Rh(III)-Photosensitized Interconversion of Norbornadiene and Quadricyclane

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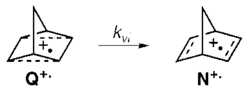
Received: June 19, 1997; In Final Form: September 4, 1997[⊗]

The utility of two Rh(III) diimine complexes, $Rh(phen)_3^{3+}$ and $Rh(phi)_2(phen)^{3+}$ (phen = 1,10-phenanthroline, phi = 9,10-phenanthrenequinone diimine), as sensitizers for the interconversion of norbornadiene (**N**) and quadricyclane (**Q**) has been investigated using steady-state photochemical and laser flash photolysis (LFP) techniques. Irradiation of acetonitrile solutions of $Rh(phen)_3^{3+}$ and **N** causes slow conversion to **Q**. The reaction is reversible; irradiation of $Rh(phen)_3^{3+}$ in the presence of **Q** leads to **N**. Irradiation of acetonitrile solutions of $Rh(phi)_2(phen)^{3+}$ and **Q** yields **N**. However, this reaction is irreversible; irradiation of the Rh(III) complex in the presence of **N** fails to afford **Q**. Irradiation of methanol solutions of either Rh(III) complex in the presence of **N** or **Q** affords minor amounts of two methanol-C7 adducts but fails to quench the **N**−**Q** interconversion reaction. The results are consistent with **N**−**Q** interconversion via an exciplex intermediate. The Rh(III)-sensitized deazatization of two cyclic azoalkane derivatives (**Azo-N**, **Azo-Q**) of **N** and **Q** was also investigated. Deazatization was achieved by $Rh(phen)_3^{3+}$ but not $Rh(phi)_2(phen)^{3+}$ sensitization. The results are consistent with a mechanism involving triplet energy transfer, but the involvement of exciplex intermediates cannot be ruled out. Bimolecular rate constants for quenching of the Rh(III) excited states by **N**, **Q**, **Azo-N**, and **Azo-Q** were determined by LFP.

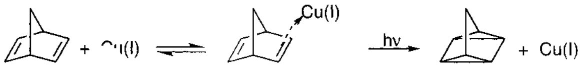
Introduction

The interconversion of norbornadiene (**N**) and quadricyclane (**Q**) has attracted considerable interest over the last two decades, largely due to its potential importance in solar energy storage.[1] Triplet-sensitized irradiation of **N** results in clean and efficient conversion ($\phi \approx 0.9$) to the higher energy isomer **Q**.[2,3] The reversion of **Q** to **N**, with the liberation of the strain energy as heat, can be affected by transition metal catalysts. The conversion of **Q** to **N** may also be facilitated by one-electron oxidation, followed by valence isomerization of $Q^{\bullet+}$ to $N^{\bullet+}$ (eq 1).[4−14] Chemically induced dynamic nuclear polarization (CIDNP) studies have established the existence of $Q^{\bullet+}$ and $N^{\bullet+}$ as two distinct species and have provided indirect evidence for the valence isomerization reaction.[15−18] We recently reported the direct detection of $Q^{\bullet+}$ by time-resolved ESR and estimated the rate constant for the valence isomerization to $N^{\bullet+}$ ($k_{vi} \approx 10^6$ s^{-1}).[19]



(1)

One significant problem with the **N**/**Q** solar energy storage system is the relatively high energy of the electronic excited states of **N**[2,3,20] and the consequent need for high-energy sensitizers, which typically absorb in the UV region. Since most solar photons lie in the visible at wavelengths longer than 450 nm, only a few percent of the solar photons may be harvested by the parent **N**/**Q** system. A significant amount of work has gone into the development of norbornadiene derivatives and sensitizers that absorb visible light.[1] For example, transition metal complexes containing copper,[7] iridium,[10] and ruthenium[11,12] have been shown to be effective in sensitizing the conversion of **N** to **Q**. Several Cu(I) compounds form ground-state charge-transfer complexes with **N** that can be selectively irradiated, resulting in efficient conversion to **Q** (eq 2).[7] The Ir(III)-sensitized conversion of **N** to **Q** involves the intermediacy of excited-state charge-transfer complexes (exciplexes) which collapse to **Q** (eq 3),[10] while $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) sensitizes the conversion of a substituted **N** to the **Q** derivative by a classical triplet energy transfer mechanism.[11]



