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Monomeric Platinum(II) Hydroxides Supported by Sterically Dominant α-Diimine Ligands

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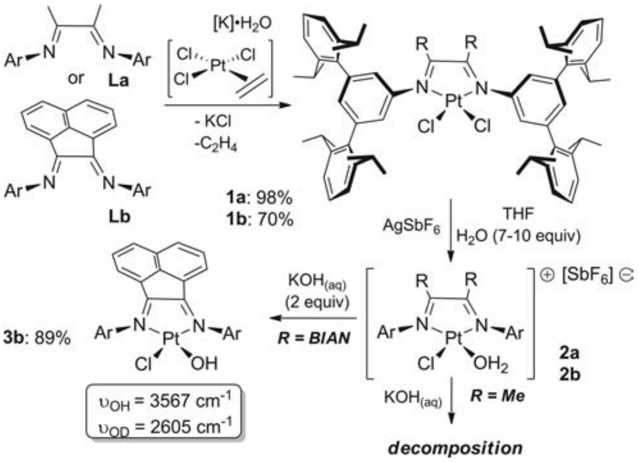
Supporting Information

ABSTRACT: The use of two new highly sterically bulky α-diimine ligands for the stabilization of neutral, monomeric platinum(II) hydroxo complexes is described. Halide abstraction from $LPtCl_2$ complexes of these ligands in the presence of water, followed by deprotonation of the cationic aquo complex, leads to LPt(OH)Cl and $LPt(OH)_2$. The latter can be reprotonated with $HNTf_2$ to yield a highly fluxional hydroxoaquoplatinum(II) cation.

The fundamental chemistry of archetypical oxygen-containing ligands (for example, M═O, M–O_2, M–OH, M–OOH, and M–OH_2) is of current interest because of their role in metal-mediated water oxidation catalysis.[1,2] An understanding of the mechanisms by which these ligands interconvert at a level commensurate with our current appreciation of the analogous hydrocarbyl ligand transformations is desirable to help with the design of improved water-splitting catalysts.[3,4] One approach to obtaining kinetic and thermodynamic information on such transformations is to prepare well-defined, monomeric examples of metal hydroxo[5] or dihydroxo[6] complexes and to study their reactivity. Despite the importance of such transformations, and the large number of metal hydroxo complexes known,[7] few studies with this emphasis have been undertaken.[8] To this end, we have become interested in synthesizing metal hydroxo complexes to assess their reactivity patterns and relevance to intermediates in water-splitting cycles. Monomeric neutral platinum(II) hydroxo complexes were among our first targets.

The monomeric platinum(II) hydroxo complexes (non-aqueous solution) that have been reported tend to be found in pincer ligand environments,[9,10] and Milstein has utilized such a complex to investigate transformations relevant to oxygen–ligand interconversions.[11] We were interested in compounds with neutral bidentate ligands to allow for a second reactive ligand site. Phosphine-stabilized monomeric platinum(II) hydroxo complexes have appeared in the literature,[12−14] but they exhibit a tendency to dimerize.[15,16] Similar reactivity patterns are seen in cationic α-diimine-stabilized platinum(II) complexes with hydroxo ligands, even when relatively large *N*-aryl groups are employed.[17−20] However, given the extensive use of α-diimine ligands to stabilize water-coordinated cations of platinum(II) relevant to C–H activation chemistry,[21,22] their greater amenability to the installation of significant steric bulk through modification of the *N*-aryl group, and their ease of handling, we sought the preparation of neutral platinum(II) hydroxide derivatives supported by a stupendously bulky diimine ligand. We have previously employed large 3,5-terphenyl *N*-aryl groups in β-diketiminato ligands to stabilize reactive organoscandium compounds[23,24] and have now extended this strategy to the diimine platform via preparation of the two new α-diimine ligands **La** (dimethyl backbone) and **Lb** (the diaryl acenaphthenequinonediimine, BIAN) shown in Scheme 1.

Scheme 1. Synthesis of Monomeric Platinum(II) Hydroxides



Ligands **La** and **Lb** were assembled via condensation of 3,5-bis(2,6-diisopropyl)aniline with the corresponding diketone and fully characterized. Reaction with the hydrate of Zeise's salt at room temperature gave the dichlorides **1a** and **1b** in 98% and 70% yield, respectively, as analytically pure brown/red solids. While the aliphatic region of the ^1H NMR spectra of these complexes offered little in the way of useful information, the signals for the R groups on the diimine backbone were diagnostic for each compound. The C_{2v} symmetry of the dichlorides was reflected in equivalent methyl groups for **1a** and three distinct resonances in the aromatic region for **1b**. In the latter complex, the signal for the proton in the position ortho to the imine carbon was particularly diagnostic, appearing as a doublet downfield of the other resonances in the molecule at 8.38 ppm (CD_2Cl_2).

