Comparative Studies with Zwitterionic Platinum(II) Bis(pyrazolyl)borate and 2,2′-Bipyridylborate Complexes

Christine M. Thomas and Jonas C. Peters*

Division of Chemistry and Chemical Engineering, Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

Received June 28, 2005

A comparison between the mononuclear platinum complexes of three structurally different monoanionic borato ligands is presented: $[Ph_2B(pyrazolyl)_2]^-$ ($[Ph_2B(pz)_2]$, **1**), [4-Ph_3B(2,2′-bipyridine)]$^-$ ([(4-BPh_3)bpy], **2**), and $[Ph_2B(CH_2PPh_2)_2]^-$ ($[Ph_2BP_2]$, **3**). The new bipyridylborate ligand **2** is introduced in this study. The relative *trans* influence of these ligands has been assessed by comparison of the structural and spectroscopic (NMR) data of the platinum dimethyl complexes $[[Ph_2B(pz)_2]Pt(Me)_2][NBu_4]$ (**4**), $[[(4\text{-}BPh_3)bpy]Pt(Me)_2][NBu_4]$ (**5**), and $[[Ph_2BP_2]Pt(Me)_2]$[ASN] (**6**). The neutral complexes $[Ph_2B(pz)_2]Pt(Me)(NCCH_3)$ (**7**), $[Ph_2B(pz)_2]Pt(Me)(CO)$ (**8**), $[Ph_2B(pz)_2]Pt(Me)(P(C_6F_5)_3)$ (**9**), $[(4\text{-}BPh_3)bpy]Pt(Me)(NCCH_3)$ (**10**), $[(4\text{-}BPh_3)bpy]Pt(Me)(CO)$ (**11**), and $[(bpy)Pt(Me)(CO)][BPh_4]$ (**12**) were prepared, and the carbonyl complexes **8**, **11**, and **12** provide information pertaining to the relative electron-releasing character of each ligand type. The CO stretching frequencies suggest that the charged borate moiety renders the borato ligands more electron-donating than their neutral analogues. Of the neutral platinum methyl solvento complexes supported by ligands **1**, **2**, and **3**, only those of **1** display very different C−H activation propensities. Upon protonation or methide abstraction in benzene at room temperature, complex **4** rapidly activates two molecules of benzene to generate $[[Ph_2B(pz)_2]Pt(Ph)_2][NBu_4]$ (**13**). Isotopic scrambling of deuterium into methane in C_6D_6 solvent suggests the intermediacy of a methane σ-adduct in this reaction. The double C−H activation reaction can be halted by addition of acetonitrile to trap the intermediate $[Ph_2B(pz)_2]Pt(Ph)(NCCH_3)$ (**14**). Complex **3** also displays reactivity toward the benzylic C−H bonds of mesitylene at room temperature to form $[Ph_2B(pz)_2]$-$Pt(pzH)(CH_2C_6H_3(CH_3)_2)$ (**15**) in modest yield.

Introduction

Motivated by the versatility of organometallic cations for processes such as polymerization, C−H bond activation, and C−E bond forming reactions (E = H, C, Si), our group has studied various neutral, formally zwitterionic complexes to examine the effect of electrophilicity on the reactivity of late transition metal centers.[1,2] These zwitterions utilize ligands in which a borate moiety is incorporated within the ligand framework but is partially insulated from the coordinated metal center. Our goal has been to study the effect of the anionic borate unit on the reactivity of these complexes by comparison to cationic complexes supported by structurally similar neutral ligands. Accordingly, previous studies in our group have focused on monoanionic bidentate ligands such as bis(phosphino)borates and bis(amino)borates, in which a borate moiety is linked to tertiary phosphine or amine donors via a methylene linker.[3] We have found that zwitterionic complexes often display reactivity quite similar to their cationic congeners, but important reactivity and mechanistic differences can be prevalent. For example, bis(phosphino)borate rhodium catalysts show tolerance to relatively polar donor solvents such as acetonitrile, in contrast to their cationic bis(phosphine) relatives.[3e] Also, comparative structural, electronic, and mechanistic studies of zwitterionic and cationic bis(phosphine) platinum(II) complexes suggest that more electron-rich, platinum(II) zwitterions are equally, if not more, competent than their isostructural cations with respect to their propensities for benzene C−H activation. Subtle mechanistic differences distinguish the benzene solution chemistry of the two systems, leading to different overall reaction rates.[3c]

Square planar platinum(II) centers supported by nitrogen donor ligands have been more thoroughly

* To whom correspondence should be addressed. E-mail: jpeters@caltech.edu.

(1) (a) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169−1203. (b) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009−3066. (c) Crabtree, R. H. *Acc. Chem. Res.* **1979**, *12*, 331−337. (d) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3089−3091.

(2) For recent discussions of C−H bond activation and functionalization mediated by cationic metal centers, see: (a) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471−2526. (b) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154−162. (c) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550−557. (d) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2181−2192. (e) Crabtree, R. H. *J. Chem. Soc., Dalton Trans*. **2001**, 2437−2450. (f) Shilov, A. E.; Shul'pin, G. B. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer: Boston, 2000.

(3) (a) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2001**, *123*, 5100−5101. (b) Betley, T. A.; Peters, J. C.; *Inorg. Chem.* **2002**, *41*, 6541−6543. (c) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125,* 8870−8888. (d) Thomas, J. C.; Peters, J. C. *Inorg. Chem.* **2003**, *42*, 5055−5073. (e) Betley, T. A.; Peters, J. C. *Angew. Chem., Int. Ed*. **2003**, *42*, 2385−2389. (f) Lu, C. C.; Peters, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 5272−5273.

10.1021/om050538j CCC: $30.25
Publication on Web 10/22/2005

examined with respect to alkane activation reactions than phosphine-supported systems.[4,5] One case pertinent to the present paper concerns various studies of the C−H activation reactivity of platinum tris(pyrazolyl)borate (Tp) complexes.[6] In this regard it is noteworthy that little attention has yet focused on bis(pyrazolyl)borate group 10 metal complexes, despite the fact that various platinum studies exploiting Tp ligands feature κ^2 Tp precursors and/or intermediates. The limited reports of platinum bis(pyrazolyl)borate systems have not described their utility for C−H activation chemistry.[7]

In addition to Tp platinum complexes, a range of Pt diimine species exhibit C−H activation activity. Among the more noteworthy diimine-type systems are the (2,2′-bipyrimidyl)platinum(II) complexes examined by Periana et al.[8] and a host of platinum diimine complexes that have proven particularly advantageous for careful mechanistic studies.[9] Platinum complexes of the 2,2′-bipyridine (bpy) ligand and its derivatives have also been investigated extensively, for example with respect to oxidative addition processes.[10,11] There are several reports that describe instances of C−H activation reactions mediated by platinum(II) bipyridyl complexes, although these reactions tend to involve intramolecular ligand C−H activation processes.[12]

In the present study, we report on platinum complexes supported by bidentate pyrazolyl and bipyridyl borate ligands. To extend borate incorporation into the ubiquitous bipyridyl ligand class, we have synthesized the ligand 2,2′-bipyridylborate [(4-BPh_3)bpy]. This ligand and the bidentate borate [$Ph_2B(pz)_2$] comprise the specific ligands of interest herein (Figure 1). We present a comparison of the structural and electronic properties of their platinum derivatives as determined by X-ray crystallography, IR spectroscopy, and ^{1}H NMR spectroscopy. Also discussed is the proclivity of several platinum derivatives to undergo C−H bond activation processes. Most interesting in this context is the discovery of a double C−H bond activation reaction: it is observed that exposure of a coordination site of the precursor $\{[Ph_2B(pz)_2]Pt(Me)_2\}^-$ in benzene solution leads to the rapid production of $\{[Ph_2B(pz)_2]Pt(Ph)_2\}^-$ at ambient temperature. This reaction is reminiscent of Goldberg's earlier discovery of a $\{\kappa^2$-[Tp*]$PtMe_2\}^-$ precursor that reacts with alkanes upon exposure of a coordination site to yield stable octahedral Pt(IV) products in which the Tp ligand is κ^3.[6e,6g,13]

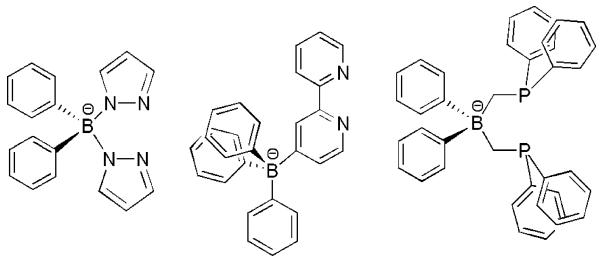


Figure 1. [$Ph_2B(pz)_2$] (**1**), [(4-BPh_3)bpy] (**2**), and [Ph_2BP_2] (**3**) ligands, each possessing a borate anion incorporated within the ligand framework.

Results and Discussion

Synthesis of Precursor Complexes. The [$Ph_2B(pz)_2$][NBu_4] (**1**) ligand was synthesized using a modification of the procedure reported in the literature.[14] Excess pyrazole and sodium tetraphenylborate were heated to a melt (80−100 °C) for several hours. This was followed by salt metathesis with NBu_4Br in CH_2Cl_2 to generate **1** in 76% yield.

The [(4-BPh_3)bpy][NBu_4] (**2**) ligand was synthesized from 4-iodo-2,2′-bipyridine[15] via formation of a bipyridyl Grignard reagent (4-MgX)bpy using ^{i}PrMgCl at −78 °C in diethyl ether (Scheme 1). The Grignard was then quenched with BPh_3 and the magnesium salt [(4-BPh_3)bpy]$_2$Mg was isolated as a red solid. It is noteworthy that traditional lithio reagents (i.e., ^{n}BuLi, ^{t}BuLi, etc.) and Mg^0 proved ineffective for the synthesis of this ligand. Strong chelation to magnesium made metalation of the magnesium derivative [(4-BPh_3)bpy]$_2$-

(4) See for example: (a) Rostovtsev, V. V.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 3608−3619. (b) Rostovtsev, V. V.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **1998**, *17*, 4530−4531. (c) Rendina, L. M.; Puddephatt, R. J. *Chem. Rev.* **1997**, *97*, 1735−1754.

(5) See for example: (a) Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804−6805. (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961−5976.

