# Ethylene Insertion in Tp′Pt(Ph)($\eta^2$-$CH_2$=$CH_2$) and C−H Activation of Ethylbenzene to Form a Platinum(IV) *ortho*-Metalated Phenethyl Complex

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Heating Tp′Pt(Ph)($\eta^2$-$CH_2$=$CH_2$) (**5**) in benzene forms an *ortho*-metalated phenethyl hydrido platinum-(IV) complex, Tp′Pt($CH_2CH_2$-*o*-$C_6H_4$)(H) (**7**). Presumably this net reaction reflects phenyl migration to ethylene to give the insertion product, Tp′$PtCH_2CH_2Ph$, as an unsaturated intermediate. Intramolecular C−H activation of an *ortho* phenyl proton from this intermediate would produce the metallacyle product. Low-temperature protonation of the phenyl ethylene complex **5** results in the formation of a cationic $\eta^2$-ethylene phenyl complex, [$\kappa^2$-(HTp′)Pt($C_6H_5$)($\eta^2$-$CH_2$=$CH_2$)][BAr′$_4$] (**6**). Low-temperature protonation of the *ortho*-metalated phenethyl complex **7** followed by addition of acetonitrile leads to reductive coupling of the Pt−H and the alkyl methylene group to give a cationic Pt(II) 2-ethylphenyl complex, [$\kappa^2$-(HTp′)-Pt($C_6H_4$-2-$CH_2CH_3$)($NCCH_3$)][BAr′$_4$] (**9**). Complex **7** has also been isolated as the sole product of gentle heating of Tp′Pt($Me)_2$(H) (**2**) with the Lewis acid B($C_6F_5)_3$ in ethylbenzene. Additional analogous Pt(IV) metallacycles, Tp′Pt($CH_2CH$(Me)-*o*-$C_6H_4$)(H) (**11a/11b**) and Tp′Pt($CH_2CH_2$-*o*-$C_6H_3$Et)(H) (**13**), have also been synthesized by this route. Note that heating of the dihydride reagent Tp′Pt(Me)$(H)_2$ (**3**) with B($C_6F_5)_3$ in either ethylbenzene or 2-propylbenzene gave only Tp′Pt(Ar)$(H)_2$ (**14** and **15**) products. Attempts to isolate an $\eta^2$-propylene phenyl complex were unsuccessful; formation of the 1,2-insertion product, Tp′Pt(CH(Me)$CH_2$-*o*-$C_6H_4$)(H) (**10**), and 2,1-insertion products, **11a** and **11b**, resulted. An in situ attempt to isolate the cationic [$\kappa^2$-(HTp′)Pt($C_6H_5$)($\eta^2$-$CH_2$=$CH(CH_3)$)][$BF_4$] resulted in the isolation of the Pt(II) phenyl aqua complex [$\kappa^2$-(HTp′)Pt($C_6H_5$)($OH_2$)][$BF_4$] (**12**) instead.

## Introduction

Generation of useful chemicals from readily available and inexpensive chemical feedstocks, such as saturated hydrocarbons, remains a major research challenge. Transition metal-mediated activation of C−H bonds is a promising approach to achieve this goal, and significant effort has been directed at understanding these processes.[1−8] While many metal reagents are capable of activating C−H bonds, few lead to catalytic formation of new C−C or C−X bonds, a prerequisite for the production of organic molecules.[9,10] Substantive advances in C−H activation of arenes with subsequent C−C bond formation have been made, although they are primarily limited to arenes with heteroatom functionality.[11] The heteroatom typically allows coordination of the arene to the metal center, thus positioning the C−H bond to be cleaved. One of the most useful transformations of this type is the ruthenium-[12−14] or rhodium-catalyzed[15] selective *ortho* alkylation of aromatic ketones with olefins.

Transformations with unactivated C−H bonds by transition metal complexes, such as hydroarylation of olefins, are rare.[16−23] A few homogeneous catalysts have been reported recently that catalyze the intermolecular hydroarylation of unactivated arenes with unactivated olefins via a C−H activation reaction. Periana and co-workers have described the regioselective hydroarylation of olefins by O-donor ligated Ir(III) catalysts, specifically,

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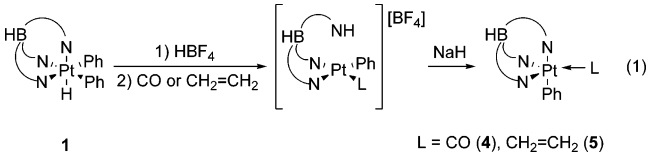
(acac-O,O)$_2$Ir(R)(py) and, more recently, (trop-O,O)$_2$Ir(Ph)(py) (acac-O,O = $\kappa^2$-*O*,*O*-acetylacetonate, trop-O,O = $\kappa^2$-*O*,*O*-tropolonato, R = $CH_3$, $C_2H_5$, Ph, $CH_2CH_2Ph$).[24−30] Gunnoe and co-workers[31−33] have reported a related Ru(II) catalyst, TpRu(CO)(NCMe)Me (Tp = hydridotris(pyrazolyl)borate), that is ∼200 times faster than previous systems[34] for the catalytic conversion of benzene and ethylene to ethylbenzene at 90 °C. These Ir(III) and Ru(II) systems preferentially undergo 2,1-insertion to form straight-chain alkylarenes. Theoretical studies suggest that these systems react through a common mechanism, which includes insertion of the $\pi$-bond of the metal-coordinated ethylene into the metal−aryl bond and C−H activation/hydrogen transfer of an unactivated benzene.[26,27,34] Of the various systems that have been reported as active catalysts for the hydroarylation of unactivated olefins, none have proven to be sufficiently active and/or selective to be commercially viable.[27]

The synthesis of Tp′Pt(Ph)($\eta^2$-$CH_2$═$CH_2$) (**5**) was undertaken in order to explore its potential as a catalyst in ethylbenzene formation, perhaps via a catalytic cycle analogous to that of the previously reported systems.[27,30,33,34] Thermolysis of complex **5** in $C_6D_6$, however, leads to formation of a stable platinum(IV) *ortho*-metalated complex, Tp′Pt($CH_2CH_2$-*o*-$C_6H_4$)(H) (**7**). While our system undergoes C−C bond formation via insertion of ethylene into the platinum phenyl linkage, subsequent intramolecular C−H activation of an *ortho*-aryl proton, yielding the metallacycle, occurs rather than intermolecular C−H activation of solvent. This *ortho*-metalated platinum hydride complex, **7**, has also been independently prepared as the sole product in the reaction of Tp′PtMe$_2$H (**2**) with ethylbenzene.

## Results and Discussion

**Tp′PtLR Complexes.** The synthesis of a variety of neutral Tp′PtLMe complexes via protonation of Tp′PtMe$_2$H (**2**), addition of a neutral trapping ligand, and subsequent deprotonation has been reported.[35] This reaction sequence has now been used to prepare analogous Tp′Pt(Ph)(L) complexes, Tp′Pt(Ph)(CO) (**4**) and Tp′Pt(Ph)($\eta^2$-$CH_2$═$CH_2$) (**5**), via a protonation/ligand addition/deprotonation sequence with Tp′PtPh$_2$H (**1**) as the metal precursor. Low-temperature addition of $HBF_4$·$Et_2O$ to a solution of Tp′PtPh$_2$H (**2**) results in the formation of the phenyl benzene adduct [$\kappa^2$-(HTp′)Pt($C_6H_5$)($\eta^2$-$C_6H_6$)][$BF_4$],[36] as indicated by the yellow solution color. Addition of ethylene or CO and warming to room temperature results in loss of the $\eta^2$-benzene ligand and formation of a Pt(II) cation, [$\kappa^2$-(HTp′)Pt($C_6H_5$)(L)][$BF_4$] (L = CO or $CH_2$═$CH_2$). Deprotonation of the free pyrazole ring with NaH in THF results in the formation of the desired neutral complexes, Tp′Pt(Ph)(CO) (**4**) and Tp′Pt(Ph)($\eta^2$-$CH_2$═$CH_2$) (**5**) (eq 1).




(1)

The geometries of analogous Tp′Pt(Me)(L) complexes depend on the identity of the neutral trapping ligand.[35] Complexes containing $\sigma$-donor ligands, such as NCMe or SMe$_2$, display simple square-planar Pt(II) geometries with one free Tp′ pyrazolyl arm, while complexes with $\pi$-acid ligands, such as CO or ethylene, bind all three Tp′ rings to the platinum center (Figure 1). Both resonance structures shown in Figure 1 for $\kappa^3$-Tp′ platinum complexes with olefin ligands are applicable. The octahedral Pt(IV) metallacyclopropane depiction is particularly useful for representing olefin orientation and for predicting coupling constants. The coordination mode of the Tp′ ligand can be determined by measuring the B−H stretching frequency, and this indirectly indicates the geometry of the platinum complex. A B−H stretching frequency above 2500 cm$^{-1}$ is indicative of $\kappa^3$-Tp′ coordination, while a B−H stretch below 2500 cm$^{-1}$ indicates $\kappa^2$-Tp′ coordination.[37] The methyl ethylene complex Tp′Pt(Me)($\eta^2$-$CH_2$═$CH_2$) displays a five-coordinate trigonal-bipyramidal geometry, whereas the methyl carbonyl complex Tp′Pt(Me)(CO) undergoes rapid interconversion between trigonal-bipyramidal and square-planar geometries on the NMR time scale. The analogous Tp′Pt(Ph)(CO) complex **4** displays a solution IR spectrum similar to the methyl carbonyl complex, with two absorptions for both the B−H stretch (2528, 2485 cm$^{-1}$) and CO stretch (2092, 2082 cm$^{-1}$). These data are consistent with rapid interconversion of the Pt(II) $\kappa^3$-Tp′ ($\nu_{B-H}$ 2528 cm$^{-1}$, $\nu_{CO}$ 2082 cm$^{-1}$) and Pt(II) $\kappa^2$-Tp′ ($\nu_{B-H}$ 2485 cm$^{-1}$, $\nu_{CO}$ 2092 cm$^{-1}$) geometries in solution.[35,38,39]

The mirror symmetry observed in the $^1$H NMR spectrum for the phenyl carbonyl complex **4** is consistent with a rapid equilibration between square-planar and trigonal-bipyramidal geometries in solution. The NMR time scale is too slow to resolve this dynamic process, but both geometries are evident in the infrared spectrum. The carbonyl carbon for complex **4** resonates at 163.7 ppm in the $^{13}$C NMR spectrum, close to the CO chemical shift in the Tp′Pt(Me)(CO) complex.[35]

Proton NMR spectra for neutral Tp′Pt(Ph)(L) complexes display a 2:1 pattern for the pyrazole resonances consistent with mirror symmetry in the Pt(II) trigonal-bipyramidal geometry.

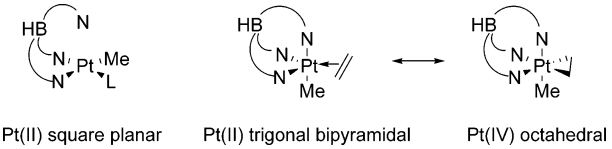



**Figure 1.** Possible geometries for neutral Tp′Pt complexes.

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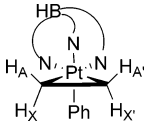



**Figure 2.** Olefin orientation in Tp′Pt(Ph)($\eta^2$-$CH_2$═$CH_2$) (**5**).

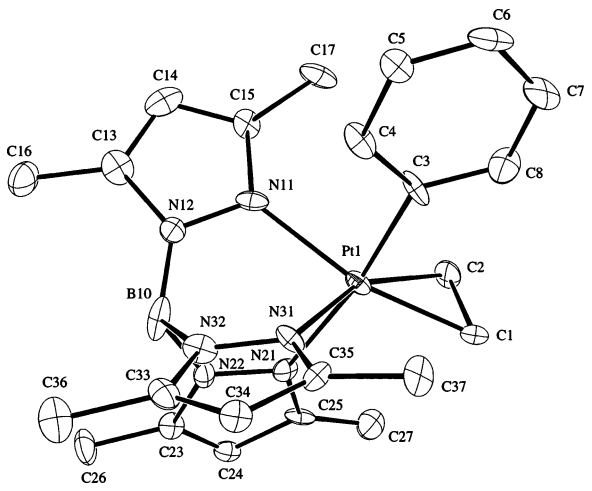



**Figure 3.** ORTEP diagram of Tp′Pt(Ph)($\eta^2$-$CH_2$═$CH_2$) (**5**). Ellipsoids are drawn at the 50% probability level.

**Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 5**

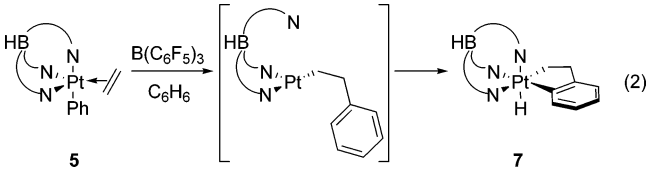
| | | | |
|---|---|---|---|
| | Bond Distances | | |
| Pt−C1 | 2.104(18) | Pt−N11 | 2.168(15) |
| Pt−C2 | 2.064(16) | Pt−N21 | 2.220(12) |
| Pt−C3 | 2.052(14) | Pt−N31 | 2.140(12) |
| C1−C2 | 1.43(3) | | |
| | Bond Angles | | |
| C1−Pt−C2 | 40.2(9) | Pt−C2−C1 | 71.4(10) |
| C1−Pt−C3 | 90.4(7) | Pt−C1−C2 | 68.4(10) |
| C2−Pt−C3 | 92.0(8) | C3−Pt−N11 | 89.4(6) |
| C1−Pt−N11 | 157.3(6) | C3−Pt−N21 | 171.7(6) |
| C1−Pt−N21 | 97.7(6) | C3−Pt−N31 | 90.8(6) |
| C1−Pt−N31 | 115.6(6) | N11−Pt−N21 | 83.8(5) |
| C2−Pt−N11 | 117.1(8) | N11−Pt−N31 | 87.1(5) |
| C2−Pt−N21 | 95.3(7) | N21−Pt−N31 | 84.1(5) |
| C2−Pt−N31 | 155.6(9) | | |

The four olefinic protons for the phenyl ethylene complex **5** are equivalent at room temperature due to a combination of mirror symmetry and rapid olefin rotation (Figure 2). At 253 K, olefin rotation is slow on the NMR time scale, and doublets are observed at 3.31 ppm ($^2J_{Pt-H}$ = 80 Hz and $^3J_{H-H}$ = 7.2 Hz) and 2.44 ppm ($^2J_{Pt-H}$ = 56 Hz and $^3J_{H-H}$ = 7.2 Hz), reflecting the AA′XX′ pattern of the static $C_s$ structure. The carbon atoms in the coordinated ethylene are isochronous and resonate at 24.2 ppm.

The structural features of the neutral phenyl ethylene platinum complex **5** were investigated by X-ray structural analysis. An ORTEP diagram of **5** shows $\kappa^3$-coordination of the Tp′ ligand (Figure 3). The platinum atom exhibits a trigonal-bipyramidal coordination geometry (Table 1). One coordinated pyrazole ring and the phenyl ligand occupy the axial positions (C3−Pt−N21 = 171.7(6)°), while the other pyrazole rings and ethylene ligand are in the equatorial plane (C2−Pt−N11 = 117.1(8)° and C1−Pt−N31 = 115.6(6)°). The ethylene ligand is oriented perpendicular to the Pt−Ph bond (C1−Pt−C3 = 90.4(7)° and C2−Pt−C3 = 92.0(8)°) with a C1−C2 bond distance of 1.43(3) Å. This coordinated olefin C−C bond distance is similar to other C−C bond lengths observed in neutral Pt(II) ethylene complexes.[40,41]

The intermediate cationic Pt(II) $\eta^2$-ethylene phenyl complex [$\kappa^2$-(HTp′)Pt($\eta^2$-$CH_2$═$CH_2$)(Ph)][$BAr'_4$] (**6**) could be detected by low-temperature $^1$H NMR spectroscopy. Protonation of complex **5** with [$H(OEt_2)_2$][$BAr'_4$] resulted in the release of one pyrazole ring from the metal center and formation of complex **6**. The $^1$H NMR spectrum for complex **6** displays an N−H resonance at 10.36 ppm for the protonated pyrazole ring. The mirror symmetry of the starting neutral platinum complex **5** has been lost, as is evident by the unique signal for each of the three nonequivalent pyrazole rings observed in the $^1$H NMR spectra. Rapid rotation of the ethylene ligand around the midpoint of the platinum−ethylene bond at room temperature is indicated by the two multiplets observed at 4.21 and 3.77 ppm with broad platinum satellites for the ethylene protons. Similar NMR data has been reported for the analogous methyl complex, [$\kappa^2$-(HTp′)Pt($\eta^2$-$CH_2$═$CH_2$)(Me)][$BAr'_4$].[35]

**Olefin Insertion.** The addition of Lewis acids to Tp′Pt$Me_2$H (**2**) and Tp′Pt$MeH_2$ (**3**) has been proposed to induce dissociation of one of the pyrazole rings from the platinum center to generate a reactive five-coordinate intermediate at ambient temperatures.[42] In an effort to uncover arene and alkane functionalization routes, the Lewis acid $B(C_6F_5)_3$ has been used to induce ethylene insertion into the platinum phenyl bond of the phenyl ethylene complex **5** at ambient temperatures (eq 2). This transformation may proceed by borane-assisted dissociation of one of the pyrazole rings, or perhaps trace protic acid is responsible for the observed reaction. In the presence of borane, insertion occurs readily at 60 °C and is followed by rapid intramolecular C−H activation of an *ortho* phenyl proton to form a Pt(IV) *ortho*-metalated phenethyl hydride complex, Tp′Pt($CH_2CH_2$-*o*-$C_6H_4$)(H) (**7**). Formation of complex **7** was also observed from the thermolysis of **5** at temperatures above 80 °C in the absence of borane. The appearance of four distinct aromatic proton signals and an upfield Pt−H resonance in the $^1$H NMR spectrum suggested the metallacyclic structure of complex **7**. Heating the phenyl carbonyl complex **4** to 90 °C in the presence of $B(C_6F_5)_3$ did not result in a similar insertion to form an acyl product, but led only to decomposition.




The formation of complex **7** leads to the question of how the Tp′Pt system differs from the previously reported catalytic systems with Ir(III) and Ru(II). A key difference in the Tp′Pt system and the Ir(III) and Ru(II) systems is the ability of Tp′Pt species to access and stabilize both Pt(II) and Pt(IV) oxidation states. Formation of the Pt(IV) metallacycle hydride complex **7** from Tp′Pt(Ph)($\eta^2$-$CH_2$═$CH_2$) (**5**) results from insertion of ethylene into the Pt−Ph bond, followed by oxidative addition of a an aryl C−H bond. In contrast, for the Ir(III) and Ru(II) systems, DFT studies suggest that following insertion and $\eta^2$-coordination of benzene, a $\sigma$-bond metathesis or an oxidative hydrogen migration pathway (OHM)—a concerted transfer of a hydrogen from the aryl carbon to the aliphatic

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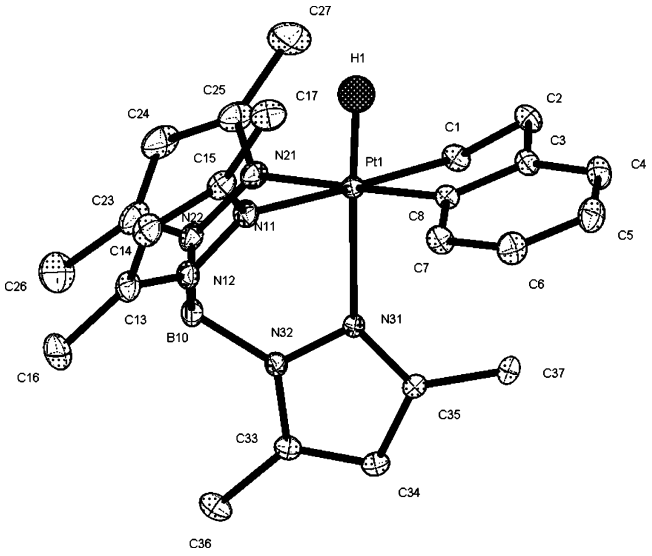



**Figure 4.** ORTEP diagram of Tp′Pt($CH_2CH_2$-*o*-$C_6H_4$)(H) (**7**). Ellipsoids are drawn at the 50% probability level. $C_6H_5Et$ and $Et_2O$ molecules are omitted for clarity.

**Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 7**

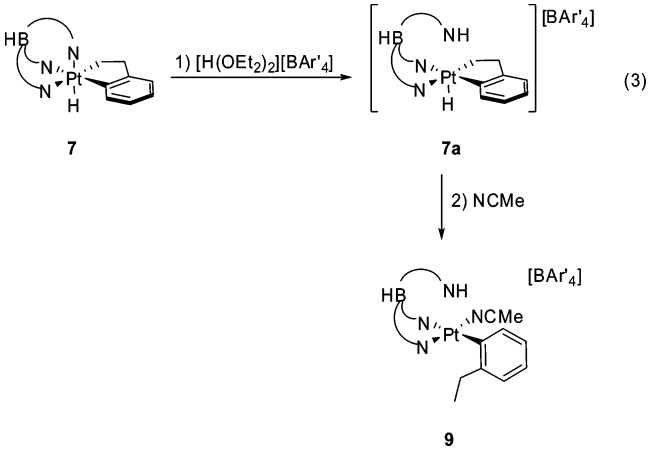
| Bond Distances | | | |
|---|---|---|---|
| Pt−C8 | 2.0176(12) | C3−C4 | 1.4031(19) |
| Pt−C1 | 2.0762(11) | C3−C8 | 1.4160(15) |
| Pt−N21 | 2.1549(11) | C4−C5 | 1.402(2) |
| Pt−N11 | 2.1662(10) | C5−C6 | 1.399(2) |
| Pt−N31 | 2.2053(9) | C6−C7 | 1.4060(19) |
| C1−C2 | 1.5468(19) | C7−C8 | 1.4055(16) |
| C2−C3 | 1.5086(18) | | |
| **Bond Angles** | | | |
| C8−Pt−C1 | 81.33(5) | N21−Pt−N31 | 87.32(4) |
| C8−Pt−N21 | 178.54(4) | N11−Pt−N31 | 86.71(4) |
| C1−Pt−N21 | 97.29(5) | C2−C1−Pt | 108.98(8) |
| C8−Pt−N11 | 97.68(4) | C3−C2−C1 | 108.07(9) |
| C1−Pt−N11 | 177.85(5) | C4−C3−C2 | 124.73(11) |
| N21−Pt−N11 | 83.69(4) | C8−C3−C2 | 115.12(11) |
| C8−Pt−N31 | 93.25(4) | C7−C8−Pt | 125.10(9) |
| C1−Pt−N31 | 95.25(4) | C3−C8−Pt | 115.61(8) |

carbon—is operative due to the absence of an easily accessible $M^{n+2}$ oxidation state required for an oxidative addition pathway.[27,33,34] In addition, the Ir(III) and Ru(II) systems are coordinatively saturated and formation of a seven-coordinate metallacycle hydride species may be unfavorable.

