Catalytic Carbon−Carbon Bond Activation and Functionalization by Nickel Complexes

Brian L. Edelbach, Rene J. Lachicotte, and William D. Jones*

Department of Chemistry, University of Rochester, Rochester, New York 14627

Received May 24, 1999

The nickel alkyne complexes (dippe)Ni(PhC≡CPh), **1**, (dippe)Ni(MeC≡CMe), **2**, (dippe)-Ni($MeO_2CC{\equiv}CCO_2Me$), **3**, (dippe)Ni($CH_3OCH_2C{\equiv}CCH_2OCH_3$), **4**, and (dippe)Ni($CF_3C{\equiv}CCF_3$), **5**, were synthesized (dippe = bis(diisopropylphosphino)ethane) and characterized by ^{1}H, ^{31}P, and ^{13}C{^{1}H} NMR spectroscopy. Complexes **1**, **2**, and **3** were characterized by X-ray crystallography. The thermolysis of complex **1** or **2** (120 °C) in the presence of excess biphenylene and excess alkyne results in very slow catalytic formation of the corresponding 9,10-disubstituted phenanthrene. However, addition of ∼6 mol % O_2 (based on the metal complex) to the reaction mixture results in an acceleration in catalysis at lower temperatures (∼70−80 °C). The thermolysis of complexes **3** or **4** with excess biphenylene and excess alkyne leads to the alkyne cyclotrimerization product as the major organic species formed in the reaction. Fluorenone was catalytically produced by heating (dippe)Ni$(CO)_2$, biphenylene, and CO. Catalytic insertion of 2,6-xylylisocyanide into the strained C−C bond of biphenylene was also achieved by heating (dippe)Ni(2,6-xylylisocyanide)$_2$, excess biphenylene, and 2,6-xylylisocyanide. Mechanistic schemes are proposed for these reactions.

Introduction

Homogeneous C−C bond cleavage and functionalization by transition metal complexes is currently an active area of research in organometallic chemistry. Stoichiometric C−C bond activation by several metal complexes has been reported.[1] Most of these examples rely on relief of ring strain,[2] attainment of aromaticity,[3] or intramolecular addition in which the C−C bond is forced into close proximity to the metal.[4]

Catalytic C−C bond activation is less common,[2k,4a,5] and most of these examples also rely on relief of ring strain. For example catalytic hydrogenolysis of biphenylene to biphenyl has been reported using (C_5Me_5)Rh-(PMe_3)H_2[5e] and several platinum, palladium, and nickel phosphine complexes.[5i] Recently, we reported that tetraphenylene can be formed catalytically from biphenylene via catalytic carbon−carbon bond activation and formation by platinum and palladium phosphine complexes.[5g] Ito et al. were able to catalytically cleave two C−C bonds of strained spiro cyclobutanones using a rhodium(I) species.[5j] Liebeskind has also used Ni$(COD)_2$ to catalyze the insertion of acetylenes into the C−C bonds of cyclobutenones to give phenols.[5l]

Catalytic cleavage of strong C−C bonds by homogeneous metal complexes is a very recent development. Milstein and co-workers reported the catalytic hydro-

(1) Murakami, M.; Yoshihiko, I. In *Topics in Organometallic Chemistry. Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer: New York, 1999; Vol. 3.

(2) (a) Adams, D. M.; Chatt, J.; Guy, R. G.; Sheppard, N. *J. Chem. Soc.* **1961**, 738−742. (b) Bailey, N. A.; Gillard, R. D.; Keeton, M.; Mason, R.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1966**, 396−398. (c) McQuillin, F. J.; Powell, K. C. *J. Chem. Soc., Dalton Trans.* **1972**, 2123-2129. (d) Barretta, A.; Cloke, F. G. N.; Feigenbaum, A.; Green, M. L. H.; Gourdon, A.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1981**, 156−158. (e) Baretta, A.; Chong, K. S.; Cloke, F. G. N.; Feigenbaum, A.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1983**, 861−864. (f) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795−1803. (g) Eisch, J. J.; Piotrowski, A. M.; Han, K. I.; Krüger, C.; Tsay, Y. H. *Organometallics* **1985**, *4*, 4−231. (h) Schwager, H.; Spyroudis, S.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1990**, *382*, 191−200. (i) Lu, Z.; Jun, C.-H.; de Gala, S. R.; Sigalas, M.; Eisenstein, O.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1993**, 1877−1880. (j) Lu, Z.; Jun, C.-H.; de Gala, S. R.; Eisenstein, O.; Crabtree, R. H. *Organometallics* **1995**, *14*, 1168−1175. (k) Perthuisot, C.; Edelbach, B. E.; Zubris, D. L.; Jones, W. D. *Organometallics* **1997**, *16*, 2016−2023. (l) Shaltout, R. M.; Sygula, R.; Sygula, A.; Fronczek, F. R.; Stanley, G. G.; Rabideau, P. W. *J. Am. Chem. Soc.* **1997**, *120*, 8835−836.

(3) (a) Kang, J. W.; Moseley, K.; Maitlis, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 5970−5977. (b) Benfield, F. W. C.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324−1331. (c) Eilbracht, P. *Chem. Ber.* **1976**, *109*, 9, 1429. (d) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222−7227. (e) Hemond, R. C.; Hughes, R. P.; Locker, H. B. *Organometallics* **1986**, *5*, 2391−2392. (f) Jones, W. D.; Maguire, J. A. *Organometallics* **1987**, *6*, 1301−1311.

(4) (a) Suggs, J. W.; Jun, C.-H. *J. Chem. Soc., Chem. Commun.* **1985**, 92−93. (b) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699−701. (c) Gozin, M.; Aizenberg, M.; Liou, S.-Y.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1994**, *370*, 42−44. (d) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1165−1166. (e) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 9774−9775. (f) Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406−12415. (g) Gandelman, M.; Vigalok, A.; Shimon, L. J. W.; Milstein, D. *Organometallics* **1997**, *16*, 3981−3986. (h) van der Boom, M. E.; Ben-David, Y.; Milstein, D. *Chem. Commun.* **1998**, 917−918. (i) van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 13415.

(5) (a) Noyori, R.; Kumagai, Y.; Umeda, I.; Takaya, H. *J. Am. Chem. Soc.* **1972**, *94*, 4018. (b) Kaneda, K.; Azuma, H.; Wayaku, M.; Teranishi, S. *Chem. Lett.* **1974**, 215. (c) Fujimura, T.; Aoki, S.; Nakamura, E. *J. Org. Chem.* **1991**, *56*, 2809, and references therein. (d) Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1991**, *113*, 2771. (e) Perthuisot, C.; Jones, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 3647−3648. (f) Murakami, M.; Amii, H.; Shigeto, K.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 8285−8290. (g) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843−2853. (h) Liou, S.-Y,; van der Boom, M. E.; Milstein D. *Chem. Commun.* **1998**, 687−688. (i) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4784−4794. (j) Murakami, M.; Takahashi, K.; Amii, H.; Ito, Y. *J. Am. Chem. Soc.* **1997**, *121*, 99307-9308. (k) Jun, C.-H.; Lee, H. *J. Am. Chem. Soc.* **1999**, *121*, 880−881. (l) Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1991**, *113*, 2771.

10.1021/om990387i CCC: $15.00 © 1999 American Chemical Society
Publication on Web 08/17/1999

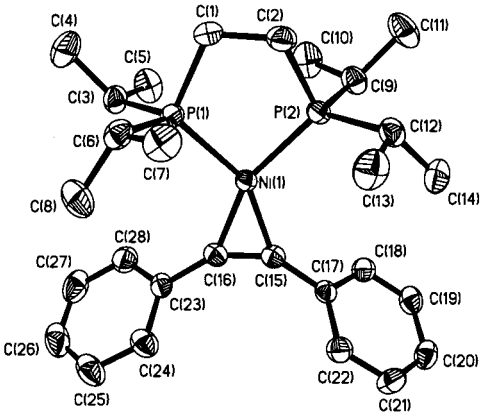


Figure 1. ORTEP drawing of (dippe)Ni(PhC≡CPh), **1**. Selected distances (Å): Ni(1)–C(16), 1.877(2); Ni(1)–C(15), 1.881(2); Ni(1)–P(1), 2.1468(6); Ni(1)–P(2), 2.1509(6); C(15)–C(16), 1.285(3).

