It is also surprising to find that at 120 K all water oxygen positions in β-CD·11D$_2$O are fully occupied except W8 (0.64), whereas at room temperature with composition β-CD·11D$_2$O most of them are only statistically filled or distributed over several sites. This suggests that water molecules have physically moved upon cooling, and the same holds for hydroxyl hydrogens engaged in flip-flops that disappeared at 120 K.

The difference of 0.6 water molecules in the two crystal structures determined at room temperature and at 120 K cannot be accounted for by errors in refinement because standard deviations of occupation factors are only of the order ±0.02. The possibility that a second modification of β-CD hydrate of composition β-CD·12D$_2$O was unwittingly used at 120 K can be discounted since it would show up in differences in unit cell constants.[20] We have to assume therefore that the 0.6 water molecule discrepancy is due to spurious water sites which did not show up clearly enough in the Fourier maps calculated with room-temperature data.

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Registry No. β-CD·11H$_2$O, 85490-99-9.

Supplementary Material Available: Listing of atomic coordinates and anisotropic temperatures for all atoms, individual bond lengths, valence angles, torsion angles, and structure amplitudes (39 pages). Ordering information is given on any current masthead page.

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(27) Shown are hydrogen-bond patterns occurring in the crystal structure of β-CD·11D$_2$O at 120 K. Because the total scheme is too complicated to be shown in one picture, it is broken up into three different schemes. In these, hydrogen bonds O-D---O are indicated by arrows pointing in the direction donor → acceptor, water molecules are denoted by W, and hydroxyl groups by two numbers, e.g., 64 means O(6)4, i.e., hydroxyl O(6) of glucose number 4 in the β-CD macrocycle. The flip-flop ring is indicated by a circle, homodromic rings by circular, one-headed arrows, and antidromic rings by circular, two-headed arrows. Water molecules W7 and W13 occur in all three schemes and are the points where the hydrogen-bonding systems are joined to form a complex three-dimensional structure. Letters in parentheses refer to paragraphs in the text.

Photofragmentation and Photosubstitution Kinetics of Dodecacarbonyltriosmium

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Abstract: The 436-nm photochemical kinetics of reactions of Os$_3$(CO)$_{12}$ in benzene with 1-octene and P(OEt)$_3$ have been studied under a wide variety of conditions. Reaction with 1-octene leads to fragmentation of the cluster whereas that with P(OEt)$_3$ leads to substitution. Both reactions proceed through the same intermediate which is shown to be a reactive isomer of Os$_3$(CO)$_{12}$, i.e., absorption of 436-nm radiation does not induce cluster fragmentation or CO dissociation. Since the reactivity of this intermediate with halocarbons is very low it is most probably not a diradical formed by homolysis of an Os–Os bond, although such a diradical could be a primary photoproduct that reacts very rapidly to form the more long-lived isomer. A possible structure for the isomer involves a CO that bridges two Os atoms (not otherwise bonded to each other), one of those Os atoms having a vacant coordination site. Attack at this site by a wide variety of donor molecules (CO, diglyme, and probably the benzene solvent, as well as the reactant molecules 1-octene and P(OEt)$_3$) can cause concerted reversion of the intermediate to Os$_3$(CO)$_{12}$. The fact that 1-octene and P(OEt)$_3$ can induce this reversion, in addition to causing forward reaction to form products, could well be the reason why the limiting quantum yields, found at high [1-octene] ($\phi_{\text{lim}} = 0.0320 \pm 0.0004$) or [P(OEt)$_3$] ($\phi_{\text{lim}} = 0.0456 \pm 0.0010$), are so low; i.e., the low quantum yields could be a reflection of the particular thermal reactivity pattern of the intermediate rather than of the photophysical behavior of Os$_3$(CO)$_{12}$. It is also the reason why limiting quantum yields are dependent on the nature of the ligand, a phenomenon also characteristic of the photokinetics of Ru$_3$(CO)$_{12}$.

The photochemical kinetics of dinuclear metal carbonyls have received considerable attention[1] since the pioneering work of Wrighton[2] but corresponding studies of metal carbonyl clusters are still quite rare. Photofragmentation is the predominant overall process in reactions of Fe$_3$(CO)$_{12}$ and Ru$_3$(CO)$_{12}$ with CO,[3-6] PPh$_3$,[3,4] and alkenes,[3-5,7] although the primary photoproduct from Ru$_3$(CO)$_{12}$ has been shown to be a reactive isomeric form of the cluster.[6] Very low quantum yields (0.001) for reactions of Ru$_3$(CO)$_{12}$ with halocarbons[5,6] have cast doubt on the earlier suggestion[3] that photolysis leads to homolysis of a Ru–Ru bond, and an alternative isomeric form has been proposed.[5,6] By contrast, Os$_3$(CO)$_{12}$ does not form Os(CO)$_5$ on photolysis under as much as 6 atm of CO,[3,8] and it undergoes simple photosubstitution with P donors.[3,8] No quantum yields were determined but reactions were reasonably fast. Again, quantum yields for reactions with halocarbons were very low (≲0.002 at 313 nm) and it was suggested[8] that the major process caused by photolysis was CO dissociation. On the other hand, photolysis of Os$_3$(CO)$_{12}$ in the presence of alkenes does lead to fragmentation[3,9] with quantum yields of ca. 0.03.[3] We have undertaken kinetic studies designed to show more clearly the type of intermediates generated by photolysis of metal carbonyl clusters and report here the photofragmentation kinetics of reaction of Os$_3$(CO)$_{12}$ with 1-octene and the photosubstitution kinetics of its reaction with P(OEt)$_3$.

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Experimental Section

$Os_3(CO)_{12}$ (Strem Chemicals), $P(OEt)_3$ (Eastman Kodak), and 1-octene (Sigma Chemicals) were used as received. Benzene (BDH AnalaR grade) was dried over molecular sieves. Diglyme (BDH Laboratory Grade) was distilled under reduced pressure over Na–Pb alloy and stored over molecular sieves under Ar. P-*n*-Bu_3 (Strem Chemicals) was distilled under reduced pressure over sodium and stored under Ar. Prepurified argon, CO, and H_2 were obtained from Canox Ltd. and CO–N_2 mixtures of known composition were obtained from Matheson Canada, Ltd.

IR spectra were measured with 1 mm path length cells (NaCl windows) with a Perkin-Elmer 298 spectrophotometer, and UV-vis spectra were measured with a Pye-Unicam SP8-400 spectrophotometer. The molar extinction coefficient of $Os_3(CO)_{12}$ at 328 nm in benzene was found to be 9300 M^{-1} cm^{-1} from a linear Beer's law plot and this value was used to estimate the initial concentration of $Os_3(CO)_{12}$ in all subsequent experiments.

A water-cooled Hanovia high pressure quartz mercury vapor lamp was used as a light source. Appropriate Corning glass filters were used to isolate 436-nm light, and a 3 M aqueous sodium nitrite solution in a 4 cm path length cell was used to cut off light with wavelengths below 436 nm.