The chirality of complex **7** is evident in the three nonequivalent pyrazole rings observed in the $^1$H NMR spectrum. The four aromatic protons are all distinct with one doublet at 6.76 ppm with $^3J_{Pt-H}$ = 38 Hz, indicative of the one aromatic proton coupled to platinum. The four bridging $CH_2CH_2$ methylene protons are diastereotopic and appear as multiplets between 3.18 and 2.63 ppm with broad platinum satellites. The platinum hydride resonates at −19.63 ppm with $^1J_{Pt-H}$ = 1391 Hz. The internal carbon of the methylene bridge resonates at 43.98 ppm, and the platinum-bound methylene carbon resonates far upfield at 8.54 ppm ($^1J_{Pt-C}$ = 601 Hz).

Clear, colorless block crystals of complex **7** were obtained, and the structure was investigated by single-crystal X-ray analysis. The hydride ligand on platinum was placed in a calculated position. Figure 4 shows the ORTEP diagram of **7**, which displays an octahedral geometry with a $\kappa^3$ coordination mode of the Tp′ ligand. The metallacycle lies in the equatorial plane opposite two pyrazole rings (C1−Pt−N11 = 177.85(5)° and C8−Pt−N21 = 178.54(4)°) (Table 2) and is twisted into an envelope conformation with C2 folded toward the platinum hydride position. The Pt−N (Pt−N31 = 2.205(1) Å) bond *trans* to the hydride is longer than the two Pt−N bonds in the equatorial plane, which have similar lengths (Pt−N11 = 2.166(1) Å and Pt−N21 = 2.155(1) Å), indicating the stronger *trans* influence of the hydride ligand. The bond distance from platinum to the methylene carbon is longer than to the arene carbon by 0.059 Å (Pt−C1 = 2.076(1) Å and Pt−C8 = 2.018(1) Å). This difference is consistent with the hybridization of the two carbons; M−C($sp^2$) bonds are shorter than M−C($sp^3$) bonds.

Low-temperature protonation of the platinum(IV) *ortho*-metalated phenethyl hydride complex Tp′Pt($CH_2CH_2$-*o*-$C_6H_4$)(H) (**7**) resulted in release of one pyrazole ring from the metal center to presumably generate a reactive five-coordinate intermediate, **7a** (eq 3). Intermediate **7a** has two possible reductive elimination pathways: the Pt−H can couple with either an aromatic or an aliphatic carbon, leaving the other end of the original metallacycle bound to platinum. Reductive elimination of the alkyl group gives exclusively a Pt(II) 2-ethylphenyl ether cation, [$\kappa^2$-(HTp′)Pt($C_6H_4$-2-$CH_2CH_3$)($OEt_2$)][BAr′$_4$] (**8**). Addition of NCMe converts this complex to the more stable acetonitrile adduct [$\kappa^2$-(HTp′)Pt($C_6H_4$-2-$CH_2CH_3$)(NCMe)][BAr′$_4$] (**9**) (eq 3). Reductive elimination of the alkyl group was detected by the appearance of an ethyl group in the $^1$H NMR spectrum. The diastereotopic methylene protons appear as a complex AB portion of an $ABX_3$ pattern at 3.25 ppm, and the methyl group resonates as a triplet at 1.37 ppm.




**7** **7a** **9** (3)

The preference for alkyl elimination can be attributed to the relative stabilities of the products formed since M−aryl bonds are stronger than M−alkyl bonds.[43−46] Factors other than M−C bond strengths have been shown to be involved in controlling the relative rates of alkyl/aryl reductive elimination,[47] but in this system the products are consistent with relative M−C bond strengths. It is possible that aryl elimination also occurs, but that the product formed rapidly rearranges to the observed 2-ethylphenyl derivative. For example, in the related (diimine)Pt(Me)(Ph)(H)(solv) system Me−H and Ph−H formation and elimination have been shown to be competitive.[48−51]

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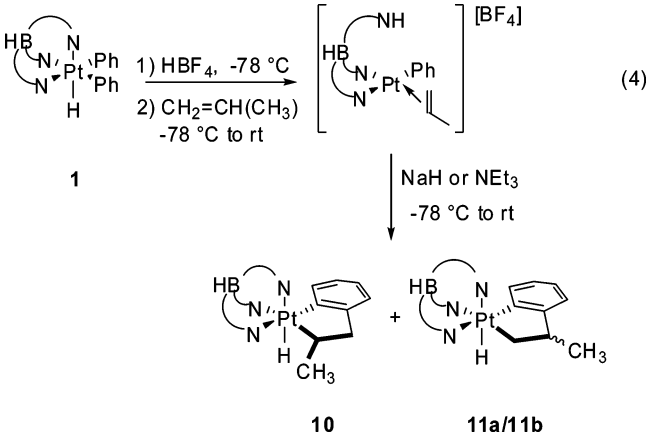
A similar rearrangement has also been studied for a related Pd system $Pd(CH_2CMe_2\text{-}o\text{-}C_6H_4)(PMe_3)_2$, synthesized from the base-induced metalation of the neophyl derivatives *trans*-$[Pd(CH_2CMe_2Ph)X(PMe_3)_2]$ (X = Cl, OAc, or OTf). When the metallacyle was protonated with HX, the reaction was reversed and the alkyl-bound complex, the neophyl derivative, was reformed via an observed $\pi,\eta^1$-arene intermediate, the $\pi,\eta^1$ designation reflecting coordination of the *ipso* carbon to palladium. Protonation of the metallacycle with $[H(OEt_2)_2][BAr'_4]$ at low temperature resulted in initial formation the $\pi,\eta^1$-arene species, which, upon warming in $Et_2O$ or THF, gave the aryl-bound $[Pd(C_6H_5\text{-}2\text{-}CMe_3)(PMe_3)][BAr'_4]$ derivative. Notably, the $\pi,\eta^1$-arene intermediate is proposed to isomerize to the aryl-bound species through a solvent-assisted rearrangement that could produce a Pd(IV) metallacycle hydrido intermediate.[46,52] The Pt(IV) metallacycle hydride complexes synthesized in this work support the feasibility of such an intermediate.

**Propylene Insertion.** In attempts to prepare the propylene analogue of **5**, Tp′Pt(Ph)($\eta^2$-$CH_2$═$CH(CH_3)$), by the same low-temperature route used to synthesize **4** and **5**, metallacycle hydride products comparable to **7** were observed after deprotonation. Following addition of $HBF_4$·$Et_2O$ at −78 °C to Tp′$PtPh_2$H (**1**), propylene was sparged into the reaction flask as the solution slowly warmed to room temperature. After 30 min, deprotonation led to one major platinum species, as determined by the $^1$H NMR spectrum of the crude reaction product, with a hydride resonating at −19.48 ppm ($^1J_{Pt-H}$ =1368 Hz) and a multiplet with platinum satellites at 5.03 ppm ($^3J_{H-H}$ = 6 Hz, $^3J_{H-H}$ = 15 Hz, $^2J_{Pt-H}$ = 50 Hz), as well as multiple new aryl peaks. When the propylene sparge was continued for 2 h prior to deprotonation, however, additional platinum hydride resonances appeared at −19.40 ppm ($^1J_{Pt-H}$ =1385 Hz) and −19.78 ppm ($^1J_{Pt-H}$ =1393 Hz), along with olefinic signals between 2.4 and 3.5 ppm and new aryl peaks. The first product is formulated as the metallacycle Tp′$Pt(CH(CH_3)CH_2\text{-}o\text{-}C_6H_4)$(H) (**10**), resulting from the 2,1-insertion of olefin into the phenyl−platinum bond. The other two species observed can be identified as diastereomers of Tp′$Pt(CH_2CH(CH_3)\text{-}o\text{-}C_6H_4)$(H) (**11a/11b**), the 1,2-insertion product (eq 4).




(4)

Low-temperature $^1$H NMR experiments were conducted to confirm complex **10** as the kinetic product of insertion and complexes **11a** and **11b** as the thermodynamic products. Upon addition of $NEt_3$ to the reaction of propylene and $[(HTp')Pt(C_6H_5)(\eta^2\text{-}C_6H_6)][BF_4]$, the 2,1-insertion product, **10**, was trapped as the major species, as evidenced by the platinum hydride signal at −19.48 ppm. The product was then separated from the salts and excess propylene, redissolved in 1,1,2,2-tetrachloroethane-$d_2$, and subsequently heated in the NMR probe. At 80 °C, formation of the 1,2-insertion products, **11a** and **11b**, and consumption of the 2,1-insertion product, **10**, was clearly evident by changes in the hydride region of the spectrum. No intermediate species was observed.

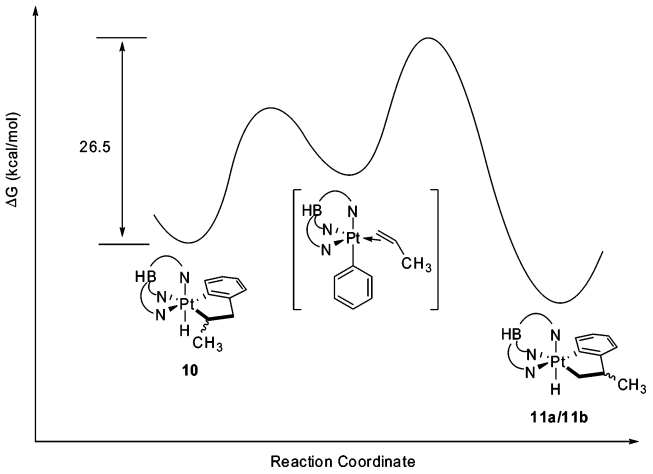



**Figure 5.** Conversion of complex **10** to complexes **11a** and **11b**.

It may be that isomerization of the 2,1-insertion product, **10**, to the 1,2-insertion products, **11a** and **11b**, proceeds through the elusive Tp′Pt(Ph)($\eta^2$-$CH_2$═$CH(CH_3)$) complex as an intermediate. This would indicate that propylene insertion into the Pt−Ph bond and formation of a C−C bond are reversible. A possible reaction coordinate is shown in Figure 5. NMR experiments at 80 °C indicate a $\Delta G^{\ddagger}$ for the conversion of **10** to **11a** and **11b** of 26.5 kcal/mol.

In a related system with cationic Pt(II) complexes of the type $[Pt(aryl)(N-N)(L)]^+$ (N−N = bidentate nitrogen ligand), α-olefins were found to insert into the Pt−aryl bond in the presence of $AgBF_4$ to form either an alkyl-bound [Pt]−$CH_2$−CHR−aryl species or an aryl-bound [Pt]−aryl−2-(CHR−$CH_3$) derivative.[43,45,53] The alkyl-bound product was formed when donor ligands, such as excess olefin, pyridine, or triphenylphosphine, were available in solution, while the aryl-bound derivative was preferred in the absence of donor ligands and is presumed to form from an intramolecular rearrangement of the alkyl-bound species.[45] The metallacycle hydride complexes here represent one type of proposed intermediate in the earlier study.[43]

Low-temperature attempts to isolate the cationic Pt(II) $\eta^2$-propylene phenyl complex, $[\kappa^2\text{-}(HTp')Pt(\eta^2\text{-}CH_2$═$CH(CH_3))(Ph)][BF_4]$, were unsuccessful. Instead a stable cationic Pt(II) phenyl aqua complex, $[\kappa^2\text{-}(HTp')Pt(Ph)(OH_2)][BF_4]$ (**12**), was isolated, presumably from adventitious water present in the $HBF_4$·$Et_2O$ solution. The $^1$H NMR spectrum for complex **12** displays a N−H resonance at 11.62 ppm for the protonated pyrazole ring and a broad singlet at 4.97 ppm for the coordinated water molecule. Similar cationic (diimine)Pt aqua complexes have been reported previously, and it is noteworthy that they activate benzene and methane C−H bonds under mild conditions.[48,54]

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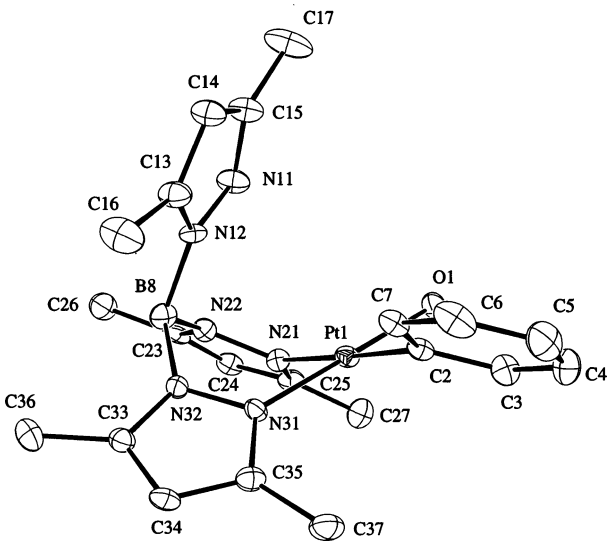


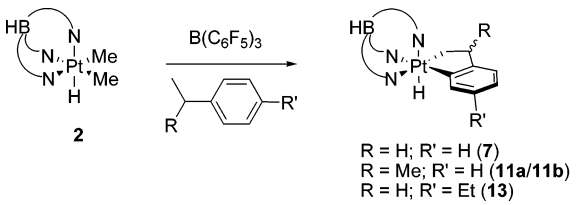

**Figure 6.** ORTEP diagram of [$\kappa^2$-(HTp′)Pt(Ph)($OH_2$)][$BF_4$] (**12**). Ellipsoids are drawn at the 50% probability level, and the [$BF_4$] counterion is omitted for clarity.

**Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 12**

| | | | |
|---|---|---|---|
| | Bond Distances | | |
| Pt−O1 | 2.075(1) | Pt−N21 | 2.095(5) |
| Pt−C2 | 1.997(6) | Pt−N31 | 1.987(5) |
| | Bond Angles | | |
| O1−Pt−C2 | 88.95(23) | C2−Pt−N21 | 178.58(24) |
| O1−Pt−N21 | 89.82(19) | C2−Pt−N31 | 93.46(24) |
| O1−Pt−N31 | 177.58(20) | N21−Pt−N31 | 87.78(21) |

The structural features of the cationic phenyl aqua complex **12** were investigated by X-ray structural analysis. An ORTEP diagram of **12** is shown in Figure 6. The protonated pyrazole nitrogen atom is turned away from the platinum square plane, an orientation seen in similar cationic (Tp′−H)Pt(II) complexes.[35] The Pt−N(21) distance of 2.095(5) Å is 0.10 Å longer than the Pt−N(31) distance of 1.987(5) Å *trans* to the water ligand, indicating the stronger *trans* influence of the phenyl ligand (Table 3). The Pt−O distance of 2.075(1) Å is similar to other Pt(II)−$OH_2$ bond distances *trans* to nitrogen ligands.[55−58]

**C−H Activation of Alkylarenes.** Mild heating of Tp′$PtMe_2H$ (**2**) in neat ethylbenzene in the presence of $B(C_6F_5)_3$ resulted in the loss of 2 equiv of methane and formation of metallacyclic complex **7** as the sole product (eq 5). When monitored by NMR, the reaction proceeded to completion at room temperature within 15 min after the addition of ethylbenzene. The diaryl hydride platinum intermediate complex, Tp′Pt($C_6H_4Et)_2H$, was not observed. Analogous reactions of **2** with either isopropyl- or 1,4-diethylbenzene also yield clean *ortho*-metalated platinum hydride complexes, Tp′Pt($CH_2CH$(Me)-*o*-$C_6H_4$)(H) (**11a/11b**) and Tp′Pt($CH_2CH_2$-*o*-$C_6H_3$(Et))(H) (**13**), respectively.




(5)

The $^1$H NMR spectrum for the platinum metallacycle derived from isopropylbenzene, complexes **11a** and **11b**, shows hydride resonances at −19.78 ($^1J_{Pt-H}$ = 1393 Hz) and −19.40 ($^1J_{Pt-H}$ = 1385 Hz) in a ratio of 2.7:1, reflecting a major, **11a**, and a minor, **11b**, isomer. These hydrides are the same as the 1,2-insertion products observed in attempts to isolate Tp′Pt(Ph)($\eta^2$-$CH_2$═$CH(CH_3)$), vide supra. While the products are chiral and formally contain only nonequivalent pyrazole rings, two of the pyrazole rings are incidentally isochronous in the room-temperature $^1$H NMR spectrum. The identity of the bridging −$CH_2CH(CH_3)$− protons was revealed by 2D NMR. For the major species, **11a**, the methine proton of the saturated bridge appears as a multiplet, resonating the furthest downfield among the bridge hydrogens at 3.20 ppm. One of the other two bridging metallacycle protons can be found at 2.77 ppm with Pt satellites ($^2J_{Pt-H}$ = 63 Hz), and the third proton is hidden under the Tp′

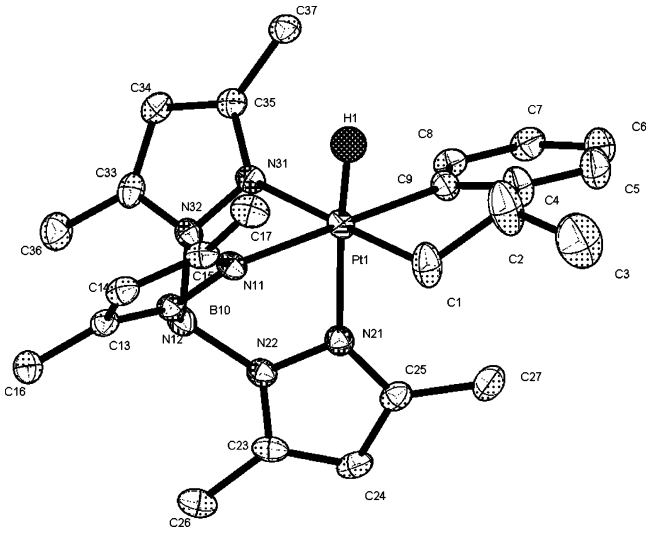



**Figure 7.** ORTEP diagram of Tp′Pt($CH_2CH$Me-*o*-$C_6H_4$)(H) (**11a**). Ellipsoids are drawn at the 50% probability level. $CH_2Cl_2$ molecule is omitted for clarity.

**Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 11a**

| | | | |
|---|---|---|---|
| | Bond Distances | | |
| Pt−C9 | 2.011(3) | C2−C4 | 1.518(5) |
| Pt−C1 | 2.054(3) | C4−C5 | 1.396(5) |
| Pt−H1 | 1.493(5) | C4−C9 | 1.401(5) |
| Pt−N31 | 2.144(3) | C5−C6 | 1.383(5) |
| Pt−N11 | 2.146(2) | C6−C7 | 1.381(5) |
| Pt−N21 | 2.180(3) | C7−C8 | 1.400(5) |
| C1−C2 | 1.558(5) | C8−C9 | 1.388(4) |
| C2−C3 | 1.459(6) | | |
| | Bond Angles | | |
| C9−Pt−C1 | 81.31(13) | C2−C1−Pt | 109.4(2) |
| C9−Pt−N31 | 98.75(11) | C3−C2−C4 | 116.0(4) |
| C1−Pt−N31 | 178.76(13) | C3−C2−C1 | 114.9(4) |
| C9−Pt−N11 | 177.83(11) | C4−C2−C1 | 106.0(3) |
| C1−Pt−N11 | 96.72(12) | C5−C4−C9 | 119.8(3) |
| C9−Pt−N21 | 91.76(11) | C5−C4−C2 | 124.8(3) |
| C1−Pt−N21 | 95.04(13) | C9−C4−C2 | 115.4(3) |
| N11−Pt−N21 | 89.29(9) | C8−C9−Pt | 124.9(2) |
| N31−Pt−N11 | 83.21(9) | C4−C9−Pt | 115.7(2) |
| N31−Pt−N21 | 86.20(9) | | |

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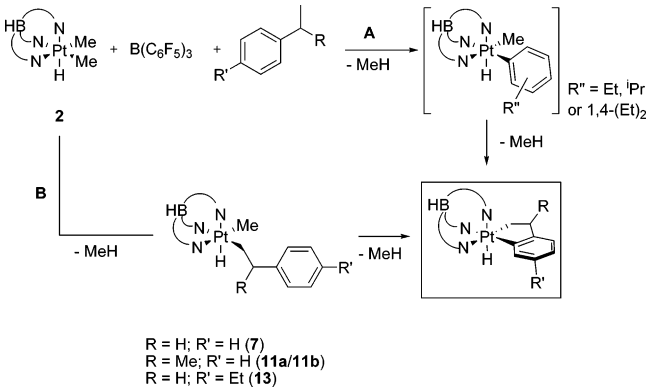
methyl peaks around 2.40 ppm. In the minor species, the methine proton signal is located at 2.95 ppm, upfield from the corresponding proton in the major isomer. The two methylene protons of **11b** are concealed by signals at 3.20 and 2.40 ppm. The methyl protons for both isomers appear as doublets between 1.31 and 1.34 ppm among the Tp′ methyl peaks.

Honey-colored crystals of what is assumed to be the major diastereomer, complex **11a**, were obtained, and the framework structure indicated by NMR studies was confirmed by X-ray analysis. Figure 7 shows the ORTEP diagram of isomer **11a**, with the methyl group positioned in an equatorial position of the five-membered ring. The solid state structure displays an octahedral geometry with a $\kappa^3$ coordination mode of the Tp′ ligand. The platinum hydride was found from the difference map and refined, indicating a Pt−H bond length of 1.493(5) Å (Table 4). The metallacycle lies in the equatorial plane opposite two pyrazole rings (C1−Pt−N31 = 178.76(13)° and C9−Pt−N11 = 177.83(11)°), and as seen in complex **7**, the $PtC_4$ ring is puckered into an envelope conformation with C2, bearing the methyl substituent, folded toward the platinum hydride. As found for complex **7**, all three Pt−N bonds have similar lengths, although the pyrazole ring located in the axial position *trans* to hydride is again slightly longer (Pt−N21 = 2.180(3) Å) than the two Pt−N bond lengths in the equatorial plane (Pt−N11 = 2.146(2) Å and Pt−N31 = 2.144(3) Å). The bond distance from platinum to the methylene carbon is longer than to the arene carbon by 0.043 Å (Pt−C1 = 2.054(3) Å and Pt−C9 = 2.011(3) Å). These bond distances are similar to those reported for TpPd($CH_2CMe_2$-*o*-$C_6H_4$)(NO).[59]

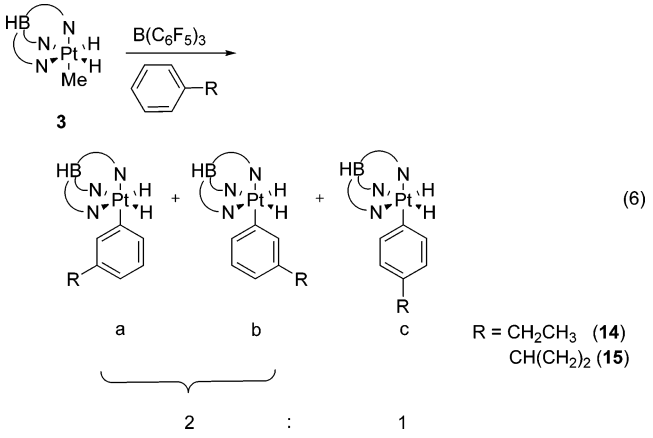
Only one pair of enantiomers is possible for the 1,4-diethylbenzene derivative, complex **13**. The $C_1$ symmetry of complex **13** is evident by the three nonequivalent pyrazole rings in the $^1$H NMR spectrum. The three aromatic protons are unique, with two doublets at 6.98 ($^3J_{H-H}$ = 6.8 Hz, $^4J_{Pt-H}$ = 18 Hz) and 6.74 ppm (d, $^3J_{H-H}$ = 6.8 Hz) and a singlet at 6.73 ppm ($^3J_{Pt-H}$ = 37 Hz). The chemical shifts for the four diastereotopic methylene protons are nearly identical to those of the ethylbenzene derivative, complex **7**. The two methylene protons of the aryl-$CH_2CH_3$ substituent are now diastereotopic, resonating at 2.70 and 2.45 ppm, and the methyl triplet at 1.08 ppm is shifted slightly upfield from that of free 1,4-diethylbenzene. The aryl−$C_{ipso}$ carbon resonates at 133.2 ppm with $^1J_{Pt-C}$ = 859 Hz. Similar coupling has been reported previously for Tp′Pt(IV)(aryl) complexes.[42,60] As found for the ethylbenzene derivative, complex **7**, the bridging methylene carbons for **13** resonate at 43.5 ppm ($^2J_{Pt-C}$ = 54 Hz) and 8.8 ppm ($^1J_{Pt-C}$ = 604 Hz).

