Further Observations on the Formation of Naphthalenes by Double Insertion of Acetylenes into Benzyne−Nickel(0) Complexes

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The reactions of acetylenes with benzyne−nickel(0) complexes Ni((1,2-η)-4,5-$X_2C_6H_2$)L_2 (X = H, L_2 = 2PEt_3 (**1**), dcpe (**2**); X = F, L_2 = 2PEt_3 (**3**), dcpe (**4**)) to give substituted naphthalenes have been investigated further in an effort to understand the factors that control the successive insertions. Complex **1** reacts with a mixture of *tert*-butylacetylene and 3-hexyne in a 1:3 molar ratio to give approximately equal amounts of 1,2-diethyl-3-*tert*-butylnaphthalene (**11**), the exclusive product of cocyclization, and 1,2,3,4-tetraethylnaphthalene (**10**), which results from double insertion of 3-hexyne. Double insertion of 1,7-octadiyne into the benzyne−nickel bond of **1** occurs exclusively in an intramolecular fashion to give 1,2,3,4-tetrahydroanthracene (**14**) in 48% isolated yield. These observations are consistent with the following postulates: (1) the first insertion occurs under steric control and forms a nickelaindene in which the substituted carbon atom is bound to nickel; (2) the second insertion occurs in the nickel−vinyl bond of this species, not the nickel−aryl bond. The second insertion is also under steric control, but the regiospecificities for *tert*-butylacetylene and 1,7-octadiyne are opposite. Addition of PEt_3 or PPh_3 suppresses (though not completely) the catalytic cyclotrimerization of methyl propiolate in the presence of **3** in favor of stoichiometric formation of a mixture of dimethyl 6,7-difluoronaphthalenedicarboxylates, the ratio of the 1,3- and 2,3-isomers, **8** and **9**, being 1:3 (PEt_3) and 1:4 (PPh_3). For *tert*-butyl propiolate in the presence of PPh_3, the ratio of 1,3- to 2,3-isomer changes to 1.6:1. These observations support the idea that for acetylenic esters both steric and electronic factors influence the second insertion. The isolated nickelaindene Ni{$C_6H_4C(CO_2Me)$=C-(CO_2Me)}(dcpe) (**18**) reacts with methyl propiolate, probably under electronic control, to give trimethyl 1,2,3-naphthalenetricarboxylate as the only product of cocyclization.

Introduction

Monomeric benzyne−nickel(0) complexes Ni((1,2-η)-4,5-$X_2C_6H_2$)L_2 (X = H; L_2 = 2PEt_3 (**1**), dcpe (**2**); X = F, L_2 = 2PEt_3 (**3**), dcpe (**4**))[1−3] undergo successive insertions with 2 equiv of acetylenes to form substituted naphthalenes;[3] the corresponding (2,3-η)-naphthalyne complexes similarly give substituted anthracenes.[4] The suggested stepwise reaction sequence for the case of a symmetrical acetylene is shown in Scheme 1. The first insertion into the benzyne−nickel bond gives a nickelaindene, a species that can be isolated from the reaction of DMAD[1] with **2** and detected by ^{31}P NMR spectroscopy in the corresponding reaction with **4**. In the second insertion step, there are two possibilities according to whether the acetylene enters the nickel-vinyl bond of the metallaindene (pathway A in Scheme 1) or the nickel−aryl bond (pathway B). The reaction is completed by reductive elimination of the zerovalent nickel fragment NiL_2 from either of the resulting seven-membered-ring metallacycles. For an unsymmetrical acetylene, the number of possible isomers at each step is doubled, depending on the direction of insertion, yet in such cases surprisingly good regioselectivities are obtained. For example, the reaction of *tert*-butylacetylene with **1** and **3** gives only the 1,3-disubstituted naphthalenes **5** and **6**, whereas that of methyl 2-butynoate with **3** gives exclusively the symmetrically substituted dimethyl 1,4-dimethylnaphthalene-2,3-dicarboxylate **7** (Scheme 2). The reaction of methyl propiolate with **3** is not so selective, however; an isomeric mixture of 1,3- and 2,3-dicarboxylates **8** and **9** is obtained. We describe here experiments that shed some light on the factors that control these insertions.

Results and Discussion

Insertion of Alkylacetylenes. It was of obvious interest to see whether different acetylenes could be cocyclized with nickel(0)−benzyne complexes and to determine the substitution pattern of the resulting naphthalenes. Earlier work[3] had shown that the reaction of Ni((1,2-η)-4,5-$F_2C_6H_2$)(PEt_3)$_2$ (**3**) with *tert*-butylacetylene to give the 1,3-disubstituted product **6** occurred between −30 °C and room temperature, whereas the corresponding reaction with 3-hexyne to give 6,7-difluoro-1,2,3,4-tetraethylnaphthalene was considerably

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(1) Abbreviations: dcpe = bis(dicyclohexylphosphino)ethane, $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$; DMAD = dimethyl acetylenedicarboxylate; Cp = η^5-C_5H_5.

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(4) Bennett, M. A.; Hockless, D. C. R.; Wenger, E. *Organometallics* **1995**, *14*, 2091.

