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Preparation of Benzyne Complexes of Group 10 Metals by Intramolecular Suzuki Coupling of *ortho*-Metalated Phenylboronic Esters: Molecular Structure of the First Benzyne-Palladium(0) Complex

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Abstract: A series of nickel(II) and palladium(II) aryl complexes substituted in the ortho position of the aromatic ring by a (pinacolato)boronic ester group, $[\mathrm{MBr}\{o\text{-}\mathrm{C_6H_4B(pin)}\}\mathrm{L_2}]$ (M = Ni, L_2 = $2PPh_3$ (**2a**), $2PCy_3$ (**2b**), $2PEt_3$ (**2c**), dcpe (**2d**), dppe (**2e**), and dppb (**2f**); M = Pd, L_2 = $2PPh_3$ (**3a**), $2PCy_3$ (**3b**), and dcpe (**3d**)), has been prepared. Many of these complexes react readily with KO^tBu to form the corresponding benzyne complexes $[\mathrm{M}(\eta^2\text{-}\mathrm{C_6H_4})\mathrm{L_2}]$ (M = Ni, L_2 = $2PPh_3$ (**4a**), $2PCy_3$ (**4b**), $2PEt_3$ (**4c**), dcpe (**4d**); M = Pd, L_2 = $2PCy_3$ (**5b**)). This reaction can be regarded as an intramolecular version of a Suzuki cross-coupling reaction, the driving force for which may be the steric interaction between the boronic ester group and the phosphine ligands present in the precursors **2** and **3**. Complex **3d** also reacts with KO^tBu, but in this case disproportionation of the initially formed η^2-C_6H_4 complex (**5d**) leads to a 1:1 mixture of a novel dinuclear palladium(I) complex, $[(\mathrm{dcpe})\mathrm{Pd}(\mu_2\text{-}\mathrm{C_6H_4})\mathrm{Pd}(\mathrm{dcpe})]$ (**6**), and a 2,2′-biphenyldiyl complex, $[\mathrm{Pd}(2,2'\text{-}\mathrm{C_6H_4C_6H_4})(\mathrm{dcpe})]$ (**7d**). Complexes **2a**, **3b**, **3d**, **4b**, **5b**, **6**, and **7d** have been structurally characterized by X-ray diffraction; complex **5b** is the first example of an isolated benzyne-palladium(0) species.

Introduction

Although benzyne and its substituted derivatives (arynes) are highly reactive, transient molecules that cannot be isolated under normal conditions, they are useful reagents in organic synthesis because they readily undergo Diels−Alder reactions, cycloadditions with 1,3-dipoles, and nucleophilic additions.[1] The benzyne fragment can also be stabilized by coordination to both early and late transition metal centers,[2−8] in the forms of both mononuclear and cluster complexes. In particular, zirconocene benzyne, $[\mathrm{Zr}(\eta^5\text{-}\mathrm{C_5H_5})_2(\eta^2\text{-}\mathrm{C_6H_4})]$, which is readily generated by elimination of methane or benzene, respectively, from $[\mathrm{Zr}(\eta^1\text{-}\mathrm{C_6H_5})(\mathrm{R})(\eta^5\text{-}\mathrm{C_5H_5})_2]$ (R = Me, Ph), undergoes stoichiometric insertions with a wide range of unsaturated molecules, thus providing a potentially useful synthetic methodology.[2,4] Benzyne-nickel(0) complexes of the type $[\mathrm{Ni}(\eta^2\text{-}4,5\text{-}\mathrm{R_2C_6H_2})(\mathrm{PEt_3})_2]$ (R = H, F) insert successively 2 equiv of alkynes to give, after reductive elimination of the $\mathrm{Ni(PEt_3)_2}$ moiety, substituted naphthalenes with fair to good regioselectivity (Scheme 1).[9−14] It would obviously be desirable to make a reaction of this type catalytic in nickel, but, unfortunately, the reaction conditions, which require alkali metal reduction of the nickel(II) precursors $[\mathrm{NiBr}(2\text{-}\mathrm{Br}\text{-}4,5\text{-}\mathrm{R_2C_6H_2})(\mathrm{PEt_3})_2]$, are incompatible with most common functional groups likely to be used as aryl substituents and with the alkynes, which have to be added after the reduction.

Recently, it has been reported that arynes, generated in situ by treatment of (2-trimethylsilyl)aryl triflates with CsF, cyclo-

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[†] Single Crystal X-ray Diffraction Unit.

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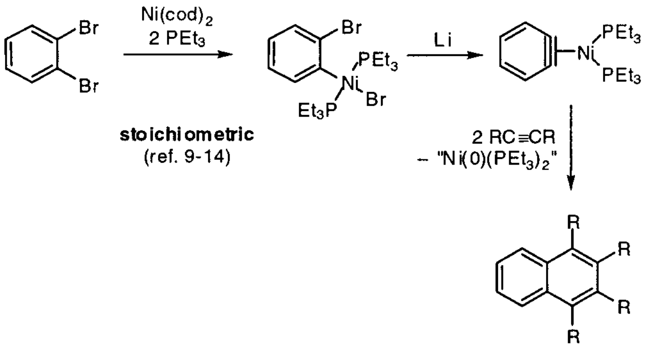
10.1021/ja0264091 CCC: $22.00

Scheme 1



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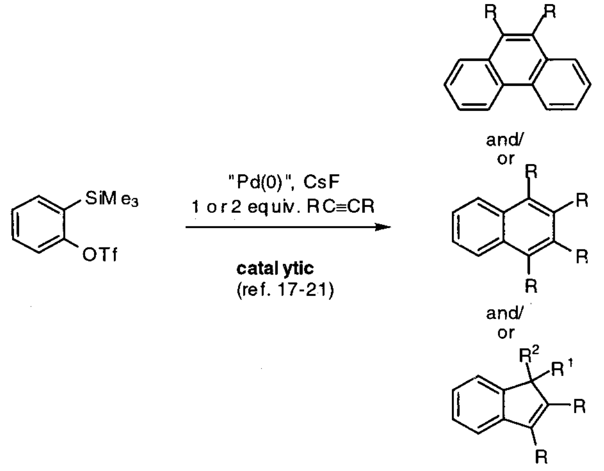
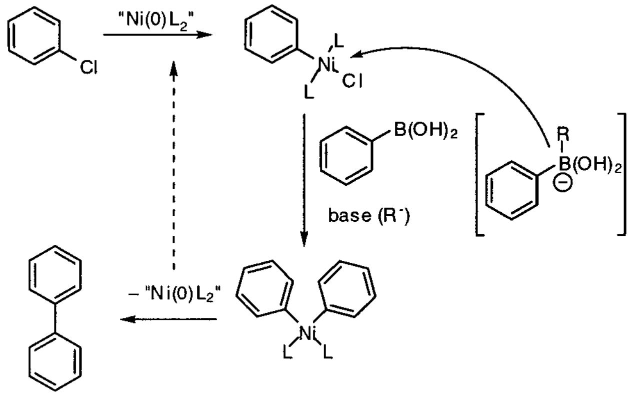
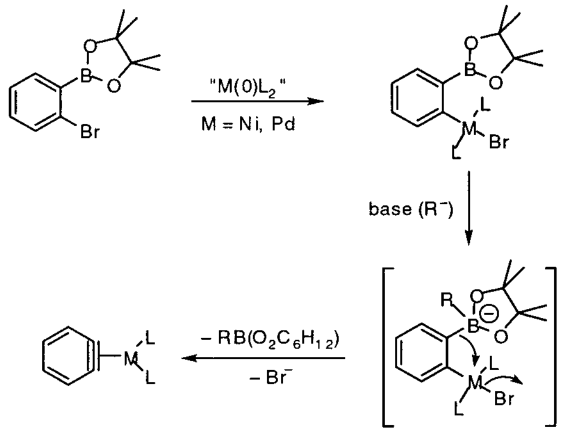


Scheme 3



Scheme 4



trimerize in the presence of catalytic amounts of a palladium(0) complex to yield triphenylenes.[15,16] By addition of 1 or 2 equiv of alkyne, these reactions can be directed to yield polyaromatic compounds such as phenanthrenes, naphthalenes, and/or indene derivatives (Scheme 2).[17−21] Most of these products probably arise from cocyclotrimerization of the free aryne with the alkynes catalyzed by the palladium complex or by insertion of the alkynes into an aryl−palladium(II) bond resulting from oxidative addition of the aryl triflate to palladium(0); although palladium(0)-benzyne complexes may have been formed, none were detected. In contrast, the catalytic carbonylation of arynes, generated in the same way, to give either anthraquinones (in the presence of cobalt carbonyls) or fluorenones (in the presence of $[RhCl(cod)]_2$) is postulated to occur via species derived by insertion of CO into a metal-benzyne complex.[22] Intermediates of this type have been observed in the stoichiometric reaction of benzyne-nickel(0) complexes with CO.[23]

We have chosen to investigate new ways of generating benzyne-nickel(0) complexes that might be compatible with a wider range of aromatic substituents and hence potentially applicable to catalytic conditions. Recently, nickel(0), assumed to be formed from the combination of a nickel(II) halide-tertiary phosphine complex and *n*-butyllithium, has been used to catalyze cross-coupling reactions of boronic esters with aryl halides, leading to the formation of biphenyls (Scheme 3).[24,25]

Mild bases such as K_3PO_4 initiate the cleavage of the boronic ester, thus forming the second aryl−Ni bond necessary for the coupling to occur. If both functionalities were present on the same arene in the form of a bromoarene substituted in the ortho position by a boronic ester, one could envisage that replacement of the bromine by the metal center and subsequent intramolecular Suzuki coupling could generate a benzyne complex (Scheme 4). We show here that this methodology is indeed feasible and can be used to form new benzyne complexes of nickel(0) and palladium(0).

Results

The nickel(II) complex $[NiBr\{o\text{-}C_6H_4B(pin)\}(PPh_3)_2]$ (**2a**)[26] was obtained by oxidative addition of *o*-bromophenyl (pinacolato)boronic ester (**1**) to a nickel(0) species prepared in situ by zinc reduction of $[NiBr_2(PPh_3)_2]$ (Scheme 5); the procedure was the same as that developed for the *o*-bromo analogue [NiBr(2-

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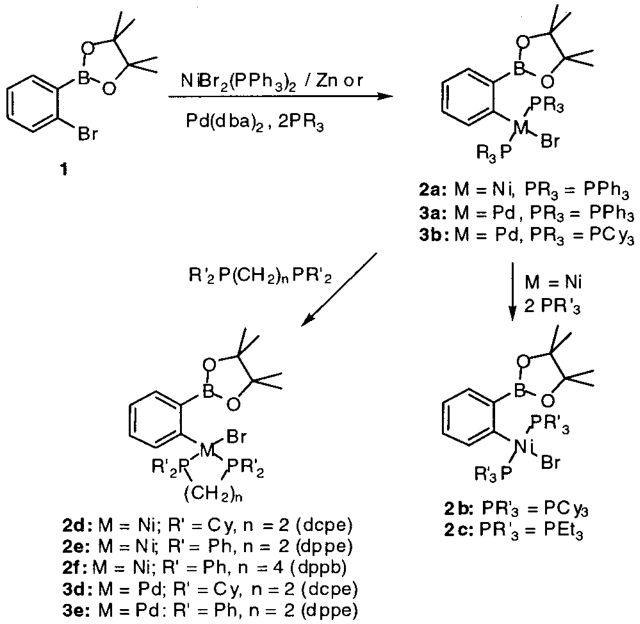
(26) Abbreviations: pin = pinacolate, $-OCMe_2CMe_2O-$; dcpe = 1,2-bis(dicyclohexylphosphino)ethane, $Cy_2PCH_2CH_2PCy_2$; dppe = 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$; dppb = 1,4-bis(diphenylphosphino)butane, $Ph_2P(CH_2)_4PPh_2$; depe = 1,2-bis(diethylphosphino)ethane, $Et_2PCH_2CH_2PEt_2$; dppm = bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$; dba = dibenzylideneacetone, PhCH=CHC(O)CH=CHPh; bipy = 2,2′-bipyridine.

Scheme 5



Br-4,5-$F_2C_6H_2$)(PPh_3)$_2$].[9] The ^{31}P NMR spectrum shows one peak at δ_P 21.4, indicative of a relative trans geometry for the two phosphine ligands. The structure of **2a** has also been confirmed by X-ray diffraction (see below).

Oxidative addition of **1** to other nickel(0) precursors, for example, [Ni(η^2-C_2H_4)(dcpe)], [$NiBr_2(PCy_3)_2$]/Zn, or [Ni(cod)$_2$]/2PEt$_3$, gave only poor yields of the corresponding nickel(II) adducts. However, these complexes could be obtained by ligand exchange reactions. Addition of various phosphines to **2a** allowed the preparation of the complexes [NiBr{*o*-C_6H_4B(pin)}-(PR_3)$_2$] (2PR$_3$ = 2PCy$_3$ (**2b**), 2PEt$_3$ (**2c**), dcpe (**2d**), dppe (**2e**), dppb (**2f**)) in excellent yields (Scheme 5), but exchange with diphosphines having larger bite angles such as {Ph$_2$P(C_6H_4)-CH_2}$_2$ or large diphosphite ligands failed. In contrast to **2a**, complexes **2b** and **2d** proved to be extremely sensitive toward hydrolysis of the aryl−B bond; thus, attempted crystallization of **2d** always gave [NiBr(C_6H_5)(dcpe)], identified by X-ray crystallography.[27] As a consequence, the exchange reactions were generally carried out in a solvent such as ether or toluene in which the resulting complexes were insoluble and could be isolated by filtration. Although complete characterization of these complexes (especially ^{13}C NMR spectra) was not always possible, the collected spectroscopic data support the formulation.

