Synthesis, Spectroscopy, and Photochemistry of Bis[bis(diphenylphosphino)methane]bis(2,5-di-isocyano-2,5-dimethylhexane)dirhodium(I)†

Chi-Ming Che,* Wai-Man Lee, and Hoi-Lun Kwong
Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong
Vivian Wing-Wah Yam
Department of Applied Science, City Polytechnic of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong
Kar-Cheong Cho
Department of Physics, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Reaction between $[Rh_2L_4]^{2+}$ (L = 2,5-di-isocyano-2,5-dimethylhexane) and dppm [bis(diphenylphosphino)methane] in acetonitrile yielded $[Rh_2L_2(dppm)_2]^{2+}$. Its optical spectrum displays an intense absorption at 595 nm, which is assigned to the transition ${}^1A_{1g}[(d_{\sigma^*})^2] \longrightarrow {}^1B_{1u}[(d_{\sigma^*})^1(p_\sigma)^1]$. Room-temperature fluorescence at 677 nm, from the ${}^1B_{1u}$ excited state, is observed in fluid solution. The ${}^3B_{1u}$ state of the rhodium complex is long-lived with a measured lifetime of 1.0 ± 0.1 µs. Studies on the quenching reactions with a series of pyridinium acceptors established that the excited reduction potential $[E^\circ(Rh_2^{3+}-Rh_2^{2+*})]$ is −1.13 V *vs.* saturated calomel electrode. The mechanism of the photoreactions of the rhodium complex with halogenocarbons is discussed.

Numerous studies on the synthesis and spectroscopy of binuclear complexes of Rh^I containing bridging diphosphines, diarsines, and di-isocyanides have been reported.[1–3] An example is the $[Rh_2(bridge)_4]^{2+}$ complex (bridge = 1,3-di-isocyanopropane)[2] which is capable of reducing protons in concentrated HCl to give molecular hydrogen upon irradiation with visible light. Other binuclear rhodium complexes with both bridging diphosphine and isocyanide ligands, $[Rh_2(RNC)_4(dppm)_2]^{2+}$ (R = Bu^t, Bu^n, or Ph; dppm = $Ph_2PCH_2PPh_2$),[1a,f] have also been reported. Our interest in the binuclear complexes of Rh^I containing both diphosphine and di-isocyanide ligands was aroused by the ability of both ligands to lock together two metal centres in close proximity and hence promote organometallic reactions involving multielectron redox processes. Moreover, the similarity of the face-to-face square planes of the dimers with other isoelectronic d^8–d^8 $[Pt_2(H_2P_2O_5)_4]^{4-}$,[4] $[Ir_2(cod)(pz)_2]$ (cod = cyclo-octa-1,5-diene, pz = pyrazolate),[5] and $[Rh_2(Bu^nNC)_4(dpam)_2]^{2+}$ [dpam = bis(diphenylarsino)methane] complexes[1d,f] as well as the rich photophysical and photochemical properties exhibited by these systems prompted us to undertake this study. As part of our research programme on photochemical C–X bond activation utilizing binuclear metal complexes, we report here the synthesis, spectroscopic and photochemical properties of a novel complex $[Rh_2L_2(dppm)_2]^{2+}$ (L = 2,5-di-isocyano-2,5-dimethylhexane).[3]

Experimental

Synthesis of Rhodium Complexes.—(*i*) $[Rh_2L_2(dppm)_2]Y_2$ (Y = Cl^- or BF_4^-). The complex $[Rh_2L_4]Cl_2$ (95 mg) prepared by the literature procedure[2d] was dissolved in acetonitrile (3–5 cm^3). A stoicheiometric amount of bis(diphenylphosphino)methane (40 mg) was slowly added to the solution with continuous stirring. The solution gradually turned blue. Upon addition of diethyl ether and cooling, a blue precipitate of $[Rh_2L_2(dppm)_2]Cl_2$ was obtained. The product was purified by slow diffusion of diethyl ether into an acetonitrile solution of the product. The BF_4^- salt was isolated by metathesis with tetrabutylammonium tetrafluoroborate {Found: C, 56.6; H, 5.1; N, 4.1. Calc. for $[Rh_2L_2(dppm)_2][BF_4]_2$: C, 56.9; H, 5.1; N, 3.8%}. U.v.–visible (MeCN): λ/nm($\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1}) 595 (16 200) and 317 (18 800). ν(CN) 2 120 cm^{-1}.

(*ii*) $[Rh_2L_2(dppm)_2Cl_2][BF_4]_2$. The complex $[Rh_2L_2(dppm)_2][BF_4]_2$ (0.1 g) was dissolved in the minimum amount of acetonitrile. Chlorine gas was slowly bubbled into the acetonitrile solution with stirring. The solution gradually turned from blue to yellow and a precipitate formed. The solvent was removed by rotary evaporation and the resulting yellow solid, $[Rh_2L_2(dppm)_2Cl_2][BF_4]_2$, was purified by crystallization from MeCN–diethyl ether {Found: C, 54.2; H, 5.0; Cl, 4.7. Calc. for $[Rh_2L_2(dppm)_2Cl_2][BF_4]_2$: C, 54.3; H, 4.9; Cl, 4.6%}. ν(CN) 2 160 cm^{-1}.

