Stoichiometric Alkane Dehydrogenation with Tp′PtMe$_2$H to Form Tp′Pt(η^2-olefin)(H) Complexes

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Gentle heating of Tp′PtMe$_2$H (**1**) in alkane solvents in the presence of B(C_6F_5)$_3$ results in C−H activation of the alkane solvent, R−H, to give Tp′Pt(Me)(H)(R) intermediates. Further heating leads to formation of Tp′Pt(η^2-olefin)(H) complexes via methane elimination followed by β-hydride elimination, a stoichiometric alkane to olefin conversion.

Introduction

The inertness of saturated hydrocarbons limits utilization of alkanes in chemical synthesis.[1−7] Although many metal reagents are now known to activate C−H bonds, few are capable of delivering productive alkane functionalization.[8−19] Alkane dehydrogenation to form the corresponding olefin is one of the simplest ways to functionalization hydrocarbons. Many transition metal catalyzed alkane dehydrogenations require stoichiometric amounts of a sacrificial olefin to accept hydrogen and effectively undergo hydrogen transfer and not net dehydrogenation.[15,20−32] Recently progress toward developing "acceptorless" dehydrogenation catalysts has been achieved utilizing pincer-ligated iridium complexes.[33−36]

Several platinum complexes have been shown to be capable of alkane dehydrogenation. The platinum examples are stoichiometric with the exception of the catalytic dehydrogenation of cyclooctane promoted by a Pt(II) phosphite complex.[37] Examples of stoichiometric alkane dehydrogenation involving platinum complexes include the following: dehydrogenation of neohexane and cyclohexane with a five-coordinate Pt(IV) complex stabilized by a β-diiminate ligand;[38] dehydrogenation of various alkanes with ([2.1.1]pyridinophane)PtMe$_2$H via methane elimination;[39] and dehydrogenation of ethers and cyclohexane with an electrophilic (tmeda)Pt(II) complex.[40]

Recently, a detailed mechanistic study on the thermolysis of Tp′PtMe$_2$H (**1**) [Tp′ = hydridotris(3,5-dimethylpyrazolyl)-borate][41] in various solvents was reported.[42] The observation that thermolysis of **1** in cyclohexane resulted in the formation of free cyclohexene prompted us to study this reaction in more

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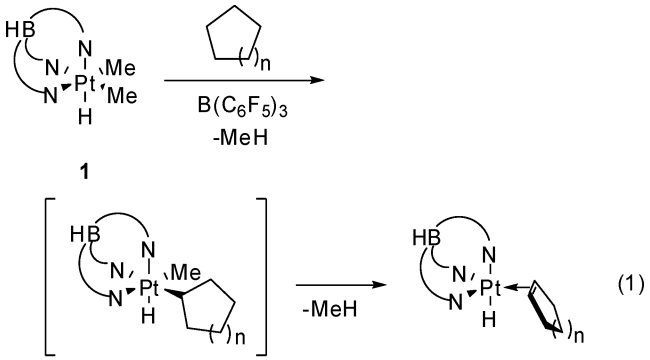
detail. The [Tp′PtMe] intermediate generated by methide abstraction from [K][Tp′PtMe$_2$] is known to activate C−H bonds to give stable Tp′Pt(Me)(H)(alkyl) complexes.[43] We now report that Tp′Pt(Me)(H)(alkyl) complexes can be generated via Lewis acid induced methane loss from Tp′PtMe$_2$H (**1**) in alkane solvents, and facile reductive elimination of methane from Tp′PtMe(H)(R) intermediates followed by β-H elimination then forms Tp′Pt(η^2-olefin)(H) products.

Results and Discussion

Neutral η^2-Olefin Complexes. Heating Tp′PtMe$_2$H (**1**) in cycloalkane solvents (cyclopentane, cyclohexane, cyclooctane; 35−50 °C) in the presence of B(C$_6$F$_5$)$_3$ results in the loss of 2 equiv of methane and formation of Tp′Pt(η^2-cycloalkene)(H) [cycloalkene = C$_5$H$_8$ (**2**), C$_6$H$_{10}$ (**3**), C$_8$H$_{14}$ (**4**)] complexes (eq 1) after 2 days. Initial loss of methane resulted in the formation of a detectable amount of intermediate species, Tp′Pt(Me)(H)-(cycloalkyl) [cycloalkane = C$_5$H$_9$ (**2a**), C$_6$H$_{11}$ (**3a**), C$_8$H$_{15}$ (**4a**)], with hydride chemical shifts similar to those previously reported.[43] When monitored by ^{1}H NMR spectroscopy in the hydride region at room temperature, the intermediates **2a**, **3a**, and **4a** are evident. These unsymmetrical intermediates, present at a low and relatively constant concentration, are consumed to form the η^2-olefin product. The Pt−H resonances for the Tp′Pt(Me)(H)(cycloalkyl) complexes appear slightly upfield of hydridodimethyl platinum reagent **1** (−20.90 ppm), at −21.08 ppm (**2a**), −21.54 ppm (**3a**), and −21.66 ppm (**4a**) in CD$_2$Cl$_2$.

