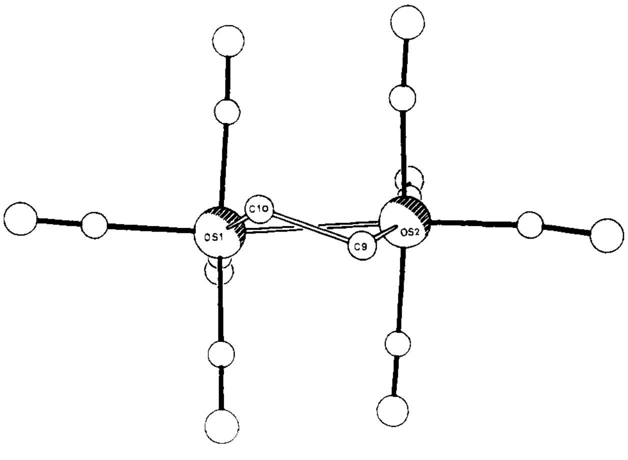
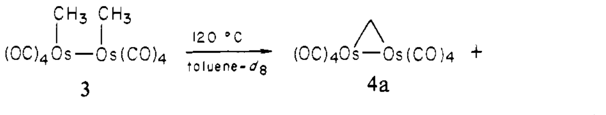


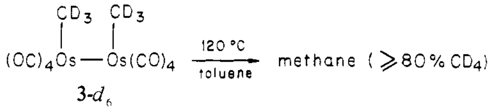
Figure 1. Molecular structure of $((\mu\text{-CC}')CH_2CH_2)Os_2(CO)_8$ (**4b**). Distances (Å): Os(1)-Os(2), 2.883 (1); Os(1)-C(10), 2.22 (2); Os(2)-C(9), 2.22 (2); C(9)-C(10), 1.53 (3). Angles (deg): Os(1)-Os(2)-C(9), 70.1 (6); Os(2)-C(9)-C(10), 105.7 (13); C(9)-C(10)-Os(1), 103.8 (12); C(10)-Os(1)-Os(2), 71.1 (5).

from ethylene and methylene-bridged dimers.

The diosmacyclopropane **4a** is also formed upon thermolysis of the dimethyl analog **3** with elimination of methane. As shown by the labeling experiments (eq 8 and 9) solvent attack is not



(8)



(9)

involved. (Again **4a** is unstable under the reaction conditions, but NMR shows that it reaches a maximum concentration of 40% of the initial concentration of **3**.) Similar reactions presumably explain the several reported cases[32] where methylene-bridged dimers are formed under conditions that would have been expected to generate dimethyl complexes. An investigation into the mechanism of methane elimination from **3** is in progress.

Acknowledgment. This work was supported by NSF Grants CHE-7920373 and CHE-8207597. The Nicolet R3m/E diffractometer and computer system were purchased with funds provided by NSF Grant CHE-8103011. We are grateful to Johnson Matthey, Inc., for a generous loan of OsO_4, to Professor J. K. Stille and K. E. Warner for helpful discussions, and to Professor R. G. Bergman for preprints of ref 8 and 9.

Registry No. **3**, 82666-17-9; **4a**, 83705-04-8; **4b**, 83705-05-9; **4c**, 83705-06-0; $Na_2[Os_2(CO)]_8$, 83705-03-7; $CH_2(OTs)_2$, 24124-59-2; $TsOCH_2CH_2OTs$, 6315-52-2; $I(CH_2)_3I$, 627-31-6; C_2H_4, 74-85-1; Os, 7440-04-2.

Supplementary Material Available: Listing of atomic coordinates and thermal parameters for $((\mu\text{-CC}')CH_2CH_2)Os_2(CO)_8$ (1 page). Ordering information is given on any current masthead page.

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Photosensitized Fragmentation of Some Dinuclear Metal Carbonyls[1]

Arnold Fox, Anthony Poë,* and Ronald Ruminski

J. Tuzo Wilson Laboratories
Erindale Campus, University of Toronto
Mississauga, Ontario, Canada L5L 1C6

Received April 19, 1982

Photoinduced homolytic fission of the metal–metal bonds in dinuclear metal carbonyls is well-known to follow absorption of light in the "metal–metal-bond region" of the complexes' UV–vis spectra.[2,3] When the radicals so produced are scavenged by halogen compounds, mononuclear carbonyl halides are usually formed. However, the success of such reactions depends on the absorption of light of the correct wavelength, one that can often lie in the near UV rather than the visible part of the spectrum.[2,4] We report here the sensitization of such reactions by biacetyl (2,3-butanedione, BA), excited to its triplet state with visible radiation. Sensitization of CO dissociation from $M(CO)_6$ (M = Cr, Mo, and W) has been observed,[5,6] and $Mn_2(CO)_{10}$ and several mononuclear carbonyls have been found to quench the phosphorescence of UO_2^{2+} in aprotic solvents.[7] No simple fragmentation reactions of metal–metal-bonded carbonyls appear to have been reported, however.