The ^{31}P NMR chemical shifts of complexes **2b**−**2f** are generally more shielded than those of their phenyl or *o*-haloaryl analogues. For example, complex **2b** shows a singlet at δ_P 6.4 for the two trans PCy$_3$ groups, cf. δ_P 9.6 for [NiCl(*o*-C_6H_4Cl)-(PCy_3)$_2$].[28] This shielding is even more pronounced for the PEt$_3$ species (δ_P 5.1 for **2c** vs 10.7 for [NiBr(*o*-C_6H_4Br)(PEt_3)$_2$][9]). The same effect is observed for the complexes formed with the chelating diphosphine ligands. The complex [NiBr{*o*-C_6H_4B-(pin)}(dcpe)] (**2d**) shows the characteristic two doublets at δ_P 59.1 and 63.7 for the cis phosphorus atoms (J_{PP} = 21.0 Hz), cf. δ_P 63.3 and 67.6 (J_{PP} = 19.4 Hz) for the hydrolysis product [NiBr(Ph)(dcpe)], δ_P 61.3 and 65.4 (J_{PP} = 17.1 Hz) for [NiBr-(*o*-C_6H_4Me)(dcpe)],[29] and δ_P 66.8 and 69.0 (J_{PP} = 30.5 Hz) for [NiBr(2-Br-4,5-$F_2C_6H_2$)(dcpe)].[9] The ^{13}C NMR spectra of the nickel(II) complexes show two characteristic signals for the boronic ester substituent at δ_C ca. 84 ppm for the quaternary carbons of the pinacolato fragment and in the region δ_C 24−26 ppm for the four CH$_3$ groups; in some cases, the latter signal shows a splitting attributable to hindered rotation around the aryl−B bond. The quaternary carbon C^1 bonded to nickel is observed as a triplet in the region δ_C 160−170 ppm with J_{PC} values of ca. 30 Hz for **2a** and **2c**, indicating that the two phosphorus atoms are mutually trans. The dppe adduct **2e** shows a doublet of doublets for C^1 with respective trans and cis J_{PC} coupling values of 83.9 and 38.5 Hz. For the dppb species **2f**, the signal for C^1 is also a triplet with J_{PC} = 33.8 Hz, but the ^{31}P NMR spectrum shows two signals with very similar chemical shifts (δ_P 11.4 and 12.0) with a coupling of 39.3 Hz that is larger than that usually observed for a cis coupling, perhaps as a consequence of distortion from planar coordination.

The palladium(II) precursors **3a** and **3b** are prepared similarly by oxidative addition of **1** with [Pd(dba)$_2$] in the presence of 2 mol equiv of PPh$_3$ or PCy$_3$, respectively, but heating to 100 °C is required (Scheme 5). With the chelating diphosphines, direct oxidative addition did not occur, and, in the case of dcpe, the species [Pd(η^2-dba)(dcpe)] was isolated.[30,31] As in the case of nickel, the dcpe and dppe species **3d** and **3e** were obtained by ligand exchange from either **3a** or **3b**, the latter complex being preferred because residual PPh$_3$ from reaction of **3a** proved more difficult to remove than that with the nickel analogue.

The ^{31}P NMR data for **3a**, **3d**, and **3e** are similar to those of their nickel counterparts, but the chemical shift of **3b** (δ_P 16.2) is very deshielded relative to that of **2b** (δ_P 6.4). The ^{13}C NMR data are similar to those of the nickel(II) products, the main difference for the cis complexes being the increased values of the couplings of C^1 with the phosphorus atom located trans to the Pd−C bond (135.7 Hz for **3d** and 129.3 Hz for **3e** vs 83.9 Hz for **2e**) and the decrease in both the cis and the trans complexes of the cis J_{PC} values (2.5 Hz for **3a**, 3.1 Hz for **3b**, and 2.5 Hz for **3e** vs 33.1 Hz for **2a**, 34.1 Hz for **2c**, and 38.5 Hz for **2e**).

The reactions of the nickel and palladium precursors **2b**−**e** and **3a**,**b**, respectively, with KO^{t}Bu give η^2-benzyne complexes (Scheme 6). Thus, on addition of KO^{t}Bu to the dcpe-nickel(II) complex **2d** in THF at room temperature, the ^{31}P NMR peaks to **2d** were replaced instantaneously by a singlet at δ_P 78.4, the chemical shift being identical to the value reported for the benzyne complex [Ni(η^2-C_6H_4)(dcpe)] (**4d**) prepared from reduction of [NiCl(*o*-C_6H_4Br)(dcpe)] with 1% Na/Hg amalgam.[29] The measured ^{1}H and ^{13}C NMR spectra were also identical to those reported previously for **4d**. The corresponding reaction with the PEt$_3$ precursor **2c** was slower, but after 2 h at room temperature the ^{31}P NMR spectrum showed the characteristic broad signal at δ_P 27.9 of the benzyne complex [Ni(η^2-

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(27) The spectroscopic data of [NiBr(Ph)(dcpe)] are analogous to those reported for the iodo complex [NiI(Ph)(dcpe)]; see ref 29. For the X-ray structure of [NiBr(Ph)(dcpe)], see: Edwards, A. J.; Retboll, M.; Wenger, E. *Acta Crystallogr., Sect. C*, submitted.

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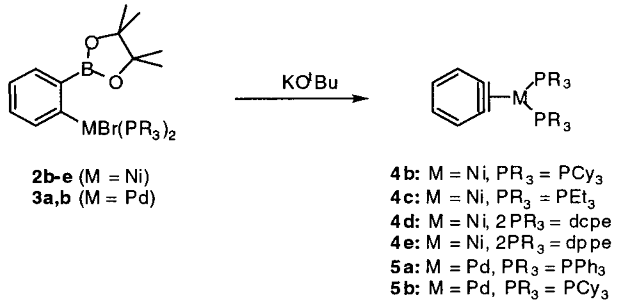
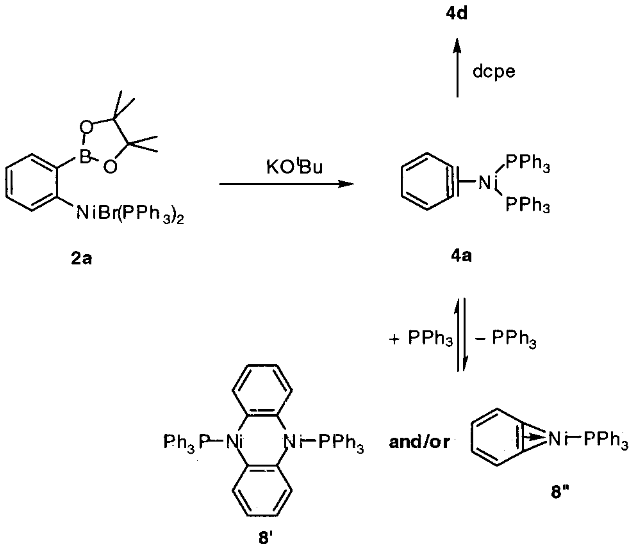
Scheme 6



Scheme 7



$C_6H_4)(PEt_3)_2]$ (**4c**), the yield as estimated from the ^{31}P NMR spectrum being >80%. All of the spectroscopic data were in agreement with those previously reported for this species.[9,32]

Reaction of the PCy_3 species **2b** with KO^{t}Bu was instantaneous; the ^{31}P NMR spectrum of the solution showed a singlet at δ_P 46.7 assignable to the benzyne complex $[Ni(\eta^2\text{-}C_6H_4)(PCy_3)_2]$ (**4b**), cf. δ_P 49.0 for the cyclohexyne analogue $[Ni(\eta^2\text{-}C_6H_8)(PCy_3)_2]$.[33] The ^{1}H NMR spectrum of **4b**, which can be extracted from the potassium salts with benzene, showed the expected AA′BB′ multiplet for the aromatic protons (δ_H 7.53 and 7.82). The ^{13}C NMR spectrum showed the quaternary carbons C^1 and C^2 of the coordinated triple bond as a doublet of doublets at δ_C 141.6 with separations arising from P−C coupling of 53.2 and 17.4 Hz. Crystals of **4b** were obtained from a solution in benzene, and the proposed structure was confirmed by X-ray diffraction analysis (see below). This complex has also been prepared by reduction of $[NiCl(o\text{-}C_6H_4\text{-}Cl)(PCy_3)_2]$ with 1% sodium amalgam.[28]

The corresponding reaction of the dppe analogue **2e** was slower and not clean. After 1.5 h at room temperature, only 20% of the desired benzyne complex $[Ni(\eta^2\text{-}C_6H_4)(dppe)]$ (**4e**) had formed. It was identified tentatively from the appearance of a singlet at δ_P 60.2 in the ^{31}P NMR spectrum of the reaction mixture, this chemical shift being identical to that of the cyclohexyne analogue $[Ni(\eta^2\text{-}C_6H_8)(dppe)]$.[33] The main product gave rise to a singlet at δ_P 44.7 assigned to $[Ni(dppe)_2]$;[34] unidentified resonances also appeared in the region δ_P 23−35. A similar reaction with **2f**, containing the larger dppb ligand, gave only $[Ni(dppb)_2]$ (δ_P 17.8).[34,35]

The reaction of the PPh_3 complex **2a** with KO^{t}Bu was more complicated. After 15 min, the ^{31}P NMR spectrum of the reaction mixture showed complete disappearance of the peak at δ_P 23.2 belonging to **2a** and appearance of a very broad, intense signal at about δ_P 0 ppm accompanied by a small singlet at δ_P 27.9. The ^{13}C NMR spectrum was surprisingly well resolved, showing peaks characteristic of symmetrically coordinated C_6H_4 at δ_C 123.3, 128.3 for the aromatic CH and at δ_C 142.8 for the two quaternary carbon atoms C^{1,2} coordinated to the metal. These signals and that for C^{ipso}−P at δ_C 137.7 showed no ^{31}P-coupling, suggesting the possibility of fast intermolecular exchange of coordinated PPh_3. The presence of species containing coordinated benzyne was confirmed by addition of 1 equiv of dcpe to the reaction mixture, which gave **4d** quantitatively together with free PPh_3. The reaction of **2a** with KO^{t}Bu was investigated by low-temperature ^{31}P NMR spectroscopy. At −70 °C, the broad peak moved to δ_P ca. −5 ppm while sharpening significantly, the peak in the region δ_P 27−28 broadened, and a new broad peak at ca. 40 ppm started to appear. At −90 °C, there were three main resonances: a very broad peak at δ_P 27−28, a fairly sharp peak at δ_P −7.0, presumably belonging to free PPh_3, and a broad peak at δ_P 40.7 ppm, the last two being in an ca. 2.5:1 intensity ratio. The peak at δ_P 40.7 is tentatively assigned to the benzyne complex $[Ni(\eta^2\text{-}C_6H_4)(PPh_3)_2]$ (**4a**), cf. δ_P 43.1 for the cyclohexyne analogue $[Ni(\eta^2\text{-}C_6H_8)(PPh_3)_2]$[33] or δ_P in the range 38−42 for $[Ni(\eta^2\text{-alkyne})(PPh_3)_2]$.[36] Unfortunately, the ^{13}C NMR spectrum recorded at −90 °C was very broad, and no conclusion could be drawn. The free PPh_3 could be removed by evaporating the mixture to dryness and washing the residue thoroughly with hexane. The ^{31}P NMR spectrum of the residue at room temperature now showed only the signal at δ_P 27−28, while its ^{13}C NMR spectrum was similar in appearance to that of the original reaction mixture except that the resonance of C^{ipso}−P was now a doublet (J_{PC} = 21.1 Hz); moreover, the integration suggested that the PPh_3 and C_6H_4 groups were now in a 1:1 ratio, whereas in the original reaction mixture the relative amount of PPh_3 was clearly much greater than 1. The ^{31}P NMR spectrum began broadening only at −90 °C; at −100 °C a very small, broad peak appeared at δ_P 40.2. Attempts to isolate a pure solid from the solution by low-temperature crystallization were unsuccessful, and both the mass spectra of the original mixture or the solid obtained after removal of free PPh_3 showed no identifiable peaks.