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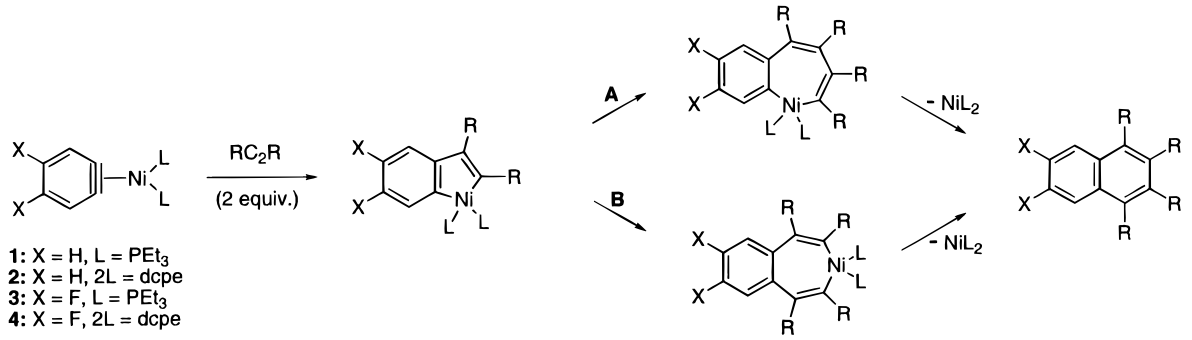
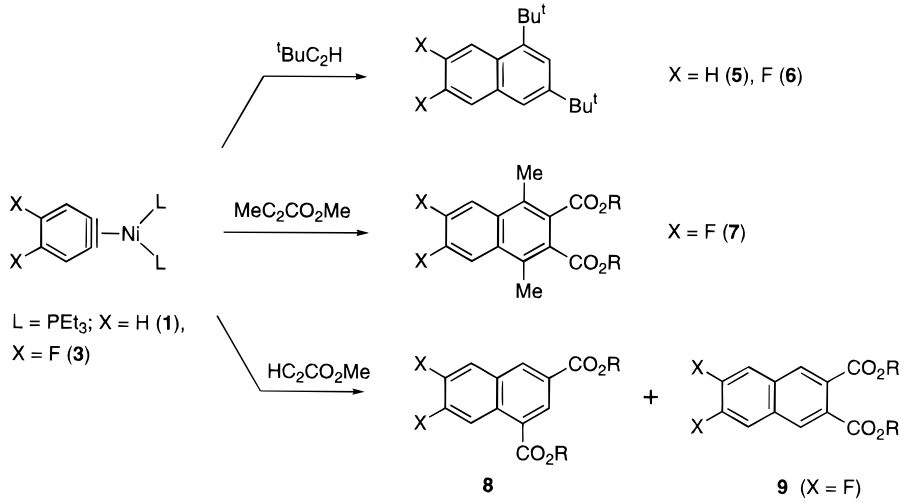
Scheme 1



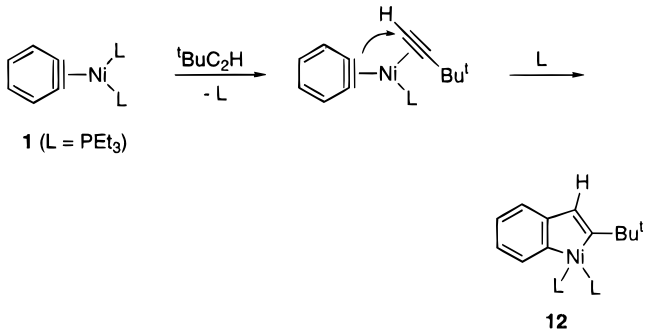
Scheme 2



slower, requiring 15 h at 65 °C for completion. We now find that the reaction of Ni((1,2-η)-C_6H_4)(PEt_3)$_2$ (**1**) with a mixture of *tert*-butylacetylene and 3-hexyne in a 1:3 molar ratio is complete after 16 h at room temperature, as shown by the total disappearance of the broad ^{31}P NMR singlet due to **1**. After chromatography, a mixture was isolated containing 1,2,3,4-tetraethylnaphthalene (**10**), formed by double insertion of 3-hexyne, and 1,2-diethyl-3-*tert*-butylnaphthalene (**11**), formed by sequential insertion of *tert*-butylacetylene and 3-hexyne; the yields based on NiBr(2-BrC_6H_4)(PEt_3)$_2$, the nickel(II) precursor to **1**, were 40% and 29%, respectively. Owing to the decomposition of the benzyne complexes during the filtration step (up to 20%), the total yields in this and the other reactions to be reported are high enough to serve as a basis for discussion of the preferred direction in each insertion step. The substitution pattern of **11** was confirmed by nuclear Overhauser experiments (see Experimental Section). No other naphthalene products were present.

This result is consistent with the pathway shown in Scheme 3, in which the Ni−C bond of **1** initially attacks the sterically less hindered carbon atom of coordinated *tert*-butylacetylene to give a metallaindene (**12**) in which the *tert*-butyl substituent is adjacent to nickel. Attempts to detect this intermediate were unsuccessful. Subsequent insertion of 3-hexyne will give **11** (Scheme 4). The regioselectivity of the first insertion is similar to that observed in the sterically controlled insertion of phenylpropyne and other unsymmetrical acetylenes into

Scheme 3



the nickel-methyl bonds of NiMe(acac)(PPh_3)[5] and of *trans*-NiClMe(PMe_3)$_2$,[6] in which the methyl group attacks the less hindered carbon of the acetylene to give a η^1-vinyl complex having the more bulky substituent next to the metal.

