*Inorg. Chem.* **2006**, *45*, 5242–5244


# Photoinitiated Electron Collection at a Metal in a Rhodium-Centered Mixed-Metal Supramolecular Complex

**Mark Elvington and Karen J. Brewer***

*Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24060-0212*

Received February 15, 2006

A mixed-metal supramolecular complex $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ has been studied and shown to undergo photoinitiated electron collection at the metal center. Reported herein is an analysis of the photochemical properties of this complex, illustrating the ability of this complex to photoreduce by two electrons by converting $Rh^{III}$ to $Rh^{I}$ and with the trimetallic assembly remaining intact. Emission-quenching experiments demonstrate efficient quenching of the Ru → dpp charge-transfer state by the Rh center and the electron-donor dimethylaniline.

The conversion of light energy into chemical energy is of great interest, with particular focus on the development of efficient solar energy conversion schemes. The metal-to-ligand charge-transfer (MLCT) excited states of ruthenium polyazine complexes have found widespread use in this arena.[1−3] Multielectron photocatalysis is a key component of schemes to convert light energy into fuels. Both solar water splitting and light-driven carbon dioxide reduction invoke multielectron reactions. Much work has focused on the development of complex supramolecular assemblies for light harvesting and directional charge separation.[4−6] Very few homogeneous systems have been studied that use light to perform multielectron reactions or collect reducing equivalents.[7−10] We report herein a Rh-centered supramolecular complex that undergoes photoinitiated electron collection at the Rh center.

Photoinitiated electron collection is a process where light energy is used to collect reducing equivalents. This multielectron photochemistry has been of interest in harvesting light energy as a means to produce multielectron-reduced substrates or fuels. A system for photoinitiated electron collection must efficiently absorb light, undergo efficient successive and/or multiple electron transfer(s), and be stable in the multielectron-reduced form, making functional photoinitiated electron collectors (PECs) elusive.

The first functioning photoinitiated EC was reported by Brewer, employing $\pi$ systems of polyazine bridging ligands (BLs) to collect electrons, $[\{(bpy)_2Ru(BL)\}_2IrCl_2]^{5+}$ (bpy = 2,2′-bipyridine).[7] This complex photochemically collects multiple electrons on the $\pi$ systems of BLs bound to a central metal.

MacDonnell, Campagna, and co-workers reported two interesting bimetallic Ru complexes that collect two or four electrons photochemically.[8] These systems function by optical excitation into a phen-type orbital on the BL followed by transfer to a lower-lying secondary $\pi^*$ acceptor orbital. Photolysis of $(phen)_2Ru(tatpq)Ru(phen)_2^{4+}$ leads to the four-electron-reduced complex tatpq = phenanthroline−pyrazine−quinone−pyrazine−phenanthroline.[8]

Bocarsly and co-workers devised promising $Pt^{IV}$-centered trimetallic complexes $[\{(NC)_5M^{II}(CN)\}_2Pt^{IV}(NH_3)_4]^{4-}$ (M = Fe, Ru, or Os) that undergo photoinitiated electron transfer.[10] In the case where M = Fe, absorption of one photon results in two-electron transfer to the central $Pt^{IV}$ followed by fragmentation of the polymetallic complex into two $Fe^{III}$ complexes and a reduced $Pt^{II}$ monometallic complex.[10]

Nocera and co-workers designed interesting metal−metal-bonded systems that undergo photochemical multielectron chemistry.[9] Photolysis of $(PPh)_3Rh^0-Rh^0(MeN(PF_2)_2)_3(CO)$

