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An Easy Conversion from Platinum(II) Reagents to Platinum(IV) Products: κ^3 to κ^2 Coordination Mode Interconversion, Phenyl Migration, and Ortho C−H Activation Cascade in a Hemilabile "Click"-Triazole Scorpionate Platinum System

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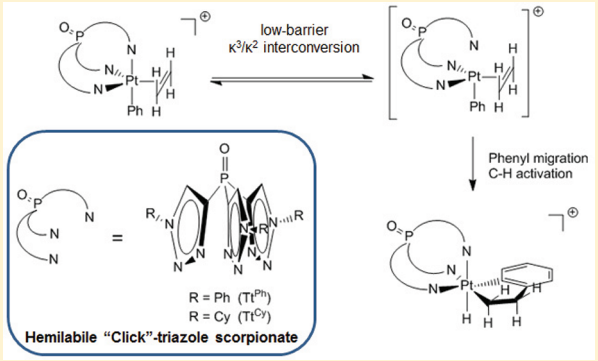
Supporting Information

ABSTRACT: A series of platinum phenyl olefin complexes has been prepared that bear hemilabile "Click"-triazole based scorpionate ligands (Tt^R). Mild heating of the olefin adducts initiates a reaction sequence to form stable, cationic Pt(IV) hydride metallacycles. An attractive mechanism involves κ^3/κ^2 conversion, phenyl migration, and ortho C−H activation. Activation parameters for the overall C−C bond-forming and C−H bond-breaking process were obtained. Insertion products from mono- and disubstituted olefins reveal a kinetic preference for phenyl migration to the less sterically hindered olefin position but a thermodynamic preference for the β-substituted metallacycle isomer, in which steric bulk is further away from the metal center and the Tt^R ligand. Thermolysis converts the kinetically favored products to their thermodynamically stable isomers via a reversible C−C bond cleavage and formation reaction. EXSY NMR and deuterium-labeling studies reveal facile scrambling processes in the metallacycles due to the hemilabile ligand.



INTRODUCTION

The incorporation of hemilable motifs into organometallic system design has become a growing area of interest, due to the ease of forming unsaturated compounds and thus initiating reactivity.[1−3] A plethora of multidentate ligand scaffolds have been reported containing weakly coordinating and easily tunable heteroatom donors that can reversibly bind to a metal center.[1−11] Although strongly donating chelates often result in stable, well-defined complexes, they can impede desirable chemical reactions.[12]

The introduction of a hemilabile functionality adds versatility by providing a flexible coordination mode geometry that can promote a variety of fundamental organometallic processes, including reductive couplings, oxidative addition, organic substrate binding, and insertion reactions.[2,11,13] For example, Lindner et al. demonstrated that the utilization of hemilabile P,O chelates assists in the Co- or Rh-catalyzed carbonylation of methyl iodide by promoting substrate binding and CO insertion reactions through flexible ligand denticity.[5,11,14−17] Shaw and co-workers have shown that a metal center's aptitude toward oxidative addition can be significantly increased by the introduction of a pendant ether that can reversibly donate and amplify the nucleophilicity of Ir in $IrCl(CO)[PMe_2(o\text{-}MeOC_6H_4)]_2$.[13] More recently, Lassaletta et al. have reported on κ^1/κ^2 interconversions in a bidentate N,N ligand Ir system that promote the catalyzed borylation of arenes.[18] Furthermore, Jiménez and co-workers have developed Ir NHC complexes with pendant hemilabile ethers and amines, which are critical to the complexes' functionality as transfer hydrogenation catalysts.[19]

Some transformations involving hemilabile ligands require an external reagent to sever the metal−ligand bond and initiate reactivity. Braunstein has reported on P,O chelated Pd complexes that do not exhibit hemilabile behavior until the addition of carbon dioxide or isocyanate, which can reversibly trap the substrate to form a C−C bond and a new dynamic system.[2,20,21] Our group has reported on both Lewis acid and thermolysis promoted κ^3/κ^2 conversions to initiate reactivity in the Tp′Pt system (Tp′ = hydridotris(3,5-dimethylpyrazolyl)-borate) (Figure 1a).[22−26] One particularly interesting example is phenyl migration to a bound olefin and subsequent intramolecular C−H activation in $Tp'Pt(Ph)(\eta^2\text{-}C_2H_4)$ to form stable metallacyclic Pt(IV) products (eq 1).[24] Such transformations occur at 60 °C in the presence of a strong Lewis acid, such as $B(C_6F_5)_3$, or at 80 °C in the absence of borane. Mechanistically, the Lewis acidic borane is postulated to promote dechelation of one of the pyrazolyl rings to form an

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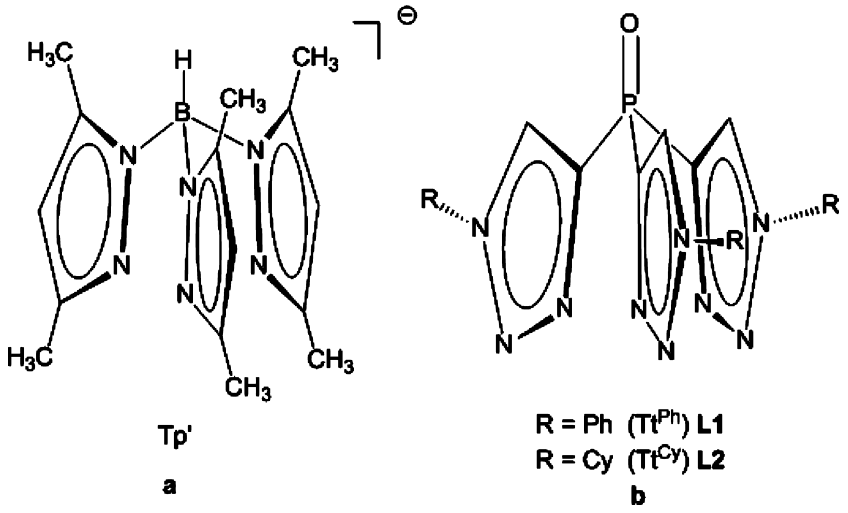
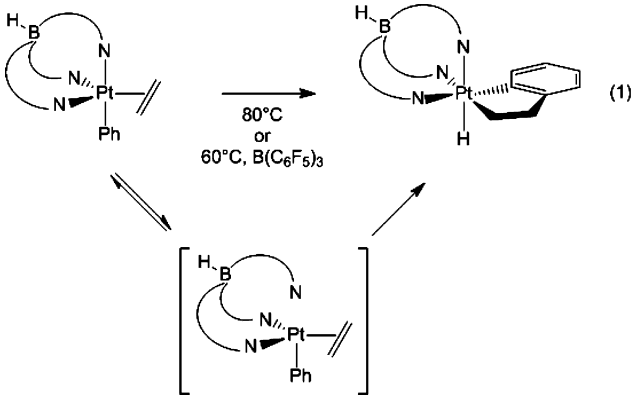


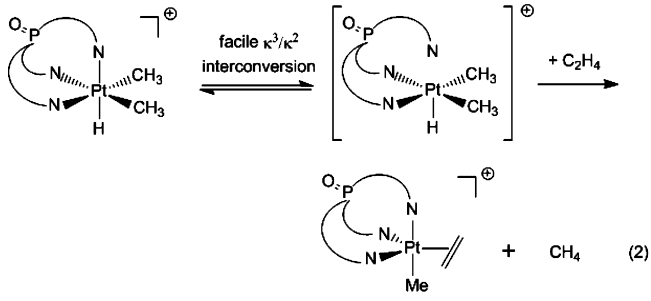
Figure 1. The Tp′ (**a**) and Tt^R (**b**) tridentate ligands.



unsaturated 16-electron intermediate from which aryl migration to the olefin occurs. The resulting three-coordinate Pt(II) species undergoes ortho C−H activation of the tethered phenyl ring to form a coordinatively saturated, 18-electron Pt(IV) product. Given the well-established trend for preliminary ligand dissociation from Pt(IV) to produce reactive intermediates,[27−36] we postulate that a κ^3/κ^2 interconversion step initiates migration in the η^2-olefin Pt(II) starting material.[24]

The utilization of hemilabile ligands can be an important factor in Pt(II)/Pt(IV) interconversion chemistry. Vedernikov and co-workers have extensively employed the hemilabile di-2-pyridylmethanesulfonate (dpms) ligand to achieve platinum−carbon functionalization in aqueous media.[7,37−43] The flexible denticity provided by the reversible sulfonate group binding in dpms assists in stabilizing oxidized Pt(IV) species en route to functionalized products. Furthermore, the dipyridyl ketone ligand used by both Puddephatt and Vedernikov readily adds nucleophiles to create an anionic ligand that can be either bidentate or tridentate.[44,45]

Recently, we have found that utilizing Lammertsma's Click-derived[46−49] 1,2,3-triazolyl-based scorpionate ligand Tt^R (Figure 1b, R = Ph (**L1**), Cy (**L2**)) lowers the barrier for κ^3/κ^2 interconversion relative to the analogous Tp′Pt system due to significantly weaker donation from the triazolyl moiety.[50] Gentle heating of the $[Tt^RPtMe_2H]^+$ cation at 35 °C induces methane elimination, and our hypothesis is that conversion to the κ^2 five-coordinate isomer is the first step. Trapping the resulting $[Tt^RPtMe]^+$ fragment with an olefin generates a five-coordinate κ^3 coordinated cation (eq 2). With this reactivity in mind, we sought



to further exploit the Tt^R ligand's facile coordination mode interconversions by exploring the Tt^RPt fragment's reactivity toward C−C bond-forming and aryl C−H activation reactions. Will replacing Tp′ with Tt^R result in lower energy barriers for the transformation of Pt(II) olefin adducts to Pt(IV) C−H activated metallacyclic products? Herein, we report the synthesis of Tt^RPt phenyl η^2-olefin complexes and their reactivity with respect to phenyl migration and subsequent C−H activation.

RESULTS AND DISCUSSION

Protonation and Trapping Reactions. In a fashion similar to the previously reported synthesis of cationic Pt(II) methyl η^2-olefin complexes $[Tt^RPtMeL][BF_4]$, we sought to generate the analogous phenyl complexes $[Tt^RPtPhL][BF_4]$. The synthetic route for the methyl derivatives involves protonation of κ^2-Tt^RPtMe_2 to form a dimethyl hydride species followed by gentle heating in the presence of an olefin to lose methane and form the trapped product. Likewise, we targeted the corresponding $[\kappa^3$-$Tt^RPtPh_2H]^+$ complexes **2** via protonation of their Pt(II) precursors κ^2-Tt^RPtPh_2 (**1**). However, addition of $HBF_4{\cdot}Et_2O$ to a methylene chloride solution of **1** at −78 °C and subsequent warming to room temperature did not produce the desired diphenyl hydride. Rather, consumption of the starting material occurred and production of benzene was observed in the ^1H NMR spectrum. Was it possible that room temperature was sufficient to promote benzene loss from the target hydride **2**? Indeed, protonation of the neutral platinum(II) reagent at low temperature and recording the ^1H NMR spectrum at −78 °C revealed clean conversion to hydride

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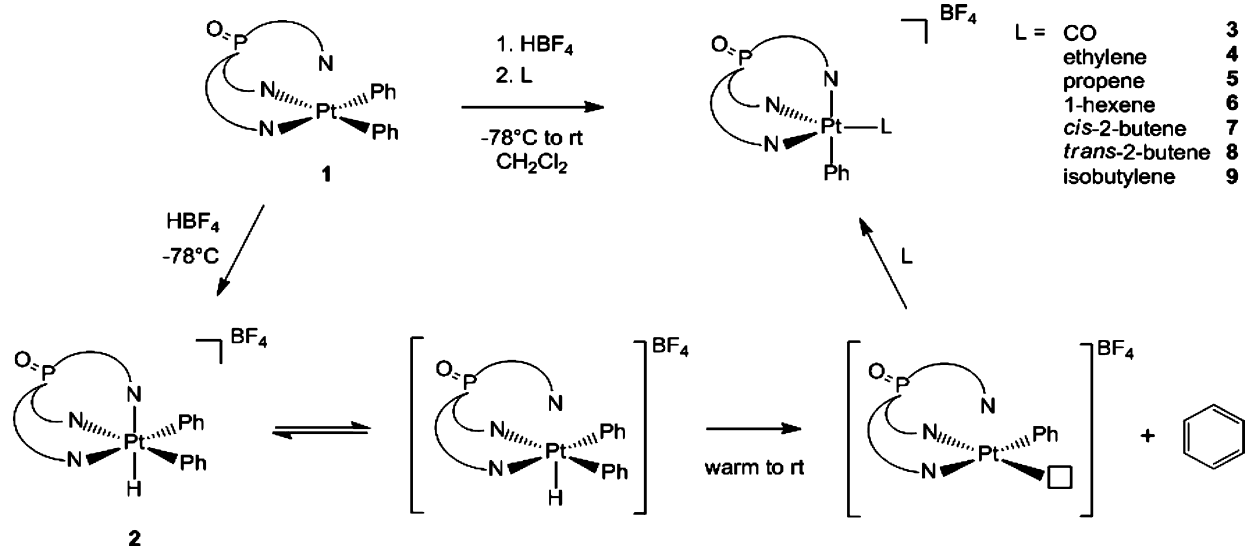
Scheme 1. Proposed Mechanism of the Protonation and Subsequent Trapping Sequence for the Conversion of 1 to 3−9



complex **2**. The diphenyl hydride complexes **2-L1** and **2-L2** display a Pt−H signal with large platinum coupling ($^1J_{Pt,H}$ = 1581 Hz (**2-L1**) and 1554 Hz (**2-L2**)), which is in accord with weak donation from the trans triazolyl nitrogen.[50] For comparison, strongly donating pyrazolyl-based systems, such as $[Tp'PtMe_2H]^+$ and $TpmPtMeH_2$ (Tpm = trispyrazolylmethane), result in a substantial decrease in the one-bond platinum−hydride coupling and are less than 1400 Hz.[51,52] A slight increase in this one-bond coupling value relative to the analogous dimethyl complexes ($^1J_{Pt,H}$ = 1541 Hz (**L1**) and 1519 Hz (**L2**)) is expected as a result of less electron donation from the phenyl ligand, thereby inducing a more electrophilic metal center and a stronger Pt−H bond.

Warming **2** to room temperature in the presence of a trapping π-acid ligand yielded the expected trapped product $[Tt^RPt(Ph)(L)][BF_4]$ (L = CO (**3**), ethylene (**4**), propylene (**5**), 1-hexene (**6**), *cis*-2-butene (**7**), *trans*-2-butene (**8**), and isobutylene (**9**)) in good to quantitative conversion by ^{1}H NMR (85−100%). Attempts at isolating adducts **5**−**9** were unsuccessful. The mechanism for this transformation is believed to mimic the $Tp'PtPh_2H$ system, notably without the need of a Lewis acid promoter.[24] Dechelation of the apical triazole ring generates a κ^2 five-coordinate unsaturated intermediate upon warming to room temperature from which benzene elimination occurs. Subsequent trapping of the resulting three-coordinate Pt(II) fragment accounts for **3**−**9** (Scheme 1).

