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An Adaptable Chelating Diphosphine Ligand for the Stabilization of Palladium and Platinum Carbenes

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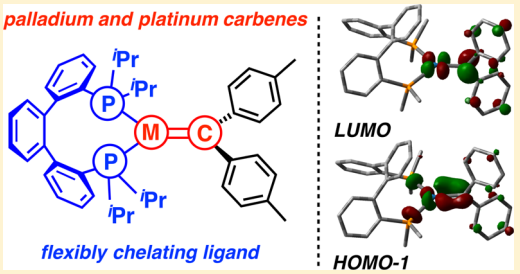
Supporting Information

ABSTRACT: Group 10 metal carbenes are proposed in catalytic transformations; however, their isolation remains difficult without the presence of a heteroatom donor. The adaptable cis and trans coordinating ligand $P^{ter}P$ (1,2-bis(2-(diisopropylphosphino)phenyl)benzene) is key in stabilizing two-coordinate palladium and platinum(0) precursors. Reacting these precursors with di-*p*-tolyldiazomethane ($(p\text{-tol})_2CN_2$) leads to the formation of the unprecedented trigonal-planar diarylcarbenes $[(P^{ter}P)M{=}C(p\text{-tol})_2]$ (M = Pd, Pt), upon transformation of the trans coordinating ligand into a wide-bite, cis-coordinating ligand. Both palladium and platinum diarylcarbenes were characterized by multinuclear NMR spectroscopy. The unusual stability of the platinum analogue allowed its characterization via X-ray crystallography. Furthermore, the reactivity of the palladium and platinum diarylcarbenes with Ph_2SiH_2 and CH_3I was investigated.



INTRODUCTION

Transition-metal carbenes have received a great deal of attention in recent years due to their various uses in organic transformations.[1−5] Specifically for group 10 metal examples, many isolated carbenes feature hereroatom stabilization, while hydrocarbon analogues ($M{=}CR_2$, R = H, alkyl, aryl) remain rare. Isolation of such compounds is desired due to their implication in a range of catalytic reactions. For example, palladium-catalyzed cross-coupling reactions between diazo compounds and an array of substrates[6] are proposed to involve the migratory insertion of a carbene fragment into palladium−C bonds; however, this proposal is based only on the identity of the observed organic products and not on studies of intermediate structures. The nature of these intermediates is difficult to probe due to their transient nature. Additionally, platinum is competent in the activation of alkynes toward nucleophilic attack. It is generally accepted that the key intermediate in this reaction involves either a platinum-stabilized carbene or a metal-bound carbocation.[5,7,8] The exact nature of this intermediate is a subject of debate, whose progress is limited again by a lack of characterized examples.

Palladium carbene species, in which the carbene is incorporated in a tridentate ligand scaffold, have been reported by us as well as by in-depth reactivity studies involving these complexes.[9−18] Specifically, our group was able to isolate a series of square-planar palladium carbenes, using the chelating diphosphine ligand $[PC(sp^2)P]^R$ (R = H, $[PC(sp^2)P]^H$ = bis(2-(diisopropylphosphino)phenyl)methylene); R = ^{t}Bu, $[PC(sp^2)P]^{tBu}$ = bis(2-(diisopropylphosphino)-4-*tert*-butylphenyl)-methylene).[10−14,19] The reactivity of these species varies from nucleophilic to electrophilic, as confirmed by DFT and experimental investigations.[10−14,19] Although this method has been beneficial for understanding the electronic structure of these four-coordinate carbenoids, it is not possible to perform their reactions catalytically due to the chelating nature of the ligand framework. It is therefore desirable to synthesize palladium and platinum species in which the carbene is not anchored to the supporting ligand, so that these transformations can be advantageous in organic synthesis.

Examples of $[M]{=}CRR'$ carbenes, where M = Ni, Pd, Pt and R, R′ = hydrogen, alkyl, or aryl substituents, are uncommon. Group 10 metal cycloheptatrienylidene complexes were synthesized; however, the delocalization in the cycloheptatrienyl ring incorporates the carbene p orbital and metal to carbon π bonding was determined to be minimal.[20,21] The cycloheptatrienylium resonance form was deemed to be favorable, indicating that these ligands behave as mainly σ donors and, therefore, are analogous to N-heterocyclic carbenes.[21] Notably, in 2002, Hillhouse and co-workers isolated a nickel diphenylcarbene, $(dtbpe)Ni{=}CPh_2$ (dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane; Figure 1); however, its heavier congeners remain elusive. Its characterization by single-crystal X-ray diffraction revealed a short Ni−C distance of 1.836(2) Å, consistent with double-bond character.[22,23] Soon after, Bröring and co-workers characterized the cationic palladium diarylcarbene $[(Trpy)PdC(p\text{-tol})_2][BAr^F{}_4]$ (Trpy = tripyrrin, *p*-tol = *p*-tolyl, $BAr^F{}_4$ = tetrakis(3,5-bis-(trifluoromethyl)phenyl)borate; Figure 1).[24] Crystallographic analysis of this species revealed a long Pd−C distance (1.976 Å) consistent with mainly σ donation from the carbene to palladium. A cationic platinum example, *trans*-$[Pt\{P^iPr_2(2,6\text{-}CH(Me)C_6H_3\}\{P^iPr_2(2,6\text{-}CH_2(Me)C_6H_3\}][PF_6]$, was later described by Carmona and co-workers and proved to be

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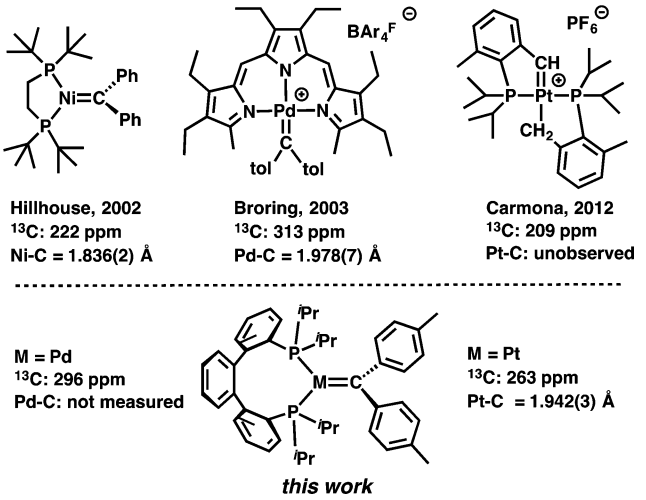


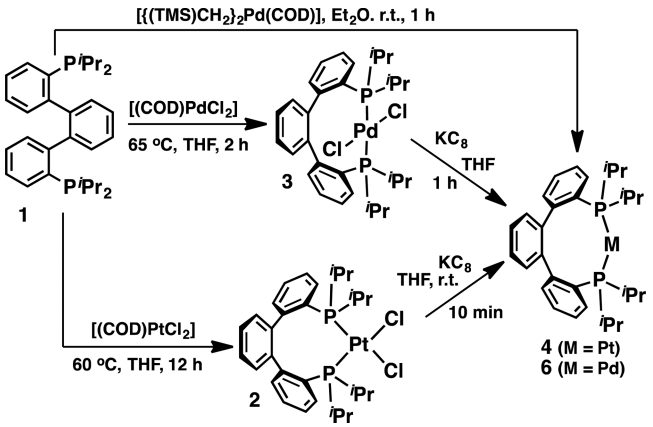
Figure 1. Isolated group 10 metal carbenes.

reactive toward nucleophiles (Figure 1). This species was not crystallographically characterized due to its high reactivity and poor thermal stability.[8,25] Additionally, Templeton and coworkers were able to observe spectroscopically a transient cationic Pt(IV) alkylidene species, $[Tp'Pt(=CHCH_3)(Me)_2][BAr^F{}_4]$ (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate); however, the instability of the species inhibited further characterization.[26] To the best of our knowledge, no platinum alkylidenes or diarylcarbenes have been structurally characterized. Herein, we present the synthesis and characterization of palladium and platinum diarylcarbenes and, therefore, complete the series of isolable group 10 metal diarylcarbenes. The platinum complex was structurally characterized, while the palladium analogue was spectroscopically characterized and showed reactivity behavior consistent with that of an alkylidene species.

RESULTS AND DISCUSSION

The reaction of $P^{ter}P$ (**1**; $P^{ter}P$ = 1,2-bis(2-(diisopropylphosphino)phenyl)benzene) with 1 equiv of $[(COD)PtCl_2]$ (COD = 1,5-cyclooctadiene) at 60 °C in THF for 12 h led to the isolation of $[(P^{ter}P)PtCl_2]$ (**2**; Scheme 1). Characterization of **2** by NMR spectroscopy at room temperature revealed broad resonances in both the ^1H and ^{31}P NMR spectra, indicating a dynamic process. Variable-temperature NMR spectroscopic studies showed a C_s-symmetric compound at 60 °C, as indicated by the equivalent environments in the ^{31}P NMR spectrum. However, when the temperature is lowered to −60 °C, the phosphine environments become nonequivalent and correspond to a cis coordination environment around the metal center ($^2J_{PP}$ = 16 Hz). The solid-state molecular structure of **2** (Figure 2) confirms the cis arrangement of the phosphines around the platinum center,[27] leaving the chlorides to occupy positions trans to each of the phosphine donors.

Scheme 1. Synthesis of the Pt(0) and Pd(0) Precursors



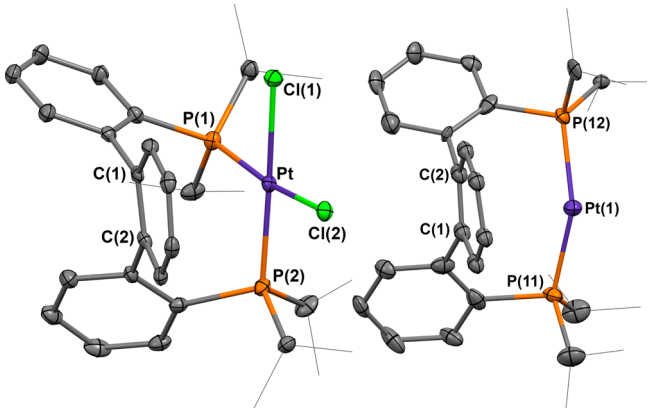


Figure 2. Molecular structures of **2** (left) and **4** (right) with displacement parameters at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): for **2**, Pt−Cl(1) = 2.3601(10), Pt−Cl(2) = 2.3490(10), Pt−P(1) = 2.2611(11), Pt−P(2) = 2.2636(11), P(1)−Pt−P(2) = 98.84(4), Cl(1)−Pt−Cl(2) = 86.22(4), P(1)−Pt−Cl(1) = 84.00(4), P(2)−Pt−Cl(2) = 90.76(4); for **4**, Pt(1)−P(11) = 2.215(3), Pt(1)−P(12) = 2.229(3), P(11)−Pt(1)−P(12) = 153.95(12).

The palladium(II) analogue can be readily synthesized by reacting $P^{ter}P$ with $[(COD)PdCl_2]$ to form $[(P^{ter}P)PdCl_2]$ (**3**; Scheme 1). In contrast to the case for **2**, the diphosphine ligand exhibits a trans coordination mode to the metal center (Figure S66 in the Supporting Information). The different ligand geometries in **2** and **3** make $P^{ter}P$ an attractive candidate for the stabilization of monomeric, two-coordinate Pd(0) and Pt(0) species, which are desirable precursors for carbene formation. For example, our group recently compared the preferentially cis coordinating $^iPr_2P(o\text{-}C_6H_4\text{-}CH_2\text{-}o'\text{-}C_6H_4)P^iPr_2$ to the more flexible, wide-bite-angle $^iPr_2P(o\text{-}C_6H_4\text{-}CH_2CH_2\text{-}o'\text{-}C_6H_4)P^iPr_2$.[28] We observed that, in the case of the former, dimeric palladium(0) compounds resulted in the absence of an additional dative ligand; however, the wide-bite-angle ligand was able to accommodate the optimal trans geometry, resulting in a two-coordinate palladium(0) compound. This choice of a flexible diphosphine ligand[29] allowed the preparation of two-coordinate palladium(0) and platinum(0) precursors which we believe play a key role in the formation of the desired carbene species. The formation of monomeric Pd(0) and Pt(0) compounds is a strategic synthetic target, since it alleviates the need for dimer[30] dissociation in subsequent reactions that might impede carbene formation. Additionally, the accessibility to cis coordination is an attractive quality for carbene formation.

Compound **2** can be reduced to $[(P^{ter}P)Pt]$ (**4**) by reacting it with 2 equiv of KC_8 at room temperature in THF (Scheme 1). The resulting species was characterized by NMR spectroscopy as well as single-crystal X-ray diffraction. The solid-state

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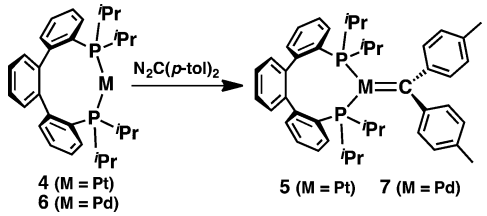
molecular structure shows a bent geometry around the metal center, as indicated by the P−Pt−P angle of 153.95° (Figure 2). Although two-coordinate platinum(0) species are known,[31−33] four- or three-coordinate complexes are common when bidentate ligands are employed.[34−38] Additionally, it is interesting to note that the structurally related para- and meta-substituted terphenyl systems reported by Agapie and co-workers (2,2″-bis(diisopropylphosphino)terphenyl) commonly exhibit an interaction between the metal center and the central aryl moiety.[39−41] In contrast with these examples, the ortho-substituted analogue described here renders the ligand too rigid to allow such an interaction. The transformation from cis to trans diphosphine coordination of $P^{ter}P$ from platinum(II) to platinum(0) demonstrates that the ligand is coordinatingly flexible, a characteristic that could be further exploited upon carbene formation.

