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# Isolation of N-Heterocyclic Alkyl Intermediates en Route to Transition Metal N-Heterocyclic Carbene Complexes: Insight into a C−H Activation Mechanism

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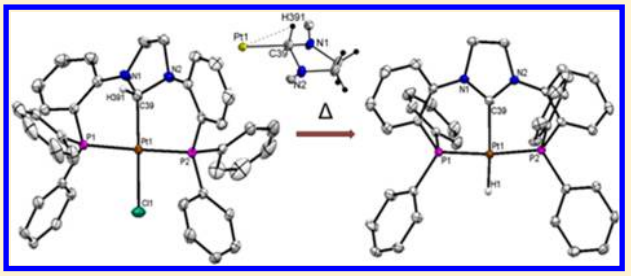
Supporting Information

**ABSTRACT:** An imidazolinium cation has been incorporated into an arene-linked diphosphine pincer ligand, $[\mathbf{2}]^+$, and the metalation of this ligand has been investigated via direct imidazolinium C−H activation to $Pd^0$ and $Pt^0$. The expected NHC-ligated metal-hydride species $[\mathbf{5}]\mathbf{PF_6}$ (M = Pt) and **6** (M = Pd) are obtained if the halide-free imidazolinium salt $[\mathbf{2}]\mathbf{PF_6}$ is used. In contrast, treatment of the imidazolinium chloride salt $[\mathbf{2}]\mathbf{Cl}$ with $M(PPh_3)_4$ leads to isolation of N-heterocyclic alkyl $M^{II}$ species **3** (M = Pd) and **4** (M = Pt), in which the imidazolinium C−H bond remains intact. Interestingly, there are no apparent agostic interactions between the imidazolinium protons and the metal centers in **3** and **4**, indicating that these species represent an unusual type of arrested C−H activation intermediate. While Pd complex **3** is thermally stable, Pt complex **4** undergoes C−H activation to afford the corresponding NHC-$Pt^{II}$-hydride species $[\mathbf{5}]\mathbf{Cl}$ upon heating. Additionally, both complexes **3** and **4** undergo rapid C−H activation upon abstraction of the metal-bound halide to form **6** and $[\mathbf{5}]\mathbf{PF_6}$, respectively. The nature of the bonding in the unusual N-heterocyclic alkyl species is investigated computationally.

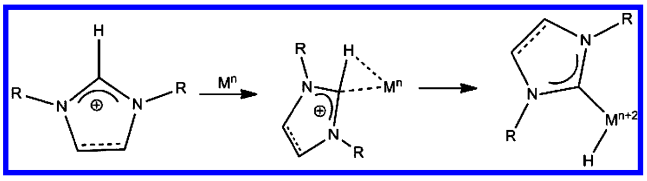


## INTRODUCTION

Transition metal-mediated C−H bond activation is a field of great interest for chemists in many areas including organic synthesis and energy-related hydrocarbon functionalization.[1−4] Depending on the electronic properties of the transition metal, C−H activation reactions can be classified into five pathways, including oxidative addition, $\sigma$-bond metathesis, metalloradical activation, 1,2-addition, and electrophilic activation.[5] Low-valent electron-rich transition metal precursors generally favor the oxidative addition pathway for C−H bond cleavage of RH, resulting in the formation of M(H)(R) species and two-electron-oxidized metal centers.[6] Prior to scission of the C−H bond, it is widely accepted that C−H bonds coordinate, forming $\sigma$-complexes, followed by C−H bond cleavage.[7,8] This mechanism is supported by a few isolated $\eta^2$ C−H agostic metal interactions in late transition metal complexes with free alkanes,[9−14] as well as arene C−H bonds within ligand frameworks whose proximity is enforced by additional chelating donors.[15−18] The latter examples are particularly relevant since C−H activation to form the metal-aryl complex can often be induced under various reaction conditions.[15,18]

Since the isolation of the first stable N-heterocyclic carbene (NHC) compound by Arduengo and co-workers in 1991,[19] NHCs have become a fixture as ligands in coordination chemistry and NHC-based homogeneous catalysis.[20−23] In general, the common preparative methods for NHC-metal complexes either require prefunctionalization of the ligand precursors or generate undesired side products.[24−27] An atom-economical pathway that has been utilized for the preparation of NHC-metal complexes is the direct imidazolium/imidazolinium C−H bond oxidative addition to low-valent late transition metal precursors to form NHC-metal-hydride complexes.[28−32] Since no intermediates featuring monodentate NHC precursors have been isolated, the mechanism for imidazolium/imidazolinium C−H bond oxidative addition is not completely clear. However, theoretical investigations by Yates and Cavell suggest that the mechanism involves the initial formation of an $\eta^2$ C−H agostic interaction,[33,34] analogous to the canonical oxidative addition mechanism for a transition metal-mediated C−H bond activation (Scheme 1). Moreover, Hill and co-workers recently reported chelation-assisted double C−H activation en route to NHC Rh and Ir complexes, and an

**Scheme 1**



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N-heterocyclic alkyl intermediate was isolated in the case of Ir.[35]

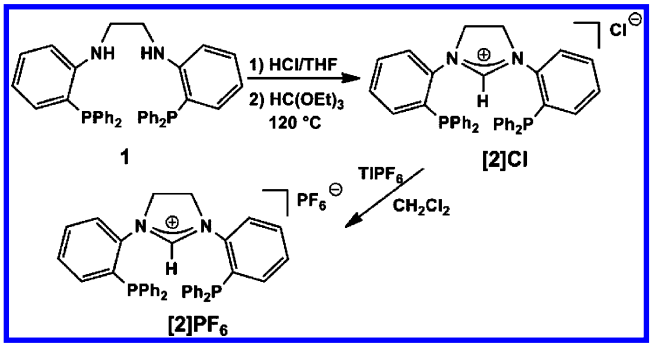
In an extension of our recent work featuring the coordination chemistry of N-heterocyclic phosphenium cations incorporated into the central position of a chelating diphosphine framework,[36−39] we chose to replace the central donor in our pincer ligand with an isolobal N-heterocyclic carbene unit. A similar ligand with diisopropylphosphine substituents was recently reported by Fryzuk and co-workers.[40] Pincer ligands have been receiving increasing attention owing to their rigidity and ability to stabilize reactive transition metal fragments,[41−45] and pincer ligands with NHC donors are now well-known.[46,47]

To extend our investigation of N-heterocyclic donor ligands to carbenes, an imidazolinium ligand precursor with diphenylphosphine-substituted *o*-phenylene linkers was synthesized straightforwardly from a known diamino/diphosphine precursor.[36] The coordination of this pincer-type imidazolinium cation to low-valent $Pd^0$ and $Pt^0$ precursors via the aforementioned C−H activation route leads to the isolation of N-heterocyclic alkyl-metal species as intermediates for the C−H bond activation process, providing valuable insight into the mechanism of imidazolinium C−H bond oxidative addition to transition metal centers.