To probe the source of methane generated early in the reaction, complex **1** was combined with cyclohexane-d_{12} and progress was monitored by ^{1}H NMR spectroscopy at 7 °C, just above the freezing point of the solvent. Initial methane loss was evident as a singlet appeared at δ = 0.19 ppm, indicating that CH$_4$ formed from Tp′Pt(CH$_3$)$_2$H first. Upon subsequent warming to 35 °C, scrambling to form CH$_n$D$_{4-n}$ (n = 3, 2, or 1) methane isotopologues was observed. These results are consistent with previously reported findings upon thermolysis of complex **1** with cyclohexane-d_{12} at 110 °C.[42]



(1)

Considering the olefin as a neutral ligand allows one to consider a d^8 Pt configuration with either a square planar or trigonal bipyramidal Pt(II) geometry (Figure 1). The coordination mode of the Tp′ ligand can be determined by measuring the B−H stretching frequency, and thus the geometry of the platinum complex follows indirectly from ν_{B-H}.[44] A B−H stretching frequency above 2500 cm^{-1} is indicative of κ^3-Tp′ coordination, while a ν_{B-H} below 2500 cm^{-1} indicates κ^2-Tp′

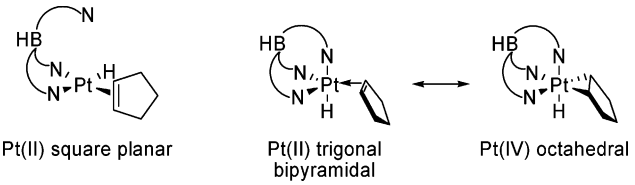


Figure 1. Possible geometries for Tp′Pt(η^2-cycloalkene)(H) complexes.

coordination.[44] The solution IR spectrum for Tp′Pt(H)(η^2-cyclo-C$_5$H$_8$), **2**, in CH$_2$Cl$_2$ indicates κ^3-coordination for Tp′, as evident by a B−H absorption at 2533 cm^{-1}. IR data for the other η^2-olefin complexes, **3** and **4**, are also consistent with κ^3-coordination. Similar neutral Tp′Pt(olefin)X complexes also exhibit κ^3-coordination of Tp′, as illustrated by the IR spectrum and ^{11}B NMR[45] chemical shift of Tp′PtMe(CH$_2$═CH$_2$) (ν_{B-H} = 2536 cm^{-1} and ^{11}B NMR δ = −8.72 ppm).[46] IR spectra for platinum olefin complexes **2**−**4** also display a platinum hydride stretch near 2270 cm^{-1}, consistent with their formulation as the β-hydride elimination product.

Both tridentate Tp′ resonance structures shown in Figure 1 are acceptable, but the platinum(IV) octahedral metallacycloalkane depiction is particularly convenient for predicting the olefin orientation. ^{1}H NMR spectra for the Tp′Pt(η^2-cycloalkene)(H) complexes display a 2:1 pattern for the pyrazole resonances consistent with mirror symmetry in the molecule. The two olefinic protons are enantiometric and appear as a multiplet with platinum satellites in accord with the platinum(IV) octahedral metallacycloalkane geometry. The olefin protons in the η^2-cyclohexene complex, **3**, resonate at 3.79 ppm, well upfield from free cyclohexene (δ = 6.02 ppm),[42] with $^2J_{Pt-H}$ = 100 Hz. The other η^2-cycloalkene complexes, **2** and **4**, show similar ^{1}H NMR spectra with olefinic signals at 3.64 ppm ($^2J_{Pt-H}$ = 94 Hz) and 3.36 ppm ($^2J_{Pt-H}$ = 90 Hz), respectively. The carbon atoms coordinated to the platinum center in the η^2-cyclohexene complex, **3**, resonate at 32.1 ppm with $^1J_{Pt-C}$ = 362 Hz.

The Pt−H resonances for the Tp′Pt(η^2-cycloalkene)(H) complexes appear far upfield at −28.57 ppm (**2**, $^1J_{Pt-H}$ = 1183 Hz), −29.19 ppm (**3**, $^1J_{Pt-H}$ = 1200 Hz), and −29.12 ppm (**4**, $^1J_{Pt-H}$ = 1198 Hz) possibly due to their location in the shielding region of the adjacent pyrazole rings. Similar Pt−H chemical shifts were observed in ([2.1.1]pyridinophane)Pt(η^2-olefin)(H) complexes.[39]

To assess the ability of Tp′PtMe$_2$H (**1**) to activate more sterically hindered C−H bonds, the reaction of **1** with *tert*-butylethane in the presence of B(C$_6$F$_5$)$_3$ was studied. The product formed, Tp′Pt(Me)H(CH$_2$CH$_2$(C(CH$_3$)$_3$), upon Lewis acid induced methane elimination, arises when the less sterically hindered primary C−H bond of the ethyl group of *tert*-butylethane is activated. The Pt−H resonates at −20.99 ppm ($^1J_{Pt-H}$ = 1443 Hz) in CD$_2$Cl$_2$. Continued heating results in elimination of a second equivalent of methane and formation of the β-H elimination product Tp′Pt(η^2-neohexene)(H) (**5**). The solution IR spectrum for Tp′Pt(H)(η^2-neohexene) in CH$_2$Cl$_2$ indicates κ^3-coordination for Tp′ (ν_{B-H} = 2535 cm^{-1}), as was seen in the η^2-cycloalkene complexes. The three olefin protons are all distinct. The internal olefin proton resonates at 3.70 ppm with $^2J_{Pt-H}$ = 97 Hz and is easily distinguished since *cis* and