The carbon monoxide complexes **3-L1** and **3-L2** display a 2:1 ratio in the Tt^R triazolyl proton signals in the ^{1}H NMR spectrum, suggesting a κ^3 trigonal-bipyramidal complex, which is consistent with the previously reported $[Tt^RPt(CH_3)(CO)][BF_4]$. A strong CO stretching absorption at high frequency (ν_{CO} 2128 and 2126 cm^{-1}, respectively) was observed, reflecting an electron-deficient metal center and limited back-donation. These high-frequency CO stretches are compatible with other Pt(II) CO cationic complexes.[50,53]

The ethylene adducts **4-L1** and **4-L2** exhibit a 2:1 ratio in each set of the Tt^R ^{1}H NMR signals, indicating C_s symmetry. The four olefinic protons in both of these complexes appear as a singlet with platinum satellites ($^2J_{Pt,H}$ = 81 and 86 Hz, respectively), reflecting rapid rotation about the bisector of the metal−ethylene triangle that averages the up and down olefin signals (H_u and H_d, Figure 2). Variable-temperature proton

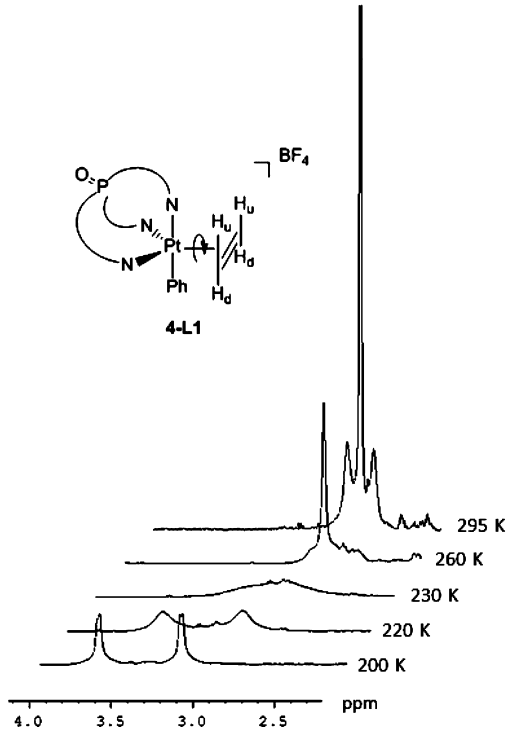


Figure 2. Variable-temperature ^{1}H NMR study of ethylene rotation in **4-L1**.

NMR studies revealed that the ethylene ligand is static at 200 K in **4-L1**, with two separate resonances (3.1 and 3.6 ppm) as a result of inequivalent sites for the bound olefin (Figure 2). The coalescence temperature for this process was found to be 229 K, which translates to a rotation barrier of 10.5 kcal/mol. The Tt^{Cy} analogue, **4-L2**, had a coalescence temperature of 238 K and a rotation barrier of 10.9 kcal/mol. The decreased energy barrier for rotation in these platinum phenyl complexes relative to the previously reported methyl analogues (11.1 kcal/mol (**L1**)

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and 11.5 kcal/mol (**L2**)) continues the expected trend that a more electron deficient metal center results in less back-bonding in the ground state.[50] The spectroscopic data collected for the mono- and disubstituted olefin complexes **5**−**9** were consistent with that of ethylene adduct **4** and the related $[Tt^RPt(Me)(L)]^+$ complexes. The activation barrier for rotation in the *trans*-2-butene adducts **7-L1** and **7-L2** was found to be 13.6 and 13.7 kcal/mol, respectively. This increase of ca. 3 kcal/mol relative to **4** is consistent with the increased steric bulk of the substituted olefin inhibiting rotation, thus suggesting that the transition state for rotation is more hindered than the ground state.

Kinetic studies on the conversion of the diphenyl hydride cation complex **2-L2** to olefin adduct **6-L2** were performed by monitoring the decay of the Pt−H signal with ^{1}H NMR spectroscopy. The reaction displayed first-order kinetics between 245 and 270 K in the presence of 1.2 equiv of 1-hexene. The conversion was also monitored using a large excess of 1-hexene (4 equiv), and the reaction rate remained constant to within experimental error, indicating a zero-order dependence on the olefin substrate. The reaction rate at 270 K was found to be $[1.38(\pm0.05)] \times 10^{-3}$ s^{-1}, giving rise to a $\Delta G^{\ddagger}_{270}$ value of 19.3(±0.1) kcal/mol. An Eyring plot (Figure 3)

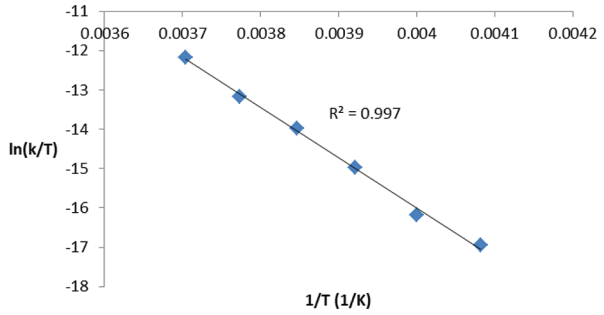
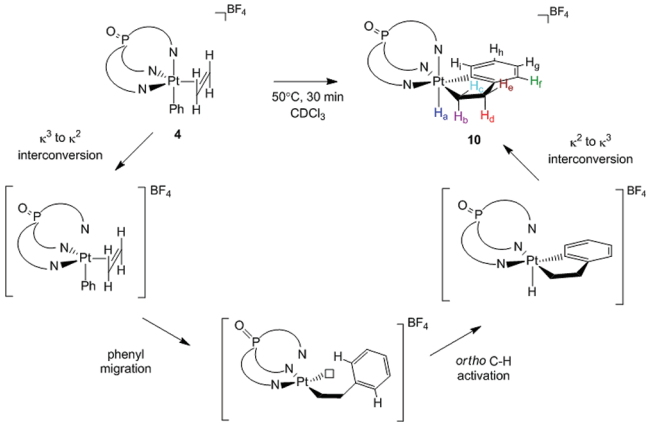


Figure 3. Eyring plot for the conversion of **2-L2** to **6-L2**.

was constructed using rate constants from a temperature range of 245−270 K: $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 25.5(±0.7) kcal/mol and +23(±3) eu, respectively. The large positive value for $\Delta S^{\ddagger}$ suggests that the rate-determining step is the reductive elimination of benzene to form two species.[54] Note that the putative η^2-benzene intermediate was never observed.

Phenyl Migration and Ortho C−H Activation. With the η^2 olefin reagents in hand, we wished to compare the migratory aptitude of the phenyl ligand in these Tt^R complexes to that of their corresponding Tp′ analogues.[24] Allowing the ethylene-bound complex **4-L1** to stand at room temperature overnight resulted in partial conversion to a new C_1-symmetric species that displayed a 1:1:1 ratio in the Tt^R proton signals. Concurrently, growth of a Pt−H signal was observed at ca. −19.0 ppm ($^1J_{Pt,H}$ = 1579 Hz). Heating the starting material at 50 °C for 30 min successfully drove the conversion quantitatively to the new product. The ^{1}H NMR spectrum is consistent with the formation of a Pt(IV) metallacyclic hydride complex, $[Tt^RPt(CH_2CH_2\text{-}o\text{-}C_6H_4)(H)][BF_4]$ (**10**), which is analogous to the insertion product formed in the Tp′Pt system. We propose a mechanism that is initiated by a facile κ^3/κ^2 conversion, resulting in an unsaturated metal species. Phenyl migration to the metal-bound ethylene would then result in a three-coordinate Pt(II) fragment. In the absence of trapping ligand, C−H activation of the ortho proton dominates and accounts for the formation of the five-membered metallacyclic hydride species (Scheme 2). Metallacycle formation under milder conditions from

Scheme 2. Proposed Mechanism for Phenyl Migration and Subsequent Ortho C−H Activation of 4 To Form the Metallacycle Hydride Complex 10



4 compared to those for the electron-rich Tp′ analogue is credited to the weakly donating hemilabile Tt^R ligand for allowing easier access to the κ^2 intermediate.[24]

Kinetic studies on the conversion of ethylene adduct **4-L2** to metallacycle complex **10-L2** were performed by monitoring the disappearance of the ortho proton of the phenyl ligand in the Pt(II) reagent. The reaction was observed between 293 and 328 K and displayed first-order kinetics. The rate at 303 K was found to be $[5.7(\pm0.9)] \times 10^{-5}$ s^{-1}, giving rise to a $\Delta G^{\ddagger}_{303}$ value of 23.7(±0.2) kcal/mol. An Eyring plot (Figure 4) was

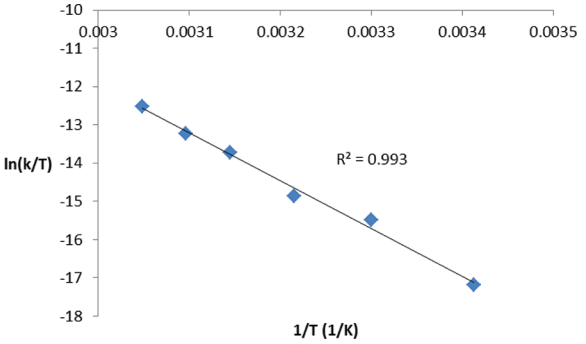


Figure 4. Eyring plot for the conversion of the ethylene adduct **4-L2** to metallacyclic hydride **10-L2**.

constructed using rate constants from this temperature range; $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 24.8 (±1.1) kcal/mol and +3.4(±3) eu, respectively. The near-zero value for $\Delta S^{\ddagger}$ is compatible with an intramolecular rearrangement.

Metallacycle Dynamics and D-Labeling Studies. With the dynamic nature of similar Tt^R dimethyl Pt−H complexes in mind,[50] we wished to examine the dynamics of the cationic metallacycle complexes. The NOESY NMR spectrum of metallacycle **10-L1** is shown in Figure 5. A cross peak that is out of phase with the diagonal signals is observed that correlates the hydride, H_a, and two of the alkyl bridge protons, H_b and H_d. This cross peak is due to a through-space NOE interaction. An intense cross peak that is in phase with the diagonal is observed between H_a and the ortho proton H_f of the aryl ring, and this cross peak

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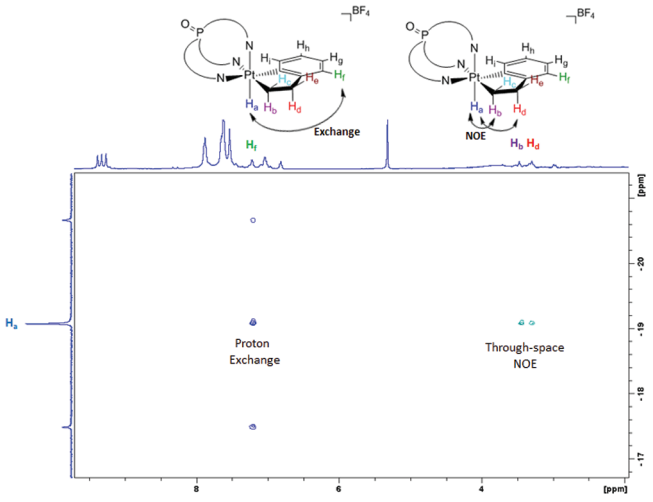


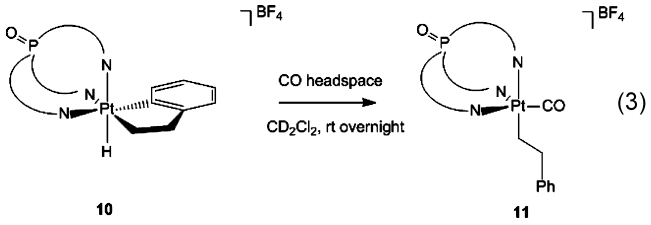
Figure 5. NOESY NMR spectrum of complex **10-L1**.

results from site exchange between these two proton positions on the NMR time scale.[55]

To confirm this exchange process, excess D_2O was added to a solution of **10-L1** and the ^1H NMR was recorded. Deuterium was rapidly incorporated into the acidic Pt−H position, as is the case for other Tt^R platinum hydride species.[50] In the aromatic region (Figure 6a), the signal for H_f significantly diminished while the signal for the adjacent proton, H_g, collapsed from a triplet to a doublet, confirming D incorporation into the adjacent H_f position. In the alkyl region near 3 ppm (Figure 6b), D incorporation was also observed for the α-carbon protons, H_b and H_c. As a result, the ^1H NMR spectrum converts from a complex pattern in the alkyl region with four inequivalent protons each with unique coupling to the other protons and also with platinum coupling to a simple spectrum of two signals.

The proposed mechanism for proton exchange in **10** is shown in Scheme 3. In analogy to elimination mechanisms from previously described dialkyl and diaryl Tt^R complexes, an initiating low-barrier κ^3/κ^2 conversion produces an unsaturated five-coordinate intermediate. In **10**, aryl elimination or alkyl elimination can occur and, in either case, free rotation of the resulting phenyl or alkyl group scrambles the ortho aryl or methyl protons, respectively. Subsequent C−H reactivation and κ^2/κ^3 conversion regenerates **10** and accounts for exchange between H_a and H_b or between H_a and H_f. The absence of an exchange cross peak between the hydride and either H_b or H_c in the NOESY NMR spectrum of **10** indicates that the C_{sp^3}−H reductive elimination is slower than C_{sp^2}−H elimination and does not occur on the NMR time scale. The relative energy barriers of these two processes are consistent with rate comparisons for methane elimination vs benzene elimination from the dimethyl and diphenyl hydride reagents, respectively.

To probe the proposed mechanism in Scheme 3, we sought to trap the putative unsaturated intermediates $[\kappa^2\text{-}Tt^RPtR]^+$. Carbon monoxide was added to the headspace of an NMR sample of **10** at room temperature and continuously mixed overnight. The ^1H NMR displayed clean conversion to a single product, $[Tt^RPt(CH_2CH_2Ph)(CO)][BF_4]$ (**11**), which is the product expected from aryl elimination (eq 3). The IR spectrum of **11** shows a single strong CO stretch (ν_{CO} 2117 cm^{-1} (**11-L1**) and 2114 cm^{-1} (**11-L2**)) at a frequency that is consistent with the related cationic complex $[Tt^RPt(CH_3)(CO)][BF_4]$. This

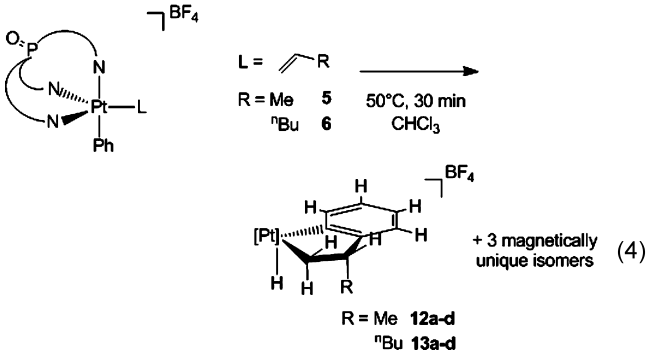


(3)

product is compatible with aryl elimination being considerably faster than alkyl elimination.

Activation parameters for the exchange process between the Pt−H position and the ortho arene position adjacent to the alkyl substituent were obtained by variable-temperature ^1H NMR studies of **10**. Upon heating to temperatures in excess of 338 K, line broadening of the hydride signal occurs and a rate constant was estimated using the slow-exchange approximation. At 345 K the rate constant was found to be 12.6 s^{-1}, giving rise to a $\Delta G^{\ddagger}_{345}$ value of 18.6 kcal/mol for this reductive coupling C−H activation process. An Eyring plot was constructed using the rate constants collected between 338 and 358 K; $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are estimated to be 23.1 kcal/mol and +12.8 eu, respectively.

Phenyl Migration in Substituted Adducts. Heating the various substituted alkene adducts **5**−**9** at 50 °C for 30 min induced phenyl migration and subsequent C−H activation to afford the corresponding metallacycle products (eqs 4−7).



