Insertion Reactions of Benzyne–Nickel(0) Complexes with Acetylenes

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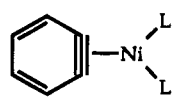
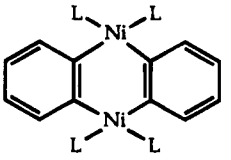
Complexes of nickel(0) containing η^2-4,5-difluorobenzyne, Ni((1,2-η)-4,5-$F_2C_6H_2$)(PEt_3)$_2$ (**10**) and Ni((1,2-η)-4,5-$F_2C_6H_2$)(dcpe) (**11**; dcpe = 1,2-bis(dicyclohexylphosphino)ethane, $Cy_2PCH_2CH_2PCy_2$) have been synthesized by alkali-metal reduction of the appropriate (2-halogenoaryl)nickel(II) halides. Spectroscopic measurements (^{13}C NMR, FAB-MS) indicate that **10**, **11**, and the parent benzyne complex Ni((1,2-η)-C_6H_4)(PEt_3)$_2$ (**2**) are monomeric, analogous to the structurally characterized species Ni((1,2-η)-C_6H_4)($Cy_2PCH_2CH_2PCy_2$). Complexes **2** and **10** undergo rapid intermolecular exchange with PEt_3 at room temperature and react with disubstituted acetylenes by double insertion into the metal–benzyne bond to form 1,2,3,4-tetrasubstituted naphthalenes. With electrophilic acetylenes ($MeO_2CC_2CO_2Me$, MeC_2CO_2Me, HC_2CO_2Me, and $CF_3C_2CF_3$) an aromatic cyclotrimer is also formed; exceptionally, hexafluorobut-2-yne also gives with **10** a phenanthrene derived from two benzyne units and the acetylene. The unsymmetrical acetylenes *tert*-butylacetylene and methyl 2-butynoate give rise to good regioselectivity in the resulting naphthalenes, the favored isomers being very dependent on the steric and electronic influence of the substituents. The dcpe complexes react similarly but more slowly with acetylenes, and with $MeO_2CC_2CO_2Me$ the monoinsertion complexes Ni{$C(CO_2Me)$=$C(CO_2Me)C_6H_2R_2$-*o*}(dcpe) (R = H, F) can be observed.

Introduction

Bis(tertiary phosphine) complexes, ML_2, of zerovalent nickel and platinum form stable complexes with many unsaturated compounds and have been used to stabilize highly reactive, nonisolable species such as small cycloalkynes and benzyne.[1] The monomeric benzyne complexes Ni(η^2-C_6H_4)L_2 (L_2 = dcpe (**1**),[2] 2 P-*i*-Pr_3) have



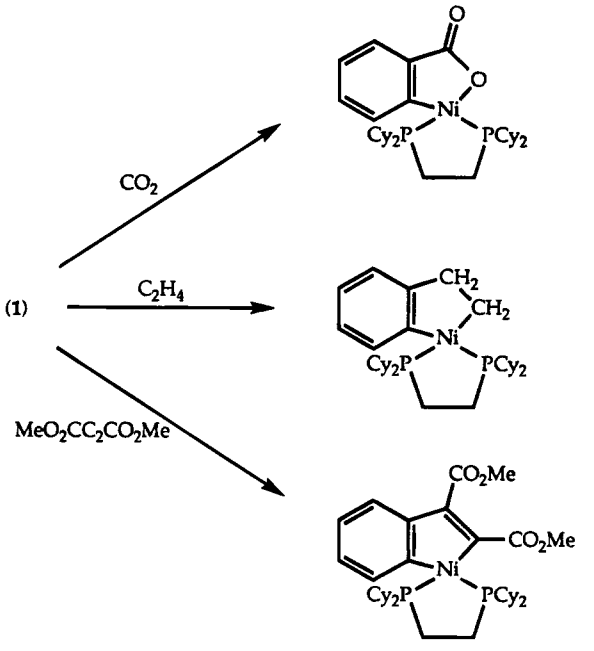
2L = dcpe (**1**), 2P-*i*-Pr_3, 2PEt_3 (**2**)



L = PEt_3 (**3**)

been made by reduction of the corresponding (2-bromophenyl)nickel(II) chloro complexes NiCl(2-BrC_6H_4)L_2 with 0.5–1% sodium amalgam,[3,4] and the dcpe complex has been structurally characterized.[3] In contrast, reduction with lithium of NiCl(2-BrC_6H_4)(PEt_3)$_2$ has been reported by Dobson *et al.*[5] to give a thermally sensitive solid of empirical formula Ni(C_6H_4)(PEt_3)$_2$

Scheme 1



which, on the basis of ^1H NMR and solution molecular weight data, was formulated as a dimeric bis(μ-*o*-phenylene)dinickel(II) complex (**3**) rather than a monomeric η^2-benzyne complex (**2**). Although **1** has been shown to undergo stoichiometric insertions with carbon dioxide, ethylene, and dimethyl acetylenedicarboxylate (Scheme 1), little else is known about the reactivity of (η^2-benzyne)nickel(0) complexes. In this paper we report the preparation and characterization of several new complexes of this class and examine their reaction with various acetylenes.

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(1) (a) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296. (b) Bennett, M. A. *Pure Appl. Chem.* **1989**, *61*, 1695.

(2) Abbreviations: dcpe = 1,2-bis(dicyclohexylphosphino)ethane, $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$; COD = 1,5-cyclooctadiene, C_8H_{12}; AIBN = azobis(isobutyronitrile).

(3) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992.

(4) Bennett, M. A.; Griffiths, K. D.; Okano, T.; Parthasarathi, V.; Robertson, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 7047.

(5) Dobson, J. E.; Miller, R. G.; Wiggen, J. P. *J. Am. Chem. Soc.* **1971**, *93*, 554.

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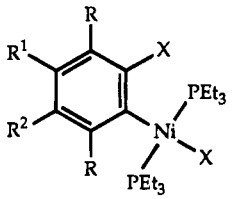
Results and Discussion

Nickel(II) Precursors. The (2-halogenophenyl)-nickel(II) halide precursors $NiX(Ar)(PEt_3)_2$ (**4**–**8**) were made in good yields by oxidative addition of the appropriate dihaloarene to $Ni(COD)_2$ in the presence of triethylphosphine (2 equiv).[6,7] The dibromoarenes re-



$R = R^1 = R^2 = H$; X = Cl (**4**)
$R = R^1 = R^2 = H$; X = Br (**5**)
$R = R^2 = H$; $R^1 = Me$; X = Cl (**6a**)
$R = R^1 = H$; $R^2 = Me$; X = Cl (**6b**)
$R = H$; $R^1 = R^2 = F$; X = Br (**7**)
$R = R^1 = R^2 = F$; X = Br (**8**)

acted faster than the dichloroarenes, in agreement with literature reports on this type of reaction.[7,8] 3,4-Dichlorotoluene gave an inseparable mixture of the 2-chloro-4-methyl and 2-chloro-5-methyl nickel(II) complexes **6a** and **6b** in a 1:4 ratio, as shown by NMR (^1H, ^{13}C, and ^{31}P NMR) spectroscopy (see Experimental Section). Although 1,2-dibromo-4,5-difluorobenzene gave the organonickel(II) complex **7** in good yield, 1,2-dibromo-3,4,5,6-tetrafluorobenzene gave an inseparable mixture of organonickel(II) complex **8** and $NiBr_2(PEt_3)_2$. More electron-rich arenes such as 1,2-dibromo-4,5-dimethoxybenzene, 1,2-dibromo-3,4,5,6-tetramethylbenzene, 1,2-dibromo-4,5-dimethylbenzene, and 1,2,4,5-tetrabromobenzene gave only small amounts of the required organonickel(II) complexes; the main products were $NiBr_2(PEt_3)_2$ and organic compounds formed by dehalogenation of the dihaloarene and coupling of the aryl residues. The lower stability of chelate (σ-aryl)-nickel(II) complexes $NiBr\{C_6H_2(CH_2NMe_2)_2$-2,6-R-4$\}$ when the *para* substituent R is electron-donating has been noted recently.[8]

These qualitative results are consistent with current views about the mechanism of oxidative addition of unactivated aromatic halides (ArX) to nickel(0) complexes.[7,9,10] In the first step, an electron is transferred from nickel(0) to the C–X bond, generating the nickel(I) radical anion intermediate $L_2Ni(XAr)^{\bullet -}$. This can either rearrange rapidly to the oxidative-addition product $NiX(Ar)L_2$ or can decompose to the nickel(I) species $NiXL_2$, which can react with more ArX to give NiX_2L_2 and the aryl radical $Ar^{\bullet -}$. The radical anion is likely to be less stable for an electron-rich aromatic system; therefore, the second pathway will be favored in this case. In 3,4-dichlorotoluene, the 4-position *para* to CH_3 is probably more electron-rich than the 3-position; hence, the initial electron transfer from nickel(0) should occur preferentially to the latter site. In agreement, 4-bromotoluene reacts about 4 times less rapidly with $Ni(PEt_3)_4$ than does bromobenzene and about 3 times less rapidly than does 2-bromotoluene.[9]

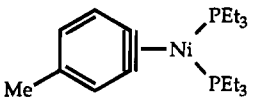
The complex $NiCl(2\text{-}BrC_6H_4)(dcpe)$ was prepared previously in two steps from $NiCl_2(dcpe)$.[3] Reduction with lithium under ethylene gave $Ni(\eta^2\text{-}C_2H_4)(dcpe)$, which was treated with *o*-dibromobenzene to give $NiBr(2\text{-}BrC_6H_4)(dcpe)$; reaction in situ with LiCl gave $NiCl(2\text{-}BrC_6H_4)(dcpe)$. A simpler route to this type of compound has been developed from the observation that reduction of $NiX_2(PPh_3)_2$ with zinc dust in the presence of an aromatic halide and a catalytic amount of AIBN gives the σ-aryl complex $NiX(Ar)(PPh_3)_2$ in good yield.[11] In this way, we have made from 1,2-dibromo-4,5-difluorobenzene the complex $NiBr(2\text{-}Br\text{-}4,5\text{-}F_2C_6H_2)(PPh_3)_2$ and displaced the PPh_3 ligands with dcpe on heating in toluene to give the required complex $NiBr(2\text{-}Br\text{-}4,5\text{-}F_2C_6H_2)(dcpe)$ (see Experimental Section).