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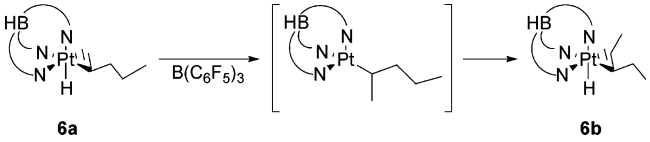
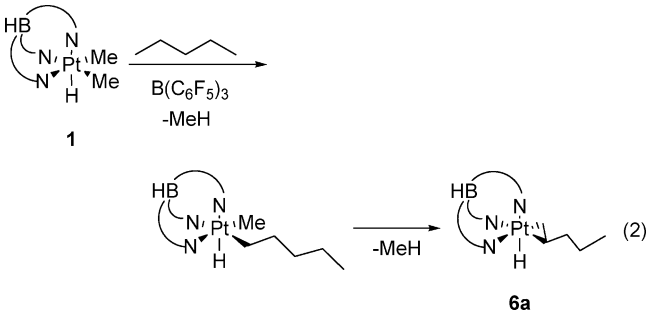


Figure 2. Possible mechanism for isomerization of Tp′Pt(η^2-1-pentene)(H) (**6a**) to Tp′Pt(η^2-2-pentene)(H) (**6b**).

trans couplings to the other olefin protons of $^3J_{H-H}$ = 8.4 Hz and $^3J_{H-H}$ = 10.8 Hz, respectively, are observed. The Pt−H resonates far upfield at −28.78 ppm ($^1J_{Pt-H}$ = 1154 Hz), similar to the Tp′Pt(η^2-cycloalkene)(H) complexes.

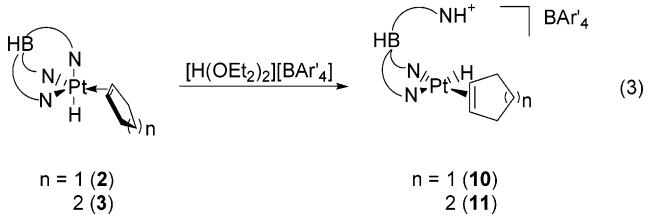
The ability of Tp′PtMe$_2$H (**1**) to activate C−H bonds regioselectively was examined by the reaction of **1** with *n*-pentane. Upon Lewis acid induced methane elimination, activation of the primary C−H bond of the solvent is indicated by the formation of Tp′Pt(1-pentyl)(Me)H, in accord with a previously reported synthesis.[43] No formation of the secondary C−H bond activation products, Tp′Pt(2-pentyl)(Me)H or Tp′Pt(3-pentyl)(Me)H, was observed under these conditions. As the reaction proceeds, elimination of a second equivalent of methane from Tp′Pt(1-pentyl)(Me)H occurs followed by β-H elimination to give the η^2-1-pentene product, Tp′Pt(η^2-CH$_2$=CHCH$_2$CH$_2$CH$_3$)(H) (**6a**) (eq 2). Increased reaction times show the appearance of a new product formulated as the η^2-2-pentene complex, Tp′Pt(η^2-CH(Me)=CH(CH$_2$CH$_3$))(H) (**6b**). Since initial results show no formation of Tp′Pt(2-pentyl)(Me)H or Tp′Pt(3-pentyl)(Me)H, which could lead directly to the η^2-2-pentene complex **6b**, formation of **6b** is most likely a result of isomerization of **6a** to the internal olefin complex via 2,1-insertion of the olefin into the Pt−H bond followed by β-H elimination (Figure 2). The ratio of **6a**:**6b** after 15 h was 4:1.



The ^{1}H NMR spectrum for the reaction of **1** with *n*-pentane after 15 h indicated the formation of only one isomer for the η^2-1-pentene complex **6a** and one for the η^2-2-pentene complex **6b** out of the two and four possible NMR distinguishable facial isomers, respectively. Differentiation between isomers **6a** and **6b** was possible by analysis of the olefin proton resonances. Formation of the η^2-1-pentene complex **6a** was confirmed by the observation of three COSY correlated olefinic protons. The two terminal olefin protons for **6a** resonate at 2.82 ppm ($^2J_{Pt-H}$ = 86 Hz, $^3J_{H-H}$ = 7.6 Hz, $^2J_{H-H}$ = 2.0 Hz) and 2.41 ppm ($^2J_{Pt-H}$ = 50 Hz, $^3J_{H-H}$ = 9.6 Hz, $^2J_{H-H}$ = 2.0 Hz) as doublets of doublets. The internal olefinic proton resonates at 3.39 ppm as a multiplet. The η^2-2-pentene isomer **6b** has only two olefinic protons, and a distinctive doublet appears for the terminal methyl group at 1.59 ppm ($^3J_{Pt-H}$ = 42 Hz).

