Similar findings have been reported in the case of pentaammineruthenium: Equilibrium studies have shown that the Ru(III) metal center is more sensitive to amine substituents than the divalent analogue.[24] As with ruthenium,[25] the coordination sphere for Os(II) probably does not contract significantly upon oxidation, since the valence electron resides in a nonbonding orbital. Hence, the increased stability of the trivalent metal center with aniline cannot be ascribed to an *increase* in steric effects upon oxidation. Rather, we feel this enhancement arises from the better σ-donating properties of the unsubstituted ligand; although dimethylaniline is slightly more basic than its parent,[26] the methyl groups apparently prevent the nitrogen from achieving its optimum bond distance.

The 8.0 kcal/mol decrease in the $N \rightarrow \pi$ isomerization energy of $[Os(NH_3)_5(PhNR_2)]^{2+}$, attributable to the methyl groups, is reflected in the rate of this isomerization as well. A rate of 8.3 s^{-1} corresponds to a decrease of 7.5 kcal/mol in the free energy of activation[27] ($\Delta G^{\ddagger}$ = 15.9 kcal/mol) compared to that for aniline ($\Delta G^{\ddagger}$ = 23.4 kcal/mol). On osmium(III) the findings are similar; in this case the difference in $N \rightarrow \pi$ isomerization rates corresponds to a 9.8 kcal/mol change in the free energy of activation. Given that these processes are intramolecular, the rate-determining step for this rearrangement for either valence state is most certainly the cleavage of the Os–N bond, the strength of which would be profoundly affected by the methyl groups. In pleasing contrast to this are the rates for $\pi \rightarrow N$ isomerization; these rates are virtually independent of the steric constraint, which implies that the rate-determining step occurs prior to the coordination of nitrogen.

A second point concerns the reversal of relative isomerization rates upon oxidation. For both complexes, the rate of $N \rightarrow \pi$ isomerization on Os(III) is significantly slower than that for the corresponding divalent species, reflecting the enhancement of the metal–nitrogen bond strength for the higher oxidation state. This is in contrast to the $\pi \rightarrow N$ isomerizations for which the converse statement is true. A comparison of these rates suggests that the metal–arene bond strength is greater for Os(II), a result that is readily attributable to metal π-back-bonding.

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Photochemistry of Diplatinum(III,III) Pyrophosphite Complexes. Efficient Photochemical Reduction of $[Pt_2(pop)_4X_2]^{4-}$ to $[Pt_2(pop)_4]^{4-}$ in Methanol

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Abstract: UV–vis irradiation of $[Pt_2(pop)_4X_2]^{4-}$ [pop = $P_2O_5H_2^{2-}$; X = Cl, Br, SCN, I, Im (ImH = imidazole)] in methanol leads to reduction to $[Pt_2(pop)_4]^{4-}$ with nearly quantitative yield (over 92%). Upon ligand-to-metal charge-transfer [$\sigma_x \rightarrow d_\sigma^*$] excitation, the quantum yield (ϕ_r) for the reduction of $[Pt_2(pop)_4X_2]^{4-}$ decreases with $X_2 = (CH_3)(I) > (SCN)_2 > I_2 > Im_2 > Cl_2 > Br_2$. The ϕ_r values are wavelength dependent, being higher with $\sigma_x \rightarrow d_\sigma^*$ excitation than that with $d_\pi \rightarrow d_\sigma^*$. Flash photolysis experiments indicate that the primary step of the photoreactions is the homolytic breakage of the Pt–X bond, $[Pt_2(pop)_4X_2]^{4-} \rightarrow [Pt^{III}Pt^{III}(pop)_4X]^{4-} + {}^{\bullet}X$.

The photochemistry of binuclear metal–metal-bonded Rh(II) and Pt(III) complexes remains relatively unexplored despite the extensive structural and spectroscopic work reported on this class of compounds.[2,3] Our interest in photochemical studies of diplatinum(III,III) pyrophosphite complexes, $[Pt_2(pop)_4X_2]^{4-}$ (pop = $P_2O_5H_2^{2-}$; X = Cl, Br, SCN, I, Im), arose as a result of previous works.[4-9] Both spectroscopic and X-ray structural data showed that the Pt–Pt bond in these Pt(III) complexes contains substantial charge-transfer character,[4-7] indicating the possibility of having redox occur upon ligand-to-metal [X → Pt(III)] charge-transfer excitation. Recent work has shown that the intensely luminescent $[Pt_2(pop)_4]^{4-}$ complex possesses rich photochemistry;[10-17] in

