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Synthesis and Reactivity of Pt^{II} Methyl Complexes Supported by Pyrazolate Pincer Ligands

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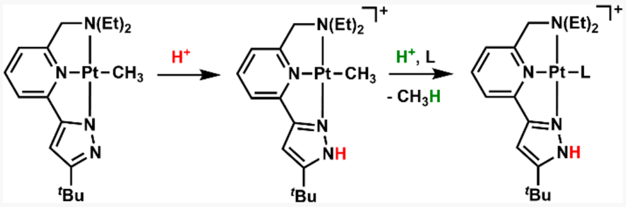
ABSTRACT: Multidentate pyrazolate ligands, 2-(5-*tert*-butylpyrazol-3-yl)-6-(diethylaminomethyl)pyridine ($(^{H}\mathbf{NNN})^{Et}$) and 2,6-bis(5-*tert*-butyl-1*H*-pyrazol-3-yl)pyridine ($^{H}\mathbf{NNN}^{H}$), were metalated with Pt^{II} to form neutral Pt(*NNN)^{Et}CH$_3$ and anionic [Y][Pt(*NNN*)-CH$_3$] (Y = Li(THF)−Cl−Li(THF)$_3$; Y = PPN) (* denotes that the pyrazolate N has been deprotonated). Reactions of these Pt^{II}−CH$_3$ complexes with acids were investigated. Protonation occurs preferentially at the pyrazolate site, and the release of methane requires additional acid.



■ INTRODUCTION

Natural gas, a significant feedstock for the chemical industry, is composed predominantly of methane.[1] Commercially viable routes that do not involve high-energy steam reforming for the conversion of methane to higher value-added products remains a challenge.[2] Aqueous direct electrophilic functionalization of methane by a Pt^{II} catalyst to generate methanol was first demonstrated by Shilov almost 50 years ago.[3] Unfortunately, the Shilov system employed Pt^{IV} as a stoichiometric oxidant. Since then, many studies of C−H functionalization using Pt^{II} complexes have been carried out as the community seeks to identify more practical catalyst systems for commercial-scale alkane functionalization.[2,4]

Key to the Shilov functionalization is C−H activation of methane by the Pt^{II} catalyst to produce a Pt^{II}−CH$_3$ species. A potentially powerful mechanism of C−H activation that has not been extensively investigated with Pt^{II} is metal−ligand cooperation (MLC). When C−H bonds are activated by a MLC mechanism, a M−C bond is formed while the proton migrates to ultimately reside on the coordinated ligand. An example of a MLC C−H activation with a late metal system has been reported by Milstein and co-workers (Figure 1).[5,6] Here, C−H oxidative addition of C$_6$H$_6$ was proposed at 2,6-bis((di*tert*-butylphosphino)methyl)pyridine (PNP) ligated Rh^{I} and Ir^{I} complexes to initially form a transient M^{III}-(H)(C$_6$H$_5$) species. The acidic hydride is then deprotonated by the carbon methylene site in the ligand backbone, a rearrangement favored by rearomatization of the pyridyl ligand. C−H activation by MLC has also been observed with other ligand functionalities, including basic nitrogen sites.[7−9]

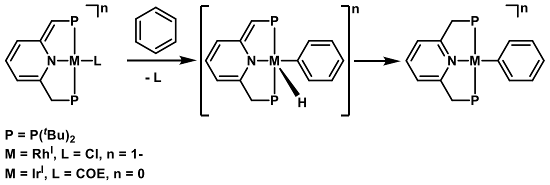


Figure 1. Previous example of ligand assisted C−H activation by Ir^{I} and Rh^{I} complex.

The protons in the multidentate pyrazolate ligand 2,6-bis(5-*tert*-butyl-1*H*-pyrazol-3-yl)pyridine ($^{H}\mathbf{NNN}^{H}$) have been reported to play a key role in N−N and N−H bond cleavage reactions of hydrazine.[10] Additionally, the pyrazolate moiety has been suggested to aid in hydrogenation reactions of ketones[11,12] and D$_2$O facilitated H−D exchange of a trispyrazolylborate (Tp) ligated Pt^{II}−CH$_3$ complex.[13] We were interested in exploring the potential of pyrazolate groups to aid in C−H bond cleavage/formation reactions. Protonation of Pt^{II}−CH$_3$ complexes has previously been reported to result in methane release.[14,15] Recently, Nozaki and co-workers reported acid addition to a Shvo-type Pt^{II}−CH$_3$ complex.[16] Experimental and theoretical evidence suggested the ligand was the initial site of protonation before methane liberation. Similarly, addition of a pyrazolate site on the ligand has the potential to promote this reactivity by providing a kinetic site for protonation. Thus, the multidentate pyrazolyl ligands $^{H}\mathbf{NNN}^{H}$ and 2-(5-*tert*-butylpyrazol-3-yl)-6-(diethylaminomethyl)pyridine ($(^{H}\mathbf{NNN})^{Et}$), which have previously been complexed to several metals (e.g., Ru^{II}, Ir^{III}, Co^{II}, and Fe^{II}),[11,17,18] were investigated on Pt^{II}. These ligands have

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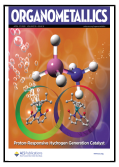

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not yet been studied in square planar d^8 metal complexes. Herein, we describe metalation of (**^{H}NNN**)^{Et} and **^{H}NNN^H** to afford stable and well-characterized d^8 square planar Pt^{II} complexes. The Pt^{II}−CH$_3$ complexes of these tridentate-pyrazolate ligands have basic nitrogen sites on the ligand available for protonation and their reactivity with acids has also been studied.

■ RESULTS AND DISCUSSION

Preparation of (*NNN)^{Et} Ligated Pt^{II} Complex. Addition of 2 equiv of 2-(5-*tert*-butylpyrazol-3-yl)-6(diethylaminomethyl)pyridine (^{H}**NNN**)^{Et} to the Pt^{II} dimer [Pt(μ-S(CH$_3$)$_2$)(CH$_3$)$_2$]$_2$ afforded monomeric Pt(*NNN)^{Et}CH$_3$ (**1**) in 79% isolated yield (Figure 2, Note: * denotes that the pyrazolate N has been deprotonated). The ^{1}H and ^{13}C{^{1}H} NMR spectra are consistent with assignment of the structure of **1** as shown in Figure 2a. Signals for the diastereotopic protons of the CH$_2$ group on the diethyl amine unit are observed at 3.20 ppm ($^2J_{H-H}$ = 12.5, $^3J_{H-H}$ = 7.3 Hz) and 2.95 ppm ($^2J_{H-H}$ = 12.5, $^3J_{H-H}$ = 7.3 Hz) in the ^{1}H NMR spectra of **1** in CD$_2$Cl$_2$, consistent with chelation of the diethyl amine moiety.[17,19] A $^2J_{Pt-H}$ of 79 Hz (0.83 ppm) in CD$_2$Cl$_2$ was observed for the Pt^{II}−CH$_3$ group in **1**. The solid-state structure of **1** was obtained through X-ray crystallography (Figure 2a). The bond lengths within the pyrazolate unit are similar to those reported for the solid-state structures of other nonprotonated pyrazolate ligands bound to metals.[11,20] The absence of a counteranion in the solid-state structure is also consistent with a deprotonated pyrazolate moiety.