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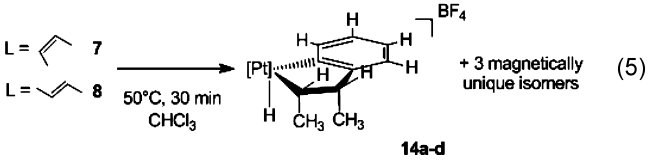

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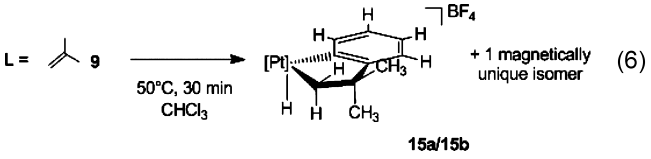

(6)

Phenyl migration of the propylene adduct **5** resulted in four unique Pt−H signals (Figure 7), reflecting the four possible insertion isomers **12a**−**d**. The methyl group on the alkyl bridge of each isomer resonates as a doublet in the 1.0−1.5 ppm region of the ^1H NMR spectrum and was confirmed to couple with the bridge methine proton by $^1H,^1H$-COSY NMR. The aryl ligand can migrate to either the α or β carbon to give rise to two structural isomers in which the methyl is located on either carbon of the alkyl bridge. A stereocenter is produced, resulting in up and down options for the methyl substituent.

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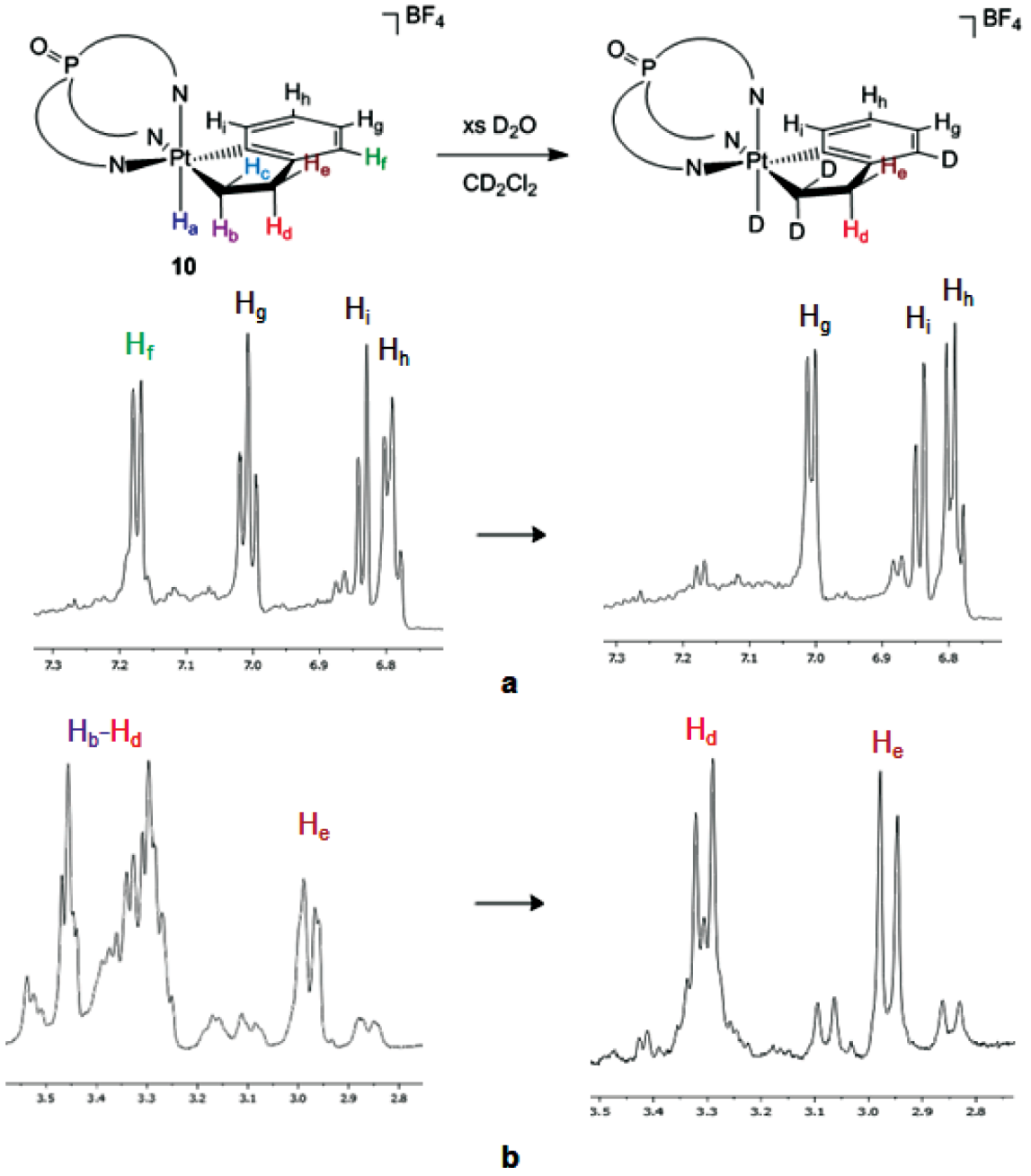
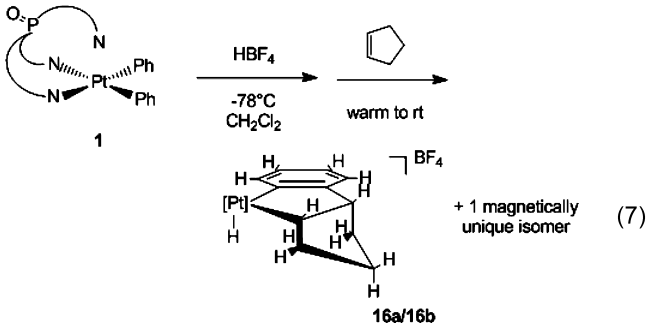


Figure 6. Aryl (a) and alkyl (b) regions of the ^{1}H NMR spectrum of **10-L1** before and after excess D_2O addition.



(7)

The metal center is also chiral, thereby generating a total of eight isomers, half of which are enantiomeric pairs that are not differentiated by routine NMR. The Pt−H signal intensity ratios display a 4:6:2:1 distribution of metallacycle products from the propylene adduct **5-L1**. To our surprise, the insertion reaction of the 1-hexene adduct **6** to afford metallacycles **13a−d** did not significantly change this isomeric distribution of products.

Metallacycle formation resulting from the *cis*-2-butene and *trans*-2-butene adducts **7** and **8** also resulted in four prominent Pt−H signals, and these isomer distributions were identical in chemical shift, platinum coupling, and ratio (2:5:4:1) to one another, indicating that both starting materials converge to the same set of isomeric products. This outcome is consistent with the fluxional nature of the parent compound **10**, in which the aryl and alkyl fragments undergo facile C−H reductive elimination and oxidative addition. Reductive elimination of the hydride and alkyl bridge followed by free rotation and reactivation erases the cis or trans relationship of the two methyl substituents in the bridge, allowing each adduct to form

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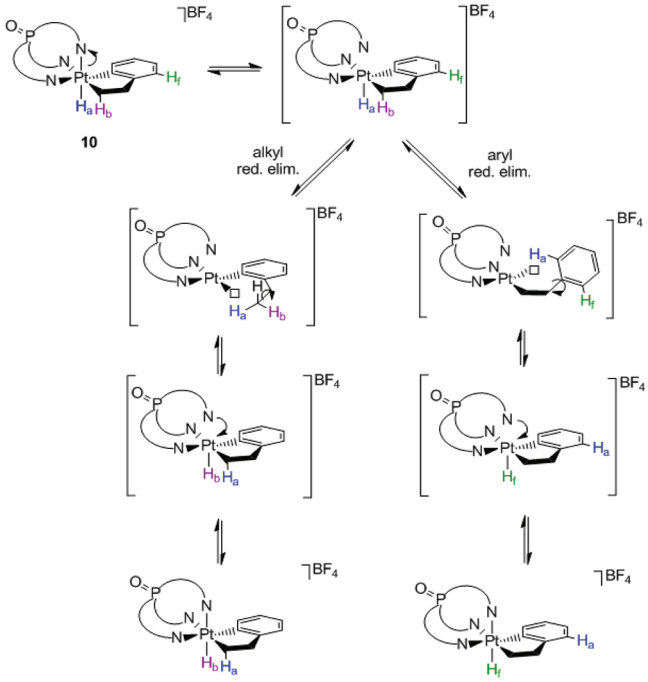
Scheme 3. Proposed Mechanism for Proton Exchange in Complex 10



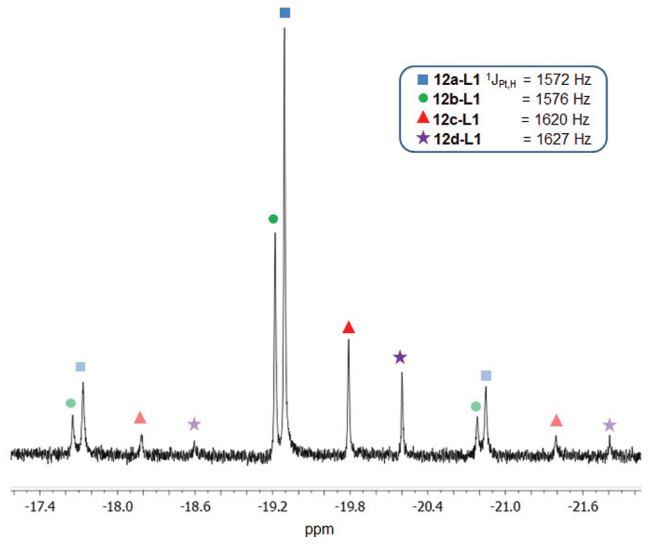


Figure 7. Pt−H region of the ^{1}H NMR spectrum of **12a−d**.

four isomers. It is conceivable that after alkyl elimination another mechanistic possibility would be C−H activation of the terminal methyl of the now three-carbon parent alkyl chain, resulting in a six-membered ring with a stereocenter at the γ carbon. Indeed, two additional Pt−H signals of minute intensity at −19.0 and −19.2 ppm with identical platinum coupling ($^1J_{Pt-H}$ = 1544 Hz) are observed in the ^{1}H NMR spectrum, which may reflect this rearrangement to form a six-membered metallacycle product.

In order to elucidate the identity of each metallacycle isomer from the corresponding Pt−H signals, we examined a simpler system—the insertion product formed from the isobutylene adduct **9**. As expected, only two Pt−H signals resulted from phenyl migration (50 °C, 30 min), reflecting geminal methyls on either the α or β carbons, **15b** and **15a**, respectively. The ^{1}H,^{13}C-HMQC NMR (Figure 8) spectrum reveals that, in the major isomer, a cross peak exists that correlates protons H_b and H_c with the α carbon, consistent with **15a**.

Migration of phenyl to the sterically hindered β carbon of isobutylene gave rise to the major isomer, a result we found counterintuitive. Monitoring the insertion by ^{1}H NMR while heating **9** at 35 °C demonstrated the appearance of both isomers in a 3:1 ratio (**15a**:**15b**). After several hours, only one Pt−H signal (that of **15a**) and a single Tt^R species remained, suggesting that **15b** undergoes rearrangement to **15a** (Figure 9). We believe that **15b**, generated from phenyl migration to the less sterically hindered α carbon, is the kinetic product of insertion. The resulting metallacycle contains geminal methyl substituents proximal to the metal center and bulky Tt^R ligand. The lower steric energy penalty associated with moving the methyl groups further away from the metal center provides a driving force to the thermodynamically favored isomer **15a**. Conversion from **15b** to **15a** presumably proceeds through the original isobutylene adduct **9** as an intermediate and implies reversible C−C bond formation. This rearrangement is consistent with similar reactivity observed in metallacycle formation from Tp′Pt(Ph)(CH_2═$CHCH_3$).[24]

The isobutylene adduct reveals the thermodynamic preference for forming isomers in which substituents are located on the β carbon, but these isomers did not assist in differentiating preferences for the up or down options at a stereocenter, such as in **12−14**. We therefore sought an adduct that would retain its cis or trans geometry regardless of rapid and reversible alkyl reductive elimination and oxidative addition. Cyclopentene served as an attractive olefin that met this criteria. When the protonation and warming sequence was performed with cyclopentene as the trapping alkene, the expected η^2-bound adduct was not produced; rather, rapid phenyl migration occurred upon alkene binding, resulting in metallacycle formation (eq 7, **16a**/**16b**). Recalling that the similar *cis*-2-butene complexes formed an isolable olefin adduct which required mild heating to induce metallacycle formation, the rapid insertion of cyclopentene demonstrates that alkene strain has a profound influence on the rate of migration of the phenyl ligand. In the ^{1}H NMR spectrum, two Pt−H signals in a 3:1 ratio were observed, reflecting the up and down orientations accessible to the original cyclopentyl ring. The NOESY NMR of this mixture (Figure 10) indicated that, in the major isomer **16a**, there is an NOE through-space interaction between the hydride H_a and four protons of the cyclopentyl ring. Likewise, in the minor isomer **16b**, a through-space interaction is present between H_a and H_b, revealing a preference for olefin substituents in the "down" position relative to the apical Tt^R nitrogen and extending in the same direction as the hydride from the plane of the metallacycle.

With these results in mind, we reexamined the more complicated propylene insertion scenario. Heating the propylene adduct **5** at 50 °C overnight and monitoring the ^{1}H NMR produced isomer ratio shifts with time reminiscent of isobutylene complex **9**. The two initial minor Pt−H signals decrease in intensity, leaving only the two major products **12a**,**b** after several hours. Ultimately, the two major isomers decompose upon prolonged heating. We believe this system displays isomer preferences similar to those described for the conversion of **9** to **15a**. The two minor isomers, **12c**,**d**, contain a methyl group on the α carbon and, upon heating, rearrange to the less sterically hindered pair of diastereomers **12a**,**b**. Given the preference for substituents to extend in the same direction

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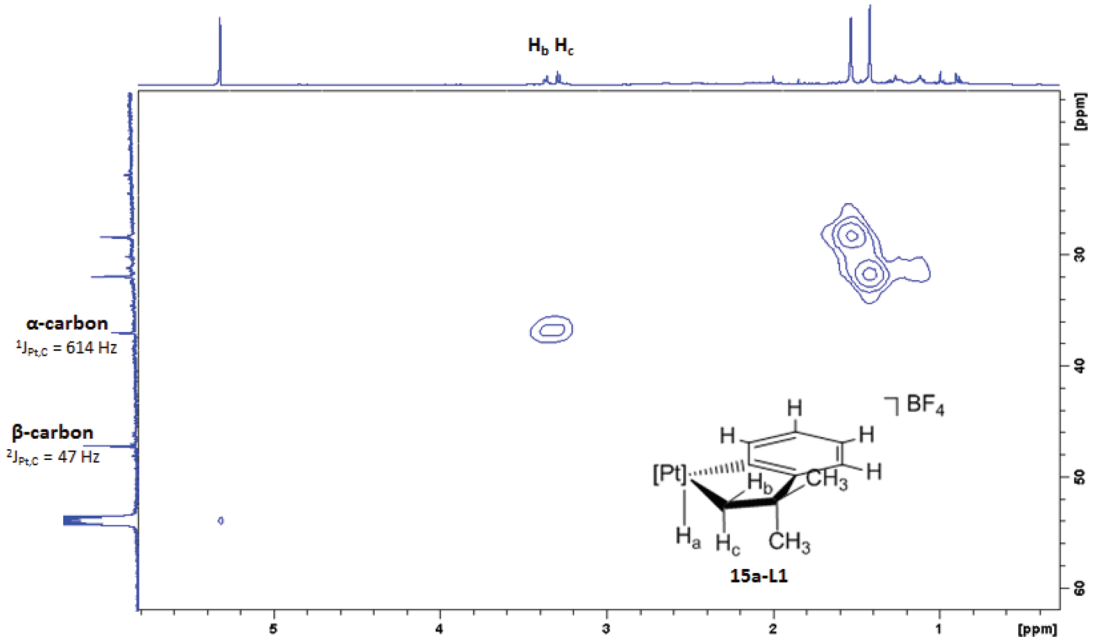

Figure 8. $^{1}H,^{13}C$-HMQC NMR spectrum of **15a-L1**. The cross peak correlating H_b and H_c with the α carbon confirms the identity of the major isomer having geminal methyl groups on the β carbon.