## RESULTS AND DISCUSSION

**Ligand Synthesis.** Synthesis of the imidazolinium ligand precursor is shown in Scheme 2. Treatment of *N*,*N*′-bis(*o*-

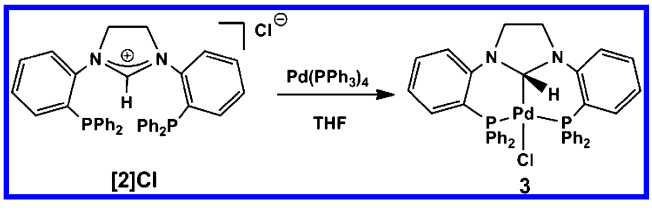
**Scheme 2**




(diphenylphosphine)phenyl)ethane-1,2-diamine[36] (**1**) with hydrochloric acid followed by treatment with triethylorthoformate affords the imidazolinium chloride salt [**2**]**Cl** as a white powder after 12 h of heating at 120 °C. The corresponding $PF_6^-$ salt [**2**]$\mathbf{PF_6}$ can be obtained via anion exchange with $TlPF_6$ (Scheme 2). The two imidazolinium ligand precursors [**2**]**Cl** and [**2**]$\mathbf{PF_6}$ have been fully characterized by NMR spectroscopy and elemental analysis.

**Addition of [2]Cl to $Pd^0$ and $Pt^0$.** The reaction of [**2**]**Cl** with $Pd(PPh_3)_4$ in THF at room temperature cleanly generates Pd complex **3**, as shown in Scheme 3. In contrast to a similar

**Scheme 3**




reaction reported by Fryzuk and co-workers in which C−H bond oxidative addition of the diisopropylphosphine-substituted analogue of [**2**]$\mathbf{PF_6}$ results in a NHC-$Pd^{II}$-hydride species,[40] no diagnostic hydride signal was observed in the $^1H$ NMR spectrum of compound **3**. Instead, a clear triplet signal at $\delta$ 4.78 ppm was observed, corresponding to a proton still bound to the central carbon, with a $^3J_{P-H}$ coupling constant of 20.2 Hz. Likewise, the $^{13}C$ NMR of **3** reveals a central carbon shift at $\delta$ 85.6 ppm, which is far too upfield for a typical NHC carbene carbon, but within the range of a regular $sp^3$-hybridized metal-alkyl carbon signal. The $^{31}P$ NMR signal of **3** is at $\delta$ 9.54 ppm and is sufficiently shifted from that of the free ligand ($\delta$ 19.0 ppm) to suggest that both phosphine arms are bound to Pd. These data indicate that compound **3** is an "arrested" intermediate that has coordinated to Pd but has not undergone C−H activation.

As expected from the spectroscopic results, the solid-state structure of **3** reveals that the central C−H bond of the ligand remains intact (Figure 1). The geometry between the central

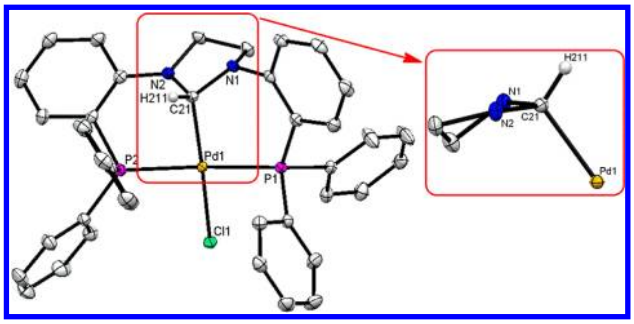



**Figure 1.** Displacement ellipsoid (50%) representation of **3**. For clarity, all hydrogen atoms except the one at the central carbon are omitted. Relevant interatomic distances (Å) and angles (deg): Pd1−C21, 2.0747(12); Pd1−P1, 2.2950(2); Pd1−P2, 2.3150(2); Pd1··H211, 2.57; N1−C21−Pd1, 119.17(8); N2−C21−Pd1, 103.55(8); N1−C21−N2, 101.70(10); Pd1··H211−C21, 109.8.

N−C−N plane and the C−Pd bond vector is considerably bent, with an angle of 126°, suggesting that the nature of the Pd-bound carbon atom is that of an X-type $sp^3$-hybridized alkyl. Consistent with this formulation, the C−N bonds associated with the central carbon of **3** (1.4398(16) and 1.4439(16) Å) are elongated relative to those in related metal-NHCs (*vide infra*) or imidazolinium cations (av C−N distance 1.307 Å obtained from Cambridge Structural Database), suggesting the disruption of any $\pi$-donation from the nitrogen lone pairs. The C−Pd distance (2.0747(12) Å) in **3** is slightly longer than that in Fryzuk's diphosphino-NHC carbene-Pd-hydride species (2.037(8) Å), even though Fryzuk's compound has a strongly *trans*-influencing hydride ligand *trans* to the NHC.[40] In addition, the hydrogen atom bound to the central carbon was located crystallographically on an electron-density difference map. Both the long Pd···H interatomic distance (∼2.57 Å) and large Pd−C−H angle (∼110°) suggest the absence of an agostic C−H−M interaction in **3**.[48] Thus, the most accurate classification of complex **3** is as an N-heterocyclic alkyl-$Pd^{II}$-Cl, an assignment further supported by the square-planar geometry at the Pd center.