η^2-Benzyne Complexes. Reduction of $NiBr(2\text{-}BrC_6H_4)(PEt_3)_2$ (**5**) by lithium in ether at −40 °C gives $Ni(C_6H_4)(PEt_3)_2$, which can be isolated as a sticky, thermally unstable solid from hexane at −60 °C but becomes a viscous oil at room temperature. The compound is difficult to obtain in crystalline form, possibly because it tenaciously retains traces of PEt_3. The ^1H NMR spectrum agrees with that reported by Dobson *et al.*[5] for the compound they isolated from lithium reduction of $NiCl(2\text{-}BrC_6H_4)(PEt_3)_2$ and formulated as **3**. However, the fast-atom bombardment mass spectrum (FAB-MS) of our compound dissolved in a degassed aprotic matrix (tetraglyme) gave the highest mass peak at m/z 370, as expected for monomeric $Ni(C_6H_4)(PEt_3)_2$, with an isotopic pattern characteristic of a compound containing only one nickel atom. The IR spectrum in hexane shows a strong band at 1590 cm^{-1}, similar to that at 1583 cm^{-1} in the spectrum of monomeric $Ni(\eta^2\text{-}C_6H_4)(dcpe)$ (**1**), which was assigned tentatively to a C≡C stretch modified by coordination.[3] These bands are notably more intense than the ν(CC) band at 1560–1570 cm^{-1} observed in $o\text{-}C_6H_4X_2$ (X = Cl, Br) and at 1554 cm^{-1} in the μ-*o*-phenylene complex $Ir_2(\eta^5\text{-}C_5Me_5)_2(CO)_2(\mu\text{-}C_6H_4)$.[12] The $^{31}P\{^1H\}$ NMR spectrum at room temperature consists of a broad singlet at δ 28.5. A sharper signal is obtained if the solution is cooled to −30 °C (no further sharpening is observed at −60 °C) or if the original sample is repeatedly recrystallized from hexane and held in vacuo for extended periods to remove as much residual PEt_3 as possible. These features point to intermolecular associative exchange of the monomer **2** with PEt_3 rather than dissociative exchange from a dimer **3**; a similar conclusion has been drawn from similar observations on the metallacycle $Ni(C_6H_4CMe_2CH_2)(PMe_3)_2$.[13] Finally, the ^{13}C NMR spectrum of **2** at 25 °C shows a singlet at δ 143.3 which can be assigned to the coordinated carbon atoms of η^2-benzyne, by analogy with the spectrum of **1**.[3] In contrast to **1**, ^{31}P coupling is not observed at room temperature owing to the rapid intermolecular exchange with PEt_3, but at −60 °C there is a doublet of doublets at δ 144.09 attributable to the X part of an AA′X spectrum (A = ^{31}P, X = ^{13}C). The separation between the outer lines 1 and 4 (J(PC) + J(P′C)) is 73.7 Hz, and that between lines 1 and 2 (or 3 and 4) is 16.5 Hz. The evidence indicates that the reduction product of **4** and **5** is a monomer, $Ni(\eta^2\text{-}C_6H_4)$-

(6) Fahey, D. R. *J. Am. Chem. Soc.* **1970**, *92*, 402.
(7) Fahey, D. R.; Mahan, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 2501.
(8) van de Kuil, L. A.; Luitjes, H.; Grove, D. M.; Zwikker, J. W.; van der Linden. J. G. M.; Roelofsen, A. M.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1994**, *13*, 468.
(9) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319.
(10) Kochi, J. K. *Pure Appl. Chem.* **1980**, *55*, 571.
(11) Bennett, M. A.; Roberts, N. K., unpublished work.
(12) Graham, W. A. G., personal communication.
(13) Carmona, E.; Gutiérrez-Puebla, E.; Marín, J. M.; Monge, A.; Paneque, M.; Poveda, M. L.; Ruiz, C. *J. Am. Chem. Soc.* **1989**, *111*, 2883.

$(PEt_3)_2$ (**2**), rather than a dimer (**3**), although the reported molecular weight data[5] are not easily explained.

In contrast to $NiCl(2\text{-}BrC_6H_4)(PEt_3)_2$ or $NiBr(2\text{-}BrC_6H_4)(PEt_3)_2$, the 2-chlorophenyl complex $NiCl(2\text{-}ClC_6H_4)(PEt_3)_2$ (**4**) is inert toward lithium, but it is reduced to **2** by 1% Na/Hg. Similarly, reduction of the isomeric mixture **6a/6b** with 1% Na/Hg gives the 4-methylbenzyne complex **9** in *ca.* 80% yield, as estimated



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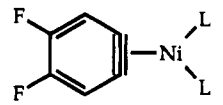


2L = 2PEt$_3$ (10), dcpe (11)

by ^{31}P NMR spectroscopy, but this also was too unstable to be purified. The difference in reactivity between **4** and **5** toward lithium indicates that the first step in the reduction of the 2-halophenyl complexes by alkali metals is abstraction of halide ion from the σ-aryl group, not from nickel(II).

Reduction of **7** with lithium in ether gives the 4,5-difluorobenzyne complex $Ni((1,2\text{-}\eta)\text{-}4,5\text{-}F_2C_6H_2)(PEt_3)_2$ (**10**), which can be isolated in 78% yield as a yellow-brown solid melting at *ca.* 20 °C. Although very air-sensitive, it is thermally more stable than **2**. The FAB mass spectrum shows the highest mass peak at m/z 406 due to the parent ion. The ^1H NMR spectrum consists of a two-proton triplet at δ 7.40 ($^3J_{HF}$ = 5 Hz) due to equivalent aromatic protons, in addition to multiplets arising from the PEt_3 protons, and there is just a singlet at δ −142.1 in the ^{19}F NMR spectrum (*cf.* the precursor **7**, whose ^{19}F NMR spectrum exhibits a pair of multiplets in a 1:1 ratio). The $^{31}P\{^1H\}$ NMR spectrum shows a broad singlet at δ 28.0, which shifts to low frequency on addition of a small amount of PEt_3. In the presence of PEt_3 (1 equiv) there is a very broad signal at δ 6, approximately midway between that of **10** and free PEt_3 (δ −19.2). Clearly, **10**, like **2**, undergoes rapid intermolecular exchange with PEt_3 on the NMR time scale at room temperature.

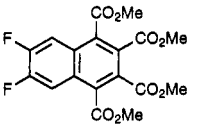
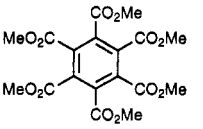
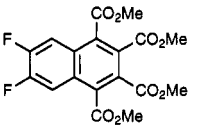
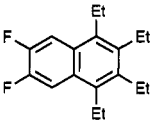
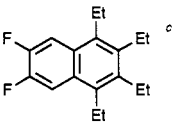
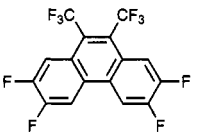
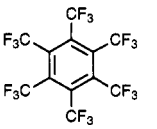
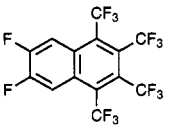
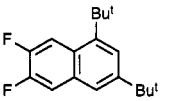
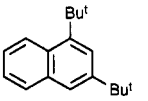
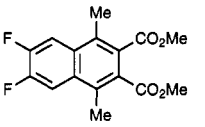
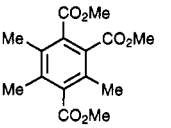
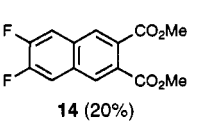
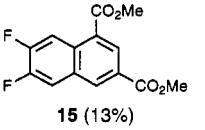
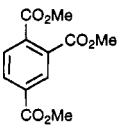
Reduction of $NiBr(2\text{-}Br\text{-}4,5\text{-}F_2C_6H_2)(dcpe)$ with lithium, either in ether or toluene at room temperature, gave the 4,5-difluorobenzyne complex $Ni((1,2\text{-}\eta)\text{-}4,5\text{-}F_2C_6H_2)(dcpe)$ (**11**) as a yellow solid in 85% yield, which is much easier to handle than **10**. It can also be made by treatment of **10** with dcpe, which provides further evidence of the lability of the PEt_3 ligands in **10**. The complex is only slightly soluble in benzene and hexane and decomposes immediately in dichloromethane. The FAB mass spectrum shows a parent ion peak at m/z 592, and the $^{31}P\{^1H\}$ and ^{19}F NMR spectra each show a sharp singlet. The ^{13}C NMR spectrum shows a symmetrical five-line multiplet at δ 137.60, the central line being less intense than the other four lines. This pattern is typical of a AA'X system, and the parameters are similar to these observed for **1**: the separation between the outer lines 1 and 5 ($J(PC) + J(P'C)$) is 85.7 Hz, and that between lines 1 and 2 (or 4 and 5) is 14.3 Hz.

Reactions with Acetylenes. We have concentrated on the reactions of the 4,5-difluorobenzyne complex **10** with acetylenes because of its relative stability and because the combination of ^{19}F and ^1H NMR spectroscopy aided product identification. These reactions did not give isolable nickel(II) complexes arising from monoinsertion into the Ni–benzyne bond. In most cases, the main products that could be isolated were the aromatic compound formed by cyclotrimerization of the acetylene and a naphthalene arising from double insertion of the acetylene into the Ni–benzyne bond and subsequent reductive elimination; formation of the aromatic cyclotrimer was generally favored with more electrophilic acetylenes. The results are summarized in Table 1. Thus, a solution of **10** in hexane reacted rapidly with dimethyl acetylenedicarboxylate (*ca.* 2 mol/mol of **10**) at −30 °C to give, after chromatography on silica gel, hexamethyl benzenehexacarboxylate (48% yield) and tetramethyl 6,7-difluoronaphthalene-1,2,3,4-tetracarboxylate (*ca.* 5% yield based on **10**), which were identified by NMR (^1H, ^{19}F) spectroscopy and mass spectrometry. The crude reaction product showed a ^{31}P NMR singlet at δ 26.6, which may be due to $Ni(PEt_3)_2(\eta^2\text{-}MeO_2CC_2CO_2Me)$. Evidently, this species acts as a catalyst precursor for the cyclotrimerization of dimethyl acetylenedicarboxylate. The reaction of **10** with 3-hexyne occurred only at room temperature to give, as the main product, 6,7-difluoro-1,2,3,4-tetraethylnaphthalene, which was isolated in 89% yield; there was no evidence in this case for the aromatic cyclotrimer C_6Et_6.

The more electrophilic acetylene hexafluoro-2-butyne reacted vigorously with **10** to give a large amount of unidentified polymeric material, but extraction with ether afforded a mixture containing $C_6(CF_3)_6$, 6,7-difluoro-1,2,3,4-tetrakis(trifluoromethyl)naphthalene (**12**), and, unexpectedly, 9,10-bis(trifluoromethyl)-2,3,6,7-tetrafluorophenanthrene (**13**) in a ratio of 1.4:1:2.4, as estimated by integration of the peaks in the ^{19}F NMR spectrum; the last compound was isolated by crystallization from CH_2Cl_2 in 25% yield. Each component showed a parent ion peak in the EI mass spectrum. The ^1H NMR spectrum of the mixture showed a triplet at δ 8.23 (J_{HF} = 9.4 Hz) due to the equivalent aromatic protons of **12** and a pair of doublets of doublets at δ 8.10 and 8.23 due to the two pairs of aromatic protons of **13**. In the region δ −50 of the ^{19}F NMR spectrum there was observed a singlet due to $C_6(CF_3)_6$, a pair of doublets due to the two pairs of CF_3 groups of **12**, and a singlet due to the equivalent CF_3 groups of **13**. Correspondingly, in the region δ −130, there was a triplet due to the equivalent aromatic fluorine atoms of **12** and a pair of triplets due to the two pairs of fluorine atoms of **13**.