Reacting an Et_2O solution of **4** with 1 equiv of $(p\text{-tol})_2CN_2$ leads to the formation of a major product, $[(P^{ter}P)Pt{=}C(p\text{-tol})_2]$ (**5**), after 2 h at room temperature (Scheme 2). The tolyl

Scheme 2. Synthesis of Diarylcarbenes 5 and 7



methyl groups resonate separately in the ^1H NMR spectrum at 2.19 and 2.22 ppm. This finding, along with the aryl region integrating to 20 total protons, indicates that the *p*-tolyl groups were incorporated into the complex. Furthermore, the ^{13}C NMR spectrum exhibits a diagnostic downfield shift at 262.8 ppm (Figure 3) as a triplet, along with platinum satellites at

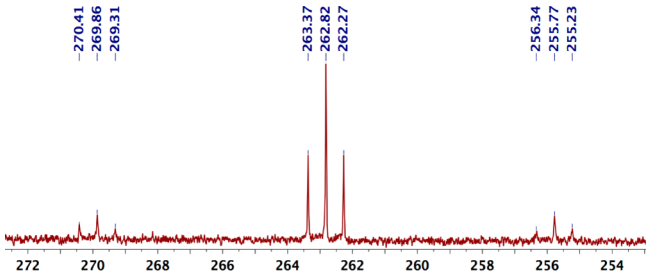


Figure 3. Carbene region of the $^{13}C\{^1H\}$ NMR spectrum for **5**.

269.9 and 255.8 ppm ($^2J_{CP}$ = 66 Hz, $^1J_{CPt}$ = 1775 Hz). This downfield chemical shift is reminiscent of other electrophilic group 10 metal carbenes. Specifically, the cationic platinum carbene *trans*-$[Pt\{P^iPr_2(2,6\text{-}CH(Me)C_6H_3)\}\{P^iPr_2(2,6\text{-}CH_2(Me)C_6H_3)\}]^+$ resonates downfield at 209 ppm; interestingly, the value of the C−Pt coupling constant reported for this complex (740 Hz) is lower than that for **5**.[8] Additionally, our group recently observed a correlation between the electronic properties of the carbene fragment and its observed chemical shift in the ^{13}C NMR spectrum. For instance, the nucleophilic carbene $[\{PC(sp^2)P\}^{tBu}Pd(PMe_3)]$ resonates relatively upfield at 136 ppm; bond polarity inversion of the carbene fragment results in electrophilic character for $[\{PC(sp^2)P^{tBu}\}Pd(PMe_3)]^+$, which has a downfield shift, at 284 ppm.[12,19] Notably, the structurally analogous trigonal-planar nickel carbene $[(dtbpe)Ni{=}CPh_2]$ exhibits spectroscopic characteristics similar to those of **5**, resonating as a triplet at 222 ppm (J_{PP} = 51 Hz).[22]

The solid-state molecular structure of **5** (Figure 4) confirms the synthesis of a trigonal-planar platinum carbene species (the

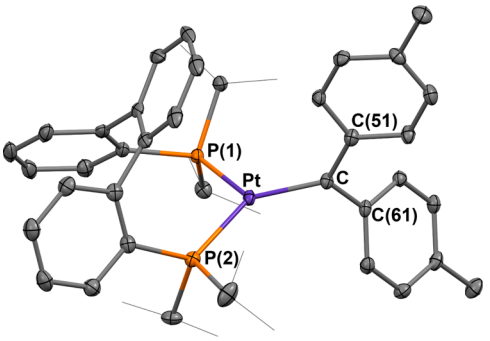


Figure 4. Molecular structure of **5** with displacement parameters at 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Pt−C = 1.942(3), Pt−P(1) = 2.2665(9), Pt−P(2) = 2.2891(10), P(1)−Pt−P(2) = 105.23(3), P(1)−Pt−C = 118.98(11), P(2)−Pt−C = 135.50(11), Pt−C−C(51) = 124.9(2), Pt−C−C(61) = 119.8(2), C(51)−C−C(61) = 115.0(3).

sums of angles are 359.68° for C and 359.71° for Pt). The Pt−C distance of 1.942(3) Å is shorter than typical Pt−C NHC distances (~2.0 Å)[42−44] and slightly shorter than those for previously reported heteroatom-stabilized platinum carbenes (1.95−2.0 Å).[26,45,46] Similarly to the previously reported nickel diphenylcarbene (dtbpe)Ni=CPh_2, the plane of the carbene ligand is almost perpendicular to the plane defined by P(1)−Pt−P(2).[22,23] This orientation allows π overlap between the platinum d orbital and a carbene p orbital. Geometry optimizations using Gaussian03 (B3LYP functional, LANL2DZ basis set) performed on **5** matched the observed solid-state structure. The frontier molecular orbitals calculated for a model of **5**, **5′**, in which the isopropyl phosphine groups were replaced by methyls, revealed the π bonding and antibonding orbitals as HOMO-1 and LUMO, respectively, found in the P(1)−Pt−P(2) plane (Figure 5). Both of these orbitals have a small σ P−Pt antibonding character.

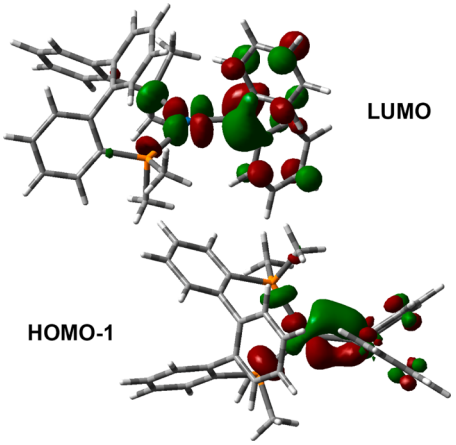


Figure 5. Frontier molecular orbitals for **5**: bonding (bottom) and antibonding (top) π symmetry orbitals for the Pt=C bond in **5**.

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It is of interest to compare the bonding observed in **5** to other examples of group 10 metal carbenes reported in the literature. Similarly to the nickel carbene reported by Hillhouse and co-workers, the bond between the metal center and the carbene fragment has a high π character due to the trigonal-planar geometry of the metal center.[22,23] This is supported by the short M−C distances of 1.942(3) Å in **5** and 1.836(2) Å in (dtbpe)Ni=CPh_2. Additionally, the presence of two separate resonances for the *p*-tolyl methyl protons in the ^{1}H NMR spectrum of **5** indicates hindered rotation around the Pt−C bond, supporting double-bond character. In contrast, our group synthesized a variety of four-coordinate palladium carbenes. These complexes range from exhibiting nucleophilic character centered on the carbene carbon to cationic character upon two-electron oxidation.[10−12] The square-planar geometry of the metal center (and the higher coordination number) resulted in a filled π antibonding orbital (HOMO) for the neutral nucleophilic carbene; the bonding is best described as a Pd−C ylide-type single bond with zwitterionic character. This is further supported by the long Pd−C distance of 2.076(3) Å. The sequential oxidation of this carbene resulted in the contraction of the Pd−C distance to 1.968(3) Å, consistent with an increase in bond order. This distance was, however, comparable to the distances observed in palladium N-heterocyclic carbenes and is best described as a cationic carbon center stabilized by π back-donation from the metal center. The weak π donor capabilities of the four-coordinate cationic palladium center results in additional electron stabilization from the bound aryl groups. This lack of π donor capabilities for group 10 metal carbenes with higher coordination numbers is further observed for the four-coordinate palladium example reported by Bröring and co-workers, [(Trpy)PdC(*p*-tol)$_2$]-[$BAr^F{}_4$], which exhibits a relatively long Pd−C distance of 1.98 Å.[24] This effect is amplified for the platinum carbenes of octahedral geometry observed by Templeton and co-workers, [Tp′Pt(=$CHCH_3$)$(Me)_2$][$BAr^F{}_4$].[26] The carbene carbon exhibits a pronounced downfield chemical shift in the ^{13}C NMR spectrum at 431 ppm. This was attributed to the cationic carbene experiencing only a weak π donation from the six-coordinate metal center.

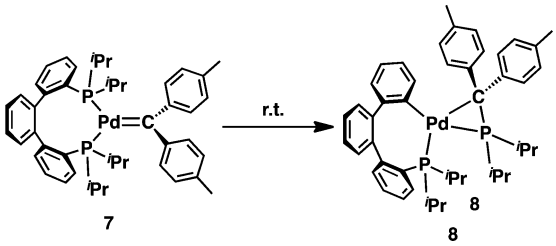
We determined that the bidentate ligand scaffold was vital for the isolation of the desired platinum carbene by employing monodentate phosphine ligands. The synthesis of the dicoordinate platinum(0) compound [$(PCy_3)_2$Pt] was therefore carried out.[33] This species reacted with 1 equiv of (*p*-tol)$_2CN_2$ until the diazo reagent was fully consumed. Instead of observing the formation of a platinum carbene, however, we observed the full conversion of the diazo species to the corresponding azine ((*p*-tol)$_2$C=N−N=C(*p*-tol)$_2$) by ^{1}H NMR spectroscopy. The compound [$(PCy_3)_2$Pt] was found unchanged at the end of the reaction. Azine formation was reported to occur through the coupling of diazo compounds with a carbene fragment.[47−49] It is therefore reasonable to propose that a platinum carbene species is an intermediate in this reaction; however, it is spectroscopically undetectable. This indicates that our coordinatingly flexible bidentate ligand aids in stabilizing the platinum carbene moiety, making its isolation feasible.

We next became interested in isolating the analogous palladium carbene. The palladium(0) precursor can be readily synthesized by reacting **1** with [{$(TMS)_2CH_2$}$_2$Pd(COD)][50] in diethyl ether at room temperature (Scheme 1). The resulting compound, [(P^{ter}P)Pd] (**6**), was characterized by NMR spectroscopy and single-crystal X-ray diffraction (Figure S67 in the Supporting Information). Similarly to **4**, the species is two-coordinate and the ligand imposes a bent geometry on the metal center.

When **6** reacts with (*p*-tol)$_2CN_2$ at room temperature, multiple species are observed in solution. Heating the reaction mixture leads to the formation of an azine species, a transformation also observed for [$(Cy_3P)_2$Pt] (see above). Exposing the reaction mixture to UV radiation for 1 h leads to a major species in solution, assignable in the ^{31}P NMR spectrum as a singlet at 48.2 ppm. This species, **7**, is the desired palladium carbene, as indicated by the presence of a triplet at 296.6 ppm in the ^{13}C NMR spectrum ($^2J_{CP}$ = 63 Hz). Attempts to obtain single crystals suitable for X-ray diffraction were hampered by its high solubility and instability; however, DFT calculations indicated that **7** is structurally and electronically similar to **5** (see the Supporting Information). The similar chemical shifts in the ^{31}P and ^{13}C NMR spectra, as well as the comparable C−P coupling constants for **5** and **7**, indicate that these two species are analogous. It is of interest to note that, to the best of our knowledge, no other palladium non-heteroatom-stabilized carbenes exhibiting a trigonal-planar geometry have been isolated.

We found that when **7** is left at room temperature overnight, full conversion to a new asymmetric product, **8** (Scheme 3), is

Scheme 3. Decomposition of 7



observed by NMR spectroscopy. The solid-state molecular structure (Figure 6) of **8** reveals a distorted-square-planar compound, in which one of the P−C_{aryl} bonds of the ligand framework was cleaved.[51,52] This results in κ^2 P−C

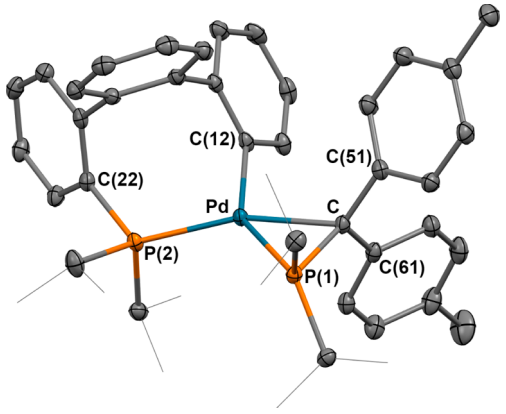


Figure 6. Molecular structure of **8** with displacement parameters at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Pd−C = 2.1794(18), Pd−P(1) = 2.2896(5), Pd−P(2) = 2.3260(5), C−P(1) = 1.8118(19), Pd−C(12) = 2.0587(19), P(1)−Pd−P(2) = 121.815(17), C(12)−Pd−C = 98.64(7), P(1)−Pd−C = 47.75(5), P(2)−Pd−C(12) = 92.84(5).

