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Cationic, Neutral, and Anionic Platinum(II) Complexes Based on an Electron-Rich PNN Ligand. New Modes of Reactivity Based on Pincer Hemilability and Dearomatization

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The synthesis and reactivity of new Pt(II) complexes, including anionic d^8 complexes, based on the electron-rich, hemilabile PNN-type pincer ligand C_5H_3N-2-$(CH_2P^tBu_2)(CH_2NEt_2)$ are described. Formation of these complexes involves dearomatization/aromatization processes of the ligand. The chloride complex $[(PNN)PtCl]^+Cl^-$ (**1**) was prepared and reacted with the base ^{t}BuOK to give the deprotonated, neutral chloride complex (PNN*)PtCl (**2**) (PNN* = C_5H_3N-2-$(CHP^tBu_2)(CH_2NEt_2)$). Reaction of **2** with ^{n}BuLi gave the corresponding neutral hydride complex (PNN*)PtH (**3**), which was readily protonated by triflic acid to give the cationic hydride complex $[(PNN)PtH]^+OTf^-$ (**4**). Unexpectedly, reaction of complex **2** with 1 equiv of RLi resulted in opening of the chelate ring, to give the corresponding anionic, dearomatized complexes $Li^+[(PNN^*)Pt(Cl)(R)]^-$ (R = methyl, **5**; phenyl, **6**). Notably, these complexes are relatively stable although they bear no stabilizing π acceptors that can lower the electron density at the metal center. Complexes **5** and **6** readily undergo protonation by HCl to form the corresponding neutral, aromatic complexes (PNN)Pt(Cl)(R) (R = methyl, **7**; phenyl, **8**), in which the hemilabile amine "arm" remains decoordinated and does not undergo protonation. Minor amounts of the dearomatized chloride complex **2** are also formed as a result of elimination of RH. Reaction of complexes **5** and **6** with water results in selective protonation−aromatization to give the corresponding complexes **7** and **8**.

Introduction

Transition metal complexes of bulky pincer-type ligands[1] have found significant applications in synthesis, bond activation, and catalysis. Among those, complexes of the pyridine-based bulky ligand ^{tBu}PNP (^{tBu}PNP = 2,6-(di-*tert*-butylphosphinomethyl)pyridine) have been explored in recent years,[2–5] and recently the hemilabile[6] PNN ligand (PNN = (2-(di-*tert*-butylphosphinomethyl)-6-diethylaminomethyl)pyridine)) was synthesized in our group.[5] The different electronic properties of the phosphine and amine ligands and the more labile coordination of the latter in the case of late transition metal complexes[7] can play important roles in catalytic and stochiometric reactions, as shown for complexes based on PCN[8,9] $C_6HR_3(CH_2P^tBu_2)[(CH_2)_xNR'_2]$ (x = 1, 2; R = H, Me; R′ = Me, Et) and PNN-type ligands. A PNN-based Ru(II) hydride

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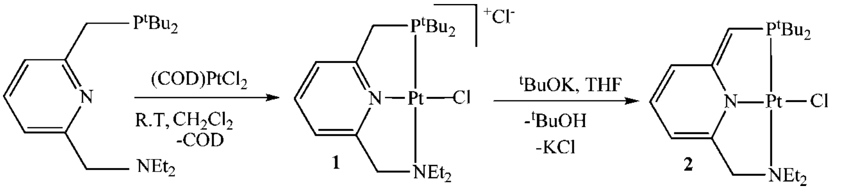
Scheme 1



complex is a highly effective catalyst for the acceptorless dehydrogenation of primary alcohols to esters under neutral conditions in high yields and high turnover numbers,[5a] for the hydrogenation of esters to alcohols under mild conditions,[5b] and for the new reaction of alcohols with amines to form amides and H_2, leading to a variety of amides.[10] The corresponding PNP Ru complexes, which are also catalytically quite active, are less efficient.[4c,5]

Herein we report the synthesis and reactivity of cationic, neutral, and anionic complexes of Pt(II) based on a hemilabile PNN system. Two major processes affect the reactivity of this system, namely, hemilability of the amine "arm" and dearomatization of the pyridine core following benzylic deprotonation. Unexpectedly, direct nucleophilic attack of organolithium reagents on a Pt−Cl center results in formation of anionic complexes without chloride substitution.

Results and Discussion

Synthesis and Characterization of PNN−Pt(II) Complexes. Upon addition of the PNN ligand to (COD)PtCl$_2$ (COD = cyclooctadiene) in methylene chloride, complex **1** was obtained in 90% yield (Scheme 1). The $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectrum of this complex shows a singlet at 49.25 ppm with Pt satellites ($J_{\mathrm{Pt-P}}$ = 3409 Hz). The ^{1}H NMR spectrum of **1** exhibits two multiplets at 3.01 and 3.39 ppm for the diastereotopic methylene protons of the diethylamine unit, indicating that the amine is coordinated to the metal center. Complex **1** was identified as the cationic [(PNN)PtCl]$^+$Cl$^-$ with one chloride coordinated to the metal center and the second chloride in the outer sphere.[11]

Colorless crystals of complex **1** suitable for X-ray diffraction analysis were obtained from a saturated benzene solution at room temperature. The platinum atom is located in the center of a square-planar structure in which the chloride ligand is located *trans* to the pyridine ring and the amine "arm" is coordinated to the metal center (Figure 1). The Pt−P and Pt−N("arm") bond lengths are comparable to the corresponding bond distances in (PCN)PtCl.[9b] However, the Pt−Cl bond length (2.296(1) Å) is significantly shorter than the corresponding bond in the PCN-based complex (2.41(1) Å)[9b] due to the stronger *trans* influence of the aryl ligand as compared to pyridine.[12] Additional bond lengths and angles are given in Table 1.

Upon treatment of complex **1** with 1.05 equiv of ^{t}BuOK at room temperature, deprotonation of the benzylic phosphine "arm" took place, resulting in the orange neutral Pt(II) complex **2** in 95% yield (Scheme 2). The $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectrum of **2** shows a singlet at 47.83 ppm with Pt satellites ($J_{\mathrm{Pt-P}}$ = 3658 Hz). Signals at 5.15, 6.25, and 6.47 ppm in the ^{1}H NMR spectrum, corresponding to three protons, indicate dearomatization of the pyridine ring. A one-proton doublet at 3.36 ppm ($J_{\mathrm{P-H}}$ = 7 Hz, $J_{\mathrm{Pt-H}}$ = 51 Hz) in the ^{1}H NMR spectrum and a doublet at 60.26 ppm ($J_{\mathrm{P-C}}$ = 70 Hz) in the $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR spectrum indicate that deprotonation at the benzylic phosphine "arm" took place. Dearomatization following deprotonation of one methylene position in pincer ligands was reported in a few cases.[3b,4g,5,13] Deprotonation of the two methylene positions in pincer ligands is also known.[14]

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Complex 1

Bond Lengths			
Pt(1)−Cl(24)	2.296(1)	P(4)−C(5)	1.841(5)
Pt(1)−N(2)	1.997(4)	P(4)−C(12)	1.864(5)
Pt(1)−N(3)	2.148(4)	N(3)−C(11)	1.496(6)
Pt(1)−P(4)	2.236(1)	N(3)−C(20)	1.513(6)
Bond Angles			
Cl(24)−Pt(1)−P(4)	98.47(4)	N(3)−Pt(1)−P(4)	168.0(1)
Cl(24)−Pt(1)−N(3)	92.5(1)	N(2)−Pt(1)−Cl(24)	176.0(1)
N(2)−Pt(1)−P(4)	85.5(1)	C(11)−N(3)−Pt(1)	107.5(3)
N(3)−Pt(1)−N(2)	83.4(1)	C(5)−P(4)−Pt(1)	100.2(2)

The neutral (PNN*)Pt(II) (PNN* = dearomatized PNN) hydride complex **3** was prepared by chloride substitution of **2** with ^{n}BuLi in THF at −20 °C, followed by β-H elimination (Scheme 2). The $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectrum of **3** shows a singlet at 59.64 ppm with Pt satellites ($J_{\mathrm{Pt-P}}$ = 3874 Hz), and in the ^{1}H NMR spectrum it exhibits the hydride as a doublet at −12.46 ppm ($J_{\mathrm{P-H}}$ = 17 Hz) with Pt satellites ($J_{\mathrm{Pt-H}}$ = 1156 Hz).