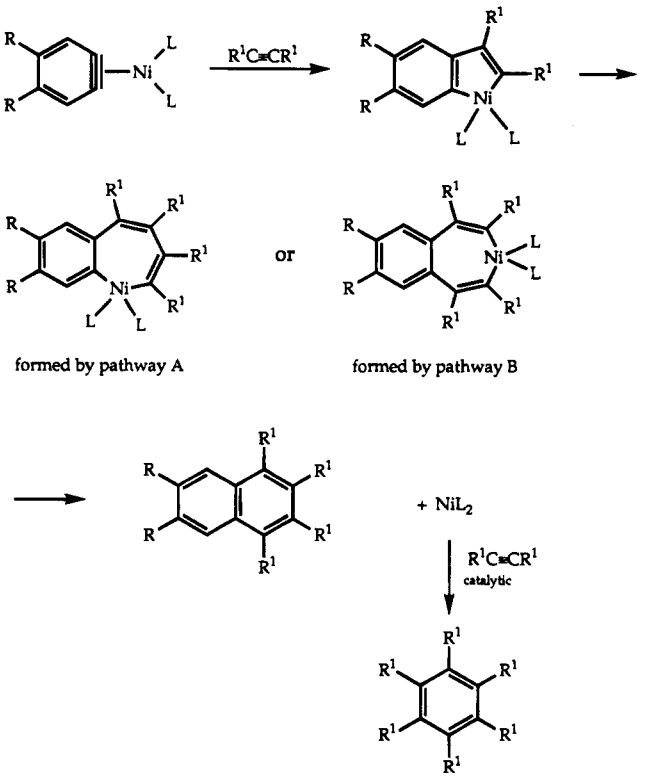
Products arising from double insertion are also obtained from the reaction of **2** and **10** with unsymmetrically substituted alkynes; the position of the substituents in the resulting naphthalene depends on the nature of the substituents. Thus, the reaction of *tert*-butylacetylene with **2** and **10** gave respectively 1,3-di-*tert*-butylnaphthalene and 1,3-di-*tert*-butyl-6,7-difluoronaphthalene. In contrast, the reaction of methyl 2-butynoate with **10** gave an approximately 1:1 mixture of the aromatic cyclotrimer trimethyl 3,5,6-trimethyl-1,2,4-benzenetricarboxylate and the symmetrically substituted derivative dimethyl 6,7-difluoro-1,4-dimethyl-2,3-naphthalenedicarboxylate, whose structure was assigned unambiguously by a nuclear Overhauser (NOE) experiment. The corresponding reaction of **10** with methyl propiolate was not regioselective, giving a 1.3:1 mixture of the symmetrically disubstituted dimethyl 6,7-difluoro-2,3-naphthalenedicarboxylate (**14**) and the unsymmetri-

Table 1. Reactions of Acetylenes with (η^2-Benzyne)nickel(0) Complexes

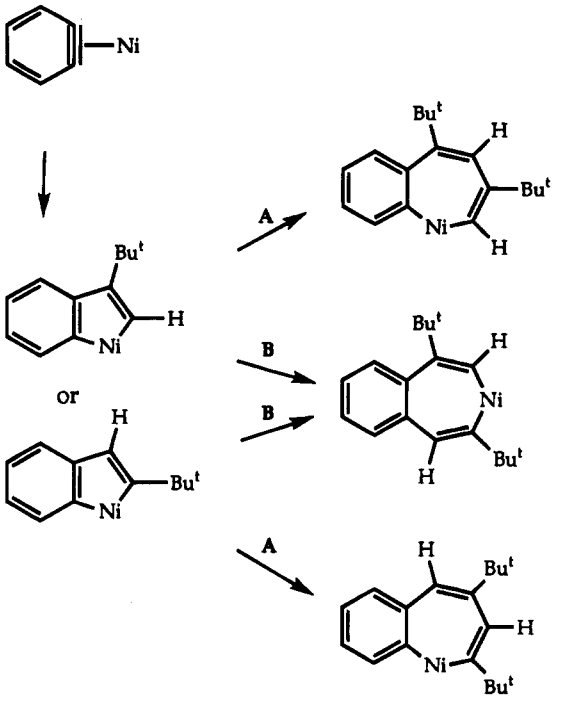
η^2-benzyne complex[a]	acetylene	organic products (yields)[b]	
10	$MeO_2CC{\equiv}CCO_2Me$	 (5%)	 (48%)
11	$MeO_2CC{\equiv}CCO_2Me$	 (43%)	
10	$EtC{\equiv}CEt$	 (89%)	
11	$EtC{\equiv}CEt$	 [c]	
10	$CF_3C{\equiv}CCF_3$	 **13** (25%)	 (16%)
		 **12** (10%)	polymer
10	$Bu^tC{\equiv}CH$	 (45%)	
2	$Bu^tC{\equiv}CH$	 (56%)	
10	$MeC{\equiv}CCO_2Me$	 (57%) (56%)	 (11%)
10	$HC{\equiv}CCO_2Me$	 **14** (20%)	 **15** (13%)
		 (12%)	

[a] Ni((1,2-η)-C_6H_4)(PEt_3)$_2$ (**2**), Ni((1,2-η)-4,5-$F_2C_6H_2$)(PEt_3)$_2$ (**10**), Ni((1,2-η)-4,5-$F_2C_6H_2$)(dcpe) (**11**). [b] Yields of naphthalene are based on the benzyne complex, yields of aromatic cyclotrimer are based on acetylene. [c] Yield not determined but probably almost quantitative.

Scheme 2



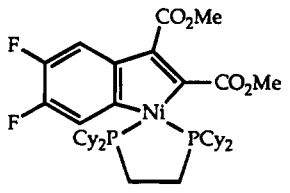
Scheme 3[a]



[a] Phosphine ligands are omitted for clarity.

cally disubstituted dimethyl 6,7-difluoro-1,3-naphthalenedicarboxylate (**15**), together with trimethyl benzene-1,2,4-tricarboxylate.

The apparent difference in behavior of the Ni(η^2-benzyne)(PEt_3)$_2$ (**2** and **10**) and Ni(η^2-C_6H_4)(dcpe) (**1**) complexes toward dimethyl acetylenedicarboxylate led us to investigate the latter in more detail. The 4,5-difluorobenzyne complex Ni((1,2-η)-4,5-$F_2C_6H_2$)(dcpe) (**11**) reacted with $MeO_2CC_2CO_2Me$ and with EtC_2Et to give the same naphthalene compounds obtained from Ni((1,2-η)-4,5-$F_2C_6H_2$)(PEt_3)$_2$ (**10**). In the case of $MeO_2CC_2CO_2Me$, however, it was possible to identify the intermediate monoinsertion product (**16**) by NMR spectroscopy, although it decomposed on attempted isolation.



16

Similarly, we found that the monoinsertion product Ni{$C_6H_4C(CO_2Me)$=$C(CO_2Me)$}(dcpe)[3] was formed only if a very dilute solution of $MeO_2CC_2CO_2Me$ was added slowly to **1** at −10 °C. Rapid addition, or use of an excess of the acetylene, led to the formation of the double-insertion product tetramethyl naphthalene-1,2,3,4-tetracarboxylate.

As mentioned above, the formation of the organic compounds can be rationalized by assuming that the acetylene undergoes sequential double insertion into the Ni–benzyne bond, as illustrated for a symmetrical acetylene in Scheme 2. The initially formed nickelaindene complex could undergo insertion of the second molecule of acetylene either into the nickel–vinyl bond, giving a 1,3-nickelabenzocycloheptatriene (pathway A), or into the nickel–aryl bond, giving a 1,4-isomer (pathway B). Pathway A is directly analogous to one of the mechanisms invoked for alkyne cyclooligomerization at transition-metal centers.[14,15] Irrespective of the route followed, reductive elimination of the nickel–carbon σ-bonds then forms the naphthalene and generates the highly reactive 14e species NiL_2, which is capable of catalyzing the cyclotrimerization of acetylenes.[16]

The pathway adopted in the insertion of an unsymmetrical acetylene in the two successive steps clearly determines the substitution pattern in the resulting naphthalene. The exclusive formation of 1,3-di-*tert*-butylnaphthalenes from **2** or **10** and *tert*-butylacetylene can be accounted for if the insertions take place by pathway A, probably under steric control, independently of the orientation of the coordinated acetylene; i.e., the *tert*-butyl group could be placed on the carbon atom not directly attached to nickel or on that directly bonded to the nickel. If pathway B were operative, the direction of the first and the second insertions would have to differ, which seems less likely (Scheme 3). In the insertion of phenylpropyne and other unsymmetrical acetylenes into the nickel-methyl bonds of NiMe(acac)(PPh_3)[17] and *trans*-NiClMe(PMe_3)$_2$,[18] the carbon atom bearing the sterically bulkier substituent is attached to the metal in the resulting η^1-vinyl product (eqs 1 and 2). In the first case, however, it has been established

(14) Winter, M. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 3, Chapter 5, p 259.

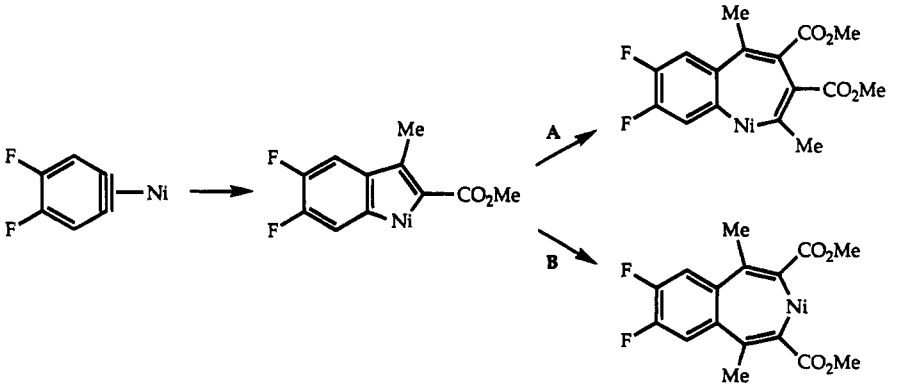
(15) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 613, 870.

(16) Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 8, p 649.

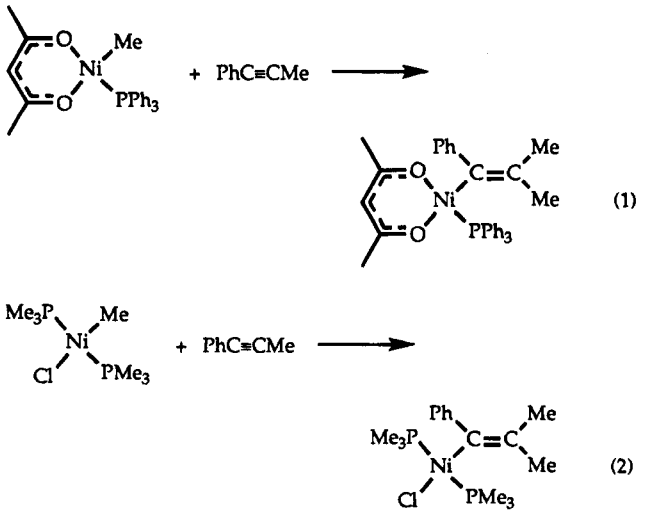
(17) Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002.

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

Scheme 4[a]



[a] Phosphine ligands are omitted for clarity.

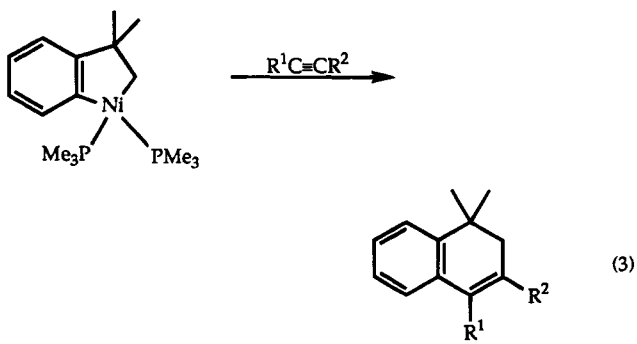


that the insertion proceeds by initial dissociation of PPh_3, probably via the intermediate NiMe(acac)(η^2-alkyne). In this intermediate, repulsion between the bulkier substituent of the unsymmetrical acetylene and the methyl group on nickel causes the latter to migrate to the sterically less hindered carbon atom. It is not known whether the acetylene insertions into **1**, **2**, **10**, and **11** are preceded by dissociation of PEt_3 (**2** and **10**) or by one-ended dissociation of dcpe (**1** and **11**); therefore, it is not clear whether the same steric argument can be invoked or whether repulsion between the bulky substituent and one of the phosphine groups is predominant.

