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C–H and C–C Bond Formation Promoted by Facile κ^3/κ^2 Interconversions in a Hemilabile "Click"-Triazole Scorpionate Platinum System

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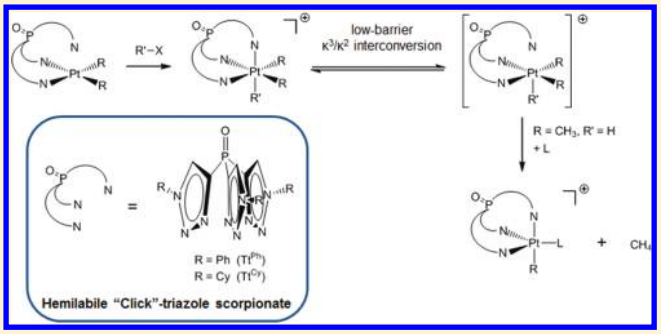
Supporting Information

ABSTRACT: A series of platinum complexes bearing 3-fold symmetrical "Click"-triazole-based scorpionate ligands (Tt^R) has been prepared. Metalation of these weakly donating ligands results in neutral Pt(II) complexes that display a κ^2 coordination mode. Such complexes are susceptible to oxidative addition using a variety of electrophilic alkyl and allyl reagents to generate isolable cationic κ^3 Pt(IV) complexes. Protonation of the κ^2 precursors results in Pt(IV) dimethyl hydride cations. Thermolysis of the dimethyl hydride species at 35 °C in the presence of a trapping π-acid ligand initiates reductive elimination of methane and formation of a Pt(II) species of the type $[Tt^{Ph}PtMe(L)][BF_4]$ (L = CO, ethylene, propylene, *cis*-2-butene, *trans*-2-butene, isobutylene) in good yield. Furthermore, the κ^3 σ-allyl complexes $[Tt^RPt(Ph)_2(CH_2CH{=}CH_2)][I]$ cleanly undergo $C_{sp2}–C_{sp2}$ reductive coupling to form biphenyl at ambient temperatures. The Tt^R ligand serves as a homofunctional hemilabile ligand and exhibits a lower barrier κ^3/κ^2 interconversion to generate reactive unsaturated five-coordinate complexes than the well-studied $Tp'PtMe_2H$ complex, which requires thermolysis at temperatures above 100 °C.



INTRODUCTION

Hemilabile ligands, in which a weakly donating group can reversibly bind to a metal center, have risen in prominence in metal–ligand system design due to the flexible coordination mode geometry and the ease of formation of unsaturated complexes, providing access to reactive intermediates.[1,2] Such systems stand in stark contrast to strongly donating ligand scaffolds that result in stable, well-defined complexes that can be reluctant reagents.[3] Numerous multidentate ligand frameworks have been reported that contain weakly coordinating and readily tunable pendant functional groups that serve the role of reversible donors.[1,2,4−10]

Our research program has focused on controlling interconversion between κ^2 and κ^3 coordination modes in the Tp′Pt system (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) (Figure 1a)). It is well established that reductive elimination from six-coordinate Pt(IV) often occurs from a five-coordinate species through preliminary ligand dissociation.[11−20] Although Tp′ is a strong donor, we have found specific conditions that allow us to control the reversible coordination of one of the pyrazolyl rings, thus granting access to the coveted five-coordinate intermediate. Thermolysis of $Tp'PtMe_2H$ above 100 °C or protonation at low temperature dechelates the apical Tp′ arm, generating a reactive unsaturated species that eliminates methane.[21] An array of reactivity patterns stemming from the resulting Tp′PtMe fragment has been documented (Scheme 1).[22−26] In the presence of cyclic alkanes, Tp′PtMe activates C–H bonds and generates dehydrogenated products after β-H elimination.[22] Trapping Tp′PtMe with carbon monoxide results in formation of the Tp′PtMe(CO) complex, which can undergo nucleophilic attack by hydroxide to generate CO_2 and a platinum dihydride species. Elimination of dihydrogen in a subsequent step represents a stoichiometric water gas shift reaction.[23] Furthermore, elimination of benzene from the

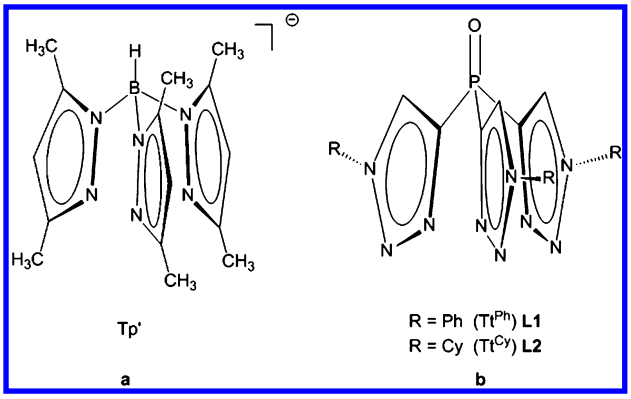


Figure 1. Tp′ (a) and Tt^R (b) tridentate ligands.

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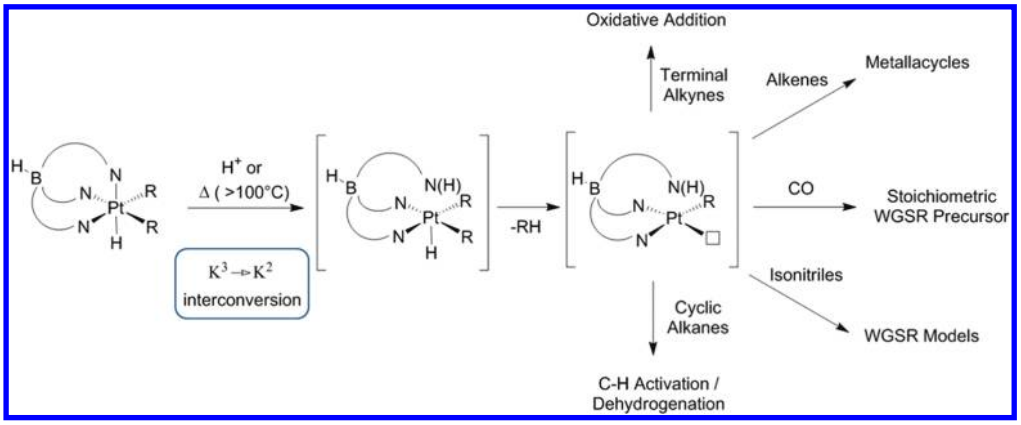
Scheme 1. Generation of the Reactive Tp′PtR Fragment and Subsequent Reactivity



analogous Tp′PtPh$_2$H and trapping with olefins lead to slow phenyl migration and ortho C−H activation to form metallacycles.[24] The initiating mechanistic step for all of these transformations is dechelation of the apical Tp′ arm to generate a reactive five-coordinate intermediate.

In hopes of facilitating conversion between κ^3 and κ^2 coordination modes for scorpionate ligands, the reactivity of the neutral trispyrazolylmethane (Tpm) ligand in an analogous Pt system was studied. To our surprise, [TpmPtMe$_2$H]$^+$ was reluctant to eliminate methane even at 100 °C.[27] It was clear that the strongly donating pyrazolyl rings have a large influence on κ^3/κ^2 interconversions. We, therefore, sought to probe reactions utilizing both a weaker tridentate nitrogen donor ligand and a more electrophilic backbone than C−H, which should allow for coordination mode interconversion under milder conditions.

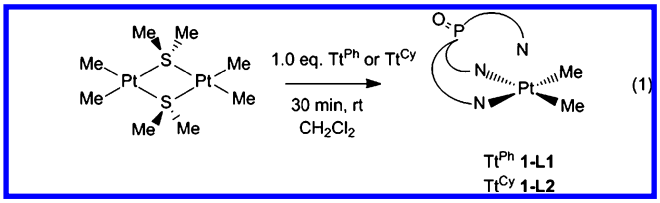
Hemilabile metal−ligand frameworks have promoted organometallic reactions in platinum chemistry. Vedernikov and co-workers have developed and employed the hemilabile di(2-pyridyl)methane sulfonate (dpms) ligand to extensively study metal−carbon functionalization using a Pt(II)/Pt(IV) system in aqueous media.[28−34] Similar to the monofunctional Tp′ ligand, the proximal sulfonate group assists in stabilizing oxidized Pt(IV) species enroute to functionalized products. Similarly, both Vedernikov and Puddephatt have utilized a dipyridylketone ligand that readily adds nucleophiles to create an anionic ligand that can be either bidentate or tridentate.[35,36]

Recently, Lammertsma and co-workers employed copper catalyzed azide−alkyne cycloaddition[37−39] (CuAAC) in the synthesis of tris(1-phenyl-1*H*-1,2,3-triazol-4-yl)phosphine oxide (**L1**) (Figure 1b), a neutral, symmetrical 1,2,3-triazolyl-based tridentate ligand, which we will abbreviate as Tt^{Ph}.[40] Despite the wide versatility and efficiency of the CuAAC reaction, utilization of 1,2,3-triazole-containing N-donor chelating ligands in transition-metal complexes is rare.[41−47] Anticipating weak donation from the triazole ring compared with pyrazole and increased electrophilicity of a P═O backbone over B−H and C−H, we were attracted to the potential of employing Tt^{Ph} to generate analogues of the Tp′PtR fragment under mild conditions. Here, we report the synthesis of a series of Tt^{R}Pt complexes and their reactivity built upon κ^3/κ^2 coordination mode flexibility, including C−X oxidative addition, C−H reductive elimination, and C−C reductive coupling, all accessible at ambient temperatures.

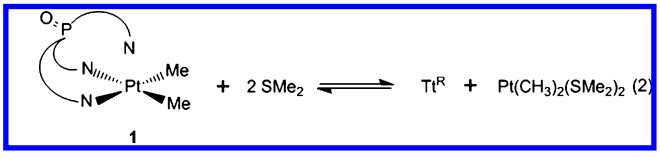
RESULTS AND DISCUSSION

Synthesis and Metalation of Tt^R. Following Lammertsma's method, Tt^{Ph} **L1** was synthesized via the CuAAC reaction between trisethynyl phosphine oxide and phenyl azide.[40] In a similar fashion, tris(1-cyclohexyl-1*H*-1,2,3-triazol-4-yl)-phosphine oxide (Tt^{Cy}) **L2** was prepared using cyclohexyl azide. The aromatic triazolyl proton of the rings in **L1** and **L2** resonates in the ^{1}H NMR spectra at 8.8 and 8.2 ppm, respectively, and serves as an excellent NMR symmetry handle.

The addition of Tt^{Ph} or Tt^{Cy} to a methylene chloride solution of [Pt(CH$_3$)$_2$(SMe$_2$)]$_2$ results in displacement of the bridging dimethyl sulfide ligands and formation of κ^2 square-planar complexes, κ^2-Tt^{Ph}Pt(CH$_3$)$_2$ (**1-L1**) or κ^2-Tt^{Cy}Pt(CH$_3$)$_2$ (**1-L2**) (eq 1), in which two triazolyl rings bind through the N3 position. The crude mixtures were chromatographed to obtain the κ^2 products as air-stable light yellow solids in 61% and 68% yield, respectively.



In accord with weak donation anticipated for the triazolyl ring, it should be noted that the Tt^R ligand readily cleaves the bridges of the platinum dimer, but it does not readily displace dimethyl sulfide present in the resulting monomer, Pt(CH$_3$)$_2$(SMe$_2$)$_2$. Instead, when more than 1 equiv of Tt^R is added to [Pt(CH$_3$)$_2$(SMe$_2$)$_2$]$_2$, the first equivalent rapidly coordinates to one-half of the platinum in the dimer, while an equilibrium is established for the remaining platinum that reflects competition between Tt^R and dimethyl sulfide to bind to Pt(II). Indeed, addition of dimethyl sulfide to clean **1** results in a mixture of bound and free Tt^R (eq 2). Attempts at heating the mixture to drive off the free dimethyl sulfide were unsuccessful and led to decomposition and undesired side reactions.



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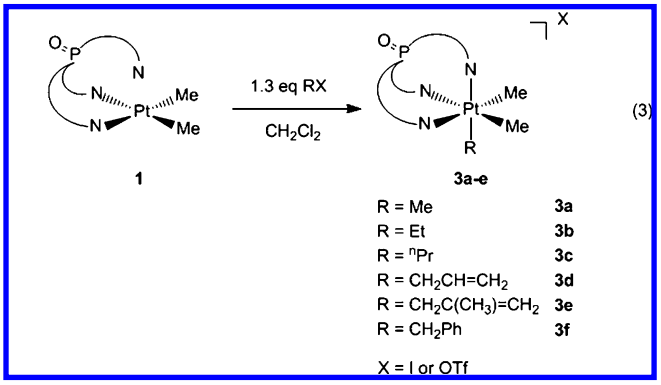
The ^{1}H NMR spectrum of κ^2-Tt^{Ph}Pt(CH$_3$)$_2$ (**1-L1**) reveals a 2:1 ratio for the triazolyl proton resonances, and a single signal for the two Pt−Me groups, indicating a C_s symmetric complex. The rather large chemical shift difference of 1 ppm between the two triazolyl proton resonances demonstrates that the apical arm is in a significantly different chemical environment, consistent with a κ^2 coordination mode. The Pt−Me resonance at 0.9 ppm with $^2J_{Pt-H}$ = 88 Hz is compatible with data for other Pt(II)−Me resonances.[25,48,49] The phosphine oxide resonance in the ^{31}P NMR spectrum moves slightly upfield from −5.7 ppm for free Tt^{Ph} to −8.4 ppm when two scorpionate arms bind to the metal. It is noteworthy that the $^1J_{P-C}$ value at the dome of the scorpionate umbrella is dependent upon the binding of the triazolyl ring, so this coupling constant serves as a convenient spectroscopic probe of the coordination mode. In **1-L1**, $^1J_{P-C}$ is 167 Hz for the lone unbound arm while $^1J_{P-C}$ decreases to 151 Hz for the two coordinated rings. Similar NMR characteristics were observed for the corresponding **1-L2** dimethyl complex. Analogous diphenyl complexes κ^2-Tt^{Ph}Pt(Ph)$_2$ (**2-L2**) and κ^2-Tt^{Cy}Pt(Ph)$_2$ (**2-L2**) were prepared in the same manner using [Pt(Ph)$_2$(SEt$_2$)$_2$]$_2$ as a platinum source, resulting in 56% and 74% yields by the Tt^R ligand (R = Ph and Cy), respectively.

Cationic Pt(IV) Alkyl and Allyl Complexes. Treatment of the dimethyl κ^2 complex **1** with electrophilic alkyl and allyl reagents resulted in oxidation of the metal center to form isolable octahedral platinum(IV) cations **3a**−**3e** (eq 3, Table 1)



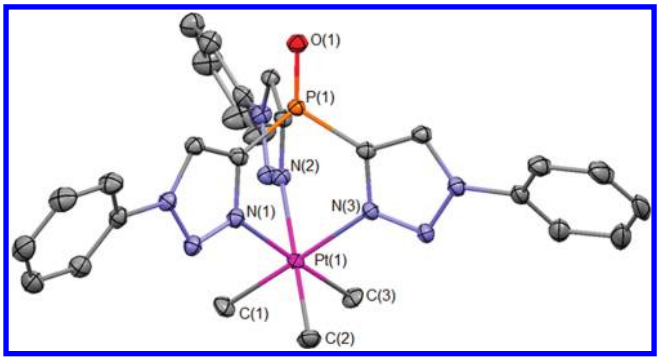


Figure 2. X-ray structure of [Tt^{Ph}PtMe$_3$][BAr′$_4$] **3a-L1**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms, the BAr′$_4$ counterion, and cocrystallized CH_2Cl_2 are omitted for clarity.

in quantitative yield by ^{1}H NMR. All compounds were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies.

