Chapter 20

Issues relevant to C-H activation at platinum(II): comparative studies between cationic, zwitterionic, and neutral platinum(II) compounds in benzene solution

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Cationic late metal systems are being highly scrutinized due to their propensity to mediate so-called electrophilic C-H activation reactions. This contribution compares the reactivity of highly reactive cationic platinum(II) systems with structurally related but neutral species. Our experimental design exploits isostructural neutral and cationic complexes supported by bis(phosphine) ligands amenable to mechanistic examination in benzene solution. The data presented herein collectively suggests that neutral platinum complexes can be equally if not more reactive towards benzene than their cationic counter-parts. Moreover, a number of unexpected mechanistic distinctions between the two systems arise that help to explain their respective reactivity.
Introduction

Recent decades have seen a flurry of interest in homogeneous organometallic species capable of mediating C-H bond activation processes. To develop inorganic systems for productive alkane or arene functionalization chemistry, an intimate understanding of the dominant factors controlling C-H activation processes is paramount. Mechanistic model studies that expose key factors controlling rates of substrate coordination, C-H bond activation, and kinetic selectivity are critical to the systematic design and re-design of potential catalyst systems.

As of late, much effort has focused on developing highly electrophilic, late metal (e.g., Rh, Ir, Pt, Hg) C-H activation systems, the presumption being that “electrophilic” systems efficiently coordinate alkanes (σ-complexes) and mediate subsequent C-H bond activation processes. This has been particularly true of cationic platinum(II) systems. Despite this fact, a collection of recent papers has put into question whether more electrophilic systems are indeed more active for C-H activation. Indeed, several neutral platinum(II) systems are now known that efficiently mediate intermolecular C-H activation processes. The first such system was reported by Goldberg and coworkers in 1997. In a key experiment, they showed that the anionic complex K[Tp’PtMe₂] reacts with B(C₆F₅)₃ to generate an unobserved, presumed 3-coordinate species, “[η₂-Tp’]PtMe”, that undergoes oxidative C-H bond addition to afford octahedral platinum(IV) alkyl hydride products, [η₃-Tp’]Pt(Me)(R)H. Building on this report, our group later identified a well-defined, neutral platinum(II) complex, [Ph₂BP₂]Pt(THF) ([Ph₂BP₂] = [Ph₂B(CH₂PPh₂)₂]), that underwent aromatic C-H bond activation processes to afford platinum(II) byproducts (e.g., [Ph₂BP₂]Pt(Ph)(THF) in benzene). While neutral, we highlighted the zwitterionic nature of this complex, owing to the fact that its anionic [Ph₂BP₂] ligand contains a partially insulated borate counter-anion. The C-H activation reaction exhibited by [Ph₂BP₂]Pt(THF) is hence reminiscent of its cationic platinum(II) relatives.

Several intriguing questions arise from our neutral [Ph₂BP₂]Pt(II) system. (1) How important/appropriate is a zwitterionic resonance contributor in describing the electronic distribution of [Ph₂BP₂]Pt(X)(L) systems? (2) Would an isostructural but formally cationic complex, (P-P)Pt(X)(L)+, exhibit similar C-H bond activation chemistry? (3) If so, how would the mechanisms by which the neutral and cationic complexes mediate such processes compare? Which system would react faster? What factors would govern their relative C-H bond activation rates? (4) How would the reactivity of neutral platinum(II) complexes that feature other donor ligands (e.g., N-donor ligands) compare?

Each of the above issues is likely to be system dependent. We therefore identified a need for a study that would cross-compare the reactivity of several
structurally related, neutral and cationic platinum(II) systems (see Figure 1). In this contribution, we discuss our recent progress in this undertaking.8

**Ligand systems**

The top row displayed in Figure 1 shows three neutral platinum(II) systems (A, C, and E) that are supported by a bidentate, uni-negative donor ligand containing a diphenylborate unit tethered to the metal via its donor arms. In this contribution, X represents a methyl ligand, and L represents a neutral donor ligand. While most of our work to date has focused on system A, we have more recently begun to examine systems of the type C and E for comparison. Aside from the obvious change in the donor group of the three systems, the possible degree of borate charge insulation is likely different. For example, in system C convenient resonance contributors are available to distribute the anionic charge throughout the ligand. In systems A and E, on the other hand, aromatic delocalization of the borate charge is not available and the zwitterionic resonance depiction is perhaps more appropriate.

While bis(pyrazolyl)borate ligands have been known for decades,9 bis(phosphino)- and bis(amino)borate ligands were unknown at the outset of our study. It was therefore necessary to tackle their syntheses first. The preparation of a variety of phenyl-substituted phosphine systems, [R₂BPR₂],10 and a methyl-substituted amine system, [Ph₂BNMe₂],11 has been reported.

![Figure 1. Design scheme to examine factors that influence C-H activation reactivity at platinum(II) centers.](image-url)
{[\text{Ph}_2\text{BL}_2]\text{PtMe}_2}^-$ Complexes

While rapid displacement of COD from (COD)PtMe$_2$ by [R$_2$BPR$_2$][NR$_4$] salts in general occurred at 22 °C, ammonium salts of [Ph$_2$B(pz)$_2$] and [Ph$_2$BN$_2$Me$_2$] were much less reactive. Dimeric [Me$_2$Pt(SMe)$_2$]$_2$ reacted more rapidly with both N-donor borate ligands, affording [[Ph$_3$B(pz)$_3$]PtMe$_2$][NBu$_4$] and [[Ph$_2$BN$_2$Me$_2$]PtMe$_2$][NEt$_4$], respectively (ASN = 5-azonia-spiro[4.4]nonane; pz = pyrazolyl). The complexes [[Ph$_2$BP$_2$]PtMe$_2$][ASN] and [[Ph$_2$B(pz)$_3$]PtMe$_2$][NBu$_4$] have been structurally characterized, and the $^2J_{\text{PtH}}$ NMR coupling constant for each complex has been measured (see Figure 2). We presume the conformation of the bis(amino)borate complex generally mimics that observed for the bis(phosphino)borate derivatives, by analogy to structurally characterized square planar [Ph$_2$BN$_2$Me$_2$]Rh complexes.$^{11}$ The borate anion in each system lies along a vector that bisects the midpoint of a square planar complex, spatially well separated from the coordinated metal center. For platinum bis(phosphino)borate complexes, the M-B distance is typically between 4.0 Å and 4.2 Å. For bis(amino)borate complexes, we estimate this distance to be between 3.65 and 3.68 Å. The conformation of square planar bis(pyrazolyl)borate complexes, in contrast, allows the borate unit to slide closer to the coordinated metal center in the solid-state. The range of M-B distances observed is quite broad (M = Rh, Pd, Pt), between 3.0 and 3.5 Å, attributable to a flexible degree of puckering exhibited by the bidentate ligand. The $^2J_{\text{PtH}}$ NMR coupling constants measured for the anionic dimethyl complexes suggest that the (phosphino)borate exhibits a stronger trans influence than the comparable bis(pyrazolyl)- and bis(amino)borate derivatives. The relative $^2J_{\text{PtH}}$ coupling constants of [[Ph$_2$BP$_2$]PtMe$_2$][ASN] and [[Ph$_2$B(pz)$_3$]PtMe$_2$][NBu$_4$] track well with their observed Pt-Me distances, the average distance in the (phosphino)borate derivative being ca. 0.1 Å longer than the (pyrazolyl)borate system.