(*iii*) $[Rh_2L_2(dppm)_2Br_2][BF_4]_2$. The dibromo salt was prepared as described above except bromine (2 cm^3) was used {Found: C, 51.4; H, 4.6; Br, 9.8. Calc. for $[Rh_2L_2(dppm)_2Br_2][BF_4]_2$: C, 51.3; H, 4.6; Br, 9.8%}. ν(CN) 2 160 cm^{-1}.

Preparation and Purification of Materials.—Acetonitrile (Mallinkrodt, ChromAR, h.p.l.c. grade) was distilled over calcium hydride and potassium permanganate before use. The pyridinium salts were prepared by refluxing the corresponding substituted pyridine with the appropriate alkylating agent such as methyl iodide in acetone–ethanol (1:1 v/v) for 4 h, followed by metathesis in water using ammonium hexafluorophosphate and recrystallization from acetonitrile–diethyl ether. The halogenocarbons were purified according to literature procedures.[6]

Physical Measurements and Instrumentation.—U.v.–visible spectra were obtained on a Shimadzu UV-240 spectrophotometer. Steady-state emission spectra were recorded on a Hitachi 650-60 fluorescence spectrophotometer. Corrected emission spectra were obtained using a Hitachi 650-0178 data processor accessory.

Luminescence quenching experiments were monitored by time-resolved (lifetime) emission measurements, and data were treated by a Stern–Volmer fit as described by $\tau_o/\tau = 1 +$

---

† *Non-S.I. unit employed:* eV ≈ 1.60 × 10^{-19} J.

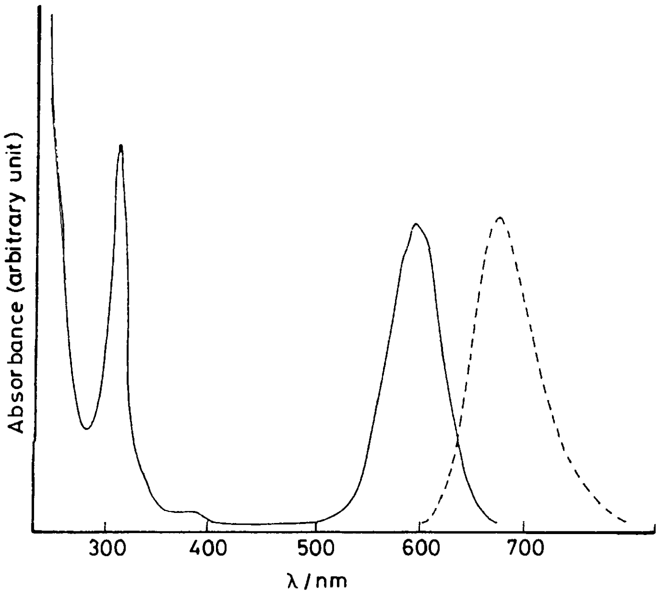

Figure 1. U.v.–visible absorption (——) and emission (– – – –) (excitation at *ca.* 590 nm) spectra of [Rh$_2$L$_2$(dppm)$_2$]$^{2+}$ in degassed acetonitrile

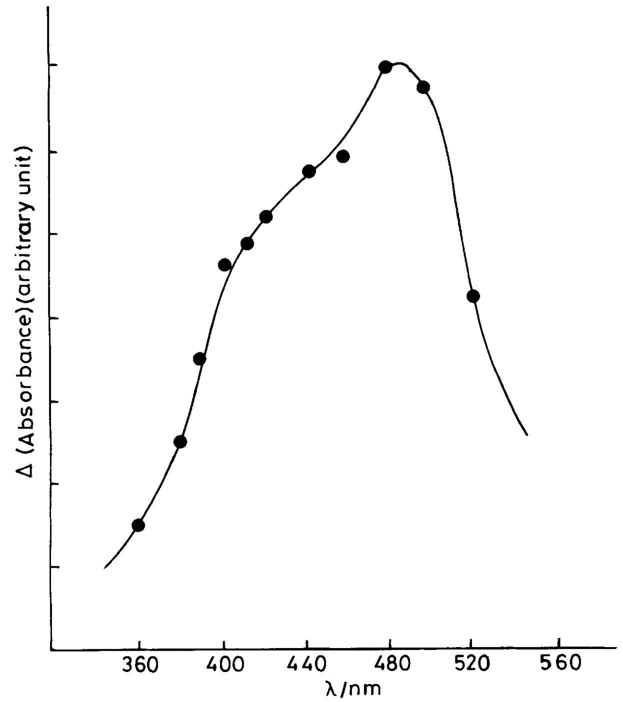

Figure 2. Transient difference absorption spectrum recorded 2 μs after flashing a degassed acetonitrile solution of [Rh$_2$L$_2$(dppm)$_2$]$^{2+}$ at 532 nm (triplet excited-state spectrum)

k$_q\tau_o$[Q] (τ_o = Excited state lifetime in the absence of quencher; τ_c = excited state lifetime in the presence of quencher; k_q = quenching rate constant; [Q] = concentration of quencher in mmol dm^{-3}). Emission lifetime measurements were made using a conventional laser system. The excitation source was the 532-nm output (second harmomic) of a Quanta-Ray Q-switched DCR-3 pulsed Nd-YAG laser (10 Hz, G-resonator) or the 588-nm output of a Quanta-Ray PDL-2 pulsed dye laser (Kiton Red) pumped by the 532-nm output of the Nd-YAG laser. Luminescence decay signals were recorded on a Tektronix model 2430 digital oscilloscope, and analysed using a program for exponential fits. All solutions for quenching studies were prepared under vacuum in a 10-cm^3 round-bottom flask equipped with a side-arm 1-cm fluorescence cuvette and sealed from the atmosphere by a Kontes quick-release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze–pump–thaw cycles.