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Table I. Yields of $[Pt_2(pop)_4]^{4-}$ from $[Pt_2(pop)_4X_2]^{4-}$ Complexes ($\sim 10^{-4}$–10^{-5} M) upon $\sigma \rightarrow d_\sigma^*$ Excitation in Methanol

complex	yield, %	approx irradn time reqd for completion, h
$[Pt_2(pop)_4Br_2]^{4-}$	92	3
$[Pt_2(pop)_4Cl_2]^{4-}$	97	$2^1/_2$
$[Pt_2(pop)_4Im_2]^{4-}$	~100	$2^1/_2$
$[Pt_2(pop)_4I_2]^{4-}$	95	$1^1/_2$
$[Pt_2(pop)_4(SCN)_2]^{4-}$	93	$^3/_4$
$[Pt_2(pop)_4(CH_3)(I)]^{4-}$	97	$^3/_4$

particular, it catalyzes the photodehydrogenation of alcohol to aldehyde or ketone and molecular hydrogen.[10] In the presence of an electron acceptor and a nucleophile X^-, the photooxidative reactions of $[Pt_2(pop)_4]^{4-}$ usually give $[Pt_2(pop)_4X_2]^{4-}$ as the final reaction product. Thus, the regeneration of $[Pt_2(pop)_4]^{4-}$ from $[Pt_2(pop)_4X_2]^{4-}$ represents an important step in any photoredox reaction catalyzed by $[Pt_2(pop)_4]^{4-}$. We describe here photochemical studies on the $[Pt_2(pop)_4X_2]^{4-}$ system. The results indicate that these complexes undergo efficient reduction to $[Pt_2(pop)_4]^{4-}$ in methanol upon UV–vis excitation. Photoinduced reductive elimination of $[Pt_2(pop)_4H_2]^{4-}$ has recently been reported by Gray and co-workers.[8]

Experimental Section

Materials. $K_4[Pt_2(pop)_4X_2]$, $K_4[Pt_2(pop)_4(CH_3)(I)]$, and $[Bu_4N]_4[Pt_2(pop)_4X_2]$ (X = Cl, Br, SCN, I, Im) were synthesized by published procedures.[4] All organic reagents were purified by standard means before being used. Deionized water and distilled methanol (spectrophotometric grade) were used throughout the photochemical experiments.

Instrumentation. Steady-state photolyses were performed by using a 350-W high-pressure mercury short-arc lamp (Illumination Industries, Inc.) coupled with a high-intensity monochromator (Bausch and Lomb).[18] Incident-light intensities were taken from the average values measured just before and after each photolysis experiment by using ferrioxalate actinometry.[18] The quantum yields (ϕ_r) for the photoreduction of $[Pt_2(pop)_4X_2]^{4-}$ to $[Pt_2(pop)_4]^{4-}$ in methanol were measured by either (a) the disappearance of the $\sigma \rightarrow d_\sigma^*$ absorption peak of $[Pt_2(pop)_4X_2]^{4-}$ or (b) the appearance of $[Pt_2(pop)_4]^{4-}$ at 367 nm. Except for $[Pt_2(pop)_4(SCN)_2]^{4-}$, both methods were tried and gave essentially the same results. For $[Pt_2(pop)_4(SCN)_2]^{4-}$, ϕ_r was measured by method a only (with the decrease in absorbance monitored at 330–340 nm). To minimize any effects arising from secondary photolysis, the ϕ_r values were determined within the first 10–20% of the photolysis reactions.[18] The transient absorption kinetic experiments were performed by using standard instrumentation in which the excitation source was the 355/266-nm output of a Quanta-Ray DCR-2Nd:YAG laser. The photoreaction was initiated by flashing a degassed methanolic solution of $[Pt_2(pop)_4X_2]^{4-}$ ($\sim 10^{-4}$–10^{-5} M). Degassing of the solution was performed by five freeze–pump–thaw cycles.

Results

Steady-State Photolysis. At room temperature, UV–vis irradiation of $[Pt_2(pop)_4X_2]^{4-}$ in methanol leads to reduction to $[Pt_2(pop)_4]^{4-}$; the spectral changes during the course of the photoreactions are shown in parts a–c of Figure 1 and Figures S1–S3 [X_2 = Im_2, 1a; Cl_2, 1b; $(CH_3)(I)$, 1c; Br_2, S1; I_2, S2; $(SCN)_2$, S3; S1–S3 are available as supplementary material]. With the exception of $[Pt_2(pop)_4(SCN)_2]^{4-}$, two isosbestic points are found in each case, indicating that no intermediate is formed in significant quantity during the conversion. The same spectral changes have also been reported in the electrochemical interconversion of $[Pt_2(pop)_4]^{4-}$ to $[Pt_2(pop)_4X_2]^{4-}$ in the presence of added halide ions X^- (X = Cl, Br, I),[19] indicating the same reaction