Upon reaction of complex **3** with 1 equiv of triflic acid, the cationic hydride Pt(II) complex **4** was formed and fully characterized by multinuclear NMR techniques (Scheme 3). The $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectrum of **4** exhibits a singlet with Pt satellites at 65.23 ppm ($J_{\mathrm{Pt-P}}$ = 3744 Hz). In the ^{1}H NMR spectrum the hydride ligand gives rise to a doublet with Pt satellites at −14.59

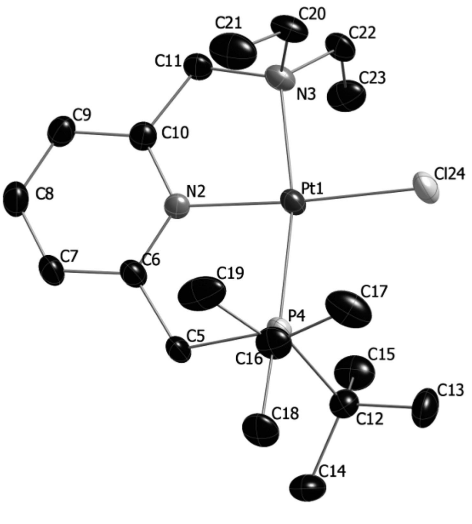


Figure 1. ORTEP view of a molecule of complex **1** at the 50% probability level. Hydrogen atoms, counteranion, and benzene were omitted for clarity.

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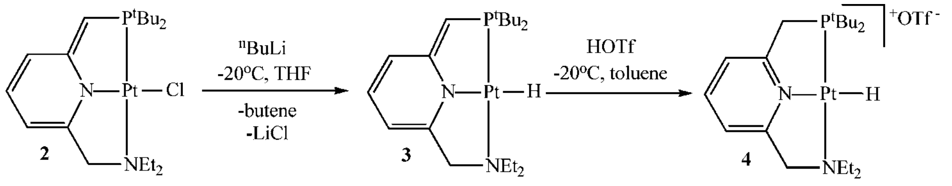
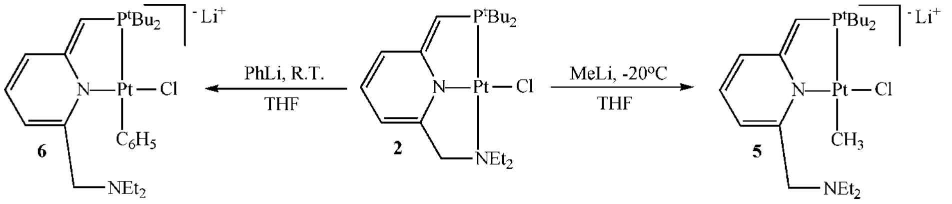
Scheme 2



Scheme 3



ppm (J_{P-H} = 18 Hz, J_{Pt-H} = 1258 Hz). Downfield-shifted signals at 7.54, 7.61, and 8.04 ppm and the two benzylic protons at 3.62 ppm (J_{P-H} = 9 Hz) indicate rearomatization of the PNN ligand.

Formation of Anionic Pt(II) Complexes Based on a Deprotonated PNN Ligand. The chemistry of anionic transition metal complexes is of significant interest due to their nucleophilic reactivity toward organic molecules,[15] their utilization in the preparation of homo- and heteronuclear transition metal clusters,[16] and their reactivity as alkylating reagents with various electrophiles[17,18] and as reducing hydride donors with polar molecules.[19–22] Formation of relatively stable anionic complexes in the absence of strong π-accepting ligands, capable of lowering the electron density at the metal center by enhancing back-bonding, is generally difficult, and relatively few examples of such compounds are known.[9a,18,20,21,23–25]

Interestingly, addition of methyllithium to a THF-d_8 solution of complex **2** at −20 °C resulted in an immediate color change from orange to red with formation of the anionic complex **5** (Scheme 3), which was characterized by multinuclear NMR techniques. The ^{31}P{^{1}H} NMR spectrum of **5** gives rise to a singlet at 56.94 ppm with Pt satellites (J_{Pt-P} = 2043 Hz). This relatively small Pt−P coupling constant, as compared to characteristic coupling of the (PNN)Pt system (about 3600 Hz), indicates substitution of the amine ligand *trans* to phosphorus by a strong σ donor.[12] The value of 2043 Hz is in line with reported values of Pt−P coupling of a phosphine located *trans* to a CH_3 ligand in an anionic PCN Pt complex.[9a] The methyl group gives rise to a three-proton doublet at 0.29 ppm (J_{P-H} = 8 Hz) with Pt satellites (J_{Pt-H} = 56 Hz) in the ^{1}H NMR spectrum and to a doublet at 5.59 ppm (J_{P-C} = 111 Hz) in the ^{13}C{^{1}H} NMR spectrum. The ^{1}H NMR spectrum indicates that the amine "arm" of the PNN ligand is not coordinated to the metal, since the methylene groups of the NEt_2 moiety exhibit a single quartet at 2.41 ppm (J_{H-H} = 7 Hz) without Pt satellites. Both ^{1}H NMR and ^{13}C{^{1}H} NMR spectra exhibit high-field signals of the dearomatized pyridine ring. A heteronuclear 2D ^{15}N−^{1}H correlation spectrum shows two ^{15}N cross-peaks, a singlet at 160.62 ppm of the pyridine nitrogen, and a singlet at 49.08 ppm of the amine nitrogen.

The Li$^+$ counterion probably stabilizes the anionic complex **5** by coordination to the amine opened "arm". In line with that, no reaction took place when MeLi was added to **2** in the presence of 12-crown-4, due to Li$^+$ complexation by the latter. Coordination of Li$^+$ might also assist in the opening of the hemilabile "arm" of complex **2**, thus providing a vacant coordination site and making possible the nucleophilic attack at the Pt center. The ^{7}Li NMR spectrum of complex **5** exhibits a broad singlet at 2.67 ppm, which suggests coordinated Li$^+$. For comparison, LiCl in THF gives rise to a narrow peak at 0 ppm. Crystallographic indication for Li$^+$ coordination was reported for the complex [(PCN)Pt(H)$_2$]$^-$Li$^+$.[9a]

A similar reactivity pattern was observed when 1 equiv of phenyllithium was added to a THF solution of complex **2** at room temperature. Rapid color change to red took place with formation of the anionic complex **6** (Scheme 4). The ^{31}P{^{1}H} NMR spectrum of **6** exhibits a singlet at 53.88 ppm with small

