

# Five-Coordinate Dihydridosilyl Platinum(IV) Complexes Supported by a Chelating Monoanionic Nitrogen-Based Ligand

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Complexes of Pt(IV) containing the bidentate ligand 3,5-diphenyl-2-(2-pyridyl)pyrrolide (PyPyr) were prepared. The ethylene complex PyPyrPt( $C_2H_4$ )Cl (1) was treated with HSiEt<sub>3</sub> or HSiEtMe<sub>2</sub> to produce the Pt(IV) silyl dihydrides PyPyrPt(H)<sub>2</sub>SiEt<sub>3</sub> (3) and PyPyrPt(H)<sub>2</sub>SiEtMe<sub>2</sub> (4), respectively. The solid-state structure of 3, determined by X-ray crystallography, reveals a dimeric structure that forms via  $\pi$ -stacking between the PyPyr ligands. Addition of Lewis bases to 3 results in either coordination to generate an octahedral Lewis base adduct (with DMAP) or silane elimination to give square-planar Pt(II) Lewis base complexes (with phosphines). Complex 3 was also found to be an active hydrosilylation catalyst for the hydrosilylation of alkynes and terminal olefins with HSiEt<sub>3</sub>.

## Introduction

Five-coordinate d<sup>6</sup> Pt(IV) complexes have attracted considerable interest as intermediates in bond activation processes and for their potential role in catalytic transformations involving oxidative additions and reductive eliminations at platinum.<sup>1-6</sup> Few five-coordinate Pt(IV) species have been isolated, and more extensive investigations into their chemical behavior appear to be limited by their inherently reactive nature. Examples of five-coordinate organometallic Pt(IV) complexes include [ $\{(o-R^{1})^{2}$  $p-R^2C_6H_2$ )NC(R<sup>3</sup>)}2CH]PtMe<sub>3</sub> (R<sup>1</sup> = Me, R<sup>2</sup> = <sup>t</sup>Bu, R<sup>3</sup> = Me,  $R^1 = Me$ ,  $R^2 = H$ ,  $R^3 = Me$ ,  $R^1 = Et$ ,  $R^2 = H$ ,  $R^3 = {}^tBu$ ,<sup>7</sup> and  $R^1 = {}^{i}Pr$ ,  $R^2 = H$ ,  $R^3 = Me^{8,9}$ ), (AmIm)PtMe<sub>3</sub> (AmIm =  $[o-C_6H_4\{N(C_6H_3^iPr_2)\}(CH=NC_6H_3^iPr_2)]^{-1}, [(BAB)PtMe_3]^{-1}$ [OTf] 1,2-bis(N-7-azaindolyl)benzene,  $OTf = O_3SCF_3$ ),<sup>11</sup> and (DtBPP)PtMe<sub>3</sub> (DtBPP=3,5-di-*tert*-butyl-2-(2-pyridyl)pyrrolide).<sup>12</sup> Given the ability of silyl ligands to support metal complexes in high oxidation states, and the established

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parallels between Si-H and C-H activation processes, 13,14 it seems that Pt(IV) silvl derivatives are appealing targets for fundamental investigations into bond activations involving platinum. In fact, only a few five-coordinate Pt(IV) complexes with silvl groups have been reported,<sup>15–18</sup> including  $[(NSiN)PtMe_2][B(C_6F_5)_4]$  (NSiN = bis(8-quinolyl)methylsilvl),  $[\kappa^2 - ((Hpz')BHpz'_2) - Pt(H)_2SiR_3][BAr'_4]$  (pz' = 3,5-dimethylpyrazole; R = Et, Ph, and Ph<sub>2</sub>H), [{(p-Cl-C<sub>6</sub>H<sub>4</sub>)NC (Me)<sub>2</sub>CH]Pt(H)<sub>2</sub>(SiR<sub>3</sub>) (R = Ph, Et, Ph<sub>2</sub>H), and (PyInd)- $Pt(SiMe_3)Me_2$  (PyInd = 2-(2'-pyridyl)indolide). Little is known about the chemical properties of such species with the exception of  $[{(p-Cl-C_6H_4)NC(Me)}_2CH]Pt(H)_2(SiR_3),$ which undergoes cycloaddition of alkynes and phosphalkynes across the chelate ring of the complex.<sup>18</sup> Here, we report ready access to five-coordinate Pt(IV) silyl dihydride complexes and their behavior as hydrosilylation catalysts. These complexes are supported by the chelating, 3,5-diphenyl-2-(2-pyridyl)pyrrolide (PyPyr) ligand. Ligands of this type have been shown to provide access to stable complexes and reactive intermediates involving Pt(IV).<sup>12,17</sup>

# **Results and Discussion**

Synthesis of Pt(II) Complexes Supported by PyPyr. The reaction of 0.5 equiv of Zeise's dimer,  $[(C_2H_4)PtCl_2]_2$ , with 1 equiv of PyPyrLi in THF produced (PyPyr)Pt( $C_2H_4$ )Cl (1) as a yellow solid in 80% yield (eq 1). A 2D NOESY NMR

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spectrum displays a correlation between the ethylene ligand and the pyridyl moiety, which is consistent with the ethylene ligand of the complex being *cis* to the pyridyl group. Similarly,



treatment of 0.5 equiv of  $[(SMe_2)PtCl_2]_2$  with PyPyrLi in THF yielded (PyPyr)Pt(SMe\_2)Cl (2) as a yellow solid in 92% yield (eq 2). The <sup>1</sup>H NMR spectrum possesses two overlapping singlets at 1.77 ppm for the thioether resonances. A 2D NOESY NMR spectrum of 2 displays a correlation between the phenyl substituents on the pyrrolide group and the methyl substituents



of the thioether, which implies that the  $SMe_2$  ligand is *cis* to the pyrrolide group. Suitable crystals of **2** were grown from vapor diffusion of pentane into a toluene solution of **2**.