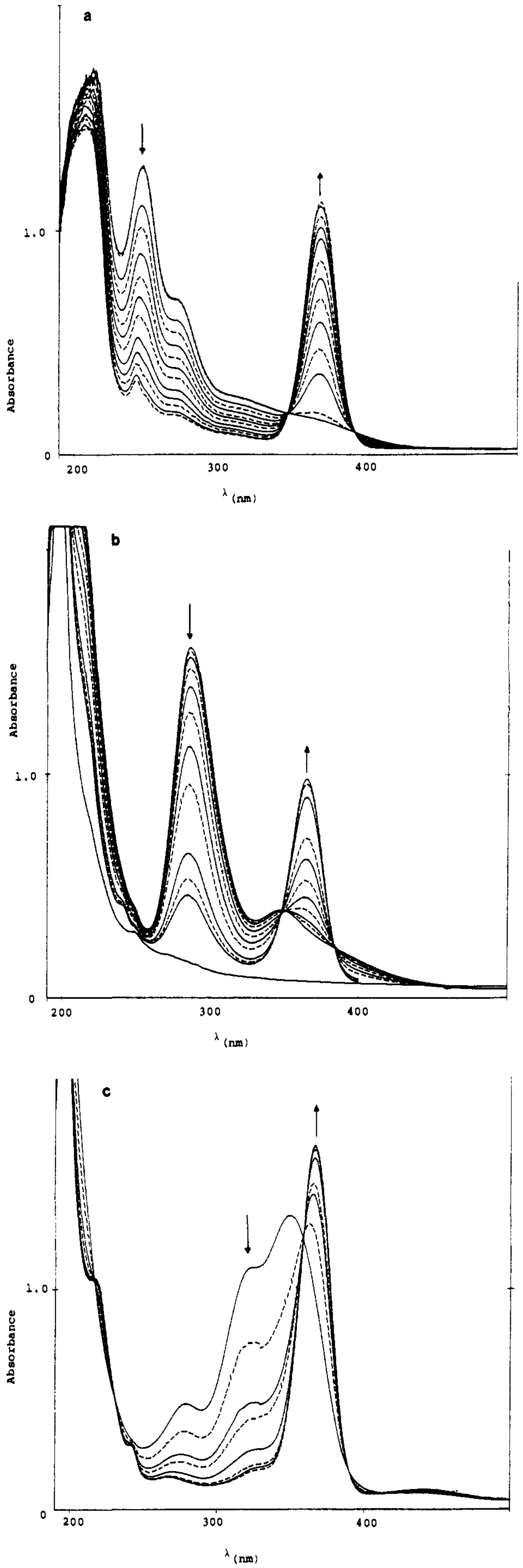

Figure 1. Spectral changes during the photoconversion of $[Pt_2(pop)_4X_2]^{4-}$ to $[Pt_2(pop)_4]^{4-}$ in methanol: (a) $[Pt_2(pop)_4Im_2]^{4-}$, (b) $[Pt_2(pop)_4Cl_2]^{4-}$, (c) $[Pt_2(pop)_4(CH_3)(I)]^{4-}$ (in 5:1 $MeOH/H_2O$ mixture).

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Table II. Quantum Yields (ϕ_r) for the Photoconversion of $[Pt_2(pop)_4X_2]^{4-}$ (2×10^{-5}–4×10^{-5} M) to $[Pt_2(pop)_4]^{4-}$ in Methanol

complex	exc λ, nm	ϕ_r
$[Pt_2(pop)_4Br_2]^{4-}$	308	1.0×10^{-2}
	340	7.0×10^{-3}
	360	4.0×10^{-3}
$[Pt_2(pop)_4Cl_2]^{4-}$	283	3.0×10^{-2}
	320	1.3×10^{-2}
	340	6.0×10^{-3}
	360	4.0×10^{-3}
$[Pt_2(pop)_4Im_2]^{4-}$	245	3.7×10^{-2}
	255	3.6×10^{-2}
	270	3.8×10^{-2}
	320	1.7×10^{-2}
	340	7.0×10^{-3}
$[Pt_2(pop)_4I_2]^{4-}$	330	4.5×10^{-2}
$[Pt_2(pop)_4(SCN)_2]^{4-}$	340	9.5×10^{-2}
	360	8.5×10^{-2}
$[Pt_2(pop)_4(CH_3)(I)]^{4-}$[a]	320	1.3×10^{-1}[b]
		1.4×10^{-1}[c]
		1.5×10^{-1}[d]
		1.6×10^{-1}[e]

[a] In MeOH/H$_2$O mixture (5:1). [b] 1.7×10^{-5} M. [c] 4×10^{-5} M. [d] 6×10^{-5} M. [e] 1×10^{-4} M.

pathway for the electrochemical and photochemical reactions.