**Mechanistic Possibilities for C−H Activation Route.** Two discrete mechanistic categories can be delineated for formation of platinum hydride complexes **7**, **11a**/**11b**, and **13** from alkyl-substituted benzenes (Scheme 1). Following Lewis acid-induced loss of methane, initial activation could take place at either an aryl (**A**) or an alkyl (**B**) C−H bond. Oxidative addition of an arene C−H bond to a metal center can be favored over alkane C−H oxidative addition both thermodynamically, due to the strength of the resultant metal−aryl bond formed, and kinetically, by lowering the barrier for C−H activation through initial $\pi$-coordination of the arene to the metal center.[36,61,62] By analogy, path **A** is probably favored here. In addition, when

**Scheme 1. Possible C−H Activation Pathways for Formation of Metallacyclic Complexes 7, 11a/11b, and 13**




the dihydride analogue, Tp′$PtMeH_2$, was reacted with either ethyl- or 2-propylbenzene in the presence of Lewis acid, only the aryl C−H activated products, Tp′$PtArH_2$ (Ar = ethylphenyl (**14**) and 2-propylphenyl (**15**)), resulted (eq 6). These results fit the pattern of previous findings for the reactivity of Tp′$PtMeH_2$ with toluene and xylenes, in which no benzylic C−H activated products were observed.[36]




(6)

Support for path **A** comes from work by Labinger, Bercaw, and co-workers that details the reactivity of diimine platinum(II) methyl cations toward alkyl-substituted benzenes. In the case of ethylbenzene, initial aryl C−H bond activation occurs exclusively, and reversibly, and the kinetic product converts intramolecularly to an $\eta^3$-benzyl product. They propose that this conversion takes place once ethylbenzene is *ortho*-activated since then it can pass through a platinum(IV) metallacycle hydride intermediate, similar to complex **7**, on the way to the final $\eta^3$-benzyl product.[63,64]

Although there is no evidence that Tp′Pt intermediates preferentially activate alkyl C−H bonds of alkylarenes, there are reports of C−H oxidative addition in other systems that are selective for alkyl over aryl C−H bonds, so path **B** in Scheme 1 deserves consideration as a viable alternative. In systems favoring alkyl C−H activation this reactivity is often explained by steric effects. For example, Tilset and co-workers found benzylic C−H bond activation of toluene and *p*-xylene by Pt(II) diimine complexes was favored when a sterically congested diimine ligand (Ar−N═CMe═N−Ar; Ar = 2,6-

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$(CH_3)_2C_6H_3$) was employed.[65] Direct activation of an ethyl C−H bond of triethylbenzene has been observed when the system contained a bulky, sterically crowded diimine ligand (Ar = 2,4,6-$Me_3C_6H_2$).[64] If path **B** is operational in our system, then the alkyl-bound alkylarene complex could go on to the final benzometallacycle. It is noteworthy that upon thermolysis, neophyl complexes $Pt(CH_2CMe_2Ph)_2L_2$ (L = N-donor or P-donor ligands) generate benzometallacycle derivatives, $Pt(CH_2CMe_2\text{-}o\text{-}C_6H_4)L_2$, and *tert*-butylbenzene. This rearrangement proceeds via intramolecular activation of the arene C−H bond.[66,67]

## Conclusion

In summary, the neutral Pt(II) phenyl ethylene complex **5** displays a five-coordinate trigonal-bipyramidal geometry, whereas the analogous Pt(II) phenyl carbonyl complex **4** undergoes rapid interconversion between the trigonal-bipyramidal and square-planar geometries in solution. Upon ethylene insertion into the Pt−phenyl bond in complex **5** at 60 °C, intramolecular C−H activation of an *ortho* proton occurs to give a stable Pt(IV) metallacycle hydride complex, **7**. Low-temperature protonation of **7** resulted in reductive elimination of the alkyl ligand to form a cationic Pt(II) 2-ethylphenyl complex. Attempts to isolate the neutral Pt(II) phenyl propylene or the cationic Pt(II) $\eta^2$-propylene phenyl complexes were unsuccessful, leading to a mixture of Pt(IV) metallacycle hydride adducts (**7** and **11a**/**11b**) or a cationic Pt(II) phenyl aqua complex (**12**), respectively.

Several Pt(IV) hydridometallacycle complexes (**7**, **11a**/**11b**, and **13**) have been synthesized through Lewis acid-assisted C−H oxidative addition of alkyl-substituted arenes to $Tp'PtMe_2H$ (**2**). The formation of these metallacycles is believed to take place via initial activation of an arene C−H bond rather than initial alkyl C−H activation. In the comparative reaction of the dihydrido reagent, $Tp'PtMeH_2$ (**3**), with alkyl-substituted arenes, only $Tp'PtArH_2$ products (**14** and **15**) resulted. While a detailed mechanism of formation of these platinum metallacycles has yet to be determined, these results indicate that an *intramolecular* rearrangement to form an *ortho*-activated aryl complex is favored over an *intermolecular* C−H activation pathway.

## Experimental Section

**Materials and Methods.** Reactions were performed under an atmosphere of dry nitrogen or argon using standard drybox techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. All glassware was oven-dried prior to use. Methylene chloride and pentane were purified under an argon atmosphere by passage through a column packed with activated alumina.[68] Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl prior to use. Deuterated methylene chloride was vacuum transferred from $CaH_2$ and degassed by several freeze−pump−thaw cycles, and deuterated 1,1,2,2-tetrachloroethane was used without further purification. Ethylbenzene, 2-propylbenzene, and 1,4-diethylbenzene were purchased from Sigma-Aldrich and dried over molecular sieves prior to use. Tris(pentfluorophenyl)borane was obtained from Strem and used without further purification.

$Tp'PtPh_2H$ (**1**), $Tp'PtMe_2H$[60] (**2**), $Tp'PtMeH_2$[69] (**3**), and $[H(OEt_2)_2][BAr'_4]$[70] were synthesized according to published procedures. Carbon monoxide and ethylene were obtained from Matheson Gas Products, Inc., and propylene was obtained from National Specialty Gases.

$^1H$ NMR and $^{13}C$ NMR spectra were recorded on a Bruker Avance 500, 400, or 300 spectrometer. $^1H$ NMR and $^{13}C$ NMR chemical shifts were referenced to residual $^1H$ and $^{13}C$ signals of the deuterated solvents. Chemical analyses were performed by Atlantic Microlabs of Norcross, GA.

**Tp′Pt(C₆H₅)(CO) (4).** $Tp'PtPh_2H$ (**1**) (0.057 g, 0.088 mmol) was placed in a 100 mL Schlenk flask under nitrogen. $CH_2Cl_2$ (15 mL) was added through the septum, and the reaction mixture was cooled to −78 °C. $HBF_4 \cdot Et_2O$ (16 μL, 0.114 mmol) was added dropwise, and the reaction was stirred for 10 min. The cold bath was removed, and $CO_{(g)}$ was purged through the solution for 30 min while warming to room temperature. After the solvent was removed in vacuo, NaH (0.003 g, 0.114 mmol) was added to the flask, which was then cooled to −78 °C. THF (15 mL) was slowly added, the cold bath was removed, and the solution was stirred for 1 h. After solvent was removed by rotary evaporation, the residue was chromatographed on alumina ($CH_2Cl_2$ as eluent), and a white solid was obtained. Yield: 35 mg (67%). IR ($CH_2Cl_2$): $\nu_{B-H}$ = 2528, 2485 $cm^{-1}$, $\nu_{CO}$ = 2092, 2082 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K, δ): 7.25 (d, $2H_{ortho}$, $^3J_{Pt-H}$ = 54 Hz, Pt−$C_6H_5$), 6.97 (m, $2H_{meta}$ and $1H_{para}$, Pt−$C_6H_5$), 5.99, 5.78 (s, 1H, 2H, Tp′C*H*), 2.41, 2.40, 2.25, 1.80 (s, 3H, 3H, 6H, 6H, Tp′C$H_3$). $^{13}C$ NMR ($CD_2Cl_2$, 298 K, δ): 163.7 (Pt−*C*≡O), 150.0, 149.8, 144.9, 144.6 (1C, 2C, 2C, 1C, Tp′*C*$CH_3$), 138.9 ($C_{meta}$, Pt−$C_6H_5$), 127.9 ($C_{ortho}$, $^1J_{Pt-C}$ = 54 Hz, Pt−$C_6H_5$), 124.7 ($C_{para}$, Pt−$C_6H_5$), 106.7, 106.6 (1C, 2C, Tp′*C*H), 15.2, 14.1, 13.3, 12.8 (1C, 2C, 1C, 2C, Tp′*C*$CH_3$).

**Tp′Pt(C₆H₅)(η²-CH₂═CH₂) (5).** $Tp'PtPh_2H$ (**1**) (0.150 g, 0.232 mmol) was placed in a 100 mL Schlenk flask under nitrogen. $CH_2Cl_2$ (15 mL) was added through the septum, and the reaction mixture was cooled to −78 °C. $HBF_4 \cdot Et_2O$ (42 μL, 0.301 mmol) was added dropwise, and the reaction was stirred for 10 min. The cold bath was removed, and ethylene was purged through the solution for 30 min while warming to room temperature. After the solvent was removed in vacuo, NaH (0.007 g, 0.301 mmol) was added to the flask, which was then cooled to −78 °C. THF (20 mL) was slowly added, the cold bath was removed, and the solution was stirred for 1 h. After solvent was removed by rotary evaporation, the residue was chromatographed on alumina ($CH_2Cl_2$ as eluent) and a white solid was obtained, which was recrystallized from $CH_2Cl_2$/methanol at −30 °C. Yield: 30 mg (22%). $^1H$ NMR ($CD_2Cl_2$, 253K, δ): 6.76 (t, $1H_{para}$, Pt−$C_6H_5$), 6.69 (t, $2H_{meta}$, Pt−$C_6H_5$), 6.23 (d, $2H_{ortho}$, $^3J_{Pt-H}$ = 39 Hz, Pt−$C_6H_5$), 5.79, 5.65 (s, 2H, 1H, Tp′C*H*), 3.31 (d, 2H, $^2J_{Pt-H}$ = 80 Hz, $^3J_{H-H}$ = 7.2 Hz, Pt−$CH_2$═$CH_2$), 2.44 (d, 2H, $^2J_{Pt-H}$ = 56 Hz, $^3J_{H-H}$ = 7.2 Hz, Pt−$CH_2$═$CH_2$), 2.42, 2.30, 2.22, 1.48 (s, 6H, 3H, 3H, 6H, Tp′C$H_3$). $^{13}C$ NMR ($CD_2Cl_2$, 253K, δ): 151.1, 149.2, 144.7, 143.7 (1C, 2C, 1C, 2C, Tp′*C*$CH_3$), 125.8, 122.8 ($C_{meta}$, $C_{ortho}$, Pt−$C_6H_5$), 118.8 ($C_{para}$, Pt−$C_6H_5$), 114.5 ($C_{ipso}$, Pt−$C_6H_5$), 108.5, 105.6 (1C, 2C, Tp′*C*H), 24.2 (Pt−*C*$H_2$═*C*$H_2$), 13.8, 13.4, 12.4, 12.1 (2C, 1C, 2C, 1C, Tp′*C*$CH_3$). Anal. Calcd for $PtBN_6C_{23}H_{31} \cdot CH_2Cl_2$: C, 42.25; H, 4.87; N, 12.32; Found: C, 43.12; H, 4.59; N, 12.05.

