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PHOTOCHEMISTRY OF BINUCLEAR d^8 COMPLEXES

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CONTENTS

A. INTRODUCTION

Binuclear metal complexes are attractive systems for the activation of organic and inorganic molecules because they offer multiple binding sites, multielectron redox capabilities and, with heteronuclear complexes, distinct metal centers that can interact differently with a given substrate [1–5]. Numerous studies have focused on the thermal reactivity of binuclear complexes with a variety of substrates; however, less attention has been paid to the activation of molecules by the electronic excited states of these complexes [6–8]. In our work, we have found that binuclear d^8 complexes exhibit rich photochemical reactivity. Our research in this area grew out of studies of the spectroscopic properties of rhodium(I) isocyanide complexes.

It had been suspected for many years that isocyanide complexes of rhodium(I) and iridium(I) might be oligomers, owing to their intense colors, which are uncharacteristic of d^8 complexes possessing π-acceptor ligands [9,10]. It was not until Mann et al. [11] demonstrated that the absorbances in the visible and near-IR region of the spectrum of $Rh(CNC_6H_5)_4^+$ were not linearly related to the concentration of monomer that the extent of oligomerization was realized. The existence of discrete dimeric species was later confirmed by X-ray diffraction analysis [12,13] and by the synthesis and characterization of Rh_2 complexes containing diisocyanoalkanes as binucleating ligands [14,15].

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The electronic structures of binuclear d^8 complexes have been discussed in terms of a simple molecular orbital (MO) model [11]. Starting from a monomer orbital scheme, two square-planar units are brought together in a face-to-face orientation. The orbitals perpendicular to the molecular plane, d_{z^2} and p_z, interact strongly, yielding $d\sigma/\sigma^*$ and $p\sigma/\sigma^*$ orbitals. To a first approximation the ground state is expected to be non-bonding, since both the $d\sigma$ and $d\sigma^*$ orbitals are filled. However, extensive spectroscopic studies of binuclear complexes have established that the metal–metal interaction in the ${}^1A_{1g}(d\sigma^*)^2$ ground state is weakly bonding [16,17]. The mixing of orbitals of the same symmetry will stabilize the lower set and destabilize the upper ones; stabilization of the filled lower set leads to metal–metal bonding.

As suggested by the MO model, and well established by numerous other studies, the lowest energy transition is $d\sigma^* \to p\sigma$ [15,18]. This excitation results in the formation of a metal–metal single bond in the excited state. The spectroscopic and photophysical properties of all binuclear d^8 complexes are dominated by the large contraction along the metal–metal coordinate that occurs upon excitation [18–20]. The $d\sigma^* \to p\sigma$ transition is metal localized; it involves the movement of an electron from an orbital localized on the exterior of the M_2 unit (the $d\sigma^*$ orbital) to an orbital localized in the interior of the dimer cage (the $p\sigma$ orbital). The excitation results in hole formation on a metal center at an open coordination site (Fig. 1). This diradical picture of the excited state is important in discussing the photochemistry and the electrochemistry of these systems.

Additional studies of binuclear rhodium(I) complexes revealed that the lowest energy singlet and triplet excited states derived from the

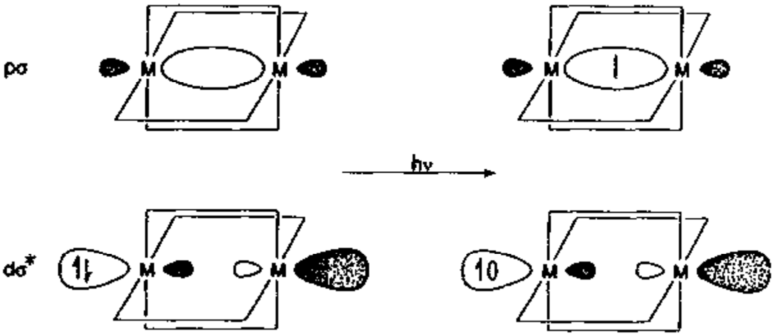


Fig. 1. Pictorial representation of the M_2-localized hole in the ${}^3(d\sigma^* p\sigma)$ state of a face-to-face binuclear d^8 complex. Prototypal complexes are $Rh_2b_4^{2+}$ (b = 1,3-diisocyanopropane), $Rh_2(TMB)_4^{2+}$ (TMB = 2,5-diisocyano-2,5-dimethylhexane), $Ir_2(TMB)_4^{2+}$, and $Pt_2(P_2O_5H_2)_4^{4-}$. Similar orbitals describe the lowest excited states of $[Ir(\mu\text{-pz})COD]_2$ (pz = pyrazole; COD = 1,5-cyclooctadiene).