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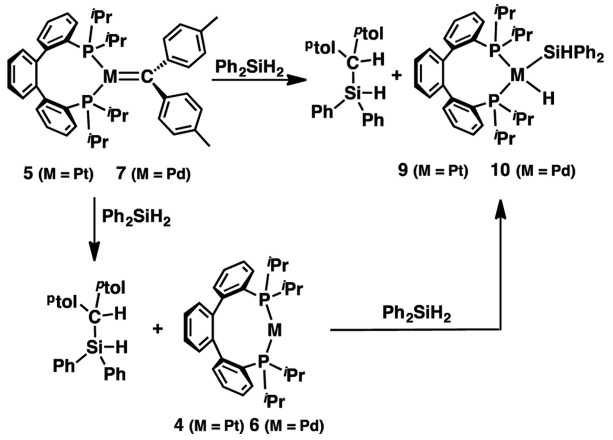
coordination of the remaining ligand fragment. The cleaved phosphine forms a new P−C bond with the di-*p*-tolylcarbene fragment, resulting in the formation of a palladacycle. On the other hand, the platinum carbene **5** is remarkably stable; no decomposition is observed even on heating in solution for 10 days at 120 °C.

With the successful isolation of the palladium and platinum diarylcarbenes, we became interested in studying their reactivity. Late-transition-metal carbenes are competent in various catalytic E−H (E = Si, N, O, S) bond insertion reactions.[53−57] Specifically, carbene insertion into silicon−hydrogen bonds has proven to be a powerful method for the formation of new Si−C bonds. Common examples often include the use of rhodium, iridium, or copper; recently,[53−55,58,59] palladium has shown similar reactivity in silicon−silicon carbene insertion reactions.[59] Carbenoid insertion into E−H bonds is proposed to occur via two major pathways, depending on the polarity of the E−H bond. For substrates with mild polarity, such as silanes, this process may occur through a concerted insertion into the E−H bond.[55,56] More polar bonds, such as O−H, S−H, and N−H, proceed by a stepwise process, in which the heteroatom is attacked by the carbene, forming an ylide intermediate, followed by hydrogen atom transfer.[58] Therefore, we became interested in the reactivity of **5** and **7** toward Si−H bonds in order to see if the synthesized carbenes performed analogously to literature examples. Reacting **5** with 2 equiv of Ph_2SiH_2 led to the observation of (di-*p*-tolylmethyl)diphenylsilane, resulting from carbene insertion into a Si−H bond of the substrate (Scheme 4), in agreement with the proposed literature mechanism in

Scheme 4. Reactions of 5 and 7 with Silanes



which a concerted insertion of the carbene fragment into the Si−H bond forms the observed organic product.[55,56] Additionally, the clean formation of ($P^{ter}P$)PtH($SiHPh_2$) (**9**) is observed; this is proposed to occur from the reaction of ($P^{ter}P$)Pt (**4**) with unreacted Ph_2SiH_2 (Scheme 4). The formation of **9** was confirmed via its independent synthesis from **4** and Ph_2SiH_2 (Figure 7).

The reaction of the palladium diarylcarbene **7** with Ph_2SiH_2 shows only trace amounts of the expected organic product (Scheme 4). Analysis of the reaction mixture reveals two palladium products: 62% of the metal silane adduct ($P^{ter}P$)Pd(Ph_2SiH_2) (**10**) and 38% of the carbene decomposition product **8**. The observed organic product to silane adduct ratio indicates that **7** undergoes decomposition before it can react fully with

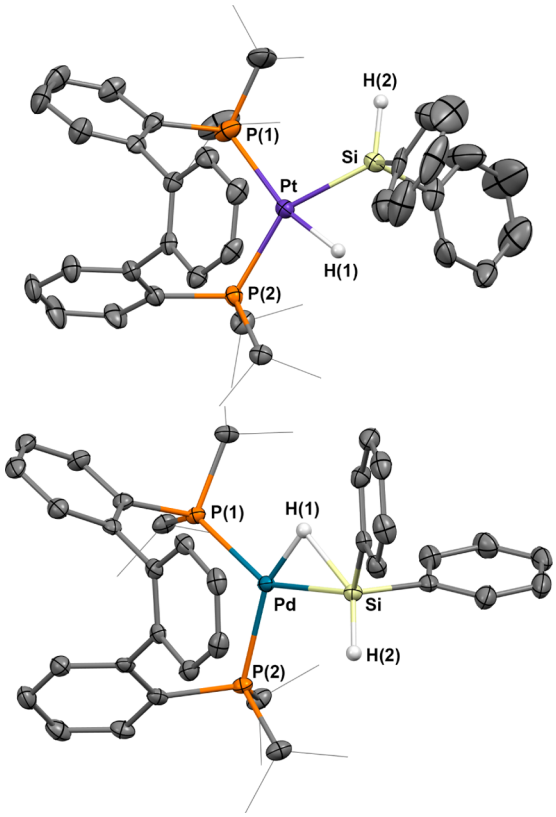


Figure 7. Molecular structures of **9** (top) and **10** (bottom) with displacement parameters at the 50% probability level. Most hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): for **9**, Pt−Si = 2.3302(16), Pt−H(1) = 1.69(6), Pt−P(1) = 2.2877(14), Pt−P(2) = 2.3335(13), Pt−H(2) = 3.28, Si−H(1) = 2.21, Si−H(2) = 1.41(5), P(1)−Pt−P(2) = 109.93(5), P(1)−Pt−Si = 100.40(6), P(2)−Pt−Si = 148.28(5), P(1)−Pt−H(1) = 163(2), P(2)−Pt−H(1) = 86(2), H(1)−Pt−Si = 64(2), Pt−Si−H(2) = 120(2); for **10**, Pd−Si = 2.3436(6), Pd−H(1) = 1.55(2), Pd−P(1) = 2.3691(5), Pd−P(2) = 2.3295(5), Pd−H(2) = 3.10, Si−H(1) = 1.87(2), Si−H(2) = 1.41(2), P(1)−Pd−Si = 146.28(2), P(2)−Pd−Si = 105.27(2), P(1)−Pd−P(2) = 108.417(19), P(1)−Pd−H(1) = 93.7(9), P(2)−Pd−H(1) = 157.7(9), H(1)−Pd−Si = 41.3(8), Pd−Si−H(2) = 108.7(10).

the substrate. Further inspection of the organic products reveals multiple carbene-related species, including the corresponding azine and 1,1,2,2-tetra-*p*-tolylethene, likely a consequence of the in situ generation of **7**. We hypothesize that the latter is a result of palladium coupling of the diazo starting material to generate the corresponding olefin, a reaction that has precedent in transition-metal chemistry. For example, ruthenium, copper, and gold compounds have proven to be competent at this transformation catalytically.[57,60−64] Such a process would represent an additional pathway for the formation of the silane adduct **10**, which would result from **6**, in turn formed by the dissociation of the carbene from **7**, explaining the relatively large amount of **10** formed. It should be noted that the platinum analogue does not lead to the same coupling between two (*p*-tol)$_2$C: fragments even upon extended heating at 120 °C, highlighting the increased stability of **5** in comparison to **7**.

As for **9**, the formation of **10** was confirmed through its independent synthesis. Evaluation of **9** and **10** via NMR spectroscopy indicates that both complexes are undergoing dynamic processes, but to a different extent. The palladium silane adduct shows equivalent environments for the two silane

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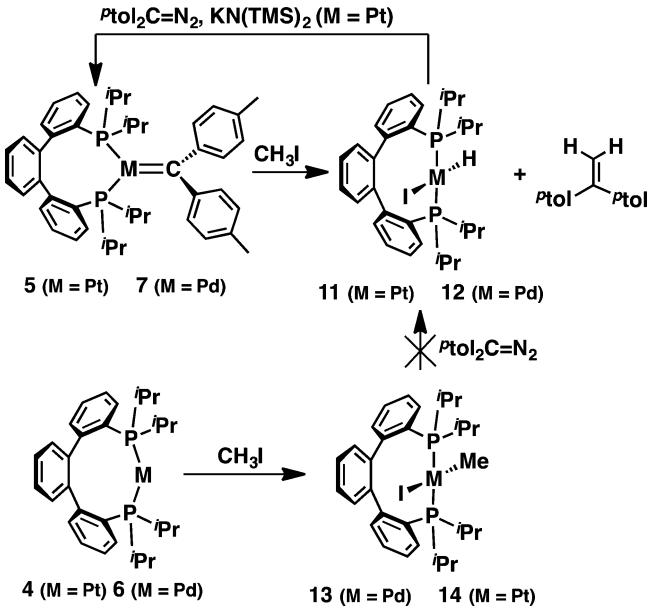
protons at 1.74 ppm. This value is shifted upfield from free silane (5.5 ppm), indicating an interaction with the metal center. Palladium silane adducts have been previously reported and commonly exhibit dynamic behavior.[65,66] It has been proposed that the two silane protons can exchange through an η^2-silane intermediate, explaining the equivalent environments observed in the ^{1}H NMR spectrum. In contrast to **10**, the platinum analogue **9** shows two distinct environments for the silane protons (−3.73 and 5.10 ppm). Additionally, its ^{31}P NMR spectrum shows two nonequivalent phosphine environments as unresolved doublets at 40.36 and 35.78 ppm. This asymmetry indicates a larger extent of silane oxidative addition in comparison to that in the palladium analogue; however, the ^{1}H NMR and ^{31}P NMR signatures are reminiscent of previously reported platinum silane adducts that exhibit fluxional behavior.[67] Examining the ^{29}Si NMR spectra for each of the compounds provides additional support for the larger extent of oxidative addition of the silane to the platinum analogue in comparison to the palladium analogue. The signal in the platinum compound is an apparent doublet at 6.6 ppm with platinum satellites (J_{SiP} = 149 Hz, J_{SiPt} = 1221 Hz). In contrast, the palladium species exhibits a singlet in the ^{29}Si NMR spectrum at −9.23 ppm. In the solid-state molecular structures (Figure 7) of both species, the Si−M−P (M = Pt, Pd) angle is larger than the optimal 90° for a square-planar geometry; however, this value is larger for the palladium (105.27(2)°) than for the platinum analogue (100.40(6)°).

In addition to Si−H bond insertion reactions, the ability of diazomethanes to react with transition-metal−carbon bonds has led to some interesting reactivity that involves carbenoid intermediates, ultimately leading to carbon−carbon cross-coupling processes. It is largely accepted that transition-metal carbenes can undergo migratory insertion into metal−R (R = alkyl, benzyl, vinyl) bonds, generating new C−C bonds.[2,6,68−74] Although palladium has been researched, it is not one of the most extensively studied transition metals. Therefore, we became interested in determining if **5** and **7** exhibited reactivity similar to that of previously reported examples.[2,6,68−74] Reacting **5** with 1 equiv of iodomethane leads to the clean formation of 1,1-di-*p*-tolylethylene (Scheme 5), along with ($P^{ter}P$)PtHI (**11**), which could be separated due to their differences in solubility. Compound **11** was characterized by single-crystal X-ray diffraction (Figure S68 in the Supporting Information) and multinuclear NMR spectroscopy (Figures S46−S48 in the Supporting Information). The hydride ligand is easily identified in the ^{1}H NMR spectrum by a triplet at −13.1 ppm, with platinum satellites ($^1J_{HPt}$ = 1200 Hz). Regeneration of the diarylcarbene **5** from **11** could be achieved through the addition of KN(TMS)$_2$ followed by the addition of the diazo reagent (Scheme 5). The analogous reaction with **7** and iodomethane led only to a trace amount of the expected organic product. The crude reaction mixture revealed that **7** reacts similarly to the platinum analogue **5**. In addition to ($P^{ter}P$)PdHI (**12**), the decomposition product **8** was observed in the reaction mixture, as well as the oxidative addition product ($P^{ter}P$)PdI(CH$_3$) (**13**). The presence of **13** was confirmed by its independent synthesis and is attributed to palladium coupling of the diazo substrate, generating the corresponding olefin along with palladium(0) (see discussion above). These results indicate, once again, that the instability of the palladium carbene inhibits its reactivity with a given substrate and, instead, leads to complicated reaction mixtures.

Scheme 5. Reactions of 5 and 7 with CH$_3$I



Group 10 metal carbenes have been invoked as intermediates in the catalytic coupling of tosylhydrazones with benzyl, vinyl, and alkyl halides.[1,2,6] This reaction is proposed to occur via the oxidative addition of the R−X (R = benzyl, vinyl, or alkyl group, X = any halogen) substrate to palladium(0), followed by the formation of the carbene from the tosyl hydrazone reagent. Insertion of the carbene into the Pd−R bond, followed by β-hydride elimination, releases the organic product. Palladium(0) is regenerated through the addition of a base. Additionally, Fryzuk and co-workers observed similar reactivity with an iridium vinylidene, Ir=C=CH$_2$[N(SiMe$_2$CH$_2$PPh$_2$)], and iodomethane.[75] They were able to observe intermediates spectroscopically and show that the transformation occurred via the insertion of the vinylidene into the iridium−carbon bond that resulted from the initial oxidative addition of the substrate to the metal center; this pathway is reminiscent of the proposed mechanism for group 10 metal coupling of diazo compounds with aryl, alkyl, and vinyl halides. In order to probe this proposed mechanism, we attempted to generate the same organic product through the reaction of the palladium (**13**) and platinum (($P^{ter}P$)PtI(CH$_3$), **14**) iodomethyl species with (*p*-tol)$_2$CN$_2$ (Scheme 5); however, no reaction occurred. This result could be due to the presence of the chelating phosphine ligand, which would lead to an unlikely five-coordinate carbene intermediate upon oxidative addition of the substrate. In our case, more likely, the R−X bond is cleaved in a cooperative manner by the metal center and the carbene moiety, similarly to what was observed for the four-coordinate group 10 metal carbenes reported previously by our group.[10]

CONCLUSIONS

We have described the synthesis and characterization of trigonal-planar palladium and platinum diarylcarbenes. The palladium carbene was spectroscopically characterized in solution; however, the instability of the species impeded its solid-state characterization. The observed palladium carbene is analogous to the isolated platinum carbene, as indicated by their similar spectroscopic signatures and further supported by DFT calculations. The $P^{ter}P$ ligand allowed the synthesis of

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trans, two-coordinate palladium(0) and platinum(0) compounds and was capable of adopting a wide-angle cis arrangement upon carbene formation, highlighting its flexibility. Additionally, the ability of P^{ter}P to stabilize two-coordinate Pd(0) and Pt(0) monomeric compounds alleviates the need to break apart dimeric species, which commonly form with ligands exhibiting a preference for cis coordination. The reactivity of the isolated palladium and platinum diarylcarbenes was investigated with Ph_2SiH_2 and CH_3I. We found that both species were competent at performing the respective transformations stoichiometrically, although the instability of the palladium compound led to more decomposition in comparison to that in the case of platinum. Current efforts are focused on developing catalytic applications involving the palladium and platinum carbenes.