[Ph$_2$BP$_2$]PtMe(L) and [Ph$_2$B(pz)$_3$]PtMe(L) Complexes

The anionic complexes [[Ph$_2$B(pz)$_3$]PtMe$_2$][NBu$_4$] and [[Ph$_2$BP$_2$]PtMe$_2$][ASN] are easily protonated by weak acids in moderately polar solvents such as THF. Their basicity provides straightforward access to complexes of the type [Ph$_3$BL$_2$]PtMeL’ by judicious choice of a bulky ammonium salt whose conjugate base is non-coordinating (e.g., HN$^+$(Pr$_2$Et)$^-$). This allows selective delivery of an L’ donor ligand. For the bis(phosphino)borate system, a wide variety of L’ ligands have been canvassed (e.g., CO, PMe$_2$, CH$_3$CN, SMe$_2$). For the C-H activation studies relevant to this contribution, we focus only the case where L’ is THF. The synthesis and structural characterization of the feature complex [Ph$_2$BP$_2$]Pt(Me)(THF) has

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been described.\textsuperscript{4,8} The bis(pyrazolyl)borate complexes \([\text{Ph}_2\text{B(pz)}_2]\text{PtMeL}’ (L’ = \text{CO}, \text{PMe}_3, \text{CH}_3\text{CN}, \text{SMe}_2)\) are similarly available, though the THF-adduct complex is too reactive to be isolated and rigorously characterized. The bis(amino)borate precursors, \([\text{Ph}_2\text{BNMe}_2]\text{PtMeL}’\), have yet to be systematically developed.

\[\text{Ph} - \text{B} \quad \text{NR}_4 \quad \text{Pt} \quad \text{Me} \]

\[2J_{\text{PtN}} = 83 \text{ Hz} \]

\[\text{Pt-B} = 3.462(1) \text{ Å} \]

\[\text{Avg Pt-C} = 2.04 \text{ Å} \]

\[\text{Ph}_2\text{B} \quad \text{Pt} \quad \text{Me} \quad \text{Ph}_2 \]

\[2J_{\text{PtN}} = 65 \text{ Hz} \]

\[\text{Pt-B} = 4.117(2) \text{ Å} \]

\[\text{Avg Pt-C} = 2.13 \text{ Å} \]

\[\text{Ph}_2\text{B} \quad \text{Pt} \quad \text{Me} \quad \text{Ph}_2 \]

\[2J_{\text{PtN}} = 87 \text{ Hz} \]

\[\text{not yet structurally characterized} \]

\[\text{Ph} - \text{B} \quad \text{Ph} \quad \text{Me} \quad \text{Pt} \quad \text{Me} \quad \text{Ph} \]

\[\text{Figure 2. Noteworthy NMR and structural parameters collected for the anionic dimethyl complexes \[\text{[[Ph}_2\text{B(pz)}_2]\text{PtMe}_2][\text{NBu}_4], \text{[[Ph}_2\text{BP}_2]\text{PtMe}_2][\text{ASN}, \text{and} \text{[[Ph}_2\text{BNMe}_2]\text{PtMe}_2][\text{NEt}_4].} \]

Electronic information from Carbonyl Model Complexes

To gain an appreciation of the relative electron-releasing character of the various \([\text{Ph}_2\text{BL}_2] \) ligands, it is instructive to consider relative CO stretching frequencies for a structurally comparable set of square planar carbonyl complexes. For the three borate ligand types under consideration, we have obtained pertinent data using rhodium(I) dicarbonyl and platinum(II) monocarbonyl platforms. We have also collected infrared data for several isostructural but formally cationic complexes. This data is summarized in Figure 3. Several conclusions can be drawn from the data. First, despite the zwitterionic
resonance contributor we have emphasized, neutral complexes supported by either the \([\text{Ph}_2\text{BP}_2]\) ligand or the \([\text{Ph}_2\text{BNMe}_2]\) ligand are appreciably less electrophilic than their cationic counter-parts in which a diphenylsilane unit substitutes the diphenylborate unit of the ligand backbone. For the platinum system in particular, the cationic complex \(\text{[(Ph}_2\text{SiP}_2)\text{Pt(Me)(CO)}][\text{B(C}_6\text{F}_5)_4]\) provides a CO stretching vibration that is 24 cm\(^{-1}\) higher in energy than its neutral derivative \(\text{[Ph}_2\text{BP}_2]\text{Pt(Me)(CO)}\) (\(\text{Ph}_2\text{SiP}_2\) refers to the neutral ligand \(\text{Ph}_2\text{Si(CH}_2\text{PPh}_2)_2\)). This implies that the cationic complex is significantly more electrophilic than its neutral congener, a conclusion that would seem to suggest there is a significant degree of electronic communication between the borate anion and the platinum center in the neutral complexes. However, examination of a series of \(\text{para-}\)-substituted aryl bis(phosphino)borates shows that substitution on the aryl borate has almost no effect on \(\nu_{\text{CO}}\), while \(\text{para-}\)-substitution of the aryl phosphine shows a stronger effect (Figure 3).\(^{10}\) Considered independently, the \(\text{para-}\)-substitution data is consistent with a localized resonance contributor for anionic bis(phosphino)borate ligands (resonance form A in figure 4), whereas the cationic versus neutral comparative data is perhaps more consistent with resonance contributors that emphasize an ylide form of the bis(phosphino)borate ligands (e.g., resonance forms B and C in Figure 4).