The X-ray crystal structure of **2** confirms the geometry deduced from NMR spectroscopy (Figure 1). Complex **2** adopts a square-planar structure with the thioether group *trans* to the pyridyl ligand and a Pt–S bond distance of 2.2723(9) Å. The small N1–Pt1–N2 bite angle of 79.4(1)° is characteristic of late transition metal complexes supported by PyPyr.<sup>12,19</sup>

Addition of HSiR<sub>3</sub> to (PyPyr)Pt(C<sub>2</sub>H<sub>4</sub>)Cl. Complex 1 was found to react with 4 equiv of Et<sub>3</sub>SiH at 25 °C in C<sub>6</sub>H<sub>6</sub> over 12 h to give (PyPyr)Pt(H)<sub>2</sub>SiEt<sub>3</sub> (3) in 95% yield after crystallization from pentane (eq 3). The <sup>1</sup>H NMR spectrum of **3** possesses two upfield hydride resonances at -15.17 ppm ( $J_{PtH}$  = 968 Hz) and -16.97 ppm ( $J_{PtH}$  = 1114 Hz), which are more similar to that of the fivecoordinate complex [ $\kappa^2$ -((Hpz')BHpz'<sub>2</sub>)-Pt(H)<sub>2</sub>SiEt<sub>3</sub>]-[BAr'<sub>4</sub>] (-16.69 ppm)<sup>16</sup> than that of the neutral six-coordinate complex Tp'Pt(H)<sub>2</sub>SiEt<sub>3</sub> (-20.15 ppm).<sup>20</sup> A 2D NOESY experiment demonstrated that the hydride ligand



resonating at -16.97 ppm displays a correlation to the phenyl substituent of the pyrrolide group, which is consistent with the hydride ligand being *cis* to the pyrrolide ligand. The <sup>29</sup>Si NMR spectrum contains a single resonance for the silyl ligand at 44.2 ppm ( $J_{PtSi} = 704.5$  Hz). The IR spectrum of **3** reveals two strong bands at 2221 and 2254 cm<sup>-1</sup> attributed to the hydride ligands; for comparison, the corresponding stretches observed for [{(p-Cl-C<sub>6</sub>H<sub>4</sub>)NC(Me)}<sub>2</sub>CH]Pt-(H)<sub>2</sub>(SiEt<sub>3</sub>)<sup>18</sup> and [ $\kappa^2$ -(((Hpz')BHpz'\_2)-Pt(H)\_2SiEt<sub>3</sub>][BAr'<sub>4</sub>]<sup>16</sup>



**Figure 1.** ORTEP diagram of the X-ray crystal structure of **2**. Hydrogen atoms and  $0.5(C_7H_8)$  are omitted for clarity. Bond lengths (Å) and angles (deg): Pt1-N1 = 2.045(3), Pt1-N2 = 2.000(3), Pt1-S1 = 2.2723(9), Pt1-C11 = 2.3196(9), N1-Pt1-N2 = 79.4(1), N1-Pt1-C11 = 94.04(8), N2-Pt1-S1 = 94.65(8), S1-Pt1-C11 = 91.58(3),N1-Pt1-S1 = 170.14(7), N2-Pt1-C11 = 173.34(8).

are at 2205 and 2258 cm<sup>-1</sup>, respectively. The formation of **3** in  $C_6D_6$ , monitored by <sup>1</sup>H NMR spectroscopy, results in production of 1 equiv of Et<sub>3</sub>SiCl and the additional byproducts Et<sub>4</sub>Si and C<sub>2</sub>H<sub>4</sub>. The reaction initially produced a stoichiometric quantity of C<sub>2</sub>H<sub>4</sub> (after 5 min), but after 1 h the ethylene was consumed with concomitant production of Et<sub>4</sub>Si via a Pt-mediated hydrosilylation of C<sub>2</sub>H<sub>4</sub> by HSiEt<sub>3</sub>. This is in contrast to the formation of  $[{(p-Cl-C_6H_4)NC-}]$ (Me)<sub>2</sub>CH]Pt(H)<sub>2</sub>(SiEt<sub>3</sub>),<sup>18</sup> which involves displacement of a pentene ligand from a Pt(II) precursor by a silane, with no hydrosilylation of the alkene. Interestingly, addition of 4 equiv of DSiEt<sub>3</sub> to 1 did not give only  $3-d_2$  as might be expected, but instead generated a mixture of 3, 3-d, and 3-d<sub>2</sub> (by <sup>1</sup>H and <sup>2</sup>H NMR spectroscopy). In a similar manner, 4 equiv of HSiMe<sub>2</sub>Et was observed to react with 1 in C<sub>6</sub>H<sub>6</sub> at 25 °C to give (PyPyr)Pt(H)<sub>2</sub>(SiMe<sub>2</sub>Et) (4) in 94% yield after 12 h (eq 3). In contrast, the addition of 4 equiv of Et<sub>3</sub>SiH to 2 at 25 °C in  $C_6H_6$  over 4 days gave no reaction by <sup>1</sup>H NMR spectroscopy.