The reaction of **10** with methyl 2-butynoate is probably under electronic control and could proceed by either pathway A or B, as shown in Scheme 4. In both cases, the observed regiochemistry can be accounted for by invoking dipolar intermediates or transition states.[19] As shown in Scheme 5, the coordinated benzyne can be imagined to attack the electron-deficient carbon atom (C^3) of coordinated methyl 2-butynoate to give the first insertion product (I). Coordination of a second molecule of methyl 2-butynoate and a similar nucleophilic attack of C^2 of the alkyne on the electron-deficient, bound carbon atom of the metallacycle leads, after cyclization, to complex II and, after reductive elimination, to the observed naphthalene (pathway A). Pathway B in this case involves a nucleophilic attack of the nickel–aryl bond of I on the positively charged carbon atom of the incoming acetylene to give, after ring closure, isomer III. A mechanism similar to that suggested for pathway A has been postulated for the formation of the unsymmetrical cyclotrimer trimethyl 1,2,4-benzenetricarboxylate from the reaction of methyl 2-butynoate with various nickel(0) precursors;[16,20] this is also the only cyclotrimerization product we observe.

The reaction of **10** with methyl propiolate is much less selective than those with methyl 2-butynoate or *tert*-butylacetylene, which may indicate that both steric and electronic controls are operative. An interesting feature of this reaction is its incompleteness: even when a large excess of methyl propiolate was used, only about half the starting complex reacted to form the double-insertion products. Presumably, as soon as enough $Ni(PEt_3)_2$ had been generated from reductive elimination to catalyze cyclotrimerization, this reaction took precedence over the double insertion.

The regioselectivity of the acetylene insertions of **2** and **10** can be compared with those into the nickel–phenyl bond of $\overline{Ni(C_6H_4CMe_2CH_2)}(PMe_3)_2$, which give, after reductive elimination, dihydronaphthalenes (eq 3).[13,21] In this case, it is suggested that the PMe_3 ligand



R[1] = H, **R** [2]= CO_2Me (**17**)
R[1] = Me, **R**[2] = CO_2Me (**18**)
R[1] = Me, **R**[2] = Ph
R[1] = H, **R**[2] = Bu^t (**19a**)
R[1] = Bu^t, **R**[2] = H (**19b**)
R[1], **R**[2] = -CH=CHCH=CH- (**20**)

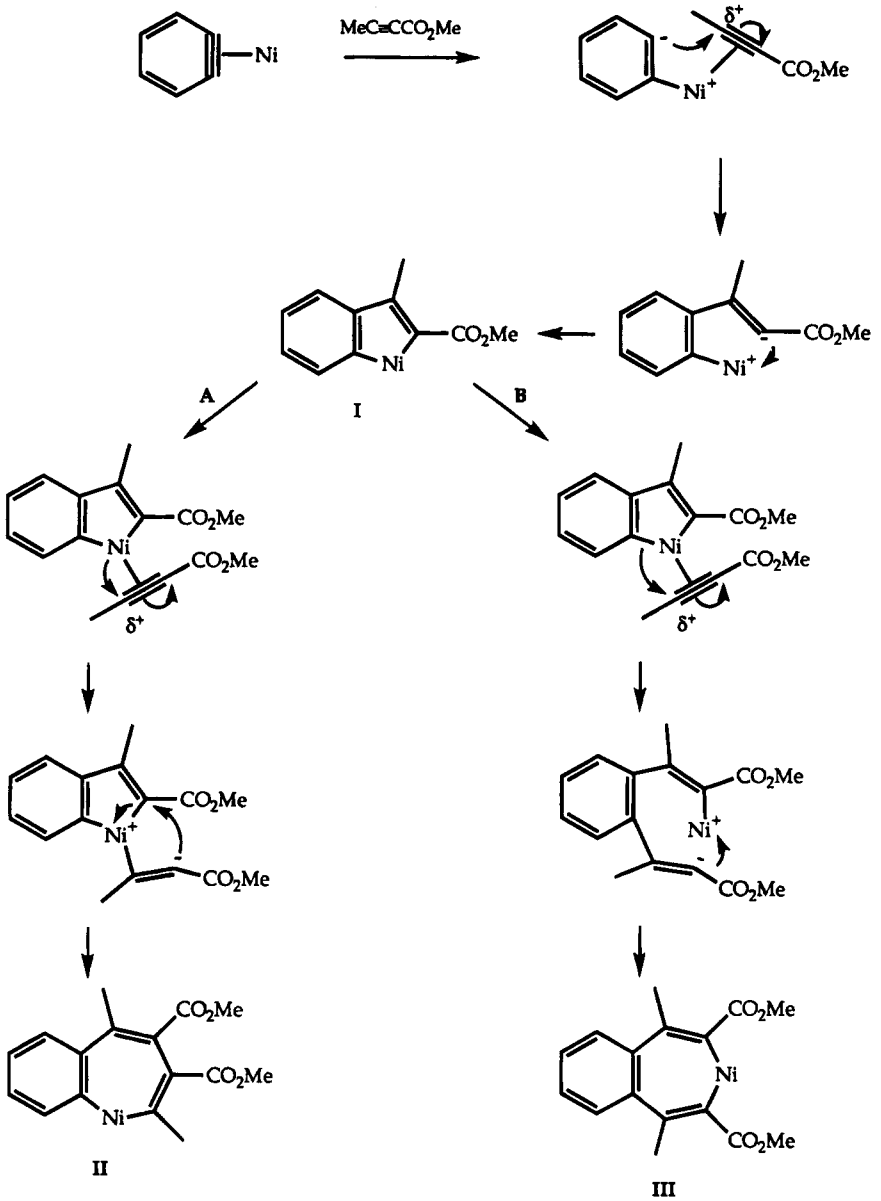
trans to the Ni–C(sp^3) bond is more labile than that trans to the Ni–C(sp^2) bond; hence, the alkyne coordinates cis to the nickel–phenyl bond and insertion occurs at this site. The reactions with methyl propiolate and methyl 2-butynoate to give **17** and **18** occur with the

(19) Maitlis, P. M. *Pure Appl. Chem.* **1972**, *30*, 427.

(20) Dierks, R.; tom Dieck, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39*, 180.

(21) Cámpora, J.; Llebaria, A.; Moretó, J. M.; Poveda, M. L.; Carmona, E. *Organometallics* **1993**, *12*, 4032.

Scheme 5[a]



[a] Phosphine ligands are omitted for clarity.

same regiospecificity as we observe for the latter acetylene and are undoubtedly under electronic control. However, *tert*-butylacetylene gives a 2.2:1 mixture of isomers **19a** and **19b**, so that in this case the sterically more crowded intermediate having the *tert*-butyl group close to the PMe_3 ligand seems to be slightly favored.

The phenanthrene **13** obtained from **10** and hexafluoro-2-butyne formally arises by coupling of two benzyne units and the acetylene. A closely related reaction is the addition of benzyne to $Ni(C_6H_4CMe_2CH_2)(PMe_3)_2$ to give the dihydrophenanthrene **20** (eq 3). Similarly, **13** could be formed by insertion of one molecule of $CF_3C{\equiv}CCF_3$ into the nickel–benzyne bond of **10** and insertion of benzyne (either coordinated or liberated by decomposition of **10**) into the resulting nickelaindene complex.

Finally, the reactions reported here can be compared with the insertions of acetylenes with other η^2-benzyne complexes, either isolated as such or generated in situ. The fragments $M(\eta^2\text{-}C_6H_4)(\eta^5\text{-}C_5H_5)_2$ (M = Ti,[22] Zr[23]) and the complex $Ru(\eta^2\text{-}C_6H_4)(PMe_3)_4$[24] undergo monoinsertion of disubstituted alkynes to give isolable metallaindenes, but these are apparently resistant to further insertion, presumably because there is no readily available coordination site for an additional acetylene molecule (see below). It is worth noting that steric effects appear to determine the formation of the predominant regioisomer arising from the insertion of tolane into the *o*-fluorobenzyne–metal bond of $Ti((1,2\text{-}\eta)\text{-}3\text{-}FC_6H_3)(\eta^5\text{-}C_5H_5)_2$.[25] One example of sequential double insertion is provided by the reactions of triphenylchromium(III) with 2-butyne or tolane, which give 1,2,3,4-tetramethylnaphthalene or 1,2,3,4-tetraphenylnaphthalene, respectively, in addition to the cyclotrimer of the acetylene.[26,27] The naphthalenes could arise from the reaction

(22) (a) Masai, H.; Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 750. (b) Mattia, J.; Humphrey, M. B.; Rogers, R. D.; Atwood, J. L.; Rausch, M. D. *Inorg. Chem.* **1978**, *17*, 3257. (c) Rausch, M. D.; Mintz, E. A. *J. Organomet. Chem.* **1980**, *190*, 65.

(23) (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047.

(24) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 3404.

(25) Butler, I. R.; Cullen, W. R.; Einstein, F. W. B.; Jones, R. H. *J. Organomet. Chem.* **1993**, *463*, C6.

of the acetylene with an intermediate (benzyne)chromium species formed by elimination of benzene from triphenylchromium(III).[28] In agreement, bis(benzyne) complexes have been isolated from reactions of homoleptic σ-aryl metalates of the heavier elements Nb, Ta, Mo, W, and Re.[29]

Conclusions

(a) Success in the preparation of (2-halogenoaryl)nickel(II) halide complexes by oxidative addition of *o*-dihaloarenes to $Ni(COD)_2$ in the presence of PEt_3 depends very much on the nature of the arene substituents and fails when these are strongly electron-donating, such as OMe.

(b) The benzyne complexes $Ni(\eta^2\text{-}C_6H_4)(PEt_3)_2$ (**2**), $Ni((1,2\text{-}\eta)\text{-}4,5\text{-}F_2C_6H_2)(PEt_3)_2$ (**10**), and $Ni((1,2\text{-}\eta)\text{-}4,5\text{-}F_2C_6H_2)$(dcpe) (**11**) have been prepared by alkali-metal reduction of the (2-halogenoaryl)nickel(II) halides and have been shown to be monomeric. Our data suggest that the previously reported μ-*o*-phenylene complex $Ni_2(\mu\text{-}C_6H_4)_2(PEt_3)_4$ (**3**) is probably monomeric $Ni(\eta^2\text{-}C_6H_4)(PEt_3)_2$.

(c) These benzyne complexes undergo double-insertion reactions with alkynes to give substituted naphthalenes, the reactivity being dependent on the nature of the auxiliary phosphine ligands. The insertion reactions of complexes **1** and **11**, containing dcpe, with dimethyl acetylenedicarboxylate are slower than the reactions of their PEt_3 analogues **2** and **10**, and monoinsertion intermediates are observed.

(d) The unsymmetrically substituted acetylenes *tert*-butylacetylene and methyl 2-butynoate give double-insertion products with good but different regioselectivities, which can be accounted for by invoking steric or electronic arguments, respectively, in each case.

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 a Varian XL-200E (^1H at 200 MHz, ^{13}C at 50.3 MHz, ^{19}F at 188.1 MHz, and ^{31}P at 80.96 MHz), a Varian Gemini-300 BB (^1H at 300 MHz and ^{13}C at 75.4 MHz), or a Varian VXR-300 instrument (^1H at 300 MHz and ^{13}C at 75.4 MHz). The chemical shifts (δ) for ^1H and ^{13}C are given in ppm relative to residual signals of the solvent, to external 85% H_3PO_4 for ^{31}P, and to internal $CFCl_3$ for ^{19}F. The spectra of all nuclei (except ^1H and ^{19}F) were ^1H-decoupled. The coupling constants (J) are given in Hz. Infrared spectra were measured in solution (NaCl cells) on a Perkin-Elmer 683 instrument. Mass spectra of the complexes were obtained on a VG ZAB2-SEQ spectrometer by the fast-atom bombardment (FAB) technique. Solutions of the samples were prepared in dry THF (for benzyne complexes) or CH_2Cl_2 and added to a matrix of glycerol or 3-nitrobenzyl alcohol or, for benzyne complexes, degassed tetraglyme. Mass spectra of organic compounds were obtained by the electron impact method (EI) on a VG Micromass 7070F spectrometer. Microanalyses were done in-house.

