# Stoichiometric and Catalytic Arene Activations by Platinum Complexes Containing Bidentate Monoanionic Nitrogen-Based Ligands

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New platinum complexes based on incorporation of the bidentate, monoanionic 2-(2′-pyridyl)indolide (PyInd) ligand, or two closely related ligands, have been prepared. Reaction of the dimethyl complex K[(PyInd)PtMe$_2$] (K[**2a**]) in benzene at 150 °C produces the diphenyl species K[(PyInd)PtPh$_2$] (K[**3a**]), a transformation that appears to proceed via direct oxidative addition of benzene to the 16-electon Pt(II) center. Complex K[**2a**] also undergoes oxidative addition of Me$_3$SiOTf (OTf = triflate) to give (PyInd)-Pt(SiMe$_3$)Me$_2$ (**4**), a rare five-coordinate Pt(IV)-silyl species. Additionally, reactions that involve stereoselective formation of products of the type (PyInd)Pt(X)(L), including the structurally characterized complexes (PyInd)Pt(Ph)(MeCN) (**6**) and (PyInd)Pt(Cl)(C$_2$H$_4$) (**7**), have been observed. These results indicate that the sites trans to the pyridinyl and indolyl fragments of the PyInd ligand are electronically differentiated. Studies of catalytic reactions that presumably proceed via the 14-electron fragment (PyInd)PtR reveal moderate activities for the hydroarylation of norbornene by benzene and other arenes at 140 °C.

## Introduction

Platinum complexes that contain nitrogen-based ligands have long been known to participate in a variety of stoichiometric and catalytic transformations of organic substrates.[1] Previous results from several research groups indicate that such nitrogen-ligated Pt species exhibit reactivity patterns not commonly observed for softer ancillary ligands such as phosphines[2] or thioethers.[3] In studies of Pt(II) complexes with bipyridine-based ligands, for example, it was demonstrated that oxidative additions of group 14 halides occur quite readily,[4] while analogous bisphosphine-Pt(II) complexes are generally less reactive in this context.[5] These and related results have been attributed to the energetic disparity between the soft Pt(II) center and the hard nitrogen-donor ligand set, which is thought to enable facile bond activation reactions that produce the harder Pt(IV) center.[1a,6] More recently, several research groups have found that Pt complexes of chelating, nitrogen-based ligands participate in oxidative additions of hydrocarbon C−H bonds.[7] This work, inspired by Shilov's report of catalytic methane oxidation,[8] has generated a great deal of interest given its potential to provide practical hydrocarbon activation systems.[9] Along these lines, (2,2′-bipyrimidine)PtCl$_2$ was reported to catalyze the conversion of methane to methyl bisulfate, although commercial application of this reaction is impeded by the harsh reaction conditions that include fuming sulfuric acid as the solvent.[10] Furthermore, Hartwig and co-workers have utilized Pt(IV) tris-pyrazolyl borate complexes as catalysts for the dehydrogenative coupling of benzene and triethylsilane, a reaction that may proceed via a Pt(II) intermediate capable of activating both C−H and Si−H bonds.[11] These results provide an impetus for the development and study of novel nitrogen-based ligands for Pt.

Studies of stoichiometric hydrocarbon activations by Pt(II) have established that 14-electron species of the type (NN)PtR, which can be neutral or cationic depending on the charge on the nitrogen-based ligand, often serve as key intermediates that

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(1) (a) Rendina, L. M.; Puddephatt, R. J. *Chem. Rev.* **1997**, *97*, 1735. (b) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497.

(2) Monaghan, P. K.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1988**, 595.

(3) Kuyper, J.; van der Laan, R.; Jenneaus, F.; Vrieze, K. *Trans. Met. Chem.* **1976**, *1*, 199.

(4) (a) Jawad, J. K.; Puddephatt, R. J. *J. Organomet. Chem.* **1976**, *117*, 297. (b) Jawad, J. K.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1466. (c) Kuyper, J. *Inorg. Chem.* **1977**, *16*, 2171. (d) Kuyper, J. *Inorg. Chem.* **1978**, *17*, 77. (e) Levy, C. J.; Puddephatt, R. J.; Vittal, J. J. *Organometallics* **1994**, *13*, 1559. (f) Levy, C. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 2108. (g) Levy, C. J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 10127. (h) Baar, C. R.; Jenkins, H. A.; Vittal, J. J.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 2805.

(5) (a) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 705. (b) Ruddick, J. D.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 2801. (c) Ruddick, J. D.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 2969. (d) Kistner, C. R.; Hutchinson, J. H.; Doyle, J. R.; Storlie, J. C. *Inorg. Chem.* **1963**, *2*, 1255. (e) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1974**, *65*, 275. (f) Clark, H. C.; Ruddick, J. D. *Inorg. Chem.* **1970**, *9*, 2556.

(6) van Asselt, R.; Rijnberg, E.; Elsevier, C. J. *Organometallics* **1994**, *13*, 706.

(7) For a recent comprehensive review, see: Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471.

(8) (a) Gol'dshleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Russ. J. Phys. Chem.* **1969**, *43*, 1222. (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2181.

(9) (a) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (b) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (c) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (d) Fekl, U.; Goldberg, K. I. *Adv. Inorg. Chem.* **2003**, *54*, 259.

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

(11) Tsukada, N.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 5022.

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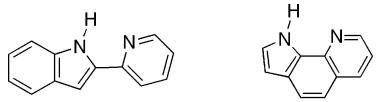



**Figure 1.** Precursors to unsymmetrical monoanionic nitrogen-based ligands.

oxidatively add C−H bonds.[12] For example, Goldberg and co-workers observed stoichiometric dehydrogenation of alkanes by the (nacnac)PtMe (nacnac$^-$ = [{2,6-$^i$Pr$_2$C$_6$H$_3$)NC(CH$_3$)}$_2$CH]$^-$) fragment, generated from a five-coordinate Pt(IV) complex (nacnac)PtMe$_3$ via the reductive elimination of ethane.[13] Similar chemistry was reported by Caulton and co-workers, who utilized a hemilabile, tridentate pyridinophane ligand to support reactive [(NN)PtR]$^+$ intermediates.[14] In search of a catalytic C−H activation system based on a neutral (NN)PtR fragment, we initiated a study of bidentate nitrogen-based ligands that contain localized neutral and anionic donors, exemplified by the deprotonated 2-(2′-pyridyl)indole (PyInd, Figure 1).[15] Two recent reports demonstrate that Pt complexes of bipyridine-derived ligands readily activate arene C−H bonds, and the similarity of the PyInd framework to that of 2,2′-bipyridine suggests that its Pt complexes will also engage in the oxidative addition of hydrocarbons.[16] It was envisioned that this activation step could be coupled with subsequent olefin insertion and reductive elimination steps to result in catalytic olefin functionalization.[17,18] Indeed, Pt complexes containing 2-(2′-pyridyl)-indole[19] and related iminopyrrole[20] ligands have already been shown to promote catalytic and stoichiometric transformations involving arenes.

Herein we report the synthesis of neutral and anionic Pt(II) complexes containing PyInd and related ligands and describe their stoichiometric and catalytic reactivity toward arenes.[21] The ability of the Pt center to react with C−H bonds is demonstrated by the activation of 2 equiv of benzene by a Pt-dimethyl complex. In addition, the stabilization of high oxidation state Pt centers by the PyInd ligand is reflected in the formation of a five-coordinate Pt(IV)-silyl complex from a Pt(II) precursor. Studies of the fundamental coordination chemistry of (NN*)Pt complexes (NN* = PyInd or a related ligand) reveal that sites trans to the pyridinyl and indolyl ligand fragments are electronically differentiated and that single isomers of (NN*)Pt(X)(L) form stereoselectively in most cases. Additionally, activities of various (NN*)Pt derivatives for the catalytic hydroarylation of norbornene are evaluated and compared.

## Results and Discussion

**Synthesis and Characterization of (NN*)Pt Complexes.** A recent report described a four-step synthesis of PyInd using protecting groups and Pd-catalyzed cross-coupling chemistry.[22] However, this ligand precursor was prepared more conveniently by the classic Fischer indole method previously utilized by Thummel and co-workers.[15] Thus, starting from readily available 2-acetylpyridine and phenylhydrazine, the corresponding phenylhydrazone derivative was formed in quantitative yield (Scheme 1). Subsequent treatment of this compound with polyphosphoric acid (PPA) at 100 °C, followed by basic workup and sublimation, provided PyInd on a 10 g scale in an overall yield of 82%. Following an analogous procedure, 2-(2′-pyridyl)-5-fluoroindole (PyInd-F) was prepared in 55% yield from 2-acetylpyridine and 4-fluorophenylhydrazine (Scheme 1).[23] In addition, pyrrolo[3,2-*h*]quinoline (PyQuin), an analogue of PyInd containing a fused ligand backbone, was synthesized via a two-step reductive cyclization route developed by Thummel and co-workers (Figure 1).[24] Deprotonation of the pyrrole with potassium hexamethyldisilazide in toluene at room temperature, followed by a pentane wash, provided the corresponding potassium salt, K[PyQuin]. In contrast, K[PyInd] and K[PyInd-F] were more conveniently obtained from the neutral indoles using potassium hydride in THF. The latter two potassium derivatives were heated to 70 °C under vacuum to remove coordinated THF.

Initial synthetic investigations targeted complexes containing an $\eta^3$-allyl ligand, which could serve as a source of the desired (NN*)PtR fragment via an $\eta^3-\eta^1$ interconversion.[25] Thus, reaction of K[PyInd] with [($\eta^3$-CH$_2$CMeCH$_2$)PtCl]$_2$ in benzene at room temperature, followed by filtration and crystallization via layering of the benzene solution with pentane, gave (PyInd)-Pt($\eta^3$-CH$_2$CMeCH$_2$) (**1a**) in 92% yield (eq 1). The unsymmetrical environment of the methallyl ligand in **1a** is evidenced by four distinct allyl methylene resonances in the $^1$H NMR spectrum (Table 1). Characteristically, the $J_{Pt-H}$ values for the syn protons of the methallyl ligand are significantly smaller than those of the anti protons.[26] Similarly, K[PyInd-F] reacted with [($\eta^3$-CH$_2$CMeCH$_2$)PtCl]$_2$ (eq 1) to yield the fluorine-containing analogue (PyInd-F)Pt($\eta^3$-CH$_2$CMeCH$_2$) (**1b**). The chemical shifts for the allyl methylene protons in this complex are very

(12) (a) Romeo, R.; Minitti, D.; Lanza, S. *Inorg. Chem.* **1979**, *18*, 2362. (b) Romeo, R.; Alibrandi, G. *Inorg. Chem.* **1997**, *36*, 4822. (c) Romeo, R. *Comments Inorg. Chem.* **2002**, *23*, 79.

(13) (a) Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804. (b) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 15286.

(14) Vedernikov, A. N.; Huffman, J. C.; Caulton, K. G. *New J. Chem.* **2003**, *27*, 665.

(15) Thummel, R. P.; Hedge, V. *J. Org. Chem.* **1989**, *54*, 1720.

(16) (a) Thomas, C. M.; Peters, J. C. *Organometallics* **2005**, *24*, 5858. (b) Zhang, F.; Kirby, C. W.; Hairsine, D. W.; Jennings, M. C.; Puddephatt, R. J. *J. Am. Chem. Soc.* **2005**, *127*, 14196.

