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Catalytic Carbon−Carbon and Carbon−Silicon Bond Activation and Functionalization by Nickel Complexes

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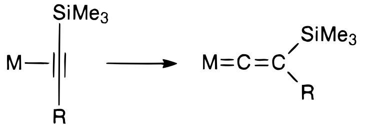
The nickel alkyne complexes (dippe)Ni($Me_3SiC{\equiv}CSiMe_3$), **1**, (dippe)Ni($Me_3CC{\equiv}CSiMe_3$), **2,** and (dippe)Ni($MeC{\equiv}CSiMe_3$), **3**, were synthesized (dippe = bis(diisopropylphosphino)ethane) and characterized by ^1H, ^{31}P, and $^{13}C\{^1H\}$ NMR spectroscopy. Complex **1** was characterized by X-ray crystallography. Heating complex **1**, **2**, or **3** with excess biphenylene and alkyne results in the catalytic formation of several novel organic compounds, several of which have been characterized by X-ray crystallography. These reactions are proposed to proceed by a competition between β-silyl migration from an acetylene insertion intermediate and elimination of phenanthrene. Mechanistic schemes are presented for these reactions.

Introduction

Homogeneous catalytic C−C bond activation and functionalization by transition metal complexes is currently an active area of research in organometallic chemistry.[1] Catalytic hydrogenolysis of biphenylene to biphenyl has been reported using $(C_5Me_5)Rh(PMe_3)H_2$[2] and several platinum, palladium, and nickel phosphine complexes.[3] Milstein and co-workers reported the catalytic hydrogenolysis and hydrosilation of a strong C−C bond using a rhodium complex.[4] Ito and co-workers treated cyclobutanone under hydrogen with a catalytic amount of a rhodium(I) complex to generate the ring-opened alcohol.[5] Jun and Lee recently reported homogeneous catalytic C−C bond cleavage of unstrained ketones.[6] Nickel(0) complexes have been employed in the formation of substituted phenols by cleaving the C−C bonds of cyclobutenones with subsequent [4+2] addition of alkynes.[7]

We have recently used (dippe)Ni($RC{\equiv}CR$) complexes as catalyst precursors for the formation of 9,10-disubstituted phenanthrenes.[8] The phenanthrene products are formed catalytically by heating (dippe)Ni($RC{\equiv}CR$) in the presence of biphenylene, the appropriate alkyne, and a small amount of O_2 to accelerate the reaction. In the present work we demonstrate that nickel complexes can catalytically functionalize biphenylene with trimethylsilyl-substituted alkynes to give 9,10-disubstituted phenanthrenes and/or products derived from addition of the C−Si bond across the C−C bond of biphenylene. Catalytic cycles are proposed for the various systems that were evaluated.

The cleavage of C−Si bonds by transition metal compounds has not been systematically studied.[9] However, several examples of C−Si bond cleavage in alkynylsilanes have been reported.[10] One common mechanism involves 1,2-silyl migration to form vinylidene complexes (eq 1).[11] Another mechanism of C−Si bond cleavage is



(1)

β-silyl migration from a metal alkyl group to the metal center.[12] This is believed to be a key step in the catalytic dehydrogenative silylation of olefins (Scheme 1).[12f]

Results and Discussion

Preparation and Characterization of Nickel Alkyne Phosphine Complexes. Several different trimethylsilylalkyne−nickel(0) complexes were prepared

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[1] Two reviews on carbon−carbon bond activation have recently been published: (a) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870. (b) Murakami, M.; Ito, Y. In *Topics in Organometallic Chemistry*; Murai, S., Ed.; Springer-Verlag: New York, 1999; Vol. 3, pp 96−129.

[2] Perthuisot, C.; Jones, W. D.; *J. Am. Chem. Soc.* **1994**, *116*, 3647.

[3] Edelbach, B. L.; Vicic, D. A.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4784.

[4] Liou, S.-Y,; van der Boom, M. E.; Milstein D. *Chem. Commun.* **1998**, 687−688.

[5] Murakami, M.; Amii, H.; Shigeto, K.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 8285.

[6] Jun, C.-H.; Lee, H. *J. Am. Chem. Soc.* **1999**, *121*, 880.

[7] Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1991**, *113*, 2771.

[8] Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1999**, *18*, 4040.

[9] Some examples include: (a) Steenwinkel, P.; James, S. L.; Grove, D. M.; Kooijman, H.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 513. (b) Hoffman, P.; Heiss, H.; Neiteler, P.; Müller, G.; Lachmann, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 880. (c) Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 419, and references therein.

[10] (a) Poist, J. E.; Kraihanzel C. S. *Chem. Commun.* **1968**, 60 (b) Ciriano, M.; Howard, J. A. K.; Spencer, J. L.; Gordon, F.; Stone, A.; Wadepohl. *J. Chem. Soc., Dalton Trans.* **1979**, 1749.

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[12] (a) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366. (b) Wakatsuki, Y.; Yamazaki, H.; Nakano, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703. (c) Marciniec B.; Pietraszuk, C. *J. Chem. Soc., Chem. Commun.* **1995**, 2003. (d) Wakatsuki, Y.; Yamazaki, H. *J. Organomet. Chem.* **1995**, *500*, 349. (e) LaPointe, A. M.; Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 906. (f) Kakiuchi, F.; Yamada, A.; Chatani, N.; Murai, S. *Organometallics* **1999**, *18*, 2033.

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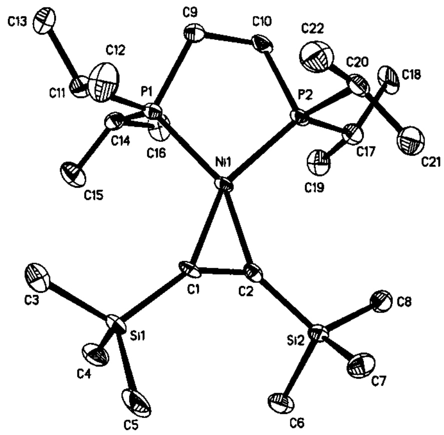
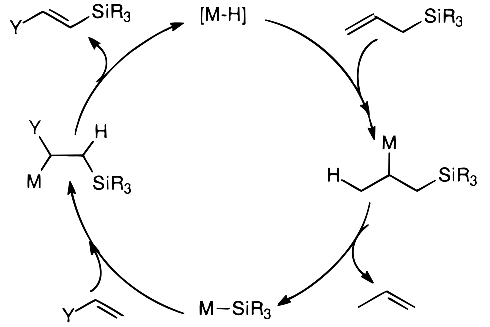


Figure 1. ORTEP drawing of (dippe)Ni(Me$_3$SiC≡CSiMe$_3$), **1**. Selected distances (Å): Ni(1)−P(1), 2.154(2); Ni(1)−P(2), 2.153(2); Ni(1)−C(1), 1.907(6); Ni(1)−C(2), 1.916(6); C(1)−C(2), 1.298(8).

Scheme 1



by addition of the alkyne to (dippe)Ni(COD) or [(dippe)NiH]$_2$. The following new compounds were synthesized: (dippe)Ni(Me$_3$SiC≡CSiMe$_3$), **1**, (dippe)Ni(Me$_3$CC≡CSiMe$_3$), **2**, and (dippe)Ni(MeC≡CSiMe$_3$), **3**. These compounds were characterized by ^{1}H, ^{31}P, and ^{13}C{^{1}H} NMR spectroscopy. The ^{13}C{^{1}H} resonances of the alkyne carbons are similar to those reported for other bis(phosphine)nickel(0) acetylene complexes.[13] Compound **1** was also characterized by X-ray crystallography (Figure 1). This compound is a distorted square planar complex (the alkyne is in the plane) with a carbon−carbon triple-bond distance of 1.298(8) Å, similar to those reported for other nickel(0) alkyne complexes with electron-donating chelating phosphines.[14]

Functionalization of Biphenylene with Silylated Acetylenes. To our knowledge the compound 9,10-bis(trimethylsilyl)phenanthrene has never been synthesized. Given the ability to functionalize the trimethylsilyl groups, we thought it desirable to attempt the preparation of this compound by heating compound **1** in the presence of biphenylene and bis(trimethylsilyl)acetylene at 120 °C. While 9,10-di(trimethylsilyl)phenanthrene was not produced, several other organic products were formed catalytically (Scheme 2). The