The transient absorption spectra and kinetics were obtained using a conventional set-up with the 532-nm output of a DCR-3 pulsed Nd-YAG laser as the excitation source. The monitoring beam was a 100-W tungsten–iodide lamp source. Transient signals were recorded as in luminescence quenching.

Results and Discussion

Spectroscopy and Photophysical Properties.—The complex [Rh$_2$L$_2$(dppm)$_2$]$^{2+}$ is easily obtained by treating [Rh$_2$L$_4$]$^{2+}$ with excess of dppm ligand. It is an air-stable blue solid, stable in aprotic solvents. Its i.r. spectrum shows only one ν(C≡N) stretch at 2 120 cm^{-1}, indicating that the two L ligands are *trans* to each other.

The electronic absorption spectrum of an acetonitrile solution of [Rh$_2$L$_2$(dppm)$_2$]$^{2+}$ exhibits bands at 595 ($\varepsilon_{max.}$ 16 200) and 317 nm ($\varepsilon_{max.}$ 18 800 dm^3 mol^{-1} cm^{-1}) (Figure 1). The presence of an intense low-energy band well separated from the higher-energy transitions in the absorption spectrum is typical of binuclear rhodium(I) complexes. With reference to previous spectroscopic works on binuclear d^8–d^8 systems,[1f,2e,7] the band at 595 nm is attributed to the $^1A_{1g} \longrightarrow 1b_{1u}$ ($^1b_{1u} \longrightarrow 2a_{1g}$) transition assuming a D_{2h} symmetry where the orbital energies are in the order: $1a_{1g}(4d_{z^2}) < 1b_{1u}(4d_{z^2}{}^*) < 2a_{1g}(5p_z) < 2b_{1u}(5p_z{}^*)$. The $1a_{1g}$ and $1b_{1u}$ orbitals are both occupied in the ground state. Interaction of the a_{1g} and b_{1u} orbital pairs, respectively, could produce weak Rh–Rh bonding. The replacement of RNC ligands in [Rh$_2$(RNC)$_4$(dppm)$_2$]$^{2+}$ by the bridging L ligands in [Rh$_2$L$_2$(dppm)$_2$]$^{2+}$ is accompanied by a red shift in the energy of the corresponding low-energy absorptions {595 nm for [Rh$_2$L$_2$(dppm)$_2$]$^{2+}$ *vs.* 523—573 nm for [Rh$_2$(RNC)$_4$(dppm)$_2$]$^{2+}$}.[1f] Apparently in [Rh$_2$L$_2$(dppm)$_2$]$^{2+}$ the bridging L ligands enforce a closer approach of the rhodium(I) centres, increasing the $d_{z^2} - d_{z^2}$ orbital interactions and decreasing the absorption energy relative to the non-bridging isocyanide ligands. Similarly, the lower *d*–*p* transition energy in [Rh$_2$L$_2$(dppm)$_2$]$^{2+}$ than in [Rh$_2$L$_4$]$^{2+}$ [2b,d] may also be attributed to the shorter bite distance of the dppm bridge relative to the L bridge, resulting in a larger metal–metal interaction.

Excitation of a degassed acetonitrile solution of [Rh$_2$L$_2$(dppm)$_2$]$^{2+}$ at 595 nm at room temperature results in photoluminescence (Figure 1). The intense emission band at 677 nm with lifetime $\tau_o < 10$ ns has been assigned as fluorescence derived from the $^1B_{1u}$ $^1(d_\sigma{}^*p_\sigma)$ state.[1f] The phosphorescence has not been recorded as it probably lies outside our instrument's spectral range (200—750 nm). However, with excitation at 532 nm and emission monitoring at 750 nm, a decay signal with τ_o of 1.0 ± 0.1 μs was recorded which is too long to be attributed to the fluorescent state. Presumably, the signal is derived from the weak emission at the tailing region of the phosphorescent band. Thus, the $^3B_{1u}$ triplet-state lifetime is estimated to be 1.0 ± 0.1 μs.

Transient absorptions at 350—550 nm with lifetime of *ca.* 1.0 μs have been observed upon 532-nm excitation of a degassed acetonitrile solution of [Rh$_2$L$_2$(dppm)$_2$]$^{2+}$, attributable to the $^3B_{1u}$ triplet absorption (Figure 2). Similar transient absorptions in the 400—550 nm region have also been observed for the [Rh$_2$L$_4$]$^{2+}$ triplet.[2b,d] The triplet decay lifetime of 1.0 μs is consistent with that obtained from emission measurements at 750 nm, thereby establishing the identity of the $^3B_{1u}$ state.