Addition of either methyl triflate or methyl iodide to **1-L1** resulted in a trimethyl species of the type [(κ^3-Tt^{Ph})PtMe$_3$][X] (X = OTf or I). The ^{1}H NMR spectrum of [(κ^3-Tt^{Ph})Pt(CH$_3$)$_3$][OTf] (**3a-L1**) shows a single resonance at 9.4 ppm for the three triazolyl ring protons, indicating an ascent in symmetry to the C_{3v} point group. The Pt−Me resonance moves downfield to 1.5 ppm and is consistent with other reported systems involving Pt(II)/Pt(IV) oxidations.[26,50−52]

Table 1. Selected Bond Lengths (Å) and Angles (°) for Complex 3a-L1

Bond Lengths			
Pt(1)−C(1)	2.039(3)	Pt(1)−N(1)	2.189(2)
Pt(1)−C(2)	2.043(3)	Pt(1)−N(2)	2.168(2)
Pt(1)−C(3)	2.045(3)	Pt(1)−N(3)	2.175(2)
P(1)−O(1)	1.468(2)		
Bond Angles			
C(1)−Pt(1)−C(2)	87.32(12)	N(1)−Pt(1)−N(2)	85.30(9)
C(2)−Pt(1)−C(3)	87.59(13)	N(2)−Pt(1)−N(3)	86.08(9)
C(3)−Pt(1)−C(1)	88.81(12)	N(3)−Pt(1)−N(1)	85.92(9)
C(1)−Pt(1)−N(3)	92.18(10)		
C(2)−Pt(1)−N(1)	93.97(11)		
C(3)−Pt(1)−N(2)	93.36(11)		

Slow diffusion of hexanes into a methylene chloride solution of **3a-L1** (after counterion exchange with [Na][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (NaBAr′$_4$)) produced clear, colorless hexagonal crystals that were suitable for X-ray crystallography. Figure 2 shows the X-ray structure of **3a-L1**, which adopts an octahedral geometry with a κ^3 coordination mode of the Tt^{Ph} ligand. The Pt−C bond lengths (2.039−2.045 Å) are consistent with other LPtMe$_3$ (L = tridentate donor) complexes.[53,54] This distance, in conjunction with the $^2J_{Pt,H}$ value of 74 Hz, is in good agreement with the well-defined trend highlighted by Goldberg et al. that correlates shorter Pt−C distances (≤2.05 Å) due to weakly donating trans ligands with larger two-bond couplings (>70 Hz) in Pt(IV)-Me compounds.[53] Comparison of the Pt−N distance in [Tt^{Ph}PtMe$_3$][BAr′$_4$] to both Tp′PtMe$_3$ and [TpmPtMe$_3$][I] reveals a consistent pattern of slight lengthening, roughly 0.02 Å, that is also compatible with less donation from the 1,2,3-triazole.[53,54] The angles around the platinum center are slightly distorted from ideal; both the N−Pt−N angles (85−86°) and the C−Pt−C (87−89°) angles are slightly pinched, resulting in larger C−Pt−N angles (92−94°). All three phenyl groups of the Tt^{Ph} ligand are twisted from their respective triazolyl ring plane, with two rotated 28° and 29° in the same direction, while the other is tilted 36° in the opposite direction.

In a similar manner to **3a**, [Tt^{R}PtMe$_2$Et][X] (**3b**) was prepared by addition of ethyl triflate or ethyl iodide to **1**. The ethyl complexes maintain the mirror plane present in their κ^2 precursors and exhibit a 2:1 ratio for the triazolyl proton resonances in the ^{1}H NMR, but the two signals are much closer in chemical shift (ca. 0.1 ppm difference), no doubt reflecting κ^3 coordination with an alkyl ligand trans to each nitrogen donor. In **3b-L1**, the methylene protons of the ethyl group appear as a quartet at 2.4 ppm with Pt satellites ($^2J_{Pt-H}$ = 75 Hz), whereas the beta protons resonate as a triplet at 0.9 ppm ($^3J_{Pt-H}$ = 56 Hz). The ability to use primary halides for alkylation of Pt(II) was further demonstrated with 1-iodopropane. Treatment of **1** with 1-iodopropane resulted in [Tt^{R}PtMe$_2$^{n}Pr][I] (**3c**). However, the reaction was significantly slower than the methyl and ethyl analogues and required stirring overnight at room temperature for completion.

1 was treated with allyl iodide, 3-bromo-2-methylpropene, or benzyl iodide to form the corresponding Pt(IV) σ-allyl or

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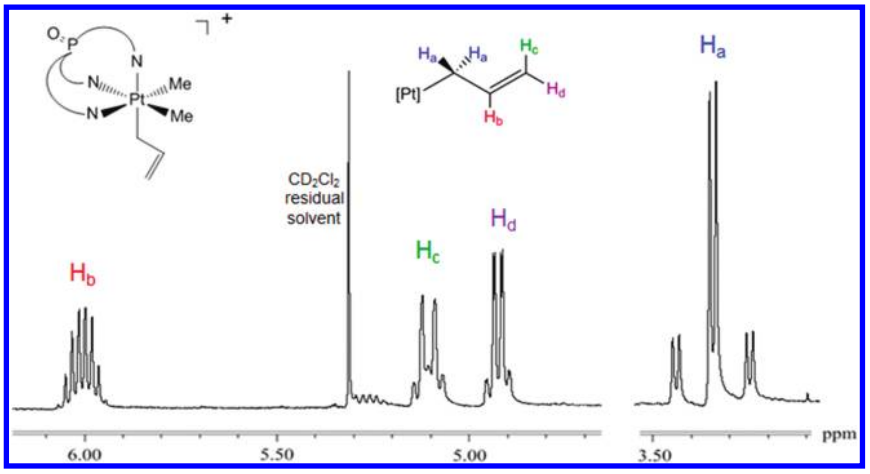
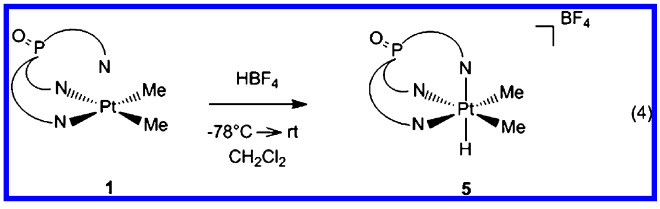


Figure 3. Allyl region of **3d-L1** in the ^{1}H NMR spectrum.

σ-benzyl complexes **3d**–**3f**. The synthesis of **3e** and **3f** was performed in the presence of 1.3 equiv of $AgBF_4$ to form the tetrafluoroborate salt. $[Tt^{Ph}PtMe_2(CH_2CH{=}CH_2)][I]$ (**3d-L1**) exhibits the characteristic 2:1 ratio and close chemical shift values of the triazolyl protons, and a downfield Pt–Me chemical shift is observed at 1.6 ppm consistent with a Pt(IV) complex with a κ^3 Tt^{Ph} coordination mode. The allyl region of the ^{1}H NMR (Figure 3) displays a typical α-olefin pattern of η^1-allyl ligands, including a doublet for the equivalent methylene protons and a large two-bond coupling to platinum, $^2J_{Pt-H}$ = 96 Hz. Platinum coupling (ca. 20 Hz) is also observed through the allyl fragment to the terminal protons which are four bonds removed from the metal center. NMR spectra of both the methyl-substituted allyl (**3e**) and benzyl (**3f**) complexes are consistent with data obtained for **3d**.

Analogous diphenyl alkyl complexes were prepared using **2-L1** and **2-L2** as starting materials. Methylation of the κ^2 complexes using methyl triflate or methyl iodide resulted in complexes of the type $[Tt^RPtPh_2Me][X]$ (X = OTf or I) (**4a**). The Pt–Me resonance moves significantly downfield to 2.3 ppm ($^2J_{Pt-H}$ = 74 Hz) as a result of deshielding by the two adjacent aromatic rings. Reaction of **2** with ethyl triflate or ethyl iodide produced the expected diphenyl ethyl complexes, $[Tt^RPtPh_2Et][X]$ (X = OTf or I) (**4b**). However, addition of 1-iodopropane did not result in oxidative addition even at longer reaction times. The presence of metal bound aromatic rings clearly reduced the nucleophilicity of the metal center relative to the Pt(II) dimethyl case.

Synthesis of $[Tt^RPtMe_2H]^+$. The addition of alkyl or allyl electrophiles to the κ^2-Tt^R complexes demonstrated that the metal center is susceptible to oxidation to form stable Pt(IV) products. With this reactivity in mind, we sought to form an analogous dimethyl hydride complex for comparison with Tp′PtMe$_2$H. Reaction of **1-L1** with mild H^+ sources, such as NH_4Cl or AcOH, did not produce the desired $[Tt^{Ph}PtMe_2H]^+$. Protonation using a strong acid, $HBF_4{\cdot}Et_2O$, was required to generate $[Tt^{Ph}PtMe_2H][BF_4]$ (**5-L1**) (eq 4).



5-L1 exhibits a hydride signal at −19.9 ppm with a large Pt coupling, $^1J_{Pt-H}$ = 1541 Hz. The one-bond Pt–H coupling is an indirect probe of the strength of the trans ligand bond to platinum. In Tp′PtMe$_2$H, the coupling is 1360 Hz, so the triazole in Tt^{Ph} is indeed a weaker donor than the pyrazole in Tp′.[55] In the Tt^{Cy} analogue $[Tt^{Cy}PtMe_2H][BF_4]$ (**5-L2**), $^1J_{Pt-H}$ is 1519 Hz, indicating that the Tt^{Cy} ligand is a slightly stronger donor than Tt^{Ph}.

In the EXSY NMR spectrum (Figure 4) of **5-L1**, an off-diagonal crosspeak with platinum satellites is present that correlates the Pt–H and the Pt–CH_3 signals. This peak is in-phase with the diagonal signals, indicating slow exchange on the NMR time scale rather than distance-dependent nuclear Overhauser effects.[56] Exchange between the hydride and methyl protons indicates a dynamic metal–ligand system at room temperature, and we postulate that this exchange proceeds through a low-barrier dechelation of the apical Tt^R ligand arm to generate a five-coordinate complex that can reductively couple H and CH_3 to form an agostic methane adduct. Such species are often proposed intermediates in metal-mediated processes involving C–H addition or elimination.[57,58] Rotation of the bound methane and oxidative addition of a different C–H bond, followed by κ^2/κ^3 conversion, completes the exchange of the methyl and hydride positions. Methane loss can occur directly from the putative η^2-CH_4 adduct, as verified by the presence of small amounts of methane at ca. 0.2 ppm in the ^{1}H NMR spectrum.[59]

This interconversion process was confirmed by the addition of D_2O and monitoring the ^{1}H NMR spectrum. Initial spectra indicate that deuterium is incorporated into the acidic hydride position. After 5 min, a new methyl signal begins to appear due to the formation of Pt–CDH_2. As deuterium incorporation proceeds, the Pt–CH_3 signal continues to decrease in intensity while the Pt–CDH_2 and, later, Pt–CD_2H signals appear and grow (Figure 5). After 30 min, the upfield region of the ^{1}H NMR displays various CH_nD_{4-n} (n = 4, 3, or 2) methane isotopologues (Figure 6) due to methane loss from the deuterated dimethyl hydride cation. The proposed mechanism for deuterium incorporation (Scheme 2) proceeds as described above, which is analogous to deuterium incorporation in the related Tp′Pt$(CH_3)_2$D.[21]

Reductive Elimination from $[Tt^RPtMe_2H]^+$. Given the dynamic nature of the $[Tt^RPtMe_2H]^+$ reagents, we wanted to drive the interconversion to the κ^2 form and favor methane loss from the unsaturated five-coordinate intermediate under mild

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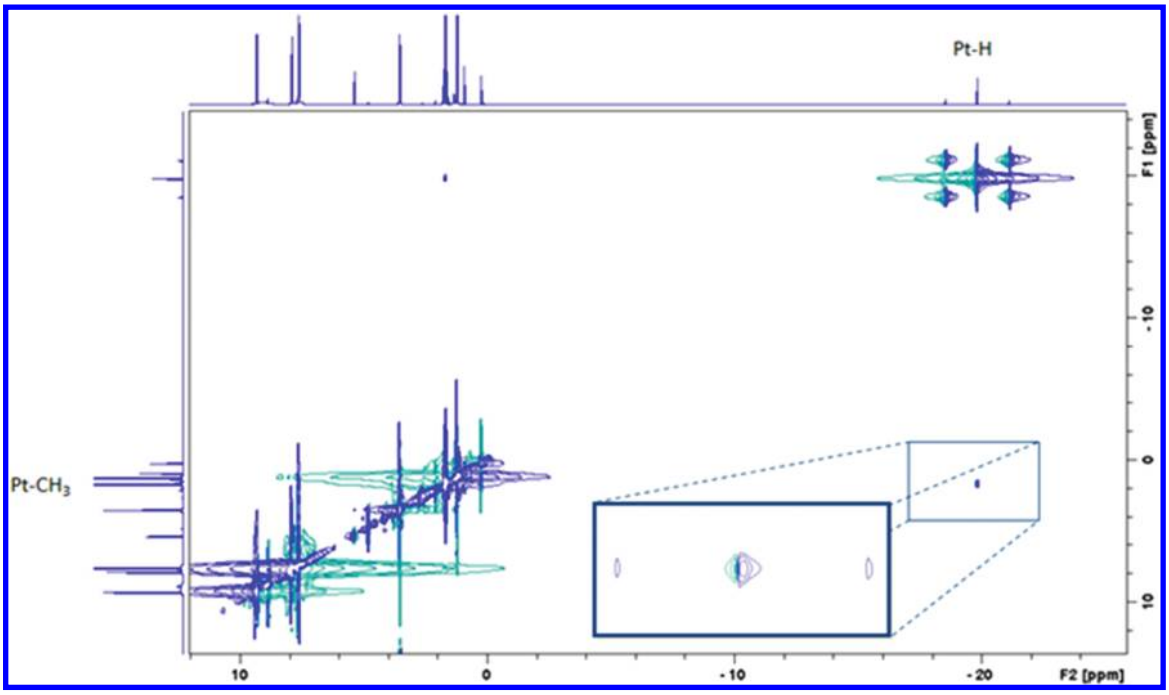

Figure 4. EXSY NMR spectrum of **5-L1**.

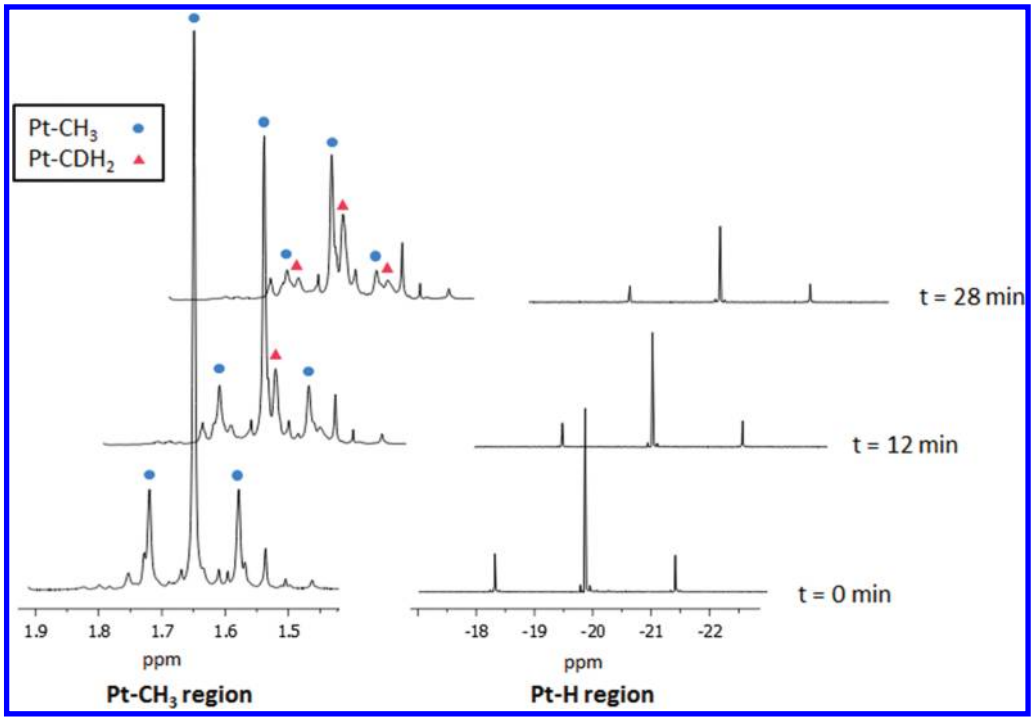

Figure 5. Methyl and hydride regions of the ^{1}H NMR spectrum in **5-L1** after addition of excess D_2O.

conditions. Indeed, heating **5** at 35 °C under a CO atmosphere for 2 h resulted in conversion to the cationic carbon monoxide complexes, [Tt^{R}PtMe(CO)][BF_4] (**6**) (eq 5) in good yield (86%) by ^{1}H NMR. The solution IR spectra of **6-L1** and **6-L2** reveal a strong CO band at 2124 and 2117 cm^{-1}, respectively. These high CO stretches (approaching that of free CO at 2139 cm^{-1}) indicate an exceptionally electron-deficient metal center, reiterating that the triazolyl ligand is a weak donor. In Tp′PtMe(CO), two distinct CO stretches (2065 and 2081 cm^{-1}) were observed that reflect the presence of both four-coordinate κ^2 and five-coordinate κ^3 isomers.[60] The existence of only one CO stretch in **6** along with the high electrophilicity at platinum is compatible with the observation of solely the κ^3 form.