**Representative [BAr′₄]⁻ NMR Data.** $^1H$ and $^{13}C$ NMR data for the $[BAr'_4]^-$ counterion for ionic products **6**, **8**, and **9** are reported separately for simplicity. $^1H$ NMR ($CD_2Cl_2$, 193 K, δ): 7.77 (br, 8H, *o*-Ar′), 7.60 (br, 4H, *p*-Ar′). $^{13}C$ NMR ($CD_2Cl_2$, 193 K, δ): 162.2 (1:1:1:1 pattern, $^1J_{B-C}$ = 50 Hz, $C_{ipso}$), 135.3 ($C_{ortho}$), 129.4 (qq, $^2J_{C-F}$ = 30 Hz, $^4J_{C-F}$ = 5 Hz, $C_{meta}$), 125.1 (q, $^1J_{C-F}$ = 270 Hz, $CF_3$), 117.9 ($C_{para}$).

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**[κ²-(HTp′)Pt(C$_6$H$_5$)(η²-CH$_2$=CH$_2$)][BAr′$_4$] (6).** Tp′PtPh$_2$H (**1**) (0.100 g, 0.154 mmol) and [H(OEt$_2$)$_2$][BAr′$_4$] (0.172 g, 0.169 mmol) were weighed into a 100 mL Schlenk flask in the drybox. The flask was cooled to −78 °C outside the drybox. $CH_2Cl_2$ (15 mL) was slowly added through the septum, and the reaction mixture was stirred for 10 min. The cold bath was removed, and ethylene was purged through the solution for 30 min while warming to room temperature. The solvent was removed in vacuo, and the residue was triturated with pentane. $^1$H NMR ($CD_2Cl_2$, 293 K, $\delta$): 10.36 (s, 1H, pz′NH), 7.10−6.78 (m, 5H, Pt−C$_6H_5$), 6.36, 6.07, 5.93 (s, 1H each, HTp′C*H*), 4.21, 3.77 (m, 2H each, broad Pt satellites, Pt−C$H_2$=C$H_2$), 2.45, 2.43, 2.38, 2.33, 2.09, 1.60 (s, 3H each, HTp′C$H_3$).

**Tp′Pt(CH$_2$CH$_2$-*o*-C$_6$H$_4$)(H) (7) by Ethylene Insertion.** Tp′Pt(Ph)(η²-CH$_2$=CH$_2$) (**5**) (0.224 g, 0.375 mmol) and 1 equiv of B(C$_6$F$_5$)$_3$ (0.192 g) were placed in a 100 mL Schlenk flask under nitrogen. Toluene (25 mL) was added, and the reaction mixture was stirred for 1 h at 60 °C. After solvent was removed in vacuo, the residue was chromatographed on alumina ($CH_2Cl_2$ as eluent) and a white solid was obtained. Yield: 111 mg (50%). $^1$H NMR ($CD_2Cl_2$, 253 K, $\delta$): 7.05 (d, 1H, Pt−CH$_2$CH$_2$-*o*-C$_6H_4$), 6.88 (t, 1H, Pt−CH$_2$CH$_2$-*o*-C$_6H_4$), 6.76 (d, 1H$_{ortho}$, $^3J_{Pt-H}$ = 38 Hz, Pt−CH$_2$CH$_2$-*o*-C$_6H_4$), 6.69 (t, 1H, Pt−CH$_2$CH$_2$-*o*-C$_6H_4$), 5.89, 5.69 (s, 2H, 1H, Tp′C*H*), 3.18 (m, 1H, Pt−C$H_2$C$H_2$-*o*-C$_6$H$_4$), 2.84 (dd, 1H, $^3J_{H-H}$ = 16.0 Hz, $^2J_{H-H}$ = 5.0 Hz, $^2J_{Pt-H}$ = 114 Hz, Pt−C$H_2$CH$_2$-*o*-C$_6$H$_4$), 2.75 (m, 1H, Pt−C$H_2$C$H_2$-*o*-C$_6$H$_4$), 2.69 (m, 1H, Pt−C$H_2$C$H_2$-*o*-C$_6$H$_4$), 2.37, 2.35, 2.34, 2.07, 1.31 (s, 6H, 3H, 3H, 3H, 3H, Tp′C$H_3$), −19.63 (s, 1H, $^1J_{Pt-H}$ = 1391 Hz, Pt−*H*). $^{13}$C NMR ($CD_2Cl_2$, 253 K, $\delta$): 157.6 (1C, Pt−CH$_2$CH$_2$-*o*-*C*$_6$H$_4$), 150.7, 150.5, 149.4, 145.2, 144.8, 144.1 (1C, 1C, 1C, 1C, 1C, 1C, Tp′*C*CH$_3$), 133.8, 133.4 (C$_{ipso}$), 124.3, 124.0, 122.1 (1C, 1C, 1C, 1C, 1C, Pt−CH$_2$CH$_2$-*o*-*C*$_6$H$_4$), 107.9, 106.6, 106.3 (Tp′*C*H), 44.0 (Pt−CH$_2$*C*H$_2$-*o*-C$_6$H$_4$), 15.2, 14.9, 12.8, 11.8 (1C, 1C, 3C, 1C, Tp′C*C*H$_3$), 8.5 (1C, $^1J_{Pt-H}$ = 601 Hz, Pt−*C*H$_2$CH$_2$-*o*-C$_6$H$_4$). Anal. Calcd for PtBN$_6$C$_{23}$H$_{31}$·1/2CH$_2$Cl$_2$: C, 44.11; H, 5.04; N, 13.13. Found: C, 44.34; H, 5.16; N, 13.04.

**[κ²-(HTp′)Pt(C$_6$H$_4$-2-CH$_2$CH$_3$)(O(CH$_2$CH$_3$)$_2$)][BAr′$_4$] (8).** Tp′Pt(CH$_2$CH$_2$-*o*-C$_6$H$_4$)(H) (**7**) (0.010 g, 0.017 mmol) and [H(OEt$_2$)$_2$][BAr′$_4$] (0.022 g, 0.022 mmol) were weighed into an NMR tube in the drybox. The NMR tube was cooled to −78 °C outside the drybox. $CD_2Cl_2$ (0.7 mL) was slowly added through the septum, and the reaction mixture was inverted several times to ensure complete mixing. $^1$H NMR ($CD_2Cl_2$, 203 K, $\delta$): 11.35 (s, 1H, pz′NH), 6.92 (d, 1H, Pt−C$_6H_4$-2-CH$_2$CH$_3$), 6.85 (t, 1H, Pt−C$_6H_4$-2-CH$_2$CH$_3$), 6.63 (t, 1H, Pt−C$_6H_4$-2-CH$_2$CH$_3$), 6.20 (d, 1H, Pt−C$_6H_4$-2-CH$_2$CH$_3$), 6.29, 5.99, 5.83 (s, 1H each, HTp′C*H*), 3.96 (q, 4H, Pt−O(C$H_2$CH$_3$)$_2$), 3.29 (dq, 2H, Pt−C$_6$H$_4$-2-C$H_2$CH$_3$), 2.37, 2.34, 2.30, 2.25, 1.79, 1.50 (s, 3H each, HTp′C$H_3$), 1.33 (t, 6H, Pt−O(CH$_2$C$H_3$)$_2$), 1.25 (t, 3H, Pt−C$_6$H$_4$-2-CH$_2$C$H_3$).

**[κ²-(HTp′)Pt(C$_6$H$_4$-2-CH$_2$CH$_3$)(NCCH$_3$)][BAr′$_4$] (9).** Tp′Pt(CH$_2$CH$_2$-*o*-C$_6$H$_4$)(H) (**7**) (0.010 g, 0.017 mmol) and [H(OEt$_2$)$_2$][BAr′$_4$] (0.022 g, 0.022 mmol) were weighed into an NMR tube in the drybox. The NMR tube was cooled to −78 °C outside the drybox. $CD_2Cl_2$ (0.7 mL) was slowly added through the septum, and the reaction mixture was inverted several times to ensure complete mixing. NCCH$_3$ (2 μL, 0.034 mmol) was added via syringe. $^1$H NMR ($CD_2Cl_2$, 273 K, $\delta$): 11.90 (s, 1H, pz′NH), 7.00 (d, 1H, Pt−C$_6H_4$-2-CH$_2$CH$_3$), 6.89 (t, 1H, Pt−C$_6H_4$-2-CH$_2$CH$_3$), 6.64 (t, 1H, Pt−C$_6H_4$-2-CH$_2$CH$_3$), 6.28 (d, 1H, Pt−C$_6H_4$-2-CH$_2$CH$_3$), 6.27, 6.04, 5.81 (s, 1H each, HTp′C*H*), 3.25 (dq, 2H, Pt−C$_6$H$_4$-2-C$H_2$CH$_3$), 2.42, 2.37, 2.35, 2.34, 2.32, 2.19, 1.44 (s, 3H each, HTp′C$H_3$ and Pt−NCC$H_3$), 1.37 (t, 3H, Pt−C$_6$H$_4$-2-CH$_2$C$H_3$).

**Tp′Pt(CH(CH$_3$)CH$_2$-*o*-C$_6$H$_4$)(H) (10) by Propylene Insertion.** Tp′PtPh$_2$H (**1**) (150 mg, 0.232 mmol) was placed in a 100 mL Schlenk flask under nitrogen. $CH_2Cl_2$ (20 mL) was added through the septum, and the reaction mixture was cooled to −78 °C. HBF$_4$·Et$_2$O (42 μL, 0.301 mmol) was added dropwise, and the reaction was stirred for 10 min. The cold bath was removed and propylene sparged into the flask for 30 min as the solution warmed slowly to room temperature. After the solvent was removed in vacuo, NaH (0.007 g, 0.301 mmol) was added to the flask, which was then cooled to −78 °C. THF (20 mL) was slowly added, the cold bath was removed, and the solution was stirred for 1 h. After solvent was removed by rotary evaporation, the residue was chromatographed on alumina ($CH_2Cl_2$ as eluent) and a colorless oil was obtained. Major product (**10**) $^1$H NMR ($CD_2Cl_2$, 303 K, $\delta$): 6.75, 6.69 (m,1H, 2H, Pt−CH(CH$_3$)CH$_2$-*o*-C$_6H_4$) 6.55 (1H, $^3J_{H-H}$ = 15 Hz, $^2J_{H-H}$ = 2.0 Hz, $^3J_{Pt-H}$ = 44 Hz, Pt−CH(CH$_3$)C$H_2$-*o*-C$_6$H$_4$), 6.69 (m, 1H, $^2J_{Pt-H}$ = 40 Hz, Pt−CH(CH$_3$)CH$_2$-*o*-C$_6H_4$) 5.84, 5.71 (s, 2H, 1H, Tp′C*H*), 5.03 (m, 1H, $^3J_{H-H}$ = 6 Hz, $^3J_{H-H}$ = 15 Hz, $^2J_{Pt-H}$ = 57 Hz, Pt−C*H*(CH$_3$)CH$_2$-*o*-C$_6$H$_4$), 2.48, 2.40, 2.39, 2.24, 1.69, 1.41 (s, 3H, 3H, 3H, 3H, 3H, 3H, Tp′C$H_3$), 1.71 (dd, 3H, $^3J_{H-H}$ = 6 Hz, $^4J_{H-H}$ = 1.6 Hz, $^2J_{Pt-H}$ = 10 Hz, Pt−CH(C$H_3$)-CH$_2$-*o*-C$_6$H$_4$), −19.48 (s, 1H, $^1J_{Pt-H}$ = 1368 Hz, Pt−*H*).