(2)

$$\mathbf{Ir} \xrightarrow{h\nu} \mathbf{Ir}^* \xrightarrow{\mathbf{N}} \left(\overset{\delta-}{\mathbf{Ir}}\text{- - -}\overset{\delta+}{\mathbf{N}}\right)^* \longrightarrow \mathbf{Q} + \mathbf{Ir} \qquad (3)$$

Rhodium(III) diimine complexes are strong photooxidants.[21−24] For example, $Rh(phen)_3^{3+}$ and $Rh(phi)_2(phen)^{3+}$ (phen = 1,10-phenanthroline, phi = 9,10-phenanthrenequinone diimine; see Chart 1) possess relatively high excited-state reduction potentials ($^*E_{(A^-/A)}$ = 2.0 V[21] and ca. 1.8 V[24] vs SCE, respectively). Given the properties of these complexes, they are obvious candidates as sensitizers for the **N**/**Q** system. However, there is only a single brief mention of the $Rh(phen)_3^{3+}$-sensitized conversion of **N** to **Q**.[6]

To gain a better understanding of the energy surfaces interconnecting **N** and **Q**, we have previously employed two cyclic azoalkanes, **Azo-N** and **Azo-Q** (see Scheme 1), as alternate precursors to the norbornadienyl and quadricyclanyl biradicals ($\mathbf{B_N}$, $\mathbf{B_Q}$)[3] and the azoalkane radical cations (**Azo-N**$^{\bullet+}$, **Azo-Q**$^{\bullet+}$) generated by one-electron oxidation.[25] The azoalkane radical cations undergo rapid deazatization to afford radical cations $N^{\bullet+}$ and $Q^{\bullet+}$, leading ultimately to the formation of the neutral hydrocarbons **N** and **Q**.[25]

In this paper, we report results of Rh(III)-photosensitized interconversion of **N** and **Q** and deazatization of **Azo-N** and **Azo-Q**. We have employed two Rh(III) sensitizers, $Rh(phen)_3^{3+}$ and $Rh(phi)_2(phen)^{3+}$, with slightly different photophysical and electrochemical properties. Bimolecular rate constants for the

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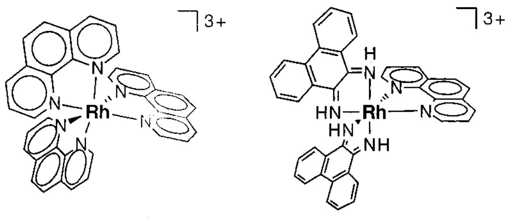
[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1997.

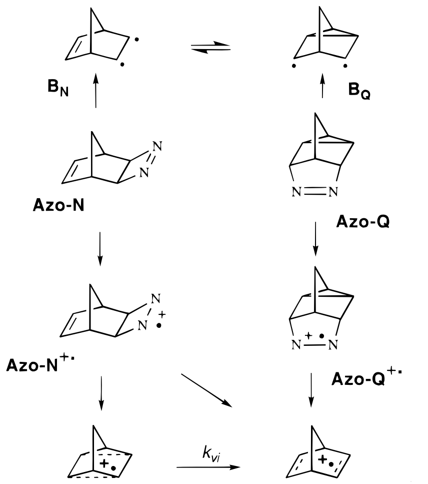
CHART 1



Rh(phen)$_3^{3+}$
$E_{(0,0)}$ = 2.75 V
*$E_{(A-/A)}$ = 2.0 V (vs. SCE)

Rh(phi)$_2$(phen)$^{3+}$
$E_{(0,0)}$ = 2.0 V
*$E_{(A-/A)}$ ~ 1.8 V (vs. SCE)

SCHEME 1

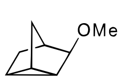


quenching of the Rh(III) excited states by **N** and **Q** and the two azoalkanes were determined by laser flash photolysis (LFP). The roles of energy transfer, electron transfer, and exciplex formation are discussed.