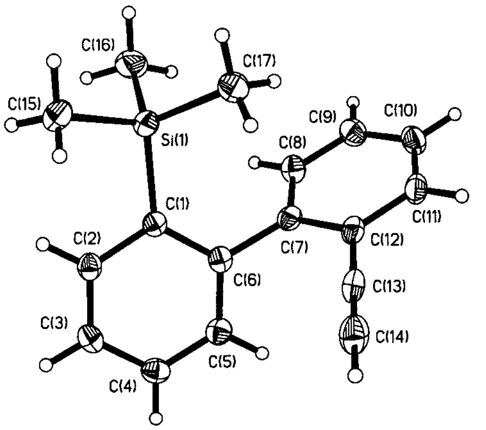
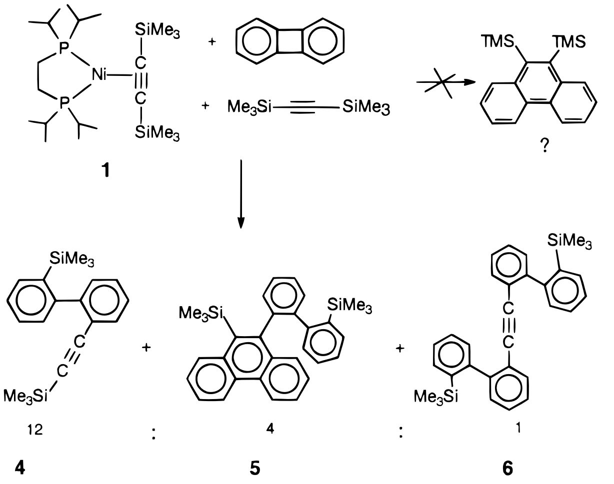


Figure 2. ORTEP drawing of 2-(ethynyl)-2′-(trimethylsilyl)biphenyl, **7**.

Scheme 2



compounds 2-(trimethylsilylethynyl)-2′-(trimethylsilyl)biphenyl, **4**, 9-trimethylsilyl-10-(2-(2′-trimethylsilylphenyl)phenyl)phenanthrene, **5**, and bis(2-(2′-trimethylsilylphenyl)phenyl)acetylene, **6**, were produced in an approximate 12:4:1 ratio (based on GC/MS). A small amount of tetraphenylene is also observed. Compounds **4** and **5** were isolated by thick layer chromatography. Compound **4** was isolated as a yellow oil (41%, 13 turnovers), which was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and GC/MS. The ^{1}H NMR spectrum indicated the presence of two different silyl methyl groups. The ^{13}C{^{1}H} NMR spectrum revealed the presence of two different acetylenic carbons. To confirm that the trimethylsilyl group and the acetylenic groups were on different benzene rings, **4** was converted to the pale yellow solid 2-(ethynyl)-2′-(trimethylsilyl)biphenyl, **7**, with potassium carbonate in methanol. An X-ray crystal structure of compound **7** confirmed that the locations of the trimethylsilyl and acetylenic groups were as indicated (Figure 2).

Compound **5** was isolated as a white solid (14%) and characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and GC/MS. The structure of the molecule was established by X-ray crystallography (Figure 3). Compound **6** is a yellow liquid, but could not be isolated in pure form, as compound **5** was always present in small amounts. The ^{1}H NMR spectrum indicates the presence of only one trimethylsilyl resonance in an 9:8 ratio with the aromatic protons. The ^{13}C{^{1}H} NMR spectrum displays

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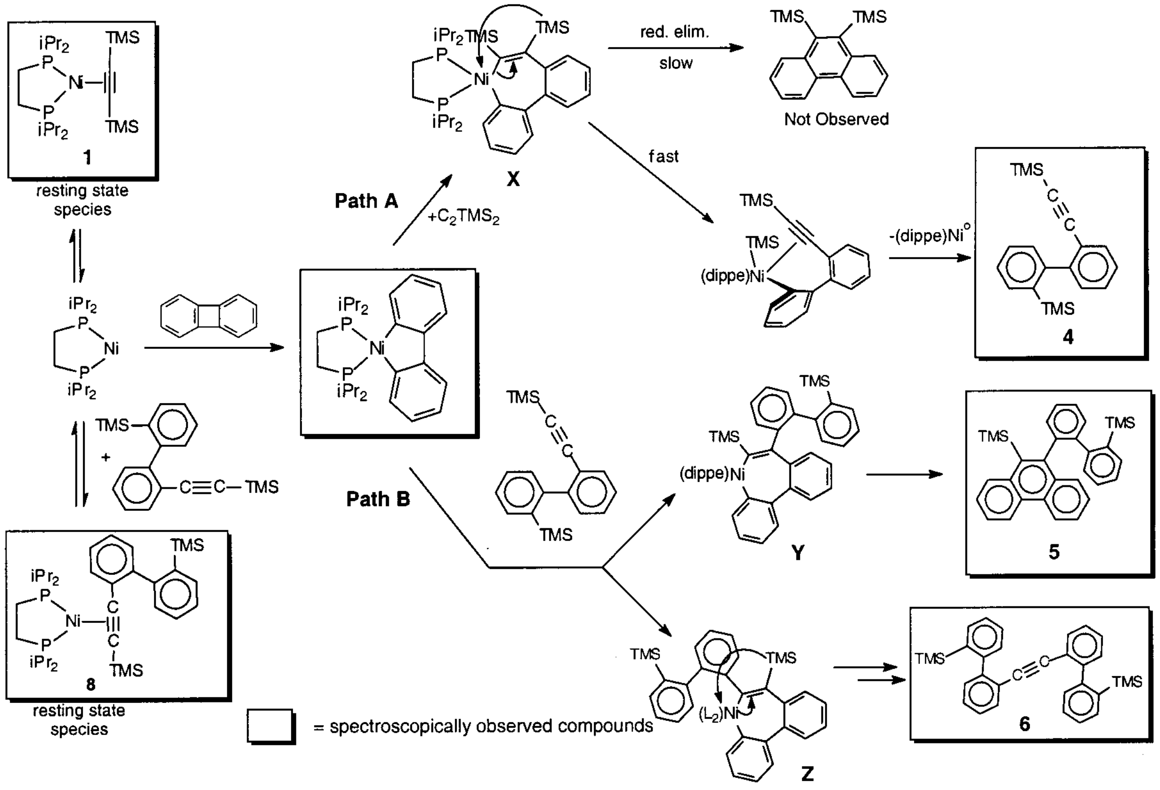
[13] Bartik, T.; Happ, B.; Iglewsky, M.; Bandmann, H.; Boese, R.; Heimbach, P.; Hoffmann, T.; Wenschuh, E. *Organometallics* **1992**, *11*, 1235.

[14] (a) Bonrath, W. Ph.D. Dissertation, University of Bochum, 1988. (b) Pörschke, K. R.; Mynott, R.; Angermund, K.; Krüger, C. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1985**, *40*, 199. (c) Pörschke, K. R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1288. (d) Bonrath, W.; Pörschke, K. R.; Wilke, G.; Angermund, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 833.

Scheme 3



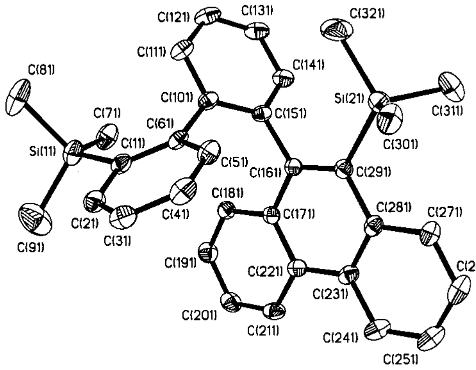


Figure 3. ORTEP drawing of 9-trimethylsilyl-10-(2-(2′-trimethylsilylphenyl)phenyl)phenanthrene, **5**.

only one type of acetylenic carbon and 12 different aromatic carbons. A GC/MS of the mixture reveals an M^+ peak at 474. These results are consistent with the formulation of compound **6** as bis(2-(2′-trimethylsilylphenyl)phenyl)acetylene.

Earlier studies with alkyl and aryl acetylenes showed that small quantities of added O_2 can accelerate these reactions.[8] The role of the O_2 was believed to be to oxidize the phosphine ligand to the phosphine oxide, generating vacant sites on the Ni^0 intermediate. Greater than 50 mol % O_2 was found to have a deleterious effect upon the reaction, presumably as reaction of the O_2 with the Ni^0 now interfered with the catalysis.