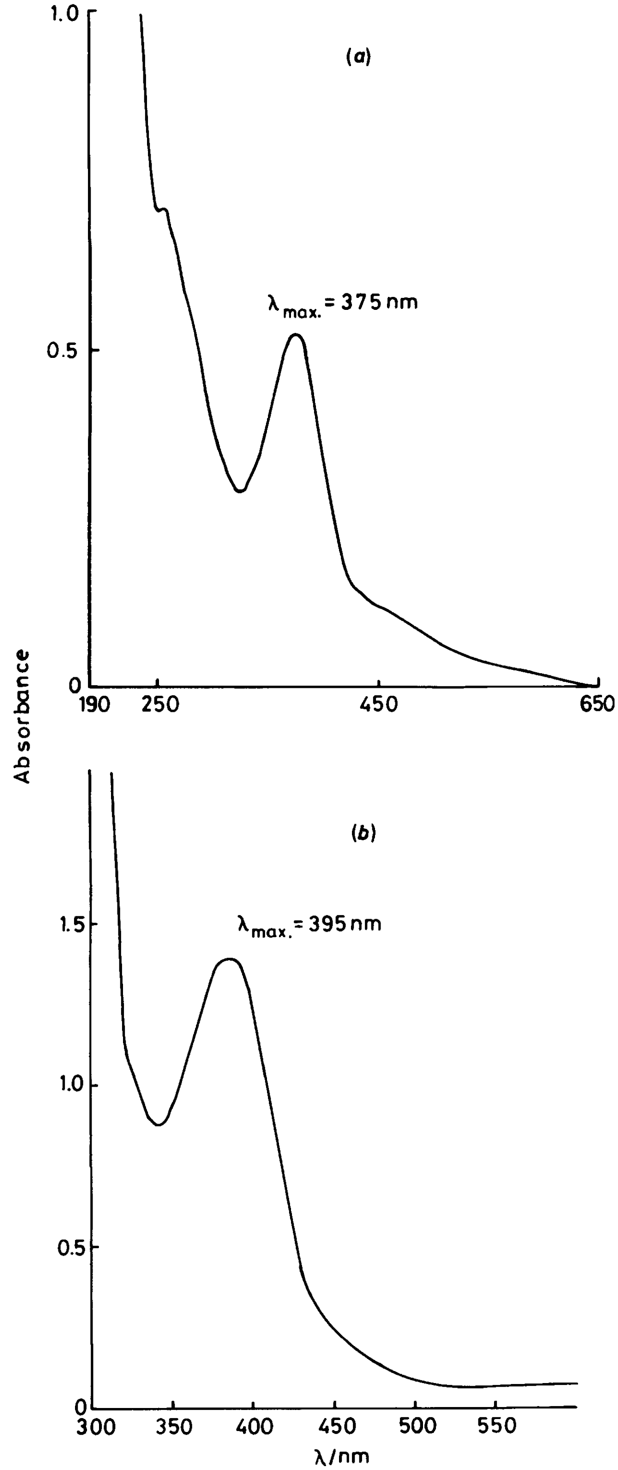

Figure 3. Electronic absorption spectra of (*a*) $[Rh_2L_2(dppm)_2Cl_2][PF_6]_2$ and (*b*) $[Rh_2L_2(dppm)_2Br_2][PF_6]_2$ in acetonitrile

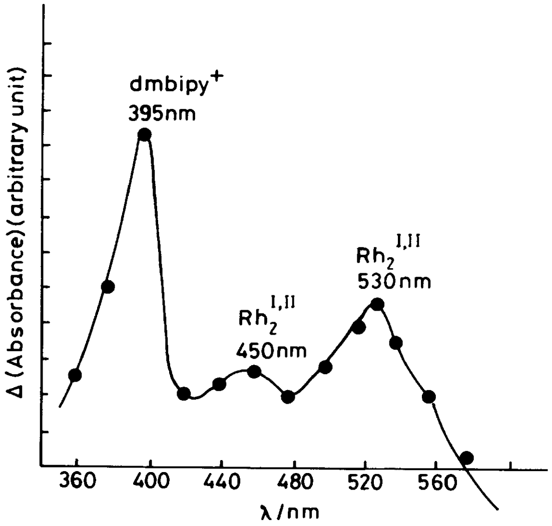

Figure 4. Transient difference absorption spectrum recorded 10 μs after flashing a degassed acetonitrile solution of $[Rh_2L_2(dppm)_2]^{2+}$ and $dmbipy^{2+}$

Redox Chemistry.—In aprotic solvents, no reversible electrochemistry of $[Rh_2L_2(dppm)_2]^{2+}$ has been observed; but the rhodium complex readily undergoes transannular thermal oxidative-addition reaction with halogen to give $[Rh_2L_2(dppm)_2X_2]^{2+}$ (X = Cl or Br). The electronic absorption spectra of $[Rh_2L_2(dppm)_2X_2]^{2+}$ (X = Cl or Br) in acetonitrile (Figure 3) exhibit bands in the 350—450 nm region, which is typical of dirhodium(II) compounds.[8] The intense absorptions at 375 and 395 nm, respectively, are attributable to the $d_\sigma \longrightarrow d_\sigma{}^*$ transition ($^1A_{1g} \longrightarrow {}^1B_{1u}$). The red shift in energy of the $d_\sigma \longrightarrow d_\sigma{}^*$ transition from Cl to Br probably arises from configuration mixing of the p_σ(X) orbital with the d_σ(Rh) orbital, suggesting the presence of charge-transfer character in the metal–metal bond.

The addition of axial ligands to the $[Rh_2L_2(dppm)_2]^{2+}$ complex to form $[Rh_2L_2(dppm)_2X_2]^{2+}$ is accompanied by a strengthening of the C≡N bond, according to i.r. spectroscopy.