(6) (a) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 12724−12725. (b) Lo, H. C.; Haskel, A.; Kapon, M.; Keinan, E. *J. Am. Chem. Soc.* **2002**, *124*, 3226−3228. (c) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 6425−6426. (d) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2000**, *19*, 3854−3866. (e) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235−10236. (f) Haskel, A.; Keinan, E. *Organometallics* **1999**, *41*, 2808−2810. (g) Jensen, M. P.; Wick, D. D.; Reinartz, S.; White, P. S.; Templeton, J. L.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 8614.

(7) (a) Onishi, M.; Hiraki, K. *Inorg. Chim. Acta* **1994**, *224*, 131−135. (b) Clark, H. C.; von Werner, K. *J. Organomet. Chem.* **1975**, *101*, 347−358. (c) Reger, D. L.; Baxter, J. C.; Lebioda, L. *Inorg. Chim. Acta* **1989**, *165*, 201−205.

(8) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560−564.

(9) (a) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846−10855. (b) Johansson, L.; Ryan, O. B.; Romming, C.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 6579−6590. (c) Johansson, L.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 739−740. (d) Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am Chem. Soc.* **2002**, *124*, 1378−1399.

(10) See for example: (a) Klein, A.; van Slageren, J.; Zalis, S. *Eur. J. Inorg. Chem.* **2003**, 1927−1938. (b) Doppiu, A.; Cinellu, M. A.; Minghetti, G.; Stoccoro, S.; Zucca, A.; Manassero, M.; Sansoni, M. *Eur. J. Inorg. Chem.* **2000**, 2555−2563. (c) Bayler, A.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2000**, *595*, 296−299. (d) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966−4968. (e) Chaudhury, N.; Puddephatt, R. J. *J. Organomet. Chem.* **1975**, *84*, 105−115. (f) Achar, S.; Catalano, V. J. *Polyhedron* **1997**, *16*, 1555−1561. (g) Hill, G. S.; Manojlovic-Muir, L.; Muir, K.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 525−530.

(11) (a) Hill, R. H.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1218−1225. (b) Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548−2550. (c) Kuyper, J. *Inorg. Chem.* **1978**, *17*, 1458−1463. (d) Kuyper, J. *Inorg. Chem.* **1977**, *16*, 2171−2176. (e) Kuyper, J. *Inorg. Chem.* **1978**, *17*, 77−81. (f) Levy, C. J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 10127−10136.

(12) (a) Minghetti, G.; Stoccoro, S.; Cinellu, M. A.; Soro, B. Zucca, A. *Organometallics* **2003**, *22*, 4770−4777. (b) Zucca, A.; Stoccoro, S.; Cinellu, M. A.; Minghetti, G.; Manassero, M.; Sansoni, M. *Eur. J. Inorg. Chem.* **2002**, 3336−3346. (c) Zucca, A.; Doppiu, A.; Cinellu, M. A.; Stoccoro, S.; Minghetti, G.; Manassero, M. *Organometallics* **2002**, *21*, 783−785. (d) Minghetti, G.; Cinellu, M. A.; Stoccoro, S.; Zucca, A.; Manassero, M. *J. Chem. Soc., Dalton Trans.* **1995**, *5*, 777−781.

(13) Aspects of this work have been briefly described in an ACS Symposium Series contribution: Peters, J. C.; Thomas, J. C.; Thomas, C. M.; Betley, T. A. *Activation and Functionalization of C−H Bonds*; Goldberg, K., Goldman, A., Eds.; ACS Symposium Series No. 885; American Chemical Society: Washington, DC, 2004; Chapter 20, pp 334−354.

(14) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288−6293.

(15) (a) Wenkert, D.; Woodward, R. B. *J. Org. Chem.* **1983**, *48*, 283−289. (b) Sprecher, M.; Breslow, R.; Uziel, O.; Link, T. M. *OPPI Briefs* **1994**, *26*, 696−701.

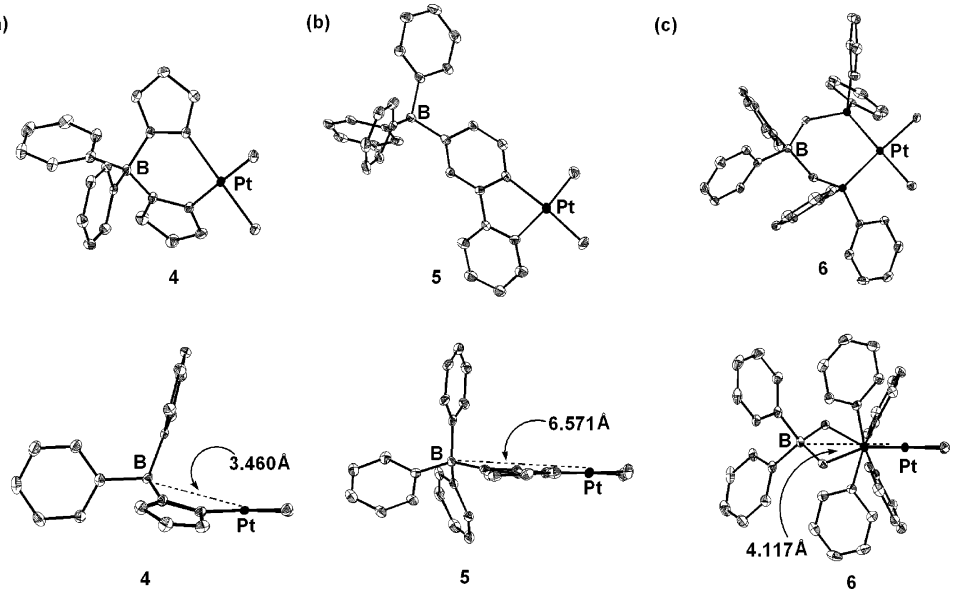


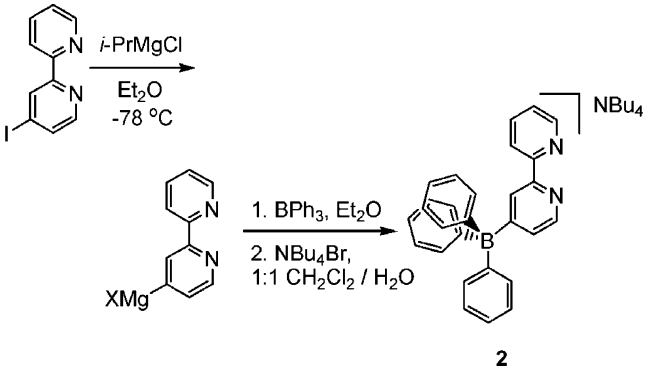
Figure 2. Displacement ellipsoid representations (50%) of two different views of (a) $[[Ph_2B(pz)_2]Pt(Me)_2][NBu_4]$ (**4**), (b) $[[(4\text{-}BPh_3)bpy]Pt(Me)_2][NBu_4]$ (**5**), and (c) $[[Ph_2BP_2]Pt(Me)_2][ASN]$ (**6**)[3a,c] displaying their geometries and Pt−B interatomic distances. The NBu_4 and ASN cations and hydrogen atoms have been omitted for clarity.

Table 1. Relevant NMR and Structural Data for Complexes 4, 5, and 6

complex	$^2J_{Pt-H}$ (Hz)	Pt−B (Å)	Pt−C (Å)	C−Pt−C (deg)	P−Pt−P or N−Pt−N (deg)
$[[Ph_2B(pz)_2]Pt(Me)_2][NBu_4]$ (**4**)	83[a]	3.460	2.040[c]	89.30 (1)	89.73(9)
$[[(4\text{-}BPh_3)bpy]Pt(Me)_2][NBu_4]$ (**5**)	85, 86[a]	6.570	2.044(3), 2.036(3)	89.52(13)	77.96(10)
$[[Ph_2BP_2]Pt(Me)_2][ASN]$ (**6**)[b]	68[a]	4.117	2.133[c]	86.6(1)	90.64(2)

[a] NMR measurements were collected in acetone-d_6 on a 300 MHz instrument. [b] Previously reported. [c] Average of both bond distances.

Scheme 1



Mg difficult; however, salt metathesis with NBu_4Br in a 1:1 mixture of CH_2Cl_2 and H_2O generated a more useful reagent, **2**, in moderate overall yield (35%). The dimethyl platinum precursors $[[Ph_2B(pz)_2]Pt(Me)_2][NBu_4]$ (**4**) and $[[(4\text{-}BPh_3)bpy]Pt(Me)_2][NBu_4]$ (**5**) were prepared in good yield (76% and >95%, respectively) by displacement of dimethyl sulfide from $[(Me)_2Pt(\mu\text{-}SMe_2)]_2$ in THF solution. Substitution reactions with $(COD)PtMe_2$ (COD = cyclooctadiene) were ineffective.

Structural and Spectroscopic Characterization Data. Single crystals of **4** and **5** suitable for X-ray diffraction were grown by vapor diffusion of petroleum ether into a concentrated THF solution.[16] The resulting structures (Figure 2) are to be compared with the structure previously reported for the bis(phosphino)-borate dimethyl complex $[[Ph_2BP_2]Pt(Me)_2][ASN]$ (**6**) (ASN = 5-azonia-spiro[4.4]nonane.[3a,c] Relevant NMR data, interatomic distances, and bond angles are presented in Table 1. All three complexes adopt a typical square planar geometry but exhibit notable differences due to geometric constraints imposed by their respective donor ligands. Both N-donor complexes **4** and **5** have C−Pt−C angles near 90°, while **6** has a slightly contracted C−Pt−C angle (86.6°). A more significant difference is observed in the ligand bite angles. While both complexes **4** and **6** have ligand bite angles near 90° (90.64° and 89.73°, respectively), the rigid bipyridine ligand leads to a much smaller N−Pt−N angle (77.96°) in complex **5**.

Another significant difference in ligand geometry is apparent upon looking into an edge of the square plane of each respective complex. While the $[(4\text{-}BPh_3)bpy]$ ligand is rigidly planar, the $[Ph_2B(pz)_2]$ ligand is canted out of the square plane and the pyrazole rings eclipse one another. The $[Ph_2BP_2]$ ligand, on the other hand, has more flexible methylene connectors that allow it to maintain a staggered conformation that minimizes steric interactions. These differences in ligand geometry lead to variations in the distance between the Pt center and the negatively charged borate moiety. Complex **4** exhibits a Pt−B distance appreciably shorter than in **6** (3.460 Å compared to 4.117 Å), while complex **5** has a much longer Pt−B interatomic distance (6.570 Å).

