temperature variation at atmospheric pressure that the radiationless relaxation of the emitting states is an activated process, the activation energies being dependent on the solvent, i.e. the second coordination sphere.[3–5] It is quite possible that the corresponding energy barrier is reduced by a pressure-induced deformation of the potential surfaces. It is worthwhile to mention that the main effect of intensity reduction occurs in a pressure range below 20–25 kbar, a region in which the complex environment (i.e. the crystal lattice, which also can be regarded as the second coordination sphere) is strongly influenced.

Conclusion

High-pressure investigations on the emission spectrum of $[Ru(bpy)_3](PF_6)_2$ single crystals have been reported for the first time. As the $\vec{E}\|\vec{c}$-polarized component carries only 5% of the emission intensity at room temperature, the $\vec{E}\perp\vec{c}$-polarized and the unpolarized spectra are comparable. A very small red shift of the emission spectrum is observed, which is explained by the simultaneous stabilization of the ligand π^* and the metal t_{2g} orbitals. Under pressure the resolution of the emission spectra is enhanced and the emission bandwidth decreases by about 30% due to a reduction of the inhomogeneous broadening of the spectra. The pressure-induced intensity reduction is possibly coupled to the change of an energy barrier involved in the radiationless relaxation of the lowest excited states. From the pressure behavior of the band shape and of the red shift, two pressure regions can be distinguished. For pressures below about 20 kbar compression of the crystal lattice seems to be the dominant effect, whereas for higher pressures intramolecular compression gains a considerable influence on the pressure behavior of the emission spectra.

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Flash Photolysis Studies of Dinuclear Manganese Carbonyl Compounds[1]

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The $Mn(CO)_4L\cdot$ (L = CO, PR_3; R = *n*-Bu, *i*-Bu, *i*-Pr, OPh) radicals have been observed directly as transient species following flash photolysis of $Mn_2(CO)_8L_2$ in hexane solution. The transient absorbance due to the radical disappears according to a second-order rate law. No difference in the decay behavior was noted when the experiments were conducted under an argon atmosphere as compared with CO. Earlier results from this laboratory in which a transient absorption was noted following flash photolysis of vacuum-degassed solutions of $Mn_2(CO)_{10}$ are shown to have been due to an experimental artifact. There is no direct evidence in the flash photolysis experimental results for dissociative loss of CO from $Mn(CO)_4L\cdot$. In addition, under the conditions of flash photolysis, $Mn(CO)_4PR_3\cdot$ is not observed to undergo replacement of phosphine by CO when a CO atmosphere is employed. The spectral characteristics of the radicals have been measured. The bimolecular rate constants for recombination of $Mn(CO)_4Pr_3\cdot$ radicals have been measured in hexane solution at 25 °C: $P(n\text{-}Bu)_3$, 1×10^8 M^{-1} s^{-1}; $P(i\text{-}Bu)_3$, 2×10^7 M^{-1} s^{-1}; $P(i\text{-}Pr)_3$, 4×10^6 M^{-1} s^{-1}; PPh_3, 1×10^7 M^{-1} s^{-1}; $P(OPh)_3$, 9×10^7 M^{-1} s^{-1}. The recombination rates are lowest for phosphorus ligands of largest steric requirement.

Introduction

It has been well established that irradiation of dinuclear metal carbonyl compounds at wavelengths corresponding to the σ–σ^* or $d\pi$–σ^* transitions results in efficient homolysis of the metal–metal bond. Studies of cross-coupling reactions of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ and of halogen atom abstraction reactions during irradiation show that metal–metal bond cleavage is homolytic, producing metal-centered radicals with 17-electron configurations.[2–4] Recombination of the radicals, eq 1, is bimolecular, with rate constant k_r near the diffusion-controlled limit.

$$M_2(CO)_{10} \underset{k_r}{\overset{h\nu}{\rightleftharpoons}} 2M(CO)_5\cdot \qquad (1)$$