The photoreactions are not affected by the presence or absence of air and can be driven to completion when the concentration of $[Pt_2(pop)_4X_2]^{4-}$ lies between 10^{-4} and 10^{-5} M. The yield of $[Pt_2(pop)_4]^{4-}$ from $[Pt_2(pop)_4X_2]^{4-}$ in each case is over 92% (Table I), indicating that the conversions are essentially quantitative. Under the same conditions as in the photochemical experiments, the thermal reactions are generally insignificant. Indeed, the $[Pt_2(pop)_4Im_2]^{4-}$ complex is stable in methanol for hours in dark conditions at room temperature. Attempts have been made to detect any oxidized organic product formed (e.g. HCOH) after the photoreactions by gas chromatography; however, no conclusive results were obtained.

Table II summarizes the quantum yields (ϕ_r) for the photoreactions in methanol. The ϕ_r values show dependence on the wavelength of excitation light; they are highest when excitations are carried out at the $\sigma \rightarrow d_\sigma^*$ transition of the $[Pt(pop)_4X_2]^{4-}$ complexes. The ϕ_r value for $[Pt_2(pop)_4(CH_3)(I)]^{4-}$ is relatively insensitive to concentration (1.7×10^{-5}–1×10^{-4} M) (Table II). For $[Pt_2(pop)_4X_2]^{4-}$, ϕ_r decreases with X_2 = (CH)(I) > $(SCN)_2$ > I_2 > Im_2 > Cl_2 > Br_2 at the $\sigma \rightarrow d_\sigma^*$ excitation. Methanol is not a unique solvent for the photoreduction of $[Pt_2(pop)_4X_2]^{4-}$ to $[Pt_2(pop)_4]^{4-}$. Similar photoreactions for $[Pt_2(pop)_4Br_2]^{4-}$ have also been observed in absolute ethanol and isopropyl alcohol.

In deionized water, prolonged steady-state irradiation ($\lambda > 300$ nm) of $[Pt_2(pop)_4X_2]^{4-}$ (X = Cl, Br, SCN) leads to reduction to $[Pt_2(pop)_4]^{4-}$. However, the photochemical reactions are complex since no isosbestic point in the UV–vis spectral changes during the course of photoreactions has been observed. Furthermore, the conversion of $[Pt_2(pop)_4X_2]^{4-}$ to $[Pt_2(pop)_4]^{4-}$ in each case is not quantitative and less than 40%. For $[Pt_2(pop)_4(CH_3)(I)]^{4-}$ in water, irradiation at 330 nm yielded $[Pt_2(pop)_4I_2]^{4-}$ and $[Pt_2(pop)_4]^{4-}$ as the final photoproducts in constrast to the photochemistry in methanol (see Figure 1c). The photoreactions in water are in general very inefficient. The quantum yields measured by the formation of $[Pt_2(pop)_4]^{4-}$ for $[Pt_2(pop)_4X_2]^{4-}$ (X = Cl, Br, SCN) are less than 10^{-3}, and flash photolysis experiments for $[Pt_2(pop)_4Cl_2]^{4-}$ and $[Pt_2(pop)_4Br_2]^{4-}$ in degassed aqueous solutions do not show any transient signal. We conclude that water is not a good solvent system for the photochemical reduction of $[Pt_2(pop)_4X_2]^{4-}$ to $[Pt_2(pop)_4]^{4-}$.

Flash Photolysis. Flash photolysis experiments were carried out with degassed solutions of $[Pt_2(pop)_4X_2]^{4-}$ at 355 nm (X_2 = Br_2) or 266 nm (X_2 = Cl_2, Im_2). In methanol, a prompt signal, which decays to $[Pt_2(pop)_4]^{4-}$, is generated immediately after the flash in each case. For $[Pt_2(pop)_4Im_2]^{4-}$, the transient absorption difference spectrum recorded 200 ms (long time) after the laser flash in shown in Figure 2. The intense 367-nm peak in the figure is due to the formation of $[Pt_2(pop)_4]^{4-}$, and this is in agreement with the results of the steady-state photolysis experiments described above. Similar findings for other $[Pt_2(pop)_4X_2]^{4-}$ complexes (X = Cl, Br) have also been observed. The nature of the prompt signal has also been investigated. The transient absorption difference spectra for $[Pt_2(pop)_4Im_2]^{4-}$, $[Pt_2(pop)_4Cl_2]^{4-}$, and $[Pt_2(pop)_4Br_2]^{4-}$ recorded immediately (1–10 μs) after the laser flash are shown in parts a–c of Figure 3. The absorption spectrum in each case agrees quantitatively with that obtained by pulse radiolysis of the corresponding $[Pt_2(pop)_4X_2]^{4-}$ complex in water,[20] indicating that the prompt signal is due to the formation of $[Pt^{II}Pt^{III}(pop)_4X]^{4-}$. For $[Pt_2(pop)_4Im_2]^{4-}$, the spectrum in Figure 3a reveals not only the formation of $[Pt^{II}Pt^{III}(pop)_4Im]^{4-}$ ($\lambda_{max} \sim 315$ nm) but also the presence of some $[Pt_2(pop)_4]^{4-}$, which could come from the rapid disproportionation reaction of $[Pt^{II}Pt^{III}(pop)_4Im]^{4-}$.[20,21] The interpretation of the spectrum in Figure 3c should be taken with caution since the absorption spectra for both $[Pt_2(pop)_4]^{4-}$ and $[Pt^{II}Pt^{III}(pop)_4Br]^{4-}$ are similar.[20] No attempt has been made to study the photochemical reactions of $[Pt_2(pop)_4(CH_3)(I)]^{4-}$ and $[Pt_2(pop)_4(SCN)_2]^{4-}$ by transient absorption spectroscopy since the complexes readily convert to $[Pt_2(pop)_4]^{4-}$ upon exposure to UV light. The mechanism for the decay of $[Pt^{II}Pt^{III}(pop)_4X]^{4-}$ to $[Pt_2(pop)_4]^{4-}$ was found to be very complicated, neither first-order nor second-order kinetics was observed.