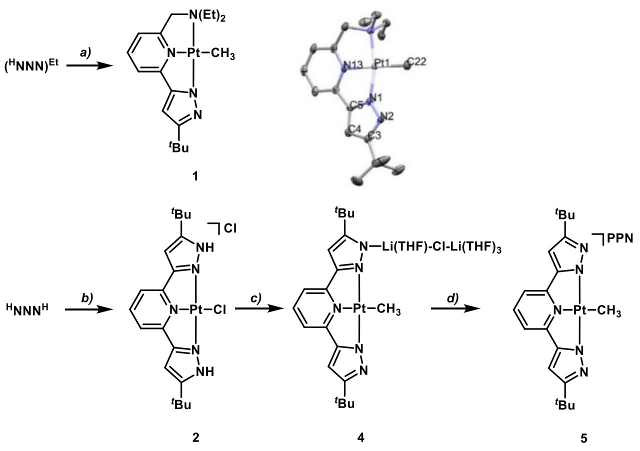


Figure 2. Synthesis of pyrazolate ligated complexes: Pt(*NNN)^{Et}CH$_3$ (**1**), [Pt(^{H}NNN^H)Cl][Cl] (**2**) [Li(THF)−Cl−Li(THF)$_3$][Pt(*NNN*)CH$_3$ (**4**) and [PPN][Pt(*NNN*)CH$_3$ (**5**). Reagents and conditions: (a) 0.5 equiv of [Pt(μ-S(CH$_3$)$_2$)(CH$_3$)$_2$]$_2$, CH$_2$Cl$_2$, RT; (b) 1 equiv of Pt(S(CH$_3$)$_2$)$_2$(Cl)$_2$, MeOH, 60 °C; (c) 6 equiv of 1.3 M CH$_3$Li in diethyl ether, THF, RT; (d) 1 equiv of [PPN][Cl], THF, RT. Thermal ellipsoid plot (50% probability) of **1**. H atoms and an equiv of CH$_2$Cl$_2$ are omitted for clarity. Selected bond distances for **1** (Å): Pt−N(13) 1.948(8), Pt−C(22) 2.062(6).

Preparation of (*NNN*) Ligated Pt^{II} Complexes. Attempts to synthesize the Pt−CH$_3$ complex with the ^{H}NNN^H (5-*tert*-butyl-1,3-bis(pyrazol-3-yl)pyridine) ligand using the above procedure were unsuccessful. However, the addition of (**^{H}NNN^H**) to Pt(S(CH$_3$)$_2$)$_2$Cl$_2$ in refluxing methanol afforded [Pt(^{H}NNN^H)Cl][Cl] (**2**) (78% isolated yield, Figure 2b). ^{1}H and ^{13}C{^{1}H} NMR spectroscopy indicate that **2** contains a symmetric ligand environment. Notably, even with rigorously dry deuterated solvents (including C$_6$D$_6$ and THF-d_8), no N−H signal was observed in the ^{1}H NMR spectra. However, characterization by elemental analysis is consistent with a cationic complex accompanied by a Cl$^-$ anion. Furthermore, stirring a solution of **2** with NaBF$_4$ in CH$_3$CN allowed isolation of [Pt(^{H}NNN^H)Cl][BF$_4$] (**3**), and the structure of **3** was confirmed by X-ray crystallography (Figure S39). A broad N−H resonance integrating to 2H at 12.08 ppm was noted in the ^{1}H NMR of **3** in dry CD$_3$CN.

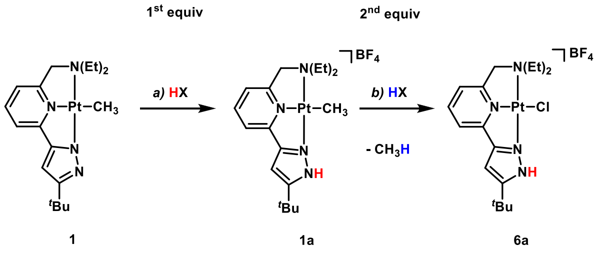
The reaction of excess CH$_3$Li (6 equiv) with **2** in THF, followed by quenching with water (3−50 equiv), afforded [Li(THF)−Cl−Li(THF)$_3$][Pt(*NNN*)CH$_3$](THF)$_4$ (**4**) in 69% isolated yield (Figure 2c). ^{1}H and ^{13}C{^{13}H} NMR spectroscopy indicates that complex **4** is symmetric with respect to the ligand in solution. A characteristic Pt-CH$_3$ resonance was observed at 1.11 ppm ($^2J_{Pt-H}$ = 79 Hz) in THF-d_8. Examination of the solid-state structure of **4** (Figure S40) revealed a pyrazolate Li−Cl−Li interaction with THF solvated Li cations. A broad singlet at −1.20 ppm is present in the ^{7}Li{^{1}H} NMR spectrum of **4** in acetone-d_6. Dissolution of isolated **4** in CD$_3$CN or acetone-d_6 results in the liberation of 4 equiv of THF, which was observed by ^{1}H NMR spectroscopy. Inner sphere Li-pyrazolate interactions have been observed in reported first-row transition-metal complexes.[18,21]

Removal of the LiClLi$^+$ cation by treatment of **4** with bis(triphenylphosphine)iminium chloride (PPNCl) yielded [PPN][Pt(*NNN*)CH$_3$] (**5**) in Figure 2d. The solid-state structure (Figure S40), the lack of a resonance in the ^{7}Li{^{1}H} NMR spectrum, and the presence of a resonance in the ^{31}P{^{1}H} spectrum, confirmed that the lithium had successfully been removed from the pyrazolate ligand. Complex **5** appears symmetric in solution by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy with a characteristic Pt−CH$_3$ resonance at 1.11 ppm ($^2J_{Pt-H}$ = 82 Hz) in CD$_3$CN.

Reactivity of Pt^{II}−CH$_3$ Pyrazolate Ligated Complexes with Acid. Reactivity of Pt−CH$_3$ complexes bearing deprotonated pyrazolate(s) in the ligand (**1**, **4**, and **5**) with Brønsted acids was probed to determine if protonation was preferred at the ligand N, the Pt^{II} center, or if direct C−H bond formation might result. **1** has a single pyrazolate, and **4** and **5** each contain two pyrazolate functionalities in the ligand.

Reaction of **1** with 1 equiv of HBF$_4$ etherate (Scheme 1a) in diethyl ether or benzene caused the precipitation of an orange solid. Upon isolation, ^{1}H and ^{13}C{^{1}H} NMR spectral data in CD$_2$Cl$_2$ were consistent with pyrazolate protonation and the formation of [Pt(^{H}NNN)^{Et}CH$_3$][BF$_4$] (**1a**). When the reaction was monitored *in situ* in C$_6$D$_6$ at room temperature,

Scheme 1. Protonation of Pt(*NNN)^{Et}CH$_3$ (1)^a



^{a}Reagents and conditions: (a) 1 equiv of HBF$_4$ etherate, C$_6$D$_6$, RT; (b) 1 equiv of HCl etherate, CD$_2$Cl$_2$, RT.

