

Preparation and Reactivity of a Monomeric Octahedral Platinum(IV) Amido Complex

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Synthesis and isolation of the monomeric octahedral platinum(IV) amido complex (NCN)PtMe₂NHPh have been accomplished upon deprotonation of the amine complex [(NCN)PtMe₂(NH₂Ph)][OTf]. The preliminary reactivity of the amido ligand has been explored.

Several studies have revealed that formally anionic heteroatomic ligands (e.g., amido, alkoxo, and related ligands) coordinated to late transition metals in low oxidation states can be quite basic and/or nucleophilic.^{1–11} For example, ruthenium(II) complexes can initiate intermolecular deprotonation of some C–H bonds to form amine/carbanion ion pairs,^{2,12–16} and an octahedral iron(II) parent amido complex has been suggested to undergo an intermolecular nucleophilic addition to free carbon monoxide.¹⁸ Recently, we have demonstrated that monomeric copper(I) amido, alkoxo, and sulfido complexes catalyze conjugate addition of amines, alcohols, and thiols to electron-deficient olefins including some vinyl arenes.^{19–22} The formal disruption of ligand-to-metal π donation due to filled $d\pi$ orbitals likely plays an important role in the reactivity of these systems by enhancing the nucleophilicity and basicity of amido, alkoxo, and related ligands.^{4,8–10}

An important distinction between amido, alkoxo, oxo, nitrene, and related ligands coordinated to middle/late transition-metal centers in high versus low oxidation state is the predilection of the former toward odd-electron radical chemistry, while the latter class of complexes typically undergoes “even-electron” reactivity.¹⁰ For example, paramagnetic ruthenium(III) hydroxo, iron(III) alkoxo, and other high oxidation oxo and imido complexes initiate C–H bond cleavage via net bond homolysis (i.e., hydrogen-atom abstraction).^{7,23,24} In contrast, diamagnetic octahedral ruthenium(II) and iron(II) complexes react with C–H bonds via even-electron acid/base reactions,^{2,12–15} and ruthenium(II) amido/hydroxo, iridium(III) methoxo, and rhodium(I) aryloxo systems activate C–H bonds through even-electron *net* 1,2-addition of C–H bonds across the M–X (X = OR, NHR) ligands.^{25–28}

The combination of a Lewis acidic metal center with a nucleophilic/basic heteroatomic ligand provides an opportunity for metal-mediated transformations. Along these lines, octahedral and d^6 group 10 complexes (Ni, Pd, and Pt) with amido, alkoxo, and related ligands represent a potentially interesting class of systems. The 4+ formal oxidation state should result in a Lewis acidic metal in addition to a filled set of $d\pi$ orbitals. Thus, such complexes might be expected to undergo even-electron chemistry, with the heteroatomic ligand acting as a base or nucleophile. Although four-coordinate palladium(II) amido, alkoxo, and related systems are key intermediates in important

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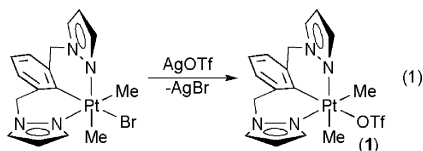
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catalytic C–N and C–O bond-forming processes²⁹ and square-planar nickel(II), palladium(II), and platinum(II) amido complexes are known,^{30,31} examples of fully characterized octahedral and monomeric metal(IV) (metal = nickel, palladium, or platinum) amido complexes are virtually unknown. The preparation and reactivity of tri- μ -amidobis[triammineplatinum(IV)] complexes have been reported,^{32–35} Peters and co-workers studied a platinum(IV) complex with a chelating pincer-type amido ligand, and Goldberg et al. have recently reported the synthesis and reactivity of platinum(IV) sulfonamide complexes.^{36,37}

The reaction of previously reported (NCN)PtMe₂Br³⁸ [NCN = 2,6-(pyrazolyl-CH₂)₂C₆H₃] with silver triflate in refluxing THF results in the formation of (NCN)PtMe₂OTf (**1**; eq 1). The ¹H NMR spectrum of complex **1** displays patterns similar to those of (NCN)PtMe₂Br but with shifted resonances. Thus, we presume that the coordination geometry of **1** is analogous to that of (NCN)PtMe₂Br with a facially coordinated NCN ligand and the triflate trans to the aryl unit. Complex **1** exhibits thermal stability because heating **1** in C₆D₆ at temperatures up to 120 °C for 20 h does not result in decomposition (¹H NMR spectroscopy).



