Cyclometalated Tridentate C-N-N Ligands with an Amine or Amido Donor in Platinum(II) and Palladium(II) Complexes and a Novel Potassium Alkoxide Aggregate

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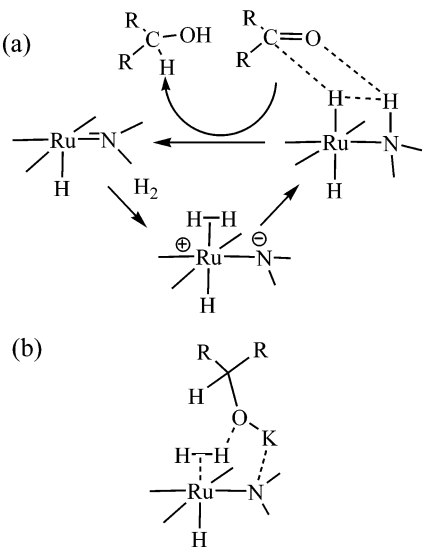
The new ligand 2-phenyl-6-(2-aminoisopropyl)pyridine, papH$_2$, was synthesized and characterized. The corresponding Pt(II) and Pd(II) complexes Pt(papH)Cl (**2**) and Pd(papH)-Cl (**3**) were synthesized and fully characterized by NMR spectroscopy and single-crystal X-ray diffraction. In each complex the κ^3N,N,C tridentate papH ligand forms two five-membered rings with the metal, one of which is created by cyclometalation of the ortho carbon of the phenyl group. Compound **2** was found to react with KO^{t}Bu to afford a Pt(II) amido complex that was isolated as [Pt(pap)]$_2$(KCl)(KO^{t}Bu)$_8$ (**4**). As revealed by single-crystal X-ray diffraction, compound **4** has a novel structure, in which two Pt(pap) moieties are attached to the K_9O_8Cl "core" of the potassium alkoxide aggregate. A solution of compound **4** does not react with H_2(g), even at 3 atm and 60 °C. A hydride complex that is suspected to be Pt-(papH)H was observed by reacting **2** with K[BH(^{s}Bu)$_3$]. This hydride does not react with acetophenone. These properties are in contrast with those of ruthenium hydrido amine/amido catalysts that readily hydrogenate acetophenone. The reaction of compound **3** with KO^{t}Bu yielded a complicated, unidentified mixture that can be reduced to Pd(0) by 3 atm of dihydrogen at ambient temperature.

Introduction

Following the development by Noyori and co-workers of highly active and selective ruthenium catalysts for the asymmetric hydrogenation of ketones,[1] a great deal of research effort has been expended to elucidate the mechanism of this catalytic hydrogenation reaction. Current evidence supports the mechanism outlined in Scheme 1 (upper cycle), starting with the dihydride catalyst *trans*-RuH$_2$((*R*)-binap)(H$_2$NCMe$_2$CMe$_2$NH$_2$),[2] the amido catalyst Ru(H)(NH$_2$CMe$_2$CMe$_2$NH)(PPh$_3$)$_2$,[2b] or precatalysts such as *trans*-RuCl$_2$(diphosphine)(diamine),[1,3] *trans*-Ru(BH$_4$)H(diphosphine)(diamine),[1c] and *trans*-RuHCl(PPh$_2$CH$_2$NHC$_6$H$_{10}$NHCH$_2$PPh$_2$)[4] in 2-propanol. As shown in Scheme 1, a *trans*-dihydride complex reacts with a ketone in the unconventional second-coordination-sphere transfer of dihydrogen to produce the alcohol and an amidohydride complex.

It has been postulated from the X-ray crystal structure determination of the dihydride that only the axial NH that is aligned with the ruthenium hydride, possibly by a hydridic−protonic RuH···HN interaction,[5] is transferred to the ketone. The crucial role of the amino ligand

Scheme 1[a]



[a] Legend: (a) catalytic cycle for the hydrogenation of ketones catalyzed by ruthenium hydridoamine complexes; (b) potassium alkoxide assisting in the splitting of the dihydrogen.

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(1) (a) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 40−73. (b) Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931−7944. (c) Sandoval, C. A.; Ohkuma, T.; Muñiz, K.; Noyori, R. *J. Am. Chem. Soc.* **2003**, *125*, 13490−13503.

(2) (a) Abdur-Rashid, K.; Faatz, M.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 7473−7474. (b) Abdur-Rashid, K.; Clapham, S. E.; Hadzovic, A.; Harvey, J. N.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 15104−15118. (c) Abbel, R.; Abdur-Rashid, K.; Faatz, M.; Hadzovic, A.; Lough, A. J.; Morris, R. H. Submitted for publication.

(3) (a) Hartmann, R.; Chen, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 3581−3585. (b) Hartmann, R.; Chen, P. *Adv. Synth. Catal.* **2003**, *345*, 1353−1359.

(4) Rautenstrauch, V.; Hoang-Cong, X.; Churlaud, R.; Abdur-Rashid, K.; Morris, R. H. *Chem. Eur. J.* **2003**, *9*, 4954−4967.

(5) (a) Stevens, R. C.; Bau, R.; Milstein, D.; Blum, O.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1990**, 1429−1432. (b) Peris, E.; Lee, J. C.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2573. (c) Lough, A. J.; Park, S.; Ramachandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356−8357. (d) Also known as dihydrogen bonding. See articles in: *Recent Advances in Hydride Chemistry*; Peruzini, M., Poli, R., Eds.; Elsevier: New York, 2001.

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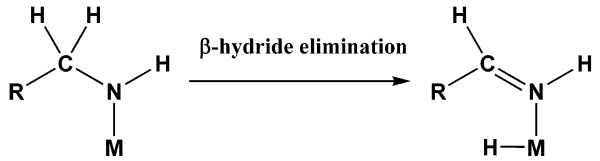
Scheme 2. β-Hydride Elimination of an Amido Ligand To Generate a Hydridoimine Complex



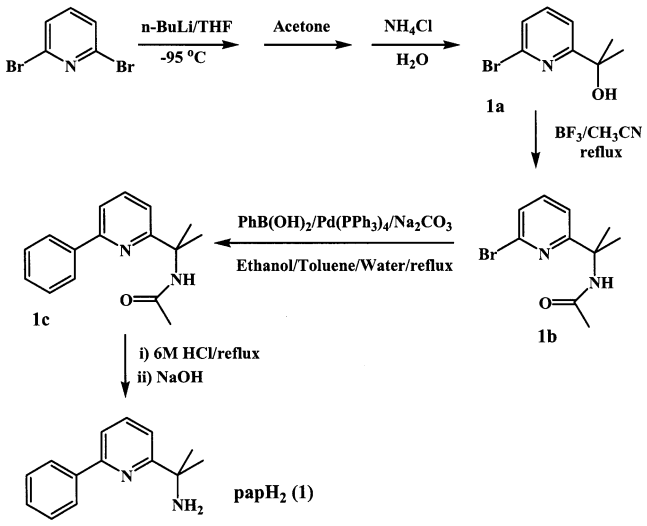
in catalysis has been given the name the "N−H effect". We have demonstrated that dihydrogen adds across the ruthenium amido (Ru═N) bond of the hydridoamido complexes to regenerate the *trans*-dihydrides in a reversible fashion via an unobserved dihydrogen σ-complex intermediate.[2] This is the turnover-limiting step in the catalytic hydrogenation process. It has long been known that transition-metal amido bonds are capable of splitting dihydrogen to form the corresponding hydridoamine species.[6] An excess of potassium alkoxide is added to 2-propanol solutions of the precatalysts to achieve an optimum rate of hydrogenation.[1] Recently Hartmann and Chen have reported that potassium ions are required for the efficient hydrogenation of acetophenone catalyzed by Noyori's catalyst.[3] One of their suggestions for the role of the potassium cation in 2-propanol is to coordinate to the amido nitrogen and to act as a Lewis acid to position an alkoxide anion to assist in the splitting of dihydrogen, as shown in the lower half of Scheme 1.

