Acknowledgment. The assistance of Dr. Larry Curtiss (Argonne National Laboratory) in carrying out the MEHT calculations and helpful discussions with Professor Roald Hoffmann (Cornell) and Dr. James McGinnis (Celanese Research Co.) are gratefully acknowledged. Support from the Alfred P. Sloan Foundation (1980–1982) is greatly appreciated. These ideas were conceived while the author was on sabbatical leave at Celanese Research Co. (Summit, NJ).

Registry No. CO, 630-08-0.

Photochemical Fragmentation of the Cluster $Ru_3(CO)_{12}$: Evidence against Homolytic Bond Cleavage[†]

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Summary: $Ru(CO)_5$ is the photoproduct when $Ru_3(CO)_{12}$ is photolyzed in octane solution containing 1 M CCl_4 and under a CO atmosphere. Although chlorocarbonylruthenium products are formed eventually, these arise from the facile thermal reaction of $Ru(CO)_5$ with the CCl_4. Quantum yields for $Ru_3(CO)_{12}$ fragmentation are markedly sensitive to the presence of CO but insensitive to that of CCl_4, arguing against proposals of diradical intermediates in this photoreaction.

Photolysis of the trinuclear cluster $Ru_3(CO)_{12}$ in hydrocarbon solutions and in the presence of soft ligands such as CO, ethylene or phosphines has long been known[1] to lead to the fragmentation of the cluster to monomeric species (e.g., eq 1). While this reaction is sufficiently facile

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

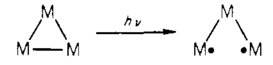
to provide a synthesis pathway for moderate concentrations of mononuclear ruthenium carbonyls in hydrocarbon solutions,[1-4] the photosynthesis procedure is not effective in more polar solvents such as tetrahydrofuran (THF) owing in part to much smaller quantum efficiences (vide infra). Furthermore, although we have found $Ru(CO)_5$ to be the photoproduct under CO at low $Ru_3(CO)_{12}$ concentrations in THF, photolysis at larger $Ru_3(CO)_{12}$ concentrations in this solvent leads to the formation of an uncharacterized, insoluble red material, presumably a polymeric ruthenium carbonyl. These marked effects of the medium on the $Ru_3(CO)_{12}$ photoreactions has stimulated our interest in the quantitative elucidation of the cluster photofragmentation mechanism.

Table I. Disappearance Quantum Yields for the Photolysis of $Ru_3(CO)_{12}$

solvent	conditions	$10^3\phi_d$
octane[c]	1 atm of CO[b]	28 ± 4
octane[d]	1 atm of C_2H_4[b]	51 ± 5
octane[e]	1 atm of Ar[b]	<0.1
CCl_4[f]	1 atm of CO	13 ± 3
CCl_4[f]	1 atm of Ar	0.7 ± 0.1
octane[f]	1 M CCl_4/1 atm of CO	24 ± 4
octane[f]	1 M CCl_4/1 atm of Ar	~0.2
THF[c]	1 atm of CO	3.5 ± 0.7
diglyme[c]	1 atm of CO	0.7 ± 0.1
octane[c]	0.5 M THF/1 atm of CO	1.7 ± 0.1
octane[c]	0.3 M diglyme/1 atm of CO	3.2 ± 0.1

[a] ϕ_d based on the decrease in intensity of the 392-nm absorption band of $Ru_3(CO)_{12}$ given that the products do not absorb light at this wavelength. $[Ru_3(CO)_{12}]$ initial $\sim 5 \times 10^{-5}$ M. $T = 25$ °C λ (irradiation) = 405 nm. The photolysis apparatus and general procedures have been described previously (Hintze, R. E.; Ford, P. C. *J. Am. Chem. Soc.* **1975**, *97*, 2664). [b] Solution prepared by flushing with respective gas, $P = 1$ atm. [c] Product formed is $Ru(CO)_5$. [d] Product formed is $Ru(CO)_4(C_2H_4)$. [e] Product unknown. [f] Products formed are chlorocarbonyls of ruthenium.