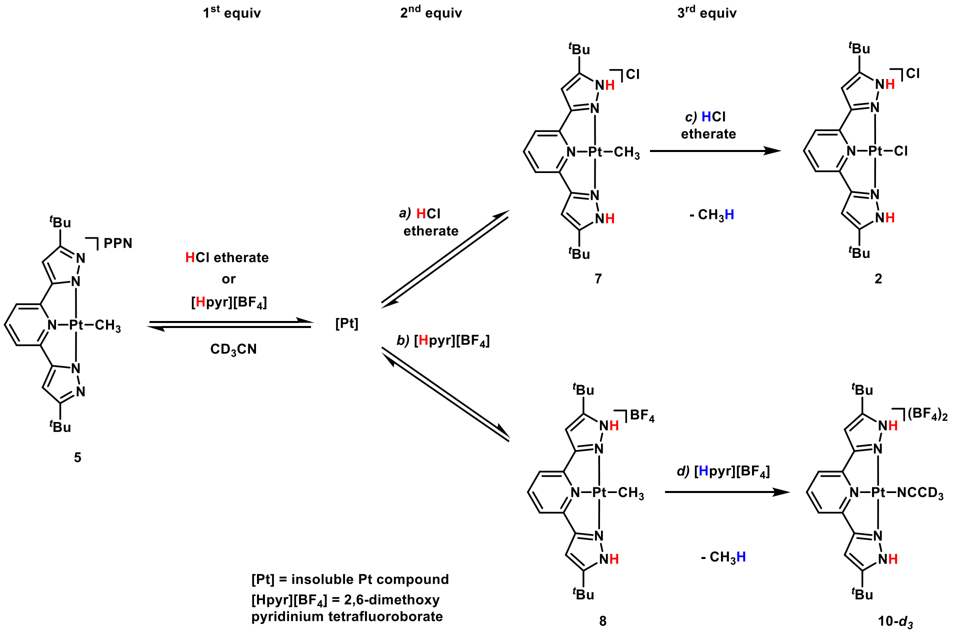


Figure 3. Speciation during the protonation of [PPN][Pt(*NNN*)CH_3] (**5**), and formation of complexes: [Pt(^{H}NNN^H)CH_3][Cl] (**7**), [Pt(^{H}NNN^H)CH_3][BF_4] (**8**), [Pt(^{H}NNN^H)Cl][Cl] (**2**), and [Pt(^{H}NNN^H)$NCCD_3$][BF_4]$_2$ (**10-*d*$_3$**) in CD_3CN. Reagents: (a) 1 equiv of HCl etherate; (b) 1 equiv of HBF_4 etherate or 2,6-dimethoxypyridinium tetrafluoroborate, (c) 1 equiv of HCl etherate, (d) 1 equiv of 2,6-dimethoxypyridinium tetrafluoroborate.

no methane evolution or Pt^{IV}−H was detected by ^{1}H NMR spectroscopy. The ^{19}F{^{1}H} NMR spectrum of **1a** displayed two broad singlets in a 1:4 ratio, consistent with an outer-sphere BF_4^- (in accordance with the natural abundance of ^{10}B:^{11}B).[22] The $^2J_{Pt-H}$ coupling of the Pt−CH_3 changed slightly upon protonation from 79 Hz for **1** to 77 Hz for **1a** in CD_2Cl_2.

The addition of an equivalent of HBF_4 in ether solution to a C_6D_6 suspension of **1a** did lead to the generation of methane at room temperature. Several broad resonances in the ^{1}H NMR spectrum were also observed, and the Pt product(s) could not be identified. Thus, when two equivalents of acid are added to the unprotonated complex **1**, the first equivalent protonates the ligand, and the second equivalent then protonates the Pt or the Pt−CH_3 bond, leading to C−H coupling. When an acid with a coordinating conjugate base, HCl in ether solution, was added to **1a**, [Pt(^{H}NNN)^{Et}Cl][BF_4] (**6a**, 69% spectroscopic yield, Scheme 1b) was observed along with the methane product. The formation of **6a** in this reaction was confirmed by independent synthesis.

The reactivity of **4** and **5** with acids was also investigated. Although **4** contains the cation, LiClLi$^+$, closely coordinated to the pyrazolate in the solid state, protonation studies in solution resulted in similar reactivity to such studies with **5**. The reactivity studies with **5** are thus presented as representative (see Supporting Information for protonation studies with **4**).

After addition of one equivalent of acid (either HCl in ether solution or 2,6-dimethoxypyridinium tetrafluoroborate) to a CD_3CN solution of **5**, a sparingly soluble yellow solid precipitated out of solution (labeled [Pt] in Figure 3), and only very broad features were visible in the ^{1}H NMR spectrum when observed *in situ* (see 1.0 equiv in Figure S36). Attempts to characterize this species independently were unsuccessful due to its limited solubility in numerous common laboratory solvents (e.g., pentane, THF, CH_2Cl_2, acetonitrile, and DMF). The addition of more acid to the reaction mixtures resulted in redissolution of the Pt complex implying further reactivity.

Addition of two equivalents of HCl in ether solution to an acetone-*d*$_6$ solution **5** resulted in the formation of [Pt(^{H}NNN^H)CH_3][Cl] (**7**, Figure 3a, 90% spectroscopic yield). When solvated in acetone-*d*$_6$, the Pt−CH_3 ligand was observed at 1.24 ppm ($^2J_{Pt-H}$ = 79 Hz), and the N−H resonance was observed downfield at 12.1 ppm. The assignment of **7** as the product in the HCl reaction was confirmed by observance of a protonated pyrazolate Pt−CH_3 cation in the solid state. Here, Cl$^-$ anion exhibited a hydrogen bonding interaction with the N−H moiety (N···Cl = 3.128(3) Å, calculated H···Cl = 2.270 Å, Figure S43). Adding an independently prepared authentic sample of **7** to a solution of **7** generated during acid addition experiments in acetone-*d*$_6$ also confirmed the assignment.

When two equivalents of 2,6-dimethoxypyridinium tetrafluoroborate were added to a CD_3CN solution of complex **5**, [Pt(^{H}NNN^H)CH_3][BF_4] (**8**) was observed *in situ* (Figure 3b, 77% spectroscopic yield). Despite multiple attempts, we were unable to isolate **8** from the protonation reaction or through anion exchange of **7** with $NaBF_4$. The ^{1}H NMR signals for complex **8** indicate that it is symmetric in solution. Additionally, the Pt−CH_3 ligand exhibits the same $^2J_{Pt-H}$ of 78 Hz as **7** in CD_3CN. The broad N−H resonance of **8** was observed downfield at 12.3 ppm (integrating to ca. 1.8 H) during the acid addition experiments. Although we were unable to isolate **8**, we were able to synthesize and isolate [Pt(^{H}NNN^H)CH_3][BAr^F_{24}] (**9**) by reaction of **7** with $NaBAr^F_{24}$. Complex **9** exhibited a similar $^2J_{Pt-H}$ of 79 Hz for the Pt−CH_3 ^{1}H NMR signal and a far downfield and broad N−H resonance at 13.4 ppm when solvated in acetone-*d*$_6$ (integrating to ca. 1.7 H).