It is well-known that group 10 metals make good catalysts in many chemical transformations. We ask the question here whether group 10 complexes can be prepared with amido ligands that can split dihydrogen in this way and be used for the hydrogenation of ketones and imines. We have reported that ruthenium amido intermediates tend to decompose through β-hydride elimination (Scheme 2) but can be isolated when the amido nitrogen has no β-hydrogens in the ligand (as in $Ru(H)(NH_2CMe_2CMe_2NH)(PPh_3)_2$).[2,7] Therefore, we designed the novel ligand 2-phenyl-6-(2-aminoisopropyl)-pyridine, $papH_2$, with two methyl groups on the α-carbon of the amino group. The phenyl group was introduced to promote cyclometalation. The presence of the Pt−C bond was desired in order to stabilize a Pt−H bond in a rare complex with only nitrogen donors as the other ligands. The other example of such a hydride is Pt(bipy-C)H, where bipy-CH is 6-(1-methylbenzyl)-2,2′-bipyridine and bipy-C is the tridentate ligand coordinated via the two bipyridine nitrogens and an ortho carbon of the phenyl of the chiral methylbenzyl group, as reported by Minghetti et al.[8] Here we report that the reaction of Pt(papH)Cl (where papH is deprotonated 2-phenyl-6-(2-aminoisopropyl)pyridine) with KO^tBu leads to the isolation of a novel platinum complex associated with potassium ions of the alkoxide base through the amido nitrogen atom.

Results and Discussion

Synthesis of 2-Phenyl-6-(2-aminoisopropyl)-pyridine, $papH_2$. The new compound $papH_2$ has been synthesized by following the route shown in Scheme 3. The lithiation of 2,6-dibromopyridine followed by the addition of excess acetone and subsequent quenching with ammonium chloride aqueous solution results in the formation of 2-bromo-6-(2-hydroxyisopropyl)pyridine (**1a**) in high yield. The crude **1a** showed a satisfactory ^1H NMR spectrum and was used in the next step without further purification. In the presence of $BF_3{\cdot}Et_2O$, **1a** reacts with acetonitrile under reflux conditions[9] to afford *N*-[1-(6-bromopyridin-2-yl)-1-methylethyl]acetamide (**1b**) in ∼30% yield, with 50% of the starting material **1a** being recovered. Increasing the reaction time or changing the amount of $BF_3{\cdot}Et_2O$ did not increase the yield significantly. In the literature, the conversion of a tertiary alcohol to the corresponding amine can be achieved by heating the alcohol with NaN_3 and an acid, followed by the reduction of the resulting azido compound to amine.[10] However, this method failed to convert **1a** to **1**. Compound **1b** is converted to *N*-[1-methyl-1-(6-phenylpyridin-2-yl)ethyl]acetamide (**1c**) in high yield by the Pd(0)-catalyzed Suzuki cross-coupling reaction[11] with $PhB(OH)_2$. Hydrolysis of **1c** by refluxing in 6 M HCl aqueous solution followed by neutralization with NaOH yields the compound $papH_2$ as a colorless liquid, quantitatively.

Scheme 3. Synthesis of the Ligand $papH_2$ (1)



Syntheses and Structures of Pt(papH)Cl (2) and Pd(papH)Cl (3). The compound $papH_2$ has two nitrogen donor atoms from an amino group and a pyridyl group that can coordinate to metal ions. In addition, the removal of the ortho proton from the phenyl group of $papH_2$ allows the ligand to chelate to metal ions in a tridentate manner. Pd(II) and Pt(II) metal ions are well-known for their ability to undergo ortho metalation by activating a C−H bond.[12] It is therefore not surprising that we have found that the $papH_2$ ligand reacted readily in this fashion with Pt(II) and Pd(II) metal ions. The compounds Pt(papH)Cl and Pd(papH)Cl can be obtained in good yield by refluxing the $papH_2$ ligand with K_2PtCl_4 or $PdCl_2$, respectively, in a dilute HCl aqueous solution (Scheme 4). This is similar to the

(6) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1−40 and references therein.

(7) A β-hydride elimination reaction in $Ir(CO)(PPh_3)_2(PhNCH_2Ph)$ has been directly observed: Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7010−7011.

(8) Minghetti, G.; Cinellu, M. A.; Stoccoro, S.; Chelucci, G.; Zucca, A. *Inorg. Chem.* **1990**, *29*, 5137−5138.

(9) Sjöberg, K. *Acta Chem. Scand.* **1968**, *22*, 1787−1790.

(10) Leffler, J. E.; Zupancic, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 259−267.

(11) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147−168.

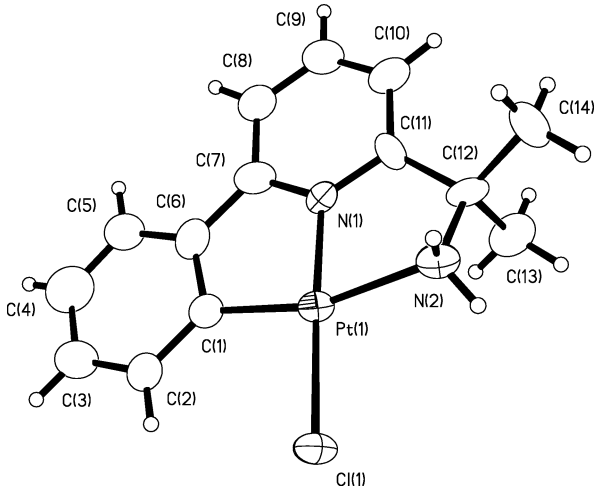


Figure 1. Molecular structure of **2**.