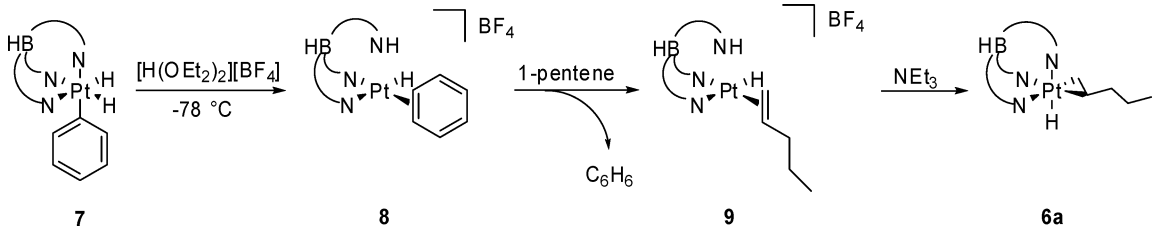
Tp′Pt(η^2-1-pentene)(H) (**6a**) has also been prepared independently via low-temperature protonation of Tp′Pt(Ph)(H)$_2$ (**7**), followed by addition of 1-pentene and subsequent deprotonation (Scheme 1). In a previous investigation of Tp′Pt(Ar)(R)(H) complexes [Ar = aryl, R = H, C$_6$H$_5$], protonation of these aryl complexes at low temperature was found to result in the formation of cationic Pt(II) η^2-arene adducts.[47] Complex **7** was protonated with HBF$_4$ at −78 °C to form [κ^2-(HTp′)Pt(η^2-benzene)(H)][BF$_4$] (**8**). Addition of excess 1-pentene to the cold solution of **8** led to formation of [κ^2-(HTp′)Pt(η^2-1-pentene)(H)][BF$_4$] (**9**) after 5 h. Complex **9** can be observed by ^{1}H NMR below 233 K as two isomers with platinum hydrides resonating at −22.19 ppm ($^1J_{Pt-H}$ = 1080 Hz) and −23.59 ppm ($^1J_{Pt-H}$ = 1176 Hz). The neutral, six-coordinate Tp′Pt(η^2-1-pentene)(H) (**6a**) was subsequently trapped by the deprotonation with NEt$_3$. Once **9** had been deprotonated, the solution could be warmed and **6a** could be isolated without further isomerization to **6b**. However, if [κ^2-(HTp′)Pt(η^2-1-pentene)(H)][BF$_4$] (**9**) was warmed prior to deprotonation, a mixture of **6a** and **6b** resulted. Synthesis of the η^2-2-pentene isomer, **6b**, by an analogous route was unsuccessful.

Cationic η^2-Olefin Complexes. Low-temperature protonation of the Tp′Pt(η^2-cycloalkene)(H) complexes, **2** and **3**, with [H(OEt$_2$)$_2$][BAr′$_4$] [BAr′$_4$ = tetrakis(3,5-trifluoromethylphenyl)-borate][48] results in removal of one of the pyrazole arms from the metal center as cationic Pt(II) η^2-olefin complexes [κ^2-(HTp′)Pt(η^2-cycloalkene)(H)][BAr′$_4$] [cycloalkene = C$_5$H$_{10}$ (**10**) and C$_6$H$_{12}$ (**11**)] (eq 3) form. The ^{1}H NMR spectra for the [κ^2-(HTp′)Pt(η^2-cycloalkene)(H)][BAr′$_4$] complexes display an N−H resonance at 9.82 (**10**) and 9.90 ppm (**11**) for the protonated pyrazole arm. The mirror symmetry of the starting neutral platinum complexes, **2** and **3**, has been lost upon protonation, as is evident in the unique signals observed for each of the three nonequivalent pyrazole arms in the ^{1}H NMR spectra.



The absence of symmetry in the protonated platinum complex is also reflected in the two inequivalent olefin proton resonances in the ^{1}H NMR spectra. The two distinct olefin protons for the η^2-cyclopentene complex **10** resonate at 5.37 ($^2J_{Pt-H}$ = 77 Hz) and 4.54 ppm ($^2J_{Pt-H}$ = 77 Hz), well downfield from their chemical shift in neutral analogue **2**. Complex **11** shows similar resonances for the coordinated cyclohexene at 5.47 ppm ($^2J_{Pt-H}$ = 70 Hz) and 4.63 ppm ($^2J_{Pt-H}$ = 74 Hz). The carbon atoms

Scheme 1. Low-Temperature Route to Tp′Pt(η^2-1-pentene)(H) (6a)



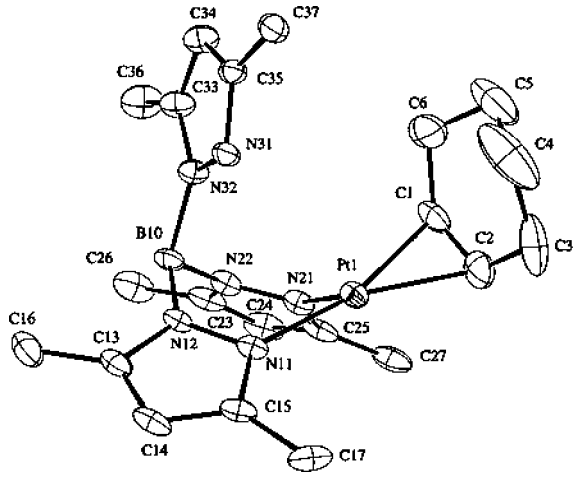


Figure 3. ORTEP diagram of [κ^2-(HTp′)Pt(η^2-cyclo-C_6H_{10})(H)][BAr′$_4$] (**11**). Ellipsoids are drawn at the 50% probability level, and the [BAr′$_4$] counterion is omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 11

