Organometallics **2002,** *21,* 1975−1981

Catalytic C−C Bond Activation in Biphenylene and Cyclotrimerization of Alkynes: Increased Reactivity of P,N- versus P,P-Substituted Nickel Complexes

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Received December 28, 2001

Reaction of $Ni(COD)_2$ with the bidentate hybrid ligand $(^iPr)_2CH_2CH_2NMe_2$ (PN) and PhC≡CR (R = Ph, ^{t}Bu, CF_3, C≡CPh) afforded the donor-stabilized mononuclear Ni(0) complexes (PN)Ni(η^2-PhC≡CR) (R = Ph (**1**), ^{t}Bu (**4**), CF_3 (**5**)) and the dinuclear compound (PN)Ni(η^2;η^2-PhC≡C−C≡CPh)Ni(PN) (**3**), respectively. In the presence of excess alkyne, compounds **1**, **3**, and **4** turned out to be active species for the catalytic carbon−carbon bond activation in biphenylene and formation of the corresponding 9,10-disubstituted phenanthrenes. However, cyclotrimerization to benzene derivatives instead of C−C bond cleavage occurred with complex **5** in the presence of excess CF_3C≡CPh and biphenylene. In contrast, the corresponding bis-phosphino-substituted species (dippe)Ni(η^2-PhC≡CR) (R = Ph (**2**), CF_3 (**9**)) showed substantially reduced catalytic activity toward phenanthrene formation or cyclotrimerization reactions.

Introduction

The selective activation of carbon−carbon bonds and their functionalization by transition metal complexes has recently attracted much interest due to its potential application in industrial petroleum refining and transformation processes. Because the target bond is both thermodynamically stable and kinetically inert, the cleavage of C−C single bonds under mild homogeneous conditions is still a fundamental challenge in organometallic chemistry. To achieve stoichiometric oxidative addition of C−C bonds to metal centers, a number of strategies have been developed, such as relief of ring strain or attainment of aromaticity. The activation of unstrained C−C bonds has been observed in the presence of highly reactive species, by forcing the target molecule into close proximity to the metal center or by the formation of strong M−aryl bonds.[1,2] Catalytic C−C bond activation and functionalization is much less common, but it has been shown in some cases that biphenylene is an appropriate substrate for this process.[3] The insertion of a reactive L_nM fragment into the central C−C bond of biphenylene generates a L_nM(2,2′-biphenyl) complex with two strong M−aryl bonds, which is thermodynamically favorable. Eisch et al. reported on the formation of 9,10-diphenylphenanthrene by heating $(PEt_3)_2$Ni(2,2′-biphenyl) in the presence of diphenylacetylene.[4] A similar result was obtained by reaction of diphenylacetylene with $CpCo(PPh_3)$(2,2′-biphenyl).[5] Our group has demonstrated the *catalytic* formation of 9,10-diphenylphenanthrene by heating a mixture of diphenylacetylene and biphenylene in the presence of the catalyst precursor (dippe)Ni(η^2-PhC≡CPh). However, oxygen was required for the catalytic process to remove the bis-phosphino ligand from the metal center and to generate a reactive Ni(0) species.[6] We have also found that (dippe)RhCl(alkyne) can be used to catalytically form phenanthrenes from biphenylene plus acetylenes,[7] but side reactions to produce cyclotrimerized arenes and fluorenes[8] were a problem in this system.

We now wish to report on the synthesis of various Ni(η^2-alkyne) complexes that are stabilized by the bidentate chelating P,N-hybrid ligand $(^iPr)_2CH_2CH_2NMe_2$ (PN).[9] According to Pearson's concept of “hard” and “soft” Lewis acids and Lewis bases, the coordinated metal−nitrogen bond in (PN)Ni(η^2-alkyne) complexes is considered to be labile.[10] The nickel compounds are expected to be more reactive toward C−C bond activation of biphenylene and functionalization reactions with alkynes compared to corresponding (dippe)Ni(η^2-alkyne) complexes.

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10.1021/om0110989 CCC: $22.00
Publication on Web 04/05/2002

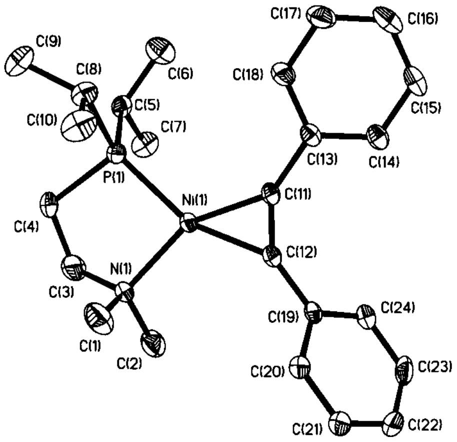
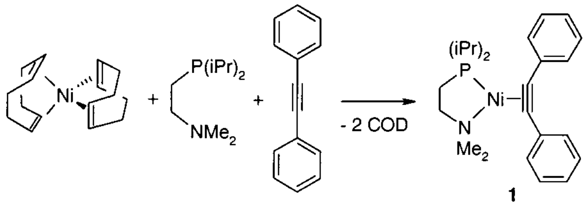


Figure 1. Molecular structure of (PN)Ni(η^2-PhC≡CPh) (**1**) (ORTEP diagram; 30% probability ellipsoids).