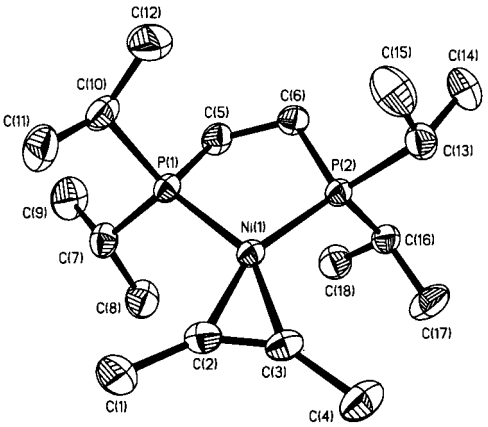


Figure 2. ORTEP drawing of (dippe)Ni(MeC≡CMe), **2**. Selected distances (Å): Ni(1)–C(2), 1.877(2); Ni(1)–C(3), 1.888(2); Ni(1)–P(1), 2.1370(5); Ni(1)–P(2), 2.1433(5); C(2)–C(3), 1.279(3).

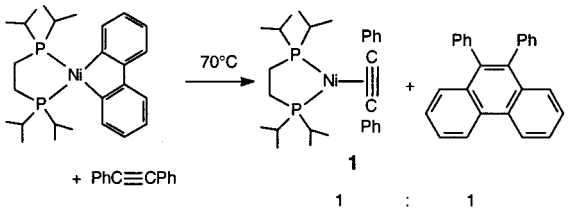
genolysis and hydrosilation of a strong C–C bond using a rhodium complex.[5h] The cleavage was aided by "forcing" the C–C bond into the proximity of the metal center. Jun and Lee reported homogeneous catalytic C–C bond cleavage of unstrained ketones.[5k] In this case, the cleavage was facilitated by chelation assistance of 2-amino-3-picoline to a rhodium(I) complex.

In this work we demonstrate that nickel complexes can catalytically functionalize biphenylene with alkynes, CO, and isocyanides to give 9,10-disubstituted phenanthrenes, fluorenone, and fluorene imines, respectively. Catalytic cycles are proposed for the various systems that were evaluated.

Results and Discussion

Preparation and Characterization of Nickel Alkyne Phosphine Complexes. Several different methodologies were used to prepare the acetylene nickel(0) phosphine complexes employed in this study. The first method involved the addition of the alkyne to (dippe)Ni(COD). In the second method the alkyne was added to $[(dippe)Ni(H)]_2$. In a third method, $(dippe)NiCl_2$ was reduced to nickel(0) with Na(Hg) amalgam in the presence of the alkyne. While the latter method oftentimes gave the highest yield, the ease of workup in the first method made it the preferred procedure in most cases. The following new compounds were synthesized via method 1: (dippe)Ni(PhC≡CPh), **1**, (dippe)Ni(MeC≡CMe), **2**, (dippe)Ni($MeO_2CC{\equiv}CCO_2Me$), **3**, (dippe)Ni($CH_3OCH_2C{\equiv}CCH_2OCH_3$), **4**, and (dippe)Ni($CF_3C{\equiv}CCF_3$), **5**. These compounds were characterized by ^1H, ^{31}P, and $^{13}C\{^1H\}$ NMR spectroscopy. Compound **5** was also characterized by ^{19}F NMR spectroscopy. The $^{13}C\{^1H\}$ resonances of the alkyne carbons are similar to those reported for other bis(phosphine)nickel(0) acetylene complexes.[6] Compounds **1**, **2**, and **3** were also characterized by X-ray crystallography (Figures 1–3). These compounds are distorted square-planar complexes (the alkyne is in the plane) with carbon–carbon triple-bond distances similar to those reported for other nickel(0) alkyne complexes with electron-donating chelating phosphines.[7]

Catalytic Formation of 9,10-(disubstituted)-Phenanthrenes. In 1985 Eisch et al. formed 9,10-diphenylphenanthrene in greater than 50% yield by heating $(PEt_3)_2Ni$(2,2′-biphenyl) at 70 °C in the presence of diphenylacetylene.[8] Wakatsuki et al. also formed 9,10-diphenylphenanthrene in 45% yield by heating diphenylacetylene and $CpCo(PPh_3)$(2,2′-biphenyl) at 95 °C for 3 days.[9] We obtained a similar result by heating a mixture of diphenylacetylene (2 equiv) and (dippe)Ni-(2,2′-biphenyl) at 70 °C. This procedure leads to the quantitative formation of 9,10-diphenylphenanthrene and complex **1** (eq 1).



(1)

To test whether the formation of 9,10-diphenylphenanthrene could be made catalytic, a mixture of complex **1** (0.028 M), biphenylene (8 equiv), and diphenylacetylene (8 equiv) was heated in toluene-d_8 at 110 °C in a resealable NMR tube for 40 h. Only a small amount of 9,10-diphenylphenanthrene had formed after this time (~0.2 turnovers). The only metal-containing compound observed by ^1H and ^{31}P NMR spectroscopy was complex **1**. However, if oxygen (~6 mol % based on complex **1**) is introduced to the NMR tube (via the addition of air), the turnover rate for the formation of 9,10-diphenylphenanthrene increases dramatically (~3 turnovers/h at 70 °C). The only metal complex identified by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy is compound **1**. A small

(6) Bartik, T.; Happ, B.; Iglewsky, M.; Bandmann, H.; Boese, R.; Heimbach, P.; Hoffmann, T.; Wenschuh, E. *Organometallics* **1992**, *11*, 1235.

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

(8) Eisch, J. J.; Piotrowski, A. M.; Han, K. I.; Krüger, C.; Tsay, Y. H. *Organometallics* **1985**, *4*, 224.

(9) Wakatsuki, Y.; Nomura, O.; Tone, H.; Yamazaki, H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1344.

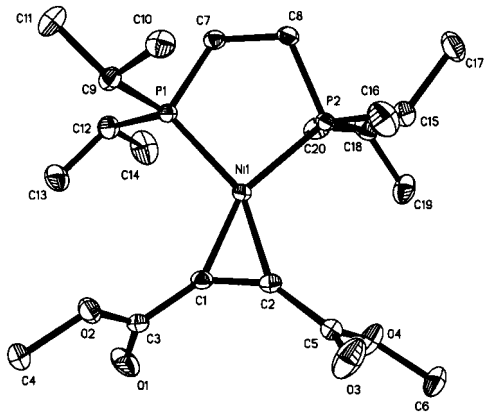


Figure 3. ORTEP drawing of (dippe)Ni($MeO_2CC{\equiv}CCO_2$-Me), **3**. Selected distances (Å): Ni(1)−C(1), 1.871(2); Ni(1)−C(2), 1.871(2); Ni(1)−P(1), 2.1491(5); Ni(1)−P(2), 2.1499(5); C(1)−C(2), 1.290(3).

amount of bis(diisopropylphosphino)ethane dioxide (δ, 52.0), bis(diisopropylphosphino)ethane monoxide (δ 51.2, J = 35 Hz and 9.8, J = 35 Hz, THF-d_8), and a pair of resonances with an AB pattern at δ 52.5 and 45.5 could also be detected in the $^{31}P\{^1H\}$ spectrum of the reaction mixture. Furthermore, the resonances in both the ^{31}P and ^1H NMR spectra were considerably broadened. A small amount of hexaphenylbenzene was observed by ^1H NMR spectroscopy as well as by GC/MS. Presumably, hexaphenylbenzene arises as a result of the catalytic cyclotrimerization of diphenylacetylene by a nickel species in the reaction mixture.[10] If complex **1** and diphenylacetylene are heated at 70 °C in the absence of biphenylene or added O_2, hexaphenylbenzene is formed catalytically.

Other alkynes were tested as potential organic precursors for the catalytic formation of 9,10-(disubstituted)phenanthrenes. In each case (dippe)Ni(alkyne), biphenylene, and the appropriate alkyne were combined in a resealable NMR tube. Oxygen (~6 mol % based on the nickel complex) was introduced via the addition of air. The mixture was then heated, and the reaction was monitored by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. The results are summarized in Scheme 1.

The reaction of complex **2** with dimethylacetylene, biphenylene, and O_2 produced 9,10-dimethylphenanthrene catalytically (~1 TO/h at 70 °C in toluene-d_8). No hexamethylbenzene was observed by ^1H NMR spectroscopy or GC/MS. The reaction of (dippe)Ni(HC≡CH) with acetylene, biphenylene, and O_2 in THF-d_8 at 85 °C produced a black intractable solid, presumably polyacetylene,[11] as the major product. The polymerization of acetylene by several metal catalysts has been reported.[11b] Traces of benzene and phenanthrene were observed in the ^1H NMR spectrum and by GC/MS.