There is evidence that the reaction with the disilylacetylene proceeds without added air, although higher temperatures (120 °C) are required to achieve a reasonable rate of catalysis. First, if the reaction is run at 110 °C with 6 mol % O_2 (via addition of air), the reaction proceeds at only twice the rate as the reaction run in the absence of air. Second, the formation of two equal intensity doublets is observed in the $^{31}P\{^1H\}$ NMR spectrum at δ 76.0 ($J = 53.3$ Hz) and δ 71.4 ($J = 53.3$ Hz) early in the catalysis. This is consistent with the formation of a (dippe)Ni(0) complex coordinated to an asymmetric acetylene. Compound **4** is the only nonsymmetrical alkyne observed in the reaction mixture, providing evidence that the new doublets in the $^{31}P\{^1H\}$ NMR spectrum arise from **4** coordinating in an η^2 fashion to (dippe)Ni(0) to give complex **8** (see Scheme 3). The identity of this compound was confirmed by independent synthesis. Addition of **4** to (dippe)Ni(COD) produces compound **8**, which has a $^{31}P\{^1H\}$ NMR spectrum identical to the compound observed in the catalytic reaction. Compound **8** was characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis. The ^1H NMR spectrum displays two trimethylsilyl resonances at δ 0.073 (s, 9 H) and -0.216 (s, 9 H). The structure of compound **8** was confirmed by X-ray crystallography (Figure 4). Heating compound **8** with excess **4** and biphenylene leads to the formation of compounds **5** and **6**. Third, when the non-phosphorus-containing species $Ni_2(COD)_2(PhC{\equiv}CPh)$ is combined with 16 equiv of bis(trimethylsilyl)acetylene and 5 equiv of biphenylene and heated at 85 °C, the major products in the reaction are tetraphenylene and compound **4**. No compound **5** or **6** is observed in the ^1H NMR spectrum. These results suggest that the phosphine complex **8** is responsible for the formation of compounds **5** and **6**. However, it is likely that some of compound **4** is formed via a non phosphine nickel compound upon addition of O_2 since a rate acceleration is observed. The mechanism depicted in Scheme 3 is proposed for the formation of compounds **4**, **5**, **6**, and **8**.

The first step is reversible loss of bis(trimethylsilyl)acetylene from compound **1** or reversible loss of alkyne

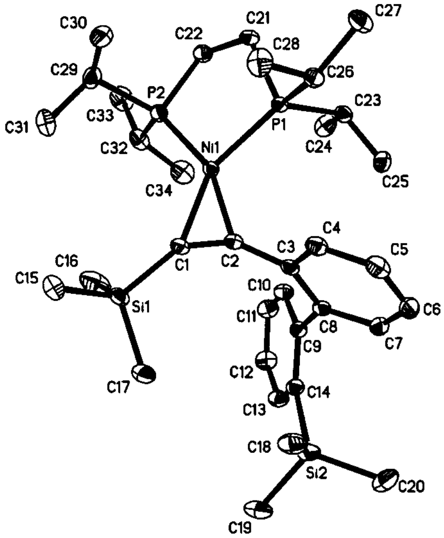


Figure 4. ORTEP drawing of (dippe)Ni(2-(trimethylsilylethynyl)-2′-(trimethylsilyl)biphenyl), **8.** Selected distances (Å): Ni(1)−P(1), 2.1601(4); Ni(1)−P(2), 2.1642(4); Ni(1)−C(1), 1.9334(14); Ni(1)−C(2), 1.8873(14); C(1)−C(2), 1.283(2).

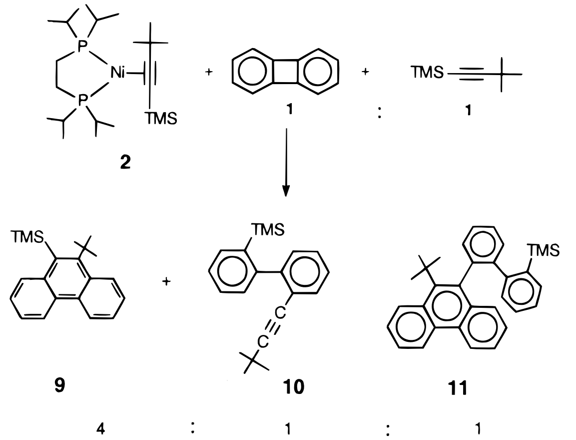
4 from compound **8** to give (dippe)Ni(0). Subsequent carbon−carbon bond activation of biphenylene by (dippe)Ni(0) gives (dippe)Ni(2,2′-biphenyl). This compound is observed in small amounts in the $^{31}P\{^1H\}$ NMR spectrum during the catalysis. Compounds **1** and **8** are the major resting state species observed in the $^{31}P\{^1H\}$ NMR spectrum during the course of the reaction. This observation is consistent with recoordination of the alkynes to (dippe)Ni(0) being more rapid than C−C cleavage of biphenylene. Reaction of (dippe)Ni(2,2′-biphenyl) with biphenylene could account for the small amount of tetraphenylene produced.[15] Two pathways are now available. Path A involves insertion of bis(trimethylsilyl)acetylene into the Ni−C bond of (dippe)Ni(2,2′-biphenyl) to give the putative cycloheptatriene compound **X**. The necessity for high temperatures to affect reasonable rates of catalysis may result from the requisite loss of one phosphine in order to accommodate alkyne coordination in the plane of the biphenyl group prior to insertion. Rapid [1,3] trimethylsilyl migration to the nickel center followed by reductive elimination of **4** regenerates the (dippe)Ni(0) fragment. The 1,3-trimethylsilyl migration must be more rapid than reductive elimination of 9,10-bis(trimethylsilyl)phenanthrene from **X** since the phenanthrene compound is not observed.

Precedent for [1,3] silyl group migration (so-called β-silyl migration) from an alkyl ligand to a metal center with concomitant loss and or coordination of alkene has been established.[12] Brookhart et al. established that rapid, reversible β-silyl migration occurred at −70 °C using cationic Pd(II) compounds.[12e] Recently, Murai and co-workers synthesized vinylsilanes from olefins using a Ru catalyst and allylsilanes as the source of organosilyl group.[12f] The key step in this reaction was the generation of a metal−silyl species via β-silyl group elimination. To our knowledge, there is no reported case of β-silyl migration from a silyl−vinyl complex.

Path B involves two possible orientations of insertion of **4** into the nickel carbon bond of (dippe)Ni(2,2′-biphenyl). First, insertion resulting in the trimethylsilyl group nearest the metal center gives compound **Y**. Reductive elimination of phenanthrene **5** regenerates (dippe)Ni(0). Second, insertion resulting in the biphenyl group nearest the metal center gives compound **Z**. Rapid 1,3 trimethylsilyl migration followed by reductive elimination gives compound **6** and (dippe)Ni(0). Insertion with the trimethylsilyl group nearest the metal center is less sterically demanding and explains the higher yield of **5** relative to **6**.

A mechanism involving oxidative addition of a Si−C(sp) bond to the nickel center and subsequent oxidative addition of the C−C bond of biphenylene via a Ni(IV) species cannot be ruled out. Caulton and co-workers have demonstrated that the cleavage of the Si−C(sp) bond of $Me_3SiC{\equiv}CSiMe_3$ to a Ru center proceeded via oxidative addition.[16] Earlier work by Stone et al. demonstrated oxidative addition of both C−Si bonds of $Me_2Si(C{\equiv}CPh)_2$ by $(PR_3)_2Pt(C_2H_4)_2$.[10b] While an oxidative addition mechanism appears viable, we favor the β-silyl migration mechanism since these reactions have been demonstrated to proceed under very mild conditions and avoid a Ni(IV) intermediate.