(17) For recent examples of transition metal-catalyzed olefin functionalizations with unactivated hydrocarbons, see: (a) Matsumoto, T.; Taube, D. J.; Periana, R. A.; Taube, H.; Yoshida, H. *J. Am. Chem.* Soc. **2000**, *122*, 7414. (b) Matsumoto, T.; Periana, R. A.; Taube, D. J.; Yoshida, H. *J. Mol. Catal. A*: *Chem.* **2002**, *180*, 1. (c) Periana, R. A.; Liu, X. Y.; Bhalla, G. *Chem. Commun.* **2002**, 3000. (d) Wong-Foy, A. G.; Bhalla, G.; Liu, X. Y.; Periana, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 14292. (e) Oxgaard, J.; Muller, R. P.; Goddardt, W. A., III; Periana, R. A. (f) Bhalla, G.; Liu, X. Y.; Oxgaard, J.; Goddard, W. A., III; Periana, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 11372. (g) Bhalla, G.; Oxgaard, J.; Goddard, W. A., III; Periana, R. A. *Organometallics* **2005**, *24*, 3229. (h) Bhalla, G.; Periana, R. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 1540. (i) Lail, M.; Arrowood, B. N.; Gunnoe, T. B. *J. Am. Chem. Soc.* **2003**, *125*, 7506. (j) Pittard, K. A.; Lee, J. P.; Cundari, T. R.; Gunnoe, T. B.; Petersen, J. L. *Organometallics* **2004**, *23*, 5514. (k) Lail, M.; Bell, C. M.; Conner, D.; Cundari, T. R.; Gunnoe, T. B.; Petersen, J. L. *Organometallics* **2004**, *23*, 5007.

(18) For reviews of early examples of olefin hydroarylations, see: (a) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633. (b) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826. (c) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731.

(19) Karshtedt, D.; Bell, A. T.; Tilley, T. D. *Organometallics* **2004**, *23*, 4169.

(20) Iverson, C. N.; Carter, C. A. G.; Baker, R. T.; Scollard, J. D.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2003**, *125*, 12674.

(21) After our initial report (see ref 19), the preparation of Pt complexes containing 2-(2′-pyridyl)indole was described by another research group: Cravotto, G.; Demartin, F.; Palmisano, G.; Penoni, A.; Radice, T.; Tollari, S. *J. Organomet. Chem.* **2005**, *690*, 2017.

(22) Liu, S.-F.; Wu, Q.; Schmider, H. L.; Aziz, H.; Hu, N.-X.; Popovic, Z.; Wang, S. *J. Am. Chem. Soc.* **2000**, *122*, 3671.

(23) Liu, Q.; Mudadu, M. S.; Schmider, H.; Thummel, R. P.; Tao, Y.; Wang, S. *Organometallics* **2002**, *21*, 4743.

(24) Wu, F.; Chamchoumis, C. M.; Thummel, R. P. *Inorg. Chem.* **2000**, *39*, 584.

(25) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. A. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; pp 175−180.

(26) Mann, B. E.; Shaw, B. L.; Shaw, G. *J. Chem. Soc. A* **1971**, 3536.

**Scheme 1**

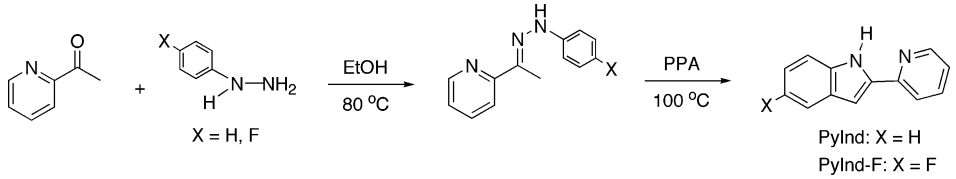
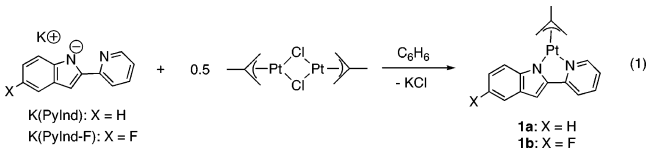



**Table 1. $^1$H NMR Chemical Shifts for the Allyl Methylene Resonances of 1a and 1b[a]**

| | $^1$H (ppm) | $^2J_{Pt-H}$ (Hz) | type of hydrogen |
|---|---|---|---|
| **1a** | 2.23 | 71.4 | anti |
| | 2.26 | 79.8 | anti |
| | 2.98 | 26.0 | syn |
| | 3.80 | 24.5 | syn |
| **1b** | 2.18 | 80.0 | anti |
| | 2.20 | 71.0 | anti |
| | 2.97 | 26.5 | syn |
| | 3.67 | 23.5 | syn |

[a] Spectra recorded in benzene-$d_6$.

similar to those in **1a** (Table 1), suggesting that the fluorine substituent on the indolyl fragment does not have a strong influence on the electron density at the Pt center. This result is consistent with Hammett correlation studies suggesting that, in aromatic systems, the electronic effect of a fluorine substituent in the para position is approximately equal to that of a proton.[27]




(1)

The solid-state structure of **1b** was determined by X-ray crystallography and is shown in Figure 2. The N−Pt−N angle is approximately 78°, indicating that PyInd-F enforces a smaller bite angle than that typically observed in Pt complexes of the $\beta$-diiminate ligands (usually close to 90°), which form six-membered chelate rings.[13a] By comparison, the N−Pt−N angle in a recently reported Pt(II) complex of an anionic 2,2′-bipyridine derivative, which features a five-membered chelate ring, is also nearly 78°.[16a] As expected, the bond between Pt and the indolyl nitrogen is shorter than that between Pt and the pyridinyl nitrogen (2.048(4) vs 2.087(5) Å), reflecting the fact that Pt forms a stronger bond with the anionic donor. Furthermore, the distance from Pt to the terminal methallyl carbon atom trans to the pyridinyl fragment, 2.104(6) Å, is shorter than that from Pt to the carbon trans to the indolyl, 2.124(6) Å. This difference suggests that the indolyl fragment has a greater trans influence than the pyridinyl, a result consistent with the fact that it is the stronger $\sigma$-donor.[7] Similar variations in Pt−C bond distances have been observed in other Pt-allyl complexes where distinct trans ligands are present.[28]

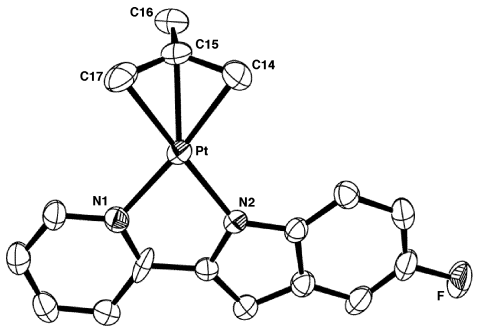
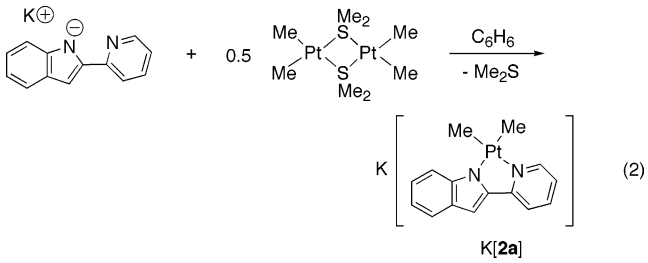



**Figure 2.** ORTEP diagram of the X-ray crystal structure of (PyInd-F)Pt($\eta^3$-$CH_2CMeCH_2$) (**1b**). Selected bond lengths (Å): Pt−N1 = 2.087(5), Pt−N2 = 2.048(4), Pt−C14 = 2.104(6), Pt−C15 = 2.103(6), Pt−C17 = 2.124(6), C14−C15 = 1.442(10), C15−C17 = 1.431(10). Selected bond angles (deg): N1−Pt−N2 = 77.98(18), C14−C15−C17 = 115.4(6).

Additional synthetic targets were anionic, dialkyl complexes of the type $[(NN^*)PtR_2]^-$, which would serve as precursors to reactive (NN*)PtR intermediates generated by alkyl group abstraction.[29] Initial attempts to form the simplest species of this type, the $[(NN^*)PtMe_2]^-$ anion, were based on reaction of K[PyInd] with $(COD)PtMe_2$ (COD = 1,5-cyclooctadiene). Even upon heating to 80 °C in THF-$d_8$, however, this reaction proceeded to only ∼50% conversion, as judged by $^1$H NMR spectroscopy. In contrast, the highly reactive precursor $[(Me_2S)PtMe_2]_2$ reacted with K[PyInd] in THF at room temperature to quantitatively form the adduct THF·K[(PyInd)$PtMe_2$] (THF·K[**2a**]) over the course of 4 h. Attempts to use this method to prepare K[**2a**] free of THF, which presumably remained coordinated to the potassium cation, proved unsuccessful, as heating under vacuum led to decomposition of the Pt complex. The THF-free complex K[**2a**] was obtained by stirring a suspension of K[PyInd] with 0.6 equiv of $[(Me_2S)PtMe_2]_2$ in benzene over the course of 10 days. Subsequent addition of pentane and decantation of the supernatant allowed the isolation of analytically pure K[**2a**] in 71% yield (eq 2). The $^1$H NMR spectrum of K[**2a**] contains two inequivalent methyl ligand resonances at 0.51 ppm ($^2J_{Pt-H}$ = 81.9 Hz) and 1.16 ppm ($^2J_{Pt-H}$ = 88.4 Hz). The rather large difference in chemical shift (approximately 0.5 ppm) suggests that the electronic environments of the two Pt-methyls are quite distinct.



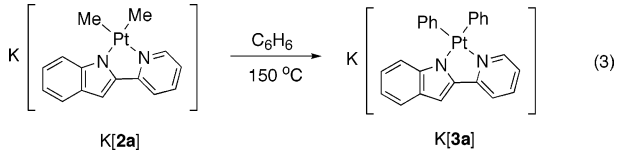

(2)

Electronic properties of the indolyl and pyridinyl fragments of the PyInd ligand in this complex were also probed with a geometry optimization of the structure of **2a** using DFT methods (see Computational Details). This calculation showed that the Pt−C bond trans to the indolyl (2.063 Å) is slightly longer than that trans to the pyridinyl group (2.056 Å). This result is consistent with the fact that, of the two nitrogen donors in PyInd, the indolyl fragment has the greater trans influence (vide supra).

(27) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1957**, *79*, 1913.
(28) See, for example: Pandolfo, L.; Paiaro, G.; Dragani, L. K.; Maccato, C.; Bertani, R.; Facchin, G.; Zanotto, L.; Ganis, P.; Valle, G. *Organometallics* **1996**, *15*, 3250.
(29) (a) Hill, G. S.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 525. (b) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1809.

The analogous PyQuin adduct K[(PyQuin)$PtMe_2$] (K[**2b**]) was obtained in 61% yield, following a procedure similar to that used to prepare K[**2a**]. The two inequivalent methyl resonances of K[**2a**] appear at 0.64 ppm ($^2J_{Pt-H}$ = 85.2 Hz) and 0.93 ppm ($^2J_{Pt-H}$ = 90.5 Hz) in the $^1$H NMR spectrum.