We have measured[8] quantum yields, ϕ_{obs}, for loss of $Mn_2(CO)_{10}$, according to reaction 1, following absorption of 436-nm radiation

$$Mn_2(CO)_{10} \xrightarrow[CCl_4]{BA,\ 436\ nm} 2Mn(CO)_5Cl \qquad (1)$$

by BA in carbon tetrachloride solutions under N_2 at 23.5 °C. Values of ϕ_{obsd} were found to increase with increasing $[Mn_2(CO)_{10}]$ to a limiting value, ϕ_l, according to eq 2 where a is a constant.

$$\phi_{obsd} = \phi_l a[Mn_2(CO)_{10}]/(1 + a[Mn_2(CO)_{10}]) \qquad (2)$$

A plot of $1/\phi_{obsd}$ against $1/[Mn_2(CO)_{10}]$ is shown in Figure 1 for data when [BA] = 0.5 or 1.0 M. A weighted least-squares analysis of these data leads to the values $\phi_l = 0.82 \pm 0.04$ and $a_{N_2} = (10.1 \pm 1.6) \times 10^3\ M^{-1}$. The standard deviation for each measurement of ϕ_{obsd} is ±9.1% when defined by $\{\sum\Delta^2/(N-2)\}^{1/2}$, Δ being the percent difference between ϕ_{obsd} and the value of ϕ calculated from the least-square parameters, and N being the number of exper-

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[1] Presented at the 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 30, 1982; INORG. 47.

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[8] $Mn_2(CO)_{10}$ (Strem Chemicals, Inc.) and $Re_2(CO)_{10}$ (Alfa Products) were used as received. $Re_2(CO)_8(PPh_3)_2$ was prepared conventionally by the thermal substitution reaction of PPh_3 with $Re_2(CO)_{10}$ and its purity checked by IR spectroscopy. Biacetyl (BDH Chemicals) was used as received. Standard photochemical techniques were used, the irradiation source being a 450-W Hanovia high-pressure quartz mercury vapor lamp, and the 436-nm line was isolated by the use of apropriate Corning Glass filters. Incident intensities (5×10^{-8} einsteins min^{-1}) were measured relative to ferrioxalate actinometry. Solutions were contained in 1.0-cm path-length silica cells fitted with a Springham high-vacuum 2-mm stopcock and were deoxygenated by several freeze–pump–thaw cycles before thermostating at 23.5 °C and irradiation with stirring. The extent of reaction of the $Mn_2(CO)_{10}$ was followed by UV–vis spectrophotometry, and in some cases the formation of $Mn(CO)_5Cl$ was monitored by IR measurements. Quantum yields for formation of $Mn(CO)_5Cl$ were an average of 1.8 times those for loss of $Mn_2(CO)_{10}$ with a mean deviation of 0.2. No other carbonyl-containing products were observed. When necessitated by the use of higher concentrations of $Mn_2(CO)_{10}$, corrections were applied for direct photolysis caused by absorption of the 436-nm light by the complex. Luminescence measurements were made by using a SLM 4800S spectrofluorimeter (SLM Instruments, Urbana, IL).

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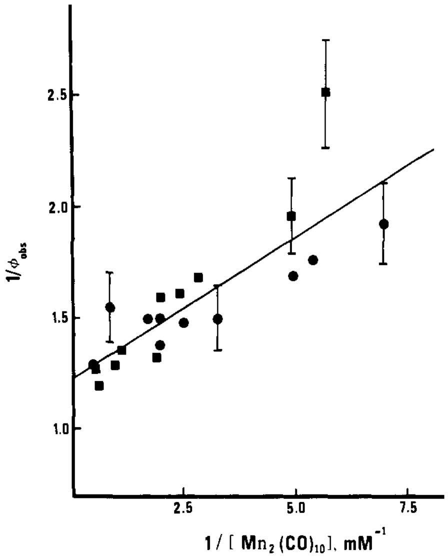

Figure 1. Dependence of $1/\phi_{obsd}$ on $1/[Mn_2(CO)_{10}]$ for photosensitization of reaction 1 in deoxygenated solutions by biacetyl (BA): (●) [BA] = 0.5 M; (■) [BA] = 1.0 M. Error bars exemplify the standary deviation of ±9% found for individual measurements of ϕ_{obsd}, and the line drawn is based on parameters obtained from a weighted least-squares analysis.