Although there are no structurally characterized C−H-bound N-heterocyclic alkyl Pd complexes in the literature for comparison, a similar Me−C-bound N-heterocyclic alkyl Pd compound was obtained via migratory insertion of a methyl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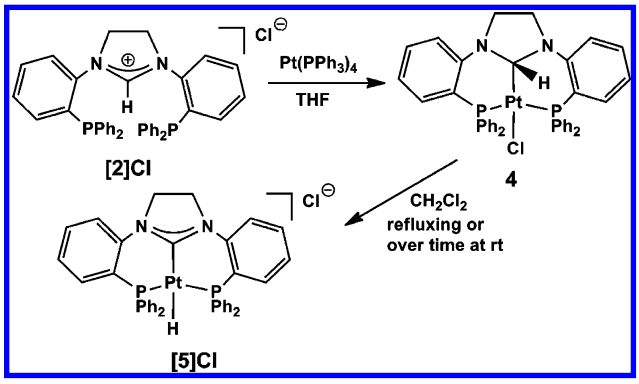
group from Pd to a free NHC ligand.[49] The long alkyl C−Pd distance in the latter compound (2.085(3) Å) is comparable with the alkyl C−Pd distance in **3** (2.0738(13) Å). As the first fully characterized example of an imidazolinium/imidazolium-derived N-heterocyclic alkyl metal complex with an intact C−H bond, complex **3** represents a stable intermediate prior to the C−H bond activation process. Several attempts to promote C−H bond activation to generate an NHC-Pd-hydride via thermolysis were unsuccessful: complex **3** is highly stable upon extended refluxing in THF, $CH_2Cl_2$, and MeCN.

In contrast to $Pd^0$, computational studies indicate that $Pt^0$ is favored to undergo C−H bond oxidative addition reactions more readily due to both a lower activation barrier and greater thermodynamic stability of the resulting $Pt^{II}(H)(R)$ species.[34] Thus, the oxidative addition of our chelating imidazolinium cation to a $Pt^0$ precursor was also investigated. Similar to the Pd case, the treatment of ligand precursor [**2**]**Cl** with $Pt(PPh_3)_4$ in THF at room temperature results in the formation of a similar N-heterocyclic alkyl-$Pt^{II}$-Cl complex, **4**, with the proton remaining on the central carbon atom (Scheme 4). The $^{31}P$

**Scheme 4**




NMR spectrum of **4** features a singlet at $\delta$ 16.6 ppm with Pt satellites ($^1J_{Pt-P}$ = 3120 Hz), suggesting Pt-bound phosphine side arms. A $^{13}C$ NMR shift at $\delta$ 66.3 ppm and a $^1H$ NMR triplet signal at $\delta$ 4.82 ppm with Pt satellites ($^3J_{P-H}$ = 12.0 Hz, $^2J_{Pt-H}$ = 52.0 Hz) correspond to the central carbon atom and the proton remaining bound to the carbon atom, respectively. These spectroscopic features are very similar to those in the Pd compound **3**, supporting the alkyl-type ligand formulation of the central donor in compound **4**.

As shown in Figure 2, the solid-state structure of **4** is quite similar to that of **3** and features a bent geometry between the N−C−N plane and the C−Pt bond vector (134.5°), suggesting an $sp^3$-hybridized central carbon atom. Again, the C−Pt bond distance in **4** (2.0423(3) Å) is slightly longer than the C−$Pt^{II}$ bond distance (2.008(4) Å) reported by Fryzuk and co-workers for the analogous NHC-Pt-hydride complex with the diisopropyl-substituted pincer ligand.[40] The hydrogen atom on the central carbon atom was located crystallographically in the electron-density difference map, further supporting the metal-alkyl nature of the central N-heterocyclic carbon. Similar to Pd derivative **3**, the long Pt···H distance (~2.56 Å) and large Pt−C−H angle (~110°) in **4** are outside the range for an agostic C−H−M interaction.[48]

In contrast to Pd complex **3**, which is thermally stable, complex **4** undergoes C−H bond activation to generate the NHC-$Pt^{II}$-hydride complex [**5**]**Cl** upon refluxing for 6 h in moderately polar solvents ($CH_2Cl_2$ or MeCN, Scheme 4).

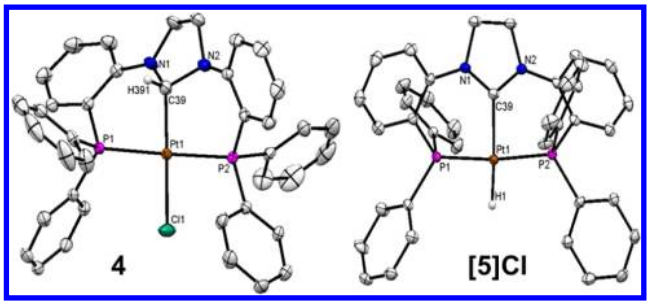



**Figure 2.** Displacement ellipsoid (50%) representation of **4** and [**5**]**Cl**. For clarity, all hydrogen atoms are omitted except the one at the central NHC carbon in **4** and the Pt hydride in [**5**]**Cl**. The $Cl^-$ counteranion in [**5**]**Cl** is also omitted for clarity. Relevant interatomic distances (Å) and angles (deg) for **4**: Pt1−C39, 2.042(3); Pt1−P1, 2.2689(8); Pt1−P2, 2.2755(8); Pt1···H391, 2.56, Pt1−C39−H391, 109.5; for [**5**]**Cl**: Pt1−C39, 2.037(2); Pt1−P1, 2.2540(6); Pt1−P2, 2.2576(6); Pt1−H1, 1.40.

