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Synthesis and Reactivity of a Neutral, Three-Coordinate Platinum(II) Complex Featuring Terminal Amido Ligation

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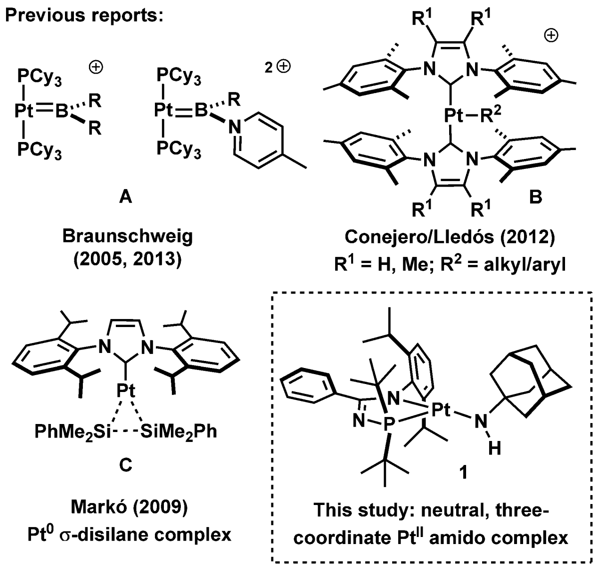
Abstract: *A crystallographically characterized three-coordinate, formally 14 electron Pt^{II} complex **1** featuring terminal amido ligation is reported. Computational analysis revealed relatively weak π donation from the amide lone pair to platinum and supports a 14-electron assignment for **1**. Stoichiometric reactivity studies confirmed the viability of net O–H and C–H addition across, as well as isonitrile insertion into, the terminal platinum–amido linkage of **1**.*



Scheme 1. Previously reported low-coordinate platinum complexes and the three-coordinate, formally 14 electron platinum(II) amido complex **1** featured herein; Cy = cyclohexyl.

Low-coordinate platinum-group metal complexes are commonly invoked as key reactive intermediates in a range of prominent organometallic transformations.[1] In this regard, there is considerable interest in preparing isolable examples of such otherwise transient species, so as to gain a more thorough appreciation of their structural and reactivity properties.

Although the conversion of stable four-coordinate (square-planar), 16-electron complexes into highly reactive three-coordinate,[2] 14-electron species is a commonly invoked mechanistic paradigm in platinum chemistry,[3] isolable three-coordinate Pt^{II} complexes have proven elusive.[4] Indeed, the coordination chemistry of d^8 species of Pt^{II} is almost exclusively dominated by square-planar species. Notwithstanding the utility of "operationally" three-coordinate Pt^{II} compounds, such as those featuring a weak agostic interaction occupying the fourth coordination site,[5] the structural characterization of genuine three-coordinate Pt^{II} species is limited to reports by the groups of Braunschweig[6] and Conejero/Lledós.[7] In each of these systems (**A** and **B** in Scheme 1), the three-coordinate Pt^{II} motif was formed by anion abstraction, thus resulting in (di)cationic complexes. Complexes of type **A** and **B** adopt T-shaped geometries, in keeping with calculations that predict the electronic stabilization of a T-shaped structure for low-spin Pt^{II}.[4] Although the apparently Y-shaped neutral Pt^{II} complex [(IPr)Pt(SiMe$_2$Ph)$_2$] (**C**) was also described,[8] subsequent analysis suggests that this complex can be more appropriately viewed as a platinum(0) σ-disilane species (Scheme 1).[9]

By comparison, isolable three-coordinate, formally 14 electron Pt^{II} complexes featuring terminal amido ligation have not been reported previously, owing in part to the considerable synthetic challenges associated with the preparation of monomeric (nonbridging) species of this type. Notably, such compounds are anticipated to be chemically distinct from **A** and **B**, because of the potential for repulsive interactions between the amido lone pair and the Pt^{II} d^8 metal center.[10] The reactivity and computational investigation of such underexplored platinum(II) amido compounds are of particular significance, in that they would serve to advance our fundamental understanding of the chemical behavior of such low-coordinate, nondative Pt–N species, as well as to provide the basis for developing new catalytic substrate transformations of nitrogen compounds to complement existing methodologies (e.g., hydroamination, Buchwald–Hartwig amination). Herein, we report the first isolable and