Pt−C1	2.189(8)	C1−C2	1.366(15)
Pt−C2	2.204(9)	C1−C6	1.510(14)
Pt−N11	2.035(6)	C2−C3	1.503(16)
Pt−N21	2.135(6)	C4−C5	1.47(3)
C1−Pt−C2	36.2(4)	C2−Pt−N21	110.0(3)
C1−Pt−N11	164.1(3)	N11−Pt−N21	85.71(22)
C1−Pt−N21	86.2(3)	Pt−C1−C2	72.5(5)
C2−Pt−N11	159.1(3)	Pt−C2−C1	71.3(5)

coordinated to the cationic platinum center in the η^2-cyclohexene complex **11** are also distinct and resonate at 82.6 and 81.5 ppm. The Pt−H resonances for **10** and **11** are shifted downfield from their neutral analogues to −23.25 ($^1J_{Pt-H}$ = 1182 Hz) and −23.75 ($^1J_{Pt-H}$ = 1226 Hz), respectively.

The structural features of the cationic η^2-cyclohexene platinum complex **11** were investigated by X-ray structural analysis. An ORTEP diagram of **11** is shown in Figure 3. The Pt−N(21) distance of 2.135(6) Å is 0.1 Å longer than the Pt−N(11) distance of 2.035(6) Å *trans* to the cyclohexene ligand, indicating the stronger *trans* influence of the hydride ligand (Table 1). The bond distance between C1−C2 (1.366(15) Å) is significantly shorter than the single bond C−C distances in the cyclohexene ring, indicating the retention of partial double bond character when coordinated to platinum(II). The tilt angle of the olefin in cyclohexene relative to the platinum square plane is 131.5°. On the basis of the geometries of other square planar platinum(II) olefin complexes, one would anticipate the orientation of the olefin in cyclohexene to be perpendicular to the platinum square plane.[46] Unfavorable steric interactions between the cyclohexene ring and the uncoordinated pyrazole ring appear to dictate the alignment of the olefin away from perpendicular relative to the platinum square plane.

Summary. Stoichiometric alkane dehydrogenation was observed when Tp′PtMe$_2$H was treated with Lewis acid in alkane solvents. The reaction is proposed to proceed via borane-induced methane elimination and subsequent C−H activation of the solvent to give a Tp′Pt(Me)(alkyl)H intermediate. Upon further heating, elimination of a second equivalent of methane occurs followed by β-H elimination to give Tp′Pt(η^2-olefin)(H) complexes. Although the selective conversion of *n*-pentane to 1-pentene was not achieved, initial results indicate regioselective activation of the stronger primary C−H bond over the weaker secondary C−H bond of *n*-pentane. Protonation of neutral Tp′Pt(η^2-cycloalkene)(H) complexes results in release of one pyrazole arm from the platinum center and formation of cationic Pt(II) η^2-cycloalkene complexes.

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.[49] Cyclopentane (Aldrich, Sure Seal), cyclohexane (Aldrich, Sure Seal), cyclooctane, and *tert*-butylethane were used as purchased. Deuterated methylene chloride was vacuum transferred from P_2O_5 and degassed by several freeze−pump−thaw cycles.

Tp′PtMe$_2$H,[50] Tp′PtPhH$_2$,[47] and [H(OEt$_2$)$_2$][BAr′$_4$][48] were synthesized according to published procedures. B(C_6F_5)$_3$ was used as obtained from Strem. [H(OEt$_2$)$_2$][BF$_4$] was obtained from Aldrich and used without further purification.

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

Representative Synthesis of Tp′Pt(η^2-olefin)(H). In a typical experiment, Tp′PtMe$_2$H (1) (0.100 g, 0.191 mmol) and 1 equiv of B(C_6F_5)$_3$ (0.098 g) were weighed into a 100 mL Schlenk flask. Then 15 mL of the alkane solvent was added via syringe through the septum. The reaction mixture was heated at 35−50 °C and stirred for 2 days. After solvent was removed in vacuo, 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.