EXPERIMENTAL SECTION

All manipulations of air- and water-sensitive compounds were performed under a dry nitrogen atmosphere using an MBraun drybox. Glassware, vials, and stir bars were dried in an oven at 120 °C overnight and evacuated for 12 h in the antechamber before being brought into the drybox. All solvents were dried by passing through a column of activated alumina, followed by storage over molecular sieves and sodium. Deuterated solvents were purchased from Cambridge Isotope Laboratories. C_6D_6 and $C_6D_5CD_3$ were dried by stirring over CaH_2 followed by filtration. $CDCl_3$ and C_6D_{12} were dried over molecular sieves. KC_8,[76] (*p*-tol)$_2$CN$_2$,[77] and [{(TMS)CH$_2$}$_2$Pd(COD)][50] were prepared according to literature procedures. All other chemicals were commercially available and were used as received. NMR spectra were obtained on Bruker 400 and Bruker 500 spectrometers at ambient temperature unless stated otherwise. Chemical shift values are reported in ppm relative to residual internal protio solvents or to a TMS standard for ^{1}H and ^{13}C{^{1}H} experiments. ^{195}Pt{^{1}H} NMR chemical shifts are relative to an external standard of Na_2PtCl_4 in D_2O, and ^{31}P{^{1}H} NMR chemical shifts are relative to an external standard of PPh_3 in C_6D_6. ^{29}Si{^{1}H} NMR chemical shifts are relative to an external standard of TMS in $CDCl_3$. Coupling constants are reported in Hz. CHN analyses were performed on a CE-440 Elemental Analyzer or by Midwest Microlab. Gaussian 03 (revision D.02) was used for all reported calculations. The B3LYP (DFT) method was used to carry out the geometry optimizations on model compounds specified in the text using the LANL2DZ basis set. The validity of the true minima was checked by the absence of negative frequencies in the energy Hessian.

Synthesis of 1,2-Bis(2-bromophenyl)benzene. The ligand precursor was synthesized according to a modified procedure.[78] *o*-Diiodobenzene (1.1 g, 3.3 mmol), 2-bromophenylboronic acid (6.7 g, 33.3 mmol), PPh_3 (843.6 mg, 3.2 mmol), $Pd(PPh_3)_4$ (350.3 mg, 0.03 mmol), and 100 mL of THF were placed in a Schlenk flask under an inert atmosphere. A 2 M KOH solution was purged with N_2, and 30 mL was transferred into the mixture. The mixture was stirred under an atmosphere of N_2 at 60 °C for 24 h. The organic layer was separated from the aqueous layer and filtered through silica. All of the volatiles were removed under reduced pressure. The residue was redissolved in hexanes and washed with H_2O_2. The organic layer was separated from the aqueous layer, dried over Na_2SO_4, and filtered over silica. If needed, the product was further purified by column chromatography (silica, *n*-hexane). The product, 1,2-bis(2-bromophenyl)benzene, was isolated as a colorless oil (1.1 g, 86%).

Synthesis of P^{ter}P (1). A solution of 1,2-bis(2-bromophenyl)-benzene (500.0 mg, 1.3 mmol) in 15 mL of Et_2O was chilled to −78 °C for 30 min, followed by the addition of *n*-butyllithium (1.62 mL, 2.6 mmol) by syringe. The mixture was warmed to room temperature and stirred for 1 h. The solution was chilled to −78 °C for 30 min before the addition of chlorodiisopropylphosphine (0.42 mL, 2.6 mmol) via syringe. The solution was stirred at room temperature for 12 h. The reaction mixture was quenched with 1 mL of a degassed 10% solution of NH_4Cl in H_2O. The solution was dried over anhydrous Na_2SO_4 and filtered through a pad of Celite. The volatiles were removed under reduced pressure. P^{ter}P (**1**) was isolated by recrystallization from a concentrated *n*-pentane solution at −35 °C. Yield: 477 mg, 80%. Data for **1** are as follows. ^{1}H NMR (500 MHz, C_6D_6): δ 0.67 (dd, 6H, CH(CH_3)$_2$, J_{HH} = 7 Hz, J_{HP} = 13 Hz), 0.90 (dd, 6H, CH(CH_3)$_2$, J_{HH} = 7 Hz, J_{HP} = 11 Hz), 0.97 (dd, 6H, CH(CH_3)$_2$, J_{HH} = 5 Hz, J_{HP} = 12 Hz), 1.11 (dd, 6H, CH(CH_3)$_2$, J_{HH} = 7 Hz, J_{HP} = 15 Hz), 1.71 (m, 2H, CH(CH$_3$)$_2$), 1.96 (m, 2H, CH(CH$_3$)$_2$), 7.00 (td, 2H, ArH, J_{HH} = 7.5 Hz, J_{HP} = 1.5 Hz), 7.08 (t, 2H, ArH, J_{HH} = 7 Hz), 7.21 (m, 6H, ArH), 7.77 (ddd, 2H, ArH, J_{HH} = 7.5 Hz, J_{HH} = 3.5 Hz, J_{HP} = 1 Hz). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 20.1 (d, CH(CH$_3$)$_2$, J_{CP} = 4 Hz), 20.2 (d, CH(CH_3)$_2$, J_{CP} = 2 Hz), 20.6 (d, CH(CH$_3$)$_2$, J_{CP} = 12 Hz), 20.8 (d, CH(CH_3)$_2$, J_{CP} = 22 Hz), 23.2 (d, CH(CH$_3$)$_2$, J_{CP} = 15 Hz), 27.8 (d, CH(CH_3)$_2$, J_{CP} = 17 Hz), 126.40 (s, Ar*C*), 126.6 (s, Ar*C*), 127.9 (s, Ar*C*), 131.9 (d, Ar*C*, J_{CP} = 3 Hz), 132.5 (d, Ar*C*, J_{CP} = 2 Hz), 133.4 (t, Ar*C*, J_{CP} = 7 Hz), 141.5 (d, Ar*C*, J_{CP} = 5 Hz), 150.3 (d, Ar*C*, J_{CP} = 31 Hz). ^{31}P{^{1}H} NMR (200 MHz, C_6D_6): δ −3.7 (s).

Synthesis of [(P^{ter}P)PtCl$_2$] (2). In a scintillation vial, a solution of P^{ter}P (**1**, 75.0 mg, 0.16 mmol) in 5 mL of THF was added to a solution of [(COD)PtCl$_2$] (60.6 mg, 0.16 mmol, 5 mL of THF). The mixture was heated for 12 h at 60 °C in a Schlenk tube. The volatiles were removed under reduced pressure and the residue was triturated with *n*-pentane (3 × 5 mL). The solvent was decanted, and the resulting white powder was washed with *n*-pentane and dried under reduced pressure. Yield: 90 mg, 76%. Data for **2** are as follows. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 1.06 (br s, 6H, CH(CH_3)$_2$), 1.35 (dd, 6H, CH(CH_3)$_2$, J_{HP} = 16 Hz, J_{HH} = 8 Hz), 1.56 (m, 12H, CH(CH_3)$_2$), 2.20 (br m, 2H, CH(CH$_3$)$_2$), 3.02 (br m, 2H, CH(CH$_3$)$_2$), 7.09 (br m, 2H, ArH), 7.15 (app t, 2H, ArH, J_{HH} = 4 Hz), 7.27 (app t, 4H, ArH, J_{HH} = 4 Hz), 7.40 (br m, 2H, ArH), 7.53 (dd, 2H, ArH, J_{HP} = 5.6 Hz, J_{HH} = 3.6 Hz). ^{1}H NMR (400 MHz, $CDCl_3$, 60 °C): δ 1.06 (br dd, 6H, CH(CH_3)$_2$, J_{HH} = 4 Hz, J_{HP} = 8 Hz), 1.34 (dd, 6H, CH(CH_3)$_2$, J_{HP} = 16 Hz, J_{HH} = 8 Hz), 1.56 (m, 12H, CH(CH_3)$_2$), 2.24 (m, 2H, CH(CH$_3$)$_2$), 3.05 (m, 2H, CH(CH$_3$)$_2$), 7.07 (br m, 2H, ArH), 7.14 (dd, 2H, ArH, J_{HH} = J_{HP} = 4 Hz), 7.24 (app t, 4H, ArH, J_{HH} = 4 Hz), 7.39 (br m, 2H, ArH), 7.51 (dd, 2H, ArH, J_{HP} = 8 Hz, J_{HH} = 4 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 20 °C): δ 21.1 (d, CH(CH$_3$)$_2$, J_{CP} = 5.8 Hz), 22.2 (s, CH(CH_3)$_2$), 22.7 (s, CH(CH_3)$_2$), 23.0 (s, CH(CH$_3$)$_2$), 23.0 (br s, CH(CH$_3$)$_2$), 26.8 (d, CH(CH$_3$)$_2$, J_{CP} = 30 Hz), 28.0 (br t, CH(CH$_3$)$_2$, J_{CP} = 15.5 Hz), 125.6 (d, Ar*C*, J_{CP} = 6.4 Hz), 127.8 (s, Ar*C*), 129.9 (s, Ar*C*), 130.5 (br s, Ar*C*), 132.9 (br s, Ar*C*), 133.7 (d, Ar*C*, J_{CP} = 8.4 Hz), 140.4 (br s, Ar*C*), 147.3 (s, Ar*C*), 147.4 (s, Ar*C*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 20 °C): δ 13.6 (br s, J_{PPt} = 3759 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, −60 °C): δ 8.8 (d, J_{PP} = 13 Hz, J_{PPt} = 3679 Hz), 15.9 (d, J_{PP} = 13 Hz, J_{PPt} = 3826 Hz). ^{195}Pt{^{1}H} NMR (86 MHz, $CDCl_3$, 20 °C): δ −4075.8 (t, J_{PtP} = 3752 Hz). Anal. Calcd for $C_{30}H_{40}Cl_2P_2Pt$: C, 49.46; H, 5.53. Found: C, 49.52; H, 5.44.

X-Ray Crystal Structure of [(P^{ter}P)PtCl$_2$]·C$_6$H$_6$ (2·C$_6$H$_6$). Single crystals were obtained as clear plates from a concentrated C_6D_6 solution at room temperature in the glovebox. Crystal and refinement data for **2·C$_6$H$_6$**: $C_{36}H_{46}Cl_2P_2Pt$; M_r = 806.66; monoclinic; space group $P2_1/n$; a = 9.9849(7) Å; b = 21.4059(14) Å; c = 15.5615(10) Å; α = 90°; β = 91.320(2)°; γ = 90°; V = 3325.2(4) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 4.501 mm^{-1}; d_{calc} = 1.611 g cm^{-3}; 47949 reflections collected; 5852 unique (R_{int} = 0.0714); giving R1 = 0.0281, wR2 = 0.0560 for 4621 data with $I > 2\sigma(I)$ and R1 = 0.0466, wR2 = 0.0602 for all 5852 data. Residual electron density (e Å^{-3}) max/min: 1.837/−1.808.

Synthesis of [(P^{ter}P)PdCl$_2$] (3). A solution of P^{ter}P (**1**; 25.0 mg, 0.05 mmol) in 5 mL of THF was added to a solution of [(COD)PdCl$_2$] (15.5 mg, 0.05 mmol) in 5 mL of THF and heated to 65 °C for 2 h in a Schlenk tube. The volatiles were removed under reduced pressure. The resulting residue was triturated with *n*-pentane (5 × 5 mL) and dried under reduced pressure. [(P^{ter}P)PdCl$_2$] (**3**) was isolated as a pale yellow powder. Yield: 29 mg, 83%. Data for **3** are as follows. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22 (app q, 6H CH(CH_3)$_2$, J_{HH} = J_{HP} = 10 Hz), 1.45 (app q, 6H, CH(CH_3)$_2$, J_{HH} = J_{HP} = 5 Hz), 1.66 (m, 12 H, CH(CH_3)$_2$), 3.05 (m, 2H, CH(CH$_3$)$_2$), 3.17 (m, 2H,

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$CH(CH_3)_2$), 7.09 (dd, 2H, Ar*H*, J_{HH} = 5 Hz, J_{HP} = 10 Hz), 7.20 (t, 2H, Ar*H*, J_{HH} = 5 Hz), 7.25 (t, 2H, Ar*H*, J_{HH} = 5 Hz), 7.36 (dd, 2H, Ar*H*, J_{HH} = 5 Hz, J_{HP} = 10 Hz), 7.40 (dd, 2H, Ar*H*, J_{HH} = 5 Hz, J_{HP} = 2 Hz), 7.55 (m, 2H, Ar*H*). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 19.4 (s, $CH(CH_3)_2$), 19.6 (s, $CH(CH_3)_2$), 20.4 (s, $CH(CH_3)_2$), 24.5 (t, $CH(CH_3)_2$, J_{CP} = 8 Hz), 25.0(t, $CH(CH_3)_2$, J_{CP} = 11 Hz), 24.4 (t, $CH(CH_3)_2$, J_{CP} = 10 Hz), 126.2 (t, ArC, J_{CP} = 3 Hz), 127.4 (s, ArC), 128.0 (s, ArC), 130.8 (s, ArC), 132.6 (s, ArC), 133.6 (t, ArC, J_{CP} = 5 Hz), 137.0(t, ArC, J_{CP} = 19 Hz), 141.7 (t, ArC, J_{CP} = 1 Hz), 145.9 (t, ArC, J_{CP} = 8 Hz). $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ 33.1 (s). Anal. Calcd for $C_{30}H_{40}Cl_2P_2Pd$: C, 56.31; H, 6.30. Found: C, 55.95; H, 6.25.

