thermally at temperatures where $MnRe(CO)_{10}$ undergoes substitution by PPh_3, showing that some CO release from decomposition occurs. $Mn(CO)_4(PPh_3)Re(CO)_5$ also gives both $Mn(CO)_4(PPh_3)Re(CO)_4(PPh_3)$ and $Mn(CO)_5Re(CO)_4(PPh_3)$ in early stages (~10%) of thermal reaction.

The principal conclusion to be drawn from our work is that the low-temperature photochemical route is the best way to effect clean formation of $Mn(CO)_4(PPh_3)Re(CO)_5$ from $MnRe(CO)_{10}$. We confirm selective loss of CO from Mn upon photoexcitation of $MnRe(CO)_{10}$.[15] Further, thermal activation of $Mn(CO)_4(PPh_3)Re(CO)_5$ yields facile rupture of the Mn–PPh_3 bond to give substitution. We find that $Mn(CO)_4(PPh_3)Re(CO)_5$ cannot survive the conditions where careful analysis of thermal chemistry of $MnRe(CO)_{10}$ (at early stages in the reaction) shows greater lability at Mn, as expected from a variety of other studies.[2,3,20]

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Photoinduced C-S Bond Cleavage by Tetrakis(pyrophosphito)diplatinum(II)

Sir:

The search for inorganic complexes for photochemical multielectron atom transfer reactions is the target of our research. Recent studies have shown that the $Pt_2(P_2O_5H_2)_4^{4-}$ complex (Pt_2) possesses unique photochemistry; for example, it facilitates photochemical H atom abstraction of alcohols and cyclohexene and cleavage of carbon–halogen bonds.[1-3] Its $^3A_{2u}$ state (denoted here $^3Pt_2^*$) is long-lived ($\tau \approx 9.8$ μs), is biradical in character, and is a powerful one-electron reductant.[4] These properties make $^3Pt_2^*$ an ideal system for mechanistic investigation of metal ion induced homolytic C–X bond cleavage reactions, which are sometimes difficult to study by conventional means. We describe here the first example of photochemical cleavage of C–S bonds by transition-metal complexes. Despite the importance of C–S bond cleavage in desulfurization reactions, relatively little is known about the actual mode of the reaction.[5]

Table I. Bimolecular Rate Constants for Quenching of $^3Pt_2^*$ by R_2S in Methanol at 25 °C

substrate	k_q, M^{-1} s^{-1}	substrate	k_q, M^{-1} s^{-1}
$(PhCH_2)_2S$	~10^7 [a]	$^tBu_2S$	6.3×10^5
Me_2S	9.7×10^5	Et_2S	4.2×10^5

[a] The k_q value is only approximate since the Stern–Volmer plot is not linear. Since the absorption and emission spectra of $Pt_2(P_2O_5H_2)_4^{4-}$ are unaffected by $(PhCH_2)_2S$, there is no ground-state association process that leads to static quenching. However, the quenching rate is found to vary with the laser energy, indicating the possibility of having secondary quenching.