Starting Materials. 1,2-Dichlorobenzene, 1,2-dibromobenzene, 1,2-dichloro-4-methylbenzene, 1,2,4,5-tetrabromobenzene, 1,2-dibromo-4,5-difluorobenzene and 1,2-dibromo-3,4,5,6-tetrafluorobenzene were obtained commercially and used as received. 1,2-Dibromo-4,5-dimethylbenzene and 1,2-dibromo-3,4,5,6-tetramethylbenzene were prepared by bromination of *o*-xylene and 1,2,3,4-tetramethylbenzene in CH_3CO_2H.[30] 1,2-Dibromo-4,5-dimethoxybenzene was prepared by bromination of 1,2-dimethoxybenzene in EtOH.[31] The complexes $NiBr_2(PPh_3)_2$[32] and $Ni(COD)_2$[33] were prepared according to the literature.

Preparations of Nickel(II) Precursors. (a) $NiCl(2\text{-}ClC_6H_4)(PEt_3)_2$ (4). To a vigorously stirred suspension of $Ni(COD)_2$ (3.155 g, 11.5 mmol) and hexane (80 mL) under nitrogen was added dropwise PEt_3 (3.7 mL, 28.7 mmol) at room temperature. After 5 min, 1,2-dichlorobenzene (1.8 mL, 16 mmol) was added to the red solution and the mixture was stirred at room temperature for 40 min, refluxed for 2 h, and then stirred again at room temperature for 16 h. The solution was filtered through Celite, and the residue was washed with toluene. The orange solution was evaporated *in vacuo* to 20 mL, methanol (40 mL) was added, and the solution was cooled to −78 °C. Solvent was decanted, and the resulting orange crystals were washed with methanol (2 × 10 mL) and dried *in vacuo* to yield 4.25 g of **4** (84%). IR (CH_2Cl_2): 3045 (w), 2975 (s), 2945 (m), 2920 (m), 2890 (m), 1565 (m), 1550 (w), 1460 (m), 1440 (m), 1415 (m), 1380 (w), 1235 (w), 1040 (s), 1015 (m) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 1.03 (quint, 18H, ^3J = 7.5, CH_3), 1.27−1.44 (m, 12H, CH_2), 6.65 (tq, 1H, ^3J = 7.7, ^4J = 1.65, H^4), 6.79 (dt, 1H, ^3J = 7.4, ^4J = 1.4, H^5), 7.07 (dd, 1H, ^3J = 7.7, ^4J = 1.4, H^3), 7.37 (dq, 1H, ^3J = 7.4, ^4J = 1.65, H^6). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 8.09 (CH_3), 13.96 (t, J_{CP} = 12.8, CH_2), 123.22 (CH), 124.13 (CH), 127.07 (CH), 138.75 (t, J_{CP} = 3.2, C^6−H), 141.43 (t, J_{CP} = 3.2, C^2), 154.36 (t, J_{CP} = 34.1, C^1). $^{31}P\{^1H\}$ NMR (80.96 MHz, C_6D_6): δ 11.7 (s). FAB-MS (glycerol, $C_{18}H_{34}Cl_2NiP_2$): *m*/*z* 295 (6), 293 (16, $Ni(PEt_3)_2$), 231 (41), 229 (100, 2-Cl-1-$PEt_3C_6H_4$); the molecular ion at *m*/*z* 440 was not observed.

(b) $NiBr(2\text{-}BrC_6H_4)(PEt_3)_2$ (5). By the same precedure, PEt_3 (6.9 mL, 46.4 mmol) was added to $Ni(COD)_2$ (5.1 g, 18.6 mmol) in hexane (120 mL). 1,2-Dibromobenzene (3.14 mL, 26 mmol) was added, and the red solution was stirred for 1.25 h at room temperature, 2 h under reflux, and 16 h at room temperature. After filtration through Celite and crystallization, 8.87 g of brown solid (**5**) was isolated (90%). IR (CH_2Cl_2): 3045 (w), 2975 (s), 2945 (m), 2920 (m), 2890 (m), 1560 (w), 1545 (w), 1460 (m), 1434 (m), 1418 (m), 1383 (w), 1233 (m), 1079 (m), 1040 (s), 1003 (m) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 1.00 (quint, 18H, ^3J = 7.5, CH_3), 1.30−1.60 (m, 12H, CH_2), 6.55 (tt, 1H, ^3J = 8, ^4J = 1.5, H^4), 7.78 (tt, 1H, ^3J = 7, ^4J = 1.5, H^5), 7.18−7.26 (m, 2H, $H^{3,6}$). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 8.41 (CH_3), 14.88 (t, J_{CP} = 12.7, CH_2), 123.85 (CH), 124.56 (CH), 130.46 (CH), 133.35 (t, J_{CP} = 4.4, C^2), 139.68 (t, J_{CP} = 3.3, C^6−H), 159.55 (t, J_{CP} = 34, C^1). $^{31}P\{^1H\}$ NMR (80.96 MHz, C_6D_6): δ 10.65 (s). FAB-MS (glycerol, $C_{18}H_{34}Br_2NiP_2$): *m*/*z* 295 (7), 293 (16, $Ni(PEt_3)_2$), 275 (100), 273 (97, 2-Br-1-$PEt_3C_6H_4$); the molecular ion at *m*/*z* 528 was not observed. Anal. Calcd for $C_{18}H_{34}Br_2NiP_2$: C, 40.72; H, 6.45; P, 11.67. Found: C, 40.09; H, 6.57; P, 11.64.

(c) $NiCl(2\text{-}Cl\text{-}4\text{-}MeC_6H_3)(PEt_3)_2$ (6a) and $NiCl(2\text{-}Cl\text{-}5\text{-}MeC_6H_3)(PEt_3)_2$ (6b). A mixture of PEt_3 (6 mL, 40.3 mmol) and $Ni(COD)_2$ (4.43 g, 16.1 mmol) in hexane (100 mL) was treated with 3,4-dichlorotoluene (2.9 mL, 22.6 mmol) and worked up as above to give 6.95 g (95%) of yellow powder which was a 4:1 mixture of **6b** and **6a** (as determined by ^1H NMR spectroscopy). The structures were assigned on the basis of

(26) (a) Zeiss, H. H.; Herwig, W. *J. Am. Chem. Soc.* **1958**, *80*, 2913. (b) Herwig, W.; Metlesics, W.; Zeiss, H. H. *J. Am. Chem. Soc.* **1959**, *81*, 6203. (c) Sneeden, R. P. A.; Zeiss, H. H. *J. Organomet. Chem.* **1969**, *20*, 153; **1972**, *40*, 163.

(27) Sneeden, R. P. A. *Organochromium Compounds*; Academic Press: New York, 1975; p 255.

(28) A (benzyne)chromium species may also be implicated in the classic Hein reaction, i.e. the conversion of triphenylchromium(III) to bis(η^6-benzene)chromium(I) and bis(η^6-benzene)(η^6-biphenyl)chromium(I): Reference 27, p 275.

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the different NMR coupling constants in a ^{13}C APT NMR experiment and by comparison with similar complexes.[34] **6a**: ^1H NMR (200 MHz, C_6D_6) δ 1.04 (quint, 18H, ^3J = 7.5, CH_3), 1.30–1.50 (m, 12H, CH_2), 2.03 (s, 3H, C^4–Me), 6.68 (br d, 1H, J = 7.5, H^5), 6.95 (d, 1H, ^3J = 7.5, H^6), 7.25 (br s, 1H, H^3); $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6) δ 8.54 (CH_3), 14.35 (t, J_{CP} = 12.5, CH_2), 20.58 (C^4–Me) (more shielded than in **6b**, which indicates the methyl group to be *para* to nickel), 125.77 (t, J_{CP} = 2.6, C^5–H), 128.29 (m, C^3–H), 132.83 (t, J_{CP} = 2.1, C^4), 138.51 (t, J_{CP} = 3.6, C^6–H), resonances due to C^1 and C^2 were not located. $^{31}P\{^1H\}$ NMR (80.96 MHz, C_6D_6) δ 11.70 (s). **6b**: IR (CH_2Cl_2) 3045 (w), 2975 (s), 2945 (m), 2920 (m), 2890 (m), 2835 (w), 1575 (w), 1555 (w), 1460 (m), 1448 (m), 1419 (m), 1383 (w), 1243 (w), 1137 (w), 1093 (m), 1040 (s), 1009 (m), 819 (m), 807 (m) cm^{-1}; ^1H NMR (200 MHz, C_6D_6) δ 1.04 (quint, 18H, ^3J = 7.5, CH_3), 1.30–1.50 (m, 12H, CH_2), 2.09 (s, 3H, C^5–Me), 6.46 (br d, 1H, ^3J = 8, H^4), 7.00 (d, 1H, ^3J = 8, H^3), 7.30 (br s, 1H, H^6); $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6) δ 8.54 (CH_3), 14.43 (t, J_{CP} = 12.5, CH_2), 21.14 (C^5–Me), 124.43 (t, J_{CP} = 2.3, C^4–H) (smallest coupling; on *para* position), 126.86 (t, J_{CP} = 2.9, C^3-H), 133.28 (t, J_{CP} = 2.6, C^5), 138.70 (t, J_{CP} = 4, C^2), 139.45 (t, J_{CP} = 3.7, C^6–H), 154.97 (t, J_{CP} = 34, C^1); $^{31}P\{^1H\}$ NMR (80.96 MHz, C_6D_6) δ 11.56 (s). FAB-MS (glycerol, $C_{19}H_{36}Cl_2NiP_2$): m/z 295 (6), 293 (15, $Ni(PEt_3)_2$), 245 (46), 243 (100, 2-Cl-5-Me-1-$PEt_3C_6H_3$); the molecular ion at m/z 454 was not observed.

(d) NiBr(2-Br-4,5-$F_2C_6H_2$)(PEt_3)$_2$ (7). To a suspension of $Ni(COD)_2$ (1.9 g, 6.9 mmol) in hexane (60 mL) at 0 °C was added successively PEt_3 (2.6 mL, 17.3 mmol) and 1,2-dibromo-4,5-difluorobenzene (2.64 g, 9.7 mmol) in solution in hexane (10 mL). The brown solution was stirred for 10 min at 0 °C and 4 h at room temperature. The solvent was removed under reduced pressure, and the brown residue was extracted with hexane (4 × 10 mL, 3 × 5 mL). The solution was filtered through Celite and evaporated to half-volume *in vacuo*. The complex was crystallized at −78 °C to yield **7** (2.9 g, 74%) as a brown solid. IR (CH_2Cl_2): 2975 (s), 2945 (m), 2920 (m), 2890 (m), 1597 (w), 1578 (w), 1458 (vs), 1215 (m), 1165 (m), 1041 (s), 876 (m) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 0.93 (quint, 18H, ^3J = 7.5, CH_3), 1.20–1.50 (m, 12H, CH_2), 6.91 (dd, 1H, J_{HF} = 10.5, J_{HF} = 7.5, H^3), 7.04 (ddt, 1H, J_{HF} = 11, J_{HF} = 9, J_{HP} = 1.8, H^6). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6): δ 8.59 (CH_3), 15.02 (t, J_{CP} = 12.9, CH_2), 119.02 (d, J_{CF} = 17.9, C^3–H), 124.62 (C^2), 125.56 (d, J_{CF} = 13.1, C^6–H), 147.14 (dd, J_{CF} = 245.1, J_{CF} = 13.8, C–F), 148.54 (dd, J_{CF} = 250.5, J_{CF} = 11.3, C–F), 155.18 (dt, J_{CP} = 34.1, J_{CF} = 3.9, C^1). ^{19}F NMR (188.1 MHz, C_6D_6): δ −144.8 (m), −142.3 (m). $^{31}P\{^1H\}$ NMR (80.96 MHz, C_6D_6): δ 10.89 (s). FAB-MS (glycerol, $C_{18}H_{32}Br_2F_2NiP_2$): m/z 565 (0.7, M + 1), 539 (2), 537 (5), 312 (13), 311 (95), 310 (14), 309 (100, 2-Br-4,5-F_2-1-$PEt_3C_6H_2$), 295 (6), 293 (15, $Ni(PEt_3)_2$). Anal. Calcd for $C_{18}H_{32}Br_2F_2NiP_2$: C, 38.14; H, 5.69; P, 10.93; Br, 28.19. Found: C, 38.52; H, 5.95; P, 10.66; Br, 28.97.

