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Photogenerated Catalysis in Metal-Organic Systems. 3.^{1a} Catalyzed Valence Isomerization of Quadricyclene to Norbornadiene via Photochemical Generation of a Strong Ground-State Oxidant

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Irradiation of an acetonitrile solution containing tris(2,2'-bipyridine)ruthenium(II) ($\text{Ru}(\text{bpy})_3^{2+}$), the methylviologen dication (MV^{2+}), and quadricyclene (Q) with 436-nm light initiates a catalytic cycle for the conversion of Q to its more stable valence isomer norbornadiene (NBD). Quantum yields of NBD production above 1 and turnovers of $\text{Ru}(\text{bpy})_3^{2+}$ greater than 10^2 have been measured. Spectral, continuous-photolysis, flash-photolysis results support a mechanism in which the primary photochemical step is oxidative quenching of the emissive metal-to-ligand charge-transfer excited state of $\text{Ru}(\text{bpy})_3^{2+}$ by MV^{2+} to form the strong ground-state oxidant, $\text{Ru}(\text{bpy})_3^{3+}$. Subsequent oxidation of Q by $\text{Ru}(\text{bpy})_3^{3+}$ regenerates the original metal complex and produces the structurally labile cation radical, $\text{Q}^{+\cdot}$. Rearrangement of $\text{Q}^{+\cdot}$ to $\text{NBD}^{+\cdot}$ and oxidation of another Q molecule by $\text{NBD}^{+\cdot}$ constitute the key chain-carrying steps in the catalytic cycle.

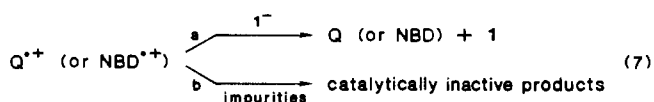
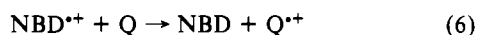
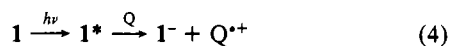
Introduction

Photogenerated catalysis² is a multistep process that begins with the light-induced generation of a ground-state catalyst C from a catalytically inactive precursor I (eq 1). In one or more subsequent thermal reactions, C converts a substrate molecule S to the final product P (eq 2). Since the catalyst generated by the



action of a single photon may result in the production of several molecules of P, the observed quantum yield of product formation can exceed unity. This chemical amplification of the initial photochemical act provides the opportunity to establish one or more catalytic cycles.

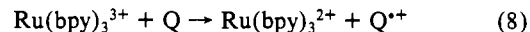
Transition-metal complexes have gained increasing popularity in the role of I^{2-4} . Photochemical reactions of complexes that have been reported to yield active thermal catalysts include ligand dissociation (especially prevalent among metal carbonyls), metal-metal bond cleavage (in dinuclear compounds and polynuclear clusters), intramolecular redox decomposition, and bimolecular electron transfer. The last type of process has been implicated in the photoinduced conversion of the highly strained hydrocarbon quadricyclene (Q) to its more stable valence isomer, norbornadiene (NBD), in the presence of the square-planar, d^8 complex $\text{PdCl}_2(\eta^4\text{-NBD})$ (1) (eq 3).^{1a,5} The essential details of the



chemistry in this system are summarized by eq 4-7. Following

excitation to a Pd-to-NBD charge-transfer excited state, the complex undergoes reductive quenching by Q (eq 4). The substantial kinetic barrier to rearrangement present in the uncharged Q molecule drops appreciably in the corresponding cation radical, $\text{Q}^{+\cdot}$, and the latter undergoes rapid and irreversible isomerization to the more stable $\text{NBD}^{+\cdot}$ cation radical (eq 5).⁶ Since oxidation of Q by $\text{NBD}^{+\cdot}$ (eq 6) is thermodynamically favorable,⁷ $\text{Q}^{+\cdot}$ is regenerated and can reenter the cycle. Repetition of eq 5 and 6 accounts for quantum yields of NBD production above 10^2 . Although large, the yields are finite, and thus one or more chain termination processes (eq 7) also must exist.

