Formation of (Diphenylphosphino)naphthalenes by Double Insertion of (Alkynyl)diphenylphosphines into Nickel(0)−Benzyne Complexes

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(Alkynyl)diphenylphosphines $Ph_2PC{\equiv}CR$ (R = H, Me, Ph, PPh_2) undergo double insertion into the nickel(0)−benzyne bond of the complexes $[Ni\{(1,2\text{-}\eta)\text{-}4,5\text{-}X_2C_6H_2\}(PEt_3)_2]$ (X = H (**1a**), F (**1b**)) to give mixtures of nickel(0) complexes containing (diphenylphosphino)naphthalenes, which in some cases are formed with high regioselectivity. Bromination of the mixtures of nickel(0) complexes obtained from $Ph_2PC{\equiv}CR$ (R = Me, Ph) and **1a** or **1b** gives in high yield the chelate $NiBr_2$ complexes $[NiBr_2\{6,7\text{-}X_2C_{10}H_2\text{-}1,4\text{-}Y_2\text{-}2,3\text{-}(PPh_2)_2\}]$ (X = H, Y = Me (**6a**), Ph (**11a**); X = F, Y = Me (**6b**), Ph (**11b**)), from which the corresponding 1,4-disubstituted 2,3-naphthylenebis(diphenylphosphines) **12a**, **13a**, **12b**, and **13b** can be liberated by treatment with NaCN in DMSO at 60 °C or dimethylglyoxime/ammonia at room temperature. Derivatives in which only one of the phosphorus atoms is oxidized, $6,7\text{-}X_2C_{10}H_2\text{-}1,4\text{-}Me_2\text{-}2\text{-}PPh_2\text{-}3\text{-}P(O)PPh_2$ (X = H (**15a**), F (**15b**)), have also been prepared. The regioselectivity of the reactions of $Ph_2PC{\equiv}CH$ with **1b** is poorer than that of $Ph_2PC{\equiv}CR$ (R = Me, Ph), and products with a 1,3-substitution pattern predominate. Reaction of $Ph_2PC{\equiv}CPPh_2$ (dppa) with **1a** gives, after addition of bromine, a pair of isomers in which $NiBr_2$ is attached to the phosphorus atoms at the 2,3- and 1,2-positions, respectively, of the tetrakis(tertiary phosphine) species $C_{10}H_4\text{-}1,2,3,4\text{-}(PPh_2)_4$ (**19**). The molecular structures of complexes **11b** and $[NiBr_2\{C_{10}H_4\text{-}1,2,3\text{-}(PPh_2)_3\text{-}4\text{-}\{P(O)Ph_2\}\text{-}\kappa P^1,P^2\}]$ (**18**), and of a disordered 73:27 mixture of the bis(diphenylphosphine oxides) $C_{10}H_4\text{-}1,4\text{-}(PPh_2)_2\text{-}2,3\text{-}\{P(O)Ph_2\}_2$ (**20**) and $C_{10}H_4\text{-}1,2\text{-}(PPh_2)_2\text{-}3,4\text{-}\{P(O)Ph_2\}_2$ (**21**) obtained by partial oxidation of **19**, have been determined by single-crystal X-ray diffraction. The regioselectivities of the insertions of $Ph_2PC{\equiv}CMe$ and $Ph_2PC{\equiv}CH$ into **1a** and **1b** are similar to those of $MeC{\equiv}CCO_2Me$ and $HC{\equiv}CCO_2Me$, respectively, and factors that influence them are discussed.

Introduction

Despite their short lifetimes under normal conditions, arynes are versatile reagents that have been widely used in organic synthesis because of their ability to undergo Diels−Alder reactions, cycloadditions with 1,3-dipoles, and additions to nucleophiles.[1−5] Additional possibilities for organic synthesis are offered by coordination to a transition-metal-containing fragment, which both stabilizes and alters the reactivity of an aryne.[6−10] We have shown that nickel(0) complexes of the type $[Ni(\eta^2\text{-aryne})L_2]$ (aryne = benzyne, 4,5-difluorobenzyne, 2,3-naphthalyne; L_2 = $2PEt_3$, dcpe[11]) undergo double insertions with alkynes.[9,12−14] After reductive elimination of the NiL_2 fragment from the presumed intermediate nickelacycle, the products are substituted naphthalenes (from the benzyne or 4,5-difluorobenzyne complexes) or anthracenes (from the 2,3-naphthalyne complexes). These insertions are often regiospecific. For example, the reaction of methyl 2-butynoate with $[Ni\{(1,2\text{-}\eta)\text{-}4,5\text{-}X_2C_6H_2\}(PEt_3)_2]$ (X = H (**1a**), F (**1b**)) leads exclusively in each case to the naphthalene having the carboxylate groups in the 2,3-positions. In contrast, *tert*-butylacetylene shows the opposite regioselectivity in its reactions with $[Ni\{(1,2\text{-}\eta)\text{-}4,5\text{-}X_2C_6H_2\}(PEt_3)_2]$ (X = H (**1a**), F (**1b**)), which give exclusively the corresponding 1,3-di-*tert*-butylnaphtha-

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(11) Abbreviations: dcpe = 1,2-bis(dicyclohexylphosphino)ethane, $Cy_2PCH_2CH_2PCy_2$; dppa = bis(diphenylphosphino)acetylene, $Ph_2P{\equiv}CPPh_2$.

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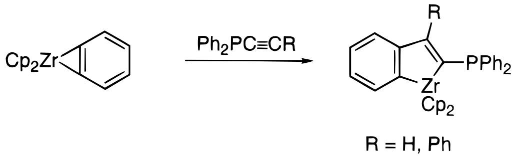
lenes. These differences have been attributed to a combination of electronic and steric effects.[9,12]

We were interested to know whether (alkynyl)diphenylphosphines such as $Ph_2PC{\equiv}CR$ and $Ph_2PC{\equiv}CPPh_2$ (dppa) would undergo double insertions with complexes **1a** and **1b** to give novel tertiary phosphines based on the naphthalene ring and, if so, with what regioselectivity. As potentially bifunctional ligands, acetylenes of this type have been used extensively in organometallic and coordination chemistry, especially for the formation of polynuclear metal complexes.[15] Apart from the results reported in our preliminary communication,[16] however, there are only two examples of the insertion of an (alkynyl)phosphine into a metal−carbon σ-bond, viz. the reactions of $Ph_2PC{\equiv}CR$ (R = H, Ph) and $t\text{-}BuP(C{\equiv}CPh)_2$ with zirconocene−benzyne, $[Cp_2Zr(\eta^2\text{-}C_6H_4)]$, a species that is generated in situ by heating $[Cp_2Zr(\eta^1\text{-}C_6H_5)_2]$.[17,18] Of particular relevance to the work described here are the reactions of $Ph_2PC{\equiv}CR$ (R = H, Ph), which give stereoselectively (2-diphenylphosphino)zirconaindene derivatives (eq 1).[17]

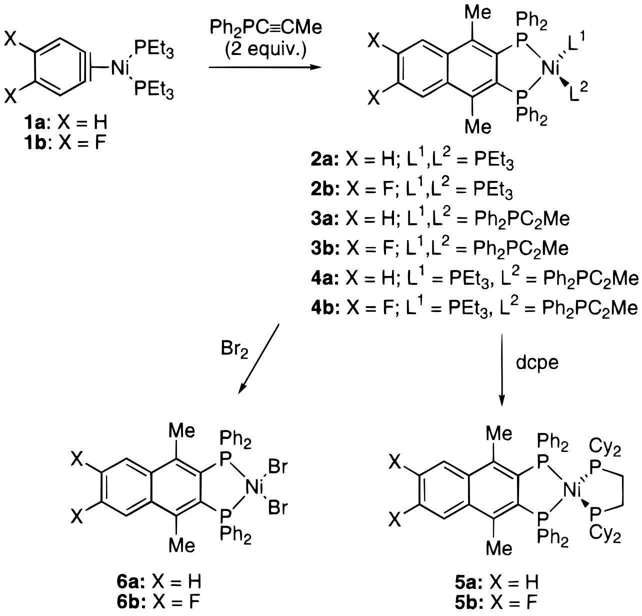


(1)

Results

(1) (1-Propynyl)diphenylphosphine, $Ph_2PC{\equiv}CMe$, and (Phenylethynyl)diphenylphosphine, $Ph_2PC{\equiv}CPh$. The benzyne−nickel(0) complexes $[Ni\{(1,2\text{-}\eta)\text{-}4,5\text{-}X_2C_6H_2\}(PEt_3)_2]$ (X = H (**1a**), F (**1b**)) react readily with $Ph_2PC{\equiv}CMe$ to give red solutions whose $^{31}P\{^1H\}$ NMR spectra are complex but consistent with the presence of three nickel(0) complexes characterized by groups of multiplets in the regions δ 50 and δ 5−10. The strongly deshielded nature of the first group suggests immediately that they arise from phosphorus atoms in a five-membered chelate ring,[19] as would be expected for coordinated 1,4-dimethyl-2,3-naphthylenebis(diphenylphosphine), $C_{10}H_4\text{-}1,4\text{-}Me_2\text{-}2,3\text{-}(PPh_2)_2$.

Scheme 1



In two of the species, the ^{31}P signals in both regions appear as triplets, with P−P couplings of ca. 25 Hz, consistent with the presence of two auxiliary P donors, i.e., PEt_3 and $Ph_2PC{\equiv}CMe$. In the third species, however, the two ancillary ligands are clearly different: the signal assigned to $C_{10}H_4\text{-}1,4\text{-}Me_2\text{-}2,3\text{-}(PPh_2)_2$ appears as a doublet of doublets, whereas the remaining signals are doublets of triplets at δ 5.4 and 9.7 and are assigned to coordinated $Ph_2PC{\equiv}CMe$ and PEt_3, respectively. Thus, the mixtures obtained by reaction of **1a** and **1b** with $Ph_2PC{\equiv}CMe$ are believed to be four-coordinate nickel(0) complexes of general formula $[Ni\{6,7\text{-}X_2C_{10}H_2\text{-}1,4\text{-}Me_2\text{-}2,3\text{-}(PPh_2)_2\}(L^1)(L^2)]$ (X = H, F), where $L^1 = L^2 = PEt_3$ (**2a,b**), $L^1 = L^2 = Ph_2PC{\equiv}CMe$ (**3a,b**), or $L^1 = PEt_3$ and $L^2 = Ph_2PC{\equiv}CMe$ (**4a,b**) (Scheme 1), all of which arise from regiospecific double insertion of the alkynylphosphine. The formulation of these very reactive and labile Ni(0) species is supported by their reaction with dcpe. Addition of the chelating ligand to the red solutions liberates the auxiliary ligands, thus simplifying the $^{31}P\{^1H\}$ NMR spectra. The products are the bis(chelate)nickel(0) complexes $[Ni\{6,7\text{-}X_2C_{10}H_2\text{-}1,4\text{-}Me_2\text{-}2,3\text{-}(PPh_2)_2\}(dcpe)]$ (X = H (**5a**), F (**5b**)), whose ^{31}P NMR spectra consist of a pair of triplets at δ ca. 47 and 52 ($^2J_{PP}$ = 27 Hz). Similar values of $^2J_{PP}$ have been reported for the complexes $[Ni(dmpe)L_2]$ (L = PMe_3, PPh_3)[20] and for other unsymmetrical nickel(0) complexes containing tertiary phosphines and coordinated olefins.[21−23] The structure of the poorly soluble complex **5a** has also been confirmed by ^1H NMR spectroscopy and mass spectrometry. Furthermore, reaction of $[Ni(\eta^2\text{-}C_2H_4)(dcpe)]$ with the free phosphine $C_{10}H_4\text{-}1,4\text{-}Me_2\text{-}2,3\text{-}(PPh_2)_2$ (see below) regenerates complex **5a**, as shown by ^{31}P NMR spectroscopy.