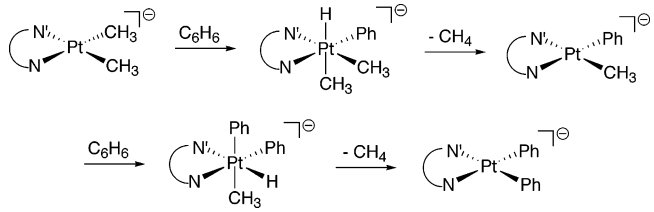
**C−H Bond Activation Reactions of (NN*)Pt Complexes.** To realize stoichiometric activations of C−H bonds by Pt(II) complexes, it is typically necessary to access a transient three-coordinate intermediate via ligand loss from a 16-electron precursor or to utilize a ligand that can be easily substituted by the hydrocarbon substrate via an associative mechanism.[30] For example, Goldberg and co-workers observed oxidative addition of benzene, cyclohexane, and pentane upon borane abstraction of a methyl group from K[($\kappa^2$-$Tp_{Me2}$)$PtMe_2$] ($Tp_{Me2}$ = 3,5-dimethyl-tris(pyrazolyl)borate).[31] Similarly, activation of $^{13}$C-labeled methane by [(tmeda)Pt(Me)($F_5$py)]X ($F_5$py = pentafluoropyridine) is thought to require the displacement of the weakly bound $F_5$py ligand by $^{13}CH_4$.[32] Complex K[**2a**], which contains no readily dissociated ligands, was not expected to react with hydrocarbons in the absence of an activator. Thus, methyl group abstraction by a Lewis acid was thought to be required to achieve the desired reactivity. Surprisingly, however, K[**2a**] was converted in benzene at 150 °C over the course of 3 days to the diphenyl complex K[**3a**] in 68% yield (eq 3). Intractable material and unreacted K[**2a**] (<10%) accounted for the remaining components of the mixture. The identity of K[**3a**] was confirmed by its independent synthesis from K[PyInd] and [($Me_2S$)$PtPh_2$]$_2$ (see Experimental Section). Further studies of this reaction were complicated by the poor solubility of K[**2a**] in benzene, but identification of methane as the only byproduct observed by $^1$H NMR spectroscopy confirms that the active Pt species is divalent. Activation of benzene by Pt(0) would require that K[**2a**] undergo a reductive elimination of ethane, which was not observed. Furthermore, thermolysis of K[**2a**] in benzene-$d_6$ led to the formation of $CH_3D$, confirming that the methane product originated from a reaction with the arene and not from an adventitious proton source.



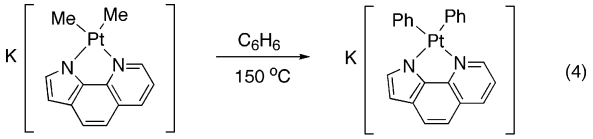

K[**2a**] K[**3a**] (3)

Although various Pt(II) complexes have been shown to react with 1 equiv of benzene to produce a Pt-phenyl product,[20,30−32] the activation of two benzene molecules at a single Pt center is rare.[34,35] One related system involves the thermolysis of (dmpe)-$PtMe_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane) in benzene

**Scheme 2**




at 180 °C, resulting in a mixture containing unreacted starting material (15%), (dmpe)PtMePh (51%), and (dmpe)$PtPh_2$ (34%).[34a] With regard to the mechanism of this transformation, Roddick and co-workers contend that it is not possible to show definitively whether it proceeds via direct oxidative addition of benzene to (dmpe)$PtMe_2$ or via the 14-electron intermediate formed by an initial dissociation of a phosphine arm. In the present study, the rigidity of the PyInd ligand appears to argue strongly against partial ligand dissociation. Even more compelling is the observation that the PyQuin complex K[**2b**], upon heating in benzene at 150 °C for 3 days, was converted in 54% yield to the diphenyl product K[**3b**] (eq 4). Since PyQuin is highly unlikely to behave as a hemilabile ligand, a direct oxidative addition pathway for C−H bond activation by K[**2b**] may be operative (Scheme 2). However, oxidative hydrogen migration[17e−g] or $\sigma$-bond metathesis[36] pathways, which do not require a fully formed Pt(IV) intermediate, cannot be completely ruled out.




K[**2b**] K[**3b**] (4)

A related, recent report describes the acid-catalyzed activation of benzene by a $PtMe_2$ derivative, supported by an anionic bis-(pyrazolyl)borate-derived ligand, to give the corresponding Pt-diphenyl complex.[16a] In this transformation, the acid presumably converts the starting platinum complex to a highly reactive 14-electron (NN)PtMe species.[30b] The possibility of catalytic benzene activation by an adventitious proton source was examined for the system reported herein. It was found that an acid additive, [$^i$$Pr_2$EtNH][$BPh_4$], had a slight accelerating effect on the rate of conversion of K[**2a**] to K[**3a**].[37] When K[**2a**] was heated in benzene at 110 °C for 20 h in the presence of 10 mol % of [$^i$$Pr_2$EtNH][$BPh_4$], K[**3a**] was formed in 83% yield, while the starting complex accounted for the remaining component of the reaction mixture. In the absence of acid, however, K[**3a**] was formed in only 58% yield under these conditions. Thus, added acid appeared to accelerate the rate of benzene activation, perhaps in the manner described above.[16a] To rule out the potential role of an adventitious acid catalyst in a conclusive manner, thermolysis of K[**2a**] was conducted in the presence

(30) (a) Johannson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846. (b) Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378. (c) Procelewska, J.; Zahl, A.; van Eldik, R.; Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 2808.

(31) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235.

(32) Holtcamp, M. W.; Henling, L. M.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* **1998**, *270*, 467.

(33) (a) Brainard, R. L.; Nutt, W. R.; Lee, T. R.; Whitesides, G. M. *Organometallics* **1988**, *7*, 2379. (b) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848. (c) Johansson, L.; Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc.* **1999**, *121*, 1974. (d) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2001**, *123*, 5100. (e) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 8870. (f) Konze, W. V.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **2002**, *124*, 12550. (g) Harkins, S. B.; Peters, J. C. *Organometallics* **2002**, *21*, 1753. (h) Song, D.; Wang, S. *Organometallics* **2003**, *22*, 2187.

(34) Pt(II) complexes: Peters, R. G.; White, S.; Roddick, D. M. *Organometallics* **1998**, *17*, 4493, and ref 16a.

(35) Pt(IV) complexes (proceeding through Pt(II) intermediates): (a) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2001**, *20*, 1709. (b) Jensen, M. P.; Wick, D. D.; Reinartz, S.; White, P. S.; Templeton, J. L.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 8614. (c) Vedernikov, A. N.; Caulton, K. G. *Chem. Commun.* **2003**, 358.

(36) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santasiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

(37) In response to a reviewer's suggestion to test for the effects of adventitious water on this reaction, a small amount of water was added to the reaction system indicated in eq 3, and complete decomposition of complex K[**2a**] was observed after 3 days of heating at 150 °C.

of 10 mol % *N,N,N′,N′*-tetramethyl-1,8-naphthalenediamine (Proton Sponge), and it was found that this additive had no effect on the reaction yield (conditions as in eq 3 above).

One potentially problematic aspect of the mechanism requiring Pt(IV) is that, given the rigidity of PyInd and PyQuin, the reductive elimination of methane must occur without prior ligand dissociation. This step, which generates an electron-deficient five-coordinate Pt(IV) intermediate, is generally thought to precede reductive eliminations from high-valent metal centers.[38] Nevertheless, using entropy of activation data and reactivity comparisons between different ligand frameworks, Goldberg and co-workers demonstrated that thermal loss of methane from (dppe)$PtMe_3H$ (dppe = 1,2-bis(diphenyphosphino)ethane) and (dppbz)$PtMe_3H$ (dppbz = 1,2-bis(diphenylphosphino)benzene) occurs without prior dissociation of a phosphine ligand arm.[38d] Thus, it is reasonable to assume that methane reductively eliminates from a six-coordinate Pt(IV) intermediate in the (NN*)Pt system (Scheme 2). Further, by the principle of microscopic reversibility, Goldberg's study suggests that direct oxidative addition of a C−H bond to a 16-electron Pt(II) complex should be feasible. In addition, a related study provides evidence of a direct intramolecular C−H activation mechanism at square planar Pt(II).[39] Theoretical calculations by Saillard and Hoffman also support the possibility of hydrocarbon activation of by square planar $d^8$ complexes without prior ligand dissociation.[40]

**Preparation of a Five-Coordinate Pt(IV)-Silyl Complex.** To provide indirect support for the oxidative addition mechanism for benzene activation, and to further probe the reactivity of (NN*)Pt(II) complexes, transformations that were expected to give isolable Pt(IV) products were targeted. Since it is well known that silyl ligands tend to support high-oxidation-state late transition metal complexes,[41,42] silicon-containing substrates were initially examined. While trimethylsilyl chloride was found to be inert toward K[**2a**], highly electrophilic trimethylsilyl triflate immediately reacted with K[**2a**] in benzene at room temperature to yield **4**, a five-coordinate Pt(IV) complex, in 82% yield (eq 5). The methyl resonance of the trimethylsilyl ligand, which appears at 0.06 ppm in the $^1$H NMR spectrum, exhibits coupling to the $^{195}$Pt nucleus ($^3J_{Pt-H}$ = 21.6 Hz). This value is similar to those in other Pt-silyl complexes that feature a three-bond Pt−H separation.[43] In addition, the $^{29}$Si NMR resonance of **4**, appearing at 38 ppm, exhibits a large one-bond coupling to $^{195}$Pt ($^1J_{Pt-Si}$ = 94 Hz). The room-temperature $^1$H NMR spectrum of **4** contains sharp ligand resonances, suggesting that the complex does not exhibit fluxional behavior on the NMR time scale.[44] However, the stable solution structure of **4** cannot

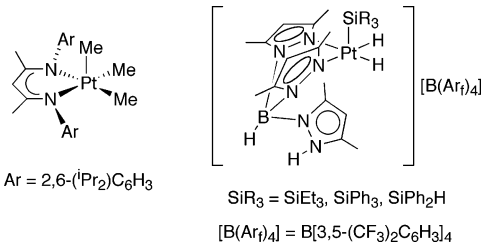
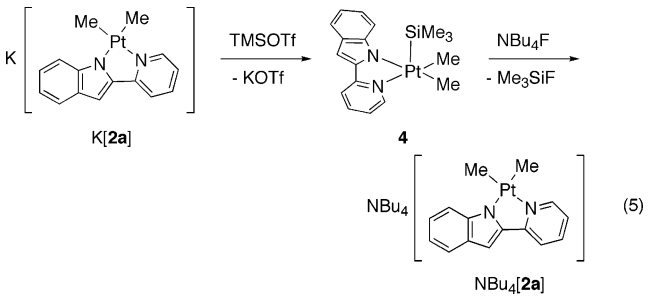



**Figure 3.** Examples of known five-coordinate Pt(IV) complexes.

be definitively assigned as square pyramidal (as drawn in eq 5) or trigonal bipyramidal on the basis of available data. Moreover, although there is no spectroscopic evidence to suggest that **4** has a dimeric structure or exists as a solvento complex, its description as a five-coordinate species must be considered tentative in the absence of an X-ray crystal structure.




(5)

It was found that **4** is thermally unstable in benzene solution and completely decomposes to tetramethylsilane and unidentified Pt-containing products over the course of 6 h at room temperature. This behavior is consistent with general reactivity patterns described for five-coordinate Pt(IV) species, which have been identified as reactive intermediates in reductive eliminations from octahedral Pt centers.[38,45] Indeed, the relative stability of **4** seems somewhat unusual, given that only two other types of five-coordinate Pt(IV) complexes have been isolated to date. Goldberg and co-workers described the preparations of (nacnac)-$PtMe_3$[46] and similar nacnac derivatives,[13b] while Templeton and co-workers reported the synthesis of cationic $[(\kappa^2\text{-}Tp_{Me2})Pt(SiR_3)(H)_2]^+$ ($R_3$ = $Et_3$, $Ph_3$, $Ph_2H$) complexes via protonation of one of the pyrazolyl arms of the octahedral $\kappa^3$-tris(pyrazolyl)borate precursors (Figure 3).[47] It is noteworthy that both of these classes of complexes were prepared directly from Pt(IV) starting materials, while **4** is a product of an oxidative addition to Pt(II). The transformation from a relatively stable square planar Pt(II) to a relatively unstable five-coordinate Pt(IV), which at first appears to be thermodynamically unfavorable, is of course driven in part by the formation of insoluble potassium triflate. Nevertheless, the facile generation of **4** attests to the ability of the PyInd ligand to stabilize high-oxidation-state Pt complexes.