$(d\sigma)^2(d\sigma^*)^1(p\sigma)^1$ electronic configuration are luminescent at ambient temperature in fluid solution [15–17,21]. Although the $^1(d\sigma^* p\sigma)$ excited state lifetime in most cases is less than 1 ns, the $^3(d\sigma^* p\sigma)$ lifetime is found to range from 30 ns to 10 μs. Ground state and $^3(d\sigma^* p\sigma)$ excited state Raman studies have shown that the metal–metal vibrational frequency increases upon excitation, corresponding to an increase in the metal–metal bond strength [19]. The increased metal–metal interaction also manifests itself in low temperature absorption spectra [18,20]. The band at 670 nm in the absorption spectrum of $Rh_2b_4^{2+}$, assigned to $^1A_{1g} \rightarrow {}^3A_{2u}$, shows a vibrational progression in a frequency of ca. 150 cm^{-1}, consistent with the Rh–Rh stretching frequency of 144 cm^{-1} obtained from Raman studies. (The ground state Rh–Rh vibrational frequency is 79 cm^{-1}.) Analysis of the band shape suggests that the Rh–Rh distance decreases by 0.3 Å in the $^3(d\sigma^* p\sigma)$ excited state.

B. EXCITED STATE REACTIONS

An electronic excited state of a metal complex is both a stronger reductant and a stronger oxidant than the ground state [22]. For this reason, binuclear d^8 complexes with relatively long-lived excited states can participate in intermolecular electron transfer reactions that are uphill for the corresponding ground state species. Such excited state electron transfer reactions often play key roles in multistep schemes for the conversion of light to chemical energy [23–25].

From spectroscopic and electrochemical studies, the $^3(d\sigma^* p\sigma)$ excited state is predicted to be a very powerful reductant, with $E°(M_2^+/{}^3M_2^*)$ estimated to range from -0.8 to -2.0 V vs. standard saturated calomel electrode (SSCE) in CH_3CN [26]. That this state is a powerful reductant has been confirmed by investigation of the electron transfer quenching of $^3(d\sigma^* p\sigma)$ $[Ir(\mu\text{-pz})COD]_2$ by a series of pyridinium acceptors with varying reduction potentials [27]. For several binuclear complexes, the excited state reduction potential cannot be calculated accurately owing to the irreversibility of the ground state electrochemistry, but it can be estimated from bimolecular electron transfer quenching experiments.

While electron transfer processes are common in inorganic photochemistry, excited state atom transfer is limited to a small class of inorganic complexes. For UO_2^{2+}, the diradical excited state (–U–O–) is active in alcohol oxidation [28]. The primary photoprocess is hydrogen atom abstraction by the oxygen-centered radical. Photoaddition to a metal center via atom transfer has been observed for binuclear metal complexes such as $Re_2(CO)_{10}$ [29–32]. The primary photoprocess is metal–metal bond homolysis. The photogenerated metal radical undergoes thermal atom abstraction reactions. Until recently, atom transfer to a metal-localized excited state had not been observed.

Atom transfer to a metal center is facilitated if there is a localized electron or hole at one or more open coordination positions. The $d\sigma^*p\sigma$ excited states of binuclear d^8 complexes satisfy this condition: the $d\sigma^*$ hole is localized at axial binding sites (Fig. 1). Probably for this reason, binuclear d^8 species exhibit rich photochemical atom transfer reactivity [26,33].

