JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Subscriber access provided by ISTANBUL TEKNIK UNIV

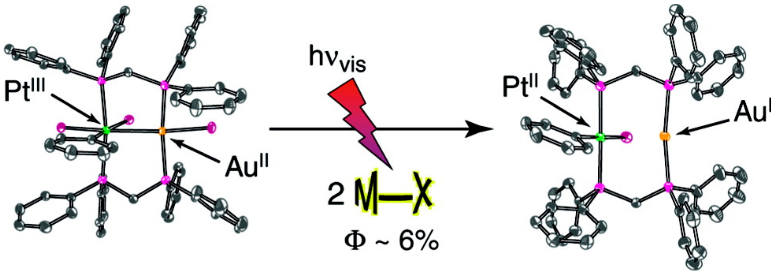
Communication

Metal–Halide Bond Photoactivation from a Pt–Au Complex

Timothy R. Cook, Arthur J. Esswein, and Daniel G. Nocera

J. Am. Chem. Soc., **2007**, 129 (33), 10094-10095• DOI: 10.1021/ja073908z • Publication Date (Web): 26 July 2007

Downloaded from http://pubs.acs.org on February 15, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 5 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

ACS Publications
High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Published on Web 07/26/2007

Metal−Halide Bond Photoactivation from a Pt^{III}−Au^{II} Complex

Timothy R. Cook, Arthur J. Esswein, and Daniel G. Nocera*

Department of Chemistry, 6-335, Massachusetts Institute of Technology, 77 Massachusetts Avenue,
Cambridge, Massachusetts 02139-4307

Received May 30, 2007; E-mail: nocera@mit.edu

Photodriven splitting of small molecules such as H_2O and HX (X = Cl, Br) to produce solar fuels[1] is hindered by the challenge of activating strong metal−halide and metal−oxo bonds that are the byproduct of H_2 elimination.[2,3] For instance, we have achieved photocatalytic hydrogen evolution from HX solutions using a dirhodium complex bridged by three dfmpa phosphazane ligands (dfmpa = $CH_3N(PF_2)_2$).[4] Two HX molecules add to the $Rh_2^{0,0}$ complex to give the hydrido−halide $Rh_2^{II,II}(H)_2(X)_2$ species from which H_2 is photoeliminated, furnishing the two-electron mixed valence complex, $Rh_2^{0,II}(X)_2$.[5] The Rh^{II}−X bond of the resulting $Rh_2^{0,II}(X)_2$ dihalide photoproduct may be activated by excitation into the $d\sigma \rightarrow d\sigma^*$ absorption manifold[6] of the bimetallic core to regenerate the $Rh_2^{0,0}$ center, thus closing the photocycle. Whereas hydrogen elimination from the $Rh_2^{II,II}(H)_2(X)_2$ species is facile, Rh^{II}−X bond activation is not, and hence this process is the overall determinant of H_2 production. An obvious strategy for improving the efficiency of H_2 production therefore is to increase the quantum yield of M−X bond activation. To this end, heterobimetallic cores provide an opportunity to incorporate a more oxidizing metal into the bimetallic center for M−X activation while at the same time preserving a site for H_2 evolution. Along these lines, the light sensitivity and two-electron chemistry of bimetallic gold−halide complexes[7,8] have led us to investigate RhAu heterobimetallic complexes.[9] We have established the oxidation of $Rh^{I}Au^{I}(tfepma)_2(CN^{t}Bu)_2Cl_2$ (tfepma = $CH_3N(P[OCH_2CF_3]_2)_2$) by two electrons to yield a direct Rh^{II}−Au^{II} bond[10] but found that the resulting complex thermally disproportionates to Rh^{III} and Au^{I} products. We surmised that an analogous $Pt^{III}Au^{II}$ system might exhibit greater covalency and hence diminished tendency for disproportionation. Although $Pt^{II}Au^{I}$ bimetallics have been synthesized[11−14] and spectroscopically examined,[15−17] the multielectron photochemistry of these $d^8\cdots d^{10}$ cores remains unexplored. In this work, we have prepared and structurally characterized the first $Pt^{III}Au^{II}$ compound[18] and show that this d^7−d^9 complex exhibits a facile two-electron chemically assisted halogen photoelimination that is promoted by visible light.

