Organonickel Chemistry at the Edge of Naphthalene

James S. Brown and Paul R. Sharp*

Department of Chemistry, University of Missouri−Columbia, Columbia, Missouri 65211

Received April 29, 2003

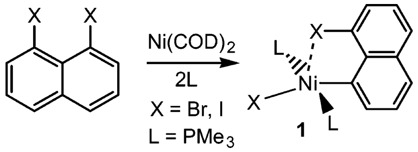
Summary: Reaction of 1,8-diiodo- or 1,8-dibromonaphthalene with a mixture of Ni(COD)$_2$ and trimethylphosphine gives the oxidative addition product Ni(PMe$_3$)$_2$(X)(C$_{10}$H$_6$X) (X = Br, I), which on reduction with Na/Hg gives perylene or, in the presence of alkynes, 1,2-disubstituted acenaphthylenes.

Introduction

Polycyclic aromatic carbon compounds (PACs),[1] including fullerenes and carbon nanotubes,[2] are a fascinating and useful class of compounds. Although many such compounds have been prepared, there is still a great need for facile and selective syntheses and derivatization techniques. Transition metal organometallic chemistry offers much in this area, and complexes where the polycyclic aromatic carbon compounds are coordinated to the face of the polycyclic through the π-system have been extensively studied.[3] In contrast, complexes with a transition metal multiply bonded to the edge of a PAC are rare.[4,5] The rich chemistry of analogous non-polycyclic complexes (metallacycle[6] and benzyne complexes[7]) suggests that the analogous polycyclic complexes will have a similar rich reaction chemistry that will allow growth and derivitization of the polycyclic system. In a previous publication, we reported the formation and reaction chemistry of a zirconacycle where zirconium is bonded to the 1,9 position at the edge of anthracene.[8] Addition of L$_2$NiBr$_2$ (L = PPh$_3$, PMe$_3$) to the zirconacycle allowed coupling of the anthracene moiety with alkynes to form larger polycyclic aceanthrylenes incorporating a five-membered ring. An alkyne reactive nickelacycle is the presumed intermediate in these reactions.[9] In this paper we report an alternative, more direct route to an analogous naphthalene nickelacycle, its decomposition to the naphthalene coupled product perylene, and its interception by alkynes to give 1,2-disubstituted acenaphthylenes.

Results

Addition of 1,8-diiodo- or 1,8-dibromonaphthalene to a yellow toluene 1:2 mixture of Ni(COD)$_2$ and PMe$_3$ results in rapid formation of a red-brown solution of the oxidative-addition product Ni(PMe$_3$)$_2$(X)(C$_{10}$H$_6$X) (**1**; X = Br, I; eq 1). Crystals of both derivatives are readily grown from toluene−hexane and were subjected to X-ray analysis. Crystal data and data collection parameters and distances and angles are provided in the Supporting Information. A drawing of the molecular structure of **1** (X = Br) is found in Figure 1.



(1)

The iodo derivative is isostructural, although the crystals are not isomorphous, and a drawing of the iodo derivative is supplied in the Supporting Information. The structures show the expected insertion of the L$_2$Ni fragment into a naphthalenic C−X bond. The resulting four-coordinate square plane, containing two *trans*

---

* Corresponding author. E-mail: SharpP@missouri.edu.

[1] Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1997.

[2] (a) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: Boston, 1996. (b) Koruga, D.; Hameroff, S. R.; Withers, J.; Loutfy, R.; Sundareshan, M. *Fullerene C60: History, Physics, Nanobiology, Nanotechnology*; North-Holland: New York, 1993. (c) Yakobson, B. I.; Smalley, R. E. *Am. Sci.* **1997**, *85*, 324−337.