Addition of one equiv HCl in ether solution to cationic **7** in CD_3CN or acetone-*d*$_6$ yielded methane and [Pt(^{H}NNN^H)Cl]-[Cl] (**2**, confirmed by ^{1}H NMR spectroscopy with addition of independently synthesized **2**, Figure 3c). After protonation, the

Cl^- counteranion of **7** preferentially coordinated to the unsaturated Pt center to form **2**, even in the presence of coordinating solvents, such as acetonitrile. 2,6-Lutidinium tetrafluoroborate (pK_a = 14.1 in acetonitrile)[23] also protonated the methyl ligand of **7** to form $[Pt(^HNNN^H)Cl][BF_4]$ (**3**) (78% isolated yield).

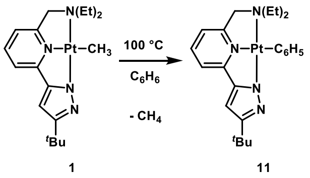
Protonation of the Pt−CH_3 moiety of cationic **8** with 2,6-dimethoxypyridinium tetrafluoroborate in CD_3CN mirrored the protonation of **7** and formed $[Pt(^HNNN^H)NCCD_3][(BF_4)_2]$ **10-*d*$_3$** (Figure 3d). Here, the acetonitrile solvent traps the unsaturated metal center to form a dicationic Pt-solvento complex. Confirmation of this species was achieved by comparison of its ^1H NMR spectrum with that of an authentic sample of **10-*d*$_3$**. A solid-state structure of **10** was also obtained (Figure S44).

Complexes **1a**, **7**, and **8** contain protonated ligands with a methyl ligand still intact after two equivalents of added acid. Generation of **1a**, **7**, and **8** in our acid addition studies indicates that the ligand pyrazolate sites are protonated in preference to the metal or metal-methyl bond. Only after ligand based pyrazolates are protonated does additional acid protonate the Pt-CH_3 moiety to liberate methane.

Thermolysis of Protonated Pt^{II}−CH_3 Pyrazolates. $[Pt(^HNNN)^{Et}CH_3][BF_4]$ (**1a**) is stable at room temperature and does not eliminate methane until subjected to relatively high temperatures (>100 °C) in C_6D_6. Upon release of methane at 100 °C, multiple unidentified [Pt] species were observed by ^1H NMR spectroscopy, along with metallic platinum. Of interest was to learn if the proton that combined with the methyl group to form methane was derived from the ligand-based N−H moeity. To shed light on this question, thermolysis was carried out with an analogue of **1a** with deuterium on the pyrazolate nitrogen, $Pt(^DNNN)^{Et}CH_3$ (generated by stirring **1a** in a D_2O/THF (1:4) mixture). Exclusive elimination of CH_4 (i.e., no CDH_3) was observed by ^1H NMR spectroscopy. While it is possible that adventitious water could result in some H/D exchange, the absence of any evidence of a CDH_3 signal suggests that the N−H may not be the source of the H that couples with the Pt-CH_3 moiety.

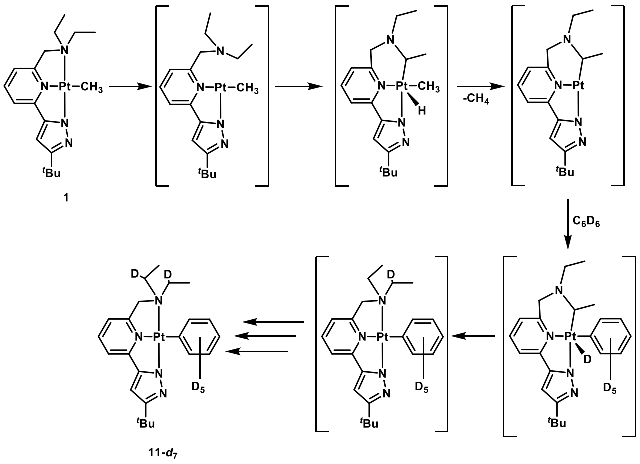
Furthermore, thermolysis of the analogous complex **1** (which lacks a proton on the pyrazolate nitrogen), also eliminated CH_4 under similar conditions (Scheme 2). Of note is that in the thermolysis of **1** in C_6D_6, $Pt(*NNN)^{Et}C_6D_5$ was observed as a major product by ^1H NMR. $Pt(*NNN)^{Et}C_6D_5$ was also detected as the main species by ESI-MS (m/z = 565.3); however, the observed mass contained two extra deuterium units. A solid-state structure was additionally obtained (Figure S45). Thermolysis of **1** in C_6H_6 yielded $Pt(*NNN)^{Et}C_6H_5$ (**11**, 25% spectroscopic yield, Scheme 2) and further confirmation of the thermolysis product was obtained through independent synthesis.

Scheme 2. Thermolysis of $Pt(*NNN)^{Et}CH_3$ (1)



Examination of the ^2H NMR spectrum (Figure S34) of the product mixture in C_6H_6 from the thermolysis of **1** in C_6D_6 revealed two broad singlets at 2.80 and 2.99 ppm, consistent with deuteration of the diastereotopic diethyl amine CH_2 group. The deuterium incorporation into the ligand is consistent with a proposed mechanism as shown in Scheme 3. At elevated temperatures, dissociation of the hemilabile diethyl amine arm occurs, followed by intramolecular C−H activation of the CH_2 alkyl on the amine to generate a cyclometalated Pt^{IV} species.[24] Reductive elimination of methane, followed by oxidative addition of the C_6D_6 solvent and subsequent reductive elimination of the amine alkyl with the deuteride on the metal, generates the observed Pt^{II}−C_6D_5 product (summarized in Scheme 3).

Scheme 3. Proposed Mechanism for D Incorporation in N^{Et} Moiety



Complex **7** was also subjected to thermolysis, and in this case, considerably higher temperatures were required to observe any reactivity. Generation of methane was not observed until 180 °C in C_6D_6, requiring almost 15 h at this temperature to reach full conversion. The Pt product of this reaction could not be conclusively identified; however, ESI-MS data indicate that it is a Pt−Cl species. Notably, the addition of 1.0 equiv of HCl in ether solution to the unknown Pt−Cl product in CD_3CN reforms **2**, indicating that the product is potentially the neutral monoprotonated analogue of **2**. More experiments are needed to confirm if the proton on the pyrazolate of **7** is the source of the proton in the methane released from **7**; however, the very high temperature required for this reaction indicates that simply having the proton nearby on the ligand does not facilitate methane release.