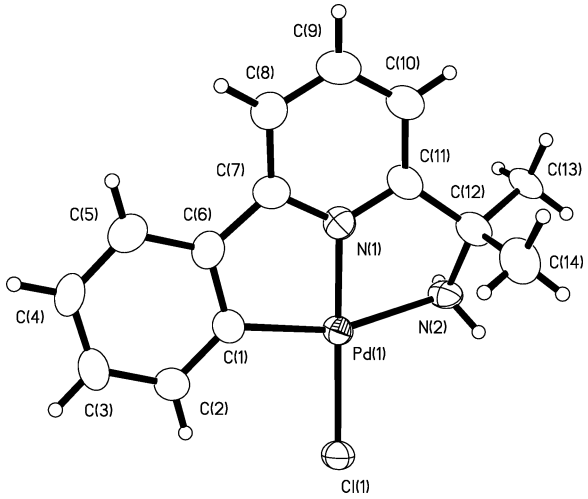
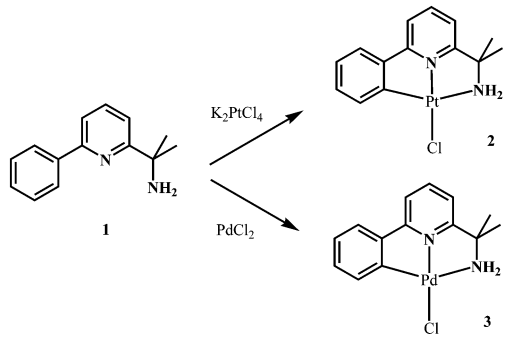


Figure 2. Molecular structure of **3**.

Scheme 4. Preparation of Complexes 2 and 3



procedure reported by Minghetti et al.[13] for the preparations of the Pt(II) and Pd(II) complexes of bipy-CH.

As shown in Figure 1, the Pt(II) center of compound **2** adopts a distorted-square-planar coordination geometry with two nitrogen donor atoms and a carbon donor atom of the tridentate ligand occupying three of the four coordination sites. The fourth ligand, chloride, is trans to the pyridyl nitrogen. The Pt(1)−N(2) bond (2.12(1) Å) is significantly longer than the Pt(1)−N(1) bond (1.95(1) Å), which could be attributed to the trans influence of the carbon donor being stronger than that of the chloride ligand. Due to the restraint of the tridentate ligand, the N(1)−Pt(1)−C(1) and N(1)−Pt(1)−N(2) angles are 83.9(5) and 79.7(4)°, respectively, instead of the 90° of ideal square-planar coordination. The molecular structure of **3** is similar to that of **2**, with the distances Pd(1)−N(1) and Pd(1)−N(2) and angles N(1)−Pd(1)−C(1) and N(1)−Pd(1)−N(2) of 1.968(5) Å, 2.169(5) Å, 82.2(2)°, and 79.6(2)°, respectively (see Figure 2).

As shown in Figure 3, molecules of **2** form face-to-face molecular pairs by dual hydrogen bonding between the chloride ligand in one molecule and the amino hydrogen atom of an adjacent molecule. The Pt···Pt distance within a molecular pair is ∼3.52 Å, about twice the van der Waals radius of Pt (1.7−1.8 Å), implying that either very weak or no metal−metal interactions contribute to the formation of molecular pairs. The neighboring molecular pairs extend the hydrogen-bonding network through the amino hydrogen atoms of one molecular pair and the chloride ligands of the other molecular pair to form quadruplex units in the crystal lattice of **2**. The average hydrogen-bonded N···Cl distance is ∼3.36 Å. A similar quadruplex arrangement is present in the crystal lattice of **3** with the average N···Cl and Pd···Pd distances of ∼3.41 and ∼3.49 Å, respectively. Interestingly, there are open channels along the *a* axis, with the cocrystallized CH_2Cl_2 and toluene solvent molecules residing inside (see Figure 4).

Reactions of 2 and 3 with Potassium *tert*-Butoxide and Dihydrogen. When compound **2** is treated with the strong base KO^{t}Bu, it readily loses one of the amino protons and the chloride ligand to form the corresponding cyclometalated amido Pt(II) species (Scheme 5). This displays a deep red color, presumably due to n(N)→d(Pt) charge transfer. In a coordinating solvent, such as THF, 1 equiv of KO^{t}Bu can convert compound **2** to the amido complex completely, while in a noncoordinating solvent, such as benzene and toluene, a large excess of KO^{t}Bu is required to complete the conversion. Presumably a THF molecule can coordinate to the platinum center in the amido complex, which helps stabilize the amido product. In the case of benzene, more O^{t}Bu$^-$ anions are required to provide a O^{t}Bu$^-$ ligand to complete the conversion. Compound **2** was converted to the amido species completely in the presence of a large excess (∼5 equiv) of KO^{t}Bu (the first step in Scheme 5). However, the isolation of the crystalline amido complex **4** only gave a ∼36% yield (the second step in Scheme 5). The very broad NMR spectrum of **4** in C_6D_6 at room temperature indicates a highly fluxional species in solution, but the actual existing form in solution has not been identified yet. The fluxionality of the amido complex might originate from the rapid exchange of the alkoxide groups or the rapid equilibrium between the alkoxide aggregates of the amido species. On the basis of the crystal structure and the NMR spectra, we postulate that the amido complex exists in

(12) (a) Cárdenas, D. J.; Echavarren, A. M.; Ramírez de Arellano, M. C. *Organometallics* **1999**, *18*, 3337−3341. (b) Van Houten, K. A.; Heath, D. C.; Barringer, C. A.; Rheingold, A. L.; Pilato, R. S. *Inorg. Chem.* **1998**, *37*, 4647−4653. (c) Neve, F.; Crispini, A.; Campagna, S. *Inorg. Chem.* **1997**, *36*, 6150−6156. (d) Lai, S. W.; Cheung, T. C.; Chan, M. C. W.; Cheung, K. K.; Peng, S. M.; Che, C. M. *Inorg. Chem.* **2000**, *39*, 255−262. (e) Albrecht, M.; Lutz, M.; Spek, A. L.; van Koten, G. *Nature* **2000**, *406*, 970−974. (f) Nonoyama, M.; Nakajima, K. *Polyhedron* **1999**, *18*, 533−543. (g) Lai, S. W.; Chan, M. C. W.; Cheung, K. K.; Peng, S. M.; Che, C. M. *Organometallics* **1999**, *18*, 3991−3997.

(13) Minghetti, G.; Cinellu, M. A.; Chelucci, G.; Gladiali, S.; Demartin, F.; Manassero, M. *J. Organomet. Chem.* **1986**, *307*, 107−114.

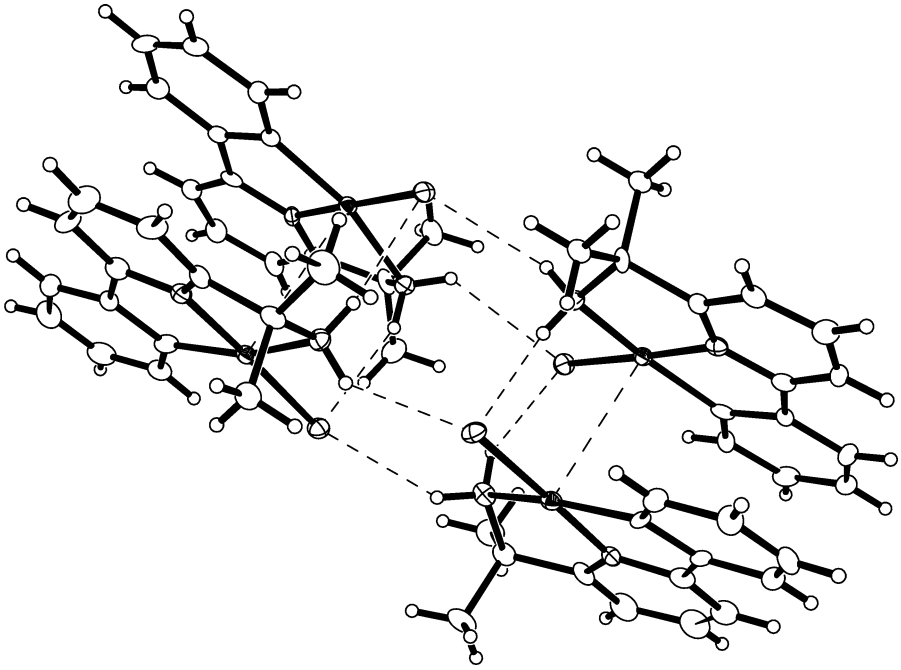


Figure 3. Diagram showing a quadruplex of **2**.