To reconcile the two seemingly disparate conclusions, it needs to be underscored that the absolute magnitude in \(\Delta\nu_{\text{CO}}\) measured between a zwitterionic complex (e.g., \(\text{[Ph}_2\text{BP}_2]\text{Pt(Me)(CO)}\)) and a cationic complex (e.g., \(\text{[(Ph}_2\text{SiP}_2)\text{Pt(Me)(CO)}][\text{BAr}_4]\)) is somewhat misleading for the following reason. In cationic late metal carbonyls, where \(\pi\)-backbonding is relatively weak, strong polarization of the CO \(\sigma\)-bond by the cationic complex is anticipated.\(^{12}\) This raises the energy of the force constant \(F_{\text{CO}}\) dramatically, and in extreme cases, polarization can dominate the observed \(F_{\text{CO}}\). In this context, cationic complexes such as \(\text{[(Ph}_2\text{SiP}_2)\text{PtMe}]^+\) are expected to have characteristically high force constants \(F_{\text{CO}}\) due to a strong polarization effect. This effect will be much reduced for CO coordinated to a neutral \(\text{[Ph}_2\text{BP}_2]\text{PtMe}\) fragment, regardless of whether or not its charge is distributed asymmetrically due to a zwitterionic resonance contributor. We therefore caution that the absolute magnitude of \(\Delta\nu_{\text{CO}}\) is not so reliable a gauge of relative backbonding ability between complexes that are \textit{formally} cationic and complexes that are \textit{formally} neutral. Large differences in polarization between isostructural cationic and neutral complexes likely compete with the electronic contributors of sigma donation, \(\pi\)-backbonding, and/or \(\pi\)-acceptor character that we typically rely upon to correlate measured \(\Delta\nu_{\text{CO}}\) values to the electron-releasing character of a ligand. The dilemma of variable polarization is avoided within a contiguous series of neutral platinum carbonyl complexes provided.\(^{10}\) The relative differences in \(\nu_{\text{CO}}\) values recorded in such a series are likely more reflective of the relative “electron-releasing” character of the donor ligand, a point we have discussed elsewhere.\(^ {10}\)
One other interesting point to note from these infrared data is that the complex [Ph$_2$B(pz)$_2$]Rh(Me)(CO) provides a CO stretch 7 cm$^{-1}$ lower in energy than in [Ph$_2$BP$_2$]Pt(Me)(CO), suggesting that the former complex, at least according to this gauge, is the more electron-rich of the two.

Figure 3. Infrared data collected for a series of rhodium and platinum carbonyl complexes. All data are reported in cm$^{-1}$ obtained by FTIR in CH$_2$Cl$_2$/KBr (BAr$_4$ = B(C$_6$F$_3$)$_2$). The complex [H$_2$B(pz)$_2$]Rh(CO)$_2$ was reported previously by Flavio et al.$^{13}$

Figure 4. Selected resonance contributors for bis(phosphino)borate ligands.
Mechanistic Comparisons Between Isostructural Neutral and Cationic Complexes

In this section we discuss the reaction profiles of the structurally related neutral and cationic platinum(II) systems, \([\text{Ph}_2\text{BP}_2]\text{Pt(Me)(THF)}\) and \([(\text{Ph}_2\text{SiP}_2)\text{Pt(Me)(THF)}][\text{B(C}_6\text{F}_3)_3]\), each of which is capable of mediating an elementary C-H bond activation process in benzene solution. Several important and unexpected mechanistic distinctions between the two systems are revealed.

Both \([\text{Ph}_2\text{BP}_2]\text{Pt(Me)(THF)}\) and \([(\text{Ph}_2\text{SiP}_2)\text{Pt(Me)(THF)}][\text{B(C}_6\text{F}_5)_4]\) are appreciably soluble in benzene solution. This fact allowed us to study their respective benzene solution chemistries by NMR spectroscopy under comparable reaction conditions. \([\text{Ph}_2\text{BP}_2]\text{Pt(Me)(THF)}\) reacts in benzene solution at 50 °C over a period of several hours to form \([\text{Ph}_2\text{BP}_2]\text{Pt(Ph)(THF)}\) as the major product (~ 80%) with concomitant liberation of methane. The cationic complex \([(\text{Ph}_2\text{SiP}_2)\text{Pt(Me)(THF)}]^+\) reacted similarly, liberating methane to produce the corresponding phenyl derivative \([(\text{Ph}_2\text{SiP}_2)\text{Pt(Ph)(THF)}]^+\). Neither of the phenyl products proved stable to extended thermolysis; however, the addition of excess THF significantly inhibited the degradation of both \([\text{Ph}_2\text{BP}_2]\text{Pt(Ph)(THF)}\) and \([(\text{Ph}_2\text{SiP}_2)\text{Pt(Ph)(THF)}]^+\). To probe these downstream reaction processes, the independently prepared phenyl complexes were warmed and monitored in benzene solution. Prolonged thermolysis of \([\text{Ph}_2\text{BP}_2]\text{Pt(Ph)(THF)}\) resulted in two apparent reaction pathways. The dominant pathway was that of disproportionation to generate the colorless molecular salt \({\{[\text{Ph}_2\text{BP}_2]\text{Pt(Ph)}\}_2}\}{{\{[\text{Ph}_2\text{BP}_2]\text{Pt(THF)}\}_2}}^+. Formation of this cation/anion pair was suggested by the appearance of two singlets \(^{31}\text{P}\{^1\text{H}\}\) NMR in a 1:1 ratio, and by a positive identification of each ion by electrospray mass spectroscopy. Additionally, the species \([[\text{Ph}_2\text{BP}_2]\text{Pt(Ph)}_2][\text{ASN}]\) was independently prepared to corroborate its spectroscopic and electrospray mass spectral data. A small amount of a presumed bridged-biphenyl species was also evident by \(^{31}\text{P}\{^1\text{H}\}\) NMR. This minor species was isolated in very low yield (~ 10%) by fractional crystallization, and an independent XRD study on crystals of this minor species established a connectivity consistent with the dinuclear complex \({\{[\text{Ph}_2\text{BP}_2]\text{Pt}_2(\mu-\eta^3:\eta^3-\text{biphenyl})}\}^+\). A similar bridged-biphenyl species was the only product observed in the cationic system. Thus, both spectroscopic and structural evidence established that \([(\text{Ph}_2\text{SiP}_2)\text{Pt(Ph)(THF)}][\text{B(C}_6\text{F}_5)_3]\) decayed quantitatively to the orange dinuclear species, \({\{([\text{Ph}_2\text{SiP}_2]\text{Pt}_2(\mu-\eta^3:\eta^3-\text{biphenyl})][\text{B(C}_6\text{F}_3)_3]\}_2\}^+.\) During the course of this study, Konze, Scott, and Kubas reported a related coupling reaction for cationic complexes of the type \([\text{R}_2\text{PC}_2\text{H}_4\text{PR}_2]\text{PtMe(OEt)}_2][\text{B(3,5-(CF}_3)_2\text{C}_6\text{H}_3)_4]\).\(^{14}\)