We conclude tentatively that **4a** is in dissociative equilibrium on the NMR time scale (fast at room temperature, slow at −90 °C) with a species $[Ni(C_6H_4)(PPh_3)]$ (**8**), which is responsible for the signal at δ_P 27−28 (Scheme 7). Complex **8** could be dinuclear, containing a pair of C_6H_4 units bridging two 14e, three-coordinate nickel(II) atoms, $[Ni_2(\mu\text{-}o\text{-}C_6H_4)_2(PPh_3)_2]$ (**8′**); a similar dinuclear formulation was postulated on the basis of molecular weight data for the product isolated from lithium reduction of $[NiCl(o\text{-}BrC_6H_4)(PEt_3)_2]$,[37] although the spectroscopic data obtained subsequently for the product from similar

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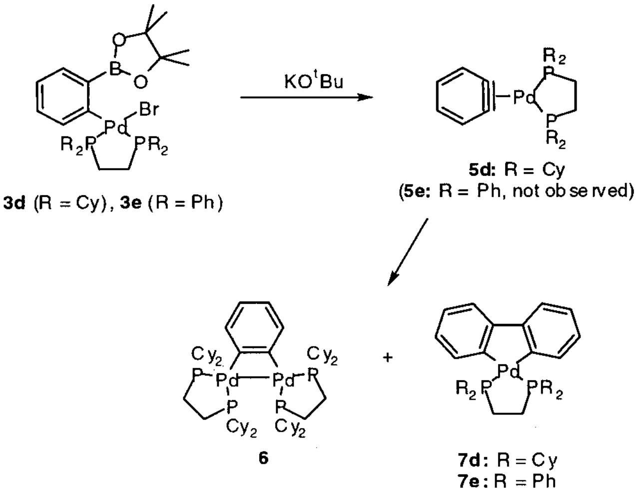
reductions were consistent with the mononuclear formulation **4c**.[9] Alternatively, one could consider a mononuclear 16e structure **8″** in which η^2-benzyne acts as a four-electron donor; this coordination mode is believed to occur in certain benzyne complexes of early transition metals, for example, $[Ta(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_6H_4)Me_2]$[38,39] and $[Ta(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_4H_6)(\eta^2\text{-}C_6H_4)]$.[40] However, the ^{13}C NMR chemical shift of the quaternary carbons bonded to nickel, observed at δ_P 142.8, is more consistent with the dimeric structure **8′**, the reported chemical shifts for η^4-benzyne complexes being considerably more deshielded (>200 ppm).[40]

The reactions of the palladium(II) complexes with KO^{t}Bu were much slower than those of nickel and generally required heating (Scheme 6).[41] The PPh_3 complex **3a** gave initially a ^{31}P NMR singlet at δ_P 41.5 that may belong to the benzyne complex $[Pd(\eta^2\text{-}C_6H_4)(PPh_3)_2]$ (**5a**), because the ^{1}H NMR spectrum showed a characteristic [AA′BB′] multiplet in the region δ_H 7.45, 8.45, but rapid decomposition hindered further identification. However, the PCy_3 complex **3b** reacted with KO^{t}Bu at room temperature overnight or at 80 °C for 2 h to give exclusively a compound showing a ^{31}P NMR singlet at δ_P 43.3 assigned to the benzyne-palladium(0) complex $[Pd(\eta^2\text{-}C_6H_4)(PCy_3)_2]$ (**5b**). The NMR data are analogous to those of **4b**; the quaternary carbon atoms of the coordinated triple bond appeared as an apparent doublet of doublets at δ_C 138.1 with separations arising from P−C coupling of 86.7 and 6.5 Hz. The FAB mass spectrum did not show any molecular ion corresponding to **5b**, but the compound crystallized from C_6D_6, and its structure was confirmed by X-ray diffraction analysis (see below).

The reaction of the palladium(II)-dcpe precursor **3d** with KO^{t}Bu was not as clean as that of its nickel analogue. After 5 min at room temperature, the ^{31}P NMR spectrum showed a small peak at δ_P 67.0 that may belong to the benzyne complex $[Pd(\eta^2\text{-}C_6H_4)(dcpe)]$ (**5d**), in addition to broad signals from **3d**. After heating at 50 °C for ca. 1 h, two new products, **6** and **7d**, had formed in approximately equal amount, characterized by two very broad signals at δ_P 60 and 69 (**6**) and a singlet at δ_P 55.1 (**7d**). When the reaction was carried out at room temperature, the same mixture was obtained after 16 h; a minor product showing two doublets at δ_P 60.7 and 64.6 (J_{PP} = 17.3 Hz), assigned to the hydrolysis product [PdBr(Ph)(dcpe)], was also formed. Poorly soluble, X-ray quality crystals of **6** deposited overnight, but they could not be redissolved in CD_2Cl_2 for spectroscopic analysis without decomposition. Diffraction analysis showed complex **6** to be a dinuclear palladium(I) species $[(dcpe)Pd(\mu\text{-}o\text{-}C_6H_4)Pd(dcpe)]$ (see below), while the second complex (**7d**) was identified as the (2,2′-biphenyldiyl)palladium(II) complex $[Pd(2,2'\text{-}C_6H_4C_6H_4)(dcpe)]$ on the basis of its ^{1}H and ^{13}C NMR spectra (see Experimental Section) (Scheme 8). Attempts to generate the benzyne complex **5d** by reduction of $[PdI(o\text{-}C_6H_4Br)(dcpe)]$ with 1% Na/Hg amalgam gave initially a solution showing the ^{31}P NMR singlet at δ_P 67.0 tentatively assigned to **5d**, but the mixture rapidly decomposed to metallic palladium and unidentified products.

Scheme 8



Reaction of the dppe complex **3e** with KO^{t}Bu led to decomposition, and ^{31}P NMR monitoring showed no peaks assignable to a benzyne complex. On standing, however, crystals deposited from the reaction mixture that were identified by X-ray analysis as being the dppe-analogue of **7d**, viz., the 2,2′-biphenyldiyl species $[Pd(2,2'\text{-}C_6H_4C_6H_4)(dppe)]$ (**7e**).

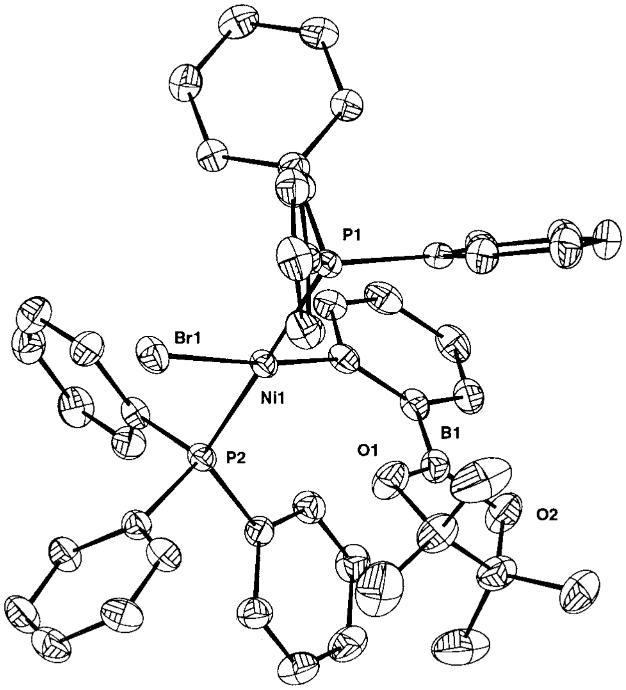


Figure 1. Molecular structure of $[NiBr\{o\text{-}C_6H_4B(pin)\}(PPh_3)_2]$ (**2a**) with selected atom labeling. Displacement ellipsoids show 50% probability levels; hydrogen atoms have been omitted for clarity.

Molecular Structures of $[NiBr\{o\text{-}C_6H_4B(pin)\}(PPh_3)_2]$ (2a), $[PdBr\{o\text{-}C_6H_4B(pin)\}(PCy_3)_2]$ (3b), $[PdBr\{o\text{-}C_6H_4B(pin)\}(dcpe)]$ (3d), $[Ni(\eta^2\text{-}C_6H_4)(PCy_3)_2]$ (4b), $[Pd(\eta^2\text{-}C_6H_4)(PCy_3)_2]$ (5b), $[(dcpe)Pd(\mu\text{-}o\text{-}C_6H_4)Pd(dcpe)]$ (6), and $[Pd(2,2'\text{-}C_6H_4C_6H_4)(dppe)]$ (7e). The molecular structures of the boronic ester precursors **2a**, **3b**, and **3d** are shown in Figures 1−3, respectively. Selected bond lengths and angles are given in Table 1.[42]

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(41) These reactions have been studied with the same batch of commercial KO^{t}Bu. The benzyne complexes are formed more rapidly if freshly sublimed base is used.

(42) The numbering scheme for the arylboronic ester moiety used throughout this paper (C1-M and C2-B) differs in some cases from that of the deposited structures.

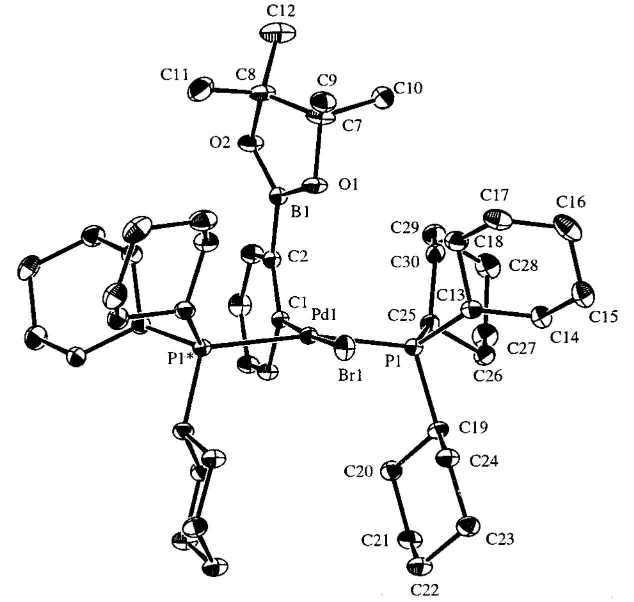

Figure 2. Molecular structure of [PdBr{*o*-$C_6H_4B(pin)$}$(PCy_3)_2$] (**3b**) with selected atom labeling; only one orientation of the disordered group is shown. Displacement ellipsoids show 30% probability levels; hydrogen atoms have been omitted for clarity. The asterisk indicates an atom generated by crystallographic symmetry.

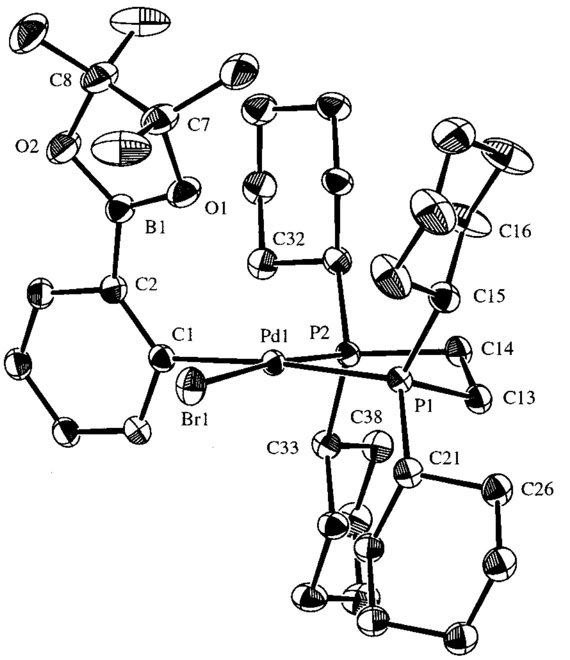

Figure 3. Molecular structure of [PdBr{*o*-$C_6H_4B(pin)$}(dcpe)] (**3d**) with selected atom labeling; only the major orientation of the disordered group is shown. Displacement ellipsoids show 30% probability levels; hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [NiBr{*o*-$C_6H_4B(pin)$}$(PPh_3)_2$] (**2a**), [PdBr{*o*-$C_6H_4B(pin)$}$(PCy_3)_2$] (**3b**), and [PdBr{*o*-$C_6H_4B(pin)$}(dcpe)] (**3d**)

	2a [M(1) = Ni]	**3b** [M(1) = Pd]	**3d** [M(1) = Pd]
M(1)−Br(1)	2.3680(4)	2.5525(7)	2.490(1)
M(1)−P(1)	2.2348(7)	2.3611(11)	2.348(2)
M(1)−P(2)	2.2372(7)	2.3611(11)[a]	2.258(2)
M(1)−C(1)	1.894(3)	2.026(5)	2.099(7)
C(2)−B(1)	1.546(4)	1.567(8)	1.561(11)
P(1)−M(1)−P(2)	174.42(3)	167.73(4)	86.3(1)
C(1)−M(1)−Br(1)	170.57(8)	176.08(15)	89.2(1)
P(2)−M(1)−Br(1)	90.81(2)	90.03(3)	174.7(1)
P(1)−M(1)−C(1)	87.35(7)	90.39(3)	174.1(2)
P(2)−M(1)−C(1)	88.70(7)	90.39(3)[a]	90.9(1)
M(1)−C(1)−C(2)	125.16(19)	124.0(4)	123.3(5)
C(1)−C(2)−B(1)	122.7(2)	126.0(5)	127.8(4)

[a] P(2) = P(1′) (generated by symmetry relation).

