# Communications

Flash Photolysis of Triruthenium Dodecacarbonyl. Evidence for Intermediates in the Competing Fragmentation and Ligand-Substitution Photoreactions of $Ru_3(CO)_{12}$

Sir:

Papers from two laboratories[1] describing quantitative investigations of the known photofragmentation[2] of $Ru_3(CO)_{12}$ to mononuclear products (e.g., eq 1) have interpreted the observed

$$Ru_3(CO)_{12} + 3\ CO \xrightarrow[\text{octane}]{h\nu} 3\ Ru(CO)_5 \qquad (1)$$

$$(2)$$
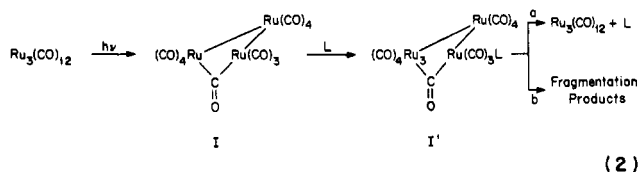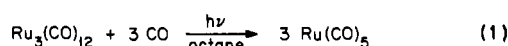
photoreactivity patterns in terms of an intermediate such as I. This intermediate, an isomer of $Ru_3(CO)_{12}$, has a vacant coordination site on one of the ruthenium centers that can be trapped by another CO or another ligand L. The resulting $Ru_3(CO)_{12}L$ species can undergo further reaction with L in subsequent steps, leading to mononuclear products or loss of L to re-form $Ru_3(CO)_{12}$. In an attempt to observe I or I' directly, we have undertaken a flash photolysis investigation of this system. Reported here is evidence for such an intermediate generated by longer wavelength flash photolysis as well as evidence for another intermediate II produced when shorter wavelength excitation is utilized. The kinetic properties as well as the wavelength behavior of the system under continuous photolysis indicate that II is an intermediate for the competing photosubstitution reaction of this triangular cluster.[3]

When an argon-purged solution of $Ru_3(CO)_{12}$ (10^{-5} M) plus THF (1.0 M) in cyclohexane was flash photolyzed ($\lambda_{irr} > 390$ nm, conventional flash apparatus, aqueous $NaNO_2$ cutoff filter)[4] at wavelengths corresponding to the lowest energy absorption band (Figure 1), a transient bleaching was observed over the spectral range 380–460 nm. The transient bleaching returned to the original base line with a first-order rate constant of 20 s⁻¹. The
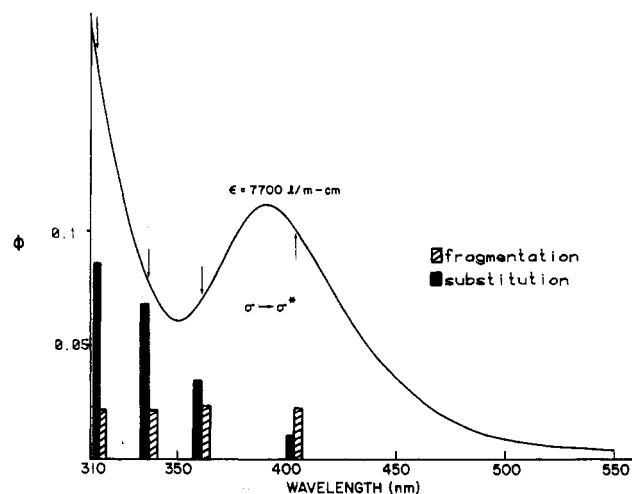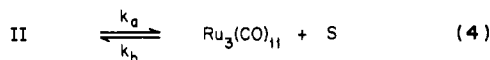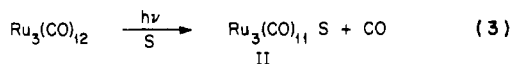
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Figure 1. Electronic absorption spectrum of $Ru_3(CO)_{12}$ with the quantum yields for fragmentation and substitution measured at the irradiating wavelengths 313, 334, 366, and 405 nm. The substitution quantum yield shown at 405 nm is the upper limit for detection. Conditions: [P(OCH₃)₃] = 0.012 M, [Ru₃(CO)₁₂] = (4–6) × 10⁻⁵ M, in 25 °C argon-purged octane solution.