■ CONCLUSIONS

In previously reported examples of addition of acid to Pt^{II}-alkyl complexes, it has sometimes been challenging to ascertain whether the metal was protonated directly or if the ligand was the kinetic site of protonation, followed by proton transfer to the metal. For example, protonation of ligated $Pt^{II}(CH_3)_2$ complexes containing a dangling N moiety in the secondary coordination sphere can lead to the generation of stable Pt^{IV} alkyl hydrides.[25−27] Low-temperature NMR studies have suggested that the dangling N moiety is the initial (kinetic) site of protonation.[28,29]

In contrast to previous studies, this work reports the use of ligands that can accept a proton but do not have the ability to reorient and stabilize Pt^{IV} hydride products. The protonation of $Pt^{II}-CH_3$ complexes supported by 2-(5-*tert*-butylpyrazol-3-yl)-6-(diethylaminomethyl)pyridine (^{H}**NNN**)^{Et} and 2,6-bis(5-*tert*-butyl-1H-pyrazol-3-yl)pyridine (^{H}**NNN**^{H}) ligands revealed that the first site of protonation was the pyrazolate and methane elimination does not occur until after all the pyrazolate sites have been protonated. Additional acid results in methane elimination at room temperature, presumably via protonation of the Pt center or the Pt-CH_3 bond. No Pt^{IV} hydrides were ever observed by ^1H NMR spectroscopy, even when the protonated complexes were subjected to thermolysis conditions. Heating of the protonated $Pt^{II}(^{H}NNN)^{Et}CH_3^+$ cationic complex (**1a**) in C_6D_6 eliminated methane at 100 °C. However, evidence indicates that the proton did not originate from the ligand N−H position. Heating of the protonated $[Pt^{II}(^{H}NNN^{H})CH_3][Cl]$ (**7**) in C_6D_6 did not result in methane release until 180 °C. While it is possible that the proton is sourced from an inter- or intramolecular pyrazolate N−H position, the high temperature of the process indicates that even if this is the case, the barrier to elimination is very high.

■ EXPERIMENTAL SECTION

General Methods. All manipulations were carried out under nitrogen atmosphere using standard Schlenk and glovebox techniques unless otherwise noted. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Dry tetrahydrofuran (THF), benzene, pentane, methylene chloride, acetonitrile, and diethyl ether were obtained by means of a Grubbs-type solvent purification system.[27] THF-d_8 and C_6D_6 were dried over sodium/benzophenone and were vacuum transferred prior to use. Acetone-d_6 and CD_3CN were dried over activated 3 Å molecular sieves. CD_2Cl_2 was dried over calcium hydride and vacuum transferred prior to use. $PtCl_2(S(CH_3)_2)_2$, $Pt(C_6H_5)_2(S(CH_3)_2)_2$, and $[Pt(CH_3)_2(\mu\text{-}S(CH_3)_2)]_2$ were synthesized following literature preparations.[30] The $^{H}NNN^{Et}$ and $^{H}NNN^{H}$ ligands were prepared according to literature procedures.[11,31] All other reagents and solvents were used as purchased from commercial suppliers.

All NMR spectra were obtained on a Bruker Avance 500 or Bruker Avance 400 MHz instrument. The spectra were recorded at 300 K. Chemical shifts are reported in units of parts per million (ppm) downfield of TMS and referenced against residual protonated solvent resonances (^1H) and characteristic solvent resonances (^{13}C). $^{31}P\{^1H\}$ NMR spectra were referenced externally to H_3PO_4 (85%, 0 ppm), and ^2H NMR spectra were referenced to the deuterium resonance of added CD_3CN (δ 1.94). $^{19}F\{^1H\}$ NMR spectra were referenced externally to C_6H_5F (−113.15 ppm). $^7Li\{^1H\}$ NMR spectra were referenced externally to LiCl (1.0 M) in D_2O (0.0 ppm). Coupling constants are reported in Hz. NMR tubes fitted with a J-Young style Teflon valve were used to obtain inert atmosphere NMR data. Elemental analyses (C, H, N) were carried out at the CENTC Elemental Analysis Facility at the University of Rochester. Accurate mass measurement analyses were conducted on a LCT Premier XE, time-of-flight, LCMS with electrospray ionization (ESI). Samples were taken up in a suitable solvent for analysis. The signals were mass measured against an internal lock mass reference of leucine enkephalin for ESI-LCMS. Waters software calibrates the instruments, and reports measurements, by use of neutral atomic masses. The mass of the electron is not included. Nominal mass accuracy ESI-MS data were obtained by use of a Waters Acquity UPLC system equipped with a Waters TUV detector (254 nm) and a Waters SQD single quadrupole mass analyzer with electrospray ionization.

*Synthesis of Pt(*NNN)^{Et}CH$_3$ (1).* A 20 mL vial was charged with a Teflon stir bar, 58.4 mg (0.204 mmol) of ^{H}**NNN**^{Et}, 58.6 mg (0.102 mmol) of $[Pt(\mu\text{-}S(CH_3)_2)(CH_3)_2]_2$, and 4 mL of dry CH_2Cl_2. The reaction was vigorously stirred for 20 min. The solvent was removed *in vacuo*, and the resulting solid was triturated (2 × 2 mL) with pentane and further dried under reduced pressures to yield an orange solid (80.1 mg, 79.2%). ^1H NMR (CD_2Cl_2, 500 MHz): δ 7.83 (1H, t, pyr-H ($^3J_{H-H}$ = 7.9 Hz)), 7.33 (1H, d, pyr-H ($^3J_{H-H}$ = 7.9 Hz)), 7.08 (1H, s, pyr-H ($^3J_{H-H}$ = 7.9 Hz)), 6.48 (1H, s, pyz-H), 4.23 (2H, s, CH_2, $^4J_{Pt-H}$ = 22 Hz), 3.20 (2H, dq, CH_2, $^2J_{H-H}$ = 12.5, $^3J_{H-H}$ = 7.3 Hz), 2.95 (2H, dq, CH_2, $^2J_{H-H}$ = 12.6, $^3J_{H-H}$ = 6.9 Hz), 1.48 (6H, t, CH_3, $^3J_{H-H}$ = 7.0 Hz), 1.34 (9H, s, CH_3), 0.83 (3H, s, Pt-CH_3, $^2J_{Pt-H}$ = 79 Hz). $^{13}C\{^1H\}$ (CD_2Cl_2, 126 MHz): δ 161.5 (s), 155.9 (s), 151.7 (s), 151.6 (s), 137.9 (s), 116.4 (s), 116.0 (s), 100.7 (s), 69.6 (s), 59.3 (s), 32.7 (s), 31.2 (s), 13.1 (s), −15.3 (s). Elemental Analysis: Anal Calcd for $C_{18}H_{28}N_4Pt$: C, 43.63; H, 5.70; N, 11.31. Found: C, 43.26; H, 5.57; N, 11.35.

Synthesis of [Pt(^{H}NNN)^{Et}CH$_3$][BF$_4$] (1a). A 20 mL vial was charged with 19.2 mg (0.0387 mmol) of **1**, a Teflon stir bar, and benzene (2 mL). The suspension was stirred vigorously while HBF_4 etherate (5.0 μL, 0.0368 mmol, 54% in diethyl ether) was added by syringe. The mixture was stirred for 5 min. Diethyl ether (10 mL) was added to completely precipitate out a yellow solid. The solid was filtered and washed with additional diethyl ether (2 × 5 mL). After the resulting solid was dissolved in minimal acetonitrile, 10 mL of diethyl ether was added to form a suspension. The suspension was filtered, and the solid was collected. It was further dried under reduced pressures (18.8 mg, 83% yield). ^1H NMR (CD_2Cl_2, 400 MHz): δ 7.90 (1H, t, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 7.41 (1H, d, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 7.18 (1H, d, pyr-H, ($^3J_{H-H}$ = 7.9 Hz), 6.53 (1H, d, pyz-H)), 4.28 (2H, t, CH_2 ($^4J_{Pt-H}$ = 24 Hz)), 3.20 (2H, dq, CH_2 ($^2J_{H-H}$ = 12.5, $^3J_{H-H}$ = 7.2 Hz)), 2.94 (2H, dq CH_2 ($^2J_{H-H}$ = 12.5, $^3J_{H-H}$ = 6.9 Hz)), 1.47 (6H, t, CH_3 ($^3J_{H-H}$ = 7.0 Hz)), 1.34 (9H, s, CH_3), 0.84 (3H, s, Pt-CH_3 ($^2J_{Pt-H}$ = 77 Hz)). $^{13}C\{^1H\}$ (CD_2Cl_2, 126 MHz): δ 160.7 (s), 156.3 (s), 152.6 (s), 150.6 (s), 138.0 (s), 117.3 (s), 117.2 (s), 101.2 (s), 69.9 (s), 59.6 (s), 32.6 (s), 30.9 (s), 13.2 (s, $^3J_{Pt-C}$ = 32 Hz), −16.0 (s). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 377 MHz): δ −152.2 (s), −152.3 (s). Attempts to characterize the material by Elemental Analysis were not successful. HRMS-ESI/Q-TOF: $[Pt(^{H}NNN)^{Et}CH_3]^+$ Theoretical Mass, m/z = 495.2019; Observed Mass, m/z = 495.2043.