Results and Discussion

We recently described the synthesis of the zerovalent Pt-alkyne complex (PN)Pt(η^2-PhC≡CPh), which is stabilized by the chelating ligand (^{i}Pr)$_2$PCH$_2$CH$_2$NMe$_2$. This compound turned out to undergo stoichiometric C(sp)−C(sp^2) bond activation in diphenylacetylene under photochemical conditions to afford the Pt(II) species (PN)Pt(Ph)(C≡CPh).[11] However, formation of a platinacyclopenta-2,5-diene complex and subsequent catalytic generation of hexaphenylbenzene were observed with excess diphenylacetylene under thermal conditions.[12]

The corresponding Ni(0) complex (PN)Ni(η^2-PhC≡CPh) (**1**) was synthesized by reaction of Ni(COD)$_2$ with (^{i}Pr)$_2$PCH$_2$CH$_2$NMe$_2$ and diphenylacetylene in pentane and was isolated as an orange, air- and moisture-sensitive solid (eq 1). The ^{1}H NMR spectrum of **1** showed



1

(1)

two sets of *o*-, *m*-, and *p*-phenyl protons of the alkyne moiety due to the asymmetric bidentate P,N ligand. Crystals of **1** suitable for X-ray diffraction were obtained by recrystallization from pentane at $T = -30$ °C. The molecular structure of **1** is illustrated in Figure 1, and selected bond lengths and angles are listed in Table 1. The structural analysis revealed the expected distorted square-planar geometry at the metal center. The alkyne ligand is positioned in the P−Ni−N plane and is bonded slightly asymmetrically to the nickel atom. The Ni−C distances are 1.845(3) and 1.904(3) Å, with the longer bond *trans* to phosphorus. Major contribution of π^* back-donation[13] is suggested by the elongated C≡C bond (1.291(5) Å) and the bending of the C≡C−C angles (145.0(3)°, 144.0(3)°) compared to free diphenylacetylene.[14] Other donor-stabilized L$_2$Ni(η^2-PhC≡CPh) complexes (L$_2$ = CN^{t}Bu, dmpe, COD, bipy, dippe) show similar C−C triple bond distances (1.276−1.300 Å) and C≡C−C bending angles (144.0−151.3°).[6,15] Ni−C bond distances in these compounds are slightly shorter when *trans* to N (~1.85 Å) than to π-acceptor ligands (~1.88 Å), as observed in **1**. In all of these complexes except the bipy derivative, the phenyl rings lie approximately in the square plane of the metal complex.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 1

Bond Lengths

Ni(1)−N(1)	2.036(3)	Ni(1)−C(12)	1.904(3)
Ni(1)−P(1)	2.1565(10)	C(11)−C(12)	1.291(5)
Ni(1)−C(11)	1.845(3)		

Bond Angles

C(11)−Ni(1)−C(12)	40.27(14)	C(12)−Ni(1)−N(1)	111.97(13)
N(1)−Ni(1)−P(1)	89.44(8)	C(12)−C(11)−C(13)	144.0(3)
C(11)−Ni(1)−P(1)	118.32(11)	C(11)−C(12)−C(19)	145.0(3)

The nickel complex **1** turned out to be an effective catalyst for the C−C bond activation in biphenylene. In the presence of **1** (8.3 mol %), a mixture of biphenylene and diphenylacetylene was quantitatively converted into 9,10-diphenylphenanthrene within 22.5 h at $T = 70$ °C (~0.5 TO/h). No cyclotrimerization of PhC≡CPh to hexaphenylbenzene was observed by ^{1}H NMR spectroscopy or GC/MS. Furthermore, **1** is the only observed species by NMR spectroscopy during the course of the reaction. The corresponding bis-phosphino-substituted complex (dippe)Ni(η^2-PhC≡CPh) (**2**), however, produced only small amounts of 9,10-diphenylphenanthrene (~0.2 turnovers) after 40 h at $T = 110$ °C. To increase the turnover rate, oxygen was required to render the process catalytic (vide supra). We attribute the enhanced reactivity of **1** compared to (dippe)Ni(η^2-PhC≡CPh) to the properties of the mixed donor ligand system; although the dimethylamino group is a good σ-donor, it also lacks in π-acceptor capability. This situation can lead to a certain lability of the coordinated Ni−NR$_2$ bond. As a result, an additional free coordination site can be generated which is essential for a catalytic cycle. We propose the mechanism shown in Scheme 1 for the formation of 9,10-diphenylphenanthrene. We assume that the first step in the production of the organic product is fast dissociation of the NR$_2$ group from the nickel atom and formation of a vacant coordination site. Subsequently the highly reactive metal center is able to cleave the C−C bond in biphenylene to generate the Ni(II) intermediate **I**. Insertion of the alkyne into the Ni−C bond then leads to the Ni(II) species **II**. Reductive

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[12] In the presence of biphenylene and diphenylacetylene no catalytic formation of the corresponding 9,10-diphenylphenanthrene was observed. Further details are reported in: Müller, C.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **2002**, *21*, 1118.

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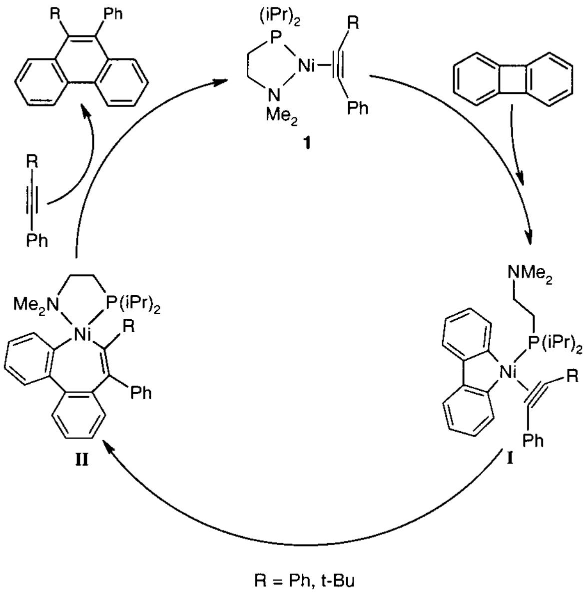
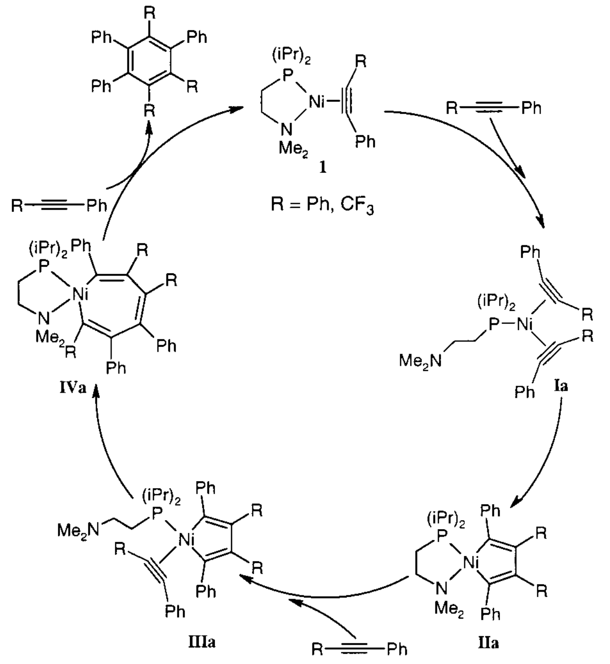
Scheme 1