A comparison of the average Pt−C bond lengths observed in these complexes is indicative of the relative *trans* influence of the borato ligands. Due to the strongly *trans* influencing nature of its phosphine donors, complex **6** exhibits an average Pt−C bond length significantly longer than either complex **4** or **5** (2.133 Å, compared to 2.040 (**4**) and 2.044/2.036 Å (**5**)). The NMR

(16) See Table 3 and the Supporting Information for crystallographic details.

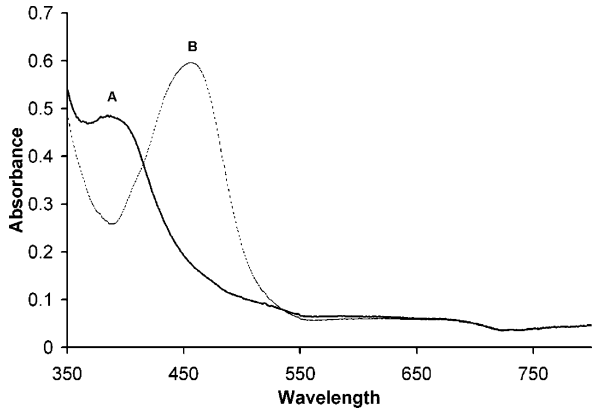


Figure 3. Optical absorption spectra of (A) **5** (solid line) and (B) (bpy)Pt(Me)$_2$ (dashed line) in acetonitrile solution at 298 K.

coupling constants are consistent with this description. For example, $^2J_{Pt-H}$ for **6** is much lower than that for either **4** or **5** (65 Hz, compared to 83 and 85/86 Hz). Evident from the NMR data and the observed Pt−C bond lengths is that the [(4-BPh$_3$)bpy] ligand in **5** and the [Ph$_2$B(pz)$_2$] ligand in **4** exert comparable *trans* influences. In addition, neutral (bpy)Pt(Me)$_2$ has an average Pt−C bond length and $^2J_{Pt-H}$ nearly identical to **5**, indicating that the borate has a negligible effect on the overall *trans* influence of the bipyridylborate ligand.

Although the [Ph$_2$BP$_2$] and [Ph$_2$B(pz)$_2$] complexes **4** and **6** are colorless, the [(4-BPh$_3$)bpy] complex **5** is intensely colored. This characteristic red-orange color can be attributed to a metal to ligand charge transfer (MLCT) {Pt d_{z^2} to ligand π^*} transition, as observed for similar bipyridine complexes.[10] Interestingly, the absorption maximum (λ_{max}) for **5** is blue shifted to 385 nm from the λ_{max} observed for the neutral (bpy)Pt(Me)$_2$ at 456 nm (Figure 3). This large blue shift is likely a qualitative measure of the degree of destabilization of the bipyridyl-centered LUMO upon incorporation of the anionic borate unit.

Protonolysis of Monoanionic Platinum Dimethyl Complexes. As has been reported previously, protonation of **6** with an ammonium salt (e.g., [HNR$_3$][BPh$_4$]) in the presence of an L donor (L = THF, CO, P(C$_6$F$_5$)$_3$, etc.) leads to clean formation of neutral [Ph$_2$BP$_2$]Pt(Me)(L) complexes.[3a,c] Likewise, it is found that protonation of **4** with [HN^{i}Pr$_2$Et][BPh$_4$] in THF in the presence of excess L cleanly generates several [Ph$_2$B(pz)$_2$]Pt(Me)(L) complexes (see Experimental Section; L = NCCH$_3$, **7**; CO, **8**; P(C$_6$F$_5$)$_3$, **9**).

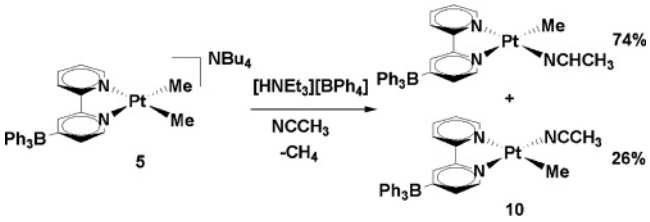
In the case of complex **5**, protonolysis by [HNEt$_3$][BPh$_4$] in acetonitrile solution led to formation of the two possible isomers of [(4-BPh$_3$)bpy]Pt(Me)(NCCH$_3$) (**10**) in a 2.8:1 ratio (Scheme 2). The major isomer formed in this reaction was determined to be that in which acetonitrile occupies the site *cis* to the borate-substituted pyridyl ring. This was established by NMR spectroscopy using a two-dimensional NOESY experiment. An identical ratio of products is observed when the reaction is performed at both high and low temperatures (−78 to 60 °C). The formation of appreciable amounts of both isomers in this reaction suggests that the *trans* effect of the pyridyl donor featuring a *p*-borate unit is quite similar to the unsubstituted donor ring.

Table 2. Infrared Carbonyl Frequencies for Platinum Methyl Carbonyl Complexes

complex	ν_{CO} (cm^{-1})[a]
[Ph$_2$B(pz)$_2$]Pt(Me)(CO) (**8**)	2078
[(4-BPh$_3$)bpy]Pt(Me)(CO) (**11**)	2098
[(bpy)Pt(Me)(CO)][BPh$_4$] (**12**)	2107
[Ph$_2$BP$_2$]Pt(Me)(CO)[b]	2094
[[Ph$_2$SiP$_2$]Pt(Me)(CO)][B(C$_6$F$_5$)$_4$][b]	2118

[a] KBr cell in CH_2Cl_2. [b] Previously reported.[3c,d,10b]

Scheme 2



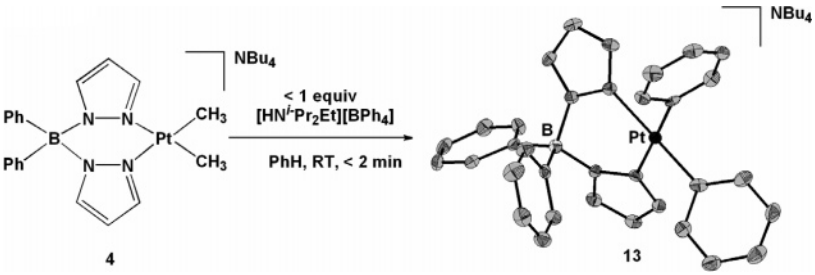
Similarly, protonation of **5** with [HNEt$_3$][BPh$_4$] in THF followed by addition of excess carbon monoxide led to the formation of both isomers of [(4-BPh$_3$)bpy]Pt(Me)(CO) (**11**) in an identical 2.8:1 ratio.

Considering Electronic Factors Using Methyl Carbonyl Derivatives. To probe the electronic differences between ligands **1**, **2**, and **3**, we have synthesized several neutral platinum methyl carbonyl complexes. The relative energies of the CO vibrations in these neutral complexes are effective indicators of the electronic environment around the platinum center. The relevant carbonyl stretching frequency data are reported in Table 2. Bis(pyrazolyl)borate complex **8** possesses a CO stretching frequency 16 cm^{-1} lower than that of the [Ph$_2$BP$_2$]Pt(Me)(CO) complex,[3c,d] indicating that, for the present square planar platinum system, the bidentate pyrazolyl ligand acts as a better electron donor than the bidentate phosphine. This result is surprising and contrasts other data from our group clearly suggesting that, in general, (phosphino)borate ligands are stronger field donors than (pyrazolyl)borates.[3c,17] The [(4-BPh$_3$)bpy] complex **11** possesses the highest CO stretching frequency (2098 cm^{-1}), suggesting that the bipyridyl ligand is the poorest donor of the three monoanionic ligands. This trend can be correlated to the Pt−B interatomic distances established for complexes **4**−**6** via X-ray diffraction (Table 1). The complex in which the borate is farthest removed from the platinum center (**5**, 6.570 Å) also corresponds to the methyl carbonyl complex with the highest CO stretching frequency (**11**). Complex **4** has the shortest Pt−B distance (3.460 Å), and its methyl carbonyl complex (**8**) exhibits the lowest CO stretching frequency.

In addition to comparing the carbonyl data among the neutral methyl carbonyl complexes, comparisons can be made between the neutral complexes and structurally analogous cationic complexes lacking a borate moiety. It is important to note, however, that the absolute difference in CO stretching frequency, at least when comparing formally neutral complexes with formally cationic complexes, is strongly influenced by electrostatic factors.[18] The difference in CO stretching frequency ($\Delta\nu_{CO}$) between the neutral complex [Ph$_2$BP$_2$]-

(17) Jenkins, D. M.; DiBilio, A. J.; Allen, M. J.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 15336−15350.

Scheme 3



Pt(Me)(CO) and the cationic complex $[[Ph_2SiP_2]Pt(Me)(CO)][B(C_6F_5)_4]$ is reported to be 24 cm^{-1}, confirming that the $[Ph_2BP_2]$ ligand is more electron-releasing than its neutral silane analogue.[3c] Although no data have been reported for a cationic analogue of **8**, the infrared data for **11** can be compared with the carbonyl stretch of 2107 cm^{-1} observed for the cationic complex $[(bpy)Pt(Me)(CO)][BPh_4]$ (**12**). On the basis of the $\Delta\nu_{CO}$ of 9 cm^{-1}, it can be concluded that the borate unit does affect the electronic environment of the platinum center, but to a much lesser extent than the borate of $[Ph_2BP_2]$. The aryl ring of the bipyridyl ligand serves as a much better insulator than the methylene linker of $[Ph_2BP_2]$.