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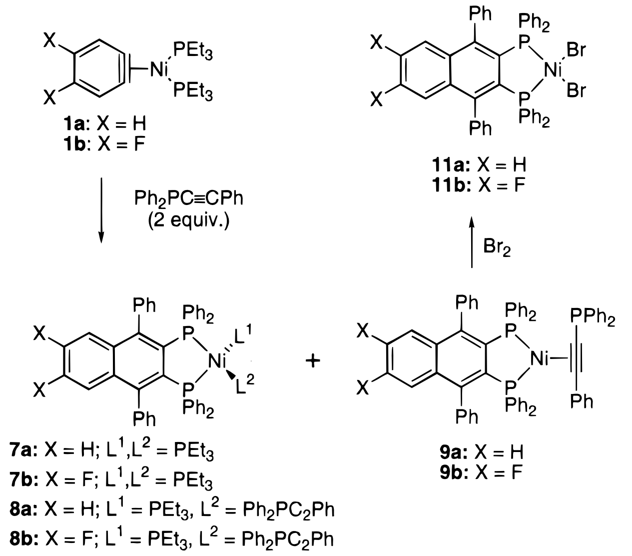
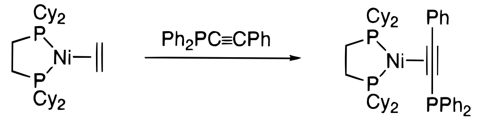
Scheme 2



Treatment of solutions containing **2a**−**4a** or **2b**−**4b** with bromine gives the dibromonickel(II) complexes [$NiBr_2\{6,7\text{-}X_2C_{10}H_2\text{-}1,4\text{-}Me_2\text{-}2,3\text{-}(PPh_2)_2\}$] (X = H (**6a**), F (**6b**)) as air-stable, orange solids in almost quantitative yield based on nickel. They have been characterized by elemental analysis, NMR (^1H, ^{31}P) spectroscopy, and, in the case of **6b**, by single-crystal X-ray diffraction.[16] The coordination geometry about the metal atom is square planar, and the coordinated PPh_2 groups are located on carbon atoms 2 and 3 of the naphthalene ring. The ^{31}P chemical shifts of **6a** and **6b** (δ 65−66) are strongly deshielded, as expected for a rigid, five-membered chelate ring; cf. δ_P 68.6 for [$Ni\{S_2C_2(CN)_2\}$-(*cis*-$Ph_2PCH{=}CHPPh_2$)].[24] In contrast with the behavior of [$Ni(\eta^2\text{-}C_6H_4)(PEt_3)_2$] (**1a**), the dcpe complex [$Ni(\eta^2\text{-}C_6H_4)(dcpe)$] shows no reaction with $Ph_2PC{\equiv}CMe$, even after 1 week at room temperature.

The ligand (phenylethynyl)diphenylphosphine, $Ph_2PC{\equiv}CPh$, also undergoes double insertions with the benzyne−nickel(0) complexes **1a** and **1b** at room temperature to generate the corresponding coordinated 1,4-diphenylnaphthylene-2,3-bis(diphenylphosphines) (Scheme 2). The products formed immediately on mixing $Ph_2PC{\equiv}CPh$ (2 mol) with **1a** or **1b** (1 mol) are the bis(triethylphosphine)nickel(0) complexes [$Ni\{6,7\text{-}X_2C_{10}H_2\text{-}1,4\text{-}Ph_2\text{-}2,3\text{-}(PPh_2)_2\}(PEt_3)_2$] (X = H (**7a**), F (**7b**)), whose $^{31}P\{^1H\}$ NMR spectra show a pair of multiplets at δ ca. 7 and 52 due to PEt_3 and the naphthylene ligand, respectively. In a slower reaction, one of the coordinated triethylphosphine ligands is replaced by $Ph_2PC{\equiv}CPh$ to give [$Ni\{6,7\text{-}X_2C_{10}H_2\text{-}1,4\text{-}Ph_2\text{-}2,3\text{-}(PPh_2)_2\}(PEt_3)(Ph_2PC{\equiv}CPh)$] (X = H (**8a**), F (**8b**)), characterized by three multiplets in the $^{31}P\{^1H\}$ NMR spectra at δ ca. 3, 7, and 52 due to coordinated $Ph_2PC{\equiv}CPh$, PEt_3, and the naphthylene ligand, respectively. In contrast with the behavior of $Ph_2PC{\equiv}CMe$, however, there is no evidence for the formation of the bis(alkynylphosphine) complex. Instead, in each case, complexes **7a,b** and **8a,b** are finally replaced by a third species characterized by the presence in its $^{31}P\{^1H\}$ NMR spectrum of a pair of multiplets in the region of δ 63 and a doublet of doublets at δ ca. −19, the P−P coupling constants being ca. 30 Hz. The multiplets at higher frequency must be assigned to inequivalent phosphorus atoms of the appropriate naphthylenebis(diphenylphosphine), while the chemical shift of the remaining signal is suggestive of an uncoordinated phosphorus atom of $Ph_2PC{\equiv}CPh$. These data are consistent with the formulation [$Ni\{6,7\text{-}X_2C_{10}H_2\text{-}1,4\text{-}Ph_2\text{-}2,3\text{-}(PPh_2)_2\}(\eta^2\text{-}Ph_2PC{\equiv}CPh)$] (X = H (**9a**), F (**9b**)), the alkynylphosphine being bound only via its triple bond to trigonal-planar-coordinated nickel(0).

This formulation is supported by the isolation of [$Ni(dcpe)(\eta^2\text{-}Ph_2PC{\equiv}CPh)$] (**10**) as a thermally sensitive yellow solid from the reaction of $Ph_2PC{\equiv}CPh$ with [$Ni(C_2H_4)(dcpe)$] (eq 2). This complex contains a parent ion peak in its FAB mass spectrum and shows a ^{31}P NMR pattern analogous to that of **9**, viz. two doublets of doublets in the region of δ 70 due to inequivalent phosphorus atoms of dcpe and a doublet of doublets at δ −14.5 due to the uncoordinated phosphorus atom of $Ph_2PC{\equiv}CPh$. In **10**, the change in the ^{13}C NMR chemical shift of the two quaternary carbons of the alkyne shows clearly that these carbons are now coordinated to the metal center; the signals appear as doublets at δ_C 87 and 108 in the free alkyne and as doublets of doublets of doublets at δ_C 141 and 150 in the complex. The structure of the analogous complex [$Ni(dcpe)(\eta^2\text{-}Ph_2PC{\equiv}CMe)$] has been confirmed by single-crystal X-ray diffraction.[25]



(2)

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Addition of bromine to the solutions of nickel(0) complexes **7a**−**9a** or **7b**−**9b** gives the corresponding orange nickel(II) complexes [$NiBr_2\{6,7\text{-}X_2C_{10}H_2\text{-}1,4\text{-}Ph_2\text{-}2,3\text{-}(PPh_2)_2\}$] (X = H (**11a**), F (**11b**)), which show the expected ^{31}P NMR singlets in the region of δ 67. The structure of complex **11b** has been confirmed by single-crystal X-ray diffraction (see below). Complex **11a** has been prepared, in 66% yield based on nickel, in a one-pot procedure starting from the precursor to **1a**, [$NiBr(2\text{-}BrC_6H_4)(PEt_3)_2$]; reduction to **1a**, insertion of $Ph_2PC{\equiv}CPh$, and bromination were carried out in successive steps. The yield is somewhat lower than that of complex **6a** obtained by use of $Ph_2PC{\equiv}CMe$, probably because the formation of the side-bonded complex **9a** scavenges some of the alkynylphosphine required for double insertion. The sterically bulky (alkynyl)diphenylphosphines $Ph_2PC{\equiv}CR$ (R = *t*-Bu, $SiMe_3$) do not react with complexes **1a** or **1b** at room temperature.

Liberation of the ditertiary phosphines from their dibromonickel(II) complexes by treatment with an excess of NaCN requires unexpectedly forcing conditions, viz. overnight heating to 60 °C in DMSO. In this way the 2,3-naphthylenebis(diphenylphosphines) $6,7\text{-}X_2C_{10}H_2\text{-}1,4\text{-}Y_2\text{-}2,3\text{-}(PPh_2)_2$ (X = H, Y = Me (**12a**); X = F, Y = Me (**12b**); X = F, Y = Ph (**13b**)) have been obtained almost quantitatively from complexes **6a**,**b** and **11b**, respectively. An alternative, milder procedure, which

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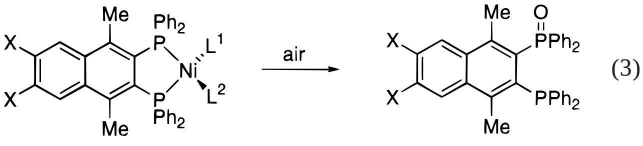
was tested with complex **11a**, is to treat the nickel(II) complex with dimethylglyoxime and aqueous ammonia at room temperature. The ligand $C_{10}H_4$-1,4-Ph_2-2,3-$(PPh_2)_2$ (**13a**) that is released quantitatively can be obtained pure by filtration through degassed acidic alumina. The naphthylenebis(diphenylphosphines) are air-stable, yellow solids that show singlet ^{31}P NMR resonances at δ ca. -1 to -6 and parent ion peaks in their electron-impact (EI) mass spectra.

Oxidation of both phosphorus atoms requires forcing conditions. The nickel(0) complexes **2a**−**4a** and **2b**−**4b** or the derived tertiary phosphines **12a**,**b** had to be treated with 30% aqueous H_2O_2 or heated in the presence of air in order to obtain the bis(diphenylphosphine oxides), 6,7-$X_2C_{10}H_2$-1,4-Me_2-2,3-$\{P(O)Ph_2\}_2$ (X = H (**14a**), F (**14b**)), quantitatively.