Results

Rh(phen)$_3^{3+}$-Sensitized Irradiations of N and Q. Steady-state irradiation (λ = 300 nm) of dilute acetonitrile solutions of Rh(phen)$_3^{3+}$ in the presence of **Q** affords **N** in 84% chemical yield at ~20% conversion. Irradiation of Rh(phen)$_3^{3+}$ in the presence of **N** under the same conditions results in the production of **Q** in 77% yield. No products other than **N** and **Q** were detected by GC or ^{1}H NMR analysis in either case. The quantum yields for Rh(phen)$_3^{3+}$-sensitized conversion of **Q** to **N** ($\phi_{\mathbf{QN}}$) and **N** to **Q** ($\phi_{\mathbf{NQ}}$) are <0.01 in both cases.[6]

Steady-state photolysis of methanol solutions of Rh(phen)$_3^{3+}$ in the presence of **Q** afforded **N** (72%) and two additional products (in 23% combined yield). These products had identical mass spectra ($M^+ = 124$; $C_7H_8 + CH_4O$), consistent with adducts between the C_7 hydrocarbon and methanol. Such adducts have been well documented;[26,27] they are assigned to ethers **1** and **2**.[27] Irradiation of methanol solutions of Rh(phen)$_3^{3+}$ in the presence of **N** yielded **Q** (76%) and the same two methanol adducts (16% combined yield).



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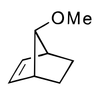

2

Rh(phi)$_2$(phen)$^{3+}$-Sensitized Irradiations of N and Q. Steady-state irradiation (λ > 400 nm) of dilute acetonitrile solutions of Rh(phi)$_2$(phen)$^{3+}$ in the presence of **Q** affords **N** in 65% yield at ca. 50% conversion. Irradiation of Rh(phi)$_2$(phen)$^{3+}$ in the presence of **N** under the same conditions resulted in slow decomposition of **N** without the formation of **Q** or any other detectable volatile products. Steady-state photolysis of a methanol solution of Rh(phi)$_2$(phen)$^{3+}$ in the presence of **Q** afforded **N** (79%) and trace amounts (ca. 1%) of the two methanol addition products at ca. 70% conversion.

TABLE 1: Oxidation Potentials, Triplet Energies, and Bimolecular Rate Constants (k_q) for Quenching of the Rh(III) Excited States by Q, N, Azo-Q, and Azo-N in Deoxygenated Acetonitrile Solution at 23 ± 2 °C[a]

quencher	$E_{(D/D^+)}$ (V vs SCE)	E_T (eV)	$k_q/10^9$ M^{-1} s^{-1} *Rh(phen)$_3^{3+}$	$k_q/10^9$ M^{-1} s^{-1} *Rh(phi)$_2$(phen)$^{3+}$
Q	0.91[b]	2.7−3.5[d]	3.1 ± 0.2	10.1 ± 0.4
N	1.56[b]	2.66[e]	1.5 ± 0.1	0.52 ± 0.02
Azo-Q	~2.1[c]	2.43[f]	2.4 ± 0.1	<0.01
Azo-N	~2.3[c]	2.60[f]	4.1 ± 0.3	<0.01

[a] Errors are reported as twice the standard deviation from the least-squares analysis of the LFP data according to eq 4. [b] Data from ref 31. [c] Reference 25. [d] Reference 3. [e] Reference 20. [f] Reference 34.

Rh(III)-Sensitized Irradiations of Azo-N and Azo-Q. Irradiation (λ = 300 nm) of an acetonitrile solution of Rh(phen)$_3^{3+}$ in the presence of **Azo-N** afforded **Q** (82%) and **N** (18%) as the sole detected products at ca. 20% conversion. Photolysis of Rh(phen)$_3^{3+}$ in the presence of **Azo-Q** under similar conditions yielded **Q** (47%) and **N** (50%). Photolysis of a methanol solution containing Rh(phen)$_3^{3+}$ and **Azo-Q** afforded **Q** (46%), **N** (47%), and methanol adducts **1** and **2** (7% combined) at 20% conversion. Similar irradiation of a methanol solution of Rh(phen)$_3^{3+}$ and **Azo-N** yielded **Q** (85%), **N** (14%), and trace amounts of **1** and **2** (~1% combined yield) at 15% conversion. Neither **Azo-Q** nor **Azo-N** decomposed upon prolonged irradiation (λ > 420 nm) of acetonitrile solutions containig Rh(phi)$_2$(phen)$^{3+}$.