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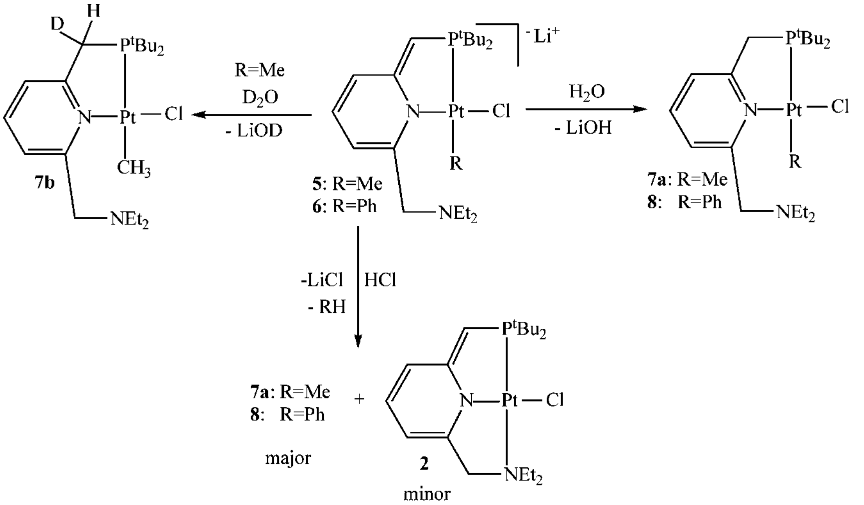
Scheme 4



Pt satellites (J_{Pt-P} = 1977 Hz). The ^{1}H NMR spectrum reveals one proton of the benzylic phosphine "arm" as a broad singlet at 3.17 ppm, and the equivalent methylene groups of the free amine "arm" appear as a quartet at 2.06 ppm (J_{H-H} = 7 Hz). The ^{13}C{^{1}H} NMR spectrum shows the *ipso* carbon of the phenyl ligand at 166.23 ppm (J_{P-C} = 127 Hz). Both ^{1}H NMR and ^{13}C{^{1}H} NMR spectra reveal a dearomatized pyridine ring. The heteronuclear 2D ^{15}N−^{1}H correlation spectrum exhibits the pyridine nitrogen as a singlet at 147.33 ppm and the amine "arm" nitrogen at 49.84 ppm. The ^{7}Li NMR spectrum of complex **6** shows a broad singlet at 1.16 ppm, which apparently corresponds to Li$^+$ coordinated to the nitrogen of the opened amine "arm".

The small Pt−P coupling in the ^{31}P{^{1}H} NMR spectrum and the large C−P coupling of the *ipso* carbon in the ^{13}C{^{1}H} NMR spectrum point to coordination of the phenyl ligand *trans* to phosphorus. Crystallographic evidence for this geometry was obtained for the analogous neutral phenyl chloride complex **8** (vide infra).

Complex **6** is expected to be more stable than complex **5**, because of the possibility of participation of the phenyl group in delocalization of the negative charge of the Pt complex. In addition, the Pt−phenyl bond is stronger than Pt−methyl.[12] Indeed, **6** can be isolated by evaporation of the solvent and extraction with benzene, which could not be applied to complex **5**. Moreover, **6** is thermally stable, whereas **5** decomposes to the starting chloride complex **2** and methane during 2−3 days.[26]

Formation of anionic complexes based on pincer type ligands as a result of nucleophilic attack was observed before with PCN-based[9a] and CNC-based[23b] Pt(II) neutral complexes. In the PCN system, which contains a six-membered (long "arm") chelate, the first equivalent of RLi (R = methyl, aryl) caused substitution of the chloride ligand, and the second equivalent led to coordination of the nucleophile to the Pt center, resulting in chelate−ring opening and formation of stable dialkyl and diaryl anionic complexes. In contrast, surprisingly, no chloride displacement was observed in the reaction of RLi with the PNN* system; rather, attack at the metal center resulted in formation of anionic (PNN*)Pt(Cl)(R) complexes with a decoordinated amine "arm".[27] This can be explained by the stronger and kinetically less labile Pt−Cl bond in the latter complexes due to the weaker *trans* effect and *trans* influence of the pyridine-type ligand as compared with the aryl ligand.[12]

The PNN* ligand enables direct coordination of the nucleophile due to dissociation of the hemilabile amine "arm", which leads to a decrease of electron density at the metal center and generation of a vacant site. The corresponding PCN ligand, in which the amine "arm" forms a five-membered amine chelate, showed no dissociation of the amine "arm" from the Pt center.[9b,28]

Reactions of the Anionic Complexes with Acid and with Water. (a) Reaction with Acid. Anionic complexes show diverse behavior when treated with acidic reagents.[14,18e,21a,23b,29] There are a number of possible outcomes to protonation of the anionic complexes **5** and **6**. It could conceivably regenerate complex **2** with formation CH_4 or C_6H_6 or regenerate the aromatic system by attacking the deprotonated benzylic phosphine "arm". Protonation at the nitrogen of the decoordinated amine "arm" is also a possibility. Interestingly, reaction of a THF solution of **5** with 1 equiv of HCl resulted mostly in protonation at the benzylic position to form the neutral complex **7a**, with only minor amounts of complex **2** being formed as a result of CH_4 elimination, **7a**:**2** = 10:1 (Scheme 4). The ^{31}P{^{1}H} NMR spectrum of **7a** gives rise to a singlet at 73.68 ppm with Pt satellites (J_{Pt-P} = 1737 Hz). The coordinated methyl group appears as a doublet at 1.49 ppm (J_{P-H} = 8 Hz) with Pt satellites (J_{Pt-H} = 64 Hz) in the ^{1}H NMR and as a doublet at 7.05 ppm (J_{P-C} = 112 Hz) in the ^{13}C{^{1}H} NMR. The benzylic phosphine "arm" exhibits a doublet at 2.72 ppm (J_{P-H} = 7 Hz) corresponding to two protons, and the methylene groups of the decoordinated amine "arm" give rise to a quartet at 2.28 ppm (J_{H-H} = 7 Hz) in the ^{1}H NMR. Both ^{1}H NMR and ^{13}C{^{1}H} NMR spectra reveal downfield signals of the rearomatized pyridine ring. The heteronuclear 2D ^{15}N−^{1}H correlation spectrum gives rise to a singlet at 231.54 ppm attributed to the

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[26] Formation of methane was detected by GC/MS. Its origin is not clear.

[27] The fact that in the reaction of ^{n}BuLi with complex **2** substitution of the chloride to form the hydride complex **3** took place (rather than formation of an anionic product) might be a result of the β-elimination process. Thus, an anionic butyl complex, analogous to **5**, might be formed first, followed by a β-H elimination process that involves chloride loss.

[28] Five-membered chelate-ring opening in a PNP Co complex was described.[25b]

[29] (a) Ellis, J. E.; Faltynek, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 1801. (b) Reinartz, S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2002**, *21*, 247.