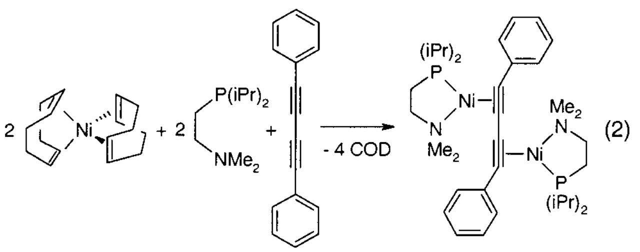
elimination of 9,10-diphenylphenanthrene and complexation of a second alkyne regenerates the Ni(0) complex **1**.

We further observed that in the absence of biphenylene, hexaphenylbenzene is formed catalytically from diphenylacetylene in the presence of **1** (initial rate: 0.4 TO/d). The lability of the M−NR$_2$ bond might facilitate the coordination of a second alkyne to generate the Ni(0) intermediate **Ia** (Scheme 2).[16] According to the commonly accepted mechanism for the cyclotrimerization of alkynes,[13e,17] reductive coupling of the ligands leads to the formation of the donor-stabilized Ni(II) metallacyclopentadiene **IIa**.[15e,18] Again, dissociation of the NR$_2$ group from the metal center provides a vacant coordination site for the third alkyne (**IIIa**), which subsequently inserts into the Ni−C bond to form the Ni(II) intermediate **IVa**. Reductive elimination of hexaphenylbenzene and complexation of an incoming alkyne regenerates the Ni(0) species **1**. *In contrast to the results described above, no hexaphenylbenzene was produced with (dippe)Ni(η^2-PhC≡CPh) (**2**) under the same reaction conditions*. Even at T = 100 °C, no cyclotrimerization reaction was observed. This observation supports the assumption that an additional free coordination site at the metal center for alkyne complexation is a prerequisite for this process. The hemilabile[19] P,N ligand offers this possibility.

Scheme 2



Catalytic C−C bond activation of biphenylene and functionalization with diphenylacetylene were also achieved by the dinuclear Ni(0) complex (PN)Ni(η^2;η^2-PhC≡C−C≡CPh)Ni(PN) (**3**).[20] This compound was synthesized by reaction of Ni(COD)$_2$ with (^{i}Pr)$_2$PCH$_2$CH$_2$NMe$_2$ and 1,4-diphenylbutadiyne in the ratio 2:2:1 in pentane according to eq 2. A mixture of biphenylene and diphenylacetylene was quantitatively converted into 9,10-diphenylphenanthrene in the presence of **3** (8.3 mol % Ni) within 22.5 h at T = 70 °C (0.5 TO/h). No



(2)

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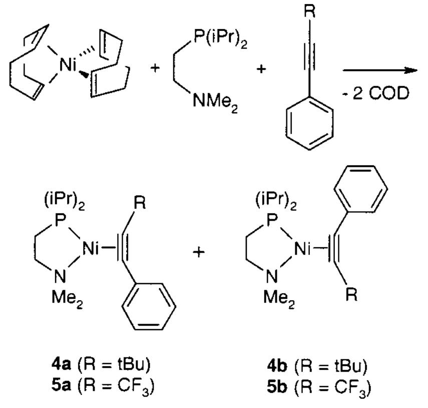
incorporation of 1,4-diphenylbutadiyne or cyclotrimerization reactions were observed. On the basis of $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy, however, we assume that compound **3** acts as a catalyst *precursor*. In the presence of excess diphenylacetylene, **3** was instantaneously converted into the η^2-diphenylacetylene complex **1** at $T = 70$ °C. As described above, this compound is most likely the active species in the phenanthrene formation.