Scheme 4



One explanation for the lack of formation of 9,10-bis(trimethylsilyl)phenanthrene is that trimethylsilyl migration in complex **X** is more rapid than reductive elimination of 9,10-bis(trimethylsilyl)phenanthrene. Another possibility may be that juxtaposition of two trimethylsilyl groups in the 9 and 10 positions is too sterically demanding, making 9,10-bis(trimethylsilyl)phenanthrene an unstable compound. To examine this latter possibility, we attempted to synthesize 9-*tert*-butyl-10-(trimethylsilyl)phenanthrene, a compound with nearly the same steric requirements as 9,10-bis(trimethylsilyl)phenanthrene. Acetylene compound **2** was dissolved in THF and heated at 120 °C in the presence of biphenylene and 1-trimethylsilyl-3,3-dimethyl-1-butyne. Three organic products were formed (Scheme 4): 9-*tert*-butyl-10-(trimethylsilyl)phenanthrene, **9**, 2-(*tert*-butylethynyl)-2′-(trimethylsilyl)biphenyl, **10**, and 9-*tert*-butyl-10-(2-(2′-trimethylsilylphenyl)phenyl)phenanthrene, **11**, in a 4:1:1 ratio (based on GC/MS).

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[15] Tetraphenylene is formed catalytically upon heating a mixture of (dippe)Ni(2,2′-biphenyl) with biphenylene in THF-d_8. See: Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843.

[16] Huang, D.; Heyn, R. H.; Bollinger, J. C.; Caulton, K. G. *Organometallics* **1997**, *16*, 292.

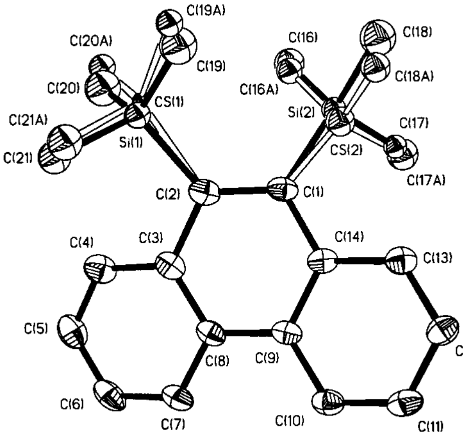


Figure 5. ORTEP drawing of 9-*tert*-butyl-10-(trimethylsilyl)phenanthrene, **9**, showing disorder of *tert*-butyl and trimethylsilyl groups.

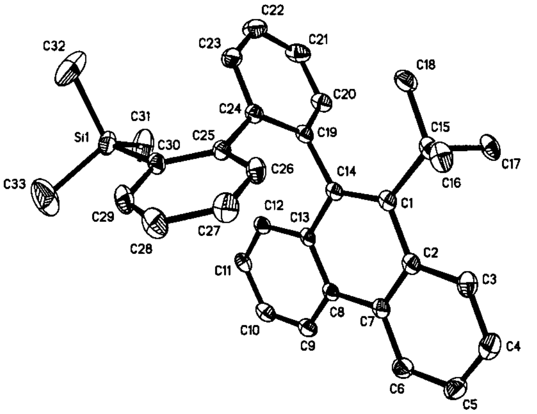
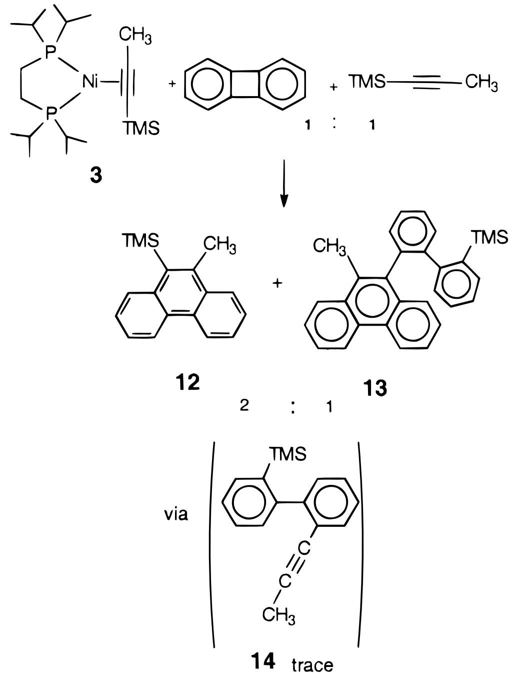


Figure 6. ORTEP drawing of 9-*tert*-butyl-10-(2-(2′-trimethylsilylphenyl)phenyl)phenanthrene, **11**.

Compound **9** was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, GC/MS, and elemental analysis. An X-ray crystal structure (Figure 5) confirmed the locations of the trimethylsilyl and *tert*-butyl groups, although these two groups were disordered. Compound **10** was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and GC/MS. The ^{13}C{^{1}H} shows two separate acetylenic carbons and one type of trimethylsilyl carbon. The aromatic region in the ^{1}H NMR is similar to that of compound **4**. Compound **11** was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, GC/MS, and elemental analysis. The structure of the molecule was established by X-ray crystallography (Figure 6).

We propose a mechanism for the formation of compounds **9**−**11** similar to that of their bis(trimethylsilyl) analogues depicted in Scheme 2. In this case however, insertion of 1-trimethylsilyl-3,3-dimethyl-1-butyne into the M−C bond of (dippe)Ni(2,2′-biphenyl) can occur with different regiochemistries, with either the *tert*-butyl group or the trimethylsilyl group on the carbon nearest the metal center. If the *tert*-butyl group is nearest the metal center, [1,3] trimethylsilyl migration and subsequent reductive elimination generates compound **10**. If the trimethylsilyl group is nearest the metal center, reductive elimination generates (dippe)Ni(0) and phenanthrene **9**. Compound **11** is formed via the same pathways as compound **5**. In this reaction no analogue of compound **6** is observed.

Scheme 5



The organic compound 9-methyl-10-(trimethylsilyl)phenanthrene, **12,** was produced in an analogous fashion by reacting a THF solution containing (dippe)Ni(MeC≡CSiMe$_3$), **3**, excess biphenylene, and 1-(trimethylsilyl)propyne at 120 °C. The two main organic products generated were 9-methyl-10-(trimethylsilyl)phenanthrene, **12**, and 9-methyl-10-(2-(2′-trimethylsilylphenyl)phenyl)phenanthrene, **13**, in a 2:1 ratio (isolated yield) (Scheme 5). A minor product was also detected by GC/MS and ^{1}H and ^{13}C{^{1}H} NMR, although it could not be isolated free from compound **3**. A GC/MS trace of this compound displayed an ion peak at 264, consistent with the molecular weight of 2-(1-propynyl)-2′-(trimethylsilyl)biphenyl, **14**. The ^{13}C{^{1}H} NMR spectrum displayed two singlets at 90.0 and 79.9 ppm, corresponding to the acetylenic carbons. Other ^{1}H and ^{13}C{^{1}H} NMR spectroscopy data are also consistent with the formulation of **14** as 2-(1-propynyl)-2′-(trimethylsilyl)biphenyl. Further support for the production of compound **14** comes from the ^{31}P{^{1}H} NMR spectrum upon completion of the reaction. Two new doublets were observed at δ 79.7 (J_{P-P} = 49.8 Hz) and 75.4 (J_{P-P} = 49.7 Hz). This observation is consistent with the formation of (dippe)Ni[(2-(1-propynyl)-2′-(trimethylsilyl)biphenyl)], which is analogous to compound **8**. Compound **12** is an off-white oil, which was characterized by GC/MS and ^{1}H and ^{13}C{^{1}H} NMR. To further confirm the structure of **12**, bromine was added to a hexane solution containing compound **12** and refluxed for 1.5 h. Two compounds were isolated: 9-bromo-10-methylphenanthrene and 9-bromomethyl-10-bromophenanthrene in an ~50:50 ratio. The ^{1}H NMR spectrum and GC/MS of 9-bromo-10-methylphenanthrene matched those reported in the literature.[17] The ^{1}H NMR spectrum of 9-bromomethyl-10-bromophenanthrene matched that reported in the literature.[18] Compound **13** was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, GC/MS, and elemental

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[17] Lambert, J. B.; Fabricius, D. M.; Hoard, J. A. *J. Org. Chem.*, **1979**, *44*, 1480.