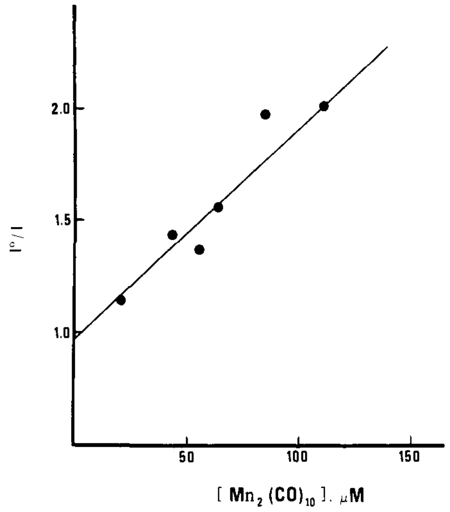

Figure 2. Stern–Volmer plot for quenching of biacetyl phosphorescence by $Mn_2(CO)_{10}$ in CCl_4. The line drawn is based on parameters obtained from a weighted least-squares analysis.

imental measurements. No significant difference is shown between the data for the two different values of [BA]. Other sets of runs led to very similar values for ϕ_l but substantially lower values of a, consistent with incomplete deoxygenation ofthe solutions, were sometimes found. When reactions were actually carried out in air-equilibrated solutions, ϕ_{obsd} increased much more slowly with $[Mn_2(CO)_{10}]$, and the values $\phi_l = 0.94 \pm 0.05$ and $a_{air} = (3.5 \pm 0.3) \times 10^2\ M^{-1}$ (standard deviation of $\phi_{obsd} = \pm 10.5\%$) were obtained from a combination of data with [BA] = 0.5 and 1.0 M.

These results were complemented by spectrofluorimetric measurements of intensities, I_f and I_p, of the fluorescence (473 nm) and phosphorescence (523 nm) of BA. In the absence of $Mn_2(CO)_{10}$ the intensity of the phosphorescence was ca. 6.5 times that of fluorescence.[9] As $[Mn_2(CO)_{10}]$ was increased, the phosphorescence intensity decreased while the fluorescence remained unaffected. The Stern–Volmer plot is shown in Figure 2 and leads to an intercept of 0.98 ± 0.05, a quenching constant, K_q, of $(9.3 \pm 1.1) \times 10^3\ M^{-1}$, and a standard deviation of I_p = 7.6%.

These results can be interpreted[11] according to eq 3–6. After

$$BA(T_1) + Mn_2(CO)_{10} \xrightarrow{k_3} BA(S_0) + Mn_2(CO)_{10}^* \quad (3)$$

$$Mn_2(CO)_{10}^* \xrightarrow{k_4} Mn_2(CO)_{10} \quad (4)$$

$$Mn_2(CO)_{10}^* \xrightarrow{k_5,\ CCl_4} 2\ Mn(CO)_5Cl \quad (5)$$

$$BA(T_1) \xrightarrow{k_6, O_2} BA(S_0) \quad (6)$$

excitation of BA to its first excited singlet state, intersystem crossing generates the triplet, $BA(T_1)$, which has a intrinsic lifetime, τ_{BA}, in the absence of quenchers. Our results show that $Mn_2(CO)_{10}$ is able to quench the triplet with a quenching constant K_q, and in so doing it acquires enough energy for it to react with the CCl_4 solvent. According to this scheme ϕ_l is given by $\phi_{isc}k_5/(k_4 + k_5)$, where $k_5/(k_4 + k_5)$ is a measure of the efficiency with which the transferred energy is used to produce chemical reaction and ϕ_{isc} is the quantum yield for formation of $BA(T_1)$ via intersystem crossing. Since $\phi_{isc} = 1$,[12] the chemical efficiency is given by ϕ_l and is ca. 80%. The values of $a_{N_2} = K_q$ and a_{air} are given by $k_3\tau_{BA}$ and $k_3/(k_6[O_2] + 1/\tau_{BA})$, respectively. The virtual identity of the values obtained for a (from the photochemistry of deoxygenated solutions) and for K_q (from the spectrofluorimetry) is in agreement with this scheme, as are the lower values of a found when deoxygenation was presumably incomplete and $[O_2]$ was finite. The values of ϕ_l from data obtained under N_2 and under air were also closely similar as required by this scheme. If the average value of $9.7 \times 10^3\ M^{-1}$ for $k_3\tau_{BA}$ is combined with the measured[13] lifetime to 0.784 ms for $BA(T_1)$ in CCl_4, then $k_3 = 1.2 \times 10^7\ M^{-1}\ s^{-1}$, a reasonably high value.[13] Combination of a_{N_2} and a_{air} ($[O_2] = 2.3 \times 10^{-3}$ M)[15] leads to $k_6 = 1.5 \times 10^7\ M^{-1}\ s^{-1}$, which is considerably smaller than the value $5 \times 10^9\ M^{-1}\ s^{-1}$ for quenching in benzene.[13]