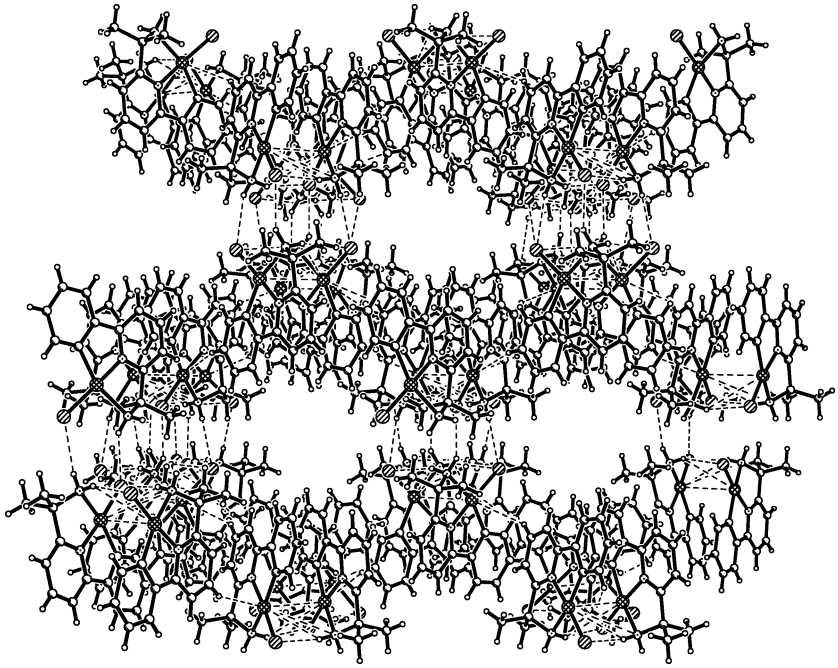


Figure 4. Diagram showing the open channels along the *a* axis in the crystal lattice of **3**.

solution as $K^+[Pt(pap)(O^tBu)]^-$ interacting with the $K^+O^tBu^-$ ion pairs, possibly in an aggregated form. The attempt to isolate crystals suitable for an X-ray diffraction study of the amido complex from the 1:1 (compound **2**:KO^tBu) ratio reaction in THF failed. It seems that the excess KO^tBu helps form an aggregate that crystallizes more easily.

The cyclometalated amido Pt(II) complex **4** has been isolated as an adduct formulated as $[Pt(pap)]_2(KCl)(KO^tBu)_8$, whose structure has been confirmed by single-crystal X-ray diffraction and is shown in Figure 5. Each molecule of **4** contains two Pt(pap) units and a ribbon of alternating K^+ cations and oxygen atoms from $^tBuO^-$ anions, which wraps around a chloride anion to form the inner "core". There are electrostatic interactions between the chloride anion and seven of the nine K^+ cations (except K(2) and K(8)) with an average interacting distance of 3.209(4) Å. The formation of an alkaline metal−oxygen network templated by a chloride ion through electrostatic interactions has also been observed in $LnNa_8(O^tBu)_{10}Cl$ (Ln = Eu, Y) by Evans et al.[14] In compound **4**, two Pt(pap) moieties are attached to each open side of the "core", respectively, through Pt(1)−O(1), N(2)−K(2), Pt(2)−O(8), and N(4)−K(8) bonds, π interactions between the phenyl rings of the pap ligands and K(1) and K(9) cations, and interactions between the nitrogen atoms and the K(4) and K(6) cations. The whole molecule has a pseudo C_2 symmetry along the Cl(1)−

(14) Evans, W. J.; Sollberger, M. S.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 4120−4127.

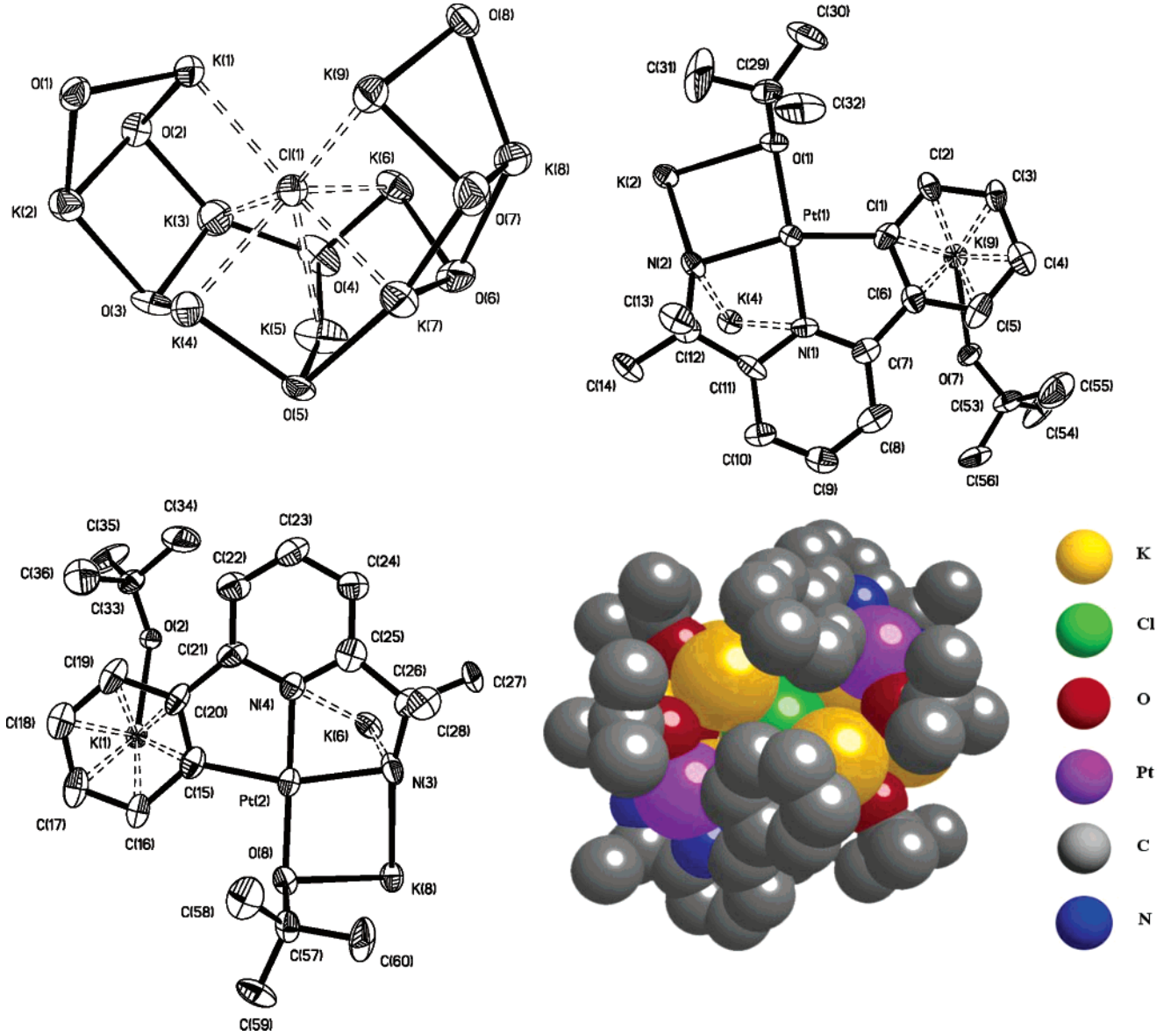
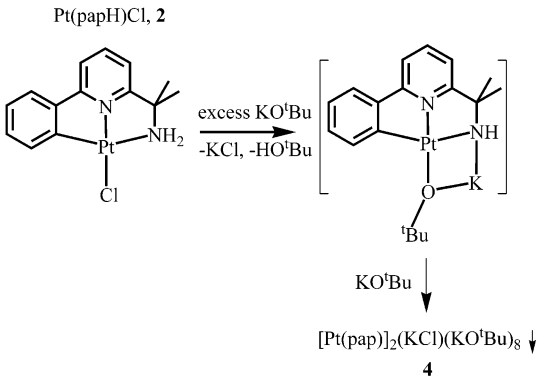