Oxidative Quenching with Pyridinium Acceptors.—The phosphorescence of $\{[Rh_2L_2(dppm)_2]^{2+}\}^*$ in acetonitrile is found to be quenched by a number of electron acceptors. 1,1′-Dimethyl-4,4′-bipyridinium (methyl viologen), $dmbipy^{2+}$, a well known one-electron oxidant, is found to quench the $\{[Rh_2L_2(dppm)_2]^{2+}\}^*$ triplet with a k_q value of 1.07×10^9 $dm^3\ mol^{-1}\ s^{-1}$. The transient difference absorption spectrum obtained 10 μs after flashing a degassed acetonitrile solution of $[Rh_2L_2(dppm)_2]^{2+}$ and $dmbipy^{2+}$ at 532 nm is shown in Figure 4. Transient absorption signals attributable to the $dmbipy^+$ species ($\lambda_{max.}$ 390 and 605 nm)[9] suggest an electron-transfer quenching mechanism [equation (1)]. The transient

$$[Rh_2L_2(dppm)_2]^{2+} + dmbipy^{2+} \longrightarrow [Rh_2L_2(dppm)_2]^{3+} + dmbipy^{+} \quad (1)$$

absorption at 605 nm, characteristic of the $dmbipy^+$ species, does not appear in the difference spectrum since it falls within the bleaching region of $[Rh_2L_2(dppm)_2]^{2+}$ at 595 nm. Transient absorptions at 450 and 530 nm are attributable to the one-electron oxidized $[Rh_2L_2(dppm)_2]^{3+}$ species. Similar observations have also been reported for the transient absorptions of $[Rh_2L_4]^{3+}$ and $[Rh_2(bridge)_4]^{3+}$ in flash-photolysis experiments with $dmbipy^{2+}$.[2d]

In addition, further to understand the electron-transfer reactivity of the $^3(d_\sigma{}^*p_\sigma)$ excited state of $[Rh_2L_2(dppm)_2]^{2+}$, a study of the electron-transfer quenching by a series of pyridinium acceptors of variable reduction potential was undertaken. The quenching rate constants are summarized in Table 1. An excited-state reduction potential $E°(Rh_2{}^{3+}–Rh_2{}^{2+*})$ of −1.13 V *vs.* saturated calomel electrode (s.c.e.) together with $\lambda = 0.47$ eV and $RT \ln K\kappa\nu = 0.48$ V *vs.* s.c.e. have been obtained by three-parameter, non-linear least-squares fit by equation (2)[10] where $k_q{}'$ are corrected for diffusional effects

Table 1. Rate constants for the quenching of $\{[Rh_2L_2(dppm)_2]^{2+}\}^*$ by a series of pyridinium acceptors in degassed acetonitrile (0.1 mol dm^{-3} $NBu^n{}_4PF_6$) at 25 °C. A stands for electron acceptor

Quencher[a]	$E(A^{+/0})$[b] V *vs.* s.c.e.	k_q/dm^3 mol^{-1} s^{-1}	k_q'/dm^3 mol^{-1} s^{-1}[c]	ln k_q'
4-Cyano-*N*-methylpyridinium	-0.67	1.25×10^8	1.26×10^8	18.65
4-Methoxy-carbonyl-*N*-methylpyridinium	-0.78	8.86×10^7	8.90×10^7	18.30
4-Amido-*N*-ethylpyridinium	-0.93	2.66×10^7	2.66×10^7	17.10
3-Amido-*N*-methylpyridinium	-1.14	9.82×10^5	9.82×10^5	13.80

[a] All the compounds are hexafluorophosphate salts. [b] Ref. 5*a*. [c] See ref. 10.

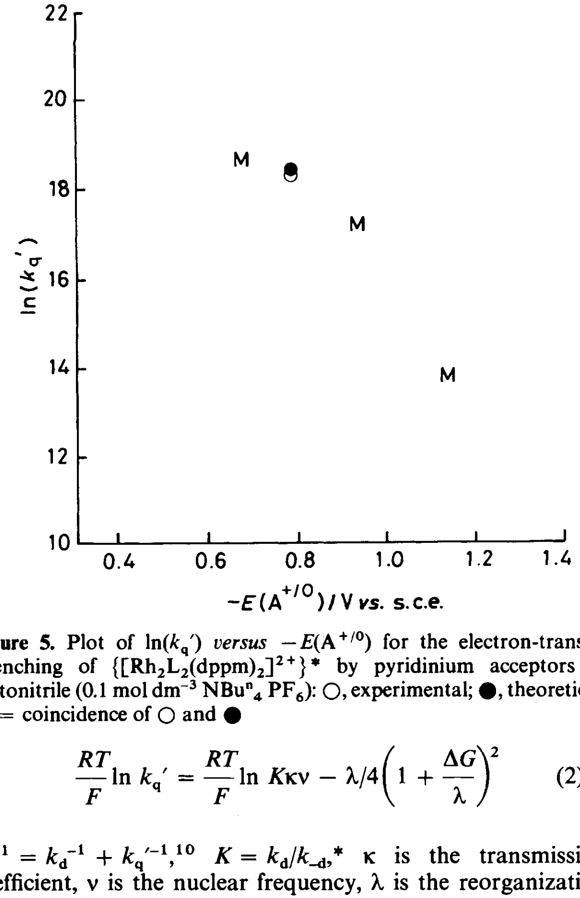

Figure 5. Plot of ln(k_q') *versus* $-E(A^{+/0})$ for the electron-transfer quenching of $\{[Rh_2L_2(dppm)_2]^{2+}\}^*$ by pyridinium acceptors in acetonitrile (0.1 mol dm^{-3} $NBu^n{}_4$ PF_6): ○, experimental; ●, theoretical; M = coincidence of ○ and ●