Both **1a** and **1b** have been characterized by single-crystal X-ray diffraction (XRD); details can be found in the Supporting Information. The central phenyl group of the terphenyl *N*-aryl

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groups is essentially perpendicular to the plane of the N_2C_2 diimine atoms; the orthogonality (relative to the central aryl ring) of the two flanking 2,6-diisopropyl rings allows the ligand to provide an effective set of flanking "steric brick walls" that protect the $PtCl_2$ core of the molecule.

A single chloride ion can be abstracted with $AgSbF_6$ in wet tetrahydrofuran (THF) to provide a mixture of monomeric THF and aquo-coordinated chloro cations. The addition of an excess of water (7−10 equiv) results in the formation of the aquo-coordinated cations **2a** and **2b** (quantitative by NMR spectroscopy), which were envisioned as precursors to neutral hydroxides via deprotonation (vide infra). Attempts to isolate these compounds were unsuccessful because concentration of the solutions initiated polymerization of THF. However, they were characterized convincingly by ^1H NMR spectroscopy and subsequent reactivity. The desymmetrization of the coordination environment at platinum was indicated by the splitting of backbone resonances into two singlets for the methyl groups in **2a** and two sets of three signals for the naphthalene backbone protons in the BIAN ligand of **2b**. Resonances for both free and bound water were apparent in the ^1H NMR spectra, indicating that the exchange between free and coordinated water is slow on the NMR time scale. Broad resonances integrating to two hydrogens appeared at 7.92−7.96 ppm for **2a** and 8.18−8.27 ppm for **2b**; the chemical shift is dependent on the concentration of water in the solution. These signals disappear upon the addition of deuterated water.

All attempts to deprotonate **2a** produced ill-defined product mixtures, likely resulting from the competing attack of base on the imine carbon or the removal of acidic α-methyl protons. The BIAN ligand obviates the latter issue, and when solutions of **2b** are treated with aqueous KOH (2 equiv), **2b** is smoothly deprotonated to produce the new monomeric platinum(II) hydroxide **3b** as a pink, air-sensitive powder (Scheme 1). Use of Hunig's base (*N*,*N*-diisopropylethylamine) also results in the facile deprotonation of **2b** to yield **3b**.

The ^1H NMR spectrum of **3b** shows the expected asymmetrical BIAN ligand aromatic proton resonances and a singlet at 1.63 ppm in THF-d_8 (2.75 ppm in C_6D_6), integrating to one hydrogen. This resonance is only observable in rigorously dried solvents and broadens into the baseline when excess water is added. The signal appears in the ^2H NMR spectrum at the same chemical shift when **3b**-d_1 is prepared using KOD in deuterated water. The O−H stretch was detected in the IR spectrum at 3567 cm^{-1}; this band shifted to 2605 cm^{-1} in **3b**-d_1.[25,26] Single crystals could be grown from a toluene/THF solution with 18-crown-6 present as a crystallization aid.[27]

The molecular structure of **3b** is shown in Figure 1, along with selected metrical data. Orientation of the *N*-terphenyl ligands is more canted out of the diimineplatinum chelate plane than in **1b** (see Figure S2 in the Supporting Information) because of packing interactions with the (unseen) 18-crown-6 guest. The Pt−O bond length is 2.139(3) Å, which compares well with the few other terminal Pt^{II}−OH bond lengths in the literature (2.025−2.194 Å).[2,8] The geometry at the platinum center is similar to that of the starting material **1b**, with the main difference being the lengthening of the Pt−N1 bond (2.104 Å) in comparison to that of Pt−N2 (2.026 Å). This latter value is closer to the Pt−N distances found in dichloride **1b**. The longer Pt−N1 length is a result of the larger trans influence of the hydroxo ligand in comparison to chloride.[12]

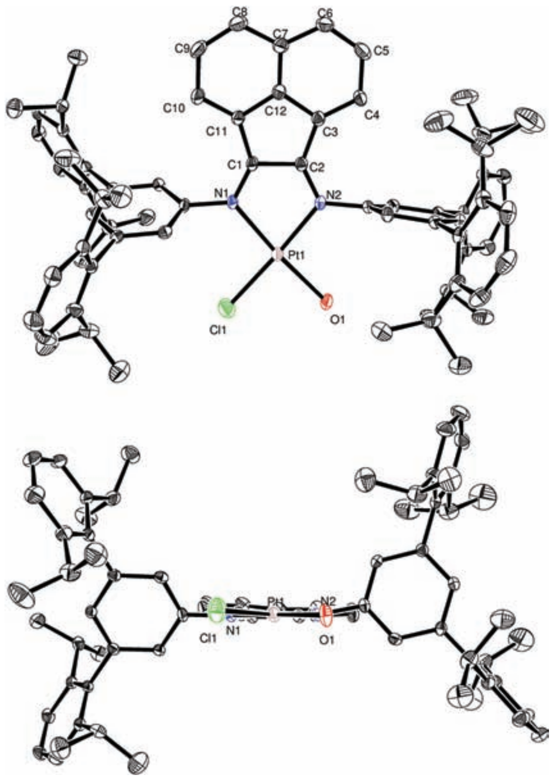
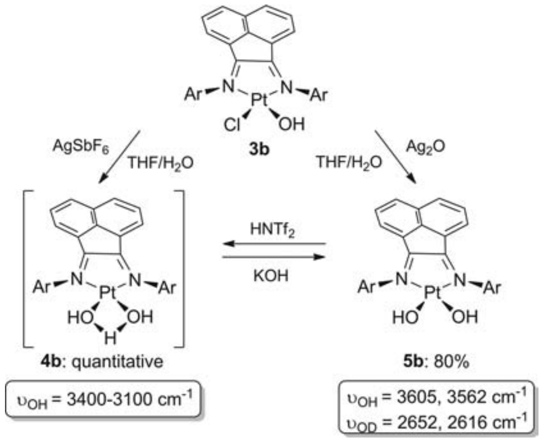