In the case of $Mn_2(CO)_{10}$, k_r, defined by the rate law $-d[Mn(CO)_5\cdot]/dt = 2k_r[Mn(CO)_5\cdot]^2$,[2] has been reported to have values of 3.9×10^9 M^{-1} s^{-1} at 20 °C in cyclohexane[5] and 9.5×10^8 M^{-1} s^{-1} at 22 °C in hexane.[6] Both sets of results are based on flash photolysis results. For $Re_2(CO)_{10}$ k_r has the value of 3.7×10^9 M^{-1} s^{-1} at 22 °C in hexane.[6] Pulsed radiolysis studies yield similar values for recombination rates in ethanol as solvent.[7]

To properly interpret some of the observed chemical behavior of the radicals it is important to know how replacement of CO on the metal center by larger ligands such as phosphines affects the rates of recombination. We know in general that recombination rates should decrease as a result of such substitution. When the ligands on the metal are sufficiently large, metal–metal bond formation is no longer energetically favored and the resulting radicals are persistent. The properties of such persistent radicals, of the form $Mn(CO)_3L_2\cdot$, where L is a bulky phosphine, have been reported.[8–10]

Aside from recombination, radicals may also undergo other reactions, notably substitution. There is substantial evidence that the radicals are highly labile. Whether that lability is related to a dissociative loss of CO from the radical, or to a

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rapid associative displacement of CO at the metal center, has been the subject of considerable discussion. An early study of the quantum yields for photosubstitution led to the view that a dissociative loss of CO is the most likely pathway for substitution into the $Mn(CO)_5\cdot$ radical.[11] A dissociative pathway has been invoked also to account for various aspects of the substitution behavior of the $Re(CO)_5\cdot$ radical.[12] On the other hand, more recent work by Poë and co-workers provides convincing evidence that, in the presence of moderate concentrations of ligands of significant nucleophilicity, an associative pathway for substitution on $Re(CO)_5\cdot$ predominates.[13]

Yesaka and co-workers have recently presented evidence from a laser photolysis study of $Mn_2(CO)_{10}$ than $Mn(CO)_5\cdot$ also undergoes substitution by $P(n\text{-Bu})_3$ via an associative process.[14] We have recently completed a kinetics study that leads us to the same conclusion.[15] Further, the associative pathway seems to dominate in the substitution behavior of ligand-substituted radicals, e.g., $Mn(CO)_3(PR_3)_2\cdot$.[10] In the case of the six-coordinate 17-electron system, $V(CO)_6$, an associative pathway for substitution was again found to prevail.[16]

In this paper we report on the results of a series of flash photolysis studies of dinuclear manganese carbonyl compounds, $Mn_2(CO)_8L_2$, where L may be a phosphine or CO. By utilizing an improved detection system we have been able to directly observe the transient absorption due to $Mn(CO)_4L\cdot$ radicals and measure their recombination rates. Use of variously substituted $Mn_2(CO)_8L_2$ compounds permits an assessment of the effect of ligand substitution on the rates of radical recombinations. Finally, we correct results reported earlier regarding what was thought to be evidence for a CO loss in a thermal process following photochemical formation of $Mn(CO)_5\cdot$ or $Re(CO)_5\cdot$ radicals.[6] Subsequent work has revealed that the observations were based on an experimental artifact.

Experimental Section

Materials. Phosphine ligands were obtained from commercial sources and used without further purification. Dimanganese decacarbonyl was acquired from commercial sources and sublimed before use. Hexane solvent was purified for flash photolysis studies by consecutive treatment with H_2SO_4/H_2O/saturated aqueous $NaHCO_3/H_2O/MgSO_4$ prior to distillation from CaH_2. Argon (NGC Industrial Gases, 99.998%) and carbon monoxide (Linde Research Grade, <5 ppm of O_2) were used without further purification.

Syntheses. Phosphine-disubstituted manganese dinuclear compounds, $Mn_2(CO)_8(PR_3)_2$ (R = *n*-Bu, *i*-Bu, *i*-Pr, Ph, OPh), were prepared as follows: $Mn_2(CO)_{10}$ (0.3 g, 1.28 mmol) and phosphine ligand (2.7 mmol) were placed in a Schlenk flask along with 75 mL of distilled hexane solvent. The solution was stirred vigorously during irradiation with a 275-W General Electric sunlamp for 8–14 h. The solvent was stripped off and the resulting orange dinuclear compound recrystallized from the appropriate orange dinuclear compound recrystallized from the appropriate solvent at −78 °C. Satisfactory elemental analyses (C, H, Mn; University of Illinois microanalytical laboratory) were obtained for all derivatives prepared. The IR spectra in the carbonyl region also established the absence of metal carbonyl impurities.