same transient behavior was noted for a similar THF/cyclohexane solution equilibrated with CO with the exception that a small amount of photofragmentation was also seen. When an analogous flash photolysis experiment was carried out under argon in neat cyclohexane, there was no observed transient or net photochemistry. Thus, it appears that I, if formed, decays within the dead time of the flash photolysis apparatus and that the transient behavior observed in the presence of THF represents formation of I', which does not undergo fragmentation for L = THF. (This is consistent with the observation that THF serves to quench the photofragmentation of $Ru_3(CO)_{12}$ when photolyzed under CO.)[1] Transient bleaching at 390 nm was also observed in cyclohexane for L = cyclohexene, P(OCH₃)₃, or PPh₃ with first-order decay rates following the sequence THF < cyclohexene < PPh₃ < P-(OCH₃)₃ ≪ CO (no transient seen). Given that THF and cyclohexene act as quenchers for photofragmentation under CO, while with L = PPh₃ or P(OCH₃)₃ photofragmentation to Ru-(CO)₄L is seen, these observations indicate a mechanism where the lifetime of I' is determined by the summed rates of the two first-order decay pathways (eq 2a,b) and the extent of net photofragmentation is governed by the partitioning between these two paths.

Flash photolysis of $Ru_3(CO)_{12}$ with higher energy light ($\lambda_{irr} > 315$ nm) leads to different behavior. For example, in THF solution under CO, transient absorption over the range 480–550 nm was seen that decayed experimentally to base line with a [CO]-dependent rate constant $k_{obsd} = k_a k_c[CO]/(k_b + k_c[CO])$.

This is consistent with photolabilization of CO followed by reaction of the transient photoproduct II with free CO,[5] e.g.

$$Ru_3(CO)_{12} \xrightarrow[S]{h\nu} \underset{II}{Ru_3(CO)_{11}} S + CO \qquad (3)$$

$$II \underset{k_b}{\overset{k_a}{\rightleftharpoons}} Ru_3(CO)_{11} + S \qquad (4)$$

$$Ru_3(CO)_{11} + CO \xrightarrow{k_c} Ru_3(CO)_{12} \qquad (5)$$

If CO loss (eq 3) were a primary photoprocess at higher energy, then photosubstitution should occur readily in the presence of other ligands. In confirmation of this expectation, 313-nm continuous photolysis of $Ru_3(CO)_{12}$ in octane containing $P(OCH_3)_3$ led to the formation of the substituted clusters $Ru_3(CO)_{12-n}L_n$ ($n = 1–4$) in competition with photofragmentation to mononuclear species as determined from electronic and IR spectra of the product mixtures.[6] The patterns of spectral changes indicate that formation of the $n = 2–4$ products is the result of sequential substitution of CO by $P(OCH_3)_3$. In the THF solution, 313-nm photolysis in the presence of added $P(OCH_3)_3$ was shown to give substituted triruthenium clusters with a quantum yield comparable to that seen in octane solution (below). However, competing photofragmentation was largely supressed owing to the quenching mechanism noted above.

That the observed photosubstitution was not just the result of cluster fragmentation followed by secondary photoreactions of the primary products as $Ru(CO)_4P(OCH_3)_3$ was tested by studying the photoreactions of this mononuclear species. Direct 313-nm photolysis of $Ru(CO)_4P(OCH_3)_3$ (0.001 M) in octane containing 0.012 M $P(OCH_3)_3$ leads only to the further substitution of $P(OCH_3)_3$ for CO on the mononuclear complex as confirmed by IR spectroscopy.[7] In addition, photolysis of $Ru(CO)_4L$ (0.001 M) in the presence of $Ru_3(CO)_{12}$ (0.0002 M) gave no substitution clusters.

Quantum yields for cluster fragmentation (Φ_f) and for the formation of $Ru_3(CO)_{11}P(OCH_3)_3$ (Φ_s) were determined spectrally and are indicated in Figure 1. Note that Φ_f is essentially wavelength independent, whereas Φ_s increases dramatically for the shorter wavelengths. Carrying out the 313-nm photolysis under a CO atmosphere ($[P(OCH_3)_3] = 0.012$ M) had opposite effects on the two photoreactions; Φ_s decreased from 0.086 to 0.043, and Φ_f increased from 0.021 to 0.029 relative to the experiment under argon. Increasing $[P(OCH_3)_3]$ to 0.1 M had the effect of increasing the yields of both reaction pathways: substitution by a factor of 2, fragmentation by 50%.