Initial investigations of the $[Pt^{II}Au^{I}(dppm)_2(CN)_2]Cl$ (dppm = $CH_2(P[Ph]_2)_2$) complex, first synthesized by Shaw and co-workers,[11] resulted in scission of the bimetallic core upon treatment with oxidants or HCl, thus prompting investigations of alternative bimetallic species. We report here the structural characterization of the $[Pt^{II}Au^{I}(dppm)_2PhCl]PF_6$ (**1**) complex of Anderson and co-workers;[19] the results of the X-ray analysis are shown in Figure 1 (left). The structure reveals a normal square planar coordination about Pt^{II} and a linear coordination of Au^{I} as shown by P(4)−Pt(1)−P(1) and C(3)−Pt(1)−Cl(1) angles of 177.42(5) and 178.70(19)°, respectively, and a P(3)−Au(1)−P(2) angle of 166.36(6)°. The Pt$\cdots$Au distance of 2.9646(3) Å is consistent with the absence of a direct metal−metal bond, as is expected for a bimetallic core in a $d^8\cdots d^{10}$ configuration.

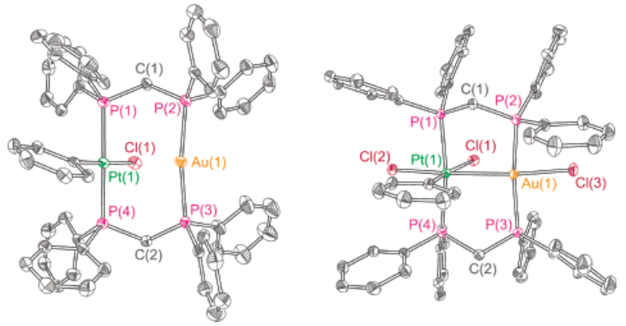


Figure 1. Thermal ellipsoid plots of **1** (left) and **2** (right) drawn at the 50% probability level. Hydrogen atoms, solvents of crystallization, and noncoordinating counterions omitted for clarity. Selected bond distances (Å): Pt(1)−Au(1), 2.9646(3) (**1**), 2.6457(3) (**2**); Pt(1)−Cl(1), 2.4362(15) (**1**), 2.4502(8) (**2**); Pt(1)−Cl(2), 2.3969(8) (**2**); Au(1)−Cl(3), 2.3909(8) (**2**). Selected bond angles (deg): Au(1)−Pt(1)−Cl(1), 72.93(4)° (**1**), 71.17(2)° (**2**); P(1)−Pt(1)−P(4), 177.42(5) (**1**), 167.92(3) (**2**); P(2)−Au(1)−P(3), 166.36(6) (**1**), 162.65(3) (**2**).

Two signals at 20.6 and 35.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum (25 °C, CD_3CN) of **1** are diagnostic of a heterobimetallic core. ^{195}Pt satellites ($^1J_{Pt-P}$ = 3040.7 Hz) flank the 20.6 ppm signal, indicative of a Pt-bound phosphorus. Oxidation of **1** by $PhI{\cdot}Cl_2$ is accompanied by a dramatic color change from pale yellow to deep red. The diagnostic resonances of **1** are replaced with two sharp signals at 15.3 and −10.5 ppm; the $^{31}P\{^1H\}$ NMR establishes that the transformation is quantitative. The observation of strong ^{195}Pt coupling to the low field resonance ($^1J_{Pt-P}$ = 1868 Hz) together with weaker coupling to the 15.3 ppm ($^1J_{Pt-P}$ = 50.7 Hz) resonance suggests that the heterobimetallic core is maintained in the reaction product. Single-crystal X-ray diffraction shows that **1** is oxidized to $[Pt^{III}Au^{II}(dppm)_2PhCl_3]PF_6$ (**2**) (Figure 1, right). The ligand topology of **1** is largely retained in **2**, the most notable difference being the inclusion of axial Cl bonding interactions in the primary coordination spheres of both the Pt and Au metal centers, as evidenced by close Pt(1)−Cl(2) and Au(1)−Cl(3) distances of 2.3969(8) and 2.3909(8) Å, respectively. A significant contraction of the Pt−Au distance from 2.9646(3) Å in **1** to 2.6457(3) Å in **2** is indicative of a formal metal−metal bond, thus completing the octahedral and square planar geometries of the Pt^{III} and Au^{II} centers, respectively. The observation of the metal−metal bond in the d^7−d^9 core of **2** is entirely consistent with Pt^{III} and Au^{II} centers, which are predominantly observed when stabilized by the formation of metal−metal bonds.[20]