$Mn_2(CO)_8$(dppe) was prepared by using the method described for $Mn_2(CO)_8$(dppm).[17a] $Mn_2(CO)_{10}$ (0.40 g, 1.03 mmol) and 1,2-bis(diphenylphosphino)ethane (0.41 g, 1.03 mmol) were added to 15 mL of refluxing decane. After 5 min, reflux was stopped. Most of the decane was removed in vacuo. The brown residue was chromatographed on a silica gel column (2.5 × 27 cm). A yellow band composed of $Mn_2(CO)_{10}$ was eluted with hexane. The product was eluted as an orange band with CH_2Cl_2/hexane (1/1). The solution was reduced in volume and the material recrystallized to give a yellow solid (50 mg). The material was successfully identified as $Mn_2(CO)_8$(dppe) and its purity checked by comparison of the solution IR with the reported values for $Mn_2(CO)_8$(dppm)[17] and with the solution IR of $Mn_2(CO)_8$(dppm) prepared by the literature method.[17a] IR (CH_2Cl_2) ν(CO): 2056 (s), 1990 (s), 1970 (s), 1933 (s), 1914 (m) cm^{-1}.

Table I. Spectroscopic Parameters Determined for $Mn(CO)_4L\cdot$ Radicals in Hexane

radical	λ_{max},[a] nm	ϵ,[b] $M^{-1}\ cm^{-1}$
$Mn(CO)_5\cdot$	830	950
$Mn(CO)_4[P(n\text{-Bu})_3]\cdot$	830	310
$Mn(CO)_4[P(i\text{-Bu})_3]\cdot$	840	500
$Mn(CO)_4[P(i\text{-Pr})_3]\cdot$	780	350
$Mn(CO)_4[P(OC_6H_5)_3]\cdot$	850	1300

[a] ±10 nm. [b] ±20%.

Flash Photolysis Studies. The flash photolysis apparatus previously described[6] has been improved by the addition of a Hamamatsu R712 photomultiplier tube (peak response at 640 nm) in a cooled photomultiplier housing and an Instruments SA, Inc., Model H-20 monochromator with gratings that provide wavelength coverage from 300 to 900 nm. The output of the photomultiplier following the flash was stored in a Biomation Model 805 waveform recorder (2048 channels, 0.2 μs to 100 ms per channel, 8-bit resolution) and then transferred to an Apple II microcomputer through an ISAAC interface, Cyborg Corp. The Apple was interfaced to a VAX 11/780 computer for transfer of data and subsequent kinetics analysis.

Samples for flash photolysis studies were prepared in a glovebox and loaded into cells fitted with a threaded Teflon stopcock. The solutions, 10^{-4}–10^{-5} M, were then degassed via several freeze–pump–thaw cycles. Argon or CO was then admitted as cover gas and the system closed off.

Flash data were analyzed by a least-squares fits of absorbances vs. time or by using rate laws appropriate to reactions of various orders. Data through the first 2 and more half-lives were employed in fitting rate law expressions. All reported rate constants are the means of values from three or more experiments, each having linear least-squares correlation coefficients greater than 0.99.

