Unexpected Photoisomerization of a Pincer-type Amido Ligand Leads to Facial Coordination at Pt(IV)

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The divalent complex (BQA)PtMe undergoes oxidative addition with MeI to afford the octahedral complex *cis*-(*mer*-BQA)PtMe$_2$I {(BQA)$^-$ = bis(8-quinolinyl)amide}. When this molecule is irradiated with visible light, it isomerizes to (*fac*-BQA)PtMe$_2$I, where the BQA ligand adopts an unexpected facial coordination mode. The amide nitrogen in this molecule is sp^3 hybridized and can be easily quarternized with HBF$_4$, resulting in [H(*fac*-BQA)PtMe$_2$I][BF$_4$], with only minor perturbation to the coordination sphere.

Pincer-type amido ligands constructed using diarylamido backbones are considerably more flexible than one might expect.[1-3] For example, the tridentate diarylamides [PNP]$^-$ and [SNS]$^-$ can exhibit the expected mer configuration when bound to a transition metal (e.g., square planar [SNS]CuCl) or can conversely adopt a highly twisted structure in bimetallic systems (e.g., D_2 {(SNS)Cu}$_2$.)[2] The inherent stability of these D_2 twisted structure types was first noted from the dimeric structure of {(BQA)Li}$_2$ (BQA = bis(8-quinolinyl)amido).[3] We now report the surprising discovery that the pincer-type BQA ligand can accommodate, and may even thermodynamically prefer, a facially coordinated geometry for a mononuclear, octahedral Pt(IV) center. This geometry gives rise to an atypical amido substituent that is sp^3 rather than sp^2 hybridized.[4] The possibility for such geometric flexibility is important to note with respect to the growing family of diarylamido pincer-type ligands.[5,6]

The system of interest was elucidated while probing the reaction chemistry of square planar (BQA)Pt–X systems (X = OTf, Me, Ph). We had previously established that

Scheme 1
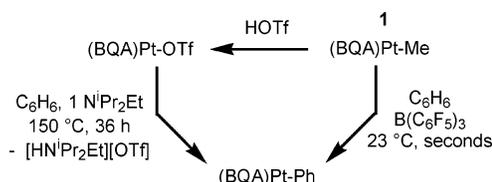
Scheme 2
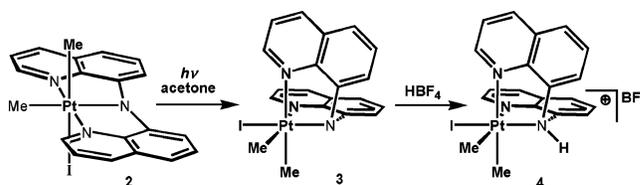
(BQA)PtOTf reacts with benzene in a base-promoted process (N^{i}Pr$_2$Et) to generate (BQA)PtPh and a stoichiometric equivalent of [HN^{i}Pr$_2$Et][OTf].[7] Whereas this reaction required elevated temperatures (ca. 150 °C) and extensive reaction times (~36 h), the addition of B(C$_6$F$_5$)$_3$ to (BQA)PtMe (**1**) in benzene facilitates a similar transformation at 23 °C within seconds (Scheme 1, see Supporting Information). Because Pt(IV) intermediates are likely operative (e.g., [(BQA)Pt(H)(Ph)(L)]$^+$)[8,9] in the transformation, we sought to examine a well-defined (BQA)Pt(II/IV) redox couple.[10]

The addition of excess MeI to **1** in acetone solution suits this purpose to afford *cis*-(*mer*-BQA)PtMe$_2$I (**2**) as a purple solid in very good yield (Scheme 2). The reaction proceeds sluggishly at 25 °C and needs to be heated at 70 °C for 18 h to reach completion. Complex **2** exhibits an intense absorption at 534 nm (ϵ 15 500 M^{-1} cm^{-1}) that is slightly red-shifted relative to **1** (λ_{max} = 527 nm (ϵ 12 000 M^{-1} cm^{-1})).[7] There are three diagnostic resonances in the ^{1}H NMR spectrum that exhibit strong ^{195}Pt–H coupling: the 2-position of the quinoline ring (8.71 ppm, $^3J_{PtH}$ = 41 Hz),

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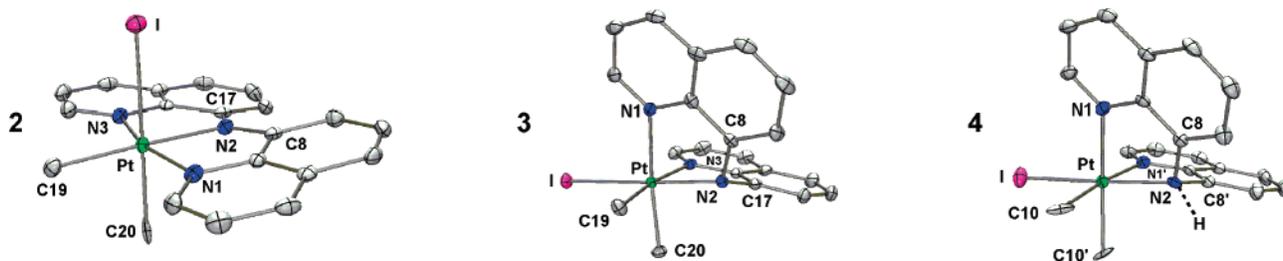
Figure 1. Solid-state molecular structures (50% ellipsoids) for **2**, **3**, and **4** (BF$_4$ anion omitted).

