

Hydroxo Radicals, C–H Activation, and Pt–C Bond Formation from 77 K Photolysis of a Platinum(IV) Hydroxo Complex

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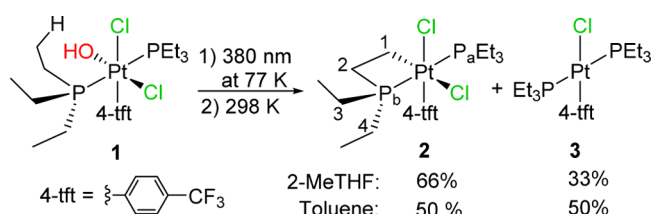
Supporting Information

ABSTRACT: Photolysis (380 nm) of *trans,cis*-Pt(PEt₃)₂(Cl)₂(OH)(4-tft) (4-tft = 4-trifluoromethylphenyl) at 77 K in 2-methyltetrahydrofuran gives triplet emission, platinum(III), and a hydroxo radical. Benzyl radical emission is observed in toluene from the reaction of a portion of the OH radicals with toluene. Warming the photolyzed solutions gives platinumacycle *trans*-Pt(CH₂CH₂PEt₃)(PEt₃)(Cl)₂(4-tft) by hydrogen-atom abstraction from a PEt₃ ligand and *trans*-Pt(PEt₃)₂(Cl)(4-tft) from net HOCl photoelimination. The platinumacycle undergoes thermal reductive elimination at 298 K or photolytic reductive elimination, even at 77 K.

Transition-metal hydroxo complexes are attracting considerable interest as key species in hydrocarbon oxidation,^{1–4} C–H activation,^{5–11} water oxidation,^{12,13} solar energy conversion and storage,^{14–18} and other catalytic schemes.^{19–24} We recently reported the synthesis and room-temperature photochemistry of platinum(IV) hydroxo complexes *trans*-Pt(PEt₃)₂(X)(Y)(OH)(R) (X and Y = Cl, Br). These complexes undergo net photoreductive elimination of HOX with oxidation of alkenes or solvent.²⁵ We now report the unusual 77 K photochemistry of one of these platinum(IV) hydroxo complexes, which leads to a sequence of hydroxo radical formation, C–H activation, Pt–C bond formation, and C–Cl reductive elimination.

Irradiation (380 nm) of *trans,cis*-Pt(PEt₃)₂(Cl)₂(OH)(4-tft) (**1**; 4-tft = 4-trifluoromethylphenyl)²⁵ for several hours in glassy 2-methyltetrahydrofuran (MeTHF) or toluene at 77 K followed by warming to room temperature gives a mixture of a new complex **2** and *trans*-Pt(PEt₃)₂(Cl)(4-tft) (**3**) (Scheme 1). (Yields in Scheme 1 were determined by ¹H NMR integration against an internal standard.) Complex **3** is the sole platinum-containing product at room temperature, and it is produced in minutes instead of hours.²⁵

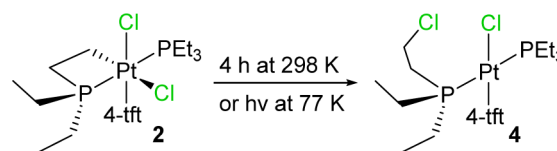
Scheme 1



New **2** is unstable at room temperature (~4 h to decay) and was not isolated but is readily characterized by NMR spectroscopy as the phosphaplatinacycle pictured in Scheme 1. Most diagnostic for the formation of **2** is the ³¹P NMR shift for the phosphorus atom in the four-membered ring. Four-membered-ring ³¹P NMR signals are strongly upfield-shifted from those not in a ring,²⁶ and this is observed in **2**, where the ring–P_b signal is at δ –65, while that for the unaltered PEt₃ ligand (P_a) is at δ –7.7, near that of **1**. The phosphorus centers are coupled to each other (doublet, ²J_{PP} = 513 Hz) and to ¹⁹⁵Pt with ¹J_{PtP} = 1853 Hz (PEt₃) and 1410 Hz (P_b). ¹H–¹H COSY and ¹H–¹³C HMQC NMR spectroscopy and comparisons to data for platinum(II) phosphaplatinacycle complexes^{27–30} allowed identification and assignment of all ¹H NMR shifts for **2**. The ring-system methylene protons appear as diastereotopic pairs. The platinum-bonded methylene group protons, H_{1a} and H_{1b}, are found at δ 2.71 and 1.73, and are bonded to the same carbon atom, C1, found at δ –0.2 in the ¹³C NMR spectrum. The P-bonded methylene group protons are located at δ 2.98 and 2.37 and are bonded to C2, found at δ 29.7 in the ¹³C NMR spectrum. The diastereotopic nature of the methylene protons establishes a *cis* configuration for the chloro ligands and the stereochemistry for **2** given in Scheme 1.