Laser Flash Photolysis. Laser flash photolysis (LFP) of dilute deoxygenated acetonitrile solutions of Rh(phen)$_3^{3+}$ affords a readily detectable transient absorption centered at 500 nm which decays with first-order kinetics ($\tau = 170 \pm 10$ ns). This transient has been assigned to the $^3(\pi,\pi^*)$ of the Rh(III) complex.[21−23] Addition of **N**, **Q**, **Azo-N**, and **Azo-Q** caused the lifetime of the transient to decrease in each case. LFP of dilute deoxygenated acetonitrile solutions of Rh(phi)$_2$(phen)$^{3+}$ affords a transient absorption centered at 460 nm which decays with first-order kinetics ($\tau = 160 \pm 10$ ns) and has been assigned to an intraligand charge transfer (ILCT) excited state.[24] The lifetime of the Rh(III) excited state was reduced by additions of **N** or **Q**; however, the lifetime of the transient was unaffected by the addition of up to 0.15 M **Azo-N** or **Azo-Q**. Bimolecular quenching rate constants (k_q) were determined from plots of the pseudo-first-order rate constant for decay of the Rh(III) excited states (k_{decay}) according to eq 4, where k_o refers to the rate constant for decay in the absence of added quencher. The quenching rate constants are listed in Table 1.

$$k_{\mathrm{decay}} = k_o + k_q[Q] \tag{4}$$

Discussion

The two Rh(III) diimine complexes sensitize the conversion of **Q** to **N**, and in the case of Rh(phen)$_3^{3+}$ the process is clearly reversible. However, the various reactions may follow different pathways depending on the photophysical and electrochemical properties of the sensitizer and quencher molecules. Our approach has been to tune the properties of the Rh(III) sensitizers by changing the ligands. For example, Rh(phen)$_3^{3+}$ possesses a higher excited-state energy and a higher excited-state reduction potential (*$E_{(A^-/A)}$) than Rh(phi)$_2$(phen)$^{3+}$ (see Chart 1). The Rh(III) complexes have short-lived singlet excited states[21−24] so that only the triplet excited states are intercepted by quenchers. The quantum yield for intersystem crossing in *Rh(phen)$_3{}^{3+}$ has been reported to be unity at room temperature.[23]

Potential reactions of the sensitizers with the donors employed include electron transfer, exciplex formation, or energy transfer. The free energy for electron transfer (ΔG) from a donor to an electronically excited acceptor may be calculated from the Rehm−Weller equation[28] (eq 5), where $E_{(0,0)}$ is the excited-

$$\Delta G = E_{(\mathrm{D/D^+})} - E_{(\mathrm{A^-/A})} - E_{(0,0)} - e^2/\epsilon a \qquad (5)$$

state energy, $E_{(\mathrm{A^-/A})}$ is the oxidation potential of the reduced acceptor, $E_{(\mathrm{D/D^+})}$ is the oxidation potential of the donor, and $e^2/\epsilon a$ is a term to account for ion pairing. The oxidative strength of an excited state is conveniently expressed by the excited-state reduction potential (eq 6).[29] Given the oxidation potentials

$$^*E_{(\mathrm{A^-/A})} = E_{(\mathrm{A^-/A})} + E_{(0,0)} \qquad (6)$$

of the four donors employed (Table 1), electron transfer from **N** and **Q** to the Rh(III) sensitizers is clearly exergonic, while electron transfer from **Azo-N** and **Azo-Q** is at least slightly endergonic. Rh(phen)$_3{}^{3+}$ possesses a relatively high excited-state energy ($E_{(0,0)} = 2.75$ eV),[21−23] leading to the possibility of triplet energy transfer in competition with electron-transfer sensitization for the donors employed. On the other hand, Rh(phi)$_2$(phen)$^{3+}$ has an excited-state energy ($E_{(0,0)} = 2.0$ eV)[24] that is lower than the triplet energies of **N**, **Q**, **Azo-N**, and **Azo-Q** (Table 1).

Interconversion of Norbornadiene and Quadricyclane. **Q** is inefficiently converted to **N** by sensitization involving both Rh(III) complexes. **N** is converted inefficiently to **Q** by Rh(phen)$_3{}^{3+}$ sensitization in acetonitrile solution, consistent with an earlier preliminary report;[6] Rh(phi)$_2$(phen)$^{3+}$-sensitized irradiation of **N** fails to yield **Q**.