The ^{1}H NMR spectrum of **6-L1** displays a 2:1 ratio for the triazolyl resonances and a Pt−Me signal at 1.4 ppm ($^2J_{Pt-H}$ = 74 Hz)

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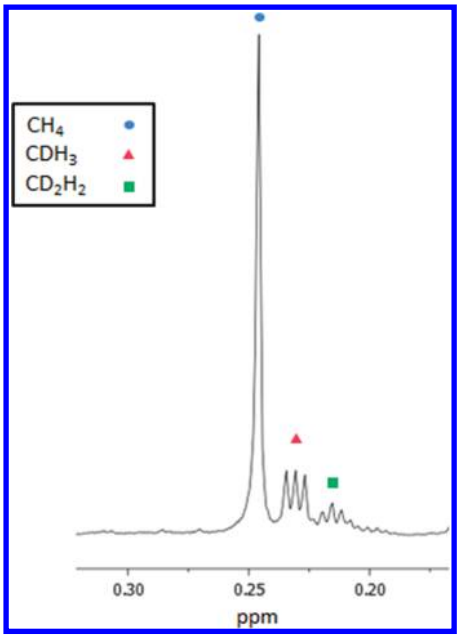
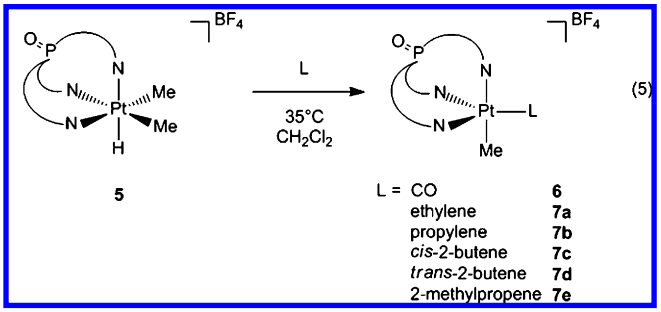


Figure 6. Methane region of the ^{1}H NMR spectrum in **5-L1** 30 min after the addition of excess D_2O.



and suggests a C_s symmetric bipyramidal geometry. The ^{13}C NMR spectrum contains the characteristic downfield metal carbonyl resonance at 161.3 ppm.

Applying the same reaction conditions, but using ethylene in place of carbon monoxide as the trapping gas, generated η^2-ethylene complexes, $[Tt^RPtMe(\eta^2\text{-}C_2H_4)][BF_4]$ (**7a**) (eq 5). The ^{13}C NMR spectra of **7a-L1** reveal $^1J_{P-C}$ values of 153 and 150 Hz for the apical and equatorial nitrogen donors, respectively, indicating that all three triazolyl arms are bound with a trigonal bipyramidal geometry about the platinum center, similar to that of **6**. The four olefinic protons in both of these complexes appear as a singlet ($^2J_{Pt-H}$ = 79 and 81 Hz, respectively), reflecting rapid rotation about the metal–ligand bond that averages the up and down (relative to the axial nitrogen) olefin signals. Variable-temperature NMR studies reveal that the olefin is static at 220 K in **7a-L1**, with two separate resonances as a result of inequivalent sites for the up and down protons of the bound alkene (Figure 7).

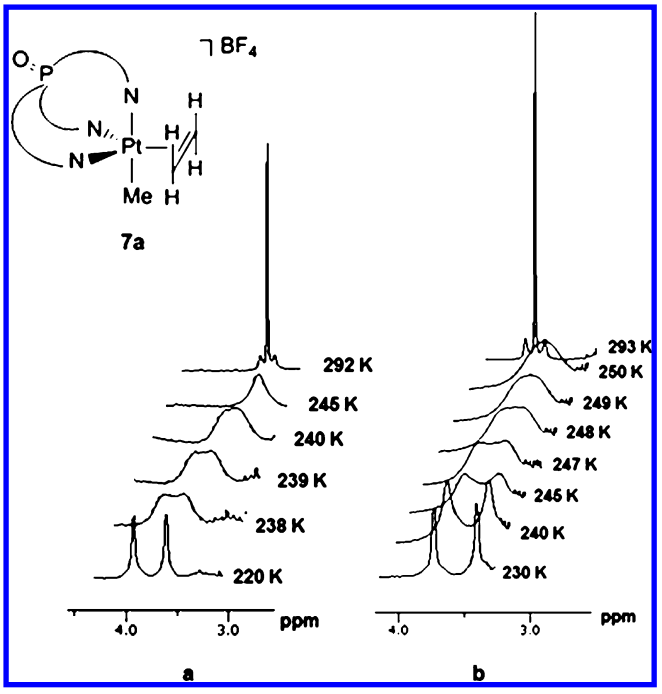
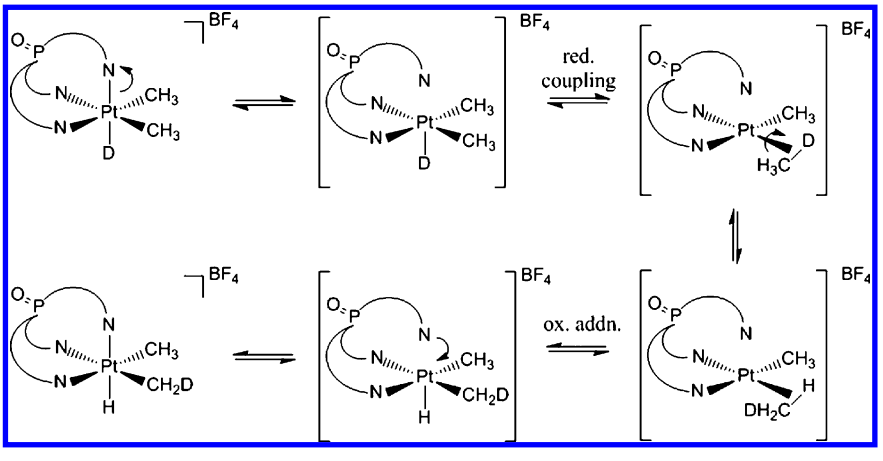


Figure 7. Variable-temperature NMR study of ethylene rotation in **7a-L1** (a) and **7a-L2** (b).

The coalescence temperature for this process was found to be 239 K for **7a-L1**, which translates to a rotation barrier of 11.1 (±0.2) kcal/mol. The Tt^{Cy} analogue, **7a-L2**, had a coalescence temperature of 248 K and a rotation barrier of 11.5 (±0.2) kcal/mol. Presumably, the Tt^{Cy} ligand is slightly more electron-rich and enhances backbonding to the olefin in the ground-state geometry.

The scope of the methane elimination/trapping sequence was expanded using the Tt^{Ph} ligand and a series of substituted

Scheme 2. Proposed Mechanism for Deuterium Incorporation into the Methyl Position



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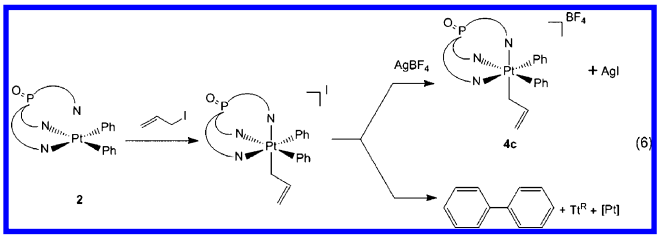
olefins. Heating **5-L1** at 35 °C for 4 h under an atmosphere of propylene, *cis*-2-butene, *trans*-2-butene, or isobutylene produced the corresponding η^2 olefin complexes **7b**–**7e** in 74–78% yield by ^{1}H NMR. [Tt^{Ph}PtMe(η^2-propylene)][BF$_4$] (**7b**) displays three unique resonances in a 1:1:1 ratio for the triazolyl protons, reflecting the descent to C_1 symmetry. In both the *cis*-2-butene and the *trans*-2-butene complexes **7c-L1** and **7d-L1**, the olefinic region of the ^{1}H NMR spectra displays two broad resonances at 298 K and indicates that room temperature is slightly below the coalescence temperature for rotation. However, in the isobutylene adduct **7e-L1**, both olefinic protons as well as both methyl groups appear as sharp singlets, revealing rapid rotation at room temperature.

Biphenyl Formation via C–C Reductive Coupling. Addition of allyl iodide or benzyl bromide to the diphenyl precursor **2** resulted in the expected product, [Tt^{R}PtPh$_2$R][I] (R = allyl **4c**, benzyl **4d**), and these Pt(IV) complexes are analogous to their dimethyl counterparts. However, whereas **3d** and **3f** are unreactive, complexes **4c** and **4d** undergo reductive C–C coupling to cleanly produce biphenyl, and this reaction is accompanied by release of Tt^R. The rate of reaction was found to be heavily influenced by the identity of the triazolyl ligand; elimination from the Tt^{Ph} allyl complex **4c-L1** was complete within 15 min at room temperature, whereas the Tt^{Cy} complex **4c-L2** proceeds slowly overnight. Counterion exchange using AgBF$_4$ shuts down the biphenyl production and results in an isolated, stable complex (eq 6).



Kinetic studies on the conversion of [**4c-L2**][I], which is formed rapidly in situ upon addition of allyl iodide to **2**, to biphenyl and free Tt^{Cy} ligand were performed with ^{1}H NMR spectroscopy by monitoring the appearance of biphenyl. The kinetics of this reaction were studied over a temperature range from 290 to 320 K; the reaction displayed second-order kinetics. The rate at 300 K was found to be 1.29 (±0.03) × 10^{-4} M^{-1} s^{-1}, giving rise to a $\Delta G^{\ddagger}_{300\ K}$ value of 22.9 (±0.2) kcal/mol. An Eyring plot (Figure 8) was constructed using rate constants from this temperature range; $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 19.1 (±1) kcal/mol and −12.6 (±4) eu, respectively.

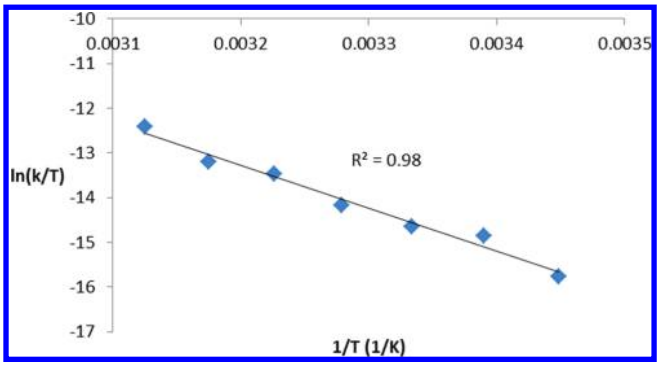
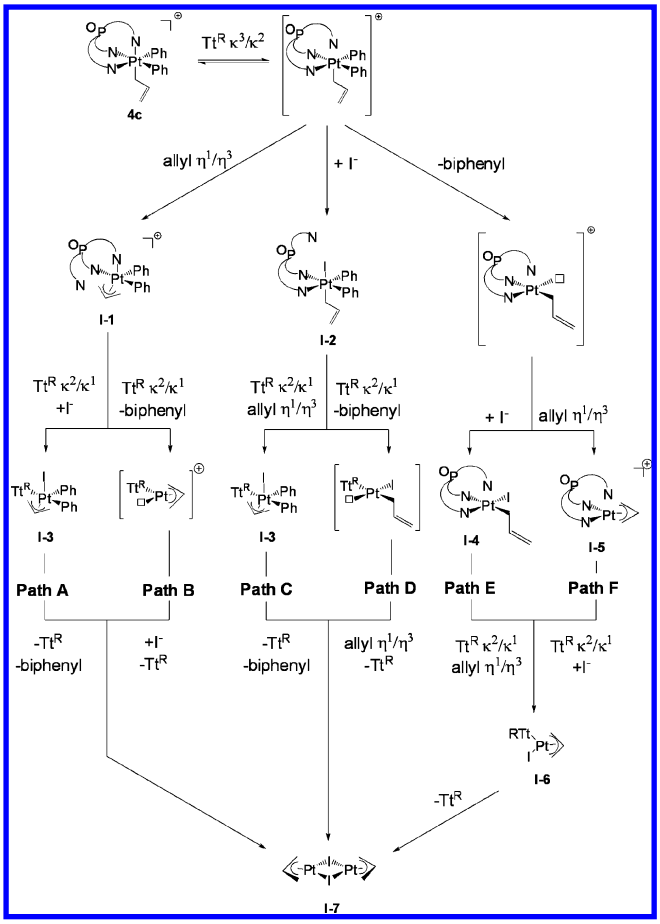


Figure 8. Eyring plot of biphenyl formation from **4c-L2**.

We believe that the mechanism for biphenyl elimination from **4c** involves a sequence that is some combination of ligand dechelation, iodide addition, and η^1-to-η^3 allyl rearrangement. Combinations of these simple steps lead to six different pathways (Scheme 3). In all cases, the initiating step is a low-

Scheme 3. Possible Mechanistic Pathways for the Elimination of Biphenyl from 4c



barrier κ^3-to-κ^2 conversion to generate an unsaturated five-coordinate intermediate. The κ^2 complex can be trapped by either a σ- to π-allyl wrap to produce intermediate **I-1** or by coordination of the iodide counterion to form **I-2**. Both **I-1** and **I-2** could undergo a reversible κ^2-to-κ^1 conversion to lose the second arm of the Tt^R ligand and again be trapped by either iodide (Path A) or the allyl (Path C), respectively. Loss of the third Tt^R arm produces an unsaturated intermediate from which biphenyl elimination can occur along with generation of the iodide-bridged π-allyl dimer **I-7**. Alternatively, biphenyl elimination could occur after the κ^2/κ^1 conversion from **I-1** (Path B) or **I-2** (Path D) and the resulting three-coordinate Pt(II) fragment could be trapped with iodide or allyl, respectively, to also yield **I-7**. The formation of a π-allyl dimer is supported by the appearance of a doublet at 1.5 ppm with Pt satellites ($^2J_{Pt,H}$ = 65 Hz) and a broad signal at 3.7 ppm while monitoring the reaction using **4c-L1** as the starting material. The two signals correlate to each other in the ^{1}H,^{1}H-COSY NMR spectrum. However, the dimer begins to decompose to Pt^0 shortly after formation.