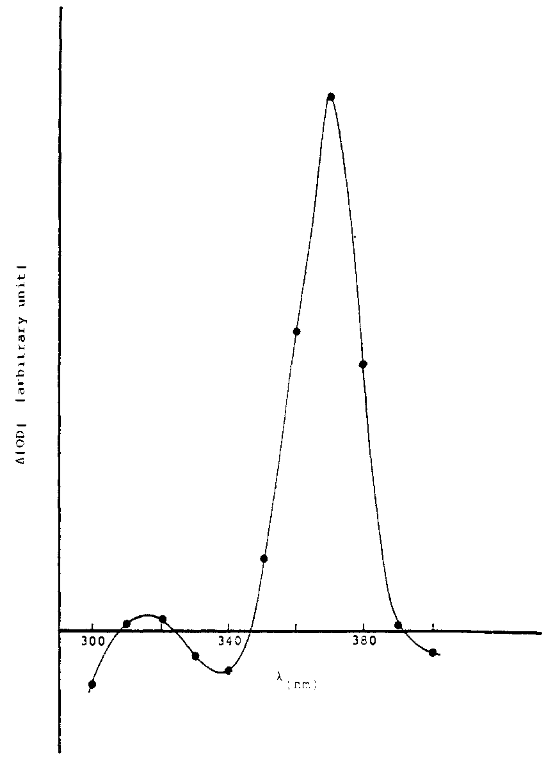

Figure 2. Transient absorption spectrum for $[Pt_2(pop)_4Im_2]^{4-}$ in methanol recorded 200 ms after the laser flash.

Discussion

For $[Pt_2(pop)_4X_2]^{4-}$, the optical spectra in the 230–450-nm region are mainly composed of two kinds of electronic transitions, namely $\sigma \rightarrow d_\sigma^*$ and $d_\pi \rightarrow d_\sigma^*$, with the former being more intense and usually higher in energy than the latter.[4,9] (The notation of the σ orbital here refers to a combination of σ_x and $d\sigma$ orbitals.) These electronic transitions are well-resolved in the cases of $[Pt_2(pop)_4Im_2]^{4-}$, $[Pt_2(pop)_4Cl_2]^{4-}$, and $[Pt_2(pop)_4Br_2]^{4-}$, a typical

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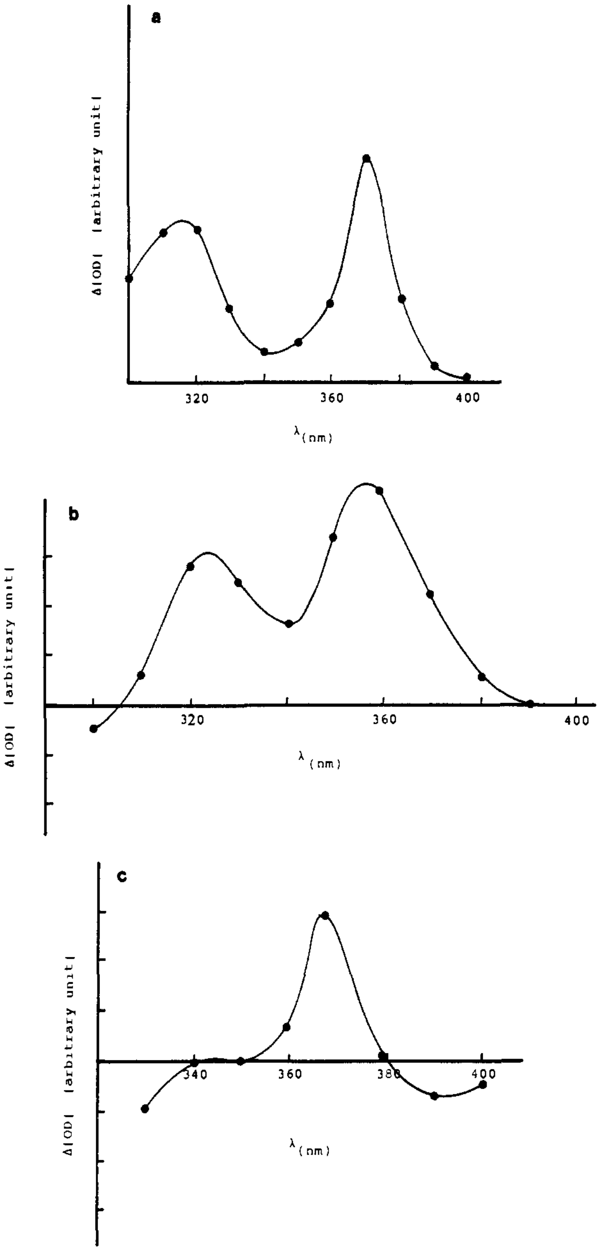