[3] Leading references: (a) Meiere, S. H.; Keane, J. M.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **2003**, *125*, 2024−2025. (b) Alvarez, C. M.; Angelici, R. J.; Sygula, A.; Sygula, R.; Rabideau, P. W. *Organometallics* **2003**, *22* (4), 624−626. (c) Evju, J. K.; Mann, K. R. *Organometallics* **2002**, *21* (5), 993−996. (d) Lee, K.; Choi, Z.-H.; Cho, Y.-J.; Song, H.; Park, J. T. *Organometallics* **2001**, *20* (26), 5564−5570. (e) Xia, A. B.; Selegue, J. P.; Carrillo, A.; Brock, C. P. *J. Am. Chem. Soc.* **2000**, *122*, 3973−3974. (f) Munakata, M.; Ning, G. L.; Suenaga, Y.; Sugimoto, K.; Kuroda-Sowa, T.; Maekawa, M. *Chem. Commun.* **1999**, 1545−1546. (g) Munakata, M.; Wu, L. P.; Ning, G. L.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Maeno, N. *J. Am. Chem. Soc.* **1999**, *121*, 4968−4976. (h) Balch, A. L.; Olmstead, M. M. *Chem. Rev.* **1998**, *98*, 2123-2165. (i) Hohmann, F.; Siemoneit, S.; Nieger, M.; Kotila, S.; Dotz, K. H. *Chem. Eur. J.* **1997**, *3*, 853−859. (j) Seiders, T. J.; Baldridge, K. K.; Oconnor, J. M.; Siegel, J. S. *J. Am. Chem. Soc.* **1997**, *119*, 4781−4782. (k) Porter, L. C.; Polam, J. R.; Bodige, S. *Inorg. Chem.* **1995**, *34*, 998−1001. (l) Rabaa, H.; Lacoste, M.; Delville-Desboise, M.-H.; Ruiz, J.; Gloaguen, B.; Ardoin, N.; Astruc, D.; Beuze, A. L.; Saillard, J.-Y.; et al. *Organometallics* **1995**, *14*, 5078−5092.

[4] Shaltout, R. M.; Sygula, R.; Sygula, A.; Fronczek, F. R.; Stanley, G. G.; Rabideau, P. W. *J. Am. Chem. Soc.* **1998**, *120*, 835−836. Arce, M. J.; Viado, A. L.; An, Y. Z.; Khan, S. I.; Rubin, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3775−3776. Bennett, M. A.; Hockless, D. C. R.; Wenger, E. *Organometallics* **1995**, *14*, 2091−2101. Buchwald, S. L.; King, S. M. *J. Am. Chem. Soc.* **1991**, *113*, 258−265. de Rege, F. M. G.; Davis, W. M.; Buchwald, S. L. *Organometallics* **1995**, *14*, 4799−4807.

[5] Tinga, M. A. G. M.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Chem. Ber.* **1994**, *127*, 1851−1856.

[6] (a) Campora, J.; Palma, P.; Carmona, E. *Coord. Chem. Rev.* **1999**, *195*, 207−281. (b) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241−2290. (c) Chappell, S. D.; Cole-Hamilton, D. J. *Polyhedron* **1982**, *1*, 739−777.

[7] (a) Majoral, J.-P.; Igau, A.; Cadierno, V.; Zablocka, M. *Top. Curr. Chem.* **2002**, *220*, 53−77. (b) Jones, W. M.; Klosin, J. *Adv. Organomet. Chem.* **1998**, *42*, 147−221. (c) Majoral, J. P.; Meunier, P.; Igau, A.; Pirio, N.; Zablocka, M.; Skowronska, A.; Bredeau, S. *Coord. Chem. Rev.* **1998**, *178−180* (part 1), 145−167. (d) Bennett, M. A.; Wenger, E. *Chem. Ber./Recl.* **1997**, *130* (8), 1029−1042. (e) Broene, R. D.; Buchwald, S. L. *Science* **1993**, *261*, 1696−1701. (f) Buchwald, S. L.; Fisher, R. A. *Chem. Scr.* **1989**, *29* (4), 417−421. (g) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047−1058. (h) Bennett, M. A. *Pure Appl. Chem.* **1989**, *61* (10), 1695.

[8] Sharp, P. R. *J. Am. Chem. Soc.* **2000**, *122*, 9880−9881.

[9] Takahashi, T.; Tsai, F. Y.; Li, Y. Z.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1999**, *121*, 11093−11100.

