

C–H Activation and C–C Coupling of Arenes by Cationic Pt(II) Complexes

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Abstract: The synthesis and characterization of cationic platinum complexes of the type $[(R_2PC_2H_4PR_2)PtMe(OEt_2)]BAR_F$ ($R = Cy, Et$) are reported. These electrophilic platinum cations are found to react quantitatively with arenes (benzene, toluene) at room temperature by undergoing intermolecular C–H activation with concomitant C–C coupling to generate complexes of the type $\{[Pt(R_2PC_2H_4PR_2)]_2(\mu-\eta^3:\eta^3\text{-biaryl})\}[BAR_F]_2$. The dianionic biaryl ligands in these compounds exhibit a rare $\mu-\eta^3:\eta^3$ -bis-allyl bonding mode and can be removed from the complex with stoichiometric oxidants to generate the free biaryl and $[(R_2PC_2H_4PR_2)Pt(\mu-X)]_2[BAR_F]_2$ ($R = Cy, Et$; $X = Cl, I$). The cationic platinum complexes $[(R_2PC_2H_4PR_2)PtMe(OEt_2)]BAR_F$ ($R = Cy, Et$) are also quite reactive with water, forming the bridging hydroxide complexes $[(R_2PC_2H_4PR_2)Pt(\mu-OH)]_2[BAR_F]_2$ ($R = Cy, Et$). A possible mechanism is proposed for the C–C coupling reaction based upon the structures of these bridging biphenyl complexes, which provides a new perspective for the related palladium-catalyzed oxidative coupling of arenes to form biaryls.

Introduction

Intense efforts have recently been devoted to the study of the C–H activation step of alkane functionalization processes.¹ The majority of this research has centered around electrophilic platinum complexes containing bidentate nitrogen ligands, with the emphasis on the catalytic transformation of methane to methanol.^{1c,2} Another field of great interest is the transition-metal-catalyzed coupling of various reagents to generate new carbon–carbon bonds, which has now evolved into a widespread synthetic technique.³ A great deal of work has also recently been devoted to the combination of these two fields, and the applications of C–H activation reactions that lead to C–C coupling are enormous.⁴ However, the majority of this work

has involved intramolecular C–H activation reactions on substrates that are already coordinated to the metal center; there are relatively few examples of intermolecular C–H activation reactions that lead to C–C coupling.⁴ One of the more studied and important examples of this type of reaction is the Pd(II)-catalyzed oxidative coupling of arenes to form biaryls.⁵ Although this reaction has been studied a great deal, the details of the mechanism have been mainly deduced indirectly.

We have been involved in the study of highly electrophilic systems for the coordination and activation of small molecules⁶ and reported a series of coordinated alkyl and aryl halides of the type $[(P\text{-}i\text{-}Pr)_3PtH(\eta^1\text{-}XR)]BAR_F$ ($BAR_F = B[3,5\text{-}C_6H_3\text{-}(CF_3)_2]_4^-$), along with analogues containing coordinated Et_2O , THF, and H_2 ligands.^{6a} Since these platinum phosphine cations are potentially more electrophilic than their nitrogen analogues, we chose to further explore these platinum phosphine cations with respect to their ability to activate C–H bonds. Our initial attempts involving complexes of the type $[(PR_3)_2PtMe(solvent)]BAR_F$ ($solvent =$ solvento ligand) resulted in electrophilic attack on the BAR_F anion by the Pt cation as opposed to C–H activation.⁷ In this paper, we report novel C–H bond cleavage reactions of aromatic substrates with complexes of the type

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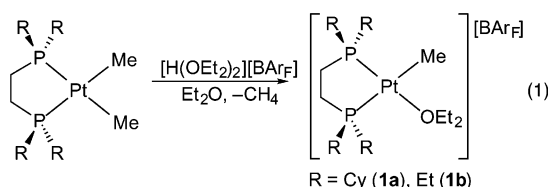
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[(diphosphine)PtMe(solvent)]BARF that lead to an unexpected C–C coupling reaction to form dianionic biaryl ligands in unusual coordination modes. The Pt–biaryl complexes can then be oxidatively cleaved to generate the free biaryls. The conclusive identification of these unique biaryl ligand structures offers a new perspective for elucidating the mechanism of the Pd(II)-catalyzed oxidative coupling of arenes, and the intermolecular C–H activation and C–C coupling reactions described in this paper are an important entry into this developing area of chemistry.

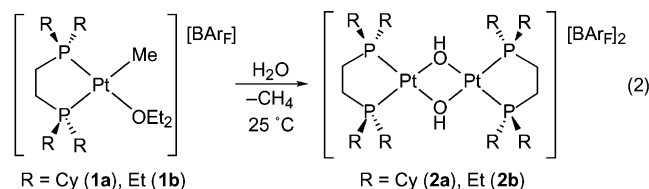
Results and Discussion

Synthesis and Characterization of Cationic Methyl Platinum Complexes. Protonation of the platinum dimethyl complexes ($R_2PC_2H_4PR_2$)PtMe₂ ($R = Cy$ (cyclohexyl), Et) with 1 equiv of $[H(OEt_2)_2][BARF]^8$ in Et₂O results in the elimination of methane to form the cationic solvento complexes $[(R_2PC_2H_4PR_2)PtMe(OEt_2)][BARF]$ ($R = Cy$, 92% yield (**1a**); Et, 89% yield (**1b**)), respectively (eq 1). These complexes can be isolated as



solids from hexanes at -30°C and were characterized by ^1H NMR, ^{31}P NMR, and elemental analyses. Particularly diagnostic are the ^{31}P NMR spectra, which exhibit two resonances with vastly different $J_{\text{P-Pt}}$ satellites (e.g., δ 70.4 (s, $J_{\text{P-Pt}} = 1870$ Hz), 50.9 (s, $J_{\text{P-Pt}} = 4520$ Hz) for **1a**) that are indicative of the much stronger trans effect of the methyl ligand relative to that of the coordinated Et₂O. These complexes are stable in Et₂O solutions at room temperature for several weeks under an inert atmosphere but decompose even in the solid state when exposed to air and moisture.