We were also interested in the catalytic C−C bond activation of biphenylene and functionalization with different alkynes, such as $^t\mathrm{BuC{\equiv}CPh}$ and $\mathrm{F_3CC{\equiv}CPh}$. The corresponding Ni($\eta^2$-alkyne) complexes were synthesized similar to the procedure described for compound **1** by reaction of $\mathrm{Ni(COD)_2}$ with 1 equiv of $(^i\mathrm{Pr})_2\mathrm{PCH_2CH_2NMe_2}$ and 1 equiv of the alkyne. (PN)Ni(η^2-$^t\mathrm{BuC{\equiv}CPh}$) (**4**) and (PN)Ni($\eta^2$-$\mathrm{F_3CC{\equiv}CPh}$) (**5**) were obtained as orange, air- and moisture-sensitive solids after recrystallization from petroleum ether/THF at $T = -30$ °C. The ^{1}H, $^{31}\mathrm{P}\{^1\mathrm{H}\}$, and $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR data showed that **4** and **5** were formed as two isomers, with the phenyl group either *trans* (**4a**, **5a**) or *cis* (**4b**, **5b**) to phosphorus (eq 3). We assume that the electron-donating ^{t}Bu group prefers the position *trans* to the nitrogen atom in **4** (**4a**:**4b** = 93:7). The molecular structure of the isoelectronic platinum complex (PN)Pt(η^2-$^t\mathrm{BuC{\equiv}CPh}$) revealed this feature.[21] The electron-withdrawing $\mathrm{CF_3}$ group, however, is preferentially oriented in the *cis* position to the nitrogen in **5** (**5a**:**5b** = 1:9). In particular, a quartet at $\delta = 59.8$ ($^4J_{\mathrm{P-F(trans)}} = 11.9$ Hz) was observed for **5b** in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum, while complex **5a** showed a singlet at $\delta = 61.4$. Complementary to this observation, a doublet at $\delta = -54.4$ ($^4J_{\mathrm{F-P(trans)}} = 12.9$ Hz) was detected for **5b** in the $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR spectrum. Compound **5a**, with the $\mathrm{CF_3}$ group *cis* to phosphorus, showed a singlet at $\delta = -57.2$. This is consistent with the fact that *trans*-coupling between two nuclei is usually much stronger compared to *cis*-coupling.



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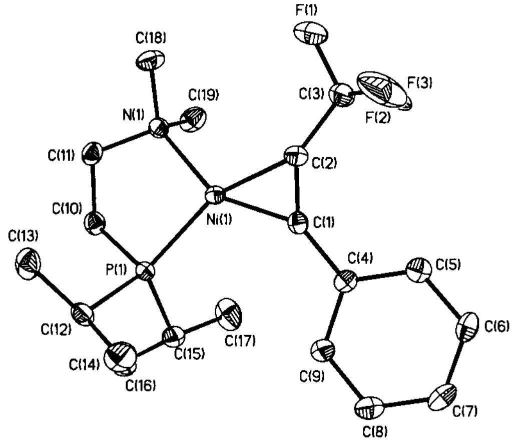


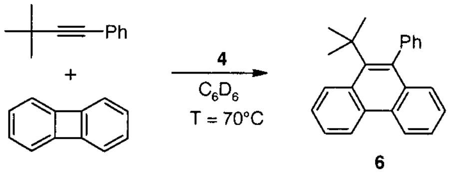
Figure 2. Molecular structure of (PN)Ni(η^2-$\mathrm{F_3CC{\equiv}CPh}$) (**5b**) (ORTEP diagram; 30% probability ellipsoids).

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 5b

Bond Lengths			
Ni(1)−N(1)	2.039(4)	Ni(1)−C(2)	1.864(4)
Ni(1)−P(1)	2.1674(13)	C(1)−C(2)	1.296(6)
Ni(1)−C(1)	1.868(4)	C(2)−C(3)	1.452(6)
Bond Angles			
C(1)−Ni(1)−C(2)	40.63(18)	C(1)−Ni(1)−P(1)	117.71(14)
N(1)−Ni(1)−P(1)	89.36(11)	C(1)−C(2)−C(3)	139.3(5)
C(2)−Ni(1)−N(1)	112.06(17)	C(2)−C(1)−C(4)	142.4(4)

A crystal of the major compound **5b** suitable for X-ray diffraction was obtained by recrystallization from petroleum ether/THF at $T = -30$ °C. The molecular structure is depicted in Figure 2, and selected bond lengths and angles are listed in Table 2. Again, the square-planar structure of **5b** and the C(2)−C(1)−C(4) angle of 142.4(4)° suggest a significant amount of π^*-back-bonding to generate d^8 Ni(II) metallacyclopropene character. The C(1)−C(2) distance is 1.296(6) Å, and the bond lengths Ni−C(1) and Ni−C(2) are 1.868(4) and 1.864(4) Å, respectively. Furthermore, the X-ray structural analysis confirmed the NMR data and showed that the $\mathrm{CF_3}$ group is indeed positioned *trans* to phosphorus, while the phenyl group is *trans* to nitrogen. Other $\mathrm{L_2Ni(PhC{\equiv}CR)}$ complexes with asymmetrically substituted acetylenes are known (R = aryl, $\mathrm{SiMe_3}$) and display similar geometric features.[13f−h,16]

Similar to **1**, (PN)Ni(η^2-$^t\mathrm{BuC{\equiv}CPh}$) turned out to be a catalyst for the production of 9-phenyl-10-*tert*-butylphenanthrene (**6**). Within 16 days at $T = 40$ °C (0.4 TO/d), a mixture of t-$\mathrm{BuC{\equiv}CPh}$ and biphenylene was quantitatively converted into the 9,10-disubstituted phenanthrene in the presence of **4** (16.6 mol %) (eq 4). We propose the same mechanism for the catalytic production of **6** as for the formation of 9,10-diphenylphenanthrene shown in Scheme 1.



(4)

In contrast, no catalytic C−C bond activation of biphenylene was observed with complex (PN)Ni(η^2-$\mathrm{F_3CC{\equiv}CPh}$) (8.3 mol %) and a mixture of $\mathrm{F_3CC{\equiv}CPh}$ and biphenylene. Instead, quantitative cyclotrimerization of the alkyne occurred, and the benzene derivatives **7** and **8** (ratio: 3:7) were generated within 4.5 h at $T = 70$ °C (∼0.9 TO/h) (eq 5). Obviously, complexation of a second alkyne with subsequent reductive coupling to a metallacyclopentadiene is much faster than oxidative addition of biphenylene to the metal center (Scheme 2). To test whether the activity of **5** toward cyclotrimerization of $\mathrm{F_3CC{\equiv}CPh}$ is again due to the hemilabile