The electronic absorption spectrum of **1** (Figure S1) features a dominant band centered at 338 nm (12 500 M^{-1} cm^{-1}). Transitions of this type in $d^8\cdots d^{10}$ complexes have been assigned to $d\sigma^* \rightarrow p\sigma$.[21] However, the small amount of Au character in the σ^* orbital of complexes such as $[Pt^{II}Au^{I}(dppm)_2(CN)_2]ClO_4$[16] suggests that this transition may also possess significant Pt $d_{z^2} \rightarrow p_z,\pi^*$ ligand charge transfer (MLCT) contributions. Upon oxidation, this promi-

10.1021/ja073908z CCC: $37.00 © 2007 American Chemical Society

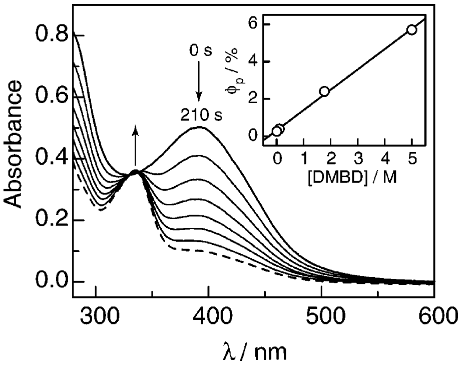
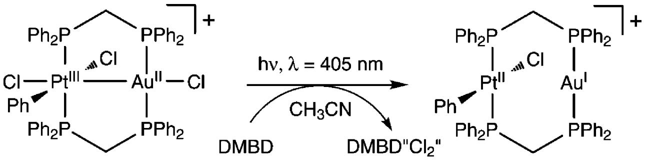


Figure 2. Spectral evolution during the photolysis of CH$_3$CN solutions of **2** (—) with monochromatic 405 nm light in the presence of 0.1 M 2,3-dimethyl-1,3-butadiene as a halogen radical trap. The final spectrum (- - -) matches that of **1**. Inset shows the linear dependence of quantum yield on trap concentration.

nent absorption band is lost and features corresponding to **2** emerge. Two new bands, observed at 278 nm (27 000 M^{-1} cm^{-1}) and 391 nm (17 000 M^{-1} cm^{-1}), are consistent with transitions originating from electron promotion from filled dσ and dπ* orbitals into an empty dσ* orbital, respectively.[22] The dσ* orbital in d^7−d^9 cores possesses significant antibonding character between the metals and axial chlorides;[10] thus, population of this empty orbital should weaken the M−X bond significantly.

Figure 2 displays the evolution of the absorption profile for the photolysis of a 30 μM solution of **2** with 405 nm light in acetonitrile in the presence of 2,3-dimethyl-1,3-butadiene (DMBD). Identical results are obtained with 446 nm excitation light. The initial spectrum, which is maintained indefinitely in the absence of light, promptly changes upon irradiation. Well-anchored isosbestic points maintained throughout the irradiation attest to a clean and quantitative photoreaction. With the appearance of the final absorption spectrum, no additional changes are observed with continued irradiation. Monitoring the photoreaction with ^{31}P{^{1}H} NMR shows that the characteristic resonances of **2** disappear with the co-incident appearance of the signals for **1**. Moreover, the final absorption spectrum is co-incident with that of independently prepared samples of **1**, thus establishing the overall photochemistry,



The quantum yield scales linearly with DMBD concentration (Figure 2, inset), attaining a maximum of 5.7% at 5 M DMBD. Irradiation in the absence of DMBD yields **1** and additional bimetallic products; ^{31}P{^{1}H} NMR spectra of reacted solutions indicate radical attack on the ligand on **1**. Such side reactions are suppressed by DMBD. Analysis of the photolyzed solution shows evidence for both DMBDCl$_2$ and (DMBDCl)$_2$ (DMBD“Cl$_2$”).