Synthesis of [Pt(^{H}NNN^{H})Cl][Cl] (2). A 100 mL Schlenk flask was charged with 282.5 mg (0.873 mmol) of ^{H}**NNN**^{H}, 339.1 mg (0.869 mmol) of $Pt(S(CH_3)_2)Cl_2$, and 15 mL of methanol in air. The solution was sparged with N_2 and heated at reflux for 2 h to yield a yellow solution. The solution was cooled to room temperature and then concentrated. Diethyl ether (20 mL) was added, precipitating a yellow solid. The solid was redissolved in methanol and concentrated. Diethyl ether was again added, and the suspension was filtered via a fritted funnel. The solid was dried under reduced pressures (437.1 mg, 84.9%). ^1H NMR (CH_3OD, 500 MHz): δ 8.27 (1H, t, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 7.96 (2H, s, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 7.09 (2H, s, pyz-H), 1.46 (18H, s, ^{t}Bu). $^{13}C\{^1H\}$ (CH_3OD, 126 MHz): δ 162.8 (s), 158.2 (s), 154.8 (s), 146.3 (s), 123.6 (s), 107.6 (s), 36.0 (s), 32.7 (s). Elemental Analysis: Anal Calcd for $C_{17}H_{25}ClN_4Pt\cdot 2H_2O$: C, 36.49; H, 4.67; N, 11.20. Found: C, 36.68; H, 4.55; N, 11.23.

Synthesis of [Pt(^{H}NNN^{H})Cl][BF$_4$] (3). A 20 mL vial was charged with 23.5 mg (0.0399 mmol) of **2**, a Teflon stir bar, 4.4 mg (0.399 mmol) of sodium tetrafluoroborate, and acetonitrile (2 mL) in air. The suspension was stirred vigorously for 1 h. The resulting suspension was filtered by a fritted funnel, and the solid was extracted with CH_2Cl_2 (2 × 2 mL). The volatiles were removed from the resulting filtrate by rotary evaporation to yield a yellow solid. The solid was redissolved in methanol and concentrated. Pentane (20 mL) was added, and the resulting suspension was filtered via fritted funnel. The solid was collected and dried under reduced pressures (21.0 mg, 82.1%). ^1H NMR (CD_3CN, 500 MHz): δ 12.07 (2H, br, N−H), 8.21 (1H, t, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 7.81 (2H, d, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 6.99 (2H, s, pyz-H), 1.43 (18H, s, CH_3), ^1H NMR (CD_3OD, 400 MHz): 8.22 (1H, t, pyr-H ($^3J_{H-H}$ = 7.8 Hz)), 7.89 (2H, d, pyr-H ($^3J_{H-H}$ = 7.8 Hz)), 7.03 (2H, s, pyz-H), 1.45 (18H, s, CH_3) $^{13}C\{^1H\}$ (CD_3CN, 126 MHz): δ 156.0 (s), 155.3 (s), 151.7 (s), 143.6 (s), 121.1 (s), 105.0 (s), 33.1 (s), 29.9 (s). ^{19}F NMR (CD_3CN, 377 MHz): δ −154.47 (s), −154.52 (s). Elemental Analysis: Anal Calcd for $C_{19}H_{25}BClF_4N_5Pt\cdot 2H_2O$: C, 33.72; H, 4.32; N, 10.35. Found: C, 33.00; H, 3.82; N, 10.46.

Synthesis of $[Li(THF){-}Cl{-}Li(THF)_3][Pt({}^{*}NNN^{*})CH_3]$ ***(4)***. A 500 mL Schlenk tube was charged with 179 mg (0.325 mmol) of **2** and 200 mL of THF. While vigorously stirring, 1.5 mL (1.95 mmol) of CH_3Li (1.3 M in diethyl ether) was added via syringe and the reaction was stirred for 2 h. Water (15.6 μL, 0.98 mmol) was added via microliter syringe and stirred for 5 min. The solution was concentrated to 5 mL, and pentane was added (50 mL) to yield a dark solid, which was removed by filtration. The filtrate was dried *in vacuo* to yield a yellow solid. (173.7 mg, 57.2%). ^{1}H NMR (THF-d_8, 500 MHz): δ 7.61 (1H, t, pyr-H ($^3J_{H-H}$ = 7.8 Hz)), 7.10 (2H, d, pyr-H ($^3J_{H-H}$ = 7.8 Hz)), 6.38 (2H, d, pyz-H), 1.32 (1H, s, CH_3), 1.11 (3H, s, Pt-CH_3, ($^2J_{Pt-H}$ = 78 Hz). ^{13}C{^{1}H} NMR (THF-d_8, 126 MHz): δ 160.7 (s), 153.5 (s), 153.2 (s), 138.6 (s), 112.1 (s), 100.4 (s), 32.8 (s), 31.4 (s), −24.0 (s). ^{7}Li{^{1}H} NMR (acetone-d_6, 155.5 MHz): δ −1.4 (s). Attempts to characterize the material by Elemental Analysis were not successful. HRMS-ESI/Q-TOF: $[Pt(^{H}NNN^{H})CH_3]^+$ Theoretical Mass, m/z = 532.1972; Observed Mass, m/z = 532.1952

Synthesis of $[PPN][Pt({}^{*}NNN^{*})CH_3]$ ***(5)***. A 25 mL Schlenk flask was charged with a Teflon stir bar, **4** (42.6 mg, 0.0792 mmol), [PPN][Cl] (43.0 mg, 0.0752 mmol), and 10 mL of THF. The suspension was vigorously stirred for 1 h to precipitate a white solid. The solid was removed by transferring the solvent using a filter cannula. The solvent was removed under reduced pressures from the filtrate to yield a solid. The solid was dissolved in 3 mL of CH_2Cl_2 and filtered through a fritted funnel. The resulting filtrate solution was dried *in vacuo* to yield an orange solid (63.0 mg, 74.3%). ^{1}H NMR (CD_3CN, 400 MHz): δ 7.63 (1H, t, pyr-H ($^3J_{H-H}$ = 7.9 Hz)), 7.58 (30H, multiplet, PPN), 7.10 (2H, d, pyr-H ($^3J_{H-H}$ = 7.9 Hz)), 6.42 (2H, s, pyz-H), 1.31 (18H, s, CH_3), 1.11 (3H, s, Pt-CH_3, ($^2J_{Pt-H}$ = 82 Hz). ^{31}P{^{1}H} (CD_3CN, 162 Hz): δ 22.00. ^{13}C{^{1}H} NMR (CD_3CN, 126 MHz): δ 161.3 (s), 153.5 (s), 153.0 (s), 139.0 (s), 133.2 (m, PPN), 130.30 (m, PPN), 128.95 (dd, $^1J_{C-P}$ = 107.8 Hz, $^3J_{C-P}$ = 1.8 Hz, PPN), 112.15 (s), 100.52 (s), 32.87 (s), 31.50 (s), −18.28 (s). Attempts to characterize the material by Elemental Analysis were not successful. HRMS-ESI/Q-TOF: Theoretical Mass $[Pt(^{H}NNN^{H})CH_3]^+$ m/z = 532.1972; Observed Mass, m/z = 532.1967.