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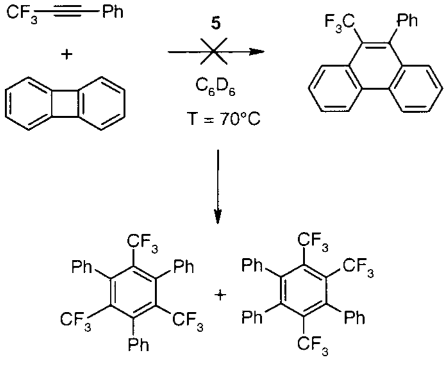
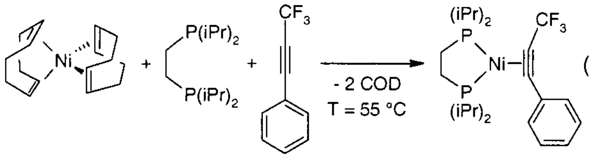
[21] Müller, C.; Lachicotte, R. J.; Jones, W. D. Unpublished results.



(5)

7 (30%) : **8** (70%)

character of the P,N ligand, we synthesized the corresponding Ni(0) complex (dippe)Ni(η^2-$F_3CC{\equiv}CPh$) (**9**). This compound was prepared according to eq 6 and was



(6)

9

obtained as an orange, air- and moisture-sensitive solid after recrystallization from petroleum ether/THF at $T = -30$ °C. The $^{31}P\{^1H\}$ NMR spectrum of **9** (C_6D_6) showed a doublet at $\delta = 83.4$ ($^2J_{P-P} = 29.7$ Hz), as well as a multiplet at $\delta = 81.4$ due to phosphorus−fluorine *trans*-coupling. A solution of **9** (8.3 mol %) and $F_3CC{\equiv}CPh$ in C_6D_6 was heated to $T = 70$ °C, and the reaction was monitored by ^1H, $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectroscopy. Only traces of the cyclotrimerization products were generated after 5.5 h. Even after prolonged heating at $T = 100$ °C (78 h) the amounts of **7** and **8** were found to be less than 1%. Furthermore, no reaction of $F_3CC{\equiv}CPh$ with biphenylene in the presence of **9** was observed either. Clearly, the mixed donor system P,N enhanced the reactivity of the Ni(0) species toward the catalytic cyclotrimerization reaction dramatically.

Conclusions

The Ni(0) complexes (PN)Ni(η^2-$PhC{\equiv}CR$) (R = Ph, ^{t}Bu) are effective catalysts for the C−C bond activation in biphenylene and functionalization with $PhC{\equiv}CPh$ or $^tBuC{\equiv}CPh$ to give 9,10-disubstituted phenanthrenes. Hexaphenylbenzene can be catalytically generated in the absence of biphenylene with (PN)Ni(η^2-$PhC{\equiv}CPh$) and excess diphenylacetylene. In the presence of (PN)Ni(η^2-$F_3CC{\equiv}CPh$), only cyclotrimerization of $F_3CC{\equiv}CPh$ rather than phenanthrene formation was observed. In contrast, the bis-phosphino-substituted complexes (dippe)Ni(η^2-$PhC{\equiv}CR$) (R = Ph, CF_3) produce only traces of phenanthrene or cyclotrimerization products under similar reaction conditions. We attribute the enhanced reactivity of P,N- versus P,P-substituted Ni(0) complexes to the hemilabile character of the P,N ligand. Furthermore, these nickel systems turned out to be more selective for phenanthrene formation from biphenylene and acetylenes than any of the (dippe)Ni(alkyne)[6] or (dippe)RhCl(alkyne)[7] complexes, described previously.

Experimental Section

General Considerations. All manipulations were carried out under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corporation glovebox unless otherwise stated. The solvents were commercially available and distilled from dark purple solutions of benzophenone ketyl. A Siemens-SMART 3-Circle CCD diffractometer was used for the X-ray crystal structure determinations. The elemental analyses were obtained from Desert Analytics (Tuscon, AZ) and Complete Analysis Laboratories, Inc. (Parsippany, NH). ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectra were recorded on a Bruker Avance-400 spectrometer, and all ^1H chemical shifts are reported relative to the residual proton resonance in the deuterated solvents. $^{31}P\{^1H\}$ NMR data are referenced to H_3PO_4 (85%), while $CFCl_3$ was used as an external standard for the $^{19}F\{^1H\}$ NMR data (δ (ppm) = 0.0). $(^iPr)_2PCH_2CH_2NMe_2$ (PN),[9] $(^iPr)_2PCH_2CH_2P(^iPr)_2$ (dippe),[22] $^tBuC{\equiv}CPh$,[23] and $F_3CC{\equiv}CPh$[24] were synthesized according to published procedures. $Ni(COD)_2$, diphenylacetylene, and 1,4-diphenylbutadiyne were obtained from Aldrich and were used without further purification.