(e) NiBr(2-BrC_6F_4)(PEt_3)$_2$ (8). As described for **7**, a suspension of $Ni(COD)_2$ (1.36 g, 4.9 mmol) in hexane (40 mL) was treated with PEt_3 (1.82 mL, 12.4 mmol). After 5 min, the solution was cooled to 0 °C and 1,2-dibromo-3,4,5,6-tetrafluorobenzene (0.95 mL, 6.9 mmol) was added slowly. The solution instantly became dark brown. After 4 h at 0 °C, the solvent was evaporated off and the brown oil was extracted with hexane. Filtration and crystallization at −78 °C gave 2.33 g of a 2:1 mixture of **8** (57%) and $NiBr_2(PEt_3)_2$. **8**: ^1H NMR (200 MHz, C_6D_6) δ 0.92 (quint, 18H, ^3J = 7.5, CH_3), 1.20–1.40 (m, 12H, CH_2); $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6) δ 8.18 (CH_3), 15.34 (t, $^1J_{CP}$ = 13.2, CH_2), 109.19 (dt, J = 18, J_{CP} = 3.2, C^2), 136.60 (dt, $^1J_{CF}$ = 246.0, J = 15.4, C–F), 138.47 (ddd, $^1J_{CF}$ = 258.1, J = 24.1, J = 12.1, C–F), 138.87 (dt, J = 53.8, J_{CP} = 30.8, C^1), 143.86 (ddd, $^1J_{CF}$ = 250.4, J = 12.1, J = 3.3, C–F), 146.01 (d, $^1J_{CF}$ = 224.1, C–F) (this complicated system was not well enough resolved to assign all the coupling constants and the C–F carbon atoms); ^{19}F NMR (188.1 MHz, C_6D_6) δ −159.5 (t, $^3J_{FF}$ = 20.7, F^4), −158.2 (dd, $^3J_{FF}$ = 19.9 and 31.7, F^5), −128.5 (dd, $^3J_{FF}$ = 20.8, $^5J_{FF}$ = 11.2, F^3), −113.5 (dd, $^3J_{FF}$ = 31.9, $^5J_{FF}$ = 11.2, F^6); $^{31}P\{^1H\}$ NMR (80.96 MHz, C_6D_6) δ 11.60 (s). $NiBr_2(PEt_3)_2$: ^1H NMR (200 MHz, C_6D_6) δ 1.11 (t, 18H, ^3J = 7.5, CH_3), 1.72 (q, 12H, ^3J = 7.5, CH_2); $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6) δ 8.69 (CH_3), 15.93 (CH_2). This ^1H NMR spectrum of $NiBr_2(PEt_3)_2$ agreed with that of an independently prepared sample and that reported in the literature.[35] Attempts to record a $^{31}P\{^1H\}$ NMR spectrum of $NiBr_2(PEt_3)_2$ were unsuccessful, perhaps because of the presence of a small amount of tetrahedral paramagnetic isomer.[36,37] Crude reaction mixtures often showed a singlet at δ 11.60 that subsequently disappeared, which may be due to $NiBr_2(PEt_3)_2$.

(f) NiBr(2-Br-4,5-$F_2C_6H_2$)(PPh_3)$_2$. A suspension of zinc dust (1.9 g, 29 mmol) in THF (20 mL) was activated by ultrasound for 30 min at room temperature and treated successively with solutions of 1,2-dibromo-4,5-difluorobenzene (6.7 g, 24.9 mmol) in THF (10 mL) and of $NiBr_2(PPh_3)_2$ (15.8 g, 21 mmol) in THF (60 mL) containing AIBN (0.25 g). The green mixture was stirred for 1.5 h at room temperature to give a brown solution. The solvent was removed by evaporation, and the complex was extracted with CH_2Cl_2. The solution was then filtered through Celite and evaporated to dryness. The yellow-brown solid was washed with hot ethanol to yield NiBr(2-Br-4,5-$F_2C_6H_2$)(PPh_3)$_2$ (11.5 g, 64%). ^1H NMR (200 MHz, C_6D_6): δ 6.26 (dd, 1H, J_{HF} = 10.5, J_{HF} = 7.2, H^3), 6.36–6.53 (app. t, 1H, J_{HF} = 9, H^6), 6.99 (br s, 18H, PPh_3), 7.82–7.95 (m, 12H, PPh_3). ^{19}F NMR (188.1 MHz, C_6D_6): δ −147.38 (m), −142.72 (m). $^{31}P\{^1H\}$ NMR (80.96 MHz, C_6D_6): δ 21.53 (s).

(g) NiBr(2-Br-4,5-$F_2C_6H_2$)(dcpe). A suspension of NiBr(2-Br-4,5-$F_2C_6H_2$)(PPh_3)$_2$ (6.27 g, 7.3 mmol) and dcpe (3.41 g, 8 mmol) in toluene (140 mL) was heated for 4 h at 50 °C. The brown solution was filtered through Celite, the residue was extracted with CH_2Cl_2, and the solvent was removed by evaporation. The complex was purified by column chromatography (silica gel, diethyl ether) and crystallized from CH_2Cl_2/hexane (1:1) to yield NiBr(2-Br-4,5-$F_2C_6H_2$)(dcpe) (3.31 g, 60%). IR (CH_2Cl_2): 2930 (s), 2850 (m), 1590 (w), 1445 (s), 1155 (w), 1000 (w) cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2): δ 1.10–2.15 (m, 40H, CH_2 of C_6H_{11}), 2.18–2.52 (m, 4H, CH_2), 2.80–3.00 (m, 4H, CH of C_6H_{11}), 6.89 (tdd, 1H, J = 10, 6, 2, H^{arom}), 7.05 (ddd, 1H, J = 10, 7, 2, H^{arom}). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 19.00–38.00 (m, CH_2 and C_6H_{11}), 119.10 (app d, $^2J_{CF}$ = 17.6, CH), 125.06 (dd, $^2J_{CF}$ = 13.2, $^3J_{CF}$ = 2.2, CH), 126.18 (br s, C^2), 147.30 (dd, $^1J_{CF}$ = 244.8, $^2J_{CF}$ = 14.3, C–F), 148.76 (dt, $^1J_{CF}$ = 249.3, $^2J_{CF}$ = 8.8, C–F), 156.92 (ddd, J_{CP} = 85.6, J_{CP} = 34.0, $^3J_{CF}$ = 4.4, C^1). ^{19}F NMR (188.1 MHz, CD_2Cl_2): δ −145.71 (m), −143.68 (m). $^{31}P\{^1H\}$ NMR (80.96 MHz, CD_2Cl_2): δ 66.77 (dd, J_{PP} = 30.5, J_{FP} = 3.4), 69.01 (d, J_{PP} = 30.5). Anal. Calcd for $C_{32}H_{50}Br_2F_2NiP_2$: C, 51.03; H, 6.69. Found: C, 50.49; H, 6.79.

Preparation of η^2-Benzyne Complexes. (a) Ni((1,2-η)-C_6H_4)(PEt_3)$_2$ (2). (i) To a 1% sodium amalgam prepared from sodium (0.43 g, 18.7 mmol) in mercury (3.15 mL) was added successively THF (20 mL) and **4** (0.52 g, 1.18 mmol). The mixture was stirred vigorously at room temperature for 23 h. The solution was then cooled to −40 °C, and hexane (20 mL) was added. The solution was filtered through Celite into a flask at 0 °C, and the solvent was evaporated *in vacuo*. The dark red residue was extracted with hexane at −40 °C, the extract was filtered, and the orange filtrate was cooled to −78 °C. The yellow powder obtained was decanted, washed with hexane at −78 °C, and dried *in vacuo* at -78 °C. The yield of **2** was 261 mg (45%).

(ii) Glass beads (10 mL volume) and lithium dispersion (30%, 100 mg) were placed in a flask under argon. The lithium was washed with hexane and dried *in vacuo*, and diethyl ether was added (30 mL). The mixture was cooled to −45 °C, and **5** (1.07 g, 2.03 mmol) was added. The mixture was stirred at −40 °C

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for 4 h, and the solvent was removed *in vacuo* at this temperature. The brown residue was extracted with hexane (6 × 5 mL) at 0 °C, and the brown extract was filtered through Celite into a flask at −78 °C and maintained at this temperature overnight. The supernatant liquid was decanted, and after it was dried in vacuo at −40 °C, **5** was isolated as a yellow-brown solid containing traces of starting complex (745 mg, 80% yield by ^{31}P NMR). IR (hexane): 3040 (w), 3000 (w), 2980 (w), 1598 (s), 1435 (m), 1125 (vs), 1030 (s), 760 (s), 730 (s) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.85−1.10 ([A_3B_2X] m, 18H, J = 7.5, CH_3), 1.45−1.63 ([A_3B_2X] m, 12H, J = 7.5, CH_2), 7.28−7.36 ([AA'BB'] m, 2H, $H^{4,5}$), 7.75−7.85 ([AA'BB'] m, 2H, $H^{3,6}$). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6): δ 9.28 (CH_3), 19.33 (m, CH_2), 122.91, 127.20 (CH), 143.34 ($C^{1,2}$). ^{13}C{^{1}H} NMR (75.4 MHz, THF-d_8, −60 °C): δ 9.14 (CH_3), 19.88 (m, CH_2), 122.72 (t, CH, J_{CP} = 4.9), 126.71 (CH), 144.09 [dd, $C^{1,2}$, separations 73.6, 16.5 (see text)]). ^{31}P{^{1}H} NMR (80.96 MHz, C_6D_6): δ 28.5 (br s). FAB-MS (tetraglyme, $C_{18}H_{34}NiP_2$): m/z 370 (100, M); no peaks due to dimer detected.

(b) Ni((1,2-η)-4-MeC$_6$H$_3$)(PEt$_3$)$_2$ (9). Following the procedure described above, the isomeric mixture **6a/6b** (777 mg, 1.7 mmol) was stirred for 18.5 h at room temperature over a 1% Na/Hg amalgam (615 mg/4 mL) in THF. The solution was decanted from the amalgam and evaporated to dryness, the residue was extracted with hexane at −40 °C (8 × 5 mL), and this solution was filtered through Celite into a flask at −78 °C. After evaporation of the solvent, the black residue was recrystallized from hexane at −78 °C to yield a brown solid which contained **9** as well as some unchanged **6a/6b**. Attempts to purify the solid further caused its decomposition. The estimated yield (^{31}P NMR) of **9** was >70%. ^{31}P{^{1}H} NMR (80.96 MHz, C_6D_6): δ 27.64 (br s).