Alternatively, stirring a solution of **4** for several days at room temperature also affords [**5**]**Cl**. The presence of a Pt-bound hydride in [**5**]**Cl** is suggested by a triplet signal at $\delta$ −3.88 ppm with Pt satellites in the $^1H$ NMR spectrum ($^1J_{Pt-H}$ = 851.5 Hz, $^2J_{P-H}$ = 24.0 Hz). In addition, a signal typical for an NHC carbon was observed in the $^{13}C$ NMR spectrum of [**5**]**Cl** at $\delta$ 194.0 ppm with both Pt satellites and coupling to $^{31}P$ ($^1J_{Pt-C}$ = 684.6 Hz, $^2J_{P-C}$ = 11.1 Hz). Both of these diagnostic spectroscopic features of [**5**]**Cl** are consistent with the bis(diisopropylphosphino)-NHC-$Pt^{II}$-hydride species reported by Fryzuk and co-workers ($\delta$ −4.43 ppm for the hydride in $^1H$ NMR; $\delta$ 196.7 ppm for the NHC carbon in $^{13}C$ NMR).[40]

The structure of [**5**]**Cl** is further confirmed by a single crystal X-ray diffraction study, as shown in Figure 2. The $Cl^-$ counteranion is ~6.8 Å away from the Pt center, confirming its outer-sphere nature. A typical planar geometry is observed between the NHC unit's N−C−N plane and C−Pt bond vector (~178.5°). The C−Pt bond distance (2.037(3) Å) in [**5**]**Cl** is nearly identical to the alkyl C−Pt bond distance in **4** (2.042(3) Å), but a rigorous comparison is difficult here due to the much stronger *trans* influence of $H^-$ in [**5**]**Cl** compared to that of $Cl^-$ in **4**. The most clear indication of the change in M−C bonding between N-heterocyclic alkyl complex **4** and NHC complex [**5**]**Cl** is the contraction of the N−C bond distances from ~1.48 Å to ~1.35 Å, consistent with the delocalized nitrogen $\pi$-donation to stabilize the singlet carbene.

The reactions shown in Scheme 4 represent the stepwise process by which an imidazolinium cation's central C−H bond is oxidatively added to a $Pt^0$ precursor. The unusual N-heterocyclic alkyl species **4** appears to be a direct intermediate en route to C−H activation by $Pt^0$ and can be isolated and fully characterized.

**Addition of [2]$PF_6$ to $Pd^0$ and $Pt^0$.** The C−H bond cleavage process described for **4** could also be promoted via halide abstraction in THF using $TlPF_6$ to cleanly generate the NHC-$Pt^{II}$-hydride complex [**5**]$PF_6$ with a $PF_6^-$ counteranion (Scheme 5). Despite the reluctance of complex **3** to undergo C−H activation under thermolytic conditions, treatment of **3** with $TlPF_6$ also promoted C−H bond cleavage to generate NHC-$Pd^{II}$-hydride complex **6**. The presence of metal hydrides was confirmed in the $^1H$ NMR spectra of [**5**]$PF_6$ and **6** ([**5**]$PF_6$: $\delta$ −3.89 ppm, $^1J_{Pt-H}$ = 854.7 Hz, $^2J_{P-H}$ = 13.2 Hz; **6**: $\delta$ −5.73 ppm, $^2J_{P-H}$ = 6.0 Hz), and typical NHC carbene carbon signals were also observed by $^{13}C$ NMR spectroscopy ([**5**]$PF_6$: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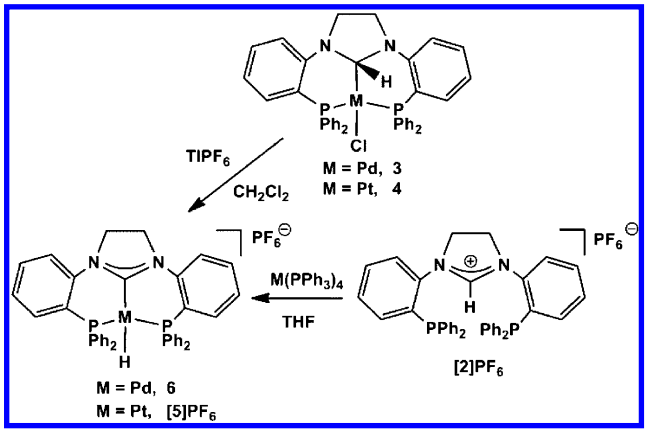
Scheme 5




194.2 ppm; **6**: 198.5 ppm). The single-crystal X-ray structure of [**5**]$PF_6$ reveals a core structure nearly identical to that of [**5**]**Cl** (see Supporting Information). Interestingly, complex **6** does not revert to **3** when treated with one equivalent of $[Et_4N]Cl$

Both [**5**]$PF_6$ and **6** can also be synthesized directly via treatment of the metal precursors $M(PPh_3)_4$ (M = Pd, Pt) with the pincer imidazolinium $PF_6^-$ salt [**2**]$PF_6$ (Scheme 5). In the case of treatment of $Pt(PPh_3)_4$ with [**2**]$PF_6$, it was observed that free $PPh_3$ (as a byproduct of the reaction) greatly effects the $^1H$ NMR chemical shift and $^1J_{Pt-H}$ of the resulting hydride product [**5**]$PF_6$. Figure 3 illustrates these changes upon

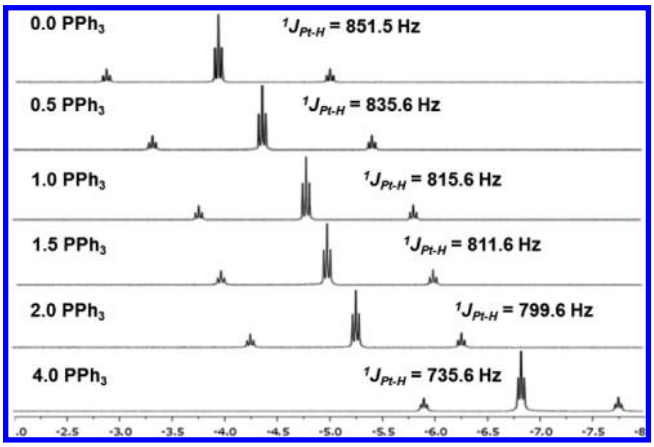
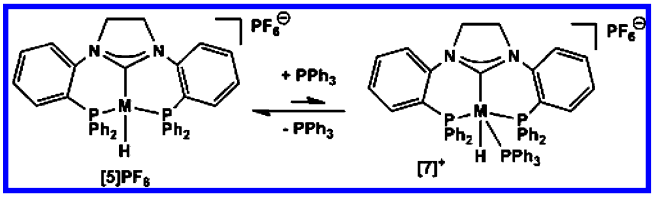