Exposure of the mixtures of nickel(0) complexes **2a**−**4a** and **2b**−**4b** to air over 24 h gives exclusively the colorless mono(diphenylphosphine oxides) 6,7-$X_2C_{10}H_2$-1,4-Me_2-2-PPh_2-3-$\{P(O)Ph_2\}$ (X = H (**15a**), F (**15b**)), which show ^{31}P NMR doublet resonances at δ ca. -6 (PPh_2) and $+31$ [$P(O)PPh_2$] ($^2J_{PP}$ = 37 Hz) and parent ion peaks in their EI mass spectra (eq 3). The formulation of **15b** has been confirmed by X-ray structural analysis.[16]

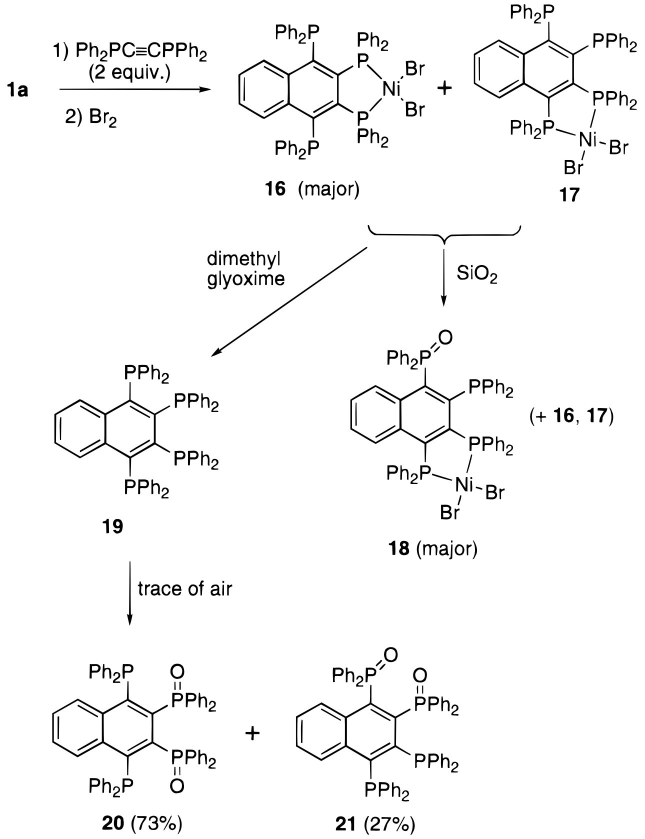


6a-8a: X = H
6b-8b: X = F

15a: X = H
15b: X = F

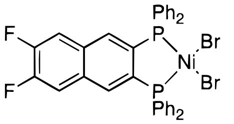
(2) Bis(diphenylphosphino)acetylene, $Ph_2PC{\equiv}CPPh_2$. Double insertion of $Ph_2PC{\equiv}CPPh_2$ with [Ni(η^2-C_6H_4)(PEt_3)$_2$] (**1a**) (Scheme 3) required heating at 50 °C for 16 h. The $^{31}P\{^1H\}$ NMR spectrum of the resulting solution is complex, although addition of bromine simplifies it. The crude orange solid isolated from the brominated solution contains the dibromonickel(II) complexes of two isomeric naphthalene-based ligands in a 2:1 ratio. The $^{31}P\{^1H\}$ NMR spectrum of the major species contains two doublets of doublets at δ_P -12.2 and 75.8, a pattern that is consistent with a symmetrical chelate complex having uncoordinated diphenylphosphino groups in the 1,4-positions, i.e., [$NiBr_2\{C_{10}H_4$-1,2,3,4-$(PPh_2)_4$-$\kappa P^2,P^3\}$] (**16**). The minor compound is less symmetrical: its $^{31}P\{^1H\}$ NMR spectrum shows four different resonances at δ -9.4, 3.8, 66.9, and 81.9, the first two being assigned to phosphorus atoms at positions 4 and 3, the last two to coordinated phosphorus atoms at positions 1 and 2. The chemical shifts and coupling constants are consistent with the formulation [$NiBr_2\{C_{10}H_4$-1,2,3,4-$(PPh_2)_4$-$\kappa P^1,P^2\}$] (**17**). Attempts to separate **16** and **17** on silica gel gave small amounts of the original mixture together with a new complex **18**, whose $^{31}P\{^1H\}$ NMR spectrum resembles that of **17** except that the resonances due to the uncoordinated phosphorus atoms P^3 and P^4 are shifted to δ 13.5 and 29.4, respectively. The IR spectrum contains a strong absorption at 1208 cm^{-1} assignable to ν(P=O), and the mass spectrum shows that one of the uncoordinated phosphorus atoms has been oxidized. The data indicate that complex **18** is [$NiBr_2\{C_{10}H_4$-1,2,3-$(PPh_2)_3$-4-$\{P(O)PPh_2\}$-$\kappa P^1,P^2\}$]; this formulation has been confirmed by X-ray structural analysis (see below). The total yield for the double-insertion reaction calculated from the recovered products **16**−**18** was ca. 90%, based on the Ni(II) precursor to **1a**, [$NiBr(2$-$C_6H_4)(PEt_3)_2$]; hence, little or no material had been lost on the silica gel column. The predominant formation of **18** as a result of chromatography can only be accounted for by mono-oxidation of **16** and **17** on the column accompanied by migration of the $NiBr_2$ fragment from phosphorus atoms P^2 and P^3 to P^1 and P^2. The observation that the relative amounts of **16** and **17** before chromatography do not change on heating suggests that the rearrangement is preceded, not followed, by oxidation of P^4.

Scheme 3



Treatment of the mixture of **16** and **17** with dimethylglyoxime in the presence of aqueous ammonia precipitates immediately the crude tetrakis(tertiary phosphine) $C_{10}H_4$-1,2,3,4-$(PPh_2)_4$ (**19**), whose $^{31}P\{^1H\}$ NMR spectrum shows a pair of triplets at δ -10.8 and 4.5 due to $P^{1,4}$ and $P^{2,3}$, respectively. Unfortunately, attempts to crystallize **19** gave only partially oxidized material, single crystals of which contained a 73:27 mixture of the bis(diphenylphosphine oxides) $C_{10}H_4$-1,4-$(PPh_2)_2$-2,3-$\{P(O)Ph_2\}_2$ (**20**) and $C_{10}H_4$-3,4-$(PPh_2)_2$-1,2-$\{P(O)Ph_2\}_2$ (**21**), as shown by X-ray structural analysis (see below).

(3) Ethynylphosphine, $Ph_2PC{\equiv}CH$. This ligand reacts with the 4,5-difluorobenzyne complex **1b** to give a dark red solution whose ^{19}F and ^{31}P NMR spectra are very complex. The $^{31}P\{^1H\}$ NMR spectrum contains signals similar to those described above corresponding to nickel(0) complexes of naphthylene-2,3-bis(diphenylphosphines), but there are also signals in the region of δ_P −5 that are likely to be due to free naphthylenebis(diphenylphosphines), together with multiplets possibly due to phosphine oxides or oligomers. The $^{31}P\{^1H\}$ NMR spectrum of the solution obtained after addition of bromine is also complex, although a resonance at δ_P 65.2 due to a minor component may be assigned to the planar chelate nickel(II) complex $[NiBr_2\{6,7-F_2C_{10}H_4-2,3-(PPh_2)_2\}]$ (**22**). The main species present shows a very broad signal at δ_P 38 and gives a green solution in CH_2Cl_2 suggestive of the presence of a paramagnetic, tetrahedrally coordinated nickel(II) complex, but we could not characterize it.



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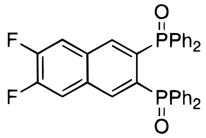

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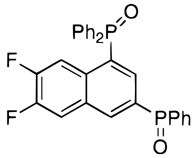

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Treatment of the nickel(0) complexes arising from reaction with $Ph_2PC{\equiv}CH$ with air and subsequently with H_2O_2 gives a mixture whose ^{19}F NMR spectrum shows the presence of only three aromatic compounds in a ratio of ca. 1:2:1. The components of the mixture could not be separated by chromatography, but some tentative assignments can be made. The first compound, which shows a triplet at δ_F −131.7 and a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ 31.0, is probably the 2,3-naphthylenebis(diphenylphosphine oxide) $6,7-F_2C_{10}H_4-2,3-\{P(O)Ph_2\}_2$ (**23**); the most abundant species contains a pair of multiplets at δ −129.4 and −133.4 in its ^{19}F NMR spectrum and a pair of doublets at δ 31.5 and 26.3 (J = 2.3 Hz) in its $^{31}P\{^1H\}$ NMR spectrum. These data suggest that the compound is the 1,3-naphthylenebis(diphenylphosphine oxide) $6,7-F_2C_{10}H_4-1,3-\{P(O)Ph_2\}_2$ (**24**); the ligand from which it is derived, $6,7-F_2C_{10}H_4-1,3-(PPh_2)_2$, is clearly incapable of chelation to a single nickel(II) atom and is likely to be responsible for the formation of the paramagnetic nickel(II) species mentioned above. The nature of the third species, which is responsible for a pair of multiplets at −130.5 and −133.7 in the ^{19}F NMR spectrum, is unknown.

The double insertion of $Ph_2PC{\equiv}CH$ with **1b** is clearly not regiospecific and, hence, synthetically not very useful. This reaction has therefore not been studied further.

Structures Determined by X-ray Crystallography. The molecular geometries of $[NiBr_2\{6,7-F_2C_{10}H_2-1,4-Ph_2-2,3-(PPh_2)_2\}]$ (**11b**) and $[NiBr_2\{C_{10}H_4-1,2,3-(PPh_2)_3-4-\{P(O)PPh_2\}-\kappa P^1,P^2\}]$ (**18**) are shown, together with the atom labeling, in Figures 1 and 2; selected interatomic distances and angles for **6b**, **11b**, and **18** are listed in Tables 1−3, respectively (those for **6b** were not given in the preliminary communication[16]). The nickel atom is bonded to the naphthylenebis(diphenylphosphine) fragments via the phosphorus atoms on C^2 and C^3 in the case of **11a** and via those on C^1 and C^2 in the case of **18**. As expected, in both complexes the coordination geometry about the metal atom is close to square planar, the mean deviation from the least-squares plane defined by Ni(1), Br(1), Br(2), P(1), and P(2) in **11** being only 0.038 Å. In **18**, the phosphorus atoms P(1) and P(2) lie 0.1585 and −0.1625 Å, respectively, from that plane. In both complexes, the naphthalene ring is planar, the dihedral angles with the coordination plane being 3.1° (**11b**) and 11.6° (**18**). Both values are considerably smaller than the value of 26.2° found in $[NiBr_2\{6,7-F_2C_{10}H_2-1,4-Me_2-2,3-(PPh_2)_2\}]$ (**6b**),[16] probably reflecting the steric interaction between the 1,4-diphenyl substituents and the PPh_2 groups in the case of **11b** and between the adjacent coordinated and uncoordinated PPh_2 groups in the case of **18**, leading in both cases to a flattening of the geometry. In agreement, the 1,4-substituents in **11b** are slightly bent away from the PPh_2 groups. The metal−ligand bond

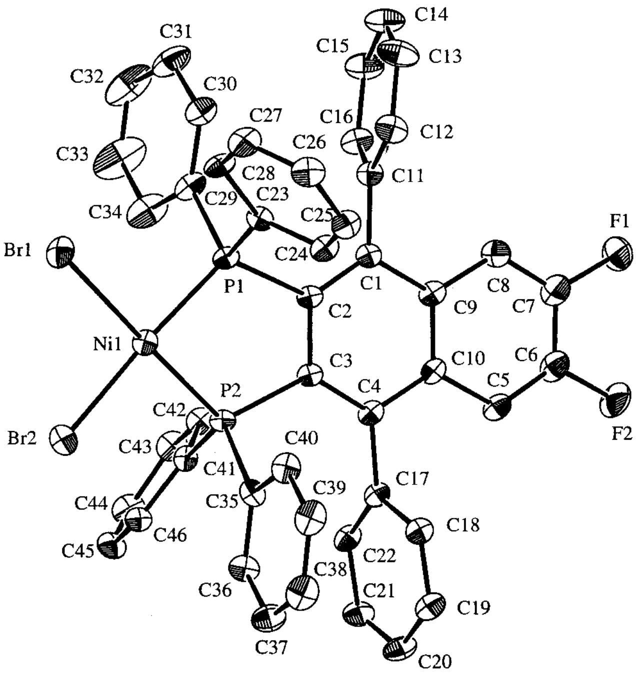

Figure 1. Molecular structure of **11b** with selected atom labeling. Thermal ellipsoids show 30% probability levels; hydrogen atoms have been omitted for clarity.