(c) Ni((1,2-η)-4,5-F$_2$C$_6$H$_2$)(PEt$_3$)$_2$ (10). A flask containing glass beads was charged with lithium (242 mg) and diethyl ether (100 mL) and cooled to −50 °C. Complex **7** (3.1 g, 5.49 mmol) in ether (2 × 20 mL) was added, and the mixture was stirred for 5 h at −40 °C. The solvent was evaporated, and the brown solid was extracted with hexane (5 × 20 mL) at −30 °C. The extract was filtered through Celite into a flask at −78 °C and cooled to −78 °C to yield 1.73 g (78%) of **10** as a brown solid. IR (hexane): 3030 (w), 1535 (w), 1440 (s), 1410 (m), 1325 (m), 1255 (m), 1240 (vs), 1140 (m), 1025 (m), 840 (m), 815 (s), 760 (s), 660 (s) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.78−1.05 ([A_3B_2X] m, 18H, J = 7.5, CH_3), 1.38−1.50 ([A_3B_2X] m, 12H, J = 7.5, CH_2), 7.40 (t, 2H, $^3J_{HF}$ = 5, $H^{3,6}$). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6): δ 8.77 (CH_3), 19.82 (d, J_{CP} = 21.4, CH_2), 108.38−108.96 ([ABX] m, CH) (assigned by APT experiment), 135.16 ($C^{1,2}$), 150.44 (dd, $^1J_{CF}$ = 249.1, $^2J_{CF}$ = 16.7, C−F). ^{19}F NMR (188.1 MHz, C_6D_6): δ −142.08 (s). ^{31}P{^{1}H} NMR (80.96 MHz, C_6D_6): δ 28.0 (br s). FAB-MS (tetraglyme, $C_{18}H_{32}F_2NiP_2$): m/z 406 (41, M), 377 (9, M − Et), 296 (37), 294 (100, Ni(PEt_3)$_2$), 282 (6), 280 (18), 265 (8), 263 (11).

(d) Attempted Preparation of Ni((1,2-η)-C$_6$F$_4$)(PEt$_3$)$_2$. A suspension of **8** (456 mg, 0.76 mmol) in ether (20 mL) was treated with lithium (37 mg) for 4 h at −40 °C. The solvent was removed by evaporation, and the resulting solid was extracted with hexane at −40 °C. The extract was filtered through Celite into a flask at −78 °C. The extract was taken to dryness, and the impure residue was extracted again with hexane. Crystallization at −78 °C gave 117 mg of solid containing the benzyne complex, traces of $OPEt_3$ (^{31}P NMR: δ 46.40), and some other unidentified impurities. ^{31}P{^{1}H} NMR (80.96 MHz, C_6D_6): δ 26.44 (br s).

(e) Ni((1,2-η)-4,5-F$_2$C$_6$H$_2$)(dcpe) (11). (i) A 30% Li dispersion (200 mg) was washed with hexane, and toluene (40 mL) was added. The suspension was cooled to −78 °C, and NiBr(2-Br-4,5-$F_2C_6H_2$)(dcpe) (0.624 g, 0.88 mmol) was added. The mixture was stirred for 45 h at room temperature, and the solution was filtered through Celite. The solvent was evaporated to a volume of 20 mL, hexane (40 mL) was added, and the complex was precipitated at −78 °C. Crystallization of the solid from THF/hexane yielded 404 mg (85%) of **11**. IR (THF): 1535 (w), 1440 (vs), 1320 (m), 1235 (s), 1135 (m), 1005 (m), 815 (m), 747 (s), 665 (s) cm^{-1}. ^{1}H NMR (200 MHz, THF-d_8): δ 1.10−2.20 (m, 48H, CH_2 and C_6H_{11}), 7.17 (dt, 2H, J = 5.3, J = 1.7, $H^{3,6}$). ^{13}C NMR (75.4 MHz, THF-d_8): δ 22.53 (t, J_{CP} = 19.8, CH_2), 25.32 (quint, J_{CP} = 19.7, CH_2), 27.09, 27.96, 28.02, 30.10, 30.46 (CH_2 of C_6H_{11}), 35.56 (t, J_{CP} = 11.0, CH of C_6H_{11}), 111.15 (m, $C^{3,6}$−H), 137.60 [5-line m, $C^{1,2}$, separations 85.7, 14.3 (see text)], 151.41 (dd, $^1J_{CF}$ = 245.9, $^2J_{CF}$ = 16.5, $C^{4,5}$). ^{19}F NMR (188.1 MHz, THF-d_8): δ −142.13 (s). ^{31}P{^{1}H} NMR (80.96 MHz, THF-d_8): δ 79.21 (s). FAB-MS (tetraglyme, $C_{32}H_{50}F_2NiP_2$): m/z 592 (22, M).

(ii) A solution of **10** (21 mg, 0.052 mmol) in THF-d_8 (0.45 mL) and dcpe (24 mg, 0.057 mmol) was prepared in a NMR tube at −78 °C. After 10 min at room temperature, ^{31}P NMR spectroscopy confirmed total conversion of **10** into **11**.

Reaction with Acetylenes. (a) Dimethyl Acetylenedicarboxylate. (i) A solution of **10** (360 mg, 0.9 mmol) in hexane (10 mL) was cooled to −30 °C, and dimethyl acetylenedicarboxylate (0.27 mL, 2.2 mmol) was added; there was an immediate reaction. The mixture was stirred for 1.5 h at −30 °C, and a red solid was formed. The solvent was removed by evaporation, and the residue was extracted with ether. The solution was filtered through Celite, and the solvent was evaporated to dryness to yield 599 mg of red oil which showed a ^{31}P NMR singlet at δ 26.64. Purification by column chromatography (silica gel, hexane/ether 5:1) yielded 150 mg of hexamethyl benzenehexacarboxylate, $C_6(CO_2Me)_6$, and 18 mg of tetramethyl 6,7-difluoro-1,2,3,4-naphthalenetetracarboxylate, 1,2,3,4-$(CO_2Me)_4$-6,7-$F_2C_{10}H_2$, which eluted first: IR ($CHCl_3$) 2960 (w), 1740 (s), 1528 (m), 1465 (m), 1445 (m), 1360 (w), 1270 (m), 1237 (m), 1165 (m) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.90 (s, 6H, OCH_3), 3.99 (s, 6H, OCH_3), 7.92 (t, 2H, J_{HF} = 9.6, $H^{5,8}$); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 53.24 (OCH_3), 53.33 (OCH_3), 113.15 (dd, $^2J_{CF}$ = 13.2, $^3J_{CF}$ = 7.7, C^5−H and C^8−H), 127.69 (t, $^3J_{CF}$ = 4.4, $C^{4a,8a}$), 128.70 ($C^{2,3}$), 132.83 ($C^{1,4}$), 152.09 (dd, $^1J_{CF}$ = 259.2, $^2J_{CF}$ = 17.6, $C^{6,7}$), 166.33 (C=O), 166.51 (C=O); ^{19}F NMR (188.1 MHz, $CDCl_3$) δ −129.45 (t, J_{HF} = 9.3); EI-MS ($C_{18}H_{14}F_2O_8$) m/z 396 (40, M), 365 (100), 162 (16), 86 (16), 84 (24). $C_6(CO_2Me)_6$: IR ($CHCl_3$) 2960 (w), 1745 (s), 1447 (m), 1365 (w), 1335 (w), 1237 (m), 1210 (m) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.86 (s, 18H); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 53.42 (OCH_3), 133.88 (C), 165.14 (C=O); EI-MS (glycerol, $C_{18}H_{18}O_{12}$) m/z 426 (1, M), 395 (100, $C_6(CO_2Me)_5(CO)$), 182 (12), 104 (11).

(ii) A solution of **11** (0.23 g, 0.39 mmol) in THF (10 mL) cooled to −78 °C was treated dropwise with a solution of dimethyl acetylenedicarboxylate (0.048 mL, 0.39 mmol) in THF (5 mL), and the mixture was stirred for 30 min at −40 °C. The ^{19}F NMR spectrum showed no evidence for the presence of the monoinsertion complex **14** (see below) but did show signals due to 1,2,3,4-$(CO_2Me)_4$-6,7-$F_2C_{10}H_2$ (see above). Purification by column chromatography (silica gel, hexane/ether (5:1)) yielded 33 mg of tetramethyl 6,7-difluoro-1,2,3,4-naphthalenetetracarboxylate (43% based on dimethyl acetylenedicarboxylate).

(iii) When the dimethyl acetylenedicarboxylate solution was added over a 20 min period to a solution of **11** at −10 °C, the monoinsertion complex **16** was formed. After the mixture was stirred for 20 min at −10 °C, the solvent was removed by evaporation and the residue was washed with hexane. Attempted crystallization from CH_2Cl_2/hexane (1:5) caused decomposition; therefore, the product **16** was identified spectroscopically. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.10−2.50 (m, 48H, CH_2 and C_6H_{11}), 3.68 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 6.72−6.92 (m, 1H, H^3or H^6), 6.97−7.15 (m, 1H, H^3 or H^6). ^{31}P{^{1}H} NMR (80.96 MHz, CD_2Cl_2): δ 63.77 (dd, J_{PP} = 24.5, J_{FP} = 3.7), 69.34 (d, J_{PP} = 24.5).

(b) 3-Hexyne. (i) As described above, a solution of **10** (360 mg, 0.9 mmol) in hexane (10 mL) was cooled to −30 °C and 3-hexyne (0.25 mL, 2.2 mmol) was added dropwise. The mixture was stirred for 15 h at 65 °C. The workup yielded 472 mg of a brown oily solid which showed ^{31}P NMR resonances at δ 26.72 and 27.06. Purification by column chromatography (silica gel, hexane/ether (5:1)) yielded 6,7-difluoro-

1,2,3,4-tetraethylnaphthalene (221 mg, 89%). IR ($CHCl_3$): 2975 (m), 2940 (w), 2910 (w), 2880 (w), 1528 (m), 1450 (m), 1267 (s), 1100 (m), 1015 (m), 817 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.21 (t, 6H, ^3J = 7.6, 2 × CH_3), 1.25 (t, 6H, ^3J = 7.6, 2 × CH_3), 2.80 (q, 4H, ^3J = 7.5, 2 × CH_2), 2.98 (q, 4H, ^3J = 7.6, 2 × CH_2), 7.71 (t, 2H, J_{HF} = 10.9, $H^{5,8}$). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 15.14 (CH_3), 15.58 (CH_3), 22.00 (CH_2), 22.68 (CH_2), 110.62 (dd, $^2J_{CF}$ = 10.5, $^3J_{CF}$ = 6.6, C^5–H and C^8–H), 128.21 ($C^{4a,8a}$), 134.93 ($C^{2,3}$), 138.38 ($C^{1,4}$), 148.97 (dd, $^1J_{CF}$ = 248.2, $^2J_{CF}$ = 17.6, $C^{6,7}$). ^{19}F NMR (188.1 MHz, $CDCl_3$): δ −139.96 (t, J_{HF} = 10.4). EI-MS ($C_{18}H_{22}F_2$): *m/z* 276 (61, M), 261 (44), 118 (21), 106 (67), 105 (66), 90 (49), 78 (57), 77 (72), 62 (100), 55 (59).

(ii) To a solution of **11** (50 mg, 0.08 mmol) in THF-d_8 (0.5 mL) in a NMR tube was added 3-hexyne (0.03 mL). The sample was heated for 16 h at room temperature. The ^{19}F NMR spectrum showed quantitative transformation of the benzyne complex into 6,7-difluoro-1,2,3,4-tetraethylnaphthalene.

