resonating ca. 40–50 ppm downfield.

A comparison of the $^1H$ NMR spectra of the CTD–catechol and the CTD–4-methylcatechol complexes (Figure 1) shows the appearance of a new feature at 105 ppm for the latter complex. This is assigned to the 4-methyl group on the substrate on the basis of studies with 4-methyl-$d_3$-catechol.[19,20] The 105 ppm feature is clearly missing in the $^1H$ NMR spectrum of the CTD-4-methyl-$d_3$-catechol complex, while the methyl resonance can be observed at 102 ppm in the $^2H$ NMR spectrum of the same complex.[21] The position of this resonance is consistent with the coordination of 4-methylcatechol to the iron through only one oxygen, the oxygen para to the methyl group. To show the similarity of the ferric center in CTD to our model systems, we have also observed the methyl resonances of the inhibitors in the CTD–*p*-cresol and the CTD–3,5-dimethylphenol complexes; these resonances are found at 87 and −23 ppm, respectively, as expected. At this point, we have not been able to observe the catecholate ring protons in the $^1H$ and $^2H$ NMR spectra; perhaps they are too broad. The other features observed in the spectra of the various complexes have yet to be assigned as well. What is clear, however, is that 4-methylcatechol binds in a monodentate configuration to the iron in CTD.

We have also studied the spectra of PCD–substrate complexes. PCD from *Pseudomonas aeruginosa*[22] is an octamer of $\alpha_2\beta_2Fe^{3+}$ units with a molecular weight of 780 000.[24,25] Figure 2 shows NMR spectra of PCD complexed with 4-methylcatechol, which is a pseudosubstrate with a cleavage rate about 1% of that of protocatechuate. Although the higher molecular weight of this enzyme gives rise to broader resonances, deuterium-labeling experiments enable us to assign the feature at 49 ppm unambiguously to the methyl group on the substrate. The isotropic shift observed indicates that, unlike in CTD, 4-methylcatechol chelates to the iron in PCD. This is an unexpected result since the ES complexes of CTD and PCD have such similar spectral properties,[1,2] but the NMR data clearly show that the two complexes are different. Our data at first glance appear to conflict with resonance Raman data on the ES complexes where features consistent with a chelated structure are observed for both complexes.[9,10] However, it has not been demonstrated that the Raman spectra are inconsistent with a monodentate structure.

We have proposed a dioxygenase mechanism[11] postulating a monodentate catecholate iron complex as the species that reacts with dioxygen because of studies demonstrating the large stabilization of the catecholate oxidation state upon chelation to a variety of metal ions, particularly iron.[26-30] According to this mechanism, the CTD ES complex is poised to react with oxygen, while the PCD ES complex would presumably have to undergo a conformational change upon oxygen binding to generate a monodentate substrate configuration. That this conformational change may occur has been suggested by studies with substrate analogues by Lipscomb et al.[31] Whatever the outcome of the mechanistic discussion, this study serves to emphasize the utility of paramagnetic NMR spectroscopy for providing details of the active-site structure in metalloproteins.

**Acknowledgment.** This work has been supported by the National Institutes of Health (GM-25422). The Bruker WM-300 NMR spectrometer was obtained in part with a grant from the National Science Foundation (CHE-7904825). R.B.L. was supported in part by a fellowship from the Exxon Foundation. L.Q. is an Alfred P. Sloan Foundation fellow (1982–1984) and the recipient of an NIH Research Career Development Award (1 K04 AM-00974).

**Registry No.** AMD, 83719-41-9.

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[19] 4-Methyl-$d_3$-catechol was synthesized by the lithium aluminum deuteride reduction of 3,4-dimethoxybenzoyl chloride in the presence of $AlCl_3$[20] and subsequent demethylation in refluxing HI. Mass spectroscopy showed a deuterium incorporation of 98%.

[20] Andrulis, P. J., Jr.; Dewar, M. J. S.; Dietz, R.; Hunt, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 5473–5478.

[21] The resonance at ca. 20 ppm integrates to approximately 8% of the peak at 102 ppm and probably arises from catechol binding to adventitiously bound iron.

[22] PCD was prepared from *Pseudomonas aeruginosa* (ATCC 23975) according to published procedures.[12,23] Enzyme with specific activity greater than 60 was used for the experiments.

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[25] Recent gel filtration experiments in our laboratory, however, suggest that PCD may be a tetramer in solution.

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[27] Rohrscheid, F.; Balch, A. L.; Holm, R. H. *Inorg. Chem.* **1966**, *5*, 1542–1551.