Synthesis of $Pt({}^{*}NNN)^{Et}Cl$ ***(6)***. A 20 mL vial was charged with 35.3 mg (0.123 mmol) of $^{H}NNN^{Et}$, 48.1 mg (0.123 mmol) of $Pt(S(CH_3)_2)_2(Cl)_2$, triethyl amine (50 μL, 0.36 mmol), and 4 mL of dry CH_2Cl_2. The reaction was vigorously stirred for 1 h. The solvent was removed, and the resulting yellow solid was washed with diethyl ether (3 × 3 mL) and dried *in vacuo* (41.9 mg, 66.0%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.97 (1H, dd, pyr-H ($^3J_{H-H}$ = 7.9 Hz, 7.8 Hz)), 7.46 (1H, d, pyr-H ($^3J_{H-H}$ = 7.9 Hz)), 7.17 (1H, d, pyr-H ($^3J_{H-H}$ = 7.8 Hz)), 6.57 (1H, s, pyz-H), 4.39 (2H, s, CH_2), 3.35 (2H, dq, CH_2, ($^2J_{H-H}$ = 12.8, $^3J_{H-H}$ = 6.7 Hz)), 2.94 (2H, dq, CH_2, ($^2J_{H-H}$ = 12.9, $^3J_{H-H}$ = 6.6 Hz)), 1.53 (6H, t, CH_3 ($^3J_{H-H}$ = 7.1 Hz)), 1.32 (9H, s, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz): δ 161.3 (s), 158.4 (s), 152.8 (s), 149.4 (s), 138.4 (s), 116.3 (s), 115.0 (s), 100.8 (s), 67.5 (s), 58.7 (s), 30.5 (s), 32.3 (s), 12.2 (s). Elemental Analysis: Anal Calcd for $C_{17}H_{25}ClN_4Pt$: C, 39.58; H, 4.88; N, 10.86. Found: C, 39.38; H, 4.81; N, 10.63.

Synthesis of $[Pt(^{H}NNN)^{Et}Cl][BF_4]$ ***(6a)***. A 20 mL vial was charged with 7.2 mg (0.014 mmol) of $Pt({}^{*}NNN)^{Et}Cl$ (**6**), a Teflon stir bar, 3.2 mg (0.014 mmol) of 2,6-dimethoxy pyridinium tetrafluoroborate and diethyl ether (3 mL). The suspension was stirred vigorously for 15 min. Diethyl ether (5 mL) was added to completely precipitate out a very light yellow solid. The supernatant was decanted, and the resulting solid was triturated with diethyl ether (4 mL) and washed with diethyl ether (2 × 3 mL). The light yellow solid was collected and dried under reduced pressures (8.1 mg, 95.8% yield). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 10.56 (1H, s, N−H), 8.29 (1H, t, pyr-H ($^3J_{H-H}$ = 8.1 Hz)), 7.86 (1H, d, pyr-H ($^3J_{H-H}$ = 8.1 Hz)), 7.79 (1H, d, pyr-H ($^3J_{H-H}$ = 8.1 Hz)), 6.90 (1H, d, pyz-H, $^4J_{H\text{-}NH}$ = 2.0 Hz), 4.69 (2H, t, CH_2 ($^4J_{Pt-H}$ = 16.6 Hz)), 3.42 (2H, dq, CH_2, $^2J_{H-H}$ = 12.7, $^3J_{H-H}$ = 7.2 Hz), 3.06 (2H, dq, CH_2 ($^2J_{H-H}$ = 12.7, $^3J_{H-H}$ = 6.9 Hz)), 1.57 (6H, t, CH_3 ($^3J_{H-H}$ = 7.1 Hz)), 1.44 (9H, s, CH_3), ^{13}C{^{1}H} (CD_2Cl_2, 126 MHz): δ 161.9 (s), 158.1 (s), 154.5 (s), 148.3 (s), 141.3 (s), 122.6 (s), 121.5 (s), 103.4 (s), 69.8 (s), 60.9 (s), 32.6 (s), 29.9 (s), 13.2 (s). ^{19}F{^{1}H} NMR (CD_2Cl_2, 377 MHz): δ −151.68 (s), −151.73 (s). Attempts to characterize the material by Elemental Analysis were not successful. HRMS-ESI/Q-TOF: $[Pt(^{H}NNN)^{Et}Cl]^+$ Theoretical Mass, m/z = 515.1473; Observed Mass, m/z = 515.1456.

Synthesis of $[Pt(^{H}NNN^{H})CH_3][Cl]$ ***(7)***. A 20 mL vial was charged with 137 mg (0.233 mmol) of **2**, a Teflon stir bar, and benzene (10 mL). While vigorously stirring, a 2.9 M CH_3MgCl (0.337 mL, 0.977 mmol) solution in THF was added via syringe and stirred for 20 min. A water (17 μL) and THF (2 mL) solution was added, and the reaction mixture was stirred for 20 min. The resulting suspension was filtered by fritted funnel, and the orange and white solid was dried under reduced pressures (155.2 mg). Note: Less than 100% yield was never attainable, even after rigorous drying. THF resonances were consistently observed by ^{1}H NMR spectroscopy and are likely indicative of the presence of MgX_2 impurities. Attempts at washing away likely impurities were unsuccessful. ^{1}H NMR (Acetone-d_6, 400 MHz): δ 13.28 (2H, br, N−H), 8.34 (1H, t, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 8.11 (2H, d, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 7.20 (2H, s, pyz-H), 1.47 (18H, s, ^{t}Bu), 1.24 (3H, s, Pt-CH_3 ($^2J_{Pt-H}$ = 79 Hz)).

Synthesis of $[Pt(^{H}NNN^{H})CH_3][BF_4]$ ***(8)***. An NMR tube fitted with a J-Young style Teflon valve was charged with **5** (5.7 mg, 0.0053 mmol). CD_3CN (0.4 mL) was then vacuum transferred to the NMR tube. 2,6-Dimethoxypyridiniumtetrafluoroborate (2.1 mg, 0.011 mmol) was then added to the NMR tube. The NMR tube was sealed, vigorously shaken, and a ^{1}H NMR spectrum was recorded. ^{1}H NMR (CD_3CN, 400 MHz): δ 11.83 (2H, br, N−H), 8.11 (1H, t, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 7.77 (2H, d, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 6.89 (2H, s, pyz-H), 1.50 (3H, s, Pt-CH_3 ($^2J_{Pt-H}$ = 79 Hz)), 1.45 (18H, s, ^{t}Bu).