X-ray quality crystals of 3 were obtained by slow evaporation of a pentane solution of 3 at 25 °C. The solid-state structure of 3 consists of two pairs of associated monomers within the asymmetric unit (Figure 2). The dimeric structures contain two molecules of 3 that orient their open coordination sites toward one another, giving rise to a Pt-Pt distance of 3.2137(9) Å. This Pt-Pt distance is longer than that expected for two Pt centers bridged by hydride ligands  $(\sim 2.7 \text{ Å})$  or for a Pt-Pt bond (2.70-3.00 Å). Thus, the proximity of the two Pt centers appears to be determined by a  $\pi$ -stacking interaction between pyridyl-pyrrolide ligands of the two complexes, resulting in distances between atoms in the different PyPyr ligands ranging from 3.3 to 3.5 Å. These distances are consistent with  $\pi$ -stacking between the pyrrolide group of one ligand and the pyridyl group of the other.<sup>21</sup> The silvl group of 3 is slightly displaced from the ideal apical position of a square-based pyramid, as indicated by inequivalent Si-Pt-N bond angles of 109.0(4)° and 112.4(4)°

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Figure 2. ORTEP diagram of  $(PyPyr)Pt(H)_2SiEt_3$  (3). Ellipsoids are drawn at 50% probability; only one dimeric unit is shown: (a) side view with CH<sub>3</sub> groups removed, (b) top view with Et and Ph groups removed. Bond lengths (Å) and angles (deg): Pt1-N12=2.07(1), Pt1-N11=2.11 (1), Pt1-Si1=2.307(6), Pt1-Pt2=3.2137(9), Pt1-H11=1.71(5), Pt1-H12=1.8(2), Pt2-N22=2.08(1), Pt2-N21=2.10(1), Pt2-Si2=2.310(6), Pt2-H21=1.70(5), Pt2-H22=1.70(5), N12-Pt1-N11=78.3(6), N12-Pt1-Si1=112.4(4), N11-Pt1-Si1=109.0(4), N12-Pt1-Pt2=87.7(4), N22-Pt2-N21=78.6(5), N22-Pt2-Si2=110.7(4), and N21-Pt2-Si2=109.6(4).

for the pyridyl and pyrrolide nitrogen atoms, respectively. The hydride ligands, which were located from the difference Fourier map, are associated with terminal Pt-H with distances of 1.71(5) and 1.8(2) Å and planarity for the PtN<sub>2</sub>H<sub>2</sub> units (maximum deviation from least-squares plane of 0.06 Å).

Addition of Lewis Bases to (PyPyr)Pt(H)<sub>2</sub>SiEt<sub>3</sub>. Complex 3 might be expected to react with Lewis bases in one of two ways: via coordination to give a six-coordinate Pt(IV) complex or by a ligand-induced reductive elimination of silane to give a four-coordinate Pt(II) hydride. Addition of 1 equiv of 4-dimethylaminopyridine (DMAP) to 3 in C<sub>6</sub>H<sub>6</sub> at 25 °C gave (PyPyr)Pt(H)<sub>2</sub>SiEt<sub>3</sub>(DMAP) (5) in 90% yield after 1 h (eq 4). The <sup>1</sup>H NMR spectrum of 5 reveals the presence of two chemically inequivalent hydrides at -16.99 ( $J_{PtH} = 1150$  Hz) and -18.10 ppm ( $J_{PtH} = 1200$  Hz), and the <sup>29</sup>Si NMR resonance is observed at 9.8 ppm. The  $\nu$ (Pt-H) stretching frequencies for 3 are observed at 2206 and 2262 cm<sup>-1</sup>, and on the basis of the spectroscopic data this complex is characterized as a six-coordinate Pt(IV) complex.



Reactions of **3** with phosphines resulted in the reductive elimination of silane. For example, addition of 1 equiv of <sup>i</sup>Pr<sub>3</sub>P to **3** in C<sub>6</sub>H<sub>6</sub> at 25 °C produced (PyPyr)Pt(<sup>i</sup>Pr<sub>3</sub>P)H (**6**) and a stoichiometric amount of HSiEt<sub>3</sub> after 1 h, and **6** was isolated as a yellow-brown solid in 72% yield (eq 5). The <sup>1</sup>H NMR spectrum of **6** contains a single upfield hydride resonance at -19.64 ppm ( $J_{PH}$  = 28.5 Hz,  $J_{PtH}$  = 1208 Hz). A 2D NOESY NMR spectrum exhibits a correlation between the hydride ligand and the phenyl substituents of the pyrrolide moiety, which confirms that the hydride is *cis* to the pyrrolide ligand. Similarly, treatment of **3** with 1 equiv of PPh<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> at 25 °C gave (PyPyr)Pt(PPh<sub>3</sub>)H (**7**) in 90% yield after 1 h (eq 5). The <sup>1</sup>H NMR spectrum of **7** contains a single upfield hydride resonance at -17.47 ppm ( $J_{PH}$ =29.5 Hz,  $J_{PtH}$ =1184 Hz). This result is in contrast to [{ $(p-Cl-C_6H_4)NC(Me)$ }<sub>2</sub>CH]Pt(H)<sub>2</sub>(SiEt<sub>3</sub>), which produces a six-coordinate Pt(IV) species upon the addition of a strong  $\sigma$ -donating phosphine such as PMe<sub>3</sub>, to give [{ $(p-Cl-C_6H_4)NC(Me)$ }<sub>2</sub>CH]Pt(H)<sub>2</sub>(SiEt<sub>3</sub>)(PMe<sub>3</sub>).<sup>18</sup> This difference in reactivity toward phosphines may be attributed to the more donating nature of the diiminate ligand of [{ $(p-Cl-C_6H_4)NC(Me)$ }<sub>2</sub>CH]Pt(H)<sub>2</sub>(SiEt<sub>3</sub>)(PMe<sub>3</sub>) (in comparison to the PyPyr ligand), which provides a more electronrich metal center that may be less prone to reductive elimination.