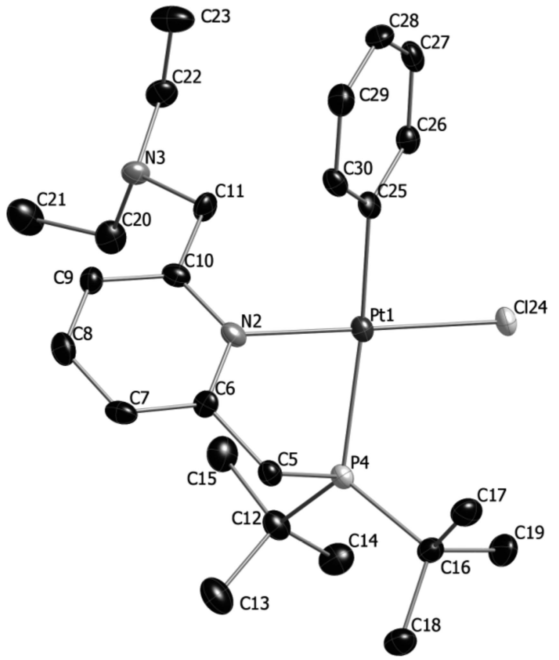


Figure 2. ORTEP view of a molecule of complex **8** at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Complex 8

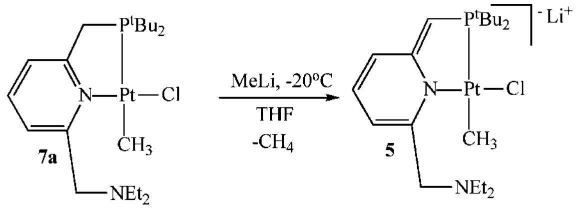
Bond Lengths			
Pt(1)−Cl(24)	2.305(1)	C(5)−C(6)	1.497(6)
Pt(1)−N(2)	2.054(3)	P(4)−C(5)	1.854(4)
Pt(1)−P(4)	2.338(1)	N(3)−C(11)	1.470(5)
Pt(1)−C(25)	2.049(4)	N(3)−C(20)	1.477(5)
Bond Angles			
Cl(24)−Pt(1)−P(4)	99.78(4)	C(25)−Pt(1)−P(4)	164.06(11)
C(25)−Pt(1)−Cl(24)	87.58(11)	N(2)−Pt(1)−Cl(24)	179.44(10)
N(2)−Pt(1)−P(4)	80.71(9)	C(30)−C(25)−Pt(1)	120.2(3)
C(25)−Pt(1)−N(2)	92.02(14)	C(5)−P(4)−Pt(1)	90.43(13)

pyridine nitrogen and a singlet at 47.54 ppm attributed to the amine nitrogen.

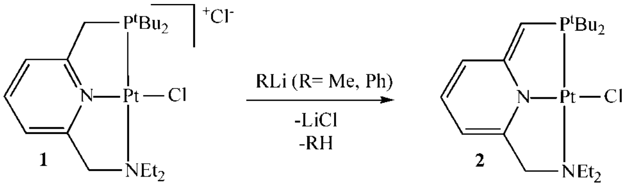
The same mode of reactivity was observed for the phenyl complex **6**. Thus, reaction of a THF solution of complex **6** with 1 equiv of HCl at room temperature resulted in formation of complexes **8** and **2** in a 25:1 ratio, respectively (Scheme 4). Complex **8** exhibits a singlet at 66.86 ppm with Pt satellites ($J_{\mathrm{Pt-P}}$ = 1694 Hz) in the ^{31}P{^{1}H} NMR spectrum. The two methylene groups of the amine "arm" give rise to a quartet at 2.15 ppm ($J_{\mathrm{H-H}}$ = 7 Hz) in the ^{1}H NMR spectra with no coupling to Pt. In the ^{13}C{^{1}H} spectrum the *ipso* signal at 157.99 ppm (d, $J_{\mathrm{P-C}}$ = 130 Hz) was found, indicating coordination of the phenyl group *trans* to the phosphine ligand. Both ^{1}H NMR and ^{13}C{^{1}H} NMR spectra reveal downfield signals of the rearomatized pyridine ring. In the heteronuclear 2D ^{15}N−^{1}H correlation spectrum the pyridine nitrogen appears as a singlet at 233.06 ppm, and the amine "arm" nitrogen gives rise to a singlet at 47.40 ppm.

Single crystals of complex **8** suitable for an X-ray diffraction study were obtained by slow evaporation of the solvent from a saturated benzene solution at room temperature. Complex **8** has a slightly distorted square-planar structure around the Pt(II) center, with the phenyl ligand located *trans* to the phosphorus atom and the chloride ligand coordinated *trans* to the pyridine ring (Figure 2). As shown by multinuclear NMR spectroscopy in solution, the amine "arm" is disconnected from the metal center, allowing coordination of the phenyl in its place. The Pt−P distance (2.338(1) Å) is much longer than the corresponding bond in **1** (2.236(1) Å), as expected from the larger *trans* influence of the phenyl ligand as compared with that of the amine moiety. Additional bond distances and bond angles of **8** are given in Table 2.

Scheme 5



Scheme 6



It is noteworthy that reaction of the protonated complex **7a** with MeLi regenerates the anionic, dearomatized system. Thus, upon reaction of **7a** with MeLi at −20 °C, an immediate color change to red took place and the anionic complex **5** was obtained (Scheme 5). No substitution of the chloride ligand to give a dimethyl complex was observed.

(b) Reaction with Water. Reaction of the anionic complexes **5** and **6** with water in a THF solution at room temperature resulted in immediate color change to orange with quantitative formation of complexes **7a** and **8**, respectively (Scheme 4). Protonation of the phosphine "arm" by water was confirmed by reaction of **5** with D_2O. The ^{1}H NMR of the product exhibits the benzylic group of the phosphine "arm" as a broad doublet at 2.69 ppm ($J_{\mathrm{P-H}}$ = 7 Hz) corresponding to one proton.

This reactivity pattern of the anionic complexes with acid and water suggests that the negative charge is not concentrated on the metal center or on the R ligand (R = aryl, methyl), but rather on the deprotonated benzylic phosphine "arm".

Significantly, although complexes **7a** and **8** are thermally stable,[30] they cannot be produced by treating the aromatized complex **1** with RLi (R = aryl, methyl). Instead, the deprotonated complex **2** was formed after addition of 1 equiv of RLi to a THF solution of complex **1** (Scheme 6). Thus, the organolithium reagents act as bases rather than as nucleophiles. As described before, decoordination of the amine "arm" and nucleophilic attack at the metal center by RLi can occur when the starting material is a complex based on the deprotonated PNN* ligand (Scheme 3). It may very well be that formation of complexes **7a** and **8** is thermodynamically more favorable than the deprotonation process of **1**, but the need to open the chelate "arm" to allow attack at the metal center may make this process kinetically unfavorable.

Summary

New cationic, neutral, and anionic Pt(II) complexes of the PNN system are reported. The PNN ligand takes an active role in the formation and reactivity of the complexes, by virtue of

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[30] While complexes **7** and **8** are highly stable at room temperature, they completely decompose during 72 h at 60 °C (complex **7**) and 72 h at 90 °C (complex **8**).

dearomatization/aromatization processes (as a result of ligand deprotonation) and hemilability. Treatment of the cationic chloride complex **1** with ^{t}BuOK resulted in deprotonation, leading to the dearomatized, neutral chloride complex **2**. Nucleophilic attack on this complex by 1 equiv of RLi did not lead to chloride substitution; rather, facile formation of the corresponding anionic complexes $Li^{+}[(PNN^{*})Pt(Cl)(R)]^{-}$ (R = methyl (**5**), phenyl (**6**)) took place, in which the amine "arm" underwent decoordination. Formation of these highly electron-rich d^8 complexes in the absence of stabilizing π acceptors is possibly assisted by coordination of Li^+ to the amine group, allowing the opening of the chelate ring followed by nucleophilic attack on Pt. Reaction of the anionic complexes **5** and **6** with HCl resulted mainly in aromatization to form the neutral complexes (PNN)Pt(Cl)(R) (R = methyl (**7**), phenyl (**8**)), RH elimination playing a minor role. This aromatization reaction was completely selective when water was used.