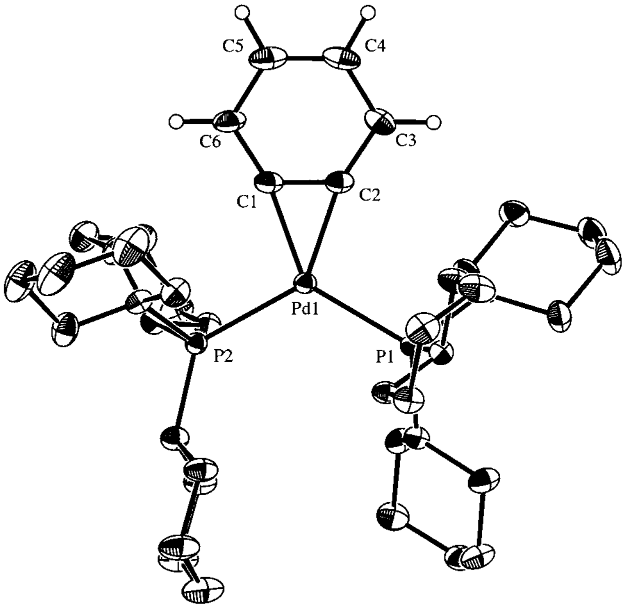

Figure 4. Molecular structure of [Pd(η^2-C_6H_4)$(PCy_3)_2$] (**5b**) with selected atom labeling. Displacement ellipsoids show 50% probability levels; hydrogen atoms of the cyclohexyl rings have been omitted for clarity.

The metal atoms in the boronic ester-substituted precursors **2a**, **3b**, and **3d** are in the expected, approximately square-planar coordination environment. The metrical data are unexceptional, the M−C and M−P distances for **2a** being similar to those reported for the ortho-substituted arylnickel(II) complexes [NiCl(*o*-C_6H_4X)$(PPh_3)_2$] (X = Me,[43] CF_3[44]), those of **3b** resembling the data for [PdCl(Ph)$(PCy_3)_2$].[45] In complex **3d**, atoms Br(1) and C(1) lie 0.2310 and 0.1889 Å, respectively, from the plane defined by Pd(1) and the two *cis*-phosphorus atoms. The significantly different Pd−P distances in **3d** [2.348(2) Å trans to η^1-aryl, 2.258(2) Å trans to Br] reflect the relative trans influence of these ligands. There is no evidence for interaction between the metal atoms and the pinacolato oxygen atoms, as judged by the M−O separations: 2.9998(12) for **2a**, 3.276(5) Å for Pd(1)−O(1) in **3b**, and 3.166(5) Å in **3d**. The phosphine ligands tend to bend away from the boronic ester substituent, the effect being particularly noticeable in the structures of **3b** and **3d** because of their bulky cyclohexylphosphine ligands. Thus, in **3b**, the P−M−P angle is 167.73(4)° (cf. 173.98(5)° for [PdCl(Ph)$(PCy_3)_2$][45] and 174.42(3)° for **2a**), while the C(1)−C(2)−B(1) angles in the η^1-aryl group are increased markedly from the expected 120° [126.0(5)° for **3b**, 127.8(4)° for **3d**].

The benzyne complexes **4b** and **5b** are isomorphous. The structure of **5b** is shown in Figure 4;[46] selected geometric parameters are listed in Table 2. They show a symmetrical η^2-coordination of the benzyne triple bond, the metal atom being

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(46) A figure showing **4b** is available in the Supporting Information.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Ni(\eta^2\text{-}C_6H_4)(PCy_3)_2]$ (**4b**) and $[Pd(\eta^2\text{-}C_6H_4)(PCy_3)_2]$ (**5b**)

	4b [M(1) = Ni]	**5b** [M(1) = Pd]
M(1)−P(1)	2.2007(12)	2.3276(14)
M(1)−P(2)	2.2002(12)	2.3415(14)
M(1)−C(1)	1.888(4)	2.042(6)
M(1)−C(2)	1.875(4)	2.032(6)
C(1)−C(2)	1.320(6)	1.324(8)
P(1)−M(1)−P(2)	122.19(5)	119.56(5)
C(1)−M(1)−P(1)	141.63(15)	140.47(18)
C(2)−M(1)−P(2)	136.93(14)	137.78(17)

in an almost perfect trigonal planar arrangement, typical of $[M(\eta^2\text{-alkyne})L_2]$ complexes of group 10 metals.[47] The two Ni−P bonds in **4b** are slightly longer than those reported for $[Ni(\eta^2\text{-}C_6H_4)(dcpe)]$ (**4d**) (ca. 2.20 Å vs 2.140(1) and 2.152(1) Å),[29] but the Ni−C bond lengths in the two complexes are similar (average value = 1.88 Å). As expected on the basis of atomic radii, the M−C and M−P bonds in **5b** are ca. 0.15 Å longer than those in **4b**; the Pd−C distances compare with those reported for the 3,5-cycloheptadien-1-yne complex $[Pd(\eta^2\text{-}C_7H_6)(PPh_3)_2]$ (2.031(4) and 2.039(4) Å).[48] The P−M−P angles are similar, 122.19(5)° for **4b** and 119. 56(5)° for **5b**, but they are much larger than the value reported for **4d** (91.8(1)°),[29] as expected from the presence in the latter of a C_2H_4 bridge between the phosphorus atoms. The lengths of the coordinated triple bond C(1)−C(2) in **4b**, **4d**, and **5b** are identical within experimental error (1.32−1.33 Å), as also are the lengths of the uncoordinated aryl C−C bonds; the latter are in the range 1.37−1.40 Å, indicating that the fragment retains aromatic character. Most other mononuclear η^2-benzyne complexes show similar trends,[49] although $[TaMe_2(\eta^2\text{-}C_6H_4)(\eta^5\text{-}C_5Me_5)]$[38,39] and $[Ir(\eta^2\text{-}C_6F_4)(\eta^5\text{-}C_5Me_5)(PMe_3)]$[50] are exceptional in having alternating long−short C−C distances in the ring.

The molecular structure of the dinuclear complex **6** is shown in Figure 5, and selected values of bond lengths and angles are given in Table 3. Each palladium atom is coordinated to a pair of phosphorus atoms from bidentate dcpe and a σ-aryl carbon atom of the bridging C_6H_4 unit. The second palladium atom occupies a fourth coordination site, the resulting geometry being highly distorted from planarity. The molecule possesses a pseudorotation symmetry axis that bisects the midpoints of the C(14)−C(15), C(11)−C(12), and Pd(1)−Pd(2) bonds. The four Pd−P bonds are of similar lengths (ca. 2.30 Å), and one phosphorus atom of each dcpe is located approximately trans to the Pd−Pd bond, the Pd−Pd−P angles being 164.2(1) and 163.1(1)°. The second phosphorus atom of one dcpe is bent away from the other, presumably because of steric repulsion between the cyclohexyl substituents. As these phosphorus atoms and the two Pd−C bonds of the *o*-phenylene bridge occupy positions that are almost transoid, a pronounced tilt is induced in the *ortho*-phenylene unit, the plane of the latter being rotated by 46° relative to the Pd−Pd axis. The two Pd−C bond lengths (ca. 2.06 Å) are in the normal range for aryl−Pd bonds, and the C−C bonds of the phenyl ring are normal. The distance between the metal atoms [2.645(1) Å] is within the range normally found for palladium(I)−palladium(I) bonds; most of the reported structures of this type show Pd−Pd bond lengths between 2.53 and 2.70 Å,[51] the shortest values being found in nonbridged dipalladium(I) species of the type $[Pd_2(NCMe)_4L_2]$ (L = NCMe, Cl, I).[52] Some examples of dinuclear complexes bridged by aliphatic groups include $[Pd_2(\mu\text{-}\eta^3\text{-}2\text{-}MeC_3H_4)(\mu\text{-}C_5H_5)(PPh_3)_2]$ (Pd−Pd = 2.679 Å),[53] $[Pd_2(\mu\text{-}\eta^3\text{-}C_3H_5)_2(PPh_3)_2]$ (2.720 Å),[54] and alkyne-bridged species $[Pd_2(\mu\text{-}C_2Ph_2)(\eta^5\text{-}C_5\text{-}$

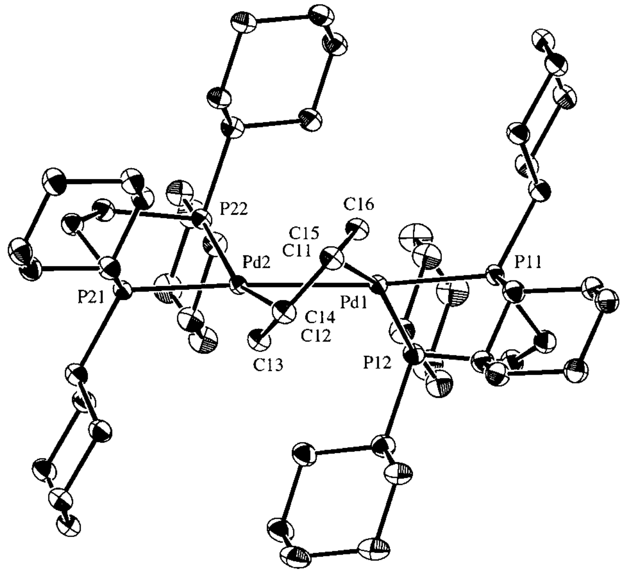

Figure 5. Molecular structure of $[(dcpe)Pd(\mu\text{-}o\text{-}C_6H_4)Pd(dcpe)]$ (**6**) with selected atom labeling; only one of the two molecules present in the asymmetric unit is shown. Displacement ellipsoids show 30% probability levels; hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[(dcpe)Pd(\mu\text{-}o\text{-}C_6H_4)Pd(dcpe)]$ (**6**)

Pd(1)−P(11)	2.296(1)	Pd(2)−P(21)	2.304(1)
Pd(1)−P(12)	2.301(1)	Pd(2)−P(22)	2.303(1)
Pd(1)−C(11)	2.061(3)	Pd(2)−C(12)	2.060(3)
Pd(1)−Pd(2)	2.645(1)	C(11)−C(12)	1.368(7)
Pd(2)−Pd(1)−P(11)	164.2(1)	Pd(1)−Pd(2)−P(21)	163.1(1)
Pd(2)−Pd(1)−C(11)	65.4(1)	Pd(1)−Pd(2)−C(12)	64.7(1)
C(11)−Pd(1)−P(12)	159.2(1)	C(12)−Pd(2)−P(22)	160.6(1)
C(11)−Pd(1)−P(11)	98.8(1)	C(12)−Pd(2)−P(21)	98.5(1)
Pd(1)−C(11)−C(12)	94.7(2)	Pd(2)−C(12)−C(11)	95.9(2)

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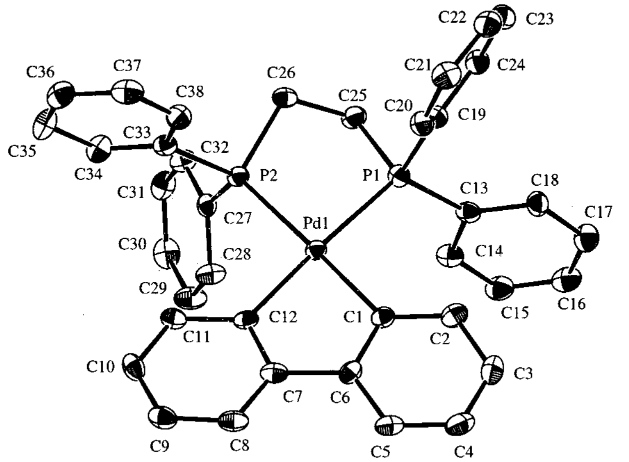

Figure 6. Molecular structure of [Pd(2,2′-$C_6H_4C_6H_4$)(dppe)] (**7e**) with selected atom labeling. Displacement ellipsoids show 30% probability levels; hydrogen atoms have been omitted for clarity.