The steric regiocontrol of the insertion of a second molecule of *tert*-butylacetylene is unlikely to differ from that of the first. Hence, the exclusive formation of 1,3-di-*tert*-butylnaphthalenes by double insertion of *tert*-butylacetylene can be accounted for most readily by assuming that the second molecule of *tert*-butylacetylene inserts into the nickel-vinyl bond of intermediate **12** (pathway A) to give the seven-membered-ring nickelacycle **13** (Scheme 4). The same sterically controlled pathway must be responsible for the major product of the slightly less selective reaction of **1** with (trimethylsilyl)acetylene. In this case, a 6:1 mixture of the 1,3-

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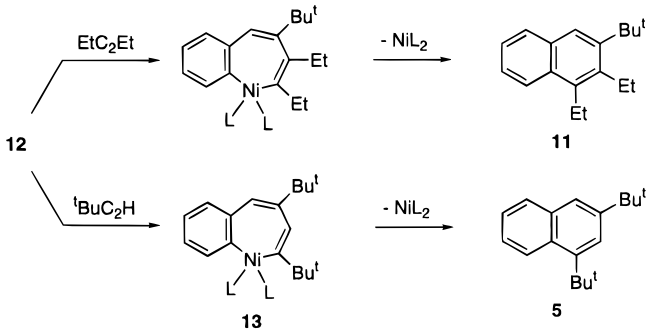
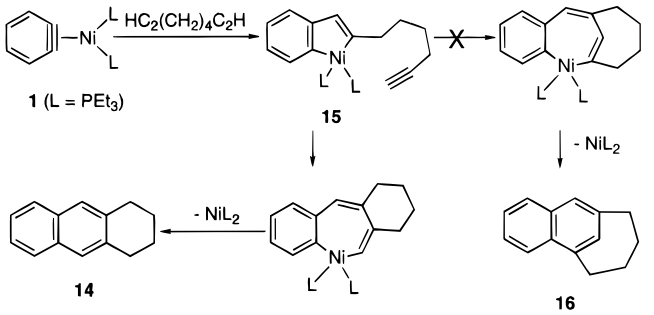
(6) Klein, H.-F.; Reitzel, L. *Chem. Ber.* **1988**, *121*, 1115.

Scheme 4



Scheme 5



and 2,3-isomers is obtained with an overall yield of 50% (based on the Ni(II) precursor), together with the enyne *trans*-$Me_3SiC{\equiv}CCH{=}CHSiMe_3$ (4% based on the acetylene) formed by dimerization of Me_3SiC_2H.

Some support for these assumptions is provided by a study of the reaction of an excess of 1,7-octadiyne with **1**, which forms 1,2,3,4-tetrahydroanthracene (**14**) in 48% isolated yield as the only double-insertion product, in addition to unidentified aromatic cyclotrimers. A plausible reaction sequence that accounts for this observation is shown in Scheme 5. The regioselectivity of insertion of the first triple bond must be the same as that found for *tert*-butylacetylene, because the metallaindene **15** having the alkyl substituent on the carbon atom bound to nickel is the only intermediate that can lead to **14**. The alkyl chain carrying the tethered triple bond is too short to allow intramolecular insertion into the nickel−aryl bond of **15**; hence, the second insertion must occur in the nickel−vinyl bond (pathway A). The direction of this insertion is, however, clearly opposite to that occurring with *tert*-butylacetylene, since the substituted carbon atom does not appear adjacent to nickel; the organic product in this case would be the bridged naphthalene **16**, which is not observed. The reversal in regiospecificity may be caused by the tendency to generate the less strained carbocycle. There is no evidence for intermolecular insertion of 1,7-octadiyne into the nickelaindene **15**, since naphthalenes containing $(CH_2)_4C_2H$ substituents are also not found.

Insertion of Acetylenic Esters. We reported[3] that methyl propiolate reacts with Ni((1,2-η)-4,5-$F_2C_6H_2$)-$(PEt_3)_2$ (**3**) to give a mixture of 1,3- and 2,3-naphthalenedicarboxylates in a *ca.* 1:1.5 mole ratio, but the yield was only 33% owing to catalytic cyclotrimerization of the acetylene. In their study of the insertion of acetylenes into the nickelacyclopentene complex Ni(CH_2-CMe_2-*o*-C_6H_4)$(PMe_3)_2$ to give 1,2-dihydronaphthalenes, Carmona *et al.*[7] showed that cyclotrimerization was impeded by addition of tertiary phosphines to trap the catalytically active Ni^0L_2 fragment, and we have made similar observations. Thus, in the presence of 2 equiv of PEt_3, reaction of methyl propiolate with **3** at −30 °C gave a 1:2.8 mixture of 1,3-$(CO_2Me)_2$-6,7-$F_2C_{10}H_4$ (**8**) and 2,3-$(CO_2Me)_2$-6,7-$F_2C_{10}H_4$ (**9**) in 56% yield; under the same conditions, use of 2 equiv of PPh_3 instead of PEt_3 gave a 1:4 ratio of **8** and **9** in 66% yield. Similarly, methyl propiolate reacted with **1** in the presence of PPh_3 (2 equiv) to give the dimethyl 1,3- and 2,3-naphthalenedicarboxylates, in a 1:3.3 ratio and 81% yield. The corresponding reaction of *tert*-butyl propiolate with **1** under the same conditions also gave a high yield of the di-*tert*-butyl compounds 1,3- and 2,3-$(CO_2$-*t*-$Bu)_2C_{10}H_6$, but the proportion of 1,3-isomer had increased markedly (mole ratio 1.6:1). In all cases, some aromatic cyclotrimer was also formed (3−20% based on the acetylenes).