Fortunately, the second, bimolecular reaction is in each case slow. Clean first order kinetics could therefore be obtained for the decay of \([\text{Ph}_2\text{BP}_2]\text{Pt(Me)(THF)}\) and \([(\text{Ph}_2\text{SiP}_2)\text{Pt(Me)(THF)}][\text{B(C}_6\text{F}_3)_3]\), respectively. To
our initial surprise, the rate of decay of the neutral system was significantly faster. At 55 °C the rate of decay of \([(\text{Ph}_2\text{SiP}_2)\text{Pt(Me)(THF)}][\text{B(}\text{C}_6\text{F}_5\text{)}_4]\) was 1.80(6) x 10^{-4} s^{-1} (t_{1/2} = 64 min), while the rate of decay of \([(\text{Ph}_2\text{BP}_2)\text{Pt(Me)(THF)}]\) was too fast to be accurately measured (31P NMR). The decay rate of \([(\text{Ph}_2\text{BP}_2)\text{Pt(Me)(THF)}]\) at 45 °C was 1.42(5) x 10^{-4} s^{-1} (t_{1/2} = 81 min). The difference in rates was much more pronounced in C_{6}D_{6} due to a large kinetic deuterium isotope effect in the cationic system (k_H/k_D = 6.52) and a negligible isotope effect in the neutral system (k_H/k_D = 1.26). These data are shown graphically in Figures 5(A), (B), and (C).

Also curious were the methane byproducts for each of these thermolysis reactions. When \([(\text{Ph}_2\text{SiP}_2)\text{Pt(Me)(THF)}][\text{B(}\text{C}_6\text{F}_5\text{)}_4]\) was incubated in C_{6}D_{6}, the methane byproduct was predominantly CH_3D, but a small amount of CH_4 was also observed (CH_4 : CH_3D = 1 : 7.6). When neutral \([(\text{Ph}_2\text{BP}_2)\text{Pt(Me)(THF)}]\) was similarly incubated, CH_4 was the dominant byproduct (CH_4 : CH_3D = 3 : 1). The ratio of methane byproducts for the latter system indicates that protons from either the \([\text{Ph}_2\text{BP}_2]\) ligand, or from THF, are incorporated into the methane byproduct to a large extent. Control experiments have established that these protons arise from the \([\text{Ph}_2\text{BP}_2]\) ligand itself due to reversible ligand metalation processes. For example, we prepared the d_{20}-labeled \([\text{Ph}_2\text{BP}_2]\) ligand \([\text{Ph}_2\text{B(CH}_2\text{P(}\text{C}_6\text{D}_3\text{)}_2]\) and examined the solution chemistry of \([\text{Ph}_2\text{B(CH}_2\text{P(}\text{C}_6\text{D}_3\text{)}_2]\text{Pt(Me)(THF)}]\) in C_{6}D_{6}. For this complex, thermolysis provided CH_3D as the dominant methane byproduct (CH_4 : CH_3D = 1.0 : 7.3). This and other mechanistically informative labeling experiments are discussed more thoroughly elsewhere. For the present contribution, we underscore the likelihood that reversible metalation at a phenylphosphine arm of
THF Ligand Self-Exchange in Benzene

An interesting question concerns the mechanism by which C₆H₆ (or C₆D₆) enters the coordination sphere in a step preceding C-H (or C-D) activation in the two systems. Benzene was chosen as the comparative solvent of choice for the two systems because both systems are appreciably soluble in benzene. Moreover, each complex is relatively stable at room temperature in benzene. This was not true of other solvents. For example, [Ph₂BP₂]Pt(Me)(THF) degrades rapidly at 22 ºC in dichloromethane, whereas both systems have very limited solubility in less reactive hydrocarbon solvents (e.g., pentane, methylcyclohexane). Under a comparative set of reaction conditions, it was consequently impractical to examine C-H activation rates and ligand exchange processes as a function of benzene concentration. We therefore chose to study THF self-exchange in benzene solution as a model for benzene replacement of THF. Once again, the cationic and neutral systems yielded disparate results.