The remaining two pathways stem from C_{sp2}–C_{sp2} elimination directly from the initial five-coordinate intermediate

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to generate a three-coordinate fragment, which, again, can be trapped by either the iodide counterion (Path E) to form **I-4** or conversion from a σ- to π-allyl wrap (Path F) to form **I-5**. A second iteration of κ^2/κ^1 Tt^R conversions and trapping yields the Pt dimer **I-7**.

It should be noted that the diphenyl methyl complex **4a** does not result in C−C bond formation, which, along with the inertness of the **4c** BF_4 counterion complex, indicates that the iodide counterion and the allyl are both critical components to biphenyl production. Assuming that the C−C coupling is not a reversible mechanistic step, this would rule out Paths B and D−F. We believe that the second-order kinetics indicate that the bimolecular reaction of the complex cation with the iodide counterion occurs on the way to the transition state. Thus, the components present in the rate-determining step cannot be used to rule out either Path A or Path C. However, the former may be more appealing due to the proximity of an internal allyl trap in competition with a bimolecular trapping with iodide. The negative entropy of activation value suggests that the trapping by iodide precedes the rate-determining step. If the $C_{sp2}-C_{sp2}$ reductive elimination step occurs after the rate-determining step, as seems likely, the associated enthalpy of activation must be less than the value of 19.1 kcal/mol measured for the enthalpy of activation for the overall reaction. Previously, 17.7 kcal/mol was reported for the enthalpy of activation for elimination from a Pt(II) metal center to give biaryl and Pt(0) products.[61]

CONCLUSION

A series of platinum complexes bearing tridentate facially coordinating "Click"-triazole scorpionate ligands (Tt^R) has been synthesized. These hemilabile ligands allow for a significantly lower barrier for κ^3/κ^2 interconversions compared with the strongly donating pyrazolyl-based Tp′. The addition of R^+ or H^+ reagents to the κ^2-coordinated precursors Tt^RPtR_2 results in an oxidized metal center to which the once-free apical triazolyl arm can rapidly and reversibly bind. Mild heating of the cationic Tt^R dimethyl hydride complexes at 35 °C suffices for conversion to an unsaturated five-coordinate species from which C−H reductive elimination and methane loss occurs. In the Tt^R diphenyl σ-allyl reagents, the weakly donating Tt^R ligand works in cooperation with the allyl fragment to produce $C_{sp2}-C_{sp2}$ coupled products. This work demonstrates the hemilability of the 1,2,3-triazole functionality and highlights their potential use in symmetrical or hybrid multidentate ligand−metal system design.

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 molecule sieves. Methylene chloride, hexanes, and pentane were purified under an argon atmosphere and passed through a column packed with activated alumina.[62] All other chemicals were used as received without further purification. Silica column chromatography was conducted with 230−400 mesh silica gel, and alumina column chromatography was conducted with 80−200 mesh alumina.

^1H, ^{31}P, and ^{13}C NMR spectra were recorded on Bruker DRX400, AVANCE400, or AMX300 spectrometers. ^1H NMR and ^{13}C NMR chemical shifts were referenced to residual ^1H and ^{13}C signals of the deuterated solvents. Elemental analyses were performed by Robertson Microlit Laboratories of Madison, New Jersey. 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})[40] (**L1**), $[Pt(CH_3)_2(SMe_2)_2]_2$,[63] $[Pt(C_6H_5)_2(SEt_2)_2]_2$,[64] $[Na][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ ($NaBAr'_4$),[65] $[H(OEt_2)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ ($HBAr'_4$),[65] benzyl iodide,[66] and tris(ethynyl)phosphine oxide[40] were synthesized using published procedures.

Synthesis of Tt^{Cy}. *Cyclohexyl Azide.* A modified version of Sharpless's procedure was performed.[67] Sodium azide (1.3 g, 20 mmol) and potassium iodide (0.034 g, 0.2 mmol) were added to a 7 mL DMF solution of cyclohexyl bromide (1.4 mL, 11.6 mmol). The reaction mixture was refluxed overnight at 90 °C. Water (20 mL) was added to the crude mixture, and the product was extracted with diethyl ether (40 mL). The organic layer was washed with H_2O (8 × 20 mL). The ether solution was dried over $MgSO_4$ and the solvent was evaporated to produce cyclohexyl azide (1.00 g, 8.0 mmol) as a yellow oil in 69% yield.

*Tris(1-cyclohexyl-1H-1,2,3-triazol-4-yl)phosphine Oxide (Tt^{Cy}) (**L2**).* A modified version of Lammertsma's synthesis of Tt^{Ph} was performed.[2] Sodium ascorbate (0.80 mL of a 1 M aqueous solution, 0.8 mmol) and $CuSO_4$ (0.35 mL of a 2 M aqueous solution, 0.7 mmol) were added to a suspension of tris(ethynyl)phosphine oxide (0.530 g, 4.4 mmol) and cyclohexyl azide (1.7 g, 13.6 mmol) in 8 mL of a 1:1 mixture of H_2O and ^tBuOH. The reaction was allowed to stir overnight at room temperature. The cloudy, peach-colored crude reaction mixture was extracted with CH_2Cl_2 and dried over $MgSO_4$. The mixture was then passed through a Celite plug, the solvent was evaporated, and the resulting oil was triturated with pentane to produce Tt^{Cy} (2.1 g, 4.2 mmol) as a white powder in 93% yield.

For simplity in presenting NMR data, the carbon atoms of the cyclohexyl group are designated by the labeling scheme in Figure 9.

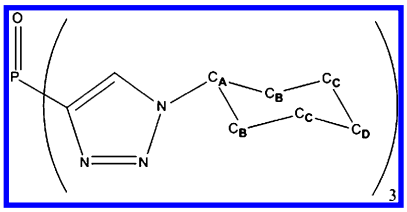

Figure 9. Carbon labels in the cyclohexyl group of the Tt^{Cy} ligand.

^1H NMR (CD_2Cl_2, 300 K, δ): 8.24 (s, 3H, $Tt^{Cy}CH$), 4.50 (m, 3H, C_A-*H*), 2.23−1.33 (m, 30H, cyclohexyl). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 291 K, δ): −6.6 (s, 1P, $Tt^{Cy}P$═O). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 300 K, δ): 140.8 (d, 3C, O═PC, $^1J_{P-C}$ = 157 Hz), 129.1 (d, 3C, O═PCCH, $^2J_{P-C}$ = 29 Hz), 61.0 (s, 3C, C_A), 33.9 (s, 6C, C_B) 25.5 (s, 6C, C_C), 25.4 (s, 3C, C_D). Anal. Calcd for $C_{24}H_{36}N_9OP$: C, 57.93; H, 7.29; N, 25.33. Found: C, 58.00; H, 7.21; N, 25.16.

Synthesis of κ^2-Tt^RPt(R′)$_2$ Complexes. *(κ^2-Tt^{Ph})Pt(CH_3)$_2$ (**1-L1**).* $[Pt(CH_3)_2(SMe_2)_2]_2$ (0.040 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 removal of the solvent, the resulting oil was chromatographed on silica gel. The column was first flushed with ethyl acetate, and this was followed by methanol. The methanol eluant was collected, and the solvent was evaporated to produce (κ^2-Tt^{Ph})Pt(CH_3)$_2$ (0.020 g, 0.030 mmol) as a pale yellow solid in 61% yield (by Tt^{Ph} ligand). ^1H NMR (CD_2Cl_2, 288 K, δ): 9.91 (s, 1H, $Tt^{Ph}CH$), 8.82 (s, 2H, $Tt^{Ph}CH$), 7.80−7.58 (m, 15H, $Tt^{Ph}C_6H_5$), 0.91 (s, 6H, $^2J_{Pt-H}$ = 88 Hz, Pt-CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K, δ): −8.4 (s, 1P, $Tt^{Ph}P$═O, $^3J_{Pt-P}$ = 26 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K, δ): 139.1 (d, 1C, O═PC, $^1J_{P-C}$ = 167 Hz), 138.2 (d, 2C, O═PC, $^1J_{P-C}$ = 151 Hz), 136.2, 136.1 (s, 1C, 2C, *ipso*-Ph), 130.2, 130.0 (s, 4C, 2C, *o*-Ph), 129.5 (s, 3C, *p*-Ph), 129.5 (d, 2C, O═PCCH, $^2J_{P-C}$ = 25 Hz), 121.0, 120.7 (s, 4C, 2C, *m*-Ph), −19.4 (s, 2C, Pt-CH_3, $^1J_{Pt-C}$ = 839 Hz). Anal. Calcd for $C_{26}H_{29}N_9OPPt$: C, 44.26; H, 3.57; N, 17.87. Found: C, 44.41; H, 3.43; N, 17.60.

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*(κ²-Tt^{Cy})Pt(CH$_3$)$_2$ (**1-L2**).* [Pt(CH$_3$)$_2$(SMe$_2$)$_2$]$_2$ (0.040 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 this was followed by methanol. The methanol eluant was collected, and the solvent was evaporated to produce (κ²-Tt^{Cy})Pt(CH$_3$)$_2$ (0.034 g, 0.048 mmol) as a white solid in 68% yield (by Tt^{Cy} ligand). ^{1}H NMR (CD_2Cl_2, 290 K, δ): 9.26, 8.29 (s, 1H, 2H, Tt^{Cy}C*H*), 4.49 (m, 3H, C$_A$-*H*), 2.20−1.27 (m, 30H, cyclohexyl), 0.69 (s, 6H, $^2J_{Pt-H}$ = 88 Hz, Pt-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 291 K, δ): −6.5 (s, 1P, Tt^{Cy}*P*═O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K, δ): 138.4 (d, 1C, O═P*C*, $^1J_{P-C}$ = 167 Hz), 137.5 (d, 2C, O═P*C*, $^1J_{P-C}$ = 151 Hz), 130.5 (d, 2C, O═PC*C*H, $^2J_{P-C}$ = 32 Hz), 129.1 (d, 1C, O═PC*C*H, $^2J_{P-C}$ = 29 Hz), 62.3, 60.7 (s, 2C, 1C, C$_A$), 33.8−33.3 (s, 1:1:1, 6C, (C$_B$), 25.4−25.1 (s, 1:1:1 and 2:1, 9C, (C$_C$ and C$_D$)), −20.1 (s, 2C, Pt-*C*H$_3$, $^1J_{Pt-C}$ = 839 Hz).

*(κ²-Tt^{Ph})Pt(Ph)$_2$ (**2-L1**).* [Pt(Ph)$_2$(SEt$_2$)$_2$]$_2$ (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 eluant was collected, and the solvent was removed by rotary evaporation to produce (κ²-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}C*H*), 7.80−7.51 (m, 15H, Tt^{Ph}C$_6$*H*$_5$), 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═P*C*, $^1J_{P-C}$ = 170 Hz), 139.0 (d, 2C, O═P*C*, $^1J_{P-C}$ = 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═P*C*), 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═PC*C*H), 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.

*(κ²-Tt^{Cy})Pt(Ph)$_2$ (**2-L2**).* [Pt(Ph)$_2$(SEt$_2$)$_2$]$_2$ (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 eluant was collected and the solvent was removed by rotary evaporation to produce (κ²-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}C*H*), 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═P*C*, $^1J_{P-C}$ = 169 Hz), 138.1 (d, 2C, O═P*C*, $^1J_{P-C}$ = 149 Hz), 129.7 (d, 1C, O═PC*C*H, $^2J_{P-C}$ = 33 Hz), 129.1 (d, 2C, O═PC*C*H, $^2J_{P-C}$ = 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 $C_{36}H_{49}N_9OPPt$: C, 51.06; H, 5.47; N, 14.89. Found: C, 50.75; H, 5.54; N, 14.62.

Synthesis of [(κ³-Tt^{Ph})Pt(R′)$_2$R″][X] Complexes. *General Method A.* To a 50 mL Schlenk flask, κ²-Tt^{R}Pt(R′)$_2$ (0.030 mmol) was placed under nitrogen. CH_2Cl_2 (10 mL) was added through the septum, and the solution was treated with 1.3 equiv (0.045 mmol) of the appropriate electrophilic reagent at room temperature. After 10 min, the solvent was evaporated, and the resulting oil was triturated with pentane to afford the trialkyl platinum product as a light yellow powder in quantitative yield by ^{1}H NMR.

General Method B. To a 50 mL Schlenk flask, κ²-Tt^{R}Pt(R′)$_2$ (0.030 mmol) and $AgBF_4$ (0.10 mmol) were placed under nitrogen. CH_2Cl_2 (10 mL) was added through the septum, and the solution was treated with 1.3 equiv (0.045 mmol) of the appropriate electrophilic reagent at room temperature. After 20 min, the cloudy solution was cannula filtered five times. The solvent was evaporated and the resulting oil was triturated with pentane to afford the trialkyl platinum product as a light yellow powder in quantitative yield by ^{1}H NMR.

*[(κ³-Tt^{Ph})PtMe$_3$][X] (**3a-L1**).* The procedure in general method A was followed using methyl iodide or methyl triflate as the electrophile. NMR data for the OTf counterion complex are reported. ^{1}H NMR (CD_2Cl_2, 300 K, δ): 9.14 (s, 3H, Tt^{Ph}C*H*), 7.85−7.60 (m, 15H, Tt^{Ph}C$_6$*H*$_5$), 1.52 (s, 9H, $^2J_{Pt-H}$ = 74 Hz, Pt-C*H*$_3$). ^{31}P NMR (CD_2Cl_2, 300 K, δ): −9.9 (s, 1P, Tt^{Ph}*P*═O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 300 K, δ): 136.2 (d, 3C, O═P*C*, $^1J_{P-C}$ = 150 Hz), 135.6 (s, 3C, *ipso*-Ph), 131.8 (s, 3C, *p*-Ph), 130.8 (d, 3C, O═PC*C*H, $^2J_{P-C}$ = 24 Hz), 130.3 (s, 6C, *o*-Ph), 121.7 (s, 6C, *m*-Ph), −6.2 (s, 3C, Pt-CH$_3$, $^1J_{Pt-C}$ = 692 Hz). Anal. Calcd for $C_{28}H_{27}F_3N_9O_4PPtS$: C, 38.71; H, 3.13; N, 14.51. Found: C, 38.68; H, 3.02; N, 14.23.

*[(κ³-Tt^{Ph})PtMe$_3$][BAr′$_4$] ([**3a-L1**][BAr′$_4$]).* In a 50 mL Schlenk flask, **3a-L1** (0.020 g, 0.027 mmol) and NaBAr′$_4$ (0.057 g, 0.080 mmol) were placed under nitrogen. CH_2Cl_2 (6 mL) was added through the septum, and the solution was allowed to stir for 1 h. The solution was cannula filtered three times and then concentrated to ca. 1 mL. Slow diffusion of hexanes into the CH_2Cl_2 solution produced clear, hexagonal crystals suitable for X-ray diffraction.

*[(κ³-Tt^{Cy})PtMe$_3$][X] (**3a-L2**).* The procedure in general method A was followed using methyl iodide or methyl triflate as the electrophile. NMR data for the OTf counterion complex are reported. ^{1}H NMR (CD_2Cl_2, 300 K, δ): 8.68 (s, 3H, Tt^{Cy}C*H*), 4.65 (m, 3H, C$_A$-*H*), 2.22−1.30 (m, 30H, cyclohexyl), 1.32 (s, 9H, $^2J_{Pt-H}$ = 73 Hz, Pt-C*H*$_3$). ^{31}P NMR (CD_2Cl_2, 300 K, δ): −7.5 (s, 1P, Tt^{Cy}*P*═O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 300 K, δ): 135.6 (d, 3C, O═P*C*, $^1J_{P-C}$ = 150 Hz), 130.1 (d, 3C, O═PC*C*H, $^2J_{P-C}$ = 24 Hz), 63.4 (s, 3C, C$_A$), 33.5 (s, 6C, C$_B$), 25.3 (s, 6C, C$_C$), 25.1 (s, 3C, C$_D$), −6.7 (s, 3C, Pt-CH$_3$, $^1J_{Pt-C}$ = 692 Hz). Anal. Calcd for $C_{28}H_{45}F_3N_9O_4PPtS$: C, 37.92; H, 5.11; N, 14.21. Found: C, 37.65; H, 4.94; N, 13.98.