(i) Hydrogen atom transfer

The $^3(d\sigma^*p\sigma)$ excited state of $Pt_2(P_2O_5H_2)_4^{4-}$ ($^3Pt_2^*$) abstracts hydrogen from a number of organic and organometallic substrates [26,33–40]. Initial work in this area focused on the catalytic conversion of isopropanol to acetone (eqn. (1)) [36]:

$$Pt_2(P_2O_5H_2)_4^{4-} + (CH_3)_2CHOH \xrightarrow{h\nu} Pt_2(P_2O_5H_2)_4^{4-} + H_2 + (CH_3)_2CO \qquad (1)$$

From detailed studies of this system, it was concluded that the primary photoprocess is abstraction of the α-hydrogen by $^3Pt_2^*$ to form a monohydride species (directly observed by transient absorption spectroscopy for a number of substrates) and the organic radical (eqn. (2))

$$^3Pt_2^* + (CH_3)_2CHOH \rightarrow Pt_2H + (CH_3)_2COH \qquad (2)$$

with the final photoproduct being Pt_2H_2 and acetone. The Pt_2H_2 complex has been characterized by spectroscopic methods [37].

Systematic studies of excited state hydrogen atom abstraction reactions have involved a binuclear iridium(I) complex, $Ir_2(TMB)_4^{2+}$ (Ir_2) [38]. Absorption spectral changes that accompany the photochemical reaction between $Ir_2(TMB)_4^{2+}$ and 9,10-dihydroanthracene include the disappearance of the $^1(d\sigma^*p\sigma)Ir_2$ band and the growth of higher energy absorptions that signal the formation of anthracene. (Resonances assignable to anthracene and Ir–H are found in ^{1}H NMR spectra.) The inorganic product from the reaction mixture has been isolated and structurally characterized as the *trans* dihydride, $Ir_2(TMB)_4H_2^{2+}$ (Ir_2H_2) [38]. An Ir–H band at 1940 cm^{-1} is observed in the IR spectrum of Ir_2H_2; this band is attributable to a terminal M–H stretch. No appreciable thermal reaction with 9,10-dihydroanthracene occurs at room temperature; however, a reaction to give anthracene and Ir_2H_2 is observed at elevated temperatures.

For 1,4-cyclohexadiene, no thermal reaction takes place (even at elevated temperatures). Photolysis of $Ir_2(TMB)_4^{2+}$ and 1,4-cyclohexadiene results in rapid disappearance of the d^8–d^8 metal complex. Resonances attributable to benzene and Ir–H are observed in ^{1}H NMR spectra. The net photoreaction is hydrogen atom transfer to the metal center:

$$Ir_2 + RH_2 \xrightarrow{h\nu} Ir_2H_2 + R \tag{3}$$

The likely steps leading to Ir_2H_2 are given in eqns. (4)–(8):

$$Ir_2 \xrightarrow{h\nu} {}^3Ir_2^* \tag{4}$$

$$^3Ir_2^* + RH_2 \rightarrow \cdot Ir_2H + RH\cdot \tag{5}$$

$$\cdot Ir_2H + RH\cdot \rightarrow Ir_2H_2 + R \tag{6}$$

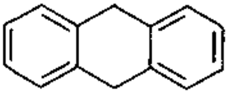
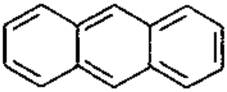
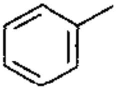
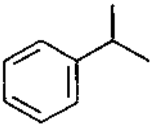
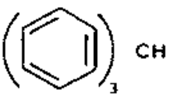
$$\cdot Ir_2H + RH_2 \rightarrow Ir_2H_2 + RH\cdot \tag{7}$$

$$\cdot Ir_2H + \cdot Ir_2H \rightarrow Ir_2H_2 + Ir_2 \tag{8}$$

The products of the photoreactions of hydrocarbons with Ir_2 are shown in Table 1. While Ir_2H_2 is not observed in all cases, only triphenylmethane

TABLE 1

Photochemical reactions of hydrocarbons with $Ir_2(TMB)_4^{2+}$

Substrate	D [a] (kcal mol^{-1})	Products
	77	Ir_2H_2, 
	73	Ir_2H_2, 
	82	Ir_2H_2 [b]
	88	No reaction [c]
	84.4	No reaction [c]
	~ 75	No reaction [c]

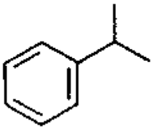
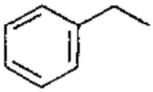
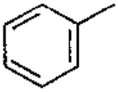
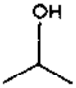
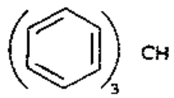
[a] C–H bond dissociation energy [38].

[b] Sluggish formation of Ir_2H_2.