The reaction of **1** with aniline in methylene chloride produces the cationic complex [(NCN)PtMe₂(NH₂Ph)][OTf] (**2**). The poor solubility of **2** in standard organic solvents led us to attempt a counterion exchange to improve the solubility. The reaction of complex **1** with aniline in CH₂Cl₂ followed by the addition of NaBAR₄^F [Ar^F = 3,5-(CF₃)₂C₆H₃] cleanly produces [(NCN)PtMe₂(NH₂Ph)][BAR₄^F] (**3**; eq 2). The solid-state structure of complex **3** has been determined from a single-crystal X-ray diffraction study (Figure 1). The Pt1–N5 bond length is 2.213(2) Å. Though a search of the Cambridge Structural Database did not yield any examples of platinum(II) aniline complexes, Radlowski et al. have reported a platinum(II) complex with two chelating amine ligands with the lengths of the four Pt–N bonds between 2.023(9) and 2.073(9) Å.³⁹

Deprotonation of **2** with BuLi produces the platinum(IV) amido complex (NCN)PtMe₂(NHPh) (**4**; eq 3). A single resonance is observed for the two symmetry-equivalent methyl ligands at 1.42 ppm (singlet with Pt satellites, ²J_{Pt–H} = 72 Hz) in the ¹H NMR spectrum and –8.6 ppm (¹J_{Pt–C} = 688 Hz) in

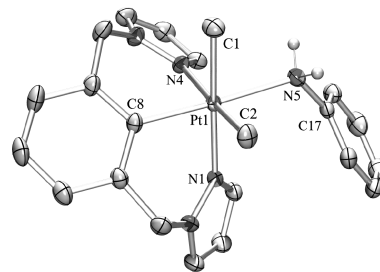
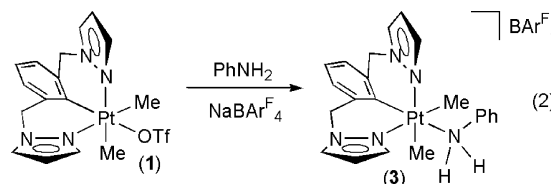
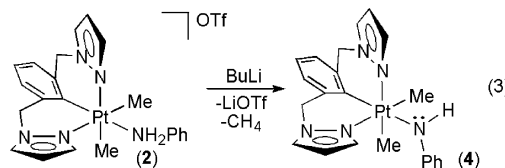


Figure 1. ORTEP of **3** (50% probability; most H atoms and the BAR₄^F counterion are excluded for clarity). Selected bond lengths (Å): Pt1–N5 2.213(2), N5–C17 1.440(3), Pt1–C8 2.022(3). Selected bond angles (deg): Pt1–N5–C17 121.0(2), C8–Pt1–N5 177.59(9).



the ¹³C NMR spectrum (in C₆D₆). The amido H atom resonates at 2.88 ppm as a broad singlet with Pt satellites visible as shoulders. In comparison, the amido H atom of TpRuL₂(NHPh) [L = P(OMe)₃ or PMe₃], also six-coordinate d⁶ anilido complexes, resonates at 1.98 and 2.80 ppm, respectively.¹⁷