*[(κ³-Tt^{Ph})PtMe$_2$Et][X] (**3b-L1**).* The procedure in general method A was followed using ethyl iodide or ethyl triflate as the electrophile. NMR data for the OTf counterion complex are reported. ^{1}H NMR (CD_2Cl_2, 300 K, δ): 9.18, 9.13 (s, 2H, 1H, Tt^{Ph}C*H*), 7.84, 7.57 (m, 15H, Tt^{Ph}C$_6$*H*$_5$), 2.41 (q, 2H, $^2J_{Pt-H}$ = 75 Hz, Pt-C*H*$_2$-CH$_3$), 1.49 (s, 6H, $^2J_{Pt-H}$ = 75 Hz, Pt-C*H*$_3$), 0.87 (t, 3H, $^3J_{Pt-H}$ = 56 Hz, Pt-CH$_2$-*C*H$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 300 K, δ): −8.6 (s, 1P, Tt^{Ph}*P*═O). ^{13}C {^{1}H} NMR (CD_2Cl_2, 293 K, δ): 136.9 (d, 1C, O═P*C*, $^1J_{P-C}$ = 151 Hz), 136.7 (d, 2C, O═P*C*, $^1J_{P-C}$ = 150 Hz), 136.2, 136.1 (s, 1C, 2C, *ipso*-Ph), 131.3, 131.2 (s, 2C, 1C, *p*-Ph), 131.0 (d, 2C, O═PC*C*H, $^2J_{P-C}$ = 24 Hz), 130.8 (d, 1C, O═PC*C*H, $^2J_{P-C}$ = 22 Hz), 130.6, 130.5 (s, 4C, 2C, *o*-Ph), 122.1, 122.0 (s, 2C, 4C, *m*-Ph), 16.0 (s, 1C, Pt-*C*H$_2$CH$_3$, $^2J_{Pt-C}$ = 33 Hz), 9.2 (s, 1C, Pt-CH$_2$*C*H$_3$, $^1J_{Pt-C}$ = 681 Hz), −4.1 (s, 2C, Pt-CH$_3$, $^1J_{Pt-C}$ = 725 Hz). Anal. Calcd for $C_{29}H_{29}F_3N_9O_4PPtS$: C, 39.46; H, 3.31; N, 14.28. Found: C, 39.16; H, 3.17; N, 13.99.

*[(κ³-Tt^{Cy})PtMe$_2$Et][X] (**3b-L2**).* The procedure in general method A was followed using ethyl iodide or ethyl triflate as the electrophile. NMR data for the OTf counterion complex are reported. ^{1}H NMR (CD_2Cl_2, 292 K, δ): 8.65, 8.60 (s, 2H, 1H, Tt^{Cy}C*H*), 4.65 (m, 3H, C$_A$-*H*), 2.22 (q, 2H, $^2J_{Pt-H}$ = 75 Hz, Pt-C*H*$_2$-CH$_3$), 2.24−1.30 (m, 30H, cyclohexyl), 1.31 (s, 6H, $^2J_{Pt-H}$ = 75 Hz, Pt-C*H*$_3$), 0.69 (s, 3H, $^3J_{Pt-H}$ = 55 Hz, Pt-CH$_2$-*C*H$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 294 K, δ): −7.7 (s, 1P, Tt^{Cy}*P*═O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 292 K, δ): 136.0 (d, 1C, O═P*C*, $^1J_{P-C}$ = 150 Hz), 135.9 (d, 2C, O═P*C*, $^1J_{P-C}$ = 150 Hz), 130.1 (d, 2C, O═PC*C*H, $^2J_{P-C}$ = 25 Hz), 139.8 (d, 1C, O═PC*C*H, $^2J_{P-C}$ = 25 Hz), 63.4 (s, 1C, 2C, C$_A$) 33.6−33.5 (s, 1:1:1, 6C, C$_B$), 25.3−25.2 (s, 1:1:1 and 2:1, 9C, C$_C$ and C$_D$), 15.8 (s, 1C, $^2J_{Pt-C}$ = 33 Hz, Pt-CH$_2$-CH$_3$), 8.4 (s, 1C, $^1J_{Pt-C}$ = 682 Hz, Pt-CH$_2$-CH$_3$), −4.9 (s, 2C, $^1J_{Pt-C}$ = 726 Hz, Pt-CH$_3$). Anal. Calcd for $C_{29}H_{47}F_3N_9O_4PPtS$: C, 38.66; H, 5.26; N, 13.99. Found: C, 38.42; H, 4.98; N, 13.87.

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[(κ³-Tt^{Ph})PtMe$_2$^{n}Pr][I] (**3c-L1**). The procedure in general method A was followed using *n*-propyl iodide as the electrophile. The reaction was stirred overnight instead of 10 min. ^{1}H NMR (CD_2Cl_2, 300 K, δ): 9.52, 9.40 (s, 2H, 1H, Tt^{Ph}C*H*), 7.89−7.58 (m, 15H, Tt^{Ph}C$_6$*H*$_5$), 2.33 (t, 2H, $^2J_{Pt-H}$ = 73 Hz, Pt-C*H*$_2$-CH$_2$-CH$_3$), 1.58 (s, 6H, $^2J_{Pt-H}$ = 74 Hz, Pt-C*H*$_3$), 1.30 (m, 2H, Pt-CH$_2$-C*H*$_2$-CH$_3$), 0.80 (t, 3H, Pt-CH$_2$-CH$_2$-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 300 K, δ): −9.8 (s, 1P, Tt^{Ph}*P*═O). ^{13}C {^{1}H} NMR (CD_2Cl_2, 300 K, δ): 136.5 (d, 1C, O═PC, $^1J_{P-C}$ = 150 Hz), 136.4 (d, 2C, O═PC, $^1J_{P-C}$ = 151 Hz), 136.4, 135.7 (s, 1C, 2C, *ipso*-Ph), 131.1 (d, 2C, O═PCCH, $^2J_{P-C}$ = 24 Hz), 130.9, 130.8 (s, 2C, 1C, *p*-Ph), 130.3, 130.2 (s, 4C, 2C, *o*-Ph), 121.8, 121.6 (s, 1C, 2C, *m*-Ph), 23.9 (s, 1C, $^3J_{Pt-C}$ = 29 Hz, Pt-CH$_2$CH$_2$CH$_3$), 17.9 (s, 1C, $^1J_{Pt-C}$ = 822 Hz, Pt-CH$_2$CH$_2$CH$_3$), 15.4 (s, 1C, $^2J_{Pt-C}$ = 80 Hz, Pt-CH$_2$CH$_2$CH$_3$), −4.6 (s, 2C, $^1J_{Pt-C}$ = 723 Hz, Pt-CH$_3$). Anal. Calcd for $C_{29}H_{31}IN_9OPPt$: C, 39.83; H, 3.57; N, 14.41. Found: C, 40.01; H, 3.47; N, 14.37.

[(κ³-Tt^{Cy})PtMe$_2$^{n}Pr][I] (**3c-L2**). The procedure in general method A was followed using *n*-propyl iodide as the electrophile. The reaction was stirred overnight instead of 10 min. ^{1}H NMR (CD_2Cl_2, 292 K, δ): 8.95, 8.88 (s, 2H, 1H, Tt^{Cy}C*H*), 4.78 (m, 3H, C$_A$-*H*), 2.13 (t, 2H, $^2J_{Pt-H}$ = 72 Hz, Pt-C*H*$_2$-CH$_2$-CH$_3$), 2.20−1.15 (m, 30H, cyclohexyl), 1.29 (s, 6H, $^2J_{Pt-H}$ = 75 Hz, Pt-C*H*$_3$), 0.70 (s, 3H, Pt-CH$_2$-CH$_2$-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 294 K, δ): −9.21 (s, 1P, Tt^{Cy}*P*═O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 292 K, δ): 135.5 (d, 1C, $^1J_{P-C}$ = 151 Hz, O═PC), 135.3 (d, 2C, $^1J_{P-C}$ = 150 Hz, O═P*C*), 130.3 (d, 2C, $^2J_{P-C}$ = 25 Hz, O═PCC*H*), 130.0 (d, 1C, $^2J_{P-C}$ = 25 Hz, O═PCC*H*), 63.0 (s, 1C, 2C, C$_A$), 33.4−33.3 (s, 1:1:1, 6C, C$_B$), 25.3−24.9 (s, 1:1:1 and 2:1, 9C, C$_C$ and C$_D$), 23.8 (s, 1C, $^3J_{Pt-C}$ = 28 Hz, Pt-CH$_2$-CH$_2$-CH$_3$), 17.3 (s, 1C, $^1J_{Pt-C}$ = 681 Hz, Pt-*C*H$_2$-CH$_2$-CH$_3$), 15.5 (s, 1C, $^2J_{Pt-C}$ = 77 Hz, Pt-CH$_2$-*C*H$_2$-CH$_3$), −5.2 (s, 2C, $^1J_{Pt-C}$ = 722 Hz, Pt-CH$_3$). Anal. Calcd for $C_{30}H_{49}IN_9O_4PPt$: C, 39.02; H, 5.53; N, 14.12. Found: C, 38.84; H, 5.25; N, 14.24.

[(κ³-Tt^{Ph})PtMe$_2$(CH$_2$CH═CH$_2$)][I] (**3d-L1**). The procedure in general method A was followed using allyl iodide as the electrophile. ^{1}H NMR (CD_2Cl_2, 294 K, δ): 9.40, 9.36 (s, 2H, 1H, Tt^{Ph}C*H*), 7.92, 7.61 (m, 15H, Tt^{Ph}C$_6$*H*$_5$), 6.01 (m, 1H, Pt-CH$_2$*C*H═CH$_2$), 5.10 (d, 1H, $^3J_{H-H}$ = 17 Hz, $^4J_{Pt-H}$ = 20 Hz, Pt-CH$_2$CH═C*H*$_{trans}$), 4.91 (d, 1H, $^3J_{H-H}$ = 9 Hz, $^4J_{Pt-H}$ = 20 Hz, Pt-CH$_2$CH⟩C*H*$_s$), 3.22 (d, 2H, $^2J_{Pt-H}$ = 96 Hz, Pt-C*H*$_2$CH⟩CH$_2$), 1.57 (s, 6H, $^2J_{Pt-H}$ = 74 Hz, Pt-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 294 K, δ): −9.91 (s, 1P, Tt^{Ph}*P*═O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K, δ): 141.5 (s, 1C, $^2J_{Pt-C}$ = 54 Hz, Pt-CH$_2$*C*H═CH$_2$), 136.4 (d, 1C, O═PC, $^1J_{P-C}$ = 150 Hz), 136.0 (d, 2C, O═P*C*, $^1J_{P-C}$ = 150 Hz), 135.6 (s, 3C, *ipso*-Ph), 131.0 (d, 1C, 2C, O═PCC*H*, $^2J_{P-C}$ = 24 Hz), 131.0 (s, 2C, 1C, *p*-Ph), 130.3, 130.2 (s, 4C, 2C, *o*-Ph), 121.7, 121.6 (s, 2C, 4C, *m*-Ph), 112.8 (s, 1C, $^3J_{Pt-C}$ = 51 Hz, Pt-CH$_2$CH═*C*H$_2$), 15.7 (s, 1C, $^1J_{Pt-C}$ = 656 Hz, Pt-CH$_2$*C*H═CH$_2$), −4.8 (s, 2C, Pt-CH$_3$, $^1J_{Pt-C}$ = 706 Hz). Anal. Calcd for $C_{29}H_{29}IN_9OPPt$: C, 39.92; H, 3.35; N, 14.45. Found: C, 39.64; H, 3.19; N, 14.19.

[(κ³-Tt^{Cy})PtMe$_2$(CH$_2$CH═CH$_2$)][I] (**3d-L2**). The procedure in general method A was followed using allyl iodide as the electrophile. ^{1}H NMR (CD_2Cl_2, 292 K, δ): 8.87, 8.82 (s, 2H, 1H, Tt^{Cy}C*H*), 5.85 (m, 1H, Pt-CH$_2$*C*H⟩CH$_2$), 4.90 (d, 1H, $^3J_{H-H}$ = 17 Hz, $^4J_{Pt-H}$ = 18 Hz, Pt-CH$_2$CH⟩C*H*$_{trans}$), 4.76 (m, 3H, C$_A$-*H*), 3.00 (d, 2H, $^2J_{Pt-H}$ = 96 Hz, Pt-C*H*$_2$CH⟩CH$_2$), 2.21−1.28 (m, 30H, cyclohexyl), 1.36 (s, 6H, $^2J_{Pt-H}$ = 74 Hz, Pt-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 300 K, δ): −8.3 (s, 1P, Tt^{Cy}*P*═O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K, δ): 142.1 (s, 1C, $^2J_{Pt-C}$ = 54 Hz, Pt-CH$_2$CH═CH$_2$), 135.6 (d, 1C, O═PC, $^1J_{P-C}$ = 150 Hz), 135.1 (d, 2C, O═PC, $^1J_{P-C}$ = 150 Hz), 130.3, 130.1 (d, 2C, 1C, O═PCC*H*, $^2J_{P-C}$ = 24 Hz), 112.3 (s, 1C, $^3J_{Pt-C}$ = 50 Hz, Pt-CH$_2$CH═*C*H$_2$), 15.2 (s, 1C, $^1J_{Pt-C}$ = 656 Hz, Pt-*C*H$_2$CH═CH$_2$), 63.2 (s, 1C, 2C, C$_A$), 33.5−33.3 (s, 1:1:1, 6C, C$_B$), 25.3−24.9 (s, 1:1:1 and 2:1, 9C, C$_C$ and C$_D$), −4.1 (s, 2C, Pt-CH$_3$, $^1J_{Pt-C}$ = 706 Hz). Anal. Calcd for $C_{29}H_{47}IN_9OPPt$: C, 39.10; H, 5.32; N, 14.15. Found: C, 38.83; H, 5.25; N, 13.88.

[(κ³-Tt^{Ph})PtMe$_2$(CH$_2$C(CH$_3$)═CH$_2$)][BF$_4$] (**3e-L1**). The procedure in general method B was followed using 3-bromo-isobutylene as the electrophile. ^{1}H NMR (CD_2Cl_2, 292 K, δ): 9.21, 9.17 (s, 2H, 1H, Tt^{Ph}C*H*), 7.84, 7.62 (m, 15H, Tt^{Ph}C$_6$*H*$_5$), 4.91, 4.85 (s, 1H, 1H, $^4J_{Pt-H}$ = 21 Hz, $^4J_{Pt-H}$ = 22 Hz, Pt-CH$_2$C(CH$_3$)⟩C*H*$_2$), 3.27 (s, 2H, $^2J_{Pt-H}$ = 96 Hz, Pt-Pt-C*H*$_2$C(CH$_3$)⟩CH$_2$), 1.58 (s, 6H, $^2J_{Pt-H}$ = 75 Hz, Pt-C*H*$_3$), 1.45 (s, 3H, $^4J_{Pt-H}$ = 10 Hz, Pt-CH$_2$C(C*H*$_3$)⟩CH$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 292 K, δ): −7.0 (s, 1P, Tt^{Ph}*P*═O). ^{13}C {^{1}H} NMR (CD_2Cl_2, 292 K, δ): 148.9 (s, 1C, $^2J_{Pt-C}$ = 26 Hz, Pt-CH$_2$CH═CH$_2$), 136.9 (d, 1C, O═PC, $^1J_{P-C}$ = 150 Hz), 136.4 (d, 2C, O═PC, $^1J_{P-C}$ = 151 Hz), 136.0 (s, 3C, *ipso*-Ph), 131.4 (s, 2C, 1C, *p*-Ph), 130.7, 130.6 (s, 4C, 2C, *o*-Ph), 130.5 (d, 2C, O═PCCH, $^2J_{P-C}$ = 24 Hz), 121.8, 121.6 (s, 2C, 4C, *m*-Ph), 112.0 (s, 1C, $^3J_{Pt-C}$ = 41 Hz, Pt-CH$_2$CH═*C*H$_2$), 23.8 (s, 1C, $^3J_{Pt-C}$ = 8 Hz, Pt-CH$_2$C(*C*H$_3$)═CH$_2$), 20.7 (s, 1C, $^1J_{Pt-C}$ = 657 Hz, Pt-CH$_2$C(CH$_3$)═CH$_2$), −2.8 (s, 2C, Pt-*C*H$_3$, $^1J_{Pt-C}$ = 709 Hz). HRMS (ESI) *m*/*z* Calcd: 759.2037 (M$^+$). Found: 759.2024.