Benzene solutions (ca. 3 mL) for photolysis were contained in 10 mm path length cells and were saturated with Ar or CO, the cells then being tightly stoppered. Benzene was used as a solvent because of the greater solubility of $Os_3(CO)_{12}$ in benzene compared with paraffin hydrocarbon solvents. The cells were positioned so that they were completely exposed to the light beam after it had passed through a 10 cm path length cell containing cold, flowing water. This meant that the intensity of absorbed light could be expressed as an intensive quantity, in units of einstein L^{-1} s^{-1}, instead of the more usual[10] extensive quantities, dependent on the volume of solution in the cell, measured when the light beam is collimated and impinges only on a limited part of the solution. This is particularly advantageous when reactions are monitored by IR measurements, and samples have to be taken from the reacting solutions at regular intervals leaving an imprecisely known volume of solution behind. The cells were always placed in an identical position so that any effects due to the noncollimation of the light beam were essentially the same from run to run. The temperature of the reacting solutions was 22 ± 1 °C.

Light intensities were routinely measured by using Aberchrome 540 actinometry[11] when Corning glass filters were used. The quantum yield for the Aberchrome 540 was taken as 0.06.[11] Intensities measured with use of this value were found to be within ca. 5% of those found with use of conventional ferrioxalate actinometry,[10] but the Aberchrome actinometer is much quicker and more convenient to use.

When the $NaNO_2$ solution was used as a filter a solution of $Os_3(CO)_{12}$ and 1.0 M 1-octene was used as a secondary actinometer, the quantum yield being taken as 0.030 (see Table I). The $NaNO_2$ filter had the advantage of letting through considerably more light so that quantum yields at higher intensities could be measured. Although longer wavelength light than 436 nm was also incident on the reaction cell, absorbance of this light by the $Os_3(CO)_{12}$ was negligible so the measured quantum yields are those appropriate only to the absorption of the 436-nm light. Knowing the reaction rates (in M s^{-1}), the quantum yield, and the fraction of light absorbed by the Aberchrome enabled the incident intensities to be estimated in einstein L^{-1} s^{-1} or, because of the 1 cm path length of the cells, as light fluxes passing into the cell in units of einstein cm^{-2} s^{-1}. Incident fluxes were measured each time a run was performed and varied typically from (8 to 37) × 10^{-10} einstein cm^{-2} s^{-1}. Effects due to any inhomogeneity of the light beam (due to its noncollimated nature) or the (relatively small) differences in the volume of the solutions will be small in view of the essentially identical procedures followed for actinometry and $Os_3(CO)_{12}$ photolysis. Effects on the *relative* quantum yields obtained with different reactants, different dissolved gases, and different reactant concentrations will be negligible.

Table I. Disappearance Quantum Yields[a] for Reactions of $Os_3(CO)_{12}$ in Benzene at 436 nm

[L], M	$10^2\phi_{av}$	[L], M	$10^2\phi_{av}$	[L], M	$10^2\phi_{av}$
With L = 1-Octene under Ar					
0.013	0.37	0.150	1.73	2.00	3.10
0.020	0.52	0.200	2.19	4.00	2.96
0.038	0.89	0.455	2.53	0.150[b]	1.83
0.060	1.05	0.910	2.95	0.191[b]	2.01
0.080	1.23	1.30	3.02	0.46[b]	2.43
0.100	1.69				
With L = 1-Octene under CO					
0.030	0.52	0.088	1.21	0.500	2.40
0.035	0.68	0.125	1.65	1.00	2.92
0.050	0.76	0.150	1.70	1.50	3.18
0.068	0.95	0.200	1.91		
With [1-Octene] = 1.0 M, and L = Diglyme under Ar					
0	3.02	1.50	1.83	3.00	1.14
0.30	2.54	2.00	1.44	3.50	1.08
1.00	1.99	2.50	1.34		
With L = $P(OEt)_3$ under Ar					
0.030	0.47[c]	0.500	2.47	1.50	3.58
0.058	0.76[c]	0.600	2.64	1.50	3.61
0.110	0.97	0.800	2.96	1.50	3.53
0.200	1.54	1.00	3.28	2.00	3.45
0.300	1.76	1.50	3.60		
With L = $P(OEt)_3$ under CO					
0.15[d]	0.91	0.90	2.84	2.00	3.17
0.30	1.41	1.20	3.34	2.30	3.21
0.30	1.24[e]	1.30	3.06	0.15	0.95[d,f]
0.50	2.01	1.50	3.23	0.15	0.96[d,g]
0.70	2.61				

[a] Values of ϕ_{av} are averages of six or four measurements of ϕ_{obsd} obtained as described in the text. I_0 = ca. 8 × 10^{-10} einstein cm^{-2} s^{-1} unless otherwise stated. [b] Runs were carried out with incident light filtered through $NaNO_2$ solution, and values of ϕ_{obsd} were measured relative to a value of 0.030 for reaction with 1.0 M 1-octene under Ar. I_0 = 36 × 10^{-10} einstein cm^{-2} s^{-1}. [c] These two values were not included in the least-squares analysis, being respectively 53% and 36% higher than values calculated according to the least-squares parameters from Table II. (N.B. of the total 62 values of ϕ_{av} determined in this study only three were omitted from the least-squares analyses. In this case it appears that these results, at the lowest values of $[P(OEt)_3]$, were subject to some systematic errors.) [d] Used to estimate $(k_v)_{CO}/k_{iv}$ = 85 ± 10 in Table III. [e] This value was not included in the least-squares analysis, being 18% lower than the value calculated from the least-squares parameters from Table II. [f] Under 25.9% CO. [g] Under 15.5% CO.

Results

Reaction of $Os_3(CO)_{12}$ with 1-Octene. Irradiation of $Os_3(CO)_{12}$ with 436-nm light in the presence of a pseudo-first-order excess of 1-octene led cleanly to a mixture of $Os(CO)_4(\eta^2\text{-octene})$ and $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-octene})$ as evidenced by the IR spectra of the product solutions from reactions carried out in isooctane. These showed bands at 2117 (w), 2102 (w), 2073 (s), 2029 (vs), 2022 (s sh), 2015 (s), 2005 (m), 1995 (m), and 1989 (br m) cm^{-1}. Apart from the band at 2005 cm^{-1} these can all be matched within a few wavenumbers with bands due to $Os(CO)_4(C_2H_4)$ and $Os_2(CO)_8(C_2H_4)$.[12] The bands can all be matched with those from a mixture of $Os(CO)_4$(methyl acrylate) and $Os_2(CO)_8$(methyl acrylate), but in this case, the bands in the product mixture are consistently lower than corresponding ones for the complexes containing the more electronegative methyl acrylate ligand.[9] The UV-vis spectra showed a sharp isosbestic point throughout the reaction. The position of the isosbestic point varied slightly from 308 to 314 nm, depending on the concentration of 1-octene. The product solutions did not absorb at 436 nm but absorption below 400 nm was such that secondary photolysis of the $Os_2(CO)_6$(octene) occurred on irradiation with light of wavelengths of 366 nm or below. The photokinetics were therefore only followed for 436-nm irradiation.