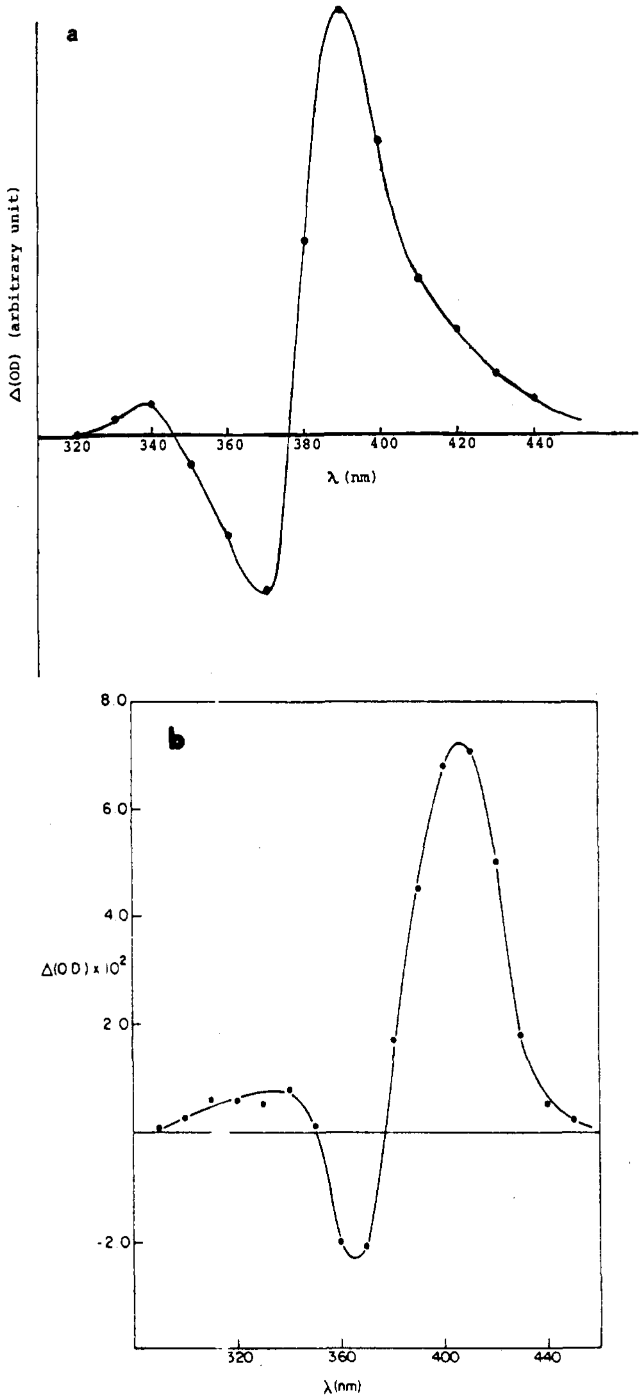

Figure 1. (a) Transient difference absorption spectrum recorded 5 μs after laser flash of a degassed methanolic solution of Pt_2 and Et_2S (~0.1 M). (b) Difference absorption spectrum between $[Pt^{II}Pt^{III}(P_2O_5H_2)_4(SCN)]^{4-}$ and $[Pt_2(P_2O_5H_2)_4]^{4-}$.

The Pt_2 complex does not react with R_2S thermally, although oxidation to $[Pt_2(P_2O_5H_2)_4(SEt_2)_2]^{2-}$ (λ_{max} 342 nm)[6] can be brought about by H_2O_2. In degassed methanol, the phosphorescence but not fluorescence of Pt_2 is quenched by R_2S (R = CH_3, C_2H_5, $(CH_3)_3C$, $PhCH_2$). Values of the quenching rate

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(1) (a) Che, C.-M.; Lee, W.-M. *J. Chem. Soc., Chem. Commun.* **1986**, 512. (b) Che, C-M.; Lee, W.-M.; Cho, K.-C.; Harvey, P. D.; Gray, H. B., submitted for publication in *J. Phys. Chem.* (c) Che, C.-M.; Cho, K.-C.; Chan, W.-S.; Gray, H. B. *Inorg. Chem.* **1986**, *25*, 4906.

(2) (a) Roundhill, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 4354. (b) Roundhill, D. M.; Atherton, S. J.; Shen, Z.-P. *J. Am. Chem. Soc.* **1987**, *109*, 6076. (c) Roundhill, D. M.; Atherton, S. J. *Inorg. Chem.* **1986**, *25*, 4071. (d) Roundhill, D. M.; Shen, Z.-P.; Atherton, S. J. *Inorg. Chem.* **1987**, *26*, 3833.

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(5) See for example: (a) Gutierrez, C. G.; Summerhays, L. R. *J. Org. Chem.* **1984**, *49*, 5206. (b) Chan, M.-C.; Cheng, K. M.; Li, M. K.; Luh, T. Y. *J. Chem. Soc., Chem. Commun.* **1985**, 1610.

(6) The $[Pt_2(P_2O_5H_2)_4(SEt_2)_2]^{2-}$ complex has also been characterized by ^{31}P NMR spectroscopy: δ 25.1, J_1(Pt–P) ≈ 2040 Hz.