[(κ³-Tt^{Cy})PtMe$_2$(CH$_2$C(CH$_3$)═CH$_2$)][BF$_4$] (**3e-L2**). The procedure in general method B was followed using 3-bromo-isobutylene as the electrophile. ^{1}H NMR (CD_2Cl_2, 300 K, δ): 8.78, 8.72 (s, 2H, 1H, Tt^{Cy}C*H*), 4.92, 4.82 (s, 1H, 1H, $^4J_{Pt-H}$ = 17 Hz, $^4J_{Pt-H}$ = 18 Hz, Pt-CH$_2$C(Me)⟩C*H*$_2$), 4.68 (m, 3H, C$_A$-*H*), 3.18 (s, 2H, $^2J_{Pt-H}$ = 94 Hz, Pt-C*H*$_2$C(CH$_3$)⟩CH$_2$), 2.37−1.41 (m, 30H, cyclohexyl), 1.42 (s, 6H, $^2J_{Pt-H}$ = 73 Hz, Pt-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 292 K, δ): −4.1 (s, 1P, Tt^{Cy}*P*═O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K, δ): 154.4 (s, 1C, Pt-CH$_2$C(CH$_3$)═CH$_2$), 135.0 (d, 1C, O═P*C*, $^1J_{P-C}$ = 154 Hz), 134.9 (d, 2C, O═PC, $^1J_{P-C}$ = 153 Hz), 130.5, 130.2 (d, 2C, 1C, O═PCCH, $^2J_{P-C}$ = 24 Hz), 104.8 (s, 1C, Pt-CH$_2$C(CH$_3$)═*C*H$_2$), 63.5, 63.4 (s, 2C, 1C, C$_A$), 33.5−33.2 (s, 1:1:1, 6C, C$_B$), 25.2−25.0 (s, 1:1:1 and 2:1, 9C, C$_C$ and C$_D$), 23.9 (s, 1C, Pt-CH$_2$C(*C*H$_3$)═CH$_2$), 19.6 (s, 1C, $^1J_{Pt-C}$ = 663 Hz, Pt-CH$_2$C(CH$_3$)═CH$_2$), −3.1 (s, 2C, Pt-*C*H$_3$, $^1J_{Pt-C}$ = 697 Hz). HRMS (ESI) *m*/*z* Calcd: 777.3446 (M$^+$). Found: 777.3412.

[(κ³-Tt^{Ph})PtMe$_2$(CH$_2$C$_6$H$_5$)][BF$_4$] (**3f-L1**). The procedure in general method A was followed using benzyl iodide as the electrophile. ^{1}H NMR (CD_2Cl_2, 292 K, δ): 9.20, 9.17 (s, 2H, 1H, Tt^{Ph}C*H*), 7.83, 7.60 (m, 15H, Tt^{Ph}C$_6$*H*$_5$), 6.96−6.84 (m, 5H, Pt-CH$_2$-C$_6$*H*$_5$), 3.82 (s, 2H, $^2J_{Pt-H}$ = 93 Hz, Pt-C*H*$_2$-C$_6$H$_5$), 1.61 (s, 6H, $^2J_{Pt-H}$ = 74 Hz, Pt-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 292 K, δ): −7.73 (s, 1P, Tt^{Ph}*P*═O). ^{13}C {^{1}H} NMR (CD_2Cl_2, 293 K, δ): 145.1 (s, 1C, $^2J_{Pt-C}$ = 48 Hz, Pt-Bn *ipso*-Ph), 136.9 (d, 1C, O═PC, $^1J_{P-C}$ = 151 Hz), 136.0 (d, 2C, O═P*C*, $^1J_{P-C}$ = 152 Hz), 136.0, 135.9 (s, 1C, 2C, Tt^{Ph} *ipso*-Ph), 131.3, 131.2 (s, 1C, 2C, Tt^{Ph} *p*-Ph), 130.7 (d, 1C, 2C, O═PCCH, $^2J_{P-C}$ = 21 Hz), 130.6, 130.5 (s, 2C, 4C, Tt^{Ph} *o*-Ph), 129.6 (s, 2C, $^3J_{Pt-C}$ = 21 Hz, Pt-Bn *o*-Ph), 128.2 (s, 2C, $^4J_{Pt-C}$ = 12 Hz, Pt-Bn *m*-Ph), 125.4 (s, 1C, $^5J_{Pt-C}$ = 14 Hz, Pt-Bn *p*-Ph), 121.9, 121.7 (s, 2C, 4C, Tt^{Ph} *m*-Ph), 17.8 (s, 1C, $^1J_{Pt-C}$ = 658 Hz, Pt-CH$_2$C$_6$H$_5$), −2.6 (s, 1C, $^1J_{Pt-C}$ = 707 Hz, Pt-CH$_3$). HRMS (ESI) *m*/*z* Calcd: 795.2037 (M$^+$). Found: 795.2012.

[(κ³-Tt^{Cy})PtMe$_2$(CH$_2$C$_6$H$_5$)][BF$_4$] (**3f-L2**). The procedure in general method A was followed using benzyl iodide as the electrophile. ^{1}H NMR (CD_2Cl_2, 292 K, δ): 8.58 (s, 3H, Tt^{Cy}C*H*), 7.00−6.80 (m, 5H, Pt-CH$_2$-C$_6$*H*$_5$), 4.62, 4.48 (m, 1H, 2H, C$_A$-*H*), 3.63 (s, 2H, $^2J_{Pt-H}$ = 94 Hz, Pt-C*H*$_2$-C$_6$H$_5$), 2.24−1.30 (m, 30H, cyclohexyl), 1.39 (s, 6H, $^2J_{Pt-H}$ = 74 Hz, Pt-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 294 K, δ): −7.0 (s, 1P, Tt^{Cy}*P*═O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 292 K, δ): 145.4 (s, 1C, $^2J_{Pt-C}$ = 47 Hz, Pt-Bn *ipso*-Ph), 135.8 (d, 1C, O═PC, $^1J_{P-C}$ = 150 Hz), 135.0 (d, 2C, O═PC, $^1J_{P-C}$ = 151 Hz), 129.7 (d, 3C, O═PCCH, $^2J_{P-C}$ = 25 Hz), 129.4 (s, 2C, $^3J_{Pt-C}$ = 21 Hz, Pt-Bn *o*-Ph), 128.1 (s, 2C, $^4J_{Pt-C}$ = 13 Hz, Pt-Bn *m*-Ph), 124.9 (s, 1C, $^5J_{Pt-C}$ = 14 Hz, Pt-Bn *p*-Ph), 63.3, 63.2 (s, 1C, 2C, C$_A$), 33.4−33.1 (s, 1:1:1, 6C, C$_B$), 25.1−25.0 (s, 1:1:1 and 2:1, 9C, C$_C$ and C$_D$), 16.9 (s, 1C, $^1J_{Pt-C}$ = 658 Hz, Pt-CH$_2$C$_6$H$_5$), −3.5 (s, 2C, $^1J_{Pt-C}$ = 706 Hz, Pt-CH$_3$). HRMS (ESI) *m*/*z* Calcd: 813.3446 (M$^+$). Found: 813.3454.

[(κ³-Tt^{Ph})Pt(Ph)$_2$Me][X] (**4a-L1**). The procedure in general method A was followed using methyl iodide or methyl triflate as the electrophile. NMR data for the OTf counterion complex are reported. ^{1}H NMR (CD_2Cl_2, 292 K, δ): 9.25, 9.23 (s, 2H, 1H, Tt^{Ph}C*H*), 7.80−7.57 (m, 15H, Tt^{Ph}C$_6$*H*$_5$), 7.23 (d, 4H, $^3J_{Pt-H}$ = 52 Hz, Pt-Ar *H*$_o$), 7.07−6.98 (m, 6H, Pt-Ar *H*$_m$ and *H*$_p$), 2.27 (s, 3H, $^2J_{Pt-H}$ = 74 Hz, Pt-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 295 K, δ): −10.1 (s, 1P, Tt^{Ph}*P*═O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K, δ): 136.8 (d, 2C, $^1J_{P-C}$ = 150 Hz, O═PC), 136.5 (d, 1C, O═PC, $^1J_{P-C}$ = 150 Hz), 136.1 (s, 4C, $^3J_{Pt-C}$ = 10 Hz, Pt-Ar *m*-Ph), 135.8, 135.7 (s, 1C, 2C, Tt^{Ph}

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ipso-Ph), 131.5 (d, 2C, $^2J_{P-C}$ = 25 Hz, O=PCCH), 131.1 (s, 3C, Tt^{Ph} *p*-Ph), 131.0 (d, 1C, $^2J_{P-C}$ = 24 Hz, O=PCCH), 130.3, 130.2 (s, 2C, 4C, Tt^{Ph} *o*-Ph), 127.9 (s, 2C, $^1J_{Pt-C}$ = 944 Hz, Pt-Ar *ipso*-Ph), 127.2 (s, 4C, $^2J_{Pt-C}$ = 56 Hz, Pt-Ar *o*-Ph), 125.0 (s, 2C, Pt-Ar *p*-Ph), 122.0, 121.8 (s, 4C, 2C, Tt^{Ph} *m*-Ph), 7.3 (s, 1C, $^1J_{Pt-C}$ = 689 Hz, Pt-CH_3). Anal. Calcd for $C_{38}H_{31}F_3N_9O_4PPtS$: C, 45.97; H, 3.15; N, 12.70. Found: C, 45.72; H, 3.26; N, 12.48.

[(κ^3-Tt^{Cy})Pt(Ph)$_2$Me][X] ***(4a-L2)***. The procedure in general method A was followed using methyl iodide or methyl triflate as the electrophile. NMR data for the OTf counterion complex are reported. ^{1}H NMR (CD_2Cl_2, 300 K, δ): 9.01, 9.00 (s, 2H, 1H, Th^{Cy}C*H*), 7.04 (d, 4H, $^3J_{Pt-H}$ = 30 Hz, H_o), 7.02−6.93 (m, 6H, H_m and H_p), 4.65 (m, 3H, NC*H*(Cy)), 2.20−1.27 (m, 30H, cyclohexyl), 2.07 (s, 3H, $^2J_{Pt-H}$ = 74 Hz, Pt-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 300 K, δ): −8.3 (s, 1P, Tt^{Cy}*P*=O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 292 K, δ): 136.4 (s, 4C, $^3J_{P-C}$ = 13 Hz, Pt-Ar *m*-Ph), 136.1 (d, 2C, O=P*C*, $^1J_{P-C}$ = 150 Hz), 135.5 (d, 1C, O=P*C*, $^1J_{P-C}$ = 151 Hz), 130.9 (d, 3C, O=PC*C*H, $^2J_{P-C}$ = 23 Hz), 128.3 (s, 2C, $^1J_{Pt-C}$ = 941 Hz, Pt-Ar *ipso*-Ph), 127.2 (s, 4C, $^2J_{Pt-C}$ = 56 Hz, Pt-Ar *o*-Ph), 125.0 (s, 2C, Pt-Ar *p*-Ph), 63.6, 63.5 (s, 2C, 1C, NCH(cyclohexyl)), 33.3−33.0 (s, 1:1:1, 6C, CB), 25.1−25.0 (s, 1:1:1 and 2:1, 9C, CC and CD), 6.5 (s, 1C, $^1J_{Pt-C}$ = 689 Hz, Pt-*C*H$_3$). HRMS (ESI) *m*/*z* Calcd: 861.3446 (M$^+$). Found: 861.3465.

[(κ^3-Tt^{Ph})Pt(Ph)$_2$Et][X] ***(4b-L1)***. The procedure in general method A was followed using ethyl iodide or ethyl triflate as the electrophile. NMR data for the OTf counterion complex are reported. ^{1}H NMR (CD_2Cl_2, 300 K, δ): 9.37, 9.25 (s, 2H, 1H, Tt^{Ph}C*H*), 7.84−7.60 (m, 15H, Tt^{Ph}C$_6$*H*$_5$), 7.20 (d, 4H, $^3J_{Pt-H}$ = 51 Hz, Pt-Ar H_o), 7.07, 6.99 (m, 6H, Pt-Ar H_m and H_p), 3.17 (q, 2H, $^2J_{Pt-H}$ = 70 Hz, Pt-C*H*$_2$-CH$_3$), 0.86 (t, 3H,$^3J_{Pt-H}$ = 54 Hz, Pt-CH$_2$-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 295 K, δ): −10.5 (s, 1P, Tt^{Ph}*P*=O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K, δ): 137.1 (d, 2C, O=P*C*, $^1J_{P-C}$ = 149 Hz), 136.9 (d, 1C, O=P*C*, $^1J_{P-C}$ = 152 Hz), 135.9 (s, 4C, Pt-Ar *m*-Ph), 135.7 (s, 3C, Tt^{Ph} *ipso*-Ph), 131.1 (d, 2C, O=PC*C*H, $^2J_{P-C}$ = 24 Hz), 131.1, 130.9 (s, 2C, 1C, Tt^{Ph} *p*-Ph), 130.8 (d, 1C, O=PC*C*H, $^2J_{P-C}$ = 24 Hz), 130.3, 130.2 (s, 4C, 2C, Tt^{Ph} *o*-Ph), 128.6 (s, 2C, $^1J_{Pt-C}$ = 907 Hz, Pt-Ar *ipso*-Ph), 127.1 (s, 4C, $^2J_{Pt-C}$ = 57 Hz, Pt-Ar *o*-Ph), 124.9 (s, 2C, Pt-Ar *p*-Ph), 121.9, 121.8 (s, 4C, 2C, Tt^{Ph} *m*-Ph), 22.3 (s, 1C, $^1J_{Pt-C}$ = 665 Hz, Pt-*C*H$_2$-CH$_3$), 16.8 (s, 1C, $^2J_{Pt-C}$ = 43 Hz, Pt-CH$_2$-*C*H$_3$). Anal. Calcd for $C_{39}H_{33}F_3N_9O_4PPtS$: C, 46.52; H, 3.30; N, 12.52. Found: C, 46.24; H, 3.28; N, 12.29.