10.1021/om030315y CCC: \$25.00
Publication on Web 07/19/2003

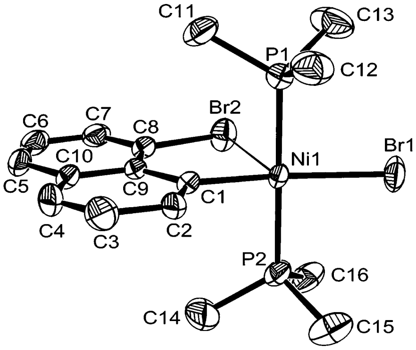


Figure 1. ORTEP drawing of $Ni(PMe_3)_2(Br)(C_{10}H_6Br)$ (**1**, X = Br).

Table 1. Yields from the Reduction of 1 (X = Br) with 6 equiv of RCCR

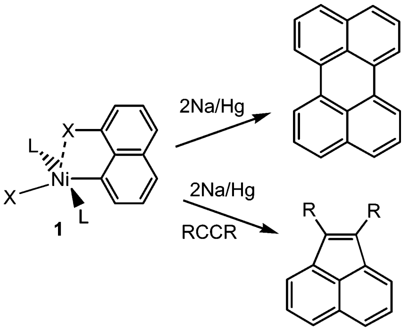
R	acenaphthylene yield (%)	perylene yield
Ph	82[a]	trace
CO_2Me	22	0
Et	~0	88
$SiMe_3$	~0	84

[a] A reaction with 2 equiv of PhCCPh gave a lower yield with a perylene:1,2-diphenylacenaphthylene ratio of 1:6.

phosphine ligands, the carbon and the halide, is approximately perpendicular to the plane of the naphthalene ring system. This positions the remaining ring-bonded *peri*-halogen atom (Br2, I2) above the four-coordinate plane and in close proximity to the Ni center. These Ni−halogen distances (Br, 2.899(1) Å; I, 2.988(2) Å) are longer than typical distances[10] but are similar to those in reported complexes described as having Ni−Br or Ni−I bonding interactions.[11] This gives the complexes a five-coordinate distorted square pyramidal geometry. The geometry of the two complexes is very similar to that observed in the five-coordinate Ni(II) complex $Ni(2\text{-}HOC_6H_4)(Br)(PMe_3)_3$,[12] which contains a PMe_3 ligand in place of the terminal halide in **1**. The bridging halide in **1** then corresponds to the terminal halide in this complex, which is also in the apical position of a square pyramid and has a rather long Ni−Br distance of 2.805(2) Å. As suggested by this long distance for a terminal halide, the bridging halide apical interaction in **1** appears to be a reluctant one, as the naphthalene framework should impose shorter distances than are observed. Ideally, the *peri*-relationship of the Ni and the halogen fixes the Ni−halogen distance at ca. 2.5 Å (the C1−C8 distance), a reasonable value for Ni(II)−Br and Ni(II)−I bond distances. That longer distances are observed indicates that a closer approach of the halogen to the Ni center is unfavorable and instead a distortion of the naphthalene framework is found. (Distortions are well known in *peri*-substituted naphthalenes with nonbonded contacts between the substituents.[13]) In the present case, the long Ni−halogen distances result in distortion of the angles around C1 and C8. In an undistorted complex these angles should be close to 120°. In **1** (X = Br) they vary from 116.0(3) to 124.9(3) Å for C1 and from 116.5(3) to 123.2(4) Å for C8, with the larger angles being the internal angles in the five-membered ring formed from Ni, C1, C9, C8, and Br2. A similar situation pertains for **1** (X = I), but the disorder in the structure (see Experimental Section) makes the angles less reliable than in the bromo derivative.

Both derivatives of **1** are slowly reduced by sodium amalgam in THF solution (Scheme 1). The initially red-brown solutions turn green over the course of a couple hours. ^{31}P NMR spectra of the solutions show unresolved broad peaks. ^{1}H NMR spectroscopy reveals the formation of peaks associated with perylene. Reaction quenching and workup give pure perylene in nearly quantitative yields.