The rapid elimination of tetramethylsilane from **4** limits reactivity studies that might be undertaken, but a clean route for converting this complex back to its precursor was found. When 1 equiv of tetrabutylammonium fluoride was added to an acetonitrile-$d_3$ solution of **4**, the anion **2a** and trimethylsilyl fluoride were immediately generated (eq 5). Other than the resonances corresponding to the *n*-butyl groups, the $^1$H NMR spectrum of $NBu_4$[**2a**] is identical to that of K[**2a**], indicating that the cation does not strongly interact with the anionic Pt

(38) (a) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457. (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961. (c) Hinman, J. G.; Baar, C. R.; Jennings, M. C.; Puddephatt, R. J. *Organometallics*, **2000**, *19*, 563. (d) Crumpton-Bregel, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 9442, and references therein.

(39) Griffiths, D. C.; Young, G. B. *Organometallics* **1989**, *8*, 875.

(40) Saillard, J. Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

(41) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

(42) For recent examples, see: (a) Gutierrez-Puebla, E.; Monge, A.; Paneque, M.; Poveda, M. L.; Taboada, S.; Trujillo, M.; Carmona, E. *J. Am. Chem. Soc.* **1999**, *121*, 346. (b) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2000**, *19*, 3854. (c) Brookhart, M.; Grant, B. E.; Lenges, C. P.; Prosenc, M. H.; White, P. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1676. (d) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 1816.

(43) See, for example: Ong, C. M.; Burchell, T. J.; Puddephatt, R. J. *Organometallics* **2004**, *23*, 1493.

(44) Attempts to observe fluxional behavior by heating **4** in benzene-$d_6$ solution to temperatures above 25 °C led to rapid decomposition of the complex.

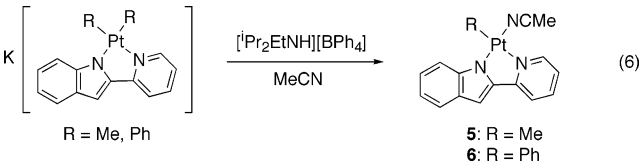
(45) Puddephatt, R. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 261.

(46) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 6423.

(47) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 6425.

complex in either case. Attack of an $X^-$ reagent onto a Pt(IV)-silyl fragment represents a silicon variant of the extensively researched product-forming step of the Shilov methane functionalization, where $OH^-$ or $Cl^-$ acts as a nucleophile toward a Pt(IV)-methyl intermediate.[8] In an effort to develop a more accurate model for the Shilov system, preparation of a Pt(IV)-trimethyl complex was attempted using K[**2a**] and reagents such as methyl iodide or methyl triflate. Unfortunately, these reactions resulted only in intractable mixtures, reflecting a probable lack of stability of low-coordinate alkyl complexes relative to their silyl analogues.

**Chemical Differentiation of Trans Sites in (PyInd)Pt Complexes.** As discussed above, $^1$H NMR characterization of complexes **1a** and K[**2a**], DFT calculations performed on **2a**, and the structural characterization of **1b** all provide evidence that the sites trans to the pyridinyl and indolyl donors of PyInd are electronically distinct. To further probe the effects of the two ligand fragments on the chemistry of (PyInd)Pt complexes, we examined reactions leading to the formation of (NN*)-Pt(X)(L) species that can hypothetically exist as mixtures of two stereoisomers. However, protonolysis of K[**2a**] with 1 equiv of [$^i$Pr$_2$EtNH][BPh$_4$] in acetonitrile generated the neutral complex (PyInd)Pt(Me)(MeCN) (**5**) as a single isomer, as evidenced by the presence of only one Pt-CH$_3$ resonance (1.45 ppm, $^2J_{Pt-H}$ = 81.0 Hz) in the $^1$H NMR spectrum of the product (eq 6). The complex was isolated in 66% yield by extraction of the crude product into dichloromethane and crystallization from a dichloromethane/pentane mixture. The arrangement of ligands about the Pt center in **5** was determined by a $^1$H NOE experiment, which indicates that the methyl ligand is cis to the indolyl fragment of PyInd. Consistent with this, Bercaw and co-workers observed that an analogous geometrical isomer was exclusively formed in the reaction of $(Me_2S)_2Pt(Me)(Cl)$ with a related 2-(*N*-arylimino)pyrrole ligand in the presence of acetonitrile.[20]




(6)

Furthermore, a similar protonolysis reaction with K[**3a**], which was conducted at 80 °C, yielded (PyInd)Pt(Ph)(MeCN) (**6**) as a single isomer with the same stereochemistry as **5** (eq 6). Relative positions of the ligands in **6** were established by the determination of its solid-state structure with X-ray crystallography, which demonstrated that the phenyl ligand is cis to the indolyl group (Figure 4). Along with the structural information obtained for **1b**, these results confirm that the indolyl fragment has the greater trans influence of the two nitrogen donors of PyInd. Presumably, protonolysis of the Pt−C bond of the methyl (or phenyl) ligand trans to the indolyl fragment occurs selectively because this produces the more thermodynamically stable of the two possible geometrical isomers of (PyInd)Pt(R)(MeCN). Thus, the acetonitrile ligand, which is less trans-influencing than either Me or Ph,[48] preferentially adopts the position trans to the indolyl donor in complexes **5** and **6**. A similar example of selective Pt−C bond cleavage by acid was observed with a Pt-dimethyl complex of a neutral unsymmetrical bidentate nitrogen-based ligand.[33h]

(48) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

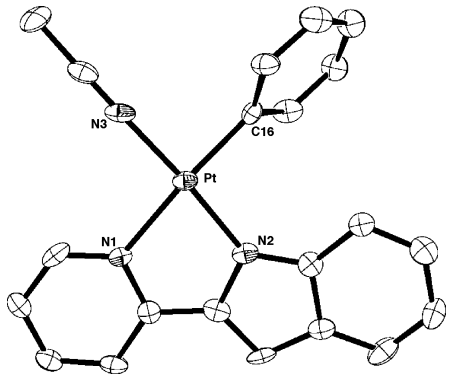



**Figure 4.** ORTEP diagram of the X-ray crystal structure of (PyInd)Pt(Ph)(MeCN) (**6**). Selected bond lengths (Å): Pt−N1 = 2.103(7), Pt−N2 = 1.986(7), Pt−N3 = 1.961(8), Pt−C16 = 2.000(9). Selected bond angles (deg): N1−Pt−N2 = 79.8(3), N1−Pt−N3 = 96.2(3), N2−Pt−N3 = 175.8(3), N1−Pt−C16 = 172.9(3), N2−Pt−C16 = 95.7(3), N3−Pt−C16 = 88.4(3).

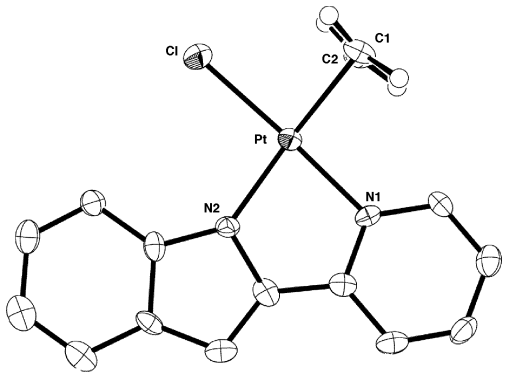
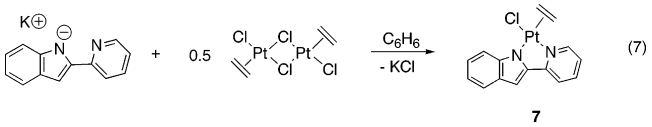



**Figure 5.** ORTEP diagram of the X-ray crystal structure of (PyInd)Pt(Cl)($C_2H_4$) (**7**). Selected bond lengths (Å): Pt−Cl = 2.292(2), Pt−N1 = 2.028(6), Pt−N2 = 1.995(6), Pt−C1 = 2.156(9), Pt−C2 = 2.146(9), C1−C2 = 1.39(1). Selected bond angles (deg): Cl−Pt−N1 = 177.4(2), Cl−Pt−N2 = 96.6(2), N1−Pt−N2 = 80.9(2).

Another potential route to complexes of the type (NN*)Pt(X)(L) involves their direct synthesis from $L_2PtX_2$ precursors. To this end, a variety of conditions were screened for reactions of K[PyInd] with $(MeCN)_2PtCl_2$ or $(Me_2S)_2PtCl_2$, but all of these attempts produced intractable mixtures of products. In contrast, K[PyInd] reacted cleanly with 0.5 equiv of $[(C_2H_4)PtCl_2]_2$ (Zeise's dimer) to form (PyInd)Pt(Cl)($C_2H_4$) (**7**) in 81% yield (eq 7).[19] The orientation of ligands in **7** was determined by $^1$H NOE experiments and X-ray crystallography, which also revealed that the bound ethylene is perpendicular to the plane of the molecule (Figure 5). The $^1$H NMR spectrum of **7** confirms that this orientation is maintained in solution, since the vinylic resonances appear as two sharp second-order multiplets (4.20 ppm, $^2J_{Pt-H}$ = 52.8 Hz and 4.51 ppm, $^2J_{Pt-H}$ = 54.0 Hz). It is surprising that the ethylene ligand, which is generally considered to have a greater trans influence than chloride,[48] adopts the position trans to the indolyl fragment. This structure may be kinetically preferred because the bridging chloride trans to the ethylene in Zeise's dimer is bound less tightly than that trans to the terminal chloride and is therefore displaced more readily by the indolyl, the more nucleophilic of the two nitrogen donors of PyInd. This explanation is supported by observations that Zeise's dimer reacts with donor ligands to form trans-dichloro products, a result that implies that the bridging chloride trans to the ethylene is indeed more labile.[49] However, attempts to convert **7** into the isomer with trans-positioned ethylene and

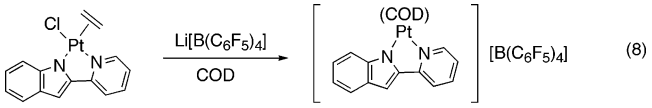
pyridinyl ligands, presumably the thermodynamically favored isomer, were unsuccessful. Thus, no reaction occurred when a 1,2-dichloroethane-$d_4$ solution of **7** was heated at 100 °C for 12 h, and the complex underwent decomposition after the temperature was increased to 120 °C. It was thought that added ethylene might facilitate this isomerization, but, when this experiment was conducted under 1 atm of ethylene, the same result was obtained.