Hydrolysis of Cationic Methyl Platinum Complexes and X-ray Structure of $[(Cy_2PC_2H_4PCy_2)Pt(\mu-OH)]_2[BARF]_2$ (2a**).** The cationic solvento complex **1a** was found to react with even adventitious amounts of water to form the bridging hydroxide complex $[(Cy_2PC_2H_4PCy_2)Pt(\mu-OH)]_2[BARF]_2$ (**2a**) (eq 2). This



complex was characterized by ^1H NMR, ^{31}P NMR, and elemental analysis, and the molecular structure was determined by X-ray diffraction. To prevent the formation of the bridging hydroxide complex **2a**, it was necessary to use diethyl ether which was freshly dried over an activated alumina column throughout the synthetic preparation of **1a**. When a stoichiometric amount of H₂O was added to a diethyl ether solution of

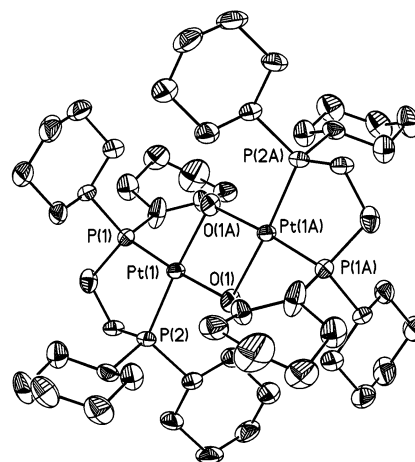


Figure 1. Molecular structure of **2a** (50% probability ellipsoids). Selected bond distances (Å) and angles (deg) for **2a**: Pt(1)–P(1), 2.2138(17); Pt(1)–O(1), 2.147(5); O(1)–Pt(1)–O(1A), 80.5(2); O(1)–Pt(1)–P(2), 96.40(15); O(1A)–Pt(1)–P(1), 95.81(14); P(1)–Pt(1)–P(2), 87.19(7).

1a, both **2a** and free CH₄ were observed by ^1H NMR. This reaction likely involves coordination of H₂O, followed by cleavage of an O–H bond and loss of CH₄ to generate a monomeric hydroxide complex, which then dimerizes to form **2a**. It is interesting to note the difference in hydrolytic reactivity between this bidentate phosphine platinum complex and its diimine and diamine analogues,^{2e–h,9} which in some cases were found to form relatively stable aqua complexes that decomposed only with certain ligand variations. The reason for this difference is not completely clear, but it is assumed that the more electrophilic phosphine system causes the aqua intermediate to be very acidic and more reactive toward protonation of the methyl ligand.

Crystals of quality suitable for X-ray diffraction analysis were obtained by cooling a concentrated solution of **2a** in pentafluoropyridine to -30°C for several days. The structure of the cation of **2a**·4NC₅F₅ is shown in Figure 1 along with selected bond lengths and bond angles. Although the OH protons were not located crystallographically, they were clearly seen in the ^1H NMR. The structure exhibits a nearly planar P₂Pt(μ-O)₂PtP₂ unit which is quite similar to analogous $[L_2Pt(\mu-OH)]^{2+}$ complexes that have been reported previously.¹⁰

C–H Activation and C–C Coupling of Benzene. When either **1a** or **1b** is heated in neat benzene at 80°C , the mostly insoluble solids transform almost immediately into deep red insoluble oils. These reactions also occur at room temperature in 4 h. The oils form red crystalline products that are isolable in nearly quantitative yields (98%), which is remarkable considering the complexity of the transformation. An NMR investigation verified that the conversion of **1a** and **1b** to $[\{Pt(R_2PC_2H_4PR_2)\}_2(\mu\text{-biphenyl})][BARF]_2$ ($R = Cy$ (**3a**), Et (**3b**)) is quantitative, with concomitant formation of methane (eq 3). Both the evolution of methane during these reactions and the ^1H NMR spectra of the products led us to believe that C–H activation had occurred. However, in addition to Pt–Ph resonances, the ^1H NMR exhibited phenyl resonances that were shifted upfield (e.g., for **3a**: 5.67 (2H), 5.48 (2H), and 4.74

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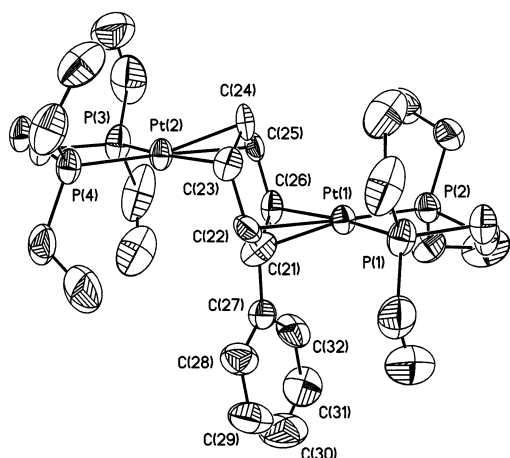
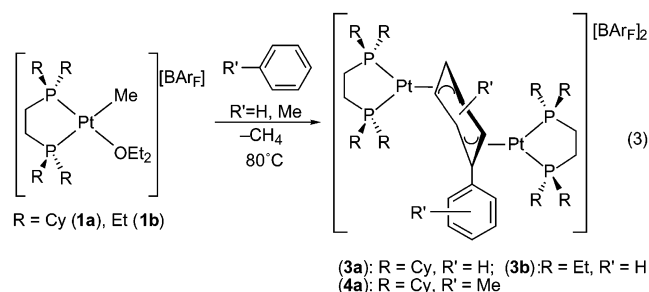


Figure 2. Molecular structure of **3b** (50% probability ellipsoids).