$$Ph \underbrace{\bigvee_{Ph}}_{Ph} H \xrightarrow{PR_3}_{C_6H_6 \ 1 \ h} Ph \underbrace{\bigvee_{Ph}}_{H} PR_3 \xrightarrow{Pt \stackrel{PR_3}{Ph}}_{Ph} Ph \underbrace{\bigvee_{Ph}}_{Ph} Ph \underbrace{\bigvee_{Ph$$

Silane Exchange of (PyPyr)Pt(H)<sub>2</sub>SiEt<sub>3</sub>. The ready loss of silane from 3 under certain conditions suggested that related Pt(IV) dihydridosilyl complexes might be obtained by exchange of the HSiEt<sub>3</sub> in 3 with free silanes. Addition of 1 equiv of HSiMe<sub>2</sub>Et in C<sub>6</sub>H<sub>6</sub> to 3 at 25 °C over 8 h gave an equilibrium mixture of 3 and 4(1:1.2). No further changes in the equilibrium were observed over 1 day at 25 °C; however, addition of excess HSiMe2Et (4 equiv) to 3 quantitatively generated 4 and HSiEt<sub>3</sub> (1 equiv) by <sup>1</sup>H NMR spectroscopy (eq 6). To investigate the mechanism of silane exchange in the reaction of 3 with HSiMe<sub>2</sub>Et, a kinetic study was initiated. At 50 °C in benzene- $d_6$ , the concentration dependence for each substrate was determined by monitoring the reaction rate under pseudo-first-order conditions. To determine the reaction order in 3, the silane exchange was followed under 10-30 equiv of excess HSiMe<sub>2</sub>Et. Under these conditions, a first-order dependence on [3] was observed. In a similar manner, the reaction order in HSiMe<sub>2</sub>Et was determined by following the silane exchange of 3 with HSiMe<sub>2</sub>Et in the presence of 10-38 equiv of excess [3]. No dependence on [HSiMe<sub>2</sub>Et] was observed, and the overall rate expression takes the following form: rate= $k_{obs}[3]$ . The lack of a dependence on the concentration of HSi-Me<sub>2</sub>Et indicates that the exchange proceeds via a dissociative pathway in which reductive elimination of HSiEt<sub>3</sub> from 3 is rate-determining. A dissociative mechanism is consistent with related displacement reactions from Pt(IV)

Table 1. Catalytic Hydrosilylation by 3<sup>a</sup>

olefin/alkyne	$T(^{\circ}\mathrm{C})$	time	product	yield (%)
C <sub>2</sub> H <sub>4</sub>	60	2 h	Et <sub>4</sub> Si	>95
1-hexene	80	1 d	cis-3-hexene	n/a
CH <sub>2</sub> CHC(CH <sub>3</sub> ) <sub>3</sub>	60	16 h	EtSi <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub>	82
1-pentyne	60	2 h	cis-Et <sub>3</sub> SiCHCH(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	>95
PhC≡CPh	80	16 h	cis-PhCHC(SiEt <sub>3</sub> )Ph	>95
MeCN	90	4 d	n/a	0
CO <sub>2</sub>	90	4 d	n/a	0

<sup>*a*</sup> Reactions were conducted with 0.1 mmol of substrate and HSiEt<sub>3</sub> and 5 mol % of **3** in 1 mL of  $C_6D_6$ . Yield and regiochemistry were determined by <sup>1</sup>H NMR spectroscopy and GC-MS relative to an internal standard.

complexes.<sup>3,22–25</sup> Interestingly, the larger silane HSiPh<sub>3</sub> does not displace HSiEt<sub>3</sub> from **3** under comparable conditions.



Catalytic Hydrosilylation by (PyPyr)Pt(H)<sub>2</sub>SiEt<sub>3</sub>. The stoichiometric hydrosilylation of ethylene in the synthesis of **3** led to the exploration of **3** as a hydrosilylation catalyst (Table 1). With 5 mol % of 3, the hydrosilylation of  $C_2H_4$ with HSiEt<sub>3</sub> in C<sub>6</sub>D<sub>6</sub> at 60 °C gave Et<sub>4</sub>Si in > 95% yield after 2 h. With 1-hexene, no hydrosilylation was detected and only olefin isomerization was observed after 1 day at 80 °C. The terminal olefin tert-butylethylene, an olefin that does not easily undergo isomerization, was hydrosilated with HSiEt<sub>3</sub> in 82% yield at 60 °C over 16 h. The hydrosilylation of alkynes by 3 was also investigated. Hydrosilylation of the terminal alkyne 1-pentyne occurred to give the cis isomer in >95% yield after 2 h at 60 °C. Interestingly, the hydrosilvlation of diphenylacetylene proceeded in high yield (>95%) at 80 °C over 16 h to give the *cis* isomer.<sup>26</sup> The smaller, less active substrates CO2 and MeCN did not undergo any detectable hydrosilylation after 90 °C in 4 days. In contrast, when  $[{(p-Cl-C_6H_4)NC(Me)}_2CH]Pt(H)_2(SiEt_3)$ was treated with ethylene and alkynes, no hydrosilylation products were observed.<sup>18</sup>

#### **Concluding Remarks**

In conclusion, Pt(IV) silyl dihydrides are readily accessed from a Pt(II) complex that undergoes multiple Si–H bond activations. One Pt(IV) silyl dihydride exhibits an unusual solid-state structure in which the basal planes of two square-based pyramidal complexes interact via  $\pi$ -stacking between the PyPyr ligands. The Pt(IV) silyl dihydride undergoes attack by Lewis bases with or without concomitant silane loss. Complex **3** also undergoes silane exchange through a dissociative pathway, presumably via the intermediate (PyPyr)PtH. This intermediate may be involved in the catalytic hydrosilylation of alkenes and alkynes by **3**.