Results and Discussion

Direct Observation of $Mn(CO)_5\cdot$ and $Mn(CO)_4PR_3\cdot$. Flash photolysis of $Mn_2(CO)_{10}$ or $Mn_2(CO)_8(PR_3)_2$ in hexane under CO atmosphere gives rise to a transient absorption in the range 700–900 nm. The absorption appears to be due to a primary photoproduct of the reaction; its absorbance decays steadily from the value observed at the shortest possible times following the flash, about 50 μs. Observations at different wavelengths afford an outline of the spectrum for the transient. Within the observable wavelength region each transient except $Mn(CO)_4P(i\text{-Pr})_3\cdot$ exhibits a λ_{max} in the region between 830 and 850 nm. For $Mn(CO)_4P(i\text{-Pr})_3\cdot$, which has a λ_{max} of 780 nm, the presence of a second absorption maximum at a longer wavelength is suggested, although only the high-energy shoulder of the absorption is seen. Spectroscopic data for the transients are compiled in Table I. Wojcicki and co-workers have reported a λ_{max} of 830 nm for $Mn(CO)_5\cdot$ in ethanol, derived from pulse radiolysis studies of $Mn_2(CO)_{10}$ and $Mn(CO)_5X$ (X = Br, I). Poliakoff and Turner reported an absorbance maximum of 798 nm for $Mn(CO)_5\cdot$ in a CO matrix at 10–20 K.[18] Peters and Vaida et al.[19] and, more recently, Yesaka and co-workers[14] have observed a transient with λ_{max} of 830 nm from their laser photolysis studies of $Mn_2(CO)_{10}$.

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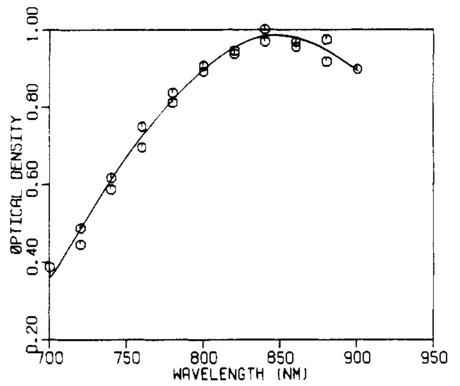

Figure 1. Absorbance spectrum of $Mn(CO)_4[P(OPh)_3]\cdot$ based on measurements following flash photolysis.

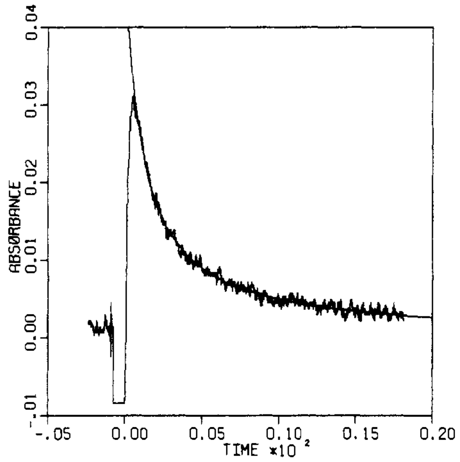

Figure 2. Change in absorbance vs. time on flash photolysis of a 2×10^{-5} M hexane solution of $Mn_2(CO)_{10}$ under 1 atm of argon.

In light of these several observations, the transient absorptions with λ_{max} in the 830–850-nm region can be confidently assigned to $Mn(CO)_5\cdot$ or $Mn(CO)_4L\cdot$ radicals formed in the flash.

A typical spectrum of a transient, observed following flash photolysis of a $Mn_2(CO)_8[P(OPh)_3]_2$ solution, is shown in Figure 1. The monosubstituted radicals have calculated extinction coefficients at λ_{max} in the range of 300–1300 M^{-1} cm^{-1} (Table I). These are reasonable values for bands presumably due to metal-centered d–d transitions. $Mn(CO)_3(PR_3)_2\cdot$ radicals exhibit two absorption maxima in the long-wavelength region in the 600–1300-nm region.[9] The wavelength limitations of our detection system preclude observation at wavelengths longer than 900 nm, but it seems likely that the $Mn(CO)_4L\cdot$ radicals also possess a second, longer wavelength absorption.