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[\{\text{Pt}(\text{Et}_2\text{PC}_2\text{H}_4\text{PEt}_2)\}_2(\mu\text{-Biphenyl})][\text{BAR}_f]_2$ (**3b**)

Distances (Å)			
Pt(2)–C(23)	2.249(10)	C(22)–C(23)	1.500(13)
Pt(2)–C(24)	2.143(11)	C(23)–C(24)	1.410(13)
Pt(2)–C(25)	2.247(8)	C(24)–C(25)	1.441(15)
C(21)–C(22)	1.374(15)	C(25)–C(26)	1.480(13)
C(21)–C(26)	1.422(12)		
Bond Angles (deg)			
P(1)–Pt(1)–P(2)	87.68(10)	C(23)–C(24)–C(25)	115.7(10)
P(3)–Pt(2)–P(4)	87.22(10)	C(24)–C(25)–C(26)	118.8(8)
C(21)–C(22)–C(23)	120.6(8)	C(25)–C(26)–C(21)	119.6(8)
C(22)–C(23)–C(24)	118.6(8)	C(26)–C(21)–C(22)	117.2(10)

ppm (1H)), indicative of π -type coordination of a phenyl ring. To characterize these products further, an X-ray diffraction study (discussed below) was carried out on **3b** (crystals of **3a** exhibited disorder, which allowed only a partial structure). Reactions similar to that in eq 3 (e.g., with complexes containing Ph_2 -



$\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ (dpppp) instead of $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$) as well as the X-ray structure of a product analogous to **3b** have recently also been found by Thomas and Peters.¹¹

X-ray Structure Determination of 3b. The molecular structure of **3b** is shown in Figure 2, and Table 1 gives metrical data. The structure indicates that **3b** is a dinuclear complex containing a bridging, dianionic biphenyl ligand in which two $(\text{Et}_2\text{PC}_2\text{H}_4\text{PEt}_2)\text{Pt}^+$ units are bonded in η^3 -fashion to opposite sides of one of the rings in the biphenyl ligand. The coordinated ring is highly distorted from planarity into a pseudo-chair conformation (bend angle of 23.3°) and is best viewed as being a dianionic, bis-allyl moiety, while the other ring in the biphenyl unit is unaffected by the coordination. This ligand can also be

represented as a phenyl-substituted benzene dianion that is bonded to two Pt(II) fragments. The bond lengths in the coordinated ring are also consistent with a bis-allyl type of bonding; the average C–C distance in the allyl units is $1.412(15)$ Å, which is a typical allylic C–C distance,¹² while the C–C distances which connect the allyl moieties are closer to C–C single bond lengths ($1.480(13)$ and $1.500(13)$ Å). Also indicative¹² of an allylic type of distortion is the short Pt–C distances to the central allylic carbon atoms ($2.083(13)$ and $2.143(11)$ Å) compared to the Pt–C distances to the outer allylic carbon atoms (average distance of $2.249(10)$ Å).

This type of bis-allyl bonding in arenes is quite unusual, and only a few examples have been reported in the literature, most of which contain boat-shaped benzene rings that are coordinated to a dinuclear center containing a metal–metal bond.¹³ Recently, Fryzuk et al. reported two dinuclear yttrium(III) complexes which contain bridging biphenyl dianions.¹⁴ In one structure, each yttrium fragment is bound in an η^6 -fashion to a different ring of the biphenyl unit; the entire biphenyl moiety is nearly planar in this complex, with a partial double bond connecting the two rings. In the other structure, both of the yttrium fragments are bonded to opposite sides of one ring of the biphenyl unit, and this ring exhibits a bis-allyl type of distortion. Although the bond lengths in this coordinated ring are similar to those in **3b**, the ring remains planar, with both yttrium fragments bonded in η^6 -fashion instead of η^3 -fashion. Evidence was also obtained for fluxionality between these two structures. However, no fluxional behavior was found in **3a** or **3b**, which retained their η^3, η^3 -bis-allyl bonding from 25 to -75°C .

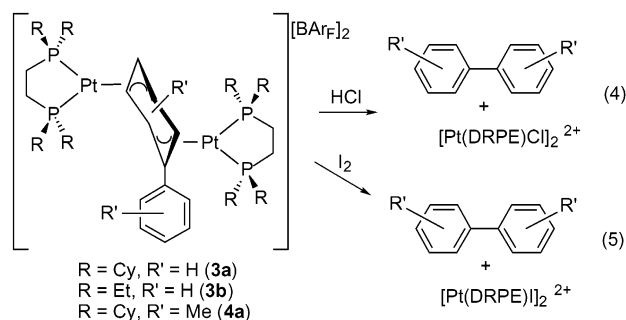
C–H Activation and C–C Coupling of Other Arenes. Complex **1a** reacts in neat toluene at 80°C almost immediately to form a red oil, which was then crystallized from a CH_2Cl_2 /hexanes mixture to give red crystals. The ^1H NMR, ^{31}P NMR, and elemental analysis are consistent with the assignment of this complex as $[\{\text{Pt}(\text{Cy}_2\text{PC}_2\text{H}_4\text{PCy}_2)\}_2(\mu\text{-bitolyl})][\text{BAR}_f]_2$ (**4a**). This species was present as a mixture of coordinated bitolyl isomers, which made it difficult to assign NMR signals. However, the characteristic upfield-shifted phenyl resonances were present in the ^1H NMR, and there were two singlets in the ^{31}P NMR ($\delta 69.9, 70.7$) with identical J_{PPt} coupling constants (3620 Hz), indicating that there are at least two isomers of this compound, depending upon coincidental resonances. In addition, a preliminary X-ray analysis indicated a structure similar to that of **3b**, but the final refinement could not be accomplished due to disorder. Complex **1a** was also dissolved in fluorobenzene and heated to 80°C , but no fluorobenzene coupling occurred, as evidenced by ^1H and ^{31}P NMR. Prolonged heating for several hours yielded methane, but no tractable solid compounds could be isolated. When **1a** was heated for several hours at 80°C in cyclohexane, methane was again evolved, but the ^1H and ^{31}P NMR spectra were identical to those in the fluorobenzene

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reaction. It is thought that at these temperatures, in the absence of a reactive substrate, intramolecular C–H activation is occurring on the phosphine ligands. However, this was not verified experimentally, as no identifiable complexes could be isolated.