Reactivity of Platinum Derivatives with Aromatic Substrates. Platinum complexes supported by ligands **1**, **2**, and **3** display varied solution chemistry in benzene. For example, we have previously reported that $[Ph_2BP_2]Pt(Me)(L)$ species are readily converted to their corresponding $[Ph_2BP_2]Pt(C_6D_5)(L)$ derivatives when gently heated in benzene-d_6 solution (where L = THF, $P(C_6F_5)_3$).[3c] For comparison we attempted to isolate the complex $[Ph_2B(pz)_2]Pt(Me)(THF)$ but found it too reactive (vide infra). The complex $[Ph_2B(pz)_2]Pt(Me)(P(C_6F_5)_3)$ (**9**) is conveniently accessible. Choice of the $P(C_6F_5)_3$ ligand is based on the presupposition that it provides a potentially labile donor ligand due to its high steric bulk and that it should feature relatively inert aryl rings. When **9** was subjected to the same reaction conditions as $[Ph_2BP_2]Pt(Me)(P(C_6F_5)_3)$ (80 °C, 24 h, C_6D_6), no reaction was observed, whereas we have previously observed that $[Ph_2BP_2]Pt(Me)(P(C_6F_5)_3)$ proceeds cleanly to the phenyl product $[Ph_2BP_2]Pt(C_6D_5)(P(C_6F_5)_3)$.[3c] The increased reactivity of $[Ph_2BP_2]Pt(Me)(P(C_6F_5)_3)$ might be attributable to the lability of the $P(C_6F_5)_3$ ligand because of a greater *trans* effect of the $[Ph_2BP_2]$ ligand, though equally likely is that steric interactions between the $[Ph_2BP_2]$ ligand and the sterically bulky $P(C_6F_5)_3$ donor serve to more greatly labilize the latter than in the case of the bis(pyrazolyl)borate system.

Another interesting difference in reactivity between complexes **4**−**6** is observed upon attempts to protolytically cleave or abstract a methyl ligand by $B(C_6F_5)_3$ in benzene solution. Thus, protonation of **4** with *1* equiv of $[HN^iPr_2Et][BPh_4]$ in benzene solution leads to the rapid C−H activation of *2* equiv of benzene, leading to the formation of a single product, $[[Ph_2B(pz)_2]Pt(Ph)_2][NBu_4]$ (**13**), with concomitant loss of *2* equiv of methane (Scheme 3).[19]

When a stronger and more soluble acid is used, such as $[H(OEt_2)_2][BAr_4]$ (Ar = $C_6H_3(CF_3)_2$), the reaction proceeds similarly but is more facile. The C−H activation process can be observed by ^1H NMR in toluene-d_8 at temperatures as low as −20 °C using the mild acid $[HN^iPr_2Et][BPh_4]$. The reaction was monitored by the production of methane and the disappearance of starting material; however, due to the formation of multiple toluene activation products, the kinetics of this reaction could not be followed closely. Addition of substoichiometric amounts of $[HN^iPr_2Et][BPh_4]$ or $[H(OEt_2)_2][BAr_4]$ (0.1 equiv) leads to much slower consumption of the starting precursor **4** (48 h), but nonetheless generates **13** quantitatively. This observation implies that acid catalyzes the double C−H activation process.

The above observations are consistent with several possible reaction mechanisms. Perhaps the simplest and most reasonable scenario, at least based upon literature precedent, concerns an associative oxidative addition/reductive elimination cycle (Scheme 4).[6,9a] The first likely step of such a mechanism (a) is protonation at the metal center to form a six-coordinate platinum(IV) species (with the other axial site presumably occupied by a solvent molecule).[20] This is followed by reductive elimination of methane and coordination of benzene to form an η^2-benzene adduct (b). The benzene molecule is then oxidatively added to form another platinum(IV) hydride (c), from which another molecule of methane is reductively eliminated (d). Oxidative addition of another benzene molecule (e) would then lead to a platinum(IV) hydride species from which the $[HNR_3][BPh_4]$ salt could be regenerated (f), allowing the reaction to proceed via addition of catalytic acid. A related cycle to consider involves initial protonation and dissociation of one of the ligand pyrazole rings to open a metal coordination site, allowing benzene to coordinate. Scenarios related to this have been previously suggested for Tp platinum(IV) complexes during acid-assisted reductive elimination processes.[6]

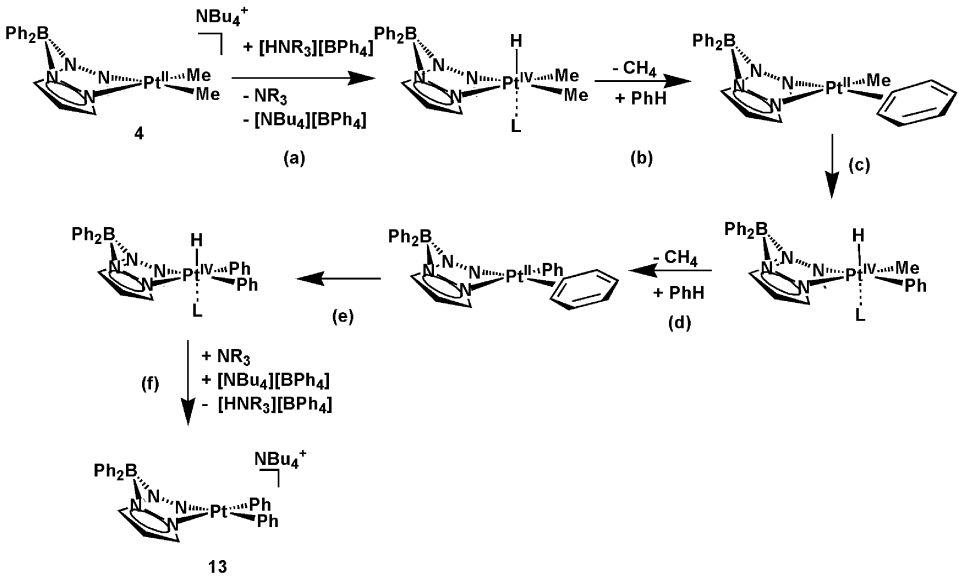
An interesting aspect of this benzene activation process is that the reaction proceeds rapidly in the presence of a labile two-electron donor such as tetrahydrofuran, but is quenched upon addition of a modestly stronger donor such as acetonitrile. Thus, protonation of **4** in benzene, followed by immediate addition of acetonitrile, leads to the formation of $[Ph_2B(pz)_2]Pt(Ph)(NCCH_3)$ (**14**) in high yield. Binding of acetonitrile to the platinum center apparently prohibits formation of the much more weakly coordinating η^2-benzene ligand (Scheme 4d).[9a] Completion of the double C−H activation process in the presence of THF implies that benzene can

(18) (a) Goldman, A. S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1996**, *118*, 12159−12166. (b) Caulton, K. G.; Fenske, R. F. *Inorg. Chem.* **1968**, *7*, 1273−1284. (c) Hush, N. S.; Williams, M. I. *J. Mol. Spectrosc.* **1974**, *50,* 349−368.

(19) See Table 3 and the Supporting Information for crystallographic details.

(20) Wik, B. J.; Lersch, M.; Tilset, M. *J. Am. Chem. Soc.* **2002**, *124*, 12116−12117.

Scheme 4



compete with THF, to some extent, for the platinum binding site. This is also true of neutral $[Ph_2BP_2]PtMe$(THF) complexes.[3a,c]

When the protonation reaction is monitored in benzene-d_6, CH_4, CH_3D, CH_2D_2, and CHD_3 are all observed by ^1H NMR. Even when a deuterated acid such as $[DN^iPr_2Et][BPh_4]$ is used, all of the mixed H/D isotopomers of methane, including CH_4, are observed. Since there is only 1 equiv of H^+ in the reaction mixture, 1 equiv each of CH_4 (where the acid is the proton source) and CH_3D (where benzene-d_6 is the proton source) might be expected. Observation of isotopic enrichment of the methane is indicative of the formation of an intermediate methane adduct that can be reversibly activated prior to dissociation.[5b,21] It is interesting to note that at −20 °C the ratio of deuterium-containing isotopomers of methane relative to CH_4 is greater, hinting that the relative rate of methane loss from the platinum methane adduct might be slowed considerably compared to the rate of H/D exchange at low temperature.

The observation that substoichiometric amounts of acid catalyze C−H activation is consistent with previous reports in which a catalytic amount of $B(C_6F_5)_3$ promotes C−H activation of solvent.[22] This extremely electrophilic Lewis acid has proven useful in abstracting a methide anion in a variety of other cases.[23] When either one or less than one equivalent of $B(C_6F_5)_3$ is added to **4**, the major product obtained is, indeed, the double benzene activation product **13**. The reaction rate is much faster than that of the Brønsted acid-assisted reaction. Such a rapid reaction at room temperature makes this reaction pathway very promising; even more encouraging is that the reaction proceeds with $B(C_6F_5)_3$ at temperatures *as low as −64 °C in toluene-d8*. Much like the acid-assisted case, all deuterium-containing isotopomers of methane (including CH_4) are observed in C_6D_6. It is difficult to exclude that the proton source for generating CH_4 in this reaction is adventitious water, similar to the result suggested by Goldberg.[6] As for the reaction with $[HNR_3][BPh_4]$, the ratio of deuterium-containing isotopomers of methane to CH_4 is greater at −64 °C than at room temperature. One can envision mechanisms similar to those suggested for the protonation route with this Lewis acid, with the exception that the first step in this case is methide abstraction rather than protonation (Scheme 5).

An estimate of the overall kinetic isotope effect for this reaction was obtained by performing the reaction with 1 equiv of $[HNR_3][BPh_4]$ in a 1:1 C_6H_6/C_6D_6 mixture. The resulting product was analyzed by ^1H NMR, and it was determined that 51% of the platinum phenyl groups in **13** were deuterated. This indicates that there is a negligible overall kinetic isotope effect ($k_H/k_D \approx 1.0$). Since there are likely multiple equilibria involved, the only conclusion that can be drawn from these data is that benzene C−H bond breaking is not significantly rate contributing.[24] We suspect that the rate-determining step is initial protonation based upon the acid concentration dependence of the overall reaction profile (i.e., the reaction slows when substoichiometric amounts of acid are added).

In contrast to complex **4**, bis(phosphino)borate complex **6** shows very different reactivity under both protonation and methide abstraction conditions in benzene. When **6** is exposed to either $B(C_6F_5)_3$ or $[HN^iPr_2Et][BPh_4]$ in benzene-d_6 at room temperature, the reaction is slower than that of **4** (∼24 h) and a complex mixture of products is formed. In addition, only CH_4 and CH_3D are observed under these conditions, indicating there is a smaller barrier to methane loss relative to the bis(pyrazolyl)borate complex. This difference can be attributed to the strong *trans* influence of the phosphine donors in **6**.