(1) (a) Campagna, S.; Serroni, S.; Puntoriero, F.; Di Pietro, C.; Ricevuto, V. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: New York, 2001; Vol. 5, p 168 and references cited therein. (b) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. A. *Coord. Chem. Rev.* **1975**, *15*, 321.
(2) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1576.
(3) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.
(4) Balzani, V.; Moggi, L.; Scandola, F. In *Supramolecular Photochemistry*; Balzani, V., Ed.; NATO Advanced Study Institute Series 214; Reidel: Dordrecht, The Netherlands, 1987; p 1 and references cited therein.
(5) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759 and references cited therein.
(6) Serroni, S.; Campagna, S.; Puntoriero, F.; Loiseau, F.; Ricevuto, V.; Passsalacqua, R.; Galletta, M. *C. R. Chim.* **2003**, *6*, 883.
(7) Molnar, S. M.; Nallas, G.; Bridgewater, J. S.; Brewer, K. J. *J. Am Chem. Soc.* **1994**, *116*, 5206.
(8) (a) Konduri, R.; Ye, H.; MacDonnell, F. M.; Serroni, S.; Campagna, S.; Rajeshwar, K. *Angew. Chem., Int. Ed.* **2002**, *41* (17), 3185. (b) Chiorboli, C.; Fracasso, S.; Scandola, F.; Campagna, S.; Serroni, S.; Konduri, R.; MacDonnell, F. M. *Chem. Commun.* **2003**, 1658. (c) Chiorboli, C.; Fracasso, S.; Ravaglia, M.; Scandola, F.; Campagna, S.; Wouters, K.; Konduri, R.; MacDonnell, F. *Inorg. Chem.* **2005**, *44* (23), 8368.
(9) (a) Heyduk, A. F.; Nocera, D. G. *Science* **2001**, *293*, 1639. (b) Nocera, D.; Heyduk, A. *PCT Int. Appl.* **2003**, 157. (c) Gray, T.; Nocera, D. *Chem. Commun.* **2005**, *12*, 1540. (d) Esswein, A.; Veige, A.; Nocera, D. *J. Am. Chem. Soc.* **2005**, *127* (47), 16641.
(10) (a) Chang, C. C.; Pfennig, B.; Bocarsly, A. B. *Coord. Chem. Rev.* **2000**, *208*, 33. (b) Watson, D. F.; Tan, H. S.; Schreiber, E.; Mordas, C. J.; Bocarsly, A. B. *J. Phys. Chem. A* **2004**, *108*, 3261. (c) Mordas, C.; Pfennig, B.; Schreiber, E.; Bocarsly, A. B. *Springer Ser. Chem. Phys.* **2003**, *71*, 453.



10.1021/ic0602648 CCC: $33.50 
Published on Web 06/17/2006

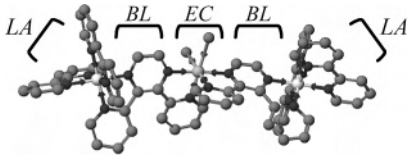


**Figure 1.** Mixed-metal supramolecular complex $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$, a molecular device for photoinitiated electron collection [light absorber (LA), bridging ligand (BL), and electron collector (EC), bpy = 2,2′-bipyridine, and dpp = 2,3-bis-2-pyridylpyrazine].

results in photodissociation of CO and coordination of hydrohalic acid. Disproportionation produces $H_2$ and $(PPh_3)_3Rh^0-Rh^0(MeN(PF_2)_2)_3X_2$ (X = halogen). Adding a halogen atom trap leads to regeneration of the catalytically active species $(PPh)_3Rh^0-Rh^0(MeN(PF_2)_2)_3$.[9]

Herein we report photochemical properties of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ [Figure 1; dpp = 2,3-bis-2-pyridylpyrazine][11] coupling two Ru light absorber (LA) units, through polyazine BLs, to a central Rh EC core. This trimetallic complex undergoes unique, previously unreported photochemistry. Photoinitiated electron collection at Rh reduces $Rh^{III}$ to $Rh^{I}$ with the trimetallic assembly remaining intact.

Tris(polyazine)rhodium(III) complexes are known to serve as electron acceptors in intermolecular electron-transfer schemes utilizing $[Ru(bpy)_3]^{2+}$ LAs.[12] Upon MLCT excitation of $[Ru(bpy)_3]^{2+}$, bimolecular electron transfer to $[Rh(bpy)_3]^{3+}$ yields $[Rh(bpy)_3]^{2+}$, which disproportionates to $[Rh(bpy)_2]^{+}$ and $[Rh(bpy)_3]^{3+}$ or in the presence of a Pt catalyst generates $H_2$.[12]

The trimetallic complex $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ displays light-absorbing properties dominated by the two Ru LA units and redox properties that illustrate the Rh(d$\sigma$*) nature of the lowest unoccupied molecular orbital (LUMO).[11] Electrochemically, this complex displays two reversible, overlapping $Ru^{II/III}$ couples at 1.63 V vs Ag/AgCl, indicating that the two Ru centers are largely electronically uncoupled (see the Supporting Information). Reductively, an irreversible $Rh^{III/II/I}$ couple at −0.37 V and two reversible $dpp^{0/-}$ couples at −0.76 and −1.00 V are observed. This illustrates the Ru(d$\pi$) nature of the highest occupied molecular orbital and Rh(d$\sigma$*) nature of the LUMO. The electronic absorption spectroscopy shows bpy- and dpp-based $\pi \rightarrow \pi^*$ transitions in the UV and Ru → bpy and Ru → dpp CT transitions in the visible.[11] The lowest energy band observed in the electronic absorption spectrum is a Ru → dpp CT transition at 520 nm.