Reactions of Bridging Biaryl Complexes. Since **3a** and **3b** formally contain a dianionic phenyl-substituted benzene ligand, they could be susceptible to hydrolysis similar to the reduced benzene intermediate in a Birch reduction. To test this, a large excess of water was added to these complexes in THF, but no reaction was evident after several days. However, when 8 equiv of HCl was added to solutions of **3a** or **3b** in CH₂Cl₂, the red color immediately disappeared. Instead of the expected phenyl-cyclohexadiene hydrolysis product, free biphenyl was obtained along with [(R₂PC₂H₄PR₂)Pt(μ-Cl)]₂[BAR_F]₂ (eq 4).¹⁵ Evidently,



Scheme 1

examples of intermolecular aryl group transfer in group 10 metals,¹⁶ and there are a few examples of transmetalation in neutral group 10 metal–aryl complexes to generate biaryl.¹⁷ In addition, there are several examples of catalytic cross-coupling reactions to generate biaryls which have proposed this transmetalation/reductive elimination mechanism.^{3d} More recently, palladium complexes of the type [PdX(Ar)(N–N)] (N–N = *N,N,N',N'*-tetramethylethylenediamine, 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine) were reported to react with AgBF₄ to form the cationic complexes [Pd(Ar)(bpy)(solv)]⁺.¹⁸ Depending on the ligand set, these complexes either were isolable or were found to spontaneously form biaryls. The formation of biaryl was proposed to go through a transmetalation/reductive elimination mechanism similar to that mentioned above, where the transmetalation was assumed to occur through a dinuclear, bridging phenyl intermediate, although no intermediates of this type were observed.

Possible Mechanism for Arene Coupling Reaction. In regard to the above discussion, complexes **3a**, **3b**, and **4a** can be viewed as representing actual isolated C–C coupled arene intermediates, the structure of which suggests a different type of coupling mechanism than those postulated previously for group 10 metal complexes. The main difference implied by the structures of our biaryl complexes is that the coupling occurs without a change in the formal oxidation state of the metal. This contrasts with previously postulated mechanisms for arene or aryl coupling, in which the formal oxidation state of the metal is reduced by 2 during a reductive elimination of the two aryl groups from a single metal center. The current results are more similar to the recently reported results of Fryzuk et al., in which complexes of the type {[PhP(CH₂SiMe₂NSiMe₂CH₂)₂PPh]M}₂(μ-Cl)₂ (M = Y and Ho) were shown to react with ArLi reagents to generate aryl-coupled products containing dianionic, μ-η⁶:η⁶-bridged biaryl ligands.¹⁴ Although the exact nature of this coupling reaction was not explored, it was assumed that the coupled products allow for a more efficient interaction of charge between the aryl groups and the metals in these predominantly ionically bonded complexes.

The novel structures of complexes **3a**, **3b**, and **4a** prompted us to postulate a possible mechanism for their formation (Scheme 2). Although we were not able to observe any intermediates in this reaction due to the low solubility of the

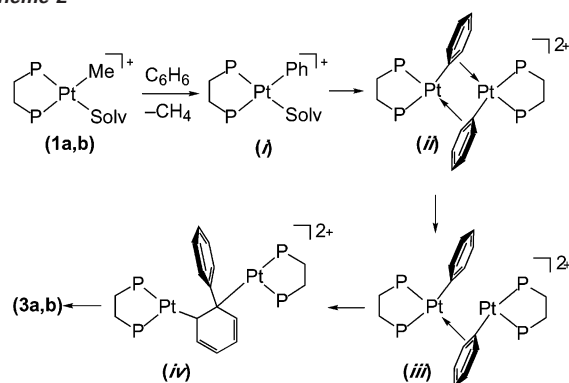
H⁺ is reduced to H₂, while the (biphenyl)²⁻ ligand is oxidized to free biphenyl. This oxidation reaction was also accomplished with elemental iodine, which resulted in the formation of free biphenyl and [(R₂PC₂H₄PR₂)Pt(μ-I)]₂[BAR_F]₂ (eq 5). The ability to release the biaryl ligands by oxidation prompted us to investigate the nature of the bitolyl isomers in **4a**. When a CH₂Cl₂ solution of **4a** was treated with iodine, the free bitolyl isomers were present along with [(R₂PC₂H₄PR₂)Pt(μ-I)]₂[BAR_F]₂ (R = Cy, Et). After the bitolyl isomers were isolated from this reaction mixture, a GC–MS analysis showed that no ortho-bitolyl isomers were formed, and that a nearly statistical mixture of *m,m'*-bitolyl, *m,p'*-bitolyl and *p,p'*-bitolyl were present. The fact that no ortho-bitolyl isomers formed is most likely due to steric effects. More importantly, the fact that a statistical mixture of mixed meta- and para-bitolyl isomers is obtained argues against an electrophilic aromatic substitution mechanism for the initial C–H activation step, which would result in an enrichment of para-bitolyl isomers.