(PN)Ni(η^2-PhC≡CPh) (1). $(^iPr)_2CH_2CH_2NMe_2$ (53.0 mg, 59.0 μL, 0.28 mmol) was added to a suspension of $Ni(COD)_2$ in pentane (4.5 mL). An orange solution was formed, and diphenylacetylene (50.0 mg, 0.28 mmol), dissolved in pentane (2.0 mL), was added. An orange solid was formed within 20 min. Stirring was continued for 1 h, and the solid was filtered and washed with cold pentane (2 × 1.0 mL). The product was dried in vacuo. **1** was obtained as an orange, air- and moisture-sensitive solid. Yield: 68.0 mg (0.16 mmol, 57%). ^1H NMR (C_6D_6): δ (ppm) 0.95 (m, 8 H, ^{i}Pr, −CH−), 1.12 (dd, $^3J_{H-P} = 16.0$ Hz, $^3J_{H-H} = 7.2$ Hz, 6 H, ^{i}Pr), 1.83 (m, 4 H, $-CH_2CH_2-$), 2.38 (s, 6 H, $N-CH_3$), 7.06 (m, 2 H, p-C_6H_5), 7.20 (pseudo-t, 2 H, m-C_6H_5), 7.31 (pseudo-t, 2 H, m-C_6H_5), 7.60 (d, $^3J_{H-H} = 7.5$ Hz, 2 H, o-C_6H_5), 7.69 (d, $^3J_{H-H} = 8.3$ Hz, 2 H, o-C_6H_5). $^{13}C\{^1H\}$ NMR (C_6D_6): δ (ppm) 18.4 ($-CH-CH_3$), 20.1 (d, $^2J_{C-P} = 9.5$ Hz, $-CH-CH_3$), 20.2 (d, $^1J_{C-P} = 9.7$ Hz, $P-CH_2-$), 24.2 (d, $^2J_{C-P} = 16.9$ Hz, −CH−), 50.8 ($N-CH_3$), 62.6 (d, $^2J_{C-P} = 10.4$ Hz, $N-CH_2-$), 123.5 (Ph−C), 124.8 (Ph−C), 126.6 (ipso-Ph−C), 126.8 (d, $^2J_{C-P} = 2.7$ Hz), 137.9 (d, $^2J_{C-P(trans)} = 9.5$ Hz, ≡C−Ph), 139.2 (d, $^2J_{C-P(cis)} = 5.3$ Hz, ≡C−Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ (ppm) 58.3. Anal. Calcd for $C_{24}H_{34}NNiP$ (426.23 g/mol): C, 67.63; H, 8.04; N, 3.29. Found: C, 67.56; H, 7.88; N, 3.18.

[(PN)Ni]$_2$(η^2;η^2-PhC≡C−C≡CPh) (3). $(^iPr)_2CH_2CH_2NMe_2$ (105.6 mg, 0.56 mmol, 117.8 μL) was added to a suspension of $Ni(COD)_2$ (153.5 mg, 0.56 mmol) in pentane (8 mL). An orange solution was formed, which was stirred for 40 min at room temperature. A solution of 1,4-diphenylbutadiyne (56.4 mg, 0.28 mmol) in pentane (2 mL) was slowly added, and the color changed to dark red. A red solid was formed immediately, which was filtered and washed with cold pentane (2 mL). The product was dried in vacuo. **3** was obtained as a red, air- and moisture-sensitive solid. Yield: 160.0 mg (0.23 mmol, 82%). ^1H NMR (C_6D_6): δ (ppm) 1.02 (m, 16 H, ^{i}Pr, −CH−), 1.27 (dd, $^3J_{H-P} = 15.8$ Hz, $^3J_{H-H} = 7.0$ Hz, 12 H, ^{i}Pr), 1.85 (m, 4 H, $P-CH_2-$), 1.97 (q, $^3J_{H-H} = 6.8$ Hz, 4 H, $N-CH_2-$), 2.55 (s, 12 H, $N-CH_3$), 7.03 (t, $^3J_{H-H} = 7.3$ Hz, 2 H, p-C_6H_5), 7.27 (t, 4 H, m-C_6H_5), 7.83 (d, $^3J_{H-H} = 7.4$ Hz, 4 H, o-C_6H_5). $^{13}C\{^1H\}$ NMR (C_6D_6): δ (ppm) 18.6 ($-CH-CH_3$), 20.4 (d, $^2J_{C-P} = 10.4$ Hz,

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$-CH-CH_3$), 20.7 (d, $^1J_{C-P} = 9.2$ Hz, $P-CH_2-$), 24.3 (d, $^2J_{C-P} = 16.5$ Hz, $-CH-$), 49.8 ($N-CH_3$), 62.8 (d, $^2J_{C-P} = 11.7$ Hz, $N-CH_2-$), 122.5 (Ph−C), 123.3 (Ph−C), 129.2 (Ph−C), 132.6 (ipso-Ph−C), 133.0 ($\equiv C-$Ph), 137.7 (d, $^2J_{C-P(trans)} = 6.9$ Hz, $\equiv C-$Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): δ (ppm) 59.0. Anal. Calcd for $C_{36}H_{58}N_2Ni_2P_2$ (698.27 g/mol): C, 61.92; H, 8.37; N, 4.01. Found: C, 62.02; H, 8.29; N, 3.98.

(PN)Ni(η^2-^{t}BuC≡CPh) (4). $(^iPr)_2CH_2CH_2NMe_2$ (12.0 mg, 13.3 μL, 0.063 mmol) was added to a suspension of $Ni(COD)_2$ (17.4 mg, 0.063 mmol) in C_6D_6 (0.6 mL). The orange solution was transferred to a vial containing ^{t}BuC≡CPh (10.0 mg, 0.063 mmol). The quantitative formation of the η^2-alkyne complex was confirmed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Subsequently, the solvent and all volatiles were evaporated in vacuo. An orange oil remained, which slowly solidified. **4** (two isomers, **4a** and **4b**) was obtained as an air- and moisture-sensitive orange solid after recrystallization from petroleum ether/THF at $T = -30$ °C. Yield: 9.0 mg (0.022 mmol, 35%). ^1H NMR (C_6D_6): δ (ppm) 0.97 (m, 8 H, ^{i}Pr, $-CH-$), 1.22 (dd, $^3J_{H-P} = 15.6$ Hz, $^3J_{H-H} = 7.1$ Hz, 6 H, ^{i}Pr), 1.43, 1.58 (2×s, 9 H, ^{t}Bu−H), 1.78 (m, 4 H, $-CH_2CH_2-$), 2.30, 2.55 (2×s, 6 H, $N-CH_3$), 7.06 (t, $^3J_{H-H} = 7.1$ Hz, 1 H, *p*-C_6H_5), 7.26 (pseudo-t, 2 H, *m*-C_6H_5), 7.43 (d, $^3J_{H-H} = 7.4$ Hz, 2 H, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ (ppm) 55.8 (7%, **4b**), 57.4 (93%, **4a**). Anal. Calcd for $C_{22}H_{38}NNiP$ (406.25 g/mol): C, 65.04; H, 9.43; N, 3.45. Found: C, 64.82; H, 9.64; N, 3.46.