We argued earlier[3] that both electronic and steric effects were important in the reaction of nickel(0)−benzyne complexes with acetylenic esters. In the first insertion step of methyl 2-butynoate, the Ni−C bond of the benzyne complex reacts with the electron-poor β-carbon atom of the alkyne to give the nickelaindene **17** (Scheme 6) in which the carboxylate-bearing carbon atom is bound to the metal atom. There is a direct analogy with the products of nucleophilic additions to alkynyl ketones or esters, for which an allenol resonance form is implicated.[8] In the case of methyl and *tert*-butyl propiolates, both electronic and steric effects should lead to the same direction of addition. The second insertion in the case of methyl 2-butynoate is probably also under electronic control, proceeding by attack on the electrophilic vinyl carbon atom of the nickelaindene (pathway A, Scheme 6). This leads to a seven-membered-ring nickelacycle containing two adjacent ester groups, which is similar to the intermediate proposed to explain the exclusive formation of trimethyl 1,2,4-benzenetricarboxylate from the cyclotrimerization of methyl 2-butynoate by various nickel(0) complexes.[9−11] Reductive elimination of NiL_2 then gives the naphthalene-2,3-dicarboxylate. For methyl and *tert*-butyl propiolates, the formation of both 1,3- and 2,3-isomers can be accounted for if both steric and electronic effects operate in the second insertion step. Specifically, the increase in proportion of the 1,3-isomer in the case of *tert*-butyl propiolate is consistent with increased steric repulsion between the ester groups in the intermediates along pathway A, causing pathway B in Scheme 6 to be favored. The same observation also tends to rule out the alternative possibility that the second insertion occurs in the nickel−aryl bond.

Steric arguments may also account for the increase in proportion of the naphthalene-2,3-dicarboxylate when the reaction of **1** with methyl propiolate is carried out in the presence of PPh_3. Coordination of this more bulky ligand in place of PEt_3 to the nickelaindene **17**

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(8) Dickstein, J. I.; Miller, S. I. In *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley: Chichester, U.K., 1978; Vol. 2, p 813.
(9) Maitlis, P. M. *Pure Appl. Chem.* **1972**, *30*, 427.
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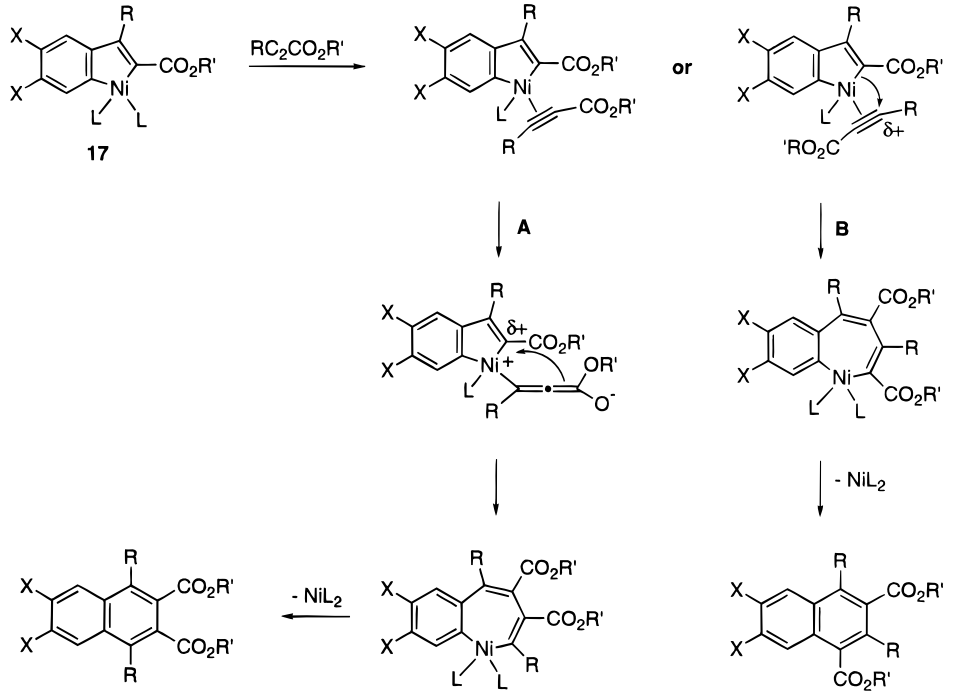
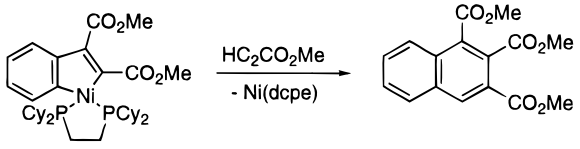
(11) Dierks, R.; tom Dieck, H. *Z. Naturforsch., B* **1984**, *39*, 180.