Figure 3. Transient absorption spectra for $[Pt_2(pop)_4X_2]^{4-}$ in methanol recorded ~2 μs after the laser flash: (a) $[Pt_2(pop)_4Im_2]^{4-}$, (b) $[Pt_2(pop)_4Cl_2]^{4-}$, (c) $[Pt_2(pop)_4Br_2]^{4-}$.

example of which is shown in Figure 4. For $[Pt_2(pop)_4(SCN)_2]^{4-}$, $[Pt_2(pop)_4(CH_3)(I)]^{4-}$, and $[Pt_2(pop)_4I_2]^{4-}$, the spectra are dominated by the intense X → Pt(III) [$\sigma_X \rightarrow d_\sigma^*$] charge-transfer transitions, and the $d_\pi \rightarrow d_\sigma^*$ transitions are hardly observed. Recent work has established that the $\sigma \rightarrow d_\sigma^*$ transitions for $[Pt_2(pop)_4Cl_2]^{4-}$ and $[Pt_2(pop)_4Br_2]^{4-}$ at 283 and 308 nm, respectively, are primarily ligand-to-metal ($\sigma_X \rightarrow d_\sigma^*$) charge transfer in nature,[7] whereas that for $[Pt_2(pop)_4Im_2]^{4-}$ at 245 nm is essentially metal-localized.

Irradiation of $[Pt_2(pop)_4X_2]^{4-}$ in the UV-vis region produces the $(\sigma)^1(d_\sigma^*)^1$ and $(d_\pi)^1(d_\sigma^*)^1$ singlet and triplet states. These excited states with one electron in the antibonding d_σ^* orbital have large distortions along the Pt-Pt coordinate and should rapidly deactivate through axial-ligand dissociation. Recent work by Gray and co-workers[9] indicated that the $(\sigma)^1(d_\sigma^*)^1$ or $(d_\pi)^1(d_\sigma^*)^1$ triplet is long-lived and hence may be responsible for the photochemical reactions.

Upon light excitation, the excited $[Pt_2(pop)_4X_2]^{4-}$ molecule may react through the following pathways:

(i) Heterolytic cleavage of the Pt-X bond with the generation of a X-Pt^{III}-Pt^{III} intermediate should rapidly react with solvent (S) or X^- to give $[Pt_2(pop)_4(X)(S)]^{3-}$ and $[Pt_2(pop)_4X_2]^{4-}$.[22]

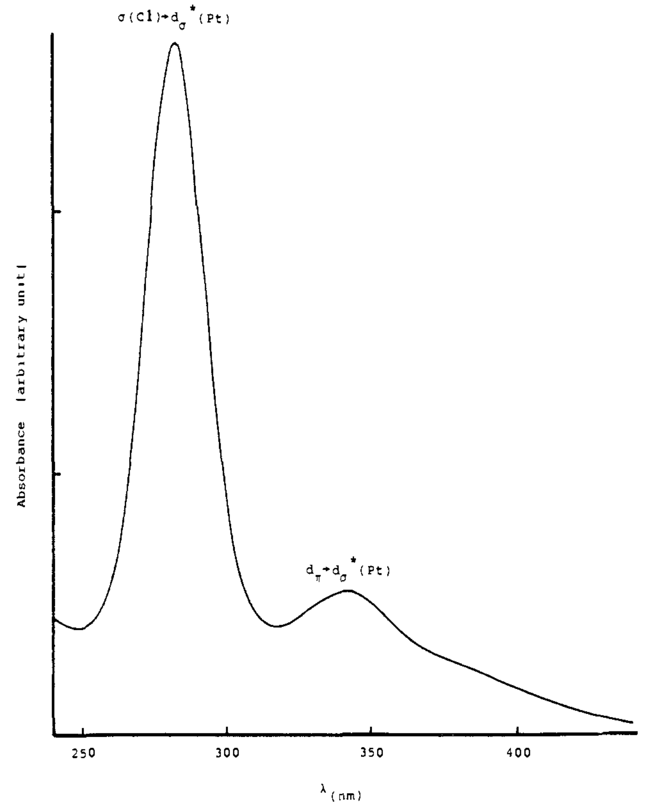

Figure 4. UV-vis spectrum of $[Pt_2(pop)_4Cl_2]^{4-}$ in methanol.