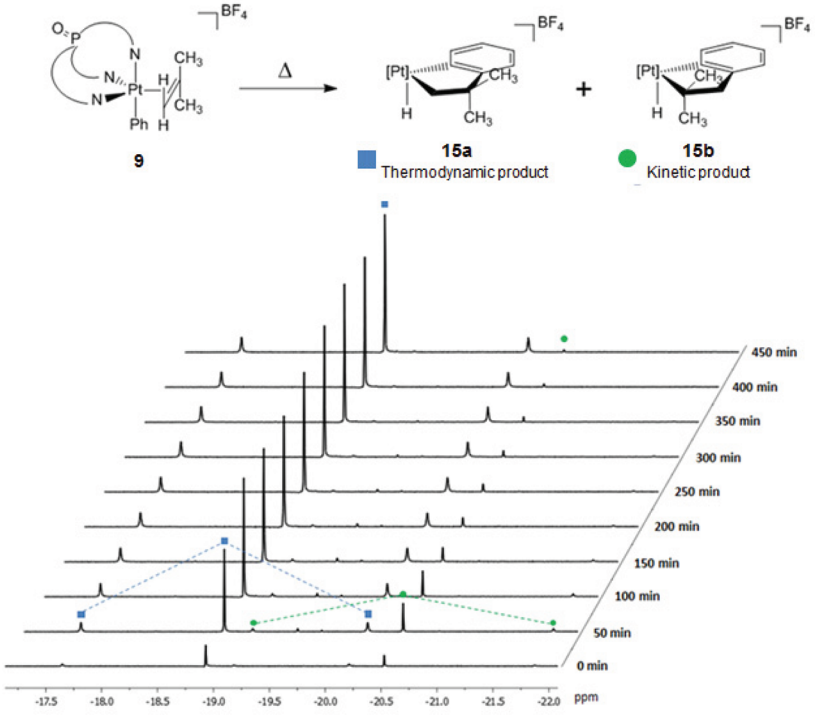

Figure 9. Pt−H region of the ^{1}H NMR spectrum of **15a**/**15b** during thermolysis at 35 °C. The initial ratio of **15a**: **to 15b** is 3:1. After several hours, **15a** is the dominant product.

as the hydride from the metallacyclic plane, we postulate that the more populated diastereomer **12a** has the methyl pointed "down" relative to the apical nitrogen (Figure 11).

Reaction Sequence Energy Barriers. The thermodynamic parameters obtained and the intermediates isolated for the reaction sequence reveal that the pathway from diphenyl hydride **2** to metallacycle products **10**−**16** traverses two significant energy barriers. After a κ^3/κ^2 conversion, the first barrier is reductive coupling and arene loss from the putative η^2-benzene adduct, which is trapped with an olefin to form a π-bound alkene complex. The second energy barrier, which is phenyl migration, varies depending on the identity of the olefin. For ethylene and simple mono- and disubstituted olefins this barrier is *greater* than that of the initial reductive coupling and allows the isolation of the η^2-alkene adduct. However, for cyclic alkenes, we postulate that the added strain provides a less hindered route for the phenyl ligand to migrate, resulting in a barrier that is *less* than the reductive coupling step.

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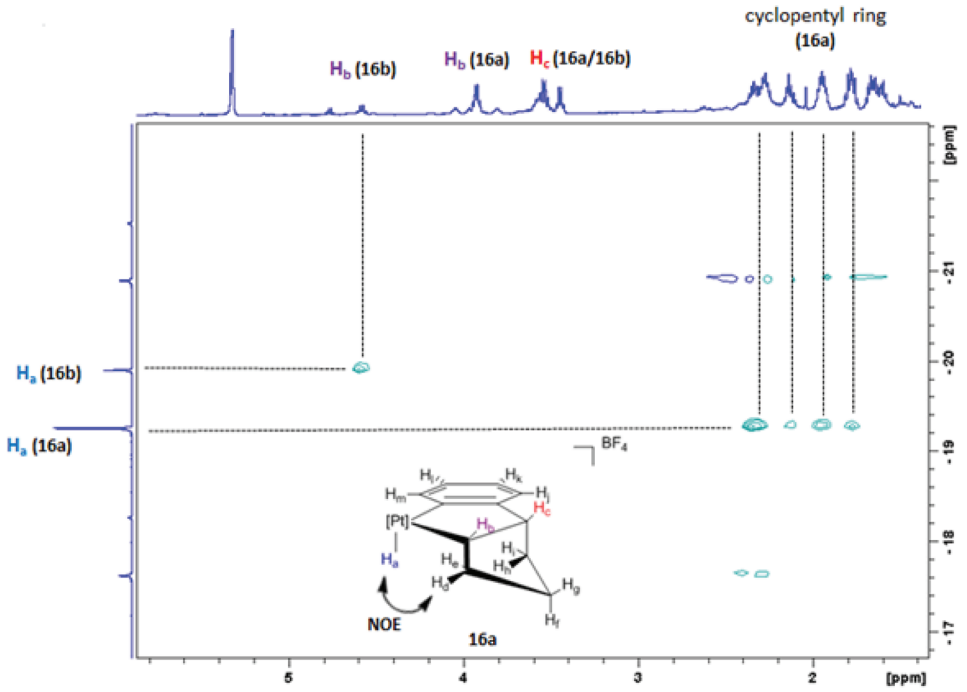


Figure 10. NOESY NMR spectrum of **16a**/**16b**.

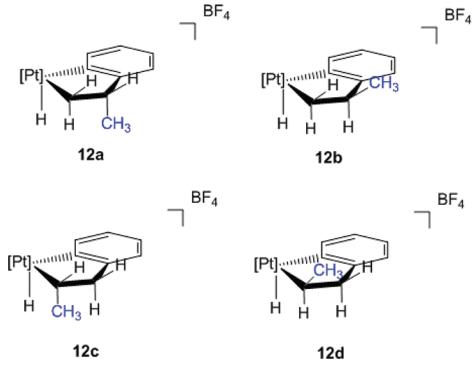
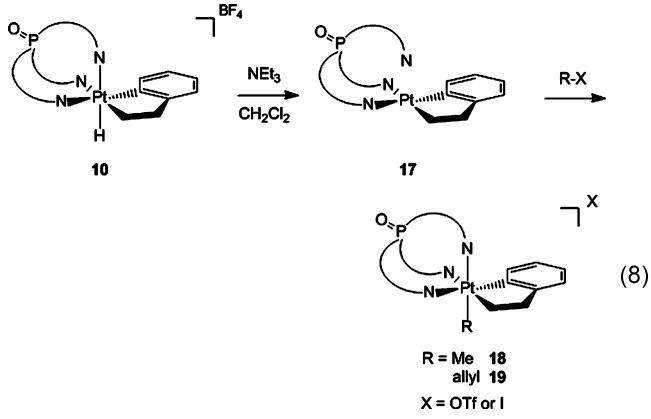


Figure 11. The four metallacycle products from propylene insertion in **5**.

After elimination of benzene from **2** and displacement by cyclopentene, the η^2-alkene adduct is not observed and the cascade continues to the final metallacyclic product.

Formation of Alkyl Metallacycle Complexes. In our studies of the dimethyl and diphenyl hydride reagents $[Tt^RPtMe_2H]^+$ and $[Tt^RPtPh_2H]^+$ **2**, we found the hydride to be acidic: addition of base regenerated the respective κ^2 Pt(II) precursors.[50] In view of the acidity of these Pt(IV) hydride complexes, triethylamine was added to a methylene chloride solution of **10-L2** in hopes of obtaining the neutral product, κ^2-$Tt^{Cy}Pt(CH_2CH_2\text{-}o\text{-}C_6H_4)$ (**17-L2**). Indeed, the addition of base generated the neutral metallacycle **17-L2** in 90% yield, as monitored by ^{1}H NMR. The Tt^R triazolyl proton signals exhibited a 1:1:1 ratio with a characteristically large chemical shift difference (ca. 0.6 ppm) between the two bound arms and the one free arm, clearly indicating κ^2 coordination of the Tt^{Cy} ligand.

Similar to the case for other κ^2-Tt^RPtR_2 compounds, the metal center in this Pt(II) metallacycle was susceptible to oxidation to form cationic Pt(IV) complexes by the addition of electrophilic alkyl or allyl reagents. Treating a methylene chloride solution of metallacycle **17** with methyl triflate at room temperature generated **18**, the methyl analogue of the hydride **10** (eq 8). Metallacycle **18** exhibits a resonance in the ^{1}H NMR spectrum at 1.5 ppm with two-bond platinum coupling of 74 Hz, which is compatible with other reported Pt(IV) methyl complexes.[26,56−58] Allowing **18** to stand at room temperature overnight did not result in the appearance of a platinum



(8)

hydride NMR signal. Note that C−C reductive elimination of the methyl group and C−H activation of the aryl would be expected to produce a Pt−H product. Similar to the synthesis of **18**, addition of allyl iodide to **17** produced the Pt allyl metallacycle **19**. The allyl complex **19** also did not result in C−C elimination and rearrangement, even upon gentle heating at 35 °C, in contrast to previously reported C−C coupling and formation of biphenyl from $[Tt^RPtPh_2(\sigma\text{-allyl})]^+$.[50] These results indicate that both **18** and **19** are static complexes at moderate temperatures and do not undergo facile reductive C−C bond formation, presumably due to a significantly higher barrier for C−C coupling than for the comparable C−H formation and cleavage reactions evident in the hydride analogues **10**−**16**.

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Summary. Pt(II) phenyl olefin complexes **4**−**9** have been prepared via benzene loss from $[Tt^{R}PtPh_2H][BF_4]$ and subsequent trapping with added olefin. Mild heating of the olefin adducts promotes migratory insertion of the olefin into the phenyl−platinum bond, and this is followed by ortho C−H activation and metallacycle formation. The mechanism for this transformation is believed to be initiated by a facile κ^3/κ^2 interconversion, leading to a reactive unsaturated Pt(II) fragment. The reversible coordination of the apical triazolyl nitrogen results in a dynamic metallacycle complex from which aryl and aliphatic elimination and reactivation readily occur. Thermolysis of the isobutylene insertion products reveals conversion of the kinetically favored α-substituted metallacycle to the thermodynamically favored β-substituted isomer, and this isomerization proceeds via a reversible C−C bond-forming step.

EXPERIMENTAL SECTION

Materials and Methods. All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk and drybox techniques. Nitrogen was purified by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. Methylene chloride, hexanes, and pentane were purified under an argon atmosphere and passed through a column packed with activated alumina. All other chemicals were used as received without further purification.

^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on Bruker DRX400, AVANCE400, and AMX300 spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts were referenced to residual ^{1}H and ^{13}C signals of the deuterated solvents. Elemental analyses were performed by Robertson Microlit Laboratories of Madison, NJ. High-resolution mass spectra were recorded on a Bruker BioTOF II ESI-TOF mass spectrometer. Mass spectral data are reported for the most abundant platinum isotope. Tris(1-phenyl-1*H*-1,2,3-triazol-4-yl)phosphine oxide (Tt^{Ph}),[49] tris(1-cyclohexyl-1*H*-1,2,3-triazol-4-yl)phosphine oxide (Tt^{Cy}),[50] and $[Pt(C_6H_5)_2(SEt_2)]_2$[59] were synthesized using published procedures.

For simplicity in presenting NMR data, the carbon atoms of the cyclohexyl group of the Tt^{Cy} ligand are designated by the labeling scheme in Figure 12. Likewise, in metallacycle complexes, the carbon atoms are designated by the labeling scheme in Figure 13.

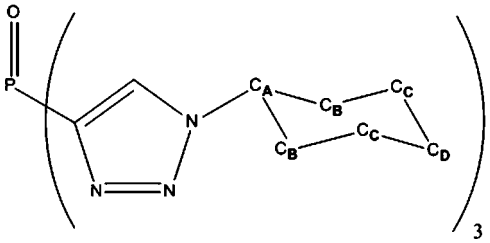

Figure 12. Carbon labels in the cyclohexyl group of the Tt^{Cy} ligand.

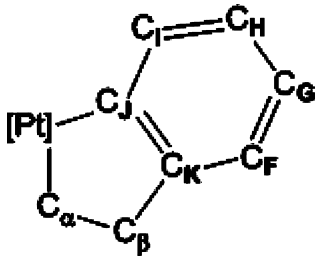

Figure 13. Carbon labels in the metallacycle complexes.

Synthesis of κ^2 $Tt^{R}PtPh_2$ Complexes. *(κ^2-Tt^{Ph})Pt(Ph)$_2$ (**1-L1**).* $[Pt(Ph)_2(SEt_2)]_2$ (0.061 g, 0.070 mmol) and Tt^{Ph} (0.033 g, 0.070 mmol) were placed in a Schlenk flask under nitrogen. CH_2Cl_2 (10 mL) was added through the septum, and the reaction mixture was stirred for 30 min at room temperature. After evaporation of the solvent, the resulting oil was purified by flash chromatography on alumina. The column was flushed with ethyl acetate and then by methanol. The methanol eluent was collected, and the solvent was removed by rotary evaporation to produce (κ^2-Tt^{Ph})Pt(Ph)$_2$ (0.033 g, 0.039 mmol) as a white solid in 56% yield. ^{1}H NMR (CD_2Cl_2, 300 K, δ): 9.27, 8.87 (s, 1H, 2H, $Tt^{Ph}CH$), 7.80−7.51 (m, 15H, $Tt^{Ph}C_6H_5$), 7.07 (d, 4H, $^3J_{Pt-H}$ = 52 Hz, Pt−Ar H_o), 6.70−6.77 (m, 6H, Pt−Ar H_m and H_p). ^{31}P{^{1}H} NMR (CD_2Cl_2, 294 K, δ): −8.7 (s, 1P, $Tt^{Ph}P$=O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K, δ): 141.0 (s, 2C, Pt−Ar *ipso*-Ph), 140.5 (d, 1C, O=PC, $^1J_{P-C}$ = 170 Hz), 139.0 (d, 2C, O=PC, $^1J_{P-C}$ = 149 Hz), 138.8 (s, 4C, Pt−Ar *m*-Ph), 136.5, 136.2 (s, 1C, 2C, Tt^{Ph} *ipso*-Ph), 130.9 (s, 2C, Tt^{Ph} *p*-Ph), 130.6 (s, 4C, Tt^{Ph} *o*-Ph), 130.5 (d, 1C, $^1J_{P-C}$ = 33 Hz, O=PC), 130.3 (s, 2C, Tt^{Ph} *o*-Ph), 130.1 (s, 1C, Tt^{Ph} *p*-Ph), 130.1 (d, 2C, $^2J_{P-C}$ = 25 Hz, O=PCCH), 126.3 (s, 4C, Pt−Ar *o*-Ph), 122.2 (s, 2C, Pt−Ar *p*-Ph), 121.4 (s, 2C, 4C, Tt^{Ph} *m*-Ph). Anal. Calcd for $C_{36}H_{28}N_9OPPt$: C, 52.18; H, 3.41; N, 15.21. Found: C, 52.35; H, 3.24; N, 15.07.