### **Experimental Section**

General Procedures. All experiments were conducted under nitrogen using standard Schlenk techniques or in a Vacuum Atmospheres drybox. Nondeuterated solvents were distilled under  $N_2$  from appropriate drying agents and stored in PTFEvalved flasks. Deuterated solvents (Cambridge Isotopes) were vacuum-transferred from appropriate drying agents.

All olefins, alkynes, 4-dimethylaminopyridine, and PPh<sub>3</sub> were purchased from Aldrich and dried over appropriate drying agents. Ethylene was obtained from Praxair and was used as received. <sup>*i*</sup>Pr<sub>3</sub>P and [(C<sub>2</sub>H<sub>4</sub>)PtCl<sub>2</sub>]<sub>2</sub> were purchased from Strem and used without further purification. The compounds 3,5-diphenyl-2-(2-pyridyl)pyrrole (PyPyr)H,<sup>27</sup> LiN(SiMe<sub>3</sub>)<sub>2</sub>,<sup>28</sup> and [(SMe<sub>2</sub>)PtCl<sub>2</sub>]<sub>2</sub><sup>29</sup> were synthesized according to a literature procedure. Silanes were purchased from Gelest or Aldrich and used without further purification.

Analytical Methods.  ${}^{1}H$ ,  ${}^{2}H$ ,  ${}^{29}Si\{{}^{1}H\}$ ,  ${}^{31}P\{{}^{1}H\}$ , and  ${}^{13}C\{{}^{1}H\}$ NMR spectra were recorded using a Bruker AVB 400, AV-500, or DRX 500 spectrometer equipped with a 5 mm broadband probe. Spectra were recorded at room temperature and referenced to the residual protonated solvent for <sup>1</sup>H or to internal tetramethylsilane for  ${}^{29}$ Si.  ${}^{31}P{}^{1}H{}$  NMR spectra were referenced relative to 85% H<sub>3</sub>PO<sub>4</sub> external standard ( $\delta = 0$ ). <sup>13</sup>C{<sup>1</sup>H} NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. Infrared spectra were recorded on a Nicolet Nexus 6700 FTIR spectrometer. Measurements were recorded for samples as Nujol mulls on KBr plates at a 4.0 cm<sup>-1</sup> resolution. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley. Identities and yields of organic products were confirmed by <sup>1</sup>H NMR spectroscopy and by GC-MS relative to an internal standard, using an Agilent Technologies 6890N GC system with an HP-5MS column.

(PyPyr)Pt(C<sub>2</sub>H<sub>4</sub>)Cl (1). To a 5 mL solution of (PyPyr)H (0.503 g, 1.70 mmol) in THF was added LiN(SiMe<sub>3</sub>)<sub>2</sub> (0.284 g, 1.70 mmol). The reaction mixture was then stirred for 30 min. After stirring, a 5 mL tetrahydrofuran solution of  $[(C_2H_4)]$ PtCl<sub>2</sub>]<sub>2</sub> (0.500 g, 1.70 mmol) was added to the reaction mixture. After 1 h of stirring the mixture, the solvent was removed in vacuo. The resulting yellow solid was dissolved in toluene, and the solution was filtered through Celite. The solvent was removed in vacuo, and the resulting solid was washed with 5 mL of pentane to give a yellow powder in 80% yield (0.755 g, 1.36 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.93 (d  $J_{\rm HH}$  = 8.5 Hz, 2H, Ar*H*), 7.49 (d  $J_{\rm HH}$  = 8.5 Hz, 2H, Ar*H*), 7.45 (t  $J_{\rm HH}$  = 8.0 Hz, 2H, ArH), 7.28-7.10 (ov m with benzene-d<sub>6</sub>, 5H, ArH), 6.49 (s, 1H, ArH), 6.32 (t  $J_{\rm HH}$  = 8.5 Hz, 1H, ArH), 6.13 (d  $J_{\rm HH}$  = 6.0 Hz, 1H, Ar*H*), 5.59 (t  $J_{HH}$  = 6.0 Hz, 1H, Ar*H*), 4.20 (br d  $J_{HH}$  = 10.0 Hz, 2H, C<sub>2</sub>H<sub>4</sub>), 3.25 (br d  $J_{HH}$  = 10.0 Hz, 2H, C<sub>2</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 157.8, 147.7, 142.7, 138.3, 136.7, 136.1, 135.7, 130.9, 129.4, 129.1, 128.6, 127.1, 126.6, 119.1, 119.0, 115.5, 73.0. Anal. Calcd (%) for C<sub>23</sub>H<sub>19</sub>N<sub>2</sub>ClPt: C, 49.87; H, 3.46; N, 5.06. Found: C, 49.74; H, 3.43; N, 5.11.