Complex **5** also shows limited reactivity with respect to C−H activation upon in situ protonation or methide

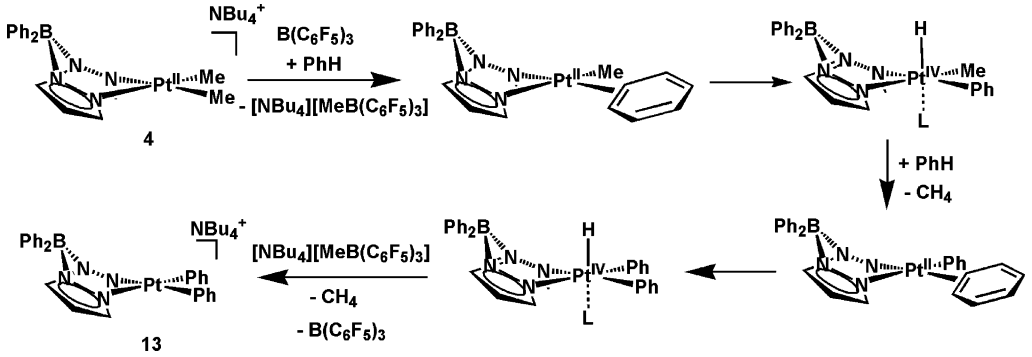
(21) Johannson, L.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 739−740.

(22) Reinhartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2001**, *20*, 1709−1712.

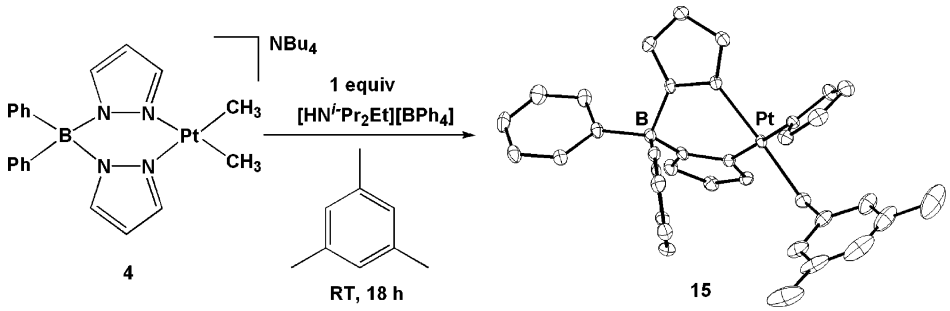
(23) (a) Hill, G. S.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 525−540. (b) Hill, G. S.; Rendina, L. M.; Puddephatt. R. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1809.

(24) Jones, W. D.; *Acc. Chem. Res.* **2003**, *36,* 140−146.

Scheme 5



Scheme 6



abstraction in benzene-d_6. Under both sets of reaction conditions, the reaction proceeds much more slowly than the $[Ph_2B(pz)_2]$ case. An ill-defined mixture of products forms, but no evidence for C−H activation is observed. CH_4 is the only methane byproduct that can be detected under these conditions.

Upon further investigation, we determined that $[Ph_2B(pz)_2]$ platinum complexes also show reactivity in the presence of acid and other aromatic substrates. Exposure of complex **4** to $[HN^iPr_2Et][BPh_4]$ in toluene and *p*-xylene gives rise to a mixture of products that includes η^1-bound benzylic species.[9b,25] In contrast, when **4** is stirred with $[HN^iPr_2Et][BPh_4]$ in mesitylene at room temperature for 18 h, the major product isolated is $[Ph_2B(pz)_2]Pt(CH_2C_6H_3(CH_3)_2)(pzH)$ (**15**) (Scheme 6).[26] This product provides an interesting example of C−H activation of an sp^3-hybridized C−H bond position, but the relatively low yield (∼50%) and the presence of a coordinated pyrazole ring establish that the formation of **15** is accompanied by undesired borate ligand degradation. The benzylic C−H activation process also occurs when the reaction is carried out in the presence of a donor ligand such as acetonitrile, THF, or pyridine, and an analogous product distribution is observed under such conditions. C−H activation was not observed with pentane, methylcyclohexane, or other nonaromatic hydrocarbons even at elevated temperatures, indicating that sp^3-hybridized C−H bond activation is operative only for more reactive benzylic C−H bonds in this system.

Concluding Remarks. Platinum bis(pyrazolyl)borate and 2,2′-bipyridylborate complexes have been prepared and compared to previously reported bis(phosphino)borate complexes in an effort to better understand the extent of charge delocalization in structurally different borato ligands. NMR and structural data for the anionic dimethyl complexes **4**, **5**, and **6** indicate that the phosphine donors of the $[Ph_2BP_2]$ ligand exert a stronger *trans* influence than the N-donor ligands; however, the $[Ph_2B(pz)_2]$ ligand has been shown through IR carbonyl stretching frequency data to be the most electron-releasing of the three ligands. This may be a result of the closer proximity of the borate unit to the metal center in complex **4** in comparison to complexes **5** and **6**.

The structural and electronic differences between these ligands appear to have a substantial effect on the reactivity of their platinum complexes with respect to C−H activation. While $[Ph_2BP_2]Pt(Me)(L)$ complexes are effective toward activation of aryl C−H bonds at elevated temperatures, analogous $[Ph_2B(pz)_2]$ complexes are completely unreactive under these conditions. $[[Ph_2B(pz)_2]Pt(Me)_2][NR_4]$ complexes, however, are highly active with respect to C−H activation of aryl C−H bonds upon protonation or methide abstraction in situ, in the absence of a donor ligand poison. These reactions are facile at temperatures well below 0 °C. Moreover, whereas coordination of a third pyrazolyl arm in the previously reported $\{\kappa^2\text{-}[Tp^*]PtMe_2\}^-$ system occurs upon methide abstraction, thereby leading to $\{\kappa^3\text{-}[Tp^*]Pt(Me)(H)(R)\}$ Pt(IV) products in the presence of alkane substrate, for the present bis(pyrazolyl)borate system only Pt(II) species are observed. Destabilization of the Pt(IV) intermediate due to the lack of a third donor chelate arm enables the double C−H activation process to proceed efficiently. We have also observed that structurally related $[Ph_2BP_2]$ and $[(4\text{-}BPh_3)bpy]$ complexes are protonated much more slowly under analogous conditions, and these systems appear to lead to very different (and ill-defined) product distributions.

(25) (a) Heyduk, A. F.; Driver, T. G.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2004**, *126* (46), 15034−15035. (b) Heyduk, A. F.; Zhong, A. H.; Labinger, J. A.; Bercaw, J. E. *Activation and Functionalization of C−H Bonds*; Goldberg, K., Goldman, A., Eds.; ACS Symposium Series No. 885; American Chemical Society: Washington, DC, 2004; pp 250−263.

(26) See Table 3 and the Supporting Information for crystallographic details.

Table 3. X-ray Diffraction Experimental Details for $[(Ph_2B(pz)_2)Pt(Me)_2][NBu_4]$ (4), $[((4\text{-}BPh_3)bpy)Pt(Me)_2][NBu_4]$ (5), $[(Ph_2B(pz)_2)Pt(C_6D_5)_2][NBu_4]$ (13), and $(Ph_2B(pz)_2)Pt(pzH)(CH_2C_6H_3(CH_3)_2)$ (15)

	4	5	13	15
chemical formula	$C_{36}H_{58}BN_5Pt$	$C_{46}H_{64}BN_3Pt$	$C_{46}H_{62}BN_5Pt$	$C_{33}H_{39}BN_4Pt$
fw	766.77	864.90	890.91	697.58
T (°C)	−177	−173	−177	−175
λ (Å)	0.71073	0.71073	0.71073	0.71073
a (Å)	9.7813(6)	9.057(1)	14.839(1)	8.2302(7)
b (Å)	23.218(1)	11.888(3)	17.029(1)	14.205(1)
c (Å)	15.7888(9)	20.348(6)	17.118(1)	14.603(1)
α (deg)	90	87.71(1)	90	67.300(1)
β (deg)	92.114(1)	84.19(2)	103.087(1)	74.056(1)
γ (deg)	90	70.316	90	82.565(1)
V (Å^3)	3583.2(4)	2052.2(8)	4213.0(6)	1513.9(2)
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Z	4	2	4	2
D_{calcd} (g/cm^3)	1.421	1.400	1.824	1.530
μ (cm^{-1})	3.947	3.453	3.368	4.662
R1, wR2[a] ($I > 2\sigma(I)$)	0.0299, 0.0721	0.0427, 0.0724	0.0306, 0.0509	0.0306, 0.0713

[a] $R1 = \Sigma||F_o| - |F_o||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)_2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Experimental Section

General Considerations. All syntheses reported were carried out using standard glovebox and Schlenk techniques in the absence of water and dioxygen, unless otherwise noted. Acetonitrile, benzene, dichloromethane, diethyl ether, petroleum ether, tetrahydrofuran, and toluene were degassed and dried by sparging with N_2 gas followed by passage through an activated alumina column. Pentane, mesitylene, and *p*-xylene were deoxygenated via sparging with N_2, dried over CaH, and distilled prior to use. Ethanol was deoxygenated via sparging with N_2, dried over NaOEt, and distilled prior to use. All solvents were stored over 3 Å molecular sieves. Deuterated benzene, chloroform, acetonitrile, acetone, and toluene were purchased from Cambridge Isotope Laboratories, Inc., degassed via repeated freeze−pump−thaw cycles, and dried over 3 Å molecular sieves. Nonhalogenated solvents were frequently tested using a standard solution of sodium benzophenone ketyl in tetrahydrofuran to confirm the absence of oxygen and moisture. $[Me_2Pt(\mu\text{-}SMe_2)]_2$,[27] $[HN^iPr_2Et][BPh_4]$,[3] $[HNEt_3][BPh_4]$,[28] $P(C_6F_5)_3$,[29] $[H(OEt_2)_2][B(C_6H_3(CF_3)_2)_4]$,[30] **3**,[3a] **6**,[3a,c,d] $(bpy)Pt(Me)_2$,[31] and 4-iodo-2,2′-bipyridine[15] were prepared using literature methods. $[DN^iPr_2Et][BPh_4]$ was prepared by acidifying an aqueous solution of N^iPr_2Et and $NaBPh_4$ with aqueous DCl. $B(C_6F_5)_3$ was recrystallized from pentane at −35 °C prior to use. All other chemicals were purchased from Aldrich, Strem, Alfa Aesar, or Lancaster and used without further purification. NMR spectra were recorded at ambient temperature, unless otherwise stated, on Varian Mercury 300 MHz, Varian Inova 500 MHz, and JEOL 400 MHz spectrometers. ^1H and ^{13}C NMR chemical shifts were referenced to residual solvent. ^{31}P NMR chemical shifts were referenced to 85% H_3PO_4. IR spectra were recorded on a Bio-Rad Excalibur FTS 3000 spectrometer controlled by Win-IR Pro software. Elemental analyses were performed by Desert Analytics, Tuscon, AZ. X-ray diffraction experiments were carried out by the Beckman Institute Crystallographic Facility on a Bruker Smart 1000 CCD diffractometer.