Emission spectroscopy was used to investigate the photophysical properties of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$. Emission from the dpp-based $^3$MLCT state at 760 nm is quenched by intramolecular electron transfer to the Rh, thereby populating the lower-lying metal-to-metal charge-transfer ($^3$MMCT) state. Compared to the model bimetallic system without Rh $\{[(bpy)_2Ru(dpp)Ru(bpy)_2]^{4+}$,[13] $\lambda_{max}^{em}$ = 744 nm, $\Phi^{em} = 1.38 \times 10^{-3}$ [measured vs $Os(bpy)_3^{2+}$]$\}$,[14]

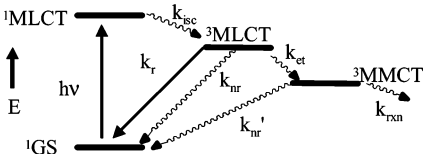


**Figure 2.** State diagram for $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$, a molecular device for photoinitiated electron collection (bpy = 2,2′-bipyridine and dpp = 2,3-bis-2-pyridylpyrazine).

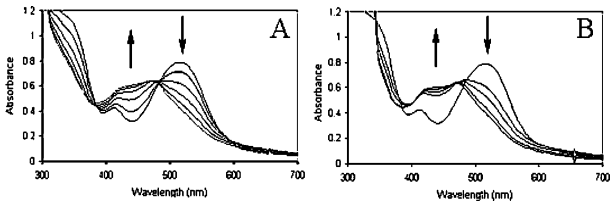


**Figure 3.** Electronic absorption spectra for the conversion of $[\{(bpy)_2Ru(dpp)\}_2Rh^{III}Cl_2]^{5+}$ to the two-electron-reduced form $[\{(bpy)_2Ru(dpp)\}_2Rh^{I}]^{5+}$ electrochemically (A) and photochemically (B) (bpy = 2,2′-bipyridine and dpp = 2,3-bis-2-pyridylpyrazine). Electrochemically (A), the complex is reduced at −0.40 V vs Ag/AgCl in deoxygenated 0.1 M $Bu_4PF_6/CH_3CN$ in an H cell. (B) The complex is photolyzed at 520 ± 10 nm in deoxygenated $CH_3CN$ with 0.29 M DMA.

the title trimetallic complex exhibits 95% quenching of the $^3$MLCT emission ($\Phi^{em} = 7.3 \times 10^{-5}$) and a concurrent reduction in the excited-state lifetime in a deoxygenated room-temperature $CH_3CN$ solution. Owing to the similar energy and Ru → $\mu$-dpp CT nature of both excited states, we estimate that $k_r$ and $k_{nr}$ are equivalent. This predicts efficient intramolecular electron transfer for $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$, $k_{et} = 1.2 \times 10^8$ s$^{-1}$, populating the Ru → Rh $^3$MMCT state (Figure 2).

The title complex $[\{(bpy)_2Ru(dpp)\}_2Rh^{III}Cl_2]^{5+}$ undergoes photoreduction in the presence of an electron donor, dimethylaniline (DMA), to produce the two-electron-reduced form $[\{(bpy)_2Ru(dpp)\}_2Rh^{I}]^{5+}$, thereby undergoing photoinitiated electron collection at the metal center. The electrochemical reduction by two electrons of $[\{(bpy)_2Ru(dpp)\}_2Rh^{III}Cl_2](PF_6)_5$ at −0.40 V leads to the formation of a $Rh^{I}$ complex, $[\{(bpy)_2Ru(dpp)\}_2Rh^{I}](PF_6)_5$, via loss of two chlorides, analogous to $[Rh(bpy)_2Cl_2]^{+}$ and $[Rh(dpp)_2Cl_2]^{+}$.[14,15] DeArmond observes that two-electron reduction of $[Rh(bpy)_2Cl_2]^{+}$ produces an irreversible oxidation due to free chloride and two $bpy^{0/-}$ couples. Similarly, reduction of $[\{(bpy)_2Ru(dpp)\}_2Rh^{III}Cl_2]^{5+}$ by two electrons results in an irreversible chloride oxidation and two low-potential $\mu$-$dpp^{0/-}$ reductions at −0.76 and −1.00 V vs Ag/AgCl. The spectroscopic changes associated with the reduction of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ are illustrated in Figure 3A. The Ru → dpp CT band shifts to higher energy for the $Rh^{I}$ complex as a result of the decreased electron-withdrawing and increased electron-donating ability of $Rh^{I}$ vs $Rh^{III}$, destabilizing the dpp $\pi$* acceptor orbitals. This shift is mirrored by a movement to higher energy of the dpp-based $\pi \rightarrow \pi^*$ band. The Ru → bpy CT band at 420 nm is relatively unaffected by Rh reduction. Photolysis of $[\{(bpy)_2Ru(dpp)\}_2Rh^{III}Cl_2]^{5+}$ in the presence of a sacrificial