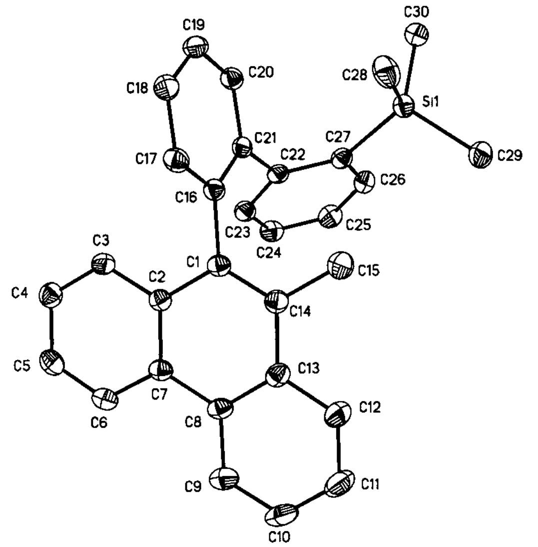

Figure 7. ORTEP drawing of 9-methyl-10-(2-(2′-trimethylsilylphenyl)phenyl)phenanthrene, **13**.

analysis. The structure of **13** was established by X-ray crystallography (Figure 7).

Conclusions

The catalytic functionalization of biphenylene with disubstituted alkynes (RC≡CR′, R = TMS, R′ = TMS or alkyl group) to give either addition products of the alkyne−Si bond across the C−C bond of biphenylene or 9,10-disubstituted phenanthrenes has been demonstrated using (dippe)Ni(RC≡CR) complexes. The array of organic products produced can be explained by alkyne insertion into a Ni(2,2′-biphenyl) bond and subsequent [1,3] trimethylsilyl migration from a vinyl ligand to a metal center versus rapid reductive elimination of the organic product. The orientation of insertion dictates which of these processes occur. In the case where the trimethylsilyl group inserts away from the metal center, [1,3] trimethylsilyl migration is more rapid than reductive elimination. These results compare with earlier biphenylene functionalizations using alkyl- and aryl-substituted acetylenes in that the latter tended to give phenanthrenes as the major products.[8]

Experimental Section

General Considerations. All manipulations were performed under an N_2 atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corporation glovebox. Tetrahydrofuran and toluene were distilled from dark purple solutions of benzophenone ketyl. Alkane solvents were made olefin-free by stirring over H_2SO_4, washing with aqueous $KMnO_4$ and water, and distilling from dark purple solutions of tetraglyme/benzophenone ketyl. Tetrahydrofuran-d_8 and toluene-d_8 were purchased from Cambridge Isotope Lab., distilled under vacuum from dark purple solutions of benzophenone ketyl, and stored in ampules with Teflon-sealed vacuum line adapters. The preparations of biphenylene,[19] dippe,[20] $Ni_2(COD)_2(PhC{\equiv}CPh)$,[21] and $[(dippe)NiH]_2$,[22] have been previously reported. All of the alkynes were purchased from Aldrich Chemical Co. The liquids were stirred over sieves, freeze−pump−thaw-degassed three times, and vacuum distilled prior to use.

All NMR spectra were recorded on a Bruker AMX400 or Avance400 spectrometer. All ^1H chemical shifts are reported in ppm (δ) relative to tetramethylsilane and referenced using chemical shifts of residual solvent resonances (THF-d_8, δ 1.73, toluene-d_8, δ 2.09). ^{31}P NMR spectra were referenced to external 30% H_3PO_4 (δ 0.0). GC/MS was conducted on a 5890 Series II gas chromatograph fitted with an HP 5970 Series mass selective detector. Analyses were obtained from Desert Analytics. A Siemens SMART system with a CCD area detector was used for X-ray structure determination.

Preparation of (dippe)Ni(Me$_3$SiC≡CSiMe$_3$), 1. (dippe)Ni(COD) (150 mg, 0.35 mmol) was dissolved in an round-bottom flask with 20 mL of benzene. Bis(trimethylsilyl)acetylene (0.8 mL, 3.5 mmol) was added dropwise to the (dippe)Ni(COD) solution and heated to reflux for 12 h, during which time the solution slowly turned golden. The mixture was filtered, and the solvent, excess COD, and bis(trimethylsilyl)acetylene were removed under vacuum with heating. The yellow powder was washed with cold MeOH. (Yield: 140 mg, 85%). X-ray quality crystals were grown by dissolving the solid in a minimum of acetone and cooling to −30 °C. NMR data for **1**: ^1H NMR (THF-d_8) δ 2.161 (sept, C*H*Me$_2$, J_{H-H} = 7.8 Hz, 4 H), 1.612 (d, PC*H$_2$*C*H$_2$*P, J_{H-P} = 7.9 Hz, 4 H), 1.144−1.000 (m, CH*Me$_2$*, 24 H), 0.218 (s, 18 H); $^{31}P\{^1H\}$ NMR (THF-d_8) δ 75.60 (s). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 157.1 (t, ≡*C*−TMS, J_{P-C} = 9.5 Hz), 26.8 (t, J_{P-C} = 9.7 Hz), 22.2 (t, J_{P-C} = 19.0 Hz), 21.2 (t, J_{P-C} = 5.0 Hz), 19.1 (s), 2.2 (s). Anal. Calcd for $C_{22}H_{50}P_2Si_2Ni$: C, 53.76; H, 10.25. Found: C, 53.35; H, 10.72.

Preparation of (dippe)Ni(Me$_3$CC≡CSiMe$_3$), 2. (dippe)Ni(COD) (200 mg, 0.47 mmol) and *tert*-butylethynyltrimethylsilane (0.49 mL, 360 mg, 2.33 mmol) were combined in an ampule with 10 mL of THF. The mixture was heated at 100 °C for 12 h. The solvent, excess COD, and alkyne were removed under vacuum. The solid was washed with cold MeOH and cold acetone, giving a green/yellow solid (yield: 95 mg, 43%). NMR data for **2**: ^1H NMR (THF-d_8) δ 2.157 (sept, C*H*Me$_2$, J_{H-H} = 6.7 Hz, 4 H), 1.658−1.521 (m, 4 H), 1.285 (s, 9 H), 1.180−1.036 (m, CH*Me$_2$*, 24 H), 0.195 (s, 9 H); $^{31}P\{^1H\}$ NMR (THF-d_8) δ 74.51 (d, J_{P-P} = 51.4 Hz), 73.88 (d, J_{P-P} = 51.3 Hz); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 172.4 (d, ≡*C*−*tert*-butyl, J_{P-C} = 35.3 Hz), 157.1 (d, ≡*C*−TMS, J_{P-C} = 29.6 Hz), 34.6 (dd, J_{P-C} = 10.1, 7.4 Hz), 33.9 (s), 27.5 (dd, J_{P-C} = 13.8, 5.9 Hz), 26.8 (dd, J_{P-C} = 13.1, 5.3 Hz), 22.7 (t, J_{P-C} = 20.2 Hz), 21.5 (m), 19.3 (d, J_{P-C} = 9.0 Hz), 3.0 (s). Anal. Calcd for $C_{23}H_{50}P_2Si_2Ni$: C, 58.11; H, 10.60. Found: C, 57.85; H, 10.55.

Preparation of (dippe)Ni(MeC≡CSiMe$_3$), 3. The compound (dippe)NiCl$_2$ (295 mg, 0.754 mmol) was suspended in 20 mL of hexanes, and 1 M Superhydride (0.69 mL, 0.69 mmol) was added dropwise at room temperature. The resulting purple solution of $[(dippe)NiH]_2$ was stirred for 0.5 h and decanted into a separate round-bottom flask. 1-Trimethylsilylpropyne (95.4 mg, 0.126 mL, 0.85 mmol) was added dropwise. Within a few minutes the solution turned a dark orange/brown. The solution was stirred for 15 min, and the solvent was removed under vacuum, giving a brown/orange oil (yield: 78 mg, 52%). NMR data for **3**: ^1H NMR (THF-d_8) δ 2.609, (d, J_{H-P} = 7.2 Hz, 3 H), 2.086 (sept, C*H*Me$_2$, J_{H-H} = 7.2 Hz, 4 H), 1.571 (d, PC*H$_2$*C*H$_2$*P, J_{H-P} = 9.3 Hz, 4 H), 1.184−0.976 (m, CH*Me$_2$*, 24 H), 0.149 (s, 9 H); $^{31}P\{^1H\}$ NMR (THF-d_8) δ 79.61 (d, J_{P-P} = 53.3 Hz), 76.54 (d, J_{P-P} = 53.3 Hz); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 154.6 (dd, ≡*C*−methyl, J_{P-C} = 36.5, 7.0 Hz), 123.9 (dd, ≡*C*−TMS, J_{P-C} = 31.6, 5.6 Hz), 26.2 (m), 22.6 (dt, J_{P-C} = 19.9, 7.6

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Hz), 20.8 (d, J_{P-C} = 9.7 Hz), 20.3 (d J_{P-C} = 8.8 Hz), 19.1 (s), 17.9(dd, J_{P-C} = 15.0, 7.8 Hz), 1.6 (s).