Similar experiments with $Re_2(CO)_{10}$ show no photosensitized reaction and no phosphorescence quenching. These phenomena are, however, both observed with $Re_2(CO)_8(PPh_3)_2$, for which $\phi_l = 0.37 \pm 0.05$ and $K_q = (4.8 \pm 0.7) \times 10^3\ M^{-1}$. The rate of energy transfer from $BA(T_1)$ is, therefore, $Mn_2(CO)_{10} > Re_2(CO)_8(PPh_3)_2 \gg Re_2(CO)_{10}$, and the efficiency with which the energy is used for producing chemical reaction is about twice as high for $Mn_2(CO)_{10}$ as for $Re_2(CO)_8(PPh_3)_2$. These results suggest that the triplet energy may be transferred *as such* to the dinuclear carbonyls. The 54.4 kcal/mol excitation should have been quite adequate to cause chemical reaction efficiently in all three cases since it greatly exceeds the activation energy for thermal reaction.[17] The photosensitization of the reaction of $Re_2(CO)_8(PPh_3)_2$ is interesting in that direct photolysis with 436-nm light does not occur since the complex does not absorb at that wavelength.[17,18] No inference can be drawn as to whether the CCl_4 attacks the triplet excited states before homolytic fission occurs or not.

These results suggest that there is considerable scope for investigating indirectly the nature of excited states of metal–metal-bonded carbonyls of this sort since the nature of the complexes can be varied steadily and widely, as can the nature of the sensitizer. Direct observation of triplet excited states seems unlikely since almost all such complexes as have been investigated show no luminescence.[19]

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(9) This can be compared with the values 6–20 and 6 found, respectively, in benzene[10] and aqueous[11] solutions.

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Acknowledgment. We thank the University of Toronto and the Natural Sciences and Engineering Research Council, Ottawa, for support of this work.

Registry No. $Mn_2(CO)_{10}$, 10170-69-1; CCl_4, 56-23-5; $Mn(CO)_5Cl$, 14100-30-2; BA, 431-03-8; $Re_2(CO)_8(PPh_3)_2$, 14172-94-2; $Re_2(CO)_{10}$, 14285-68-8; O_2, 7782-44-7.

Definitive Evidence for Cycloheptatetraene from Dehydrobromination of Bromocycloheptatrienes

James W. Harris and W. M. Jones*

Department of Chemistry, University of Florida
Gainesville, Florida 32611

Received June 4, 1982

Thermolysis or photolysis of the tosylhydrazone salt of tropone in the presence of styrene gives the cyclopropane product **5**[1] (Scheme I). In the presence of 1,3-diphenylbenzo[*c*]furan, thermolysis[2] gives the adduct **6**. Dehydrobromination of the mixture of bromocycloheptatrienes **4** with base in the presence of the same two acceptors gives the same adducts.[3,4] As photolysis or thermolysis of tosylhydrazone salts typically leads to carbenes[5] and since cyclopropanes are typical carbene–olefin adducts,[5] it has been assumed that **5** arises from addition of the carbene to styrene. Likewise dehydrobromination of bromocycloheptatrienes such as **4** would be expected to occur by β and vinylogous β eliminations[6] to give the allene **3**. Furthermore, adduct **6** is that expected of Diels–Alder addition of an allene to the diene. It has therefore been quite reasonably assumed that **6** arises from the allene **3**. Finally, since both adducts **5** and **6** are formed from both **1** and **4**, it has ben presumed that the intermediates are interconvertible and that both are formed from each precursor.