(11) Holder, A. A.; Swavey, S.; Brewer, K. J. *Inorg. Chem.* **2004**, *43*, 303.
(12) (a) Brown, G. M.; Chan, S. F.; Creutz, C.; Schwarz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 7638. (b) Creutz, C.; Keller, A. D.; Sutin, N.; Zipp, A. P. *J. Am. Chem. Soc.* **1982**, *104*, 3618.
(13) Fuchs, Y.; Lofters, S.; Dieter, T.; Shi, W.; Morgan, S.; Strekas, T. C.; Gafney, H. D.; Baker, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 2691.
(14) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630.
(15) Rasmussen, S. C.; Richter, M. M.; Yi, E.; Place, H.; Brewer, K. J. *Inorg. Chem.* **1990**, *29*, 3926.

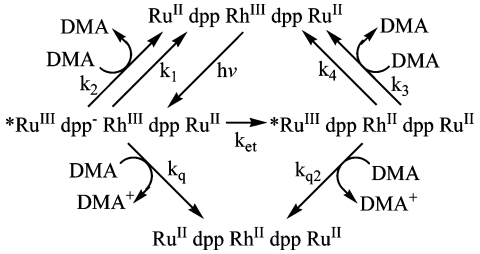


**Figure 4.** Proposed mechanism for photoinitiated electron transfer. bpy, Cl, and charges are omitted for clarity. $Ru^{II}dppRh^{III}dppRu^{II}$ = $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ (bpy = 2,2′-bipyridine and dpp = 2,3-bis-2-pyridylpyrazine). DMA = dimethylaniline. $k_1$ and $k_4$ are the unimolecular decay pathways from the $^3$MLCT and $^3$MMCT states, respectively, whereas $k_2$ and $k_3$ are the bimolecular deactivation rates from the same states. $k_{et}$ is the rate of electron transfer to generate the $^3$MMCT state. $k_q$ and $k_{q2}$ are the rates of reductive quenching by DMA to generate the $Rh^{II}$ complex from the $^3$MLCT and $^3$MMCT states, respectively.

electron donor, DMA, leads to the production of the same $[\{(bpy)_2Ru(dpp)\}_2Rh^{I}]^{5+}$ species (Figure 3B). The changes in the high-energy visible region of the spectrum are obscured in the photochemical experiment because of intense absorbance by DMA. The spectroscopic changes associated with the photochemical reduction (Figure 3B) are identical with those seen in the electrochemical reduction (Figure 3A). This study illustrates the ability of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$ to undergo photoinitiated electron collection at the Rh center.

A kinetic investigation has been undertaken to probe photoreduction of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ in more detail. The generation of the two-electron-reduced form of our trimetallic complex, $[\{(bpy)_2Ru(dpp)\}_2Rh^{I}]^{5+}$, appears to occur through production of the $Rh^{II}$ form, consistent with the electrochemical properties of $[Rh(bpy)_2Cl_2]^+$ and $[Rh(dpp)_2Cl_2]^+$.[15,16] Our kinetic analysis focuses on the initial photochemical steps leading to the first-electron reduction of the trimetallic complex (Figure 4).

An emission-quenching analysis by the sacrificial donor DMA provides insight into the reactivity of the $^3$MLCT state (Figures 2 and 4). The interaction between $[Ru(bpy)_3]^{2+}$ and DMA has been studied previously.[17] For $[Ru(bpy)_3]^{2+}$, the $^3$MLCT is quenched by DMA at a rate of $7.1 \times 10^7$ $M^{-1}$ $s^{-1}$. For $*Ru(bpy)_3^{2+}$, the excited-state reduction potential is 0.77 V and the oxidation potential for DMA is 0.81 V (vs SCE).[16] The excited-state reduction potential for $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ is 0.90 V, increasing the driving force for reductive quenching of the Ru → dpp CT state. The $^3$MLCT state of the trimetallic complex undergoes competitive electron transfer to Rh to generate the $^3$MMCT state. This gives rise to a complicated mechanism.