Synthesis of $[Pt(^{H}NNN^{H})CH_3][BAr^{F}_{24}]$ ***(9)***. A 20 mL vial was charged with 46.0 mg (0.078 mmol) of **2**, a Teflon stir bar, and benzene (3 mL). While stirring vigorously, 0.117 mL (0.328 mmol) of CH_3MgCl (2.9 M in THF) was added via syringe, and the resulting mixture was stirred for 20 min. A solution of water (5 μL, 0.224 mmol) and THF (1 mL) was added, and the reaction mixture was stirred for an additional 20 min. The resulting suspension was filtered by a fritted funnel, and the mixture of orange and white solid was collected into a 20 mL vial (35.5 mg). The vial was then charged with $NaBAr^{F}_{24}$ (49.8 mg, 0.0562 mmol), acetone (3 mL), and a Teflon stir bar and stirred for 1.5 h to form a suspension. The solvent was reduced by half under vacuum, and then 10 mL of diethyl ether was added. The resulting suspension was filtered by PTFE (0.4 μm) syringe filter. The filtrate was concentrated, and 10 mL of pentane was added to form a suspension. The supernatant was decanted, and the resulting orange oil was pumped to dryness to yield an orange solid (62.7 mg, 56.7% yield). ^{1}H NMR (Acetone-d_6, 500 MHz): δ 13.13 (2H, s, N−H), 8.38 (1H, t, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 8.17 (2H, d, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 7.78 (8H, br s, BAr^{F}_{24}), 7.78 (4H, s, BAr^{F}_{24}), 7.23 (2H, s, pyz-H), 1.47 (18H, s, ^{t}Bu), 1.21 (3H, s, Pt-CH_3, ($^2J_{Pt-H}$ = 79 Hz). ^{13}C{^{1}H} (Acetone-d_6, 126 MHz): δ 162.8 (q, $^1J_{BC}$ = 50.0 Hz), 159.1 (s), 157.2 (s), 149.9 (s), 142.5 (s), 135.7 (s), 130.2 (q, $^3J_{CF}$ = 32.6 Hz), 125.5 (q, $^1J_{CF}$ = 271.9 Hz), 120.8 (s), 118.6 (s), 104.9 (s), 33.0 (s), 30.0 (s), −22.7 (s). ^{19}F{^{1}H} NMR (CD_2Cl_2, 377 MHz): δ −62.85 (s). Attempts to characterize the material by Elemental Analysis were not successful. HRMS-ESI/Q-TOF: $[Pt(^{H}NNN^{H})\text{-}CH_3]^+$ Theoretical Mass, m/z = 532.1972; Observed Mass, m/z = 532.2000.

Synthesis of $[Pt(^{H}NNN^{H})NCCH_3][BF_4]_2$ ***(10)***. A 20 mL vial was charged with 31.3 mg (0.0533 mmol) of **2**, a Teflon stir bar, 20.7 mg (0.107 mmol) of silver tetrafluoroborate, and acetonitrile (3 mL). The suspension was stirred vigorously for 1 h. The resulting suspension was filtered through a PTFE (0.4 μm) syringe filter. The filtrate was concentrated, and diethyl ether (5 mL) was added to precipitate a light yellow solid. The supernatant was decanted, and the solid was washed with diethyl ether (2 × 5 mL) and dried under reduced pressures (27.2 mg, 66.5%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 12.92 (2H, s, N−H), 8.23 (1H, t, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 7.72 (2H, d, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 6.75 (2H, s, pyz-H), 2.94 (3H, s, $NCCH_3$) 1.48 (18H, s, CH_3), ^{1}H NMR (CD_3CN, 500 MHz): 12.12 (2H, s, N−H), 8.29 (1H, t, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 7.88 (2H, d, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 7.05 (2H, s, pyz-H), 1.45 (18H, s, CH_3), ^{13}C{^{1}H} (CD_3CN, 126 MHz): δ 160.9 (s), 155.1 (s), 152.3 (s), 146.1 (s), 121.7 (s), 105.7 (s), 33.1 (s), 29.8 (s) ^{19}F NMR (CD_3CN, 377 MHz): δ −150.89 (s), −150.94 (s). Elemental Analysis: Anal Calcd for $C_{21}H_{28}B_2F_8N_6Pt$: C, 34.40; H, 3.85; N, 11.46. Found: C, 34.21; H, 3.52; N, 11.22.

Synthesis of $Pt(^*NNN)^{Et}C_6H_5$ ***(11)***. An NMR tube fitted with a J-Young style Teflon valve was charged with $Pt(S(CH_3)_2)_2(C_6H_5)_2$ (7.0 mg, 0.0147 mmol), $^{\mathbf{H}}\mathbf{NNN}^{\mathbf{Et}}$ (4.2 mg, 0.0147 mmol), and CD_2Cl_2. The reaction was heated to 60 °C for 2.5 h. After it was cooled, the yellow solution was concentrated in a 20 mL vial in air. Diethyl ether (2 mL) was then added until a yellow suspension formed. The suspension was decanted, and then the solid was washed with pentane (1 × 2 mL) and further dried under reduced pressures to obtain a pale yellow solid (6.6 mg, 80.5%). ^{1}H (400 MHz, CD_2Cl_2): δ 7.84 (1H, t, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 7.53 (2H, d, pyr-H ($^3J_{H-H}$ = 7.0 Hz, $^3J_{Pt-H}$ = 39.4 Hz)), 7.37 (1H, d, pyr-H ($^3J_{H-H}$ = 8.0 Hz)), 7.14–7.00 (3H, m, Ar−H and pyr-H overlapping), 6.92 (1H, t, Ar−H ($^3J_{H-H}$ = 7.3 Hz)), 6.48 (1H, s, pyz-H), 4.31 (2H, s, CH_2), 3.10 (2H, dq, CH_2 ($^2J_{H-H}$ = 10.4, $^3J_{H-H}$ = 7.1 Hz)), 2.79 (2H, dq, CH_2 ($^2J_{H-H}$ = 13.7, $^3J_{H-H}$ = 7.0 Hz)), 1.53 (6H, CH_3 ($^3J_{H-H}$ = 7.1 Hz)), 1.27 (9H, s, CH_3). $^{13}C\{^1H\}$ (CD_2Cl_2, 126 MHz): δ 162.1 (s), 157.3 (s), 152.2 (s), 151.6 (s), 147.4 (s), 138.7 (s), 137.9 (s), 127.0 (s), 122.6 (s) 116.4 (s), 115.4 (s), 101.1 (s), 69.2 (s), 60.0 (s), 32.6 (s), 31.2 (s), 13.3 (s). HRMS-ESI/Q-TOF: $[Pt(^HNNN^{Et})C_6H_5]^+$ Theoretical Mass, m/z = 557.2176; Observed Mass, m/z = 557.2187.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00023.

NMR characterization data and additional solid-state structures with data tables (PDF)

Accession Codes

CCDC 1949454−1949459, 1949477, and 1949480 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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