The use of acetylenes with electron-withdrawing substituents led to the formation of more cyclotrimerization product relative to the phenanthrene product. The reaction of **4** with 1,4-dimethoxy-2-butyne and biphenylene in toluene at 70 °C resulted in the formation of the cyclotrimerization product hexakis(methoxymethyl)benzene and 9,10-bis(methoxymethyl)phenanthrene in a 7:1 ratio (based on ^1H NMR spectroscopy). Heating a THF mixture of complex **3** with dimethyl acetylenedicarboxylate and biphenylene at 85 °C results in exclusive formation of the cyclotrimerization product benzenehexacarboxylic acid hexamethyl ester. Perhaps the alkyne with the most electron-withdrawing substituents is hexafluoro-2-butyne. Hexafluoro-2-butyne was reacted with complex **5** and biphenylene at 85 °C in THF-d_8 in a resealable NMR tube. An orange solid formed when the reaction mixture was cooled to room temperature, assigned as the polymer of hexafluoro-2-butyne.[12] Neither the cyclotrimerization product nor the phenanthrene product was observed by high temperature (65 °C) ^1H or ^{19}F NMR spectroscopy.

Mechanism of Phenanthrene Formation. Several observations offer suggestions as to the possible mechanism of these reactions. As mentioned earlier the formation of 9,10-(diphenyl)phenanthrene is extremely slow without prior addition of O_2 to the reaction mixture, even at elevated temperatures (120 °C). However, heating a mixture of (dippe)Ni(PhC≡CPh), diphenylacetylene, and biphenylene at 70 °C following the addition of ~6 mol % O_2 results in the rapid formation of 9,10-(diphenyl)phenanthrene as well as a small amount of bis(diisopropylphosphino)ethane dioxide. The resonances in the ^1H NMR spectrum of the sample are broad under these conditions, but the resonances in the ^1H NMR spectrum sharpen if this solution is degassed and filtered to remove any suspended particles. Continued heating of the mixture results in the catalytic formation of 9,10-diphenylphenanthrene at approximately the same turnover rate as before filtering and O_2 removal. If a small amount of dippe is added to the reaction mixture at this point, catalysis stops. If a sufficient amount of O_2 is admitted to oxidize the excess phosphine as well as a small amount of (dippe)Ni(PhC≡CPh), the catalytic formation of 9,10-diphenylphenanthrene continues. Addition of *1 equiv* of O_2 (relative to the metal complex) to a reaction mixture containing (dippe)Ni(PhC≡CPh), diphenylacetylene, and biphenylene results in the formation of bis(diisopropylphosphino)ethane dioxide, free acetylene, and "Ni metal". Heating this reaction mixture does not give 9,10-diphenylphenanthrene. If an aliquot of a spent catalytic reaction is added to an NMR tube containing (dippe)Ni(PhC≡CPh), diphenylacetylene, and biphenylene and the mixture is then heated at 85 °C without added O_2, 9,10-diphenylphenanthrene is formed catalytically, albeit at a somewhat slower rate.

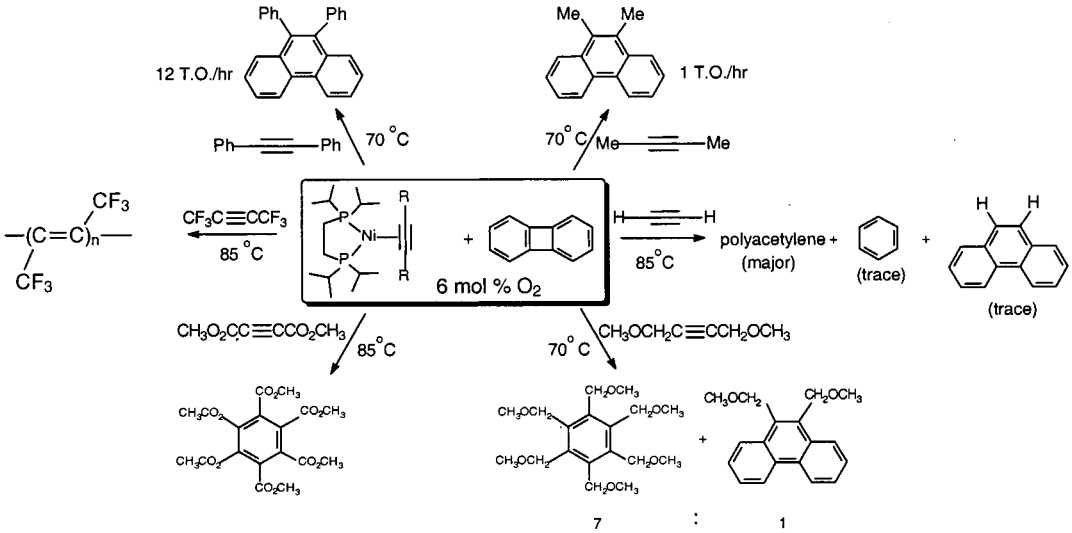
Other related complexes were examined for the similar catalytic formation of phenanthrene. An NMR tube containing (bipy)Ni(PhC≡CPh) (bipy = bipyridine), diphenylacetylene, and biphenylene was heated at 85 °C in THF-d_8. 9,10-(Diphenyl)phenanthrene was formed catalytically, but the turnover rate was slower (~1.2 TO/h) than that observed with the (dippe)Ni(PhC≡CPh) and added O_2. Addition of ~6 mol % O_2 (via addition of air) to the reaction mixture had *no effect* on the turnover

(10) The cyclotrimerization of substituted acetylenes by nickel complexes is well-known. For example see: Reppe, W.; von Kutepow, N.; Magin, A. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 7. Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic Press: New York, 1975; Vol. 2. Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1998**, *120*, 1672, ref 3.

(11) (a) Daniels, W. E. *J. Org. Chem.* **1964**, *29*, 2936. (b) Shirakawa, H. *Synth. Met.* **1995**, *69*, 3. (c) Shirakawa, H. *Mol. Cryst. Liq. Cryst.* **1989**, *171*, 235.

(12) Nishimura. S.; Nagai, A.; Takahashi, A.; Narita, T.; Hagiwara, T.; Hamana, H. *Macromolecules* **1992**, *25*, 1648.

Scheme 1



rate. Except for slight broadening of the resonances in the ^{1}H NMR spectrum, no other changes were observed upon addition of O_2.

The phosphine-free complex $Ni_2(COD)_2(PhC{\equiv}CPh)$[13] was added to a THF solution of diphenylacetylene and biphenylene. The ^{1}H NMR spectrum reveals an equilibrium between the dimer $Ni_2(COD)_2(PhC{\equiv}CPh)$ and the monomer (COD)Ni(PhC≡CPh). Heating the mixture at 85 °C initially leads to the formation of hexaphenylbenzene, COD, and a small amount of 9,10-diphenylphenanthrene. However, with continued heating more COD is released and the rate of formation of 9,10-diphenylphenanthrene exceeds that of hexaphenylbenzene. No change in the rate of formation of phenanthrene is observed when a 2:1 mixture of complex **1** and $Ni_2(COD)_2(PhC{\equiv}CPh)$ is heated at 85 °C with diphenylacetylene and biphenylene. The concentration of complex **1** is unchanged over the course of the reaction.

The complex $(PPh_3)_2Ni(PhC{\equiv}CPh)$[14] was found to also be an excellent catalyst for the insertion of diphenylacetylene into biphenylene in the presence of O_2. A solution containing $Ni(PPh_3)_2(PhC{\equiv}CPh)$ (0.024 M) and equimolar substrates (0.25 M each) gave about a 20% yield of diphenylphenanthrene upon standing for 24 h following addition of 8% O_2. A small quantity of $O{=}PPh_3$ was seen by ^{31}P NMR spectroscopy (δ 26.03, ~3%). Heating the THF solution to 60 °C resulted in the complete conversion to product in 15–20 min.

One possible mechanism for the catalytic formation of these phenanthrenes may involve reversible loss of the coordinated alkyne to give [(dippe)Ni(0)]. The C–C bond of biphenylene is then cleaved by [(dippe)Ni(0)], resulting in the formation of (dippe)Ni(2,2-biphenyl). Alkyne coordination to give a five-coordinate complex followed by insertion of alkyne into the Ni–aryl bond and reductive elimination of phenanthrene regenerates (dippe)Ni(0). In the absence of added O_2 this mechanism may well be operating, albeit slowly. Huggins and Bergman established that for complexes of the type $Ni(acac)(L)CH_3$ (where L = phosphine) the alkyne must enter a square-planar coordination site prior to insertion. They noted that insertion of alkynes into the metal alkyl bond is preceded by loss of phosphine.[15] Samsel and Norton arrived at similar conclusions for intramolecular acetylene insertion into Pd–carbon bonds.[16] In the present case the chelating dippe ligand disfavors phosphine dissociation, thereby decreasing the likelihood of forming a square-planar intermediate with the alkyne in that plane.