The electronic spectrum of $Ru_3(CO)_{12}$ is dominated by a strong absorption band (λ_{max} 392 nm in octane (ϵ_{max} 7.7 × 10^3 L mol^{-1} cm^{-1})) attributed to a transition from an orbital which is bonding with regard to the metal–metal bond framework to one which is antibonding in this regard.[5,6] It has been suggested[3,7] that the photofragmentation resulting from irradiation in this wavelength region may proceed via the cleavage of a single Ru–Ru bond to produce the open chain diradical A (eq 2) in the primary



(2)

A

M = $Ru(CO)_4$

photoreaction step. A similar mechanistic proposal has been made for the photofragmentations of $Os_3(CO)_{12}$[8] and of $HMCo_3(CO)_{12}$.[9] Reaction with CCl_4 to give chlorocarbonyl products has been argued as evidence for formation of metal radicals in photoreactions of $Os_3(CO)_{12}$[8] and of numerous dinuclear metal–metal bonded complexes.[7,10] We have shown that 405-nm photolysis of $Ru_3(CO)_{12}$ in CCl_4 solution indeed does lead to formation of chlorocarbonyl ruthenium products; however, the quantum yield for the photofragmentation (ϕ_d) is a factor of 20 larger under CO (1 atm) than under argon (Table I). Even greater differences are seen with the ϕ_d values measured in octane solution with CCl_4 (1 M) added. When this solution is equilibrated with CO (1 atm), ϕ_d is indistinguishable from that value measured in the absence of CCl_4. Under an argon atmosphere, ϕ_d in the octane/1 M CCl_4 solution is 2 orders of magnitude smaller, although apparently somewhat larger than seen in octane solution alone.

Examination of product solution infrared spectra leads to particularly important observations. Photolysis of $Ru_3(CO)_{12}$ in octane/1 M CCl_4 solution under CO (1 atm) for a time period sufficient to cause an 80% decrease of

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[†] Dedicated in memory of Professor Rowland Pettit.

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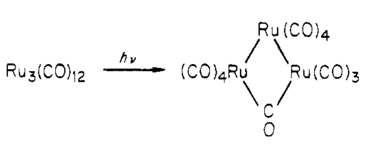
the ν_{CO} bands of the starting material (2062 (vs), 2032 (s), and 2012 (m) cm^{-1}) is accompanied by the appearance of very prominent new absorbances at 2040 (s) and 1999 (vs) cm^{-1} characteristic of $Ru(CO)_5$![11] Only minor other absorbances at 2074, 2082, 2108 (w), 2130, and 2140 cm^{-1}, suggesting the presence of some chlorocarbonyl ruthenium species,[12] were found in this initial spectrum. Continued photolysis leads to complete conversion to the latter products.[13] However, the identical products are formed if $Ru_3(CO)_{12}$ in octane solution is photolyzed under CO to completion giving only $Ru(CO)_5$, then CCl_4 is subsequently added, and the system is allowed to react in the dark. This thermal chlorination of $Ru(CO)_5$ in octane/1 M CCl_4 occurred with a first-order rate constant of about 1×10^{-4} s^{-1} at room temperature (~20 °C). The products of $Ru_3(CO)_{12}$ photolysis in octane/1 M CCl_4/Ar (1 atm) led to the slow formation of a product solution exhibiting a number of ν_{CO} bands in the IR, the more prominent of which were noted above as products under CO (1 atm).

The above results in CCl_4 solution demonstrate clearly that the principal photofragmentation pathway in octane does not occur via the intermediacy of a reactive diradical species. The role of CO in determining the quantum yields, the observation of $Ru(CO)_5$ as the primary photoreaction product under CO and in the presence of CCl_4, and the failure of CCl_4 to affect ϕ_d under CO (1 atm) indicate that the excited states and intermediates along the primary photoreaction potential surface are not intercepted by CCl_4 and that the eventual chlorocarbonyl products are the result of secondary thermal reactions of the $Ru(CO)_5$ product. A minor fragmentation pathway via radical intermediates may be reflected by the small ϕ_d values seen under argon. However, reaction of CCl_4 with the unsaturated intermediate proposed below might also account for this minor pathway.