Ph_5)(L)(L′)] (2.541−2.639 Å) [L,L′ = η^5-C_5Ph_5;[55] L = bipy, L′ = absent, MeCN, P(OPh)$_3$].[56]

The structure of **6** is exceptional in several respects. It is the first example of an *ortho*-phenylene bridging two palladium(I) centers. Some examples with palladium(II) are known in which the two metal atoms are not bonded (Pd···Pd separation > 3.5 Å), the complexes containing additional bridging ligands such as dppm, dialkyl sulfide, OAc, or $Ph_2PCH_2SCH_2Ph$.[57−59] Examples of complexes having a metal−metal bond bridged by an *ortho*-phenylene unit are known for iron, [Fe_2(μ-*o*-C_6F_4)-(CO)$_8$],[60] and iridium, [Ir_2(μ-*o*-C_6H_4)(η^5-C_5H_5)$_2$(CO)$_2$][61] and [Ir_2-(μ-*o*-C_6H_4)(μ-PPh_2)(μ-H)(η^5-C_5H_5)$_2$],[62] but in all of these cases the aromatic bridge is coplanar with the two metal atoms. Complex **6** is unique in the observed tilting of its *ortho*-phenylene bridge. The closest analogy to such a tilted bridge comes from a dinuclear iridium complex, [Ir_2(μ-1-η^1-1,2-η^2-*p*-C_6H_4OMe)(η^5-C_5Me_5)$_2$(CO)$_2$], in which the aryl group is coordinated simultaneously in a σ-fashion to one iridium atom and π-bonded to the second metal center, the resulting bridge being not symmetrical.[63] Similar π-interactions in complex **6** between Pd(1)−C(12) and Pd(2)−C(11) [2.565(4) Å and 2.589(4) Å, respectively] cannot be ruled out, but these distances are much longer than the Ir−phenyl π-bonds mentioned above [Ir−C(π) = 2.324(7) and 2.394(7) Å; Ir−C(σ) = 2.054(7) Å] or those observed in dipalladium(I) π-bridged complexes, cf. Pd−C distances of 2.12−2.16 Å in the η^3-allyl species [Pd_2(μ-η^3-C_3H_5)$_2$(PPh_3)$_2$].[54]

The molecular structure of the 2,2′-biphenyldiyl complex **7e** is shown in Figure 6, and selected values of bond lengths and angles are given in Table 4. The palladium atom has the expected square planar coordination, the biphenyldiyl unit being coplanar with the plane defined by Pd and the two phosphorus atoms (the two carbon atoms C1 and C12 lie only −0.0057 and 0.0631 Å, respectively, from the latter plane). The Pd−C and Pd−P distances are similar to those discussed above, and this structure is analogous to those reported for other 2,2′-biphenyldiyl complexes of group 10 metals, viz., [Ni(2,2′-$C_6H_4C_6H_4$)(dcpe)],[64] [Ni(2,2′-$C_6H_4C_6H_4$)(dippe)],[65] [Pt(2,2′-$C_6H_4C_6H_4$)(PPh_3)$_2$],[66] and [Pd(2,2′-$C_6H_4C_6H_4$)(depe)].[67]

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [Pd(2,2′-$C_6H_4C_6H_4$)(dppe)] (**7e**)

Pd(1)−P(1)	2.321(2)	Pd(1)−P(2)	2.320(2)
Pd(1)−C(1)	2.066(6)	Pd(1)−C(12)	2.059(6)
C(7)−C(12)	1.397(8)	C(1)−C(6)	1.389(8)
C(6)−C(7)	1.483(9)		
P(1)−Pd(1)−P(2)	84.52(5)	C(1)−Pd(1)−C(12)	80.3(2)
P(2)−Pd(1)−C(1)	178.1(2)	P(1)−Pd(1)−C(12)	177.1(1)

Discussion

In this work, we have demonstrated that benzyne complexes of nickel(0) and, for the first time, palladium(0)[68] can be generated by an intramolecular Suzuki coupling occurring within an arylmetal(II) complex containing an ortho-substituted boronic ester group. The required precursors are prepared by oxidative addition of the *o*-bromophenyl(pinacolato) boronic ester **1** to nickel(0) or palladium(0) complexes; the process occurs readily only when the auxiliary ligands are monodentate tertiary phosphines (PPh_3 for Ni; PPh_3, PCy_3 for Pd) and is unsatisfactory for bidentate tertiary diphosphines, probably because of the steric bulk of the pinacolato substituent. Steric interactions between this group and the phosphines are evident in the X-ray structures of **2a**, **3b**, and **3d**. In accord with the usual trend,[69] the oxidative additions to nickel(0) are, qualitatively, much faster than those to palladium(0). For the Pd−PCy_3 system, which reacts faster than the Pd−PPh_3 one, oxidative addition probably occurs to an intermediate containing only one bulky PR_3 group in the coordination sphere, as proposed for the rapid Suzuki coupling reactions observed with palladium catalysts bearing very bulky phosphine ligands.[70,71] Fortunately, the precursors containing bidentate tertiary diphosphine ligands can readily obtained by ligand substitution from the complexes containing monodentate phosphines **2a**, **3a**, and **3b**.

The reactivity of the palladium(II) and nickel(II) complexes depends strongly on the steric bulk of the auxiliary phosphine ligands. Hydrolytic cleavage of the aryl−B bond occurs most readily with the nickel complexes containing the cyclohexyl-substituted ligands PCy_3 (**2b**) and dcpe (**2d**). The palladium analogues are less prone to hydrolysis, whereas the PPh_3 complexes of both Ni and Pd, **2a** and **4a**, and the PEt_3 complex

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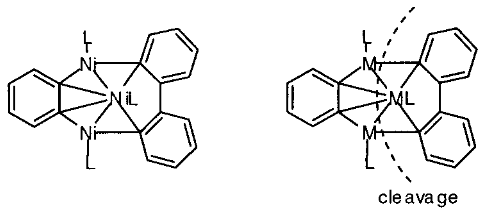

Figure 7. Schematic representation of the trinuclear nickel complexes reported in ref 71, and illustration of the cleavage postulated for the formation of **6** and **7d**.

of Ni, **2c**, seem to be inert to water. Qualitatively, a similar trend is observed for the rates of the reactions of the boronic ester complexes with KO^{t}Bu to give benzyne complexes, viz., dcpe > PCy_3 > PPh_3 > PEt_3 and Ni > Pd, suggesting that the reactions are sterically driven. Presumably, the mechanism of this intramolecular Suzuki coupling reaction (postulated in Scheme 4) is similar to that of the intermolecular version (Scheme 3), in which the base is commonly assumed to attack directly at boron to generate a carbanion, although initial substitution of the halide at the metal center cannot be excluded. At this stage it is not clear why, in the case of palladium, weaker bases than KO^{t}Bu are ineffective, and further studies of a range of bases with both nickel and palladium are required.

The new procedure has allowed the preparation of novel C_6H_4 complexes of palladium(0) and palladium(I) which do not survive the strongly reducing alkali metal reagents that have previously been required for forming benzyne complexes of nickel(0). In contrast to [Pd(η^2-C_6H_4)(PCy_3)$_2$] (**5b**), the dcpe analogue **5d** is unstable to disproportionation, giving the novel metal−metal bonded dipalladium(I) species [(dcpe)Pd(μ_2-C_6H_4)-Pd(dcpe)] (**6**) and the 2,2′-biphenyldiyl complex [Pd(2,2′-$C_6H_4C_6H_4$)(dcpe)] (**7d**). The mechanism of this process is unknown, although the fact that these two species are always formed in equimolar ratio suggests a common intermediate. One possibility could be the fragmentation of a trinuclear cluster similar to the compound [Ni_3(μ_3-C_6H_4)(μ_3-2,2′-$C_6H_4C_6H_4$)(P^i-Pr_3)$_3$] that was isolated as a minor product of the reduction of [NiCl(o-C_6H_4Cl)(P^iPr_3)$_2$] with 1% Na/Hg amalgam (Figure 7).[72]

Reaction of the dppe complex **3e** with KO^{t}Bu also leads to formation of a 2,2′-biphenyldiyl complex (**7e**), although in this case neither the benzyne-palladium(0) complex [Pd(η^2-C_6H_4)-(dppe)] (**5e**) nor the corresponding μ-o-phenylenedipalladium-(I) complex could be detected. 2,2′-Biphenyldiyl complexes related to **7d** and **7e** have also been obtained from the insertion of free benzyne into nickel(0)− and platinum(0)−benzyne bonds[64,66] and by oxidative cleavage of the C−C bond of biphenylene with nickel(0).[73] The first of these processes provides an alternative route to **7e**; partial decomposition of **5e** could liberate benzyne, which could react immediately with its progenitor.

Conclusion

Benzyne complexes of nickel(0) and, for the first time, palladium(0) can be generated by a KO^{t}Bu-promoted, intramolecular coupling of an arylmetal(II) complex ortho-substituted with a boronic ester group. The reactions occur more rapidly with nickel than with palladium and more rapidly with sterically demanding tertiary phosphines in the coordination sphere. Because the formation of the arylmetal(II) precursors by oxidative addition is faster with nickel than with palladium, the former would appear to be more suitable for developing a catalytic cycle based on benzyne complexes. Catalytic reactions with alkynes and the extension of the methodology to other transition metals are currently being investigated.

Experimental Section

General Procedures. All experiments were carried out under nitrogen. All solvents were dried and degassed prior to use. NMR spectra were recorded on a Varian XL-200E (^{1}H at 200 MHz, ^{13}C at 50.3 MHz, ^{31}P at 81.0 MHz), a Varian Gemini 300BB or Varian Mercury 300 (^{1}H at 300 MHz, ^{13}C at 75.4 MHz, ^{31}P at 121.4 MHz), or a Varian Inova-500 instrument (^{1}H at 500 MHz, ^{13}C at 125.7 MHz). The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvent and to external 85% H_3PO_4 for ^{31}P. The spectra of all nuclei (except ^{1}H) were ^{1}H-decoupled. The coupling constants (J) are given in Hz with an estimated error of ±0.2 Hz. Infrared spectra were measured on a Perkin-Elmer Spectrum One instrument. Mass spectra of the complexes were obtained on a ZAB-SEQ4F spectrometer by the fast-atom bombardment (FAB) technique using matrixes of either dry tetraglyme or 3-nitrophenyl octyl ether (NOPE), and those of the organic ligands on a Fisons VG Autospec instrument by electron impact (EI). Unfortunately, the benzyne complexes and several of the nickel(II) precursors were sensitive to heat and sometimes moisture, and, generally, they were too difficult to handle to obtain satisfactory analyses. When elemental analyses were possible, they were carried out in-house.

Starting Materials. The complexes [$NiBr_2(PPh_3)_2$],[74] [Ni(cod)$_2$],[75] [Ni(η^2-C_2H_4)(dcpe)],[29] and [$Pd_2(dba)_3$·dba][76] (also referred to as [Pd-(dba)$_2$] in the text) were prepared according to published procedures. o-Bromophenylboronic acid was obtained commercially and used as received.

***o*-C$_6$H$_4$BrB(pin) (1).** Commercial o-$C_6H_4BrB(OH)_2$ (1.8 g, 8.95 mmol) was suspended in pentane (20 mL), and pinacol (1.06 g, 8.95 mmol) was added. The slurry slowly solubilized while being stirred for 2 h at room temperature. The solution was decanted, dried over $MgSO_4$, and evaporation of the solvent yielded **1** (2.1 g, 84%) as a colorless liquid. Impurities that were present in the ^{1}H NMR spectrum of the starting boronic acid could not be removed, and the product was used directly for the preparation of the complexes. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.36 (s, 12H, CH_3), 7.18−7.27 (m, 2H, $H^{4,5}$), 7.50−7.54 (m, 1H, $H^{6 \text{ or } 3}$). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$): δ 24.5 (CH_3), 83.9 (O−C), 125.9 (CH), 127.9 (C^1−Br), 131.5 (CH), 132.2 (CH), 136.1 (CH); C^2−B not observed. EI-MS ($C_{12}H_{16}BBrO_2$): m/z 282 (27, M^+), 267 (25, M^+ − Me), 203 (100, M^+ − Br), 183 (67, $C_6H_4BrBOH^+$), 161 (78).

(i) Preparation of Aryl-Ni(II) and Pd(II) Complexes. [NiBr{*o*-C$_6$H$_4$B(pin)}(PPh$_3$)$_2$] (2a). A suspension of zinc powder (200 mg, 3.1 mmol) in THF (5 mL) was activated by ultrasound for 1 h. [$NiBr_2$-(PPh_3)$_2$] (2.02 g, 2.7 mmol) and o-C_6H_4BrB(pin) (2.0 g, 7.1 mmol) were added, and the suspension was stirred for 2 h at room temperature during which time the color changed from green to yellow/brown. The solution was evaporated to dryness, and the residue was washed successively with 30 mL and 70 mL portions of ether. The powder was redissolved with CH_2Cl_2, and this filtrate was evaporated to dryness leaving a yellow powder. Yield: 2.1 g (89%). Single crystals of **2a** were obtained from a toluene solution layered with hexane. ^{1}H NMR

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(300 MHz, $\mathrm{C_6D_6}$): δ 1.29 (s, 12H, $\mathrm{CH_3^{pin}}$), 6.32 (t, 1H, J 7.4, $\mathrm{H^{4\ or\ 5}}$), 6.48 (t, 1H, J 7.0, $\mathrm{H^{5\ or\ 4}}$), 7.05−7.15 (m, 18H, $\mathrm{H^{PPh}}$), 7.33 (d, 1H, J 7.1, $\mathrm{H^{3\ or\ 6}}$), 7.78 (d, 1H, J 7.4, $\mathrm{H^{6\ or\ 3}}$), 7.85−7.98 (m, 12H, $\mathrm{H^{PPh}}$). ^{13}C-{^{1}H} NMR (75.4 MHz, $\mathrm{CD_2Cl_2}$): δ 25.5 ($\mathrm{CH_3^{pin}}$), 83.6 (C^{pin}−O), 120.9 (t, J_{PC} 2.4, CH), 126.7 (t, J_{PC} 2.2, CH), 127.7 (t, J_{PC} 4.8, $\mathrm{CH}^{m-\mathrm{PPh}}$), 129.6 (s, $\mathrm{CH}^{p-\mathrm{PPh}}$), 132.4 (t, J_{PC} 21.2, $\mathrm{C}^{i-\mathrm{PPh}}$), 135.2 (t, J_{PC} 5.3, $\mathrm{CH}^{o-\mathrm{PPh}}$), 135.8 (t, J_{PC} 4.6, $\mathrm{C^6}$−H), 138.7 (t, J_{PC} 2.5, $\mathrm{C^3}$−H), 162.5 (t, J_{PC} 33.1, $\mathrm{C^1}$−Ni); $\mathrm{C^2}$−B not observed. ^{31}P{^{1}H} NMR (81.0 MHz, $\mathrm{CD_2Cl_2}$): δ 21.4. FAB-MS ($\mathrm{C_{48}H_{46}BBrNiO_2P_2}$, NOPE): *m/z* 866 ($\mathrm{M^+}$, very weak), 785 ($\mathrm{M^+}$ − Br). Anal. Calcd for $\mathrm{C_{48}H_{46}BBrNiO_2P_2}$: C, 66.55; H, 5.35. Found: C, 66.10; H, 5.71.