(PyPyr)Pt(SMe<sub>2</sub>)Cl (2). To a 5 mL solution of PyPyrH (0.450 g, 1.52 mmol) in THF was added LiN(SiMe<sub>3</sub>)<sub>2</sub> (0.254 g, 1.52 mmol). The reaction mixture was then stirred for 30 min. After stirring, a 5 mL tetrahydrofuran solution of  $[(SMe_2)-PtCl_2]_2$  (0.500 g, 1.52 mmol) was added to the reaction mixture.

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After 1 h of stirring, the solvent was removed under vacuum. The resulting yellow solid was dissolved in benzene and filtered through Celite. The volatile material was removed in vacuo, and the resulting solid was washed with 5 mL of pentane three times to give a yellow powder in 92% yield (0.823 g, 1.40 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  9.30 (d  $J_{HH}$  = 5.2 Hz, 1H, Ar*H*), 7.66 (d  $J_{HH}$  = 6.0 Hz, 2H, Ar*H*), 7.53 (d  $J_{HH}$  = 6.0 Hz, 2H, Ar*H*), 7.30–7.10 (ov m with benzene- $d_6$ , 7H, Ar*H*), 6.62 (s, 1H, Ar*H*), 6.42 (t  $J_{HH}$  = 6.0 Hz, 1H, Ar*H*), 5.94 (t  $J_{HH}$  = 6.0 Hz, 1H, Ar*H*), 7.10 (v q  $J_{PtH}$  = 32.5 Hz, 6H, S(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  158.2, 147.5, 145.8, 137.6, 137.4, 131.7, 128.9, 128.4, 128.3, 126.9, 126.6, 117.2, 116.9, 114.3, 21.3. Anal. Calcd (%) for C<sub>23</sub>H<sub>21</sub>ClN<sub>4</sub>Pt: C, 46.98; H, 3.60; N, 4.76. Found: C, 46.45; H, 3.82; N, 4.33.

(**PyPyr)Pt(H)**<sub>2</sub>SiEt<sub>3</sub> (3). To a 5 mL solution of (PyPyr)Pt (C<sub>2</sub>H<sub>4</sub>)Cl (0.100 g, 0.18 mmol) in benzene was added HSiEt<sub>3</sub> (0.084 g, 0.72 mmol). The reaction mixture was stirred for 12 h, and then the volatile material was removed in vacuo. The resulting red solid was dissolved in pentane and crystallized by slow evaporation to give red plates in 95% yield (0.104 g, 0.17 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 8.07 (d  $J_{HH}$  = 5.0 Hz, 1H, ArH), 7.97 (d  $J_{HH}$  = 7.0 Hz, 2H, ArH), 7.55 (d  $J_{HH}$  = 7.0 Hz, 2H, ArH), 7.4 (t  $J_{HH}$  = 7.5 Hz, 1H, ArH), 6.98 (s, 1H, ArH), 6.51 (t  $J_{HH}$  = 7.0 Hz, 9H, SiCH<sub>2</sub>CH<sub>3</sub>), 0.66 (t  $J_{HH}$  = 4.5 Hz, 9H, SiCH<sub>2</sub>CH<sub>3</sub>), 0.66 (t  $J_{HH}$  = 4.5 Hz, 6H, SiCH<sub>2</sub>CH<sub>3</sub>), -15.17 (d  $J_{HH}$  = 7.5 Hz,  $J_{PtH}$  = 968 Hz, 1H, PtH), -16.97 (d  $J_{HH}$  = 7.5 Hz,  $J_{PtH}$  = 1114 Hz, 1H, PtH). <sup>1</sup>H, <sup>29</sup>Si {<sup>1</sup>H} HMBC NMR: δ 44.2 (s  $J_{PtSi}$  = 704.5 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 158.0, 152.6, 146.8, 138.5, 138.2, 137.0, 132.9, 129.6, 129.0, 128.4, 127.9, 127.5, 126.5, 126.2, 118.4, 118.2, 113.9, 10.9, 7.6. Anal. Calcd (%) for C<sub>27</sub>H<sub>32</sub>N<sub>2</sub>PtSi: C, 53.36; H, 5.31; N, 4.61. Found: C, 53.08; H, 5.24; N, 4.46. IR (cm<sup>-1</sup>): ν<sub>PtH</sub> 2221, 2254.

