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

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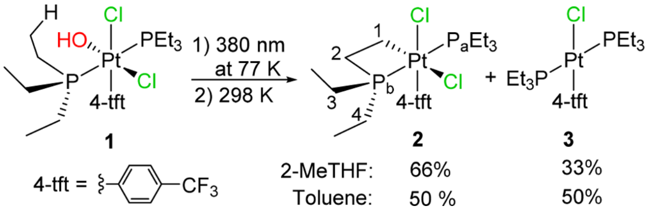
Supporting Information

ABSTRACT: Photolysis (380 nm) of *trans,cis*-Pt(PEt_3)$_2$(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 platinacycle *trans*-Pt($CH_2CH_2PEt_2$)(PEt_3)(Cl)$_2$(4-tft) by hydrogen-atom abstraction from a PEt_3 ligand and *trans*-Pt(PEt_3)$_2$(Cl)(4-tft) from net HOCl photoelimination. The platinacycle 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(PEt_3)$_2$(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(PEt_3)$_2$(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(PEt_3)$_2$(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]

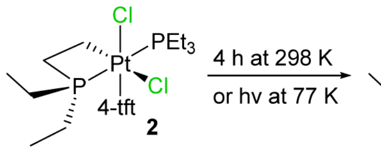
Scheme 1



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 ^{31}P NMR shift for the phosphorus atom in the four-membered ring. Four-membered-ring ^{31}P 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 PEt_3 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 ^{195}Pt with $^1J_{PtP}$ = 1853 Hz (PEt_3) and 1410 Hz (P_b). $^1H−^1H$ COSY and $^1H−^{13}C$ 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 ^{13}C 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 ^{13}C 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, platinacycle **2** completely converts to Pt(PEt_3)($Et_2PCH_2CH_2Cl$)(Cl)(4-tft) (**4**) by reductive elimination (Scheme 2). The ^{31}P NMR spectrum of **4** shows two closely spaced signals at δ 13.7 and 13.0 with ^{195}Pt 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-

Scheme 2



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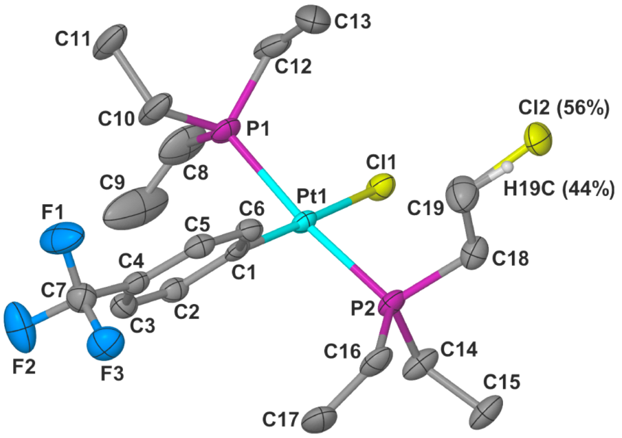
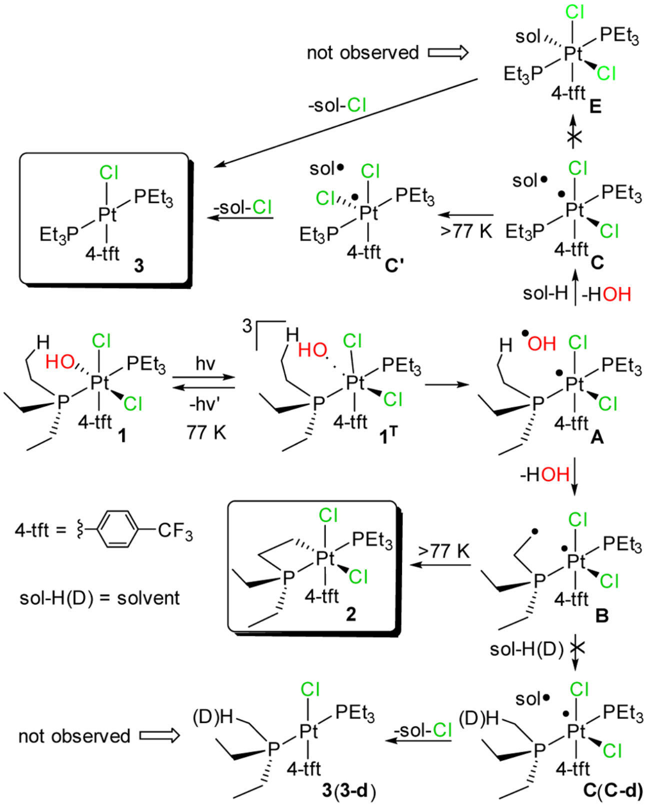


Figure 1. Drawing of the solid-state structure of cocrystallized **3** (44%) and **4** (56%).

Scheme 3



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 (λ_{max} = 620 nm). The emission lifetime (38 μs) 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 ($\mathbf{1}^{T}$) 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 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 elimination[25])? 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 photoreductions of transition-metal complexes that are accompanied by hydrocarbon oxidation[25,35−39] may occur by a similar process,

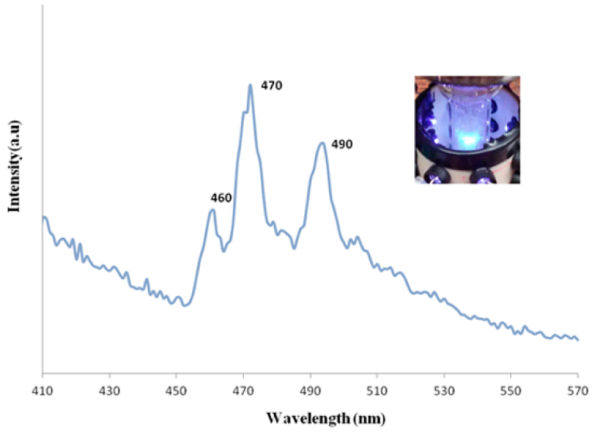


Figure 2. Benzyl radical emission spectrum from a toluene-photolyzed sample of **1** at 77 K. Inset: visible blue emission during photolysis (λ = 380 nm).

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.

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