(ii) Homolytic cleavage of the Pt-X bond generates the mixed-valence X-Pt^{III}-Pt^{II} intermediate.

(iii) The excited $[Pt_2(pop)_4X_2]^{4-}$ complexes may undergo direct two-electron reduction to $[Pt_2(pop)_4]^{4-}$, in a way similar to the solution chemistry of monomeric platinum(IV) complexes.[23]

Pathways i and ii are expected on the basis of the bonding picture. The excited state of $[Pt_2(pop)_4X_2]^{4-}$, either $(\sigma)^1(d_\sigma^*)^1$ or $(d_\pi)^1(d_\sigma^*)^1$, has one electron in the antibonding d_σ^* orbital that should weaken the Pt-Pt and Pt-X bonds. In methanol, the photoreactions are the reduction of $[Pt_2(pop)_4X_2]^{4-}$ to $[Pt_2(pop)_4]^{4-}$. The results on flash photolysis experiments provide no evidence for pathway i but strongly indicate that the primary step is the homolytic breakage of the Pt-X bond.

$$[Pt_2(pop)_4X_2]^{4-} \xrightarrow{h\nu} [Pt^{II}Pt^{III}(pop)_4X]^{4-} + X^{\bullet} \quad \text{[pathway ii]}$$

In fact, the nice isosbestic points found in the photoconversion of $[Pt_2(pop)_4X_2]^{4-}$ to $[Pt_2(pop)_4]^{4-}$ in methanol also preclude a Pt^{III}-Pt^{III} intermediate, $[Pt_2(pop)_4(X)(S)]^{3-}$, which is expected to be stable in solution within the time scale of photochemical experiments.[22] From Table II, it is obvious that the ϕ_r values depend on the wavelength of excitation light, suggesting that more than one reactive state may be involved. If the $(\sigma)^1(d_\sigma^*)^1$ and $(d_\pi)^1(d_\sigma^*)^1$ triplets are responsible for the photochemical reactions, the results in Table II are easily understandable. The much higher ϕ_r values upon $\sigma \rightarrow d_\sigma^*$ excitation than with $d_\pi \rightarrow d_\sigma^*$ excitation are primarily due to the fact that the X → Pt(III) charge-transfer character in the $(\sigma)^1(d_\sigma^*)^1$ state should promote redox reaction with the formation of X-Pt^{III}-Pt^{II} and $X^{\bullet}$ species.

The pathways by which the $[Pt^{II}Pt^{III}(pop)_4X]^{4-}$ and $X^{\bullet}$ radicals decay have not been fully elucidated. The $X^{\bullet}$ radicals could

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(22) The $[Pt_2(pop)_4(Cl)(OH_2)]^{3-}$ and $[Pt_2(pop)_4(Br)(OH_2)]^{3-}$ complexes have been generated in aqueous solutions and characterized spectroscopically. These complexes are stable in water for more than 1 h but rapidly react with added nucleophile Y^- to give $[Pt_2(pop)_4(X)(Y)]^{4-}$ (X = Cl, Br; Y = Cl, Br, SCN). Che, C. M.; Lau, T. C.; Lo, C. F.; Poon, C. K.; Gray, H. B., to be submitted for publication.

(23) For example, see: Skinner, C. E.; Jones, M. M. *J. Am. Chem. Soc.* **1969**, *91*, 4405-4408.

possibly be scavenged by the solvent or undergo radical recombination reactions whereas the $[Pt^{II}Pt^{III}(pop)_4X]^{4-}$ species may undergo disproportionation to give $[Pt_2(pop)_4]^{4-}$ and $[Pt_2(pop)_4X_2]^{4-}$ as suggested by previous work.[20,21,24] From Table II, the ϕ_r values for $[Pt_2(pop)_4X_2]^{4-}$ depend on the nature of axial ligands and decrease with $X_2 = (CH_3)(I) > (SCN)_2 > I_2 > Im_2 > Cl_2 > Br_2$. With the exception of $[Pt_2(pop)_4Cl_2]^{4-}$, this trend parallels the corresponding decrease in Pt–Pt bond distances [X_2, *d*(Pt–Pt) in angstroms: $(CH_3)(I)$, 2.78 (1); $(SCN)_2$, 2.760 (1); I_2, 2.754 (1); Im_2, 2.745 (1); Br_2, 2.723 (4); Cl_2, 2.695 (1)].[6,25–28]