Reaction of (dippe)Ni($Me_3SiC{\equiv}CSiMe_3$) with Biphenylene and Bis(trimethylsilyl)acetylene. An ampule was charged with (dippe)Ni($Me_3SiC{\equiv}CSiMe_3$) (25 mg, 0.050 mmol), biphenylene (240 mg, 1.58 mmol), and bis(trimethylsilyl)acetylene (281 mg, 1.58 mmol). The mixture was dissolved in 5 mL of THF and heated at 120 °C for 3 days in an ampule sealed with a Teflon valve to avoid entry of air, after which only a trace of biphenylene and bis(trimethylsilyl)acetylene remained. The reaction mixture was applied to a thick layer SiO_2 chromatography (TLC) plate, and a 12:1 (v/v) solution of hexanes$-CH_2Cl_2$ was used as eluent. Three major bands were observed under UV light. The product of band 1 ($R_f \approx 0.5$) was extracted with CH_2Cl_2. The isolated product was a yellow oil (207 mg, 41%) and identified as 2-(trimethylsilylethynyl)-2′-(trimethylsilyl)biphenyl, **4**, by ^1H, $^{13}C\{^1H\}$ NMR spectroscopy and GC/MS. **4** was also characterized by derivatization to **7** as described below.

Bands 2 and 3 ($R_f \approx 0.4$ and 0.35, respectively) were isolated. ^1H NMR spectroscopy displayed a mixture of products. Therefore the contents of the two bands were combined and applied to a TLC plate. A 300:20:2 (v/v/v) solution of hexanes$-CHCl_3$-ethyl acetate was used as eluent. Two bands were observed under UV light. A GC trace of band 1 ($R_f \approx 0.45$) contained three compounds. One compound was isolated by adding ~2 mL of hexanes. A white solid precipitated (56 mg). The white solid was identified as 9-trimethylsilyl-10-(2-(2′-trimethylphenyl)phenyl)phenanthrene, **5**, by ^1H NMR, GC/MS, elemental analysis, and X-ray crystallography. A GC trace of the remaining yellow solution displayed **5** as well as two other compounds. Another 49 mg of **5** was precipitated by dissolving the yellow solid in hot ethanol and cooling to −30 °C. The solvent was removed from the remaining yellow liquid, giving 67 mg of yellow solid. GC/MS revealed a small amount of **5**, tetraphenylene, and one other compound. The tetraphenylene was isolated by applying the mixture to a TLC plate and using a 300:12 (v/v) hexanes$-CH_2Cl_2$ solution as eluent. Tetraphenylene (8 mg) was isolated from an $R_f \approx 0.3$ band. One other band with $R_f \approx 0.4$ was isolated, giving a yellow solid (60 mg). GC/MS of this band revealed a 2.5:1 mixture of **5** and bis(2-(2′-trimethylsilylphenyl)phenyl)acetylene, **6**, which could not be separated. **6** was identified by GC/MS and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.

Preparation of 2-(Ethynyl)-2′-(trimethylsilyl)biphenyl, 7. A 25 mL round-bottom flask was charged with **8** (207 mg, 0.64 mmol), potassium carbonate (364 mg, 2.64 mmol), and 15 mL of methanol. The mixture was stirred at room temperature for 1.5 h. The excess potassium carbonate was filtered, and the product was extracted from the filtrate with pentane. The pentane was removed under vacuum, giving a yellow solid (138 mg, 86%). X-ray quality crystals were grown by dissolving in hot ethanol and slow cooling to room temperature.

Preparation of (dippe)Ni[(2-(trimethylsilylethynyl)-2′-(trimethylsilyl)biphenyl)], 8. (dippe)Ni(COD) (232 mg, 0.54 mmol) and 2-(trimethylsilylethynyl)-2′-(trimethylsilyl)biphenyl, **4** (192 mg, 0.596 mmol), were combined in an ampule with 3 mL of THF. The mixture was heated at 60 °C for 48 h. The solvent and excess COD were removed under vacuum, giving a brown oil. The oil was dissolved in a minimum of acetone and cooled to −30 °C. The resulting yellow powder was filtered and washed with cold acetone (yield: 230 mg, 66%). X-ray quality crystals were grown by dissolving the yellow powder in a minimum of acetone and cooling to −30 °C. NMR data for **8**: ^1H NMR (THF-d_8) δ 7.570 (d, J_{H-H} = 7.4 Hz, 1 H), 7.446 (d, J_{H-H} = 7.3 Hz, 1 H), 7.263 (d, J_{H-H} = 7.3 Hz, 1 H), 7.184−6.989 (m, 4 H), 6.948 (t, J_{H-H} = 7.8 Hz, 1 H), 2.117 (sept, C*H*Me_2, J_{H-H} = 7.6 Hz, 2 H), 2.09−1.94 (m, 2 H), 1.65−1.51 (m, 2 H), 1.21−0.98 (m, CH*Me*$_2$, 24 H), 0.75−0.43 (bs, 2 H), 0.073 (s, 9 H), −0.216 (s, 9 H); $^{31}P\{^1H\}$ NMR (THF-d_8) δ 76.0 (J = 53.3 Hz) and δ 71.4 (J = 53.3 Hz). Anal. Calcd for $C_{34}H_{58}P_2Si_2Ni$: C, 63.45; H, 9.08. Found: C, 63.48; H, 9.28.

Characterization Data for 2-(Trimethylsilylethynyl)-2′-(trimethylsilyl)biphenyl, 4. ^1H NMR (C_6D_6): δ 7.633−7.580 (m, 1 H), 7.500−7.462 (m, 1 H), 7.246−7.193 (m, 3 H), 7.133−7.094 (m, 1 H), 6.295 (dq, J_{H-H} = 6.9, 2 Hz, 2 H), 0.078 (s, 9 H), 0.009 (s, 9 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.9 (s), 138.6 (s), 134.7 (s), 131.9 (s), 130.3 (s), 130.1 (s), 128.4 (s), 127.8 (s), 127.4 (s), 126.8 (s), 124.1 (s), 117.6 (s), 105.4 (≡*C*−Ph), 98.7 (≡*C*−TMS), −0.49 (s), −0.25 (s). MS, 322 (M^+). **9-Trimethylsilyl-10-(2-(2′-trimethylsilylphenyl)phenyl)phenanthrene, 5.** ^1H NMR (CD_2Cl_2): δ 8.711−8.667 (m, 1 H), 8.575−8.537 (m, 1 H), 8.418−8.369 (m, 1 H), 7.649−7.598 (m 2 H), 7.574−7.424 (m, 6 H), 7.398−7.360 (m, 1 H), 7.208 (t, J_{H-H} = 6.7, 1.2 Hz, 1 H), 7.141 (bd, J_{H-H} = 8.0 Hz, 1 H), 6.974 (t, J_{H-H} = 7.4, 1.1 Hz, 1 H), 6.754 (t, J_{H-H} = 7.3, 1.5 Hz, 1 H), 0.271 (s, 9 H) 0.235 (s, 9 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 146.9 (s), 146.8 (s), 142.6 (s), 141.5 (s), 139.8 (s), 137.0 (s), 136.3 (s), 135.2 (s), 133.7 (s), 132.4 (s), 130.7 (s), 130.5 (s), 130.2 (s), 129.9 (s), 129.7 (s), 128.8 (s), 128.1 (s), 127.8 (s), 127.1 (s), 127.0 (s), 126.1 (s), 126.04 (s), 126.03 (s), 125.8 (s), 123.4 (s), 122.3 (s), 2.62 (s), 2.06 (s). MS, 474 (M^+). Anal. Calcd for $C_{33.5}H_{35.5}Si_2$ (benzene in the lattice): C, 81.40; H, 7.24; Si, 11.35. Found: C, 81.45; H, 7.37; Si, 11.18. **Bis(2-(2′-trimethylsilylphenyl)phenyl)acetylene, 6.** ^1H NMR (CD_2Cl_2): δ 7.640−7.600 (m, 2 H), 7.40−7.14 (m, 14 H, overlapping **5**). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 147.7 (s), 146.3 (s), 141.8 (s), 134.7 (s), 132.1 (s), 130.5 (s), 130.0 (s), 129.4 (s), 128.4, 127.9 (s), 127.6 (s), 127.4 (s), 92.9 (s, ≡*C*−Ph), 0.312 (s). MS: 474 (M^+).