The course of the reactions was followed by absorbance measurements at 328 nm, the absorbance maximum for $Os_3(CO)_{12}$. The concentration, C_t, of unreacted $Os_3(CO)_{12}$ at any time, t, was estimated from eq 1. The initial concentration, C_0, was generally

$$C_t = C_0(A_t - A_\infty)/(A_0 - A_\infty) \qquad (1)$$

ca. 2 × 10^{-4} M and the absorbance varied from A_0 = ca. 1.8 down

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Table II. Kinetic Parameters Obtained from a Weighted Linear Least-Squares Dependence of $1/\phi_{av}$ on $1/[L]$

L	atmosphere	gradient, M	intercept	$10^2\phi_{lim}$	(ϕ_{av}),[a] %
1-octene	Ar	3.27 ± 0.13	31.5 ± 0.4	3.17 ± 0.04[b]	6.5
1-octene	CO	4.63 ± 0.22	29.3 ± 0.9	3.41 ± 0.11[b]	7.4
$P(OEt)_3$	Ar	9.12 ± 0.47	21.8 ± 0.5	4.59 ± 0.11[c]	5.2
$P(OEt)_3$	CO	13.0 ± 1.3	22.5 ± 1.2	4.44 ± 0.24[c]	8.6
1-octene[d]	Ar	17.0 ± 0.09[e]	33.2 ± 0.9		4.9

[a] Value of $\sigma(\phi_{av})$ found from the deviations of the experimental values of $1/\phi_{av}$ from those calculated by using the least-squares intercepts and gradients. (See Appendix.) [b] The weighted average of these values is 3.20 ± 0.04. [c] The weighted average of these values is 4.56 ± 0.10. [d] Data from dependence of $1/\phi_{av}$ on [diglyme] for reaction with 1.0 M 1-octene in the presence of 0–3.5 M diglyme. [e] Unit of the gradient is M^{-1}.

to A_∞ = ca. 0.75. In addition to A_∞, a total of 8 absorbance measurements were made over the first 25–30% of each reaction. Alternate values (first and third, second and fourth, etc.) were used to estimate six values for the rates, R, from absorbance differences of ca. 0.05–0.1. Average values of I_a were estimated from eq 2 where A_{436} was the average absorbance at 436 nm over the time period from which the particular rate was calculated. Values of the quantum yields, $\phi_{obsd} = R/I_a$, for disappearance of

$$I_a = I_0\{1 - \exp(-A_{436})\} \qquad (2)$$

$Os_3(CO)_{12}$ were found to show no consistent dependence on C_t, i.e., on the extent of reaction followed (e.g., Table IV, supplementary material). Values of ϕ_{av}, the average at each concentration of 1-octene, are given in Table I for reactions in solutions equilibrated with atmospheres of Ar or CO. The values of ϕ_{av} increase with [1-octene] but approach a limiting value. The data are in good accord with eq 3, where L = 1-octene, ϕ_{lim} is the limiting value of ϕ_{av} corresponding to very high concentrations

$$\phi_{av} = a\phi_{lim}[L]/\{1 + a[L]\} \qquad (3)$$

of 1-octene, and a is a constant. This accord is demonstrated by the good linearity of the plots of $1/\phi_{av}$ against 1/[1-octene] shown in Figure 1. Values of $1/\phi_{lim}$ and $1/a\phi_{lim}$ were obtained respectively from the intercepts and gradients found by linear least-squares analysis in which each value of ϕ_{av} was assumed to have the same percent uncertainty.[13] They are given in Table II together with their standard deviations, values of ϕ_{lim} obtained from the inverse of the intercept, and values of $\sigma(\phi_{av})$, the probable errors (standard deviations) of each determination of ϕ_{av} (see Appendix). The fit to eq 3 is excellent, and the parameters obtained are of high precision. This is due both to the extensive replication of data and to the wide ranges of [L] used.

The series of reactions, monitored in exactly the same way but with [1-octene] = 1.0 M and various concentrations of diglyme, show that diglyme retards the reaction (Table I). A plot of $1/\phi_{av}$ vs. [diglyme] is shown in Figure 2 to be linear. A plot of ϕ_0/ϕ_{av} vs. [diglyme] is also linear, the intercept being 1.01 ± 0.05, so Stern–Volmer behavior is being followed.

Reaction of $Os_3(CO)_{12}$ with $P(OEt)_3$. Reactions with $P(OEt)_3$ in benzene proceed with formation of $Os_3(CO)_{11}\{P(OEt)_3\}$ as evidenced by the appearance of absorbance bands at 337 nm and 2053 cm^{-1}, the same values as were found after thermal reaction of $Os_3(CO)_{11}(NCMe)$ with $P(OEt)_3$. Extended photolysis led to complete disappearance of the band at 2068 cm^{-1} due to $Os_3(CO)_{12}$ and to eventual formation of $Os_3(CO)_{10}\{P(OEt)_3\}_2$ and other products. Quantum yields were obtained from data over the first 25–35% reaction when the only product observed was $Os_3(CO)_{11}\{P(OEt)_3\}$. The absorbance at 328 nm did not change appreciably during this proportion of the reaction, and reactions were therefore monitored by measurement of the decreasing absorbance in the IR of the band at 2068 cm^{-1} due to $Os_3(CO)_{12}$ shown by samples removed from the silica cell in which reaction was proceeding. Samples were taken after the cell was removed from the light beam and the solution remaining in the cell was then re-equilibrated with the appropriate gas and the cell tightly stoppered before it was replaced in the light beam. Thermal reactions were sufficiently slow that no reaction took place while the cell was removed from the light beam for sampling. The extinction coefficient of the IR band at 2068 cm^{-1} was measured before any irradiation by direct comparison of its absorbance with

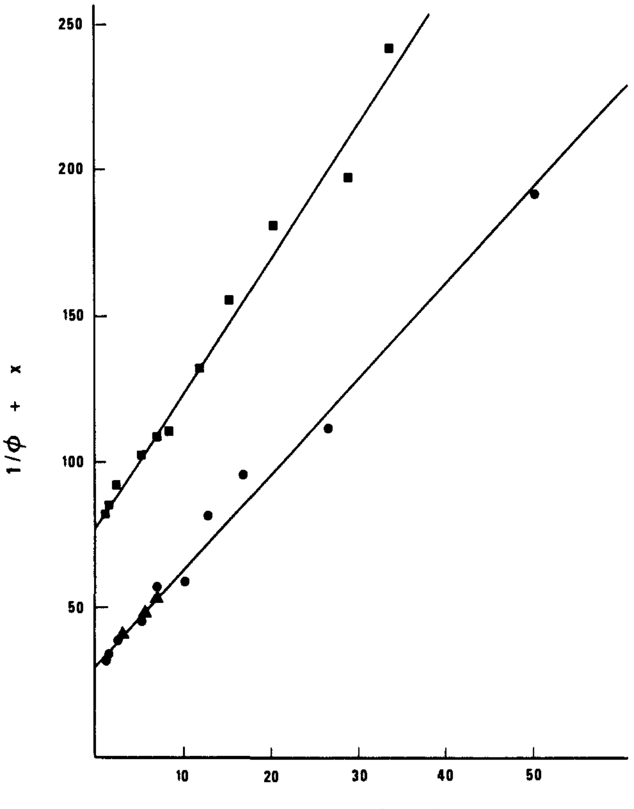

Figure 1. Dependence of $1/\phi$ on 1/[1-octene]: (●) reaction under Ar, $x = 0$, I_0 = ca. 8×10^{10} einstein cm^{-2} s^{-1}; (▲) reaction under Ar, $I_0 = 36 \times 10^{-10}$ einstein cm^{-2} s^{-1}; (■) reaction under CO, $x = 50$.