Such a correlation of ϕ_r values with *d*(Pt–Pt) bond distances is not unreasonable given the fact that the photoreaction

$$[Pt_2(pop)_4X_2]^{4-} \xrightarrow{h\nu} [Pt_2(pop)_4]^{4-}$$

involves breakage of the metal–metal bond. The reactive $[Pt^{II}Pt^{III}(pop)_4X]^{4-}$ intermediate and $[Pt_2(pop)_4]^{4-}$ products with $(d_\sigma)^2(d_\sigma{}^*)^1$ and $(d_\sigma)^2(d_\sigma{}^*)^2$ configurations, respectively, should have weaker Pt–Pt bond strengths than the starting $[Pt_2(pop)_4X_2]^{4-}$ species $[(d_\sigma)^2]$. In fact, the $[Pt_2(pop)_4(CH_3)(I)]^{4-}$ complex, having the highest ϕ_r value[29] (Table II), has a Pt–Pt bond distance (2.782 (1) Å) close to that found in the partially oxidized linear-chain $[[Pt_2(pop)_4Br]^{4-}]$ compound (2.793 (1) Å).[25]

Conclusion

The efficient and stoichiometric photoconversion of $[Pt_2(pop)_4X_2]^{4-}$ to $[Pt_2(pop)_4]^{4-}$ in methanol makes $[Pt_2(pop)_4]^{4-}$ distinctly different from other binuclear d^8–d^8 complexes such as $[Rh_2(TMB)_4]^{2+}$ (TMB = 2,4-dimethyl-2,5-diisocyanohexane).[3] The high ϕ_r value observed for $[Pt_2(pop)_4(CH_3)(I)]^{4-}$ suggests the potential usefulness of $[Pt_2(pop)_4]^{4-}$ in catalyzing photochemical C–X (X = halogen) bond-breakage reactions. Even though $[Pt_2(pop)_4]^{4-}$ is stable in aqueous solution, the complex nature of the photochemistry of $[Pt_2(pop)_4X_2]^{4-}$ in water precludes it to be a good solvent system for photocatalysis work.

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Registry No. $[Pt_2(pop)_4Br_2]^{4-}$, 87374-25-2; $[Pt_2(pop)_4Cl_2]^{4-}$, 87355-26-8; $[Pt_2(pop)_4Im_2]^{4-}$, 114944-21-7; $[Pt_2(pop)_4I_2]^{4-}$, 87355-25-7; $[Pt_2(pop)_4(SCN)_2]^{4-}$, 102133-43-7; $[Pt_2(pop)_4(CH_3)(I)]^{4-}$, 114928-99-3; $[Pt_2(pop)_4]^{4-}$, 80011-25-2.

Supplementary Material Available: Figures S1–S3 show spectral changes of photoreactions (3 pages). Ordering information is given on any current masthead page.

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(29) The high ϕ_r value for $[Pt_2(pop)_4(CH_3)(I)]^{4-}$ may also due to the fact that the reductively eliminated product, CH_3I, is nonoxidizing.

Aprotic Conjugate Addition of Allyllithium Reagents Bearing Polar Groups to Cyclic Enones. 1. 3-Alkylallyl Systems

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Abstract: The conjugate addition of lithiated (*E*)- and (*Z*)-oct-2-enyl sulfoxides and phosphine oxides, but-2-enyl sulfoxides, phosphine oxides and phosphonates, and 3,3-dimethylallyl and allyl sulfoxides to cyclic enones has been examined. The *E* and *Z* carbanions react in highly diastereoselective fashion with five-membered cyclic enones to deliver respectively syn and anti vinylic sulfoxides, phosphine oxides, and phosphonates. Hexamethylphosphoric triamide has no regiochemical influence on these reactions. The regiochemical and stereochemical outcomes of these reactions are rationalized in terms of planar lithiated reagents in which Li^+ is bound to oxygen attached to sulfur or phosphorus of the polar group and a 10-membered "trans-decalyl"- or "trans-fused chair–chair"-like transition-state model in which the lithiated reagent adopts an endo orientation over one face of the enone such that for the *E* reagent, the 3-alkyl group is pseudoequatorial, and for the *Z*, pseudoaxial.

The aprotic conjugate addition of lithiated stabilized carbanions to conjugated enones is a well-known reaction that has received considerable attention, from both exploratory mechanistic[1–4] and synthetic[5] viewpoints. In many cases, the propensity of such carbanions to undergo carbonyl addition with conjugated enones

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