Experimental Section

General Procedures. All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with an MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under an argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glovebox over 4 Å molecular sieves. Commercially available reagents were used as received. The ligand PNN[5] and the complex $Pt(COD)Cl_2$[31] were prepared according to literature procedures. The NMR spectra were recorded at 250 (^{1}H), 101 (^{31}P), and 235 MHz (^{19}F) using a Bruker DPX 250 spectrometer, at 400 (^{1}H), 100 (^{13}C), 162 (^{31}P), and 155 MHz (^{7}Li) using a Bruker AMX-400 NMR spectrometer, and at 500 (^{1}H), 126 (^{13}C), 202 MHz (^{31}P), and 50.7 MHz (^{15}N in 2D $^{15}N-^{1}H$ correlation) using a Bruker DPX 500 spectrometer. All spectra were recorded at 23 °C (if not specified otherwise). The long-range $^{2}D^{15}N-^{1}H$ correlation spectrum was measured using the Bruker standard microprogram GHMBC by an inverse gradient selected experiment using a 5 mm Bruker inverse multinuclear resonance probe with a single-axis (*z*) gradient coil. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. ^{1}H NMR chemical shifts are referenced to the residual hydrogen signal of the deuterated solvents, and in $^{13}C\{^{1}H\}$ NMR the ^{13}C signal of the deuterated solvents was used as a reference. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. ^{19}F NMR chemical shifts were referenced to C_6F_6 (−163 ppm). ^{15}N NMR chemical shifts are reported as referenced downfield to liquid ammonia. In ^{7}Li NMR measurements LiCl was used as a standard (LiCl in THF = 0 ppm). Screw-cap 5 mm NMR tubes were used in the NMR follow-up experiments. Abbreviations used in the description of NMR data are as follows: Ar aryl, br broad, s singlet, d doublet, t triplet, q quartet, m multiplet, v virtual. Elemental analyses were performed by H. Kolbe, Microanalytisches Laboratorium, Germany. The X-ray data were collected on a Nonius KappaCCD diffractometer, Mo Kα ($\lambda = 0.71073$ Å) with a graphite monochromator at $T = 120(2)$ K. The data were processed with Denzo-Scalepack. The structures were solved by direct methods with SHELXS and were refined by full matrix least-squares based on F^2 with SHELXL-97.

Preparation of $[(PNN)PtCl]^{+}Cl^{-}$ (1). To a methylene chloride solution (8 mL) of $(COD)PtCl_2$ (308 mg, 0.89 mmol) was added the PNN ligand (300 mg, 0.93 mmol), resulting in an immediate color change to yellowish. The $^{31}P\{^{1}H\}$ NMR spectrum of the solution revealed formation of complex **1**. The solvent was removed under vacuum, and the residue was washed with pentane and extracted with methylene chloride. Solvent evaporation yielded 471 mg (0.80 mmol, 90% yield) of cream-colored complex **1**.

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): 49.25 (s, J_{Pt-P} =3409 Hz). ^{1}H NMR (CD_2Cl_2): 8.13 (dt, J_{H-H} = 8 Hz, J_{P-H}=8 Hz,1H, pyridine-H4), 7.97 (d, J_{H-H} = 8 Hz, 1H, pyridine-H5), 7.84 (d, J_{H-H} = 8 Hz, 1H, pyridine-H3), 4.70 (s, 2H, CH_2N), 3.93 (d, J_{P-H} = 10 Hz, J_{Pt-H} = 26 Hz, 2H, CH_2P), 3.39 (m, 2H, $NCHHCH_3$), 3.01 (m, 2H, $NCHHCH_3$), 1.48 (t, J_{H-H} = 7 Hz, $N(CH_2CH_3)_2$ 1.46 (d, J_{P-H} = 16 Hz, $P(C(CH_3)_3)_2$; the last two reported signals are overlapped, and their integral corresponds to 24H. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): 162.20 (bs, Py-C2), 161.95 (bs, Py-C6), 140.47 (s, Py-C4), 128.62 (s, Py-C5), 121.64 (s, Py-C3), 65.75 (s, Py-CH_2N), 55.97 (s, $N(CH_2Me)_2$), 36.19 (d, J_{PC} = 27 Hz, $P(C(CH_3)_3)_2$), 36.11 (d, J_{PC} = 32 Hz, PCH_2), 28.69 (s, $P(C(CH_3)_3)_2$),12.28 (s, $N(CH_2CH_3)_2$ (assignment of $^{13}C\{^{1}H\}$ NMR signals was confirmed by ^{13}C DEPT). Anal. Found (calcd for $C_{19}H_{35}P_1N_2Pt_1Cl_2+0.5(CH_2Cl_2)$): C, 37.36 (37.12); H, 6.49 (5.75); N, 4.46 (4.44).

X-ray Structural Analysis of 1. Complex **1** was crystallized from a saturated benzene solution at room temperature to give colorless crystals. Crystal data: $C_{19}H_{35}Cl_2N_2P_1Pt_1 + C_6H_6$, 0.3 × 0.2 × 0.05 mm^3, triclinic, space group $P\bar{1}$, $a = 9.1580(2)$ Å, $b = 10.9628(2)$ Å, $c = 16.0184(2)$ Å, $\alpha = 77.293(1)°$, $\beta = 76.973(1)°$, $\gamma = 69.110(1)°$ from 25 degrees of data, $V = 1446.51(4)$ Å^3, $Z = 2$, fw = 666.56, D_c = 1.530 Mg/m^3, μ = 5.104 mm^{-1}. Data collection and treatment: 28 500 reflections collected, $-11 \le h \le 11$, $-13 \le k \le 14$, $0 \le l \le 20$, 6593 independent reflections (R_{int} = 0.080); 293 parameters refined with no restraints, final R_1 = 0.0326 for data with $I > 2\sigma(I)$ and R_1 = 0.0365 on 6592 reflections, wR_2 = 0.0911, goodness-of-fit on F^2 = 1.086, largest electron density peak = 2.576 e/Å^3.

Preparation of (PNN*)PtCl (2). To a THF (5 mL) suspension of complex **1** (53.4 mg, 0.091 mmol) was added ^{t}BuOK (11.2 mg, 0.095 mmol), resulting in a color change from yellowish to orange. The solvent was removed under vacuum, and the complex was extracted with benzene. Solvent evaporation yielded 47.9 mg (0.087 mmol, 95% yield) of complex **2** as an orange solid.

$^{31}P\{^{1}H\}$ NMR (C_6D_6): 47.83 (s, J_{Pt-P} = 3658 Hz). ^{1}H NMR (C_6D_6): 6.47 (ddd, J_{H-H} = 9 Hz, J_{H-H} = 6 Hz, J_{P-H} = 2 Hz, 1H, pyridine-H4), 6.25 (d, J_{H-H} = 9 Hz, 1H, pyridine-H5), 5.15 (d, J_{H-H} = 6 Hz, 1H, pyridine-H3), 3.36 (d, J_{P-H} = 7 Hz, J_{Pt-H} = 51 Hz, 1H, $=CHP$), 2.98 (s, 2H, CH_2N), 2.95 (m, 2H, $NCHHCH_3$), 2.17 (m, 2H, $NCHHCH_3$), 1.47 (d, J_{P-H} = 14 Hz, 18H, $P(C(CH_3)_3)_2$, 1.17 (t, J_{H-H} = 7 Hz, 6H, $N(CH_2CH_3)_2$. $^{13}C\{^{1}H\}$ NMR (C_6D_6): 169.29 (d, J_{PC} = 10 Hz, Py-C2), 156.81 (s, Py-C6), 131.98 (s, Py-C4), 112.81 (d, J_{P-C} = 12 Hz, Py-C3), 95.85 (s, Py-C5), 64.12 (s, Py-CH_2N), 60.26 (d, J_{P-C} = 70 Hz, $=CHP$), 54.25 (s, $N(CH_2CH_3)_2$), 36.91 (d, J_{PC} = 33 Hz, $P(C(CH_3)_3)_2$), 29.08 (d, J_{PC} = 3 Hz, $P(C(CH_3)_3)_2$), 11.60 (s, $N(CH_2CH_3)_2$) (assignment of $^{13}C\{^{1}H\}$ NMR signals was confirmed by ^{13}C DEPT). Anal. Found (calcd for $C_{19}H_{34}P_1N_2Pt_1Cl_1+0.5(C_6H_6)$): C, 44.91 (44.71); H, 6.65 (6.31); N, 5.20 (4.73).