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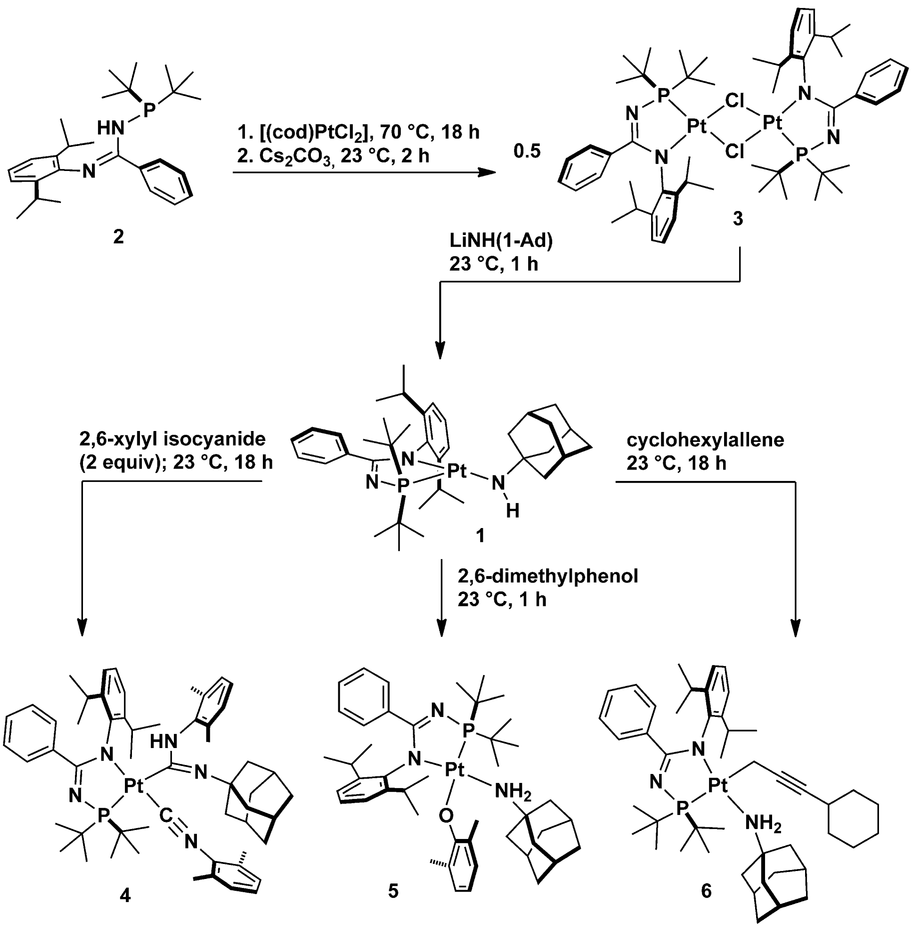
crystallographically characterized three-coordinate Pt^{II} complex featuring terminal amido ligation (complex **1**, Scheme 1). The stability of the complex is ensured by a sterically demanding *N*-phosphinoamidinate ancillary coligand.[11] DFT calculations suggest relatively weak π donation from the amide lone pair to the platinum center and support a 14-electron assignment for **1**. Stoichiometric reactivity studies confirmed the viability of net O–H and C–H addition across, as well as isonitrile insertion into, the Pt–NH(1-adamantyl) linkage of the formally 14 electron complex **1**. DFT calculations also provided insight into the reactivity and mechanisms of such O–H and C–H addition reactions.