**Figure 3.** Hydride region of the $^1H$ NMR spectrum ($CD_2Cl_2$) of [**5**]$PF_6$ in the presence of varying relative concentrations of $PPh_3$, illustrating the effect of added $PPh_3$ on the hydride chemical shift and $^1J_{Pt-H}$.

addition of varying amounts of $PPh_3$ to isolated [**5**]$PF_6$. To explain this phenomenon, we propose the equilibrium shown in Scheme 6, in which [**5**]$PF_6$ reversibly coordinates $PPh_3$ in solution to form the five-coordinate phosphine adduct **7**. In the

Scheme 6




presence of higher concentrations of $PPh_3$ in solution, the equilibrium in Scheme 6 is shifted more toward complex $[7]^+$, resulting in a smaller $^1J_{Pt-H}$ coupling constant because the bound $PPh_3$ donor ligand decreases the Pt-hydride $\sigma$ interaction. A very similar five-coordinate pincer-ligated $Pt^{II}(H)(PPh_3)$ complex was recently reported using an analogous ligand with a central N-heterocyclic phosphite donor.[39] Complex $[7]^+$ is apparently less thermodynamically favored than [**5**]$PF_6$ and can be observed only in solution; attempts to isolate $PPh_3$ adduct $[7]^+$ were unsuccessful and always resulted in the regeneration of complex [**5**]$PF_6$ in pure crystalline form. To further probe the phosphine-binding equilibrium, a less bulky and more electron-donating phosphine, $PMe_3$, was added to [**5**]$PF_6$. In this case, a similar $PMe_3$ adduct of the NHC-$Pt^{II}$-hydride can be observed in solution by NMR spectroscopy and can be isolated in the solid state (see Experimental Section).

**Computational Studies.** As complexes **3** and **4** represent isolable precursors to C−H activation of imidazolinium cations, computational investigations were undertaken to better understand the bonding in these complexes. Geometry optimizations of complexes **4** and [**5**]**Cl** were carried out using Gaussian 09 (B3LYP/LANL2DZ),[50] and the computed geometries were in reasonable agreement with those obtained via X-ray crystallography (see Supporting Information). As observed experimentally, the $Cl^-$ counterion in the optimized structure of [**5**]**Cl** is >3 Å from the Pt center, precluding Pt−Cl bonding interactions. The bonding between Pt and the N-heterocycle in complexes **4** and [**5**]**Cl** was examined using natural bond orbital (NBO) analysis,[51] and the Pt−C NBOs are shown in Figure 4. On the basis of the contributions from each atom to

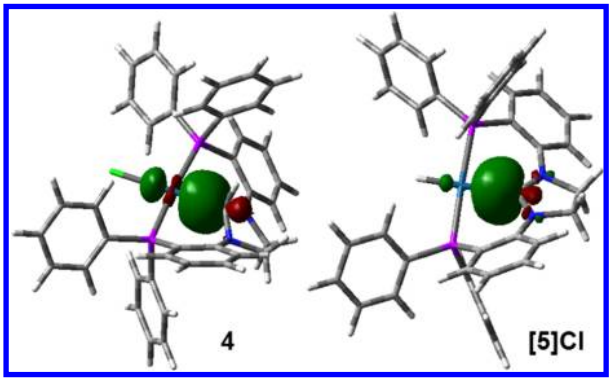



**Figure 4.** Pictorial representations of the Pt−C natural bond orbitals computed for complexes **4** and [**5**]**Cl**. NBO of **4**: 35.6% Pt, 64.4% C (26.6% s/73.4% p). NBO of [**5**]**Cl**: 23.4% Pt, 76.6% C (43.7% s/56.3% p).

the NBO, the Pt−C NBO of **4** is more covalent (35.6% Pt/64.4% C) than that of [**5**]**Cl** (23.4% Pt/76.6% C), as would be expected based on the anionic alkyl nature of the carbon donor in **4** compared to the NHC $\sigma$-donor nature of the carbon donor in [**5**]**Cl**. Likewise, the orbital contributions in the NBO from the carbon atom in complex **4** (26.6% s/73.4% p) are indicative of $sp^3$ hybridization, while there are significantly more s orbital contributions to the Pt−C NBO (43.7% s/56.3% p) from the carbon atom in [**5**]**Cl**.

## ■ CONCLUSION

Similar to the widely accepted mechanism for C−H bond activation by transition metal centers, C−H bond oxidative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addition of imidazolinium cations might have also been expected to undergo the initial formation of an agostic C−H−M species followed by C−H bond cleavage and two-electron oxidation of the metal center. In contrast to this canonical mechanism, we have found that, at least in the case of chelate-enforced imidiazolinium C−H activation, a different mechanism is possible. Herein we have isolated intermediates on the C−H activation pathway of a diphosphine-substituted imidazolinium species with Pt and Pd, showing that in some cases the initial step is not formation of a side-bound C−H agostic interaction, but rather involves formal two-electron oxidation of an electron-rich metal center and formation of an N-heterocyclic alkyl intermediate species. In this particular case, the C−H bond cleavage step occurs at a later stage.

Similar C−H activation of an imidazolinium-containing diphosphine pincer ligand was reported by Fryzuk and co-workers, but an N-heterocyclic alkyl species was not isolated in their studies.[40] Some key differences between the two systems can explain the slightly different observations, namely, (1) the isopropyl substituents on the phosphines in Fryzuk's ligand were electron-releasing enough to promote more rapid C−H activation or (2) the absence of coordinating anions such as $Cl^-$ in their studies precluded stabilization of N-heterocyclic alkyl intermediates. It is also interesting that, although monodentate imidazolinium and imidazolium cations have been shown to oxidatively add to low-valent metal centers, no other reports of N-heterocyclic alkyl intermediates on these pathways have been reported. Here we suggest that the rigid chelating nature of our ligand is the key to this phenomenon. Chelation of the phosphine donor arms constrains the geometry of the N-heterocycle such that approach to the metal center is restricted. Another possible factor is the delocalization of the NHC nitrogen lone pairs throughout the aromatic rings that are forced to be in the same plane as the N-heterocycle by chelation. We have previously suggested that such delocalization weakens the ability of these nitrogen donors to stabilize a singlet configuration at the central donor atom (previously an N-heterocyclic phosphenium cation),[38] and this factor could play a role in the chemistry described herein as well.