[c] No observed formation of Ir_2H_2.

TABLE 2

Stern–Volmer quenching rate constants for $Ir_2(TMB)_4^{2+}$ and $Pt_2(P_2O_5H_2)_4^{4-}$

Substrate	D [a] (kcal mol^{-1})	$^3Ir_2^*$ [b] ($M^{-1}\ s^{-1}$)	$^3Pt_2^*$ [c] ($M^{-1}\ s^{-1}$)
	82	7.9×10^5 ($k_H/k_D > 3$)	1.2×10^6
	73	5.2×10^5	8.2×10^6
	84.4	3.1×10^5	$<10^4$
	85.5	2.3×10^5	
	88.0	9.7×10^4	$<10^4$
		6.5×10^4	
	91.0		5×10^3
	~75	$<4\times10^5$	$<2\times10^4$

[a] C–H bond dissociation energy [38].

[b] Ref. 38.

[c] Refs. 35 and 38–40.

fails to quench the $^3(d\sigma^*p\sigma)$ excited state of Ir_2. Photochemical conversion of the organic substrates may occur with no build-up of inorganic product. For $Pt_2(P_2O_5H_2)_4^{4-}$, excited state quenching by toluene and cumene has been observed; steady state photolysis ($\lambda_{ex} = 370$ nm) produces H_2 and organic radical products [39].

The kinetics of hydrogen atom transfer reactions of $^3Ir_2^*$ and $^3Pt_2^*$ with a series of organic donors have been investigated (Table 2) [38]. If the $^3M_2^*$ reaction is a sterically unencumbered atom transfer process, the rate should track the homolytic C–H bond energies of the substrates. Indeed, in one

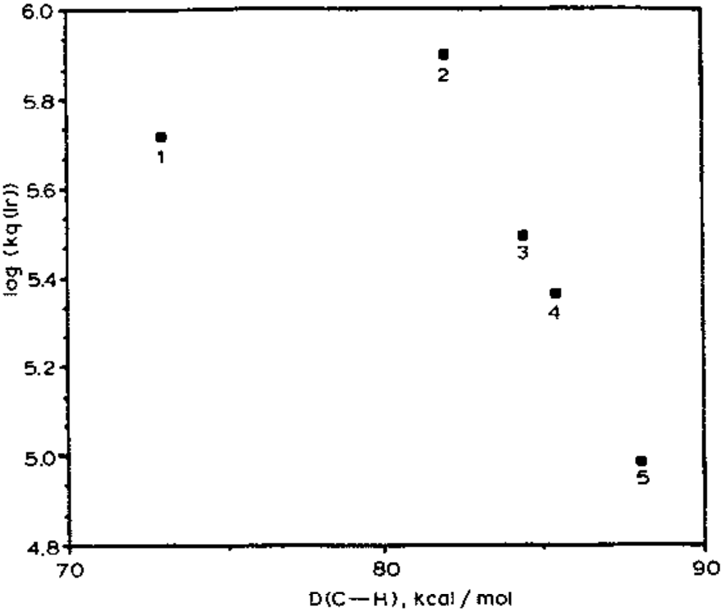


Fig. 2. Plot of log k_q vs. the C–H bond dissociation energy (D(C–H)) for the hydrogen atom transfer quenching of $^3Ir_2^*$ by hydrocarbon substrates: 1, cyclohexadiene; 2, cyclohexene; 3, cumene; 4, ethylbenzene; 5, toluene.

series of quenchers, the rate constant for $^3Ir_2^*$ decreases with increasing C–H bond energy (Fig. 2) [38]. However, for the reaction with cyclohexene, the homolytic C–H bond energy of which is ca. 10 kcal mol^{-1} greater than that of 1,4-cyclohexadiene, a larger rate constant is observed. Smith [38] argued that steric effects may be important in the $^3Ir_2^*$ reactions. Recent work has shown that the structure of 1,4-cyclohexadiene is almost planar [41]. The structure of cyclohexene is a skewed boat [42]. For a linear M–H–C transition state, a much less favorable steric interaction is expected for the planar 1,4-cyclohexadiene. The angle defined by the M–H–C vector and the plane containing the allyl unit is much smaller for 1,4-cyclohexadiene than for cyclohexene.