After several hours at room temperature in toluene-*d*₈ or MeTHF, or more rapidly in chloroform, platinumacycle **2** completely converts to Pt(PEt₃)(Et₂PCH₂CH₂Cl)(Cl)(4-tft) (**4**) by reductive elimination (Scheme 2). The ³¹P NMR

Scheme 2



spectrum of **4** shows two closely spaced signals at δ 13.7 and 13.0 with ¹⁹⁵Pt satellites (*J*_{PtP} = 2770 and 2722 Hz, respectively). The shifts and coupling constants are very similar to those of **3**,²⁵ consistent with the formation of an analogous platinum(II) complex. The ¹H NMR spectrum shows a distinctive set of multiplets at δ 3.87 and 2.25 assigned to the chloroethyl group. A crystal grown from the mixture of **3** and **4** was subjected to X-ray crystal structure analysis, which showed that **3** and **4** cocrystallized in an 11:14 ratio (Figure 1). Complex **2** also photo-

Received: September 24, 2014

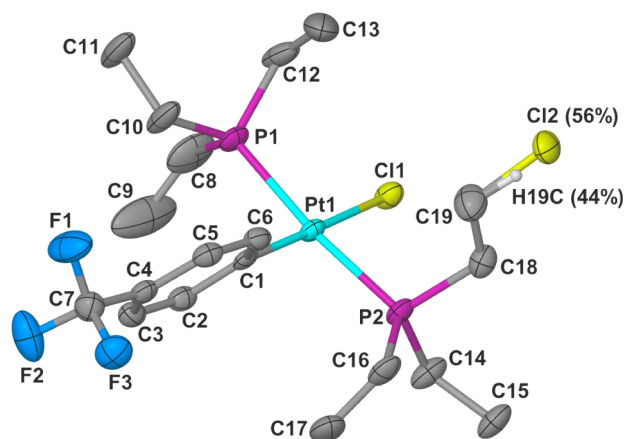


Figure 1. Drawing of the solid-state structure of cocrystallized **3** (44%) and **4** (56%).

decomposed (380 nm) to 4 at room temperature or at 77 K. (A gold(III) complex was recently reported to undergo photolytic reductive elimination of aryl chloride.³¹)

In addition to its photochemical reactivity, **1** is photoluminescent in MeTHF glass at 77 K. Irradiation at 380 nm gives visible salmon-pink emission ($\lambda_{\text{max}} = 620 \text{ nm}$). The emission lifetime ($38 \mu\text{s}$) and intensity decrease as the photolysis progresses indicate that emission is from a triplet excited state of a species that is photodecaying; in other words, the emission is from a triplet of **1**. Remarkably, our previously reported density functional theory calculations of the lowest-energy triplet and singlet of the PMe_3 analogue of **1** gave a ground-state singlet to lowest-energy triplet gap corresponding to 630 nm.²⁵ The calculations also indicate high spin density on a loosely bonded OH ligand in the triplet excited state. Switching the solvent from MeTHF to toluene- d_8 changes the emission to blue, which, in contrast to the salmon-pink emission, brightens as photolysis progresses. The blue emission spectrum (Figure 2) is characteristic of the benzyl radical.^{32–34}

The picture (Scheme 3) that thus emerges is that photolysis of **1** in a 77 K matrix generates a triplet excited state (1^T) that decays to the ground state by emission or progresses to a geminate platinum(III)/OH radical pair (**A**). The highly reactive OH radical then abstracts hydrogen atoms from the solvent (upper