*(κ^2-Tt^{Cy})Pt(Ph)$_2$ (**1-L2**).* $[Pt(Ph)_2(SEt_2)]_2$ (0.061 g, 0.070 mmol) and Tt^{Cy} (0.035 g, 0.070 mmol) were placed in a Schlenk flask under nitrogen. CH_2Cl_2 (10 mL) was added through the septum, and the reaction mixture was stirred for 30 min at room temperature. After removal of the solvent, the resulting oil was purified by flash chromatography on alumina. The column was first flushed with ethyl acetate and then by methanol. The methanol eluent was collected, and the solvent was removed by rotary evaporation to produce (κ^2-Tt^{Cy})Pt(Ph)$_2$ (0.043 g, 0.051 mmol) as a white solid in 74% yield (by Tt^{Cy} ligand) . ^{1}H NMR (CD_2Cl_2, 291 K, δ): 8.96, 8.36 (s, 1H, 2H, $Tt^{Cy}CH$), 7.04 (d, 4H, $^3J_{Pt-H}$ = 63 Hz, $^3J_{H-H}$ = 7 Hz, H_o), 6.72−6.80 (m, 6H, H_m and H_p), 4.50 (m, 3H, NC*H*Cy), 1.21−2.22 (m, 30H, cyclohexyl). ^{31}P{^{1}H} NMR (CD_2Cl_2, 293 K, δ): −7.09 (s, 1P, $Tt^{Cy}P$=O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 292 K, δ): 141.7 (s, 2C, *ipso*-Ph), 139.1 (s, 4C, *m*-Ph), 139.1 (d, 1C, O=PC, $^1J_{P-C}$ = 169 Hz), 138.1 (d, 2C, O=PC, $^1J_{P-C}$ = 149 Hz), 129.7 (d, 1C, O=PCCH, $^2J_{P-C}$ = 33 Hz), 129.1 (d, 2C, O=PCCH, $^2J_{P-C}$ = 24 Hz), 126.1 (s, 4C, *o*-Ph), 121.9 (s, 2C, *p*-Ph), 62.4, 61.2 (s, 2C, 1C, C_A), 33.8−33.1 (s, 1:1:1, 6C, C_B), 25.4−25.1 (s, 1:1:1 and 2:1, 9C, C_C and C_D). HRMS (ESI): *m*/*z* calcd 979.2265 (M + Cs^+), found 979.2296. Anal. Calcd for $C_{36}H_{28}N_9OPPt\cdot{}^1/_2CH_2Cl_2$: C, 49.30; H, 5.29; N, 14.18. Found: C, 48.54; H, 5.24; N, 14.22.

Synthesis of $[(\kappa^3\text{-}Tt^{R})Pt(Ph)_2H][X]$ Complexes. *[(κ^3-Tt^{Ph})Pt(Ph)$_2$H][BF$_4$] (**2-L1**).* $Tt^{Ph}PtPh_2$ (**1-L1**; 0.030 g, 0.035 mmol) was weighed into an NMR tube in a drybox. CD_2Cl_2 (0.6 mL) was added through the septum, and the solution was cooled to −78 °C outside of the drybox. The methylene chloride solution was treated with 1 equiv of $HBF_4\cdot Et_2O$ (4.5 μL, 0.035 mmol) and placed inside the cold probe of the NMR spectrometer. The ^{1}H NMR spectrum showed quantitative conversion to **2-L1**. ^{1}H NMR (CD_2Cl_2, 195 K, δ): 9.41, 9.30 (s, 1H, 2H, $Tt^{Ph}CH$), 7.79−6.96 (m, 25H, $Tt^{Ph}C_6H_5$ and Pt−C_6H_5), −19.18 (s, 1H, $^1J_{Pt-H}$ = 1581 Hz, Pt−H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 195 K, δ): −6.5 (s, 1P, $Tt^{Ph}P$=O). ^{13}C {^{1}H} NMR (CD_2Cl_2, 195 K, δ): 137.2 (s, 3C, Tt^{Ph} *ipso*-Ph), 134.9 (d, 2C, O=PC, $^1J_{P-C}$ = 155 Hz), 134.5 (s, Pt−Ar *m*-Ph), 134.4 (d, 1C, O=PC, $^1J_{P-C}$ = 155 Hz), 130.7 (s, 3C, Tt^{Pt} *p*-Ph), 130.5 (d, 3C, O=PCCH, $^2J_{P-C}$ = 30 Hz), 129.8 (s, 6C, Tt^{Ph} *o*-Ph), 128.2 (s, 2C, Pt−Ar *ipso*-Ph), 127.3 (s, 4C, $^2J_{Pt-C}$ = 62 Hz, Pt−Ar *o*-Ph), 124.9 (s, 2C, Pt−Ar *p*-Ph), 120.9 (s, 6C, Tt^{Ph} *m*-Ph).

*[(κ^3-Tt^{Cy})Pt(Ph)$_2$H][BF$_4$] (**2-L2**).* The same procedure was performed using the analgous $Tt^{Cy}Pt(Ph)_2$ (**1-L2**) starting material. Quantitative conversion to **2-L2** was observed. ^{1}H NMR (CD_2Cl_2, 200 K, δ): 8.81, 8.75 (s, 1H, 2H, $Tt^{Cy}CH$), 7.16 (s, 4H, $^3J_{Pt-H}$ = 53 Hz, Pt−Ar H_o), 6.99, 6.90 (m, 6H, Pt−Ar H_m and H_p), 4.67, 4.58 (m, 1H, 2H, C_A-*H*), 2.10−1.09 (m, 30H, cyclohexyl), −19.40 (s, 1H, $^1J_{Pt-H}$ = 1554 Hz, Pt−*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 200 K, δ): −5.7 (s, 1P, $Tt^{Cy}P$=O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 200 K, δ): 137.3 (s, 4C, Pt−Ar *m*-Ph), 134.3, 133.7 (d, 2C, 1C, O=PC, $^1J_{P-C}$ = 150 Hz), 129.2 (d, 3C, O=PCCH, $^2J_{P-C}$ = 23 Hz), 127.9 (s, 2C, Pt−Ar *ipso*-Ph), 127.2 (s, 4C, $^2J_{Pt-C}$ = 60 Hz, Pt−Ar *o*-Ph), 124.6 (s, 2C, Pt−Ar *p*-Ph), 62.5, 62.4 (s, 1C, 2C, C_A), 32.7−32.2 (s, 6C, C_B), 24.4−23.9 (s, 9C, C_C and C_D).

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Elimination and Trapping Reactions. In a typical experiment, **1** (0.035 mmol) was placed in a Schlenk flask under nitrogen. Methylene chloride (10 mL) was added through the septum, and the solution was cooled to −78 °C in a dry ice/isopropyl alcohol bath. The solution was treated with 1 equiv of $HBF_4{\cdot}Et_2O$ (0.035 mmol). The mixture was warmed to room temperature while being sparged with the appropriate trapping gas. The solvent was removed by rotary evaporation and the resulting oil triturated with pentane to afford the desired trapped product **3**−**9** as a white powder in high yield by ^{1}H NMR.

*[(κ^3-Tt^{Ph})Pt(CO)(Ph)][BF$_4$] (**3-L1**).* ^{1}H NMR exhibited quantitative conversion to **3-L1**. ^{1}H NMR (CD_2H_2, 291 K, δ): 9.45, 9.34 (s, 1H, 2H, Tt^{Ph}C*H*), 7.90−715 (m, 25H, Tt^{Ph}C$_6$*H*$_5$ and Pt−C$_6$*H*$_5$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 291 K, δ): −5.7 (s, 1P, Tt^{Ph}*P*═O). ^{13}C {^{1}H} NMR (CD_2Cl_2, 284 K, δ): 159.1 (s, 1C, Pt−*C*O), 138.2 (d, 3C, O═P*C*, $^1J_{P-C}$ = 160 Hz), 137.1 (s, 2C, Pt−Ar *m*-Ph), 135.8, 135.6 (s, 2C, 1C, Tt^{Ph} *ipso*-Ph), 132.3 131.9 (d, 1C, 2C, O═PC*C*H, $^2J_{P-C}$ = 23 Hz), 131.6, 130.9 (s, 1C, 2C, Tt^{Pt} *p*-Ph), 130.6, 130.4 (s, 2C, 4C, Tt^{Ph} *o*-Ph), 128.9 (s, 2C, Pt−Ar *o*-Ph), 126.8 (s, 1C, Pt−Ar *p*-Ph), 122.9 (s, 1C, Pt−Ar *ipso*-Ph), 121.9, 121.4 (s, 2C, 4C Tt^{Ph} *m*-Ph). IR (CH_2Cl_2 solution) ν_{CO} = 2128 cm^{-1}. HRMS (ESI): *m*/*z* calcd 779.1360 (M$^+$), found 779.1376. Anal. Calcd for $C_{32}H_{27}BF_4N_9OPPt$: C, 42.97; H, 2.68; N, 14.55. Found: C, 43.45; H, 2.91; N, 14.15.

*[(κ^3-Tt^{Cy})Pt(CO)(Ph)][BF$_4$] (**3-L2**).* ^{1}H NMR exhibited quantitative conversion to **3-L2**. ^{1}H NMR (CD_2Cl_2, 292 K, δ): 8.82, 8.72 (s, 1H, 2H, Tt^{Cy}C*H*), 7.31−7.11 (m, 5H, Pt−C$_6$*H*$_5$), 4.55, 4.52 (m, 1H, 2H, C$_A$-*H*), 2.31−1.30 (m, 30H, cyclohexyl). ^{31}P{^{1}H} NMR (CD_2Cl_2, 292 K, δ): −6.8 (s, 1P, Tt^{Cy}*P*═O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 292 K, δ): 159.5 (s, 1C, Pt−*C*O), 137.2 (d, 3C, O═P*C*, $^1J_{P-C}$ = 155 Hz), 137.2 (s, 2C, Pt−Ar *m*-Ph), 131.4 (d, 3C, O═PC*C*H, $^2J_{P-C}$ = 28 Hz), 128.7 (s, 2C, Pt−Ar *o*-Ph), 126.6 (s, 1C, Pt−Ar *p*-Ph), 123.4 (s, 1C, Pt−Ar *ipso*-Ph), 63.9, 62.8 (s, 1C, 2C, C$_A$), 33.2, 33.1 (s, 6C, C$_B$), 25.2−25.0 (s, 9C, C$_C$ and C$_D$). IR (CH_2Cl_2 solution): ν_{CO} 2126 cm^{-1}. HRMS (ESI): *m*/*z* calcd 797.2769 (M$^+$), found 797.2777. Anal. Calcd for $C_{31}H_{41}N_9O_2PPt{\cdot}{}^1/_2CH_2Cl_2$: C, 40.84; H, 4.54; N, 13.61. Found: C, 41.25; H, 4.36; N, 13.29.

*[(κ^3-Tt^{Ph})Pt(η^2-C$_2$H$_4$)(Ph)][BF$_4$] (**4-L1**).* ^{1}H NMR exhibited quantitative conversion to **4-L1**. ^{1}H NMR (CD_2Cl_2, 260 K, δ): 9.28, 9.27 (s, 1H, 2H, Tt^{Ph}C*H*), 8.03−7.49 (m, 15H, Tt^{Ph}C$_6$*H*$_5$), 7.10−7.01 (m, 5H, Pt−C$_6$*H*$_5$), 3.50 (s, 4H, $^2J_{Pt-H}$ = 81 Hz, Pt−C$_2$*H*$_4$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 260 K, δ): −7.6 (s, 1P, Tt^{Ph}*P*═O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 260 K, δ): 136.9 (d, 2C, O═P*C*, $^1J_{P-C}$ = 152 Hz), 136.7 (s, 2C, Pt−Ar *m*-Ph), 136.5 (d, 1C, O═P*C*, $^1J_{P-C}$ = 150 Hz), 135.6, 135.5 (s, 2C, 1C, Tt^{Ph} *ipso*-Ph), 131.2, 130.8 (s, 1C, 2C, Tt^{Pt} *p*-Ph), 130.4 (s, 6C, Tt^{Ph} *o*-Ph), 127.8 (s, 2C, Pt−Ar *o*-Ph), 124.9 (s, 1C, Pt−Ar *p*-Ph), 122.2 (s, 1C, Pt−Ar *ipso*-Ph), 121.8, 121.5 (s, 2C, 4C, Tt^{Ph} *m*-Ph), 41.8 (s, 2C, $^1J_{Pt-C}$ = 316 Hz, Pt−*C*$_2$H$_4$). HRMS (ESI): *m*/*z* calcd 779.1724 (M$^+$), found 779.1693. Anal. Calcd for $C_{32}H_{27}BF_4N_9OPPt$: C, 44.36; H, 3.14; N, 14.55. Found: C, 44.62; H, 2.96; N, 14.30.

*[(κ^3-Tt^{Cy})Pt(η^2-C$_2$H$_4$)(Ph)][BF$_4$] (**4-L2**).* ^{1}H NMR exhibited quantitative conversion to **4-L2**. ^{1}H NMR (CD_2Cl_2, 270 K, δ): 8.70 (s, 3H, Tt^{Cy}C*H*), 7.89 (d, 2H, Pt−Ar H_o), 7.04−6.97 (m, 3H, Pt−Ar H_m and H_p), 4.63 (m, 3H, C$_A$-*H*), 3.25 (s, 4H, $^2J_{Pt-H}$ = 86 Hz, Pt−C$_2$*H*$_4$), 2.20−1.31 (m, 30H, cyclohexyl). ^{31}P{^{1}H} NMR (CD_2Cl_2, 270 K, δ): −8.2 (s, 1P, Tt^{Cy}*P*═O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 270 K, δ): 137.1 (s, 2C, Pt−Ar *m*-Ph), 135.6 (d, 2C, O═P*C*, $^1J_{P-C}$ = 151 Hz), 135.3 (d, 1C, O═P*C*, $^1J_{P-C}$ = 150 Hz), 130.2 (d, 1C, O═PC*C*H, $^2J_{P-C}$ = 24 Hz), 129.8 (d, 1C, O═PC*C*H, $^2J_{P-C}$ = 24 Hz), 127.6 (s, 2C, Pt−Ar *o*-Ph), 124.6 (s, 1C, Pt−Ar *p*-Ph), 122.1 (s, 1C, Pt−Ar *ipso*-Ph), 63.1, 62.7 (s, 1C, 2C, C$_A$), 38.0 (s, 2C, $^1J_{Pt-C}$ = 363 Hz, Pt−*C*$_2$H$_4$), 33.2−32.9 (s, 6C, C$_B$), 25.0−24.7 (s, 9C, C$_C$ and C$_D$). HRMS (ESI): *m*/*z* calcd 797.3133 (M$^+$), found 797.3108.

*[(κ^3-Tt^{Ph})Pt(η^2-propylene)(Ph)][BF$_4$] (**5-L1**).* ^{1}H NMR exhibited 85% conversion to **5-L1**. ^{1}H NMR (CD_2Cl_2, 298 K, δ): 9.33, 9.31, 9.25 (s, 1H, 1H, 1H, Tt^{Ph}C*H*), 7.86−7.44 (m, 15H, Tt^{Ph}C$_6$*H*$_5$), 7.32−6.96 (m, 5H, Pt−C$_6$*H*$_5$), 5.26 (m, 1H, H$_2$C═C*H*CH$_3$), 4.71 (d, 1H, $^3J_{H-H}$ = 8 Hz, Pt−$H_{cis\ to\ H}$HC═CHCH$_3$), 4.67 (d, 1H, $^3J_{H-H}$ = 14 Hz, $H_{trans\ to\ H}$HC═CHCH$_3$), 1.39 (d, 3H, $^3J_{H-H}$ = 6 Hz, H$_2$C═CHC*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 255 K, δ): −4.6 (s, 1P, Tt^{Ph}*P*═O). ^{13}C {^{1}H} NMR (CD_2Cl_2, 255 K, δ): 137.8 (d, 1C, O═P*C*, $^1J_{P-C}$ = 162 Hz), 137.1 (d, 1C, O═P*C*, $^1J_{P-C}$ = 156 Hz), 136.5 (d, 1C, O═P*C*, $^1J_{P-C}$ = 151 Hz), 135.5, 135.4, 135.3 (s, 1C, 1C, 1C, Tt^{Ph} *ipso*-Ph), 134.9 (s, 2C, Pt−Ar *m*-Ph), 132.1 (d, 2C, O═PC*C*H, $^2J_{P-C}$ = 24 Hz), 131.7 (d, 1C, O═PC*C*H, $^2J_{P-C}$ = 24 Hz), 131.0 (s, 2C, Pt−Ar *o*-Ph), 130.7, 130.3, 130.2 (s, 1C, 1C, 1C, Tt^{Ph} *p*-Ph), 130.2 (s, 6C, Tt^{Ph} *o*-Ph), 127.9 (s, 1C, Pt−Ar *p*-Ph), 124.7 (s, 1C, Pt−Ar *ipso*-Ph), 121.5, 121.0, 120.9 (s, 2C, 2C, 2C, Tt^{Ph} *m*-Ph), 93.8 (s, 1C, H$_2$C═CHCH$_3$), 70.7 (s, 1C, H$_2$C═CHCH$_3$), 20.6 (s, 1C, H$_2$C═CHCH$_3$). HRMS (ESI): *m*/*z* calcd 793.1881 (M$^+$), found 793.1816.