X-ray Crystallography Procedures. X-ray quality crystals were grown as indicated in the experimental procedures per individual complex. The crystals were mounted on a glass fiber with Paratone N oil. Structures were determined using direct methods with standard Fourier techniques using the Bruker AXS software package. Table 3 includes the X-ray diffraction experimental details, while the full crystallographic tables are included in the Supporting Information.

$[Ph_2B(pz)_2][Na(pzH)_2]$. A mixture of solid $NaBPh_4$ (8.908 g, 26.03 mmol) and solid pyrazole (22.731 g, 333.9 mmol) was heated to a melt and stirred in a 50 mL flask fitted with a Dean−Stark trap and condenser to collect benzene as it distilled from the reaction mixture. The reaction was heated at 80−100 °C until a nearly stoichiometric amount of benzene (4.22 mL, 1.81 equiv) was collected (3 h). The reaction was extracted with boiling hexanes (4 × 200 mL). The solids were then dried under reduced pressure to yield a white powder (8.0090 g, 67.1%). *Note: This is a variation of the literature method,*[14] *which is reported to provide [$Ph_2B(pz)_2$][Na]. The literature method replaces the extraction with a distillation to remove the excess pyrazole.*

$[Ph_2B(pz)_2][NBu_4]$ (1). Solid $[Ph_2B(pz)_2][Na(pzH)_2]$ (3.7573 g, 8.1982 mmol) was dissolved in dichloromethane (80 mL) along with NBu_4Br (2.6733 g, 8.2924 mmol). The hazy solution was stirred for 10 min and filtered over Celite on a sintered glass frit. The filtrate was concentrated by rotary evaporation. Hexanes (80 mL) was added and stirred vigorously, forming white solids. The solids were collected by filtration and washed with toluene (3 × 20 mL) and hexanes (2 × 20 mL). The resulting solids were suspended in toluene (20 mL) and stirred for 5 min, then collected by filtration and washed with hexanes (2 × 20 mL). The resulting white solids were dried under reduced pressure (4.2889 g, 96.6%). ^1H NMR (300 MHz acetone-d_6): δ 7.40 (d, 2H, $^3J_{H-H}$ = 1.8 Hz, pz-3H), 7.21 (m, 4H, *o*-Ph), 7.15 (d, 2H, $^3J_{H-H}$ = 2.4 Hz, pz-5H), 6.97−7.05 (m, 6H, *m,p*-Ph), 5.95 (dd, 2H, $^3J_{H-H}$ = 1.8, 2.1 Hz, pz-4H), 3.70 (m, 8H, NBu_4), 1.77 (m, 8H, NBu_4), 1.40 (m, 8H, NBu_4), 0.97 (t, 12H, $^3J_{H-H}$ = 7.8 Hz, NBu_4).

$[(4\text{-}BPh_3)bpy][NBu_4]$ (2). Solid 4-iodo-2,2′-bipyridine (1.3330 g, 4.72 mmol) was dissolved in Et_2O (50 mL) and cooled to −78 °C with stirring (upon cooling, the mixture becomes heterogeneous). To this suspension was added ^iPrMgCl (2.36 mL, 2.0 M in Et_2O, 4.72 mmol) dropwise over 10 min. The suspension became deep red upon addition. After stirring for 1 h, BPh_3 (1.1413 g, 4.72 mmol) in THF (10 mL) was added and the resulting solution was allowed to warm to room temperature over 3 h. The resulting red solids were collected on a sintered glass frit and washed with Et_2O (3 × 10 mL). The solids were taken up in CH_2Cl_2 (20 mL), and solid NBu_4Br (1.5216 g, 4.72 mmol) was added. 40 mL of H_2O was added

(27) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643−1648.
(28) Rodima, T.; Kaljurand, I.; Pihl, A.; Maeemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2002**, *67* (6), 1873−1881.
(29) Kemmitt, R. D. W.; Nichols, D. I.; Peacock, R. D. *J. Am. Chem. Soc. A* **1968**, 2149−2152.
(30) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.
(31) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 444−449.

and the mixture was stirred vigorously for 30 min. The CH_2Cl_2 layer was then collected and washed with additional H_2O (2 × 20 mL). The combined CH_2Cl_2 layers were collected, dried with Na_2SO_4, and evaporated in vacuo. The remaining solids were recrystallized via vapor diffusion of petroleum ether into THF to yield white needles (0.8187 g, 1.28 mmol, 27%). ^{1}H NMR (300 MHz, acetone-d_6): δ 8.65 (br m, 1H, 3-bpy), 8.41−8.45 (m, 2H, 6,3′-bpy), 8.19 (d, 1H, $^3J_{H-H}$ = 5.1 Hz, 6′-bpy), 7.73 (ddd, 1H, $^3J_{H-H}$ = 8.4, 7.2, 2.1 Hz, 4′-bpy), 7.35 (m, 7H, *o*-Ph + 5-bpy), 7.18 (m, 1H, 4′-bpy), 6.96 (t, 6H, $^3J_{H-H}$ = 7.5 Hz, *m*-Ph), 6.81 (m, 3H, $^3J_{H-H}$ = 6.9 Hz, *p*-Ph), 3.44 (m, 8H, NBu_4), 1.82 (m, 8H, NBu_4), 1.42 (m, 8H, NBu_4), 0.98 (t, 12H, $^3J_{H-H}$ = 7.2 Hz, NBu_4). ^{13}C NMR (75.409 MHz, acetone-d_6): δ 160.5, 149.9, 137.5, 137.4, 133.8, 131.9, 130.3, 126.8, 123.4, 123.2, 121.9, 59.8 (NBu_4), 24.9 (NBu_4), 20.8 (NBu_4), 14.4 (NBu_4). Anal. Calcd for $C_{44}H_{58}BN_3$: C, 82.60; H, 9.14; N, 6.57. Found: C, 82.04; H, 9.24; N, 6.81.

[(Ph$_2$B(pz)$_2$)Pt(Me)$_2$][NBu$_4$] (4). Solid $[Me_2Pt(\mu\text{-}SMe_2)]_2$ (0.3775 g, 1.215 mmol) and solid **1** (0.6573 g, 1.213 mmol) were suspended in tetrahydrofuran (10 mL). The resulting cloudy white mixture was stirred for 3 h, then dried in vacuo. The resulting solids were collected on a sintered glass frit and washed with petroleum ether (3 × 5 mL) and benzene (3 × 5 mL). The off-white solids were dried further in vacuo to yield analytically pure **4** (0.7091 g, 76.1%). Crystals for X-ray diffraction were grown via vapor diffusion of petroleum ether into tetrahydrofuran. ^{1}H NMR (300 MHz acetone-d_6): δ 7.76 (m, 2H, $^3J_{Pt-H}$ = 5.4 Hz, pz-3H), 7.12 (dd, 2H, $^3J_{H-H}$ = 2.3, 0.9 Hz, *p*-Ph), 7.08 (d, 2H, $^3J_{H-H}$ = 1.2 Hz, pz-5H), 7.06 (m, 4H, *o*-Ph), 6.83 (dd, 4H, $^3J_{H-H}$ = 6.9, 3.0 Hz, *m*-Ph), 6.05 (t, 2H, $^3J_{H-H}$ = 1.8 Hz, pz-4H), 3.45 (m, 8H, NBu_4), 1.80 (m, 8H, NBu_4), 1.40 (m, 8H, NBu_4), 0.97 (t, 12H, $^3J_{H-H}$ = 7.8 Hz, NBu_4), 0.36 (s, 6H, $^2J_{Pt-H}$ = 83 Hz, Me). ^{13}C NMR (75.409 MHz, acetone-d_6): δ 138.0, 135.6, 134.7, 126.9, 125.7, 103.0, 59.2 (s, NBu_4), 24.5 (s, NBu_4), 20.3 (s, NBu_4), 14.0 (s, NBu_4), −18.9 (s, Pt-Me). Anal. Calcd for $C_{36}H_{58}BN_5Pt$: C, 56.39; H, 7.62; N, 9.13. Found: C, 56.68; H, 7.78; N, 9.28.

[((4-BPh$_3$)bpy)Pt(Me)$_2$][NBu$_4$] (5). Solid $[Me_2Pt(\mu\text{-}SMe_2)]_2$ (0.0267 g, 0.0466 mmol) was dissolved in THF (3 mL). To this stirring solution was added **2** (0.0596 g, 0.0933 mmol) in THF (5 mL), and the mixture was allowed to stir for 1 h. The resulting red solution was dried in vacuo and the remaining solids were washed with Et_2O (3 × 5 mL) to afford analytically pure product as a red-orange powder (0.0804 g, 0.0930 mmol, 99%). ^{1}H NMR (300 MHz, acetone-d_6): δ 9.11 (d, 1H, $^3J_{H-H}$ = 7.5 Hz, $^3J_{Pt-H}$ = 24 Hz, 6-bpy), 8.71 (d, 1H, $^3J_{H-H}$ = 5.4 Hz, $^3J_{Pt-H}$ = 21 Hz, 6′-bpy), 8.24 (br s, 1H, 3-bpy), 8.13 (ddd, 1H, $^3J_{H-H}$ = 9.6, 8.1, 0.3 Hz, 5′-bpy), 7.79 (d, 1H, $^3J_{H-H}$ = 7.8 Hz, 3′-bpy), 7.58 (br s, 1H, 5-bpy), 7.48 (m, 1H, 4′-bpy), 7.31 (br s, 6H, *o*-Ph), 7.01 (t, 6H, $^3J_{H-H}$ = 5.4 Hz, *m*-Ph), 6.87 (t, 3H, $^3J_{H-H}$ = 7.5 Hz, *p*-Ph), 3.41 (m, 8H, NBu_4), 1.79 (m, 8H, NBu_4), 1.39 (m, 8H, NBu_4), 0.96 (t, 12H, $^3J_{H-H}$ = 7.5 Hz, NBu_4), 0.92 (3H, $^2J_{Pt-H}$ = 86 Hz, Pt-Me), 0.82 (3H, $^2J_{Pt-H}$ = 85 Hz, Pt-Me). ^{13}C NMR (75.409 MHz, acetone-d_6): δ 160.3, 159.7, 153.3, 147.3, 143.7, 137.6, 137.0, 136.0, 131.4, 127.1, 123.7, 123.2, 59.5 (NBu_4), 24.8 (NBu_4), 20.7 (NBu_4), 14.4 (NBu_4), −15.0 (Me), −15.3 (Me). Anal. Calcd for $C_{46}H_{64}BN_3Pt$: C, 63.88; H, 7.46; N, 4.86. Found: C, 63.91; H, 7.80; N, 4.65.