2-(Ethynyl)-2′-(trimethylsilyl)biphenyl, 7. ^1H NMR (C_6D_6): δ 7.624−7.597 (m, 1 H), 7.495−7.452 (m, 1 H), 7.293−7.250 (m, 1 H), 7.236−7.191 (m, 2 H), 7.115−7.075 (m, 1 H), 6.914 (dq, J_{H-H} = 7.1, 2.7 Hz, 2 H), 2.976 (s, 1 H), 0.075 (s, 9 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 146.7 (s), 146.4 (s), 138.2 (a), 134.1 (s), 132.2 (s), 130.0 (s), 129.2 (s), 127.7 (s), 127.5 (s), 126.8 (s), 126.1 (s), 121.6 (s), 82.4 (s, ≡*C*−Ph), 80.0 (s, ≡*C*−H), −0.54 (s). MS: 250 (M^+). Anal. Calcd for $C_{17}H_{18}Si$: C, 81.54; H, 7.25; Si, 11.22. Found: C, 81.14; H, 7.17; Si, 12.08.

Reaction of (dippe)Ni($Me_3CC{\equiv}CSiMe_3$) with Biphenylene and 1-Trimethylsilyl-3,3-dimethyl-1-butyne. An ampule was charged with (dippe)Ni($Me_3CC{\equiv}CSiMe_3$) (50 mg, 0.11 mmol), biphenylene (200 mg, 1.31 mmol), and 1-trimethylsilyl-3,3-dimethyl-1-butyne (203 mg, 0.275 mL, 1.31 mmol). The mixture was dissolved in 5 mL of THF and heated at 120 °C for 4 days as before. The solvent was removed under vacuum, and the mixture dissolved in a minimum of CH_2Cl_2 and applied to a thick layer chromatography (TLC) plate. A 6:1 (v/v) solution of hexanes$-CH_2Cl_2$ was used as eluent. Two major bands were observed under UV light. The product of band 1 ($R_f \approx 0.8$) was extracted with CH_2Cl_2, giving 315 mg of a viscous yellow oil. GC/MS revealed two compounds in a 4:1 ratio, each with a molecular weight of 306. The major product was isolated as a white solid by dissolving the mixtures in a minimum of hexanes and cooling to −30 °C. The solid was washed with cold methanol. X-ray quality crystals were grown by dissolving in C_6H_6, layering with methanol, and cooling to −30 °C. This compound was characterized by ^1H NMR spectroscopy, GC/MS, elemental analysis, and X-ray crystallography and determined to be 9-*tert*-butyl-10-(trimethylsilyl)phenanthrene, **9**. The filtrate was stripped of solvent, redissolved in a minimum of CH_2Cl_2, and applied to a *thin* layer chromatography plate. A 30:1:0.1 (v/v/v) solution of hexanes−acetonitrile−ethyl acetate was used as eluent. Two bands were observed. Band 1a ($R_f \approx 0.85$) yielded an oil identified as 2-(*tert*-butylethynyl)-2′-(trimethylsilyl)biphenyl, **10**, and characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy as well as GC/MS. Band 1b was compound **9**.

Band 2 ($R_f \approx 0.65$) was extracted with CH_2Cl_2. The solvent was removed under vacuum to give 75 mg of a white solid. This compound was further purified by dissolving in hot ethanol and cooling to −30 °C. X-ray quality crystals were

Table 1. X-ray Data Collection and Refinement Parameters for 1, 5, 7, 8, 9, 11, and 13

	1	**5**	**7**	**8**	**9**	**11**	**13**
chem formula	$C_{22}H_{50}P_2Si_2Ni$	$C_{33.5}H_{35.5}Si_2$	$C_{17}H_{18}Si$	$C_{34}H_{58}P_2Si_2Ni$	$C_{21}H_{26}Si$	$C_{33}H_{34}Si$	$C_{30}H_{28}Si$
fw	491.45	494.3	250.40	643.63	306.51	458.69	416.61
cryst syst	triclinic	triclinic	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic
space group, *Z*	$P\bar{1}$, 2	$P\bar{1}$, 4	$P2_1/n$, 8	$P2_1/n$, 4	$P2_12_12_1$, 4	$P\bar{1}$, 2	C2/*c*, *8*
a, Å	10.2830(9)	10.4834(2)	19.4741(8)	12.68430(10)	8.97110(10)	9.5282(2)	24.5023(10)
b, Å	10.7457(9)	12.9347(2)	7.3014(3)	19.6756(2)	12.15930(10)	10.316 A	13.0864(5)
c, Å	14.6014(12)	22.4424(3)	21.1731(8)	15.16810(10	16.1896(2)	14.1657(3)	17.9748(7)
α, deg	109.5490(10)	75.9890	90	90	90	70.0820(10)	90
β, deg	95.350(2)	88.1280	96.2460(10)	92.4660(10)	90	86.0750(10)	125.8500(10)
γ, deg	102.166(2)	75.5630	90	90	90	89.0570(10)	90
vol, $Å^3$	1462.6(2)	2858.17	2992.7(2)	3782.02(5)	1766.00(3)	1306.03(4)	4671.7(3)
temp, °C	−80	−80	−80	−80	−80	−80	−80
no. of data collected	6010	12093	11646	22758	7683	5661	9905
no. of unique data	3833	7679	4146	8785	2520	3607	3330
$R1(F_o)$, $wR2(F_o^2)$ $(I > 2\sigma(I))$	0.0623, 0.1300	0.0461, 0.1081	0.0512, 0.1116	0.0300, 0.0730	0.0428, 0.0942	0.0595, 0.1432	0.0368, 0.0866
$R1(F_o)$, $wR2(F_o^2)$, all data	0.0923, 0.1434	0.0597, 0.1159	0.0756, 0.1234	0.0379, 0.0768	0.0545, 0.0990	0.0731, 0.1509	0.0462, 0.0916
goodness of fit	1.000	1.025	1.013	1.013	0.988	0.968	1.060

grown by dissolving in hot ethanol and slowly cooling to room temperature. The resulting solid was washed with cold methanol to give 9-*tert*-butyl-10-(2-(2′-trimethylsilylphenyl)phenyl)-phenanthrene, **11**. This compound was characterized by ^1H NMR spectroscopy, GC/MS, elemental analysis, and X-ray crystallography.

Characterization Data for 9-*tert*-Butyl-10-(trimethylsilyl)phenanthrene, 9. ^1H NMR (CD_2Cl_2): *δ* 8.592−8.440 (m, 3 H), 8.155−8.100 (m, 1 H), 7.600−7.476 (m, 4 H), 1.730 (s, 9 H), 0.506 (s, 9 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 157.7 (s), 137.9 (s), 137.6 (s), 132.9 (s), 131.8 (s), 129.5−129.6 (m), 128.7 (s), 127.0 (s), 125.8 (s), 125.4 (s),125.3 (s), 123.6 (s), 122.9 (s), 39.7 (s), 34.3 (s), 5.6 (s). MS: 306 (M^+). Anal. Calcd for $C_{21}H_{26}Si$: C, 82.29; H, 8.55; Si, 9.16. Found: C, 82.21; H, 8.61; Si, 8.99.