Aryl Coupling Background. The catalytic oxidative coupling of arenes by palladium acetate with oxygen is a well-known reaction. Although the mechanism of this reaction has been debated, the most often cited version (Scheme 1) involves electrophilic aromatic substitution of the arene by palladium to form a σ-arylpalladium(II) moiety with loss of a proton (step a). This σ-arylpalladium(II) species is then proposed to undergo transmetalation to give a diarylpalladium(II) species (step b), which can then undergo reductive elimination to give the biaryl product and a Pd(0) species (step c), which is reoxidized by oxygen. Although no intermediates have been directly observed to verify this mechanism of C–C coupling, there are several

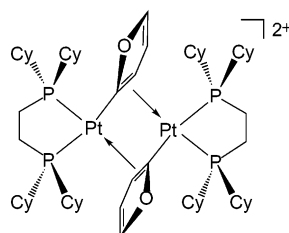
(15) The compounds [(R₂PC₂H₄PR₂)Pt(μ-Cl)]₂[BAR_F]₂ (R = Cy, Et) were characterized by comparing their ¹H and ³¹P NMR spectra to those of authentic samples (prepared by reacting (R₂PC₂H₄PR₂)Pt(Me)(Cl) with [H(OEt)₂]₂[BAR_F] in Et₂O).

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Scheme 2



starting materials and products in the benzene solvent, we propose that the first step of this reaction occurs through C–H activation of benzene, with a subsequent liberation of methane to generate a cationic platinum phenyl complex (**i**). Recent kinetic studies on benzene C–H activation reactions at cationic platinum centers containing diimine ligands suggest that these reactions occur by a mechanism involving coordination of an η^2 -benzene, followed by reversible oxidative addition of benzene C–H bonds, reversible formation of a methane C,H- σ -complex, and finally methane loss.^{2b} A similar mechanism is most likely occurring in our diphosphine system, and methane formation was detected by ^1H NMR in sealed NMR tube reactions. As further support, a complex analogous to **i** has been spectroscopically observed as an intermediate in a similar system where the phosphine is dppp.¹¹ The C–C coupling reaction is then proposed to occur via an η^1, η^2 -bridged phenyl dimer (**ii**), which has a putative structure very similar to that of an η^1, η^2 -bridged 2-furyl dimer synthesized by reacting **1a** with furan. However,



no C–C coupling occurred between the bridging 2-furyl groups in this complex.¹⁹ There are also several transition metal complexes containing bridging aryl groups that have been structurally characterized.²⁰

To verify that two initially formed platinum phenyl complexes are reacting to generate a dimeric complex (**ii**), as opposed to a platinum phenyl complex reacting with free benzene solvent, we carried out an experiment in which $(\text{Cy}_2\text{PC}_2\text{H}_4\text{PCy}_2)\text{Pt}(\text{Ph})(\text{Me})$ was reacted with 1 equiv of $[\text{H}(\text{OEt}_2)_2][\text{BAR}_f]$ in C_6D_6 solvent. After the reaction was heated to 80 °C for 5 min, a dark red oil was obtained which was isolated, dissolved in $\text{CD}_2\text{-Cl}_2$, and shown by NMR to consist of **3a** with no deuterium

incorporation. This strongly suggests that a dimeric intermediate such as **ii** is involved in the coupling reaction. We feel that the η^1, η^2 -bridged nature of this intermediate is reasonable, especially in light of the recent spectroscopic and structural characterization of cationic η^2 -benzene complexes of platinum(II)²¹ and a dinuclear palladium complex with an η^2 -phenyl interaction.²² Since η^2 -coordination of a benzene ring is expected to dearomatize and consequently activate the ring to some degree, we propose that, after dissociation of one of the η^2 -benzene ligands to generate compound **iii**, a migratory insertion of the η^2 -benzene ligand into the Pt–Ph bond occurs to form complex **iv**, which can be viewed as containing two η^1 -allyl interactions. This complex then undergoes η^1 – η^3 -type allyl migration reactions on the ring to which the Pt fragments are attached to generate the final product, **3a,b**.²³ The fact that **3** does not show any fluxionality in solution from 25 to –75 °C suggests that the solid-state structure, which contains a phenyl group substituent on the central position of one of the allyl units, also represents the most stable conformation in solution. Although, to the best of our knowledge, no one has previously suggested the migratory insertion of an η^2 -benzene ligand into a Pt–Ph bond, it seems reasonable that this could occur based upon the preponderance of small-molecule insertion reactions into group 10 metal–aryl bonds. In addition, migratory insertion reactions of palladium aryls with coordinated dienes to give coordinated allyls are known.²⁵ It has been claimed that these reactions are more facile than olefin insertions because of the stability of the metal allyl complex that forms.^{25a} This may be a driving force in the formation of **3a,b**. In further support for this type of insertion reaction, the migration of a methyl group to the arene ring has been reported in the complex $(\eta^6\text{-benzene})\text{Mn}(\text{Me})(\text{CO})_2$ to give the *endo*-methylcyclohexadienyl product.²⁶ It is also possible that these types of insertion mechanisms are actually operating in the reported examples of aryl-coupling reactions mentioned above. The fact that the biaryl ligands in **3a**, **3b**, and **4a** are removed by mild oxidants also supports this hypothesis.

Summary

The reaction of the cationic platinum complexes $[(\text{R}_2\text{PC}_2\text{H}_4\text{-PR}_2)\text{PtMe}(\text{OEt}_2)]\text{BAR}_f$ ($\text{R} = \text{Cy}$ (**1a**), Et (**1b**)) with aromatic substrates was expected to give C–H activation to form σ -aryl complexes of the type $[(\text{R}_2\text{PC}_2\text{H}_4\text{PR}_2)\text{Pt}(\text{Ar})(\text{Solv})]\text{BAR}_f$ with elimination of methane. However, even at room temperature these reactions proceed quantitatively to form the C–C coupled products **3a**, **3b**, and **4a**, which contain bridging, dianionic biaryl ligands. It is likely that σ -aryl complexes are first formed in these reactions by C–H activation on the arene substrates,