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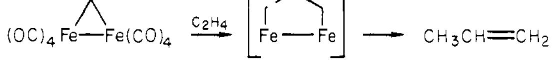
# Synthesis and Structure of Diosmacycloalkanes. Reversible Addition of Ethylene to a Methylene-Bridged Dimer

Keith M. Motyl, Jack R. Norton,* Cynthia K. Schauer, and Oren P. Anderson*

*Department of Chemistry, Colorado State University*
*Fort Collins, Colorado 80523*

*Received September 2, 1982*

Methylene-bridged dimers and their derivatives have been implicated in olefin metathesis,[1] acetylene polymerization,[2] and other important processes.[3,4] They also serve as models for the surface methylene groups that Pettit and co-workers have shown to be involved in the Fischer–Tropsch reaction[5] and in the hydrogenolysis of linear hydrocarbons.[6] Considerable interest has therefore been aroused by the report (also from Pettit's group[7]) that propene is formed from the reaction of $(\mu\text{-}CH_2)Fe_2(CO)_8$ (**1**) with ethylene, and by their proposal that the reaction (eq 1) involves a diferracyclopentane intermediate.



**1**

(1)

This hypothesis has stimulated efforts at the synthesis of dimetallacycloalkanes in general and has led to the successful preparation of $((\mu\text{-}CC')CH_2CH_2CH_2)$-$Co_2(CO)_2Cp_2$ (**2**) by Theopold and Bergman.[8] However, although propene is formed upon thermolysis of **2**, generation of the latter by the reaction of ethylene with the corresponding methylene-bridged dimer has not proven possible.[9,10] We now report the

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[1] (a) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1. (b) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911 and references therein.

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[8] Theopold, K. H.; Bergman, R. G. *Organometallics*, in press.

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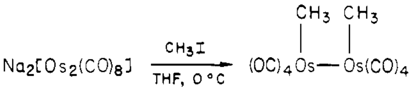
direct observation of 1,2-diosmacyclopentane formation by ethylene addition to the osmium analogue of **1** and the synthesis and structural characterization of the first 1,2-dimetallacyclobutane.

The dinuclear dihydride $Os_2(CO)_8H_2$,[11] which can be prepared in 24% yield by the controlled thermolysis of *cis*-$Os(CO)_4H_2$,[12] can be converted quantitatively to the known[13] dinuclear diiodide $Os_2(CO)_8I_2$ by treatment with methyl iodide (eq 2). Reduction

$$Os(CO)_4H_2 \xrightarrow{\Delta} Os_2(CO)_8H_2 \xrightarrow[CH_3I]{excess} Os_2(CO)_8I_2 \quad (2)$$

$$Os_2(CO)_8I_2 \xrightarrow[THF]{Na/Hg} Na_2[Os_2(CO)_8] \quad (3)$$



$$Na_2[Os_2(CO)_8] \xrightarrow[THF,\ 0\ °C]{CH_3I} (OC)_4\overset{CH_3}{\overset{|}{Os}}-\overset{CH_3}{\overset{|}{Os}}(CO)_4 \quad (4)$$

with sodium amalgam in THF (eq 3) gives a solution that apparently contains the dinuclear dianion $[Os_2(CO)_8]^{2-}$.[14-16] Addition of an excess of methyl iodide to the dianion solution readily gives $Os_2(CO)_8(CH_3)_2$ (**3**);[17] addition of the dianion solution to 1-2 equiv of difunctional alkylating agents gives the 1,2-diosmacycloalkanes **4a-c** (eq 5). For the diosmacyclopentane **4c**[18]

$$Na_2[Os_2(CO)_8] \xrightarrow[\substack{THF,\ 0\ °C \\ X\ =\ I,\ OTs}]{X(CH_2)_nX} (OC)_4\overbrace{Os(CH_2)_nOs}(CO)_4 \quad (5)$$

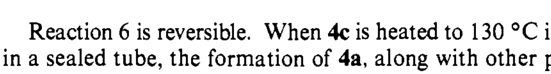
**4a**, $n = 1$
**b**, $n = 2$
**c**, $n = 3$

the use of 1,3-diiodopropane gave reasonable results, but for the smaller rings, **4a**[19] and **4b**,[20] the use of $CH_2(OTs)_2$[21-23] and $TsOCH_2CH_2OTs$ proved more satisfactory. Yields based on $Os_2(CO)_8I_2$ ranged from 10% (**4b**) to 35% (**4a**), although the conversion from the dianion was probably higher.[14]

All three of the diosmacycloalkanes are air-stable, white, crystalline solids. The structure of the diosmacyclobutane **4b** has been confirmed by X-ray diffraction[24] and is shown in Figure 1. The molecule has approximate $C_2$ symmetry. A 27° twist about the Os-Os bond keeps the $Os(CO)_4$ units out of the sterically unfavorable eclipsed configuration at the expense of bending the $Os_2C_2$ ring and slightly compressing[25] (105°) the Os-C-C angles. The $\mu$-1,2-ethanediyl bridge contains a normal (1.53 (3) Å) carbon-carbon single bond. The two osmium-carbon bond lengths (2.22 (2) Å) equal the sum of the covalent radii calculated from the Os-Os and C-C bond lengths.[26] The fact that a single $^1H$ NMR peak is observed down to -50 °C implies that the $Os_2C_2$ ring in **4b** is quite flexible.