Tp′Pt(η^2-cyclo-C_5H_8)(H) (2). Anhydrous cyclopentane (15 mL) was added to the solids as described above. The reaction mixture was stirred for 2.5 days at 35 °C. Yield: 85 mg (79%). IR (CH_2Cl_2): ν_{B-H} = 2533 cm^{-1}, ν_{Pt-H} = 2265 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 253 K, δ): 5.83, 5.64 (s, 2H, 1H, Tp′C*H*), 3.64 (m, 2H, $^2J_{Pt-H}$ = 94 Hz, Pt(C*H*=C*H*CH$_2$CH$_2$CH$_2$)), 2.32, 2.30, 2.16, 2.15 (s, 6H, 3H, 6H, 3H, Tp′CH_3), 2.00, 1.71, 1.16 (m, m, m, 6H, Pt(CH=CHCH_2CH_2CH_2), −28.57 (s, 1H, $^1J_{Pt-H}$ = 1183 Hz, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 253 K, δ): 148.9, 144.5, 143.9 (3C, 1C, 2C, Tp′*C*CH$_3$), 107.8, 104.9 (1C, 2C, Tp′*C*H), 38.4, 32.2, 22.0 (2C, 2C, 1C, Pt(*C*H=*C*HCH$_2$*C*H$_2$*C*H$_2$), 14.6, 13.2, 12.4, 12.2 (2C, 1C, 2C, 1C, Tp′C*C*H$_3$). Anal. Calcd for PtBN$_6$C$_{20}$H$_{31}$·CH$_2$Cl$_2$: C, 39.03; H, 5.15; N, 13.00. Found: C, 40.03; H, 5.15; N, 12.79.

Tp′Pt(η^2-cyclo-C_6H_{10})(H) (3). Anhydrous cyclohexane (15 mL) was added to the solids as described above. The reaction mixture was stirred for 2 days at 50 °C. Yield: 70 mg (64%). IR (KBr): ν_{B-H} = 2516 cm^{-1}, ν_{Pt-H} = 2269 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 263K, δ): 5.83, 5.64 (s, 2H, 1H, Tp′C*H*), 3.79 (m, 2H, $^2J_{Pt-H}$ = 100 Hz, Pt(C*H*=C*H*CH$_2$CH$_2$CH$_2$CH$_2$)), 2.32, 2.31, 2.21, 2.19 (s, 6H, 3H,

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6H, 3H, Tp′CH_3), 2.09, 1.62, 1.28 (m, m, m 8H, Pt(CH═CHCH_2-CH_2CH_2CH_2)), −29.19 (s, 1H, $^1J_{Pt-H}$ = 1200 Hz, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 263 K, δ): 150.8, 149.0, 144.5, 143.9 (1C, 2C, 1C, 2C, Tp′*C*CH_3), 108.3, 105.1 (1C, 2C, Tp′*C*H), 32.1 (2C, $^1J_{Pt-C}$ = 362 Hz, Pt(*C*H═*C*HCH$_2$CH$_2$CH$_2$CH$_2$), 29.6, 22.1 (2C, 2C, Pt(CH═CHCH_2CH_2CH_2CH_2),) 14.7, 12.6, 12.5, 11.8 (2C, 1C, 2C, 1C, Tp′CCH_3). Anal. Calcd for $PtBN_6C_{21}H_{33}$·0.5 CH_3OH: C, 43.66; H, 5.96; N, 14.21. Found: C, 43.13; H, 5.66; N, 14.34.

Tp′Pt(η²-cyclo-C_8H_{14})(H) (4). Cyclooctane (15 mL) was added to the solids as described above. The reaction mixture was stirred for 2 days at 50 °C. Yield: 91 mg (79%). IR (CH_2Cl_2): ν_{B-H} = 2533 cm^{-1}, ν_{Pt-H} = 2275 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 263 K, δ): 5.82, 5.67 (s, 2H, 1H, Tp′C*H*), 3.36 (m, 2H, $^2J_{Pt-H}$ = 90 Hz, Pt(C*H*═C*H*CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 2.32, 2.31, 2.20, 2.19 (s, 3H, 6H, 6H, 3H, Tp′CH_3), 1.66−1.41 (m, 12H, Pt(CH═CHCH_2CH_2CH_2-CH_2CH_2CH_2), −29.12 (s, 1H, $^1J_{Pt-H}$ = 1198 Hz, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 263 K, δ): 151.0, 148.9, 144.0, 143.9 (1C, 2C, 1C, 2C, Tp′*C*CH_3), 108.4, 105.0 (1C, 2C, Tp′*C*H), 37.5 (2C, $^1J_{Pt-C}$ = 362 Hz, Pt(*C*H═*C*HCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 33.5, 31.7, 26.6 (2C, 2C, 2C, Pt(CH═CH*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$),) 14.9, 12.6, 12.5, 12.0 (2C, 1C, 2C, 1C, Tp′C*C*H_3). Anal. Calcd for $PtBN_6C_{23}H_{37}$·CH_2Cl_2: C, 41.87; H, 5.71; N, 12.21. Found: C, 42.17; H, 5.80; N, 12.39.

Tp′Pt(η²-neohexene)(H) (5). Anhydrous *tert*-butylethane (15 mL) was added to the solids as described above. The reaction mixture was stirred for 3 days at 35 °C. Yield: 72 mg (65%). IR (CH_2Cl_2): ν_{B-H} = 2535 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 240 K, δ): 5.82, 5.67 (s, 2H, 1H, Tp′C*H*), 3.70 (dd, 1H, $^2J_{Pt-H}$ = 97 Hz, $^3J_{H-H}$ = 8.4 Hz, $^3J_{H-H}$ = 10.8 Hz, Pt−CH_2═C*H*(C(CH_3)$_3$), 2.45 (dd, 1H, Pt−CH_2═CH(C(CH_3)$_3$), 2.35, 2.27, 2.18 (s, 9H, 3H, 6H, Tp′CH_3), 1.05 (s, 9H, Pt−CH_2═CH(C(CH_3)$_3$), −28.78 (s, 1H, $^1J_{Pt-H}$ = 1154 Hz, Pt-*H*). The other inequivalent olefin proton resonance is obscured by the Tp′(CH_3) resonances in the range from 2.35 to 2.18 ppm. Satisfactory analytical data were not obtained.