[(κ^3-Tt^{Cy})Pt(Ph)$_2$Et][X] ***(4b-L2)***. The procedure in general method A was followed using ethyl iodide or ethyl triflate as the electrophile. NMR data for the OTf counterion complex are reported. ^{1}H NMR (CD_2Cl_2, 292 K, δ): 8.86, 8.77 (s, 2H, 1H, Th^{Cy}C*H*), 7.03−6.93 (m, 10H, Pt-C$_6$*H*$_5$), 4.63, 4.58 (m, 2H, 1H, C$_A$-*H*), 2.94 (q, 2H, $^2J_{Pt-H}$ = 67 Hz, Pt-C*H*$_2$-CH$_3$), 2.95−1.26 (m, 30H, cyclohexyl), 0.61 (s, 3H, $^3J_{Pt-H}$ = 54 Hz, Pt-CH$_2$-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 300 K, δ): −7.2 (s, 1P, Tt^{Cy}*P*=O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 292 K, δ): 136.3 (d, 2C, O=P*C*, $^1J_{P-C}$ = 148 Hz), 136.2 (s, 4C, Pt-Ar *m*-Ph), 136.0 (d, 1C, O=P*C*, $^1J_{P-C}$ = 150 Hz), 130.4 (d, 2C, O=PC*C*H, $^2J_{P-C}$ = 24 Hz), 130.1 (d, 1C, O=PC*C*H, $^2J_{P-C}$ = 25 Hz), 129.0 (s, 2C, $^1J_{Pt-C}$ = 968 Hz, Pt-Ar *ipso*-Ph), 127.2 (s, 4C, $^2J_{Pt-C}$ = 57 Hz, Pt-Ar *o*-Ph), 125.0 (s, 2C, Pt-Ar *p*-Ph), 63.4, 63.3 (s, 2C, 1C, C$_A$), 33.3−33.2 (s, 1:1:1, 6C, C$_B$), 25.1−24.9 (s, 1:1:1 and 2:1, 9C, C$_C$ and C$_D$), 21.4 (s, 1C, $^1J_{Pt-C}$ = 665 Hz, Pt-CH$_2$-CH$_3$), 16.9 (s, 1C, $^2J_{Pt-C}$ = 43 Hz, Pt-CH$_2$-*C*H$_3$). HRMS (ESI) *m*/*z* Calcd: 875.3602 (M$^+$). Found: 875.3565.

[(κ^3-Tt^{Ph})Pt(Ph)$_2$(CH$_2$CH=CH$_2$)][BF$_4$] ***(4c-L1)***. The procedure in general method B was followed using allyl iodide as the electrophile. ^{1}H NMR (CD_2Cl_2, 294 K, δ): 9.28, 9.30 (s, 2H, 1H, Tt^{Ph}C*H*), 7.80, 7.58 (m, 15H, Tt^{Ph}C$_6$*H*$_5$), 7.22 (d, 4H, $^3J_{Pt-H}$ = 50 Hz, Pt-Ar H_o), 7.08, 7.02 (m, 6H, Pt-Ar H_m and H_p), 5.83 (m, 1H, Pt-CH$_2$C*H*⟩CH$_2$), 5.10 (d, 1H, $^3J_{H-H}$ = 19 Hz, $^4J_{Pt-H}$ = 18 Hz, Pt-CH$_2$CH⟩C*H*$_{trans\ to\ H}$), 4.92 (d, 1H, $^3J_{H-H}$ = 10 Hz, $^4J_{Pt-H}$ = 15 Hz, Pt-CH$_2$CH⟩C*H*$_{s\ to\ H}$), 3.90 (d, 2H, $^2J_{Pt-H}$ = 86 Hz, Pt-C*H*$_2$CH⟩CH$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 270 K, δ): −8.0 (s, 1P, Tt^{Ph}*P*=O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K, δ): 140.9 (s, 1C, $^2J_{Pt-C}$ = 65 Hz, Pt-CH$_2$CH=CH$_2$), 136.8 (d, 2C, O=P*C*, $^1J_{P-C}$ = 150 Hz), 136.7 (d, 1C, O=P*C*, $^1J_{P-C}$ = 150 Hz), 136.1 (s, 4C, Pt-Ar *m*-Ph), 135.7 (s, 3C, Tt^{Ph} *ipso*-Ph), 131.2, 131.1 (s, 2C, 1C, Tt^{Ph} *p*-Ph), 130.9 (d, 3C, O=PCCH, $^2J_{P-C}$ = 24 Hz), 130.5, 130.4 (s, 4C, 2C, Tt^{Ph} *o*-Ph), 128.5 (s, 2C, $^1J_{Pt-C}$ = 951 Hz, Pt-Ar *ipso*-Ph), 127.3 (s, 4C, $^2J_{Pt-C}$ = 56 Hz, Pt-Ar *o*-Ph), 125.2 (s, 2C, Pt-Ar *p*-Ph), 121.8, 121.7 (s, 2C, 4C, Tt^{Ph} *m*-Ph), 115.4 (s, 1C, $^3J_{Pt-C}$ = 49 Hz, Pt-CH$_2$CH=*C*H$_2$), 27.3 (s, 1C, $^1J_{Pt-C}$ = 643 Hz, Pt-*C*H$_2$CH=CH$_2$). HRMS (ESI) *m*/*z* Calcd: 869.2194 (M$^+$). Found: 869.2152.

[(κ^3-Tt^{Cy})Pt(Ph)$_2$(CH$_2$CH=CH$_2$)][BF$_4$] ***(4c-L2)***. The procedure in general method B was followed using allyl iodide as the electrophile. ^{1}H NMR (CD_2Cl_2, 294 K, δ): 8.87, 9.30 (s, 2H, 1H, Tt^{Cy}C*H*), 7.07−6.97 (m, 10H, Pt-C$_5$*H*$_6$), 5.80 (m, 1H, Pt-CH$_2$C*H*⟩CH$_2$), 5.10 (d, 1H, $^3J_{H-H}$ = 17 Hz, $^4J_{Pt-H}$ = 19 Hz, Pt-CH$_2$CH⟩C*H*$_{trans\ to\ H}$), 4.80 (d, 1H, $^3J_{H-H}$ = 9 Hz, Pt-CH$_2$CH⟩C*H*$_{s\ to\ H}$), 4.66, 4.59 (m, 2H, 1H, C$_A$-*H*), 3.71 (d, 2H, $^2J_{Pt-H}$ = 87 Hz, Pt-C*H*$_2$CH⟩CH$_2$), 2.02−1.71 (m, 30H, cyclohexyl). ^{31}P{^{1}H} NMR (CD_2Cl_2, 294 K, δ): −6.3 (s, 1P, Tt^{Ph}*P*=O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 270 K, δ): 141.2 (s, 1C, $^2J_{Pt-C}$ = 64 Hz, Pt-CH$_2$CH=CH$_2$), 136.0 (s, 4C, Pt-Ar *m*-Ph), 135.1 (d, 2C, O=P*C*, $^1J_{P-C}$ = 151 Hz), 134.8 (d, 1C, O=P*C*, $^1J_{P-C}$ = 152 Hz), 130.5 (d, 2C, O=PCCH, $^2J_{P-C}$ = 23 Hz), 130.3 (d, 1C, O=PCCH, $^2J_{P-C}$ = 21 Hz), 128.3 (s, 2C, $^1J_{Pt-C}$ = 944 Hz, Pt-Ar *ipso*-Ph), 127.3 (s, 4C, $^2J_{Pt-C}$ = 55 Hz, Pt-Ar *o*-Ph), 125.2 (s, 2C, Pt-Ar *p*-Ph), 112.4 (s, 1C, $^3J_{Pt-C}$ = 49 Hz, Pt-CH$_2$CH=*C*H$_2$), 63.4, 63.3 (s, 2C, 1C, C$_A$), 33.3−33.2 (s, 1:1:1, 6C, C$_B$), 26.0 (s, 1C, $^1J_{Pt-C}$ = 644 Hz, Pt-CH$_2$CH=CH$_2$), 25.1−24.9 (s, 1:1:1 and 2:1, 9C, C$_C$ and C$_D$). HRMS (ESI) *m*/*z* Calcd: 887.3602 (M$^+$). Found: 887.3564.

[(κ^3-Tt^{Ph})Pt(Ph)$_2$(CH$_2$Ph)][BF$_4$] ***(4d-L1)***. The procedure in general method B was followed using benzyl iodide as the electrophile. ^{1}H NMR (CD_2Cl_2, 296 K, δ): 9.35, 9.32 (s, 2H, 1H, Tt^{Ph}C*H*), 7.72−7.51, (m, 15H, Tt^{Ph}C$_6$*H*$_5$), 7.28−7.03 (m, 10H, Pt-Ar), 6.83−6.72 (m, 5H, Pt-CH$_2$-C$_6$*H*$_5$), 4.51 (s, 2H, $^2J_{Pt-H}$ = 88 Hz, Pt-C*H*$_2$-C$_6$H$_5$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 296 K, δ): −7.06 (s, 1P, Tt^{Ph}*P*=O). ^{13}C {^{1}H} NMR (CD_2Cl_2, 296 K, δ): 143.6 (s, 1C, $^2J_{Pt-C}$ = 52 Hz, Pt-Bn *ipso*-Ph), 136.9 (d, 1C, O=P*C*, $^1J_{P-C}$ = 151 Hz), 136.6 (d, 2C, O=P*C*, $^1J_{P-C}$ = 151 Hz), 136.1 (s, 4C, Pt-Ar *m*-Ph), 135.9, 135.8 (s, 1C, 2C, Tt^{Ph} *ipso*-Ph), 131.3, 130.9 (s, 1C, 2C, Tt^{Ph} *p*-Ph), 131.0 (d, 1C, 2C, O=PCCH, $^2J_{P-C}$ = 25 Hz), 130.5, 130.4 (s, 2C, 4C, Tt^{Ph} *o*-Ph), 130.1 (s, 2C, $^3J_{Pt-C}$ = 24 Hz, Pt-Bn *o*-Ph), 128.4 (s, 2C, Pt-Bn *m*-Ph), 128.0 (s, 2C, Pt-Ar *ipso*-Ph), 127.5 (s, 4C, $^2J_{Pt-C}$ = 54 Hz, Pt-Ar *o*-Ph), 126.4 (s, 1C, $^5J_{Pt-C}$ = 12 Hz, Pt-Bn *p*-Ph), 125.5 (s, 2C, Pt-Ar *p*-Ph), 121.7, 121.6 (s, 2C, 4C, Tt^{Ph} *m*-Ph), 27.5 (s, 1C, $^1J_{Pt-C}$ = 660 Hz, Pt-*C*H$_2$C$_6$H$_5$). HRMS (ESI) *m*/*z* Calcd: 919.2350 (M$^+$). Found: 919.2314.

[(κ^3-Tt^{Cy})Pt(Ph)$_2$(CH$_2$Ph)][BF$_4$] ***(4d-L2)***. The procedure in general method B was followed using benzyl iodide as the electrophile. ^{1}H NMR (CD_2Cl_2, 292 K, δ): 8.97, 8.87 (s, 2H, 1H, Tt^{Cy}C*H*), 7.13−6.58 (m, 15H, Pt-CH$_2$-C$_6$*H*$_5$ and Pt-C$_6$*H*$_5$), 4.64, 4.50 (m, 1H, 2H, C$_A$-*H*), 4.29 (s, 2H, $^2J_{Pt-H}$ = 89 Hz, Pt-C*H*$_2$-C$_6$H$_5$), 2.12−1.25 (m, 30H, cyclohexyl). ^{31}P{^{1}H} NMR (CD_2Cl_2, 294 K, δ): −9.5 (s, 1P, Tt^{Cy}*P*=O). ^{13}C{^{1}H} NMR (CD_2Cl_2, 292 K, δ): 144.4 (s, 1C, $^2J_{Pt-C}$ = 52 Hz, Pt-Bn *ipso*-Ph), 136.3 (s, 4C, $^3J_{Pt-C}$ = 7 Hz, Pt-Ar *m*-Ph), 135.9, 135.7 (d, 1C, 2C, O=P*C*, $^1J_{P-C}$ = 148 Hz), 130.7, 130.6 (d, 3C, O=PCCH, $^2J_{P-C}$ = 24 Hz), 130.0 (s, 2C, $^3J_{Pt-C}$ = 24 Hz, Pt-Bn *o*-Ph), 128.4 (s, 2C, $^4J_{Pt-C}$ = 10 Hz, Pt-Bn *m*-Ph), 128.3 (s, 2C, $^1J_{Pt-C}$ = 947 Hz, Pt-Ar *ipso*-Ph), 127.3 (s, 4C, $^2J_{Pt-C}$ = 55 Hz, Pt-Ar *o*-Ph), 126.0 (s, 1C, $^5J_{Pt-C}$ = 12 Hz, Pt-Bn *p*-Ph), 125.2 (s, 2C, Pt-Ar *p*-Ph), 63.3, 63.2 (s, 1C, 2C, C$_A$), 33.7−32.8 (s, 1:1:1, 6C, C$_B$), 26.0 (s, 1C, $^1J_{Pt-C}$ = 659 Hz, Pt-CH$_2$C$_6$H$_5$), 25.0−24.9 (s, 1:1:1 and 2:1, 9C, C$_C$ and C$_D$). HRMS (ESI) *m*/*z* Calcd: 937.3758 (M$^+$). Found: 937.3724.

Synthesis of [(κ^3-Tt^R)Pt(Me)$_2$H][X] Complexes. *[(κ^3-Tt^{Ph})PtMe$_2$H][BF$_4$]* ***(5-L1)***. Into a 50 mL Schlenk flask was placed κ^2-Tt^{Ph}Pt(CH$_3$)$_2$ (0.021 g, 0.030 mmol) under nitrogen. CH_2Cl_2 (10 mL) was added through the septum, and the flask was cooled to −78 °C. The solution was then treated with 1.0 equiv (3.7 μL, 0.030 mmol) of ca. 8.0 M HBF$_4$·Et$_2$O, and it was allowed to warm to room temperature. The solvent was evaporated and the resulting solid was triturated with pentane to afford [(κ^3-Tt^{Ph})Pt(Me)$_2$H][BF$_4$] (0.023 g, 0.029 mmol) as a white powder. ^{1}H NMR (CD_2Cl_2, 294 K, δ): 9.30 (s, 2H, 1H, Tt^{Ph}C*H*), 7.85−7.24 (m, 15H, Tt^{Ph}C$_6$*H*$_5$), 1.60 (s, 6H, $^2J_{Pt-H}$ = 70 Hz, Pt-C*H*$_3$), −19.91 (s, 1H, $^1J_{Pt-H}$ = 1541 Hz, Pt-H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 300 K, δ): −6.6 (s, 1P, Tt^{Ph}*P*=O). ^{13}C {^{1}H} NMR (CD_2Cl_2, 293 K, δ): 135.7 (d, 2C, O=P*C*, $^1J_{P-C}$ = 152 Hz),

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135.6, 135.5 (s, 1C, 2C, Tt^{Ph} *ipso*-Ph), 135.4 (d, 1C, O=PC, $^1J_{P-C}$ = 150 Hz), 130.9 (d, 2C, O=PCCH, $^2J_{P-C}$ = 24 Hz), 130.7 (s, 3C, Tt^{Pt} *p*-Ph), 130.1 (s, 6C, Tt^{Ph} *o*-Ph), 121.5 (s, 6C, Tt^{Ph} *m*-Ph), −14.6 (s, 2C, Pt-CH_3, $^1J_{Pt-C}$ = 620 Hz).

*[(κ^3-Tt^{Ph})PtMe$_2$H][BAr′$_4$] ([**5-L1**][BAr′$_4$])*. Into a 50 mL Schlenk flask was placed κ^2-$Tt^{Ph}Pt(CH_3)_2$ (0.021 g, 0.030 mmol) under nitrogen. CH_2Cl_2 (10 mL) was added through the septum, and the flask was cooled to −78 °C. The platinum complex was treated with a methylene chloride solution containing 1.0 equiv (0.023 g, 0.030 mmol) of HBAr′$_4$ via cannula transfer. The mixture was allowed to warm to room temperature, and the solvent was concentrated to ca. 1 mL. Slow diffusion of hexanes produced clear, hexagonal crystals. Anal. Calcd for $C_{58}H_{37}BF_{24}N_9OPPt$: C, 44.40; H, 2.38; N, 8.04. Found: C, 44.08; H, 2.44; N, 8.16.