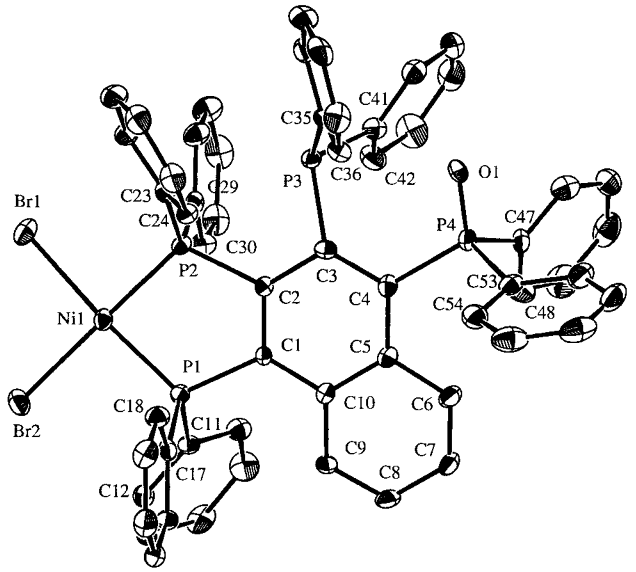

Figure 2. Molecular structure of **18** with selected atom labeling. Thermal ellipsoids show 30% probability levels; hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 6b[a]

Ni(1)−Br(1)	2.3400(8)	Ni(1)−Br(2)	2.3253(7)
Ni(1)−P(1)	2.144(1)	Ni(1)−P(2)	2.144(1)
P(1)−C(2)	1.829(4)	P(2)−C(3)	1.833(4)
C(1)−C(2)	1.389(5)	C(2)−C(3)	1.428(5)
C(3)−C(4)	1.377(5)	C(1)−C(9)	1.416(5)
C(4)−C(10)	1.439(5)	C(1)−C(11)	1.496(6)
C(4)−C(12)	1.495(6)		
Br(1)−Ni(1)−Br(2)	93.05(3)	Br(1)−Ni(1)−P(1)	91.28(4)
Br(1)−Ni(1)−P(2)	176.36(4)	Ni(1)−P(1)−C(2)	109.9(1)
C(2)−C(1)−C(11)	123.4(4)	C(3)−C(4)−C(12)	124.0(4)

[a] For the numbering scheme, refer to ref 16.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 11b

Ni(1)−Br(1)	2.336(2)	Ni(1)−Br(2)	2.331(2)
Ni(1)−P(1)	2.143(2)	Ni(1)−P(2)	2.127(2)
P(1)−C(2)	1.854(7)	P(2)−C(3)	1.836(7)
C(1)−C(2)	1.38(1)	C(2)−C(3)	1.42(1)
C(3)−C(4)	1.39(1)	C(1)−C(9)	1.43(1)
C(4)−C(10)	1.43(1)	C(1)−C(11)	1.49(1)
C(4)−C(17)	1.49(1)		
Br(1)−Ni(1)−Br(2)	94.18(6)	Br(1)−Ni(1)−P(1)	89.40(7)
Br(1)−Ni(1)−P(2)	175.89(8)	Ni(1)−P(1)−C(2)	110.6(2)
C(2)−C(1)−C(11)	125.3(7)	C(3)−C(4)−C(17)	123.9(7)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 18

Ni(1)−Br(1)	2.335(2)	Ni(1)−Br(2)	2.338(2)
Ni(1)−P(1)	2.124(3)	Ni(1)−P(2)	2.137(3)
P(1)−C(1)	1.84(1)	P(2)−C(2)	1.859(8)
P(3)−C(3)	1.851(8)	P(4)−C(4)	1.85(1)
C(1)−C(2)	1.39(1)	C(2)−C(3)	1.44(1)
C(3)−C(4)	1.42(1)	C(1)−C(10)	1.44(1)
C(4)−C(5)	1.42(1)	P(4)−O(1)	1.463(6)
Br(1)−Ni(1)−Br(2)	94.06(7)	Br(1)−Ni(1)−P(2)	88.29(8)
Br(1)−Ni(1)−P(1)	173.5(1)	Ni(1)−P(1)−C(1)	110.6(3)
P(1)−C(1)−C(2)	116.0(6)	P(2)−C(2)−C(3)	123.3(6)
P(3)−C(3)−C(2)	111.2(6)	P(4)−C(4)−C(3)	119.1(6)

lengths in both complexes are similar to each other and to those in **6b** (Ni−Br, 2.333 Å (av) (**6b**), 2.335 Å (av) (**11b**), 2.337 Å (av) (**18**); Ni−P, 2.144(1), 2.144(1) Å (**6b**), 2.143(2), 2.127(2) Å (**11b**), 2.124(3), 2.137(3) Å (**18**)). The P−O bond length in **18** (1.463(6) Å) is comparable with that of 6,7-$F_2C_{10}H_2$-1,4-Me_2-2-(PPh_2)-3-{P(O)Ph_2} (**15b**) (1.489(5) Å)[16] and with those in a wide range of tertiary phosphine oxides.[26]

The unit cell of the crystal isolated from attempted crystallization of the tetrakis(tertiary phosphine) **19** contains two isomeric bis(tertiary phosphine oxides), $C_{10}H_4$-1,4-(PPh_2)$_2$-2,3-{P(O)PPh_2}$_2$ (**20**) (73% occupancy) and $C_{10}H_4$-1,2-(PPh_2)$_2$-3,4-{P(O)PPh_2}$_2$ (**21**) (27% occupancy). The structure of **20** is shown in Figure 3. Owing to disorder arising from the alternative locations of an oxygen atom on P(1) or P(3), the bond lengths are unreliable and are therefore not tabulated. However, an interesting consequence of the steric crowding is that the naphthalene units are not planar. The substituted carbon atoms C(1), C(2), C(3), and C(4) are respectively 0.17(2), 0.31(3), 0.01(3), and −0.10(2) Å out of the plane defined by the other carbon atoms (C(5)−C(10)) of the naphthalene ring. As a consequence of the steric repulsion between O(2) and O(3), the phosphorus atoms P(2) and P(3) also deviate considerably from this plane, the dihedral angle between the planes P(2)−C(2)−C(3) and P(3)−C(3)−C(2) being 42.2(13)°. Similar steric distortions of the aromatic ring have been reported for benzenes having more than two adjacent PPh_2 groups, e.g. for 1,2,3,4-tetrakis(diphenylphosphino)benzene and its chalcogen adducts, which were studied by ^{31}P NMR spectroscopy,[27] or for 1,2,3,5-tetrakis(diphenylthiophosphino)benzene, whose X-ray structure analysis showed dihedral angles P−C−C−P of up to 70°.[28]

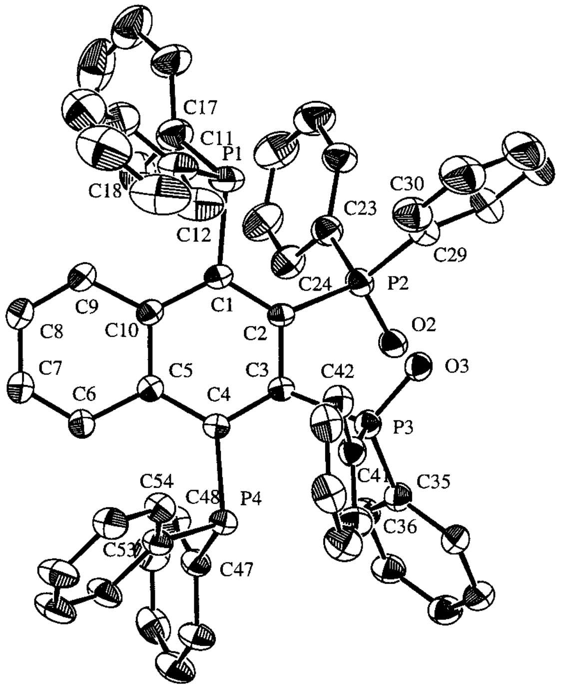

Figure 3. Molecular structure of **20** with selected atom labeling. Thermal ellipsoids show 30% probability levels; hydrogen atoms have been omitted for clarity.

Discussion

The double insertion of (alkynyl)diphenylphosphines into the nickel−carbon bonds of the benzyne complexes **1a** and **1b** leads to naphthalene-based diphenylphosphines and derived phosphine oxides that would be difficult to make by conventional methods. In particular, the reactions with $Ph_2PC{\equiv}CR$ (R = Me, Ph) occur with high regioselectivity to give nickel(0) complexes containing the corresponding 2,3-naphthylenebis(diphenylphosphines) 6,7-$X_2C_{10}H_2$-1,4-Y_2-2,3-(PPh_2)$_2$ (X = H, Y = Me (**12a**); X = F, Y = Me (**12b**); X = H, Y = Ph (**13a**); X = F, Y = Ph (**13b**)), which behave as bidentate ligands and can be isolated from the reactions via their five-membered-ring chelate $NiBr_2$ complexes.[29] Few examples of naphthalene-based bis(tertiary phosphines) are known. The closest analogue is 1-phenylnaphthalene-2,3-bis(diphenylphosphine), which is obtained via its $PtCl_2$ complex by thermal coupling of the pendant alkynyl groups of *cis*-[$PtCl_2$($Ph_2PC{\equiv}CPh$)$_2$].[30,31] The

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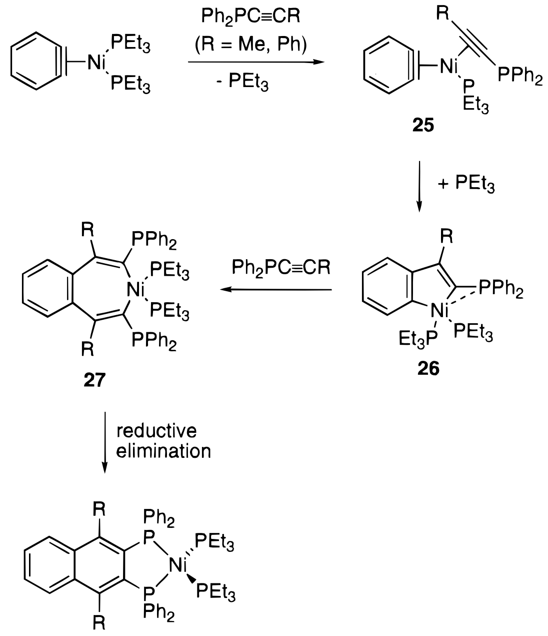
Scheme 4



compounds 1,8-naphthylenebis(dimethylphosphine)[32] and 1,8-naphthylenebis(diphenylphosphine)[33] have been obtained from the reaction of 1,8-dilithionaphthalene with the appropriate phosphinous chloride; the second compound forms six-membered-ring chelate complexes with $PtCl_2$ and $PdCl_2$.

In view of the bulk of the PPh_2 group, the regioselectivity observed with $Ph_2PC\equiv CR$ (R = Me, Ph) cannot be determined primarily by steric effects but must result from electronic control. The regioselectivity is similar to that with methyl 2-butynoate, $MeC\equiv CCO_2Me$, whose double insertion with **1a** and **1b** is also believed to be under electronic control.[12,14] The similarity in the directing effects of PPh_2 and CO_2Me as substituents on a $C\equiv C$ bond is supported by theoretical calculations, which show alkynylphosphines and acetylenic esters to be polarized similarly, although there is no delocalization of the π-system onto the phosphorus atom.[34]

A possible mechanism for the double insertion of $Ph_2PC\equiv CR$ (R = Me, Ph) into the nickel(0)–benzyne bond of **1a** is outlined in Scheme 4. In the first step, the alkynylphosphine displaces a PEt_3 ligand to give a η^2-alkyne complex (**25**), analogous to the spectroscopically detected complexes **9a** and **9b**, and to **10**. The first insertion, resulting from attack of the nucleophilic benzyne complex on the electrophilic carbon atom of the alkyne, then gives the five-membered nickelacycle **26**, in which the carbon atom bearing the PPh_2 group is attached to nickel, i.e., a (2-diphenylphosphino)nickelaindene, analogous to the similarly prepared (2-diphenylphosphino)zirconaindene (eq 1).[17]

The second insertion can take place in either the nickel–vinyl or nickel–phenyl bond of **26**. In the corresponding reaction of $MeC\equiv CCO_2Me$ with **1b**, we favored insertion into the nickel–vinyl bond in the second step on electronic grounds.[9,12,14] However, DFT calculations show nickel–vinyl and nickel–phenyl bonds to be very similar in energy[35] and, in this case, the presence of the PPh_2 group may tilt the balance in favor of the nickel–phenyl bond. Thus, if the second insertion occurs in the same sense as the first one, the product will be the seven-membered nickelacycle **27**. Many examples of similar metallacycles that result from insertion of an unsaturated substrate into a five-membered nickelacycle are known.[36] Reductive elimination from **27** then gives the appropriate naphthylene-2,3-bis(diphenylphosphine), which will readily capture the nickel(0) fragment to give the observed mixture of nickel(0) complexes.