(7)

**7**

In a preliminary communication, we reported that equimolar combinations of **7** and other Pt(II) complexes with Ag(I) activators catalyze the hydroarylaton of unfunctionalized olefins by benzene and other arenes.[19] To understand the nature of the active Pt species in this catalysis, attempts were made to isolate and characterize the products of chloride abstraction from **7**. While the reaction of **7** with AgOTf did not produce a stable complex, the combination of **7** with $Li[B(C_6F_5)_4]$ in the presence of 1 equiv of cyclooctadiene led to formation of the diolefin complex **8** (eq 8). The unsymmetrical environment of the COD ligand is reflected by the distinct chemical shifts of the two types of vinylic protons, which resonate at 5.53 ppm ($^2J_{Pt-H}$ = 71.0 Hz) and 6.84 ppm ($^2J_{Pt-H}$ = 83.0 Hz). This complex did not catalyze the hydrophenylation of olefins such as norbornene, a result that can be attributed to the inability of monoolefin substrates to displace the chelating diene from Pt. Nevertheless, the successful synthesis of **8** demonstrates that a Pt-diolefin complex is a reasonable intermediate in the catalytic hydroarylation of olefins by **7** and other Pt(II) complexes. Further evidence for the formation of such a complex is provided in a report that describes a related Pt-based system for catalytic olefin hydroamination.[50]




(8)

**7** **8**

**Catalytic Hydroarylation of Norbornene by (NN*)Pt Complexes.** Observations of stoichiometric activation of benzene by complexes of the type $K[(NN^*)PtMe_2]$ (vide supra) prompted an investigation of the activities of (NN*)Pt species in catalytic arene functionalizations. These efforts focused on access to reactive 14-electron intermediates formulated as (NN*)PtR, which were expected to undergo subsequent activations of arene and olefin substrates. Such a fragment can be generated via an $\eta^3-\eta^1$ interconversion of the methallyl ligand in **1a** or **1b**, borane abstraction of a methyl ligand from K[**2a**], or loss of acetonitrile from **5**. All of these potential catalyst systems were screened to determine their activities for the hydrophenylation of norbornene, and the results of this study are given in Table 2. It was found that, at 10 mol % catalyst loading relative to norbornene, low to moderate yields of *exo*-phenylnorbornane were obtained upon heating in neat benzene at 140 °C for 16 h (eq 9). In all of these reactions, two products

**Table 2. (NN*)Pt Catalysts for the Hydrophenylation of Norbornene[a]**

| catalyst | yield (%) |
|---|---|
| **1a** | 38 |
| **1b** | 41 |
| $K[\mathbf{2a}] + B(C_6F_5)_3$ | 27 |
| **5** | 26 |

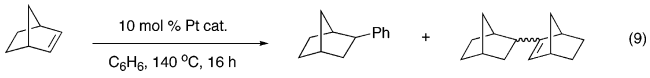
[a] Conditions as in eq 9.

**Table 3. Hydroarylation of Norbornene with Substituted Arenes[a]**

| arene | yield (%) |
|---|---|
| benzene | 38 |
| toluene | 28[b] |
| chlorobenzene | 58[b] |
| fluorobenzene | 0 |
| *p*-xylene | 0 |

[a] Catalyst: **1a**, conditions as in eq 9. [b] Mixture of para-, meta-, and ortho-substituted products.

of norbornene dimerization, which were possibly formed via a vinylic activation pathway, were the major contaminants (combined yields of 30−45%). The fact that comparable yields were obtained with all of the catalyst formulations suggests that, under the reactions conditions, these Pt precursors are converted to similar kinds of reactive intermediates (vide infra).




(9)

To assess the substrate scope of norbornene hydroarylations catalyzed by **1a**, the reactivity of other arenes in this system was investigated. While toluene was reactive, as expected, it was surprising to find that chlorobenzene also hydroarylated norbornene to form *exo*-chlorophenylnorobornane as a mixture of para, meta, and ortho isomers (Table 3). Thus, the potentially reactive C−Cl bond in this substrate was unaffected. For toluene, the *o*:*m*:*p* ratio of norbornene hydorarylation products was measured to be 0.4:1:0.6.[51]

In contrast, fluorobenzene and *p*-xylene did not participate in the hydroarylation of norbornene, and only products of norbornene dimerization were observed in these reactions. Olefins other than norbornene, including cyclohexene, cyclopentene, 1-octene, and vinyltrimethylsilane, were also screened as candidates for hydrophenylation, and all were found to be unreactive. This lack of reactivity can be contrasted with the broad substrate scope achieved with the previously reported cationic fragment $[(NN^*)PtL]^+$ (derived from **7** and $AgBF_4$) and related cationic Pt complexes, which catalyzed the hydroarylation of olefins that are inherently less reactive than norbornene, including cyclohexene and propylene.[19]

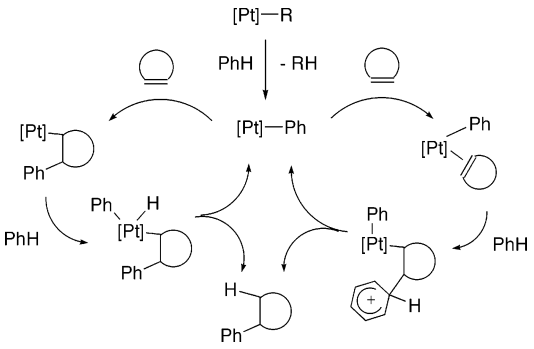
Given the data available for related catalytic systems, two mechanistic possibilities seem reasonable for this transformation. On one hand, the Pt center may activate norbornene toward attack by an arene nucleophile, a step that can be followed by the liberation of *exo*-phenylnorbornane after a proton transfer (Scheme 3). Such a mechanism was proposed for electrophilic Pt-based hydroarylation,[19,52] hydroamination,[50,53] and hydrovinylation[54] catalysts. On the other hand, the fragment (NN*)PtR (R = 2-butenyl for **1a** or **1b**; R = Me for K[**2a**] or **5**) may initiate a catalytic cycle via reaction with benzene to give (NN*)PtPh. After olefin insertion into the Pt−aryl bond, the resulting

(49) (a) van Baar, J. F.; Vrieze, K.; Stufkens, D. J. *J. Organomet. Chem.* **1974**, *81*, 247. (b) Maresca, L.; Natile, G.; Cattalini, L.; Gasparrini, F. *J. Chem. Soc., Dalton Trans.* **1976**, *12*, 1090. (c) Albinati, A.; Isaia, F.; Kaufmann, W.; Sorato, C.; Venanzi, L. M. *Inorg. Chem.* **1989**, *28*, 1112.

(50) Karshtedt, D.; Bell, A. T.; Tilley, T. D. *J. Am. Chem. Soc.* **2005**, *127*, 12640.

(51) These products were identified using the GC data available in: Malinowska, A.; Czelusniak, I.; Górski, M.; Szymanska-Buzar, T. *Tetrahedron Lett.* **2005**, *46*, 1427, and $^1H$ NMR data from references therein.

**Scheme 3**




Pt-alkyl intermediate can release the hydroarylation product after undergoing benzene activation and C−H bond reductive elimination (Scheme 3). This latter scenario, or some variant thereof, appears to account for hydroarylations catalyzed by Ir[17a−h] and Ru[17i−k] complexes, which contain hard oxygen- and nitrogen-based ligands, respectively.

Although it is not clear which of the mechanistic pathways delineated in Scheme 3 is operative in this system, the propensity of (NN*)Pt complexes to participate in stoichiometric benzene activations (vide infra) points to an olefin insertion/C−H bond oxidative addition pathway. In addition, the observation of *m*-tolylnorbornane as the major product of norbornene hydroarylation by toluene argues strongly against the olefin activation mechanism, which is expected to result in preferential formation of the para product.[19] The C−H bond activation mechanism is further supported by the stoichiometric reaction of the phenyl complex **6** with 2 equiv of norbornene. When heated for 12 h at 140 °C in fluorobenzene-$d_5$, an unreactive arene, these reactants are converted to *exo*-phenylnorbornane (in 64% yield based on Pt) and unidentified Pt-containing species. It is likely that the organic product results from the insertion of norbornene into the Pt−C bond of **6**, followed by vinylic C−H bond activation of the second equivalent of norbornene and reductive C−H bond elimination. This experiment also explains the observation of norbornene dimerization products in the catalytic system described above. These products presumably result from the insertion of norbornene into the Pt−C bond of a Pt-vinyl intermediate. Further efforts to study the mechanism of this catalysis by identifying possible intermediates in nobornene hydroarylations promoted by in situ-generated (NN*)PtR species were complicated by the presence of multiple Pt complexes observed by $^1$H NMR spectroscopy under the reaction conditions (140 °C, benzene-$d_6$). This may not be surprising, considering the possibility that both aryl and vinyl C−H activation pathways, potentially involving distinct catalytically active species, may account for the observed organic products.

Nevertheless, the operation of an electrophilic mechanism in (NN*)PtR-catalyzed hydroarylations cannot be ruled out on the basis of available data. Indeed, a possible explanation for the milder reaction conditions achieved in the $[(NN^*)PtL]^+$, relative to the (NN*)PtR, system may hinge on the highly carbocationic character of an olefin coordinated to a positively charged platinum center.[54b] Thus, even relatively weak nucleophiles such as olefins[54a] and arenes[19,52] may attack a carbon atom of the Pt-olefin complex, forming a C−C bond (Scheme 3). In the case of neutral (NN*)PtR catalysts, a coordinated olefin would be significantly less electrophilic, requiring more forcing reaction conditions that could result in lower selectivities.

## Concluding Remarks

Deprotonated 2-(2′-pyridyl)indole and related species containing localized neutral and anionic nitrogen donor sites represent a promising class of ancillary ligands in Pt chemistry. These frameworks support unusually reactive Pt complexes, enabling the activation of benzene that apparently proceeds via direct oxidative addition of a C−H bond to a 16-electron Pt(II) center. While hydrocarbon activations by (NN)Pt complexes are known, these reactions typically require the generation of a 14-electron intermediate, such as the ($\kappa^2$-$Tp_{Me2}$)PtMe fragment reported by Goldberg and co-workers.[31] Additionally, the PyInd ligand supports a stable five-coordinate Pt(IV)-silyl complex, which is only the third type of an isolated five-coordinate Pt(IV) species[46,47] and the first in which the Pt(IV) complex was prepared from a Pt(II) precursor.

The bidentate monoanionic ligands reported herein also allow for the generation of highly reactive, neutral, 14-electron species of the type (NN*)PtR, which are implicated as active intermediates in the catalytic hydroarylation of norbornene by (NN*)Pt complexes. Further synthetic investigations demonstrate that the sites trans to the pyridinyl and indolyl fragments of PyInd are electronically differentiated, and this facilitates stereoselective preparation of complexes of the type (PyInd)Pt(X)(L). These attractive features of PyInd and similar ligands offer promise for future efforts to develop novel catalytic and stoichiometric substrate transformations.

## Experimental Section

**Synthetic Methods.** All experiments were conducted under a nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres drybox, unless otherwise noted. Dry, oxygen-free solvents were used throughout. Olefin impurities were removed from pentane by treatment with concentrated $H_2SO_4$, 0.5 N $KMnO_4$ in 3 M $H_2SO_4$, and saturated $NaHCO_3$. Pentane was then dried over $MgSO_4$, stored over activated 4 Å molecular sieves, and distilled over potassium benzophenone ketyl under a nitrogen atmosphere. Thiophene impurities were removed from benzene (or toluene) by treatment with $H_2SO_4$ and saturated $NaHCO_3$. Benzene (or toluene) was then dried over $MgSO_4$ and distilled from potassium metal under a nitrogen atmosphere. Tehtrahydrofuran was distilled from sodium benzophenone ketyl, and acetonitrile was distilled from $CaH_2$. Chlorobenzene and fluorobenzene were vacuum-transferred from $CaH_2$.