The dependence of the observed rate constant for self-exchange, kₙₑₓ (determined by magnetization transfer), on the concentration of THF was strikingly different between the neutral and cationic platinum systems. For neutral [Ph₂BP₂]Pt(Me)(THF), kₙₑₓ showed no [THF] dependence. In sharp contrast, cationic [(Ph₂SiP₂)Pt(Me)(THF)][B(C₆F₅)₄] showed a first-order dependence on [THF] for the observed rate constant. The extrapolated intercept for the plot of kₙₑₓ versus THF equivalents for [(Ph₂SiP₂)Pt(Me)(THF)]⁺ intersects at the origin and thereby suggests negligible mechanistic dependence on the solvent (benzene) and/or the [B(C₆F₅)₄] anion. The absolute difference in the rate constant of THF self-exchange (kₙₑₓ) at a given temperature between the two systems was only modest. For example, at 25 ºC, the rate constant for [Ph₂BP₂]Pt(Me)(THF) (kₑₓ(298K) = 12.0 s⁻¹) is ~ one third as large as that for [(Ph₂SiP₂)Pt(Me)(THF)]⁺ (kₑₓ(298K) = 38.5 M⁻¹ s⁻¹). More interesting was that the temperature dependence of kₑₓ varied dramatically between the two systems. The rate constant kₑₓ of [Ph₂BP₂]Pt(Me)(THF) was examined over the temperature range 11.2 - 48.9 ºC and provided an entropy and enthalpy of activation as follows: ΔS‡ = 0.1 ± 5.4 e.u.; ΔΗ‡ = 16.0 ± 1.6 kcal/mol. Analogous data collected for cationic [(Ph₂SiP₂)Pt(Me)(THF)]⁺ over the temperature range 16.0 - 44.6 ºC provided distinctly different values: ΔS‡ = -30.2 ± 5.2 e.u. and ΔΗ‡ = 1.9 ± 0.5 kcal/mol.
The activation parameters obtained for \([\text{Ph}_2\text{SiP}_2\text{Pt(Me)(THF)}][\text{B(C}_6\text{F}_3)_3]\) are consistent with a classic associative mechanism of ligand exchange, in accord with the linear dependence of the exchange rate constant on THF concentration. ¹⁵ Associative ligand exchange is commonplace for ligand substitution in square planar platinum(II) systems and is the mechanism we had anticipated. Interpreting the activation parameters and lack of THF dependence on \(k_{\text{ex}}\) of \([\text{Ph}_3\text{BP}_2\text{Pt(Me)(THF)}]\) is less straightforward. Perhaps the simplest scenario to put forward for ligand exchange is therefore that of a purely dissociative mechanism which proceeds via a neutral 3-coordinate intermediate, “\([\text{Ph}_3\text{BP}_2\text{Pt(Me)}]\)”. Given the increased electron-richness of the platinum center in the neutral system, dissociation of a \(\sigma\)-donor ligand might be expected to be more favorable. However, simple dissociative exchange mechanisms are rarely observed in platinum(II) substitution chemistry. Even in cases where they have been reported, such as the systems elegantly put forth by Romeo,¹⁶ certain assumptions are required to suggest the presence of a truly 3-coordinate intermediate species. Therefore, two additional mechanisms for THF exchange in \([\text{Ph}_3\text{BP}_2\text{Pt(Me)(THF)}]\) need also to be considered: solvolytic displacement of the bound THF by benzene itself, and an anchimeric mechanism whereby a bond pair from the ancillary \([\text{Ph}_2\text{BP}_2]\) ligand coordinates the platinum center prior to appreciable Pt-O bond breaking. These latter two possibilities constitute associative interchange mechanisms involving discrete 5-coordinate, rather than 3-coordinate, intermediates. While we cannot distinguish between dissociative, solvent-assisted, or ligand-assisted exchange pathways from the THF exchange data alone, solution NMR data obtained for \([\text{Ph}_3\text{BP}_2\text{Pt(Me)(THF)}]\) encourages us to suggest that an anchimeric pathway for ligand exchange is most likely operative for the neutral complex \([\text{Ph}_3\text{BP}_2\text{Pt(Me)(THF)}]\) in benzene (Figure 6). We speculate that a similar mechanism is operative for exchange of THF by benzene in the overall C-H activation process in the neutral system.

Figure 6. Possible mechanisms for THF ligand self-exchange in benzene for the complexes \([\text{Ph}_2\text{SiP}_2\text{Pt(Me)(THF)}][\text{B(C}_6\text{F}_3)_3]\) (top) and \([\text{Ph}_3\text{BP}_2\text{Pt(Me)(THF)}]\) (bottom). Note: An anchimeric exchange pathway for \([\text{Ph}_3\text{BP}_2\text{Pt(Me)(THF)}]\) involving the phenyl groups of the phosphine donor arms is also likely, but is not shown explicitly.
Direct Evidence for Reversible Metalation Processes in
[Ph₂BP₂]Pt(Me)(THF) and for a Pt(IV) Hydride Intermediate

When a sample of [Ph₂BP₂]Pt(Me)(THF) slightly wetted with excess THF was dissolved in benzene-d₆, its ¹H and ³¹P{¹H} NMR spectra were unremarkable. This was also true of related spectra for an analytically pure sample of cationic [(Ph₂SiP₂)Pt(Me)(THF)][B(C₆F₅)₄]. However, when analytically pure [Ph₂BP₂]Pt(Me)(THF), obtained by careful drying under an argon purge to remove residual THF, was dissolved in benzene-d₆ and examined at 25 °C by ³¹P{¹H} NMR spectroscopy, additional signals were observed that clearly indicated the presence of species distinct from [Ph₂BP₂]Pt(Me)(THF), and distinct from its known products of benzene-C-H activation. A series of NMR experiments (¹H, ³¹H{³¹P}, ³¹P{³¹H}, and ¹³C{¹H}) were performed on [Ph₂BP₂]Pt(Me)(THF), the d₂₀-labeled derivative [Ph₂B(CH₂P(C₆D₅)₂)₂]Pt(Me)(THF), and the ¹³C-labeled derivative [Ph₂BP₂]Pt(¹³CH₃)(THF) to assign the number and nature of the new species present. The interested reader is referred to the full paper for complete details. The collective NMR data allows us to draw three important conclusions. First, when [Ph₂BP₂]Pt(Me)(THF) is dissolved in C₆D₆ at 25 °C, three distinct, methyl-containing secondary species can be detected, in addition to the expected and dominant complex, [Ph₂BP₂]Pt(Me)(THF). This is most evident from a ¹³C{¹H} NMR spectrum of [Ph₂BP₂]Pt(¹³CH₃)(THF). Second, the dominant secondary complex contains a hydride ligand whose signal persists in the spectrum of d₂₀-labeled [Ph₂B(CH₂P(C₆D₅)₂)₂]Pt(Me)(THF). This secondary species appears to be a platinum(IV) hydride that is generated by ortho-metalation of the diphenylborate subunit. Possible structures of the spectroscopically observable platinum(IV) intermediate are proposed below in Figure 7. As a final point, we emphasize that the starting complex [Ph₂BP₂]Pt(Me)(THF), as well as the secondary species observed at 25 °C, are all consumed and ultimately funneled along the intermolecular benzene C-H activation pathway over a period of several hours at 45 °C. Important data detailed above for the neutral and cationic platinum(II) systems are summarized in Table 1.

![Figure 7. Possible structures for the platinum(IV) methyl hydride intermediate.](image-url)
Table 1. Summary of key comparative data relevant to the overall mechanism of benzene C-H activation between the cationic and neutral complexes \([\text{Ph}_2\text{SiP}_2]\text{Pt(Me)(THF)}\) and \([\text{Ph}_2\text{BP}_2]\text{Pt(Me)(THF)}\).