General Procedure for the Preparation of [NiBr{*o*-$\mathrm{C_6H_4}$B(pin)}-$\mathrm{L_2}$] (2b−2e). These complexes were prepared by replacement of the $\mathrm{PPh_3}$ ligands in **2a** using as solvent toluene (**2d**) or ether (**2b**, **2c**, **2e**) from which the product precipitated. This procedure avoided hydrolysis of the products, which decomposed on attempted purification. The preparation of **2d** is given as a characteristic example.

[NiBr{*o*-$\mathrm{C_6H_4}$B(pin)}(dcpe)] (2d). Solid [NiBr{*o*-$\mathrm{C_6H_4}$B(pin)}-$\mathrm{(PPh_3)_2}$] (**2a**) (1.38 g, 1.59 mmol) and dcpe (700 mg, 1.65 mmol) were dissolved in toluene (5 mL), and the mixture was stirred for 2 h at room temperature. The pure product, **2d**, precipitated as a yellow powder, which was isolated by filtration. Yield: 1.16 g (95%). ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$): δ 0.90−2.02 (m, 48H), 1.27 (s, 12H, $\mathrm{CH_3^{pin}}$), 6.79 (t, 1H, J 7.2, CH), 6.94 (t, 1H, J 7.4, CH), 7.55 (app d, 2H, J 7.8, CH). ^{31}P {^{1}H} NMR (81.0 MHz, $\mathrm{C_6D_6}$): δ 59.1 (d), 63.7 (d, J_{PP} 21.0). FAB-MS ($\mathrm{C_{38}H_{64}BBrNiO_2P_2}$, NOPE): *m/z* 765 ($\mathrm{MH^+}$), 683 ($\mathrm{M^+}$ − Br).

[NiBr{*o*-$\mathrm{C_6H_4}$B(pin)}$\mathrm{(PCy_3)_2}$] (2b). This was similarly prepared in ether. Yield 94%. ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$): δ 0.90−1.40 (m, 20H, $\mathrm{CH_2}$), 1.39 (s, 6H, $\mathrm{CH_3^{pin}}$), 1.50−1.95 (m, 40H, $\mathrm{CH_2}$), 2.05−2.30 (m, 6H, PCH), 6.62 (br t, 1H, J 7.2, $\mathrm{H^{4\ or\ 5}}$), 6.79 (br t, 1H, J 7.2, $\mathrm{H^{5\ or\ 4}}$), 7.43 (br d, 1H, J 7.2, $\mathrm{H^{3\ or\ 6}}$), 7.74 (br d, 1H, J 7.2, $\mathrm{H^{6\ or\ 3}}$). ^{31}P{^{1}H} NMR (81.0 MHz, $\mathrm{CD_2Cl_2}$): δ 6.4. FAB-MS ($\mathrm{C_{48}H_{82}BBrNiO_2P_2}$, NOPE): *m/z* 902 ($\mathrm{M^+}$, very weak), 822 ($\mathrm{MH^+}$ − Br).

The ^{13}C NMR spectra of **2b** and **2d** could not be recorded because the solutions decomposed.

[NiBr{*o*-$\mathrm{C_6H_4}$B(pin)}$\mathrm{(PEt_3)_2}$] (2c). This was prepared as described above using ether as solvent. The sensitive complex was isolated as a brown oil containing traces of $\mathrm{PPh_3}$ after evaporation of the solvent in vacuo and was not purified further. The yield was quantitative as estimated by ^{31}P NMR spectroscopy. This compound was best converted immediately into the corresponding benzyne complex **4c** by treatment with KO^{t}Bu. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 0.90−1.04 (m, 18H, $\mathrm{CH_3^{PEt}}$), 1.24 (s, 12H, $\mathrm{CH_3^{pin}}$), 1.30−1.45 (m, 12H, $\mathrm{CH_2^{PEt}}$), 6.70−6.90 (m, 2H, $\mathrm{H^{4,5}}$), 7.56 (d, 1H, J 7.8, $\mathrm{H^{3\ or\ 6}}$), 7.87 (d, 1H, J 7.1, $\mathrm{H^{6\ or\ 3}}$). ^{13}C {^{1}H} NMR (75.4 MHz, $\mathrm{C_6D_6}$): δ 8.7 (s, $\mathrm{CH_3^{PEt}}$), 15.5 (t, J_{PC} 12.1, $\mathrm{CH_2^{PEt}}$), 25.5 ($\mathrm{CH_3^{pin}}$), 83.7 (C^{pin}−O), 120.9 (t, J_{PC} 2.6, $\mathrm{C^{4\ or\ 5}}$−H), 136.0 (t, J_{PC} 2.8, $\mathrm{C^3}$−H), 136.3 (t, J_{PC} 4.3, $\mathrm{C^6}$−H), 167.9 (t, J_{PC} 34.2, $\mathrm{C^1}$−Ni); one aromatic CH located underneath residual solvent peaks, while $\mathrm{C^2}$−B was not located. ^{31}P{^{1}H} NMR (81.0 MHz, $\mathrm{CD_2Cl_2}$): δ 5.1.

[NiBr{*o*-$\mathrm{C_6H_4}$B(pin)}(dppe)] (2e). This was prepared similarly to **2b** in 92% yield. ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$): δ 1.36 (s, 6H, $\mathrm{CH_3^{pin}}$), 1.38 (s, 6H, $\mathrm{CH_3^{pin}}$), 1.45−1.70 (m, 4H, $\mathrm{PCH_2}$), 6.35−6.41 (m, 1H, $\mathrm{H^{4\ or\ 5}}$), 6.60−6.70 (m, 1H, $\mathrm{H^{5\ or\ 4}}$), 7.05−7.65 (m, 22H, $\mathrm{H^{PPh}}$ + $\mathrm{H^{3,6}}$). ^{13}C{^{1}H} NMR (75.4 MHz, $\mathrm{CD_2Cl_2}$): δ 22.8 (dd, J_{PC} 26.8, 22.4, $\mathrm{PCH_2}$), 23.9 ($\mathrm{CH_3^{pin}}$), 25.4 ($\mathrm{CH_3^{pin}}$), 31.0 (dd, J_{PC} 25.6, 12.7, $\mathrm{PCH_2}$), 83.4 (s, $\mathrm{OC^{pin}}$), 121.1 (s, CH), 127.7 (d, J_{PC} 9.9, $\mathrm{CH^{PPh}}$), 128.7 (d, J_{PC} 9.4, $\mathrm{CH^{PPh}}$), 128.8 (d, J_{PC} 10.3, $\mathrm{CH^{PPh}}$), 128.9 (d, J_{PC} 8.5, $\mathrm{CH^{PPh}}$), 128.9 (d, J_{PC} 6.4, CH), 129.8 (d, J_{PC} 2.8, $\mathrm{CH^{PPh}}$), 130.3 (d, J_{PC} 2.0, $\mathrm{CH^{PPh}}$), 130.7 (d, J_{PC} 2.3, $\mathrm{CH^{PPh}}$), 131.4 (d, J_{PC} 2.5, $\mathrm{CH^{PPh}}$), 132.5 (d, J_{PC} 9.3, $\mathrm{CH^{PPh}}$), 132.6 (d, J_{PC} 7.8, $\mathrm{CH^{PPh}}$), 134.3 (d, J_{PC} 11.1, $\mathrm{CH^{PPh}}$), 134.9 (d, J_{PC} 11.3, $\mathrm{CH^{PPh}}$), 136.4 (dd, J_{PC} 2.3, 2.9, CH), 137.1 (dd, J_{PC} 7.0, 1.7, $\mathrm{C^6}$−H), 170.0 (dd, J_{PC} 83.9, 38.5, $\mathrm{C^1}$−Ni); C−P and $\mathrm{C^2}$−B were not located. ^{31}P {^{1}H} NMR (81.0 MHz, $\mathrm{C_6D_6}$): δ 30.9 (d), 54.8 (d, J_{PP}17.9). FAB-MS ($\mathrm{C_{38}H_{40}BBrNiO_2P_2}$, NOPE): *m/z* 740 ($\mathrm{M^+}$), 659 ($\mathrm{M^+}$ − Br).

[NiBr{*o*-$\mathrm{C_6H_4}$B(pin)}(dppb)] (2f). This was obtained as above in 92% yield. ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$): δ 0.5−1.5 (m, 8H, $\mathrm{CH_2}$), 1.3 (br s, 12H, $\mathrm{CH_3^{pin}}$), 6.3−7.8 (m, 24H, $\mathrm{H^{arom}}$). ^{13}C{^{1}H} NMR (50.3 MHz, $\mathrm{CD_2Cl_2}$): δ 24.8−26.3 (m, $\mathrm{CH_2}$), 25.5 (s, $\mathrm{CH_3^{pin}}$), 25.7 (s, $\mathrm{CH_3^{pin}}$), 84.0 (s, $\mathrm{OC^{pin}}$), 121.1 (s, CH), 127.5−130.0 (m, CH), 130.6−131.3 (m, $\mathrm{C^{PPh}}$), 131.4−136.0 (m, CH), 163.2 (t, J_{PC} 33.8, $\mathrm{C^1}$−Ni). ^{31}P {^{1}H} NMR (81.0 MHz, $\mathrm{C_6D_6}$): δ 11.4 (d), 12.0 (d, J_{PP} 39.3).

[PdBr{*o*-$\mathrm{C_6H_4}$B(pin)}$\mathrm{(PPh_3)_2}$] (3a). A mixture of [Pd$\mathrm{(dba)_2}$] (300 mg, 0.52 mmol), $\mathrm{PPh_3}$ (574 mg, 1.14 mmol), and **1** (382 mg, 0.7 mmol) in toluene (20 mL) was stirred for 1 h at room temperature and then heated for 100 °C for 5 h until ^{31}P NMR monitoring showed the reaction to be complete. The solvent was evaporated, and the pale yellow powder was washed first with a mixture of toluene (2 mL) and hexane (5 mL) and then with just hexane. Recrystallization from a $\mathrm{CH_2Cl_2}$ solution layered with hexane yielded **3a** as an off-white solid. ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$): δ 1.19 (s, 12H, $\mathrm{CH_3^{pin}}$), 6.50 (app [AA′BB′] m, 2H, $\mathrm{H^{4,5}}$), 6.81−6.84 (m, 1H, $\mathrm{H^{3\ or\ 6}}$), 7.19−7.24 (m, 1H, $\mathrm{H^{6\ or\ 3}}$), 7.27 (br tt, 12H, J 7.2, 1.2, $\mathrm{H^{PPh}}$), 7.38 (br t, 6H, J 7.3, $\mathrm{H^{PPh}}$), 7.49−7.55 (m, 12H, $\mathrm{H^{PPh}}$). ^{13}C{^{1}H} NMR (50.3 MHz, $\mathrm{CD_2Cl_2}$): δ 25.2 (s, $\mathrm{CH_3{}^{pin}}$), 83.5 (s, $\mathrm{C^{pin}}$−O), 121.8 (s, CH), 127.9 (t, J_{PC} 5.0, $\mathrm{CH^{PPh}}$), 128.6 (s, CH), 129. 9 (s, $\mathrm{CH^{PPh}}$), 132.0 (t, J_{PC} 22.2, $\mathrm{C^{PPh}}$), 135.1 (s, CH), 135.2 (t, J_{PC} 6.3, $\mathrm{CH^{PPh}}$), 139.0 (s, $\mathrm{C^6}$−H), 165.5 (t, J_{PC} 2.5, $\mathrm{C^1}$−Pd); $\mathrm{C^2}$−B not located. ^{31}P{^{1}H} NMR (81.0 MHz, $\mathrm{CD_2Cl_2}$): δ 23.2. FAB-MS ($\mathrm{C_{48}H_{46}BBrO_2P_2Pd}$): *m/z* 833 ($\mathrm{MH^+}$ − Br), 630 ($\mathrm{Pd(PPh_3)_2{}^+}$), 571 ($\mathrm{MH^+}$ − Br − $\mathrm{PPh_3}$). Anal. Calcd for $\mathrm{C_{48}H_{46}BBrO_2P_2Pd{\cdot}{}^1/_2CH_2Cl_2}$: C, 60.91; H, 4.95. Found: C, 61.26; H, 5.00.