Unfortunately, as clean as this picture may appear at first sight, on further reflection it loses its crispness. In the first place, as originally pointed out by Waali,[6] both **5** and **6** could originate from a single intermediate, the allene; the latter by a Diels–Alder reaction and the former by an allowed ($\pi^2s + \pi^8s$) cycloaddition by using the termini of the eight-electron conjugated allene π system. He has recently extended this argument with MNDO/3 calculations from which he has concluded that cycloheptatrienylidene does not represent an energy minimum; instead it is the transition state for the interconversion of enantiomeric allenes. As such, of course, it is not available for biomolecular chemistry. On the other hand, in principle the carbene could also be the sole intermediate responsible for biomolecular chemistry since it not only could cycloadd as a typical carbene to give **5** but could also add to one double bond of the furan to give an adduct that could rapidly rearrange to **6**.[1]

In this communication we report experimental data that unequivocally answer some but not all of the above questions. Our results prove the following: (a) dehydrobromination of the bromocycloheptatrienes gives an intermediate that is best represented by the allene structure; (b) this is the intermediate that is responsible for adduct **6**. We also report weak evidence that favors a carbene as the progenitor of the spirononatriene **5**.

Scheme I

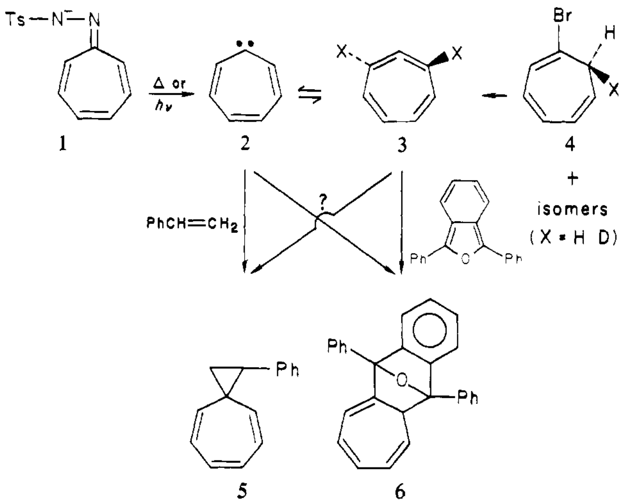

Table I. Specific Rotations of Allene Adducts

bromocycloheptatrienes[a]	base	solvent	*T*, °C	$[\alpha]^{25}{}_D$,[b] deg
4, X = H	potassium menthoxide	THF	0	3.40
4, X = H	potassium menthoxide	THF	45	2.60
4, X = H	potassium menthoxide	THF	65	0.74
4, X = D	potassium *tert*-butoxide	THF	25	−1.84
4, X = D	potassium *tert*-butoxide	THF	53	−1.38
4, X = D	potassium *tert*-butoxide	diglyme	100[c]	−0.60

[a] A mixture of 1-, 2-, and 3-bromocycloheptatrienes was used for all runs. [b] Rotations were measured in methylene chloride by using a 1.0-dm polarimeter cell. Sample sizes were typically about 100 mg and gave observed rotations of about 0.100–0.200 ± 0.002°. Repetitive runs showed deviations in specific rotation of 0.15° or less. The rather large deviation is believed to be due to the presence of small amounts of the exo isomer as a contaminant to the primary endo adduct. The former could not be separated by standard chromatography methods. The presence of this contaminant vitiates any conclusions based on changes in rotation. However, conclusions based solely on the presence or absence of rotation should be secure since there was no other detectable contaminant. [c] Optically active adduct did not racemize under these conditions.

Our approach was the same as that used to probe the structure of 1,2-cyclohexadiene, 1,2-cycloheptadiene, and 2,3,6-bicyclo[3.2.1]octatriene:[8] chirality. Since **3** is chiral and **2** is achiral, only the allene could give an optically active adduct **6**. The problem, then, was to generate the intermediate under conditions where by (assuming the allene structure) an excess of one of the enantiomers would be formed. To accomplish this, we used two approaches. In the first, a THF solution of a mixture of bromocycloheptatrienes **4** (X = H) was allowed to react with the potassium salt of menthol. The resulting adducts were isolated and, indeed, found to be active (Table I). This result suggested the allene as the intermediate but was not unequivocal because the presence of menthol (either free or as the salt) could create a chiral environment during the cycloaddition (although probably not[8b]). We therefore used a second less equivocal approach. In this case a primary deuterium isotope effect was used to lead to an enantiomeric excess of the intermediate. Thus, a mixture of optically active monodeuteriobromocycloheptatrienes (**4**, X = D; typical $[\alpha]^{25}{}_D$ −0.164°) was prepared by reducing bromotropylium bromide with $LiAlD_3$·quinine.[9] Since cis elimination of DBr from,

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