<table>
<thead>
<tr>
<th>(\text{Ph}_2\text{SiP}_2\text{Pt(Me)(THF)})</th>
<th>(\text{Ph}_2\text{BP}_2\text{Pt(Me)(THF)})</th>
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- \(\nu(\text{CO})\) of \([\text{Ph}_2\text{SiP}_2]\text{Pt(Me)(CO)})[\text{B(C}_6\text{F}_5)_4]\) = 2118 cm\(^{-1}\)
- \(\nu(\text{CO})\) of \([\text{Ph}_2\text{BP}_2]\text{Pt(Me)(THF)}\) = 2094 cm\(^{-1}\)
- Rate of C-H activation at 55 °C: \(k = 1.80(6) \times 10^4\) s\(^{-1}\)
- Rate of C-D activation at 55 °C: \(k = 2.76(7) \times 10^5\) s\(^{-1}\)
  \(k_{\text{H}}/k_{\text{D}} = 6.52\)
- Rate of C-H activation at 45 °C: \(k = 1.42(5) \times 10^4\) s\(^{-1}\)
- Rate of C-D activation at 45 °C: \(k = 1.13(3) \times 10^5\) s\(^{-1}\)
  \(k_{\text{H}}/k_{\text{D}} = 1.26\)
- Mechanism of THF self-exchange is associative. Activation parameters: \(\Delta S^\ddagger = -30.2 \pm 5.2\) e.u. and \(\Delta H^\ddagger = 1.9 \pm 0.5\) kcal/mol
- Mechanism of THF self-exchange is ligand-assisted (or dissociative). Activation parameters: \(\Delta S^\ddagger = -0.1 \pm 5.4\) e.u. and \(\Delta H^\ddagger = 16.0 \pm 1.6\) kcal/mol
- \(\text{CH}_3 : \text{CH}_2D\) ratio in methane byproduct after thermolysis in \(\text{C}_6\text{D}_6\): 1.0 : 7.6
- \(\text{CH}_3 : \text{CH}_2D\) ratio in methane byproduct after thermolysis in \(\text{C}_6\text{D}_6\): 3.0 : 1.0
- Negligible deuterium incorporation into the \((\text{Ph}_2\text{SiP}_2)\) ligand after thermolysis in benzene-\(d_6\).
- Significant deuterium incorporation into the \([\text{Ph}_2\text{BP}_2]\) ligand after thermolysis in benzene-\(d_6\).
- \((\text{Ph}_2\text{SiP}_2)\) metalation in benzene solution is kinetically non-competitive with benzene C-H activation processes.
- \([\text{Ph}_2\text{BP}_2]\) metalation in benzene solution are kinetically very competitive with benzene C-H activation processes.

Discussion of the overall mechanisms of benzene C-H activation

The benzene solution chemistry we have observed for the neutral complex \([\text{Ph}_2\text{BP}_2]\text{Pt(Me)(THF)}\) is generally comparable to that observed for its isostructural but cationic relative \([\text{Ph}_2\text{SiP}_2]\text{Pt(Me)(THF)}][\text{B(C}_6\text{F}_5)_4]\). The zwitterionic descriptor offered for \([\text{Ph}_2\text{BP}_2]\text{Pt(Me)(THF)}\) is therefore useful in that it predicts its overall C-H activation reactivity. However, important mechanistic differences exist that can be attributed to the role that the bis(phosphine)-ligand auxiliary plays in each respective system. These mechanistic distinctions most likely reflect electronic rather than steric differences.

In Figure 8, we outline the simplest plausible mechanism (Path A) by which cationic \((\text{Ph}_2\text{SiP}_2)\text{Pt(Me)(THF)}^+\) undergoes intermolecular benzene
activation. The outlined mechanism is consistent with all of our data, and is generally similar to that proposed for other \( \text{L}_2\text{Pt(Me)}^+ \) systems that have been thoroughly described elsewhere. Key points to note in Path A are that benzene coordination to the cationic platinum center is likely an associative process, and the benzene activation step is likely to be rate-determining, intimated by the large primary kinetic isotope effect that was observed for \( \text{(Ph}_2\text{SiP}_2\text{)}\text{Pt(Me)}(\text{THF})^+ \) \( (k_{\text{H}}/k_{\text{D}} \sim 6.52) \). While we favor a benzene C-H activation step for the cationic system that occurs by oxidative addition from platinum(II) to give a platinum(IV) phenyl hydride, our data offers no direct evidence for this hypothesis.

Neutral \( \text{[Ph}_2\text{BP}_2\text{]}\text{Pt(Me)(THF)} \) differs from \( \text{(Ph}_2\text{SiP}_2\text{)}\text{Pt(Me)}(\text{THF})^+ \) in that the bis(phosphine) auxiliary is intimately involved in both ligand exchange, and in C-H activation processes operative in benzene solution. The zero-order dependence in THF for THF self-exchange reflects the ability of the \( \text{[Ph}_2\text{BP}_2\text{]} \) ligand to assist in ligand exchange by an \( \eta^3 \)-binding mode, an intramolecular process akin to a solvent-assisted ligand substitution process. While THF loss might also be dissociative based upon our exchange data, the prevailing ligand metatation chemistry of \( \text{[Ph}_2\text{BP}_2\text{]}\text{Pt(Me)(THF)} \) persuades us to discount this latter possibility. A propensity for the \( \text{[Ph}_2\text{BP}_2\text{]} \) ligand to achieve an \( \eta^3 \)-binding mode dramatically impacts the nature of the C-H activation processes that are observed in benzene solution.