Deuterated solvents were purchased from Cambridge Isotopes and dried with appropriate drying agents. Unless otherwise noted, all reagents were purchased from Aldrich or Strem Chemicals and used without further purification. Base-free $Li[B(C_6F_5)_4]$ was obtained from Boulder Scientific. Norbornene was purified by sublimation. Other olefin substrates were dried over sodium metal and vacuum-transferred onto activated molecular sieves before use, and $B(C_6F_5)_3$ was recrystallized from pentane at −35 °C. The compounds $(COD)PtMe_2$,[55] $[(C_2H_4)PtCl_2]_2$,[56] $[(Me_2S)PtMe_2]_2$,[57] $[(Me_2S)PtPh_2]_2$,[58] $[(\eta^3\text{-}CH_2CMeCH_2)PtCl]_2$,[26] PyInd,[16] K[PyInd],[19]

(52) Youn, S. W.; Pastine, S. J.; Sames, D. *Org. Lett.* **2004**, *6*, 581.
(53) (a) Wang, X.; Widenhoefer, R. A. *Organometallics* **2004**, *23*, 1649. (b) Qian, H.; Widenhoefer, R. A. *Org. Lett.* **2005**, *7*, 2635. (c) Brunet, J.-J.; Cadena, M.; Chu, N. C.; Diallo, O.; Jacob, K.; Mothes, E. *Organometallics* **2004**, *23*, 1264. (d) Brunet, J.-J.; Chu, N. C.; Diallo, O. *Organometallics* **2005**, *24*, 3104.
(54) (a) Hahn, C.; Cucciolito, M. E.; Vitagliano, A. *J. Am. Chem. Soc.* **2002**, *124*, 9038. (b) Hahn, C. *Chem.−Eur. J.* **2004**, *10*, 5888.
(55) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.
(56) Chatt, J.; Searle, M. L. *Inorg. Synth.* **1957**, *5*, 210.
(57) Hill, G. S.; Irwin, M. J.; Levy, C. J.; Rendina, L. M.; Puddephatt, R. J. *Inorg. Synth.* **1998**, *32*, 149.

PyInd-F,[23] PyQuin,[24] [$^i$Pr$_2$EtNH][BPh$_4$],[33d] and (PyInd)Pt(Cl)(C$_2$H$_4$) (**7**)[19] were prepared according to literature procedures.

**Analytical Methods.** All NMR spectra were recorded at room temperature, using a Bruker DRX-500 spectrometer equipped with a 5 mm BBI probe, a Bruker AVB-400 spectrometer equipped with a 5 mm BB probe, or a Bruker AVQ-400 spectrometer equipped with a 5 mm QNP probe. $^1$H (500.1 MHz) and $^{13}$C{$^1$H} (124.7 MHz) NMR spectra were referenced internally by the solvent signal relative to tetramethylsilane, while $^{19}$F{$^1$H} (376.5 MHz) NMR spectra were referenced to an internal hexafluorobenzene standard and $^{29}$Si (79.5 MHz) NMR spectra were referenced to an internal tetramethylsilane standard. Unless otherwise noted, spectra for all NMR-active nuclei of a given compound were obtained in the same solvent. Multiplets that are predicted to be doublets of doublets but appear as pseudotriplets are denoted as "pt".

Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley. Identities of organic products were confirmed by $^1$H NMR spectroscopy and by GC-MS, using an Agilent Technologies 6890N GC system with an HP-5MS column. FAB-MS spectra were recorded on a ZAB2-EQ spectrometer from Micromass.

**Potassium 2-(2′-Pyridyl)-5-fluoroindolide, K[PyInd-F].** This compound was synthesized from PyInd-F (3.00 g, 13.0 mmol) and KH (0.52 g, 13.0 mmol) by a procedure analogous to that used to prepare K[PyInd],[19] yielding K[PyInd]-F as a yellow-green solid (2.92 g, 83%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 6.54 (pt, $^3J$ = 8.5 Hz, 1H), 6.84 (s, 1H), 6.99 (pt, $^3J$ = 5.5 Hz, 1H), 7.05 (d, $^3J$ = 11.0 Hz, 1H), 7.32 (t, $^3J$ = 7.5 Hz, 1H), 7.62 (pt, $^3J$ = 7.5 Hz, 1H), 7.88 (d, $^3J$ = 8.5 Hz, 1H), 8.41 (s, 1H). $^{13}$C{$^1$H} NMR: $\delta$ 98.6, 102.6 ($^2J_{C-F}$ = 21.3 Hz), 105.7 ($^2J_{C-F}$ = 26.3 Hz), 118.6 ($^3J_{C-F}$ = 10.0 Hz), 120.7 ($^1J_{C-F}$ = 128.8 Hz), 132.0 ($^3J_{C-F}$ = 10.0 Hz), 136.8, 146.9, 149.8, 150.8, 156.2, 158.0, 159.3. $^{19}$F{$^1$H} NMR: $\delta$ −131.1. Anal. Calcd for C$_{13}$H$_8$FKN$_2$: C, 62.37; H, 3.22; N, 11.19. Found: C, 62.00; H, 3.35; N, 11.14.

**Potassium Pyrrolido[3,2-*h*]quinoline, K[PyQuin].** The solids pyrrolo[3,2-*h*]quinoline (2.20 g, 13.1 mmol) and potassium hexamethyldisilazide (2.61 g, 13.1 mmol) were combined in a Schlenk flask and suspended in 15 mL of cooled (0 °C) toluene. This mixture was stirred vigorously and allowed to reach room temperature over the course of 1 h. Stirring then continued for an additional 5 h, and the solvent was removed under reduced pressure. The resulting residue was washed with pentane (3 × 10 mL) and dried in vacuo for 16 h, providing K[PyQuin] as a powdery dark green solid (2.10 g, 78%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 6.49 (d, $^3J$ = 1.5 Hz, 1H), 7.03 (d, $^3J$ = 8.5 Hz, 1H), 7.11 (dd, $^3J$ = 8.0 Hz, $^3J$ = 4.5 Hz, 1H), 7.51 (d, $^3J$ = 1.5 Hz, 1H), 7.71 (d, $^3J$ = 8.5 Hz, 1H), 8.10 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.5 Hz, 1H), 8.56 (dd, $^3J$ = 4.5 Hz, $^4J$ = 1.5 Hz, 1H). $^{13}$C NMR: $\delta$ 100.9, 113.9, 116.2, 123.0, 124.0, 130.4, 136.1, 138.2, 141.7, 144.2, 146.7. Anal. Calcd for C$_{11}$H$_7$KN$_2$: C, 64.05; H, 3.42; N, 13.58. Found: C, 64.30; H, 3.25; N, 12.32.

**(PyInd)Pt($\eta^3$-CH$_2$CMeCH$_2$) (1a).** To a suspension of [($\eta^3$-CH$_2$-CMeCH$_2$)PtCl]$_2$ (0.246 g, 0.434 mmol) in 8 mL of benzene was added K[PyInd] (0.200 g, 0.868 mmol) as a solid. The reaction mixture was allowed to stir for 16 h and filtered, and the solvent volume was reduced to ca. 3 mL. The resulting solution was layered with 10 mL of pentane and stored at room temperature for 1 day, leading to the precipitation of a yellow solid. The solvent was decanted, and the resulting solid was washed with pentane and dried in vacuo, yielding **1a** (0.352 g, 92%). $^1$H NMR (benzene-$d_6$): $\delta$ 1.86 ($^3J_{Pt-H}$ = 66.0 Hz, 3H, C*H*$_3$), 2.23 ($^2J_{Pt-H}$ = 71.4 Hz, 1H, C*H*), 2.26 ($^2J_{Pt-H}$ = 79.8 Hz, 1H, C*H*), 2.98 ($^2J_{Pt-H}$ = 26.0 Hz, 1H, C*H*), 3.80 ($^2J_{Pt-H}$ = 24.5 Hz, 1H, C*H*), 6.01 (pt, $^3J$ = 7.3 Hz, 1H), 6.72 (pt, $^3J$ = 7.0 Hz, 1H), 7.01 (s, 1H), 7.12 (d, $^3J$ = 8.0 Hz, 1H), 7.28 (pt, $^3J$ = 7.5 Hz, 1H), 7.43 (pt, $^3J$ = 7.0 Hz, 1H), 7.84 (d, $^3J$ = 8.3 Hz, 1H), 7.92 (d, $^3J$ = 7.5 Hz, 1H), 8.10 (d, $^3J$ = 5.0 Hz, 1H). $^{13}$C{$^1$H} NMR: $\delta$ 23.1, 31.4, 46.6, 105.7, 111.8, 116.9, 118.7, 119.2, 120.2, 121.5, 122.8, 131.2, 137.2, 146.9, 148.1, 152.1, 157.9. Anal. Calcd for C$_{17}$H$_{16}$N$_2$Pt: C, 46.05; H, 3.64; N, 6.32. Found: C, 46.09; H, 3.69; N, 6.02.

**(PyInd-F)Pt($\eta^3$-CH$_2$CMeCH$_2$) (1b).** Following the procedure analogous to that used to prepare **1a**, with [($\eta^3$-CH$_2$CMeCH$_2$)PtCl]$_2$ (0.158 g, 0.279 mmol) and K[PyInd-F] (0.119 g, 0.558 mmol) as the reactants, **1b** was obtained as a powdery yellow-orange solid (0.224 g, 87%). $^1$H NMR (benzene-$d_6$): $\delta$ 1.84 ($^3J_{Pt-H}$ = 66.5 Hz, 3H, C*H*$_3$), 2.18 ($^2J_{Pt-H}$ = 80.0 Hz, 1H, C*H*), 2.20 ($^2J_{Pt-H}$ = 71.0 Hz, 1H, C*H*), 2.97 ($^2J_{Pt-H}$ = 26.5 Hz, 1H, C*H*), 3.67 ($^2J_{Pt-H}$ = 23.5 Hz, 1H, C*H*), 6.03 (pt, $^3J$ = 6.0 Hz, 1H), 6.77 (pt, $^3J$ = 8.0 Hz, 1H), 6.82 (s, 1H), 7.07 (d, $^3J$ = 8.0 Hz, 1H), 7.20 (pt, $^3J$ = 8.5 Hz, 1H), 7.58 (m, 2H), 8.08 (d, $^3J$ = 5.0 Hz, 1H). $^{13}$C{$^1$H} NMR: $\delta$ 23.0, 31.6, 46.6, 102.4 ($^3J_{C-F}$ = 6.7 Hz), 105.1 ($^2J_{C-F}$ = 22.5 Hz), 111.4 ($^2J_{C-F}$ = 25.0 Hz), 112.1, 117.8 ($^3J_{C-F}$ = 9.2 Hz), 119.9 ($^1J_{C-F}$ = 158.8 Hz), 120.6, 137.3, 144.8, 148.0, 152.1, 156.9, 157.6, 159.2. $^{19}$F{$^1$H} NMR: $\delta$ −125.3. Anal. Calcd for C$_{17}$H$_{15}$N$_2$FPt: C, 44.25; H, 3.28; N, 6.07. Found: C, 43.93; H, 3.10; N, 6.11.