(Ph$_2$B(pz)$_2$)Pt(Me)(NCCH$_3$) (7). Solid **4** (0.0595 g, 0.0775 mmol) and solid $[HN^iPr_2Et][BPh_4]$ (0.0343 g, 0.0764 mmol) were combined in a mixture of tetrahydrofuran (2 mL) and acetonitrile (3 drops). The resulting clear solution was stirred for 2 h at room temperature and then dried in vacuo. The remaining solids were extracted with benzene and filtered through Celite to remove $[NBu_4][BPh_4]$. The filtrate was dried in vacuo to yield analytically pure product as an off-white solid (60%). ^{1}H NMR (300 MHz benzene-d_6): δ 7.77 (d, 1H, $^3J_{H-H}$ = 2.1 Hz, $^3J_{Pt-H}$ = 25 Hz, pz-3′H), 7.59 (d, 1H, $^3J_{H-H}$ = 2.4 Hz, pz-3H), 7.49 (d, 1H, $^3J_{H-H}$ = 2.1 Hz, pz-5′H), 7.38 (d, 1H, $^3J_{H-H}$ = 2.7 Hz, pz-5H), 7.27 (m, 10H, Ph), 6.14 (t, 1H, $^3J_{H-H}$ = 2.1 Hz, pz-4H), 5.88 (m, 1H, $^3J_{H-H}$ = 2.1 Hz, pz-4′H), 1.09 (s, 3H, $^2J_{Pt-H}$ = 77.2 Hz, Pt-Me), 0.24 (s, 3H, $^4J_{Pt-H}$ = 6.9 Hz, NCC*H*$_3$). ^{13}C NMR (75.409 MHz, benzene-d_6): δ 140.8, 139.4, 138.5, 137.2, 135.1, 127.9, 127.1, 126.0, 104.9, 104.6, 30.7 (N*C*CH$_3$), 1.56 (NC*C*H$_3$), −18.8 (Pt-Me). ES-MS (*m*/*z*, negative): 549 (M − H$^+$). Anal. Calcd for $C_{21}H_{22}BN_5Pt$: C, 45.83; H, 4.03; N, 12.73. Found: C, 46.64; H, 3.99; N, 12.02.

(Ph$_2$B(pz)$_2$)Pt(Me)(CO) (8). Solid **4** (0.0480 g, 0.0625 mmol) was dissolved in tetrahydrofuran (2 mL) under N_2 in a 25 mL Schlenk flask equipped with a rubber septum. CO was bubbled through the solution using a long needle for 2 min. To this was added a solution of $[HN^iPr_2Et][BPh_4]$ (0.278 g, 0.0619 mmol) in tetrahydrofuran (3 mL) via syringe. The solution immediately turned yellow upon addition of the ammonium salt, but slowly faded to a cloudy white slurry over a period of 5 min. Solvent was removed in vacuo. The resulting solids were extracted with benzene (3 × 2 mL) and filtered through Celite. Solvent was removed from the filtrate to yield white solids (85%). ^{1}H NMR (300 MHz benzene-d_6): δ 7.44 (m, 2H, pz-3H), 7.33 (m, 2H, pz-5H), 7.24 (m, 4H, *o*-Ph), 7.23 (m, 4H, *m*-Ph), 7.07 (m, 2H, *p*-Ph), 5.87 (m, 1H, $^3J_{H-H}$ = 2.1 Hz, pz-4H), 5.77 (t, 1H, $^3J_{H-H}$ = 1.5 Hz, pz-4H), 0.79 (s, 3H, $^2J_{Pt-H}$ = 70.2 Hz, Pt-Me). IR (cm^{-1}): 2087. Anal. Calcd for $C_{20}H_{19}BN_4OPt$: C, 44.71; H, 3.56; N, 10.43. Found: C, 46.59; H, 3.58; N, 11.02. Samples of this species repeatedly analyzed high in carbon content.

(Ph$_2$B(pz)$_2$)Pt(Me)(P(C$_6$F$_5$)$_3$) (9). Solid **4** (0.0347 g, 0.0452 mmol), solid $[HN^iPr_2Et][BPh_4]$ (0.0271 g, 0.0603 mmol), and solid $P(C_6F_5)_3$ (0.0449 g, 0.0844 mmol) were suspended in tetrahydrofuran (2 mL) and stirred for 30 min. The solvent was removed from the resulting mixture in vacuo. The remaining solids were extracted with benzene/petroleum ether (10:1) and filtered through Celite. These extracts were dried in vacuo, and the resulting off-white solids were extracted into petroleum ether and recrystallized at −35 °C. The resulting white solids were washed with cold petroleum ether (1 mL) to yield analytically pure product (42.4%). ^{1}H NMR (300 MHz, benzene-d_6): δ 7.47 (d, 1H, $^3J_{H-H}$ = 2.1 Hz, pz-3H), 7.42 (d, 2H, $^3J_{H-H}$ = 2.1 Hz, pz-3H, pz-5H), 7.32 (m, 4H, *o*-Ph), 7.21−7.27 (m, 6H, *m,p*-Ph), 6.50 (d, 1H, $^3J_{H-H}$ = 1.8 Hz, pz-5H), 5.78 (m, 1H, pz-4H), 5.53 (t, 1H, $^3J_{H-H}$ = 2.4 Hz, pz-4H), 0.36 (d, 3H, $^2J_{Pt-H}$ = 72 Hz, $^3J_{P-H}$ = 6.0 Hz, Pt-Me). ^{31}P NMR (121.368 MHz, benzene-d_6): δ −36.21 (s, $^1J_{Pt-P}$ = 5800 Hz). ^{13}C NMR (75.409 MHz, benzene-d_6): δ 150.0 (m, $P(C_6F_5)_3$), 146.6 (m, $P(C_6F_5)_3$), 142.8 (m, $P(C_6F_5)_3$), 140.1, 139.8, 139.3, 138.9, 137.5, 133.4, 127.1, 105.4, 104.8, −14.9 (Pt-Me). Anal. Calcd for $C_{37}H_{19}BF_{15}N_4PPt$: C, 42.67; H, 1.84; N. 5.38. Found: C, 42.50; H, 2.07; N, 5.06.

((4-BPh$_3$)bpy)Pt(Me)(NCCH$_3$) (10). Solid **5** (0.0481 g, 0.0557 mmol) was stirred in THF with $[HNEt_3][BPh_4]$ (0.0234 g, 0.0557 mmol). To this mixture was added 3 drops of acetonitrile. After 1 h, the solvent was evaporated in vacuo. The resulting solids were extracted into benzene (2 × 10 mL). These extracts were dried in vacuo to yield both isomers in a 2.8:1 ratio (0.0286 g, 0.0440 mmol, 79%). ^{1}H NMR (300 MHz, acetone-d_6): δ 8.91 (d, 1H, $^3J_{H-H}$ = 8.7 Hz, 6-bpy), 8.41 (d, 1H, $^3J_{H-H}$ = 5.4 Hz, 6′-bpy), 8.31 (br s, 1H, 3-bpy), 8.21 (ddd, 1H, $^3J_{H-H}$ = 8.4, 3.0, 1.2 Hz, 4′-bpy), 7.92 (d, 1H, $^3J_{H-H}$ = 9.0 Hz, 3′-bpy), 7.66 (m, 2H, 5-bpy, 5′-bpy), 7.32 (m, 6H, *o*-Ph), 7.03 (t, 6H, $^3J_{H-H}$ = 7.2 Hz, *m*-Ph), 6.90 (m, 3H, $^3J_{H-H}$ = 7.2 Hz, *p*-Ph), 2.79 (major)/2.84 (minor) (s, 3H, NCCH$_3$, $^4J_{Pt-H}$ = 25 Hz), 0.94 (major)/0.86 (minor) (s, 3H, Pt-Me, $^2J_{Pt-H}$ = 73 Hz). ^{13}C NMR for major isomer (75.409 MHz, acetone-d_6): δ 161.7, 160.5 (br), 156.4, 148.8, 145.8, 141.3, 136.9, 135.9, 132.1, 128.1, 127.5, 124.1, 123.5, 41.4, 4.5, −14.0 (Me). Anal. Calcd for $C_{31}H_{28}BN_3Pt$: C, 57.42; H, 4.35; N. 6.48. Found: C, 57.17; H, 4.13; N, 5.99.

((4-BPh$_3$)bpy)Pt(Me)(CO) (11). Solid **5** (0.0356 g, 0.0412 mmol) was stirred in THF with $[HNEt_3][BPh_4]$ (0.0173 g, 0.0412 mmol). This mixture was placed under a blanket of CO and stirred for 1 h. The solvent was evaporated in vacuo, and the resulting solids were extracted into benzene (2 × 10 mL).

These extracts were dried in vacuo to yield both isomers in a 2.8:1 ratio (0.0227 g, 0.0357 mmol, 87%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.65 (d, 1H, $^3J_{H-H} = 5.7$ Hz, $^3J_{Pt-H} = 21$ Hz, 6-bpy), 8.52 (br s, 1H, 3-bpy), 8.32 (d, 1H, $^3J_{H-H} = 5.7$ Hz, $^3J_{Pt-H} = 33$ Hz, 6′-bpy), 8.12 (ddd, 1H, $^3J_{H-H} = 8.3$, 8.3, 1.5 Hz 4′-bpy), 8.01 (d, 1H, $^3J_{H-H} = 8.4$ Hz, 3′-bpy), 7.56 (m, 1H, 5-bpy), 7.32 (m, 7H, *o*-Ph, 5′-bpy), 7.13 (t, 6H, $^3J_{H-H} = 7.2$ Hz, *m*-Ph), 7.00 (m, 3H, $^3J_{H-H} = 7.2$ Hz, *p*-Ph), (major)/(minor) 1.27/1.19 (s, 3H, Pt-Me, $^2J_{Pt-H} = 69$ Hz). ^{13}C NMR for major isomer (75.409 MHz, CD_2Cl_2): δ 192.0, 160.0 (br), 151.1, 143.1, 142.8, 141.5, 135.8, 135.4, 134.7, 131.6, 128.1, 127.1, 123.9, 123.7, −12.3 (Me). IR (CH_2Cl_2): 2098 cm^{-1}. Anal. Calcd for $C_{30}H_{25}BN_2OPt$: C, 56.71; H, 3.97; N. 4.41. Found: C, 59.70; H, 4.02; N, 4.98. Samples of this species repeatedly analyzed high in carbon content.