Scheme 6



would favor intermediates in which the ester group of the incoming acetylene was remote from L, thus favoring pathway A over pathway B in Scheme 6.

We attempted to isolate or detect a nickelaindene intermediate in the reaction of Ni((1,2-η)-C_6H_4)(dcpe) (**2**) with 1 equiv of methyl propiolate but obtained only low yields of naphthalene-1,3- and 2,3-dicarboxylates in addition to unidentified decomposition products. Evidently, the first-formed nickelaindene is more reactive toward acetylenes than is the initial benzyne complex. However, the isolable nickelaindene Ni{C_6H_4C(CO_2Me)=C(CO_2Me)}(dcpe) (**18**),[2] which is formed by careful treatment of **2** with less than 1 equiv of DMAD, reacted with methyl propiolate to give only one double-insertion product, trimethyl 1,2,3-naphthalenetricarboxylate (eq 1); there was no evidence for formation of the 1,2,4-



(1)

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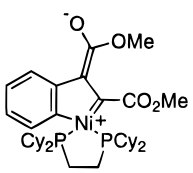
isomer. This reaction presumably is controlled mainly by electronic effects associated with the two ester groups in **18**, which increase the electrophilicity of the nickel-bound carbon atom. These effects may also account for the fact that **18** is more stable than other nickelaindenes, the nickel–vinyl bond being stabilized by the carbene-like resonance form **19**. However, we cannot



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exclude the possibility that methyl propiolate inserts into the nickel–aryl bond of **18** (pathway B); electronic and steric effects would favor formation of the regioisomer having the ester-substituted carbon atom attached to nickel, and reductive elimination would also give the 1,2,3-tricarboxylate isomer.

Finally, it is of interest to compare the regioselectivities we observe with those found in the transformation of cobalt(I)-acetylene complexes CoCp(PPh_3)(η^2-RC_2R') to cobaltacyclopentadienes Co{C(R)=C(R′)C(R″)=C(R‴)}(Cp)(PPh_3) by reaction with acetylenes R″C_2R‴.[12] In this case, steric factors were suggested to be predominant because products containing carbon atoms bearing the bulkiest substituent adjacent to cobalt tended to be favored. Although the direction of addition is similar to that we find for the first insertion, it differs from that for the second insertion. For example, whereas we observe only the naphthalene-2,3-dicarboxylate **7** from **3** and methyl 2-butynoate, reaction of CoCp(PPh_3)(η^2-MeC_2CO_2Me) with methyl 2-butynoate gives two products, Co{C(CO_2Me)=C(Me)C(CO_2Me)=C(Me)}(Cp)(PPh_3) (50% yield) and Co{C(CO_2Me)=C(Me)C(Me)=C(CO_2Me)}(Cp)(PPh_3) (9% yield), in neither of which are the ester groups on adjacent carbon atoms as they are in **7**. These differences support our argument that electronic effects are important, especially in the second insertion step. However, an alternative possibility that cannot be excluded is that the cobalt reactions, which are carried out overnight at room temperature, are under thermodynamic control, whereas the generally faster reactions of nickel(0)–benzyne complexes with acetylenes are governed kinetically.

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Experimental Section

General Procedures. All experiments were performed under an inert atmosphere with use of standard Schlenk techniques, and all solvents were dried and degassed prior to use. All reactions involving benzyne complexes were carried out under argon. NMR spectra were recorded on Varian XL-200E (^{1}H at 200 MHz, ^{13}C at 50.3 MHz, ^{19}F at 188.1 MHz, and ^{31}P at 80.96 MHz), Varian Gemini-300 BB (^{1}H at 300 MHz, ^{13}C at 75.4 MHz, and ^{31}P at 121.4 MHz), Varian VXR-300 (^{1}H at 300 MHz, and ^{13}C at 75.4 MHz), and Varian Inova-500 instruments (^{1}H at 500 MHz). The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvent and to external 85% H_3PO_4 for ^{31}P. The spectra of all nuclei (except ^{1}H and ^{19}F) were ^{1}H-decoupled. The coupling constants (J) are given in Hz. Infrared spectra were measured in solution (KBr cells) on a Perkin-Elmer 683 instrument. Mass spectra of the organic compounds were obtained by the electron impact (EI) method on a VG Micromass 7070F or a Fisons Instruments VG AutoSpec spectrometer. The GC-mass spectra were recorded on a HP5890-5970 system.

The ratios of the products in the organic mixtures were calculated from their ^{1}H NMR integrals unless otherwise specified.

Starting Materials. The benzyne complexes Ni(η^2-C_6H_4)(PEt_3)$_2$ (**1**) and Ni(η^2-C_6H_4)(dcpe) (**2**) were obtained by reduction of the corresponding 2-bromoaryl−nickel(II) bromides with lithium in ether.[2,3] *tert*-Butyl propiolate was obtained commercially and used as received.