- (19) The complexes $[(\text{Cy}_2\text{P}(\text{CH}_2)_2\text{PCy}_2)\text{Pt}(\mu\text{-}\eta^1\text{-}\eta^2\text{-OC}_4\text{H}_9)]_2[\text{BAR}_f]_2$ and also $[(\text{Cy}_2\text{P}(\text{CH}_2)_2\text{PCy}_2)\text{Pt}(\mu\text{-S-C-SC}_4\text{H}_9)]_2[\text{BAR}_f]_2$ were prepared and structurally characterized by X-ray diffraction. Full experimental details, characterization, and properties of these complexes will be disclosed in a separate manuscript.
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followed by formation of dinuclear phenyl-bridged complexes which undergo C–C coupling to form the final products. It is proposed that this C–C coupling occurs via migratory insertion of an η^2 -coordinated benzene ligand attached to platinum into a Pt–Ph bond. The dianionic biaryl ligands in these complexes were removed easily by mild oxidants to generate the corresponding free biaryls, while the formal oxidation state of the platinum metal does not change throughout this transformation. This is in contrast to the previously proposed formation of biaryls from metal–aryl complexes involving transmetalation reactions to generate bis-aryl metal complexes, which undergo reductive elimination to give the biaryl and a reduced metal species. However, it is possible that the mechanism proposed in this paper may be operating in some of these other systems as well and may provide insight into catalyst development and mechanistic understanding in these systems. Complex **1** is also quite reactive with water, forming the bridging hydroxide complexes $[(R_2PC_2H_4PR_2)Pt(\mu-OH)]_2[BAr_F]_2$ ($R = Cy, Et$) with even adventitious amounts of water. It is intriguing that these diphosphine platinum cations and related species can be so highly tuned as to exhibit dramatically different reactivities depending on the nature of the bidentate ligands; e.g., the dppp analogue of **1** is stable to adventitious water.¹¹ The reason for this is not completely clear, but it would appear that factors in addition to electronics control the protonation of the methyl ligand in the presumed aquo intermediate. Also, the diimine and diamine analogues^{2e–h,9} have been shown to be only moderately reactive with water and, most significantly, undergo C–H activation with aromatic substrates to generate relatively stable Pt–aryl complexes that do not undergo C–C coupling.

Experimental Section

General Procedures. All manipulations were performed in dry glassware under a helium atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. All NMR spectra were recorded on a Unity Series 300 MHz spectrometer. Toluene, hexanes, and Et₂O were dried by passing through activated alumina and copper oxide. CH₂Cl₂ was dried over P₂O₅. C₆H₆ was dried over NaK, and C₆H₅F was dried over CaH₂. The complexes (R₂PC₂H₄PR₂)PtMe₂, (R₂PC₂H₄PR₂)Pt(Me)(Ph), and (R₂PC₂H₄PR₂)Pt(Me)(Cl) ($R = Cy$ (cyclohexyl), Et) were prepared according to the literature.²⁷ The compounds [H(OEt₂)₂BAr_F] and NaBAr_F were prepared according to the literature,²⁸ but NaBAr_F was dried by azeotropic distillation in benzene for better exclusion of water.

Preparation of [(Cy₂PC₂H₄PCy₂)Pt(Me)(OEt₂)]BAr_F (1a**).** To a stirred Et₂O solution (10 mL) of [H(OEt₂)₂BAr_F] (0.438 g, 0.433 mmol) at room temperature was added (Cy₂PC₂H₄PCy₂)Pt(Me)₂ (0.280 g, 0.433 mmol) as a solid. Evolution of methane began immediately, and after 5 min the solution was clear and colorless. The volume was reduced to 2 mL, and 15 mL of hexanes was then added to obtain an oily solid. The flask was placed in a freezer at –30 °C for 1 day to obtain a white, crystalline solid. The filtrate was decanted off, and the solids were washed with 3 × 5 mL of hexanes and dried under vacuum to give pure **1a** (0.605 g, 89%). Anal. Calcd for C₆₃H₇₃BF₂₄OP₂Pt: C, 48.19; H, 4.69. Found: C, 48.08; H, 4.96. ¹H NMR (C₆H₅F, –30 °C): δ 0.497 (d, 3H, $J_{HP} = 5.7$ Hz, $J_{HPt} = 36$ Hz); 1.12 (t, 6H); 1.55–1.62 (m); 1.70–1.79 (m); 1.90 (m, 4H); 3.63 (q, 4H); 7.65 (s, 4H); 8.29 (s, 8H). ³¹P NMR (C₆H₅F, –30 °C): δ 70.4 (s, $J_{PPt} = 1870$ Hz); 50.9 (s, $J_{PPt} = 4520$ Hz).

Preparation of [(Et₂PC₂H₄PEt₂)Pt(Me)(OEt₂)]BAr_F (1b**).** To a stirred Et₂O solution (10 mL) of [H(OEt₂)₂BAr_F] (0.469 g, 0.464 mmol) at room temperature was added (Et₂PC₂H₄PEt₂)Pt(Me)₂ (0.200 g, 0.464 mmol) as a solid. Evolution of methane began immediately, and after 5 min the solution was clear and colorless. The volume was reduced to 3 mL, and 10 mL of hexanes was then added to obtain a light yellow, oily solid. The flask was placed in a freezer at –30 °C for 1 day to obtain a white, crystalline solid. The filtrate was decanted off, and the solids were washed with 3 × 5 mL of hexanes and dried under vacuum to give **1b** (0.577 g, 92%). ¹H NMR (C₆H₅F, –30 °C): δ 0.525 (d, 3H, $J_{HP} = 6.0$ Hz, $J_{HPt} = 39.6$ Hz); 1.13 (t, 6H); 1.43 (m); 1.61 (m); 2.10–2.55 (m); 3.58 (q, 4H); 7.67 (s, 4H); 8.31 (s, 8H). ³¹P NMR (C₆H₅F, –30 °C): δ 61.1 (s, $J_{PPt} = 1814$ Hz); 50.7 (s, $J_{PPt} = 4330$ Hz).