Figure 5. Molecular structure of **4**: (upper left) structure of the K_9O_8Cl core, with all the ^{t}Bu groups omitted for clarity; (upper right and bottom left) structure of $K^+[Pt(pap)(O^tBu)]^-$, interacting with two other K^+ cations; (bottom right) space-filling diagram.

Scheme 5. Reaction of 2 with KO^{t}Bu

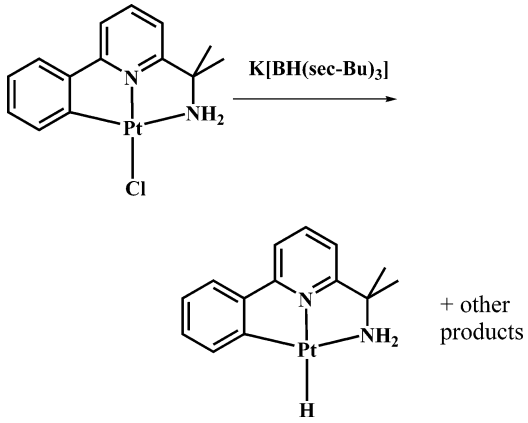


K(5) direction. Each Pt center again adopts a distorted-square-planar geometry with C-N-N donor atoms from the pap ligand occupying three coordination sites and one O donor atom from the O^{t}Bu$^-$ anion occupying the fourth site trans to the pyridyl nitrogen atom. The Pt(1)−C(1) bond in **4** is slightly longer than in **2**, while the Pt(1)−N(2) bond in **4** is slightly shorter than in **2**.

Similar to the case for the Ru(II) amido complexes, **4** is extremely air-sensitive in solution but stable in the solid state for several hours. Unlike the Ru amido complexes that heterolytically split dihydrogen readily in solution to form the corresponding hydrido amino species, the solution of **4** does not react with dihydrogen even under 3 atm of dihydrogen at 60 °C. The amido complex solution obtained from the 1:1 (compound **2**:KO^{t}Bu) reaction in THF also does not react with 3 atm dihydrogen. Cowan and Trogler reported that the hydrogenolysis of *trans*-$Pt(PEt_3)_2H(NHPh)$ produced[15a] $Pt(PEt_3)_2H_2$ and $PhNH_2$ via an associative mechanism.[15b] No parallel reactivity was observed in the present work, and the reason for this is not fully understood yet. Unlike compound **2**, compound **3** reacts with KO^{t}Bu in solution to afford a complicated, unidentified mixture,

(15) (a) Cowan, R. L.; Trogler, W. C. *Organometallics* **1987**, *6*, 2451−2453. (b) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750−4761.

Scheme 6. Reaction of 2 with K[BH(ˢBu)₃]



which can be reduced to Pd(0) under 3 atm of H_2 gas at room temperature.

Reactions of 2 with $NaBH_4$ and K((ˢBu)₃BH). The Pt(II) hydride complex Pt(bipy-C)H was made by hydride transfer from $NaBH_4$ to Pt(bipy-C)Cl.[8] However, the reaction of compound **2** with $NaBH_4$ in alcohol solution produces Pt(0) directly instead of the desired platinum hydride Pt(papH)H (**5**). The compound **5** is thought to be present as an impure product from the reaction of compound **2** with 1 equiv of K[BH(ˢBu)₃] (Scheme 6). The ^1H NMR spectrum of the crude product shows a signal at −11.41 ppm with platinum satellites ($^1J_{Pt-H} = 1409.4$ Hz) thought to be due to **5**, on the basis of the similarity to Pt(bipy-C)H (−13.6 ppm, $^1J_{Pt-H} = 1606$ Hz). Compound **5** in this mixture does not lose dihydrogen under argon or vacuum. It does not react with excess acetophenone and does not catalyze its hydrogenation when under 3 atm of H_2. These properties are in contrast with those of the ketone hydrogenation catalysts *trans*-$RuH_2(H_2NCMe_2CMe_2NH_2)$(binap) and *trans*-$RuH_2(H_2NCMe_2CMe_2NH_2)(PPh_3)_2$, which are only stable under dihydrogen and rapidly react with acetophenone.[2a,b]