*[(κ^3-Tt^{Cy})Pt(η^2-propylene)(Ph)][BF$_4$] (**5-L2**).* ^{1}H NMR exhibited 86% conversion to **5-L2**. ^{1}H NMR (CD_2Cl_2, 298 K, δ): 8.72, 8.67 (s, 2H, 1H, Tt^{Cy}C*H*), 7.20 (d, 2H, Pt−Ar H_o), 6.98−6.90 (m, 3H, Pt−Ar H_m and H_p), 5.01 (m, 1H, H$_2$C═C*H*CH$_3$), 4.63, 4.55 (m, 1H, 2H, C$_A$-*H*), 4.47 (d, 1H, $H_{cis\ to\ H}$HC═CHCH$_3$), 4.45 (d, 1H, $H_{trans\ to\ H}$HC═CHCH$_3$), 2.27−1.26 (m, 30H, cyclohexyl). ^{31}P{^{1}H} NMR (CD_2Cl_2, 255 K, δ): −6.1 (s, 1P, Tt^{Cy}*P*═O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 270 K, δ): 137.1 (d, 1C, O═P*C*, $^1J_{P-C}$ = 159 Hz), 137.0 (d, 1C, O═P*C*, $^1J_{P-C}$ = 159 Hz), 136.4 (d, 1C, O═P*C*, $^1J_{P-C}$ = 152 Hz), 135.5 (s, 2C, Pt−Ar *m*-Ph), 131.0 (d, 1C, O═PC*C*H, $^2J_{P-C}$ = 24 Hz), 130.5 (d, 1C, O═PC*C*H, $^2J_{P-C}$ = 26 Hz), 130.2 (d, 1C, O═PC*C*H, $^2J_{P-C}$ = 27 Hz), 127.0 (s, 2C, Pt−Ar *o*-Ph), 124.4 (s, 1C, Pt−Ar *p*-Ph), 121.6 (s, 1C, Pt−Ar *ipso*-Ph), 62.9, 62.3, 62.0 (s, 1C, 1C, 1C, C$_A$), 60.7 (s, 1C, H$_2$C═CHCH$_3$), 33.5−32.5 (s, 6C, C$_B$), 25.6−24.7 (s, 9C, C$_C$ and C$_D$), 14.1 (s, 1C, H$_2$C═CHCH$_3$). HRMS (ESI): *m*/*z* calcd 811.3289 (M$^+$), found 811.3308.

*[(κ^3-Tt^{Ph})Pt(η^2-1-hexene)(Ph)][BF$_4$] (**6-L1**).* ^{1}H NMR exhibited 96% conversion to **6-L1**. ^{1}H NMR (CD_2Cl_2, 275 K, δ): 9.39, 9.35, 9.30 (s, 1H, 1H, 1H, Tt^{Ph}C*H*), 7.88−7.51 (m, 15H, Tt^{Ph}C$_6$*H*$_5$), 7.35−6.96 (m, 5H, Pt−C$_6$*H*$_5$), 4.98 (m, 1H, H$_2$C═C*H*(Bu)), 4.60, 4.50 (s, 2H, *H*$_2$C═CH(Bu)), 1.73−0.64 (m, 9H, H$_2$C═CH(*Bu*)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 255 K, δ): −4.9 (s, 1P, Tt^{Ph}*P*═O). ^{13}C {^{1}H} NMR (CD_2Cl_2, 275 K, δ): 138.0 (d, 1C, $^1J_{P-C}$ = 161 Hz, O═P*C*), 137.7 (d, 2C, $^1J_{P-C}$ = 160 Hz, O═P*C*), 135.7 (s, 3C, Tt^{Ph} *ipso*-Ph), 135.2 (s, 2C, Pt−Ar *m*-Ph), 132.3 (d, 2C, $^2J_{P-C}$ = 28 Hz, O═PC*C*H,), 131.3 (d, 2C, O═PC*C*H), 130.8, 130.7, 130.4 (s, 1C, 1C, 1C, Tt^{Ph} *p*-Ph), 130.3 (s, 6C, Tt^{Ph} *o*-Ph), 127.2 (s, 2C, Pt−Ar *o*-Ph), 124.9 (s, 1C, Pt−Ar *p*-Ph), 121.7 (s, 1C, Pt−Ar *ipso*-Ph), 121.7, 121.2 (s, 2C, 4C, Tt^{Ph} *m*-Ph), 96.8 (s, 1C, H$_2$C═CH(Bu)), 68.7 (s, 1C, H$_2$C═CH(Bu)), 34.5 (s, 1C, H$_2$C═CH(CH$_2$CH$_2$CH$_2$CH$_3$)), 31.7 (s, 1C, H$_2$C═CH-(CH$_2$CH$_2$CH$_2$CH$_3$)), 22.3 (s, 1C, H$_2$C═CH(CH$_2$CH$_2$CH$_2$CH$_3$)), 13.9 (s, 1C, H$_2$C═CH(CH$_2$CH$_2$CH$_2$CH$_3$)). HRMS (ESI): *m*/*z* calcd 835.2350 (M$^+$), found 835.2335.

*[(κ^3-Tt^{Cy})Pt(η^2-1-hexene)(Ph)][BF$_4$] (**6-L2**).* ^{1}H NMR exhibited 94% conversion to **6-L2**. ^{1}H NMR (CD_2Cl_2, 298 K, δ): 8.66, 8.65, 8.61 (s, 1H, 1H, 1H, Tt^{Cy}C*H*), 7.33 (d, 2H, Pt−Ar H_o), 7.00−6.93 (m, 3H, Pt−Ar H_m and H_p), 4.77 (m, 1H, H$_2$C═C*H*(Bu)), 4.62, 4.56 (m, 1H, 2H, C$_A$−*H*), 4.29 (d, 1H, $^3J_{H-H}$ = 18 Hz, $H_{trans\ to\ H}$C═CH(Bu)), 4.26 (d, 1H, $^3J_{H-H}$ = 9 Hz, $H_{cis\ to\ H}$C═CH(Bu)), 2.23−0.77 (m, cyclohexyl and H$_2$C═CH(*Bu*)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 275 K, δ): −7.3 (s, 1P, Tt^{Cy}*P*═O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 275 K, δ): 137.2 (d, 1C, O═P*C*, $^1J_{P-C}$ = 154 Hz), 136.7 (d, 2C, O═P*C*, $^1J_{P-C}$ = 146 Hz), 135.6 (s, 2C, Pt−Ar *m*-Ph), 130.8 (d, 1C, O═PC*C*H, $^2J_{P-C}$ = 24 Hz), 130.5 (d, 1C, O═PC*C*H, $^2J_{P-C}$ = 27 Hz), 130.2 (d, 1C, O═PC*C*H, $^2J_{P-C}$ = 26 Hz), 127.7 (s, 2C, Pt−Ar *o*-Ph), 124.6 (s, 1C, Pt−Ar *p*-Ph), 121.8 (s, 1C, Pt−Ar *ipso*-Ph), 87.2 (s, 1C, H$_2$C═C*H*(Bu)), 77.6 (s, 1C, H$_2$C═CH(Bu)), 63.9, 62.5, 62.4 (s, 1C, 1C, 1C, C$_A$), 33.2−33.1 (s, 7C, C$_B$ and H$_2$C═CH(CH$_2$CH$_2$CH$_2$CH$_3$)), 31.8 (s, 1C, H$_2$C═CH-(CH$_2$CH$_2$CH$_2$CH$_3$)), 25.0−24.9 (s, 9C, C$_C$ and C$_D$), 22.4 (s, 1C, H$_2$C═CH(CH$_2$CH$_2$CH$_2$CH$_3$)), 13.9 (s, 1C, H$_2$C═CH-(CH$_2$CH$_2$CH$_2$CH$_3$)). HRMS (ESI): *m*/*z* calcd 853.3758 (M$^+$), found 853.3746.

*[(κ^3-Tt^{Ph})Pt(η^2-cis-2-butylene)(Ph)][BF$_4$] (**7-L1**).* ^{1}H NMR exhibited 85% conversion to **7-L1**. ^{1}H NMR (CD_2Cl_2, 275 K, δ): 9.36, 9.32 (s, 1H, 2H, Tt^{Cy}C*H*),), 7.86−7.49 (m, 15H, Tt^{Ph}C$_6$*H*$_5$), 7.09−6.90 (m, 5H, Pt−Ar), 5.50 (s, 2H, CH$_3$C*H*═C*H*CH$_3$), 1.49 (s, 6H, C*H*$_3$CH═CHC*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 295 K, δ): −8.9 (s, 1P, Tt^{Cy}*P*═O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 275 K, δ): 140.6 (d, 1C, O═P*C*, $^1J_{P-C}$ = 159 Hz), 138.8 (d, 2C, O═P*C*, $^1J_{P-C}$ = 159 Hz), 136.3 (s, 1C, Tt^{Ph} *ipso*-Ph), 135.7 (s, 2C, Pt−Ar *m*-Ph), 134.9 (s, 2C, Tt^{Ph} *ipso*-Ph), 131.3 (d, 1C, O═PC*C*H, $^2J_{P-C}$ = 28 Hz), 130.5 (d, 2C, O═PC*C*H, $^2J_{P-C}$ = 23 Hz),

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130.4−129.76 (4C, 2C, 2C, 1C, Tt^{Ph} *o*-Ph and *p*-Ph), 127.3 (s, 2C, Pt−Ar *o*-Ph), 124.4 (s, 1C, Pt−Ar *p*-Ph), 121.1, 121.0 (s, 2C, 4C, Tt^{Ph} *m*-Ph), 90.9 (s, 2C, $CH_3CH{=}CHCH_3$), 15.6 (s, 2C, $CH_3CH{=}CHCH_3$). HRMS (ESI): *m*/*z* calcd 807.2037 (M^+), found 807.2019.

*[(κ^3-Tt^{Cy})Pt(η^2-cis-2-butylene)(Ph)][BF_4] (**7-L2**).* ^{1}H NMR exhibited 95% conversion to **7-L2**. ^{1}H NMR (CD_2Cl_2, 275 K, δ): 8.62 (s, 3H, $Tt^{Cy}CH$), 7.07−6.87 (m, 5H, Pt−Ar), 5.32 (s, 2H $(CH_3)CH{=}CH(CH_3)$), 4.62, 4.53 (m, 1H, 2H, C_A−*H*), 2.23−1.22 (m, 30H, cyclohexyl), 1.41 (d, $(CH_3)CH{=}CH(CH_3)$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 275 K, δ): −8.7 (s, 1P, $Tt^{Cy}P{=}O$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 275 K, δ): 137.5 (d, 3C, O=PC, $^1J_{P-C}$ = 156 Hz), 135.0 (s, 2C, Pt−Ar *m*-Ph), 131.3, 130.6 (d, 1C, 2C O=PCCH, $^2J_{P-C}$ = 24 Hz, 28 Hz), 127.1 (s, 2C, Pt−Ar *o*-Ph), 124.7 (s, 1C, Pt−Ar *ipso*-Ph), 124.2 (s, 1C, Pt−Ar *p*-Ph), 88.8 (s, 2C, $(CH_3)CH{=}CH(CH_3)$), 63.1, 62.3 (s, 1C, 2C, C_A), 33.6−33.0 (s, 6C, C_B), 25.3−24.9 (s, 9C, C_C and C_D), 15.5 (s, 2C, $(CH_3)HC{=}CH(CH_3)$). HRMS (ESI): *m*/*z* calcd 825.3446 (M^+), found 825.3477.

*[(κ^3-Tt^{Ph})Pt(η^2-trans-2-butene)(Ph)][BF_4] (**8-L1**).* ^{1}H NMR exhibited 91% conversion to **8-L1**. ^{1}H NMR (CD_2Cl_2, 300 K, δ): 9.37, 9.34, 9.17 (s, 1H, 1H, 1H, $Tt^{Ph}CH$), 7.86−7.35 (m, 15H, $Tt^{Ph}C_6H_5$), 7.28 (d, 2C, Pt−Ar H_o), 7.00−6.94 (m, 3H, Pt−Ar H_m and H_p), 5.68, 4.79 (s, 1H, 1H, $(CH_3)HC{=}CH(CH_3)$). 1.63, 1.33 (s, 3H, 3H, $(CH_3)CH{=}CH(CH_3)$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 260 K, δ): −8.5 (s, 1P, $Tt^{Ph}P{=}O$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 260 K, δ): 139.1 (d, 1C, O=PC, $^1J_{P-C}$ = 163 Hz), 137.5 (d, 1C, O=PC, $^1J_{P-C}$ = 148 Hz), 137.2 (d, 1C, O=PC, $^1J_{P-C}$ = 151 Hz), 135.7, 135.6, 135.3 (s, 1C, 1C, 1C, Tt^{Ph} *ipso*-Ph), 135.3 (s, 2C, Pt−Ar *m*-Ph), 132.5 (d, 1C, O=PCCH, $^2J_{P-C}$ = 24 Hz), 131.6 (d, 1C, O=PCCH, $^2J_{P-C}$ = 25 Hz), 131.0 (d, 1C, O=PCCH, $^2J_{P-C}$ = 25 Hz), 131.0, 130.8, 130.0 (s, 1C, 1C, 1C, Tt^{Ph} *p*-Ph), 130.2 (s, 6C, Tt^{Ph} *o*-Ph), 128.4 (s, 1C, Pt−Ar *ipso*-Ph), 126.4 (s, 2C, Pt−Ar *o*-Ph), 124.5 (s, 1C, Pt−Ar *p*-Ph), 121.7, 120.9 (s, 2C, 4C, Tt^{Ph} *m*-Ph), 96.0, 93.2 (s, 1C, 1C, $(CH_3)HC{=}CH(CH_3)$), 20.7, 19.5 (s, 1C, 1C, $(CH_3)HC{=}CH(CH_3)$). HRMS (ESI): *m*/*z* calcd 807.2037 (M^+), found 807.2071.

*[(κ^3-Tt^{Cy})Pt(η^2-trans-2-butene)(Ph)][BF_4] (**8-L2**).* ^{1}H NMR exhibited 90% conversion to **8-L2**. ^{1}H NMR (CD_2Cl_2, 260 K, δ): 8.73, 8.71, 8.56 (s, 1H, 1H, 1H, $Tt^{Cy}CH$), 7.24 (d, 2H, Pt−Ar H_o), 6.96−6.88 (m, 3H, Pt−Ar H_m and H_p), 5.55, 4.75 (s, 1H, 1H, $(CH_3)CH{=}CH(CH_3)$), 4.62, 4.49 (m, 2H, 1H, C_A−*H*), 2.24−1.23 (m, 36H, cyclohexyl and $(CH_3)CH{=}CH(CH_3)$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 260 K, δ): −6.2 (s, 1P, $Tt^{Cy}P{=}O$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 260 K, δ): 137.8 (d, 1C, O=PC, $^1J_{P-C}$ = 162 Hz), 136.8 (d, 1C, O=PC, $^1J_{P-C}$ = 148 Hz), 136.1 (d, 1C, O=PC, $^1J_{P-C}$ = 153 Hz), 135.5 (s, 2C, Pt−Ar *m*-Ph), 131.6 (d, 1C, O=PCCH, $^2J_{P-C}$ = 20 Hz), 131.4 (d, 1C, O=PCCH, $^2J_{P-C}$ = 24 Hz), 130.4 (d, 1C, O=PCCH, $^2J_{P-C}$ = 30 Hz), 128.4 (s, 1C, Pt−Ar *ipso*-Ph), 127.3 (s, 2C, Pt−Ar *o*-Ph), 124.1 (s, 1C, Pt−Ar *p*-Ph), 94.5, 91.8 (s, 1C, 1C, $(CH_3)CH{=}CH(CH_3)$), 63.1, 62.6, 61.7 (s, 1C, 1C, 1C, C_A), 34.2−32.7 (s, 6C, C_B), 25.0−24.8 (s, 9C, C_C and C_D), 20.6, 19.5 (s, 1C, 1C, $(CH_3)HC{=}CH(CH_3)$). HRMS (ESI): *m*/*z* calcd 825.3446 (M^+), found 825.3420.