Table 2. Rate constants for the quenching of $\{[Rh_2L_2(dppm)_2]^{2+}\}^*$ by a series of halogenocarbons in degassed acetonitrile at 25 °C

Quencher	$E(RX–RX^{\cdot-})$/V *vs.* s.c.e.[a]	$10^{-5}k_q$/dm^3 mol^{-1} s^{-1}
Allyl bromide	-1.29	2.74
Isopropyl iodide	-1.58	2.20
Methyl iodide	-1.63	1.41
Ethyl iodide	-1.67	2.18
Chloroform	-1.67	1.58
n-Butyl bromide	-2.27	1.59
Cyclopentyl bromide	-2.30	1.17

[a] Ref. 11.

$$\frac{RT}{F}\ln k_q' = \frac{RT}{F}\ln K\kappa\nu - \lambda/4\left(1 + \frac{\Delta G}{\lambda}\right)^2 \qquad (2)$$

$k_q^{-1} = k_d^{-1} + k_q'^{-1}$,[10] $K = k_d/k_{-d}$,* κ is the transmission coefficient, ν is the nuclear frequency, λ is the reorganization energy associated with the inner and outer co-ordination spheres, and ΔG, the standard free-energy change of the reaction, is given by equation (3), for oxidative quenching,

$$\Delta G = -[E(Q–Q^-) - E(Rh_2{}^{3+}–Rh_2{}^{2+*})] + w_p - w_r \qquad (3)$$

where w_r and w_p are the work terms required to bring reactants or products to the mean separation for reaction. The work term associated with $[Rh_2L_2(dppm)_2]^{2+}$ and a pyridinium acceptor is 0.01—0.03 eV. This contribution was neglected in the analysis of the electron-transfer rate data. Figure 5 shows the theoretical fit. The close agreement between the theoretical curve and the experimental data is in accordance with the fact that the photoreactions are outer-sphere electron transfer in nature.

The $E°(Rh_2{}^{3+}–Rh_2{}^{2+*})$ of -1.13 V *vs.* s.c.e. is comparable to the value of -1.25 V for $\{[Rh_2L_4]^{2+}\}^*$.[2d] This is supported by a similar rate constant for the quenching of $\{Rh_2L_4{}^{2+}\}^*$ by dmbipy^{2+} ($k_q = 1.1 \times 10^9$ dm^3 mol^{-1} s^{-1}). The calculated reorganization energy of 0.47 eV is considerably lower than that (0.74 eV) for $\{[Ru(bipy)_3]^{2+}\}^*$ (bipy = 2,2′-bipyridine).[10] This may be ascribed to a smaller outer-sphere reorganization energy because of the larger size of the rhodium complex.

Photoredox Reactions with Halogenocarbons.—Previous work showed that steady-state irradiation of a degassed acetonitrile solution of $[Rh_2L_2(dppm)_2]^{2+}$ and RX (CH_2Cl_2, $CHCl_3$, or CCl_4) at 595 nm results in the formation of $[Rh_2L_2(dppm)_2Cl_2]^{2+}$, the quantum yield of which decreases in the order $CH_2Cl_2 < CHCl_3 < CCl_4$.[3] In this work, the mechanism of the photoredox reactions with halogenocarbons has been investigated by Stern–Volmer quenching and flash photolysis. No thermal reaction between the alkyl halides and $[Rh_2L_2(dppm)_2]^{2+}$ was observed under the conditions of the photochemical experiments. The intensity of the fluorescence at 677 nm was not affected by alkyl halides but the phosphorescence was found to be quenched, indicating that the photoreactions are derived from the $^3(d_\sigma{}^*p_\sigma)$ excited state. The quenching rate constants determined from the equation $\tau_0/\tau = 1 + k_q\tau_0[RX]$ are summarized in Table 2. The values are low and show little if any dependence on the reduction potentials of alkyl halides. Flash photolysis of a degassed acetonitrile solution of $[Rh_2L_2(dppm)_2]^{2+}$ and $CHCl_3$ gives rise to transient absorptions at 450 and 515 nm [Figure 6(*a*)], similar to the absorption of $[Rh_2L_2(dppm)_2]^{3+}$ (Figure 4). Figure 6(*b*) shows the transient difference spectrum recorded 30 µs after flash photolysis of a degassed acetonitrile solution of $[Rh_2L_2(dppm)_2]^{2+}$ and allyl bromide. The spectra in Figure 6(*a*) and (*b*), though similar, are not identical; the difference is more pronounced in the visible region (500—550 nm).

There are two possible mechanistic pathways by which $\{[Rh_2L_2(dppm)_2]^{2+}\}^*$ reacts with alkyl halides; namely, atom transfer (a.t.) and electron transfer (e.t.)[2h] (Scheme 1). For the

Atom transfer:

$$\{[Rh^I–Rh^I]^{2+}\}^* + X–R \longrightarrow [Rh–Rh\cdots X\cdots R]^{2+} \longrightarrow [Rh^I–Rh^{II}–X]^{2+} + R^\cdot$$

Electron transfer:

$$\{[Rh^I–Rh^I]^{2+}\}^* + X–R \longrightarrow [Rh^I–Rh^{II}]^{3+} + RX^{\cdot-}$$

$$RX^{\cdot-} \longrightarrow R^\cdot + X^-$$

Scheme 1.