Preparation of [(Cy₂PC₂H₄PCy₂)Pt(μ -OH)]₂[BAr_F]₂ (2a**).** Compound **1a** (0.200 g, 0.127 mmol) was dissolved in C₆H₅F (5 mL), and 2 equiv of H₂O (0.00459 g, 0.254 mmol) was then added with stirring. A white precipitate began to form immediately. After the mixture was stirred for 2 h at room temperature, the white solids were collected on a coarse frit, washed with 3 × 5 mL benzene, and dried under vacuum to give pure **2a** (0.175 g, 92%). Anal. Calcd for C₁₁₆H₁₂₂B₂F₄₈O₂P₄Pt₂: C, 46.51; H, 4.10. Found: C, 46.53; H, 4.08. ¹H NMR (CD₂Cl₂, 25 °C): δ –0.382 (s, 2H); 1.30–1.37 (m); 1.76–1.89 (m); 2.07 (m, 8H); 7.57 (s, 8H), 7.73 (s, 16H). ³¹P NMR (CD₂Cl₂, 25 °C): δ 60.4 (s, $J_{PPt} = 3500$ Hz).

Preparation of [{Pt(Cy₂PC₂H₄PCy₂)]₂(μ -biphenyl)][BAr_F]₂ (3a**).** Compound **1a** (0.300 g, 0.191 mmol) was suspended in benzene (5 mL) and heated to 80 °C for 5 min (alternatively, this reaction was done at 25 °C for 4 h with the same results). A dark red oil formed with gas evolution (a sealed-tube reaction showed this gas to be CH₄). The solution was cooled to room temperature, the solvent was decanted off of the oil, and the oil was washed with 3 × 5 mL of benzene and dried in a vacuum to give an oily solid. The solids were dissolved in CH₂Cl₂ (3 mL) and layered with hexanes (10 mL) to obtain red crystals of pure **3a** (0.291 g, 98%). Anal. Calcd for C₁₂₈H₁₃₀B₂F₄₈P₄Pt₂: C, 49.34; H, 4.21. Found: C, 49.13; H, 4.34. ¹H NMR (CD₂Cl₂, 25 °C): δ 1.21–1.31 (m); 1.69–1.83 (m); 2.33 (m, 8H); 4.74 (t, 1H, $J_{HPt} = 29$ Hz); 5.48 (m, 2H); 5.67 (m, 2H); 7.12 (m, 2H); 7.30 (t, 2H); 7.42 (t, 1H); 7.57 (s, 8H), 7.73 (s, 16H). ³¹P NMR (CD₂Cl₂, 25 °C): δ 71.8 (s, $J_{PPt} = 3640$ Hz).

Preparation of [{Pt(Et₂PC₂H₄PEt₂)]₂(μ -biphenyl)][BAr_F]₂ (3b**).** Compound **1b** (0.250 g, 0.185 mmol) was suspended in benzene (5 mL) and reacted at either 80 or 25 °C as above. The crude oily solid was dissolved in CH₂Cl₂ (2 mL) and layered with hexanes (15 mL) to obtain red crystals of pure **3b** (0.243 g, 98%). X-ray quality crystals were obtained by layering a THF solution of **3b** with hexanes and storing at –30 °C for several days. Anal. Calcd for C₉₆H₈₂B₂F₄₈P₄Pt₂: C, 42.97; H, 3.08. Found: C, 42.77; H, 3.26. ¹H NMR (CD₂Cl₂, 25 °C): δ 0.835 (m); 1.19 (m); 2.12 (m, 8H); 4.82 (t, 1H, $J_{HP} = 6.60$ Hz, $J_{HPt} = 24.6$ Hz); 5.32 (m, 2H); 5.57 (m, 2H); 7.07 (m); 7.16 (m); 7.32 (m); 7.57 (s, 8H), 7.73 (s, 16H). ³¹P NMR (CD₂Cl₂, 25 °C): δ 57.0 (s, $J_{PPt} = 3670$ Hz).

Preparation of [{Pt(Cy₂PC₂H₄PCy₂)]₂(μ -bitolyl)][BAr_F]₂ (4a**).** Compound **1a** (0.300 g, 0.191 mmol) was suspended in toluene (5 mL) and reacted at either 80 or 25 °C as above. The crude oily solid was dissolved in CH₂Cl₂ (3 mL) and layered with hexanes (15 mL) to obtain red crystals of pure **4a** (0.294 g, 98%). Anal. Calcd for C₁₃₀H₁₃₄B₂F₄₈P₄Pt₂: C, 49.66; H, 4.30. Found: C, 49.54; H, 4.38. ¹H NMR (CD₂Cl₂, 25 °C): (many signals overlapping because of isomeric mixture) δ 1.21–1.35 (m); 1.64–1.75 (m); 2.25 (m); 4.95–5.08 (m); 5.57 (m); 5.71 (m); 5.83 (m); 6.94 (br); 7.24 (br); 7.28 (br); 7.31 (br); 7.34 (br); 7.37 (br); 7.57 (s, 8H), 7.73 (s, 16H). ³¹P NMR (CD₂Cl₂, 25 °C): δ 70.7 (s, $J_{PPt} = 3620$ Hz), δ 69.9 (s, $J_{PPt} = 3620$ Hz).

Reactions of **3a and **3b** with HCl.** A solution containing 0.0500 mmol of either **3a** or **3b** in 5 mL of CH₂Cl₂ was treated with 0.40 mL of a 1.0 M solution of HCl in Et₂O. The red color of the solution

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disappeared immediately to give a light yellow solution. The solvents were removed under vacuum, and the remaining light yellow solids were extracted with 3×10 mL of hexanes. The hexane extracts were combined, and the solvent was removed to give a white solid, which was found by ^1H NMR and GC–MS to be pure biphenyl. The remaining yellow solids were dissolved in CD_2Cl_2 , and the spectra were identical to those of samples of $[(\text{R}_2\text{PC}_2\text{H}_4\text{PR}_2)\text{Pt}(\mu\text{-Cl})_2][\text{BARf}]_2$ ($\text{R} = \text{Cy}, \text{Et}$) which were prepared by reacting $(\text{R}_2\text{PC}_2\text{H}_4\text{PR}_2)\text{Pt}(\text{Me})(\text{Cl})$ with $[\text{H}(\text{OEt})_2][\text{BARf}]$ in Et_2O .