Although bimolecular electron transfer from Q to an electronically excited transition-metal complex (e.g. eq 4) provides a convenient entry into the catalytic cycle defined by eq 5 and 6, this pathway is limited to complexes whose excited states are relatively strong oxidants ($E_{\text{red}}^* > 0.9$ V vs SCE). This thermodynamic requirement would seem to preclude the use of the well-known photosensitizer $\text{Ru}(\text{bpy})_3^{2+}$ (bpy is 2,2'-bipyridine), since reductive quenching of its long-lived and emissive Ru-to-bpy charge-transfer excited state ($E_{\text{red}}^* = 0.8$ V vs SCE⁸) by Q is endoergic. Consistent with this expectation, we have found that the luminescence from this state is unquenched by Q. Interestingly, however, the oxidized complex, $\text{Ru}(\text{bpy})_3^{3+}$, is an appreciably stronger oxidizing agent ($E_{\text{red}} = 1.29$ V vs SCE⁸) than the excited state, and the process described by eq 8 is energetically favorable.



Consequently, generation of the oxidized ruthenium complex in the presence of Q can, in principle, initiate a catalytic cycle analogous to that discussed above.

In this report we describe our efforts to devise a system for the catalytic conversion of Q to NBD on the basis of the strategy of photochemically generating a strong ground-state oxidant.⁹ Three components comprise the initial system selected for study: $\text{Ru}(\text{bpy})_3^{2+}$, methylviologen dication (MV^{2+}), and Q. The metal complex functions as a photosensitizer and is the primary light-absorbing species; upon population of its emissive metal-to-ligand charge-transfer excited state (denoted by an asterisk), the complex undergoes oxidative quenching by MV^{2+} according to eq 9. This



- (1) (a) This is Document No. NDRL-2920 from the Notre Dame Radiation Laboratory. Part 2: Kelley, C. K.; Kutal, C. *Organometallics* **1985**, *4*, 1351. (b) University of Georgia. (c) Notre Dame Radiation Laboratory.
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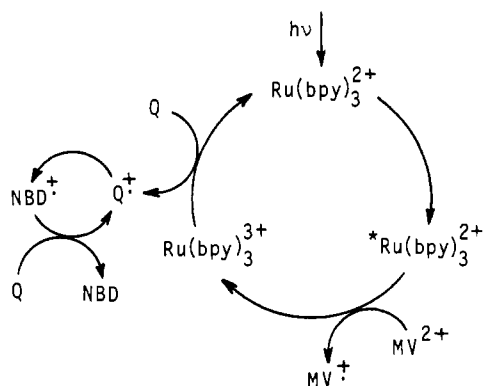
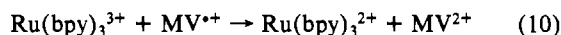


Figure 1. Proposed photogenerated catalytic cycle for the valence isomerization of Q to NBD.

quenching step, which occurs with a bimolecular rate constant of $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile,¹⁰ is well characterized and generates a species, MV^{2+} , with distinctive spectral properties.¹¹ Unproductive reverse electron transfer between the primary photoproducts (eq 10) should be inhibited if sufficient Q is present



to scavenge $\text{Ru}(\text{bpy})_3^{3+}$ (eq 8).¹² The latter process produces Q^+ and regenerates the original ruthenium complex. As depicted in Figure 1, the net result of this coupled series of reactions is the initiation of a photogenerated catalytic cycle for the conversion of Q to NBD. Reported below are spectral, continuous-photolysis, and flash-photolysis results that support this proposed mechanistic scheme.

Experimental Section

(a) Reagents. Norbornadiene (Aldrich) was purified by three distillations from potassium metal under a nitrogen atmosphere. Quadricyclene was prepared and purified by a procedure described previously.¹³ A commercial sample of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (G. F. Smith) was recrystallized from water and then methanol; the spectral properties of the resulting material closely matched those reported in the literature.¹⁴ Methylviologen dichloride (Aldrich) was converted to the hexafluorophosphate salt by dissolution in water followed by precipitation with ammonium hexafluorophosphate. The solid was filtered, washed with water, and then recrystallized from acetonitrile/water. The acetonitrile (UV grade, Burdick and Jackson) used in the spectral and photochemical studies was distilled from phosphorus pentoxide; the distillate was refluxed over calcium hydride for 1 h and then slowly distilled and stored under a nitrogen atmosphere.