**K[(PyInd)PtMe$_2$] (K[2a]).** To a stirred suspension of K[PyInd] (0.230 g, 0.990 mmol) in 6 mL of benzene was added a solution of [(Me$_2$S)PtMe$_2$]$_2$ (0.341 g, 0.594 mmol) in 2 mL of benzene. After this mixture was allowed to stir vigorously for 10 days, the solvent volume was reduced to ca. 2 mL, and 10 mL of pentane was added. After the precipitate was allowed to settle, the supernatant was decanted, and the resulting yellow-green solid was washed twice with pentane and dried in vacuo, yielding K[**2a**] (0.322 g, 71%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 0.52 ($^2J_{Pt-H}$ = 81.9 Hz, 3H, C*H*$_3$), 1.16 ppm ($^2J_{Pt-H}$ = 88.4 Hz, 3H, C*H*$_3$), 6.72 (pt, $^3J$ = 6.6 Hz, 1H), 6.81 (pt, $^3J$ = 8.4 Hz, 1H), 6.88 (s, 1H), 6.97 (pt, $^3J$ = 5.7 Hz, 1H), 7.67 (d, $^3J$ = 7.5 Hz, 1H), 7.78 (m, 3H), 8.78 (d, $^3J$ = 5.7 Hz, 1H). $^{13}$C{$^1$H} NMR: $\delta$ −24.1, −15.1, 99.8, 116.8, 117.0, 120.4, 120.6, 121.1, 121.8, 132.5, 135.6, 145.9, 149.3, 149.4, 160.1. Anal. Calcd for C$_{15}$H$_{15}$KN$_2$Pt: C, 39.38; H, 3.30; N, 6.12. Found: C, 38.99; H, 3.32; N, 5.73.

**K[(PyQuin)PtMe$_2$] (K[2b]).** Following the procedure analogous to that used to prepare K[**2a**], with [(Me$_2$S)PtMe$_2$]$_2$ (0.262 g, 0.436 mmol) and K[PyQuin] (0.150 g, 0.727 mmol) as the reactants, K[**2b**] was obtained as a powdery yellow solid, which was recrystallized from a THF/pentane mixture (1:2 by volume) and dried in vacuo to yield an analytically pure product (0.190 g, 61%). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 0.64 ($^2J_{Pt-H}$ = 85.2 Hz, 3H, C*H*$_3$), 0.93 ppm ($^2J_{Pt-H}$ = 90.5 Hz, 3H, C*H*$_3$), 6.50 (d, $^3J$ = 1.9 Hz, 1H), 7.09 (d, $^3J$ = 8.7 Hz, 1H), 7.18 (dd, $^3J$ = 8.1 Hz, $^3J$ = 5.1 Hz, 1H), 7.47 (d, $^3J$ = 1.9 Hz, 1H), 7.65 (d, $^3J$ = 8.7 Hz, 1H), 8.24 (d, $^3J$ = 8.1 Hz, 1H), 8.76 (d, $^3J$ = 5.1 Hz, 1H). $^{13}$C{$^1$H} NMR: $\delta$ −26.2, −20.2, 99.9, 102.3, 115.5, 116.7, 123.8, 125.0, 129.6, 134.4, 135.8, 144.1, 145.7. Anal. Calcd for C$_{13}$H$_{13}$KN$_2$Pt·0.25(THF): C, 37.31; H, 3.36; N, 6.23. Found: C, 37.09; H, 3.05; N, 5.85. The presence of 0.25 equiv of THF was confirmed by $^1$H NMR integration.

**K[(PyInd)PtPh$_2$] (K[3a]).** Following the procedure analogous to that used to prepare K[**2a**], with K[PyInd] (0.100 g, 0.430 mmol) and [(Me$_2$S)PtPh$_2$]$_2$ (0.212 g, 0.258 mmol) as the reactants, K[**3a**] was obtained as a flaky bright yellow solid (0.192 g, 77%). $^1$H NMR (THF-$d_8$): $\delta$ 6.52 (m, 2H), 6.55 (pt, $^3J$ = 7.0 Hz, 1H), 6.68 (dd, $^3J$ = 9.0 Hz, $^3J$ = 7.0 Hz, 2H), 6.74 (pt, $^3J$ = 6.0 Hz, 1H), 6.82 (dd, $^3J$ = 9.0 Hz, $^3J$ = 7.0 Hz, 4H), 6.89 (s, 1H), 7.31 (d, $^3J$ = 9.0 Hz, 1H), 7.68 (m, 6H), 8.00 (d, $^3J$ = 5.5 Hz, 1H). $^{13}$C{$^1$H} NMR: $\delta$ 97.9, 113.8, 114.8, 116.8, 117.6, 117.7, 117.8 (two overlapping signals), 117.9, 123.8, 124.4, 126.1, 129.2, 133.5, 137.5, 138.2, 144.4, 145.6, 146.0, 153.2, 157.3. Anal. Calcd for C$_{25}$H$_{19}$-KN$_2$Pt: C, 51.63; H, 3.29; N, 4.82. Found: C, 51.43; H, 3.51; N, 4.61.

**K[(PyQuin)PtPh$_2$] (K[3b]).** Following the procedure analogous to that used to prepare K[**2a**], with K[PyQuin] (0.050 g, 0.242 mmol) and [(Me$_2$S)PtPh$_2$]$_2$ (0.097 g, 0.145 mmol) as the reactants,

(58) Rashidi, M.; Fakhroeian, Z.; Puddephatt, R. J. *J. Organomet. Chem.* **1991**, *406*, 261.

K[**3b**] was obtained as a yellow solid (0.118 g, 88%). $^1$H NMR (THF-$d_8$): $\delta$ 6.52 (br s, 1H), 6.73 (pt, $^3J$ = 7.0 Hz, 2H), 6.85 (m, 4H), 7.04 (pt, $^3J$ = 6.3 Hz, 1H), 7.08 (d, $^3J$ = 9.0 Hz, 1H), 7.32 (br s, 1H), 7.46 (d, $^3J$ = 7.0 Hz, 2H), 7.56 (pt, $^3J$ = 9.0 Hz, 3H), 8.07 (d, $^3J$ = 4.5 Hz, 1H), 8.14 (d, $^3J$ = 7.5 Hz, 1H). $^{13}$C{$^1$H} NMR: $\delta$ 100.7, 115.2, 117.6, 120.9, 121.3, 123.7, 124.0, 126.6, 126.8, 129.4, 135.3, 136.1, 140.7, 140.9, 142.2, 144.9, 145.1, 147.0, 151.8. Anal. Calcd for $C_{23}H_{17}KN_2Pt$: C, 49.72; H, 3.08; N, 5.04. Found: C, 49.34; H, 2.99; N, 4.95.

**(PyInd)Pt(SiMe$_3$)Me$_2$ (4).** To a suspension of K[**2a**] (0.080 g, 0.175 mmol) in 2 mL of benzene, trimethylsilyl triflate (0.038 g, 0.175 mmol) was added as a solution in 1 mL of benzene. After stirring for 20 min, the solvent was removed in vacuo and the resulting residue was extracted with 2 mL of dichloromethane and rapidly filtered. To this solution, 10 mL of pentane was added, causing **4** to precipitate as a powdery brown solid (0.070 g, 82%). $^1$H NMR (dichloromethane-$d_2$): $\delta$ 0.06 ($^3J_{Pt-H}$ = 21.6 Hz, 9H, Si-*Me*$_3$), 1.01 ($^2J_{Pt-H}$ = 62.4 Hz, Pt-C*H*$_3$), 1.69 ($^2J_{Pt-H}$ = 70.4 Hz, Pt-C*H*$_3$), 6.91 (pt, $^3J$ = 7.2 Hz, 1H), 7.03 (pt, $^3J$ = 6.0 Hz, 1H), 7.05 (s, 1H), 7.18 (pt, $^3J$ = 6.0 Hz, 1H), 7.57 (d, $^3J$ = 8.0 Hz, 1H), 7.72 (d, $^3J$ = 8.0 Hz, 1H), 7.84 (pt, $^3J$ = 7.2 Hz, 1H), 7.94 (d, $^3J$ = 8.0 Hz, 1H), 8.51 (d, $^3J$ = 6.0 Hz, 1H). $^{13}$C{$^1$H} NMR: $\delta$ −7.7, 0.2, 3.1, 102.7, 109.0, 113.9, 115.4, 117.9, 120.6, 121.0, 121.1, 122.2, 128.2, 131.6, 138.6, 144.9. $^{29}$Si{$^1$H-INEPT} NMR: $\delta$ 38 ($^1J_{Pt-Si}$ = 94 Hz). Anal. Calcd for $C_{18}H_{24}N_2PtSi$: C, 43.98; H, 4.92; N, 5.70. Found: C, 43.63; H, 4.72; N, 5.44.

**(PyInd)Pt(Me)(MeCN) (5).** To a solution of K[**2a**] (0.080 g, 0.175 mmol) in 3 mL of acetonitrile was added [$^i$Pr$_2$EtNH][BPh$_4$] (0.084 g, 0.175 mmol) as a solid. After stirring for 2 h, the solvent was removed and the resulting residue was extracted into 5 mL of dichloromethane and filtered. The solvent volume was then reduced to ca. 1 mL, and the resulting solution was layered with 10 mL of pentane and stored at −35 °C for 2 days, leading to precipitation of **5** as a microcrystalline red solid (0.054 g, 66%). $^1$H NMR (dichloromethane-$d_2$): $\delta$ 1.45 ($^2J_{Pt-H}$ = 81.0 Hz, 3H, Pt-C*H*$_3$), 2.42 (s, 3H, C*H*$_3$CN), 6.90 (pt, $^3J$ = 7.5 Hz, 1H), 7.00 (m, 2H), 7.12 (pt, $^3J$ = 4.3 Hz, 1H), 7.52 (d, $^3J$ = 8.0 Hz, 1H), 7.73 (d, $^3J$ = 8.5 Hz, 1H), 7.84 (m, 2H), 8.40 (d, $^3J$ = 4.3 Hz, 1H). $^{13}$C{$^1$H} NMR: $\delta$ −25.9, 4.3, 102.2, 115.0, 117.5, 119.6, 120.9, 121.3, 121.9, 130.2, 137.4, 145.5, 147.7, 148.0, 156.3. Complex **5** was judged to be pure by $^1$H NMR, but a satisfactory combustion analysis could not be obtained. HRMS (FAB): *m*/*z* for $[C_{16}H_{15}N_3Pt]^+$ ($M^+$): calcd 443.0893, obsd 443.0892 (for $^{194}$Pt).

**(PyInd)Pt(Ph)(MeCN) (6).** To a solution of K[**3a**] (0.070 g, 0.120 mmol) in 3 mL of acetonitrile was added [$^i$Pr$_2$EtNH][BPh$_4$] (0.057 g, 0.129 mmol) as a solid. The reaction mixture was allowed to stir for 2 h at 80 °C in a Teflon-sealed flask and allowed to cool to room temperature, and volatile materials were then removed under reduced pressure. The resulting residue was extracted into 5 mL of dichloromethane and filtered. The solvent volume was then reduced to ca. 1 mL, and the resulting solution was layered with 10 mL of pentane and stored at −35 °C for 2 days, leading to precipitation of **6** as a microcrystalline yellow-orange solid (0.049 g, 81%). $^1$H NMR (dichloromethane-$d_2$): $\delta$ 2.35 (s, 3H, C*H*$_3$CN), 5.88 (d, $^3J$ = 8.5 Hz, 1H), 6.55 (pt, $^3J$ = 8.0 Hz, 1H), 6.75 (pt, $^3J$ = 7.5 Hz, 1H), 6.99 (s, 1H), 7.12 (m, 6H), 7.43 (d, $^3J$ = 7.5 Hz, 1H), 7.56 (d, $^3J$ = 7.0 Hz, 1H), 7.85 (m, 2H), 8.40 (d, $^3J$ = 5.5 Hz, 1H). $^{13}$C{$^1$H} NMR: $\delta$ 4.3, 102.5, 116.4, 117.6, 119.5, 120.6, 121.1, 121.5, 123.4, 126.8, 130.0, 131.2, 138.0, 138.9, 146.1, 146.7, 147.5, 156.4. Anal. Calcd for $C_{21}H_{17}N_3Pt$: C, 49.80; H, 3.38; N, 8.30. Found: C, 49.77; H, 3.57; N, 8.12.