(PN)Ni(η^2-CF_3C≡CPh) (5). $Ni(COD)_2$ (27.2 mg, 0.099 mmol) was suspended in C_6D_6 (0.5 mL), and $(^iPr)_2CH_2CH_2NMe_2$ (18.7 mg, 20.8 μL, 0.099 mmol) was added. The orange solution was transferred to a vial containing CF_3C≡CPh (16.8 mg, 0.099 mmol). The color changed to yellow, and the quantitative formation of the η^2-alkyne complex was confirmed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The solvent and all volatiles were evaporated in vacuo to afford an orange oil, which slowly solidified. **5** was obtained as an orange, air- and moisture-sensitive solid after recrystallization from petroleum ether/THF at $T = -30$ °C (two isomers, **5a** and **5b** in a ratio of 1:9). Yield: 27.0 mg (0.065 mmol, 66%). ^1H NMR (C_6D_6): δ (ppm) 0.83 (dd, $^3J_{H-P} = 12.6$ Hz, $^3J_{H-H} = 6.9$ Hz, 6 H, ^{i}Pr, **5b**), 0.88 (m, 2 H + 2 H, $-CH-$, **5a**, **5b**), 0.96 (dd, $^3J_{H-P} = 16.3$ Hz, $^3J_{H-H} = 7.1$ Hz, 6 H + 6 H, ^{i}Pr, **5a**, **5b**), 1.16 (dd, $^3J_{H-P} =$, 16.2 Hz, $^3J_{H-H} = 7.6$ Hz, 6 H, ^{i}Pr, **5a**), 1.70 (m, 4 H + 4 H, $-CH_2CH_2-$, **5a**, **5b**), 2.24 (s, 6 H, $N-CH_3$, **5a**), 2.44 (s, 6 H, $N-CH_3$, **5b**), 7.04 (m, 1 H + 1 H, *p*-C_6H_5, **5a**, **5b**), 7.16 (pseudo-t, 2 H, *m*-C_6H_5, **5b**), 7.23 (pseudo-t, 2 H, *m*-C_6H_5, **5a**), 7.56 (d, $^3J_{H-H} = 7.8$ Hz, 2 H, *o*-C_6H_5, **5a**), 7.65 (d, $^3J_{H-H} = 7.1$ Hz, 2 H, *o*-C_6H_5, **5b**). $^{31}P\{^1H\}$ NMR (C_6D_6): δ (ppm) 59.8 (q, $^4J_{P-F} = 11.9$ Hz, *trans*-$P-CF_3$), 61.4 (*cis*-$P-CF_3$). $^{19}F\{^1H\}$ NMR (C_6D_6): δ (ppm) −57.2 (s, *cis*-$P-CF_3$), −54.4 (d, $^4J_{F-P} = 12.9$ Hz, *trans*-$P-CF_3$). Anal. Calcd for $C_{19}H_{29}F_3NNiP$ (418.15 g/mol): C, 54.58; H, 6.99; N, 3.35. Found: C, 54.29; H, 7.08; N, 3.37.

(dippe)Ni(η^2-F_3CC≡CPh) (9). A solution of bis(diisopropylphosphino)ethane (22.6 mg, 0.086 mmol) in C_6D_6 (0.5 mL) was added to $Ni(COD)_2$ (23.7 mg, 0.086 mmol). An orange solution was formed, which was transferred to a vial containing F_3CC≡CPh (14.7 mg, 0.086 mmol). The NMR tube was heated to $T = 55$ °C for 4 h. The formation of the η^2-alkyne complex was confirmed by ^1H, $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectroscopy. Subsequently the solvent and all volatiles were evaporated in vacuo and the residue was recrystallized from petroleum ether/THF at $T = -30$ °C. **9** was obtained as an orange, air- and moisture-sensitive solid. Yield: 14.0 mg (0.029 mmol, 33%). ^1H NMR (C_6D_6): δ (ppm) 0.77 (dd, $^3J_{H-P} = 12.4$ Hz, $^3J_{H-H} = 7.0$ Hz, 6 H, ^{i}Pr), 0.85 (dd, $^3J_{H-P} = 12.6$ Hz, $^3J_{H-H} = 7.0$ Hz, 6 H, ^{i}Pr), 0.93 (dd, $^3J_{H-P} = 16.0$ Hz, $^3J_{H-H} = 7.2$ Hz, 6 H, ^{i}Pr), 1.15 (m, 10 H, ^{i}Pr, $-CH-$), 1.83, 1.95 (2×m, 2 × 2 H, $-CH_2-CH_2-$), 7.05 (t, $^3J_{H-H} = 7.3$ Hz, 1 H, *p*-C_6H_5), 7.21 (pseudo-t, 2 H, *m*-C_6H_5), 7.73 (d, $^3J_{H-H} = 7.7$ Hz, 2 H, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ (ppm) 81.4 (m, *trans*-P−F), 83.4 (d, $^2J_{P-P} = 29.7$ Hz). $^{19}F\{^1H\}$ NMR (C_6D_6): δ (ppm) −55.8 (d, $^4J_{F-P} = 9.1$ Hz). Anal. Calcd for $C_{23}H_{37}F_3NiP_2$ (491.25 g/mol): C, 54.58; H, 6.99. Found: C, 54.58; H, 7.68.