X-ray Crystal Structure of [($P^{ter}P$)PdCl$_2$] (3). Single crystals were obtained as yellow needles from a concentrated THF solution layered with *n*-pentane at −35 °C in the glovebox. Crystal and refinement data for **3**: $C_{30}H_{40}Cl_2P_2Pd$; M_r = 639.86; triclinic; space group $P\bar{1}$; a = 11.1678(7) Å; b = 15.7553(9) Å; c = 16.9878(10) Å; α = 88.891(2)°; β = 73.797(2)°; γ = 80.222(2)°; V = 2827.4(3) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 0.977 mm^{-1}; d_{calc} = 1.503 g cm^{-3}; 60818 reflections collected; 9962 unique (R_{int} = 0.0408); giving R1 = 0.0313, wR2 = 0.0756 for 8177 data with $I > 2\sigma(I)$ and R1 = 0.0426, wR2 = 0.0803 for all 9962 data. Residual electron density (e Å^{-3}) max/min: 0.962/−0.550.

Synthesis of [($P^{ter}P$)Pt] (4). A suspension of KC_8 (17.4 mg, 0.13 mmol) in 5 mL of THF was added dropwise to a solution of [($P^{ter}P$)PtCl$_2$] (**2**; 46.1 mg, 0.06 mmol) in 5 mL of THF. The mixture was stirred at room temperature for 10 min. The volatiles were removed under reduced pressure, followed by extraction with *n*-pentane. The crude product was isolated as an orange powder (40.1 mg, 96%). Analytically pure **4** was isolated by recrystallization from a concentrated solution of *n*-pentane at −35 °C (10 mg, 36%). Data for **4** are as follows. ^1H NMR (500 MHz, C_6D_6): δ 1.11 (app q, 6H, $CH(CH_3)_2$, J_{HH} = 5 Hz), 1.20 (m, 12H, $CH(CH_3)_2$), 1.29 (app q, 6H, $CH(CH_3)_2$, J_{HP} = 10 Hz), 2.29 (m, 4H, $CH(CH_3)_2$), 6.91 (t, 2H, Ar*H*, J_{HH} = 10 Hz), 7.00 (t, 2H, Ar*H*, J_{HH} = 7.5 Hz), 7.04 (m, 2 H, Ar*H*), 7.16 (m, 4H, Ar*H*), 7.43 (d, 2H, Ar*H*, J_{HH} = 6.5 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 18.1 (s, $CH(CH_3)_2$), 21.3 (s, $CH(CH_3)_2$), 21.3 (t, $CH(CH_3)_2$, J_{CP} = 5.3 Hz), 22.4 (t, $CH(CH_3)_2$, J_{CP} = 3.5 Hz), 23.9 (t, $CH(CH_3)_2$, J_{CP} = 11.4 Hz), 29.4 (t, $CH(CH_3)_2$, J_{CP} = 8.6 Hz), 125.0 (s, ArC), 125.7 (s, ArC), 127.2 (s, ArC), 131.4 (s, ArC), 132.1 (s, ArC), 132.5 (s, ArC), 141.6 (s, ArC), 149.6 (d, J_{CP} = 8 Hz, ArC). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 63.3 (s, J_{PPt} = 4597 Hz). $^{195}Pt\{^1H\}$ NMR (86 MHz, C_6D_6): δ −5759.1 (t, J_{PtP} = 4515 Hz). Anal. Calcd for $C_{30}H_{40}P_2Pt$: C, 54.79; H, 6.13. Found: C, 54.65; H, 5.88.

X-ray Crystal Structure of [($P^{ter}P$)Pt] (4). Single crystals were obtained as yellow blocks from a concentrated *n*-pentane solution at −35 °C in the glovebox. Crystal and refinement data for **4**: $C_{30}H_{40}P_2Pt$; M_r = 657.65; triclinic; space group $P\bar{1}$; a = 10.4152(16) Å; b = 17.115(3) Å; c = 17.993(3) Å; α = 69.156(4)°; β = 89.994(4)°; γ = 80.636(4)°; V = 2951.6(8) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 4.877 mm^{-1}; d_{calc} = 1.480 g cm^{-3}; 54024 reflections collected; 10422 unique (R_{int} = 0.0921); giving R1 = 0.0945, wR2 = 0.2311 for 7847 data with $I > 2\sigma(I)$ and R1 = 0.1138, wR2 = 0.2477 for all 10422 data. Residual electron density (e Å^{-3}) max/min: 3.415/−2.528.

Synthesis of [($P^{ter}P$)Pt═C(*p*-tol)$_2$] (5). A solution of [($P^{ter}P$)Pt] (**4**; 43.9 mg, 0.07 mmol) in 5 mL of Et_2O was mixed with a solution of $(p\text{-tol})_2CN_2$ (14.8 mg, 0.07 mmol) in 5 mL of Et_2O. The reaction mixture was stirred at room temperature for 2 h. The volatiles were removed under reduced pressure and the residue was redissolved in *n*-pentane. The solution was filtered through a pad of Celite and concentrated in vacuo. The product crystallized at −35 °C from this concentrated solution. Yield: 18 mg, 40%. Data for **5** are as follows. ^1H NMR (500 MHz, C_6D_6): δ 0.99 (m, 12H, $CH(CH_3)_2$), 1.09 (app q, 6H, $CH(CH_3)_2$, J = 7.2 Hz), 1.40 (app q, 6H, $CH(CH_3)_2$, J = 8 Hz), 2.24 (s, 3H, $C_6H_4CH_3$), 2.27 (br t, 3H, $C_6H_4CH_3$, J_{HP} = 4 Hz), 2.45 (m, 2H, $CH(CH_3)_2$), 2.54 (m, 2H, $CH(CH_3)_2$), 6.85 (m, 2H, Ar*H*), 6.89 (m, 2H, Ar*H*), 7.08 (br m, 2H, Ar*H*), 7.20 (m, 5H, Ar*H*), 7.39 (m, 2H, Ar*H*), 7.45 (m, 2H, Ar*H*), 7.49 (m, 2H, Ar*H*). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 18.2 (s, $CH(CH_3)_2$, J_{CPt} = 141 Hz), 20.3 (s, $CH(CH_3)_2$, J_{CPt} = 26 Hz), 20.8 (s, $CH(CH_3)_2$, J_{CPt} = 20 Hz), 21.5 (s, $C_6H_4CH_3$), 21.59 (t, $CH(CH_3)_2$, J_{CP} = 1 Hz), 27.2 (t, $CH(CH_3)_2$, J_{CP} = 10 Hz), 31.8 (s, $C_6H_4CH_3$), 35.6 (t, $CH(CH_3)_2$, J_{CP} = 14 Hz, J_{CPt} = 95 Hz), 126.4 (s, ArC), 126.5 (t, ArC, J_{CP} = 10 Hz), 127.4 (s, ArC), 127.4 (s, ArC), 129.0 (s, ArC), 129.8 (s, ArC), 130.1 (s, ArC), 132.4 (br s, ArC), 133.3 (t, ArC, J_{CP} = 4 Hz), 133.6 (t, ArC, J_{CP} = 5 Hz), 142.5 (s, ArC), 146.9 (t, ArC, J_{CP} = 8 Hz), 154.5 (t, ArC, J_{CP} = 11 Hz), 155.4 (t, ArC, J_{CP} = 25 Hz), 262.8 (t, Pt = C(*p*-tol)$_2$, J_{CP} = 65.5 Hz, J_{CPt} = 1775 Hz. $^{31}P\{^1H\}$ NMR (200 MHz, C_6D_6): δ 51.8 (s, J_{PPt} = 2234 Hz). $^{195}Pt\{^1H\}$ NMR (86 MHz, C_6D_6): δ −3702.0 (t, J_{PtP} = 2234 Hz). Anal. Calcd for $C_{45}H_{54}P_2Pt$: C, 63.44; H, 6.39. Found: C, 63.50; H, 6.31.

X-ray Crystal Structure of [($P^{ter}P$)Pt═C(*p*-tol)$_2$] (5). Single crystals were obtained as dark red blocks from a concentrated solution of *n*-pentane at −35 °C in the glovebox. Crystal and refinement data for **5**: $C_{45}H_{54}P_2Pt$; M_r = 851.91; monoclinic; space group $P2_1/c$; a = 14.9955(10) Å; b = 14.4043(9) Å; c = 18.4309(12) Å; α = 90°; β = 103.3790(10)°; γ = 90°; V = 3873.0(4) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 3.736 mm^{-1}; d_{calc} = 1.461 g cm^{-3}; 89959 reflections collected; 9615 unique (R_{int} = 0.0819); giving R1 = 0.0315, wR2 = 0.0573 for 7469 data with $I > 2\sigma(I)$ and R1 = 0.0544, wR2 = 0.0634 for all 9615 data. Residual electron density (e Å^{-3}) max/min: 1.875/−1.473.

Synthesis of [(PterP)Pd] (6). *Method A.* In a 20 mL scintillation vial, a solution of $P^{ter}P$ (**1**; 50.0 mg, 0.11 mmol) in 5 mL of Et_2O was added to [(COD)Pd($CH_2TMS)_2$] (33.6 mg, 0.11 mmol). The mixture was stirred at room temperature for 1 h. The orange solution was filtered through a pad of Celite, concentrated under reduced pressure, and layered with *n*-pentane. The product **6** crystallized from this solution at −35 °C. Yield: 28 mg, 46%.

Method B. Potassium graphite (KC_8, 12.0 mg, 0.09 mmol) was suspended in THF (5 mL) and added to a solution of **3** (27.7 mg, 0.04 mmol) in 5 mL of THF dropwise. The solution was stirred at room temperature for 30 min. The volatiles were removed under reduced pressure. The residue was extracted with 10 mL of *n*-pentane. The *n*-pentane solution was filtered through a plug of Celite and concentrated under reduced pressure. Pure **6** crystallized from this concentrated solution at −35 °C. Yield: 11 mg, 45%. Data for **6** are as follows. ^1H NMR (400 MHz, C_6D_6): δ 1.02 (app q, 6H $CH(CH_3)_2$, J = 14 Hz), 1.11 (m, 12H, $CH(CH_3)_2$), 1.24 (app q, 6H, $CH(CH_3)_2$, J = 17 Hz), 2.16 (m, 4H, $CH(CH_3)_2$), 6.92 (td, 2H, Ar*H*, J_{HH} = 7 Hz, J_{HP} = 2 Hz), 6.98 (t, 2H, Ar*H*, J_{HH} = 7 Hz), 7.03 (m, 2H, Ar*H*), 7.07 (m, 2H, Ar*H*), 7.17 (d, 2H, Ar*H*, J_{HH} = 7 Hz), 7.39, (d, 2H, Ar*H*, J_{HH} = 8 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 18.2 (s, $CH(CH_3)_2$), 21.3 (s, $CH(CH_3)_2$), 22.5 (t, $CH(CH_3)_2$, J_{CP} = 7 Hz), 28.0 (t, $CH(CH_3)_2$, J_{CP} = 7 Hz), 124.1 (s, ArC), 125.9 (s, ArC), 127.1 (s, ArC), 131.6 (s, ArC), 132.2 (s, ArC), 132.3 (t, ArC, J_{CP} = 4 Hz), 136.6 (s, ArC), 140.4 (t, ArC, J_{CP} = 11 Hz), 149.8 (t, ArC, J_{CP} = 11 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 34.1 (s). Anal. Calcd for $C_{35}H_{52}P_2Pd{\cdot}C_5H_{12}$: C, 65.57; H, 8.18. Found: C, 65.91; H, 8.52.

X-ray Crystal Structure of [($P^{ter}P$)Pd]·1/2C_5H_{12} (6·1/2C_5H_{12}). Single crystals were obtained as yellow needles from a concentrated *n*-pentane solution at −35 °C in the glovebox. Crystal and refinement data for **6·1/2C_5H_{12}**: $C_{65}H_{92}P_4Pd_2$; M_r = 1210.07; monoclinic; space group $P2_1/c$; a = 18.1059(11) Å; b = 10.3894(6) Å; c = 31.9405(19) Å; α = 90°; β = 100.5762(12)°; γ = 90°; V = 5906.2(6) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 0.756 mm^{-1}; d_{calc} = 1.361 g cm^{-3}; 89377 reflections collected; 10395 unique (R_{int} = 0.0579); giving R1 = 0.0385, wR2 = 0.0912 for 7971 data with $I > 2\sigma(I)$ and R1 = 0.0574, wR2 = 0.0977 for all 10395 data. Residual electron density (e Å^{-3}) max/min: 2.437/−2.412.