Conclusions

In summary, the novel $papH_2$ ligand and its cyclometalated Pt(II) and Pd(II) complexes Pt(papH)Cl and Pd(papH)Cl have been synthesized and fully characterized. Bearing an amino group in the papH ligand, the compound Pt(papH)Cl reacts readily with KOᵗBu in solution to form the corresponding amido complex K[Pt(pap)(OᵗBu)]. While the dehydrohalogenation reaction produced an amido complex, as in the case of our ruthenium catalysts, this complex still contains a coordinated alkoxide, unlike the ruthenium catalysts. The Pt(II) amido complex has been isolated as $[Pt(pap)]_2(KO^tBu)_8(KCl)$, with O^tBu^- anions coordinated to Pt(II) centers and K^+ cations bonded to the amido nitrogen donor atoms. This may be relevant to Hartmann and Chen's explanation for the beneficial effect of potassium ions on the activity of Noyori ketone hydrogenation catalysts. Unfortunately, $[Pt(pap)]_2(KO^tBu)_8(KCl)$ does not split dihydrogen to form the corresponding hydrido amine Pt(II) complex, presumably because the coordinated O^tBu^- ligand is trans to the pyridine nitrogen donor that has a relatively weak trans influence and, thus, might not dissociate easily to allow dihydrogen to enter the coordination sphere. The fact that the independently prepared hydridoamine complex Pt(papH)H does not react with acetophenone might be explained by two factors. First, the complex might be a poor hydride donor, because this ligand is trans to the low-trans-influence nitrogen donor. Second, it does not have the geometry of the ruthenium diamine dihydride catalysts that have a hydride *fac* to the chelating amine, thereby enabling an alignment of M−H and N−H bonds by an MH···HN hydridic−protonic interaction.[1a,2] The research on group 10 complexes of ligands with a NCN donor set, where one of the nitrogen donor atoms is from an amido group, is being conducted currently in our laboratory. Such a ligand might remedy the problems identified here, because the carbon donor in the middle has a strong trans influence that may labilize the trans ligand and increase the hydridic character of a Pt(N−C−N)H complex. These are crucial characteristics of ketone hydrogenation catalysts.

Experimental Section

Unless otherwise stated, all preparations and manipulations were carried out under a purified argon atmosphere with the use of standard Schlenk, vacuum line, and glovebox techniques in dry, oxygen-free solvents. The workup of organic products was conducted in air. All solvents used in the syntheses and spectroscopic measurements were purified according to the literature methods. Deuterated solvents were degassed and dried over molecular sieves. K_2PtCl_4 was purchased from Strem Chemical Co. All other chemicals were purchased from Aldrich Chemical Co. NMR spectra were recorded on Varian Unity 500 and 400 and Gemini 300 MHz spectrometers. ^1H chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. Elemental analyses were done in the Chemistry Department.

Synthesis of 1a. BuLi (1.6 M in hexanes, 31 mL, 50 mmol) was diluted with 30 mL of THF. The resulting solution was cooled to −95 °C. Then 2,6-dibromopyridine (11.85 g in 70 mL of THF, 50 mmol) was added slowly with vigorous stirring. The resulting dark green suspension was stirred at −95 °C for 15 min, followed by the addition of 6 mL of acetone. The resulting mixture was further stirred at −95 °C for 30 min, warmed to ambient temperature, and stirred overnight to afford an orange solution. A saturated NH_4Cl solution (50 mL) was added with vigorous stirring. The organic layer was combined with the CH_2Cl_2 extract of the aqueous layer, washed with brine, and dried over Na_2SO_4. The removal of the solvents gave a brown oil of crude **1a** in 96% yield (10.4 g). The crude product was used without further purification. ^1H NMR ($CDCl_3$, 25 °C, ppm): δ 7.59 (t, $J = 7.8$ Hz, 1H), 7.40 (dd, $J = 7.8$ Hz, $J = 2.2$ Hz, 2H), 4.24 (s, br, 1H, OH), 1.57 (s, 6H, CH_3).

Synthesis of 1b. To a solution of **1a** (5.00 g, 0.023 mol) in 20 mL of CH_3CN was added 10 mL of $BF_3{\cdot}Et_2O$. The resulting solution was refluxed for 72 h, cooled to ambient temperature, neutralized with NaOH aqueous solution, and extracted with CH_2Cl_2. The CH_2Cl_2 extracts were combined, washed with brine, and dried over Na_2SO_4. The solvent was then removed under vacuum, and the residue was flushed through a silica gel column to afford, after evaporation, the white solid **1b** in 30% yield (1.77 g). ^1H NMR ($CDCl_3$, 25 °C, ppm): δ 7.58 (t, $J = 8.0$ Hz, 1H), 7.39 (dd, $J = 8.0$, $J = 3.0$ Hz, 2H), 6.99 (s, br, 1H, NH), 2.06 (s, 3H, $COCH_3$), 1.76 (s, 6H, CH_3).

Synthesis of 1c. To a mixture of $Pd(PPh_3)_4$ (0.26 g, 0.22 mmol) and **1b** (1.9 g, 7.4 mmol) in 16 mL of toluene was added $PhB(OH)_2$ (1.09 g, 8.88 mmol, in 5 mL of EtOH) and Na_2CO_3 (1.57 g, 14.8 mmol, in 8 mL of H_2O). The resulting mixture was then refluxed for 16.5 h. The organic phase was combined with the CH_2Cl_2 extract of the aqueous phase and dried under

Table 1. Crystallographic Data

	2	**3**	**4**
formula	$C_{14}H_{15}N_2ClPt$	$C_{14}H_{15}N_2ClPd\cdot 0.25C_7H_8\cdot 0.25CH_2Cl_2$	$C_{60}H_{100}N_4O_8ClK_9Pt_2\cdot 1.5C_6H_6$
fw	441.82	397.40	1900.15
T, K	150(2)	150(2)	150(2)
wavelength, Å	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	orthorhombic	monoclinic
space group	*Pc*	$Pna2_1$	$P2_1/n$
a, Å	17.456(4)	21.336(4)	23.154(5)
b, Å	13.216(3)	21.469(4)	14.737(3)
c, Å	12.616(3)	14.219(3)	27.657(6)
α, deg	90	90	90
β, deg	104.71(3)	90	114.75(3)
γ, deg	90	90	90
V, Å^3	2815.1(10)	6513(2)	8570(3)
Z	8	16	4
D_{calcd}, g cm^{-3}	2.085	1.621	1.473
μ, cm^{-1}	101.42	13.78	37.77
2θ(max), deg	55.00	54.96	54.96
no. of rflns	22922	53425	66539
no, of rflns used	11271	14488	19507
no. of params	650	735	783
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0439 wR2 = 0.0945	R1 = 0.0442 wR2 = 0.0898	R1 = 0.0740 wR2 = 0.1490
R indices (all data)[a]	R1 = 0.0627 wR2 = 0.1043	R1 = 0.0740 wR2 = 0.1023	R1 = 0.2247 wR2 = 0.2024
goodness of fit on F^2	1.022	1.056	0.947

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w[(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

vacuum. The residue was flushed through a silica gel column to afford, after evaporation, the white solid **1c** in 86% yield (1.62 g). ^{1}H NMR ($CDCl_3$, 25 °C, ppm): δ 8.04 (m, 2H), 7.83 (t, J = 7.8 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.60−7.43 (m, 3H), 7.38 (d, J = 7.8 Hz, 1H), 2.13 (s, 3H, $COCH_3$), 1.85 (s, 6H, CH_3). The NH signal was not observed. ^{13}C NMR: δ 169.4, 164.3, 155.1, 139.2, 138.0, 129.1, 128.8, 126.8, 118.5, 117.9, 56.7, 27.5, 24.9. Anal. Calcd for $C_{16}H_{18}N_2O$: C, 75.56; H, 7.13; N, 11.01. Found: C, 75.76; H, 7.40; N, 11.08.