Our synthetic route to the targeted three-coordinate Pt^{II} amido complex **1** began with the treatment of the *N*-phosphinoamidine **2** with $[(cod)PtCl_2]$, followed by exposure to a base to afford the dinuclear platinum(II) *N*-phosphinoamidinate complex **3** as a yellow solid in 60% yield (Scheme 2). The dinuclear character of **3** was confirmed on the basis of X-ray diffraction data (see Figure S1).[12] The treatment of **3** (0.5 equiv) with LiNH(1-Ad) afforded **1** as an orange solid in 75% yield. Both NMR spectroscopy and elemental analysis indicated that **1** had the empirical formula [(P,N)Pt(NH(1-Ad))], without additional coligands.

Subsequent crystallographic characterization established the identity of **1** as a three-coordinate Pt^{II} complex featuring terminal (1-adamantyl)amido ligation (Figure 1). The coordination geometry at platinum in **1** deviates significantly from the T-shaped configuration observed for **A** and **B**, owing in part to the steric demands of the chelating *N*-phosphinoamidinate ligand (P-Pt-N2 bite angle: 77.88(5)°). Furthermore, the inequivalent P-Pt-N3(1-Ad) (129.82(7)°) and N2(aryl)-Pt-N3(1-Ad) (151.77(9)°) angles ($\Sigma_{\text{L-Pt-L}}$ 359.5°) indicate that the geometry about platinum in **1** cannot simply be described as trigonal or Y-shaped. To the best of our knowledge, no other crystallographically characterized Pt^{II}–NH(alkyl) complex (three- or four-coordinate) has been reported previously.[13] However, a survey of crystallographically characterized four-coordinate Pt^{II}–NH(aryl) complexes revealed $Pt–N_{amido}$ distances (1.984(5)–2.125(5) Å)[14] that are statistically longer than the Pt–NH(1-Ad) distance found in **1** (1.914(2) Å). Although **1** proved to be unstable in air, no decomposition was observed upon heating solutions of **1** in THF at 75 °C over the course of 72 h on the basis of ^{31}P NMR spectroscopic analysis.

In an effort to evaluate possible $Pt_{d\pi}–N(1\text{-Ad})_{\pi}$ interactions in **1**, we conducted a variable-temperature solution ^{1}H NMR (300 MHz) study. At room temperature, **1** exhibited sharp C–H resonances and effective C_S symmetry that rendered the isopropyl methine hydrogen atoms equivalent on the NMR timescale, in keeping with rapid rotation about the Pt–NH(1-Ad) bond. Upon cooling, decoalescence of the methine signal occurred ($T_C = -65$ °C), with two somewhat broad methine proton signals observed at −80 °C (see Figure S2 in the Supporting Information). Analysis of these NMR line-shape changes by use of the Gutowsky–Holm approximation[15] yielded an estimated $\Delta G^{\ddagger}$ value of 9.8 kcal mol^{-1}.[16] These observations suggest the absence of a strong Pt–NH(1-Ad) multiple bond in **1**, in keeping with our DFT results (see below).

The migratory insertion of unsaturated substrates (e.g. alkenes, alkynes, isonitriles) into late-metal–amido linkages is a powerful elementary step in the functionalization of organonitrogen compounds.[10c,17] In a preliminary effort to ascertain whether such insertion reactions were feasible in the present system, we treated **1** with 2,6-xylyl isocyanide (2 equiv). Gratifyingly, the resulting platinum-functionalized amidine **4** was isolated as an analytically pure yellow solid (Scheme 2). The connectivity within **4**, as observed in the crystal structure (Figure 1), can be viewed as arising



Scheme 2. Synthesis and reactivity of the three-coordinate, formally 14 electron platinum(II) amido complex **1**; 1-Ad = 1-adamantyl, cod = 1,5-cyclooctadiene.