---

* In this work, k_d and K are taken to be 2.0×10^{10} dm^3 mol^{-1} s^{-1} and 1—2 dm^3 mol^{-1}, respectively.

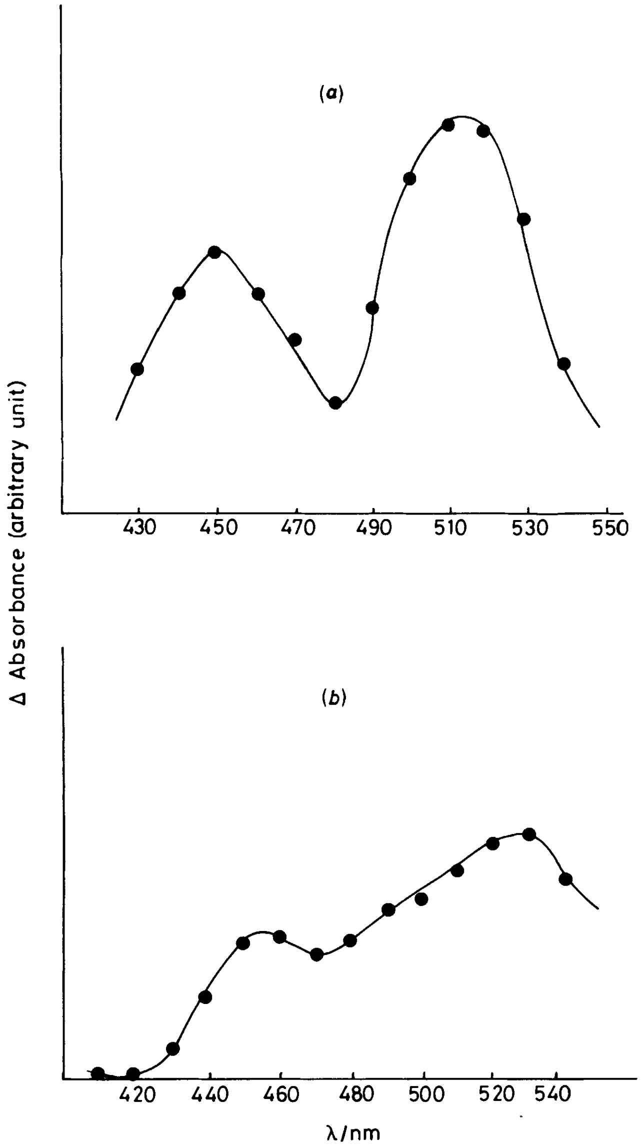

Figure 6. Transient difference spectra obtained (*a*) 10 μs after flash photolysis of $[Rh_2L_2(dppm)_2]^{2+}$ (10^{-5} mol dm^{-3}) and chloroform (4 mol dm^{-3}) and (*b*) 30 μs after laser flash photolysis of $[Rh_2L_2(dppm)_2]^{2+}$ ($\approx 10^{-5}$ mol dm^{-3}) with allyl bromide ($\approx$ 1 mol dm^{-3}), in degassed acetonitrile

e.t. pathway the rhodium complex produced on flash photolysis of $[Rh_2L_2(dppm)_2]^{2+}$ with an alkyl halide should be $[Rh_2L_2(dppm)_2]^{3+}$, whereas for the a.t. pathway the reaction product should be $[Rh_2L_2(dppm)_2X]^{2+}$. The results of the flash photolysis experiments in this work cannot be used to assign unambiguously the mechanism of the photoreactions. Although there are some differences between Figures 6(*a*) and (*b*) they are not large. Furthermore, Figure 6(*a*) is very similar to the transient spectrum of $[Rh_2L_2(dppm)_2]^{3+}$ produced by oxidative quenching of $\{[Rh_2L_2(dppm)_2]^{2+}\}^*$ with dmbipy^{2+}.

However, we tend to favour an inner-sphere type of mechanism where excited-state a.t. occurs with synchronous e.t. This is because of the insufficient driving force for an outer-sphere electron-transfer quenching mechanism, governed by the $E^\circ(Rh_2^{3+}\text{-}Rh_2^{2+*})$ value of -1.13 V *vs.* s.c.e. and the low reduction potentials of the alkyl halides employed (Table 2).[11] Thus the photoreaction of $[Rh_2L_2(dppm)_2]^{2+}$ with chloroform can be described by Scheme 2. The low-energy absorption

$$[Rh^I\text{-}Rh^I]^{2+} \xrightarrow{h\nu} \{[Rh^I\text{-}Rh^I]^{2+}\}^*$$

$$\{[Rh^I\text{-}Rh^I]^{2+}\}^* + RX \rightleftharpoons [Rh^I\text{-}Rh^I\cdots XR]^{2+} \longrightarrow [Rh^I\text{-}Rh^I\cdots X\cdots R]^{2+}$$

$$[Rh^I\text{-}Rh^I\cdots X\cdots R]^{2+} \longrightarrow [Rh^I\text{-}Rh^{II}\text{-}X]^{2+} + R^{\bullet}$$

$$[Rh^I\text{-}Rh^{II}\text{-}X]^{2+} + RX \longrightarrow [X\text{-}Rh^{II}\text{-}Rh^{II}\text{-}X]^{2+} + R^{\bullet}$$

Scheme 2.

bands in Figures 6(*a*) and (*b*) may be attributed to the $d_\sigma \longrightarrow d_\sigma^*$ transitions of the $[Rh^I\text{-}Rh^{II}\text{-}X]^{2+}$ species, which may be similar in energy if charge-transfer mixing between the Rh–X and Rh–Rh bonds is small.