The double insertion of $Ph_2PC\equiv CH$ is less regioselective than those of $Ph_2PC\equiv CR$ (R = Me, Ph); a similar trend is evident in the behavior of $HC\equiv CCO_2Me$ and $MeC\equiv CCO_2Me$.[9,12] It seems likely that the first insertion occurs with the same regioselectivity as those for $Ph_2PC\equiv CR$ to give the corresponding (2-diphenylphosphino)nickelaindene **26** (R = H); cf. the reactions of $Ph_2PC\equiv CR$ (R = H, Ph) with $[Cp_2Zr(\eta^2\text{-}C_6H_4)]$ (eq 1).[17] Loss of regiocontrol may occur in the second insertion, perhaps as a result of competitive insertion with the same regioselectivity into the nickel–phenyl and nickel–vinyl bonds of the nickelaindene.

The formation of the η^2-alkyne complexes **9a**,**b** and **10** is also of interest. In general, P-donor coordination of (alkynyl)diphenylphosphines is favored kinetically and there are numerous complexes or clusters in which dppa acts as a bridging ligand through its phosphorus atoms.[37] Only a few compounds are known in which alkyne coordination is favored over P-donor coordination, e.g. $[Co_2(CO)_6\{\mu\text{-}\eta^2\text{-}(C_6F_5)_2PC\equiv CR\}]$ (R = Me, Ph),[15a] $[(CpNi)_2(\mu\text{-}\eta^2\text{-}Ph_2PC\equiv C\text{-}t\text{Bu})]$,[38] and $[W(CO)(\eta^2\text{-}Ph_2PC\equiv CPPh_2)(S_2CNEt_2)_2]$;[39] more commonly the $Ph_2PC\equiv CR$ ligands bridge a pair of metal atoms via phosphorus and the triple bond, as in $[Ni_2(CO)_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}Ph_2PC\equiv C\text{-}t\text{Bu})]$.[38] In our case, although a P-coordinated species may be an intermediate in the formation of **10**, the complex having the alkyne bonded to nickel is clearly the thermodynamically favored species.

Finally, an interesting feature of the new naphthalene-based bis(tertiary phosphines) is that they undergo selective oxidation to mixed tertiary phosphine–phosphine oxide compounds when their nickel(0) complexes are exposed to air. The only polyfunctional tertiary phosphines known to undergo mono-oxidation in air are *o*-phenylenebis(methylphenylphosphine), $o\text{-}C_6H_4(PMePh)_2$,[40] and 1,2,3,4-tetrakis(diphenylphosphino)benzene; in the latter compound only the phosphorus atom

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bonded to C^1 is oxidized.[27] Bis(tertiary phosphine) monoxides are potentially useful ligands for some homogeneously catalyzed processes, yet few satisfactory, general synthetic methods are available.[41] The selectivity to air oxidation in the case of the naphthalene-based ligands may result from steric protection and electronic deactivation of one phosphorus atom induced by oxidation at its rigidly held neighbor or from a selective monooxidation induced by the presence of the chelated nickel(0) center. As the free naphthylenebis(diphenylphosphines) are quite resistant to aerial oxidation, the latter mechanism is favored.

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 81.0 MHz), a Varian Gemini-300 BB (^1H at 300 MHz, ^{13}C at 75.4 MHz, and ^{31}P at 121.4 MHz), or a Varian Inova-500 instrument (^1H at 500 MHz, ^{13}C at 125.7 MHz, and ^{31}P at 202.4 MHz). The chemical shifts (δ) for ^1H 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 ^1H and ^{19}F) were ^1H-decoupled. The coupling constants (J) are given in Hz. Infrared spectra were measured on Perkin-Elmer 683 or FT-1800 instruments. Mass spectra were obtained on a Fisons VG ZAB2-SEQ spectrometer by the fast-atom bombardment (FAB) technique, on a Fisons VG Autospec spectrometer by electron impact (EI), or on a Fisons VG Quattro II by electrospray (ESI). Microanalyses were done in-house.

In several cases, especially for the tertiary phosphines and phosphine oxides, the uninformative ^1H and ^{13}C NMR spectra, which consist of broad multiplets in the aromatic region δ_H 6.8–8.5 and δ_C 122–135, are not reported in detail.

Starting Materials. 1,2-Dibromobenzene, 1,2-dibromo-4,5-difluorobenzene, acetylene (ethyne), phenylacetylene, propyne, 3,3-dimethyl-1-butyne, bis(diphenylphosphino)acetylene (dppa), and (trimethylsilyl)acetylene were obtained commercially and used as received. Chlorodiphenylphosphine was obtained commercially and distilled under an inert, reduced-pressure atmosphere before use. The aryl–nickel(II) complexes [NiBr-(2-Br-4,5-$X_2C_6H_2$)(dcpe)] (X = H, F) were prepared by zinc reduction of [$NiBr_2(PPh_3)_2$][42] in the presence of the appropriate 1,2-dibromoarene and subsequent replacement of PPh_3 by dcpe. The complexes [NiBr(2-Br-4,5-$X_2C_6H_2$)($PEt_3)_2$] (X = H, F) were prepared by reaction of [$Ni(COD)_2$][43] with the corresponding dibromoarene in the presence of 2.5 equiv of PEt_3.[12] The complex [$Ni(C_2H_4)$(dcpe)] was prepared as described previously.[44]

The (alkynyl)diphenylphosphines $Ph_2PC{\equiv}CR$ (R = H, Me, Ph, *t*-Bu) were prepared by following the published procedures.[45,46] Complete NMR data for these compounds have not been published; they are given below, together with some values for the corresponding oxides.

$Ph_2PC{\equiv}CMe$. ^1H NMR (300 MHz, C_6D_6): δ 1.53 (s, 3H, CH_3), 7.02–7.11 (m, 6H, Ar H), 7.64–7.67 (m, 4H, Ar H). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ −31.4 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 4.9 (s, CH_3), 76.4 (s, $CH_3\mathit{C}{\equiv}C$), 106.1 (s, $CH_3C{\equiv}\mathit{C}$), 128.7 (d, J(PC) 7.7, CH), 129.0 (s, CH), 132.9 (d, J(PC) 21.0, CH), 137.73 (d, J(PC) 8.0, C).

$Ph_2P(O)C{\equiv}CMe$. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ 7.3 (s).

$Ph_2PC{\equiv}CPh$. ^1H NMR (300 MHz, C_6D_6): δ 6.84–6.94 (m, 3H, Ar H), 7.00–7.11 (m, 6H, Ar H), 7.31–7.36 (m, 2H, Ar H), 7.73–7.80 (m, 4H, Ar H). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 86.6 (d, J(CP) 8.9, $PhC{\equiv}\mathit{C}$), 108.1 (d, J(CP) 4.5, $Ph\mathit{C}{\equiv}C$), 122.9 (C), 128.2 (CH), 128.6 (d, J(PC) 7.5), 128.6, 128.9, 131.8 (CH), 132.7 (d, J(PC) 21.5, CH), 136.6 (d, J(PC) 7.1, C). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ −32.5 (s).

$Ph_2PC{\equiv}C$-*t*-Bu. ^1H NMR (300 MHz, C_6D_6): δ 1.36 (s, 9H, $C(CH_3)_3$), 7.31–7.39 (m, 6H, Ar H), 7.58–7.66 (m, 4H, Ar H). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ −34.0 (s).

$Ph_2P(O)C{\equiv}C$-*t*-Bu. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ 5.1 (s).

$Ph_2PC{\equiv}CH$. ^1H NMR (300 MHz, C_6D_6): δ 2.68 (d, 1H, ^1J(PH) 2.48, $C{\equiv}CH$), 6.9–7.05 (m, 6H, Ar H), 7.59–7.67 (m, 4H, Ar H). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ −33.3 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 96.6 (br s, $H\mathit{C}{\equiv}C$), 111.1 (s, $HC{\equiv}\mathit{C}$), 128.9 (d, J(PC) 9.4, CH), 129.3 (s, CH), 133.0 (d, J(PC) 24.0, CH), 136.1 (d, J(PC) 8.3, C).

$Ph_2P(O)C{\equiv}CH$. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ 5.6 (s).

((Trimethylsilyl)ethynyl)diphenylphosphine, $Ph_2PC{\equiv}CSiMe_3$. This oil was prepared similarly to $Ph_2PC{\equiv}C$-*t*-Bu[45] by deprotonation of $Me_3SiC{\equiv}CH$ with *n*-BuLi at −78 °C and reaction of the resulting lithioacetylide with Ph_2PCl. ^1H NMR (300 MHz, C_6D_6): δ 0.13 (s, 9H, CH_3), 6.96–7.09 (m, 6H, Ar H), 7.70–7.77 (m, 4H, Ar H). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ −0.1 (s, CH_3), 103.3 (d, J(CP) 13.2, $Me_3SiC{\equiv}\mathit{C}$), 117.4 (s, $Me_3Si\mathit{C}{\equiv}C$), 129.0 (d, J(PC) 7.7), 129.5 (s), 132.8 (d, J(PC) 20.9, CH), 136.5 (d, J(PC) 6.6, C). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2): δ −31.1 (s).

Insertion Reactions of $Ph_2PC{\equiv}CMe$ with [Ni{(1,2-η)-4,5-$X_2C_6H_2$}($PEt_3)_2$] (X = H (1a), F (1b)). A filtered, yellow solution of **1a** in hexane (30 mL), prepared by reduction of [NiBr(2-BrC_6H_4)($PEt_3)_2$] (531 mg, 1 mmol) with lithium (231 mg, 10 mmol, 30% dispersion in paraffin) in ether at −40 °C,[12] was cooled to −78 °C. A solution of diphenyl-1-propynylphosphine (560 mg, 2.5 mmol) in hexane (5 mL) was added. The initially formed orange suspension was then warmed to room temperature, and the resulting dark red solution was stirred at room temperature for a further 4 h. The $^{31}P\{^1H\}$ NMR spectrum showed the presence of three nickel(0) complexes of general formula [Ni{$C_{10}H_4$-1,4-Me_2-2,3-($PPh_2)_2$}(L^1)(L^2)] (L^1 = L^2 = PEt_3 (**2a**), L^1 = L^2 = $Ph_2PC{\equiv}CMe$ (**3a**), L^1 = PEt_3 and L^2 = $Ph_2PC{\equiv}CMe$ (**4a**)), together with free PEt_3 and $Ph_2PC{\equiv}CMe$. The relative ratio of the complexes changes from one experiment to the other, depending on the excess of $Ph_2PC{\equiv}CMe$ present.

2a. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ 10.9 (t, ^2J(PP) 25.6, PEt_3), 50.9 (t, ^2J(PP) 25.6, $C_{12}H_{10}(PPh_2)_2$).

3a. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ 7.9 (t, ^2J(PP) 22.8, $Ph_2PC{\equiv}CMe$), 51.5 (t, ^2J(PP) 22.8, $C_{12}H_{10}(PPh_2)_2$).