Synthesis of papH$_2$ (1). 1c (0.6 g, 2.36 mmol) was refluxed in 40 mL of 6 M HCl for 20 h in air. The resulting solution was neutralized with NaOH (aq) and extracted with CH_2Cl_2. The removal of the solvent afforded a colorless oil of papH$_2$ in 96% yield (0.48 g). ^{1}H NMR ($CDCl_3$, 25 °C, ppm): δ 8.14 (m, 2H), 7.77 (t, J = 7.8 Hz, 1H), 7.65 (dd, J = 7.8 Hz, J = 0.9 Hz, 1H), 7.58−7.46 (m, 3H), 7.43 (dd, J = 7.8 Hz, J = 0.9 Hz, 1H), 2.11 (s, 2H), 1.62 (s, 6H). ^{13}C NMR: δ 167.8, 155.7, 139.6, 137.3, 129.0, 128.7, 126.9, 117.8, 116.8, 54.0, 31.1. Anal. Calcd for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.19. Found: C, 79.52; H, 7.33; N, 12.99.

Synthesis of Pt(papH)Cl (2). K_2PtCl_4 (0.415 g, 1 mmol) and papH$_2$ (0.3 g, 1.4 mmol) were refluxed in 60 mL of 1 M HCl aqueous solution in air for 4 h until the red color of K_2PtCl_4 completely disappeared. The mixture was cooled to ambient temperature, and the light yellow precipitate of **2** was collected by vacuum filtration, washed with water, ethanol, and ether, and dried under vacuum (70% yield, 0.31 g). ^{1}H NMR (CD_2Cl_2, 25 °C, ppm): δ 7.57 (t, J = 7.8 Hz, 1H), 7.47 (dd, J = 6.6 Hz, J = 1.2 Hz, 1H), 7.20−7.10 (m, 2H), 7.10−6.98 (m, 2H), 6.65 (d, J = 7.8 Hz, 1H), 4.54 (s, 2H), 1.73 (s, 6H). ^{13}C NMR: δ 165.6, 163.7, 147.0, 141.4, 137.5, 133.0, 129.6, 123.6, 122.9, 117.7, 116.9, 65.4, 30.3. Anal. Calcd for $C_{14}H_{15}N_2PtCl$: C, 38.06; H, 3.42; N, 6.34. Found: C, 37.99; H, 3.57; N, 6.30.

Synthesis of Pd(papH)Cl (3). $PdCl_2$ (0.198 g, 1.1 mmol) and papH$_2$ (0.250 g, 1.2 mmol) were heated in 100 mL of 0.06 M HCl aqueous solution in air until the color of $PdCl_2$ disappeared (<3 h). The mixture was cooled to ambient temperature, and the resulting light yellow precipitate of **3** was collected by vacuum filtration and washed with water, ethanol, and ether (88% yield, 0.35 g). ^{1}H NMR (CD_2Cl_2, 25 °C, ppm): δ 7.57 (t, J = 7.8 Hz, 1H), 7.34 (dd, J = 7.5 Hz, J = 1.2 Hz, 1H), 7.18−7.06 (m, 2H), 6.97 (td, J = 7.5 Hz, J = 1.2 Hz, 1H), 6.91−6.80 (m, 2H), 3.94 (s, 2H), 1.74 (s, 6H). ^{13}C NMR: δ 166.4, 163.0, 154.4, 147.9, 138.4, 134.6, 129.0, 123.9,

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

Compound **2**

Pt(1)−N(1)	1.95(1)	Pt(3)−N(5)	1.95(1)
Pt(1)−C(1)	1.98(1)	Pt(3)−C(29)	1.98 (1)
Pt(1)−N(2)	2.12 (1)	Pt(3)−N(6)	2.12 (1)
Pt(1)−Cl(1)	2.322(3)	Pt(3)−Cl(3)	2.329(4)
Pt(2)−N(3)	1.97(1)	Pt(4)−N(7)	1.94 (1)
Pt(2)−C(15)	1.99 (2)	Pt(4)−C(43)	1.99(1)
Pt(2)−N(4)	2.13 (1)	Pt(4)−N(8)	2.12 (1)
Pt(2)−Cl(2)	2.312(3)	Pt(4)−Cl(4)	2.304(3)
N(1)−Pt(1)−C(1)	83.9(5)	N(5)−Pt(3)−C(29)	82.9(5)
N(1)−Pt(1)−N(2)	79.7(4)	N(5)−Pt(3)−N(6)	80.5(4)
C(1)−Pt(1)−N(2)	162.9(5)	C(29)−Pt(3)−N(6)	162.8(5)
N(1)−Pt(1)−Cl(1)	177.5(3)	N(5)−Pt(3)−Cl(3)	177.3(3)
C(1)−Pt(1)−Cl(1)	98.0(4)	C(29)−Pt(3)−Cl(3)	98.1(4)
N(2)−Pt(1)−Cl(1)	98.5(3)	N(6)−Pt(3)−Cl(3)	98.6(3)
N(3)−Pt(2)−C(15)	81.6(5)	N(7)−Pt(4)−C(43)	82.6(5)
N(3)−Pt(2)−N(4)	81.0(4)	N(7)−Pt(4)−N(8)	80.6(5)
C(15)−Pt(2)−N(4)	161.9(5)	C(43)−Pt(4)−N(8)	163.0(5)
N(3)−Pt(2)−Cl(2)	177.9(3)	N(7)−Pt(4)−Cl(4)	179.0(4)
C(15)−Pt(2)−Cl(2)	98.4(4)	C(43)−Pt(4)−Cl(4)	97.9(4)
N(4)−Pt(2)−Cl(2)	99.2(3)	N(8)−Pt(4)−Cl(4)	98.9(3)

Compound **3**

Pd(1)−N(1)	1.968(5)	Pd(3)−N(5)	1.956(5)
Pd(1)−C(1)	2.003(6)	Pd(3)−C(29)	1.995(6)
Pd(1)−N(2)	2.169(5)	Pd(3)−N(6)	2.177(5)
Pd(1)−Cl(1)	2.314(2)	Pd(3)−Cl(3)	2.334(2)
Pd(2)−N(3)	1.958(5)	Pd(4)−N(7)	1.966(5)
Pd(2)−C(15)	1.981(6)	Pd(4)−C(43)	1.984(6)
Pd(2)−N(4)	2.158(5)	Pd(4)−N(8)	2.165(5)
Pd(2)−Cl(2)	2.326(2)	Pd(4)−Cl(4)	2.319(2)
N(1)−Pd(1)−C(1)	82.2(2)	N(5)−Pd(3)−C(29)	82.4(2)
N(1)−Pd(1)−N(2)	79.6(2)	N(5)−Pd(3)−N(6)	79.06(19)
C(1)−Pd(1)−N(2)	160.7(2)	C(29)−Pd(3)−N(6)	160.6(2)
N(1)−Pd(1)−Cl(1)	174.7(1)	N(5)−Pd(3)−Cl(3)	178.0(1)
C(1)−Pd(1)−Cl(1)	96.8(2)	C(29)−Pd(3)−Cl(3)	97.4(2)
N(2)−Pd(1)−Cl(1)	101.9(1)	N(6)−Pd(3)−Cl(3)	101.2(1)
N(3)−Pd(2)−C(15)	82.5(2)	N(7)−Pd(4)−C(43)	82.4(3)
N(3)−Pd(2)−N(4)	78.8(2)	N(7)−Pd(4)−N(8)	79.7(2)
C(15)−Pd(2)−N(4)	160.6(2)	C(43)−Pd(4)−N(8)	160.8(2)
N(3)−Pd(2)−Cl(2)	175.7(1)	N(7)−Pd(4)−Cl(4)	173.0(1)
C(15)−Pd(2)−Cl(2)	97.4(2)	C(43)−Pd(4)−Cl(4)	96.9(2)
N(4)−Pd(2)−Cl(2)	101.8(1)	N(8)−Pd(4)−Cl(4)	101.8(1)