In Figure 8, we outline three mechanistic pathways to account for the solution chemistry of \( \text{[Ph}_2\text{BP}_2\text{]}\text{Pt(Me)(THF)} \). These are labeled Path B, Path C, and Path D, respectively. Association of an aryl ring from the diphenylborate unit of \( \text{[Ph}_2\text{BP}_2\text{]}\text{Pt(Me)(THF)} \) leads down Path B to a metatation process that generates a platinum(IV) methyl hydride complex (product B), an intermediate that can be spectroscopically detected. We do not think product B precedes an intermolecular benzene C-H activation step. Rather, we think that metatation at the diphenylborate unit is reversible, and that product B is ultimately funneled along Paths C and D. Common to Paths C and D is an \( \eta^3 \)-binding mode for the \( \text{[Ph}_2\text{BP}_2\text{]} \) auxiliary that involves the arylphosphine donor rather than the diphenylborate unit. Path C proceeds along a simpler scenario that invokes a \( \text{[Ph}_2\text{BP}_2\text{]} \)-assisted benzene-\( \text{d}_6 \) substitution for THF, followed by oxidative addition of benzene-\( \text{d}_6 \) and reductive elimination of \( \text{CH}_3\text{D} \), the methane byproduct expected. The key distinction between Path C and Path A is the mechanism by which benzene enters the platinum coordination sphere. Our intuition is to suggest that the rate-determining step along Path C is the C-H activation step, and that the negligible primary kinetic isotope effect that was measured for \( \text{[Ph}_2\text{BP}_2\text{]}\text{Pt(Me)(THF)} \) \( (k_{\text{H}}/k_{\text{D}} \sim 1.26) \) was due to the kinetic dominance of the fourth path, Path D. In this last pathway, arylphosphine ligand metatation processes occur that produce platinum(IV) methyl hydride-species distinct from product B (shown in Path B). Subsequent to ligand metatation, benzene-\( \text{d}_6 \) enters the platinum coordination sphere at one of several
Figure 8. Postulated mechanisms for the intermolecular C-H activation of benzene for cationic [(Ph₂SiP₂)Pt(Me)(THF)][B(C₆F₅)₄] (Path A), and neutral [Ph₂BP₂]Pt(Me)(THF) (Paths B, C, and D). RDS refers to the suggested rate-determining step along each path.
indistinguishable stages, each of which involves the reductive elimination of CH$_4$ (for simplicity only one scenario is presented in Figure 8 explicitly). C-D activation of benzene-$d_6$, followed by a reverse metalation process that transfers deuteride into the [Ph$_2$BP$_2$] ligand, ultimately leads to the phenyl platinum complex. **Path D** thus accounts for the high degree of CH$_4$ released by [Ph$_2$BP$_2$]Pt(Me)(THF) in benzene-$d_6$, and the incorporation of deuteride into the [Ph$_2$BP$_2$] ligand. We are comfortable explicitly invoking platinum(IV) intermediates along both **Paths C** and **D** that arise from oxidative addition of benzene-$d_6$, because of our spectroscopic evidence for a platinum(IV) species resulting from [Ph$_2$BP$_2$] metalation (product **B**, **Path B**). Also, we emphasize that our inability to detect the platinum(IV) hydride species produced by [Ph$_2$BP$_2$] metalation along **Path D** is because the ligand metalation process is itself rate-determining. A key piece of evidence that supports this assertion is that in both benzene and benzene-$d_6$, the rate of decay of the $d_{20}$-labeled derivative [Ph$_2$B(CH$_2$P(C$_6$D$_5$)$_2$$_2$)Pt(Me)(THF) is significantly slower than that of [Ph$_2$BP$_2$]Pt(Me)(THF) itself ($k_{1H}/k_{1D} \approx 3$ in benzene-$d_6$). Under conditions in which **Path D** dominates and ligand metalation is rate-determining, this is just what we expect.

The observation that the rate of decay of $d_{20}$-[Ph$_2$BP$_2$]Pt(Me)(THF) is modestly slower in benzene-$d_6$ than in protio benzene ($k_{1H}/k_{1D} \approx 1.8$) is perhaps more curious, but is conveniently explained as follows: deuteration of the aryl positions of the [Ph$_2$BP$_2$] ligand slows the rate of ligand metalation, and thereby attenuates the overall rate by which $d_{20}$-[Ph$_2$BP$_2$]Pt(Me)(THF) traverses down **Path D**. This in turn funnels more of the system down **Path C**, a path insensitive to arylphosphine deuteration. In this manner, a pre-equilibrium shift in benzene-$d_6$ serves to amplify the primary kinetic isotope effect of **Path C**, and thereby exposes C-H activation as rate-determining along this path as well. We can therefore suggest that a C-H activation process of some sort is rate-determining for each of the four distinct pathways that are outlined in Figure 8.

**Comparing the [Ph$_2$BP$_2$] and [Ph$_2$B(pz)$_2$] Systems with Respect to C-H Activation**

We had also hoped to compare the benzene C-H activation chemistry of [Ph$_2$BP$_2$]Pt(Me)(THF) with the bis(pyrazolyl)borate complex [Ph$_2$B(pz)$_2$]Pt(Me)(THF). Unfortunately, the latter complex proved too reactive to isolate or even spectroscopically identify in benzene solution. We therefore canvassed the relative reactivities of the anionic dimethyl complexes, [[Ph$_2$BL$_2$]PtMe$_2$][NR$_4$], in benzene solution upon addition of [HN$'$Pr$_2$Et][BPh$_4$] or B(C$_6$F$_3$)$_3$ to expose a coordination site in situ. Several qualitative differences in the reactivity of the two systems were immediately apparent. When a slurry of [[Ph$_2$BP$_2$]PtMe$_2$][ASN] was exposed to one equiv of either B(C$_6$F$_3$)$_3$ or HN$'$Pr$_2$Et$'$ in C$_6$D$_6$, ill-defined chemistry occurred at a very slow rate. The
starting material persisted for hours, and the only identifiable byproducts were CH₄ and CH₃D. Consumption of the starting material proceeded much more rapidly on addition of either reagent in the presence of several equiv of THF. Under these conditions, [Ph₂BP₂]Pt(Me)(THF) is generated immediately. In contrast, the addition of B(C₆F₅)₃ or [HNᵢPr₂Et][NBu₄] at 22 °C to a slurry of [Ph₂B(pz)₂]PtMe₂][NR₄] in benzene rapidly (< 5 min) and cleanly produced the diphenyl complex, [Ph₂B(pz)₂]PtTHF][NBu₄], with the concomitant evolution of each of the possible methane isotopomers (CH₄, CH₃D, CH₂D₂, CHD₃, CD₄). This latter reaction occurred at the same rate in both C₆H₆ and C₆D₆: a competition experiment using a 1:1 mixture of C₆H₆:C₆D₆ and subsequent examination of the products by ¹H NMR demonstrated that approximately 50% of the platinum-phenyl groups were Pt-C₆H₅, consistent with no significant kinetic isotope effects. It appears that methane loss is rate limiting in the (pyrazolyl)borate system, but not in the bis(phosphino)borate system. Even more interesting is that catalytic quantities (0.1 – 0.25 equiv) of [HNᵢPr₂Et][BPh₄] and B(C₆F₅)₃ drive the conversion of [Ph₂B(pz)₂]PtMe₂][NR₄] to [Ph₂B(pz)₂]Pt(C₆D₆₂][NR₄]. Addition of 0.1 equiv of B(C₆F₅)₃ mediates the conversion rapidly (< 5 min). Currently, we cannot distinguish whether methide abstraction initiates subsequent arene activation, or whether trace “HOB(C₆F₅)₃” initiates the activation chemistry by protonation at platinum followed by methane loss. In the case of [HNᵢPr₂Et][BPh₄], there is little doubt that protonation (presumably at platinum) is the first step that exposes a site by methane loss. An additional point is that the activation chemistry will occur below – 20 °C in toluene-d₈. In a VT experiment carried out from – 60 °C to 0 °C, a stoichiometric mixture of [HNᵢPr₂Et][BPh₄] and [Ph₂B(pz)₂]PtMe₂][NBu₄] began to produce deuterated methane isotopomers as low as – 40 °C. A mixture of platinum products resulted consistent with toluene-d₈ C-D activation in various positions. ¹H NMR data verified a product consistent with benzylic activation. We also canvassed the reaction of [HNᵢPr₂Et][BPh₄] and [Ph₂B(pz)₂]PtMe₂][NBu₄] in mesitylene. In this case, we were able to isolate and structurally characterize a product establishing benzylic activation. Unfortunately, the pyrazole ligand occupying the fourth coordination site shows that some [Ph₂B(pz)₂] ligand degradation occurred (Figure 9). While we have yet to probe the mechanism of the double C-H bond activation reaction, we suggest a plausible mechanism that might account for the ability of catalytic [HNᵢPr₂Et][BPh₄] to mediate the overall process (Figure 10).
Figure 9. C-H bond activation of mesitylene with concomitant ligand degradation. Displacement ellipsoid representation of \([\text{Ph}_2\text{B(pz)}_2\text{Pt(CH}_2\text{-3,5-Me}_2\text{Ph})\text{(pyrazole)}] \) is also shown.