A solution of $Mn_2(CO)_8$(dppe) in hexane was subjected to flash photolysis. No transient absorption was observed in the region between 700 and 900 nm at a time 50 μs or longer after the flash. We conclude that although metal–metal bond homolysis probably occurs under the flash conditions, recombination of the radicals so formed is comparatively rapid because the metal centers are held in close proximity by the presence of the bidentate phosphine ligand attached to each metal. A maximum half-life of about 5×10^{-5} s can be estimated for the diradical formed in the flash of $Mn_2(CO)_8$(dppe). By comparison, organic diradicals possess lifetimes in the range of 10^{-5}–10^{-9} s.[20]

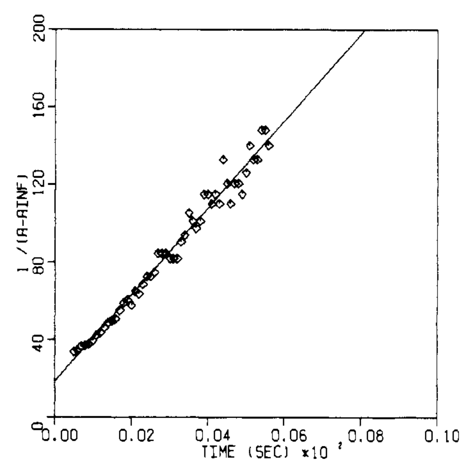

Figure 3. Second-order kinetic plot of $1/(A - A_{inf})$ vs. time for the recombination of $Mn(CO)_5\cdot$ radicals at 26 °C after flash photolysis of a hexane solution of $Mn_2(CO)_{10}$.

A representative trace of absorbance vs. time for $Mn(CO)_5\cdot$ is shown in Figure 2. The line through the trace represents the best fit to a second-order rate law for the disappearance. A second-order rate plot of the data is linear through more than 2 half-lives, as illustrated in Figure 3. From the slope *m* of the second-order rate plot, the path length *b*, and second-order rate constant k_r,[6] the extinction coefficient, ϵ, for the transient absorption at 830 nm can be calculated: $\epsilon = 2k_r/mb$. A value of 950 M^{-1} cm^{-1} was calculated in good agreement with the value of 800 M^{-1} cm^{-1} reported by Wojcicki et al. for ethanol solvent.[7]

When an argon atmosphere rather than CO is employed for $Mn_2(CO)_{10}$ solutions, there is no observable difference in the time dependence of the trace at 830 nm following the flash. This suggests that dissociative loss of CO from the radical, giving rise to a species with significantly different absorbance at 830 nm, is not extensive during the lifetime of the radical under these conditions.[14] Assuming that a loss of 10% of the radical would lead to observable effects, the first-order rate constant for dissociative loss of CO from $Mn(CO)_5\cdot$ must be less than about 10^2 s^{-1}.

If indeed the rate constant for loss of CO from $Mn(CO)_5\cdot$ is less than 10^2 s^{-1}, the range of possible rate constants for CO loss that would be consistent with the photosubstitution results[10] is quite narrow, because it was estimated on the basis of those data that the rate constant for dissociative los of CO must be on the order of 10 s^{-1} or greater. We were thus led to question earlier results from this laboratory that indicated substantial loss of CO from the $Mn(CO)_5\cdot$ radical following flash photolysis.[6] The basis of the conclusion in the eariler work was an apparent large excess absorbance noted when $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ was flashed in hexane solutions that had been vacuum degassed. A similar result was not seen when a CO atmosphere was present. As a control, degassed solvent had also been subjected to flash, and no excess absorbance noted. We have repeated the earlier experiments using an argon atmosphere rather than keeping the system under vacuum. Under these conditions there is no evidence of the transient behavior shown in Figure 2 of ref 6. The absorbances seen previously were due to transient bubble formation that occurred only when an absorbing species was present in solution to absorb radiation from the flash. The bubbles are sufficiently short-lived to have disappeared within 0.5 s. As a check, a degassed solution of benzophenone under vacuum was flashed; the same transient effects were noted.