Potential reactions of the Rh(III) sensitizers with **N** and **Q** are summarized in Scheme 2. Plausible mechanisms of Rh(phen)$_3{}^{3+}$-sensitized conversion of **N** to **Q** involve triplet energy transfer (eqs 8 and 9) or formation of a (charge-transfer) exciplex (eq 13) which decays in part to **Q** (eq 14). Full electron transfer generating free $\mathbf{N}^{\bullet+}$ (eq 10) followed by valence isomerization to $\mathbf{Q}^{\bullet+}$ and back electron transfer (eq 12) to yield **Q** can be ruled out since $\mathbf{N}^{\bullet+}$ is significantly lower in energy than $\mathbf{Q}^{\bullet+}$.[30] Triplet energy transfer is predicted to be an unlikely process due to the endothermicity of the reaction; the triplet energy of **N** (~3.0 eV)[2,3] is significantly higher than the excited-state energy of Rh(phen)$_3{}^{3+}$ (2.75 eV).[21−23] However, recent photoacoustic calorimetry experiments indicated that the triplet energy of **N** (2.66 eV)[20] may be somewhat lower; thus, energy transfer may be involved in the generation of **Q** in this case. However, classical vertical triplet energy transfer is unlikely to be important in the Rh(phen)$_3{}^{3+}$-sensitized conversion of **N** to **Q**, given the low efficiency of the reaction ($\phi < 0.01$)[6] compared to that obtained with aryl ketone triplet sensitizers ($\phi \approx 0.9$).[2]

SCHEME 2

$$\mathrm{Rh(III)} \xrightarrow{h\nu} {}^3\mathrm{Rh(III)}^* \qquad (7)$$

$$^3\mathrm{Rh(III)}^* + \mathrm{D} \rightarrow \mathrm{Rh(III)} + {}^3\mathrm{D}^* \qquad (8)$$
$$(\mathrm{D} = \mathrm{N}, \mathrm{Q})$$

$$^3\mathrm{D}^* \rightarrow \mathrm{Q\ and/or\ N} \qquad (9)$$

$$^3\mathrm{Rh(III)}^* + \mathrm{D} \rightarrow \mathrm{Rh(II)} + \mathrm{D}^{\bullet+} \qquad (10)$$

$$\mathrm{Q}^{\bullet+} \rightarrow \mathrm{N}^{\bullet+} \qquad (11)$$

$$\mathrm{Rh(II)} + \mathrm{D}^{\bullet+} \rightarrow \mathrm{Rh(III)} + \mathrm{D} \qquad (12)$$

$$^3\mathrm{Rh(III)}^* + \mathrm{D} \rightarrow ({}^{\delta-}\mathrm{Rh(III)}\text{- - -}\mathrm{D}^{\delta+})^* \qquad (13)$$

$$({}^{\delta-}\mathrm{Rh(III)}\text{- - -}\mathrm{D}^{\delta+})^* \rightarrow \mathrm{Rh(III)} + \mathrm{N\ and/or\ Q} \qquad (14)$$

The Rh(phen)$_3{}^{3+}$-sensitized conversion of **Q** to **N** could involve full electron transfer, as the valence isomerization of $\mathbf{Q}^{\bullet+}$ to $\mathbf{N}^{\bullet+}$ (eq 11) has been well documented.[15,16,19] The alternative possibility is reaction via exciplex intermediates (eqs 13 and 14). Classical vertical triplet energy transfer can be ruled out due to the endothermicity of the process; however, we note that nonvertical energy transfer mechanisms have been proposed to account for the inefficient triplet-sensitized conversion of **Q** to **N**.[2]

The excited state of Rh(phen)$_3{}^{3+}$ is quenched efficiently by both **N** and **Q** ($k_q \approx 10^9$ M^{-1} s^{-1}) despite the low quantum yields for their interconversion under these conditions. The rate constant for quenching by **Q** is twice as large as the value for **N**, consistent with their redox potentials[31] (Table 1) and indicating the involvement of charge-transfer processes. The quenching rate constants do not correlate with the triplet energies of **N** and **Q**.