It is not likely that the reactions of $^3Ir_2^*$ and $^3Pt_2^*$ with hydrocarbons involve energy transfer or electron transfer. Another quenching mechanism, suggested for the reactions of $^3Pt_2^*$ with simple alkenes, is an inner-sphere process that involves the formation of a diradical intermediate [43]:

$$^3Pt_2^* + RCH{=}CHR \rightarrow \cdot M_2\text{–}CHR\text{–}CHR\cdot \qquad (9)$$

$$M_2\text{–}CHR\text{–}CHR\cdot \rightarrow Pt_2 + RCH{=}CHR \qquad (10)$$

The second step in this mechanism involves the collapse of the diradical intermediate back to the alkene and the ground state metal complex. The rapid formation of Ir_2H_2 with 1,4-cyclohexadiene and the large kinetic isotope effect observed for cyclohexene do not support a mechanism of this sort in the case of $^3Ir_2^*$.

(ii) Alkyl halide reductions

Irradiation of binuclear d^8 complexes in the presence of alkyl halides yields products that can be rationalized in terms of excited state electron transfer followed by dissociative decomposition of RX^- and rapid scavenging of R· and X^- [26,33,44–47]. The back electron transfer reaction is inhibited by the decomposition of the alkyl halide radical anion. Photolysis of $Ir_2(TMB)_4^{2+}$ in 1,2-dichloroethane cleanly generates $Ir_2(TMB)_4Cl_2^{2+}$ (Fig. 3) [38]. The presumed organic product is ethylene. Similarly, $Rh_2b_4^{2+}$ reacts

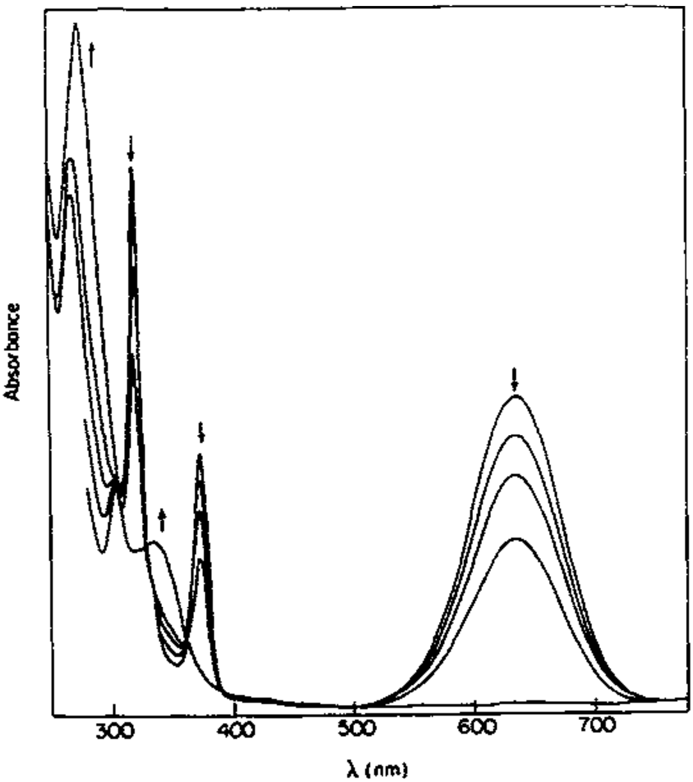


Fig. 3. Spectral changes upon irradiation of $[Ir_2(TMB)_4](B(C_6H_5)_4)_2$ in neat 1,2-dichloroethane ($\lambda_{ex} > 604$ nm).

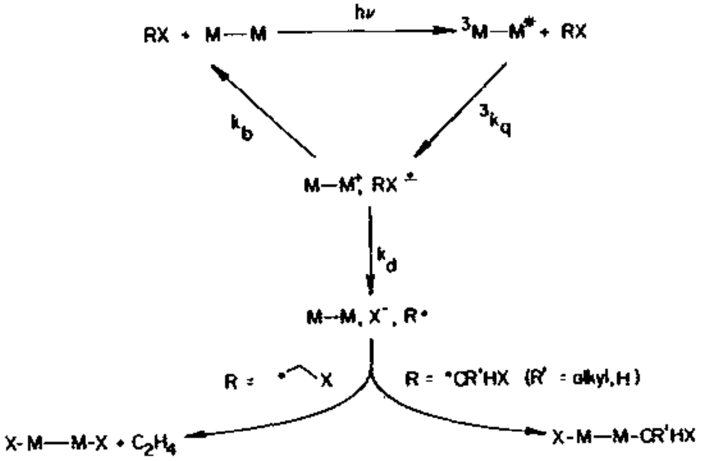


Fig. 4. $S_{RN}1$ mechanistic scheme for halocarbon photo-oxidative addition.

photochemically with 1,2-dichloroethane ($\lambda_{ex} > 500$ nm). The inorganic product is $Rh_2b_4Cl_2^{2+}$.

