, respectively,[13] and the sum of the covalent radii of Ni and Si, which is about 2.34−2.41 Å.[14] The nickel−silicon distance in **3** may also be compared to those calculated for the theoretical compounds $Ni(SiH_2)_6$ and $Ni(SiH_2)_5$ (Ni−Si = 2.41 and 2.20 Å, respectively).[15] Though the Ni−Si distance might indicate a weak Ni−Si bond, we have no unambiguous evidence that this is so.

It is well-known that polycarbosilanes containing main-chain acetylenic units have electron delocalization through the Si atoms via σ^*-π hyperconjugation.[16] In $\sigma^*-\pi$ hyperconjugation, it is generally accepted that Si can stabilize partial β-positive and α-negative charges provided the Si−C bond is coplanar with the vacant orbital on the β-carbon.[17] Asymmetrically substituted acetylenes show a significant increase in polarization on coordination to Ni(0).[18] Polarization of an acetylene bond should give rise to different bonding distances for each of the acetylenic carbons to the complexed metal as in $(Ph_3P)_2Ni[PhCCSiMe_3]$.[18] Consistent with this, the Ni−C1 and Ni−C10 distances are longer (ca. 0.05 Å) than the Ni−C2 and Ni−C9 distances. This may partially account for the expansion of the C1−Si−C10 angle and the novel trans geometry of the complexed acetylenes directly adjacent to the silicon.

Analogs of **2** and **3** with two electron-donating groups (diisopropyl) on silicon and germanium analogs of **2** and **3** have been synthesized. The reactivities of complex **3** with carbon monoxide and oxygen are under investigation. These will be discussed in a subsequent paper.

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Supplementary Material Available: Crystallographic data for **2** and **3**, including tables of data collection and structure determination details, atomic coordinates, bond distances and angles, and thermal parameters (19 pages). Ordering information is given on any current masthead page.

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