Conclusion

The $[Rh_2L_2(dppm)_2]^{2+}$ complex represents another binuclear d^8–d^8 system, which undergoes photoinduced halogen-atom transfer reactions. Although the excited-state energy of the present system is substantially lower than that of $[Pt_2(H_2P_2O_5)_4]^{4-}$,[4] which has been subjected to extensive study, it has the advantage over the platinum complex in that it absorbs strongly in the visible region, thereby suggesting its high potential for solar-energy utilization. Moreover, the present study does support Gray's previous work[2a–f] in that the dirhodium(I) system is likely to show promising photochemical properties and deserves our attention in the design of new photocatalysts based on binuclear d^8–d^8 complexes.

Acknowledgements

We acknowledge support from the University of Hong Kong and the Croucher Foundation. H. L. K. and W. M. L. acknowledge the receipt of a studentship, administered by the Croucher Foundation. Helpful discussion with Professor H. B. Gray is also acknowledged.

References

1 See, for example, (*a*) A. L. Balch, *J. Am. Chem. Soc.*, 1976, **98**, 8049; (*b*) A. R. Sanger, *J. Chem. Soc., Dalton Trans.*, 1977, 120; (*c*) A. L. Balch and B. Tulyathan, *Inorg. Chem.*, 1977, **16**, 2840; (*d*) A. L. Balch, J. W. Labadie, and G. Delker, *ibid.*, 1979, **18**, 1224; (*e*) J. T. Mague and S. H. DeVries, *ibid.*, 1980, **19**, 3743; (*f*) W. A. Fordyce and G. A. Crosby, *J. Am. Chem. Soc.*, 1982, **104**, 985.

2 (*a*) N. S. Lewis, K. R. Mann, J. G. Gordan II, and H. B. Gray, *J. Am. Chem. Soc.*, 1976, **98**, 7461; (*b*) K. R. Mann, J. A. Thich, R. A. Bell, C. L. Coyle, and H. B. Gray, *Inorg. Chem.*, 1980, **19**, 2462; (*c*) V. M. Miskowski, G. L. Nobinger, D. S. Kliger, G. S. Hammond, N. S. Lewis, K. R. Mann, and H. B. Gray, *J. Am. Chem. Soc.*, 1978, **100**, 485; (*d*) S. J. Milder, R. A. Goldbeck, D. S. Kliger, and H. B. Gray, *ibid.*, 1980, **102**, 6761; (*e*) S. F. Rice and H. B. Gray, *ibid.*, 1981, **103**, 1593; (*f*) S. F. Rice, S. J. Milder, H. B. Gray, R. A. Goldbeck, and D. S. Kliger, *Coord. Chem. Rev.*, 1982, **43**, 349; (*g*) D. C. Boyd, P. A. Matsch, M. M. Mixa, and K. R. Mann, *Inorg. Chem.*, 1986, **25**, 3331; (*h*) G. S. Rodman, C. A. Daws, and K. R. Mann, *ibid.*, 1988, **27**, 3347.

3 C. M. Che and W. M. Lee, *J. Chem. Soc., Chem. Commun.*, 1986, 616.

4 D. M. Roundhill, H. B. Gray, and C. M. Che, *Acc. Chem. Res.*, 1989, **22**, 55; A. P. Zipp, *Coord. Chem. Rev.*, 1988, **84**, 47.

5 (*a*) J. L. Marshall, S. R. Stobart, and H. B. Gray, *J. Am. Chem. Soc.*, 1984, **106**, 3027; (*b*) J. V. Caspar and H. B. Gray, *ibid.*, p. 3029; (*c*) J. R. Winkler, J. L. Marshall, T. L. Netzel, and H. B. Gray, *ibid.*, 1986, **108**, 2263.

6 D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' 2nd edn., Pergamon, Oxford, 1980.

7 W. A. Fordyce, J. G. Brummer, and G. A. Crosby, *J. Am. Chem. Soc.*, 1981, **103**, 7061; S. F. Rice and H. B. Gray, *ibid.*, 1983, **105**, 4571.

8 K. R. Mann, N. S. Lewis, V. M. Miskowski, D. K. Erwin, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, 1977, **99**, 5525; V. M.

Miskowski, T. P. Smith, T. M. Loehr, and H. B. Gray, *ibid.*, 1985, **107**, 7925.

9 E. M. Kosower and J. L. Cotter, *J. Am. Chem. Soc.*, 1964, **86**, 5524.

10 C. R. Bock, J. A. Connor, A. R. Gutierrez, T. J. Meyer, D. G. Whitten, B. P. Sullivan, and J. K. Nagle, *J. Am. Chem. Soc.*, 1979, **101**, 4815.

11 A. J. Bard and H. Lund, 'Encyclopedia of Electrochemistry of the Elements,' Organic Section, Marcel Dekker, New York, 1980, vol. 14; C. K. Mann and K. K. Barnes, 'Electrochemical Reactions in Non-aqueous Systems,' Marcel Dekker, New York, 1970.

Received 23rd *October* 1989; *Paper* 9/04555D