An $S_{RN}1$ mechanism (Fig. 4) has been proposed to explain the photoreduction of alkyl halides by certain binuclear d^8 complexes [26]. For $[Ir(\mu\text{-}pz)COD]_2$, the excited state reduction potential of which is less than -1.5 V(SSCE), an outer-sphere electron transfer reaction is plausible. Reduction potentials for alkyl halides of interest are generally more negative than -1.5 V(SSCE) [48]. The quenching rate constant for the reaction of the $^3(d\sigma^* p\sigma)$ excited state of $[Ir(\mu\text{-}pz)COD]_2$ with 1,2-dichloroethane agrees with the rate expected for outer-sphere electron transfer to an acceptor with a reduction potential of -2.0 V(SSCE) [45]. However, outer-sphere electron transfer is not a likely pathway for complexes with $E^\circ(M_2^+/^3M_2^*) > -1.0$ V(SSCE).

An alternative to outer-sphere electron transfer, which yields similar photoredox products with alkyl halides, is excited state atom transfer (Fig.

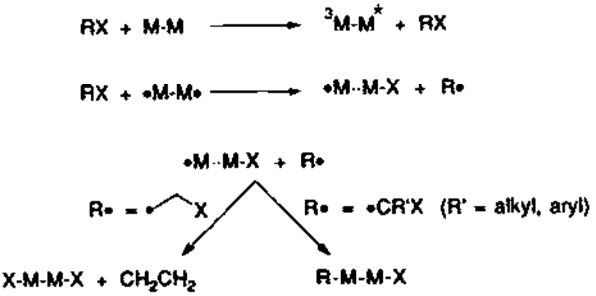


Fig. 5. Atom transfer mechanism for halocarbon photo-oxidative addition.

5). Data obtained for $Pt_2(P_2O_5H_2)_4^{4-}$ indicate that alkyl and aryl halides react with the $^3(d\sigma^*p\sigma)$ excited state via halogen atom transfer [33]. The $^3(d\sigma^*p\sigma)$ excited state abstracts the halogen atom, generating a d^8–d^7 monohalide species and an organic radical. An atom transfer mechanism is also favored for the reaction between $^3Ir_2^*$ and 1,2-dichloroethane.

The Ir_2–1,2-dichloroethane photoredox reaction is very clean for $\lambda_{ex} > 500$ nm. As λ_{ex} is decreased to 400 nm, however, secondary photolysis occurs. The most likely reaction is photochemical degradation of $Ir_2(TMB)_4Cl_2^{2+}$ [49]. Higher energy irradiation of $Rh_2b_4^{2+}$ in 1,2-dichloroethane also results in complex behavior. The rapid disappearance of $Rh_2b_4^{2+}$ with the growth of $Rh_2b_4Cl_2^{2+}$ is observed initially; loss of $Rh_2b_4Cl_2^{2+}$ is accompanied by the appearance of bands attributable to oligomeric rhodium species [50].

C. ELECTROCATALYSIS

If production of an oxidizing hole in the $d\sigma^*$ orbital is the key to photochemical atom transfer, then electrochemical generation of such a hole should produce a highly reactive intermediate that would mimic the initial step in the $^3(d\sigma^*p\sigma)$ reaction. Several binuclear d^8 complexes undergo reversible one-electron oxidations in non-coordinating solvents [51–53]. The complex $Rh_2(TMB)_4^{2+}$ possesses a quasi-reversible one-electron oxidation at 0.74 V(SSCE) in CH_2Cl_2 solution. Electrochemical oxidation of $Rh_2(TMB)_4^{2+}$ in the presence of 1,4-cyclohexadiene is accompanied by an enhanced anodic current with loss of the cathodic wave, behavior which is indicative of an electrocatalytic process [38]. Bulk electrolysis of $Rh_2(TMB)_4^{2+}$ in an excess of 1,4-cyclohexadiene results in the formation of benzene and two protons ($C_6H_8 \rightarrow C_6H_6 + 2H^+ + 2e^-$ ($E° = 0.4$ V vs. normal hydrogen electrode)). The maximum number of turnovers is limited by the amount of substrate relative to solvent. The complex $Rh_2(TMB)_4^{2+}$ is slowly lost owing to a competitive reaction with CH_2Cl_2 to produce $Rh_2(TMB)_4Cl_2^{2+}$.