The addition of O_2 might facilitate the loss of coordinated alkyne by oxidizing (dippe)Ni(PhC≡CPh) to give the cationic nickel species $[(dippe)Ni(PhC{\equiv}CPh)]^+$. If loss of alkyne and subsequent cleavage of biphenylene is more rapid from $[(dippe)Ni(PhC{\equiv}CPh)]^+$ than from the neutral species, the rate of catalysis might increase, providing that insertion into the Ni–aryl bond is accessible in this case. To test this hypothesis, two oxidizing agents more potent than O_2 were tested: 1,1′-diacetylferrocene silver tetrafluoroborate (+0.49 V vs Fc) and $Fe(bipy)_3(PF_6)_2$ (+0.66 V vs Fc).[17] A THF solution of (dippe)Ni(PhC≡CPh), diphenylacetylene, biphenylene, and 6 mol % (based on **1**) 1,1′-diacetylferrocene silver tetrafluoroborate was heated at 85 °C. No 9,10-diphenylphenanthrene was observed after 12 h. Addition of ~10 mol % O_2 and continued heating resulted in catalytic formation of 9,10-diphenylphenanthrene. A similar reaction using $Fe(bipy)_3(PF_6)_2$ as the oxidizing agent did not lead to the production of 9,10-diphenylphenanthrene under similar conditions. These observations argue against oxidation of the metal acetylene complex by O_2.

The rate of catalysis was monitored as a function of O_2 concentration. Six NMR tubes were prepared, each containing **1**, biphenylene (10 equiv), and diphenylphenanthrene (10 equiv) in THF-d_8. Various amounts of oxygen (6, 13, 20.5, 28, 40, and 52 mol % based on **1**) were admitted (via air) to the NMR tubes. A $^{31}P\{^1H\}$ NMR spectrum of the mixtures after addition of O_2 revealed a small amount of bis(diisopropylphosphino)-

(13) Muetterties, E. L.; Pretzer, W. R.; Thomas, M. G.; Beier, B. F.; Thorn, D. L.; Day, V. W.; Anderson, A. B. *J. Am. Chem. Soc.* **1978**, *100*, 2090.
(14) Rosenthal, U. *Z. Anorg. Allg. Chem.* **1981**, *482*, 179. Greaves, E. O.; Lock, C. J. L.; Maitlis, P. M. *Can. J. Chem.* **1968**, *46*, 3879.
(15) Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002.
(16) Samsel, E. G.; Norton, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 5505.
(17) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

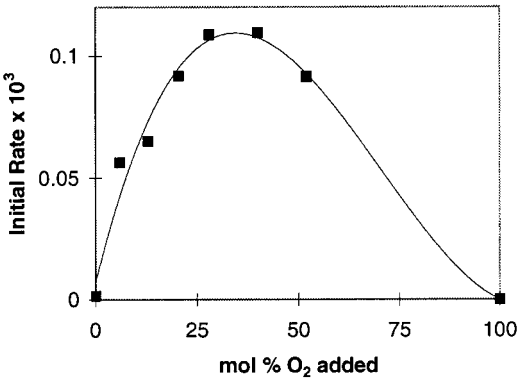


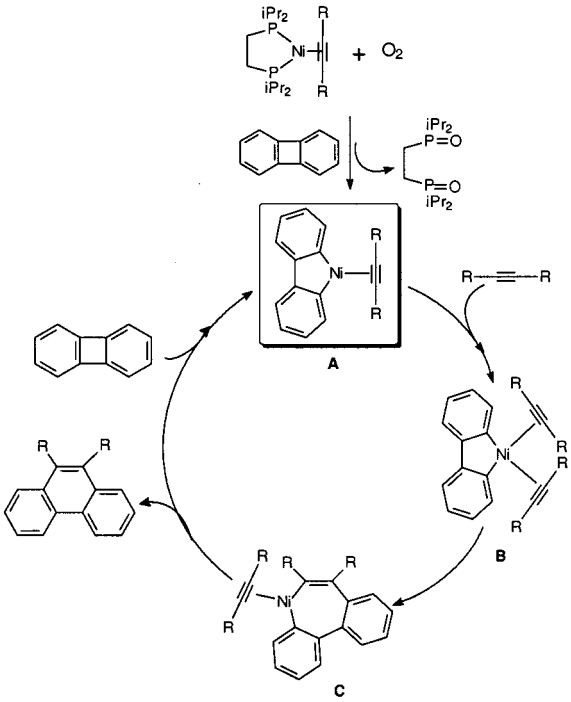
Figure 4. Initial rate of formation of 9,10-diphenylphenanthrene vs mol % O_2 for the reaction of **1** (0.030 M) with diphenylacetylene (0.30 M) and biphenylene (0.30 M) at 60 °C. The initial rate (M^{-1} s^{-1}) was calculated from the slope of concentration of 9,10-diphenylphenanthrene vs time during the first 10 min of reaction.

ethane dioxide and bis(diisopropylphosphino)ethane monoxide and the two doublet of doublets resonances at δ 52.5 and 45.6. The latter resonances are consistent with the formation of a Ni complex coordinated to one bis(isopropyl) phosphine, while the other bis(isopropyl) phosphine is oxidized and no longer coordinated to the metal center. The concentration of all these species increased relative to **1** as more O_2 was admitted. The NMR tubes were heated at 60 °C, and the initial rate of catalysis was monitored via ^{1}H NMR spectroscopy. The results are displayed in Figure 4. Increasing the concentration of O_2 increases the initial rate of catalysis moderately up to ~30−40 mol % O_2, after which point additional O_2 leads to a decrease in the rate of catalysis. All of the reactions went to completion with the exception of the 6 mol % O_2 reaction, which stopped with ~2 equiv of biphenylene and diphenylphenanthrene remaining. A ^{31}P{^{1}H} NMR spectrum of the mixtures after consumption of biphenylene and phenanthrene revealed no changes in the relative amounts of the phosphine-containing species.

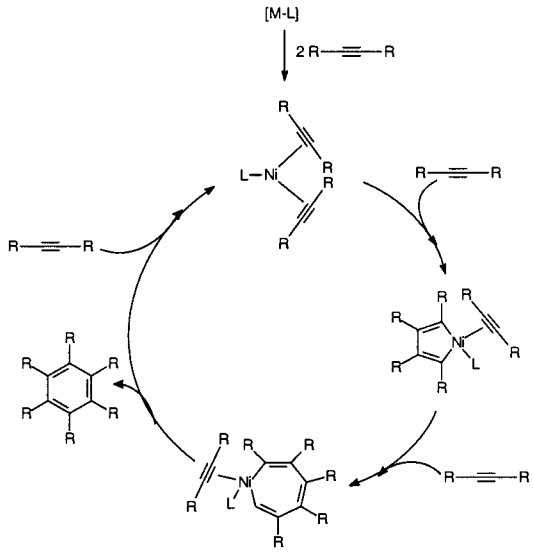
Given the observations discussed above, the following conclusions can be drawn. First, O_2 can be ruled out as a one-electron oxidizing agent in these reactions since oxidants stronger than O_2 had no effect on the rate of catalysis. Second, oxygen is not required once catalysis begins, as it can be removed and catalysis continues. Third, coordinated phosphine is not required for the catalysis since $Ni_2(COD)_2(PhC{\equiv}CPh)$ and (bipy)Ni(PhC≡CPh) work. These observations imply that the role of oxygen might simply be to remove the phosphine ligand from the metal center (as phosphine oxide), thereby forming a more active catalyst.

Since we were unable to observe the active catalyst spectroscopically, we can only speculate as to its structure. The catalytic cycle depicted in Scheme 2 represents a plausible mechanistic pathway for the formation of 9,10-disubstituted phenanthrenes. The addition of O_2 leads to release of the phosphine in its oxidized form. Subsequent cleavage of the strained C−C bond in biphenylene by the putative Ni(0) species results in the formation of intermediate **A** (Scheme 2). This complex coordinates a second acetylene molecule to generate **B**. While the structure of **B** is unlikely to be a square-planar complex, if one of the alkynes is coordinated in

Scheme 2



Scheme 3



the plane of the biphenyl group, rapid insertion into the Ni−C bond can occur, generating compound **C**. Complex **C** can reductively eliminate the phenanthrene and regenerate **A**. Intermediates **A**, **B**, and **C** would all display only aromatic resonances in the ^{1}H NMR spectrum and would be difficult to identify under the reaction conditions.

This catalytic cycle is similar to the commonly accepted mechanism for the cyclotrimerization of alkynes outlined in Scheme 3.[18] In the present case, after the reductive elimination of the organic product, C−C cleavage of biphenylene gives the boxed species **A** rather than the bis(η^2-coordinated)alkyne complex depicted in Scheme 3. It has been established that the nickel(0)−alkyne bond strength is greatest for compounds containing donor ligands and/or acetylenes with electron-

(18) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081.