(c) Hexafluoro-2-butyne. Complex **10** was prepared *in situ* from **7** (505 mg, 0.89 mmol) by reduction with 30% Li dispersion (118 mg) in ether (20 mL) for 3 h at −30 °C, the reaction progress being monitored by ^{31}P NMR spectroscopy. The solvent was evaporated, the residue was washed with hexane at −30 °C, and the extract was filtered through Celite and its volume reduced *in vacuo* to 20 mL. Exposure of the solution at −30 °C to an atmosphere of hexafluoro-2-butyne caused an instantaneous reaction. After the mixture was stirred for 30 min at −20 °C and 1 h at room temperature, the solvent was evaporated to yield 1.8 g of a brown insoluble polymer. The solid was extracted with ether and purified by column chromatography (silica gel, hexane/ether (5:1)) to yield 194 mg of a 2.4:1.4:1 mixture (ratio calculated from the ^{19}F NMR spectrum) of 9,10-bis(trifluoromethyl)-2,3,6,7-tetrafluorophenanthrene (**13**), hexakis(trifluoromethyl)benzene, and 6,7-difluoro-1,2,3,4-tetrakis(trifluoromethyl)naphthalene (**12**; 44 mg (25%) isolated by crystallization from CH_2Cl_2). $C_6(CF_3)_6$: ^{19}F NMR (188.1 MHz, $CDCl_3$) δ −52.24 (s, CF_3); EI-MS ($C_{12}F_{18}$) *m/z* 486 (13, M), 467 (40), 417 (34), 69 (100, CF_3). 6,7-F_2-1,2,3,4-$(CF_3)_4$-$C_{10}H_2$ (**12**): ^1H NMR (200 MHz, $CDCl_3$) δ 8.23 (t, J_{HF} = 9.4, $H^{5,8}$); ^{19}F NMR (188.1 MHz, $CDCl_3$) δ −50.74 (d, J = 12.2, CF_3), −53.55 (d, J = 12.2, CF_3), −125.46 (t, J = 9.8, $F^{6,7}$); EI-MS ($C_{14}H_2F_{14}$) *m/z* 436 (51, M), 417 (25, M − F), 386 (22), 367 (56, M − CF_3), 348 (4), 317 (20), 298 (7), 229 (7), 149 (14), 77 (11), 69 (100, CF_3). 2,3,6,7-F_4-9,10-$(CF_3)_2$-$C_{14}H_4$ (**13**): ^1H NMR (200 MHz, $CDCl_3$) δ 8.10 (br dd, 2H, J = 11.8, J = 8.3, H^{arom}), 8.23 (dd, 2H, J = 11.4, J = 7.6, H^{arom}); ^{19}F NMR (188.1 MHz, $CDCl_3$) δ −52.49 (s, CF_3), −130.54 (t, J = 10.5, F^{arom}), −133.33 (t, J = 10.5, F^{arom}); EI-MS ($C_{16}H_4F_{10}$) *m/z* 386 (57, M), 367 (9), 336 (6), 317 (34), 85 (31), 71 (50), 69 (68, CF_3), 57 (100).

(d) *tert*-Butylacetylene. (i) A solution of **2** (0.38 g, 1 mmol) in hexane (20 mL) was cooled to −30 °C, and *tert*-butylacetylene (0.45 mL, 4 mmol) in ether (2 mL) was added. The mixture was stirred for 1 h at −30 °C and 4.5 h at room temperature, the progress of the reaction being monitored by ^{31}P NMR spectroscopy. The solvent was removed by evaporation, and the residue, taken up in ether, was filtered through a silica gel column. The compound was purified by preparative TLC (silica gel, hexane/ether (1:1)), and 135 mg (56%) of 1,3-di-*tert*-butylnaphthalene was isolated: ^1H NMR (200 MHz, $CDCl_3$): δ 1.53 (s, 9H, $C(CH_3)_3$), 1.75 (s, 9H, $C(CH_3)_3$), 7.48–7.56 (m, 2H, $H^{6,7}$), 7.70–7.76 (m, 2H, $H^{2,4}$) (no coupling observed with the other protons), 7.92–7.98 (m, 1H, H^5), 8.46–8.54 (m, 1H, H^8) ($H^{5,8}$ became approximate doublets by irradiation at δ 7.47). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 31.22 (CH_3), 31.84 (CH_3), 34.92 (C), 36.26 (C), 122.18 (CH), 122.34 (CH), 123.94 (CH), 124.56 (CH), 126.55 (CH), 129.66 (CH), 135.13 ($C^{4a,8a}$), 145.40 ($C^{1 \text{ or } 3}$), 147.19 ($C^{1 \text{ or } 3}$). EI-MS ($C_{18}H_{24}$): *m/z* 240 (30, M), 225 (100), 141 (11), 77 (10), 57 (73).

(ii) A solution of **10** (0.331 g, 0.8 mmol) in THF (20 mL) was prepared at −50 °C, and *tert*-butylacetylene (0.5 mL, 4.5 mmol) in solution in THF (5 mL) was added. The mixture was stirred for 1 h at −30 °C and 20 h at room temperature. Workup as described above and crystallization from CH_2Cl_2/hexane gave 99 mg (45%) of 1,3-di-*tert*-butyl-6,7-difluoronaphthalene. ^1H NMR (300 MHz, CD_2Cl_2): δ 1.40 (s, 9H, $C(CH_3)_3$), 1.60 (s, 9H, $C(CH_3)_3$), 7.57 (dd, 1H, J = 8.7, 8.1, H^4), 7.57 (dt, 1H, J_{HF} = 21, J = 0.5, H^8), 7.62 (br s, 1H, H^2), 8.15 (dd, 1H, J_{HF} = 14.7, J = 8.7, H^5). ^{13}C NMR (75.4 MHz, CD_2Cl_2): δ 31.36 (CH_3), 31.87 (CH_3), 35.36 (C), 36.57 (C), 113.63 (d, $^2J_{CF}$ = 15.6, $C^{5 \text{ or } 8}$–H), 115.07 (d, $^2J_{CF}$ = 15.4, $C^{5 \text{ or } 8}$–H), 122.05 (d, J = 3.2, $C^{2 \text{ or } 4}$–H), 123.20 (d, J = 2.3, $C^{2 \text{ or } 4}$–H), 126.78 (d, $^3J_{CF}$ = 5.9, $C^{4a \text{ or } 8a}$), 132.91 (d, $^3J_{CF}$ = 7.7, $C^{4a \text{ or } 8a}$), 145.77 (d, J = 4.4, $C^{1 \text{ or } 3}$), 148.49 (dd, $^1J_{CF}$ = 244.8, $^2J_{CF}$ = 15.4, C–F), 148.61 (d, J = 2.2, $C^{1 \text{ or } 3}$), 149.20 (dd, $^1J_{CF}$ = 248.1, $^2J_{CF}$ = 15.4, $C^{1 \text{ or } 3}$). ^{19}F NMR (188.1 MHz, CD_2Cl_2): δ −140.57 (m), −138.86 (m).

(e) Methyl 2-Butynoate. A solution of **10** (0.345 mg, 0.85 mmol) in THF (20 mL) was cooled to −78 °C, and a solution of methyl 2-butynoate (0.34 mL, 3.4 mmol) in THF (5 mL) was added. The solution was stirred for 5.5 h while being warmed to room temperature. The solvent was removed by evaporation. Filtration of an ether solution through a silica gel column yielded 257 mg of a clean 1.3:1 mixture of dimethyl 6,7-difluoro-1,4-dimethyl-2,3-naphthalenedicarboxylate (57%) and trimethyl 1,2,4-benzenetricarboxylate.[19] The compounds were separated by column chromatography (silica gel, hexane/ether (1:1)), and the structure of the naphthalene compound was assigned unambiguously by ^1H NMR spectroscopy. A nuclear Overhauser effect (NOE) experiment yielded a 18% response from the naphthalenic protons in $C^{5,8}$ on irradiation of the signal attributed to the methyl protons (δ 2.62). IR (CH_2Cl_2): 3010 (w), 2955 (m), 1730 (vs, C=O), 1525 (s), 1435 (s), 1230 (vs), 1170 (s), 1080 (m), 1030 (m), 873 (m), 860 (m), 805 (w) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 2.62 (s, 6H, 2 × CH_3), 3.90 (s, 6H, 2 × CO_2CH_3), 7.82 (t, 2H, J_{HF} = 10.1, $H^{5,8}$). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 16.34 (CH_3), 52.75 (OCH_3), 112.40 (m, CH), 129.38 (C), 130.46 (C), 131.65 (C), 150.79 (dd, $^1J_{CF}$ = 252.5, $^2J_{CF}$ = 16.4, CF), 169.13 (C=O). ^{19}F NMR (188.1 MHz, CD_2Cl_2): δ −134.38 (t, J_{HF} = 10.2). EI-MS ($C_{16}H_{14}F_2O_4$): *m/z* 308 (26, M), 277 (77), 276 (100), 261 (33), 218 (87), 190 (73), 151 (31), 57 (53).

(f) Methyl Propiolate. A solution of **10** (331 mg, 0.82 mmol) in THF (20 mL) was cooled to −50 °C, and a solution of methyl propiolate (0.36 mL, 4 mmol) in THF (5 mL) was added. The solution was stirred for 1 h at −30 °C and 20 h at room temperature, but the reaction was not complete as shown by ^{31}P NMR spectroscopy. An excess of methyl propiolate was added, but no decrease in the residual amount of **10** was observed. The solvent was removed by evaporation, and the crude red oil, as an ether extract, was filtered through a silica gel column. The ^{19}F NMR spectrum of the crude compound showed a 1.3:1 mixture of the symmetrically substituted dimethyl 6,7-difluoro-2,3-naphthalenedicarboxylate (**14**) and the unsymmetrical dimethyl 6,7-difluoro-1,3-naphthalenedicarboxylate (**15**). Separation on preparative TLC (silica gel, hexane/ether (1:1)) yielded 30 mg (13%) of **15** and 171 mg of a 3:1 mixture of trimethyl 1,2,4-benzenetricarboxylate and **14** (20%). The structure of **14** was assigned by a NOE experiment. Irradiation of the signal due to $H^{5,8}$ (δ 7.71) gave a 16% response from the remaining aromatic protons. 2,3-$(CO_2Me)_2$-6,7-$F_2C_{10}H_4$ (**14**): ^1H NMR (200 MHz, CD_2Cl_2) δ 3.91 (s, 6H, 2 × OCH_3), 7.71 (t, 2H, J_{HF} = 9.2, $H^{5,8}$), 8.18 (s, 2H, $H^{1,4}$); ^{19}F NMR (188.1 MHz, CD_2Cl_2) δ −133.32 (t, J_{HF} = 9.2). 1,3-$(CO_2Me)_2$-6,7-$F_2C_{10}H_4$ (**15**): IR (CH_2Cl_2) 2950 (w), 1715 (s), 1515 (s), 1465 (m), 1435 (w), 1375 (w), 1285 (w), 1235 (s), 1220 (m), 1130 (m), 855 (m) cm^{-1}; ^1H NMR (200 MHz, CD_2Cl_2) δ 3.98 (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 7.77 (dd, 1H, J_{HF} = 10.4, J_{HF} = 8.3, $H^{5 \text{ or } 8}$), 8.68 (br s, 1H, $H^{2 \text{ or } 4}$), 8.77 (br s, 1H, $H^{2 \text{ or } 4}$), 8.91 (dd, 1H, J_{HF} = 13.4, J_{HF} = 8.3, $H^{5 \text{ or } 8}$); ^{19}F NMR (188.1 MHz, CD_2Cl_2) δ −135.88 (m), −130.56 (m).

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