[PdBr{*o*-$\mathrm{C_6H_4}$B(pin)}$\mathrm{(PCy_3)_2}$] (3b). A mixture of [Pd$\mathrm{(dba)_2}$] (1 g, 1.74 mmol), $\mathrm{PCy_3}$ (1 g, 3.57 mmol), and **1** (500 mg, 1.77 mmol) in toluene (30 mL) was stirred at room temperature for 10 min during which time a yellow solution was formed. The reaction was complete after heating at 100 °C for 15 min. The solvent was evaporated, the residue was suspended in hexane, and the suspension was filtered through Celite. The residual powder was washed several times with ether until dba was no longer eluted, and then the solid was redissolved with $\mathrm{CH_2Cl_2}$ and eluted from the Celite plug. The solvent was removed to yield pure **3b** (970 mg, 59%) as a white powder. Single crystals were obtained from a $\mathrm{CH_2Cl_2}$ solution layered with hexane. ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$): δ 1.2−2.4 (m, 66H, Cy), 1.55 (s, 12H, $\mathrm{CH_3^{pin}}$), 7.07 (t, 1H, J 7.2, $\mathrm{H^{arom}}$), 7.22 (t, 1H, J 7.5, $\mathrm{H^{arom}}$), 7.83 (app d, 2H, J 7.8 Hz, $\mathrm{H^{arom}}$). ^{13}C{^{1}H} NMR (75.4 MHz, $\mathrm{CH_2Cl_2/C_6D_6}$): δ 25.2 (s, $\mathrm{CH_3{}^{pin}}$), 27.1 (s, $\mathrm{CH_2}$), 28.0−28.3 (m, $\mathrm{CH_2}$), 30.3 (s, $\mathrm{CH_2}$), 34.1 (t, J_{PC} 9.2, PCH), 83.7 (s, $\mathrm{C^{pin}}$−O), 121.3 (s, CH), 129.2 (s, CH), 137.0 (s, CH), 138.8 (t, J_{PC} 3.8, $\mathrm{C^6}$−H), 165.4 (t, J_{PC} 3.1, $\mathrm{C^1}$−Pd); $\mathrm{C^2}$−B not located. ^{31}P {^{1}H} NMR (81.0 MHz, $\mathrm{CH_2Cl_2/C_6D_6}$): δ 16.2. FAB-MS ($\mathrm{C_{48}H_{82}BBrO_2P_2Pd}$, NOPE): *m/z* 870 ($\mathrm{MH^+}$ − Br), 589.

[PdBr{*o*-$\mathrm{C_6H_4}$B(pin)}(dcpe)] (3d). A mixture of [PdBr{*o*-$\mathrm{C_6H_4}$B-(pin)}$\mathrm{(PCy_3)_2}$] (**3b**) (465 mg, 0.49 mmol) and dcpe (230 mg, 0.54 mmol) in toluene (5 mL) was stirred for 1 h at 50 °C during which time a white powder formed. The solid was filtered off and washed with toluene. Drying in vacuo gave pure **3d** (315 mg, 79%). Single crystals suitable for X-ray analysis were obtained from a $\mathrm{CH_2Cl_2}$ solution layered with hexane. ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$): δ 0.95−2.20 (m, 48H, dcpe), 1.36 (s, 6H, $\mathrm{CH_3^{pin}}$), 1.38 (s, 6H, $\mathrm{CH_3^{pin}}$), 6.71 (t, 1H, J 7.1, $\mathrm{H^{4\ or\ 5}}$), 6.91 (t, 1H, J 7.3, $\mathrm{H^{5\ or\ 4}}$), 7.44 (app t, 1H, J 6.1, $\mathrm{H^6}$), 7.54 (d, 1H, J 7.4, $\mathrm{H^3}$). ^{13}C{^{1}H} NMR (50.3 MHz, $\mathrm{CD_2Cl_2}$): δ 19.5 (dd, J_{PC} 19.2, 10.2, $\mathrm{PCH_2}$), 23.0−24.0 (m, $\mathrm{PCH_2}$), 23.6 (s, $\mathrm{CH_3^{pin}}$), 24.2 (s, $\mathrm{CH_3^{pin}}$), 25.9−30.3 (m, $\mathrm{CH_2}$), 31.5 (d, J_{PC} 23.8, PCH), 34.0 (d, J_{PC} 18.2, PCH), 35.3 (dd, J_{PC} 14.7, 2.5, PCH), 36.4 (d, J_{PC} 26.8, PCH), 83.2 (s, $\mathrm{C^{pin}}$−O), 121.9 (s, CH), 128.3 (d, J_{PC} 8.4, CH), 135.4 (d, J_{PC} 5.2, CH), 136.2 (d, J_{PC} 10.2, CH), 170.3 (d, J_{PC} 135.7, $\mathrm{C^1}$−Pd); $\mathrm{C^2}$−B not located. ^{31}P{^{1}H} NMR (81.0 MHz, $\mathrm{CD_2Cl_2}$): δ 58.6 (d), 61.9 (d, J_{PP} 20.5). FAB-MS ($\mathrm{C_{38}H_{64}BBrO_2P_2Pd}$, NOPE): *m/z* 731 ($\mathrm{M^+}$ − Br), 609.

[PdBr{*o*-$\mathrm{C_6H_4}$B(pin)}(dppe)] (3e). A mixture of [PdBr{*o*-$\mathrm{C_6H_4}$B-(pin)}$\mathrm{(PCy_3)_2}$] (**3b**) (203 mg, 0.21 mmol) and dppe (85 mg, 0.21 mmol) in toluene (10 mL) was heated for 30 min at 95 °C. Evaporation followed by suspension in ether and filtration gave pure **3e** (100 mg, 60%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.24−1.38 (m, 2H, PCH), 1.60 (br s, 13H, CH_3^{pin} + PCH), 1.80−1.92 (m, 1H, PCH), 6.78 (br t, 1H, *J* 7.2, $H^{4\text{ or }5}$), 6.85 (br dd, 2H, *J* 8.4, 3.0, H^{PPh}), 7.11 (td, 2H, *J* 7.5, 2.4, H^{PPh}), 7.28−7.34 (m, 2H, H^{PPh}), 7.36−7.54 (m, 11H, H^{arom}), 7.75 (ddd, 2H, *J* 11.7, 8.4, 1.5, H^{PPh}), 7.89−7.96 (m, 2H, H^{PPh}), 8.02−8.08 (m, 2H, H^{PPh}). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2): δ 22.9 (dd, J_{PC} 25.3, 12.0, PCH_2), 23.9 (s, CH_3^{pin}), 25.3 (s, CH_3^{pin}), 30.7 (dd, J_{PC} 30.6, 21.9, PCH_2), 83.1 (s, C^{pin}−O), 122.1 (d, J_{PC} 1.4, C^4−H), 127.9 (d, J_{PC} 10.4, CH^{PPh}), 128.4 (dd, J_{PC} 8.7, 2.1, $C^{3\text{ or }5}$−H), 128.8 (d, J_{PC} 9.9, CH^{PPh}), 129.0 (d, J_{PC} 10.9, CH^{PPh}), 129.0 (d, J_{PC} 9.0, CH^{PPh}), 130.3 (d, J_{PC} 2.8, CH^{PPh}), 130.5 (d, J_{PC} 18.2, C^{PPh}), 130.6 (d, J_{PC} 2.2, CH^{PPh}), 130.8 (d, J_{PC} 2.3, CH^{PPh}), 131.6 (d, J_{PC} 2.6, CH^{PPh}), 131.9 (d, J_{PC} 20.9, C^{PPh}), 132.5 (d, J_{PC} 9.0, CH^{PPh}), 132.9 (d, J_{PC} 11.0, CH^{PPh}), 133.5 (d, J_{PC} 33.3, C^{PPh}), 134.0 (d, J_{PC} 12.3, CH^{PPh}), 134.8 (d, J_{PC} 12.9, CH^{PPh}), 136.5 (dd, J_{PC} 5.0, 2.7, $C^{5\text{ or }3}$−H), 137.1 (dd, J_{PC} 10.1, 1.8, C^6−H), 169.5 (dd, J_{PC} 129.3, 2.5, C^1−Pd); one C−P and C^2−B were not located. ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2): δ 30.1 (d), 49.5 (d, J_{PP} 18.0). FAB-MS ($C_{38}H_{40}BBrO_2P_2Pd$, NOPE): *m/z* 707 (M^+ − Br).

(ii) Preparation of the Benzyne-Ni(0) and -Pd(0) Complexes. General Procedure for the Preparation of Ni-Benzyne Complexes [Ni(η^2-C_6H_4)L_2] (4a−f). The nickel(II) precursors **2a−f** (ca. 150 mg) were mixed with solid KO^{t}Bu (2−3 equiv), and THF (2 mL) was added. The mixtures were stirred at room temperature and monitored by ^{31}P NMR spectroscopy. Once the reaction was complete, the solvent was removed in vacuo, and the residue was washed with hexane to yield creamy white powders that were reactive to air and moisture, especially the complexes of monodentate phosphines. Further spectroscopic measurements were run on C_6D_6 extracts, when possible.

[Ni(η^2-C_6H_4)(PPh_3)$_2$] (4a). The reaction required 15 min at room temperature. Product **4a** shows complex exchange processes of the PPh_3 ligands in solution (see text). ^{1}H NMR (200 MHz, C_6D_6, room temperature): δ 6.94−7.03 (br m, 11H, H^{arom}), 7.36−7.46 (br m, 8H, H^{arom}). ^{13}C {^{1}H} NMR (75.4 MHz, C_6D_6, room temperature): δ 123.3 (s, CH^{C6H4}), 128.3 (s, CH^{C6H4}), 128.5 (s, CH^{PPh}), 128.8 (d, J_{PC} 11.0, CH^{PPh}), 134.2 (d, J_{PC} 17.9, CH^{PPh}), 137.7 (s, C^{PPh}), 142.8 (s, $C^{1,2}$−Ni). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, room temperature): δ 0 ± 2 (br), 26.9 (**8**, <10%). ^{31}P{^{1}H} NMR (81.0 MHz, $C_6D_5CD_3$, −90 °C): δ 40.7.

The solvent was removed in vacuo, and the residue was washed with hexane. This procedure removed free PPh_3 leaving a solid which may be the dinuclear species [(Ph_3P)Ni(μ-*o*-C_6H_4)$_2$Ni(PPh_3)] (**8′**). ^{13}C {^{1}H} NMR (75.4 MHz, C_6D_6, room temperature): δ 123.3 (s, CH^{C6H4}), 128.3 (s, CH^{C6H4}), 128.5 (d, J_{PC} 12.9, CH^{PPh}), 129.0 (br s, CH^{PPh}), 134.2 (d, J_{PC} 25.8, CH^{PPh}), 137.3 (d, J_{PC} 21.1, C^{PPh}), 142.8 (s, $C^{1,2}$−Ni). ^{31}P-{^{1}H} NMR (81.0 MHz, C_6D_6, room temperature): δ 26.9.

[Ni(η^2-C_6H_4)(PCy_3)$_2$] (4b). Addition of THF to a mixture of **2b** and KO^{t}Bu caused an immediate reaction, and ^{31}P NMR monitoring indicated the yield of **4b** to be >80%. Single crystals suitable for X-ray diffraction analysis were obtained from a solution in benzene that had been used for NMR spectroscopy. ^{1}H NMR (300 MHz, C_6D_6): δ 1.3−2.3 (m, 66H), 7.52−7.54 (m, 2H, $CH^{benzyne}$), 7.80−7.83 (m, 2H, $CH^{benzyne}$). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6): δ 27.1 (s, CH_2), 28.1 (d, J_{PC} 8.9, CH_2), 31.8 (d, J_{PC} 12.4, CH_2), 36.9 (3 line m, sepn of outer lines = 17.9, PCH), 123.3 (t, J_{PC} 4.0, $C^{3,6}$−H), 128.3 (s, $C^{4,5}$−H), 141.6 (app dd, sepns 53.2, 17.4, $C^{1,2}$−Ni). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6): δ 46.7 (br). FAB-MS ($C_{42}H_{70}NiP_2$, tetraglyme): *m/z* 695 [MH^+]. Anal. Calcd for $C_{42}H_{70}NiP_2$: C, 72.52; H, 10.14. Found: C, 73.26; H, 10.18.

[Ni(η^2-C_6H_4)(PEt_3)$_2$] (4c). The reaction was complete after 2 h at room temperature. The spectroscopic data (^{1}H, ^{13}C, and ^{31}P NMR, FAB-MS) were identical to those previously reported.[9]

[Ni(η^2-C_6H_4)(dcpe)] (4d). The reaction was instantaneous and quantitative as shown by ^{31}P NMR spectroscopy. The spectroscopic data (^{1}H, ^{13}C, and ^{31}P NMR, FAB-MS) were identical to those previously reported.[29]

[Ni(η^2-C_6H_4)(dppe)] (4e). Monitoring by ^{31}P NMR spectroscopy of the reaction of **2e** with KO^{t}Bu showed formation of **4e** after 1.5 h at room temperature (ca. 20%) together with [Ni(dppe)$_2$] (δ_P 44.7)[34] as the major compound and other unidentified species giving signals in the region δ_P 23−35.

4e. ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6): δ 60.2.

Attempted Preparation of [Ni(η^2-C_6H_4)(dppb)] (4f). Very slow reaction of **2f** with KO^{t}Bu led to formation of [Ni(dppb)$_2$] (δ_P 17.8),[34] the structure of which was confirmed by X-ray analysis of crystals deposited from the C_6D_6 extract used for NMR investigation.[35]

[Pd(η^2-C_6H_4)(PPh_3)$_2$] (5a). Reaction of the palladium precursor **3a** in THF/C_6D_6 (0.5 mL, 0.1 mL) with KO^{t}Bu showed initially a peak in the ^{31}P NMR spectrum at δ_P 41.5 that may belong to the benzyne complex **5a**. Rapid decomposition hindered further characterization.