(b) Equipment and Procedures. Electronic absorption spectra were recorded on a Cary 15 spectrophotometer. Luminescence intensity measurements were taken with a Perkin-Elmer MPF-44B spectrofluorimeter. Continuous photolyses were conducted with a 200-W high-pressure mercury-arc lamp whose output was passed through a Bausch and Lomb high-intensity monochromator.

In a typical photochemical experiment, an acetonitrile solution containing $\text{Ru}(\text{bpy})_3^{2+}$, MV^{2+} , Q, and nonane (added as an internal standard for gas chromatographic analysis) was placed in a 1-cm rectangular quartz cell, deaerated by bubbling with a stream of argon for 30 min, and then irradiated with stirring in a thermostated cell holder maintained at 25 °C. A companion dark sample was run to determine the extent of

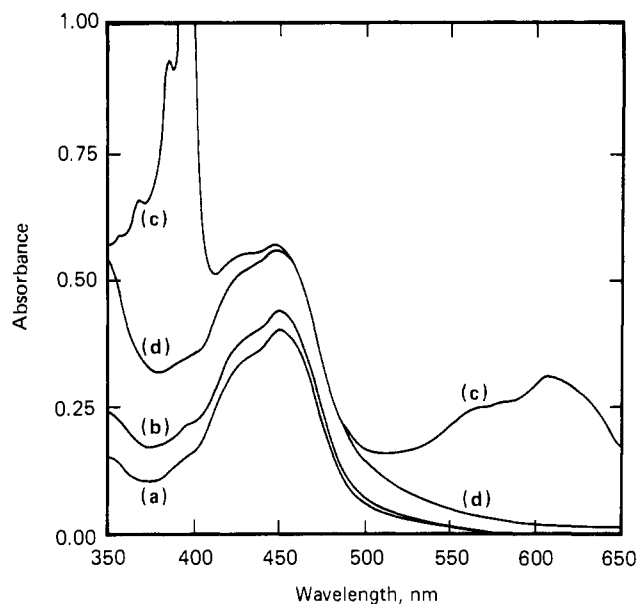


Figure 2. Electronic absorption spectra of various samples in acetonitrile: (a) $2.73 \times 10^{-5} \text{ M Ru}(\text{bpy})_3^{2+}$; (b) $2.73 \times 10^{-5} \text{ M Ru}(\text{bpy})_3^{2+} + 2.83 \times 10^{-3} \text{ M MV}^{2+} + 0.61 \text{ M Q}$; (c) sample b immediately after irradiation at 436 nm for 925 s; (d) sample c after sitting in the dark for 1 h.

any thermal reaction. Incident light intensity was measured by Reineckate actinometry.¹⁵ Aliquots of the irradiated and dark samples were analyzed by gas chromatography on a Varian 2700 instrument equipped with a flame ionization detector. A 12 ft \times 1/8 in. stainless steel column packed with 5% OV-101 on Chromosorb G HP and maintained at 90 °C afforded a separation of NBD and Q with retention times of 8 and 12 min, respectively. Gas chromatographic peak areas were integrated with a Perkin-Elmer Sigma 10 data system.

Quantum yields for norbornadiene production, ϕ_{NBD} , were calculated according to the expression given in eq 11, where I denotes the incident

$$\phi_{\text{NBD}} = \frac{\text{mol of NBD formed}}{I \times t \times \% \text{ quenching} \times \% A_{\text{Ru}}} \quad (11)$$

light intensity in einsteins s^{-1} , t is time of irradiation in seconds, % quenching represents the percentage of $\text{Ru}(\text{bpy})_3^{2+}$ excited states that are quenched by MV^{2+} , and $\% A_{\text{Ru}}$ is the average value of the percentage of the incident light absorbed by $\text{Ru}(\text{bpy})_3^{2+}$ during photolysis. Both the % quenching and $\% A_{\text{Ru}}$ values were corrected for competitive and unproductive absorption of the incident light by a ground-state Q-MV^{2+} complex (vide infra). It was necessary to use an average value for $\% A_{\text{Ru}}$ because the accumulation of the strongly absorbing photoproduct, MV^{2+} (Figure 2), during the course of photolysis caused a continuous change in absorbance at the excitation wavelength.