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Table II. Bimolecular Rate Constants for the Reaction $^3Pt_2^* + R{-}X \rightarrow [Pt^{II}Pt^{III}{-}X] + R^\bullet$ in Methanol at 25 °C and C–X Bond Energies

R–X	bond energy, kJ mol^{-1} [a]	rate constant, M^{-1} s^{-1}
H–allyl	362	$(5.4 \pm 0.5) \times 10^6$ (cyclohexene)[b]
Br–alkyl	293–286	$(4.4 \pm 0.4) \times 10^7$ (^{n}BuBr)[c]
RS–alkyl	270	$(9.7 \pm 0.8) \times 10^5$ (Me_2S)[d]

[a] *CRC Handbook of Chemistry and Physics*, 67th Ed.; CRC: Boca Raton, FL, 1986–1987. [b] Che, C.-M.; Lee, W. M.; Cho, K.-C., results to be submitted for publication. [c] Reference 1b. [d] This work.

constants (k_q) in methanol deduced from the equation $\tau_0/\tau = 1 + k_q\tau_0[R_2S]$ at 25 °C are summarized in Table I. Since the quenchers do not absorb in the visible region, quenching by an energy-transfer pathway is unlikely. Flash-photolysis experiments give evidence that the reactions occurring between $^3Pt_2^*$ and R_2S are predominately atom transfer in nature[7] as shown in eq 1.

$$^3Pt_2^* + R_2S \rightarrow [Pt^{II}Pt^{III}{-}SR] + R^\bullet \qquad (1)$$

The transient difference absorption spectrum recorded instantaneously (5 μs) after the laser flash of a degassed methanolic solution of Pt_2 and Et_2S has an intense band at 390 nm, as shown in Figure 1a. The same spectra are also obtained with $(PhCH_2)_2S$. Figure 1b shows the difference absorption spectrum between $[Pt^{II}Pt^{III}(P_2O_5H_2)_4(SCN)]^{4-}$ and Pt_2.[1c,8] The two spectra are vitually identical, suggesting that the 390-nm peak in Figure 1a is due to the σ(RS) → $d\sigma^*$(PT) charge-transfer transition of $[Pt^{II}Pt^{III}{-}SR]$, which is expected to have energy similar to that of the σ(NCS) → $d\sigma^*$(Pt) transition of $[Pt^{II}Pt^{III}(P_2O_5H_2)_4(SCN)]^{4-}$. Evidence for the $R^\bullet$ radical in eq 1 also comes from the identification of the $PhCH_2CH_2Ph$ product[9] obtained by broad-band irradiation ($\lambda > 350$ nm) of Pt_2 and $(PhCH_2)_2S$ in degassed methanol for 5 h.[10]

Unlike other $[Pt^{II}Pt^{III}(pop)_4X]^{4-}$ complexes (X = Im, H, Cl), which rapidly disproportionate in solution,[2b,8,11] these $[Pt^{II}Pt^{III}{-}SR]$ species remain stable in methanol over a period of 50 ms. The RS ligand is a powerful σ-donor, thus stabilizing the $[Pt^{II}Pt^{III}]$ system through extensive charge-transfer mixing with the $d\sigma$(Pt–Pt) bond. Previous work also indicated that the stability of the $[Pt^{II}Pt^{III}X]$ system increases with increasing nucleophilicity of X, in the order X = Cl < Br < SCN.[1c]

From Table I, the k_q values are in the order $R_2S = (PhCH_2)_2S > Me_2S > {}^tBu_2S > Et_2S$. Except for Me_2S, the k_q values are in parallel with the stabilities of the $R^\bullet$ intermediates.[12] Table II summarizes the rate constants of the reaction $^3Pt_2^* + R{-}X \rightarrow [Pt^{II}Pt^{III}{-}X] + R^\bullet$ together with the C–X bond energies. The unexpectedly low k_q values for R_2S, whose bond energies are the lowest when compared with those for C–H and C–Br bonds, reflect the importance of the steric effect of R_2S in affecting the atom-transfer reactions of $^3Pt_2^*$.