Elimination of halogen from dihalide complexes of transition metals has remained largely unexplored owing to the difficulties associated with executing this reaction.[23] Unfavorable thermodynamic constraints demand that the reaction be performed under forcing conditions.[24] Notwithstanding, the production of H$_2$ from simple substrates such as mineral acids demands that this reaction be overcome using visible light. Our previous work on the d^7−d^9 complex, Rh^{0}Rh^{II}(dfpma)$_3$Cl$_2$(η^1-dfpma), eliminates halogen in neat trap (i.e., THF) but only at a maximum quantum yield of 0.6% and with UV light (λ_{max} = 350 nm) as the impetus. In the d^7−d^9 complex of **2**, the chemically assisted photoelimination may be performed with visible light and occurs with a 10-fold increase in efficiency. The high quantum yield suggests that intermediates will be of sufficient concentration such that they may be captured by transient laser kinetics techniques. As such, spectroscopic experiments to elucidate the mechanism of M−X bond activation are currently underway.

Acknowledgment. This research was supported by the NSF (Grant CHE-0132680). Grants from the NSF also provided instrument support to the DCIF at MIT (CHE-9808061, DBI-9729592).

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.

References

(1) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15729.
(2) Pistorio, B. J.; Nocera, D. G. *Chem. Commun.* **1999**, 1831.
(3) Pistorio, B. J.; Nocera, D. G. *J. Photochem. Photobiol. A* **2004**, *162*, 563.
(4) Heyduk, A. F.; Nocera, D. G. *Science* **2001**, *293*, 1639.
(5) Esswein, A. J.; Veige, A. S.; Nocera, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 16641.
(6) Heyduk, A. F.; Macintosh, A. M.; Nocera, D. G. *J. Am. Chem. Soc.* **1999**, *121*, 5023.
(7) Fackler, J. P., Jr. *Inorg. Chem.* **2002**, *41*, 6959.
(8) Mazany, A. M.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 801.
(9) Dempsey, J. L.; Esswein, A. J.; Manke, D. R.; Rosenthal, J.; Soper, J. D.; Nocera, D. G. *Inorg. Chem.* **2005**, *44*, 6879.
(10) Esswein, A. J.; Dempsey, J. L.; Nocera, D. G. *Inorg. Chem.* **2007**, *46*, 2362.
(11) Hassan, F. S. M.; Markham, D. P.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 279.
(12) Langrick, C. R.; Pringle, P. G.; Shaw, B. L *J. Chem. Soc., Dalton Trans.* **1984**, 1233.
(13) Cooper, G. R.; Hutton, A. T.; Langrick, C. R.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1984**, 855.
(14) Langrick, C. R.; Shaw, B. L. *J. Chem. Soc., Datlon Trans.* **1985**, 511.
(15) Xia, B.-H.; Zhang, H.-X.; Che, C.-M.; Leung, K.-H.; Phillips, D. L.; Zhe, N.; Zhou, Z.-Y. *J. Am. Chem. Soc.* **2003**, *125*, 10362.
(16) Yip, H.-K.; Lin, H.-M.; Cheung, K.-K.; Che, C.-M.; Wang, Y. *Inorg. Chem.* **1994**, *33*, 1644.
(17) Yin, G.-Q.; Wei, Q.-H.; Zhang, L.-Y.; Chen, Z.-N. *Organometallics* **2005**, *25*, 580.
(18) Per a search of the CDC database for all PtAu heterobimetallics.
(19) Xu, C.; Anderson, G. K.; Brammer, L.; Braddock-Wilking, J.; Rath, N. P. *Organometallics* **1996**, *15*, 3972.
(20) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999; pp 1079 and 1100.
(21) Balch, A. L.; Catalano, V. J.; Olmstead, M. M. *Inorg. Chem.* **1990**, *29*, 585.
(22) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier; New York, 1984; Chapter 7.
(23) Crabtreee, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; Wiley-Interscience: New York, 2001.
(24) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Venturi, C.; Zuccaccia, C. *J. Organomet. Chem.* **2006**, *691*, 3881.

JA073908Z