Future studies will focus on establishing other unusual reactivity patterns with these chelating ligands with the ultimate goal of understanding the role of the chelating framework in reaction pathways such as the C−H activation reported herein.

## EXPERIMENTAL SECTION

**General Considerations.** All syntheses reported were carried out using standard glovebox and Schlenk techniques in the absence of water and dioxygen, unless otherwise noted. Benzene, *n*-pentane, tetrahydrofuran, toluene, diethyl ether, and dichloromethane were degassed and dried by sparging with ultra high purity argon gas followed by passage through a series of drying columns using a Seca Solvent System by Glass Contour. All solvents were stored over 3 Å molecular sieves. Deuterated benzene, dichloromethane, and tetrahydrofuran were purchased from Cambridge Isotope Laboratories, Inc., degassed via repeated freeze−pump−thaw cycles, and dried over 3 Å molecular sieves. Solvents were frequently tested using a standard solution of sodium benzophenone ketyl in tetrahydrofuran to confirm the absence of oxygen and moisture. Compound **1**,[36] $Pd(PPh_3)_4$,[52] and $Pt(PPh_3)_4$[53] were synthesized using literature procedures. All other chemicals were purchased from Aldrich, Strem, or Alfa Aesar and used without further purification. NMR spectra were recorded at ambient temperature unless otherwise stated on a Varian Inova 400 MHz instrument. $^1H$ and $^{13}C$ NMR chemical shifts were referenced to residual solvent and are reported in ppm. $^{31}P$ NMR chemical shifts (in ppm) were referenced to 85% $H_3PO_4$ (0 ppm), and $^{19}F$ NMR chemical shifts (in ppm) were referenced to $CCl_3F$ (−2.3 ppm). Elemental microanalyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ, USA.

**X-ray Crystallography.** All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated Mo K$\alpha$ radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections, were carried out using the Bruker Apex2 software.[54] Preliminary cell constants were obtained from three sets of 12 frames. Crystallographic data and refinement parameters are provided in Table S1, and further experimental crystallographic details are described for each compound in the Supporting Information.

**Computational Details.** All calculations were performed using Gaussian09[50] for the Linux operating system. Density functional theory calculations were carried out using the B3LYP hybrid functional, with Becke's three-parameter exchange functional (B3)[55] and the correlation functional of Lee, Yang, and Parr (LYP).[56] A mixed-basis set was employed, using the LANL2DZ(d,p) double-$\zeta$ basis set with effective core potentials for phosphorus, chlorine, and platinum[57−59] and D95 V[60] for carbon, nitrogen, and hydrogen. Using crystallographically determined geometries as a starting point, the geometries were optimized to a minimum, followed by analytical frequency calculations to confirm that no imaginary frequencies were present. NBO[51] calculations were performed on the optimized geometries of **4** and [**5**]**Cl** without including any solvation corrections. XYZ coordinates of the optimized geometries of all computed complexes are provided in the Supporting Information.

**3-Bis(*o*-diphenylphosphino)phenyl-1*H*-imidazolinium Chloride, [2]Cl.** To a 50 mL THF solution of **1** (356 mg, 0.614 mmol) was added 2.5 mL of 1.0 M hydrochloric acid solution in diethyl ether slowly at room temperature. The reaction mixture was allowed to stir for 1 h, and then the volatiles were removed *in vacuo*. Triethylorthoformate (15 mL) was added to the white solid residue, and the mixture was heated to reflux under a dinitrogen atmosphere for 12 h to ensure complete reaction. Upon completion, the reaction mixture was cooled to room temperature. The resulting white powder was collected via filtration, washed with diethyl ether, and further dried *in vacuo* to yield analytically pure product. Yield: 289 mg, 75.1%. $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ 8.21 (m, 2H, Ar-*H*), 8.14 (s, 1H, C-*H*), 7.52 (m, 2H, Ar-*H*), 7.38−7.35 (m, 14H, Ar-*H*), 7.32−7.28 (m, 8H, Ar-*H*), 6.98 (m, 2H, Ar-*H*), 4.26 (s, 4H, $CH_2$). $^{31}P$ NMR (161.8 MHz, $CD_2Cl_2$): $\delta$ 17.98 (s). $^{13}C$ NMR (100.5 MHz, $CD_2Cl_2$): $\delta$ 158.7, 138.9, 134.6, 134.4, 134.3, 134.2, 131.2, 130.6, 129.9, 129.2, 128.7, 54.1. Anal. Calcd for $C_{39}H_{33}ClN_2P_2$: C, 74.70; H, 5.30; N, 4.47. Found: C, 74.67; H, 5.24; N, 4.40.

**3-Bis(*o*-diphenylphosphino)phenyl-1*H*-imidazolinium hexafluorophosphate, [2]$PF_6$.** To a suspension of $TlPF_6$ (147 mg, 0.419 mmol) in 10 mL of dichloromethane was added white solid [**2**]**Cl** (263 mg, 0.419 mmol). The reaction mixture was allowed to stir at room temperature for 12 h to ensure completion, and the resulting mixture was filtered through Celite. Removal of volatiles from the resulting clear colorless solution *in vacuo* afforded a white solid as an analytically pure product. Yield: 289 mg, 93.5%. $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ 7.55 (m, 2H, Ar-*H*), 7.53 (s, 1H, C-*H*), 7.45−7.39 (m, 16H, Ar-*H*), 7.34−7.30 (m, 8H, Ar-*H*), 7.04 (m, 2H, Ar-*H*), 4.19 (s, 4H, $CH_2$). $^{31}P$ NMR (161.8 MHz, $CD_2Cl_2$): $\delta$ 16.6 (s, 2P, Ar-*P*), −143.3 (septet, 1P, $PF_6$). $^{13}C$ NMR (100.5 MHz, $CD_2Cl_2$): $\delta$ 157.8, 134.9, 134.4, 134.2, 134.1, 131.3, 131.1, 130.3, 129.5, 129.4, 127.0, 53.1. Anal. Calcd for $C_{39}H_{33}F_6N_2P_3$: C, 63.59; H, 4.52; N, 3.80. Found: C, 63.51; H, 4.46; N, 3.73.