Flash photolyses were performed with equipment that has been described in detail elsewhere.¹⁶ Excitation wavelengths were confined to the region $\geq 520 \text{ nm}$ by means of a cutoff filter.

Results and Discussion

(a) Spectral and Solution Properties. The electronic absorption spectrum of $2.73 \times 10^{-5} \text{ M Ru}(\text{bpy})_3^{2+}$ in acetonitrile is presented in Figure 2 (curve a). Upon addition of $2.83 \times 10^{-3} \text{ M MV}^{2+}$ and 0.61 M Q, the spectrum undergoes a general increase in absorbance extending out to 540 nm (curve b). Since neither MV^{2+} nor Q absorbs appreciably above 350 nm, this behavior must reflect the formation of one or more ground-state complexes between the components in the system. Spectral studies of the various binary combinations revealed that significant complexation only occurs between MV^{2+} and Q; a solution of these two reagents displays a featureless absorption rising from about 540 nm toward shorter wavelengths.

This complex formation process was analyzed by using the dilution method of Cilento and Sanioto.¹⁷ In brief, a solution of MV^{2+} and Q was prepared and its absorbance, A , measured

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(12) (a) It should be recalled that reverse electron transfer (eq 10) can occur in two stages: (i) extremely rapid recombination of geminate $\text{Ru}(\text{bpy})_3^{3+}/\text{MV}^{2+}$ pairs that have not escaped from their original solvent cages and (ii) slower, diffusional recombination of free $\text{Ru}(\text{bpy})_3^{3+}$ and MV^{2+} ions that had escaped into the bulk solution. Only $\text{Ru}(\text{bpy})_3^{3+}$ ions in the latter category are expected to be sufficiently long-lived to undergo scavenging by Q (eq 8). In aqueous solution, the efficiency of cage escape for photogenerated $\text{Ru}(\text{bpy})_3^{3+}/\text{MV}^{2+}$ pairs is ~ 0.25 .^{12b} (b) Chan, S.-F.; Chou, M.; Creutz, C.; Matsubara, T.; Sutin, N. *J. Am. Chem. Soc.* **1981**, *103*, 369.

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Table I. Quantum Yields for Production of NBD in the Ru(bpy)₃²⁺-MV²⁺-Q System

run	[MV ²⁺], M × 10 ³	% quenching ^a	φ _{NBD} ^b
A	1.92	20.9	1.6
B	2.83	35.3	1.2
C	4.76	59.6	0.91

^aPercentage of *Ru(bpy)₃²⁺ quenched by MV²⁺; measured by luminescence spectroscopy. ^bExperimental conditions: sample volume 4 mL; [Ru(bpy)₃²⁺] = 2.7–3.1 × 10⁻⁵ M; [Q] = 0.61 M; samples irradiated at 436 nm for 900–925 s; incident light intensity 2.0 × 10⁻⁸ einstein s⁻¹.

at 350 nm. Various amounts of solvent were then added, and the absorbance was redetermined after each dilution. The linearity of the plot of V vs $(VA)^{-1}$, where V denotes the total volume of the sample, is diagnostic of a 1:1 stoichiometry for the complex (eq 12). This plot also yields values for the association constant,



K , and the extinction coefficient of the complex at the monitoring wavelength; we find $K = 0.3 \text{ M}^{-1}$ and $\epsilon_{350} = 1.1 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$. The small K value indicates a rather weak interaction between MV²⁺ and Q. At the concentrations typically employed in the photochemical studies, approximately 16% of the added MV²⁺ exists in complexed form.