Others have reported flash photolysis experiments involving vacuum-degassed solutions[5] but apparently did not encounter bubble formation. The incidence of such an effect is probably related among other things to the total energy output of the

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Table II. Comparison of Recombination Rate Constants as a Function of Steric (θ) and Electronic (ν) Properties of L on $Mn(CO)_4L\cdot$

L	ν,[a] cm^{-1}	θ,[a] deg	k_r, $M^{-1}\ s^{-1}$
CO		95	9×10^8
$P(n\text{-}C_4H_9)_3$	2062	132	1×10^8
$P(i\text{-}C_4H_9)_3$	2061	144	2×10^7
$P(i\text{-}C_3H_7)_3$	2060	160	4×10^6
$P(OC_6H_5)_3$	2086	130	9×10^7
$P(C_6H_5)_3$	2070	144	1×10^7

[a] Reference 22. [b] Measured in hexane at 25 ± 2 °C.

flash lamp. In any case, the fact that there is no evidence of a difference in character of the absorbance between solutions under argon and those under CO means that there is *no* direct evidence in the flash photolysis results for dissociative CO loss from either $Mn(CO)_5\cdot$ or $Re(CO)_5\cdot$, as previously argued. If we assume, as above, that dissociation of CO from about 10% of the radicals in the solutions under argon would lead to observable differences in the absorbance traces following the flash, we can again place an upper limit of about $10^2\ s^{-1}$ on the rate constant for CO loss from either radical.

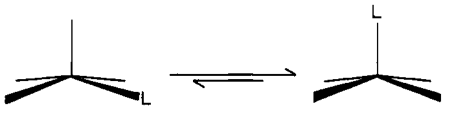
The decay of monosubstituted radicals, $Mn(CO)_4PR_3\cdot$, was monitored under either a CO or an argon atmosphere. As with $Mn(CO)_5\cdot$ the kinetics of decay and the spectral characteristics of the radical band were unaffected by the nature of the atmosphere. After 30 or more flash cycles under a CO atmosphere, results identical with those obtained with an argon atmosphere were observed. These observations rule out formation of $Mn(CO)_5\cdot$ by CO substitution in any measurable amounts under the conditions of the flash experiment. While CO substitution of $Mn_2(CO)_8(PR_3)_2$ by continuous photolysis has been reported previously,[11] it should be kept in mind that in continuous photolysis the concentration of radicals present at any time is very small. Hence the lifetime of a radical in solution is much longer, permitting reactions such as CO substitution to occur.

Rates of Recombination of $Mn(CO)_4PR_3\cdot$ Radicals. Hexane solutions of $Mn_2(CO)_8(PR_3)_2$ were subjected to flash photolysis with the monitor monochromator set at the wavelength of the absorbance maximum corresponding to the σ–σ^* transition.[21] The flash produces a transient loss in that absorbance, due to homolysis of the metal–metal bond. The absorbance did not entirely return to its original value following the first few flashes, presumably due to scavenging of impurities by the radicals. However, after the first few flash cycles the solutions exhibited photochromic behavior, and no loss in absorbance was seen, even after several flashes.

In each case the absorbance recovery following the flash exhibited second-order kinetics behavior. Table II contains the measured second-order recombination rate constants. Note that the rate constants are smaller than the value $9 \times 10^8\ M^{-1}\ s^{-1}$ observed for $Mn_2(CO)_{10}$ by factors ranging from 9 to more than 200. In the trialkylphosphine series the rate constant decreases steadily with increasing cone angle, θ, a measure of the bulk of the ligands.[22] The electronic characteristics of these ligands are essentially constant, as measured by the effect of the ligand on the A_1 symmetry stretching mode of $Ni(CO)_3PR_3$ compounds,[22] listed in Table II as ν. The ligands $P(OPh)_3$ and $P(n\text{-}Bu)_3$ have approximately the same cone angle but differ significantly in electronic character. The fact that the recombination rate constants for the corresponding $Mn(CO)_4PR_3\cdot$ radicals are about the same suggests that the rate constants are affected mainly by steric factors, and not much by electronic affects, among this group of ligands. Similar comments are applicable to the comparison between PPh_3 and $P(i\text{-}Bu)_3$.