**Tp′Pt(CH(CH$_3$)CH$_2$-*o*-C$_6$H$_4$)(H) (10) and Tp′Pt(CH$_2$CH-(CH$_3$)-*o*-C$_6$H$_4$)(H) (11a/11b) Mixture by Propylene Insertion.** Tp′PtPh$_2$H (**1**) (100 mg, 0.154 mmol) was placed in a 100 mL Schlenk flask under nitrogen. $CH_2Cl_2$ (20 mL) was added through the septum, and the reaction mixture was cooled to −78 °C. HBF$_4$·Et$_2$O (28 μL, 0.200 mmol) was added dropwise, and the reaction was stirred for 10 min. Propylene was condensed into the solution and allowed to stir for 1 h at −78 °C. The cold bath was removed and the solution warmed slowly to room temperature under propylene. After 1 h, the propylene purge was stopped and the flask again cooled to −78 °C. NEt$_3$ (28 μL, 0.200 mmol) was slowly added, and the solution was left to stir for 90 min at −78 °C. The solution was allowed to warm as solvent was removed in vacuo. The residue was taken up in $CH_2Cl_2$/hexanes (3/20 mL) and the solution transferred away from the salts via cannula. The product was chromatographed on silica ($CH_2Cl_2$ as eluent) and a white powder obtained. $^1$H NMR ($CD_2Cl_2$, 293 K, $\delta$): −19.40 (s, 1H, $^1J_{Pt-H}$ =1385 Hz, Pt−*H*, **11b**), −19.48 (s, 1H, $^1J_{Pt-H}$ =1368 Hz, Pt−*H*, **10**), and −19.78 (s, 1H, $^1J_{Pt-H}$ =1393 Hz, Pt−H, **11a**) ratio: **11b** (1.3):**10** (1.0):**11a** (1.3).

**[κ²-(HTp′)Pt(C$_6$H$_5$)(OH$_2$)][BF$_4$] (12).** Tp′PtPh$_2$H (**1**) (0.150 g, 0.232 mmol) was placed in a 100 mL Schlenk flask under nitrogen. $CH_2Cl_2$ (30 mL) was added through the septum, and the reaction mixture was cooled to −78 °C. HBF$_4$·Et$_2$O (35 μL, 0.254 mmol) was added dropwise, and the reaction was stirred for 10 min. The cold bath was removed, and propylene was purged through the solution for 30 min while warming to room temperature. The solvent was removed in vacuo, and the residue was triturated with pentane. A white solid was obtained, which was recrystallized from $CH_2Cl_2$/pentane at −30 °C. Yield: 148 mg (95%). $^1$H NMR ($CD_2Cl_2$, 293 K, $\delta$): 11.62 (s, 1H, pz′NH), 6.89 (m, 3H, Pt−C$_6H_5$), 6.71 (d, 2H$_{ortho}$, Pt−C$_6H_5$), 6.25, 6.09, 5.83 (s, 1H each, HTp′C*H*), 4.97 (s, 2H, Pt−O$H_2$), 2.43, 2.42, 2.38, 2.35, 2.13, 1.56 (s, 3H each, HTp′C$H_3$).

**General C−H Activation of Alkylarene (7, 11a/11b, and 13).** Tp′Pt(Me)$_2$(H) (**2**) (0.075 g, 0.143 mmol) and 1 equiv of B(C$_6$F$_5$)$_3$ (0.073 g) were placed in a 100 mL Schlenk flask under nitrogen.

An alkyl-substituted benzene (20 mL) was added, and the reaction mixture was stirred overnight at 35 °C. After solvent was removed in vacuo, the resultant brown residue was chromatographed on alumina ($CH_2Cl_2$ as eluent) and a yellow oil was collected. A white solid was obtained upon recrystallization in $CH_2Cl_2$/methanol at −30 °C.

**Tp′Pt(CH₂CH₂-*o*-C₆H₄)(H) (7).** Tp′Pt(Me)₂(H) (**2**) (0.075 g, 0.143 mmol) and 1 equiv of $B(C_6F_5)_3$ (0.073 g) were combined as described with 20 mL of ethylbenzene. The product was recrystallized in ethylbenzene at 0 °C. Yield: 55 mg (64%).

**Tp′Pt(CH₂CH(CH₃)-*o*-C₆H₄)(H) (11a/11b).** Tp′Pt(Me)₂(H) (**2**) (0.075 g, 0.143 mmol) and 1 equiv of $B(C_6F_5)_3$ (0.073 g) were combined as described with 20 mL of 2-propylbenzene. $^1$H NMR **11a** ($CD_2Cl_2$, 298 K, $\delta$): 7.05−6.65 (4H, Pt−CH₂CH(CH₃)-*o*-C₆*H*₄), 5.89, 5.69 (s, 2H, 1H, Tp′C*H*), 3.19 (m, 1H, Pt−CH₂C*H*(CH₃)-*o*-C₆H₄), 2.79 (dd, 1H, $^3J_{H-H}$ = 7.5 Hz, $^2J_{Pt-H}$ = 63 Hz, Pt−C*H*₂CH(CH₃)-*o*-C₆H₄), 2.4 (m, 1H, Pt−C*H*₂CH(CH₃)-*o*-C₆H₄), 2.44−2.35 (s, 12H, Tp′C*H*₃), 2.09 (s, 3H, Tp′C*H*₃), 1.33 (d, 3H, Pt−CH₂CH(C*H*₃)-*o*-C₆H₄), 1.30 (s, 3H, Tp′C*H*₃), −19.78 (s, 1H, $^1J_{Pt-H}$ = 1393 Hz, Pt−*H*). $^{13}$C NMR ($CD_2Cl_2$, 298 K, $\delta$): 159.0 (s, 1C, $^2J_{Pt-C}$ = 90 Hz, Pt−CH₂CH(CH₃)-*o*-*C*₆H₄), 150.5 (s, 1C, $^2J_{Pt-C}$ = 21 Hz, Tp′*C*CH₃), 150.4 (1C, $^2J_{Pt-C}$ = 26 Hz, Tp′*C*CH₃) 149.4 (1C, $^2J_{Pt-C}$ = 16 Hz, Tp′*C*CH₃), 145.2, 144.7, 144.1 (s, 1C, 1C, 1C, Tp′*C*CH₃), 133.7 (s, 1C, Pt−CH₂CH(CH₃)-*o*-*C*₆H₄), 133.0 (s, 1C, $^1J_{Pt-C}$ = 837 Hz, $C_{ipso}$) 124.9 (s, 1C, $J_{Pt-C}$ = 43 Hz, Pt−CH₂CH(CH₃)-*o*-*C*₆H₄), 124.0 ($J_{Pt-C}$ = 7 Hz, Pt−CH₂CH(CH₃)-*o*-*C*₆H₄), 122.7 (1C, $J_{Pt-C}$ = 54 Hz, Pt−CH₂CH(CH₃)-*o*-*C*₆H₄), 107.9, 106.6 ($^3J_{Pt-C}$ = 11.5 Hz), 106.2 ($^3J_{Pt-C}$ = 9.8 Hz) (1C, 1C, 1C, Tp′*C*H), 47.9 (1C, $^2J_{Pt-C}$ = 64 Hz, Pt−CH₂*C*H(CH₃)-*o*-C₆H₄), 20.7 ($^3J_{Pt-C}$ = 83 Hz., Pt−CH₂CH(*C*H₃)-*o*-C₆H₄), 18.4 (d, $^1J_{Pt-C}$ = 601 Hz, Pt−*C*H₂CH(CH₃)-*o*-C₆H₄), 15.15 ($^3J_{Pt-C}$ = 17 Hz), 14.92 ($^3J_{Pt-C}$ = 17 Hz), 12.82, 12.8, 12.79, 12.17 (1C, 1C, 1C, 1C, 1C, 1C, Tp′C*C*H₃).

$^1$H NMR **11b** ($CD_2Cl_2$, 243 K, $\delta$): 7.05−6.65 (4H, Pt−CH₂CH(CH₃)-*o*-C₆*H*₄), 5.89, 5.69 (s, 2H, 1H, Tp′C*H*), 3.12 (m, 1H, $^2J_{Pt-H}$ = 108 Hz, Pt−C*H*₂CH(CH₃)-*o*-C₆H₄), 2.92 (dd, 1H, $^3J_{H-H}$ = 6.5 Hz, Pt−CH₂C*H*(CH₃)-*o*-C₆H₄), 2.4 (m, 1H, Pt−C*H*₂CH(CH₃)-*o*-C₆H₄) 2.44−2.35 (s, 12H, Tp′C*H*₃), 2.11 (s, 3H, Tp′C*H*₃), 1.31 (d, 3H, Pt−CH₂CH(C*H*₃)-*o*-C₆H₄), 1.26 (s, 3H, Tp′C*H*₃), −19.4 (s, 1H, $^1J_{Pt-H}$ = 1385 Hz, Pt−*H*). $^{13}$C NMR ($CD_2Cl_2$, 298 K, $\delta$): 162.5 (s, 1C, Pt−CH₂CH(CH₃)-*o*-*C*₆H₄), 150.5, 150.3, 149.4, 145.2, 144.8, 144.1 (s, 1C, 1C, 1C, 1C, 1C, 1C, Tp′*C*CH₃), 134.0 (s, 1C, Pt−CH₂CH(CH₃)-*o*-*C*₆H₄), 131.0 (s, 1C, $C_{ipso}$) 124.6 (s, 1C, $J_{Pt-C}$ = 40 Hz, Pt−CH₂CH(CH₃)-*o*-*C*₆H₄), 124.2 ($J_{Pt-C}$ = 7 Hz, Pt−CH₂CH(CH₃)-*o*-*C*₆H₄), 122.1 (1C, $J_{Pt-C}$ = 46 Hz, Pt−CH₂CH(CH₃)-*o*-*C*₆H₄), 107.9, 106.6, 106.2 (1C, 1C, 1C, Tp′*C*H), 46.5 (1C, $^2J_{Pt-C}$ = 34 Hz, Pt−CH₂*C*H(CH₃)-*o*-C₆H₄), 23.5 (1C, Pt−CH₂CH(*C*H₃)-*o*-C₆H₄), 18.1 (d, $^1J_{Pt-C}$ = 612 Hz, Pt−*C*H₂CH(CH₃)-*o*-C₆H₄), 15.2 ($^3J_{Pt-C}$ = 17 Hz), 15.1 ($^3J_{Pt-C}$ = 17 Hz), 12.82, 12.8, 12.79, 11.6 (1C, 1C, 1C, 1C, 1C, Tp′C*C*H₃). Anal. Calcd for $PtBN_6C_{24}H_{33}\cdot CH_2Cl_2$: C, 43.12; H, 5.07; N, 12.35. Found: C, 43.79; H, 5.20; N, 12.35.