Preparation of (PNN*)PtH (3). To a THF solution (4 mL) of complex **2** (167 mg, 0.302 mmol) was added 212 μL of a THF solution of ^{n}BuLi (1.5 M, 0.109 mmol) at −20 °C. The solution was warmed to room temperature, and the solvent was removed under vacuum. Complex **3** was extracted with benzene, and the benzene was removed under vacuum to yield 152 mg (0.294 mmol, 97% yield) of complex **3** as a dark orange solid.

$^{31}P\{^{1}H\}$ NMR (C_6D_6): 59.64 (s, J_{Pt-P} = 3874 Hz). ^{1}H NMR (C_6D_6): 6.65 (ddd, J_{H-H} = 9 Hz, J_{H-H} = 8 Hz, J_{P-H} = 2 Hz, 1H, pyridine-H4), 6.45 (d, J_{H-H} = 9 Hz, 1H, pyridine-H5), 5.38 (d, J_{H-H} = 7 Hz, 1H, pyridine-H3), 3.49 (d, J_{P-H} = 7 Hz, 2H, $=CHP$), 3.15 (s, 2H, CH_2N), 2.51 (m, 4H, NCH_2CH_3), 1.46 (d, J_{H-H} = 14 Hz, 18H, $P(C(CH_3)_3)_2$, 1.16 (t, J_{H-H} = 7 Hz, 6H, $N(CH_2CH_3)_2$,

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(31) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

−12.46 (t, $J_{P-H} = 17$ Hz, $J_{Pt-H} = 1156$ Hz, 1H, Pt-*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): 167.73 (d, $J_{P-C} = 11$ Hz, Py-C2), 156.74 (d, $J_{PC} = 3$ Hz, Py-C6), 132.6 (d, $J_{P-C} = 2$ Hz, Py-C4), 112.43 (d, $J_{P-C} = 16$ Hz, Py-C3), 95.88 (s, Py-C5), 67.46 (d, $J_{P-C} = 2$ Hz, *J*Py-CH_2N), 59.21 (d, $J_{P-C} = 69$ Hz, =CHP), 55.77 (d, $J_{P-C} = 2$ Hz, N(CH_2CH_3)$_2$), 35.94 (d, $J_{PC} = 35$ Hz, P(*C*(CH_3)$_3$)$_2$), 29.61 (d, $J_{P-C} = 4$ Hz, $J_{Pt-C} = 32$ Hz, P(C(*C*H_3)$_3$)$_2$), 13.25 (s, $J_{Pt-C} = 36$ Hz, N(CH_2*C*H_3)$_2$) (assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by ^{13}C DEPT). Anal. Found (calcd for $C_{19}H_{35}P_1N_2Pt_1+0.5(C_6H_6)$): C, 46.77 (47.47); H, 7.11 (6.88); N, 4.86 (5.03).

Preparation of [(PNN)PtH]$^+$OTf$^-$ (4). To a toluene solution (1 mL) of complex **3** (16 mg, 0.031 mmol) was added 1 equiv of HOTf (2.7 μL, 0.031 mmol) at −20 °C. An immediate color change from orange to yellowish took place. The solution was warmed to room temperature, and the solvent was removed under vacuum. Complex **4** was washed with pentane and extracted with THF. Solvent removal under vacuum yielded 21.3 mg (0.03 mmol, 98% yield) of complex **4** as a light yellowish solid.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): 65.23 (s, $J_{Pt-P} = 3744$ Hz). ^{1}H NMR (CD_2Cl_2): 8.04 (t, $J_{H-H} = 8$ Hz, 1H, pyridine-H4), 7.61 (d, $J_{H-H} = 8$ Hz, 1H, pyridine-H5), 7.54 (d, $J_{H-H} = 8$ Hz, 1H, pyridine-H3), 4.47 (s, 2H, C*H*$_2$N), 3.62 (d, $J_{P-H} = 9$ Hz, 2H, C*H*$_2$P), 3.29 (m, 2H, NC*H*HCH$_3$), 3.21 (m, 2H, NCH*H*CH$_3$), 1.48 (t, $J_{H-H} = 7$ Hz, 6H, N(CH_2C*H*$_3$)$_2$), 1.35 (d, $J_{P-H} = 15$ Hz, 18H, P(C(C*H*$_3$)$_3$)$_2$), −14.59 (d, $J_{P-H} = 18$ Hz, $J_{Pt-H} = 1258$ Hz, 1H, Pt-*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 159.91 (bs, Py-C2), 159.41 (bs, Py-C6), 138.98 (s, Py-C4), 128.62 (s, Py-C5), 120.96 (s, Py-C3), 68.09 (s, Py-CH_2N), 57.72 (s, N(*C*H$_2$Me)$_2$), 35.70 (d, $J_{P-C} = 30$ Hz, P*C*H$_2$), 35.14 (d, $J_{P-C} = 29$ Hz, P(*C*(CH_3)$_3$)$_2$), 28.76 (d, $J_{P-C} = 4$ Hz, P(C(*C*H$_3$)$_3$)$_2$),13.75 (s, N(CH_2*C*H$_3$)$_2$ (assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by ^{13}C DEPT). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): −79.68 (s, *free* SO_3CF_3). Anal. Found (calcd for $C_{20}H_{36}P_1N_2Pt_1SO_3F_3$): C, 36.53 (35.98); H, 6.11 (5.44); N, 4.01 (4.20).

Preparation of [(PNN*)Pt(Cl)(CH$_3$)]$^-$Li$^+$ (5). To a d_8-THF solution (0.5 mL) of complex **2** (20 mg, 0.036 mmol) at −20 °C was added 38 μL of a diethyl ether solution of MeLi (1 M, 0.038 mmol), resulting in a color change from orange to red. Formation of complex **5** was immediately revealed by $^{31}P\{^1H\}$ NMR. Complex **5** was converted to complex **2** during 3−4 days at room temperature. GC/MS analysis of a 10 μL sample of the gas phase from the screw-cap tube revealed formation of CH_4.