Catalytic Formation of 9,10-Diphenylphenanthrene. A solution of **1** (8.5 mg, 0.02 mmol), diphenylacetylene (42.7 mg, 0.24 mmol), and biphenylene (36.4 mg, 0,24 mmol) in C_6D_6 (0.6 mL) was transferred to a resealable NMR tube. The sample was heated to $T = 70$ °C, and the reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Complete conversion to the disubstituted phenanthrene was achieved within 22.5 h. Subsequently, the solution was diluted in a mixture of pentane and dichloromethane (5 mL) and filtered to remove decomposition products. The solvents and all volatiles were evaporated in vacuo to yield pure 9,10-diphenylphenanthrene (78.0 mg, 0.236 mmol, 98%). ^1H NMR (C_6D_6): δ (ppm) 6.95 (t, $^3J_{H-H} = 7.2$ Hz, 2 H, *p*-C_6H_5), 7.04 (pseudo-t, 4 H, *m*-C_6H_5), 7.10 (d, $^3J_{H-H} = 7.6$ Hz, 4 H, *o*-C_6H_5), 7.30, 7.44 (2×pseudo-t, 2 × 2 H, C_6H_4), 7.76, 8.60 (2×d, $^3J_{H-H} = 8.0$ Hz, 2 × 2 H, C_6H_4). The reaction was repeated with complex **3** (7.0 mg, 0.01 mmol) instead of **1** at $T = 70$ °C. Quantitative formation of 9,10-diphenylphenanthrene from diphenylacetylene (42.7 mg, 0.24 mmol) and biphenylene (36.4 mg, 0.24 mmol) was achieved within 22.5 h. The reaction was worked up as described above to yield 76.0 mg (0.23 mmol, 96%) of 9,10-diphenylphenanthrene.

Catalytic Formation of Hexaphenylbenzene. A solution of **1** (4.7 mg, 0.01 mmol) and diphenylacetylene (20.2 mg, 0.113 mmol) in C_6D_6 (0.6 mL) was transferred to a resealable NMR tube and heated to $T = 70$ °C. The reaction was monitored by ^1H and ^{31}P NMR spectroscopy and went to completion within 60 days. To isolate the organic product, the solution was diluted in dichloromethane (10 mL) and filtered to remove decomposition products. The solvent and all volatiles were evaporated in vacuo to afford pure hexaphenylbenzene (19.3 mg, 96%). ^1H NMR (C_6D_6): δ (ppm) 6.73 (t, $^3J_{H-H} = 7.3$ Hz, 6 H, *p*-C_6H_5), 6.83 (pseudo-t, 12 H, *m*-C_6H_5), 7.12 (d, $^3J_{H-H} = 7.1$ Hz, 12 H, *o*-C_6H_5).

Catalytic Formation of 9-Phenyl-10-*tert*-butylphenanthrene (6). A solution of **4** (20.3 mg, 0.05 mmol), biphenylene (45.0 mg, 0.3 mmol), and ^{t}BuC≡CPh (46.8 mg, 0.3 mmol) was transferred to a resealable NMR tube and heated to $T = 40$ °C. The reaction was monitored by ^1H NMR spectroscopy. Within 16 days the organic product was quantitatively generated. The solution was diluted in a mixture of pentane and chloroform (5 mL) and filtered to remove decomposition products. The solvents and all volatiles were evaporated in vacuo, and the residue was recrystallized from acetone at $T = -30$ °C to afford colorless crystals. Yield: 77.3 mg (0.25 mmol, 83%). ^1H NMR (C_6D_6): δ (ppm) 1.42 (s, 9 H, ^{t}Bu), 7.23 (d, $^3J_{H-H} = 8.5$ Hz, 1 H), 7.33 (m, 3 H), 7.44 (m, 3 H), 7.55 (m, 3 H), 8.61 (d, $^3J_{H-H} = 8.9$ Hz, 1 H), 8.66 (d, $^3J_{H-H} = 7.5$ Hz, 1 H), 8.76 (d, $^3J_{H-H} = 8.0$ Hz, 1 H). Anal. Calcd for $C_{24}H_{22}$ (310.44 g/mol): C, 92.86; H, 7.14. Found: C, 93.04; H, 7.36.

Catalytic Formation of Tris(trifluoromethyl)triphenylbenzene (7, 8). A solution of **5** (6.5 mg, 0.016 mmol) and F_3CC≡CPh (31.7 mg, 0.187 mmol) in C_6D_6 (0.6 mL) was heated to $T = 70$ °C in a resealable NMR tube. The reaction was monitored by ^1H and $^{19}F\{^1H\}$ NMR spectroscopy. Within 4.5 h the benzene derivatives **7** and **8** were generated quantitatively. The solution was diluted in pentane (5 mL), and decomposition products were removed by filtration. The solution was concentrated to ∼2 mL and stored at $T = -30$ °C. A mixture of **7** and **8** (ratio 3:7) was obtained as a colorless solid after decanting the mother liquor and drying the residue in vacuo. Yield: 25.0 mg (0.049 mmol, 79%). $^{19}F\{^1H\}$ NMR (C_6D_6): δ (ppm) −55.9 (q, $J_{F-F} = 16.6$ Hz, 3 F, **8**), −54.6 (q, $J_{F-F} = 16.6$ Hz, 3F, **8**), −52.9 (s, 3 F, **8**), −51.4 (s, **7**). Anal. Calcd for $C_{27}H_{15}F_9$ (510.42 g/mol): C, 63.54; H, 2.96. Found: C, 63.37; H, 3.28.

Acknowledgment is made to the U.S. Department of Energy, grant FG02-86ER13569, for their support of this work. C.M. thanks the Deutsche Forschungsgemeinschaft (DFG) for a postdoctoral fellowship. We also thank Dr. Nicole Brunkan for assistance with compound characterization.

Supporting Information Available: Details of data collection parameters, bond lengths, bond angles, fractional atomic coordinates, and anisotropic thermal parameters for **1** and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0110989