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Chlorine Photoelimination from a Diplatinum Core: Circumventing the Back Reaction

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Solar energy may be stored by using it to rearrange the bonds of H_2O and HX (X = Cl, Br) to H_2/O_2 and H_2/X_2, respectively.[1,2] From a mechanistic standpoint, the oxidative half-reaction of HX is more attractive than H_2O because it only involves the coupling of a two-electron oxidation to H_2 generation. The water oxidation half-reaction requires four electrons, and necessarily involves the intimate coupling of electron to proton transfer.[3,4] Unlike the $1e^-$ chemistry of redox symmetric bimetallic complexes,[2,5] we have developed a method for hydrogen production from HX solutions utilizing a bimetallic photocatalyst that operates in two discrete two-electron steps for hydrogen evolution and halogen elimination.[6,7] A hydrido-halide $Rh_2^{II,II}(H)_2(X)_2$ species is generated from the addition of two HX molecules to a parent $Rh_2^{0,0}$ complex. H_2 photoelimination is facile to furnish a two-electron mixed valence complex, $Rh_2^{0,II}(X)_2$; photoelimination of halogen, however, from $Rh_2^{0,II}(X)_2$ is not. Hence the overall efficiency for the H_2 photocycle is limited by the efficiency of halogen photoelimination. More generally, overcoming the strong metal−halide bond is an important overall determinant of H_2 production in most HX photocycles. If no pathway for bond activation is accessible, productive chemistry ceases upon hydrogen evolution.[8] Even if halogen photoelimination is achieved, halogen must be trapped since the back-reaction of the primary photoelimination products is rapid and favorable.[9] For this reason, the overall photoefficiency typically scales with the efficiency of the chemical trap. Traps are problematic in that the trap−X bond provides the thermodynamic driving force,[10,11] thus obviating energy storage implications. In addition, the detailed process by which photoelimination proceeds is obscured as both $X^\bullet$ and X_2 can react with most traps. Improved efficiencies for H_2 production therefore require increased quantum yields for M−X bond activation and new strategies to prevent the back reaction of primary photoproducts.

Our most recent investigations of HX photocycles have focused on improving the efficiency of the halogen elimination step of the photocycle by incorporating oxidizing metals, such as Au and Pt into bimetallic cores.[12,13] Whereas a PtAu bimetallic trihalogen complex shows markedly improved photoefficiencies for photoelimination,[13] it nonetheless requires a halogen trap. We now report a system that addresses both challenges of a high photoefficiency for X_2 elimination in the absence of a trap. Photolysis of a $Pt_2^{III,III}$ complex with UV or visible light (355−510 nm) eliminates halogen to deliver a two-electron mixed-valent $Pt_2^{I,III}$ with a high quantum yield in solution. Photolysis of the complex in the solid state yields Cl_2 with no need for a halogen trap.