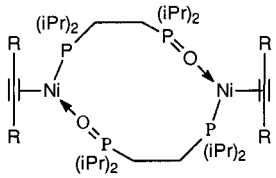


Figure 5. Possible structure of oxidized intermediate.

withdrawing groups. Furthermore, the degree of complexation is directly proportional to the rate of cyclotrimerization of alkynes.[19] This may account for the relative increase in cyclotrimerization to phenanthrene formation when alkynes with acceptor groups are employed.

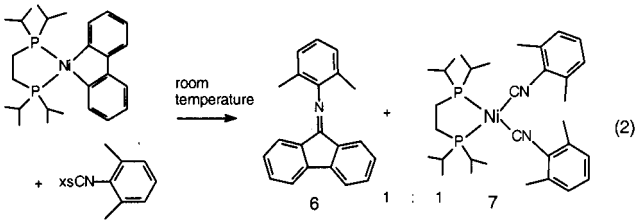
Another possible intermediate in the formation of the phenanthrenes may be the dimer shown in Figure 5. In this case one arm of the bis(phosphine) is oxidized and coordinated to one metal center, while the other phosphine is coordinated to a different metal center. As discussed above, the $^{31}P\{^1H\}$ spectrum displayed resonances for a species with an A_2B_2 pattern. A simulated fit of these NMR resonances is consistent with the structure depicted in Figure 5 (see Supporting Information). Release of the oxygenated phosphine from a nickel would result in a 14-electron Ni(0) complex capable of cleaving the C–C bond of biphenylene. Subsequent insertion of acetylene and reductive elimination of the phenanthrene regenerates a Ni(0) species. The rate of catalysis should increase as the concentration of this complex increases if such a species is an intermediate in the catalytic formation of phenanthrenes. While the concentration of this compound was largest upon addition of 52 mol % O_2 (based on **1**), the initial rate of catalysis was decreased relative to addition of 40 mol % O_2. This observation is inconsistent with a monooxidized phosphine Ni complex being an intermediate in the major pathway to phenanthrene formation. However the intermediate shown in Figure 5 cannot be ruled out as part of an alternative pathway for the formation of phenanthrenes.

Catalytic Carbonylation of Biphenylene. Previously we have demonstrated that $(C_5Me_5)Rh(CO)_2$ reacts with biphenylene in the presence of CO to give fluorenone catalytically.[2k] In the present study we found that (dippe)Ni(2,2′-biphenyl) reacted with biphenylene under a CO atmosphere at room temperature to give fluorenone and (dippe)$Ni(CO)_2$ in a 1:1 ratio (based on ^1H NMR spectroscopy). Eisch et al. obtained similar results when they treated $(PEt_3)_2Ni$(2,2′-biphenyl) with CO at −78 °C.[8] Fluorenone was also formed in 43% yield by mixing $CpCo(PPh_3)$(2,2′-biphenyl) and CO at room temperature.[9]

Heating a THF-d_8 mixture of (dippe)$Ni(CO)_2$ at 95 °C with 5 equiv of biphenylene under an atmosphere of CO resulted in the catalytic formation of fluorenone (~2 TO/day). The resting state species is (dippe)$Ni(CO)_2$. Scheme 4 shows the proposed mechanism for the formation of fluorenone. The first step is reversible loss of CO from the resting state species (dippe)$Ni(CO)_2$ to give the putative 14-electron complex (dippe)Ni(CO). This is followed by carbon–carbon bond cleavage of biphenylene and CO insertion into the Ni–C bond of the coordinated biphenyl. Displacement of fluorenone by CO regenerates (dippe)Ni(CO). Coordination of CO to (dippe)Ni(CO) to form (dippe)$Ni(CO)_2$ is probably more rapid than cleavage of biphenylene, which is consistent with the observation that the resting state species is (dippe)$Ni(CO)_2$.

There is spectroscopic evidence for the formation of compound **X** under certain conditions. If the reaction is performed in an NMR tube with thorough mixing, an orange solution results and the only nickel species observed in the ^1H and ^{31}P NMR spectra is (dippe)Ni-$(CO)_2$. However, if CO mixing is inefficient, as in an unshaken NMR tube, the solution is red. A ^1H NMR spectrum of the red sample displays four isopropyl methyl resonances at δ 1.450 (J_{P-H} = 15.2, 7.1 Hz), 1.364 (J_{P-H} = 13.4, 7.1 Hz), 0.662 (J_{P-H} = 13.4, 7.0 Hz), and 0.316 (J_{P-H} = 15.3, 7.1 Hz) as well as new aromatic resonances (some are obscured by fluorenone). The ^{31}P NMR spectrum displays two new doublets at δ 77.52 (J_{P-P} = 55.2 Hz) and 69.16 (J_{P-P} = 56.4 Hz), consistent with a nickel species containing inequivalent phosphines. Compound **X** has inequivalent phosphines by virtue of CO insertion into the Ni–C bond, and the isopropyl methyl groups on each phosphorus are diastereotopic. The fact that this compound is only observed under CO-deficient conditions is consistent with the CO-facilitated reductive elimination of fluorenone from **X**.

Catalytic Production of Fluorene Imines. The migratory insertion of isocyanides, CNR, into metal–carbons bonds is a well-known reaction in organometallic chemistry. Insertion of isocyanides into Ni–aryl bonds has been established.[20] Insertion of isocyanide into a Co–aryl bond was accomplished by heating a mixture of 2,6-xylyl isocyanide and CpCo-(PPh_3)(2,2′-biphenyl) at 110 °C for 9 h, resulting in the formation of (2,6-xylyl)-fluoren-9-ylideneamine, **6**, in 44% yield.[9] In this study, compound **6** and (dippe)Ni-(CN-2,6-xylyl)$_2$, **7**, were formed in a 1:1 ratio in quantitative yield at room temperature by mixing (dippe)-Ni(2,2′-biphenyl) and 2,6-xylyl isocyanide (eq 2).

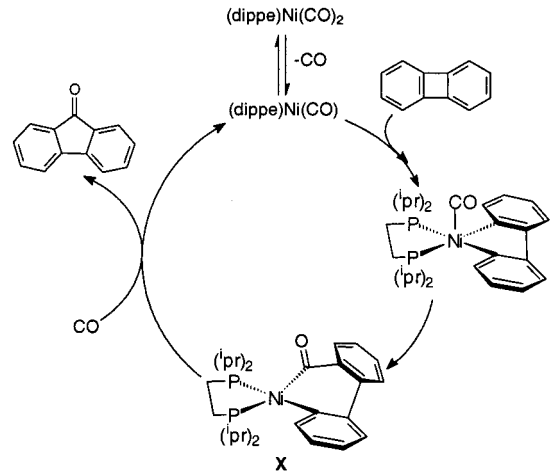


Heating compound **7** at 107 °C with 2 equiv of biphenylene results in the formation of compound **6**, a small amount of tetraphenylene, and a new nickel complex, **Z**. The new nickel compound displays four broad isopropyl methyl resonances centered at δ 1.40, 1.19, 0.779, and 0.208 as well as new aromatic resonances (some are obscured by compound **6**). The ^{31}P NMR spectrum displays two new doublets with an AB pattern at δ 62.23 (J_{P-P} = 54.2 Hz) and 61.83 (J_{P-P} = 51.7 Hz) and a small amount of (dippe)Ni(2,2′-biphenyl). These results are consistent with a nickel species containing inequivalent phosphines. Compound **Z** has inequivalent phosphines by virtue of isocyanide inser-

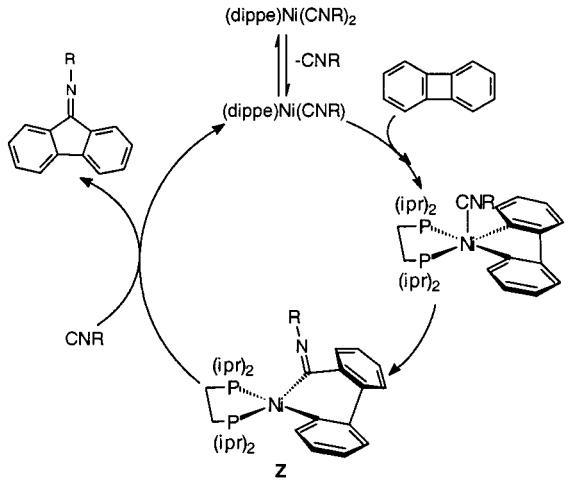
(19) Rosenthal, U.; Schulz, W. *J. Organomet. Chem.* **1987**, *321*, 103.

(20) (a) Cámpora, J.; Gutiérrez, E.; Monge, A.; Poveda, M. L.; Carmona, E. *Organometallics* **1992**, *11*, 2644. (b) Cámpora, J.; Gutiérrez, E.; Monge, A.; Poveda, M. L.; Ruiz, C.; Carmona, E. *Organometallics* **1993**, *12*, 4025.