Figure 1. Molecular structure of **3b** in the solid state (hydrogens, one molecule of 18-crown-6, and toluene removed for clarity). Ellipsoids are at 30% probability. Selected bond lengths (Å) and angles (deg): Pt−O1, 2.139(3); Pt−Cl1, 2.249(2); Pt−N1, 2.104(3); Pt−N2, 2.026(4); O1−Pt−N1, 175.1(1); O1−Pt−N2, 95.96(1); Cl1−Pt−O1, 88.1(1); Cl1−Pt−N1, 96.7(1); Cl1−Pt−N2, 174.9(1).

Scheme 2. Reactivity of Platinum(II) Hydroxides



Resubjecting isolated **3b** to the conditions used to generate cations **2** led to the hydroxy aqua cation **4b** (Scheme 2). A larger excess of water was required to cleanly produce **4b**, and in contrast to **2b**, the ^1H NMR spectrum of **4b** indicated that it has a symmetrical coordination environment, suggesting an averaged structure, as shown in Scheme 2, in which the three hydrogens undergo rapid exchange. Attempted isolation again resulted in polymerization of the THF solvent, so **4b** was treated in situ with aqueous KOH, resulting in rapid deprotonation to yield the neutral *cis*-dihydroxo complex **5b**, which was more rigorously characterized because of its ready isolation.

Dihydroxo complex **5b** was also accessible directly from **3b** by stirring with a THF/water suspension of Ag_2O overnight; this allowed for isolation of **5b** as a dark-purple solid in 80% yield (Scheme 2). The *cis*-hydroxide **5b** also shows symmetrical BIAN ligand resonances in the ^1H NMR but distinct from those observed for its protonated derivative **4b**. In dry solvents, a singlet integrating to two protons was observed at 1.02 ppm in THF-d_8 (1.52 ppm in C_6D_5Br) for the Pt−OH protons. This assignment was confirmed through the synthesis of **5b**-d_2 and observation of a broad resonance at ≈1 ppm in the ^2H NMR spectrum. In the IR spectrum of **5b**, two equal-intensity bands are observed at 3605 and 3562 cm^{-1} and are assigned to the symmetric and antisymmetric O−H stretches. These bands appear at 2652 and 2619 cm^{-1} in the spectrum of **5b**-d_2.[28] Crystals suitable for XRD analysis were grown by the slow diffusion of hexanes into a THF/toluene solution of **5b** at −30 °C. Unfortunately, the molecule cocrystallized with both toluene and THF molecules in the lattice, which were severely disordered. While the data could not be refined to an acceptable standard, the analysis certainly established the connectivity within the platinum complex, firmly identifying it as the dihydroxo species, as indicated by the spectroscopic data.

With isolated **5b** in hand, it was possible to generate solutions of the protonated complex **4b** in the absence of excess water by treating **5b** with triflimidic acid, $HNTf_2$, in C_6D_5Br. The addition of 1 equiv of $HNTf_2$ to **5b** gave a new set of ligand resonances consistent with the formation of **4b**; a second 1 equiv of acid had no effect on the position of these resonances, indicating that protonation to form the diaquo dication is not occurring. A solution of **4b** obtained in this manner was cooled from 298 K to the freezing point of C_6D_5Br (243 K), and a broad signal integrating to three hydrogens was observed to migrate from 7.14 to 7.51 ppm as the temperature was lowered. Although the resonance broadened, it did not undergo coalescence, indicating that the protons were still in rapid exchange at 243 K. The solution IR of this sample showed a broad band spanning from 3400 to 3100 cm^{-1}. Together these data suggest that the proton bridges the two Pt−OH moieties in a symmetrical ground-state structure in which the bridging and terminal protons rapidly exchange, but a hydroxoaquo ground state cannot be ruled out. Notably, Hunig's base, which is capable of deprotonating **2b**, does not deprotonate **4b**, which supports the μ-H^+ structure depicted in Scheme 2.

In conclusion, we report a route to platinum(II) hydroxo compounds stabilized by sterically demanding α-diimine ligands and we are now exploring the reactivity of coordinated hydroxo ligands.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental procedures, spectral data for **3b**, **4b**, and **5b**, X-ray structures of **1a**, **1b**, and **5b**, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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