*[(κ^3-Tt^{Ph})Pt(η^2-isobutylene)(Ph)][BF_4] (**9-L1**).* ^{1}H NMR exhibited 87% conversion to **9-L1**. ^{1}H NMR (CD_2Cl_2, 260 K, δ): 9.38, 9.34 (s, 1H, 2H, $Tt^{Ph}CH$), 7.87−7.46 (m, 15H, $Tt^{Ph}C_6H_5$), 7.23−6.98 (m, 5H, Pt−C_6H_5), 4.78 (s, 2H, $H_2C{=}C(CH_3)_2$), 1.16 (s, 6H, $H_2C{=}C(CH_3)_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 260 K, δ): −8.4 (s, 1P, $Tt^{Ph}P{=}O$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 260 K, δ): 138.1 (d, 2C, O=PC, $^1J_{P-C}$ = 158 Hz), 137.3 (1, 1C, O=PC, $^1J_{P-C}$ = 149 Hz), 135.6, 135.5 (s, 1C, 2C, Tt^{Ph} *ipso*-Ph), 134.6 (s, 2C, Pt−Ar *m*-Ph), 132.4 (d, 2C, O=PCCH, $^2J_{P-C}$ = 24 Hz), 131.4 (d, 1C, O=PCCH, $^2J_{P-C}$ = 28 Hz), 130.5−130.0 (s, 1C, 1C, 1C, Tt^{Ph} *p*-Ph), 130.2, 130.0 (s, 4C, 2C, Tt^{Ph} *o*-Ph), 127.6 (s, 2C, Pt−Ar *o*-Ph), 124.4 (s, 1C, Pt−Ar *p*-Ph), 121.6, 121.0 (s, 2C, 4C, Tt^{Ph} *m*-Ph), 73.3 (s, 1C, $H_2C{=}C(CH_3)_2$), 29.1 (s, 2C, $H_2C{=}C(CH_3)_2$). HRMS (ESI): *m*/*z* calcd 807.2037 (M^+), found 807.1966.

*[(κ^3-Tt^{Cy})Pt(η^2-isobutylene)(Ph)][BF_4] (**9-L2**).* ^{1}H NMR exhibited 92% conversion to **9-L2**. ^{1}H NMR (CD_2Cl_2, 292 K, δ): 8.72 (s, 3H, $Tt^{Cy}CH$), 7.09 (d, 2H, Pt−Ar H_o), 6.93, 6.92 (m, 3H, Pt−Ar H_m and H_p), 4.70 (s, 2H, $H_2C{=}C(CH_3)_2$), 4.62, 4.51 (m, 1H, 2H, C_A−*H*), 2.25−1.17 (m, 36H, cyclohexyl), 1.10 (s, 6H, $H_2C{=}CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 260 K, δ): −5.2 (s, 1P, $Tt^{Cy}P{=}O$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 260 K, δ): 137.2 (d, 2C, O=PC, $^1J_{P-C}$ = 158 Hz), 136.7 (d, 1C, O=PC, $^1J_{P-C}$ = 147 Hz), 134.6 (s, 2C, Pt−Ar *m*-Ph), 134.2 (s, 1C, Pt−Ar *ipso*-Ph), 131.5 (d, 1C, O=PCCH, $^2J_{P-C}$ = 25 Hz), 130.8 (d, 2C, O=PCCH, $^2J_{P-C}$ = 28 Hz), 127.4 (s, 2C, Pt−Ar *o*-Ph), 124.2 (s, 1C, Pt−Ar *p*-Ph), 73.2 (s, 1C, $^1J_{Pt-C}$ = 190 Hz, $H_2C{=}CH(CH_3)_2$), 63.1, 62.1 (s, 1C, 2C, C_A), 28.9 (s, 2C, $H_2C{=}CH(CH_3)_2$), 33.0, 32.9 (s, 2C, 4C, C_B), 25.2−24.7 (s, 9C, C_C and C_D). HRMS (ESI): *m*/*z* calcd 825.3446 (M^+), found 825.3413.

Phenyl Migration Reactions. In a typical experiment, Tt^RPt(Ph)(L) (**4**−**9**; 0.035 mmol) was weighed into an NMR tube in the glovebox. $CDCl_3$ (0.6 mL) was added through the septum. The sample was heated in a 50 °C oil bath for 30 min. The solution was transferred to a round-bottom flask, and the solvent was removed by rotary evaporation. The resulting oil was triturated with pentane to afford the metallacycle product as a pale yellow power in high yield by ^{1}H NMR.

*[κ^3-Tt^{Ph}Pt(CH_2CH_2-*o*-C_6H_4)(H)][BF_4] (**10-L1**) by Ethylene Insertion.* Quantitative conversion from **4-L1** was observed by ^{1}H NMR. ^{1}H NMR (CD_2Cl_2, 293 K, δ): 9.420, 9.35.,9.29 (s, 1H, 1H, 1H, $Tt^{Ph}CH$), 7.91−7.51 (m, 15H, Tt^{Ph} C_6H_5), 7.21 (d, 1H, H_f), 7.05 (t, 1H, H_g), 7.01 (d, 1H, H_i), 6.81 (t, 1H, H_h), 3.47 (m, 1H, H_a), 3.31, (m, 2H, H_b and H_c), 2.97 (m, 1H, H_d, $^3J_{Pt,H}$ = 117 Hz), −19.0 (s, 1H, Pt−H, $^1J_{Pt,H}$ = 1579 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K, δ): −6.3 (s, 1P, $Tt^{Cy}P{=}O$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K, δ): 156.6 (s, 1C, C_K, $^2J_{Pt,C}$ = 125 Hz), 137.0, 136.0 (d, 2C, 1C, O=PC, $^1J_{P-C}$ = 151, 152 Hz), 135.9, 135.8, 135.8 (s, 1C, 1C, 1C, Tt^{Ph} *ipso*-Ph), 132.0 (s, 1C, C_I), 131.4, 131.3, 131.3 (s, 1C, 1C, 1C, Tt^{Ph} *p*-Ph), 131.1−130.8 (d, 3 O=PCCH), 130.8 (s, 1C, C_J), 130.6, 130.5 (s, 4C, 2C, Tt^{Ph} *o*-Ph), 125.7 (s, 1C, C_G), 125.2 (s, 1C, C_H, $^3J_{Pt,C}$ = 43 Hz), 123.5 (s, 1C, C_F, $^3J_{Pt,C}$ = 47 Hz), 122.0, 121.8, 121.8 (s, 2C, 2C, 2C, Tt^{Ph} *m*-Ph), 42.3 (s, 1C, C_β, $^2J_{Pt,C}$ = 53 Hz), 19.2 (s, 1C, C_α, $^1J_{Pt,C}$ = 599 Hz). HRMS (ESI): *m*/*z* calcd 779.1724 (M^+), found 779.1699. Anal. Calcd for $C_{32}H_{27}BF_4N_9OPPt$: C, 44.36; H, 3.14; N, 14.55. Found: C, 44.61; H, 3.18; N, 14.27.

*[κ^3-Tt^{Cy}Pt(CH_2CH_2-*o*-C_6H_4)(H)][BF_4] (**10-L2**) by Ethylene Insertion.* Quantitative conversion from **4-L2** was observed by ^{1}H NMR. ^{1}H NMR (CD_2Cl_2, 293 K, δ): 8.79, 8.75, 8.69 (s, 1H, 1H, 1H, $Tt^{Cy}CH$), 7.17 (d, 1H, H_f), 7.00 (t, 1H, H_g), 6.83 (d, 1H, H_h), 6.79 (t, 1H, H_i), 4.69, 4.67, 4.57 (m, 1H, 1H, 1H, C_A−*H*), 3.25−2.87 (m, 4H, H_a−H_d), 2.24−1.15 (m, 30H, cyclohexyl), −19.4 (s, 1H, Pt−H, $^1J_{Pt,H}$ = 1559 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K, δ): −3.7 (s, 1P, $Tt^{Cy}P{=}O$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K, δ): 156.7 (s, 1C, C_K, $^2J_{Pt,C}$ = 125 Hz), 135.6, 135.6, 134.9 (d, 1C, 1C, 1C, O=PC, $^1J_{P-C}$ = 152, 151, 153 Hz), 132.0 (s, 1C, C_I), 130.9 (s, 1C, C_J, $^1J_{Pt,C}$ = 900 Hz), 130.6, 130.5, 130.0 (d, 1C, 1C, 1C O=PCCH, $^2J_{P-C}$ = 24, 25, 23 Hz), 125.5 (s, 1C, C_G), 125.0 (s, 1C, C_H, $^3J_{Pt,C}$ = 42 Hz), 123.4 (s, 1C, C_F, $^3J_{Pt,C}$ = 47 Hz), 63.7, 63.6, 63.3 (s, 1C, 1C, 1C, C_A), 42.4 (s, 1C, C_β, $^2J_{Pt,C}$ = 54 Hz), 33.6−33.0 (s, 6C, C_B), 25.2−24.9 (s, 9C, C_C and C_D), 18.3 (s, 1C, C_α, $^1J_{Pt,C}$ = 597 Hz). HRMS (ESI): *m*/*z* calcd 797.3133 (M^+), found 797.3132.

*[κ^3-Tt^{Ph}Pt($CH_2CH(CH_3)$-*o*-C_6H_4)(H)][BF_4] (**12a-L1/12b-L1**) and [κ^3-Tt^{Ph}Pt($CH(CH_3)CH_2$-*o*-C_6H_4)(H)][BF_4] (**12c-L1/12d-L1**) Mixture by Propylene Insertion.* ^{1}H NMR ($CDCl_3$, 298 K, δ): −18.9 (s, 1H, $^1J_{Pt-H}$ = 1576 Hz, Pt−H, **12b**), −19.0 (s, 1H, $^1J_{Pt-H}$ = 1572 Hz, Pt−H, **12a**), −19.6 (s, 1H, $^1J_{Pt-H}$ = 1620 Hz, **12c**), −19.99 (s, 1H, $^1J_{Pt-H}$ = 1627 Hz, **12d**). Ratio: **12b**:**12a**:**12c**:**12d** = 4.1:6.3:1.7:1.

*[κ^3-Tt^{Cy}Pt($CH_2CH(CH_3)$-*o*-C_6H_4)(H)][BF_4] (**12a-L2/12b-L2**) and [κ^3-Tt^{Cy}Pt($CH(CH_3)CH_2$-*o*-C_6H_4)(H)][BF_4] (**12c-L2/12d-L2**) Mixture by Propylene Insertion.* ^{1}H NMR ($CDCl_3$, 298 K, δ): −19.04 (s, 1H, $^1J_{Pt-H}$ = 1545 Hz, Pt−H, **12b**), −19.21 (s, 1H, $^1J_{Pt-H}$ = 1542 Hz, Pt−H, **12a**), −19.70 (s, 1H, $^1J_{Pt-H}$ = 1585 Hz, **12c**), −20.10 (s, 1H, $^1J_{Pt-H}$ = 1590 Hz, **12d**). Ratio: **12b**:**12a**:**12c**:**12d** = 3.1:4.9:1.6:1.

*[κ^3-Tt^{Ph}Pt($CH_2CH(^nBu)$-*o*-C_6H_4)(H)][BF_4] (**13a-L1/13b-L1**) and [κ^3-Tt^{Ph}Pt($CH(^nBu)CH_2$-*o*-C_6H_4)(H)][BF_4] (**13c-L1/13d-L1**) Mixture by 1-Hexene Insertion.* ^{1}H NMR ($CDCl_3$, 298 K, δ): −18.8 (s, 1H, $^1J_{Pt-H}$ = 1576 Hz, Pt−H, **13b**), −19.0 (s, 1H, $^1J_{Pt-H}$ = 1577 Hz,

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Pt−H, **13a**), −19.5 (s, 1H, $^1J_{Pt-H}$ = 1624 Hz, **13c**), −19.9 (s, 1H, $^1J_{Pt-H}$ = 1627 Hz, **13d**). Ratio: **13b**:**13a**:**13c**:**13d** = 6.2:5.9:2.3:1.

*[κ³-Tt^{Cy}Pt(CH$_2$CH(^{n}Bu)-o-C$_6$H$_4$)(H)][BF$_4$] (**13a/13b-L2**) and [κ³-Tt^{Cy}Pt(CH(^{n}Bu)CH$_2$-o-C$_6$H$_4$)(H)][BF$_4$] (**13c/13d-L2**) Mixture by 1-Hexene Insertion.* ^{1}H NMR (CDCl$_3$, 298 K, δ): −19.04 (s, 1H, $^1J_{Pt-H}$ = 1548 Hz, Pt−H, **13b**), −19.23 (s, 1H, $^1J_{Pt-H}$ = 1548 Hz, Pt−H, **13a**), −19.65 (s, 1H, $^1J_{Pt-H}$ = 1594 Hz, **13c**), −20.07 (s, 1H, $^1J_{Pt-H}$ = 1600 Hz, **13d**). Ratio: **13b**:**13a**:**13c**:**13d** = 4.4:4.0:1.6:1.

*[κ³-Tt^{Ph}Pt(CH(CH$_3$)CH(CH$_3$)-o-C$_6$H$_4$)(H)][BF$_4$] (**14a-L1−14d-L1**) Mixture by 2-Butene Insertion.* ^{1}H NMR (CDCl$_3$, 298 K, δ): −19.3 (s, 1H, $^1J_{Pt-H}$ = 1613 Hz, Pt−H, **14c**), −19.3 (s, 1H, $^1J_{Pt-H}$ = 1614 Hz, Pt−H, **14a**), −19.8 (s, 1H, $^1J_{Pt-H}$ = 1633 Hz, **14b**), −20.2 (s, 1H, $^1J_{Pt-H}$ = 1649 Hz, **14d**). Ratio: **14c**:**14a**:**14b**:**14d** = 1.6:4.7:4.4:1.

*[κ³-Tt^{Cy}Pt(CH(CH$_3$)CH(CH$_3$)-o-C$_6$H$_4$)(H)][BF$_4$] (**14a-L1−14d-L2**) Mixture by 2-Butene Insertion.* ^{1}H NMR (CDCl$_3$, 298 K, δ): −19.4 (s, 1H, $^1J_{Pt-H}$ = 1572 Hz, Pt−H, **14c**), −19.5 (s, 1H, $^1J_{Pt-H}$ = 1574 Hz, Pt−H, **14a**), −20.0 (s, 1H, $^1J_{Pt-H}$ = 1586 Hz, **14b**), −20.3 (s, 1H, $^1J_{Pt-H}$ = 1600 Hz, **14d**). Ratio: **14c**:**14a**:**14b**:**14d** = 1.3:5.0:5.3:1.