The continuous and kinetic flash photolysis results described here indicate the presence of two reactive intermediates, each key to independent pathways, leading respectively to photofragmentation or to ligand photosubstitution of $Ru_3(CO)_{12}$. The intermediate for photosubstitution appears to be $Ru_3(CO)_{11}$ or $Ru_3(CO)_{11}S$ (S = solvent); however, the current evidence does not differentiate between formation of II via simple dissociation from

a cluster excited state or via a more complex mechanism.[8] In addition, these observations further emphasize the important roles played by the reaction medium and excitation energy in directing the course of this photochemistry. Studies in progress are focused on the further elucidation of the quantitative aspects of the reaction dynamics of the observed intermediates.

(8) However, Wrighton and co-workers have identified (via FTIR techniques) a species equivalent to II in the low-temperature (77 K) photoreactions of $Ru_3(CO)_{12}$ in hydrocarbon matrices containing the donor ligand 2-CH₃-THF (private communication from M. S. Wrighton).

Department of Chemistry   **Marc F. Desrosiers**
University of California   **David A. Wink**
Santa Barbara, California 93106   **Peter C. Ford***

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Failure of Stranks' Postulate and the Volume Profile for the Aquation of $Co(NH_3)_5X^{n+}$

Sir:

In summary, it can be shown that (i) eq 1 is incorrect, (ii) eq 3 is correct, but this does not justify eq 1, and (iii) in reaction 2, the entering H_2O and the leaving X almost equally participate in the transition state.

In 1974 Stranks made a postulate concerning the partial molal volume ($\bar{V}$) of complex ion in its transition state of ligand substitution.[1] Activation volumes (ΔV^*) for many complex ion reactions were interpreted on the basis of this postulate.[2,3] He has assumed that the intrinsic component ($\bar{V}_{int}$) of $\bar{V}$ of a five-coordinate intermediate is approximately equal to that of its six-coordinate precursor

$$\bar{V}_{int}(ML_5{}^{m+}) \simeq \bar{V}_{int}(ML_5X^{n+}) \qquad (1)$$

where $\bar{V}_{int} = \bar{V} - \bar{V}_{el}$ and $\bar{V}_{el}$ is the contribution from the electrostatic interaction of the charged complex ion with the solvent.[1] Since the magnitude of $\bar{V}_{el}$ should be similar for octahedral complexes of the same charge,[4] eq 1 automatically means that $\bar{V}(ML_5X^{n+})$ is approximately constant throughout a series of ML_5X^{n+} complexes with a fixed n value. However, $\bar{V}(Co(NH_3)_5X^{2+})$ ranges from 63.6 cm³ mol⁻¹ for X = F⁻ to 94.8 cm³ mol⁻¹ for X = I⁻ and $\bar{V}(Co(NH_3)_5X^{3+})$ ranges from 60.3 cm³ mol⁻¹ for X = H_2O to 122.9 cm³ mol⁻¹ for X = $OC(NHCH_3)_2$.[5] When it is considered that the magnitudes of ΔV^* or reaction volume (ΔV) in water are in a range from −30 to +30 cm³ mol⁻¹, eq 1 is obviously incorrect.[6]

Later, Palmer and Kelm assumed the existence of $Co(NH_3)_5{}^{3+}$ in the transition state of the aquation

$$Co(NH_3)_5X^{n+} + H_2O \rightarrow Co(NH_3)_5H_2O^{3+} + X \qquad (2)$$

and demonstrated that

$$\bar{V}(Co(NH_3)_5{}^{3+}) = \bar{V}(Co(NH_3)_6{}^{3+}) \qquad (3)$$

(5) Over this monitoring wavelength range, the intermediate I′ has no absorbance. However, when the transient behavior resulting from short-wavelength flash photolysis in the presence of various ligands was monitored at 390 nm, temporal absorbance changes consistent with the behavior expected for the simultaneous formation of both I′ and II were observed.

(6) These products' spectra were compared to the spectra of authentic samples of $Ru_3(CO)_{12-n}(P(OCH_3)_3)_n$ ($n = 1–3$) prepared by Dr. R. Trautman and D. Taube of this laboratory. The cluster $n = 4$, previously unreported, is presumed present from the shift in the band maximum with increased subsitution; for $n = 1–3$, the λ_{max} is 402, 416, and 426 nm, respectively. From the reaction mixture a fourth cluster was isolated with a λ_{max} at 445 nm. The $Ru_3(CO)_{11}(P(OCH_3)_3)$ cluster has been reported: Bruce, M. I.; Keheo, D. C.; Matisons, J. G.; Nicholson, B. K.; Rieger, P. H.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1982**, 442–444.

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