(PyPyr)Pt(H)<sub>2</sub>SiEtMe<sub>2</sub> (4). To a 5 mL solution of (PyPyr)Pt (C<sub>2</sub>H<sub>4</sub>)Cl (0.100 g, 0.18 mmol) in benzene was added HSiEtMe<sub>2</sub> (0.064 g, 0.73 mmol). The reaction mixture was stirred for 12 h, and then the volatile material was removed in vacuo. The resulting red solid was dissolved in THF/pentane (1:1), and the mixture was concentrated to 1 mL. Slow evaporation of the reaction mixture gave red plates in 94% yield (0.098 g, 0.17 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  10.05 (br s, 1H, ArH), 8.34 (d  $J_{\rm HH} = 5.0$  Hz, 1H, ArH), 7.96 (d  $J_{\rm HH} = 7.2$  Hz, 2H, ArH), 7.56 (d  $J_{\rm HH} = 6.8$  Hz, 2H, ArH), 7.39 (d  $J_{\rm HH} = 5.0$  Hz, 2H, ArH), 7.26 (ov m, 5H, ArH), 6.81 (t J<sub>HH</sub> = 7.5 Hz, 1H, ArH), 6.63 (s, 1H, Ar*H*), 6.46 (t  $J_{\rm HH}$  = 7.5 Hz, 1H, Ar*H*), 0.76 (t  $J_{\rm HH}$  = 6.5 Hz, 3H, SiCH<sub>2</sub>CH<sub>3</sub>), 0.67 (t  $J_{\rm HH}$  = 6.5 Hz, 2H, SiCH<sub>2</sub>CH<sub>3</sub>), 0.22 (s  $J_{\text{SiH}} = 8.0$  Hz,  $J_{\text{PtH}} = 16.4$  Hz, 6H, SiCH<sub>3</sub>), -15.36 (d  $J_{\text{HH}} =$ 7.2 Hz,  $J_{\text{PtH}} = 1000$  Hz, 1H, Pt*H*), -16.89 (d  $J_{\text{HH}} = 7.2$  Hz,  $J_{\text{PtH}} = 1154$  Hz, 1H, Pt*H*). <sup>1</sup>H, <sup>29</sup>Si{<sup>1</sup>H} HMBC NMR:  $\delta$  29.2. <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  152.6, 150.7, 148.8, 138.5, 137.6, 135.5, 132.7, 131.9, 128.8, 128.5, 127.1, 126.4, 123.8, 120.1, 119.2, 118.0, 110.4, 7.75, 4.56, 1.00. Anal. Calcd (%) for C<sub>25</sub>H<sub>26</sub>N<sub>2</sub>PtSi: C, 51.98; H, 4.54; N, 4.85. Found: C, 52.37; H, 4.83; N, 4.80. IR (cm<sup>-1</sup>):  $\nu_{PtH}$  2220, 2252.

(PyPyr)Pt(H)<sub>2</sub>SiEt<sub>3</sub>(DMAP) (5). To a 5 mL solution of (PyPyr)Pt(H)<sub>2</sub>SiEt<sub>3</sub> (0.080 g, 0.13 mmol) in benzene was added DMAP (0.017 g, 0.12 mmol). The reaction mixture was stirred for 1 h, and then the volatile material was removed in vacuo. The resulting brown solid was dissolved in 1 mL of THF, and pentane was allowed to diffuse into the reaction mixture. Brown plates were isolated in 90% yield (0.087 g, 0.12 mmol). <sup>1</sup>H NMR  $(C_6D_6)$ :  $\delta$  8.28 (d  $J_{HH}$  = 5.0 Hz, 2H, ArH), 8.13 (d  $J_{HH}$  = 7.2 Hz, 2H, Ar*H*), 7.81 (d  $J_{HH}$  = 7.2 Hz, 2H, Ar*H*), 7.54 (d  $J_{HH}$  = 7.2 Hz, 1H, ArH), 7.36–7.27 (ov m, 6H, ArH), 7.09 (d  $J_{\rm HH}$  = 7.5 Hz, 1H, ArH), 6.95 (t J<sub>HH</sub> = 6.4 Hz, 1H, ArH), 6.61 (s, 1H, ArH), 5.98 (t  $J_{\rm HH}$  = 6.4 Hz, 1H, ArH), 5.89 (d  $J_{\rm HH}$  = 5.0 Hz, 2H, ArH), 2.03 (s, 6H, NCH<sub>3</sub>), 0.98 (t J<sub>HH</sub> = 5.4 Hz, 9H, SiCH<sub>2</sub>CH<sub>3</sub>), 0.80 (t  $J_{\rm HH} = 5.4$  Hz, 6H, SiC $H_2$ CH<sub>3</sub>), -16.99 (d  $J_{\rm HH} = 6.4$  Hz,  $J_{\text{PtH}} = 1150 \text{ Hz}, 1\text{H}, \text{Pt}H), -18.10 \text{ (d } J_{\text{HH}} = 6.4 \text{ Hz}, J_{\text{PtH}} = 1200 \text{ Hz}, 1\text{H}, \text{Pt}H).$ <sup>1</sup>H, <sup>29</sup>Si{<sup>1</sup>H} HMBC NMR:  $\delta$  9.8. <sup>13</sup>C {<sup>1</sup>H} NMR: δ 157.7, 152.0, 148.7, 145.5, 139.7, 136.8, 135.8,

132.3, 129.5, 128.7, 128.5, 128.2, 126.7, 126.3, 125.5, 123.8, 118.7, 117.7, 113.5, 110.4, 34.5, 11.2, 8.4. Anal. Calcd (%) for  $C_{34}H_{42}N_4PtSi: C, 55.95; H, 5.80; N, 7.68.$  Found: C, 56.28; H, 5.68; N, 7.76. IR (cm<sup>-1</sup>):  $\nu_{PtH}$  2206, 2262.