Though bimetallic complexes of group 10 metals bridged by diphosphine ligands typically promote insertion reactions,[14−18] they can drive oxidative chemistry.[19] With regard to the latter, we were intrigued by the oxidative chemistry of $Pd_2(P{-}P)_2X_2$ (P−P = dimethylphosphinomethane, diethylphosphinomethane) by halogens to yield valence symmetric face-to-face $Pd_2^{II,II}(P{-}P)_2X_4$ (X = Cl, Br) and μ-X_2 complexes (X = I).[20] We find that the $d^8\cdots d^8$ cores of these complexes can disproportionate to deliver $d^7{-}d^9$ mixed-valence complexes in the presence of phosphazane ligands. Suitable Pt^0 and Pt^{II} sources (e.g., $({}^{tBu}dba)_3Pt_2$ and $Pt(cod)Cl_2$, ^{tBu}dba = 4′-*tert*-butyl dibenzylideneacetone, cod = 1,5-cyclooctadiene) react with the phosphazane tfepma (tfepma = $((CF_3CH_2O)_2P)_2NCH_3$) to yield $Pt_2^{I,I}(tfepma)_2Cl_2$ (**1**) in analogy to the synthesis of $Pt_2^{I,I}$ phosphine complexes.[21] The solid state structure of **1**, shown in Figure 1, reveals a short Pt−Pt contact of 2.6187(6) Å, similar to that of other $M_2(P{-}P)_2X_2$ bimetallics and consistent with a metal−metal bond.[17,22] A $^{31}P\{^1H\}$ resonance at 113.57 ppm disappears upon the addition of 1 equiv of $PhI\cdot Cl_2$ to a solution of **1** and two resonances appear at 100.52 and 60.62 ppm, corresponding to phosphorus atoms coordinated to the Pt^I and Pt^{III}, respectively, of $Pt_2^{I,III}(tfepma)_2Cl_4$ (**2**). X-ray diffraction studies confirm the two-electron mixed-valent nature of **2** (Figure 1). The Pt(1)−Pt(2) distance of 2.6187(7) Å establishes that a metal−metal bond is maintained upon oxidation. The coordination of Cl(3) and Cl(4) to Pt(2), ($d_{Pt(2)-Cl(3)}$ = 2.323(2) Å and $d_{Pt(2)-Cl(4)}$ = 2.338(2) Å) completes the pseudo-octahedral geometry about the Pt^{III} center. The structure of **2** is unique among the oxidation products of $M_2(P{-}P)_2X_2$ bimetallics, as it represents the first example of a group 10 two-electron mixed-valent compound. Oxidation of **2** with 1 equiv of $PhI\cdot Cl_2$, or treatment of **1** with 2 equiv of $PhI\cdot Cl_2$, affords a red solution of $Pt_2^{III,III}(tfepma)_2Cl_6$ (**3**). The $^{31}P\{^1H\}$ NMR spectrum of **3** shows a single resonance at 52.22 ppm. As with **1** and **2**, X-ray diffraction analysis of the complex indicates the presence of a direct Pt−Pt interaction (d_{Pt-Pt} = 2.7037(3) Å) for two metals possessing an octahedral coordination environment.

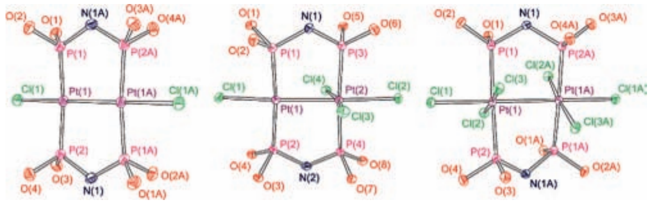

Figure 1. Thermal ellipsoid plots of **1** (left) **2** (center) and **3** (right) drawn at the 50% probability level; **1** and **3** crystallize with half a molecule per asymmetric unit. (O)−CH_2CF_3 and (N)−CH_3 groups of the phosphazanes are omitted for clarity.

The diplatinum-based suite of $d^7{-}d^7$, $d^9{-}d^7$, and $d^9{-}d^9$ complexes defined by **3**, **2**, and **1**, respectively, complement the previously described dirhodium suite of complexes of the same d-electron count.[9] As shown in Supporting Information, Figure S7, the electronic profiles of **1**−**3** are dominated by excited states of dσ* parentage as observed for the spectroscopy of $d^7{-}d^7$, $d^9{-}d^7$, and $d^9{-}d^9$ dirhodium complexes.[23] As the dσ* absorption profile possesses both M−M and M−X antibonding character, electronic excitation into the empty dσ* orbital is expected to promote halogen

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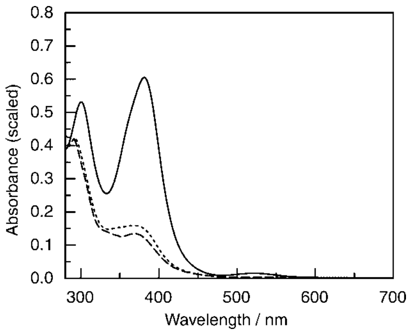

Figure 2. Electronic absorption spectra of **3** (solid), **2** (dashed), and the solid state photolysis product (dotted) in CH_2Cl_2. $\lambda_{irr} > 350$ nm.