Scheme 1



Addition of diphenylacetylene to solutions of **1** prior to reduction results in a different outcome. The red-brown solutions again turn green over the course of a couple hours, but now ^{31}P NMR spectra show a sharp peak at positions expected for the alkyne complex $L_2Ni(RCCR)$.[14] ^{1}H NMR spectroscopy shows the formation of small amounts of perylene along with new peaks in the aromatic region. Reaction workup and product isolation reveal that the new aromatic product is the 1,2-diphenylacenaphthylene (Scheme 1, R = Ph). Yields vary according to the amount of alkyne added, with increasing alkyne concentration giving greater yields of the acenaphthylene at the expense of perylene formation. A similar reaction with dimethylacetylenedicarboxylate also yields the acenaphthylene ($R = CO_2Me$), but RCCR ($R = Et, SiMe_3$) do not yield the corresponding acenaphthylenes. The results of these reactions are summarized in Table 1 for **1** (X = Br).

Discussion

A proposed sequence for the reduction process and the formation of perylene and the acenaphthylenes is shown in Scheme 2. The reduction of **1** to the nickelacycle **2** is modeled after the reduction of $L_2Ni(X)(2\text{-}XC_6H_4)$ to the Ni benzyne complexes $L_2Ni(C_6H_4)$ as executed by Ben-

---

[10] Orphen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans. (Suppl.)* **1989**, S1−S81.

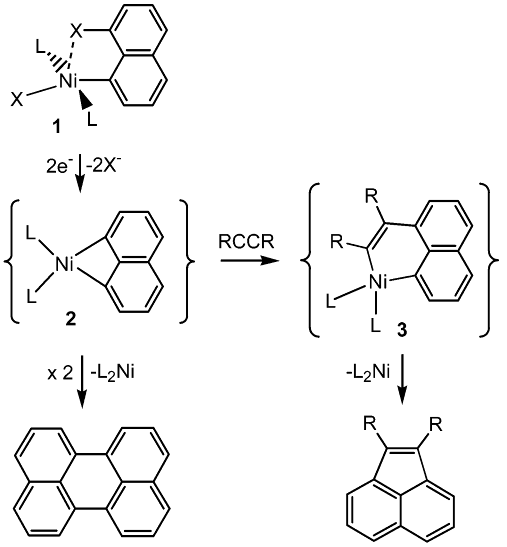
[11] (a) Kajiwara, T.; Yamaguchi, T.; Kido, H.; Kawabata, S.; Kuroda, R.; Ito T. *Inorg. Chem.* **1993**, *32* (23), 4990−4991. (b) Fox, S.; Stibrany, R. T.; Potenza, J. A.; Schugar, H. J. *Inorg. Chim. Acta* **2001**, *316* (1−2), 122−126. (c) Krueger, T.; Krebs, B.; Henkel, G. *Angew. Chem.* **1992**, *104* (1), 71−72; *Angew. Chem., Int. Ed. Engl.* **1992**, *31* (1), 55−56. (d) Bellitto, C.; Dessy, G.; Fares, V. *Inorg. Chem.* **1985**, *24* (18), 2815−2820. (e) Sacconi, L.; Dapporto, P.; Stoppioni, P. *Inorg. Chem.* **1977**, *16* (2), 224−227.

[12] Klein, H.-F.; Dal, A.; Jung, T.; Flörke, U.; Haupt, H.-J. *Eur. J. Inorg. Chem.* **1998**, *12*, 2027−2032.

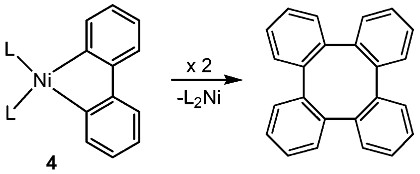
[13] Leading references: (a) Kilian, P.; Slawin, A. M. Z.; Woolins, J. D. *Chem. Eur. J.* **2003**, *9*, 215−222. (b) Bock, H.; Sievert, M.; Havlas, Z. *Chem. Eur. J.* **1994**, *4*, 677−685. (c) Seyferth, D.; Vick, S. C. *J. Organomet. Chem.* **1977**, *141*, 173−187.