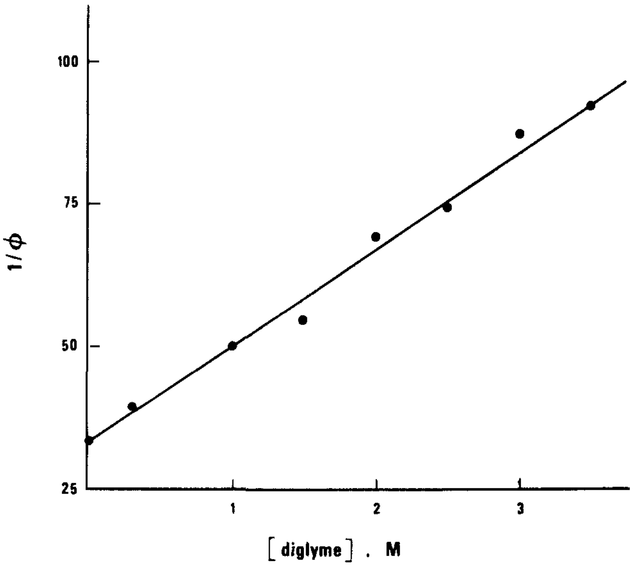

Figure 2. Dependence of $1/\phi$ on [diglyme] for reaction with 1.0 M 1-octene.

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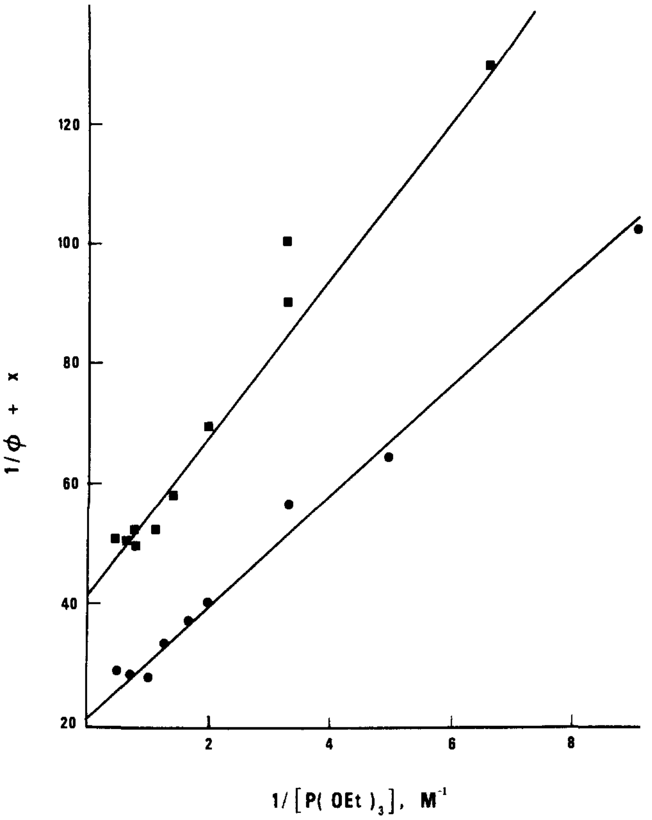

Figure 3. Dependence of $1/\phi$ on $1/[P(OEt)_3]$: (●) reaction under Ar, $x = 0$; (■) reaction under CO, $x = 20$.

the UV absorbance at 328 nm measured at the same time so that concentration changes during the periods of irradiation could be calculated from the fractional decrease in the absorbance at 2068 cm^{-1}. Six absorbance measurements were made over the first 25–35% of reactions so that 4 different values of the rate could be obtained by using absorbances of alternate samples. The total absorbance change was only ca. 0.1 so, in order to maximize the precision, the spectrum of each sample was run 3 times on the slowest possible scan speeds and the absorbances, if different, were averaged. Absorbance differences used for calculating the rates were ca. 0.03–0.04.

The values of I_a were estimated from a knowledge of the extinction coefficients of 560 M^{-1} cm^{-1} for $Os_3(CO)_{12}$ and 1550 M^{-1} cm^{-1} for $Os_3(CO)_{11}\{P(OEt)_3\}$, at 436 nm. The proportion of the total absorbance at a given stage of the reaction that was due to absorbance by $Os_3(CO)_{12}$ rather than $Os_3(CO)_{11}\{P(OEt)_3\}$ was calculated and I_a(total) was multiplied by this fraction to give the value of I_a necessary to calculate ϕ_{obsd}. Thus after 5% reaction ca. 85% of the total light absorbed was absorbed by $Os_3(CO)_{12}$ and, after 25% reaction, this had decreased to ca. 50%.

No change of ϕ_{obsd} with C_t (i.e., with time) was observed. Values of ϕ_{av}, the average of the four measurements of ϕ_{obsd} at each value of $[P(OEt)_3]$, are shown in Table I and are also in good accord with eq 3 (L = $P(OEt)_3$). Plots of $1/\phi_{av}$ against $1/[P(OEt)_3]$ are shown in Figure 3 for reactions under Ar or CO. Least-squares values of the various parameters are given in Table II, again showing the high precision resulting from replication and wide ranges of [L].

A value $10^2\phi_{av} = 3.38 \pm 0.05$ was found for reaction with 1.0 M P-n-Bu$_3$ which compares with the value of 3.23 estimated for reaction with 1.0 M $P(OEt)_3$ from the data in Table II. Reaction with 1.16 M $P(OEt)_3$ *and* 1.27 M 1-octene occurred with $10^2\phi_{av} = 3.39 \pm 0.08$.

Discussion

The Reaction Scheme. Any mechanistic scheme for these reactions has to take into account the following observations:

(1) The values of ϕ_{av} increase with [L] (L = 1-octene or $P(OEt)_3$) to limiting values, ϕ_{lim}, in qualitatively the same way irrespective of whether L is 1-octene or $P(OEt)_3$, or of whether the reactions are carried out under Ar or CO. When reaction is followed with mixtures of $P(OEt)_3$ and 1-octene the value of ϕ_{av} is *not* equal to the sum of the values observed separately.

(2) The values of ϕ_{lim} are quite low and those for $P(OEt)_3$ and 1-octene are distinguishably different from each other. (The difference between the respective weighted averages of $10^2\phi_{lim}$ in Table II is 1.36 ± 0.11.)

(3) The effect of the presence of CO on both the fragmentation and substitution reactions is to reduce the rate of rise to ϕ_{lim} with increasing [L] but not to affect the value of ϕ_{lim}. (The gradients quoted in Table II and shown in Figures 2 and 3 for reactions under CO are larger than for reactions under Ar by 1.36 ± 0.26 M and 3.88 ± 1.38 M for the fragmentation and substitution reactions, respectively.)