Synthesis of [($P^{ter}P$)Pd═C(*p*-tol)$_2$] (7). [($P^{ter}P$)Pd] (**6**) was dissolved in hexanes and placed in a quartz J. Young NMR tube along with $(p\text{-tol})_2CN_2$ and a C_6D_6 capillary. The solution was exposed to UV radiation and monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After 1 h of UV exposure, a mixture of products was observed, including 73% [($P^{ter}P$)Pd═C(*p*-tol)$_2$] (**7**), 17% [($P^{ter}P$)Pd] (**6**), 7% decomposition of the carbene to [(2″-diisopropylphosphino-{1,1′:2′,1″-terphenyl}-2-yl)Pd(η^2-*P*,*C*-^{i}Pr$_2$P═C(*p*-tol)$_2$)] (**8**), and 4% of an unidentified product. Further exposure of the solution to UV radiation resulted in further conversion to the insertion product **8**. Storing the mixture obtained after 1 h of UV exposure in the dark at room temperature

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resulted in full conversion to **8** after 12 h (vide infra). Data for **7** are as follows. ^{1}H NMR (500 MHz, C_6D_{12}): δ 0.80 (app q, 6H, CH(CH_3)$_2$, J = 5 Hz), 0.88 (app q, 6H, CH(CH_3)$_2$, J = 5 Hz), 1.01 (app q, 6H, CH(CH_3)$_2$, J = 10 Hz), 1.44 (app q, 6H, CH(CH_3)$_2$, J = 5 Hz), 2.20 (s, 3H, $C_6H_4CH_3$), 2.33 (s, 3H, $C_6H_4CH_3$), 2.50 (m, 2H, $CH(CH_3)_2$), 6.82 (m, 6H, Ar*H*), 6.94 (m, 2H, Ar*H*), 7.09 (m, 6H, Ar*H*), 7.18 (dd, 2H, Ar*H*, J_{HH} = 5 Hz, J_{HP} = 10 Hz), 7.25 (d, 2H, Ar*H*, J_{HH} = 10 Hz), 7.41 (dd, 2H, Ar*H*, J_{HH} = 5 Hz, J_{HP} = 10 Hz). ^{13}C{^{1}H} NMR (126 MHz, $C_6D_5CD_3$, −15 °C): δ 17.8 (s, CH(CH_3)$_2$), 22.0−19.0 (obscured by solvent peak, CH(CH_3)$_2$), 22.7 (app t, CH(CH_3)$_2$, J_{CP} = 11 Hz), 33.0 (t, $CH(CH_3)_2$, J_{CP} = 11 Hz), 122.3 (s, Ar*C*), 126.1 (s, Ar*C*), 126.3 (t, Ar*C*, J_{CP} = 13 Hz), 127.1 (s, Ar*C*), 131.9 (s, Ar*C*), 133.1 (t, Ar*C*, J_{CP} = 9 Hz), 134.5 (s, Ar*C*), 135.9 (s, Ar*C*), 141.9 (s, Ar*C*), 146.8 (dd, Ar*C*, J_{CP} = 4 Hz, J_{CP} = 9 Hz), 155.2 (t, Ar*C*, J_{CP} = 15 Hz), 156.2 (t, Ar*C*, J_{CP} = 14 Hz, Ar*C*), 160.2 (s, Ar*C*), 296.4 (t, Pd=*C*(*p*-tol)$_2$, J_{CP} = 63 Hz). ^{31}P{^{1}H} NMR (200 MHz, C_6D_{12}): δ 52.4 (s).

Synthesis of 8. A benzene solution of [(P^{ter}P)Pd] (**6**; 54.9 mg, 0.10 mmol, 0.7 mL) and (*p*-tol)$_2$CN$_2$ (21.4 mg, 0.10 mmol) was placed in a quartz J. Young NMR tube and exposed to UV radiation for 5 h. The volatiles were removed under reduced pressure. The crude residue was dissolved in 2 mL of *n*-pentane. [(2″-Diisopropylphosphino-{1,1′:2′,1″-terphenyl}-2-yl)Pd(η^2 -P,C-^{i}Pr$_2$P=C(*p*-tol)$_2$)] (**8**) crystallized at −35 °C as pale orange crystals. Yield: 40 mg, 73%. Data for **8** are as follows. ^{1}H NMR (500 MHz, C_6D_6): δ 0.27 (dd, 3H, CH(CH_3)$_2$, J_{HH} = 7 Hz, J_{HP} = 18 Hz), 0.92 (m, 6H, CH(CH_3)$_2$), 1.0 (dd, 3H, CH(CH_3)$_2$, J_{HH} = 7 Hz, J_{HP} = 15 Hz), 1.09 (dd, 3H, CH(CH_3)$_2$, J_{HH} = 7 Hz, J_{HP} 11 Hz), 1.17 (dd, 3H, CH(CH_3)$_2$, J_{HH} = 7 Hz, J_{HP} = 17 Hz), 1.34 (dd, 3H, CH(CH_3)$_2$, J_{HH} = 7 Hz, J_{HP} = 15 Hz), 1.52 (dd, 3H CH(CH_3)$_2$, J_{HH} = 7 Hz, J_{HP} = 16 Hz), 1.99 (m, 1H, $CH(CH_3)_2$), 2.11 (s, 3H, $C_6H_4CH_3$), 2.16 (s, 3H, $C_6H_4CH_3$), 2.29 (m, 1H, $CH(CH_3)_2$), 2.37 (m, 1H, $CH(CH_3)_2$), 2.47 (m, 1H, $CH(CH_3)_2$), 6.80 (tt, 1H, Ar*H*, J_{HH} = 7 Hz, J_{HP} = 2 Hz), 6.99 (m, 14 H, Ar*H*), 7.32 (d, 2H, Ar*H*, J_{HH} = 8 Hz), 7.36 (t, 1H, Ar*H*, J_{HH} = 7 Hz), 7.40 (dd, 1H, Ar*H*, J_{HH} = 7 Hz, J_{HP} = 2 Hz), 7.53 (d, 2H, Ar*H*, J_{HH} = 8 Hz). ^{13}C{^{1}H} NMR (126 Hz, C_6D_6): δ 18.4 (br s, CH(CH_3)$_2$), 19.8 (d, CH(CH_3)$_2$, J_{CP} = 7 Hz), 20.2 (d, CH(CH_3)$_2$, J_{CP} = 7 Hz), 20.4 (d, CH(CH_3)$_2$, J_{CP} = 3 Hz), 20.5 (d, CH(CH_3)$_2$, J_{CP} = 3 Hz), 20.7 (d, CH(CH_3)$_2$, J_{CP} = 4 Hz), 21.0(s, $C_6H_4CH_3$), 21.0(d, CH(CH_3)$_2$, J_{CP} = 14 Hz), 21.2 (s, $C_6H_4CH_3$), 22.3 (d, CH(CH_3)$_2$, J_{CP} = 6 Hz), 22.5 (d, CH(CH_3)$_2$, J_{CP} = 4 Hz), 23.1 (d, CH(CH_3)$_2$, J_{CP} = 23.7 (d, CH(CH_3)$_2$, J_{CP} = 18 Hz), 32.3 (dd, CH(CH_3)$_2$, J_{CP} = 13 Hz, J_{CP} = 10 Hz), 122.5 (s, Ar*C*), 124.6 (dd, Ar*C*, J_{CP} = 6 Hz, J_{CP} = 3 Hz), 125.3 (s, Ar*C*), 126.3 (d, Ar*C*, J_{CP} = 6 Hz), 127.2 (dd, Ar*C*, J_{CP} = 6 Hz, J_{CP} = 3 Hz), 127.5 (s, Ar*C*), 128.4 (s, Ar*C*), 129.0 (s, Ar*C*), 129.2 (s, Ar*C*), 128.8 (app t, Ar*C*, J_{CP} = 4 Hz), 130.9 (d, Ar*C*, J_{CP} = 7 Hz), 131.5 (s, Ar*C*), 131.9 (s, Ar*C*), 133.1 (d, Ar*C*, J_{CP} = 9 Hz), 134.5 (s, Ar*C*), 134.8 (s, Ar*C*), 136.9 (s, Ar*C*), 140.7 (d, Ar*C*, J_{CP} = 3 Hz), 141.6 (d, Ar*C*, J_{CP} = 4 Hz), 147.1 (dd, *C*(*p*-tol)$_2$, J_{CP} = 8 Hz, J_{CP} = 4 Hz), 148.2 (d, Ar*C*, J_{CP} = 3 Hz), 149.2 (d, Ar*C*, J_{CP} = 4 Hz), 149.6 (s, Ar*C*), 149.8 (s, Ar*C*), 167.8 (d, Ar*C*, J_{CP} = 21 Hz), 168.6 (d, Ar*C*, J_{CP} = 21 Hz). ^{31}P{^{1}H} NMR (200 MHz, C_6D_6): δ 13.6 (d, J_{PP} = 14 Hz), 38.2 (d, J_{PP} = 14 Hz). Anal. Calcd for $C_{45}H_{54}P_2Pd$: C, 70.81; H, 7.13. Found: C, 70.67; H, 6.99.

X-ray Crystal Structure of 8. Single crystals were obtained as orange blocks from a concentrated *n*-pentane solution at −35 °C in the glovebox. Crystal and refinement data for **8**: $C_{45}H_{54}P_2Pd$; M_r = 763.22; monoclinic; space group $P2_1/c$; a = 12.1666(3) Å; b = 12.6383(3) Å; c = 25.2046(6) Å; α = 90°; β = 91.1130(10)°; γ = 90°; V = 3874.86(16) Å^3; Z = 4; T = 120(2) K; λ = 1.54178 Å; μ = 4.856 mm^{-1}; d_{calc} = 1.308 g cm^{-3}; 74785 reflections collected; 7560 unique (R_{int} = 0.0424); giving R1 = 0.0250, wR2 = 0.0674 for 7051 data with $I > 2\sigma(I)$ and R1 = 0.0272, wR2 = 0.0689 for all 7560 data. Residual electron density (e Å^{-3}) max/min: 0.965/−0.485.

Synthesis of [(Cy_3P)$_2$Pt]. To a suspension of [(COD)PtCl$_2$] (30.0 mg, 0.08 mmol) in 5 mL of THF was added a solution of Cy_3P (45.0 mg, 0.16 mmol) in 5 mL of THF. The mixture was stirred at room temperature for 12 h. The volatiles were removed under reduced pressure, and the residue was triturated with *n*-pentane (5 × 5 mL). The residue was dried under reduced pressure. [(Cy_3P)$_2$PtCl$_2$] was isolated as a white powder. Yield: 53.2 mg, 80.2%. The ^{1}H and ^{31}P{^{1}H} NMR spectra are consistent with the reported literature values.[79] The product, [(PCy_3)$_2$PtCl$_2$], was used in the next step without further purification. In a 20 mL scintillation vial, [(PCy_3)PtCl$_2$ (53.2 mg, 0.06 mmol) was dissolved in 5 mL of THF. A suspension of KC_8 (17.4 mg, 0.13 mmol) in 5 mL of THF was added to this solution. The mixture was stirred at room temperature for 3 h. The volatiles were removed under reduced pressure. The product was extracted in *n*-pentane and filtered through a pad of Celite. The volatiles were removed under reduced pressure and the product, [(PCy_3)$_2$Pt], was isolated as a yellow powder. Yield: 27.0 mg, 55%. The ^{1}H and ^{31}P{^{1}H} NMR spectra are consistent with the reported literature values.[32]

Reaction of [(Cy_3P)$_2$Pt] with (*p*-tol)$_2$CN$_2$. [(Cy_3P)$_2$Pt] (27.0 mg, 0.04 mmol) was dissolved in C_6D_6 and added to (*p*-tol)$_2$CN$_2$ (7.8 mg, 0.04 mmol). The mixture was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy until full conversion of (*p*-tol)$_2$CN$_2$ to (*p*-tol)$_2$C=N−N=C(*p*-tol)$_2$ was achieved (12 h). No conversion of [(PCy_3)$_2$Pt] was observed. The ^{1}H NMR spectrum for (*p*-tol)$_2$C=N—N=C(*p*-tol)$_2$ is consistent with the reported literature values.[80]

Reaction between [(P^{ter}P)Pt=C(*p*-tol)$_2$] (5) and H_2SiPh_2. A C_6D_6 solution of [(P^{ter}P)Pt=C(*p*-tol)$_2$] (**5**; 28.1 mg, 0.04 mmol) was placed in a J. Young NMR tube along with 2 equiv of Ph_2SiH_2 (0.02 mL, 0.08 mmol). The solution was heated to 120 °C for 3 days and monitored by ^{31}P{^{1}H} NMR spectroscopy to ensure full consumption of **5**. The volatiles were removed, and the crude residue was dissolved in *n*-pentane. The solution was chilled to −35 °C to induce precipitation of [(P^{ter}P)Pt(H)SiHPh$_2$] (**9**), leaving the organic product, (di-*p*-tolylmethyl)diphenylsilane (69% crude NMR yield), in the mother liquor. The final organic product was purified by column chromatography (silica, hexanes). Data for (di-*p*-tolylmethyl)-diphenylsilane are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 6H, $C_6H_4CH_3$), 4.09 (d, 1H, $CH(p\text{-tol})_2$, J_{HH} = 1 Hz), 5.18 (d, 1H, Si*H*Ph$_2$, J_{HH} = 1 Hz, J_{HSi} = 160 Hz), 6.98 (d, 4H, Ar*H*, J_{HH} = 8 Hz), 7.05 (d, 4H, Ar*H*, J_{HH} = 8 Hz), 7.26 (m, 4 H, Ar*H*), 7.31 (m, 6H, Ar*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 29.9 (s, $C_6H_4CH_3$), 127.9 (s, Ar*C*), 129.2 (s, Ar*C*), 129.2 (s, Ar*C*), 129.7 (s, Ar*C*), 133.5 (s, Ar*C*), 135.0 (s, Ar*C*), 135.9 (s, Ar*C*), 129.0 (s, Ar*C*).