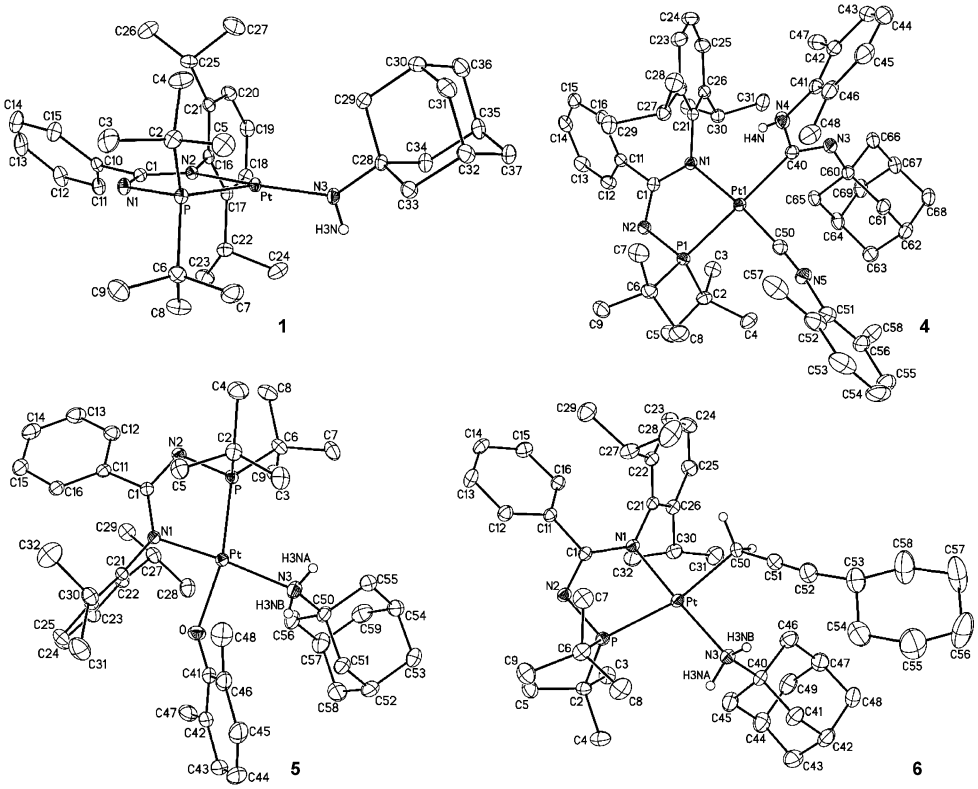


Figure 1. Crystallographically determined structures of **1**, **4**, **5**, and **6**. Selected interatomic distances [Å] and angles [°]: for **1**: Pt–P 2.2004(6), Pt–N2(aryl) 2.0360(19), Pt–N3(1-Ad) 1.914(2); P-Pt-N2(aryl) 77.88(5), P-Pt-N3(1-Ad) 129.82(7), N2(aryl)-Pt-N3(1-Ad) 151.77(9), Pt-N3-C28 135.87(16); for **4**: Pt–P 2.3157(9), Pt–N1(aryl) 2.086(3); for **5**: Pt–P 2.2186(6), Pt–N1(aryl) 2.0318(18), Pt–N3(1-Ad) 2.108(2), Pt–O 2.0760(17); for **6**: Pt–P 2.3000(8), Pt–N1(aryl) 2.049(3), Pt–N3(1-Ad) 2.100(3), Pt–C50 2.133(3), C50–C51 1.455(5), C51–C52 1.210(6), C52–C53 1.481(6).

from desired 1,1-insertion of isonitrile into the Pt–NH(1-Ad) linkage of **1**, followed by tautomerization and the coordination of a second equivalent of isonitrile.