Reaction of Ni((1,2-η)-C_6H_4)(PEt_3)$_2$ (1) with a Mixture of *tert*-Butylacetylene and 3-Hexyne. A solution of **1** in hexane (35 mL), prepared by reduction with lithium of NiBr(2-BrC_6H_4)(PEt_3)$_2$ (0.57 g, 1.07 mmol) in ether (20 mL), was cooled to −50 °C, and THF (10 mL) was added. A mixture of *tert*-butylacetylene (0.132 mL, 1.07 mmol) and 3-hexyne (0.365 mL, 3.21 mmol) in THF (3 mL) was added dropwise, and the solution was warmed to room temperature. After 16 h, the ^{31}P NMR spectrum showed only a signal at δ 26.8, due to either Ni(EtC_2Et)(PEt_3)$_2$ or Ni(Bu^tC_2H)(PEt_3)$_2$. Filtration through silica gel (CH_2Cl_2) and separation by preparative TLC (hexane) yielded 178 mg of a 42:58 mixture of 1,2-diethyl-3-*tert*-butylnaphthalene (**11**) (29% based on Ni(II) precursor) and 1,2,3,4-tetraethylnaphthalene (**10**) (40%). **11:** ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.27 (t, 3H, J = 7.4, CH_3), 1.30 (t, 3H, J = 7.5, CH_3), 1.53 (s, 9H, $C(CH_3)_3$), 3.12 (q, 2H, J = 7.4, CH_2), 3.19 (q, 2H, J = 7.5, CH_2), 7.32−7.48 (m, 2H, $H^{6,7}$), 7.73 (s, 1H, H^4), 7.77 (d, 1H, J = 7.6, H^5), 7.98 (d, 1H, J = 7.8, H^8); a NOE experiment gave a 30% response of the singlet at δ 7.73 and a 11% response for the quartet at δ 3.19 on irradiation of the ^{t}Bu signal at δ 1.53; ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 15.83, 16.74 (CH_3), 21.34, 23.62 (CH_2), 32.30 (CH_3), 36.47 (C), 123.45, 123.70, 125.30, 128.74 (CH), 130.57, 132.16, 138.82, 139.04, 145.98 (C) one CH signal is hidden by the CH signals of 1,2,3,4-tetraethylnaphthalene at δ 124.43 and 124.47; EI-MS ($C_{18}H_{24}$): m/z 240 (100, M^+), 225 (89), 211 (22), 165 (32). **10**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25 (t, 6H, J = 7.5), 1.31 (t, 6H, J = 7.5), 2.85 (q, 4H, J = 7.5), 3.11 (q, 4H, J = 7.5), 7.44 ([AB] m, 2H), 8.07 ([AB] m, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 15.62, 15.95 (CH_3), 21.78, 22.85 (CH_2), 124.43, 124.47 (CH), 130.91, 135.29, 137.67 (C).

Reaction of Ni((1,2-η)-C_6H_4)(PEt_3)$_2$ (1) with (Trimethylsilyl)acetylene. A solution of **1** in hexane (40 mL) and THF (10 mL), prepared by reduction with lithium of NiBr(2-BrC_6H_4)(PEt_3)$_2$ (0.655 g, 1.23 mmol) in ether (30 mL), was cooled to −60 °C. (Trimethylsilyl)acetylene (0.8 mL, 6 mmol) was added dropwise and the mixture stirred for 4.5 h while being warmed to room temperature. The ^{31}P NMR spectrum of the solution showed a singlet at δ 16.6 and total disappearance of **1**. Purification by preparative TLC (hexane) gave 214 mg of an inseparable mixture of 1,3-(Me_3Si)$_2$$C_{10}H_6$, 2,3-($Me_3Si$)$_2$$C_{10}H_6$, and the enyne *trans*-$Me_3SiC{\equiv}CCH{=}CHSiMe_3$ in a ratio of 62:10:27 (GC−MS, column HP-5, temperature 70−250 °C, rate 15°/min). The yields of the 1,3- and 2,3-isomers are 43% and 7%, respectively (based on NiBr(2-BrC_6H_4)(PEt_3)$_2$). 1,3-(Me_3Si)$_2$$C_{10}H_6$: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.34 (s, 9H), 0.46 (s, 9H), 7.46−7.53 (m, 2H, $H^{6,7}$), 7.82 (d, 1H, J = 1.3, $H^{2\text{ or }4}$), 7.86−7.88 (m, 1H, $H^{5\text{ or }8}$), 8.03 (app t, 1H, J = 1, $H^{4\text{ or }2}$), 8.07−8.10 (m, 1H, $H^{8\text{ or }5}$); EI-MS ($C_{16}H_{24}Si_2$) m/z 272 (48, M^+), 257 (100), 241 (10), 121 (10), 73 (24). 2,3-(Me_3Si)$_2$$C_{10}H_6$: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.43 (s, 18H), 7.50 ([AB] m, 2H), 7.80 ([AB] m, 2H), 8.16 (s, 2H, $H^{1,4}$); EI-MS ($C_{16}H_{24}Si_2$) m/z 272 (45, M^+), 257 (76), 241 (100), 183 (8), 73 (21). *trans*-(Me_3SiC_2)CHCH($SiMe_3$): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.07 (s, 9H), 0.18 (s, 9H), 5.96 (d, 1H, J = 19.4), 6.51 (d, 1H, J = 19.4); EI-MS ($C_{10}H_{20}Si_2$) m/z 196 (19, M^+), 181 (100), 155 (17), 123 (14), 97 (10), 73 (62).