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[7] An oxidative-quenching pathway is unlikely since R_2S is electrochemically reduced only with an applied potential less than −2.75 V vs Ag/AgCl. Reductive quenching of $^3Pt^{2*}$ with R_2S will give the $[Pt^IPt^{II}]$ intermediate, which absorbs at 410 nm (Che, C.-M.; Atherton, S. J.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 5143) and is very unstable. This is in contrast to the results of flash-photolysis experiments.

[8] Che, C.-M.; Gray, H. B.; Atherton, S. J.; Lee, W. M. *J. Phys. Chem.* **1986**, *90*, 6747.

[9] $PhCH_2CH_2Ph$ is identified by ^1H NMR spectroscopy and mass spectral analysis.

[10] No Pt^{III}_2 product was found by ^{31}P NMR spectroscopy. Instead, some decomposition of Pt_2 was observed. Recent studies have shown that $[Pt_2(P_2O_5H_2)X_2]^{4-}$ easily undergoes reduction to $[Pt_2(P_2O_5H_2)_4]^{4-}$ in methanol upon irradiation with UV light ($\lambda > 300$ nm) (Che, C.-M., Lee, W. M.; Cho, K.-C. *J. Am. Chem. Soc.* **1988**, *110*, 5407). Thus, it is not suprising to find that steady-state irradiation ($\lambda > 300$ nm) of $[Pt_2(P_2O_5H_2)_4]^{4-}$ with R_2S in methanol does not produce $[Pt_2(P_2O_5H_2)_4(R)(SR)]^{4-}$, which is expected to be very reactive toward photochemical reductive elimination.

[11] Roundhill, D. M.; Atherton, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 6829.

[12] Similar reactivities of R_2S with tri-*n*-butyltin hydride have also been found.[5a]

Uranium(VI)–Oxo–Alkoxide Cluster Synthesis via Ligand Redistribution

Sir:

Although a number of well-characterized uranium alkoxide complexes in a variety of formal oxidation states (+3 → +6) have been reported,[1-5] there are few examples of uranyl (UO_2^{2+}) alkoxide complexes[6-11] and only two structurally characterized members of this class.[12,13] There is disagreement in the literature as to the exact composition of binary uranyl alkoxides. Gilman and co-workers[7] proposed complexes of the stoichiometry $UO_2(OR)_2(ROH)_{3-4}$, while Bradley and co-workers[8] reported that uranyl complexes of secondary and tertiary alkoxides disproportionate in alcoholic solution to form compounds of the formula $UO(OR)_4(ROH)$. In both cases, formula assignments were based solely on elemental analyses.

In the course of our investigations of the nonaqueous chemistry of the uranyl ion, we have examined the reactions of anhydrous uranyl halides (UO_2X_2) with alkali-metal alkoxides in aprotic solvents. Addition of a tetrahydrofuran solution of potassium *tert*-butoxide to a stirred THF slurry of anhydrous uranyl chloride results in the slow (8–10 h) formation of a red solution and an insoluble precipitate. Filtration of the suspension, followed by concentration and cooling of the filtrate, results in the isolation of orange-red crystals (**1**) in a yield of ca. 30% based on UO_2Cl_2.[14] The ^1H NMR spectrum of the complex in toluene-d_8 at −35 °C consists of four sharp singlets at δ 2.08, 1.95, 1.66, and 1.55 in a 1:1:2:1 ratio. There are no resonances in the spectrum that can be attributed to free or coordinated tetrahydrofuran. The Nujol mull IR spectrum shows two U–O stretching modes at 931 and 898 cm^{-1}.

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[14] IR (Nujol mull): 1365 m, 1356 m, 1225 w, 1193 w, 1166 m, 1021 w, 976 w, 931 s, 898 s, 772 m, 761 w, 719 w, 643 w br, 608 m, 509 w, 498 w, 456 m br cm^{-1}. Anal Calcd for $U_3O_{14}C_{40}H_{90}$: C, 31.8; H, 6.02. Found: C, 31.8; H, 6.07. The crystals decompose at 165 °C without melting.