**Tp′Pt(CH₂CH₂-*o*-C₆H₃(CH₂CH₃))(H) (13).** Tp′Pt(Me)₂(H) (**2**) (0.075 g, 0.143 mmol) and 1 equiv of $B(C_6F_5)_3$ (0.073 g) were combined as described with 20 mL of 1,4-diethylbenzene. $^1$H NMR ($CD_2Cl_2$, 298 K, $\delta$): 6.98 (d, 1H, $^3J_{H-H}$ = 6.8 Hz, $^4J_{Pt-H}$ = 18 Hz, Pt−CH₂CH₂-*o*-C₆*H*₃(CH₂CH₃)), 6.74 (d, 1H, $^3J_{H-H}$ = 6.8 Hz, Pt−CH₂CH₂-*o*-C₆*H*₃(CH₂CH₃)), 6.73 (s, 1H$_{ortho}$, $^3J_{Pt-H}$ = 37 Hz, Pt−CH₂CH₂-*o*-C₆*H*₃(CH₂CH₃)), 6.16, 5.90 (d, 1H$_{para}$, 1H$_{meta}$, $^3J_{H-H}$ = 3.3 Hz, Pt−CH₂CH₂-*o*-C₆*H*₃(CH₂CH₃)), 5.90, 5.89, 5.71 (s, 1H, 1H, 1H, Tp′C*H*), 3.18 (m, 1H, Pt−CH₂C*H*₂-*o*-C₆H₃-(CH₂CH₃)), 2.85 (dd, 1H, $^2J_{H-H}$ = 5.6, $^2J_{H-H}$ = 15.2, $^2J_{Pt-H}$ = 114 Hz, Pt−C*H*₂CH₂-*o*-C₆H₃(CH₂CH₃)), 2.76 (m, 1H Pt−CH₂C*H*₂-*o*-C₆H₃(CH₂CH₃) 2.70 (1H, $^3J_{H-H}$ = 8.0 Hz, Pt−CH₂CH₂-*o*-C₆H₃(C*H*₂CH₃)), 1.08 (t, 3H, $^3J_{H-H}$ = 7.6 Hz, Pt−CH₂CH₂-*o*-C₆H₃(CH₂C*H*₃)), −19.73 (s, 1H, $^1J_{Pt-H}$ = 1395 Hz, Pt−*H*). $^{13}$C NMR ($CD_2Cl_2$, 298 K, $\delta$): 154.6 (1C, $^2J_{Pt-C}$ = 108 Hz, Pt−CH₂CH₂-*o*-*C*₆H₃(CH₂CH₃)), 150.8 ($^2J_{Pt-C}$ = 22.0 Hz), 150.4 ($^2J_{Pt-C}$ = 25.0 Hz), 149.3 ($^2J_{Pt-C}$ = 19.0 Hz), 145.1, 144.7, 144.1 (1C, 1C, 1C, 1C, 1C, 1C, Tp′*C*CH₃), 140.4 ($J_{Pt-C}$ = 46 Hz), 133.4, 133.2 (1C$_{ipso}$, $^1J_{Pt-C}$ = 859 Hz, Pt−CH₂CH₂-*o*-*C*₆H₃(CH₂CH₃)), 123.6, 121.8 ($^2J_{Pt-C}$ = 46 Hz), (1C, 1C, 1C, 1C, 1C, Pt−CH₂CH₂-*o*-*C*₆H₃(CH₂CH₃)), 107.9 ($^3J_{Pt-C}$ = 11.6 Hz), 106.6 ($^3J_{Pt-C}$ = 11.4 Hz), 106.3 ($^3J_{Pt-C}$ = 9.0 Hz) (1C, 1C, 1C, Tp′*C*H), 43.5 (1C, $^2J_{Pt-C}$ = 54.0 Hz, Pt−CH₂*C*H₂-*o*-C₆H₃(CH₂CH₃)), 29.1 (1C, Pt−CH₂*C*H₂-*o*-C₆H₃(*C*H₂CH₃)) 16.8, 15.2 ($^3J_{Pt-C}$ = 16.6 Hz), 14.9 ($^3J_{Pt-C}$ = 16.4 Hz), 12.85, 12.78 (1C, 1C, 1C, 2C, 1C, Tp′C*C*H₃), 11.8 (1C, $^2J_{C-C}$ = 2 Hz, Pt−CH₂CH₂-*o*-C₆H₃(CH₂*C*H₃)), 8.8 (1C, $^1J_{Pt-C}$ = 604 Hz, Pt−*C*H₂CH₂-*o*-C₆H₃(CH₂CH₃)). Anal. Calcd for $PtBN_6C_{25}H_{35}\cdot CH_2Cl_2$: C, 48.00; H, 5.67; N, 13.44. Found: C, 47.06; H, 5.64; N, 12.70.

**General Procedure for the Synthesis of Tp′Pt(Ar)(H)₂ Complexes (14, 15).** Tp′PtMe(H)₂ (**3**) (0.075 g, 0.147 mmol) and 1 equiv of $B(C_6F_5)_3$ (0.075 g) were placed in a 100 mL Schlenk flask under nitrogen. Aromatic solvent (15 mL) was subsequently added, and the reaction mixture was stirred overnight at 35 °C. After solvent removal in vacuo, the resultant residue was chromatographed on alumina ($CH_2Cl_2$ as eluent) and a white solid was obtained, which was recrystallized from pentanes at −30 °C.

**Tp′Pt(C₆H₄CH₂CH₃)(H)₂ (14).** Tp′PtMe(H)₂ (**3**) (0.050 g, 0.098 mmol) and $B(C_6F_5)_3$ (0.050 g, 0.098 mmol) were combined as described above with 15 mL of anhydrous ethylbenzene. $^1$H NMR ($CD_2Cl_2$, 298 K, $\delta$): 6.76, 6.72 (br, Pt−C₆*H*₄Et), 5.87, 5.84 (s, 1H, 2H, Tp′−C*H*), 2.47, 2.41, 2.40, 2.24, 2.22, 2.09 (Tp′−C*H*₃) 2.54, 1.43 (m, 1H, 1H, C₆H₄C*H*₂CH₃), 1.19 (t, 3H, $^3J_{H-H}$ = 7.5 Hz, C₆H₄CH₂C*H*₃), −18.74, −18.77 (s, 2H, ca. 2:1, $^1J_{Pt-H}$ = 1290 Hz, $^1J_{Pt-H}$ = 1289, Pt−*H*). $^{13}$C NMR ($CD_2Cl_2$, 298 K, $\delta$): 149.6 (s, 2C, $^2J_{Pt-C}$ = 21 Hz, Tp′*C*CH₃), 149.4 (s, 1C, $^2J_{Pt-C}$ = 25 Hz, Tp′*C*CH₃), 144.5, 143.9 (s, 1C, 2C, Tp′*C*CH₃), 126.3, 122.2, 121.4 (s, Pt−*C*₆H₄Et) 105.6 (s, 2C, $^2J_{Pt-C}$ = 9.8 Hz, Tp′*C*H) 104.9 (s, 1C, $^2J_{Pt-C}$ = 10 Hz, Tp′*C*H), 31.5, 29.2, 15.4 (s, 1C, $^2J_{Pt-C}$ = 33 Hz, Tp′C*C*H₃), 13.8 (s, 2C, $^2J_{Pt-C}$ = 18 Hz, Tp′C*C*H₃) 13.7, 12.1 (s, 1C, 2C, Tp′C*C*H₃).

**Tp′Pt(C₆H₄CH(CH₃)₂)(H)₂ (15).** Tp′PtMe(H)₂ (**3**) (0.050 g, 0.098 mmol) and $B(C_6F_5)_3$ (0.050 g, 0.098 mmol) were combined as described above with 15 mL of 2-propylbenzene. $^1$H NMR ($CD_2Cl_2$, 298 K, $\delta$): 6.76, 6.71 (br, Pt−C₆*H*₄$^i$Pr), 5.85, 5.82 (s, 1H, 2H, Tp′−C*H*), 2.45, 2.39, 2.22, 2.07 (Tp′−C*H*₃) 2.73 (m, 1H,

Pt−$C_6H_4CH(CH_3)_2$), 1.18 (d, 6H, Pt−$C_6H_4CH(CH_3)_2$) −18.78, −18.80 (s, 2H, ca. 2:1, $^1J_{Pt-H}$ = 1292, $^1J_{Pt-H}$ = 1289 Hz, Pt−*H*).

**Structural Data for 5.** Crystals from $CH_2Cl_2$/methanol; $C_{23}H_{31}N_6BPt$, $M$ = 597.43; orthorhombic, space group $P2_1nb$; $Z$ = 4; $a$ = 7.9063(4) Å, $b$ = 11.9371(6) Å, $c$ = 25.2697(12) Å; α = 90°, $\beta$ = 90°, $\gamma$ = 90°; $U$ = 2384.91(20) Å$^3$; $D_c$ = 1.664 Mg m$^{-3}$; $T$ = −100 °C; max 2$\theta$: 50°; Mo Kα radiation ($\lambda$ = 0.71073 Å); 4011 unique reflections were obtained, and 2493 of these with $I > 2.5\sigma(I)$ were used in the refinement; data were collected on a Bruker SMART diffractometer, using the omega scan method. For significant reflections merging *R*-value: 0.044. Residuals: $R_F$: 0.043; $R_w$: 0.045 (significant reflections); GoF: 1.0495.

**Structural Data for 7.** Crystals were obtained from ethylbenzene; $C_{27}H_{36}N_6BPt$, $M$ = 650.52; monoclinic, space group $P2_1/c$; $Z$ = 4; $a$ = 8.0135(8) Å, $b$ = 24.027(3) Å, $c$ = 14.0296(14) Å; α = 90°, $\beta$ = 99.090 (4)°, $\gamma$ = 90°; $U$ = 2667.3(5) Å$^3$; $D_c$ = 1.620 Mg m$^{-3}$; $T$ = 100(2) K; max 2$\theta$: 50°; Mo Kα radiation ($\lambda$ = 0.71073 Å); 202 152 unique reflections were obtained and 27 982 of these with $I > 2\sigma(I)$ were used in the refinement; data were collected on a Bruker SMART APEX-II diffractometer, using the omega scan method. For significant reflections merging *R*-value: 0.0604. Residuals: $R_F$: 0.0297; $R_w$: 0.0613 (significant reflections); GoF: 1.120.

**Structural Data for 11.** Crystals were obtained from $CH_2Cl_2$/methanol; $C_{25}H_{35}N_6Cl_2BPt$, $M$ = 696.39; monoclinic, space group $C2/c$; $Z$ = 8; $a$ = 28.0057(6) Å, $b$ = 12.4619(3) Å, $c$ = 15.5140(3) Å; α = 90°, $\beta$ = 94.3510(10)°, $\gamma$ = 90°; $U$ = 5398.8(2) Å$^3$; $D_c$ = 1.714 Mg m$^{-3}$; $T$ = 100(2) K; max 2$\theta$: 50°; Mo Kα radiation ($\lambda$ = 0.71073 Å); 56 961 unique reflections were obtained and 6519 of these with $I > 2.5\sigma(I)$ were used in the refinement; data were collected on a Bruker SMART APEX-II diffractometer, using the omega scan method. For significant reflections merging *R*-value: 0.0296. Residuals: $R_F$: 0.0251; $R_w$: 0.0518 (significant reflections); GoF: 1.041.

**Structural Data for 12.** Crystals from $CH_2Cl_2$/pentane; $C_{21.5}H_{31}N_6ClF_4B_2OPt$, $M$ = 717.67; triclinic, space group $P\bar{1}$; $Z$ = 4; $a$ = 9.1331(2) Å, $b$ = 12.6495(3) Å, $c$ = 24.9106(5) Å; α = 102.218(1)°, $\beta$ = 95.437(1)°, $\gamma$ = 96.559(1)°; $U$ = 2773.27(11) Å$^3$; $D_c$ = 1.719 Mg m$^{-3}$; $T$ = −100 °C; max 2$\theta$: 50°; Mo Kα radiation ($\lambda$ = 0.71073 Å); 9783 unique reflections were obtained and 7764 of these with $I > 2.5\sigma(I)$ were used in the refinement; data were collected on a Bruker SMART diffractometer, using the omega scan method. For significant reflections merging *R*-value: 0.039. Residuals: $R_F$: 0.037; $R_w$: 0.038 (significant reflections); GoF: 1.8003.

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**Supporting Information Available:** Experimental details and stacked plot for the heating of complex **10** and complete crystallographic data for complex **5** and CIF files for structures **7**, **11**, and **12** are available. This information is available free of charge via the Internet at http://pubs.acs.org.

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