A single crystal of **4** suitable for an X-ray diffraction study was grown from a saturated benzene solution, and the solid-state structure is shown in Figure 2. The Pt1–N5 bond length for complex **4** is 2.087(2) Å, which is 0.126 Å shorter than the Pt1–N5 bond length [2.213(2) Å] in the cationic aniline complex **3**. As is expected for platinum(IV) versus ruthenium(II), the Pt1–N5 bond of **4** is slightly shorter than the Ru–N_{amido} bond [2.101(2) Å] of TpRu[P(OMe)₃]₂(NHPh).¹⁷ The anilido lone pair of complex **4** can potentially back-donate into the π* orbitals of the anilido phenyl ring, which would shorten the N_{amido}–C_{phenyl} bond. Indeed, the N5–C17 bond length of complex **4** is 1.376(3) Å, which is shorter than 1.440(3) Å for the cationic complex **3**; however, the orientation of the phenyl substituent of the anilido ligand of **4** is not oriented to maximize overlap with the amido lone pair [the Pt1–N5–C17–C18 dihedral angle is 35.6(3)°]. The twisting of the phenyl ring out of the H_{amido}–N5–C17 plane might be due to a steric interaction between C18(H) and the methyl ligand C15(H). Cowan and Troglar have reported the solid-state structure for the platinum(II) amido complex *trans*-PtH(NHPh)(PEt₃)₂.⁴⁰ Consistent with a comparison between Pt^{II} and Pt^{IV}, the Pt^{II}–N_{amido} bond was found to be longer than that for **4** at 2.125(5) Å, with a N_{amido}–C_{phenyl} bond shorter than that of **4** at 1.343(8) Å. Espinet et al. have also reported the solid-state structure for a platinum(II) amido complex, albeit with a substituted anilido ligand.⁴¹

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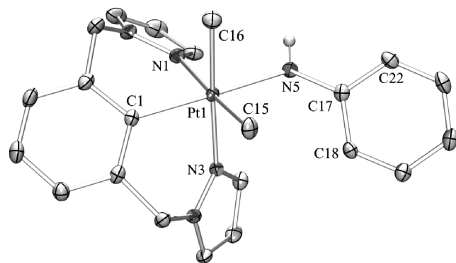
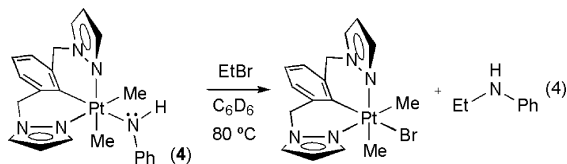


Figure 2. ORTEP of **4** (50% probability; most H atoms are excluded for clarity). Selected bond lengths (Å): Pt1–N5 2.087(2), N5–C17 1.376(3), Pt1–C1 2.046(2). Selected bond angles (deg): Pt1–N5–C17 130.6(1), C1–Pt1–N5 174.65(7).

Although the *p*-iodo substitution precludes a direct comparison, the Pt–N_{amido} bond for *trans*-[PtCl{NH(*p*-IC₆H₄)}](PEt₃)₂ was found to be slightly shorter than that for **4** at 2.006(4) Å.

The downfield region of the ¹H NMR spectrum of complex **4** in toluene-*d*₈ is consistent with N_{amido}–C_{phenyl} bond rotation that is rapid on the NMR time scale: a single triplet is observed for the *m*-anilido protons (7.20 ppm) with overlapping triplet and doublet for the *p*- and *o*-anilido protons (6.59–6.64 ppm), respectively. We conducted variable-temperature NMR studies in an effort to explore the possibility of hindered Pt–N_{amido} and N–C_{phenyl} bond rotation.⁴² Upon cooling to –50 °C, the onset of broadening was observed for the resonances due to the amido phenyl group; however, cooling to –70 °C did not result in decoalescence of these resonances, and we were not able to obtain kinetic data for hindered N–C bond rotation.

We have previously reported that TpRuL₂X (X = OH, NH₂, or NHPh) complexes possess nucleophilic amido/hydroxo ligands.^{2,7,43} In order to directly compare the nucleophilicity of TpRu(PMe₃)₂(NHPh) and complex **4**, we compared the rate of nucleophilic substitution reactions with EtBr (eq 4). At 80 °C, complex **4** reacts with EtBr to produce EtN(H)Ph and (NCN)PtMe₂Br with *k*_{obs} = 1.4(1) × 10^{–4} s^{–1} (*t*_{1/2} ~ 1.4 h). This corresponds to Δ*G*[‡] of 27.0 kcal/mol, smaller than the corresponding Δ*G*[‡] of 29.0 kcal/mol (80 °C) for TpRu(PMe₃)₂(NHPh) (*t*_{1/2} ~ 22 h). Thus, the relative rates of reaction of ethyl bromide with TpRu(PMe₃)₂(NHPh) and complex **4** are not dramatically different, while copper(I) anilido complexes show substantially enhanced reactivity with Δ*G*[‡] values of ~22 kcal/mol at room temperature.