Table I also summarizes ϕ_d values in tetrahydrofuran and diglyme solutions under CO (1 atm).[14] In each case, ϕ_d is markedly smaller than in octane under otherwise comparable conditions. That such changes are not simply due to solvent effects is demonstrated by decreased ϕ_d values in octane when small concentrations of THF or diglyme are added (Table I). Under such conditions low concentrations of these donor cosolvents added to octane act as quenchers of the photofragmentation, the quantitative behavior following Stern–Volmer type kinetics (ϕ_0/ϕ vs. [Q] plots linear).[15] However, the identical product ($Ru(CO)_5$) is formed by photolysis in octane, THF, or diglyme solutions.

That the reaction quantum yields are little affected by CCl_4, a radical trap, but are significantly affected by the presence of weak Lewis bases indicates that the key intermediate(s) in the photofragmentation is not radical in nature but is coordinatively unsaturated. We propose the species B shown in eq 3. Once formed by photolysis, B could be trapped by a weak donor such as THF or (competitively) by CO or other π-acid ligand (e.g., C_2H_4, Table I). Fragmentation of the resulting $Ru_3(CO)_{12}L$ adduct may prove facile; however, fragmentation of the analogous adduct of a hard base, for example, THF, may be much less so owing to the probable need to stabilize intermediates of low coordination number. Thus, the latter species would be expected to collapse back to the more stable $Ru_3(CO)_{12}$ starting material with loss of THF.



B

(3)

Studies are in progress to identify key intermediates of the proposed photofragmentation mechanism and to characterize better the thermal reactions of $Ru(CO)_5$ with CCl_4. It is notable that $Fe(CO)_5$ is essentially unreactive with CCl_4 under comparable conditions.[16,17]

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Registry No. $Ru_3(CO)_{12}$, 15243-33-1; $Ru(CO)_5$, 16406-48-7; CO, 630-08-0; CCl_4, 56-23-5.

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[12] These absorbances are consistent with the spectrum of $Ru_2(CO)_6Cl_4$: Johnson, B. F. G.; Johnston, R. D.; Lewis, J. *J. Chem. Soc. A* **1969**, 792–797.

[13] Note that $Ru(CO)_5$ does not absorb 405-nm light significantly so that further reactions of this species under these conditions represents thermal not photochemical processes.

[14] CO solubilities at 25 °C are relatively insensitive to the nature of these solvents ranging only from 0.006 mol/(L atm) in diglyme [M.S. Dissertation, J. Hildebrand, University of California, Santa Barbara, 1979] to ~0.012 M/(L atm) in octane [value estimated from that found in heptane, "Encyclopedia of Chemical Technology", 3rd ed.; Wiley: New York, 1978; Vol. 4, p 775].

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Synthesis, Structure, and Reactivity of $Ru(\eta^6\text{-}C_6Me_6)[\eta^4\text{-}C_6Me_4(CH_2)_2]$. An Unusual Transition-Metal *o*-Xylylene Complex[†]

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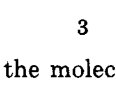
Summary: Deprotonation of $[Ru(C_6Me_6)_2]^{2+}$ generates the new *o*-xylylene complex $Ru(C_6Me_6)[C_6Me_4(CH_2)_2]$. The X-ray crystallographic study confirms that the metal is coordinated to the endocyclic diene system. The exocyclic methylenes are nucleophilic and can be reacted with electrophiles in a stepwise manner. This has allowed the isolation of a new *exo*-(methylene)cyclohexadienyl complex.

Transition metals are often valuable in stabilizing organic molecules which cannot survive in common laboratory conditions. For instance, many examples of cyclobutadiene complexes have been reported, and their use in organic synthetic applications has been explored.[1] *o*-Xylylene, **1**, is another example of this type of reactive species. Here again, coordination of the molecule to a transition metal yields a stable complex. With this ligand,

1

2



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[†] Dedicated to the memory of Professor Roland Pettit.

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