(4) For the fragmentation reaction with 1-octene, values of ϕ_{av} that are significantly less than ϕ_{lim} are not affected when I_a is changed by a factor of almost 5 (Table I).

(5) The effect of diglyme on reactions with 1-octene is to decrease the values of ϕ_{av} according to Stern–Volmer systematics (Figure 2).

Observation (1) shows that reactions occur via photogeneration of a reactive intermediate or intermediates than can revert to $Os_3(CO)_{12}$ in competition with reaction with L to form products. The same intermediate must be involved in reactions with $P(OEt)_3$ and 1-octene because otherwise the value of ϕ_{av} observed with the mixtures would be equal to the sum of those observed with each reactant individually. Observation (3) shows that the reactive intermediate is not $Os_3(CO)_{11}$ and that CO dissociation plays a negligible role in the reaction. If the less-than-limiting values of ϕ_{av} for reactions under Ar were low because of reaction of photogenerated $Os_3(CO)_{11}$ with the small, equivalent amount of CO released, then the coordinatively unsaturated $Os_3(CO)_{11}$ must be extraordinarily sensitive to CO compared with 1-octene or $P(OEt)_3$. This is because [CO] must be $\lesssim 5 \times 10^{-5}$ M, even when L = $P(OEt)_3$ and CO is actually released during the reaction, yet this amount of CO would have to compete quite successfully with $P(OEt)_3$ when its concentration is as high as 0.3 M (Table I). If this were so one would expect that an increase of [CO] to ca. 10^{-2} M (as when reactions are carried out in solutions equilibrated with 1 atm of CO) would almost completely inhibit the reaction whereas, at $[P(OEt)_3] = 0.3$ M, ϕ_{av} is only decreased by ca. 25%. This argument applies even more strongly to fragmentation reactions with 1-octene when no CO release is required by the stoichiometry. Finally one would expect a substantial decrease in ϕ_{obsd} as more and more CO is released during the course of reaction with $P(OEt)_3$. No such decrease was observed.

Observation (4) shows that reactive fragments such as $Os_2(CO)_8$ and $Os(CO)_4$ are not photogenerated intermediates,[9] the recombination of which leads to the lower values of ϕ_{av} at lower [1-octene]. This regeneration would be a second-order reaction in competition with pseudo-first-order reactions of the fragments with 1-octene. This would imply that ϕ_{av} would be significantly dependent on I_a,[14,15] yet this is not what is observed. Such photoinduced fragmentation would be expected to lead to formation of $Os(CO)_4L$ in reactions when L = P donor yet no such mononuclear products have been observed here or elsewhere.[3,8]

We must therefore conclude that the reactions proceed via a common photogenerated intermediate which must be a chemically reactive isomeric form of $Os_3(CO)_{12}$. This conclusion, coupled with the other observations described above, can most simply be accounted for in terms of the reactions shown in Scheme I. $Os_3(CO)_{12}^*$ represents the electronically excited form of $Os_3(CO)_{12}$ produced by absorption of the 436 nm quantum of light. Reaction i represents the deexcitation of $Os_3(CO)_{12}^*$ that probably occurs by radiationless decay.[16] Reaction ii involves conversion of the electronically excited $Os_3(CO)_{12}^*$ to the chemically reactive

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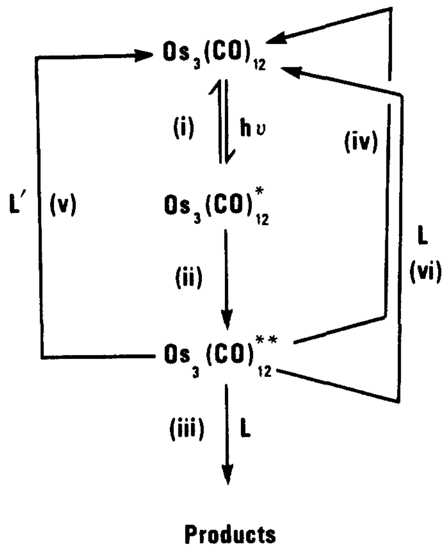
(14) Laine, R. M.; Ford, P. C. *Inorg. Chem.* **1977**, *16*, 388–391.

(15) Fox, A.; Poë, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 2497–2499.

(16) No reports of emission from $Os_3(CO)_{12}$ at ambient temperatures appear to have been made.

Scheme I



isomeric intermediate $Os_3(CO)_{12}$**. This intermediate must be relatively long lived because it is capable of discrimination between a number of bimolecular reaction paths. Thus, it can undergo reaction iii with a suitably reactive ligand L and form products. This reaction can involve substitution (with P-donor ligands) or fragmentation (with olefines). Alternatively, $Os_3(CO)_{12}$** can revert to $Os_3(CO)_{12}$ in one of three possible ways, i.e., via reaction iv, involving "spontaneous" first-order reversion that occurs without intervention by any added reagents (reaction iv might, of course, involve pseudo-first-order reaction induced by the solvent); via reaction v, involving bimolecular attack on $Os_3(CO)_{12}$** by an added Lewis base, L', that is not sufficiently reactive to cause formation of any reaction products; and via reaction vi, which involves attack on $Os_3(CO)_{12}$** by the same ligand, L, that is capable of producing products but that can also cause reversion to $Os_3(CO)_{12}$.

The Rate Equation and Derivation of Relative Rate Constants. The reaction scheme leads to the rate equation shown, in alternative forms, in eq 4 and 5. ϕ_{max} is defined as $k_{ii}/(k_i + k_{ii})$ and represents the quantum yield for formation of $Os_3(CO)_{12}$**. Equation 4 allows for an increase in ϕ with increasing [L] until

$$\phi = \phi_{max}k_{iii}[L]/\{k_{iii}[L] + k_{iv} + k_v[L'] + k_{vi}[L]\} \quad (4)$$

$$1/\phi = (k_{iii} + k_{vi})/k_{iii}\phi_{max} + (k_{iv} + k_v[L'])/k_{iii}\phi_{max}[L] \quad (5)$$

a limitingvalue, shown in eq 6, is reached. Plots of $1/\phi$ against $1/[L]$ will be linear (Figures 1 and 3), and the inverse of the

$$\phi_{lim} = \phi_{max}k_{iii}/(k_{iii} + k_{vi}) \quad (6)$$

intercepts gives the value of ϕ_{lim} (Table II). These can be dependent on the nature of L because of different ratios k_{iii}/k_{vi}. The ratio gradient/intercept of the inverse plots will lead to values of $k_{iv}/(k_{iii} + k_{vi})$ in the absence of added L'. When [L'] = finite and constant the inverse plots will have higher gradients as shown in Figures 1 and 3 for reactions carried out under CO. Alternatively, if [L] is constant and [L'] is varied, as is the case for reaction with 1 M 1-octene in the presence of various concentrations of diglyme, then a plot of $1/\phi$ against [L'] will be linear as in Figure 2. Behavior of this type is also shown by reactions with $[P(OEt)_3] = 0.15$ M in solutions equilibrated with 100%, 25.9%, and 15.5% CO. The proposed scheme is therefore fully consistent with all the trends shown by the data.