Tp′Pt(η²-pentene)(H). Anhydrous *n*-pentane (20 mL) was added to the solids as described above. The reaction mixture was stirred for 15 h at 30 °C. The ratio of Tp′Pt(η²-1-pentene)(H) (**6a**) to Tp′Pt(η²-2-pentene)(H) (**6b**) was 4:1 with a yield of 34 mg (63%). IR (CH_2Cl_2): ν_{B-H} = 2535 cm^{-1}. ^{1}H NMR for **6a** (CD_2Cl_2, 298 K, δ): 5.83, 5.67 (s, 2H, 1H, Tp′C*H*), 3.39 (m, 1H, Pt−CH_2═C*H*CH$_2$CH$_2$CH$_3$), 2.82 (dd, 1H, $^2J_{Pt-H}$ = 86 Hz, $^3J_{H-H}$ = 7.6 Hz, $^2J_{H-H}$ = 2.0 Hz, Pt−CH_2═CHCH$_2$CH$_2$CH$_3$, 2.41 (dd, 1H, $^2J_{Pt-H}$ = 50 Hz, $^3J_{H-H}$ = 9.6 Hz, $^2J_{H-H}$ = 2.0 Hz, Pt−CH_2═CHCH$_2$CH$_2$-CH$_3$, 2.38−2.12 (s, 18H, Tp′CH_3), 1.71, 1.32 (m, 2H, 2H, Pt−CH_2═CHCH_2CH_2CH$_3$), 0.99 (t, Pt−CH_2═CHCH$_2$CH$_2$CH_3), −29.14 (s, 1H, $^1J_{Pt-H}$ = 1144 Hz, Pt-*H*). ^{1}H NMR for **6b** (CD_2Cl_2, 298 K, δ): 5.83, 5.67 (s, 2H, 1H, Tp′C*H*), 3.45 (m, 2H, Pt−C*H*(CH$_3$)═C*H*(CH$_2$-CH$_3$), 2.38−2.12 (s, 18H, Tp′CH_3), 1.59 (d, 3H, $^3J_{Pt-H}$ = 42 Hz, Pt−CH(CH_3)═CH(CH$_2$CH$_3$)), 1.45 (m, 2H, Pt−CH(CH$_3$)═CH(CH_2-CH$_3$)), 1.07 (t, 3H, Pt−CH(CH$_3$)═CH(CH$_2$CH_3)), −29.50 (s, 1H, $^1J_{Pt-H}$ = 1208 Hz, Pt-*H*).

Synthesis of Tp′Pt(η²-1-pentene)(H) (6a). Tp′Pt(Ph)(H)$_2$ (**7**) (85 mg, 0.148 mmol) was placed in a 50 mL Schlenk flask under N_2 and dissolved in 15 mL of CH_2Cl_2. The solution was cooled to −78 °C, and 1.1 equiv of HBF_4 (22 μL, 0.162 mmol) was added via syringe. After 15 min, 190 μL (1.48 mmol) of cold 1-pentene was added to the solution. After 5 h, NEt_3 (22 μL, 0.148 mmol) was added to the cold solution to depronate. After 1.5 h, the cold bath was removed and solvent pulled off in vacuo, resulting in an oily, yellow product. The product was taken up in minimal CH_2Cl_2 and 5× hexanes were added to crash out the salts. The liquid was filtered away from the salts via cannula transfer and the filtrate condensed to a white powder by rotoevaporation. Yield: 69 mg (83%).

[κ²-(HTp′)Pt(η²-1-pentene)(H)][BF_4] (9). An NMR tube was charged with 15 mg of Tp′Pt(η²-1-pentene)(H) (**6a**) (0.0266 mmol), and the solids were dissolved in 0.7 mL of anhydrous CD_2Cl_2 in the drybox. Outside the drybox, the tube was cooled to −78 °C, and 3.6 μL of [H(OEt_2)$_2$][BF_4] (0.0266 mmol) was added. The sample was kept below 233 K. ^{1}H NMR (CD_2Cl_2, 233 K, δ): −22.19 (s, 1H, $^1J_{Pt-H}$ = 1080 Hz, Pt-*H*), −23.59 (s, 1H, $^1J_{Pt-H}$ = 1176 Hz, Pt-*H*).

Representative [BAr′$_4$]$^-$ NMR Data. ^{1}H and ^{13}C NMR data for the [BAr′$_4$]$^-$ counterion are reported separately for simplicity. ^{1}H 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, *C*F_3), 117.9 (C_{para}).