**(N-Heterocyclic alkyl)Pd−Cl (3).** $Pd(PPh_3)_4$ (207 mg, 0.179 mmol) was dissolved in 10 mL of THF, and to this stirring yellow solution was added [**2**]**Cl** (112 mg, 0.179 mmol). The mixture became a clear yellow solution in 5 min. The reaction was allowed to stir at room temperature for 12 h, resulting in formation of a yellow precipitate. The yellow solid was collected via filtration and dried *in vacuo* to afford analytically pure product. Yield: 95.0 mg, 72.3%. $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ 7.67 (m, 4H, Ar-*H*), 7.50−7.32 (m, 18H, Ar-*H*), 6.94 (m, 2H, Ar-*H*), 6.88 (m, 2H, Ar-*H*), 6.81 (t, 2H, Ar-*H*), 4.78 (t, 1H, C-*H*, $^3J_{P-H}$ = 20.2), 3.55 (m, 2H, $CH_2$), 3.14 (m, 2H,


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$CH_2$). $^{31}P$ NMR (161.8 MHz, $CD_2Cl_2$): $\delta$ 9.54 (s). $^{13}C$ NMR (100.5 MHz, $CD_2Cl_2$): $\delta$ 150.0, 134.8, 134.3, 131.7, 130.4, 130.2, 128.5, 128.3, 120.2, 118.8, 85.6, 49.5. Anal. Calcd for $C_{39}H_{33}ClN_2P_2Pd$: C, 63.86; H, 4.53; N, 3.82. Found: C, 63.80; H, 4.50; N, 3.81.

**(N-Heterocyclic alkyl)Pt−Cl (4).** $Pt(PPh_3)_4$ (72.4 mg, 0.0582 mmol) was dissolved in 10 mL of THF, and to this yellow solution was added ligand precursor [**2**]**Cl** (36.5 mg, 0.0582 mmol). The reaction was allowed to stir at room temperature for 1 h; then volatiles were removed *in vacuo*. The residue was washed with diethyl ether to afford a yellow solid as crude product. Single crystals suitable for X-ray diffraction were obtained via vapor diffusion of diethyl ether into a concentrated THF solution of **4**. Yield: 35.0 mg, 73.2%. $^1H$ NMR (400 MHz, *d*-THF): $\delta$ 7.63 (m, 4H, Ar-*H*), 7.46 (m, 4H, Ar-*H*), 7.36 (m, 8H, Ar-*H*), 7.28 (m, 6H, Ar-*H*), 6.84−6.71 (m, 4H, Ar-*H*), 6.61 (t, 2H, Ar-*H*), 4.82 (dt, 1H, C-*H*, $^3J_{P-H}$ = 12.0 Hz, $^2J_{Pt-H}$ = 52.0 Hz), 3.35 (m, 2H, $CH_2$), 3.05 (m, 2H, $CH_2$). $^{31}P$ NMR (161.8 MHz, $d_8$-THF): $\delta$ 16.6 (d, 1P, Ar-*P*, $^1J_{Pt-P}$ = 3120 Hz). $^{13}C$ NMR (100.5 MHz, $CD_2Cl_2$): $\delta$ 151.0, 134.8, 134.3, 132.1, 130.7, 130.5, 128.4, 128.1, 118.1, 116.3, 66.3, 48.6. Anal. Calcd for $C_{39}H_{33}ClN_2P_2Pt$: C, 56.97; H, 4.05; N, 3.41. Found: C, 56.91; H, 4.06; N, 3.28.

**[NHC-Pt-H][Cl], [5]Cl.** Compound **4** (22.8 mg, 0.0277 mmol) was dissolved in deuterated dichloromethane and transferred to a J. Young tube. The yellow solution was heated at 60 °C in an oil bath. The reaction progress was monitored by both $^1H$ and $^{31}P$ NMR spectroscopy. After 12 h, the volatiles were removed to afford a yellow solid as an analytically pure product. Single crystals suitable for X-ray diffraction were obtained via vapor diffusion of diethyl ether into a concentrated dichloromethane solution of [**5**]**Cl**. Yield: 20.8 mg, 91.2%. $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ 7.64−7.47 (m, 22H, Ar-*H*), 7.24 (t, 4H, Ar-*H*), 6.931 (m, 2H, Ar-*H*), 3.98 (s, 4H, $CH_2$), −3.88 (dt, 1H, C*H*, $^1J_{Pt-H}$ = 851.5 Hz, $^2J_{P-H}$ = 13.0 Hz),. $^{31}P$ NMR (161.8 MHz, $CD_2Cl_2$): $\delta$ 16.3 (d, 1P, Ar-*P*, $^1J_{Pt-P}$ = 2620 Hz). $^{13}C$ NMR (100.5 MHz, $CD_2Cl_2$): $\delta$ 194.0, 144.5, 134.1, 134.0, 133.2, 132.1, 129.2, 128.3, 126.0, 120.3, 119.2, 50.3. Anal. Calcd for $C_{39}H_{33}ClN_2P_2Pt$: C, 56.97; H, 4.05; N, 3.41. Found: C, 56.92; H, 4.19; N, 3.31.