The values of the intercepts and/or gradients of the plots in the figures enable calculations of various relative rate constants to be made. Since ϕ_{max} and k_{iv} are common to both reactions, the relative gradients for reactions with 1-octene and $P(OEt)_3$ under Ar provide a value of 2.79 ± 0.18 for $(k_{iii})_{oct}/(k_{iii})_p$. The ratio intercept/gradient provides $(k_{iii} + k_{vi})/k_{iv}$ for both reactants, and values of $(k_v)_{CO}[CO]/k_{iv}$ can be obtained from the difference between the gradients under CO and under Ar, divided by the gradient under Ar. Independent values can be obtained from data for reactions with 1-octene and $P(OEt)_3$. A rather more precise value of $(k_v)_{CO}/k_{iv}$ can be obtained from the differences between the value of $1/\phi_{av}$ for reaction with 0.15 M $P(OEt)_3$ under Ar and those for reactions with the same concentration of $P(OEt)_3$ under 16%, 26%, and 100% CO. The concentration of CO under 100% CO is taken to be 0.66×10^{-2} M.[17] All three independent estimates are in good agreement. A value of $(k_v)_{dig}/k_{iv}$ can be obtained from the gradients in the presence and absence of diglyme. The values for these rate constant ratios are all shown in Table III. The respective values of $(k_{iii} + k_{vi})$ etc. allow the calculation of $10^2\phi_{av}$ for mixtures of 1.16 M $P(OEt)_3$ and 1.27 M 1-octene. A value of 3.27 ± 0.17 is found which is in excellent agreement with the experimental value of 3.39 ± 0.08. The fact that the quantum yields for reaction with 1.0 M $P(OEt)_3$ or P-n-Bu_3 are almost identical suggests that the various rate constants for these two P-donor ligands are very similar.

Table III. Relative Rate Constants for Reactions of $Os_3(CO)_{12}$**

rate constant, k, M^{-1} s^{-1}	k/k_{iv}, M^{-1}			
$(k_v)_{CO}$[a]	63 ± 12[b]	65 ± 23[c]	85 ± 10[d]	75 ± 8[e]
$(k_v)_{dig}$[a]	5.2 ± 0.4			
$(k_{iii})_p + (k_{vi})_p$[a]	2.40 ± 0.18			
$(k_{iii})_{oct} + (k_{vi})_{oct}$[a]	9.64 ± 0.50			
$(k_{iii})_p$	2.4[f]	1.1[g]	0.55[h]	0.11[i]
$(k_{iii})_{oct}$	6.8[f]	3.1[g]	1.55[h]	0.31[i]
$(k_{vi})_p$	0[f]	1.3[g]	1.85[h]	2.3[i]
$(k_{vi})_{oct}$	2.9[f]	6.6[g]	8.1[h]	9.3[i]

[a] Independent of value of ϕ_{max}. [b] From difference between gradients of inverse plots for reaction with 1-octene under Ar and CO. [c] From difference between gradients of inverse plots for reaction with $P(OEt)_3$ under Ar and CO. [d] From data for reaction with 0.15 M $P(OEt)_3$ under 0%, 15.5%, 25.9%, and 100% CO. [e] Weighted average of preceding three values. [f] If $(k_{vi})_p = 0$ and, hence, $\phi_{max} = 0.0456$. [g] If $\phi_{max} = 0.1$. [h] If $\phi_{max} = 0.2$. [i] If $\phi_{max} = 1.0$.

Values of k_{iii} and k_{vi} cannot be estimated individually and precisely from the data available here. However, since $(k_{iii})_{oct}/(k_{iii})_p = 2.8$ and $\{(k_{iii})_{oct} + (k_{vi})_{oct}\}/\{(k_{iii})_p + (k_{vi})_p\} = 4.0$ it follows that $(k_{vi})_p < (k_{vi})_{oct}$ and it is therefore possible that $(k_{vi})_p = 0$. The intercepts of the inverse plots for reaction with $P(OEt)_3$ then give $\phi_{max} = 0.0456$ (Table II), and it cannot be less than this. Taking $(k_{vi})_p = 0$ it is then easy to obtain values of $(k_{iii})_p$, $(k_{iii})_{oct}$, and $(k_{vi})_{oct}$, relative to k_{iv}. On the other hand, we know that ϕ_{max} cannot be greater than 1.0 when the intercepts provide values of (k_{iii}/k_{vi}) for both reactants. Values of $(k_{iii})_p$, $(k_{vi})_p$, $(k_{iii})_{oct}$, and $(k_{vi})_{oct}$ can then all be obtained relative to k_{iv}. The two sets of parameters corresponding to the limiting values of 0.0456 and 1.0 for ϕ_{max} are both included in Table III. The sets differ from each other quite pronouncedly for the following reason. If ϕ_{max} is small then the small values of ϕ_{lim} are caused mainly by this factor and the importance of the k_{vi} terms is correspondingly less, the values of $k_{iii} + k_{vi}$ being determined wholly or to a major extent by the k_{iii} term. If ϕ_{max} is large then the only reason why the values of ϕ_{lim} are so small is because the k_{vi} terms are relatively much more important than the k_{iii} terms. With the data available here there is no way of knowing which of the extreme sets or which intermediate set (two of which are also given in Table III) is the correct one. However, it seems improbable that $P(OEt)_3$ would be completely ineffective at inducing reversion of $Os_3(CO)_{12}$** to $Os_3(CO)_{12}$ when diglyme and 1-octene (and, probably, benzene) are quite good, and it therefore seems likely that $\phi_{max} \gtrsim 0.1$. In this case the ratio of rate constants for reversion compared with those for forward reaction vary from ca. 1 to 20 for $P(OEt)_3$ and ca. 2 to 30 for 1-octene. The order of effectiveness in inducing reversion when $\phi_{max} = 0.1$–1.0 is always 1-octene > diglyme > $P(OEt)_3$, and 1-octene is always more effective in inducing reaction (fragmentation) than is $P(OEt)_3$ (substitution).

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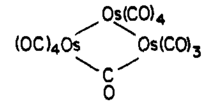
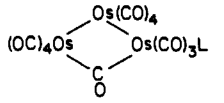
(17) Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1–9. Weast, R. C., Ed. *Handbook of Chemistry and Physics*; The Chemical Rubber Co.: Cleveland, OH, 1980; p D208.

The value of $(k_v)_{CO}$ in Table III should more properly be taken to represent $(k_{iii})_{CO} + (k_{vi})_{CO}$ since the substitution of a free CO for a coordinated one would not have been detected. We do not know the relative contributions of $(k_{iii})_{CO}$ and $(k_{vi})_{CO}$ to the observed value of ca. 75 M^{-1} (Table III), but any roughly equal division would imply that CO is the most effective ligand of all those studied at inducing either reversion or forward reaction (substitution) in $Os_3(CO)_{12}^{**}$.