The product studies in neat methanol were key to elucidating the reaction mechanisms. Under these conditions, any free radical cations (i.e. $\mathbf{N}^{\bullet+}$, $\mathbf{Q}^{\bullet+}$) should be trapped by methanol with formation of methyl ethers;[26,27] the rate of trapping $\mathbf{Q}^{\bullet+}$ by pure methanol is faster than valence isomerization to $\mathbf{N}^{\bullet+}$.[27] The fact that the formation of **N** from **Q** (and vice versa) is not quenched effectively by methanol rules out significant involvement of *full* electron transfer generating free radical ions. However, the formation of some methyl ethers (10−20%) in both reactions requires the involvement of at least partial charge transfer. The observation of ethers **1** and **2** does not allow one to differentiate between free radical ions and exciplex intermediates. The ethers may arise by *exo* attack of methanol on free radical ions, $\mathbf{N}^{\bullet+}$ and/or $\mathbf{Q}^{\bullet+}$, or on an *endo* exciplex.[27] Both reactions have precedent: with 1,4-dicyanobenzene as sensitizer, $\mathbf{N}^{\bullet+}$ and $\mathbf{Q}^{\bullet+}$ are trapped by *exo* attack;[26,27] likewise, with 1-cyanonaphthalene (CNN) as electron acceptor, an *endo* exciplex (or encounter complex) between **N** and CNN is captured from the *exo* face.[32]

We formulate the Rh(phen)$_3{}^{3+}$-sensitized interconversion of **N** and **Q** via excited-state complexes (exciplexes), [Rh−**N**]* and [Rh−**Q**]*, with substantial charge-transfer character (eqs 13 and 14). Such reactions have precedent; for example, the conversion of **N** to **Q**, sensitized by an Ir(III) diimine complex, has been rationalized via an exciplex mechanism.[10] Exciplex intermediates have been invoked also in the 1-cyanonaphthalene-sensitized irradiation of **N**[27,32] or of an **N** derivative.[33] However, the valence isomerization within the complex is inefficient in both directions; thus, the exciplexes preferentially decay to the starting materials.

The Rh(phi)$_2$(phen)$^{3+}$-sensitized conversion of **Q** to **N** most likely proceeds via exciplex intermediates. Vertical triplet energy transfer is ruled out due to the relatively low excited-state energy of Rh(phi)$_2$(phen)$^{3+}$ (Table 1). Electron transfer from **N** and **Q** to the rhodium excited state is predicted to be exergonic in both cases. Indeed, the rate constant for quenching of the Rh(phi)$_2$(phen)$^{3+}$ excited state by **Q** is near the diffusion-controlled limit in acetonitrile, whereas the rate constant for quenching by **N** is ~20 times slower, consistent with their relative oxidation potentials.[31] Again, the formation of **N** from **Q** cannot be quenched in neat methanol, consistent with the lack of formation of free radical ions to a significant extent. The key difference appears to be that the [Rh(phi)$_2$(phen)$^{3+}$−**Q**]* exciplex decomposes in part to **N**, while the [Rh(phi)$_2$(phen)$^{3+}$−**N**]* exciplex does not yield **Q** in detectable amounts.

Deazatization of Azo-N and Azo-Q. Both azoalkanes undergo efficient deazatization upon Rh(phen)$_3$$^{3+}$ sensitization, affording mixtures of **N** and **Q**. Product studies and LFP experiments provide key evidence for the role of electron- or energy-transfer-induced deazatization (Scheme 3). Electron transfer from **Azo-Q** to *Rh(III) is slightly endergonic, whereas electron transfer from **Azo-N** is clearly endergonic. On the other hand, triplet energy transfer from *Rh(phen)$_3$$^{3+}$ to both azoalkanes is exergonic (Table 1).[34] Triplet (benzophenone, acetophenone)-sensitized deazatization of both **Azo-N** and **Azo-Q** affords **Q** in ~90% yield.[3] Thus, the formation of **Q** upon sensitized deazatization of the azoalkanes potentially serves as a probe for the involvement of triplet energy transfer (eqs 15 and 16).