*[(κ^3-Tt^{Cy})PtMe$_2$H][BF$_4$] (**5-L2**)*. The same procedure was performed using the analgous $Tt^{Cy}Pt(CH_3)_2$ complex. ^{1}H NMR (CD_2Cl_2, 292 K, δ): 8.88, 8.87 (s, 1H, 2H, $Tt^{Cy}CH$), 4.62 (m, 3H, C_A-*H*), 2.20−1.22 (m, 30H, cyclohexyl), 1.39 (s, 6H, $^2J_{Pt-H}$ = 70 Hz, Pt-CH_3), −20.07 (s, 1H, $^1J_{Pt-H}$ = 1519 Hz, Pt-*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 292 K, δ): −5.6 (s, 1P, $Tt^{Cy}P$=O). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K, δ): 134.6 (d, 2C, O=P*C*, $^1J_{P-C}$ = 150 Hz), 134.2 (d, 1C, O=PC, $^1J_{P-C}$ = 150 Hz), 130.6 (d, 3C, O=PCCH, $^2J_{P-C}$ = 24 Hz), 63.0 (s, 3C, C_A), 33.0−32.8 (s, 1:1:1, 6C, C_B), 24.9−24.6 (s, 1:1:1 and 2:1, 9C, C_C and C_D), −15.6 (s, 2C, Pt-CH_3, $^1J_{Pt-C}$ = 623 Hz).

Elimination and Trapping Reactions. In a typical experiment, a Schlenk flask was charged with 0.030 mmol of [(κ^3-Tt^R)Pt(Me)$_2$H][BF$_4$] **5** under nitrogen. CH_2Cl_2 (6 mL) was added through the septum, and the flask was warmed to 35 °C. The headspace was purged with the trapping gas (L) and stirred for 2 h (L = CO or olefin). The solvent was evaporated and the resulting oil was triturated with pentane to produce [Tt^RPt(Me)(L)][BF_4] as a light yellow powder in good yield by ^{1}H NMR.

*[(κ^3-Tt^{Ph})PtMe(CO)][BF$_4$] (**6-L1**)*. Yield: 86% by ^{1}H NMR. ^{1}H NMR (CD_2H_2, 293 K, δ): 9.29 (s, 3H, $Tt^{Ph}CH$), 7.88, 7.56 (m, 15H, Tt^{Ph}-C_6H_5), 1.44 (s, 3H, $^2J_{Pt-H}$ = 74 Hz, Pt-CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 282 K, δ): −7.8 (s, 1P, $Tt^{Ph}P$=O). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 284 K, δ): 161.3 (s, 1C, Pt-CO), 135.9, 135.6 (s, 2C, 1C, Tt^{Ph} *ipso*-Ph), 132.3 (d, 1C, $^2J_{P-C}$ = 26 Hz, O=PCCH), 131.4 (d, 2C, $^2J_{P-C}$ = 24 Hz, O=PCCH), 131.0 (s, 3C, Tt^{Pt} *p*-Ph), 130.6, 130.4 (s, 2C, 4C, Tt^{Ph} *o*-Ph), 121.9, 121.6 (s, 2C, 4C Tt^{Ph} *m*-Ph), −14.6 (s, 1C, Pt-CH_3). IR (CH_2Cl_2 solution) ν_{CO} = 2124 cm^{-1}. Anal. Calcd for $C_{26}H_{21}BF_4N_9O_2PPt$: C, 38.82; H, 2.63; N, 15.67. Found: C, 38.77; H, 2.91; N, 15.39.

*[(κ^3-Tt^{Cy})PtMe(CO)][BF$_4$] (**6-L2**)*. Yield: 85% by ^{1}H NMR. ^{1}H NMR (CD_2Cl_2, 292 K, δ): 8.73 (s, 3H, $Tt^{Cy}CH$), 4.63 (m, 3H, C_A-*H*), 2.24−1.25 (m, 30H, cyclohexyl), 1.41 (s, 6H, $^2J_{Pt-H}$ = 71 Hz, Pt-CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 292 K, δ): −8.6 (s, 1P, $Tt^{Cy}P$=O). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 292 K, δ): 161.8 (s, 1C, Pt-*C*O), 136.9 (d, 3C, $^1J_{P-C}$ = 157 Hz, O=P*C*), 132.0 (d, 2C, $^2J_{P-C}$ = 29 Hz, O=PCCH), 130.1 (d, 1C, $^2J_{P-C}$ = 24 Hz, O=PCCH), 63.7, 63.0 (s, 1C, 2C, C_A), 33.4−33.2 (s, 6C, C_B), 25.2−25.0 (s, 1:1:1 and 2:1, 9C, C_C and C_D), −15.3 (s, 1C, $^1J_{Pt-C}$ = 522 Hz, Pt-CH_3). IR (CH_2Cl_2 solution) ν_{CO} = 2117 cm^{-1}. HRMS (ESI) *m*/*z* Calcd: 735.2612 (M$^+$). Found: 735.2657. Anal. Calcd for $C_{26}H_{39}BF_4N_9O_2PPt$: C, 37.97; H, 4.78; N, 15.33. Found: C, 37.97; H, 4.78; N, 15.33.

*[(κ^3-Tt^{Ph})PtMe(η^2-C_2H_4)][BF$_4$] (**7a-L1**)*. Yield: 85% by ^{1}H NMR. ^{1}H NMR (CD_2Cl_2, 298 K, δ): 9.39, 9.34 (s, 2H, 1H, $Tt^{Ph}CH$), 7.84−7.44 (m, 15H, $Tt^{Ph}C_6H_5$), 3.33 (s, 4H, $^2J_{Pt-H}$ = 79 Hz, Pt-C_2H_4), 1.05 (s, 3H, $^2J_{Pt-H}$ = 63 Hz, Pt-CH_3), $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 300 K, δ): −7.6 (s, 1P, $Tt^{Ph}P$=O). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K, δ): 137.2 (d, 1C, O=P*C*, $^1J_{P-C}$ = 153 Hz), 136.7 (d, 2C, $^1J_{P-C}$ = 150 Hz, O=P*C*), 135.6, 135.5 (s, 2C, 1C, Tt^{Ph} *ipso*-Ph), 131.1, 130.9 (s, 1C, 2C, Tt^{Pt} *p*-Ph), 130.3 (s, 6C, Tt^{Ph} *o*-Ph), 121.4, 121.3 (s, 4C, 2C, Tt^{Ph} *m*-Ph), 40.9 (s, 2C, Pt-C_2H_4), −12.3 (s, 1C, Pt-CH_3). Anal. Calcd for $C_{59}H_{37}BF_{24}N_9OPPt$ (BAr′$_4$ counterion): C, 44.83; H, 2.36; N, 7.97. Found: C, 45.11; H, 2.38; N, 7.69.

*[(κ^3-Tt^{Cy})PtMe(η^2-C_2H_4)][BF$_4$] (**7a-L2**)*. Yield: 81% by ^{1}H NMR. ^{1}H NMR (CD_2Cl_2, 292 K, δ): 8.69, 8.62 (s, 2H, 1H, $Tt^{Cy}CH$), 4.63, 4.54 (m, 2H, 1H, C_A-*H*), 3.00 (s, 4H, $^2J_{Pt-H}$ = 81 Hz, Pt-C_2H_4) 2.23−1.25 (m, 30H, cyclohexyl), 0.85 (s, 6H, $^2J_{Pt-H}$ = 63 Hz, Pt-CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 292 K, δ): −7.7 (s, 1P, $Tt^{Cy}P$=O). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K, δ): 136.4 (d, 2C, $^1J_{P-C}$ = 152 Hz, O=P*C*), 135.2 (d, 1C, $^1J_{P-C}$ = 150 Hz, O=P*C*), 130.3 (d, 1C, $^2J_{P-C}$ = 24 Hz, O=PCCH), 129.9 (d, 1C, $^2J_{P-C}$ = 25 Hz, O=PCCH), 63.2, 63.0 (s, 1C, 2C, C_A), 37.1 (s, 2C, $^1J_{Pt-C}$ = 361 Hz, Pt-C_2H_4), 33.5−33.3 (s, 1:1:1, 6C, C_B), 25.2−25.0 (s, 1:1:1 and 2:1, 9C, C_C and C_D), −13.3 (s, 1C, $^1J_{Pt-C}$ = 620 Hz, Pt-CH_3). HRMS (ESI) *m*/*z* Calcd: 735.2976 (M$^+$). Found: 735.2953.

*[(κ^3-Tt^{Ph})PtMe(η^2-propylene)][BF$_4$] (**7b-L1**)*. Yield: 77% by ^{1}H NMR. ^{1}H NMR (CD_2Cl_2, 300 K, δ): 9.34, 9.21, 9.19 (s, 1H, 1H, 1H, $Tt^{Ph}CH$), 7.89, 7.59 (m, 15H, $Tt^{Ph}C_6H_5$), 5.03 (m, 1H, H_2C=C*H*CH_3), 4.35 (d, 1H, $^3J_{H-H}$ = 13 Hz, $H_{trans\ to\ H}C$=$CHCH_3$), 4.28 (d, 1H, $^3J_{H-H}$ = 7 Hz, $H_{s\ to\ H}C$=$CHCH_3$), 1.51 (d, 3H, $^3J_{H-H}$ = 6 Hz, Pt-H_2C=CHCH_3), 0.95 (s, 3H, $^2J_{Pt-H}$ = 63 Hz, Pt-CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 300 K, δ): −9.8 (s, 1P, $Tt^{Ph}P$=O). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K, δ): 136.0, 135.8 (s, 3C, Tt^{Ph} *ipso*-Ph), 131.9 (d, 2C, O=PCCH, $^2J_{P-C}$ = 24 Hz), 131.4, (s, 3C, Tt^{Ph} *p*-Ph), 130.6 (s, 6C, Tt^{Ph} *o*-Ph), 121.7, 121.6 (s, 4C, 2C, Tt^{Ph} *m*-Ph), 88.7 (s,1C, H_2C=*C*HCH$_3$), 64.6 (s, 1C, H_2C=CHCH$_3$), 20.0 (s, 1C, H_2C=CHCH$_3$), −8.6 (s, 1C, Pt-CH_3). HRMS (ESI) *m*/*z* Calcd: 731.1724 (M$^+$). Found: 731.1691.

*[(κ^3-Tt^{Ph})PtMe(η^2-*s*-2-butene)][BF$_4$] (**7c-L1**)*. Yield: 78% by ^{1}H NMR. ^{1}H NMR (CD_2Cl_2, 298 K, δ): 9.40, 9.27 (s, 2H, 1H, $Tt^{Ph}CH$), 7.87, 7.49 (m, 15H, $Tt^{Ph}C_6H_5$), 5.02 (d, 2H, $(CH_3)HC$=*C*H(CH_3)), 1.59 (d, 6H, (CH_3)HC=CH(CH_3)), 0.68 (s, 3H, Pt-CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, δ): −7.3 (s, 1P, $Tt^{Ph}P$=O). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, δ): 136.1, 135.9 (s, 1C, 2C, Tt^{Ph} *ipso*-Ph), 132.0 (d, 2C, O=PCCH, $^2J_{P-C}$ = 29 Hz), 131.4−130.3 (s, 9C, Tt^{Ph} *o*-Ph and *p*-Ph), 121.9−121.6 (s, 6C, Tt^{Ph} *m*-Ph), 87.0 (s, 2C, $(CH_3)HC$=CH(CH_3)), 14.2 (s, 2C, $(CH_3)HC$=CH(CH_3)), −1.8 (s, 1C, Pt-CH_3). HRMS (ESI) *m*/*z* Calcd: 745.1881 (M$^+$). Found: 745.1851.

*[(κ^3-Tt^{Ph})PtMe(η^2-*trans*-2-butene)][BF$_4$] (**7d-L1**)*. Yield: 74% by ^{1}H NMR. ^{1}H NMR (CD_2Cl_2, 270 K, δ): 9.38, 9.21, 9.11 (s, 1H, 1H, 1H, $Tt^{Ph}CH$), 7.88, 7.62 (m, 15H, $Tt^{Ph}C_6H_5$), 5.48, 4.71 (m, 1H, 1H, $(CH_3)HC$=*C*H(CH_3)), 1.82, 1.30 (d, 3H, 3H, (CH_3)HC=CH(CH_3)), 0.98 (s, 3H, $^2J_{Pt-H}$ = 64 Hz, Pt-CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 270 K, δ): −9.5 (s, 1P, $Tt^{Ph}P$=O). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 270 K, δ): 139.2 (d, 1C, $^1J_{P-C}$ = 164 Hz, O=P*C*), 137.1 (d, 1C, $^1J_{P-C}$ = 150 Hz, O=P*C*), 137.0 (d, 1C, $^1J_{P-C}$ = 146 Hz, O=P*C*), 135.8, 135.7, 135.7 (s, 1C, 1C, 1C, Tt^{Ph} *ipso*-Ph), 132.6 (d, 1C, O=PCCH, $^2J_{P-C}$ = 26 Hz), 132.1 (d, 1C, O=PCCH, $^2J_{P-C}$ = 25 Hz), 131.0 (d, 1C, O=PCCH, $^2J_{P-C}$ = 30 Hz), 131.2−130.3 (s, 9C, Tt^{Ph} *o*-Ph and *p*-Ph), 121.7, 121.6, 121.0 (s, 2C, 2C, 2C, Tt^{Ph} *m*-Ph), 90.1, 90.0 (s, 1C, 1C, $(CH_3)HC$=*C*H(CH_3)), 19.7 (s, 2C, $(CH_3)HC$=CH(CH_3)), −7.6 (s, 1C, Pt-CH_3). HRMS (ESI) *m*/*z* Calcd: 745.1881 (M$^+$). Found: 745.1833.

*[(κ^3-Tt^{Ph})PtMe(η^2-isobutylene)][BF$_4$] (**7e-L1**)*. Yield: 78% by ^{1}H NMR. ^{1}H NMR (CD_2Cl_2, 298 K, δ): 9.29, 9.17 (s, 2H, 1H, $Tt^{Ph}CH$), 7.87, 7.56 (m, 15H, $Tt^{Ph}C_6H_5$), 4.53 (s, 2H, $^2J_{Pt-H}$ = 67 Hz, H_2C=C$(CH_3)_2$), 1.52 (s, 6H, H_2C=C$(CH_3)_2$), 1.07 (s, 3H, Pt-CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K, δ): −8.7 (s, 1P, $Tt^{Ph}P$=O). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K, δ): 138.3 (d, 2C, $^1J_{P-C}$ = 156 Hz, O=P*C*), 137.6 (d, 1C, $^1J_{P-C}$ = 156 Hz, O=P*C*), 135.9 (s, 3C, Tt^{Ph} *ipso*-Ph), 132.3 (d, 3C, O=PCCH, $^2J_{P-C}$ = 24 Hz), 131.3, 130.9 (s, 1C, 2C, Tt^{Ph} *p*-Ph), 130.6, 130.2 (s, 4C, 2C, Tt^{Ph} *o*-Ph), 121.7 (s, 6C, Tt^{Ph} *m*-Ph), 110.5 (s, 1C, H_2C=*C*H$(CH_3)_2$), 67.6 (s, 1C, H_2C=CH$(CH_3)_2$), 28.5 (s, 1C, H_2C=CH$(CH_3)_2$), −5.3 (s, 1C, Pt-CH_3). HRMS (ESI) *m*/*z* Calcd: 745.1881 (M$^+$). Found: 731.1875.

*Structural Data for [**3a-L1**][BAr′$_4$]*. Crystals were obtained from CH_2Cl_2/hexanes: $C_{60}H_{41}BCl_2F_{24}N_9OPPt$, *M* = 1667.79; monoclinic, space group $P2_1/c$; Z = 4; *a* = 16.2833(2) Å, *b* = 15.5893(2) Å, *c* = 25.8409(2) Å; α = 90°, β = 93.93700(10)°, γ = 90°; *U* = 6543.85(14) Å^3; D_c = 1.693 mg/cm^3; *T* = 100(2) K; θ range = 2.72−70.06°; reflections collected = 129 300; independent reflections = 12 190; data were collected on a Bruker-AXS SMART Apect-II diffractometer; goodness-of-fit = 1.073.

■ ASSOCIATED CONTENT

Supporting Information

Representative ^{1}H and ^{13}C NMR spectra, kinetic studies data of biphenyl formation from **4c-L2**, and cif file for structure **3a-L1**.

This material is available free of charge via the Internet at http://pubs.acs.org.

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