The pathway proposed to explain the oxidation of 1,4-cyclohexadiene is shown in Fig. 6. Oxidation of $Rh_2(TMB)_4^{2+}$ generates the reactive d^8–d^7 complex, $Rh_2(TMB)_4^{3+}$. The metal complex abstracts a hydrogen atom from the organic substrate, generating a monohydride species and an organic radical. It is known that hydride complexes of $Rh_2(TMB)_4^{2+}$ are unstable [54]. (No reaction between $Rh_2(TMB)_4^{2+}$ and HCl is observed at room temperature in the absence of air, suggesting that the equilibrium between the d^8–d^8 and d^7–d^7 species lies far to the side of the d^8–d^8 complex.) Therefore the monohydride rapidly loses H^+, regenerating $Rh_2(TMB)_4^{2+}$. The cycle accounts for the generation of H^+ (identified electrochemically at

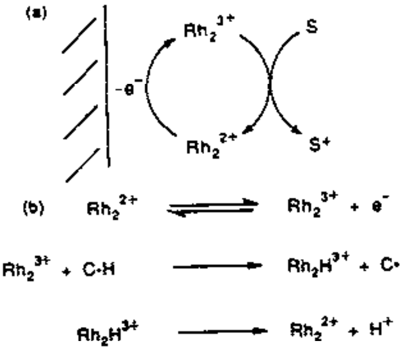


Fig. 6. (a) Pictorial representation of an electrocatalytic cycle that regenerates the Rh_2^{2+} complex. (b) Atom transfer pathway for electrochemical oxidation of 1,4-cyclohexadiene.

a platinum button electrode and by the decrease in pH) and the electrocatalytic behavior of $Rh_2(TMB)_4^{2+}$.

The competitive reaction of $Rh_2(TMB)_4^{2+}$ with CH_2Cl_2 can also be interpreted in terms of a pathway similar to that for the hydrogen atom abstraction. The d^8–d^7 complex abstracts a halogen atom, generating a monohalide species. The monohalide, rather than losing halide to regenerate $Rh_2(TMB)_4^{2+}$, reacts to yield $Rh_2(TMB)_4Cl_2^{2+}$.

Our work has established that highly reactive d^8–d^7 species can be formed by electrochemical oxidation, and that complexes with a $d\sigma^*$ hole exhibit rich atom abstraction chemistry. The ability to generate reactive d^8–d^7 complexes electrochemically should make it possible to carry out reactions with the most inert hydrocarbons. While the $^3(d\sigma^* p\sigma)$ state may be energetic enough to react with hydrocarbons with D(C–H) in excess of 100 kcal mol^{-1}, the expected rates for these reactions are orders of magnitude less than the lower limit set by the triplet lifetime. For $^3Pt_2^*$, k_q values are roughly 10^4 M^{-1} s^{-1} for substrates with D(C–H) approximately 90 kcal mol^{-1} [33]. Electrochemically generated d^8–d^7 complexes should, in principle, be more versatile than excited states with nanosecond to microsecond lifetimes.

Systems using binuclear d^8 complexes covalently linked to pyridinium acceptors yield charge-separated species upon excitation [55]. Excited state electron transfer generates the one-electron oxidized metal complex and the one-electron reduced pyridinium. Our work on the atom abstraction chemistry of complexes with a $d\sigma^*$ hole has shown that it should be possible to intercept the d^8–d^7 species of the charge-separated state, thereby inhibiting the back electron transfer step. The development of an inorganic or organometallic system where coupled electron transfer (photo-induced charge separation) and atom transfer (chemistry at the oxidized metal) steps lead to energy storage may be a viable goal.

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