SCHEME 3

$$^{3}\mathrm{Rh(III)}^{*} + \text{Azo-D} \rightarrow \mathrm{Rh(III)} + {}^{3}\text{Azo-D}^{*} \quad (\mathrm{D} = \mathrm{N}, \mathrm{Q}) \qquad (15)$$

$$^{3}\text{Azo-D}^{*} \rightarrow \mathrm{Q} \qquad (16)$$

$$^{3}\mathrm{Rh(III)}^{*} + \text{Azo-D} \rightarrow \mathrm{Rh(II)} + \text{Azo-D}^{\bullet +} \qquad (17)$$

$$\mathrm{Rh(II)} + \text{Azo-D}^{\bullet +} \rightarrow \mathrm{Rh(III)} + \text{Azo-D} \qquad (18)$$

$$\text{Azo-D}^{\bullet +} \rightarrow \mathrm{D}^{\bullet +} \qquad (19)$$

$$\mathrm{Rh(II)} + \mathrm{D}^{\bullet +} \rightarrow \mathrm{Rh(III)} + \mathrm{D} \qquad (20)$$

$$^{3}\mathrm{Rh(III)}^{*} + \text{Azo-D} \rightarrow [\text{Rh- - -Azo-D}]^{*} \qquad (21)$$

$$[\text{Rh- - -Azo-D}]^{*} \rightarrow \mathrm{Q}\ \text{and/or}\ \mathrm{N} \qquad (22)$$

On the other hand, **Azo-N** and **Azo-Q** show remarkably different reactivity upon singlet-sensitized one-electron oxidation.[25] **Azo-Q** affords **N** exclusively, while **Azo-N** affords **Q** as the major product (80%).[25] The formation of **Q** as major product in the Rh(phen)$_3$$^{3+}$-sensitized irradiation of **Azo-N** is consistent with either energy or electron transfer. However, the comparable yields of **N** and **Q** obtained from **Azo-Q** indicate that both electron and energy transfer processes may be involved.

Rh(phen)$_3$$^{3+}$ sensitizaton in neat methanol does not quench the formation of **N** and **Q**; this indicates that, consistent with the suggested free energies (eq 5), the deazatization mechanism does not involve full electron transfer generating free radical ions (eqs 17−20). However, the minor additional amounts of methyl C_7 ethers are consistent with the involvement of partial charge transfer (exciplexes) as a possible minor pathway (eqs 21 and 22).

Both **Azo-N** and **Azo-Q** quench *Rh(phen)$_3$$^{3+}$ with similar rate constants ($k_q \approx 10^9$ M^{-1} s^{-1}) despite their different oxidation potentials; indeed, quenching by **Q** and **N** has rate constants of similar magnitude despite their significantly lower oxidation potentials (Table 1). This clearly points to the involvement of energy transfer quenching by the azoalkanes (eq 15).

Sensitization by Rh(phi)$_2$(phen)$^{3+}$ failed to cause deazatization of either azoalkane. Likewise, both **Azo-N** and **Azo-Q** failed to quench *Rh(phi)$_2$(phen)$^{3+}$ at a measurable rate, consistent with the predicted free energies of electron and energy transfer sensitization.

Summary and Conclusions

The Rh(phen)$_3$$^{3+}$-sensitized irradiation of **N** or **Q** results in inefficient conversion to the respective valence isomer. The valence isomerization most likely proceeds via an exciplex (charge-transfer) intermediate rather than via free radical ions or via vertical triplet energy transfer. This conclusion is based (i) on the formation of methanol adducts but the inability to quench **N**−**Q** interconversion in methanol; (ii) on low quantum yields for **N**−**Q** interconversion in both directions; (iii) despite the near diffusion-controlled quenching of the Rh(III) excited state by both **N** and **Q**; (iv) on the correlation of the *Rh(phen)$_3$$^{3+}$ quenching rate constants of **N** and **Q** with their oxidation potentials; and (v) on the predicted exergonicity of electron transfer vs the predicted endergonicity of vertical triplet energy transfer. Rh(phi)$_2$(phen)$^{3+}$ sensitizes the conversion of **Q** to **N**; however, this reaction is irreversible. Irradiation of the Rh(III) complex in the presence of **N** fails to afford **Q**. Again, the methanol trapping experiments and the bimolecular quenching rate constants support a mechanism involving the intermediacy of an exciplex.