(b) Continuous-Photolysis Studies. Photochemical studies of the Ru(bpy)₃²⁺-MV²⁺-Q system were conducted at 436 nm in acetonitrile solution. At the concentrations employed (see Table I), Ru(bpy)₃²⁺ was the principal light-absorbing species (accounting for >90% of the absorbed photons) while MV²⁺ quenched 20–60% of the resulting Ru-to-bpy charge-transfer excited states.¹⁸ Analyses of photolyzed samples by gas chromatography revealed that NBD had been produced. Control experiments established that the formation of this product does not occur in the dark or in the absence of Ru(bpy)₃²⁺ or MV²⁺.

Figure 2 illustrates the spectral changes that accompany the photoinduced production of NBD in the Ru(bpy)₃²⁺-MV²⁺-Q system. The intense new bands appearing at ~395 nm and 606 nm (curve c) are characteristic of the methylviologen cation radical, MV^{•+},¹⁰ generated via the oxidative quenching of *Ru(bpy)₃²⁺ (eq 9). While highly exoergic reverse electron transfer between the primary photoproducts (eq 10) provides a pathway for the disappearance of both species on a μs–ms time scale,¹⁹ MV^{•+} persists for at least several minutes following the cessation of photolysis.²⁰ Such behavior can be attributed to the competitive scavenging of Ru(bpy)₃³⁺ by Q (eq 8), which, relative to MV^{•+}, is present in enormous excess. This process regenerates Ru(bpy)₃²⁺ and creates Q^{•+}, a key chain-carrying species in the catalytic conversion of Q to NBD (eq 5 and 6).

Table I summarizes quantum yield data from a series of experiments in which the MV²⁺ concentration, and thus the percent quenching of *Ru(bpy)₃²⁺, was varied. Two important points emerge from these results. First, the finding that φ_{NBD} can exceed unity establishes the existence of a photogenerated catalytic cycle for the conversion of Q to NBD in the Ru(bpy)₃²⁺-MV²⁺-Q system. Second, the inverse dependence of φ_{NBD} upon percent quenching supports the proposed involvement of eq 9 in the mechanism outlined in Figure 1. Specifically, higher quenching levels are accompanied by increases in the concentration of the primary photoproducts, Ru(bpy)₃³⁺ and MV^{•+}. Consequently, the unproductive reverse electron-transfer reaction between these species (eq 10) experiences a greater rate enhancement than the competitive process involving reduction of Ru(bpy)₃³⁺ by Q (eq

8).²¹ The net result is a decrease in the amount of the catalytically active Q^{•+} produced and a concomitant drop in φ_{NBD}.

Decomposition of one or more components involved in the photogenerated catalytic system occurs upon prolonged photolysis, as evidenced by a decrease in φ_{NBD}. In one set of experiments, for example, the quantum yield dropped from 1.5 to 0.8 for photolysis times of 900 and 8100 s, respectively. Moreover, the absorption spectrum of a photolyzed solution that had sat in the dark for sufficient time to allow for disappearance of MV^{•+} exhibits enhanced absorption throughout the near-ultraviolet and visible regions (Figure 2; compare curves b and d). Notwithstanding this degradation problem,²² the photoinduced production of NBD is characterized by a high turnover of the Ru(bpy)₃²⁺ sensitizer. In the 8100-s experiment mentioned above, 240 mol of NBD was produced/mol of metal complex initially present in the sample.

(c) Flash-Photolysis Studies. Information about the transient photochemical behavior of the Ru(bpy)₃²⁺-MV²⁺-Q system was obtained from a series of flash-photolysis experiments. Initially, an acetonitrile solution of Ru(bpy)₃²⁺ (10⁻⁴ M) was irradiated with pulses of polychromatic light (λ ≥ 520 nm) having a duration of ~30 μs. No transients were detected following decay of the flash, consistent with the submicrosecond lifetime of *Ru(bpy)₃²⁺.⁸ In a second experiment, flash irradiation of a solution containing Ru(bpy)₃²⁺ and MV²⁺ (10⁻³–10⁻² M) generated a transient that could readily be identified as MV^{•+} by its spectral characteristics (e.g. curve c in Figure 2). This species, which arose from the oxidative quenching process given by eq 9, decayed in the μs–ms time regime with second-order kinetics. The characteristics of the latter process are consistent with occurrence of reverse electron transfer between the primary photoproducts according to eq 10. In the final experiment, flash photolyzing a solution of Ru(bpy)₃²⁺, MV²⁺, and Q (~0.1 M) resulted in the appearance of MV^{•+} but, in contrast to the rapid decay observed in experiment 2, the cation radical persisted for at least several seconds after the flash. This behavior parallels that seen in continuous photolysis and lends credence to the proposal that reduction of Ru(bpy)₃³⁺ by Q (eq 8) retards the undesirable back-electron-transfer reaction (eq 10).