Synthesis of [(P^{ter}P)Pt(H)SiHPh$_2$] (9). One equivalent of Ph_2SiH_2 (7.6 μL, 0.04 mmol) was added via syringe to a solution of [(P^{ter}P)Pt] (**4**; 26.8 mg, 0.04 mmol) in Et_2O. The mixture was stirred at room temperature for 1 h. The volatiles were removed under reduced pressure. The crude residue was washed with cold *n*-pentane, leaving **9** as a clean tan powder (31 mg, 90%). Data for **9** are as follows. ^{1}H NMR (400 MHz, C_6D_6): δ −3.73 (dd, 1H, Pt*H*, J_{HP} = 144 Hz, J_{HP} = 20 Hz, J_{HPt} = 868 Hz), 0.88 (m, 4H, CH(CH_3)$_2$), 1.04 (m, 14H, CH(CH_3)$_2$), 1.24 (m, 6H, CH(CH_3)$_2$), 2.44 (m, 3H, $CH(CH_3)_2$), 3.21 (m, 1H, $CH(CH_3)_2$), 5.10 (m, 1H, Si*H*), 6.85 (m, 6H, Ar*H*), 6.92 (t, 1H, Ar*H*, J_{HH} = 8 Hz), 7.0 (t, 1H, Ar*H*, J_{HH} = 8 Hz), 7.07 (m, 3H, Ar*H*), 7.18 (m, 2H, Ar*H*), 7.30 (t, 3H, Ar*H*, J_{HH} = 8 Hz), 7.39 (t, 2H, Ar*H*, J_{HH} = 8 Hz), 7.98 (d, 2H, Ar*H*, J_{HH} = 8 Hz), 8.07 (d, 2H, Ar*H*, J_{HH} = 8 Hz). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 17.8 (br s, CH(CH_3)$_2$), 18.4 (br s, CH(CH_3)$_2$), 20.0 (s, CH(CH_3)$_2$), 20.1 (s, CH(CH_3)$_2$), 20.4 (s, CH(CH_3)$_2$), 20.2 (s, CH(CH_3)$_2$), 22.4 (br m, CH(CH_3)$_2$), 22.3 (d, CH(CH_3)$_2$, J_{CP} = 11 Hz), 26.7 (br d, CH(CH_3)$_2$, J_{CP} = 23 Hz), 27.9 (d, CH(CH_3)$_2$, J_{CP} = 14 H), 28.1 (d, CH(CH_3)$_2$, J_{CP} = 13 Hz), 33.9 (br d, CH(CH_3)$_2$, J_{CP} = 23 Hz), 126.1 (s, Ar*C*), 126.7 (s, Ar*C*), 127.1 (s, Ar*C*), 127.2 (s, Ar*C*), 27.3 (s, Ar*C*), 127.6 (s, Ar*C*), 126.7 (s, Ar*C*), 128.1 (Ar*C*, obscured by solvent peaks), 129.5 (s, Ar*C*), 130.1 (s, Ar*C*), 130.8 (br s, Ar*C*), 132.9 (d, Ar*C*, J_{CP} = 7 Hz), 133.5 (d, Ar*C*, J_{CP} = 7 Hz), 136.6 (s, Ar*C*, J_{CPt} = 30 Hz), 137.8 (s, Ar*C*, J_{CPt} = 34 Hz), 140.8 (s, Ar*C*), 141.5 (s, Ar*C*), 146.2 (s, Ar*C*), 146.4 (s, Ar*C*), 147.3 (s, Ar*C*), 148.2 (s, Ar*C*). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 34.7 (unresolved d, J_{PPt} = 2718 Hz), 40.4 (unresolved d, J_{PPt} = 1837 Hz). ^{195}Pt {^{1}H} NMR (C_6D_6, 86 MHz): δ −3644.2 (dd, J_{PtP} = 2750 Hz, J_{PtP} = 1848 Hz). ^{29}Si {^{1}H} NMR (C_6D_6, 80 MHz): δ 6.6 (app d, J_{SiP} = 149 Hz, J_{SiPt} = 1221 Hz) Anal. Calcd for $C_{42}H_{52}P_2PtSi$: C, 59.91; H, 6.23. Found: C, 60.01; H, 6.20.

X-ray Crystal Structure of [(P^{ter}P)Pt(H)SiHPh$_2$] (9). Single crystals were obtained as pale yellow blocks from a concentrated *n*-pentane solution at −35 °C in the glovebox. Crystal and refinement

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data for **9**: $C_{32}H_{52}P_2PtSi$; M_r = 841.95; orthorhombic; space group *Pbca*; a = 17.0851(7) Å; b = 18.5952(8) Å; c = 23.7353(11) Å; α = 90°; β = 90°; γ = 90°; V = 7540.7(6) Å^3; Z = 8; T = 120(2) K; λ = 0.71073 Å; μ = 3.867 mm^{-1}; d_{calc} = 1.483 g cm^{-3}; 116275 reflections collected; 6635 unique (R_{int} = 0.1308); giving R1 = 0.0348, wR2 = 0.0606 for 4506 data with $I > 2\sigma(I)$ and R1 = 0.0729, wR2 = 0.0672 for all 6635 data. Residual electron density (e Å^{-3}) max/min: 0.938/−0.948.

Reaction between [(P^{ter}P)Pd═C(*p*-tol)$_2$] (7) and H_2SiPh_2. To an *n*-hexane solution of [(P^{ter}P)Pd] (**6**; 20.0 mg, 0.04 mmol) was added 1 equiv of (*p*-tol)$_2$CN$_2$ (7.8 mg, 0.04 mmol). The solution was transferred to a quartz J. Young NMR tube along with a C_6D_6 capillary. The mixture was exposed to UV radiation and monitored by $^{31}P\{^1H\}$ NMR spectroscopy to ensure adequate conversion to [(P^{ter}P)Pd═C(*p*-tol)$_2$] (**7**). Next, 1 equiv of Ph_2SiH_2 was added (6.5 μL, 0.04 mmol). The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy to ensure full consumption of **7**. The evaluation of the crude ^1H NMR spectrum revealed 14% conversion to (di-*p*-tolylmethyl)diphenylsilane. The $^{31}P\{^1H\}$ NMR spectrum showed 62% conversion to [(P^{ter}P)Pd-(H)SiHPh$_2$] (**10**) and 38% conversion to the decomposition product **8**.

Synthesis of [(P^{ter}P)Pd(H)SiHPh$_2$] (10). To an Et$_2$O solution of [(P^{ter}P)Pd] (**6**; 50.0 mg, 0.09 mmol) was added 1 equiv of Ph_2SiH_2 (0.02 mL, 0.09 mmol). The mixture was stirred at room temperature for 1 h. The volatiles were removed, and the crude residue was redissolved in *n*-pentane. The solution was chilled to −35 °C, resulting in the recrystallized product (**10**; 48 mg, 72%). Data for **10** are as follows. ^1H NMR (400 MHz, C_6D_6): δ 0.94 (app q, 6H, CH(CH_3)$_2$, J_{HP} = 6 Hz), 1.13 (app q, 6H, CH(CH_3)$_2$, J_{HP} = 8 Hz), 1.20 (m, 12H, CH(CH_3)$_2$), 1.74 (s, 2H, SiH_2), 2.24 (m, 2H, CH(CH$_3$)$_2$), 2.56 (m, 2H, CH(CH$_3$)$_2$), 6.88 (m, 8 H, ArH), 7.06 (dd, 2H, ArH, J_{HH} = 8 Hz, J_{HP} = 4 Hz), 7.22 (m, 4H, ArH), 7.30 (t, 4H, ArH, J_{HH} = 8 Hz), 7.98 (d, 4H, ArH, J_{HH} = 8 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ18.9 (s, CH(CH$_3$)$_2$), 20.4 (s, CH(CH$_3$)$_2$), 20.7 (t, CH(CH$_3$)$_2$, J_{CP} = 3 Hz), 22.6 (t, CH(CH$_3$)$_2$, J_{CP} = 7 Hz), 26.3 (t, CH(CH$_3$)$_2$, J_{CP} = 5 Hz), 29.6 (t, CH(CH$_3$)$_2$, J_{CP} = 10 Hz), 126.4 (s, ArC), 126.9 (s, ArC), 127.5 (s, ArC), 128.0 (s, ArC), 130.5 (s, ArC), 130.9 (s, ArC), 131.9 (d, ArC, J_{CP} = 3 Hz), 133.0 (t, ArC, J_{CP} = 4 Hz), 136.5 (s, ArC), 140.1 (s, ArC), 43.2 (s, ArC), 47.7 (t, ArC, J_{CP} = 11 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 30.4 (s). $^{29}Si\{^1H\}$ NMR (C_6D_6, 80 MHz): δ −9.2 (s). Anal. Calcd for $C_{42}H_{52}P_2PdSi$: C, 66.96; H, 6.96. Found: C, 67.12; H, 7.14.

X-ray Crystal Structure of [(P^{ter}P)Pd(H)SiHPh$_2$] (10·C$_5$H$_{12}$). Single crystals were obtained as pale yellow blocks from a concentrated *n*-pentane solution at −35 °C in the glovebox. Crystal and refinement data for **10**·C_5H_{12}: $C_{47}H_{62.15}P_2PdSi$; M_r = 823.54; triclinic; space group $P\bar{1}$; a = 9.7476(3) Å; b = 13.3740(5) Å; c = 17.3877(6) Å; α = 72.9060(10)°; β = 83.9190(10)°; γ = 81.8410(10)°; V = 2139.73(13) Å^3; Z = 2; T = 120(2) K; λ = 0.71073 Å; μ = 0.567 mm^{-1}; d_{calc} = 1.278 g cm^{-3}; 57530 reflections collected; 7535 unique (R_{int} = 0.0396); giving R1 = 0.0256, wR2 = 0.0632 for 6926 data with $I > 2\sigma(I)$ and R1 = 0.0286, wR2 = 0.0643 for all 7535 data. Residual electron density (e Å^{-3}) max/min: 0.700/−0.343.

Reaction between [(P^{ter}P)Pt═C(*p*-tol)$_2$] (5) and CH_3I. One equivalent of CH_3I (2.5 μL, 0.04 mmol) was added to a C_6D_6 solution of [(P^{ter}P)Pt═C(*p*-tol)$_2$] (**5**; 25.0 mg, 0.04 mmol). The mixture was heated to 120 °C for 12 h in a Schlenk flask. The volatiles were removed under reduced pressure. The residue was extracted with *n*-pentane. The organic product, 1,1-di-*p*-tolylethylene (5.5 mg, 71%), was isolated from this *n*-pentane solution. The residual powder contained [(P^{ter}P)Pt(H)I (**11**; 22 mg, 86%). Data for **11** are as follows. ^1H NMR (400 MHz, C_6D_6): δ −13.10 (t, 1H, PtH, J_{HP} = 3 Hz, J_{HPt} = 1200 Hz), 0.86 (app q, 6H, CH(CH_3)$_2$, J_{HP} = 8 Hz), 1.04 (app q, 6H, CH(CH_3)$_2$, J_{HP} = 4 Hz), 1.26 (app q, 6H, CH(CH_3)$_2$, J_{HP} = 8 Hz), 1.47 (app q, 6H, CH(CH_3)$_2$, J_{HP} = 8 Hz), 2.20 (m, 2H, CH(CH$_3$)$_2$), 2.93 (m, 2H, CH(CH$_3$)$_2$), 6.83 (m, 4H, ArH), 6.92 (t, 2H, ArH, J_{HP} = 8 Hz), 7.0 (m, 2H, ArH), 7.29 (dd, 2H, ArH, J_{HH} = 8 Hz, J_{HP} = 4 Hz), 7.34 (m, 2H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 20.2 (s, CH(CH$_3$)$_2$, J_{CPt} = 19 Hz), 21.0(s, CH(CH$_3$)$_2$), 21.6 (s, CH(CH$_3$)$_2$), 21.8 (t, CH(CH$_3$)$_2$), 23.2 (t, CH(CH$_3$)$_2$, J_{CP} = 15 Hz), 29.2 (t, CH(CH$_3$)$_2$, J_{CP} = 12 Hz), 124.7 (t, ArC, J_{CP} = 4 Hz), 127.2 (s, ArC), 128.0(s, ArC), 132.6 (s, ArC, J_{CPt} = 17 Hz), 132.6 (s, ArC), 132.9 (t, ArC, J_{CP} = 4 Hz), 138.8 (t, ArC, J_{CP} = 23 Hz), 140.6 (t, ArC, J_{CP} = 3 Hz), 149.6 (t, ArC, J_{CP} = 8 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 35.2 (s, J_{PPt} = 2874 Hz). Data for 1,1-di-*p*-tolylethylene are as follows. Isolated yield: 5 mg, 0.027 mmol, 71%. ^1H NMR (400 MHz, C_6D_6): δ 2.12 (s, 6H, $C_6H_5CH_3$), 5.41 (s, 2H, $CH_2C(p\text{-tol})_2$), 6.97 (d, 4H, ArH, J_{HH} = 8 Hz), 7.32 (d, 4H, ArH, J_{HH} = 8 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 21.1 (s, $C_6H_5CH_3$), 113.0 (s, $CH_2C(p\text{-tol})_2$), 128.7 (s, ArC), 129.2 (s, ArC), 137.5 (s, ArC), 139.5 (s, ArC). Anal. Calcd for $C_{30}H_{41}IP_2Pt$: C, 45.87; H, 5.26. Found: C, 45.61; H, 5.12.