Scheme 4



Scheme 5



tion into the Ni−C bond. Addition of excess 2,6-xylyl isocyanide to compound **Z** gives **6** and **7**. These results are consistent with compound **Z** being the isocyanide insertion product depicted in Scheme 5.

Interestingly, heating a mixture of **7**, biphenylene, and 2,6-dimethylphenyl isocyanide does not lead to immediate formation of **6**. An induction period is observed; however, once catalysis begins, the turnover rate is greater than 10/day at 107 °C. Similar behavior is observed with (dppe)Ni(2,6-xylyl isocyanide)$_2$, **8** (no significant rate acceleration was observed). In light of the similarities between the CO and isocyanide reactions, an analogous catalytic cycle for the formation of **6** is depicted in Scheme 5.

Conclusions

The catalytic functionalization of biphenylene with disubstituted alkynes to give 9,10-disubstituted phenanthrenes has been demonstrated using (dippe)Ni(RC≡CR) complexes as catalyst precursors. Alkynes containing electron-donating or mildly electron-withdrawing groups α to the alkyne carbon favor phenanthrene formation vs cyclotrimerization product. However, cyclotrimerization products increase relative to phenanthrene formation as the substituents on the α carbon become more electron withdrawing. Terminal alkynes favor polymer formation. The active catalyst appears to be a non-phosphorus-containing Ni species which can be generated by addition of O_2 to (dippe)Ni(RC≡CR). Experimental evidence suggests that the role of oxygen is to remove the dippe ligand by oxidation, thereby generating the active catalyst. Catalytic carbonylation of biphenylene to generate fluorenone was also achieved with (dippe)Ni(CO)$_2$ as the catalyst precursor. Finally, it was demonstrated that isocyanides can insert into the C−C bond of biphenylene to generate fluorene imines.

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 Labs, distilled under vacuum from dark purple solutions of benzophenone ketyl, and stored in ampules with Teflon-sealed vacuum line adapters. The preparations of 1,1′-diacetylferrocene silver tetrafluoroborate,[21] biphenylene,[22] neopentylisocyanide,[23] dippe,[24] (bipy)Ni(PhC≡CPh),[25] Ni$_2$(COD)$_2$(PhC≡CPh),[13] (dippe)Ni(COD),[26] [(dippe)NiH]$_2$,[5i] (dippe)Ni(2,2′-biphenyl),[27] 2,2′-dilithiobiphenyl,[28] (dippe)Ni(HC≡CH),[7a] (dippe)Ni(CO)$_2$,[7a] and (PPh$_3$)$_2$Ni(Ph≡CPh)[14] have been previously reported. Ni(COD)$_2$, Fe(bipy)$_3$(PF$_6$)$_2$, and all of the alkynes with the exception of 1,4-dimethoxy-2-butyne were purchased from Aldrich Chemical Co. The alkyne 1,4-dimethoxy-2-butyne was purchased from Lancaster. 2,6-Xylyl isocyanide was purchased from Fluka, 2,2′-dibromobiphenyl was purchased from Alfa Aesar (Avocado), and dppe was purchased from Strem. 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 (^{1}H, ^{31}P, ^{13}C) or Avance400 (^{1}H, ^{31}P, ^{13}C, ^{19}F) spectrometer. All ^{1}H 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). ^{19}F NMR spectra were referenced to external $C_6F_5CF_3$. $CFCl_3$ appears at δ +62.54 relative to internal $C_6H_5CF_3$ in THF-d_8 solvent. 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(PhC≡CPh), 1. (dippe)Ni(COD) (186 mg, 0.43 mmol) and diphenylacetylene (93 mg, 0.52 mmol) were dissolved in 8 mL of benzene in an ampule. The solution was heated at 65 °C for 36 h. The solvent was removed under vacuum, and the orange solid was dissolved in a minimum of

(21) Carty, P.; Dove, M. F. A. *J. Organomet. Chem.* **1971**, *28*, 125.
(22) Yates, P. *Organic Synthesis*; Wiley: New York, 1968; Collect. Vol. 48, p 12.
(23) Schuster, R. E. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. 5, p 772.
(24) Cloke, F. G. N.; Gibson, V. C. Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1988**, 2227.
(25) Rosenthal, U.; Nauck, C.; Arndt, P.; Pulst, S.; Baumann, W.; Burlakov, V. V.; Görls, H. *J. Organomet. Chem.* **1994**, *484*, 81.
(26) Bonrath, W.; Pörschke, K. R.; Wilke, G.; Angermund, K.; Krüger, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 833. Werner Bonrath, Ph.D. Thesis, Max-Planck-Institute für Kohlenforschung, 1988.
(27) Edelbach, B. E.; Vicic, D. A.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4784.
(28) Gardner, S. A.; Gordon, H. B.; Rausch, M. D. *J. Organomet. Chem.* **1973**, *60*, 179.

THF, layered with hexanes, and cooled to −30 °C overnight. Orange crystals were isolated by filtration (yield: 165 mg of orange X-ray quality crystals, 77%). NMR data for **1**: ^{1}H NMR (THF-d_8): δ 7.349 (d, J_{H-H} = 7.4 Hz, 4 H), 7.152 (t, J_{H-H} = 7.4 Hz, 4 H), 6.987 (t, J_{H-H} = 7.3 Hz, 2 H), 2.127 (sept, C*H*Me$_2$, J_{H-H} = 7.2 Hz, 4 H), 1.657 (d, PC*H*$_2$C*H*$_2$P, J_{H-P} = 9.2 Hz, 4 H), 1.078 (quintet, CH*Me*$_2$, J_{H-H} = 7.2, J_{P-H} = 7.2 Hz, 24 H). ^{31}P{^{1}H} NMR (THF-d_8): δ 79.35 (s). ^{13}C{^{1}H} NMR (THF-d_8): δ 141.3 (t, ≡*C*−Ph, J_{P-C} = 7.1 Hz), 132.3 (s), 128.3 (d, J_{P-C} = 8.6 Hz), 127.3 (s), 124.9 (s), 26.7 (t, J_{P-C} = 10.4 Hz), 22.2 (t, J_{P-C} = 19.1 Hz), 20.4 (t, J_{P-C} = 4.0 Hz), 19.1 (s). Anal. Calcd for $C_{28}H_{42}P_2Ni$: C, 67.35; H, 8.48. Found: C, 67.49; H, 8.55.

Preparation of (dippe)Ni(MeC≡CMe), 2. (dippe)Ni(COD) (150 mg, 0.35 mmol) was dissolved in a round-bottom flask with 10 mL of benzene. Dimethylacetylene (55 μL, 0.70 mmol) was dissolved in 5 mL of benzene and added dropwise to the (dippe)Ni(COD) solution. The mixture was stirred at room temperature for 3 days, during which time the solution slowly turned orange, then dark orange. The solvent was removed under vacuum, and the orange solid was washed with cold methanol to remove excess COD. The solid was dissolved in a minimum of acetone and cooled to −30 °C overnight (yield: 86 mg of yellow X-ray quality crystals, 66%). NMR data for **2**: ^{1}H NMR (THF-d_8): δ 2.400 (d, J_{H-H} = 5.2, 2.9 Hz, 6 H), 2.024 (sept, C*H*Me$_2$, J_{H-H} = 6.9 Hz, 4 H), 1.532 (d, PC*H*$_2$C*H*$_2$P, J_{H-P} = 8.6 Hz, 4 H), 1.124 (q, CH*Me*$_2$, J_{H-H} = J_{P-H} = 8.0 Hz, 12 H), 1.037 (q, CH*Me*$_2$, J_{H-H} = J_{P-H} = 5.8 Hz, 12 H). ^{31}P{^{1}H} NMR (THF-d_8): δ 80.16 (s). ^{13}C{^{1}H} NMR (THF-d_8): δ 124.3 (t, ≡*C*-Me, J_{P-C} = 19.7 Hz), 26.0 (t, J_{P-C} = 10.0 Hz), 22.9 (t, J_{P-C} = 19.5 Hz), 20.2 (t, J_{P-C} = 4.4 Hz), 19.3 (s), 15.4 (t, J_{P-C} = 11.1 Hz). Anal. Calcd for $C_{18}H_{38}P_2Ni$: C, 57.63; H, 10.21. Found: C, 57.43; H, 10.47.