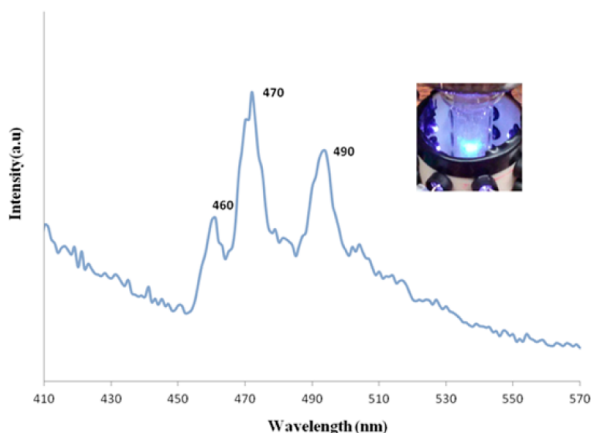
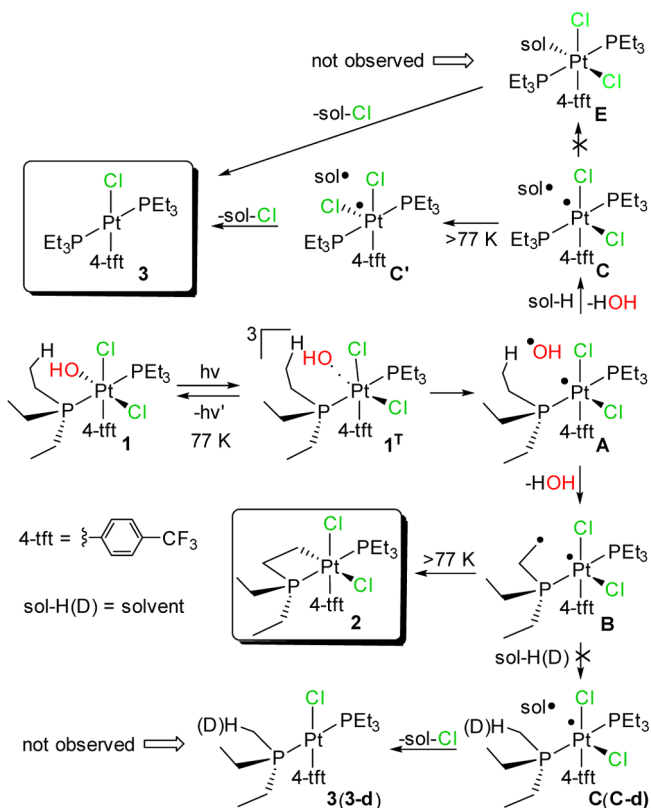


Figure 2. Benzyl radical emission spectrum from a toluene-photolyzed sample of **1** at 77 K. Inset: visible blue emission during photolysis ($\lambda = 380$ nm).

Scheme 3



part of Scheme 3) or the PEt_3 ligand (lower part of Scheme 3), with the ratio depending on the solvent. Greater solvent reaction occurs with the weak C–H bonds of the toluene methyl group and less with the stronger 2-MeTHF bonds (Scheme 1). Warming the frozen matrix results in carbon/platinum(III) radical pair (**B**) coupling to form platinacycle **2**. Platinacycle **2** formation must occur as the frozen matrix is warmed because **2** is photosensitive to reductive elimination, even at 77 K. The possibility that coupling of the solvent and platinum(III) radicals occurs upon warming to give a platinum/solvent complex (**E**) that then reductively eliminates to give chlorinated solvent and **3** can be eliminated because **E** complexes are not observed by low-temperature NMR of a photolyzed sample warmed from 77 K to -60°C ; only **3** and **4** are detected. Another possible pathway to **3** is the abstraction of a solvent hydrogen atom by the phosphine ethyl radical in **B** to give a solvent radical that then abstracts a chlorine radical from platinum(III) complex **C** (lower part of Scheme 3). This can be eliminated because deuterium incorporation into the phosphine ligand of **3** is predicted (**3-d**) in deuterated solvents but is not observed (toluene- d_8).

A question that arises is, why is the 77 K frozen matrix photochemistry of **1** different from the room temperature solution photochemistry (net HOCl elimination²⁵)? A likely explanation is that in the frozen matrix the PEt_3 ligand may be locked into a position favorable for abstraction and the chlorine ligand may be inhibited from attaining a position favorable for abstraction.

The relatively efficient formation of **2** and the subsequent reductive elimination of the C–Cl bond are notable. Although we did not observe the intermolecular equivalent reactions with solvent, the formation of **2** does suggest that other photo-reductions of transition-metal complexes that are accompanied by hydrocarbon oxidation^{25,35–39} may occur by a similar process,

that is, metal–ligand radical pair generation, ligand radical–hydrocarbon reaction, metal–C radical coupling (M–C bond formation), and reductive elimination. It should also be noted that the photochemistry described here shows parallels to the thermal chemistry of iron halogenases,⁴⁰ where hydrogen-atom transfer to an oxo ligand generates the carbon radical that then couples with a halogen ligand.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures, characterization data (NMR spectra), and X-ray structural data (CIF file for **3**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

All authors have given approval to the final version of the manuscript and contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Dr. Charles Barnes for X-ray data collection and processing and Dr. Wei Wycoff for assistance with the NMR measurements. Support was provided by the U.S. Department of Energy, Office of Basic Energy Sciences (Grant DE-FG02-88ER13880).

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