Although there have been previous reports of $\mu$-1,2-ethanediyl dimers without metal-metal bonds,[4b,27] **4b** is the first 1,2-dimetallacyclobutane. Bergman and co-workers obtained no such product from the reaction of $ICH_2CH_2I$ with $Na[CpCo(CO)_2]$; even a stabilized derivative, from the diiodide of benzocyclobutadiene, was formed in only 16% yield and proved unstable at room temperature.[8]

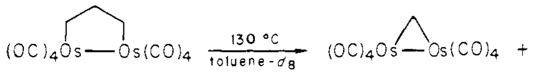
The infrared spectrum[28] of the diosmacyclopropane **4a** shows the features characteristic[29] of a methylene bridge: antisymmetric C-H stretch at 2958 (vw), symmetric C-H stretch at 2933 (vw), $CH_2$ wag at 943 (m), and $CH_2$ rock at 780 (vw) $cm^{-1}$. **4a** can be converted to **4c** in good yield (85% by NMR) by treatment with 1.0 atm (8.4 equiv) of ethylene at 100 °C; the diosmacyclopentane can be isolated by TLC (silica gel/hexane). Reaction 6 is the first case of directly observable dimetallacyclopentane formation from an olefin and a methylene-bridged dimer containing two transition metals.[30,31]



(6)

**4a** **4c**

Reaction 6 is reversible. When **4c** is heated to 130 °C in toluene in a sealed tube, the formation of **4a**, along with other products, is observed (eq 7). (**4a** is unstable at 130 °C, but NMR monitoring of the reaction mixture shows that it reaches a maximum concentration of 10% of the initial concentration of **4c**.) The formation of propene from **4c** and the formation of **4c** from ethylene and **4a** offer direct evidence in support of the Pettit[1b,7] (eq 1) and Bergman[9] mechanisms for the formation of propene



$$C_2H_4\ (0\ 56\ equiv) + CH_3CH{=}CH_2\ (0\ 21\ equiv) + CH_4\ (0\ 32\ equiv) \quad (7)$$

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(10) Theopold and Bergman[9] suggest that the reaction requires a coordinatively unsaturated dicobaltacyclopropane and that the resulting coordinatively unsaturated dicobaltacyclopentane eliminates propene before it recoordinates the dissociated CO.

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(14) We have not yet isolated a salt of the dianion. The IR of the THF solution after reduction ($\nu_{CO}$ 1978 (vs), 1949 (s), 1878 (s), 1834 (m) $cm^{-1}$) contains bands similar to those[15] of $Na_2[Fe_2(CO)_8]$ in THF; the absence of bridging carbonyls suggests that $Na_2[Os_2(CO)_8]$ has a nonbridged structure like that of $Na_2[Fe_2(CO)_8]$.[16] However, the additional band in the IR spectrum of the $Os_2(CO)_8I_2$ reduction solution suggests that something besides $[Os_2(CO)_8]^{2-}$ may also be present. The addition of 2 equiv of $CF_3CO_2H$ converts the IR spectrum of the reduction solution principally to that of $Os_2(CO)_8H_2$.[11,12]

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(18) $^1H$ NMR (benzene-$d_6$) $\delta$ 3.12 (2 H), 1.10 (4 H); IR (hexane) 2122 (vw), 2079 (m), 2042 (m), 2034 (vs), 2022 (m), 2014 (m), 1996 (w) $cm^{-1}$. Anal. Calcd for $C_{11}H_6O_8Os_2$: C, 20.43; H, 0.93. Found: C, 20.80; H, 1.01. A parent ion with the appropriate isotopic distribution was observed in the mass spectrum.

(19) $^1H$ NMR (benzene-$d_6$) $\delta$ 3.73 (s); IR (hexane) 2128 (vw), 2082 (m), 2036 (vs), 2022 (m), 2004 (m), 1966 (m, sh) $cm^{-1}$. Anal. Calcd for $C_9H_2O_8Os_2$: C, 17.48; H, 0.32. Found: C, 17.53; H, 0.43. A parent ion with the appropriate isotopic distribution was observed in the mass spectrum.

(20) $^1H$ NMR (benzene-$d_6$) $\delta$ 1.51 (s); IR (hexane) 2122 (vw), 2077 (m), 2030 (vs), 2020 (m, sh), 2012 (m), 1994 (m) $cm^{-1}$. A parent ion with the appropriate isotopic distribution was observed in the mass spectrum.

(21) Emmons, W. D.; Ferris, A. F. *J. Am. Chem. Soc.* **1953**, *75*, 2257.