4a. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ 5.6 (dt, ^2J(PP) 41.2, 25.4, $Ph_2PC{\equiv}CMe$), 10.1 (dt, ^2J(PP) 41.2, 21.6, PEt_3), 51.2 (dd, ^2J(PP) 25.4, 21.6, $C_{12}H_{10}(PPh_2)_2$).

A similar reaction was carried out with the 4,5-difluorobenzyne complex **1b**; $^{31}P\{^1H\}$ NMR monitoring showed the formation of the corresponding 6,7-difluoro-substituted nickel(0) complexes **2b**–**4b**, whose ^{31}P NMR spectroscopic data were similar to those of **2a**–**4a**.

[Ni{6,7-$X_2C_{10}H_2$-1,4-Me_2-2,3-($PPh_2)_2$}(dcpe)] (X = H (5a), F (5b)). In qualitative reactions, dcpe (small excess) was added to solutions containing **2a**–**4a** and **2b**–**4b**, and the mixtures were stirred for 2 h at room temperature. The $^{31}P\{^1H\}$ and ^{19}F NMR spectra indicated the formation of **5a** or **5b**, together with free PEt_3 and $Ph_2PC{\equiv}CMe$. Complex **5a** was isolated as a beige solid by removing the solvent in vacuo and washing

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with hexane. The compound was not analytically pure, but attempts to crystallize it were unsuccessful owing to its poor solubility.

5a. ^{1}H NMR (300 MHz, C_6D_6): δ 1.15−2.15 (m, 48H, dcpe), 2.29 (6H, CH_3), 6.80−7.25 (m, 14H), 7.75 ([AB]m, 2H), 7.97−8.05 (m, 8H). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ 47.2 (t, ^2J(PP) 26.6), 52.1 (t, ^2J(PP) 26.6). FAB-MS ($C_{62}H_{78}NiP_4$, tetraglyme): *m/z* 1004 (20, M^+). High-resolution MS: calcd for $C_{62}H_{78}NiP_4$, 1004.440 754; found, 1004.444 885.

5b. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ 47.4 (t, ^2J(PP) 27.4), 52.3 (t, ^2J(PP) 27.4). ^{19}F NMR (188.1 MHz, C_6D_6): δ −139.6 (app t, *J*(FH) 10.2).

[NiBr$_2$\{6,7-X$_2$C$_{10}$H$_2$-1,4-Me$_2$-2,3-(PPh$_2$)$_2$\}] (X = H (6a), F (6b)). A solution of bromine (0.15 mL, 2.9 mmol) in hexane (5 mL) was added dropwise over 5 min to a solution containing **2a**−**4a** (1 mmol) at −30 °C (prepared as described above), and the mixture was stirred for 2 h at room temperature. Filtration of the resulting orange precipitate in air afforded the nickel(II) complex **6a** (696 mg, 95% yield based on the nickel(II) precursor). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.21 (s, 6H, CH_3), 7.37−7.50 (m, 12H, Ar H), 7.89−7.98 (m, 8H, Ar H), 7.66−8.05 (m, 4H, Ar H). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2): δ 65.5 (s). EI-MS ($C_{36}H_{30}Br_2NiP_2$): *m/z* 663 (100, M^+ − Br). Anal. Calcd for $C_{36}H_{30}Br_2NiP_2$: C, 58.18; H, 4.04; P, 8.35. Found: C, 58.40; H, 4.24; P, 8.85.

In a similar reaction, the mixture of nickel(0) complexes **2b**−**4b** was treated with bromine to give **6b** in 97% yield (based on the nickel(II) precursor). Single crystals suitable for X-ray diffraction were obtained from CH_2Cl_2/hexane. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.18 (s, 6H, CH_3), 7.46−7.59 (m, 12H, Ar H), 7.81 (t, ^1J(FH) 10.1, 2H, Ar H), 7.91−7.98 (m, 8H, Ar H). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2): δ 20.38 (CH_3), 112.23 (m, CH), 129.16 (t, *J*(CP) 5.6, CH), 131.53 (CH), 133.07 (t, *J*(CP) 4.8, CH), 133.34, (t, *J*(CP) 6.3, $C^{1,4}$), 135.20 (t, *J*(CP) 46.5, C^{phenyl}), 140.22 (t, *J*(CP) 9.7, $C^{2,3}$), 151.55 (br dd, *J* 281, 24, CF); $C^{4a,8a}$ not located. $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2): δ 65.8 (s). ^{19}F NMR (188.1 MHz, CD_2Cl_2): δ −132.6 (app t, *J*(FH) 10.1). EI-MS ($C_{36}H_{28}Br_2F_2NiP_2$): *m/z* 778 (46, M^+), 697 (65, M^+ − Br), 504 (100). Anal. Calcd for $C_{36}H_{28}Br_2F_2NiP_2$: C, 55.50; H, 3.62; Br, 20.51. Found: C, 55.36; H, 3.66; Br, 20.33.

6,7-X$_2$C$_{10}$H$_2$-1,4-Me$_2$-2-PPh$_2$-3-\{P(O)Ph$_2$\} (X = H (15a), F (15b)). Ether (20 mL, nondegassed) was added to a mixture of **2a**−**4a** (prepared as described above), and the mixture was stirred for 24 h in air at room temperature. During this time, the dark red solution changed to clear yellow. Removal of all volatiles in vacuo and dissolution of the residue in acetone (5 mL) gave a solution that was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy to contain **15a** as the only naphthalene-based product, together with the phosphine oxides of the auxiliary ligands. ^{1}H NMR (200 MHz, C_6D_6): δ 2.25 (s, 3H, CH_3), 2.79 (s, 3H, CH_3), 6.85−7.95 (m, 24H). $^{31}P\{^1H\}$ NMR (81.0 MHz, d_6-acetone): δ −6.6 (d, ^3J(PP) 37.4), 31.0 (d, ^3J(PP) 37.4). EI-MS ($C_{36}H_{30}OP_2$): *m/z* 540 (29, M^+), 422 (100, M^+ − Ph), 314 (45, M^+ − PPh_2).

The 6,7-difluoro analogue 6,7-$F_2C_{10}H_2$-1,4-Me_2-2-PPh_2-3-\{P(O)Ph_2\} (**15b**) was prepared similarly by exposure of a solution of **2b**−**4b** to air. Dissolution of the residue in acetone and slow evaporation of the solution gave single crystals of **15b** suitable for X-ray diffraction. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.11 (s, 3H, CH_3), 2.75 (s, 3H, CH_3), 6.90−8.00 (m, 22H). $^{31}P\{^1H\}$ NMR (81.0 MHz, d_6-acetone): δ −6.3 (d, ^3J(PP) 36.7), 31.0 (d, ^3J(PP) 36.7). ^{19}F NMR (188.1 MHz, C_6D_6): δ −135.3 (m) −136.0 (m). EI-MS ($C_{36}H_{28}F_2OP_2$): *m/z* 576 (40, M^+), 499 (100, M^+ − Ph), 391 (38, M^+ − PPh_2). High-resolution MS: calcd for $C_{36}H_{28}F_2OP_2$, 576.158 834 9; found, 576.158 054.

6,7-X$_2$C$_{10}$H$_2$-1,4-Me$_2$-2,3-\{P(O)Ph$_2$\}$_2$ (X = H (14a), F (14b)). An excess of aqueous H_2O_2 (30 vol, 10 mL) was added to a solution containing **2a**−**4a** (prepared as described above), and the mixture was stirred for 24 h in air at room temperature. During this time, the dark red solution changed to clear yellow. Removal of all volatiles in vacuo and dissolution of the resulting residue in acetone (5 mL) gave a solution which was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy to contain **14a** as the only naphthalene-based product, together with the phosphine oxides of the auxiliary ligands. Extraction with benzene and crystallization gave pure **14a** as a colorless solid. ^{1}H NMR (200 MHz, C_6D_6): δ 2.48 (br s, 6H, CH_3), 6.85−7.15 (m, 12H), 7.28 ([AB]m, 2H), 7.65−7.85 (m, 8H). $^{31}P\{^1H\}$ NMR (81.0 MHz, d_6-acetone): δ 34.3 (br s). EI-MS ($C_{36}H_{30}O_2P_2$): *m/z* 556 (32, M^+), 479 (100, M^+ − Ph). High-resolution MS: calcd for $C_{36}H_{30}O_2P_2$, 556.172 107; found, 556.171 083. Anal. Calcd for $C_{36}H_{30}O_2P_2$: C, 77.69; H, 5.43. Found: C, 77.71; H, 5.57.

The analogous 6,7-difluoro-substituted bis(phosphine oxide) **14b** was formed similarly. IR (KBr disk): ν(P=O) 1118 cm^{-1}. $^{31}P\{^1H\}$ NMR (81.0 MHz, d_6-acetone): δ 33.4 (br s). ^{19}F NMR (188.1 MHz, C_6D_6): δ −133.9 (br). EI-MS ($C_{36}H_{28}F_2O_2P_2$): *m/z* 592 (36, M^+), 515 (100, M^+ − Ph).

6,7-X$_2$C$_{10}$H$_2$-1,4-Me$_2$-2,3-(PPh$_2$)$_2$ (X = H (12a), F (12b)). A solution of [NiBr$_2$\{$C_{10}H_4$-1,4-Me_2-2,3-(PPh_2)$_2$\}] (**6a**; 218 mg, 0.29 mmol) in DMSO (20 mL) was treated with NaCN (575 mg, 11.7 mmol), and the mixture was heated to 60 °C overnight with stirring. After addition of hexane (25 mL) and distilled water (20 mL), separation and evaporation of the organic phase afforded **12a** quantitatively as a yellow solid. ^{1}H NMR (200 MHz, C_6D_6): δ 2.28 (s, 6H, CH_3), 6.95−7.15 (m, 12H), 7.23 ([AB] m, 2H), 7.45−7.55 (m, 8H), 7.77 ([AB] m, 2H). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ 20.5 (CH_3), 125.3, 126.9, 127.6 (CH), 128.6 (t, ^3J(CP) 2.7, CH), 132.0 (t, ^2J(CP) 8.9, CH), 135.3 ($C^{4a,8a}$), 137.9 (t, ^1J(CP) 4.4, C^{phenyl}), 139.5 (t, ^2J(CP) 4.4, $C^{1,4}$), 140.8 (t, *J*(CP) 18.1, $C^{2,3}$). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ −5.6 (s). EI-MS ($C_{36}H_{30}P_2$): *m/z* 524 (58, M^+), 447 (100, M^+ − Ph). High-resolution MS: calcd for $C_{36}H_{30}P_2$, 524.182 278; found, 524.181 939.

The analogous compound 6,7-$F_2C_{10}H_2$-1,4-Me_2-2,3-(PPh_2)$_2$ (**12b**) was liberated quantitatively from **6b** in the same way. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): δ −5.6 (s). ^{19}F NMR (188.1 MHz, C_6D_6): δ −138.5 (app t, *J*(FH) 10.3). EI-MS ($C_{36}H_{28}F_2P_2$): *m/z* 560 (64, M^+), 483 (100, M^+ − Ph).

Elemental analyses of **12a** and **12b** were unsatisfactory because the compounds tenaciously retain organic solvents.