**[NHC-Pt-H][$PF_6$], [5]$PF_6$.** $Pt(PPh_3)_4$ (228 mg, 0.183 mmol) was dissolved in 10 mL of THF, and to this yellow solution was added ligand precursor [**2**]$PF_6$ (135 mg, 0.183 mmol). The mixture was allowed to stir at room temperature for 12 h to ensure reaction completion. Volatiles were removed in vacuo, and the residue was washed with diethyl ether to afford a yellow solid as the crude product. Single crystals suitable for X-ray crystallography were obtained via vapor diffusion of diethyl ether into a concentrated dichloromethane solution of [**5**]$PF_6$. Yield: 151 mg, 88.3%. $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ 7.63−7.55 (m, 14H, Ar-*H*), 7.53−7.47 (m, 8H, Ar-*H*), 7.26 (m, 4H, Ar-*H*), 6.91 (m, 2H, Ar-*H*), 4.02 (s, 4H, $CH_2$), −3.89 (dt, 1H, C*H*, $^1J_{Pt-H}$ = 854.7 Hz, $^2J_{P-H}$ = 13.2 Hz). $^{31}P$ NMR (161.8 MHz, $CD_2Cl_2$): $\delta$ 16.5 (d, 1P, Ar-*P*, $^1J_{Pt-P}$ = 2619 Hz), −143.9 (septet, 1P, $PF_6$, $^1J_{P-F}$ = 710 Hz). $^{13}C$ NMR (100.5 MHz, $CD_2Cl_2$): $\delta$ 194.2, 144.8, 134.3, 134.2, 133.4, 132.4, 129.4, 128.6, 126.3, 120.6, 119.4, 50.7. Anal. Calcd for $C_{39}H_{33}F_6N_2P_3Pt$: C, 50.28; H, 3.57; N, 3.01. Found: C, 50.23; H, 3.66; N, 2.97.

**[NHC-Pd-H][$PF_6$] (6).** To a white suspension of $TlPF_6$ (26.0 mg, 0.0744 mmol) in 5 mL of dichloromethane was added a yellow solution of compound **3** (54.6 mg, 0.0744 mmol) in 10 mL of dichloromethane. The mixture was allowed to stir at room temperature for 12 h, and the clear yellow solution was collected via filtration through Celite. Removal of volatiles *in vacuo* afforded a yellow solid as crude product. Crystallization via vapor diffusion of diethyl ether into a concentrated dichloromethane solution of the crude product afforded analytically pure product. Yield: 46.5 mg, 74.0%. $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ 7.61−7.54 (m, 14H, Ar-*H*), 7.48 (t, 8H, Ar-*H*), 7.24−7.18 (m, 4H, Ar-*H*), 6.88 (m, 2H, Ar-*H*), 3.96 (s, 4H, $CH_2$), −5.73 (t, 1H, C*H*, $^3J_{P-H}$ = 6.0 Hz). $^{31}P$ NMR (161.8 MHz, $CD_2Cl_2$): $\delta$ 25.4 (s, 2P, Ar-*P*), −143.9 (septet, 1P, $PF_6$, $^1J_{P-F}$ = 710 Hz). $^{13}C$ NMR (100.5 MHz, $CD_2Cl_2$): $\delta$ 198.5, 144.1, 134.3, 134.1, 133.1, 132.2, 129.5, 128.7, 126.4, 120.7, 120.0, 50.7. Anal. Calcd for $C_{39}H_{33}F_6N_2P_3Pd$: C, 55.56; H, 3.95; N, 3.32. Found: C, 55.64; H, 3.92; N, 3.26.

**Studies of $PPh_3$ Binding to [5]$PF_6$.** Compound [**5**]$PF_6$ was dissolved in deuterated dichloromethane and transferred into a J. Young tube. To the light yellow solution was added different amounts of $PPh_3$ (ranging from 0.5 equiv to 4 equiv), and $^1H$ NMR and $^{31}P$ NMR spectra were recorded after addition of each amount of $PPh_3$ to the reaction. $^1H$ NMR of hydride shifts (400 MHz, $CD_2Cl_2$): $\delta$ 0.0 equiv $PPh_3$, −3.93 ($^1J_{Pt-H}$ = 851.5 Hz); 0.5 equiv $PPh_3$, −4.39 ($^1J_{Pt-H}$ = 835.6 Hz); 1.0 equiv $PPh_3$, −4.80 ($^1J_{Pt-H}$ = 815.6 Hz); 1.5 equiv $PPh_3$, −4.97 ($^1J_{Pt-H}$ = 811.6 Hz); 2.0 equiv $PPh_3$, −5.26 ($^1J_{Pt-H}$ = 799.6 Hz); 4.0 equiv $PPh_3$, −6.84 ($^1J_{Pt-H}$ = 735.6 Hz). $^{31}P$ NMR shifts (161.8 MHz, $CD_2Cl_2$): $\delta$ 0.0 equiv $PPh_3$, 16.22 ($^1J_{Pt-P}$ = 2620 Hz); 0.5 equiv $PPh_3$, 14.60 ($^2J_{Pt-H}$ = 2633 Hz); 1.0 equiv $PPh_3$, 13.17 ($^1J_{Pt-H}$ = 2646 Hz); 1.5 equiv $PPh_3$, 12.60 ($^1J_{Pt-H}$ = 2650 Hz); 2.0 equiv $PPh_3$, 11.71 ($^1J_{Pt-H}$ = 2699 Hz); 4.0 equiv $PPh_3$, 6.97 ($^1J_{Pt-H}$ = 2701 Hz). All the other resonances stay the same as those reported above for [**5**]$PF_6$, without detectable changes.

**$PMe_3$ Adduct of [5]$PF_6$.** Compound [**5**]$PF_6$ (24.5 mg, 0.0298 mmol) was dissolved in 10 mL of dichloromethane, and to this light yellow solution was added 10 equiv of $PMe_3$. The mixture became a yellow solution immediately. After 10 min, the volatiles were removed *in vacuo*, and the residue was washed with diethyl ether (3 × 5 mL) to afford a yellow solid. Yield: 24.7, 92.1%. $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ 7.70 (m, 2H, Ar-*H*), 7.52 (t, 2H, Ar-*H*), 7.37 (m, 4H, Ar-*H*), 7.28 (m, 16H, Ar-*H*), 7.11 (t, 2H, Ar-*H*), 6.95 (m, 2H, Ar-*H*), 4.36 (br, 4H, $CH_2$), 1.10 (d, 9H, $CH_3$), −12.71 (br, 1H, Pt*H*, $^1J_{Pt-H}$ = 563.7 Hz). $^{31}P$ NMR (161.8 MHz, $CD_2Cl_2$): $\delta$ −12.1 (br, 1P, Ar-*P*, $^1J_{Pt-P}$ = 2754 Hz), −48.2 (br, 1P, $PMe_3$).

## ■ ASSOCIATED CONTENT

### Supporting Information

Crystallographic data and refinement parameters for **3**, **4**, [**5**]**Cl**, and [**5**]$PF_6$, crystallographic data in CIF format, computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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