Emission from the $^3$MLCT state of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ is quenched efficiently by DMA (Figure 5A). Using the mechanism in Figure 4, $\Phi_o^{em}/\Phi^{em} = 1 + (k_q + k_2)/\{(k_1 + k_{et})[DMA]\}$. The slope of the Stern−Volmer plot (using $k_1 = k_r + k_{nr} = 1.2 \times 10^8$ $s^{-1}$) yields $k_q + k_2 = 2 \times 10^{10}$ $M^{-1}$ $s^{-1}$, consistent with efficient $^3$MLCT emission quenching. Back electron transfer for amine quenching of ruthenium

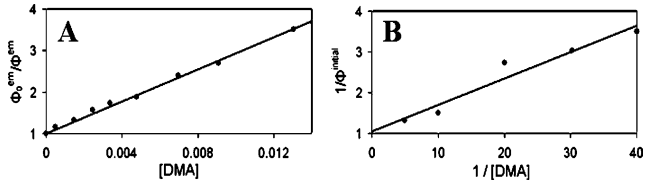


**Figure 5.** Stern−Volmer plots for (A) emission quenching of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2]^{5+}$ by DMA and (B) product formation of the one-electron-photoreduced $Rh^{II}$ product (bpy = 2,2′-bipyridine and dpp = 2,3-bis-2-pyridylpyrazine).

polyazine systems is often efficient, reducing the net product formation. In the case of $*Ru(bpy)_3^{2+}$ quenched by DMA, $k_q = 7.1 \times 10^7$ $M^{-1}$ $s^{-1}$ and $k_b = 4.1 \times 10^9$ $M^{-1}$ $s^{-1}$.[17]

To investigate the formation of the photoreduced $Rh^{II}$ product in more detail, a Stern−Volmer analysis of product formation was undertaken (Figure 5B). At early photolysis times, the formation of $Rh^{II}$ dominates and would display Ru → dpp CT transitions intermediate between the $Rh^{III}$ and $Rh^{I}$ forms. At high [DMA], $\Phi_{initial}$ approaches unity. Product formation can occur from the $^3$MLCT or $^3$MMCT state or a combination of both. Kinetically, if product formation comes from the $^3$MLCT state, $1/\Phi = (k_1 + k_{et})/(k_q[DMA]) + (k_q + k_2)/k_q$. Conversely, if product formation comes from the $^3$MMCT state, $1/\Phi = (1/\Phi_{^3MMCT})(k_4/(k_{q2}[DMA]) + (k_{q2} + k_3)/k_q)$. Both pathways predict the linear plot of $1/\Phi$ vs 1/[DMA] observed in Figure 5B, which yields a slope of 0.065 and a *y* intercept of 1.05. If the $Rh^{II}$ product results from the $^3$MLCT state, $k_q$ would be $1.9 \times 10^9$ $M^{-1}$ $s^{-1}$. The higher $k_q$ for quenching of the trimetallic complex by DMA relative to $[Ru(bpy)_3]^{2+}$ would be consistent with the increased driving force for electron transfer. If the $Rh^{II}$ product results from quenching of the $^3$MMCT state, $k_4/k_{q2}$ is 0.062 and the value of $k_{q2}$ would depend on the lifetime of the $^3$MMCT state. Related trichelated systems show rapid back electron transfer ($7.1 \times 10^9$ $s^{-1}$),[18] which would require a very rapid $k_{q2}$. The above emission-quenching analysis and this product formation analysis suggest that both the $^3$MLCT and $^3$MMCT states may lead to photoreduced products.

The ability to reduce a metal center by multiple electrons within a supramolecular architecture that remains intact is unique and promising. The photoreduced product $[\{(bpy)_2Ru(dpp)\}_2Rh]^{5+}$ is coordinatively unsaturated, available to interact with substrates. Interestingly, this reduced complex still possesses an intense MLCT band that might be exploited for further photochemical reduction. Studies exploring the photochemical properties of this complex in more detail are underway.

**Acknowledgment** is made to the donors of the American Chemical Society Petroleum Research Fund for support of this work.

**Supporting Information Available:** Cyclic voltammogram of $[\{(bpy)_2Ru(dpp)\}_2RhCl_2](PF_6)_5$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0602648

(16) Kew, G.; DeArmond, M. K.; Hanck, K. J. *J. Phys. Chem.* **1974**, *78*, 727.

(17) (a) Anderson, C. P.; Salmon, D. J.; Meyer, T. J.; Young, R. C. *J. Am. Chem. Soc.* **1977**, *99* (6), 1980. (b) Haga, M.; Dodsworth, E.; Eryavec, G.; Seymour, P.; Lever, B. *Inorg. Chem.* **1985**, *24*, 1901.

(18) Indelli, M. T.; Bignozzi, C. A.; Harriman, A.; Schoonover, J. R.; Scandola, F. *J. Am. Chem. Soc.* **1994**, *116*, 3775.