There is considerable interest in exploiting 1,2-E–H bond addition (E = main-group element) across late-metal–amido fragments in the development of new substrate transformations.[10] In this regard, the basic and nucleophilic character of terminal amido groups within four-coordinate formally 16 electron platinum(II) amido complexes as a result of the disruption of nitrogen-to-platinum π bonding has been established.[14d] However, given our view of three-coordinate **1** as a formally 14 electron species on the basis of DFT data (see below), we wondered if analogous E–H bond addition reactions would be inhibited by the expected propensity of **1** to bind two-electron donors. In an initial test of this hypothesis, **1** was treated with 2,6-xylenol (Scheme 2); from this reaction mixture, the analytically pure [(P,N)Pt(O-2,6-xylyl)(NH_2(1-Ad))] complex **5**, arising from net O–H bond addition across the Pt–NH(1-Ad) linkage of **1**, was obtained as a pale-yellow solid. The crystal structure of the formally 16 electron Pt^{II} complex **5** (Figure 1) features a Pt–NH_2(1-Ad) distance of 2.108(2) Å, which is notably longer (by about 0.2 Å) than the Pt–NH(1-Ad) distance found in **1**. The Pt–O(2,6-xylyl) distance in **5** (2.0760(17) Å) falls within the range observed in some other four-coordinate, formally 16 electron platinum(II) aryloxy complexes.[14a,d,18]

Encouraged by the observed net O–H addition across the Pt–NH(1-Ad) linkage of **1**, we turned our attention to exploring the reactivity of **1** with cyclohexylallene, given the dual propensity of allenes to participate in migratory insertion reactions and undergo deprotonation by Brønsted bases.[19] The exposure of **1** to cyclohexylallene enabled the isolation of analytically pure pale-yellow **6** (Scheme 2). Single-crystal X-ray data (Figure 1) and solution NMR data support the identification of **6** as the depicted alkynyl species.

To examine the unique bonding of **1** and the mechanisms/activation barriers for the addition of phenol O–H and allene C–H bonds across the Pt–NH(1-Ad) group, we carried out DFT calculations in Gaussian 09[20] (see the Supporting Information for details; the free energies (and enthalpies in parenthesis) reported refer to M06/6-311+G(2d,p)[LANL2TZ-(f)]//M06/6-31G(d,p)-[LANL2DZ]).[21] This methodology provided geometries very close to the crystal structures of **1**, **4**, **5**, and **6**. For example, the calculated Pt–C, Pt–N, Pt–O, and Pt–P distances deviate from the values found crystallographically by an average of only 0.05 Å, and the P-Pt-N2 and P-Pt-N3(1-Ad) angles in **1** differ by approximately 4°. For all reaction pathways examined, solvation was incorporated by using the implicit SMD model of *n*-pentane.[22]

Although **1** is formally a 14-electron Pt^{II} complex, there is the possibility that the NH(1-Ad) amido group can donate an electron pair to the Pt center, which would correspond to Pt–NHR↔Pt=NHR resonance and an increase in the electron count around Pt. Inspection of the M06 molecular orbitals (Figure 2) indeed shows overlap of the NH(1-Ad) amido electron pair with the Pt metal center in the highest occupied molecular orbital (HOMO), but the wavefunction has a significant degree of localization on the amido nitrogen atom. This result suggests that **1** is best described as a 14-electron complex. There is also the possibility that the nitrogen atom of the P,N ligand is involved in π donation to Pt; however, overall there is a N_π–$Pt_{d\pi}$ antibonding interaction.

The reaction of 2,6-xylenol with **1** leads to the Pt^{II} aryloxy complex **5** by net addition of the O–H bond across the Pt–N bond (Scheme 2). Despite an extensive search, we could not locate a stable π coordination structure between 2,6-xylenol and **1**. Instead, there is an O-coordination complex that