$^{31}P\{^1H\}$ NMR (d_8-THF): 56.94 (s, $J_{Pt-P} = 2043$ Hz). ^{1}H NMR (d_8-THF): 6.18 (ddd, $J_{H-H} = 9$ Hz, $J_{H-H} = 7$ Hz, $J_{P-H} = 2$ Hz, 1H, pyridine-H4), 5.72 (d, $J_{H-H} = 9$ Hz, 1H, pyridine-H5), 5.60 (d, $J_{H-H} = 7$ Hz, 1H, pyridine-H3), 3.60 (s, 2H, C*H*$_2$N), 3.26 (bs, 2H, =C*H*P), 2.41 (q, $J_{H-H} = 7$ Hz, 2H, NC*H*HCH$_3$), 1.32 (d, $J_{P-H} = 12$ Hz, 18H, P(C(C*H*$_3$)$_3$)$_2$, 0.95 (t, $J_{H-H} = 7$ Hz, 6H, N(CH_2C*H*$_3$)$_2$, 0.29 (d, $J_{P-H} = 8$ Hz, $J_{Pt-H} = 56$ Hz, 3H, Pt−C*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): 177.14 (d, $J_{P-C} = 20$ Hz, Py-C2), 159.68 (s, Py-C6), 132.59 (s, Py-C4), 112.69 (d, $J_{P-C} = 15$ Hz, Py-C3), 96.37 (s, Py-C5), 65.56 (d, $J_{P-C} = 56$ Hz, =CHP), 62.78 (s, Py-CH_2N), 48.17 (s, N(*C*H$_2$CH$_3$)$_2$), 36.55 (d, $J_{P-C} = 17$ Hz, P(*C*(CH_3)$_3$)$_2$), 29.89 (d, $J_{P-C} = 5$ Hz, P(C(*C*H$_3$)$_3$)$_2$), 13.33 (s, N(CH_2CH_3)$_2$), 5.59 (d, $J_{P-C} = 111$ Hz, Pt-*C*H$_3$) (assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by ^{13}C DEPT). ^{15}N NMR from ^{15}N−^{1}H correlation (d_8-THF): 160.62 (s, Py-*N*), 49.08 (s, Py-CH_2*N*). ^{7}Li NMR (d_8-THF): 2.67 (bs). ES-MS: *m/z*− 567.80 (M) (calcd 567.20), 603.81 (M + H + Cl) (calcd 603.66), *m/z*+ 533.08 (M + H − Cl) (calcd 532.75).

Preparation of [(PNN*)Pt(Cl)(C$_6$H$_5$)]$^-$Li$^+$ (6). To a THF solution (1.5 mL) of complex **2** (20 mg, 0.036 mmol) was added 30.6 μL of a THF solution of PhLi (1.3 M, 0.040 mmol), resulting in a color change from orange to red. Formation of complex **6** was immediately revealed by $^{31}P\{^1H\}$ NMR. The solvent was removed under vacuum for 1 h, and the residual solid was extracted with benzene. Benzene evaporation yielded 19 mg (0.030 mmol, 83% yield) of complex **6** as a bourdeaux solid.

$^{31}P\{^1H\}$ NMR (d_8-THF): 53.88 (s, $J_{Pt-P} = 1977$ Hz). ^{1}H NMR (d_8-THF): 7.33 (m, 2H, Ar) 6.71 (t, $J_{H-H} = 7$ Hz, 2H, Ar), 6.58 (t, $J_{H-H} = 7$ Hz, 1H, Ar), 6.16 (bt, $J_{H-H} = 7$ Hz, 1H, pyridine-H4), 5.73 (d, $J_{H-H} = 8$ Hz, 1H, pyridine-H5), 5.41 (d, $J_{H-H} = 6$ Hz, 1H, pyridine-H3), 3.54 (s, 2H, C*H*$_2$N), 3.17 (bs, 1H, C*H*P), 2.06 (q, $J_{H-H} = 7$ Hz, 2H, NC*H*HCH$_3$), 1.33 (d, $J_{P-H} = 12$ Hz, 18H, P(C(C*H*$_3$)$_3$)$_2$, 0.63 (t, $J_{H-H} = 7$ Hz, 6H, N(CH_2C*H*$_3$)$_2$. $^{13}C\{^1H\}$ NMR (d_8-THF): 177.13 (d, $J_{P-C} = 20$ Hz, Py-C6), 166.23 (d, $J_{P-C} = 127$ Hz, *ipso* of phenyl, coordinated *trans* to P), 159.96 (s, Py-C2), 138.28 (s, Ar), 131.16 (d, $J_{P-C} = 15$ Hz, Ar), 129.47 (s, Ar), 127.69 (s, Ar), 125.56 (bs, Ar), 121.48 (s, Py-C3), 112.18 (bs, Ar), 102.92 (d, Py-C5), 63.82 (s, Py-*C*H$_2$N), 47.81 (s, N(*C*H$_2$CH$_3$)$_2$), 35.53 (d, $J_{P-C} = 19$ Hz, *C*H$_2$P), 34.61 (d, $J_{P-C} = 10$ Hz, P(*C*(CH_3)$_3$)$_2$), 29.05 (bs, P(C(*C*H$_3$)$_3$)$_2$), 12.27 (s, N(CH_2*C*H$_3$)$_2$), (assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by ^{13}C DEPT). ^{15}N NMR from ^{15}N−^{1}H correlation (d_8-THF): 147.33 (s, Py-*N*), 49.84 (s, Py-CH_2*N*). ^{7}Li NMR (d_8-THF): 1.16 (bs). ES-MS: *m/z* 629.98 (M + H) (calcd 630.10), 666.97 (M + 2H + Cl) (calcd 666.56), *m/z*+ 595.20 (M + H − Cl) (calcd 594.65) (major), 554.09 (M + 2H − C_6H_5) (calcd 554.01).

Reactivity of Anionic Complexes. Reaction of [(PNN*)Pt(Cl)(CH$_3$)]$^-$Li$^+$ (5) with HCl. To a THF solution (1.5 mL) of complex **2** (20 mg, 0.036 mmol) at −20 °C was added 38.4 μL of a THF solution of MeLi (1 M, 0.039 mmol), resulting in the formation of complex **5**. This was followed immediately by addition of 9 μL of dioxane solution of HCl (4 M, 0.036 mmol) at room temperature, resulting in a color change to orange light. The $^{31}P\{^1H\}$ NMR spectrum at room temperature revealed formation of complex **7a** as a major product and **2** as a minor product, in a 10:1 ratio, respectively. The solvent was removed under vacuum, and complex **7a** was extracted with benzene. Benzene evaporation yielded 19 mg (0.025 mmol, 93% yield) of complex **7** as an orange solid.

Complex 7a. $^{31}P\{^1H\}$ NMR (C_6D_6): 73.68 (s, $J_{Pt-P} = 1737$ Hz). ^{1}H NMR (C_6D_6): 7.49 (d, $J_{H-H} = 7$ Hz,1H, pyridine-H5), 6.98 (t, $J_{H-H} = 7$ Hz, 1H, pyridine-H4), 6.47 (d, $J_{H-H} = 7$ Hz, 1H, pyridine-H3), 4.30 (s, 2H, C*H*$_2$N), 2.72 (d, 2H, $J_{P-H} = 7$ Hz, C*H*$_2$P), 2.28 (q, $J_{H-H} = 7$ Hz, 2H, NC*H*HCH$_3$), 1.49 (d, $J_{P-H} = 8$ Hz, $J_{Pt-H} = 64$ Hz, 3H, Pt-C*H*$_3$), 1.17 (d, $J_{P-H} = 13$ Hz, 18H, P(C(C*H*$_3$)$_3$)$_2$, 0.86 (t, $J_{H-H} = 7$ Hz, 6H, N(CH_2C*H*$_3$)$_2$. $^{13}C\{^1H\}$ NMR (C_6D_6): 166.26 (Py-C6), 164.40 (d, $J_{P-C} = 7$ Hz, Py-C2), 136.34 (s, Py-C4), 123.82 (s, Py-C5), 120.89 (d, $J_{P-C} = 7$ Hz, Py-C3), 61.89 (s, Py-*C*H$_2$N), 47.37 (s, N(*C*H$_2$CH$_3$)$_2$), 35.55 (d, $J_{P-C} = 21$ Hz, *C*H$_2$P), 34.54 (d, $J_{P-C} = 8$ Hz, P(*C*(CH_3)$_3$)$_2$), 29.02 (d, $J_{P-C} = 5$ Hz, P(C(*C*H$_3$)$_3$)$_2$), 12.26 (s, N(CH_2*C*H$_3$)$_2$), 7.05 (d, $J_{P-C} = 112$ Hz, Pt-*C*H$_3$) (assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by ^{13}C DEPT). ^{15}N NMR from ^{15}N−^{1}H correlation (C_6D_6): 231.54 (s, Py-*N*), 47.54 (s, Py-CH_2*N*). ES-MS: *m/z*− 567.98 (M − H) (calcd 567.20), 603.99 (M + Cl) (calcd 603.66), *m/z*+ 533.21 (M − Cl) (calcd 532.75) (major), 553.19 (M − CH_3) (calcd 554.17). Anal. Found (calcd for $C_{20}H_{38}P_1N_2Pt_1Cl+0.5(C_6H_6)$): C, 45.31 (45.50); H, 6.62 (6.81); N, 5.14 (4.61).