Table 1. Bond Lengths and Angles for (*mer*-BQA)PtMe$_2$I (**2**), (*fac*-BQA)PtMe$_2$I (**3**), and [H(*fac*-BQA)PtMe$_2$I][BF$_4$] (**4**)

	2	3	4		2	3	4
Pt−N1	2.008(4) Å	2.137(3) Å	2.152(4) Å	N2−Pt−I	90.16(9)°	177.73(7)°	177.95(15)°
Pt−N2	2.033(3) Å	2.036(3) Å	2.135(6) Å	N2−Pt−N1	81.47(16)°	81.06(10)°	80.62(11)°
Pt−N3	2.017(4) Å	2.146(3) Å	−^{b}	N2−Pt−N3	81.82(16)°	80.53(10)°	−^{b}
Pt−I	2.783(1) Å	2.630(2) Å	2.598(1) Å	N1−Pt−N3	163.22(17)°	97.50(10)°	94.67(12)°
Pt−C19^a	2.088(5) Å	2.052(3) Å	2.152(4) Å	C19{10}−Pt−C20{10}^{a}	87.15(17)°	90.55(12)°	87.08(16)°
Pt−C20	2.102(5) Å	2.045(3) Å	−^{b}	C8−N2−C17{8′}^{c}	131.93(42)°	114.82(25)°	114.02(17)°

^{a} C17, C19, and C20 corresponds to **2** and **3**, C8′ and C10 corresponds to **4**. ^{b} Values are omitted because they are generated by the symmetry transformation {x, −y + 1/2, z}. ^{c} C8′ generated by a symmetry transformation {x, −y + 1/2, z}.

the equatorial methyl group trans to the amido N atom (1.67 ppm, $^2J_{PtH}$ = 60 Hz), and the axial methyl group (1.43 ppm, $^2J_{PtH}$ = 70 Hz). These assignments are supported by a 1D NOE coupling experiment, performed by saturation (0.5 s mixing time) of the 2-position proton of the quinoline ring. As expected, NOE is observed to the equatorial methyl protons, but no NOE is observed to the axial methyl protons. The solid-state structure of **2** was determined by X-ray diffraction (Figure 1) and confirms the cis relationship between the methyl groups and axial placement of the iodo ligand.

Oxidative addition using d_3-MeI under the same conditions affords a 1:1 mixture of axial and equatorial CD$_3$ products (^{1}H and ^{2}H NMR). This result suggests a labile iodide ligand in acetone solution that facilitates methyl group isomerization, in accord with observations made by Puddephatt and co-workers concerning the {*cis*-1-(N=CHC$_6$H$_4$)-2-(N=CHC$_6$H$_5$)C$_6$H$_{10}$}PtMe$_2$I system.[11]

We noted that **2** decays in solution in the presence of ambient room light but is stable when stored in the dark. It was subsequently found that photolysis of **2** using a 100 W incandescent light bulb over 48 h effects a gradual color change from purple to red. The ^{1}H NMR spectrum of the solution establishes quantitative conversion to a single new complex with one methyl group resonance at 1.25 ppm ($^2J_{PtH}$ = 71 Hz) that integrates to 6H and exhibits no NOE to the 2-position protons of the quinoline rings. In a control experiment, complex **2** proved to be completely stable in acetone solution when incubated at 70 °C in the absence of light over a period of 24 h. Also, irradiation of an acetone-d_6 solution of **2** with a 300 W medium-pressure Hg light source filtered with a 560 nm long pass filter and a 2 mm path of water (to screen infrared radiation) converted **2** to its new isomer in ca. 3 h as monitored by UV−vis. These data are suggestive of a photoisomerization process and led us to the initial but incorrect assumption that **2** had

photoisomerized to *trans*-(*mer*-BQA)PtMe$_2$I, an isomer of **2** in which the iodide ligand is coordinated in the equatorial position, trans to the amido N atom.