While eq 8 removes one potential reaction partner of MV^{•+}, it creates another, namely Q^{•+}. This hydrocarbon cation radical and its immediate offspring, NBD^{•+}, each are thermodynamically capable of oxidizing MV^{•+} back to MV²⁺ (eq 13). Since rapid



and complete regeneration of MV²⁺ is not observed, alternative pathways for scavenging Q^{•+} and/or NBD^{•+} must be available. Presumably, these pathways involve combination with O₂ or other trace impurities in the solvent (eq 7b).

Concluding Remarks

Photoactivation of the three-component system Ru(bpy)₃²⁺-MV²⁺-Q initiates a catalytic cycle for the valence isomerization of Q to NBD. The essential steps in this process can be deduced from the following observations. (1) Direct spectroscopic detection of MV^{•+} in both continuous- (Figure 2, curve c) and flash-photolysis experiments establish the occurrence of eq 9. (2) The longevity of this cation radical and the high turnover of Ru(bpy)₃²⁺ provide strong circumstantial evidence for the operation of eq 8. (3) Values of φ_{NBD} above unity (Table I) are diagnostic of a chain process such as that described by eq 5 and 6. Collectively, these steps constitute the mechanism of photogenerated catalysis proposed in Figure 1.

(18) No distinction is made between quenching by MV²⁺ and the Q-MV²⁺ complex. See: Prasad, D. R.; Hoffman, M. Z. *J. Phys. Chem.* **1984**, *88*, 5560.

(19) Electron transfer between Ru(bpy)₃³⁺ and MV^{•+} occurs with a bimolecular rate constant of 8.1 × 10⁹ M⁻¹ s⁻¹ in acetonitrile.¹⁰

(20) This persistence of MV^{•+} occurs in deaerated solutions; upon exposing an irradiated sample to air, the characteristic blue color of the cation radical disappears rapidly.

(21) For example, a 2-fold increase in the concentrations of Ru(bpy)₃³⁺ and MV^{•+} quadruples the rate of eq 10 while it only doubles that of eq 8 (at constant Q concentration).

(22) (a) While the details of the decomposition pathway(s) were not investigated, one possibility is photosubstitution of a bpy ligand in Ru(bpy)₃²⁺; this latter process is reported to occur with a quantum yield of 10⁻² in acetonitrile.^{22b} Decomposition products arising from the reactive organic species generated during the course of photolysis (e.g. cation radicals such as MV^{•+} and NBD^{•+}) also are conceivable. (b) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613.

While the system investigated in this study can operate with quantum yields above unity, its overall performance characteristics are far from ideal. Competitive absorption by photogenerated MV^{2+} , for example, causes a serious inner-filter problem (Figure 2, curve c) and effectively precludes the use of excitation wavelengths above 500 nm. Replacement of MV^{2+} by a quencher that, upon reduction by $*Ru(bpy)_3^{2+}$, undergoes irreversible decomposition to weakly absorbing products²³ might lead to significant improvement in this respect. Such a quencher also would tend to minimize reverse electron transfer between the primary photoredox products (e.g. eq 10) and thereby enhance the yield of $Ru(bpy)_3^{3+}$ that can be scavenged by Q.

Finally, photochemical generation of a strong ground-state oxidant appears to be a viable strategy for initiating radical-

cation-mediated catalytic reactions of organic molecules.²⁴ As such, it provides an alternative to the more common approach involving direct reaction of an organic substrate with a photoexcited electron acceptor (e.g. eq 4). Additional studies of transition-metal-containing photoinitiator systems and their possible incorporation into photosensitive materials²⁵ are being pursued.