[14] (a) Bochmann, M.; Hawkins, I.; Hursthouse, M. B.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1990**, 1213−1219. (b) Poerschke, K. R.; Mynott, R.; Angermund, K.; Krueger, C. *Z. Naturforsch., B* **1985**, *40B*, 199−209.

Scheme 2



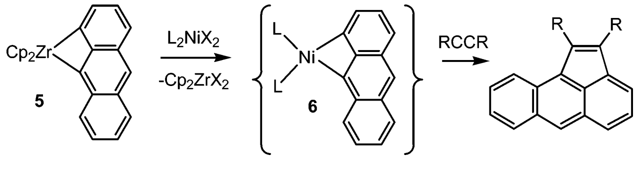
nett and co-workers.[7c,g] However, **2** is apparently unstable under the reaction conditions and decomposes producing perylene. While the platinum triethylphosphine analogue of **2** is known and is stable at ambient temperatures,[15] the low stability of **2** was not unanticipated. The related five-membered nickelacycle **4** (L = PEt$_3$), formed by low-temperature insertion of "L$_2$Ni" into the C−C bond of biphenylene, is unstable at ambient temperatures and decomposes to the analogous coupled product tetraphenylene (eq 2).[16,17] In contrast,



(2)

the platinum analogue of **4** is stable at 80 °C.[18] In addition, alkyne trapping reactions of the four-membered nickelacycle **6** (Scheme 3) formed by metallacycle transfer from Cp$_2$Zr(1,9-anthracenediyl) **5** to L$_2$NiX$_2$ (X = Cl, Br) indicate that **6** (L = PPh$_3$) is not stable above 10 °C,[8,19] although the difference in phosphine ligand (PPh$_3$ versus PMe$_3$) may alter stability.

Scheme 3



The trapping of **2** by alkynes was also expected in analogy with the anthracene derivative **5** (L = PPh$_3$, PMe$_3$), which reacts readily with alkynes to produce aceanthrylenes[8,19] (Scheme 3). However, **5** is successfully trapped by RCCR for R = Et and SiMe$_3$, whereas the naphthalene derivative **2** is not suggesting that **2** is less stable than **5** or slower to react with alkynes before decomposition.

An alternative to nickelacycle **2** in the reduction of **1** is radical formation. Radical coupling could give perylene, and radical trapping by the alkynes could give the acenaphthylenes. Cycloaddition of alkynes to radicals is known.[20] To investigate this possibility, we added 9,-10-dihydroanthracene to the reduction reaction. Perylene was again obtained along with unreacted 9,10-dihydroanthracene. Naphthalene and anthracene, the expected products of hydrogen atom abstraction from 9,10-dihydroanthracene, were not detected.

Conclusions

Oxidative addition of one C−X bond of 1,8-dihalonaphthalene to the L$_2$Ni fragment yields a five-coordinate Ni(II) complex where coordination of the remaining carbon-bonded halogen is forced on the Ni center by the constraints of the naphthalene geometry. Reduction of the Ni(II) oxidative addition complexes most likely provides access to the unstable nickelacycle L$_2$Ni(1,8-naphthalenediyl) (L = PMe$_3$) **2**, which decomposes giving perylene. Nickelacycle **2** is trapped by alkynes in a cycloaddition reaction yielding 1,2-disubstituted acenaphthylenes.

Experimental Section

Unless stated otherwise, all experiments were performed under a dinitrogen atmosphere using a VAC drybox or by Schlenk techniques. Solvents were dried and deoxygenated by standard procedures.[21] Sodium amalgam[22] and 1,8-diiodo- and dibromonaphthalene were prepared as previously reported. PMe$_3$ (1 M THF solution), Ni(COD)$_2$, and alkynes were purchased from Aldrich or Acros Chemical Companies and used as received. NMR spectra were recorded on a Bruker ARX-250, 300, or 500 NMR instrument at ambient probe temperatures. Infrared spectra were obtained with a Nicolet Nexis spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts are reported in parts per million and are referenced to TMS (^{1}H, ^{13}C) or external 85% H$_3$PO$_4$ (^{31}P) standards. Desert Analytics performed the elemental analyses.