Compound **4**

Pt(1)−N(1)	1.939(9)	K(4)−N(1)	3.308(9)
Pt(1)−C(1)	2.02(1)	K(6)−N(4)	2.99(1)
Pt(1)−O(1)	2.039(8)	K(6)−N(3)	3.45(1)
Pt(1)−N(2)	2.096(9)	K(9)−C(3)	3.20(1)
Pt(2)−N(3)	1.95(1)	K(9)−C(4)	3.22(1)
Pt(2)−C(15)	2.00(1)	K(9)−C(2)	3.34(1)
Pt(2)−O(8)	2.019(9)	K(9)−C(5)	3.39(1)
Pt(2)−N(4)	2.12(1)	K(9)−C(6)	3.48(1)
K(2)−N(2)	2.85(1)	K(9)−C(1)	3.52(1)
K(8)−N(4)	2.91(1)	Cl(1)−K(1)	3.117(4)
K(1)−C(18)	3.26(1)	Cl(1)−K(6)	3.140(4)
K(1)−C(19)	3.28(1)	Cl(1)−K(4)	3.150(4)
K(1)−C(17)	3.29(1)	Cl(1)−K(9)	3.163(4)
K(1)−C(20)	3.39(1)	Cl(1)−K(7)	3.209(4)
K(1)−C(16)	3.42(1)	Cl(1)−K(3)	3.295(4)
K(1)−C(15)	3.48(1)	Cl(1)−K(5)	3.388(5)
K(4)−N(2)	3.01(1)		
N(1)−Pt(1)−C(1)	82.4(5)	N(3)−Pt(2)−C(15)	80.5(5)
N(1)−Pt(1)−O(1)	176.5(3)	N(3)−Pt(2)−O(8)	179.1(4)
C(1)−Pt(1)−O(1)	99.4(5)	C(15)−Pt(2)−O(8)	99.1(5)
N(1)−Pt(1)−N(2)	81.3(4)	N(3)−Pt(2)−N(4)	81.0(4)
C(1)−Pt(1)−N(2)	163.0(5)	C(15)−Pt(2)−N(4)	161.1(5)
O(1)−Pt(1)−N(2)	96.8(4)	O(8)−Pt(2)−N(4)	99.3(4)

123.1, 117.6, 116.9, 63.3, 30.9. Anal. Calcd for $C_{14}H_{15}N_2PdCl\cdot 0.25C_7H_8$: C, 50.29; H, 4.55; N, 7.45. Found: C, 50.06; H, 4.71; N, 7.05.

Synthesis of [Pt(pap)]$_2$(KO^{t}Bu)$_8$(KCl) (4). KO^{t}Bu (112 mg, 1 mmol) and **2** (88 mg, 0.2 mmol) were mixed in benzene and stirred vigorously for 15 h to produce a deep red solution with a white precipitate. The solid was removed by filtration through Celite. The subsequent slow evaporation of the filtrate afforded red crystals of **4**, which were washed with hexanes and dried under vacuum (36% yield, 68 mg). ^{1}H NMR (C_6D_6, 25 °C, ppm): δ 7.52 (d, br, J = 8.0 Hz, 2H), 7.37 (m, br, 4H), 7.16 (d, br, J = 8.0 Hz, 2H), 6.78 (d, br, J = 7.6 Hz, 2H), 6.71 (d, br, J = 7.2 Hz, 2H), 6.19 (d, br, J = 7.6 Hz, 2H), 1.39 (s, br; 18H), 1.25 (s, br, 12H), 1.20 (s, br, 54H). The amido N−H signal was not observed. ^{13}C NMR: δ 166.0 (br), 137.4 (br), 134.4 (br), 132.8 (br), 131.0 (br), 129.2 (br), 124.3 (br), 121.7 (br), 118.0 (br), 117.4 (br), 115.0 (br), 72.3 (br), 69.5 (br), 66.9 (br), 35.6 (br), 35.4 (br), 32.0 (br). Anal. Calcd for $C_{60}H_{100}N_4ClO_8K_9Pt_2\cdot 1.5C_6H_6$: C, 43.62; H, 5.78; N, 2.95. Found: C, 43.22; H, 5.37; N, 2.79.

Synthesis of Pt(papH)H (5). To a solution of **2** (88 mg, 3 mL of THF, 0.2 mmol) was added K((s^{t}Bu)$_3$BH) (0.2 mL, 1.0 M in THF, 0.2 mmol). The mixture was stirred overnight and filtered through Celite. Hexanes (10 mL) was added to the filtrate to precipitate a dark orange solid, which was collected by filtration, washed with hexanes, and dried under vacuum (yield of the crude **5**: 24 mg). The hydride was not successfully purified by recrystallization. ^{1}H NMR (C_6D_6, 25 °C): δ −11.41 (satellite, $^1J_{Pt-H}$ = 1409.4 Hz).

X-ray Crystallographic Analysis. Single crystals of **2** and **3** were obtained from slow diffusion of toluene into their CH_2Cl_2 solutions, respectively, while single crystals of **4** were obtained from slow evaporation of its benzene solution. The crystals were mounted at the end of glass fibers. Single-crystal X-ray diffraction data were collected using a Nonius Kappa-CCD diffractometer with Mo Kα radiation (λ = 0.710 73 Å) operating at 50 kV and 30 mA at 150 K. No significant decay was observed during the data collection. The data were integrated and scaled using the Denzo-SMN package. The structures were solved and refined using SHELXTL V6.10.[16] Neutral atom scattering factors were taken from ref 17. All structures were solved by the Patterson method. Crystals of **2** and **4** belong to the monoclinic space groups *Pc* and $P2_1/n$, respectively, while crystals of **3** belong to the orthorhombic space group $Pna2_1$. Benzene molecules were located in the crystal lattice of **4** (1.5 benzene per molecule of **4**). Toluene and CH_2Cl_2 molecules were located in the crystal lattice of **3** (0.25 CH_2Cl_2 and 0.25 toluene per molecule of **3**). All non-hydrogen atoms were refined anisotropically, the positions for all hydrogen atoms were calculated, and their contributions were included in the structure factor calculations. Crystallographic data are given in Table 1, and selected bond lengths and angles are given in Table 2.

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Supporting Information Available: Tables giving crystallographic data for **2**−**4**; the data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0496232

(16) SHELXTL NT Crystal Structure Analysis Package, Version 6.10; Bruker AXS, Analytical X-ray System, Madison, WI, 2000.

(17) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4, Table 2.2A.