Acknowledgment. Financial support for this work was provided by the National Science Foundation (Grant CHE-8210558) and by the Office of Basic Energy Sciences of the Department of Energy.

(23) Various cobalt(III) ammine complexes, for example, undergo efficient reduction by $*Ru(bpy)_3^{2+}$ to yield weakly absorbing Co(II) species.⁸

- (24) For examples of this strategy in purely organic systems, see: Gotoh, T.; Kato, M.; Yamamoto, M.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1981**, 90. Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499.
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Thermal and Photolytic Reactions of Nitrosyl-Carbonyl Complexes of Rhodium and Iridium with Triphenylphosphine

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The photolysis of $[Rh(NO)(CO)(PPh_3)_2]$ in the presence of PPh_3 in dichloromethane results in the expulsion of NO rather than CO and the formation of *trans*- $[Rh(CO)Cl(PPh_3)_2]$. The thermal reaction and photoreaction of $[Ir(NO)(CO)Cl(PPh_3)_2]BF_4$ (**1**) with PPh_3 lead to dissociation of NO and the formation of the Ir(II) radical $[Ir(CO)Cl(PPh_3)_3]BF_4$ (**2**). The demonstration of the homolytic cleavage of the Ir-NO bond of **1** provides support for the proposal that the photodissociation of NO instead of CO in the compounds $[M(NO)(CO)(PPh_3)_2]$ (where M is Rh or Ir) proceeds from a charge-transfer state that has a bent M-N-O bond.

Introduction

The substitution of the nitrosyl ligand in complexes by other ligands is not commonly observed. The substitution or expulsion of CO instead of NO in the photolyses of $[Mn(NO)(CO)_4]$,¹ $[Co(NO)(CO)_3]$,²⁻⁵ and $[(C_5H_5)M(NO)(CO)_2]$, where M is Cr, Mo, or W,⁶ in solution and $[Co(NO)(CO)_3]$,⁷ $[Mn(NO)(CO)_4]$,⁸ $[Mn(NO)_3(CO)]$,⁹ and $[Fe(NO)_2(CO)_2]$ ¹⁰ in inert-gas matrices may be attributed to the stronger M-NO bond compared to the M-CO bond due to the stronger π -acceptor property of NO compared to that of CO. The substitution of CO in preference to NO in thermal reactions is also known for complexes such as $[Fe(NO)_2(CO)_2]$,¹¹ $[RFe(NO)(CO)_3]$,¹² $[(C_5H_5)Mn(CO)_2(NO)]^+$,¹³⁻¹⁵ $[Ir(NO)(CO)(PPh_3)_2]$,¹⁶ and other complexes with carbonyl and nitrosyl ligands. In contrast to this usual reactivity pattern, the photolysis of $[Ir(NO)(CO)(PPh_3)_2]$ in the presence of PPh_3 has been recently shown to lead to dissociation of NO rather than CO.¹⁷ To elucidate this apparently anomalous observation, we have investigated the photolytic reactions of PPh_3 with the compounds $[Rh(NO)(CO)(PPh_3)_2]$, $[Rh(NO)(PPh_3)_3]$, and $[Ir(NO)(CO)Cl(PPh_3)_2]BF_4$. The thermal reaction of the last compound with PPh_3 has been found to proceed with cleavage of the Ir-NO bond and formation of a relatively stable iridium(II) radical. Dissociation of NO from metal nitrosyl complexes has been recently proposed to be generally responsible for nitrosyl transfer and dioxygenation reactions.¹⁸

Experimental Section

Literature methods were used to prepare $[Rh(NO)(CO)(PPh_3)_2]$,¹⁹ $[Rh(NO)(PPh_3)_3]$,²⁰ and $[Ir(NO)(CO)Cl(PPh_3)_2]PF_6$.²¹ Photolyses were conducted with a 450-W medium-pressure mercury vapor lamp

jacketed with a Pyrex immersion well. Photolyses at 0 and $-78.5^\circ C$ were conducted by placing the lamp in its Pyrex immersion well and the sample in a tube in a Dewar containing ice water or a dry ice-acetone mixture. Infrared data of samples photolyzed in a liquid 0.5-mm NaCl

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