(PMe$_3$)$_2$Ni(X)(C$_{10}$H$_6$X) (1). X = I. To a stirred suspension of Ni(COD)$_2$ (49.7 mg, 0.263 mmol) in 5 mL of toluene was added 0.526 mL of 1 M PMe$_3$ (0.526 mmol) in THF. The solution was stirred for 5 min to ensure a complete reaction. The resulting solution was then added to 1,8-diiodonaphthalene (100 mg, 0.263 mmol) dissolved in 1 mL of toluene with stirring. The mixture was stirred for 2 h at room temperature and then concentrated under reduced pressure. Hexane (4 mL) was added and the mixture was cooled to −34 °C to produce the pure insertion product as brown-red crystals. Yield: 74 mg (53%). Anal. Calc (found) for C$_{16}$H$_{24}$I$_2$P$_2$Ni: C, 32.53 (32.21); H, 4.09 (4.39). ^{1}H NMR (250 MHz, C$_6$D$_6$): 0.91 (t, $^3J_{HH}$ = 3.7 18H PMe$_3$), 6.80 (t, $^3J_{HH}$ = 7.6, 1H), 7.10 (m, 2H), 7.53 (d, $^3J_{HH}$ = 8.1, 1H), 7.79 (d, $^3J_{HH}$ = 5.8, 1H), 8.13 (d, $^3J_{HH}$ = 7.2, 1H). ^{13}C{^{1}H} NMR (62.8 MHz, C$_6$D$_6$): 15.12 (t, J_{CP} = 15.0, PMe$_3$),

---

(15) Tinga, M. A. G. M.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Chem. Ber.* **1994**, *127*, 1851−1856.

(16) Eisch, J. J.; Piotrowski, A. M.; Han, K. I.; Krüger, C.; Tsay, Y. H. *Organometallics* **1985**, *4*, 224−231.

(17) The analogous PMe$_3$ complex is a postulated intermediate in the Ni(0) catalytic conversion of biphenylene to tetraphenylene: Schwager, H.; Spyroudis, S.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1990**, *382*, 191−200.

(18) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843−2853.

(19) Ramakrishna, T. V. V.; Sharp, P. R. Work in progress.

(20) Leading reference: Kokubo, K.; Yamaguchi, H.; Kawamoto, T.; Oshima, T. *J. Am. Chem. Soc.* **2002**, *124*, 8912−8921.

(21) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15* (5), 1518−1520.

(22) Templeton, J. L.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 2293−2299.

121.75 (s), 124.07 (s), 124.83 (s), 125.07 (s), 128.64 (s), 129.00 (s), 131.18 (s), 134.00 (s), 140.80 (s) 164.15 (s, C−Ni). $^{31}P\{^1H\}$ NMR (101 MHz, C_6D_6): −17.8.

X = Br. PMe_3 (700 μL of a 1 M THF solution, 0.700 mmol) was added to a stirred suspension of $Ni(COD)_2$ (96.2 mg, 0.350 mmol) in 5 mL of toluene. The solution was stirred for 5 min to ensure complete reaction. The solution was then added slowly to a stirred solution of 1,8-dibromonaphthalene (100 mg, 0.350 mmol) in toluene (5 mL). The mixture was stirred for 2 h at room temperature and then concentrated to about 2 mL under reduced pressure. Hexane (5 mL) was added, and the solution was placed at −34 °C overnight to induce crystallization (red-brown crystals). Yield: 129 mg (74.3%). Anal. Calc (found) for $C_{16}H_{24}Br_2P_2Ni$: C, 38.68 (38.95); H, 4.87 (5.05). ^1H NMR (250 MHz, C_6D_6): 0.75 (t, $^3J_{HH} = 3.8$ 18H PMe_3), 6.85 (t, $^3J_{HH} = 7.8$, 1H), 7.02 (t, $^3J_{HH} = 7.5$, 1H), 7.13 (presumed d, 1H, partially obscured by solvent peak), 7.43 (d, $^3J_{HH} = 7.9$, 1H), 7.70 (d, $^3J_{HH} = 7.3$, 1H), 7.83 (d, $^3J_{HH} = 6.7$, 1H). $^{13}C\{^1H\}$ NMR (62.8 MHz, C_6D_6): 12.64 (t, $J_{CP} = 13.9$), 122.00 (s), 124.53 (s), 125.02 (s), 127.53 (s), 128.48 (s), 129.48 (s), 132.59 (t), 136.25 (s), 137.79 (s), 162.43 (s, C−Ni). $^{31}P\{^1H\}$ NMR (101 MHz, C_6D_6): −16.8.