[Pd(η^2-C_6H_4)(PCy_3)$_2$] (5b). Reaction of **3b** (52 mg, 0.05 mmol) with KO^{t}Bu (20 mg, 0.18 mmol) in toluene (3 mL) for 16 h at room temperature gave **5b** in >90% yield as shown by ^{31}P NMR spectroscopy. X-ray quality crystals were obtained from an NMR solution in C_6D_6. ^{1}H NMR (300 MHz, C_6D_6): δ 1.05−2.25 (m, 66H, Cy), 7.41−7.49 (m, 2H, $CH^{benzyne}$), 7.71−7.77 (m, 2H, $CH^{benzyne}$). ^{13}C {^{1}H} NMR (75.4 MHz, C_6D_6): δ 26.9 (s, CH_2), 28.1 (d, J_{PC} 8.9, CH_2), 31.0 (d, J_{PC} 12.4, CH_2), 37.0 (d, J_{PC} 17.9, PCH), 122.7 (t, J_{PC} 9.1, $C^{3,6}$−H), 128.3 (s, $C^{4,5-}$H), 138.1 (app dd, sepns 86.7, 6.5, $C^{1,2}$−Pd). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6): δ 43.3.

Attempted Preparation of [Pd(η^2-C_6H_4)(dcpe)] (5d). A suspension of **3d** (ca. 20 mg) and KO^{t}Bu (excess) in a mixture of THF (0.5 mL) and C_6D_6 (0.2 mL) was prepared in a NMR tube, and the reaction was monitored by ^{31}P NMR spectroscopy (see text). Small amounts of complex **5d** were initially formed, but disproportionation gave two major products (ratio ca. 1:1) that could be readily separated; single crystals of the poorly soluble dimer [(dcpe)Pd(μ-*o*-C_6H_4)Pd(dcpe)] (**6**) deposited from the mixture, while the 2,2′-biphenyldiyl species **7d** remained in solution.

5d. ^{31}P {^{1}H} NMR (81.0 MHz, C_6D_6): δ 67.0.

[(dcpe)Pd(μ-*o*-C_6H_4)Pd(dcpe)] (6). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6): δ 60 (br), 69 (br).

[Pd(2,2′-$C_6H_4C_6H_4$)(dcpe)] (7d). ^{1}H NMR (500 MHz, C_6D_6): δ 1.0−2.4 (m, 48H, dcpe), 7.19−7.21 (m, 4H, H^{arom}), 7.70 (d, 2H, *J* 7.0, $H^{3,3'}$), 7.76−7.81 (m, 2H, $H^{6,6'}$). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6): δ 20.8 (t, J_{PC} 36.1, PCH_2), 26.6−34.7 (m, CH_2^{dcpe}), 36.0 (t, J_{PC} 7.2, PCH), 120.2 (s, CH), 124.3 (s, CH), 125.2 (t, J_{PC} 11.9, CH), 140.3 (t, J_{PC} 15.0, CH), 160.1 (s, $C^{2,2'}$), 171.4 (dd, J_{PC} 116.6, 10.5, $C^{1,1'}$-Pd). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6): δ 55.1.

Attempted Preparation of [Pd(η^2-C_6H_4)(dppe)] (5e). Reaction of [PdBr{*o*-C_6H_4B(pin)}(dppe)] (**3e**) with KO^{t}Bu, carried out as described above, led to complete decomposition. The poorly soluble complex [Pd(2,2′-$C_6H_4C_6H_4$)(dppe)] (**7e**) crystallized from the solution and was identified only by X-ray diffraction analysis and FAB-MS. FAB-MS ($C_{38}H_{32}P_2Pd$, NOPE): *m/z* 757 (MH^+).

X-ray Crystallography of 2a·1.5C_6H_5Me, 3b, 3d, 4b·C_6H_6, 5b·C_6H_6, 6·C_6H_5Me, and 7e. Crystal data, details of data collection, data processing, structure analyses, and structure refinements are given in Table 5.

The crystals were mounted on a quartz fiber, and data were collected at 200 K on a Nonius Kappa CCD diffractometer equipped with a 95 mm camera and graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The data were measured by use of COLLECT,[77] while the intensities of the reflections were processed and the data reduced by use of the computer programs Denzo and Scalepak.[78] The structures

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(77) *COLLECT Software*, Nonius BV, 1997−2001.

(78) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. 276, pp 307−326.

Table 5. Crystal and Structure Refinement Data for Compounds **2a**, **3b**, **3d**, **4b**, **5b**, **6**, and **7e**

	2a	**3b**	**3d**	**4b**	**5b**	**6**	**7e**
(a) Crystal Data							
chemical formula	$C_{48}H_{46}BBrNiO_2P_2 \cdot 1.5C_7H_8$	$C_{48}H_{82}BBrO_2P_2Pd$	$C_{38}H_{64}BBrO_2P_2Pd$	$C_{42}H_{70}NiP_2 \cdot C_6H_6$	$C_{42}H_{70}P_2Pd \cdot C_6H_6$	$C_{58}H_{100}P_4Pd_2 \cdot C_6H_5Me$	$C_{38}H_{32}P_2Pd$
fw	1004.39	950.24	811.98	773.79	821.48	1226.26	657.02
crystal system	triclinic	orthorombic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	*Pnma* (No. XX)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	9.92980(10)	20.3184(3)	8.7037(1)	9.99820(10)	10.1512(1)	13.9055(2)	11.7245(4)
b (Å)	12.95530 (10)	22.7581(4)	12.4606(1)	28.9827(3)	29.5301(3)	19.0192(2)	18.1595(8)
c (Å)	20.4921(3)	10.5870(1)	36.1403(4)	15.1034(5)	15.0770(2)	24.0778(3)	14.7765(6)
α (deg)	85.1981(4)					80.6763(5)	
β (deg)	88.5163(4)		94.6632(5)	96.1217(5)	97.1577(6)	85.7074(4)	99.223(2)
γ (deg)	72.3410(4)					89.81279(6)	
V (Å^3)	2503.14(5)	4895.5	3906.56(6)	4351.63(9)	4484.35(9)	6265.9(1)	3105.4(2)
D_{calc} (g cm^{-3})	1.333	1.289	1.380	1.181	1.217	1.300	1.405
Z	2	4	4	4	4	4	4
μ (mm^{-1})	1.292 (Mo Kα)	1.298 (Mo Kα)	1.614 (Mo Kα)	0.550 (Mo Kα)	0.516 (Mo Kα)	0.714 (Mo Kα)	0.726 (Mo Kα)
(b) Data Collection, Processing, and Refinement							
2θ max (deg)	55.04	50.06	50.08	54.98	51.28	55.06	50.46
data collected (h,k,l)	(−12,−16,−26) to (12,16,26)	(−24,−27,−12) to (24,27,12)	(−10,−14,−43) to (10,14,43)	(−12,−37,−19) to (12,35,19)	(−12,−35,−17) to (12,35,17)	(−18,−23,−31) to (18,24,31)	(−13,−21,−17) to (14,21,17)
total reflections	75 844	59 885	46 354	75 271	68 283	124 400	39 996
unique reflections (R_{int}/%)	11 494 (5.1)	4440 (5.0)	3896 (4.5)	9960 (5.4)	8375 (6.5)	28 627 (5.9)	5561 (6.1)
observed reflections	5981 [$I > 3\sigma(I)$]	4042 [$I > 2\sigma(I)$]	5487 [$I > 3\sigma(I)$]	3614 [$I > 3\sigma(I)$]	4548 [$I > 3\sigma(I)$]	17 995 [$I > 3\sigma(I)$]	3843 [$I > 3\sigma(I)$]
absorp. corr. (trans. factors)	integration (0.745 to 0.939)	integration (0.848 to 0.950)	integration (0.743 to 0.942)	integration (0.870 to 0.979)	integration (0.931 to 0.975)	integration (0.852 to 0.922)	integration (0.921 to 0.966)
no. of parameters	583	290	120	449	460	244	370
R	0.0286	0.049	0.0631	0.0403	0.0630	0.0667	0.0531
R_w	0.0318	0.077	0.1135	0.0452	0.0350	0.1029	0.0634

of **3b** and **3d** were solved by Patterson method (PATTY),[79] while the others were solved by direct methods by use of SIR92[80] for **5b**$\cdot C_6H_6$, **6**$\cdot C_6H_5Me$, and **7e**, and SIR97[81] for **2a**$\cdot 1.5C_6H_5Me$ and **4b**$\cdot C_6H_6$.

The structure of **2a**$\cdot 1.5C_6H_5Me$ consists of one molecule of complex with one toluene molecule that is well ordered, while the second toluene lies about a center of inversion in a well-resolved 50:50 disordered fashion. Hydrogen atoms were included at geometrically determined positions (C−H 1.00 Å) and periodically recalculated, but they were not refined. The maximum and minimum peaks in the final difference Fourier map were 0.38 and −0.38 e/Å^3, respectively.

In the structure of **3b**, the molecule is located on a crystallographic mirror plane. The boronic ester unit, $C_6H_{12}BO_2$, is not planar but is disordered across this plane. The unit possesses approximate C_2 symmetry, and restraints were added to the B−O distances. All non-H atoms were refined anisotropically, apart from the B atom that lies too close to the mirror plane. The hydrogen atoms were included in the refinement at idealized positions (C−H 0.95 Å) and frequently recalculated. The maximum and minimum peaks in the final difference Fourier map were 0.54 and −0.65 e/Å^3, respectively, the maximum being located in the vicinity of the disordered boronic ester group.

The crystal of **3d** showed a small amount of twinning, and the boronic ester part, $C_6H_{12}BO_2$, was disordered over two orientations in a 0.706:0.294 ratio. The refinement was carried out with the help of the constrained least squares refinement program RAELS2000.[82] The four cyclohexyl groups were defined relative to the phosphorus atom to which they were attached and were constrained to be identical. Atoms C1−C6 of the aromatic ring were constrained to be planar. Multiple axial systems[83] allowed the local mirror-related boronic ester fragments [B1, O1, O2, C7−C12] and [B1′, O1′, O2′, C7′−C12′] to have local coordinates defined relative to C6 with B1 in the plane of C6, O1, and O2. These fragments were constrained to have local 2-fold symmetry, and C6−B1 and C6−B1′ were restrained to be collinear. The thermal displacement parameters were obtained using rigid body parametrizations.[84] The H atoms were recalculated at chemically sensible positions after each refinement cycle. The above modeling allowed 120 independent variables to adequately refine the structure. The data fit suggests that the final atomic parameters are reliably determined and the quoted errors are meaningful. The maximum and minimum peaks in the final difference Fourier map were 1.25 and −1.10 e/Å^3.

In the crystal structure of **4b**$\cdot C_6H_6$, each molecular species was accompanied by one molecule of benzene that was perfectly defined. The non-hydrogen atoms were refined anisotropically by full matrix least squares. Hydrogen atoms were included at geometrically determined positions (C−H 1.00 Å) and periodically recalculated, but they were not refined. The maximum and minimum peaks in the final difference Fourier map were 0.88 and −0.35 e/Å^3. The structure of **5b**$\cdot C_6H_6$ was isomorphous to **4b**$\cdot C_6H_6$, but the crystal was thin and twinned, producing two sets of reflections. One set was indexed and the intensities extracted from it, while the other set was ignored. The maximum and minimum peaks in the final difference Fourier map were 2.10 and −1.66 e/Å^3, respectively, the biggest ones being located near the Pd atom.

The structure of **6**$\cdot C_6H_5Me$ possesses a pseudo translational symmetry with the toluene molecule departing somewhat from it, and the constrained least squares refinement program RAELS2000 was used.[82] Atoms in each of the two molecules of **6** present in the asymmetric unit are approximately related by a local 2-fold rotation axis, and this is reflected in the atom labeling. The 16 cyclohexyl groups were defined relative to the phosphorus atom to which they were attached and were constrained to be identical. The toluene molecules were constrained to be planar. The thermal displacement parameters were obtained using rigid body parametrizations.[84] The Pd and P atoms were effectively

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refined as isolated anisotropic atoms by allowing extra parametrization, but constrained so that pseudo translationally related atoms had identical parameters.[85] The H atoms were recalculated at chemically sensible positions after each refinement cycle. The structure was adequately refined using only 244 independent variables. The data fit suggests that the final atomic parameters are reliably determined and the quoted errors are meaningful for the average geometry. The maximum and minimum peaks in the final difference Fourier map were 2.28 and −1.95 e/Å^3.

The crystal of **7e** was of poor quality with a high mosaic spread, but the derived data were able to produce a final structure of reasonable quality. The non-hydrogen atoms were refined anisotropically by full matrix least squares. Hydrogen atoms were included in the refinement at geometrically determined positions (C−H 0.95 Å) which were periodically recalculated. The maximum and minimum peaks in the final difference Fourier map were 1.44 and −0.86 e/Å^3, respectively, the biggest ones being located near the Pd atom.

The calculations were performed with use of the crystallographic software packages teXsan,[86] maXus,[87] RAELS2000,[82] and CRYSTALS.[88] The neutral atom scattering factors were taken from ref 89. The mass attenuation coefficients used were those implemented in maXus.[87]

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Supporting Information Available: CIF files giving full crystallographic data for **2a**·1.5C_6H_5Me, **3b**, **3d**, **4b**·C_6H_6, **5b**·C_6H_6, **6**·C_6H_5Me, and **7e**, and figure for **4b**·C_6H_6 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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