Reaction of Ni((1,2-η)-C_6H_4)(PEt_3)$_2$ (1) with 1,7-Octadiyne. A solution of **1** in hexane (40 mL), prepared by reduction with lithium of NiBr(2-BrC_6H_4)(PEt_3)$_2$ (0.439 g, 0.8 mmol) in ether (15 mL), was cooled to −50 °C. 1,7-Octadiyne (0.27 mL, 2.5 equiv) was added dropwise and the mixture stirred for 1 h while being warmed to room temperature. The ^{31}P NMR spectrum of the solution showed an AB quartet at δ 28.01 and 24.45 (J = 28), probably due to Ni(η-1,7-octadiyne)(PEt_3)$_2$. Separation by preparative TLC gave an unidentified cyclotrimerization product (67 mg) and 1,2,3,4-tetrahydroanthracene[13] (**14**) (70 mg, 48% based on NiBr(2-BrC_6H_4)(PEt_3)$_2$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.82−1.87 (m, 4H), 2.93−3.00 (m, 4H), 7.32−7.37 ([AA′BB′] m, 2H), 7.53 (br s, 2H), 7.67−7.72 ([AA′BB′] m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 23.35, 29.74 (CH_2), 124.84, 126.60, 126.92 (CH), 132.05, 136.18 (C). EI-MS ($C_{14}H_{14}$): m/z 182 (100, M^+), 165 (32), 154 (70), 141 (40), 106 (61), 105 (59), 77 (51).

Reaction of Ni((1,2-η)-4,5-$F_2C_6H_2$)(PEt_3)$_2$ (3) with Methyl Propiolate in the Presence of PEt_3. A solution of **3**, prepared from NiBr(2-Br-4,5-$F_2C_6H_2$)(PEt_3)$_2$ (0.611 g, 1.08 mmol), was treated with methyl propiolate (0.24 mL, 2.7 mmol) in the presence of PEt_3 (0.32 mL, 2.16 mmol). The mixture was stirred for 3 h while being warmed from −60 to −15 °C. Separation by preparative TLC gave 16 mg of **8** (6%) and 175 mg of a 1.3:5.6:1 mixture of 1,3-(CO_2Me)$_2$-6,7-$F_2C_{10}H_4$ (**8**) (9%), 2,3-(CO_2Me)$_2$-6,7-$F_2C_{10}H_4$ (**9**) (42%), and 1,2,4-(CO_2Me)$_3$$C_6H_3$.

Reaction of Ni((1,2-η)-4,5-$F_2C_6H_2$)(PEt_3)$_2$ (3) with Methyl Propiolate in the Presence of PPh_3. A solution of **3** in hexane (60 mL), prepared by reduction with lithium of NiBr(2-Br-4,5-$F_2C_6H_2$)(PEt_3)$_2$ (0.676 g, 1.2 mmol) in ether (30 mL), was treated with a solution of methyl propiolate (0.27 mL, 3 mmol) in THF (5 mL) in the presence of PPh_3 (0.628 g, 2.4 mmol). The mixture was stirred for 1.5 h while being warmed to −30 °C. After removal of the solvent by evaporation, separation by preparative TLC (hexane/ether 3:1) gave 41 mg of **8** (13% based on Ni(II) precursor) and 286 mg of a 1.5:1 mixture of **9** (53%) and 1,2,4-(CO_2Me)$_3$$C_6H_3$.

Reaction of Ni((1,2-η)-C_6H_4)(PEt_3)$_2$ (1) with Methyl Propiolate in the Presence of PPh_3. A solution of **1** in hexane (50 mL), prepared by reduction with lithium of NiBr(2-BrC_6H_4)(PEt_3)$_2$ (0.645 g, 1.2 mmol) in ether (30 mL), was cooled to −78 °C. A solution of PPh_3 (0.628 g, 2.4 mmol) in THF (20 mL) was added, followed by a solution of methyl propiolate (0.27 mL, 3 mmol) in THF (5 mL). The mixture was stirred for 2 h while being warmed to −15 °C. Monitoring by ^{31}P NMR spectroscopy showed total disappearance of the starting complex. After removal of the solvent by evaporation, separation by preparative TLC (hexane/ether 2:1) gave 56 mg of 1,3-(CO_2Me)$_2$$C_{10}H_6$ (19% based on Ni(II) precursor) and 242 mg of a 3:1 mixture of 2,3-(CO_2Me)$_2$$C_{10}H_6$ (62%) and 1,2,4-(CO_2Me)$_3$$C_6H_3$.

Reaction of Ni((1,2-η)-C_6H_4)(PEt_3)$_2$ (1) with *tert*-Butyl Propiolate in the Presence of PPh_3. Under the same conditions as described above, a solution of **1**, prepared from NiBr(2-BrC_6H_4)(PEt_3)$_2$ (0.65 g, 1.22 mmol), was treated with

(13) Tius, M. A.; Gomez-Galeno, J. *Tetrahedron Lett.* **1986**, *27*, 2571.