Reduction of 1. Compound **1** (X = Br) (40 mg, 0.0080 mmol) was dissolved in THF and stirred over 0.5% Na/Hg (1.0 g, 0.22 mmol) for 2 h. The reaction was quenched with 10 mL of 1 M HCl and extracted with 10 mL and 2 × 5 mL of Et_2O. The volatiles were removed from the combined extracts in vacuo. The residue was dissolved in hexane, placed on a silica gel column, and eluted with hexanes. The perylene fraction was collected and evaporated to dryness and the perylene identified by comparison of its properties with an authentic sample. Yield: 10 mg (98%). A similar reaction with an added 2 equiv of 9,10-dihydroanthracene gave only perylene and recovered 9,10-dihydroanthracene.

Reduction of 1 in the Presence of Alkynes (RCCR). Compound **1** (X = Br) (21.6 mg, 0.00435 mmol) and the alkyne (0.0264 mmol, 6 equiv) were dissolved in 4 mL of THF and stirred over 0.5% Na/Hg (1.0 g, 0.22 mmol) for 2 h. The reaction was quenched with 5 mL of 1 M HCl or $NaHCO_2$(aq) (R = $SiMe_3$) and extracted with 10 mL and 2 × 5 mL of Et_2O. The volatiles were removed from the combined extracts in vacuo. The residue was dissolved in hexane, placed on a silica gel column, and eluted with hexanes. The perylene and acenaphthylene fractions were collected and evaporated to dryness. Yields are given in Table 1. Acenaphthylenes were identified by comparison of their ^1H NMR spectra with published data.[23]

Crystal Structure Analysis. Crystal data, reflection collection, and processing parameters, and solution and refinement data are summarized in Table 1 and given as a complete listing in the Supporting Information. Crystals were grown as described above. In both cases, a sample of crystals was placed in a pool of heavy oil. One crystal was selected and removed from the oil with a glass fiber. With the oil-covered crystal adhering to the end of the glass fiber, the sample was transferred to an N_2 cold stream on the diffractometer. Data collection and processing proceeded normally for both derivatives, and both structures were solved by indirect methods. Refinement and location of all atoms proceeded rapidly with the bromide. For the iodide, complete carbon atom location was difficult, and it became apparent that a secondary position for the ring-bound iodine atom was present, indicating likely disorder. A disorder model featuring a 2-fold rotation about the Ni−C9 vector, leaving the PMe_3 ligands and the Ni unaltered, was developed and successfully refined. The two possible orientations refined to an occupancy ratio of 0.8:0.2. In the minor orientation the naphthalene was refined as a rigid group with isotropic carbon atoms. All other atoms were refined anisotropically with no restraints.

Acknowledgment. We thank the National Science Foundation for supporting this work (CHE-0101348) and for providing a portion of the funds for the purchase of the NMR (CHE 9221835) equipment. We also thank Dr. Charles Barnes for assistance with the crystal structure determinations.

Supporting Information Available: A listing of crystal data and structure refinement, atomic coordinates, anisotropic displacement parameters, bond distances, and bond angles for **1** (X = I, Br) and a drawing of **1** (X = I) showing the disorder. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030315Y

---

(23) Dyker, G. *J. Org. Chem.* **1993**, *58*, 234−238.