Preparation of (dippe)Ni(MeO$_2$CC≡CCO$_2$Me), 3. (dippe)Ni(COD) (100 mg, 0.233 mmol) was dissolved in a round-bottom flask with 15 mL of THF. Dimethyl acetylenedicarboxylate (21 μL, 0.17 mmol) was dissolved in 5 mL of THF and added dropwise to the (dippe)Ni(COD) solution. The solution immediately turned orange/brown. The mixture was stirred for 12 h, the solvent and excess COD were removed under vacuum, and the orange solid was redissolved in 25 mL of THF. An additional 31 μL of dimethylacetylenedicarboxylate dissolved in 5 mL of THF was added dropwise to the mixture, the mixtire was stirred for 12 h at room temperature, and the solvent and excess COD were removed under vacuum. The solid was dissolved in a minimum of THF and layered with hexanes. After 12 h, the mother liquor was removed from the clear crystals (benzenehexacarboxylic acid hexamethyl ester) and cooled to −30 °C. After 2 days, 30 mg of orange, X-ray quality crystals of **3** were isolated (yield: 28%). NMR data for **3**: ^{1}H NMR (THF-d_8): δ 3.625(s, 6 H), 2.106 (sept, C*H*Me$_2$, J_{H-H} = 7.8 Hz, 4 H), 1.703 (d, PC*H*$_2$C*H*$_2$P, J_{H-P} = 9.5 Hz, 4 H), 1.109 (overlapping quartets, CH*Me*$_2$, J_{H-H} = J_{P-H} = 6.9 Hz, 24 H). ^{31}P{^{1}H} NMR (THF-d_8): δ 71.24 (s). Anal. Calcd for $C_{20}H_{38}O_4P_2Ni$: C, 51.87; H, 8.27. Found: C, 51.89; H, 8.20.

Preparation of (dippe)Ni(CH$_3$OCH$_2$C≡CCH$_2$OCH$_3$), 4. (dippe)Ni(COD) (200 mg, 0.47 mmol) was dissolved in a round-bottom flask with 20 mL of THF. 1,4-Dimethoxy-2-butyne (80 mg, 100 μL, 0.70 mmol) was added, and the mixture was heated to 70 °C for 2 h. The solvent, COD, and excess 1,4-dimethoxy-2-butyne were removed under vacuum, giving a dark oil (125 mg, 62%). NMR data for **4**: ^{1}H NMR (THF-d_8): δ 4.661, (s, 4 H), 3.289, (s, 6 H), 2.093 (sept, C*H*Me$_2$, J_{H-H} = 7.1 Hz, 4 H), 1.582 (d, PC*H*$_2$C*H*$_2$P, J_{H-P} = 8.6 Hz, 4 H), 1.117 (1:22:1 quartet, CH*Me*$_2$, J_{H-H} = J_{P-H} = 7.1 Hz, 12 H), 1.036 (q, CH*Me*$_2$, J_{H-H} = J_{P-H} = 7.1 Hz, 12 H). ^{31}P{^{1}H} NMR (THF-d_8): δ 82.32 (s). ^{13}C{^{1}H} NMR (THF-d_8): δ 129.9 (t, ≡*C*−CH$_2$, J_{P-C} = 19.5 Hz), 72.2 (t, J_{P-C} = 9.7 Hz), 57.2 (s), 26.2 (t, J_{P-C} = 10.4 Hz), 22.7 (t, J_{P-C} = 19.3 Hz), 20.3 (t, J_{P-C} = 4.1 Hz), 19.2 (s).

Preparation of (dippe)Ni(CF$_3$C≡CCF$_3$), 5. (dippe)Ni(COD) (250 mg, 0.58 mmol) was dissolved in a 50 mL round-bottom flask with 20 mL of THF. Hexafluoro-2-butyne (1 atm) was added to the flask. The solution immediately turned orange. The solvent, excess COD, and alkyne were removed under vacuum. The orange/brown solid was dissolved in a minimum of hexanes and cooled to −30 °C. The orange crystals were washed with cold MeOH (yield: 172 mg, 61%). NMR data for **5**: ^{1}H NMR (THF-d_8): δ 2.146 (sept, C*H*Me$_2$, J_{H-H} = 7.5 Hz, 4 H), 1.791 (d, PC*H*$_2$C*H*$_2$P, J_{H-P} = 8.5 Hz, 4 H), 1.133 (overlapping quartet, CH*Me*$_2$, 24 H). ^{31}P{^{1}H} NMR (THF-d_8): δ 85.74 (s). ^{19}F NMR (THF-d_8): δ 11.12 (d, J_{F-P} = 7.6 Hz). ^{13}C{^{1}H} NMR (THF-d_8): δ 125.9 (t, J_{P-C} = 10.4 Hz), 123.3 (t, J_{P-C} = 10.4 Hz), 26.0 (d, J_{P-C} = 24.0 Hz), 22.1 (t, J_{P-C} = 19.3 Hz), 19.9 (t, J = 3.0 Hz), 19.0 (s). Anal. Calcd for $C_{18}H_{32}P_2F_6Ni$: C, 44.78; H, 6.68. Found: C, 44.54; H, 7.09.

Preparation of (dippe)Ni(CN-2,6-xylyl)$_2$, 7. (dippe)Ni(COD) (430 mg, 1.0 mmol) was dissolved in 15 mL of THF. To this solution was added 2,6-dimethylbenzene isocyanide (340 mg, 2.58 mmol) dropwise at room temperature. The mixture was stirred for 2 h, during which time it became orange in color. The solvent and excess COD were removed under vacuum, leaving an orange oil behind (yield: 459 mg, 79%). NMR data for **8**: ^{1}H NMR (THF-d_8): δ 7.0−6.9 (m, 6 H), 2.369 (s, 6 H), 2.020 (sept, C*H*Me$_2$, J_{H-H} = 6.8 Hz, 4 H), 1.527 (d, PC*H*$_2$C*H*$_2$P, J_{H-P} = 8.4 Hz, 4 H), 1.206 (q, CH*Me*$_2$, J_{H-H} = J_{P-H} = 7.0 Hz, 12 H), 1.037 (q, CH*Me*$_2$, J_{H-H} = 7.1 Hz, 12 H). ^{31}P{^{1}H} NMR (THF-d_8): δ 76.59 (s).

Preparation of (dppe)Ni(CN-2,6-xylyl)$_2$, 8. (dppe)Ni(COD) (150 mg, 0.265 mmol) was dissolved in 5 mL of THF. To this solution was added 2,6-dimethylbenzene isocyanide (70 mg, 0.533 mmol) dropwise at room temperature. The mixture was stirred for 2 h, during which time it became orange in color. The solvent and excess COD were removed under vacuum. The solid was extracted with a minimum of hexanes, filtered through a glass plug, and cooled to −30 °C, giving orange crystals (yield: 130 mg, 68%). NMR data for **8**: ^{1}H NMR (THF-d_8): δ 7.79−7.72 (m, 8 H), 7.27−7.17 (m, 12 H), 6.94 (s, 6 H), 2.25 (d, PC*H*$_2$C*H*$_2$P, J_{H-P} = 15.3 Hz, 4 H), 2.16 (s, 12 H). ^{31}P{^{1}H} NMR (THF-d_8): δ 46.32 (s). Anal. Calcd for $C_{44}H_{42}P_2N_2Ni$: C, 73.46; H, 5.88. Found: C, 73.26; H, 5.78.

General Procedure for Catalytic Formation of Phenanthrenes. A solution containing the metal complex (0.033 M), biphenylene (0.33 M), and the appropriate acetylene (0.36 M) was prepared in 0.6 mL of toluene-d_8 or THF-d_8 and added to a resealable NMR tube. The NMR tube was degassed and filled with 700 mm N_2. The NMR tube was then momentarily opened to air, which introduced an additional 60 mm air into the tube, resulting in ~6 mol % O_2 vs the metal complex (total P = 760 mm = 748 mm N_2 + 12 mm O_2; V_{tube} = 2.0 mL; T = 300 K; mmol O_2 = PV/RT = (12/760 atm)(0.002 L)/[(0.082 L·atm/mol·K)(300 K)] × 1000 = 0.0013 mmol O_2 = 6.5% based on Ni). The NMR tube was heated at the appropriate temperature (see Scheme 1) in a constant-temperature oil bath thermostatically controlled (±0.5 °C). The NMR tube was removed at various intervals and cooled to room temperature, and a ^{1}H NMR spectrum was recorded. The catalytic turnover number was calculated from the ratio of phenanthrene product to metal species. Initial rates were used to calculate the turnover rate. Toluene-d_8 and THF-d_8 work equally well with virtually no difference in turnover rate.