Reaction of Ph$_2$PC≡CPh with [Ni\{(1,2-η)-4,5-X$_2$C$_6$H$_2$\}(PEt$_3$)$_2$] (X = H (1a), F (1b)). The reaction was carried out as described for $Ph_2PC{\equiv}CMe$ using **1a**, formed from reduction of [NiBr(2-BrC_6H_4)(PEt_3)$_2$] (538 mg, 1 mmol), and $Ph_2PC{\equiv}CPh$ (550 mg, 1.9 mmol). $^{31}P\{^1H\}$ NMR monitoring showed the initial formation of [Ni\{$C_{10}H_4$-1,4-Ph_2-2,3-(PPh_2)$_2$\}(L^1)(L^2)] (L^1 = L^2 = PEt_3 (**7a**), L^1 = PEt_3 and L^2 = $Ph_2PC{\equiv}CPh$ (**8a**)), together with free PEt_3. Complex **7a** formed first, but after 1 h at room temperature **8a** was the major compound. After 3 h, these compounds had disappeared and [Ni\{$C_{10}H_4$-1,4-Ph_2-2,3-(PPh_2)$_2$\}(η^2-$Ph_2PC{\equiv}CPh$)] (**9a**) was the main product. $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6): **7a**, δ 6.7 (m, PEt_3), 51.8 (m, $C_{12}H_{10}$(PPh_2)$_2$); **8a**, δ 3.4 (dt, ^2J(PP) 47.8, 21.5, $Ph_2PC{\equiv}CPh$), 7.4 (dt, ^2J(PP) 47.8, 23.8, PEt_3), 52.3 (app t, *J*(PP) 22.6, $C_{12}H_{10}$(PPh_2)$_2$); **9a**, δ −19.4 (dd, ^3J(PP) 32.9, 29.4, $Ph_2PC{\equiv}CPh$), 61.6 (dd, ^2J(PP) 32.4, ^3J(PP) 29.6, $C_{22}H_{14}$(PPh_2)$_2$), 63.5 (app t, *J*(PP) 32.8, $C_{22}H_{14}$(PPh_2)$_2$).

A similar reaction was carried out using [NiBr(2-Br-4,5-$F_2C_6H_2$)(PEt_3)$_2$] (567 mg, 1 mmol) and $Ph_2PC{\equiv}CPh$ (570 mg, 2 mmol). $^{31}P\{^1H\}$ NMR monitoring of the insertion showed the formation of products with spectroscopic parameters similar to those of **7a** and **8a**, together with [Ni\{6,7-$F_2C_{10}H_2$-1,4-Ph_2-2,3-(PPh_2)$_2$\}(η^2-$Ph_2PC{\equiv}CPh$)] (**9b**) as the major compound. **9b**: $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6) δ −19.2 (dd, ^3J(PP) 33.3, 29.9, $Ph_2PC{\equiv}CPh$), 62.2 (dd, ^2J(PP) 33.2, ^3J(PP) 29.9, $C_{22}H_{12}F_2$(PPh_2)$_2$), 63.5 (app t, *J*(PP) 33.3, $C_{22}H_{12}F_2$(PPh_2)$_2$).

[NiBr$_2$\{6,7-X$_2$C$_{10}$H$_2$-1,4-Ph$_2$-2,3-(PPh$_2$)$_2$\}] (X = H (11a), F (11b)). Addition of a solution of bromine (0.15 mL) in THF (10 mL) to a solution of **7a**−**9a** (1 mmol) at −30 °C, followed by stirring for 16 h at room temperature, gave a beige suspension in a greenish solution. The solution was decanted and the solid purified by filtration through a silica gel column

(CH_2Cl_2). Removal of the solvent gave pure **11a** as an orange-red powder (570 mg, 66% yield based on Ni(II) precursor). The compound was recrystallized from a CH_2Cl_2 solution layered with hexane. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 6.35 (d, 4H, *J* 7.6), 6.89 (d, 4H, *J* 7.7), 7.10 ([AA′BB′]m, 2H), 7.20 (t, 2H, *J* 7.3), 7.27−7.38 (m, 10H), 7.44−7.56 (m, 12H). $^{13}C\{^{1}H\}$ NMR (50.3 MHz, CD_2Cl_2): δ 127.55, 127.73, 128.02 (CH), 128.64 (t, *J* 5.9, CH), 129.00, 130.52 (CH), 130.89 (t, *J* 1.7, CH), 131.32 (C), 133.11 (t, *J* 4.7, CH), 133.85 (t, *J* 46.4, $P-C^{phenyl}$), 136.30 (t, *J* 1.8, $C^{4a,8a}$), 136.69 (t, *J* 2.8, $C^{1,4}$), 147.64 (t, *J* 9.0, $C^{2,3}$). $^{31}P\{^{1}H\}$ NMR (81.0 MHz, CD_2Cl_2): δ 66.7 (s). EI-MS ($C_{46}H_{34}Br_2NiP_2$): *m*/*z* 787 (65, $M^+ - Br$), 741 (35), 706 (40), 571 (95), 443 (52), 286 (100). Anal. Calcd for $C_{46}H_{34}Br_2NiP_2{\cdot}CH_2Cl_2$: C, 59.29; H, 3.81. Found: C, 59.44; H, 4.06.

The nickel(II) complex **11b** was obtained similarly by addition of a hexane solution of bromine to an aliquot of the mixture of Ni(0) complexes **7b**−**9b** prepared as described above. Red single crystals suitable for X-ray diffraction were obtained from CH_2Cl_2/hexane. $^{31}P\{^{1}H\}$ NMR (81.0 MHz, CD_2Cl_2): δ 67.1 (s). ^{19}F NMR (188.1 MHz, CD_2Cl_2): δ −132.26 (app t, *J*(FH) 10.3). FAB-MS (3-nitrophenyloctyl ether, $C_{46}H_{32}Br_2F_2NiP_2$): *m*/*z* 902 (8, M^+), 823 (100, $M^+ - Br$). Anal. Calcd for $C_{46}H_{32}Br_2F_2NiP_2{\cdot}2CH_2Cl_2$: C, 53.71; H, 3.36; P, 5.78. Found: C, 53.81; H, 3.95; P, 5.92.

6,7-$X_2C_{10}H_2$-1,4-Ph_2-2,3-$(PPh_2)_2$ (X = H (13a), F (13b)). Under nitrogen, a solution of $[NiBr_2\{C_{10}H_4\text{-}1,4\text{-}Ph_2\text{-}2,3\text{-}(PPh_2)_2\}]$ (**11a**; 45 mg) in acetone was treated with an excess of dimethylglyoxime (20 mg) and one drop of degassed concentrated aqueous NH_4OH. After 3 h at room temperature, ^{31}P NMR spectroscopy showed the formation of **13a** to be quantitative. The solvent was evaporated, the red solid was extracted with benzene, and the resulting yellowish solution was filtered through degassed silylated silica gel. Chromatographic purification through degassed acidic alumina (ether) gave pure **13a** as a yellow solid. ^{1}H NMR (500 MHz, C_6D_6): δ 6.69 (t, 4H, *J* 7.8), 8.82−6.85 (m, 6H), 6.92 ([AA′BB′]m, 2H), 6.93−6.98 (m, 12H), 7.29−7.32 (m, 8H), 7.38 ([AA′BB′]m, 2H). $^{31}P\{^{1}H\}$ NMR (121.4 MHz, C_6D_6): δ −1.3 (s). $^{13}C\{^{1}H\}$ NMR (125.7 MHz, C_6D_6): δ 126.51 (CH), 127.13 (t, *J*(CP) 27.4, CH), 127.66, 127.91 (CH), 128.07 (d, *J*(CP) 2.3, CH), 128.29, 130.67 (CH), 132.76 (t, *J*(CP) 10.3, CH), 136.30 (C), 137.57 (t, *J*(CP) 2.1, C), 139.38 (dd, *J*(CP) 14.4, 13.0, $P-C^{phenyl}$), 139.54 (C), 146.63 (t, *J*(CP) 5.1, $C^{2,3}$). EI-MS ($C_{46}H_{34}P_2$): *m*/*z* 648 (M^+, 31), 571 (100). High-resolution MS: calcd for $C_{46}H_{34}P_2$, 648.213 578; found, 648.213 845.

The bis(phosphine) **13b** was released from the dibromide **11b** by heating with NaCN in DMSO as described for **12a**. $^{31}P\{^{1}H\}$ NMR (81.0 MHz, C_6D_6): δ −6.9 (s). ^{19}F NMR (188.1 MHz, C_6D_6): δ −137.9 (app t, *J*(FH) 10.2).

Reaction between $Ph_2PC{\equiv}CPPh_2$ and $[Ni(\eta^2\text{-}C_6H_4)(PEt_3)_2]$ (1a). A hexane solution of **1a**, obtained from lithium reduction of $[NiBr(2\text{-}BrC_6H_4)(PEt_3)_2]$ (508 mg, 0.96 mmol), was cooled to −60 °C. Bis(diphenylphosphino)acetylene (680 mg, 1.73 mmol) was added as a solid, followed by THF (10 mL). The cold bath was removed, and the solution was stirred for 3 h and then heated at 50 °C for 16 h. After being cooled to −10 °C, the solution was treated with a solution of bromine (0.15 mL) in THF (10 mL) and the mixture was stirred for 2 h at room temperature. The solvent was removed in vacuo. The residue was extracted with THF, and the solution was filtered through Celite. Removal of the solvent yielded a crude solid containing $[NiBr_2\{C_{10}H_4\text{-}1,2,3,4\text{-}(PPh_2)_4\text{-}\kappa P^2,P^3\}]$ (**16**) and $[NiBr_2\{C_{10}H_4\text{-}1,2,3,4\text{-}(PPh_2)_4\text{-}\kappa P^1,P^2\}]$ (**17**) in a 2:1 ratio, together with other phosphorus-containing products (as shown by ^{31}P NMR spectroscopy). Attempted separation on a degassed silica gel column (CH_2Cl_2) gave 423 mg of a 1:1:0.7 mixture of **16**, **17**, and $[NiBr_2\{C_{10}H_4\text{-}1,2,3\text{-}(PPh_2)_3\text{-}4\text{-}\{P(O)PPh_2\}\text{-}\kappa P^1,P^2\}]$ (**18**). Further elution with acetone yielded another 520 mg of red **18**. Single crystals for X-ray analysis of **18** were obtained from a hot mixture of chlorobenzene, toluene, and acetone. The total yield of double-insertion products, calculated from **16**−**18**, was 90%, based on the Ni(II) precursor.

The first fraction eluted from the column, containing mainly the isomeric mixture of **16** and **17**, was treated with dimethylglyoxime (150 mg) in acetone (20 mL) and 10 drops of concentrated aqueous NH_4OH. A colorless solid was formed immediately. The solution was decanted, and the residue was extracted with DMSO. Addition of hexane and stirring gave a sticky solid which was identified as being the tetrakis(tertiary phosphine) $C_{10}H_4$-1,2,3,4-$(PPh_2)_4$ (**19**). Attempted crystallization from DMSO/ether gave a mixture of dioxides, **20** and **21**, identified by X-ray crystallography (see below).

16: $^{31}P\{^{1}H\}$ NMR (81.0 MHz, d_6-acetone) δ −12.2 (dd, *J*(PP) 16.0, 11.8, $P^{1,4}$), 75.8 (dd, *J*(PP) 16.0, 11.8, $P^{2,3}$).

17: $^{31}P\{^{1}H\}$ NMR (81.0 MHz, d_6-acetone) δ −9.4 (app t, *J*(PP) 3.3, P^4), 3.8 (d, *J*(PP) 26.9, P^3), 66.9 (dd, 75.7, 3.7, P^1), 81.9 (ddd, *J*(PP) 75.8, 27.0, 2.7, P^2).