Reaction of [(PNN*)Pt(Cl)(CH$_3$)]$^-$Li$^+$ (5) with Water. To a THF solution (1.5 mL) of complex **2** (20 mg, 0.036 mmol) at −20 °C was added 38.4 μL of a THF solution of MeLi (1 M, 0.039 mmol), resulting in the formation of complex **5**. Upon injection of excess H_2O (1 μL, 0.056 mmol) into a THF solution of **5** in a 5 mm screw-cap tube equipped with a septum, a color change to yellow took place and formation of the neutral complex **7** was immediately revealed by $^{31}P\{^1H\}$ NMR spectroscopy. The solvent was removed under vacuum, and complex **7a** was extracted with benzene. Benzene evaporation yielded 15.5 mg (0.027 mmol, 76% yield) of complex **7a** as an orange solid.

Reaction of [(PNN*)Pt(Cl)(C$_6$H$_5$)]$^-$Li$^+$ (6) with HCl. To a THF solution (1.5 mL) of complex **6** (23 mg, 0.036 mmol) was added 9 μL of a dioxane solution of HCl (4 M, 0.036 mmol) at room temperature, resulting in a color change to light orange. The $^{31}P\{^1H\}$NMR spectrum revealed formation of complex **8** as a major product and **2** as a minor product, in a 25:1 ratio, respectively. The solvent was removed under vacuum, and complex **8** was extracted with 20 mL of pentane (complex **2** was extracted from the residue with benzene). Pentane evaporation yielded 16 mg (0.025 mmol, 71% yield) of complex **8** as an orange solid.

Complex 8. $^{31}P\{^1H\}$ NMR (C_6D_6): 66.86 (s, J_{Pt-P} = 1694 Hz). ^1H NMR (C_6D_6): 7.65 (t, J_{H-H} = 7 Hz, 2H, Ar), 7.44 (m, 2H, Ar), 7.20 (t, J_{H-H} = 8 Hz, 1H, Ar), 7.02 (m, 2H, Ar), 6.49 (d, J_{H-H} = 8 Hz, 1H, Ar), 3.50 (s, 2H, $C\mathit{H}_2N$), 2.83 (d, J_{P-H} = 7 Hz, 2H, $C\mathit{H}_2P$), 2.15 (q, J_{H-H} = 7 Hz, 2H, $NC\mathit{H}HCH_3$), 1.16 (d, J_{P-H} = 13 Hz, 18H, $P(C(C\mathit{H}_3)_3)_2$, 0.73 (t, J_{H-H} = 7 Hz, 6H, $N(CH_2C\mathit{H}_3)_2$. $^{13}C\{^1H\}$ NMR (C_6D_6): 167.61 (s, Py-C6), 163.94 (d, J_{P-C} = 7 Hz, Py-C2), 157.99 (d, J_{P-C} = 130 Hz, *ipso* of phenyl, coordinated *trans* to P), 136.93 (s, Ar), 136.7 (s, Py-C4), 128.97 (s, Py-C5), 127.43 (d, J_{P-C} = 9 Hz, Ar), 126.78 (d, J_{P-C} = 8 Hz, Ar), 124.31 (s, Ar), 123.58 (s, Ar), 120.51 (d, J_{P-C} = 4 Hz, Py-C3), 63.82 (s, Py-CH_2N), 47.81 (s, $N(\mathit{C}H_2CH_3)_2$), 35.53 (d, J_{P-C} = 19 Hz, $\mathit{C}H_2P$), 34.61 (d, J_{P-C} = 10 Hz, $P(\mathit{C}(CH_3)_3)_2$), 29.05 (bs, $P(C(\mathit{C}H_3)_3)_2$), 12.27 (s, $N(CH_2\mathit{C}H_3)_2$), (assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by ^{13}C DEPT). ^{15}N NMR from $^{15}N-^1H$ correlation (C_6D_6): 233.06 (*s*, Py-N), 47.40 (s, Py-$CH_2\mathit{N}$). ES-MS: *m/z*- 629.98 (M) (calcd 630.10), 666.97 (M + H + Cl) (calcd 666.56), *m/z* + 554.09 (M + H − C_6H_5) (calcd 554.00) (major), 595.20 (M + H − Cl) (calcd 595.65). Anal. Found (calcd for $C_{25}H_{40}P_1N_2Pt_1Cl + C_6H_6$): C, 52.23 (52.57); H, 6.88 (6.55); N, 4.26 (3.96).

X-ray Structural Analysis of 8. Complex **8** was crystallized from a saturated benzene solution by slow evaporation of the solvent at room temperature to give colorless needles. Crystal data: $C_{25}H_{40}ClN_2PPt$, 0.10 × 0.03 × 0.01 mm^3, monoclinic, space group $P2_1/n$, $a = 12.6781(3)$ Å, $b = 10.0244(2)$ Å, $c = 20.8930(6)$ Å, $\beta = 102.328(1)°$ from 20 degrees of data, $V = 2594.07(11)$ Å^3, $Z = 4$, fw = 630.10, D_c =1.613 Mg/m^3, μ = 5.588 mm^{-1}. Data collection and treatment: 17 274 reflections collected, $-16 \le h \le 16$, $0 \le k \le 13$, $0 \le l \le 27$, 6235 independent reflections (R_{int} = 0.052). Solution and refinement: 279 parameters refined with no restraints, final $R_1 = 0.0317$ for data with $I > 2\sigma(I)$ and $R_1 = 0.0534$ on 5891 reflections, $wR_2 = 0.0583$, goodness-of-fit on $F^2 = 0.978$, largest electron density peak = 2.635 e/Å^3.

Reaction of $[(PNN^*)Pt(Cl)(C_6H_5)]^-Li^+$ (6) with Water. To a NMR tube equipped with a septum containing a THF solution (1.5 mL) of complex **6** (20 mg, 0.031 mmol) was injected 2 μL (0.112 mmol) of H_2O. A color change from red to orange took place, and formation of complex **8** was revealed by $^{31}P\{^1H\}$ NMR. The solvent was removed under vacuum, and the complex was extracted with benzene. Benzene evaporation yielded 17 mg (0.027 mmol, 87% yield) of complex **8** as an orange solid.

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Supporting Information Available: CIF files containing X-ray crystallographic data for complexes **1** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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