**[(PyInd)Pt(COD)][B(C$_6$F$_5$)$_4$] (8).** To a stirred solution of **7** (0.100 g, 0.221 mmol) and 1,5-cyclooctadiene (0.024 g, 0.221 mmol) in 7 mL of dichloromethane was added Li[B(C$_6$F$_5$)$_4$] (0.152 g, 0.221 mmol) as a solid. The reaction mixture was stirred for 16 h and filtered, and the solvent volume was reduced to ca. 2 mL. The solution was then layered with 3 mL of hexane and stored at −35 °C for 5 days, yielding **8** as a dark red oily solid (0.164 g, 63%). $^1$H NMR (dichloromethane-$d_2$): $\delta$ 2.62 (m, 8H, C$H_2$), 5.53 ($^2J_{Pt-H}$ = 71.0 Hz, 2H, C*H*), 6.84 ($^2J_{Pt-H}$ = 83.0 Hz, 2H, C*H*), 6.93 (d, $^3J$ = 10.0 Hz, 1H), 7.11 (pt, $^3J$ = 9.5 Hz, 1H), 7.15 (s, 1H), 7.26 (m, 2H), 7.64 (d, $^3J$ = 10.0 Hz, 1H), 7.75 (d, $^3J$ = 7.5 Hz, 1H), 8.01 (m, 2H). $^{13}$C{$^1$H} NMR: $\delta$ 29.7, 31.9, 100.8, 101.0, 108.7, 112.5, 121.7, 122.1, 123.4, 123.5, 127.0, 131.1, 135.5 (br), 137.6 (br), 139.7 (br), 142.7, 144.0, 146.1, 146.8 (br), 149.5, 157.3. $^{19}$F{$^1$H} NMR: $\delta$ −166.6 (t, $^3J$ = 15.0 Hz, 2F), −162.8 (t, $^3J$ = 20.7 Hz, 1F), −132.3 (br s, 2F). Anal. Calcd for $C_{45}H_{21}BF_{20}N_2Pt$: C, 45.97; H, 1.80; N, 2.38. Found: C, 45.92; H, 1.92; N, 2.32.

**Thermolysis of K[2a].** A 15 mg amount of K[**2a**] was suspended in 1 mL of benzene and placed in an NMR tube (a small amount of cyclohexane-$d_{12}$ was added to obtain a lock signal), which was subsequently flame-sealed and heated to 150 °C in a temperature-controlled bath for 3 days. A $^1$H NMR spectrum was obtained, confirming the formation of methane. The solvent was then removed under reduced pressure, and the resulting residue was redissolved in THF-$d_8$. The $^1$H and $^{13}$C NMR spectra of the product were subsequently obtained and compared to those of the authentic sample of K[**3a**] (see above), confirming that K[**3a**] was the major product (68% yield). An internal ferrocene standard was used to quantify the yield of the reaction. The reaction with benzene-$d_6$ was conducted under the same conditions, and a $^1$H NMR spectrum was obtained before the solvent was removed. While $CH_3D$ was observed in the reaction mixture, ethane was not.

**Thermolysis of K[2b].** This reaction was conducted under the same conditions as indicated for K[**2a**] (54% yield). The identity of K[**3b**] as the major product was established by comparison of its $^1$H and $^{13}$C NMR spectra to those of the authentic sample (vide supra).

**Reaction of 4 with NBu$_4$F.** To a sample of **4** (0.0090 g, 0.018 mmol) dissolved in 0.2 mL of acetonitrile-$d_3$ was added NBu$_4$F (0.0048 g, 0.018 mmol) as a solution in 0.2 mL of acetonitrile-$d_3$. A $^1$H NMR spectrum of this reaction mixture was obtained, confirming the presence of **2a** (by comparison with the $^1$H NMR spectrum of K[**2a**]) and trimethylsilyl fluoride (0.11 ppm, $^3J_{F-H}$ = 7.5 Hz) as the only products.

**Reaction of 6 with Norbornene.** To a sample of **6** (0.0150 g, 0.030 mol) dissolved in 0.2 mL of fluorobenzene-$d_5$ was added 2 equiv of norbornene (0.0057 g, 0.060 mmol) dissolved in 0.2 mL of fluorobenzene-$d_5$. The resulting mixture was heated for 12 h at 140 °C, and the organic products were analyzed by $^1$H NMR and GC-MS, revealing the formation of *exo*-phenylnorbornane (64% yield) and a small amount of norbornene dimerization products (ca. 15% yield).

**General Procedure for Catalytic Runs.** Reactions were conducted in 5 mm Wilmad NMR tubes equipped with a J. Young Teflon-valve seal, which were heated in temperature-controlled oil baths. Samples were prepared in a drybox by dissolving the catalyst and norbornene in neat arene. Reaction progress was monitored by $^1$H NMR spectroscopy (a small amount of cyclohexane-$d_{12}$ was added to all samples in order to obtain a lock signal). Product yields were quantified by GC, using a calculated response factor to account for the difference in ionization between the integration standard (naphthalene) and *exo*-phenylnorbornane.

**X-ray Structure Determination of 1b.** X-ray-quality crystals of **1b** were obtained by vapor diffusion of pentane into a toluene solution at room temperature. The X-ray analysis of **1b** was carried out at the Advanced Light Source facility of the Lawrence Berkeley National Laboratory. Measurements were made on a Bruker Platinum 200 CCD area detector with Si(111) channel cut crystal-monochromated synchrotron radiation. The data were processed using the methods indicated below for compounds **6** and **7** and are summarized in Table 4.

**General Considerations for the Determinations of X-ray Structures of 6 and 7.** The X-ray analyses of compounds **6** and **7**

**Table 4. Summary of Crystallographic Data for 1b, 6, and 7·0.5$CH_2Cl_2$**

| | 1b | 6 | 7·0.5$CH_2Cl_2$ |
|---|---|---|---|
| formula | $PtFN_2C_{17}H_{15}$ | $PtN_3C_{21}H_{17}$ | $PtCl_3N_2C_{15.5}H_{14}$ |
| MW | 461.40 | 506.48 | 529.74 |
| cryst color, habit | red, plate | pale yellow, platelike | orange, blocklike |
| cryst dimens | 0.04 × 0.03 × 0.02 mm | 0.19 × 0.15 × 0.05 mm | 0.09 × 0.09 × 0.20 mm |
| cryst syst | monoclinic | monoclinic | monoclinic |
| cell determination ($2\theta$ range) | 5487 (5.42° < $2\theta$ < 58.08°) | 4501 (4.00° < $2\theta$ < 49.00°) | 2804 (5.00° < $2\theta$ < 49.00°) |
| lattice type | primitive | primitive | *C*-centered |
| lattice params | $a$ = 10.386(2) Å | $a$ = 10.295(2) Å | $a$ = 20.614(3) Å |
| | $b$ = 13.784(3) Å | $b$ = 26.794(6) Å | $b$ = 15.956(2) Å |
| | $c$ = 10.202(2) Å | $c$ = 12.618(3) Å | $c$ = 9.241(1) Å |
| | $\beta$ = 110.111(5)° | $\beta$ = 93.410(3)° | $\beta$ = 101.447(1)° |
| | $V$ = 8876(1) Å$^3$ | $V$ = 3474(1) Å$^3$ | $V$ = 2979.2(6) Å$^3$ |
| space group | $P2_1/c$ (#14) | $P2_1/c$ (#14) | $C2/c$ (#15) |
| $Z$ value | 4 | 8 | 8 |
| $D_{calc}$ | 2.131 g/cm$^3$ | 1.936 g/cm$^3$ | 2.362 g/cm$^3$ |
| $\mu$ | synchrotron, 12.10 cm$^{-1}$ | Mo Kα, 80.52 cm$^{-1}$ | Mo Kα, 99.13 cm$^{-1}$ |
| temperature | −100 °C | −140 °C | −135 °C |
| scan type | $\omega$ (0.3° per frame) | $\omega$ (0.3° per frame) | $\omega$ (0.3° per frame) |
| no. of reflns measd | total: 10 808 | total: 15 281 | total: 6678 |
| | unique: 2957 ($R_{int}$ = 0.0391) | unique: 4042 ($R_{int}$ = 0.043) | unique: 2710 ($R_{int}$ = 0.045) |
| corrections | Lorentz−polarization | Lorentz−polarization | Lorentz−polarization |
| | abs ($T_{max}$ = 0.7939, $T_{min}$ = 0.6432) | abs ($T_{max}$ = 1.00, $T_{min}$ = 0.48) | abs ($T_{max}$ = 1.00, $T_{min}$ = 0.45) |
| structure solution | direct methods (SIR97) | direct methods (SIR97) | direct methods (SIR97) |
| refinement | full-matrix least-squares | full-matrix least-squares | full-matrix least squares |
| no. reflns obsd | 2571 [$I > 2.0\sigma(I)$] | 4151 [$I > 3.0\sigma(I)$] | 1893 [$I > 3.0\sigma(I)$] |
| no. variables | 190 | 451 | 198 |
| $R$; $R_w$; $R_{all}$ | 0.0301; 0.0743; 0.0357 | 0.038; 0.042; 0.062 | 0.032; 0.037; 0.050 |
| GOF | 1.107 | 1.37 | 1.23 |
| max. peak in final diff map | 1.933 e$^-$/Å$^3$ | 1.30 e$^-$/Å$^3$ | 1.00 e$^-$/Å$^3$ |
| min. peak in final diff map | −0.561 e$^-$/Å$^3$ | −2.57 e$^-$/Å$^3$ | −1.51 e$^-$/Å$^3$ |

were carried out at the UC Berkeley CHEXRAY crystallographic facility. Measurements were made on a Bruker SMART CCD area detector with graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71069 Å). Data were integrated by the program SAINT and analyzed for agreement using XPREP. Empirical absorption corrections were made using SADABS. Structures were solved by direct methods and expanded using Fourier techniques. All calculations were performed using the teXsan crystallographic software package. Selected crystal and structure refinement data are summarized in Table 4.

**X-ray Structure Determination of 6.** X-ray-quality crystals of **6** formed upon slow evaporation of a dilute dichloromethane solution. The compound crystallizes in the centric monoclinic space group $P2_1/c$ with two molecules in the asymmetric unit and eight molecules in the unit cell. The pyridinyl moieties of the ligands in adjacent molecules are essentially parallel to each other and have a plane-to-plane closest approach of about 3.25 Å. All hydrogen atom positions were calculated but not refined.

**X-ray Structure Determination of 7.** X-ray quality crystals of **7** formed upon slow evaporation of a dilute dichloromethane solution. The compound crystallizes with one molecule of **7** and one-half molecule of dichloromethane in the asymmetric unit, and the dichloromethane sits on the crystallographic 2-fold axis in the cell. Non-hydrogen atoms were refined anisotropically. The data set was of sufficient quality that the positions of the four hydrogen atoms of the ethylene ligand could be refined with the thermal parameters fixed at reasonable values. Other hydrogens were included in calculated positions and not refined.

## Computational Details

**Method.** Quantum mechanical calculations were performed at the University of California, Berkeley Molecular Graphics Facility using a 98 cpu-cluster with 2.8 GHz Xeon processors. The DFT calculation on **2a** was carried out by implementing the B3LYP exchange−correlation functional[59] with the LACVP**++ basis set, using Jaguar 5.5. The geometry of **2a** was fully optimized in the gas phase without symmetry constraints. Vibrational frequencies were calculated to ensure that local minima lacked any negative frequencies.

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**Supporting Information Available:** X-ray crystallographic data for **1b**, **6**, and **7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(59) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.