(22) The fact that these reactions succeed suggests that the synthesis of dimetallacyclolalkanes from dinuclear dianions is best accomplished by successive $S_N2$ reactions (two-electron processes) under conditions where one-electron transfers are minimized. We are aware of only one, unsuccessful, previous attempt[23] at the synthesis of methylene-bridged dimers from $CH_2(OTs)_2$.

(23) Berke, H.; Weiler, G. *Angew. Chem., Int. Ed. Eng.* **1982**, *21*, 150.

(24) **4b**: $a = 7.355$ (1) Å, $b = 13.522$ (2) Å, $c = 13.544$ (2) Å, $\beta = 101.01$ (1)° at -140 °C; space group $P2_1/c$, with $Z = 4$. Of 2651 reflections measured, 2018 were taken as observed ($I > 2.5\sigma(I)$). Least-squares refinement (empirical absorption correction, 181 parameters) to convergence gave $R = 0.062$, $R_w = 0.080$, and GOF = 1.44.

(25) A planar $Os_2C_2$ ring with the observed bond lengths would have an approximate tetrahedral (108°) angle at carbon.

(26) The sum of covalent radii for an Os-C single bond has been given elsewhere as 2.211 Å: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1978**, *17*, 1291.

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(28) These spectra were obtained on Nicolet MX-S and MX-1 FT IR spectrometers. We thank Professor D. E. Leyden and the Nicolet Instrument Corp. for use of these instruments.

(29) Oxton, I. A.; Powell, D. B.; Sheppard, N.; Burgess, K.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1982**, 719.

(30) The synthesis of titanacyclobutanes from olefins and $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$ has recently been reported.[31]

(31) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876. Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *Ibid.* **1981**, *103*, 7358.

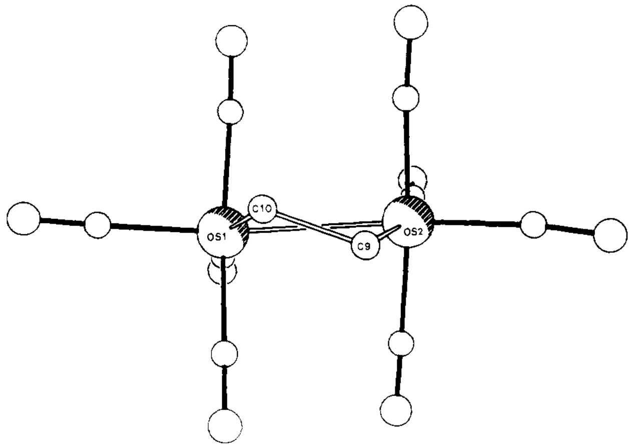
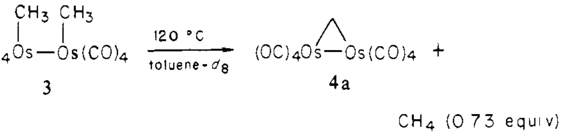


**Figure 1.** Molecular structure of $((\mu\text{-CC}')CH_2CH_2)Os_2(CO)_8$ (**4b**). Distances (Å): Os(1)-Os(2), 2.883 (1); Os(1)-C(10), 2.22 (2); Os(2)-C(9), 2.22 (2); C(9)-C(10), 1.53 (3). Angles (deg): Os(1)-Os(2)-C(9), 70.1 (6); Os(2)-C(9)-C(10), 105.7 (13); C(9)-C(10)-Os(1), 103.8 (12); C(10)-Os(1)-Os(2),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

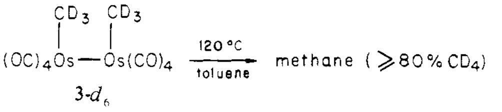
from ethylene and methylene-bridged dimers.

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



$$(OC)_4Os(CH_3)\text{—}Os(CH_3)(CO)_4 \xrightarrow[\text{toluene-}d_8]{120\ °C} (OC)_4Os(CH_2CH_2)Os(CO)_4 + CH_4\ (0\ 73\ \text{equiv}) \quad (8)$$

3 → 4a



$$(OC)_4Os(CD_3)\text{—}Os(CD_3)(CO)_4 \xrightarrow[\text{toluene}]{120\ °C} \text{methane}\ (\geqslant 80\%\ CD_4) \quad (9)$$

3-$d_6$

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, $\phi_{\text{obs}}$, for loss of $Mn_2(CO)_{10}$, according to reaction 1, following absorption of 436-nm radiation

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

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

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

A plot of $1/\phi_{\text{obsd}}$ 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 $\phi_{\text{obsd}}$ is ±9.1% when defined by $\{\sum\Delta^2/(N-2)\}^{1/2}$, $\Delta$ being the percent difference between $\phi_{\text{obsd}}$ and the value of $\phi$ 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 ($5 \times 10^{-8}$ 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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