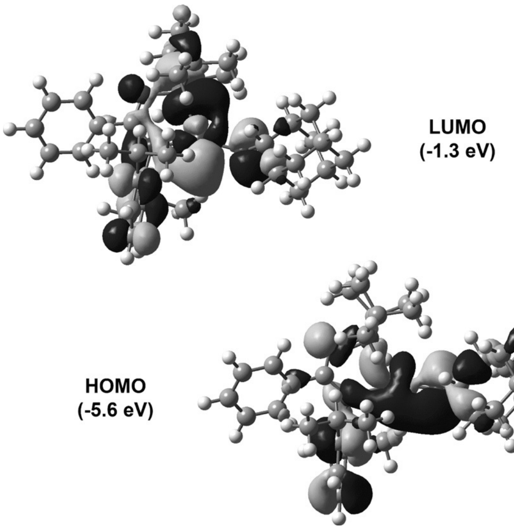
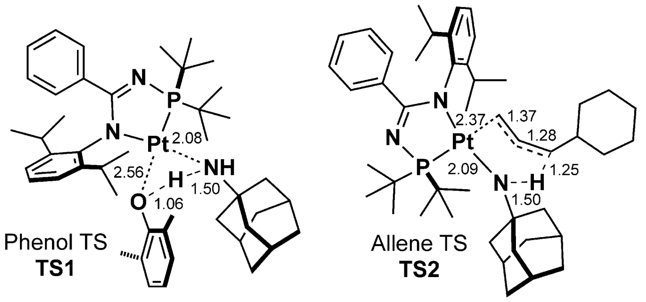


Figure 2. HOMO and LUMO orbitals for **1**.



Phenol TS
TS1

Allene TS
TS2

Scheme 3. Transition-state structures (bond lengths in Å).

precedes O–H bond addition and leads to **TS1** (Scheme 3) with $\Delta G^{\neq} = 12.5$ kcal mol^{-1} relative to separated reactants.[23] This transition state is similar to that of other 1,2-addition reactions to metal–amido complexes and involves simultaneous phenol deprotonation and formation of the Pt–OAr bond. The polar nature of the breaking O–H bond and forming N–H bond suggests that this transition state is probably best described in terms of intramolecular proton transfer followed by ion-pair collapse to form the Pt–O bond. Intrinsic reaction coordinate (IRC) calculations indicate that **TS1** directly connects **5** with the O-coordination complex and no intervening species. We also examined intermolecular proton transfer and an oxidative-addition/reductive-elimination sequence. Both of these pathways were thermodynamically more than 10 kcal mol^{-1} higher in energy than **TS1**.

Cyclohexylallene C–H addition to **1** leads to the platinum(II) alkynyl complex **6** (Scheme 2). We first considered the isomerization of cyclohexylallene to the internal alkyne, followed by direct 1,2-addition of a methyl group C–H bond across the platinum–amido group. Although isomerization of the allene to an alkyne is thermodynamically reasonable ($\Delta G = -5.3$ kcal mol^{-1}), the barrier for 1,2-addition of the sp^3 C–H bond is 31.4 kcal mol^{-1}, which is relatively large as compared to that for alternative reaction pathways. Similarly to the reaction with 2,6-xylenol, the reaction pathways for intermolecular proton transfer and oxidative addition/reductive elimination between cyclohexylallene and **1** are not energetically viable.[23] The lowest-energy reaction pathway identified that leads to **6** occurs via **TS2** (Scheme 3) with $\Delta G^{\neq} = 22.3$ kcal mol^{-1} ($\Delta H^{\neq} = 4.5$ kcal mol^{-1}) relative to reactants. This transition state involves concomitant C–H deprotonation by the terminal NH(1-Ad) fragment, allene-to-alkyne π-electron rearrangement, and nucleophilic attack of the allene CH$_2$ terminus to the Pt metal center. IRC calculations confirm that **TS2** probably connects **6** with an endergonic allene–platinum π-coordination complex ($\Delta G = 7.6$ kcal mol^{-1}).

In summary, we have described the unprecedented three-coordinate Pt^{II} complex **1** featuring terminal amido ligation. The complex was characterized by the use of NMR spectroscopic, X-ray crystallographic, and DFT methods. No evidence for stabilizing agostic interactions was found, and computational analysis supports a 14-electron formulation with minimal Pt–N π bonding. Net O–H and C–H addition reactions across, as well as isonitrile insertion into, the terminal platinum–amido linkage were observed. The coordinative/electronic unsaturation of the platinum amido species **1** described herein makes it an attractive precursor for investigations of intermolecular substrate activation and functionalization. Studies to probe such reactivity are currently under way.

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