PPh_3 (0.63 g, 2.4 mmol) and with *tert*-butyl propiolate (0.411 mL, 3 mmol). Separation by preparative TLC gave 181 mg of 1,3-$(CO_2{}^tBu)_2C_{10}H_6$ (45% based on Ni(II) precursor) and 175 mg of a 2:1 mixture of 2,3-$(CO_2{}^tBu)_2C_{10}H_6$ (28%) and 1,2,4-$(CO_2{}^tBu)_3C_6H_3$. 1,3-$(CO_2{}^tBu)_2C_{10}H_6$: IR (CH_2Cl_2) 3010 (w), 2980 (m), 2935 (w), 1710 (vs), 1625 (w), 1507 (w), 1477 (w), 1455 (w), 1395 (m), 1370 (s), 1313 (s), 1250 (s), 1157 (vs), 1010 (m), 850 (m), 780 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.64 (s, 9H, ^{t}Bu), 1.67 (s, 9H, ^{t}Bu), 7.54 (ddd, 1H, J = 8.1, 6.9, 1.2, $H^{6\text{ or }7}$), 7.66 (ddd, 1H, J = 8.5, 6.8, 1.4, $H^{7\text{ or }6}$), 7.95 (dd, 1H, J = 8, 1.4, H^5), 8.58 (d, 1H, J = 1.8, $H^{2\text{ or }4}$), 8.62 (br d, 1H, J = 2, $H^{4\text{ or }2}$), 8.85 (br d, 1H, J = 8.5, H^8); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 28.1, 28.2 (CH_3), 81.5, 81.8 (C), 125.8, 126.6 (CH), 127.2, 127.3 (C), 128.9, 129.4, 129.8 (CH), 132.9, 133.1 (C), 134.6 (CH), 165.1, 166.5 (CO); EI-MS ($C_{20}H_{24}O_4$) m/z 328 (M^+, 24), 272 (16), 255 (18), 216 (100), 199 (32); HR-MS calcd for $C_{20}H_{24}O_4$ 328.167 460, found 328.166 606. 2,3-$(CO_2{}^tBu)_2C_{10}H_6$: ^1H NMR (200 MHz, $CDCl_3$) δ 1.60 (s, 18H, ^{t}Bu), 7.54 ([AB] m, 2H, $H^{6,7}$), 7.87 ([AB] m, 2H, $H^{5,8}$), 8.12 (s, 2H, $H^{1,4}$). 1,2,4-$(CO_2{}^tBu)_3C_6H_3$: ^1H NMR (200 MHz, $CDCl_3$) δ 1.56 (s, 9H, ^{t}Bu), 1.57 (s, 18H, ^{t}Bu), 7.62 (dd, 1H, J = 8.0, 0.5, H^6), 8.03 (dd, 1H, J = 8.0, 1.7, H^5), 8.21 (dd, 1H, J = 1.7, 0.5, H^3).

Sequential reaction of Ni((1,2-η)-C_6H_4)(dcpe) (2) with DMAD and Methyl Propiolate. A solution of DMAD (0.021 mL, 0.17 mmol) in THF (2 mL) was slowly added over 20 min to a crude solution of **2** (0.187 g, *ca*. 0.3 mmol) in THF (10 mL) at −10 °C, and the mixture was stirred for 30 min. The ^{31}P NMR spectrum of the solution showed the two doublets at δ 67.9 and 62.1 of the monoinsertion complex **18**. A solution of methyl propiolate (0.04 mL, 0.45 mmol) in THF (3 mL) was then added and the solution stirred for 16 h at room temperature (no complex remained, as shown by ^{31}P NMR spectroscopy). The solvent was evaporated, the residue was extracted with ether, and the extract was filtered through silica gel. Separation by preparative TLC (ether−hexane 1:1) gave 10 mg of tetramethyl 1,2,3,4-naphthalenetetracarboxylate and 33 mg of trimethyl 1,2,3-naphthalenetricarboxylate[14] (64% based on DMAD). 1,2,3-$(CO_2Me)_3C_{10}H_5$: IR (CH_2Cl_2) 3060 (w), 2955 (m), 2845 (w), 1725 (vs), 1515 (w), 1460 (m), 1435 (s), 1295 (s), 1250(vs) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 4.01 (s, 3H, OCH_3), 4.06 (s, 3H, OCH_3), 4.12 (s, 3H, OCH_3), 7.67 (ddd, 1H, J = 8.5, 7, 1.4, $H^{6\text{ or }7}$), 7.77 (ddd, 1H, J = 8.5, 7, 1.4, $H^{7\text{ or }6}$), 7.91 (ddd, 1H, J = 8.5, 1.4, 0.8, H^5), 8.73 (s, 1H, H^4), 8.99 (dt, 1H, J = 8.5, 1.1, H^8); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$) 52.6, 52.9, 53.1 (CH_3), 123.3 (C), 126.1, 126.7, 128.0 (CH), 128.5 (C), 129.1 (CH), 129.9 (C), 130.3 (CH), 133.0, 139.1 (C), 165.3, 166.8, 169.0 (CO); EI-MS ($C_{16}H_{14}O_4$) m/z 302 (52, M^+), 271 (100), 84 (50), 49 (52).

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