The Nature of $Os_3(CO)_{12}^{**}$ and Its Reactions. Photoreactions of $Os_3(CO)_{12}$ with seeveral chlorocarbon solvents proceed with very much smaller quantum yields[8] than those with 1-octene, $P(OEt)_3$, or P-*n*-Bu_3. It therefore seems unlikely[5,6,8] that $Os_3(CO)_{12}^{**}$ is a diradical species formed by photoinduced homolysis of one of the Os–Os bonds. $Os_3(CO)_{12}Cl_2$ does undergo photofragmentation reaction with CCl_4 with quite high efficiency and the Os-centered radicals presumably formed in this reaction must be effective scavengers of Cl atoms from CCl_4.[8] An alternative formulation, I, is characterized by the presence of a vacant coordination site on one Os atom created by metal migration, i.e.,


I

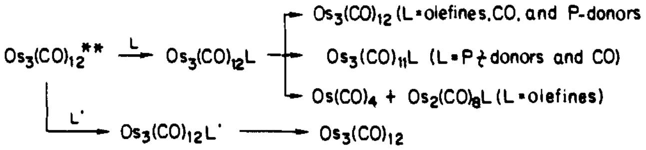

II

the electron pair formally involved in an Os–Os bond has migrated onto the C atom of a CO ligand. The process can also be looked on as the insertion of a terminal CO ligand into an Os–Os bond. Attack by L at the vacant coordination site would give the 18-electron molecule II. This can undergo various further reactions which determine both the nature of the products and the values of the limiting quantum yield.

When L = 1-octene, $Os_3(CO)_{12}$(1-octene) can undergo fragmentation to form $Os(CO)_4$(1-octene) and $Os_2(CO)_8$, or $Os(CO)_4$ and $Os_2(CO)_8$(1-octene). The unsaturated fragments can then react rapidly with another 1-octene molecule. For reasons which will be considered below, we favor the latter pair as being initial products of the fragmentation. Alternatively, when L = $P(OEt)_3$, the intermediate $Os_3(CO)_{12}\{P(OEt)_3\}$ undergoes CO dissociation, reformation of the Os–Os bond, and consequent formation of $Os_3(CO)_{11}\{P(OEt)_3\}$. We envisage this process to be concerted, a terminal CO being lost from the Os atom and the bridging CO being reconverted to a terminal one with Os–Os bond formation all at the same time. This is because of the nature of the reversion processes v and vi, and probably process iv as well. Thus, $Os_3(CO)_{12}L$ could lose L instead of CO. If it did this in a concerted manner it would lead directly to $Os_3(CO)_{12}$, but if it lost it to reform $Os_3(CO)_{12}^{**}$ instead then L would not be inducing direct reversion to $Os_3(CO)_{12}$ which, in the absence of L′, would occur only via reaction iv. ϕ_{lim} could not then be dependent on the nature of L as is observed here and as is also found for photofragmentation reactions of $Ru_3(CO)_{12}$.[6,18] This analysis applies even more strikingly to the effect of L′. If L′ adds to the vacant coordination site to form $Os_3(CO)_{12}L'$ this must react directly to form $Os_3(CO)_{12}$ and not form it via reversion to $Os_3(CO)_{12}^{**}$. In the latter case, formation of $Os_3(CO)_{12}L'$ would simply be a dead end, kinetically irrelevent side reaction and L′ could not influence the kinetics. Although we have only studied these reactions with benzene as a solvent, photofragmentation of $Ru_3(CO)_{12}$ with CO and P donors is very solvent dependent, the solvent affecting the rate of rise to ϕ_{lim} but not ϕ_{lim} itself.[6,18] Reaction iv can, therefore, be very solvent dependent, and the solvent is probably acting as another example of L′.

This analysis implies that reactions iii and vi have an initial step in common, namely formation of $Os_3(CO)_{12}L$ as shown in Scheme II. This has no effect on the rate equation apart from the fact that k_{iii} and k_{vi} represent combinations of rate constants. It is, of course, possible that reversion of $Os_3(CO)_{12}^{**}$ to $Os_3(CO)_{12}$ is caused by attack by L or L′ at a different position from the vacant coordination site, but this seems to us to be less likely.

Scheme II



This part of the overall mechanism shown in Scheme II is very similar to that proposed[19] by Ford et al. for photolysis of $Ru_3(CO)_{12}$ apart from the fact that $Ru_3(CO)_{12}L$ appears only to undergo fragmentation while $Os_3(CO)_{12}L$ can undergo fragmentation or substitution, depending on the nature of L. Another feature is the fact that $Os_3(CO)_{12}L$ can revert to $Os_3(CO)_{12}$ instead of forming products. This is also possible for $Ru_3(CO)_{12}L$ since ϕ_{lim} for photolysis of $Ru_3(CO)_{12}$ is also dependent on the nature of L.[6,18,20]

The photolyses of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ are characterized much more by their similarity than by their differences. Apart from the fact that $Os_3(CO)_{12}L$ undergoes CO loss rather than fragmentation when L is a P-donor ligand, the patterns of behavior are qualitatively identical and quantitatively very similar. It is interesting that the olefine in $Os_3(CO)_{12}$(olefine) is capable of causing Os–Os bond breakage whereas CO, PPh_3,[8] $P(OEt)_3$, or even P-*n*-Bu_3 are not. All these ligands are capable of causing $Ru_3(CO)_{12}L$ to undergo fragmentation.[3-9]

The greater ease of fragmentation of $Ru_3(CO)_{12}L$ is easily understood. Bonds between second-row metals are generally weaker than those between third-row metals,[22] and Ru–Ru bonds are specifically weaker than Os–Os bonds.[23] Why olefins seem to be the only ligand type capable of causing fragmentation of $Os_3(CO)_{12}L$ is less clear. If, however, the initial fragmentation products are, indeed, $Os_2(CO)_8L$ and $Os(CO)_4$, as proposed above, then their formation when L = olefins but not when L = P donors or CO can be understood in terms of the evidently[9] much greater stability of $Os_2(CO)_8$(ol) compared with $Os_2(CO)_8L$ (L = P donor or CO).[24]

It is important to note that it is the thermal reactivity of intermediates such as $M_3(CO)_{12}^{**}$ and $M_3(CO)_{12}L$ that determines the natures of the photochemically produced products and the photochemical kinetics. It is also entirely possible that ϕ_{max} is as high as 1.0. The low values of ϕ_{lim} for these clusters are not necessarily due to any photophysical factors but could be due to a relatively high ability of L to cause $M_3(CO)_{12}^{**}$ to revert to $M_3(CO)_{12}$ rather than to form products. The initial photochemical product could also be a diradical species, produced by photoinduced homolysis of one M—M bond, provided that the diradical reverts to $M_3(CO)_{12}$ or forms $M_3(CO)_{12}^{**}$ more rapidly than it reacts with CCl_4, etc. The low, but finite, quantum yields for reactions with halocarbons[5,6,8] would then be the consequence of a small amount of successful scavenging of the diradicals in neat halocarbon solution.[25] Initial formation of diradicals could explain the formation of a bridging CO species such as I. Unpaired electron density in 17-electron metal-centered radicals is partly delocalized onto the CO ligands.[27] Pairing of one electron, centered on a metal atom, with another, centered on a C atom,

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(18) Brodie, N.; Malito, J.; Markiewicz, S.; Poë, A. J., unpublished observations.