[(bpy)Pt(Me)(CO)][BPh$_4$] (12). Solid (bpy)Pt(Me)$_2$ (0.0260 g, 0.0682 mmol) was stirred in THF, and CO was bubbled through the solution for 20 min. To this was added a solution of [HNEt$_3$][BPh$_4$] (0.0287 g, 0.0682 mmol) in THF. This mixture was allowed to stir under a blanket of CO for 1 h. The solvent was evaporated in vacuo, and the resulting solids were washed with benzene (2 × 10 mL) and dried in vacuo to yield the yellow product (∼80%). Spectroscopic data were similar to those reported previously for [(bpy)Pt(Me)(CO)]$^+$ cations.[10b] ^{1}H NMR (300 MHz, acetone-d_6): δ 9.07 (d, 1H, $^3J_{H-H} = 9.0$ Hz, 6-bpy), 8.98 (d, 1H, $^3J_{H-H} = 7.5$ Hz, 6′-bpy), 8.66 (d, 1H, $^3J_{H-H} = 5.7$ Hz, 3-bpy), 8.48 (m, 2H, 4′-bpy, 3′-bpy), 8.40 (m, 1H, 4′-bpy), 7.91 (m, 1H, 5-bpy), 7.40 (m, 1H, 5′-bpy), 7.33 (m, 8H, BPh$_4$), 6.92 (t, 8H, $^3J_{H-H} = 7.8$ Hz, BPh$_4$), 6.77 (t, 4H, $^3J_{H-H} = 6.9$ Hz, BPh$_4$), 1.28 (s, 3H, Pt-Me, $^2J_{Pt-H} = 68$ Hz). ES-MS (*m*/*z*): 394 [M]$^+$. IR (CH_2Cl_2): 2107 cm^{-1}.

Generation of [(Ph$_2$B(pz)$_2$)Pt(C$_6$D$_5$)$_2$][NBu$_4$] (13). Solid **4** (0.0345 g, 0.0449 mmol) and solid [HN^{i}Pr$_2$Et][BPh$_4$] (0.0200 g, 0.0045 mmol) were stirred in benzene-d_6 (2 mL) for 30 min. The resulting reaction mixture was filtered through Celite. Upon standing for 1 h, solids precipitated. These off-white solids were collected and washed with petroleum ether (3 × 2 mL) and benzene (2 × 2 mL). The remaining solids were dried further in vacuo to yield clean product (87% yield was detected by NMR using a ferrocene standard; however, only 40% was isolated). Crystals were grown for X-ray diffraction by dissolving product in benzene and layering with petroleum ether at room temperature. ^{1}H NMR (300 MHz, benzene-d_6): δ 7.58 (d, 2H, $^3J_{H-H} = 2.7$ Hz, pz-3H), 7.19 (m, 4H, $^3J_{H-H} = 6.6$ Hz, *o*-BPh), 7.40 (t, 4H, $^3J_{H-H} = 7.2$ Hz, *m*-BPh), 7.31 (m, 2H, *p*-BPh), 7.28 (d, 2H, $^3J_{H-H} = 1.2$ Hz, pz-5H), 5.92 (t, 2H, $^3J_{H-H} = 2.1$ Hz, pz-4H), 1.73 (br m, 8H, NBu$_4$), 0.89 (m, 8H, NBu$_4$), 0.77 (t, 12H, $^3J_{H-H} = 7.8$ Hz, NBu$_4$), 0.66 (m, 8H, NBu$_4$). ^{13}C NMR (75.409 MHz, acetone-d_6): δ 150 (br), 142 (br), 141.3, 140 (br), 136.4 (br), 135.6, 134.9, 127.1, 126.1, 103.0, 59.2 (NBu$_4$), 24.4 (NBu$_4$), 20.4 (NBu$_4$), 13.9 (NBu$_4$). ES-MS(−) (*m*/*z*): 648 [M]. Anal. Calcd for $C_{46}H_{52}D_{10}BN_5Pt$: C, 61.32; H, 8.05; N, 7.77. Found: C, 61.66; H, 6.84; N, 8.13. Alternatively, **5** can be prepared by (a) using 0.1 equiv [HN^{i}Pr$_2$Et][BPh$_4$], but reaction time must be lengthened from 30 min to 48 h; (b) using [H(OEt$_2$)$_2$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$] in place of [HN^{i}Pr$_2$Et][BPh$_4$]; (c) using B(C$_6$F$_5$)$_3$ in place of [HN^{i}Pr$_2$Et][BPh$_4$]. Using 0.05 equiv of B(C$_6$F$_5$)$_3$ and using 1.0 equiv results in nearly identical reaction time and yield.

(Ph$_2$B(pz)$_2$)Pt(C$_6$D$_5$)(NCCH$_3$) (14). Solid **4** (0.0366 g, 0.0477 mmol) and solid [HN^{i}Pr$_2$Et][BPh$_4$] (0.0223 g, 0.0496 mmol) were dissolved in benzene-d_6 (2 mL). Three drops of acetonitrile were added, and the mixture was stirred for 1 h. The resulting solution was filtered through Celite, and the filtrate was dried in vacuo. The resulting solids were extracted into petroleum ether and dried in vacuo to yield spectroscopically pure product as an off-white solid (∼80%). ^{1}H NMR (300 MHz, benzene-d_6): δ 7.58 (d, 1H, $^3J_{H-H} = 2.4$ Hz, pz-3H), 7.45 (m, 2H, pz-3H, pz-5H), 7.28−7.36 (m, 5H, *o*-Ph, pz-5H), 7.18 (t, 4H, $^3J_{H-H} = 7.2$ Hz, *m*-Ph), 7.06 (t, 2H, $^3J_{H-H} = 9.3$ Hz, *p*-Ph), 6.09 (t, 1H, $^3J_{H-H} = 2.1$ Hz, pz-4H), 5.63 (t, 1H, $^3J_{H-H} = 2.2$ Hz, pz-4H), −0.02 (s, 3H, $^4J_{Pt-H} = 7.2$ Hz, Pt-NCCH$_3$). ^{13}C NMR (75.409 MHz, benzene-d_6): δ 144.2, 139.9, 138.5, 138.2, 137.7, 137.2, 135.0, 127.7, 127.3, 124.2, 104.8 (pz-4), 30.8 (N*C*CH$_3$), 1.3 (NC*C*H$_3$). Anal. Calcd for $C_{26}H_{19}D_5BN_5Pt$: C, 50.58; H, 4.73; N, 11.34. Found: C, 50.72; H, 4.16; N, 11.17.

Reaction of Complex 4 with [HNEt$_3$][BPh$_4$] in Toluene and *p*-Xylene. Solid **4** (0.0657 g, 0.0885 mmol) was stirred in toluene (or *p*-xylene) (10 mL) for 3 h with [HN^{i}PrEt$_2$][BPh$_4$] (0.0398 g, 0.0886 mmol). The resulting solution was filtered through Celite, and the filtrate was then dried in vacuo. Solution NMR data revealed the following diagnostic signals: *toluene*: ^{1}H NMR (300 MHz, benzene-d_6): δ 3.24 (s, $^2J_{Pt-H} = 99$ Hz, benzylic activation), 2.36, 2.31, 2.24 (aryl activation products, *o*, *p*, *m*, respectively); *p*-xylene: ^{1}H NMR (300 MHz, acetone-d_6): δ 2.90 (s, $^2J_{Pt-H} = 104$ Hz, benzylic activation).

(Ph$_2$B(pz)$_2$)Pt(pzH)(CH$_2$C$_6$H$_3$(CH$_3$)$_2$) (15). Solid **4** (0.0115 g, 0.0149 mmol) was stirred in mesitylene (2 mL) for 18 h with [HNEt$_3$][BPh$_4$] (0.0066 g, 0.0153 mmol). Volatiles were removed from the resulting solution in vacuo. The remaining solids were extracted with benzene (3 × 1 mL) and filtered through Celite. The filtrate was dried in vacuo to yield **15** as a white solid (∼50%). Crystals of **15** suitable for X-ray diffraction were obtained by vapor diffusion of petroleum ether into a concentrated benzene solution. ^{1}H NMR (300 MHz, benzene-d_6): δ 12.5 (br, 1H), 7.79 (d, 1H, $^3J_{H-H} = 1.8$ Hz, pz-3H), 7.58 (d, 1H, $^3J_{H-H} = 2.4$ Hz, pz-3H), 7.49 (d, $^3J_{H-H} = 2.1$ Hz, 1H, pz-3H), 7.07−7.26 (m, 10H, BPh), 6.88 (m, 1H, Mes), 6.65 (m, 1H, pz-5H), 6.58 (m, 1H, pz-5H), 6.43 (m, 2H, Mes), 6.03 (m, 1H, pz-5H), 5.96 (t, 1H, $^3J_{H-H} = 2.1$ Hz, pz-4H), 5.87 (t, $^3J_{H-H} = 2.1$ Hz, 1H, pz-4H), 5.36 (m, 1H, pz-4H), 3.07 (s, 2H, C*H*$_2$, $^2J_{Pt-H} = 104.9$ Hz), 2.13 (s, 6H, CH$_3$). XRD analysis confirmed the identity of this degradation product. Further characterization of this material was not pursued.

Acknowledgment. The authors acknowledge J. Christopher Thomas for insightful discussions. BP (Methane Conversion Cooperative) and the NSF (CHE-01232216) are acknowledged for funding. Larry Henling and Theodore A. Betley are acknowledged for crystallographic assistance.

Supporting Information Available: Crystallographic data for **4**, **5**, **13**, and **15** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050538J