[κ²-(HTp′)Pt(η²-cyclo-C_5H_8)(H)][BAr′$_4$] (10). Tp′Pt(η²-C_5H_8)(H) (2) (0.125 g, 0.239 mmol) and [H(OEt_2)$_2$][BAr′$_4$] (0.290 g, 0.287 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 (20 mL) was slowly added through the septum, and the reaction mixture was stirred for 10 min. The cold bath was removed, and the reaction was stirred for 30 min while warming to room temperature. The solvent was removed in vacuo, and the residue was triturated with pentane. Colorless crystals were obtained from CH_2Cl_2/pentane at −30 °C. Yield: 66 mg (20%). ^{1}H NMR (CD_2Cl_2, 293 K, δ): 9.82 (s, 1H, pz′N*H*), 6.24, 6.09, 6.00 (s, 1H each, HTp′C*H*), 5.37 (m, 1H, $^2J_{Pt-H}$ = 77 Hz, Pt(C*H*═C*H*CH$_2$CH$_2$CH$_2$)), 4.54 (m, 1H, $^2J_{Pt-H}$ = 77 Hz, Pt(C*H*═C*H*CH$_2$CH$_2$CH$_2$)), 2.37, 2.36, 2.27, 2.22, 1.83 (s, 6H, 3H, 3H, 3H, 3H, HTp′CH_3), 2.09, 1.65, 1.42 (m, 2H each, Pt(CH═CHCH_2CH_2CH_2)), −23.25 (s, 1H, $^1J_{Pt-H}$ = 1182 Hz, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 293 K, δ): 153.8, 153.2, 150.2, 149.2, 148.7, 144.3 (HTp′*C*CH_3), 110.2, 109.4, 108.1 (HTp′*C*H), 86.9, 85.7 (Pt(*C*H═*C*HCH$_2$CH$_2$CH$_2$), 35.6, 34.3, 21.0 (Pt(CH═CH*C*H$_2$*C*H$_2$*C*H$_2$) 16.4, 14.2, 13.3, 11.6, 11.4 (Tp′C*C*H_3). Anal. Calcd for $PtB_2F_{24}N_6C_{52}H_{44}$: C, 43.81; H, 3.11; N, 5.89. Found: C, 44.01; H, 3.12; N, 5.61.

[κ²-(HTp′)Pt(η²-cyclo-C_6H_{10})(H)][BAr′$_4$] (11). Tp′Pt(η²-C_6H_{10})(H) (**3**) (0.042 g, 0.072 mmol) and [H(OEt_2)$_2$][BAr′$_4$] (0.089 g, 0.088 mmol) were weighed into a 50 mL Schlenk flask in the drybox. The flask was cooled to −78 °C outside the drybox. CH_2Cl_2 (10 mL) was slowly added through the septum, and the reaction mixture was stirred for 10 min. The cold bath was removed, and the reaction was stirred for 30 min while warming to room temperature. The solvent was removed in vacuo, and the residue was triturated with pentane. Colorless crystals were obtained from CH_2Cl_2/pentane at −30 °C. Yield: 67 mg (73%). ^{1}H NMR (CD_2Cl_2, 293 K, δ): 9.90 (s, 1H, pz′N*H*), 6.25, 6.10, 6.00 (s, 1H each, HTp′C*H*), 5.47 (m, 1H, $^2J_{Pt-H}$ = 70 Hz, Pt(*C*H═*C*HCH$_2$CH$_2$CH$_2$CH$_2$)), 4.63 (m, 1H, $^2J_{Pt-H}$ = 74 Hz, Pt(C*H*═C*H*CH$_2$CH$_2$CH$_2$CH$_2$)), 2.39, 2.38, 2.36, 2.26, 2.24, 1.80 (s, 3H each, HTp′CH_3), 1.70−1.27 (m, 8H, Pt(CH═CHCH_2CH_2CH_2CH_2)), −23.75 (s, 1H, $^1J_{Pt-H}$ = 1226 Hz, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 293 K, δ): 153.7, 153.3, 150.2, 149.1, 148.8, 144.3 (HTp′*C*CH_3), 110.3, 109.5, 108.0 (HTp′*C*H), 82.6, 81.5 (Pt(*C*H═*C*HCH$_2$CH$_2$CH$_2$CH$_2$)), 30.3, 29.6, 21.3, 20.9 (Pt(CH═CH*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_2$)), 14.5, 14.1, 13.3, 11.6, 11.5 (Tp′C*C*H_3). Anal. Calcd for $PtB_2F_{24}N_6C_{53}H_{46}$: C, 44.22; H, 3.22; N, 5.84. Found: C, 44.26; H, 3.09; N, 5.78.

Structural Data for 11. Crystals from CH_2Cl_2/pentane; $C_{53}H_{45.34}N_6F_{24}B_2Pt$, M = 1438.98; triclinic, space group $P\bar{1}$; Z = 2; a = 12.6222(4) Å, b = 12.6738(4) Å, c = 18.3604(5) Å; α = 87.648(1)°, β = 82.375(1)°, γ = 83.164(1)°; U = 2889.52(15) Å^3;

D_c = 1.654 Mg m^{-3}; T = −100 °C; max 2θ = 50°; Mo Kα radiation (λ = 0.71073 Å); 10 163 unique reflections were obtained and 8156 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 = 0.032; residuals, R_F = 0.050; R_w = 0.060 (significant reflections); GoF = 1.7330.

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Supporting Information Available: Complete crystallographic data for **8**. This information is available free of charge via the Internet at http://pubs.acs.org.

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