X-ray Crystal Structure of [(P^{ter}P)Pt(H)I] (11). Single crystals were obtained as colorless blocks from a concentrated diethyl ether solution at −35 °C in the glovebox. Crystal and refinement data for **11**: $C_{30}H_{40}IP_2Pt$; M_r = 784.55; tetragonal; space group $I\bar{4}$; a = 23.0436(16) Å; b = 23.0436(16) Å; c = 13.4662(12) Å; α = 90°; β = 90°; γ = 90°; V = 7150.7(12) Å^3; Z = 8; T = 120(2) K; λ = 0.71073 Å; μ = 4.891 mm^{-1}; d_{calc} = 1.458 g cm^{-3}; 54859 reflections collected; 6276 unique (R_{int} = 0.0457); giving R1 = 0.0178, wR2 = 0.0359 for 5877 data with $I > 2\sigma(I)$ and R1 = 0.0217, wR2 = 0.0379 for all 6276 data. Residual electron density (e Å^{-3}) max/min: 0.711/−0.379.

Conversion of [(P^{ter}P)Pt(H)I] (11) to [(P^{ter}P)Pt═C(*p*-tol)$_2$] (5). One equivalent of KN(SiMe$_3$)$_2$ (4.7 mg, 0.02 mmol) was added to an Et$_2$O solution of [(P^{ter}P)Pt(H)I (**11**; 18.4 mg, 0.02 mmol) in a scintillation vial. The mixture was stirred at room temperature for 2 h. The volatiles were removed under reduced pressure, and the residue was extracted with *n*-pentane. The solution was filtered over a pad of Celite. The ^1H and $^{31}P\{^1H\}$ NMR spectra indicated full conversion to [(P^{ter}P)Pt] (**4**). The addition of 1 equiv of (*p*-tol)$_2$CN$_2$ led to quantitative conversion to [(P^{ter}P)Pt═C(*p*-tol)$_2$] (**5**).

Reaction between [(P^{ter}P)Pd═C(*p*-tol)$_2$] (7) and CH_3I. [(P^{ter}P)Pd] (**6**; 20.0 mg, 0.04 mmol) was dissolved in *n*-hexane along with (*p*-tol)$_2$CN$_2$ (7.8 mg, 0.04 mmol). The solution was transferred to a quartz J. Young NMR tube along with a C_6D_6 capillary. The mixture was exposed to UV radiation for 1 h. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy to ensure adequate conversion to [(P^{ter}P)Pd═C(*p*-tol)$_2$] (**7**). Once the conversion to carbene **7** was achieved, 1 equiv of CH_3I (2.2 μL, 0.04 mmol) was added to the solution. The mixture was monitored by $^{31}P\{^1H\}$ NMR spectroscopy to ensure full consumption of the carbene. Typical reaction times were 3 h. By ^1H NMR spectroscopy, 13% conversion to 1,1-di-*p*-tolylethylene was detected. The two isomers of the byproduct [(P^{ter}P)Pd(H)I] (**12**) were observed, as indicated by two upfield resonances at −10.45 ppm (t, PdH, J_{HP} = 12 Hz) and −11.11 ppm (t, PdH, J_{HP} = 12 Hz), supporting the formation of the iodohydride complex. Evaluation of the crude $^{31}P\{^1H\}$ NMR spectrum revealed a mixture of **12** (36.01 (s) and 34.90 ppm (s)), **13**, and the decomposition product **8**.

Synthesis of [(P^{ter}P)Pd(CH$_3$)I] (13). One equivalent of CH_3I (3 μL, 0.04 mmol) was added to an Et$_2$O solution of [(P^{ter}P)Pd] (**6**; 24.3 mg, 0.04 mmol). The mixture was stirred for 1 h at room temperature. The volatiles were removed under reduced pressure, and the resulting residue was triturated with *n*-pentane. The residue was dried under reduced pressure, and the product **13** was isolated as a tan powder (29 mg, 96%). Data for **13** are as follows. ^1H NMR (400 MHz, C_6D_6, major isomer): δ −0.11 (t, 3H, PdCH_3, J_{HP} = 8 Hz), 1.07 (app q, 6H, CH(CH_3)$_2$, J_{HP} = 8 Hz), 1.29 (app q, 6H, CH(CH_3)$_2$, J_{HP} = 8 Hz), 1.46 (app q, 6H, CH(CH_3)$_2$, J_{HP} = 4 Hz), 1.72 (app q, 6H, CH(CH_3)$_2$, J_{HP} = 8 Hz), 2.53 (m, 2H, CH(CH$_3$)$_2$), 3.52 (m, 2H, CH(CH$_3$)$_2$), 6.88 (t, 2H, ArH, J_{HH} = 8 Hz), 6.95 (t, 2H, ArH, J_{HH} = 8 Hz), 7.13 (app t, 2H, ArH, J_{HP} = 4 Hz), 7.3 (m, 6H, ArH). ^1H NMR (400 MHz, C_6D_6, minor isomer): δ 0.26 (t, 3H, PdCH_3, J_{HP} = 4 Hz), CH(CH_3)$_2$ signals are obscured by major isomer, 2.84 (m, 2H, CH(CH$_3$)$_2$), 4.08 (m, 2H, CH(CH$_3$)$_2$), 7.07 (m, 2H, ArH), 7.56 (m, 2H, ArH), 6 aryl protons are obscured by the major isomer. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, major isomer): δ 4.7 (t, (PdCH$_3$, J_{CP} = 2 Hz), 20.3 (s, CH(CH$_3$)$_2$), 20.5 (s, CH(CH$_3$)$_2$), 21.3 (s, CH(CH$_3$)$_2$), 24.4 (t, CH(CH$_3$)$_2$, J_{CP} = 9 Hz), 24.7 (t, CH(CH$_3$)$_2$, J_{CP} = 8 Hz), 32.1 (t, CH(CH$_3$)$_2$, J_{CP} = 9 Hz), 125.7 (t, ArC, J_{CP} = 2 Hz), 127.3 (s, ArC), 128.1 (s, ArC), 130.3 (s, ArC), 130.8 (s, ArC), 134.2 (t, ArC, J_{CP} = 4

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Hz), 139.3 (t, ArC, J_{CP} = 26 Hz), 141.3 (t, ArC, J_{CP} = 3 Hz), 146.4 (t, ArC, J_{CP} = 8 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, minor isomer): δ −5.0 (br s, $PdCH_3$), 19.2 (s, $CH(CH_3)_2$), 19.8 (s, $CH(CH_3)_2$), 19.9 (t, $CH(CH_3)_2$, J_{CP} = 2 Hz), 24.0 (t, $CH(CH_3)_2$, J_{CP} = 8 Hz), 25.1 (t, $CH(CH_3)_2$, J_{CP} = 8 Hz), 28.3 (t, $CH(CH_3)_2$, J_{CP} = 12 Hz), 122.7(s, ArC), 124.6 (s, ArC), 126.6 (s, ArC), 130.6 (s, ArC), 132.6 (s, ArC), 133.7 (t, ArC, J_{CP} = 4 Hz), 138.4 (t, ArC, J_{CP} = 17 Hz), 143.1 (s, ArC), 145.1 (t, ArC, J_{CP} = 8 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 36.9 (s, major isomer), 31.7 (s, minor isomer). Anal. Calcd for $C_{31}H_{43}IP_2Pd$: C, 52.37; H, 6.10. Found: C, 51.99; H, 5.83.

Synthesis of [(PterP)Pt(CH$_3$)I] (14). To an Et_2O solution of [($P^{ter}P$)Pt] (**4**; 20.9 mg, 0.03 mmol) was added 1 equiv of CH_3I (2 μL, 0.03 mmol). The mixture was stirred for 1 h at room temperature, resulting in the formation of a precipitate. The suspension was decanted, and the resulting powder was triturated with *n*-pentane and dried under reduced pressure. [($P^{ter}P$)Pt(CH_3)I (**14**; 20 mg, 94%) was isolated as a tan powder. Data for **14** are as follows. ^1H NMR (400 MHz, C_6D_6): δ −0.11 (t, 3H, PtCH_3, J_{HP} = 8 Hz, J_{HPt} = 72 Hz), 1.07 (app q, 6H, CH(CH_3)$_2$, J_{HP} = 4 Hz), 1.28 (m, 6H, CH(CH_3)$_2$), 1.47 (m, 6H, CH(CH_3)$_2$), 1.68 (app q, 6H, CH(CH_3)$_2$, J_{HP} = 8 Hz), 2.63 (m, 2H, CH(CH$_3$)$_2$), 3.62 (m, 2H, CH(CH$_3$)$_2$), 6.86 (t, 2H, ArH, J_{HH} = 4 Hz), 6.94 (t, 2H, ArH, J_{HH} = 4 Hz), 7.09 (dd, 2H, ArH, J_{HH} = 6 Hz, J_{HP} = 4 Hz), 7.3 (m, 6H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ −7.9 (t, $PtCH_3$, J_{CP} = 6 Hz), 20.2 (s, $CH(CH_3)_2$, J_{CPt} = 21 Hz). 20.9 (s, $CH(CH_3)_2$), 21.1 (s, $CH(CH_3)_2$), 24.1 (t, $CH(CH_3)_2$, J_{CP} = 12 Hz), 24.2 (t, $CH(CH_3)_2$, J_{CP} = 7 Hz), 31.0 (t, $CH(CH_3)_2$, J_{CP} = 14 Hz), 125.5 (t, ArC, J_{CP} = 3 Hz), 127.3 (s, ArC), 127.68 (s, ArC), 130.6 (s, ArC, J_{CPt} = 29 Hz), 131.3 (s, ArC), 134.0 (t, ArC, J_{CP} = 4 Hz), 138.9 (t, ArC, J_{CP} = 22 Hz), 142.1 (s, ArC), 146.4 (t, ArC, J_{CP} = 8 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 30.8 (s). $^{195}Pt\{^1H\}$ NMR (C_6D_6, 86 MHz): δ −3123.5 (t, J_{PtP} = 2901 Hz). Anal. Calcd for $C_{31}H_{43}IP_2Pt$: C, 46.56; H, 5.42. Found: C, 46.50; H, 5.66.

X-ray Crystal Structure of [($P^{ter}P$)Pt(CH$_3$)I] (14). Single crystals were obtained as colorless blocks from a concentrated solution of toluene layered with *n*-pentane at −35 °C in the glovebox. Crystal and refinement data for **14**: $C_{30}H_{40}IP_2Pt$; M_r = 799.58; monoclinic; space group $P2_1/n$; a = 10.2030(9) Å; b = 14.0134(13) Å; c = 20.8771(19) Å; α = 90°; β = 93.5760(10)°; γ = 90°; V = 2979.2(5) Å^3; Z = 3; T = 120(2) K; λ = 0.71073 Å; μ = 5.8721 mm^{-1}; d_{calc} = 1.783 g cm^{-3}; 45156 reflections collected; 5254 unique (R_{int} = 0.0395); giving R1 = 0.0157, wR2 = 0.0343 for 4809 data with $I > 2\sigma(I)$ and R1 = 0.0196, wR2 = 0.0351 for all 5254 data. Residual electron density (e Å^{-3}) max/min: 0.481/−0.366.

Reaction of [($P^{ter}P$)Pt(CH$_3$)I] (14) or [($P^{ter}P$)Pd(CH$_3$)I] (13) with (*p*-tol)$_2$CN$_2$. To a THF solution of either [($P^{ter}P$)Pt(CH_3)I (**14**; 20.8 mg, 0.03 mmol) or [($P^{ter}P$)Pd(CH_3)I (**13**; 18.0 mg, 0.03 mmol) was added 1 equiv of (*p*-tol)$_2CN_2$ (7.0 mg, 0.03 mmol). The mixture was stirred at room temperature for 4 h. Evaluation of the crude reaction mixture by ^1H and ^{31}P NMR spectroscopy showed no reaction. Exposing the reaction mixtures to UV radiation led to decomposition of the diazo reagent to the corresponding azine compound, leaving the palladium and platinum starting materials unchanged.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00924.

NMR spectra for compounds **1**−**11** and **13**, X-ray structures for compounds **3**, **6**, **11**, and **14**, and DFT calculation details (PDF)

Crystallographic data (CIF)

Cartesian coordinates for the calculated structures (XYZ)

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Notes

The authors declare no competing financial interest.

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