2-(*tert*-Butylethynyl)-2′-(trimethylsilyl)biphenyl, 10. ^1H NMR ($CDCl_3$): *δ* 7.609−7.562 (m, 1 H), 7.408−7.133 (m, 7 H), 0.947 (s, 9 H), −0.033 (s, 9 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): *δ* 148.2 (s), 147.1 (s), 138.6 (s), 134.4 (s), 131.2 (s), 130.0 (s), 129.96 (s), 128.3 (s), 127.3 (s), 126.7 (s), 126.4 (s), 124.7 (s), 102.8 (≡*C*−Ph), 78.7 (≡*C*−*tert*-butyl), 30.5 (s), 14.1 (s), 0.21 (s). MS: 306 (M^+). **9-*tert*-Butyl-10-(2-(2′-trimethylsilylphenyl)phenyl)phenanthrene, 11.** ^1H NMR (THF-d_8): *δ* 8.744−8.735 (m, 1 H), 8.610 (d, J_{H-H} = 8.2 Hz, 1 H), 8.543 (d, J_{H-H} = 7.2 Hz, 1 H), 7.566−7.477 (m, 5 H), 7.446−7.363 (m, 4 H), 7.199 (bs, 2 H), 6.918 (dt, J_{H-H} = 7.2, 1.6 Hz, 1 H), 6.590 (bs, 1 H), 1.480 (bs, 9 H), 0.263 (s, 9 H). $^{13}C\{^1H\}$ NMR (330 K, THF-d_8): *δ* 147.4 (s), 143.3 (s), 142.7 (s), 142.4 (s), 140.5 (s), 136.8 (s), 136.5 (s), 134.8 (s), 133.2 (s), 132.9 (s), 132.4 (s), 130.6 (s), 130.43 (s), 130.39 (s), 129.7 (s), 129.2 (s), 127.9 (s), 127.7 (s), 127.1 (s), 126.6 (s), 126.5 (s), 126.1 (s), 125.3 (s), 124.2 (s), 122.7 (s), 122.66 (s), 39.2 (s), 35.6 (s), 2.5 (s). MS: 458 (M^+). Anal. Calcd for $C_{33}H_{34}Si$: C, 86.41; H, 7.47; Si, 6.12. Found: C, 86.49; H, 7.44; Si, 5.93.

Reaction of (dippe)Ni(MeC≡CSiMe$_3$) with Biphenylene and 1-Trimethylsilylpropyne. An ampule was charged with (dippe)Ni(MeC≡CSiMe$_3$) (130 mg, 0.30 mmol), biphenylene (250 mg, 1.64 mmol), and 1-trimethylsilylpropyne (184 mg, 0.243 mL, 1.64 mmol). The mixture was dissolved in 5 mL of THF and heated at 120 °C for 7 days as before. The solvent was removed under vacuum, and the mixture was dissolved in a minimum of CH_2Cl_2 and applied to a thick layer chromatography (TLC) plate. A 25:1 (v/v) solution of hexanes−CH_2Cl_2 was used as eluent. Four major bands were observed under UV light. The product of band 1 ($R_f \approx 0.7$) was extracted with CH_2Cl_2. The isolated product was determined to be residual biphenylene (∼15 mg). Band 2 ($R_f \approx 0.6$) was a yellow oil (217 mg), which was dissolved in hot ethanol and isolated by cooling to −30 °C. The orange solid melts as it is warmed to room temperature. This material was identified as the known compound[23] 9-methyl-10-(trimethylsilyl)phenanthrene, **12**, by ^1H, $^{13}C\{^1H\}$ NMR spectroscopy and GC/MS. Band 3 ($R_f \approx 0.5$) was isolated and determined to be tetraphenylene (∼15 mg). Band 4 was extracted with CH_2Cl_2; the resulting viscous oil was dissolved in hot ethanol and cooled to −30 °C. The resulting white solid (150 mg) of 9-methyl-10-(2-(2′-trimethylsilylphenyl)phenyl)phenanthrene, **13**, was washed with cold methanol and characterized by ^1H NMR spectroscopy, GC/MS, elemental analysis, and X-ray crystallography.

Characterization Data for 9-Methyl-10-(trimethylsilyl)phenanthrene, 12. ^1H NMR (C_6D_6): *δ* 8.512−8.419 (m, 2 H), 8.233 (d, J_{H-H} = 8 Hz, 1 H), 7.912−7.855 (m, 1 H), 7.435−7.342, (m, 4 H), 2.580 (s, 3 H), 0.477 (s, 9 H). $^{13}C\{^1H\}$ NMR (C_6D_6): *δ* 144.2 (s), 136.0 (s), 134.5 (s), 132.4 (s), 131.5 (s), 130.1 (s), 129.2 (s), 126.9 (s), 126.7 (s), 125.7 (s), 125.4 (s), 124.8 (s), 123.5 (s), 123.0 (s), 21.9 (s), 4.2 (s). MS, 264 (M^+). **9-Methyl-10-(2-(2′-trimethylsilylphenyl)phenyl)phenanthrene, 13.** ^1H NMR (THF-d_8): *δ* 8.726−8.633 (m, 2 H), 7.996 (bd, J_{H-H} = 7.2 Hz, 1 H), 7.590−7.277 (m, 10 H), 6.866 (t, J_{H-H} = 7.2 Hz, 1 H), 6.7449 (bd, J_{H-H} = 7.2 Hz, 1 H), 6.564 (t, J_{H-H} = 7.2 Hz, 1 H), 1.730 (bs, 9 H), 0.515 (s, 9 H). $^{13}C\{^1H\}$ NMR (336 K, THF-d_8): *δ* 145.3 (s), 142.4 (s), 138.3 (s), 137.4 (s), 135.1 (bs), 134.0 (s), 130.1 (s), 130.8 (s), 129.1 (s), 129.0 (bs), 128.5 (s), 128.0 (s), 126.4 (s), 126.0 (s), 125.73 (s), 125.70 (s), 125.2 (s), 124.8 (bs), 124.7 (s), 124.5 (s), 124.1 (s), 123.6 (s), 121.6 (s), 121.2 (s), 16.2 (s), 0.08 (s). MS: 416 (M^+). Anal. Calcd for $C_{30}H_{28}Si$: C, 86.49; H, 6.77; Si, 6.74. Found: C, 86.41; H, 7.46; Si, 6.79.

2-(1-Propynyl)-2′-(trimethylsilyl)biphenyl, 14. ^1H NMR (C_6D_6): *δ* 1.423 (s, 9 H), 0.129 (s, 3 H). The aromatic protons were obscured by compound **12**. $^{13}C\{^1H\}$ NMR (C_6D_6): *δ* 90.0 (s), 79.9 (s), 0.61 (s). The other carbon resonances were obscured by compound **12**. MS: 264 (M+).

X-ray Structural Determination of 1, 5, 7, 8, 9, 11, and 13. All of the crystals were mounted on glass fibers under Paratone-8277 (Exxon) and immediately placed in a cold nitrogen stream at −80 °C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Siemens SMART CCD area detector system equipped with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1321 frames of data (1.3 hemispheres), using a detector-to-crystal distance of 5.094 cm (maximum 2*θ* angle of 56.52°), were collected using a narrow frame method with scan widths of 0.3° in *ω* and exposure times of 30 s/frame for all of the crystals except for **5**, which was collected at 10 s exposures. The total data collection time was approximately

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(23) Marcinow, A.; Clawson, D. K.; Rabideau, P. W. *Tetrahedron* **1989**, *45*, 5441.

13 h for 30 s exposures and 7 h for 10 s exposures. Frames were integrated either to 0.75 Å or to 0.90 Å with the Siemens SAINT program. The unit cell parameters for all of the crystals were based upon the least-squares refinement of three-dimensional centroids of >2000 reflections.[24] Data were corrected for absorption using the program SADABS.[25] The space group assignments were made on the basis of systematic absences and intensity statistics by using the XPREP program. The structure solutions were achieved by direct methods and refined employing full-matrix least-squares on F^2 (Siemens, SHELXTL,[26] version 5.04). There was nothing unusual about the solution and refinement of any of the structures, with the exceptions of **5**, **7**, and **9**: Both **5** (P (#2), $Z = 4$) and **7** ($P2_1/n$, $Z = 8$) contain two independent molecules in the asymmetric unit; the TMS and *t*-Bu groups exhibit disorder in **9**, and the disordered atoms were refined isotropically. For all of the structures except **9**, the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens were included in idealized positions, except H1 and H2 were located and their positions and isotropic thermal parameter refined for **7**. Further experimental details of the X-ray diffraction studies are provided in Table 1. Full experimental details of the X-ray diffraction studies, as well as positional parameters, anisotropic thermal parameters, bond lengths and angles, and fixed hydrogen positional parameters are given in the Supporting Information. In all ORTEPS, ellipsoids are shown at the 30% level and hydrogen atoms have been omitted for clarity.

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Supporting Information Available: Tables of crystallographic data including atomic coordinates, thermal parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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[24] It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10× the listed value.

[25] The SADABS program is based on the method of Blessing: see Blessing, R. H. *Acta Crystallogr., Sect A* **1995**, *51*, 33.

[26] *SHELXTL: Structure Analysis Program, version 5.04*; Siemens Industrial Automation Inc.: Madison, WI, 1995.