The basicity of the amido and hydroxo ligands for the series of ruthenium complexes has also been examined through reactions with organic substrates with acidic C–H bonds. For example, the reaction of TpRu(PMe₃)₂NHPh with phenylacetylene at 80 °C results in the formation of TpRu(PMe₃)₂(C≡CPh) and free aniline.² Similarly, the reaction of **4** with phenylacetylene produces free aniline and (NCN)PtMe₂(C≡CPh) (**5**) after

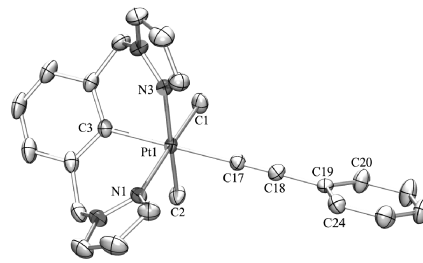
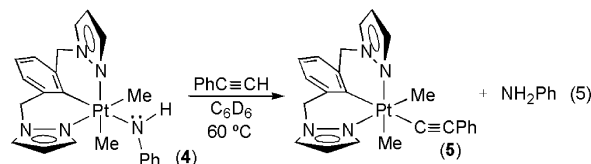
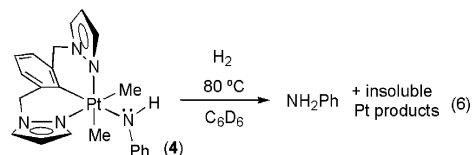


Figure 3. ORTEP of **5** (30% probability; H atoms are excluded for clarity.) Selected bond lengths (Å): Pt1–C17 2.062(5), C17–C18 1.180(8), C18–C19 1.459(7), Pt1–C3 2.065(5). Selected bond angles (deg): Pt1–C17–C18 179.4(6), C17–C18–C19 178.1(7), C3–Pt1–C17 177.3(2).

12 h at 60 °C (eq 5). An X-ray structure has been obtained from a single crystal of **5**, and the data reveal a pseudooctahedral coordination geometry (Figure 3). The Pt1–C17 bond length is 2.062(5) Å, and the acetylide fragment is nearly linear with Pt1–C17–C18 and C17–C18–C19 bond angles of 179.4(6)° and 178.1(7)°, respectively.



In order to test the thermal stability of complex **4**, we heated a C₆D₆ solution of **4** to 120 °C. After 90 h, ethane and methane were observed in minimal quantities (by ¹H NMR spectroscopy) with little change to the resonances due to **4**. The formation of neither aniline nor additional Pt species was observed. Thus, complex **4** is thermally robust. The reaction of complex **4** with H₂ at 80 °C initially results in the formation of a second complex with the {(NCN)PtMe₂} fragment (this complex could not be isolated) with concomitant production of free aniline. Continued heating for 90 h results in a decrease in the resonances due to (NCN)PtMe₂ systems (¹H NMR) and production of free aniline (eq 6). Thus, we presume that dihydrogen is being activated to release aniline and form insoluble Pt decomposition products.



In summary, we have synthesized a new platinum(IV) amido complex. Despite the thermal stability of **4**, the anilido complex reacts with acidic C–H bonds and H₂. Simple nucleophilic substitution reactions with EtBr place the nucleophilicity of the anilido of **4** between that of TpRu(PMe₃)₂NHPh, which reacts more slowly than **4**, and monomeric Cu–NHPh complexes, which react more rapidly than **4**.^{4,8–10}

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Supporting Information Available: Details of the synthesis and characterization of all complexes, reactivity studies, and complete data from the X-ray crystal diffraction studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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