Figure 10. Mechanistic scenario that might account for the ability of \([\text{HNPr}_2\text{Et}]\text{[BPh}_4\text{]}\) to catalyze the conversion of \([\text{Ph}_2\text{B(pz)}_2\text{PtMe}_2]\text{[NBu}_4\text{]}\) to \([\text{Ph}_2\text{B(pz)}_2\text{PtPh}_2]\text{[NBu}_4\text{]}\) in benzene solution. A displacement ellipsoid representation of the anion in \([\text{Ph}_2\text{B(pz)}_2\text{PtPh}_3]\text{[NBu}_4\text{]}\) is also shown.
Summary

This contribution has emphasized the reactivity of several platinum(II) complexes with respect to arene C-H bond activation. Most noteworthy are the results that compare the benzene solution chemistry of a neutral and cationic platinum(II) complex in which the platinum centers reside in an isostructural environment. Our data reveals that, even for very similar complexes, the mechanism of a C-H bond activation process can be dramatically different for two complexes capable of mediating the same overall reaction. Key differences described herein concern respective mechanisms of ligand exchange, and the relative propensity for inter- versus intramolecular arene C-H bond activation processes. Two surprising results uncovered within the neutral system \([Ph_2BP_2]Pt(Me)(THF)\) concern the (i) lack of THF dependence on the rate of THF self-exchange in benzene, and (ii) the presence of a spectroscopically observable platinum(IV) methyl hydride complex that is presumed to be in equilibrium with the \([Ph_2BP_2]Pt(Me)(THF)\) in benzene solution.

We had hoped to correlate key mechanistic differences between the cationic complex \([(Ph_2SiP_2)Pt(Me)(THF)][B(C_6F_5)_4]\) and the neutral complex \([Ph_2BP_2]Pt(Me)(THF)\) to electronic factors, the neutral system being the more electron-rich of the two despite the fact that it can be represented as a zwitterion. A key question with which we continue to struggle is the degree to which measured CO stretching frequencies can be used to correlate the relative electrophilicity of two isostructural complexes where one is cationic and one is neutral. The increased polarizability of CO when bound to a cationic platinum center complicates this issue. While comparisons that rely on such data are in and of themselves limited in a quantitative sense, our intuition is still to suggest the neutral zwitterion \([Ph_2BP_2]Pt(Me)(THF)\) is appreciably more electron rich at platinum than the cation \([(Ph_2SiP_2)Pt(Me)(THF)][B(C_6F_5)_4]\).

The final section in this contribution briefly compared the reactivity of a bis(pyrazolyl)borate platinum(II) system with the bis(phosphino)borate system. While these two systems are similar, the nature of the donor atoms coordinating platinum are distinct. Marked differences in reactivity were discerned, the bis(pyrazolyl)borate being the more reactive of the two under the conditions discussed.\(^{18}\) An intriguing double C-H bond activation reaction was identified that converted \({\{Ph_3B(pz)_3\}PtMe_2}\{NBu_4\}\) directly to \({\{Ph_2B(pz)_2\}PtPh_2}\{NBu_4\}\) rapidly in benzene at room temperature and below. The reaction is initiated by both stoichiometric and catalytic quantities of either \(B(C_6F_5)_3\) or \([HN\Pr_2Et][BPh_3]\). It appears that benzene C-H activation at \([Ph_2B(pz)_2]\)Pt(II) can be very facile, occurring at temperatures as low as -40 °C, in cases where coordinating donor ligands other than benzene solvent are removed from the reaction system. In this regard, generating neutral platinum species in situ may afford highly productive C-H activation systems, but their activation chemistry needs to be controlled to produce high selectivity.

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References


15 Langford, C. H.; Gray, H. B. Ligand Substitution Processes; Benjamin: New
   York, 1966; pp 18-54.
17 The mechanistic scheme shown in figure 10 does not consider protonation at
   one of the pyrazolyl arms as a means to expose a coordination site for arene
   coordination/activation. Such a scenario would also be reasonable and could
   account for the observed diphenyl product. For a reference that pertains to the
   protonation of (pyrazolyl)borate ligands in a related context see: Reinartz, S.;
18 In separate studies, we have found examples whereby [Ph₂BP₂]Pt(Me)(L)
   complexes undergo benzene C-H activation more readily than
   [Ph₂B(pz)₂]Pt(Me)(L) complexes. For example, the complex
   [Ph₂BP₂]Pt(Me)(P(C₆F₅)₃) degrades quantitatively to [Ph₂BP₂]Pt(Ph)(P(C₆F₅)₃)
   in benzene at 80 °C, whereas [Ph₂BP₂(pz)₂]Pt(Me)(P(C₆F₅)₃) is stable for
   prolonged periods at temperatures above 100 °C in benzene (see ref 8).