Reactions of 3a and 3b with I_2 . To a stirred solution containing 0.0500 mmol of either **3a** or **3b** in acetone was added a 2-fold excess of iodine (0.0254 g, 0.100 mmol). The color changed from dark red to light red immediately. The solvent was removed under vacuum, and the solids were extracted with 3×10 mL of hexanes. The hexane extracts were combined, and the solvent was removed to give pure biphenyl as above. The remaining light yellow solids were found to contain $[(\text{R}_2\text{PC}_2\text{H}_4\text{PR}_2)\text{Pt}(\mu\text{-I})_2][\text{BARf}]_2$ ($\text{R} = \text{Cy}, \text{Et}$) based upon the similarity of the spectra to those of $[(\text{R}_2\text{PC}_2\text{H}_4\text{PR}_2)\text{Pt}(\mu\text{-Cl})_2][\text{BARf}]_2$ prepared above.

Reaction of 4a with I_2 . A stirred solution containing 0.0500 mmol of **4a** in acetone was treated with I_2 as above, with similar results and workup. The hexane extracts were combined, and the solvent was removed to give a white solid, which was found by ^1H NMR to contain a mixture of bitolyl isomers. The isomeric mixture was found by GC–MS to consist of 3,3'-dimethylbiphenyl (43.7%), 3,4'-dimethylbiphenyl (44.1%), and 4,4'-dimethylbiphenyl (12.2%), which is very close to a statistical mixture (4:4:1) of these isomers.

X-ray Crystal Structure Determinations. Crystals of **2a** and **3b** were mounted from a matrix of mineral oil. The crystals were immediately placed on a Bruker P4/CCD/PC diffractometer and cooled to 203 K using a Bruker LT-2 temperature device. The data were collected using a sealed, graphite-monochromatized $\text{MoK}\alpha$ X-ray source. A hemisphere of data was collected using a combination of ϕ and ω scans, with 30 s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement were handled using SMART software.²⁹ Frame integration and final cell parameter calculation were carried out using SAINT software.³⁰ The data were corrected for absorption using the SADABS program.³¹ Decay of reflection intensity was not observed. A two-fold disorder in **2a** was modeled in the carbon atom positions C9, C11, and C12 (cyclohexyl carbon atoms); each of these positions was split over two, one-half occupancy sites. Hydrogen atom positions were fixed ($\text{C-H} = 0.96$ Å for methane, 0.97 Å for methylene, and 0.93 Å for aromatic). The hydrogen atoms were refined using the riding model, with isotropic temperature factors fixed to 1.2 (methylene and aromatic) or 1.5 (methyl) times the equivalent isotropic U of the carbon atom to which they were bound.

Table 2. Crystal and Data Collection Parameters for $[(\text{Cy}_2\text{PC}_2\text{H}_4\text{PCy}_2)\text{Pt}(\mu\text{-OH})_2][\text{BARf}]_2 \cdot 4\text{NC}_5\text{F}_5$ (**2a**) and $\{\text{Pt}(\text{Et}_2\text{PC}_2\text{H}_4\text{PEt}_2)_2(\mu\text{-Biphenyl})\}[\text{BARf}]_2$ (**3b**)

	2a	3b
formula	$\text{C}_{136}\text{H}_{120}\text{B}_2\text{F}_{68}\text{N}_4\text{O}_2\text{P}_4\text{Pt}_2$	$\text{C}_{96}\text{H}_{82}\text{B}_2\text{F}_{48}\text{P}_4\text{Pt}_2$
formula weight	3670.04	2683.30
color	colorless	red
crystal system	triclinic	triclinic
space group	$P1$	$P1$
a , Å	14.1156(8)	13.0443(6)
b , Å	15.2352(9)	18.1546(9)
c , Å	19.112(1)	24.857(1)
α , deg	74.306(1)	110.108(1)
β , deg	70.329(1)	98.902(1)
γ , deg	82.550(1)	98.738(1)
V , Å ³	3722.5(4)	5326.0(4)
Z	1	2
temp, K	203(2)	203(2)
$R(\text{int})$	0.0202	0.0212
no. of params refined	856	1369
final R indices	$R_1 = 0.0603$, $(I > 2\sigma(I))$ $wR_2 = 0.1687$	$R_1 = 0.0657$, $wR_2 = 0.1714$
R indices (all data)	$R_1 = 0.0709$, $wR_2 = 0.1792$	$R_1 = 0.0876$, $wR_2 = 0.1856$
GOF on F^2	1.178	1.277

The final model did not include hydrogen atom positions on the disordered cyclohexyl group in **2a**, and hydrogen atoms were not placed on the bridging portion of the biphenyl ligand in **3b**. The final refinement for **2a** and **3b** included anisotropic temperature factors on all non-hydrogen atoms except for solvent atom positions.³² Structure solution, refinement, graphics, and preparation of publication materials were performed using SHELXTL.³³ Additional details of data collection and structure refinement are listed in Table 2.

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Supporting Information Available: X-ray data for **2a** and **3b** (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(29) SMART, Version 4.210; Bruker Analytical X-ray Systems, 6300 Enterprise Lane, Madison, WI 53719, 1996.

(30) SAINT, Version 4.05; Bruker Analytical X-ray Systems, 6300 Enterprise Lane, Madison, WI 53719, 1996.

(31) Sheldrick, G. SADABS; University of Göttingen, Germany, 1996.

(32) $R_1 = \sigma(|F_o| - |F_c|)/\sigma(F_o)$ and $R_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2) + (a^*P)^2]$, where $a = 0.1170$ for **2a**, and 0.095 for **3b**.

(33) SHELXTL, Version 5.1; Bruker Analytical X-ray Systems, 6300 Enterprise Lane, Madison, WI 53719, 1997.