(19) Desrosiers, M. F.; Wink, D. A.; Ford, P. C. *Inorg. Chem.* **1985**, *24*, 1-2.

(20) Photosubstitution of $Co(CO)_3(NO)$ has been proposed[21] to proceed via an isomeric reactive intermediate with a vacant coordination site. Values of ϕ_{lim} in this case are also dependent on the nature of the entering ligand.

(21) Evans, W.; Zink, J. I. *J. Am. Chem. Soc.* **1981**, *103*, 2635-2640.

(22) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71-110.

(23) Quicksall, C. O.; Spiro, T. G. *Inorg. Chem.* **1968**, *7*, 2365-2369.

(24) Moss, J. R.; Graham, W. A. G. *J. Chem. Soc., Dalton Trans.* **1977**, 95-99.

(25) Recombination of Re-centered diradicals, generated photochemically from $Re_2(CO)_8(\mu$-dppm), is very rapid although Cl abstraction from CCl_4 can compete to some extent.[26]

(26) Lee, K.-W.; Pennington, W. T.; Cordes, A. W.; Brown, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 631-641.

(27) Herrinton, T. R.; Brown, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 5700-5703 and references therein.

could compete with pairing of two unpaired electrons both centered on a metal atom. Besides the detailed distribution of unpaired electrons between the metal and the CO ligands, steric effects could also be important here.

These considerations suggest that discussion of the photochemical behavior of metal carbonyl clusters, in terms either of spectroscopic data or of theoretical calculations on the clusters themselves,[28] is quite misdirected. Finally, it seems very likely that higher energy photolysis of $Os_3(CO)_{12}$ will induce CO dissociation, as well as formation of $Os_3(CO)_{12}^{**}$, as has been found for $Ru_3(CO)_{12}$.[19]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council, Ottawa, for support.

Appendix

The quantum yield data were analyzed statistically as follows. Reactions with 1-octene under Ar provided thirteen sets of six values of ϕ_{obsd}, one set for each run with a defined value of [1-octene]. The deviation of each member of a set from the average, ϕ_{av}, of the set provided a value of $\Delta = 100(\phi_{obsd} - \phi_{av})/\phi_{av}$. The 78 values of Δ were used to calculate $\sigma(\phi_{obsd}) = 100\{\Sigma\Delta^2/(78 - 13)\}^{1/2} = 8.5\%$ by the method of pooled variances[13] which assumes that a constant value of $\sigma(\phi_{obsd})$ expressed as a percentage uncertainty is applicable to all the measurements. This value for the probable error of a single determination of ϕ_{obsd} was useful in enabling the conclusion to be drawn that ϕ_{obsd} showed no significant trend with time during any given reaction. It also provided an estimate for $\sigma(\phi_{av})$ of $8.5/\sqrt{6} = 3.5\%$. Similarly, the 66 values of ϕ_{obsd} from the eleven different values of [1-octene] used for reaction under CO led to $\sigma(\phi_{obsd}) = 7.5\%$ and $\sigma(\phi_{av}) = 3.1\%$, and the 45 values of ϕ_{obsd} at [1-octene] = 1.0 M and 8 different values of [diglyme] led to $\sigma(\phi_{obsd}) = 6.6\%$ and $\sigma(\phi_{av}) = 2.7\%$. These three independent estimates of the internal consistency of the measurements of ϕ_{obsd} during a run show that the assumption of an essentially constant value of $\sigma(\phi_{obsd})$ for reaction with 1-octene is a good one, even when reactions are carried out under quite different conditions. Pooling all 192 values of ϕ_{obsd} gave $\sigma(\phi_{obsd}) = 7.9\%$ and $\sigma(\phi_{av}) = 3.2\%$. A similar pooling of all 108 values of ϕ_{obsd} from four measurements at each of fourteen different values of $[P(OEt)_3]$ for reactions under Ar, and thirteen different values of $[P(OEt)_3]$ for reactions under CO, led to $\sigma(\phi_{obsd}) = 8.9\%$ and $\sigma(\phi_{av}) = 8.9/\sqrt{4} = 4.5\%$.

These values of $\sigma(\phi_{obsd})$ are based on the internal consistency of measurements within a given run and do not allow for uncertainties that arise from uncertainties in [1-octene] etc. in different reaction mixtures. A measure of the combined uncertainties can be obtained from the goodness of fit of the data to eq 3. Thus, if Δ is the percent deviation, $100(\phi_{av} - \phi_{calcd})/\phi_{calcd}$, of a value of ϕ_{av} from that calculated according to the least-squares parameters for the dependence of $1/\phi_{av}$ on 1/[1-octene], $1/[P(OEt)_3]$, or [diglyme], then the probable error in ϕ_{av}, $\sigma(\phi_{av})$, is given by $100\{\Sigma\Delta^2/(N - 2)\}^{1/2}t_{N-2}(95\%)/1.96$: N is the number of values of ϕ_{av} (one for each value of [1-octene], etc.), t_{N-2} (95%) is the "Student's t value"[13] for 95% confidence and $N - 2$ degrees of freedom, and 1.96 is the "Student's t value" for 95% confidence and an infinite number of degrees of freedom. The value $1.96\sigma(\phi_{av})$ is, therefore, an exact measure of the 95% confidence limit for each value of ϕ_{av} so that, in this sense, the values of $\sigma(\phi_{av})$ are exactly equivalent to what would have been obtained from an infinite number of measurements. The values of $\sigma(\phi_{av})$ listed in Table II were obtained in this way and are necessarily as large or larger than those derived simply from the internal consistency during each reaction. The uncertainties listed for the parameters in Table II are derived from these larger values of $\sigma(\phi_{av})$.

These different ways of analyzing the reproducibility of the data provide an objective assessment which is remarkably consistent and which emphasizes the good precision of the measurements of individual values of ϕ_{obsd}. The excellent precision obtained for the values of ϕ_{av} and the derived parameters results from the extensive replication of the values of ϕ_{obsd} and the wide ranges of [L] that were used.

Registry No. $Os(CO)_4(B)$ (B = η^2-octene), 101954-35-2; $Os_2(CO)_8(B)$ (B = μ-η^1,η^2-octene), 101954-36-3; $Os_3(CO)_{11}\{P(OEt)_3\}$, 101954-37-4; $Os_3(CO)_{10}\{P(OEt)_3\}_2$, 101954-38-5; $Os_3(CO)_{12}$, 15696-40-9; $P(OEt)_3$, 122-52-1; CO, 630-08-0; 1-octene, 111-66-0; diglyme, 111-96-6; benzene, 71-43-2.

Supplementary Material Available: Table of values of ϕ_{obsd} for reaction with 1-octene under Ar (1 page). Ordering information is given on any current masthead page.

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[28] E.g.: Delley, B.; Manning, M. C.; Ellis, D. E.; Berkowitz, J.; Trogler, W. C. *Inorg. Chem.* **1982**, *21*, 2247–2253 and references therein.