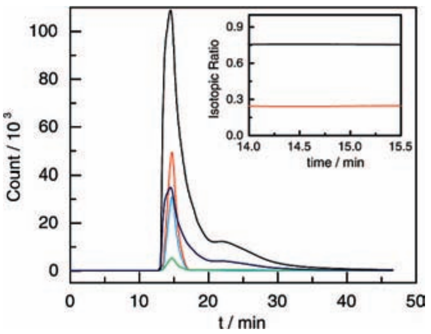

Figure 3. Mass spectrometry analysis of the gas evolved from solid state photolysis of **3**. Traces correspond to ^{35}Cl (black), $^{35}Cl^{35}Cl$ (red), ^{37}Cl (purple), $^{35}Cl^{37}Cl$ (blue), $^{37}Cl^{37}Cl$ (green) mass fragments. Inset shows the fractional amount of ^{35}Cl (red) and ^{37}Cl (black) present.

elimination as we have observed for the M−X bond photoactivation of Rh_2[9] and PtAu[13] systems.

Irradiation of 43 μM solutions of **3** in benzene with either 405 or 510 nm light in the presence of 2,3-dimethyl-1,3-butadiene (DMBD) leads to rapid conversion to **2** as monitored by both UV−vis spectroscopy (Figure S8) and $^{31}P\{^1H\}$ NMR (Figure S13). The quantum yield for Pt−Cl bond activation is high. Figure S9 shows the measured photoreaction quantum yields (Φ_p) as related to the DMBD concentration. The observed quantum yield of 38% for halogen photoelimination far exceeds all previously reported values.[6,13] Since both 405 and 510 nm light give the same efficiency for halogen elimination, a common excited-state must be reached by the 385 and 520 nm transition bands. Photolysis of **3** in benzene in the absence of DMBD results in reductive fragmentation of the bimetallic core to yield $Pt(tfepma)Cl_2$. Conversely, photolysis of **3** in THF in the absence of DMBD results in its quantitative conversion to **2**. Based on dirhodium photochemistry,[6,7] the photoeliminated halogen is efficiently trapped by α-H abstraction from THF.

The resulting suite of compounds preserves a metal−metal bond across a four-electron transformation with a $Pt_2^{I,III}$ species mixed-valence species as the linchpin. The presence of metal−metal bonding across the series provides an accessible excited-state with σ^* character from which photochemistry can originate, in much the same way as has been previously reported for Rh_2 dimers.[9,23]

A halogen trap is circumvented if the photoreaction is performed in the solid state. Irradiation of solid powder samples of **3** in vacuo and in ambient conditions results in elimination of Cl_2 to produce (based on UV−vis, $^{31}P\{^1H\}$ and ^1H analysis, Figures 2, S12, and S14) **2** in 70% synthetic yield along with its isomer, the *cis*,*trans*-$Pt_2^{II,II}(tfepma)_2Cl_4$ compound (see Supporting Information for structural and NMR data) in 15% yield. Generation of chlorine gas in these solid state experiments was confirmed by a mass spectrometric (MS) analysis of the gas in the headspace of a sealed, evacuated high-pressure glass vessel in which **3** was irradiated. Mass fragments corresponding to $^{35,35}Cl_2$, $^{37,37}Cl_2$, $^{35,37}Cl_2$, $^{35}Cl\cdot$, and $^{37}Cl\cdot$ are all observed (Figure 3); the $Cl\cdot$ results from Cl_2 fragmentation upon electron impact ionization. The experimental abundance of ^{35}Cl and ^{37}Cl of 0.756(1) and 0.244(1), respectively, is in good agreement with the natural abundance of these isotopes in chlorine gas (75.78(4) and 24.22(4), respectively[24]). Since the possibility of a bimolecular reaction is removed in the solid state and no trap is present to collect ejected $Cl\cdot$ radicals, an intramolecular elimination of Cl_2 from the excited-state of **3** is invoked.

The development of HX splitting photocatalysis is expanded by the results reported herein: (1) high quantum yields for halogen photoelimination have been achieved and (2) the evolution of Cl_2 upon solid-state photolysis of **3** represents the first example of the thermodynamically unfavorable halogen elimination without the use of a chemical trap. Since Cl_2 addition proceeds facilely under the conditions of photolysis, we have shown authentic energy storage reactivity in the absence of a halogen trap. Further work is underway to unify the H_2 and X_2 photochemistry and to elucidate mechanistic details of M−X bond activation for the compounds reported here.

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Note Added after ASAP Publication. Typographical errors in the compound descriptions presented in the online abstract (ASAP 12/18/08) have been corrected. The revised abstract was reposted on January 7, 2009.

Supporting Information Available: Tables of bond lengths and angles, full experimental details and crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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