*[κ³-Tt^{Ph}Pt(CH$_2$C(CH$_3$)$_2$-o-C$_6$H$_4$)(H)][BF$_4$] (**15a-L1**) and [κ³-Tt^{Ph}-Pt(C(CH$_3$)$_2$CH$_2$-o-C$_6$H$_4$)(H)][BF$_4$] (**15b-L1**) Mixture by Isobutylene Insertion.* ^{1}H NMR (CDCl$_3$, 298 K, δ): −18.8 (s, 1H, $^1J_{Pt-H}$ = 1569 Hz, Pt−H, **15a**), −20.7 (s, 1H, $^1J_{Pt-H}$ = 1648 Hz, Pt−H, **15b**). Ratio: **15a**:**15b** = 31:1. Complete spectroscopic characterization of **15a** can be found in the Supporting Information.

*[κ³-Tt^{Cy}Pt(CH$_2$C(CH$_3$)$_2$-o-C$_6$H$_4$)(H)][BF$_4$] (**15a-L2**) and [κ³-Tt^{Cy}-Pt(C(CH$_3$)$_2$CH$_2$-o-C$_6$H$_4$)(H)][BF$_4$] (**15b-L2**) Mixture by Isobutylene Insertion.* ^{1}H NMR (CDCl$_3$, 298 K, δ): −19.1 (s, 1H, $^1J_{Pt-H}$ = 1540 Hz, Pt−H, **15a**), −20.6 (s, 1H, $^1J_{Pt-H}$ = 1620 Hz, Pt−H, **15b**). Ratio: **15a**:**15b** = 4.7:1.

*[κ³-Tt^{Ph}Pt(CHC(CH$_2$)$_3$-o-C$_6$H$_4$)(H)][BF$_4$] (**16a-L1/b-L1**) Mixture by Cyclopentene Insertion.* Tt^{Ph}PtPh$_2$ (**1**; 0.030 g, 0.036 mmol) was placed in a Schlenk flask under nitrogen. Methylene chloride (10 mL) was added through the septum, and the solution was cooled to −78 °C in a dry ice/isopropyl alcohol bath. The solution was treated with HBF$_4$·Et$_2$O (4.5 μL, 0.035 mmol) and cyclopentene (16.4 μL, 0.18 mmol). The mixture was warmed to room temperature. The solvent was removed by rotary evaporation and the resulting oil triturated with pentane to afford a mixture of **16a** and **16b** as a white powder in high yield by ^{1}H NMR. ^{1}H NMR (CDCl$_3$, 298 K, δ): −19.3 (s, 1H, $^1J_{Pt-H}$ = 1626 Hz, Pt−H, **16a**), −19.9 (s, 1H, $^1J_{Pt-H}$ = 1621 Hz, Pt−H, **16b**). Ratio: **16a**:**16b** = 2.8:1. Complete spectroscopic characterization of **16a** can be found in the Supporting Information.

*[κ³-Tt^{Cy}Pt(CHC(CH$_2$)$_3$-o-C$_6$H$_4$)(H)][BF$_4$] (**16a-L2/b-L2**) Mixture by Cyclopentene Insertion.* ^{1}H NMR (CDCl$_3$, 298 K, δ): −19.4 (s, 1H, $^1J_{Pt-H}$ = 1594 Hz, Pt−H, **16a**), −20.0 (s, 1H, $^1J_{Pt-H}$ = 1586 Hz, Pt−H, **16b**). Ratio: **16a**:**16b** = 2.7:1.

CO Trapping Reactions. *[(κ³-Tt^{Ph})Pt(CO)(CH$_2$CH$_2$Ph)][BF$_4$] (**11-L1**).* [Tt^{Ph}Pt(CH$_2$CH$_2$-o-C$_6$H$_4$)(H)][BF$_4$] (**10-L1**; 0.015 g, 0.017 mmol) was weighed in an NMR tube. The tube was purged with CO, and CD$_2$Cl$_2$ (0.6 mL) was added through the septum. The sample was placed in an NMR tube spinner overnight at room temperature. **11-L1** was generated in 95% conversion by ^{1}H NMR. ^{1}H NMR (CD$_2$H$_2$, 295 K, δ): 9.35 (s, 3H, Tt^{Ph}C*H*), 7.85−7.22 (m, 25H, Tt^{Ph}C$_6$*H*$_5$ and Pt−CH$_2$CH$_2$C$_6$*H*$_5$), 2.89, 2.72 (t, 2H, Pt−C*H*$_2$C*H*$_2$Ph). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 291 K, δ): −4.9 (s, 1P, Tt^{Ph}*P*═O). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 284 K, δ): 161.3 (s, 1C, Pt−CO), 144.4 (s, 1C, Pt−CH$_2$CH$_2$Ph *ipso*-Ph), 130.7 (s, 3C, Tt^{Pt} *p*-Ph), 130.7, 130.4 (s, 6C, Tt^{Ph} *o*-Ph), 128.9 (s, 2C, Pt−CH$_2$CH$_2$Ph *o*-Ph), 128.8 (s, 2C, Pt−CH$_2$CH$_2$Ph *m*-Ph), 126.4 (s, 2C, Pt−CH$_2$CH$_2$Ph *p*-Ph), 121.8, 121.6 (s, 2C, 4C Tt^{Ph} *m*-Ph), 38.5 (s, 1C, Pt−CH$_2$CH$_2$Ph), 12.5 (s, 1C, Pt−CH$_2$CH$_2$Ph). IR (CH$_2$Cl$_2$ solution): ν_{CO} 2171 cm^{-1}. HRMS (ESI): *m*/*z* calcd 807.1673 (M$^+$), found 807.1658.

*[(κ³-Tt^{Cy})Pt(CO)(CH$_2$CH$_2$Ph)][BF$_4$] (**11-L2**).* [Tt^{Cy}Pt(CH$_2$CH$_2$-o-C$_6$H$_4$)(H)][BF$_4$] (**10-L2**; 0.015 g, 0.017 mmol) was weighed in an NMR tube. The tube was purged with CO, and CD$_2$Cl$_2$ (0.6 mL) was added through the septum. The sample was placed in an NMR tube spinner overnight at room temperature. **11-L1** was generated in 93% conversion by ^{1}H NMR. ^{1}H NMR (CD$_2$Cl$_2$, 292 K, δ): 8.72 (s, 3H, Tt^{Cy}C*H*), 7.28−7.26 (m, 5H, Pt−CH$_2$CH$_2$C$_6$*H*$_5$), 4.63 (m, 3H, C$_A$−*H*), 2.80, 2.56 (t, 2H, 2H, Pt−C*H*$_2$C*H*$_2$C$_6$H$_5$), 1.93−0.88 (m, 30H, cyclohexyl). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 292 K, δ): −8.7 (s, 1P, Tt^{Cy}*P*═O). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 292 K, δ): 161.2 (s, 1C, Pt−CO), 144.6 (s, 1C, Pt−CH$_2$CH$_2$Ph *ipso*-Ph), 137.6−136.5 (d, 3C, O═P*C*), 131.9−131.1 (d, 3C, O═PC*C*H), 128.9 (s, 1C, Pt−CH$_2$CH$_2$Ph *o*-Ph), 128.8 (s, 1C, Pt−CH$_2$CH$_2$Ph *m*-Ph), 126.3 (s, 1C, Pt−CH$_2$CH$_2$Ph *p*-Ph), 63.6, 63.0 (s, 1C, 2C, C$_A$), 38.5 (s, 1C, Pt−CH$_2$*C*H$_2$Ph), 33.3 (s, 6C, C$_B$), 25.2−25.0 (s, 9C, C$_C$ and C$_D$), 11.5 (s, 1C, Pt−*C*H$_2$CH$_2$Ph). IR (CH$_2$Cl$_2$ solution): ν_{CO} 2114 cm^{-1}. HRMS (ESI): *m*/*z* calcd 825.3082 (M$^+$), found 825.3055.

Deprotonation and Alkylation Reactions. *κ²-Tt^{Cy}Pt(CH$_2$CH$_2$-o-C$_6$H$_4$) (**17-L2**).* [Tt^{Cy}Pt(CH$_2$CH$_2$-o-C$_6$H$_4$)(H)][BF$_4$] (**10-L2**; 0.030 g, 0.034 mmol) was placed in a Schlenk flask under nitrogen. Methylene chloride (10 mL) was added through the septum. The solution was treated with triethylamine (14 μ, 0.102 mmol) and stirred for 20 min. The solvent was removed by rotary evaporation and the resulting oil triturated with pentane to afford **17-L1** in 90% conversion from **10-L2** by ^{1}H NMR. ^{1}H NMR (CD$_2$Cl$_2$, 293 K, δ): 8.97, 8.37, 8.33 (s, 1H, 1H, 1H, Tt^{Cy}C*H*), 7.12−6.71 (m, 4H, Pt−C$_6$*H*$_4$), 4.63, 4.53, 4.25 (m, 1H, 1H, 1H, C$_A$−*H*), 2.58−1.29 (m, 4H, 30H, Pt−C*H*$_2$C*H*$_2$, cyclohexyl). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 293 K, δ): −7.1 (s, 1P, Tt^{Cy}*P*═O). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 293 K, δ): 162.8 (s, 1C, C$_K$), 138.6, 137.5, 137.6 (d, 1C, 1C, 1C, O═P*C*, $^1J_{P-C}$ = 151 Hz, 151 Hz, 170 Hz), 134.5 (s, 1C, C$_I$), 131.2, 129.3, 128.9 (d, 1C, 1C, 1C, O═PCC*H*, $^2J_{P-C}$ = 33, 25, 26 Hz), 129.0 (s, 1C, C$_J$), 122.8 (s, 1C, C$_G$), 122.7 (s, 1C, C$_H$), 121.4 (s, 1C, C$_F$), 62.6, 62.4, 60.6 (s, 1C, 1C, 1C, C$_A$), 41.7 (s, 1C, C$_β$), 33.8−32.3 (s, 6C, C$_B$), 25.3−24.9 (s, 9C, C$_C$ and C$_D$), 8.1 (s, 1C, C$_α$, $^1J_{Pt,C}$ = 834 Hz). HRMS (ESI): *m*/*z* calcd 797.3133 (M + H$^+$), found 797.3168.

*[κ³-Tt^{Cy}Pt(CH$_2$CH$_2$-o-C$_6$H$_4$)(CH$_3$)][OTf] (**18-L2**).* **17-L2** (0.010 g, 0.013 mmol) was placed in a Schlenk flask under nitrogen. Methylene chloride (10 mL) was added through the septum. The solution was treated with 1.2 equiv of methyl triflate and stirred for 20 min. The solvent was removed by rotary evaporation and the resulting oil triturated with pentane to afford the alkylated product as a pale yellow powder. ^{1}H NMR showed quantitative conversion from **17-L2**. ^{1}H NMR (CD$_2$Cl$_2$, 293 K, δ): 8.68, 8.65, 8.57 (s, 1H, 1H, 1H, Tt^{Cy}C*H*), 7.15−6.78 (m, 4H, Pt−C$_6$*H*$_4$), 4.73, 4.66, 4.52 (m, 1H, 1H, 1H, C$_A$−*H*), 2.58−1.29 (m, Pt−C*H*$_2$C*H*$_2$, cyclohexyl), 1.47 (s, Pt−C*H*$_3$, $^2J_{Pt,H}$ = 74 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 293 K, δ): −7.9 (s, 1P, Tt^{Cy}*P*═O). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 293 K, δ): 155.9 (s, 1C, C$_K$, $^2J_{Pt,C}$ = 118 Hz), 135.9, 135.6, 135.3 (d, 1C, 1C, 1C, O═P*C*, $^1J_{P-C}$ = 151 Hz each), 131.2 (s, 1C, C$_I$), 129.9, 129.8, 129.3 (d, 1C, 1C, 1C, O═PCC*H*, $^2J_{P-C}$ = 24, 23, 23 Hz), 129.0 (s, 1C, C$_J$, $^1J_{Pt,C}$ = 956 Hz), 125.3 (s, 1C, C$_G$), 124.9 (s, 1C, C$_H$, $^3J_{Pt,C}$ = 44 Hz), 123.9 (s, 1C, C$_F$, $^3J_{Pt,C}$ = 48 Hz), 63.5, 63.0 (s, 2C, 1C, C$_A$), 37.8 (s, 1C, C$_β$, $^2J_{Pt,C}$ = 27 Hz), 33.7−32.9 (s, 6C, C$_B$), 25.2−24.8 (s, 9C, C$_C$ and C$_D$), 21.7 (s, 1C, C$_α$, $^1J_{Pt,C}$ = 667 Hz), −6.0 (s, 1C, Pt−CH$_3$, $^1J_{Pt,C}$ = 690 Hz). HRMS (ESI): *m*/*z* calcd 811.3289 (M$^+$), found 811.3301.

*[κ³-Tt^{Cy}Pt(CH$_2$CH$_2$-o-C$_6$H$_4$)(CH$_2$CH═CH$_2$)][I] (**19-L2**).* **17-L2** (0.010 g, 0.013 mmol) was placed in a Schlenk flask under nitrogen. Methylene chloride (10 mL) was added through the septum. The solution was treated with 1.2 equiv of allyl iodide and stirred for 20 min. The solvent was removed by rotary evaporation and the resulting oil triturated with pentane to afford the alkylated product as a pale yellow powder. ^{1}H NMR showed quantitative conversion from **17-L2**. ^{1}H NMR (CD$_2$Cl$_2$, 293 K, δ): 8.71, 8.70, 8.56 (s, 1H, 1H, 1H, Tt^{Cy}C*H*), 7.14−6.78 (m, 4H, Pt−C$_6$*H*$_4$), 5.76 (m, 1H, Pt−CH$_2$C*H*═CH$_2$), 4.85 (d, 1H, Pt−CH$_2$CH═C*H*$_{trans\ to\ H}$, $^3J_{H,H}$ = 17 Hz, $^4J_{Pt,H}$ = 23 Hz), 4.75, 4.70, 4.51 (m, 1H, 1H, 1H, C$_A$-*H*), 4.61 (dd, 1H, Pt−CH$_2$CH═C*H*$_{cis\ to\ H}$, $^3J_{H,H}$ = 10 Hz), 3.26−2.84 (m, 4H, Pt−C*H*$_2$C*H*$_2$), 2.29−1.25 (m, 30 H, cyclohexyl). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 293 K, δ): −8.3 (s, 1P, Tt^{Cy}*P*═O). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 293 K, δ): 155.7 (s, 1C, C$_K$, $^2J_{Pt,C}$ = 109 Hz), 141.9 (s, 1C, Pt−CH$_2$*C*H═CH$_2$, $^2J_{Pt,C}$ = 60 Hz), 136.0, 135.8, 135.6 (d, 1C, 1C, 1C, O═P*C*, $^1J_{P-C}$ = 149 Hz each), 131.0 (s, 1C, C$_I$), 130.1, 129.9, 129.3 (d, 1C, 1C, 1C, O═PCC*H*, $^2J_{P-C}$ = 24,

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26, 24 Hz), 129.1 (s, 1C, C_J), 125.4 (s, 1C, C_G), 124.8 (s, 1C, C_H, $^3J_{Pt,C}$ = 40 Hz), 123.7 (s, 1C, C_F, $^3J_{Pt,C}$ = 50 Hz), 112.9 (s, 1C, Pt−$CH_2CH{=}CH_2$, $^3J_{Pt,C}$ = 51 Hz), 63.5, 63.0 (s, 2C, 1C, C_A), 37.6 (s, 1C, C_β, $^2J_{Pt,C}$ = 21 Hz), 33.7−33.0 (s, 6C, C_B), 25.2−24.8 (s, 9C, C_C and C_D), 23.7 (s, 1C, C_α, $^1J_{Pt,C}$ = 679 Hz), 16.1 (s, 1C, Pt−$CH_2CH{=}CH_2$, $^1J_{Pt,C}$ = 655 Hz). HRMS (ESI): *m*/*z* calcd 837.3446 (M^+), found 837.3464.

■ ASSOCIATED CONTENT

Supporting Information

Text and figures giving representative ^1H and ^{13}C NMR spectra, complete characterization data for complexes **15a-L1** and **16a-L1**, and kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ DEDICATION

Dedicated to the memory of Prof. F. Gordon A. Stone.

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