Phenanthrene Catalytic Rate as a Function of O$_2$ Concentration. Six resealable NMR tubes containing (dippe)Ni(PhC≡CPh) (0.030 M), biphenylene (0.30 M), and diphenylacetylene (0.30 M) were prepared with dioxane as an internal standard in THF-d_8. Each tube was charged with O_2 (via air) as described above: 6, 13, 20.5, 28 40, and 52 mol % based on **1**. The tubes were thoroughly mixed for several minutes and filtered through a glass plug. A ^{31}P{^{1}H} spectrum of each sample displayed **1**, bis(diisopropylphosphino)ethane dioxide (δ, 52.0), bis(diisopropylphosphino)ethane monoxide (δ 51.2, J = 35 Hz and 9.8, J = 35 Hz, THF-d_8), and a pair of resonances with A_2B_2 patterns at δ 52.5 and 45.5. A simulation

of the resonances of the latter compound is consistent with the dimer depicted in Figure 5 (see Supporting Information). Each tube was then heated in an NMR probe at 60 °C. The reactions were monitored by ^{1}H NMR spectroscopy. A plot of concentration of 9,10-diphenylphenanthrene vs time was generated using only initial reaction times (10−12 min). The slope was calculated for each reaction. The results are depicted in Figure 4.

General Procedure for Catalytic Formation of Fluorenone. A solution containing (dippe)Ni(CO)$_2$ (0.056 M) and biphenylene (0.28 M) was prepared in THF-d_8 and added to a resealable NMR tube. The NMR tube was charged with 1 atm of CO. The NMR tube was heated at 100 °C in a constant-temperature oil bath thermostatically controlled (±0.5 °C). The NMR tube was removed at various intervals and cooled to room temperature, and a ^{1}H NMR spectrum was recorded. The catalytic turnover number was calculated from the ratio of fluorenone product to metal species with hexamethylbenzene as internal standard. Initial rates were used to calculate the turnover rate.

General Procedure for Catalytic Formation of Fluorene Imine. A solution containing (dippe)Ni(CN-2,6-xylyl)$_2$ (0.038 M), biphenylene (0.22 M), and 2,6-xylylisocyanide was prepared in THF-d_8 and added to a resealable NMR tube. The NMR tube was heated at 107 °C in a constant-temperature oil bath thermostatically controlled (±0.5 °C). The NMR tube was removed at various intervals and cooled to room temperature, and a ^{1}H NMR spectrum was recorded. The catalytic turnover number was calculated from the ratio of product to metal species. Initial rates were used to calculate the turnover rate.

X-ray Structural Determination of 1. A colorless needle of approximate dimensions 0.28 × 0.22 × 0.18 mm^3 was cut from a large cluster of crystals and mounted under Paratone-8277 on a glass fiber 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) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of 30 s/frame using a detector-to-crystal distance of 5.09 cm (maximum 2θ angle of 56.6°). The total data collection time was approximately 12 h. Frames were integrated to a maximum 2θ angle of 56.6° with the Siemens SAINT program to yield a total of 16186 reflections, of which 6280 were independent (R_{int} = 2.72%, R_{sig} = 3.74%)[29] and 5392 were above 2$\sigma(I)$. Laue symmetry revealed a monoclinic crystal system, and the final unit cell parameters (at −80 °C) were determined from the least-squares refinement of three-dimensional centroids of 8192 reflections.[30] Data were corrected for absorption with the SADABS[31] program. The space group was assigned as $P2_1/n$, and the structure was solved by using direct methods and refined employing full-matrix least-squares on F^2 (Siemens, SHELXTL,[32] version 5.04). For a Z value of 4, there is one molecule in the asymmetric unit. All of the atoms were refined anisotropically, and hydrogen atoms were included in idealized positions giving a data:parameter ratio of approximately 20:1. The structure refined to a goodness of fit (GOF)[33] of 1.160 and final residuals[34] of R1 = 4.42% ($I > 2\sigma(I)$), wR2 = 7.87% ($I > 2\sigma(I)$). Table 1 gives selected data collection parameters. In ORTEP diagrams, ellipsoids are shown at the 30% level and hydrogen atoms have been omitted for clarity.

Table 1. Selected X-ray Data for 1, 2, and 3

crystal parameters	1	2	3
chemical formula	$C_{28}H_{42}P_2Ni$	$C_{18}H_{38}P_2Ni$	$C_{20}H_{38}P_2O_4Ni$
fw	499.27	375.13	463.15
cryst syst	monoclinic	monoclinic	monoclinic
space group, Z	$P2_1/n$	$P2_1$	$P2_1/n$
a, Å	9.15130(10)	7.83800(10)	10.7338(2)
b, Å	27.18890(10)	13.6572(3)	9.62210(10)
c, Å	11.11780(10)	10.24810(10)	23.1508(2)
β, deg	104.8630(10)	104.78	94.8240(10)
vol, Å^3	2673.71(4)	1060.73(3)	2382.58(5)
temp, °C	−80	−80	−80
ρ_{calc}, g cm^{-3}	1.240	1.175	1.291
no. of data collected	16186	6673	14048
no. of unique data	6280	4230	5545
no. of observed data	5392	4072	4484
no. of params varied	280	200	254
R1(F_o), wR2(F_o^2) ($I > 2\sigma(I)$)	0.0442, 0.0787	0.0243, 0.0585	0.0328, 0.0718
R1(F_o), wR2(F_o^2), all data	0.0559, 0.0827	0.0259, 0.0594	0.0477, 0.0768
goodness of fit	1.160	1.038	1.039

X-ray Structural Determination of 2. A pale yellow crystal of approximate dimensions 0.38 × 0.26 × 0.22 mm^3 was cut from a cluster, mounted under Paratone-8277, and immediately placed in a cold nitrogen stream at −80 °C on the X-ray diffractometer. The X-ray intensity data were collected as for **1** above. Frames were integrated with the Siemens SAINT program to yield a total of 6673 reflections, of which 4230 were independent (R_{int} = 1.47%, R_{sig} = 2.84%) and 4072 were above 2$\sigma(I)$. Laue symmetry revealed a monoclinic crystal system, and the final unit cell parameters (at −80 °C) were determined from the least-squares refinement of three-dimensional centroids of 5901 reflections. Data were corrected for absorption with the SADABS program. The space group was assigned as $P2_1$ and the structure was solved by using direct methods and refined employing full-matrix least-squares on F^2 (Siemens, SHELXTL, version 5.04). For a Z value of 2, there is one molecule in the asymmetric unit. All of the non-H atoms were refined anisotropically, and the hydrogen atoms were included in idealized positions giving a data:parameter ratio of approximately 20:1. The structure refined to a goodness of fit (GOF) of 1.038 and final residuals of R1 = 2.43% ($I > 2\sigma(I)$), wR2 = 5.85% ($I > 2\sigma(I)$). Table 1 gives selected data collection parameters.

X-ray Structural Determination of 3. A yellow fragment of approximate dimensions 0.24 × 0.28 × 0.40 mm^3 was cut from a large cluster of crystals, mounted under Paratone-8277 on a glass fiber, and immediately placed in a cold nitrogen stream at −80 °C on the X-ray diffractometer. The X-ray intensity data were collected as for **1** above. Frames were integrated to a maximum 2θ angle of 56.6° with the Siemens SAINT program to yield a total of 14048 reflections, of which 5545 were independent (R_{int} = 2.94%, R_{sig} = 4.03%) and 4484 were above 2$\sigma(I)$. Laue symmetry revealed a monoclinic crystal system, and the final unit cell parameters (at −80 °C) were determined from the least-squares refinement of three-dimensional centroids of 8192 reflections. Data were corrected for absorption with the SADABS program. The space group was assigned as $P2_1/n$, and the structure was solved by using direct methods and refined employing full-matrix least-squares on F^2 (Siemens, SHELXTL, version 5.04). For a Z value of 4, there is one molecule in the asymmetric unit. All of the atoms were refined anisotropically, and hydrogen atoms were in-

(29) $R_{int} = \sum|F_o^2 - F_o^2(\text{mean})|/\sum[F_o^2]$; $R_{sigma} = \sum[\sigma(F_o^2)]/\sum[F_o^2]$.

(30) 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.

(31) The SADABS program is based on the method of Blessing; see: Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

(32) *SHELXTL: Structure Analysis Program, version 5.04*; Siemens Industrial Automation Inc.: Madison, WI, 1995.

(33) GOF = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where n and p denote the number of data and parameters.

(34) R1 = $(\sum||F_o^2| - |F_c||)/\sum|F_o|$; wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [(\max;0,F_o^2) + 2F_c^2]/3$.

cluded in idealized positions giving a data:parameter ratio of approximately >15:1. The structure refined to a goodness of fit (GOF) of 1.039 and final residuals of R1 = 3.28% ($I > 2\sigma(I)$), wR2 = 7.18% ($I > 2\sigma(I)$).

Acknowledgment is made to the U.S. Department of Energy (Grant FG02-86ER13569) for their support of this work.

Supporting Material Available includes a simulation of the ^{31}P NMR spectrum for the intermediate shown in Figure 5 and 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.

OM990387I