Single crystals of the new product were subjected to XRD analysis, which firmly established the identity of the photoproduct as *cis*-(*fac*-BQA)PtMe$_2$I, **3** (Figure 1). The BQA ligand in **3** is coordinated facially, and the two methyl groups are cis disposed to one another (90.5(1)°) and, therefore, trans to the quinolinyl N-donor nitrogen ligands. The most interesting structural aspect of **3** is that the amide donor is highly pyramidalized and is best described as sp^3 hybridized, reflected by the contraction of the C8−N2−C17 angle from 131.93(42)° in **2** to 114.82(25)° in **3**. This geometry at nitrogen had not to our knowledge been previously observed for transition metal diarylamide complexes. Also distinctive in the structure of **3** is that the iodide ligand now resides at the position trans to the amido N donor and that the Pt−I bond distance exhibits a significant contraction (ca. 0.15 Å) upon isomerization from **2** to **3** (see Table 1 for all key structural parameters). This contraction presumably reflects the greater trans influence of a methyl versus the amido substituent. The approximately tetrahedral geometry at the amide nitrogen in **3** causes a dramatic decrease in its lone pair donation to Pt, indicated by a large shift in an amide-to-Pt LMCT band (534 nm in **2**; 422 nm in **3**). The charge-transfer assignment is supported by the empirical observation that addition of HBF$_4$ etherate to **3** in CH$_2$Cl$_2$ completely bleaches the absorption band at 422 nm but does not affect the low-energy band at 510 nm (Figure 2).

HBF$_4$ addition to **3** produces the protonated complex **4** (Figure 1), which is isolated in near quantitative yield (97%) as a rose-colored solid. Its ^{1}H NMR spectrum shows a signature downfield resonance (10.33 ppm), exhibiting ^{195}Pt satellites ($^2J_{PtH}$ = 21 Hz) for the N−H proton, and a new and broad absorption in the IR spectrum at 3127 cm^{-1} attributable to the N−H vibration. ^{195}Pt coupling to the two methyl groups ($^2J_{PtH}$ = 70 Hz) is virtually unchanged. A 1D-NOE (1.0 s mixing time) experiment with saturation of the

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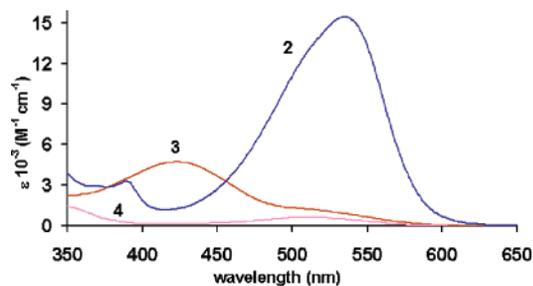
Figure 2. Absorption spectra of **2**, **3**, and **4** in CH_2Cl_2.

N−H proton resonance indicates coupling to both the 8-position proton of the aryl ring (8.78 ppm) and the methyl ligands (1.54 ppm).

The solid-state structure of **4** was determined by X-ray diffraction (Figure 1) and is consistent with the solution data. Most notably, the Pt−N2 (the amido substituent in **3**) and the Pt−Me bond distances each elongate by ca. 0.1 Å. H11, the proton on N2, is hydrogen bonded to the BF_4^- counteranion (N2−F1 = 2.821(7) Å). Neutral diarylamine adducts of transition metals are very uncommon, and the Pt−N2 bond of **4** is amongst the shortest of its type to be reported. For comparison, unchelated diphenylamine adducts of $AlCl_3$ [12] and $GaMe_2Cl$ [13] have been reported and exhibit C_{aryl}−N−C_{aryl} bond angles of 110.5(4)° and 105.2(2)°, respectively. These angles are contracted by comparison to the C8−N2−C8′ angles of **3** (114.82(25)°) and **4** (114.02(17)°).

Anionic tridentate ligands that are able to isomerize from *mer* to *fac* in octahedral or pseudooctahedral complexes are very unusual.[4,14−16] The (BQA)Pt^{IV} system is particularly intriguing because the reaction is photolytically driven. Shaw and co-workers have reported the octahedral complex L′Ru-(CO)Cl_2 {L′ = ((Ph_2P)CH_2('Bu)C=N−)_2} which undergoes

a related mer to fac photoisomerization.[17] However, (BQA)-$PtMe_2I$ and L′Ru(CO)Cl_2 are dissimilar because the latter system involves an isomerization resulting from the photolytic dissociation of CO and does not feature a highly pyramidalized geometry about the central nitrogen.

One possible mechanism for the conversion of **2** to **3** proceeds through an intermediate in which the iodide ligand has dissociated prior to photoisomerization. Absorption of a photon by this intermediate would destabilize the metal−amide bond, allowing for relaxation to a structure that accommodates an sp^3-hybridized geometry about the amide nitrogen. This isomer could then be trapped by coordination of iodide to generate the observed product **3**. This scenario is hypothetical, but consistent with the observation that the iodide ligand appears to be quite labile in acetone, allowing rapid scrambling of the two methyl ligands. Also, the photoisomerization process is severely attenuated when the acetone solution is saturated with NaI. The observed shortening of the Pt−I bond distance in **3** compared to **2**, without an appreciable change in the Pt−N2 bond distance, supports the idea of a strengthened Pt−I interaction in **3**.

To conclude, the photoisomerization process described herein underscores the geometric flexibility accessible to the [BQA]$^-$ ligand. Despite its typical preference to bind in a planar tridentate fashion, it can adopt quite distorted structures, as in the fac platinum(IV) complexes **3** and **4**. Given this and related findings[1−3] caution should be exercised when generally referring to ligands such as these as *pincer-type*.

Supporting Information Available: X-ray crystallographic files (CIF) and complete synthetic details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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