18: IR (KBr) 3052 (m), 1582 (w), 1479 (s), 1435 (s) 1208 (s, P═O), 1111 (s), 1097 (s), 737 (vs), 692 (vs), 642 (vs) cm^{-1}; $^{31}P\{^{1}H\}$ NMR (81.0 MHz, d_6-acetone) δ 13.5 (d, *J*(PP) 27.5, P^3), 29.4 (d, *J*(PP) 3.9, P^4), 64.9 (dd, *J*(PP) 76.9, 4.0, P^1), 84.1 (dd, *J*(PP) 76.8, 27.3, P^2); FAB-MS (NBA, $C_{58}H_{44}Br_2NiOP_4$) *m*/*z* 1019 (38, $M^+{-}Br$), 803 (100, $C_{10}H_4(PPh_2)_3(OPPh_2)$).

19: $^{31}P\{^{1}H\}$ NMR (81.0 MHz, d_6-DMSO) δ −10.8 (t, *J*(PP) 13.7, $P^{1,4}$), 4.5 (t, *J*(PP) 13.7, $P^{2,3}$).

Reaction of $Ph_2PC{\equiv}CH$ with $[Ni\{(1,2\text{-}\eta)\text{-}4,5\text{-}F_2C_6H_2\}(PEt_3)_2]$ (1b). Both the reactions of **1a** and **1b** (1 mmol) with 2 equiv of $Ph_2PC{\equiv}CH$ (420 mg, 2 mmol) gave very complicated mixtures, as shown by ^{31}P NMR spectroscopy. That obtained from **1b** was used in subsequent experiments.

A solution of bromine (0.15 mL, 2.9 mmol) in hexane (5 mL) was added dropwise to the reaction mixture obtained from **1b**. The resulting orange precipitate was separated by filtration and washed with hexane. The ^{31}P NMR spectrum indicated the presence of various dibromonickel(II) species (see text). The peaks listed below are believed to be due to $[NiBr_2\{6,7\text{-}F_2C_{10}H_2\text{-}2,3\text{-}(PPh_2)_2\}]$ (**22**).

22: $^{31}P\{^{1}H\}$ NMR (81.0 MHz, CD_2Cl_2) δ 65.8 (s); ^{19}F NMR (188.1 MHz, CD_2Cl_2) δ −132.6 (app t, *J*(FH) 10.1); EI-MS ($C_{36}H_{28}F_2P_2NiBr_2$) *m*/*z* 778 (46, M^+), 697 (65, $M^+ - Br$), 504 (100).

Formation of $[Ni(\eta^2\text{-}Ph_2PC{\equiv}CPh)(dcpe)]$ (10). A suspension of $[Ni(C_2H_4)(dcpe)]$ (224 mg, 0.44 mmol) in ether (10 mL) was cooled to 0 °C under nitrogen. $Ph_2PC{\equiv}CPh$ (126 mg, 0.44 mmol) was added as a solid, and the orange solution was stirred for 0.5 h at room temperature. $^{31}P\{^{1}H\}$ NMR analysis of the resulting yellow solution showed quantitative formation of **10**, which can be isolated as a yellow solid by layering the solution with hexane. Although stable in solution, solid samples of **10** decompose on storage over a period of days. ^{1}H NMR (200 MHz, C_6D_6): δ 0.90−2.20 (m, 48H), 6.85−7.20 (m, 9H), 7.20−7.40 (m, 2H), 7.70−7.85 (m, 4H). $^{13}C\{^{1}H\}$ NMR (125.7 MHz, C_6D_6): δ 22.0 (t, *J*(CP) 19.5, CH_2), 22.6 (t, *J*(CP) 19.4, CH_2), 26.6 (CH_2), 27.5−27.7 (m, CH_2), 29.1, 29.4 (CH_2), 30.0−30.2 (m, CH_2), 35.1 (dd, *J*(CP) 16.0, 3.4, CH), 35.7 (dd, *J*(CP) 16.7, 3.8, CH), 122.9 (C of *Ph*C≡C), 124.4 (CH), 127.5, 127.8, 127.9 (CH), 128.2 (d, *J*(CP) 7, CH), 133.9 (d, *J*(CP) 20.1, CH), 141.4 (ddd, *J*(CP) 10.5, 5.0, 3.2, P*C*≡C), 142.0 (dd, *J*(CP) 14.8, 4.0, C of PPh_2), 150.3 (ddd, *J*(CP) 41.0, 19.0, 5.3, PC≡*C*). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 81.0 MHz): δ −14.5 (dd, $^{3}J(PP)$ 24.9, $^{3}J(PP)$ 34.5, $Ph_2PC{\equiv}CPh$), 68.3 (dd, $^{2}J(PP)$ 41.9, $^{3}J(PP)$ 24.7), 70.1 (dd, $^{2}J(PP)$ 41.9, $^{3}J(PP)$ 34.6, dcpe). FAB-MS ($C_{46}H_{63}NiP_3$, tetraglyme): *m*/*z* 766 (3, M^+).

X-ray Crystallography. Crystal data, details of data collection, data processing, structure analysis, and structure refinement are given in Table 4.

All three structures were solved by direct methods (SIR92)[47] and were expanded with use of Fourier techniques (DIRDIF94).[48] The crystal structure of **11b**·$3CH_2Cl_2$ revealed a crystallographic asymmetric unit comprising one clearly defined molecule of **11b** and three molecules of partly disordered CH_2-

Table 4. Crystal and Structure Refinement Data for Compounds 11b, 18, and 20/21

	$[NiBr_2\{6,7\text{-}F_2C_{10}H_2\text{-}1,4\text{-}Ph_2\text{-}2,3\text{-}(PPh_2)_2\text{-}\kappa P^{2,3}\}]$ (**11b**)	$[NiBr_2\{C_{10}H_4\text{-}1,2,3\text{-}(PPh_2)_3\text{-}4\text{-}\{P(O)PPh_2\}\text{-}\kappa P^1,P^2\}]$ (**18**)	$C_{10}H_4(PPh_2)_2\{P(O)Ph_2\}_2$ (**20/21**)
(a) Crystal Data			
chem formula	$C_{46}H_{32}Br_2F_2NiP_2 \cdot 3CH_2Cl_2$	$C_{58}H_{44}Br_2NiOP_4 \cdot 1.21C_7H_8 \cdot 0.29C_3H_6O$	$C_{58}H_{44}O_2P_4 \cdot 2C_2H_6OS$
fw	1158.01	1227.72	1053.14
cryst syst	monoclinic	triclinic	monoclinic
unit cell dimens			
a (Å)	17.976(4)	13.431(2)	21.296(6)
b (Å)	28.384(9)	13.715(3)	11.996(3)
c (Å)	9.385(4)	16.000(2)	23.157(7)
α (deg)		94.70(1)	
β (deg)	90.21(3)	104.06(1)	111.18(3)
γ (deg)		96.27(1)	
V (Å^3)	4789(3)	2823.8(8)	5516(3)
space group	$P2_1/a$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/a$ (No. 14)
D_c (g cm^{-3})	1.606	1.444	1.268
Z	4	2	4
F(000)	2320	1255.56	2208
color, habit	brown-red, block	orange, plate	yellow, block
cryst dimens (mm)	0.33 × 0.30 × 0.18	0.30 × 0.15 × 0.05	0.19 × 0.16 × 0.15
μ (cm^{-1})	66.00 (Cu Kα)	35.69 (Cu Kα)	2.60 (Mo Kα)
(b) Data Collection and Processing			
diffractometer	Rigaku AFC6R	Rigaku AFC6R	Philips PW1100/20
X-radiation	Cu Kα (graphite monochromated)	Cu Kα (graphite monochromated)	Mo Kα (graphite monochromated)
scan mode	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
ω-scan width (deg)	$1.20 + 0.30 \tan \theta$	$1.20 + 0.30 \tan \theta$	$1.0 + 0.34 \tan \theta$
2*θ* limits (deg)	120.2	120.0	40.0
data collected (*h,k,l*)	(−20,0,0) to (20,31,10)	(−15,−15,−17) to (15,0,17)	(−20,0,0) to (19,11,22)
no. of rflns			
total	7822	8823	5677
unique (R_{int} (%))	7323 (10.7)	8415 (5.4)	5178 (6.0)
obsd	5008 ($I > 2\sigma(I)$)	4666 ($I > 2\sigma(I)$)	2035 ($I > 3\sigma(I)$)
abs cor (transmissn factors)	azimuthal scans (0.23−0.31)	azimuthal scans (0.65−0.84)	none
decay (%)	nil	nil	13
(c) Structure Analysis and Refinement			
struct soln	direct methods (SIR92)		
refinement	full-matrix least squares		
no. of params	578	668	215
R(obsd data) (%)	6.2	6.0	8.1
R_w(obsd data) (%)	7.4	7.9	11.6

Cl_2. Several of the atoms of the CH_2Cl_2 molecules were split over two sites, and relative occupancies were refined. Restraints were placed on the C−Cl distances in these cases. The disordered carbon atoms were refined with isotropic displacement factors, while all other non-hydrogen atoms were refined anisotropically by full-matrix least squares. Hydrogen atoms were included at calculated positions (C−H = 0.95 Å) and held fixed. The maximum and minimum peaks in the final difference Fourier map were 1.40 and −1.41 e/Å^3, respectively, the major features being associated with the solvent molecules. All calculations were performed with use of teXsan structure analysis software.[49]

In the crystal structure of **18**$\cdot 1.21C_7H_8 \cdot 0.29C_3H_6O$, the molecular species (**18**) was clearly defined, but disordered solvent molecules were also present; one series of peaks was assigned to disordered toluene and the other to a disordered mixture of toluene and acetone. Restraints were imposed upon these solvent molecules and relative occupancies refined where appropriate.[50] All non-hydrogen atoms were refined anisotropically by full-matrix least squares, except for those of the disordered solvent molecules. Hydrogen atoms were included at calculated positions (C−H = 0.95 Å); they were not refined, but their positions were recalculated regularly. The maximum and minimum peaks in the final difference Fourier map were 1.22 and −0.52 e/Å^3, respectively, the largest features being associated with the bromine atoms and solvent molecules. teXsan[49] and XTAL[50] software was used.

The crystal structure of **20**/**21**·2DMSO revealed a molecular species with oxygen atoms bonded to P(1) and P(3) having only partial occupancy. Data were weak, and only 2035 out of 5178 independent reflections were considered to be reliable; therefore, the comprehensive constrained least-squares refinement program RAELS96 was used to minimize the number of parameters required to describe the structure.[51] Constraints enabled 215 variables to adequately describe the refinement of the 77 non-hydrogen atoms in the asymmetric cell.[52,53] The asymmetric unit contains a mixture of two isomers (**20**/**21**) in a 73:27 ratio, which differ only in the location of the oxygen atoms attached to phosphorus atoms. Atom O(2) is attached to P(2), whereas the remaining oxygen atom is attached either to P(1) (occupancy 0.27) or to P(3) (occupancy 0.73). Two molecules of DMSO are also present, one of which is 0.69/0.31 disordered. The DMSO molecule was constrained to contain an exact mirror plane, while differences in the P−O bond

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lengths were constrained to approach zero. All atoms were described by refinable rigid body thermal parametrizations.[52] The hydrogen atoms were relocated in sensible chemical positions after each refinement cycle. The maximum and minimum peaks in the final difference Fourier map were 1.0 and −1.3 e/Å^3, respectively. Calculations were performed with the crystallographic software packages teXsan,[49] XTAL,[50] and RAELS96.[51]

The neutral atom scattering factors were taken from ref 54 for structure **11b** and from ref 55 for structures **18** and **20/21**. $\Delta f'$ and $\Delta f''$ values and mass attenuation coefficients were taken from ref 55 for all three structures.

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Supporting Information Available: Figures giving additional views and tables giving X-ray crystallographic data for **11b**·3CH$_2$Cl$_2$, **18**·1.21C$_7$H$_8$·0.29C$_3$H$_6$O, and **20**/**21**·2DMSO. This material is available free of charge via the Internet at http://pubs.acs.org.

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