Azo-N and **Azo-Q** were deazatized by Rh(phen)$_3$$^{3+}$ but not Rh(phi)$_2$(phen)$^{3+}$ sensitization. The results are consistent with a mechanism involving classical triplet energy transfer; however, the involvement of exciplex intermediates cannot be ruled out.

Experimental Section

Materials and Solvents. Norbornadiene (Aldrich) was passed through activated alumina before use; quadricyclane was used as received. 3,4-Diazatricyclo[4.2.1.0^{2,5}]nona-3,7-diene (**Azo-N**),[35] 3,4-diazaquadricyclo[6.1.0.0^{2,6}0^{5,9}]non-3-ene (**Azo-Q**),[36,37] Rh(phen)$_3$$^{3+}$•3PF$_6$$^-$,[38] and Rh(phi)$_2$(phen)$^{3+}$•3PF$_6$$^-$ [24,39] were synthesized according to literature procedures. Acetonitrile (Aldrich spectrophotometric grade) was distilled from calcium hydride immediately before use. Methanol (Aldrich spectrophotometric grade) was used as received.

Product Analysis and Characterization. Gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, a Hewlett-Packard 3392A integrator, and an HP-1 capillary column (25 m × 0.2 mm; Hewlett-Packard, Inc.). The GC injector port was maintained below 175 °C to avoid thermal decomposition of the azoalkanes. GC/MS analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a HP-5917A mass-selective detector and a HP-1 capillary column (25 m × 0.2 mm; Hewlett-Packard, Inc.). ^{1}H NMR spectra were recorded on a Bruker AC80 (80 MHz) NMR spectrometer in acetonitrile-d_3 solution. Ultraviolet−visible absorption spectra were recorded on a Hewlett-Packard HP8452A UV spectrometer.

Steady-State Photolyses. The Rh(phen)$_3$$^{3+}$-sensitized steady-state photolysis experiments were carried out in a Rayonet photochemical reactor equipped with six or 12 RPR-300 (300 nm) lamps. For the Rh(phi)$_2$(phen)$^{3+}$-sensitized photolyses, a 150 W Xe lamp was used in conjunction with a glass cutoff filter ($\lambda > 400$ nm). Solutions containing 0.02−0.05 M substrate, ca. 10^{-4} M Rh(III) complex, and 0.003 M *m*-tolunitrile (internal GC standard) in 1 × 1 cm^2 quartz cells were deoxygenated prior to photolysis with a stream of dry argon for 15 min and sealed with rubber septa. Alternatively, deoxygentated acetonitrile-d_3 solutions of the substrates, sensitizer, and dichloromethane (internal standard) were irradiated in 5 mm o.d. NMR tubes. Products were identified by ^{1}H NMR, GC/MS, and co-injection. Product yields were determined by GC and ^{1}H NMR analysis of the crude photolysates and are based on disappearance of starting material based on the relative peak areas versus internal standard. Quantum yields were determined by valerophenone actinometry.[40]

Laser Flash Photolysis Experiments. Laser flash photolysis experiments employed the pulses (308 nm, ca. 80 mJ/pulse, 20 ns) from a Lambda Physik Lextra 50 excimer laser or a Lambda Physik FL 3002 dye laser (Stilbene 420, 420 nm, ca. 2 mJ/pulse, 20 ns) and a computer-controlled system which has been described elsewhere.[41] The dye laser was pumped by the excimer laser. Solutions of the Rh(III) complexes were prepared such that the absorbance at the excitation wavelength was ca. 0.3. Transient absorption spectra were recorded employing a Suprasil quartz flow cell (1 × 1 cm^2) and a flow system to ensure that a fresh volume of sample was irradiated by each laser pulse. Quenching rate constants were measured using argon-saturated static samples contained in 1 × 1 cm^2 Suprasil quartz cells.

Acknowledgment. The authors thank the National Science Foundation for generous support of this research and C. Turro for the preparation of the rhodium complexes. G.W.S. thanks NSERC (Canada) for a postdoctoral fellowship.

Supporting Information Available: Ground-state and transient UV−vis absorption spectra of the two Rh(III) sensitizers and a representative kinetic decay trace of the $Rh(phen)_3^{3+}$ excited state generated by LFP (5 pages). See any current masthead page for ordering information.

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