(PyPyr)Pt(P'Pr<sub>3</sub>)H (6). To a 5 mL solution of (PyPyr)Pt- $(H)_2SiEt_3$  (0.100 g, 0.164 mmol) in benzene was added P<sup>i</sup>Pr<sub>3</sub> (0.0265 g, 0.165 mmol). The reaction mixture was stirred for 1 h, and then the volatile material was removed in vacuo. The resulting brown solid was dissolved in 1 mL of THF, and pentane was allowed to diffuse into the solution. Brown blocks were isolated in 72% yield (0.0770 g, 0.118 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.12 (d  $J_{\rm HH}$  = 7.5 Hz, 2H, ArH), 7.62 (d  $J_{\rm HH}$  = 7.5 Hz, 2H, ArH), 7.51 (d  $J_{\rm HH}$  = 8.0 Hz, 1H, ArH), 7.35–7.20 (ov m, 5H, ArH), 6.83 (s, 1H, ArH), 6.60 (t  $J_{\rm HH} = 7.5$  Hz, 1H, ArH), 6.15 (t J<sub>HH</sub>=6.0 Hz, 1H, ArH), 1.78 (m, 3H, PCH), 0.99 (m, 18H, PCHCH<sub>3</sub>), -19.64 (d J<sub>PH</sub> = 28.5 Hz, J<sub>PtH</sub> = 1208 Hz, 1H, PtH). <sup>31</sup>P{<sup>1</sup>H} NMR: 41.2 (s  $J_{PPt} = 3688$  Hz). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 159.5, 150.2, 148.7, 139.6, 137.5, 135.9, 131.6, 129.2, 128.7, 128.3, 126.9, 126.0, 125.6, 123.8, 118.8, 116.8, 113.7, 24.2  $(J_{CP} = 32.0 \text{ Hz})$ , 19.5. Anal. Calcd (%) for  $C_{30}H_{37}N_2PPt$ : C, 55.29; H, 5.72; N, 4.30. Found: C, 54.89; H, 5.44; N, 4.09.

(**PyPyr)Pt(PPh<sub>3</sub>)H (7).** To a 5 mL solution of (PyPyr)Pt-(H)<sub>2</sub>SiEt<sub>3</sub> (0.020 g, 0.033 mmol) in benzene was added PPh<sub>3</sub> (0.0085 g, 0.033 mmol). The reaction mixture was allowed to stir for 1 h, and then the volatile material was removed in vacuo. The brown solid was dissolved in 1 mL of THF, and pentane was allowed to diffuse into the solution. Brown blocks were isolated in 90% yield (0.023 g, 0.031 mmol). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 8.21 (d J<sub>HH</sub> = 7.5 Hz, 2H, Ar*H*), 7.65 (ov m, 7H, Ar*H*), 7.47 (ov m, 3H, Ar*H*), 7.23 (ov m, 3H, Ar*H*), 6.92 (ov m, 13H, Ar*H*), 6.49 (t J<sub>HH</sub> = 7.5 Hz, 1H, Ar*H*), 5.72 (t J<sub>HH</sub> = 6.0 Hz, 1H, Ar*H*), -17.47 (d J<sub>PH</sub>=29.5 Hz, J<sub>PtH</sub>=1184 Hz, 1H, Pt*H*). <sup>31</sup>P{<sup>1</sup>H} NMR: 21.9 (s J<sub>PPt</sub>=1918 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 148.8, 139.2, 137.3, 136.0, 135.5, 135.0, 134.1 (J<sub>CP</sub> = 15.0 Hz), 129.8 (J<sub>CP</sub> = 7.5 Hz), 129.5, 129.2, 128.5, 127.4, 126.7, 125.7, 123.8, 120.1, 119.2, 118.7, 116.8, 113.8, 110.5. Anal. Calcd (%) for C<sub>39</sub>H<sub>31</sub>N<sub>2</sub>PPt: C, 62.15; H, 4.15; N, 3.72. Found: C, 62.29; H, 4.56; N, 3.06.

General Procedure for Catalytic Runs. Reactions were conducted in 5 mm Wilmad NMR tubes equipped with a J. Young Teflon-valve seal, which were heated in temperature-controlled oil baths. Samples were prepared in the drybox by dissolving the catalyst, silane, and alkyne or olefin in  $C_6D_6$ . Gases were condensed on a Schlenk line using a volumetric gas bulb. Reaction progress was monitored by <sup>1</sup>H NMR spectroscopy. Product identities and yields were determined by <sup>1</sup>H NMR spectroscopy and GC-MS relative to an internal standard.

Kinetic Measurements. Reactions were monitored by <sup>1</sup>H NMR spectroscopy, on a Bruker AV-500 spectrometer, using 5 mm Wilmad NMR tubes fitted with septa. The samples were prepared by dissolution of 3 in 1 mL of  $C_6D_6$  that was added to the NMR tube, which was sealed. The NMR tube was then cooled to 0 °C in an ice bath. To this cooled solution was added via a syringe HSiEtMe2. The NMR tube was quickly placed in the probe, which was preheated to 50 °C. The probe temperature was calibrated using a neat methanol sample prior to the experiment and was monitored throughout the experiment with a thermocouple. Single-scan spectra were obtained using an automated acquisition program that was started immediately after placing the sample in the probe, and the peaks were integrated relative to the intensity of a known concentration of a hexamethylbenzene standard. Rate constants were obtained by nonweighted linear least-squares fit of the integrated firstorder rate law.

X-ray Structure Determination. The X-ray analyses of 2 and 3 were carried out at UC Berkeley CHEXRAY crystallographic facility. Measurements were made on a Bruker APEX CCD area detector with graphite-monochromated Mo Ka radiation ( $\lambda = 0.71073$  Å). Data were integrated by the program SAINT and analyzed for agreement using XPREP. Empirical absorption corrections were made using SADABS. The structure was solved by direct methods and expanded using Fourier techniques. All calculations were performed using the SHELXTL crystallographic package. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated position with the exception of the hydride ligands of **3**, which were located from the difference Fourier map.

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Supporting Information Available: Kinetic analysis and complete X-ray crystallographic data for 2 and 3. This material is available free of charge via the Internet at http://pubs.acs.org.