The flash experiments on $Mn_2(CO)_8(PR_3)_2$ compounds were conducted under 1 atm CO pressure, to reduce decomposition. However, if a substantial fraction of the $Mn(CO)_PR_3\cdot$ radicals formed in the flash underwent replacement of phosphine by CO, the recovery of absorption in the 350-nm region would not lead to correct values for the second-order rate constants we wished to measure. To ensure that this was not a problem, studies of the extent of replacement of phosphine ligand by CO were carried out by using IR cells and a small photoflash unit. There was little evidence of phosphine ligand replacement after several flashes. In addition, the transient absorption behavior was mathematically modeled for various mixtures of $Mn(CO)_5\cdot$ and $Mn(CO)_4PR_3\cdot$ radicals, assuming the experimentally determined values for recombination rate constants to form $Mn_2(CO)_{10}$ and $Mn_2(CO)_8(PR_3)_2$ and assuming that the rate constant for formation of $Mn_2(CO)_9(PR_3)$ is the geometric mean of the other two values. In these simulations, the experimentally determined extinction coefficients of the dinuclear species at the monitor wavelength were used where these are known. The simulations showed that experimentally observable nonlinearities in the second-order rate plots should be evident when the extent of replacement of phosphine by CO in the $Mn(CO)_4PR_3\cdot$ radicals exceeds about 10%. There was no evidence of nonlinearity in our rate plots. As mentioned above, repetitive flash cycles for $Mn_2(CO)_8(PR_3)_2$ under CO yield constant kinetics parameters as measured under argon, indicating that $Mn_2(CO)_9L$ and $Mn_2(CO)_{10}$ are not formed in measurable amounts. We therefore believe that such processes are not operative to an extent that affects the rate constant results listed in Table II.

Poë has argued that the nature of the phosphine ligand in the $Mn_2(CO)_8(PR_3)_2$ compounds affects the strength of the metal–metal bond in the dinuclear species in which the phosphine ligands occupy positions along the metal–metal bond axis.[23] Strong σ donor ligands with little π acid character are thought to incur larger $d\pi$–$d\pi$ electron repulsions between the metals, leading to weaker metal–metal bonds. The fact that these effects are not reflected in significant barriers to the recombinations of the radicals suggests that the transition state in the recombination is very early; that is, there is very little bond making in the transition state. A low barrier to recombination is evident also in the generally high values for the recombination rate constants. Even the slowest recombination rate, for $Mn(CO)_4P(i\text{-}Pr)_3\cdot$, is at most only about 3 orders of magnitude less than the diffusion-controlled limit. In the product dinuclear compounds following radical recombination, the phosphine ligands are located in the axial positions. There is abundant evidence that this location is determined by steric rather than electronic considerations. In the case of substituted $Re_2(CO)_{10}$ compounds, for which more data are available, smaller phosphorus donor ligands, as well as smaller ligands of other types, with lower π-bonding capacity and larger σ donor capability than CO, occupy radial positions. There is some basis for supposing further that, in $Mn(CO)_4L\cdot$ radicals, most ligands preferentially occupy one of the basal positions in the square-pyramidal structure.[8] This means that a rearrangement must precede recombination of $Mn(CO)_4PR_3\cdot$ radicals:



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(21) Absorbance maxima for the phosphine disubstituted dimers were determined for hexane solutions: $Mn_2(CO)_8[P(n\text{-}Bu)_3]_2$, 355 nm; $Mn_2(CO)_8[P(i\text{-}Bu)_3]_2$, 357 nm; $Mn_2(CO)_8[P(i\text{-}Pr)_3]_2$, 362 nm; $Mn_2(CO)_8[P(OC_6H_5)_3]_2$, 353 nm.

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The energy requirement for the rearrangement probably constitutes nearly all of the difference in free energy barriers for recombinations of $Mn(CO)_5\cdot$ and $Mn(CO)_4PR_3\cdot$ radicals. This energy requirement is not very large; for the bulkiest ligand, $P(i\text{-}Pr)_3$, the difference in ΔG^* for recombination of the $Mn(CO)_4P(i\text{-}Pr)_3\cdot$ and $Mn(CO)_5\cdot$ radicals amounts to only 14 kJ/mol (3.3 kcal/mol). Recombination to yield the diaxial product is highly selective as demonstrated by the observation that when a solution of the diaxially substituted $Mn_2(CO)_8L_2$ compound in an IR cell is repeatedly flashed with a photoflash lamp, there is no appearance of other isomers, as determined by IR. The identical experiment performed in CCl_4 has $Mn(CO)_4LCl\cdot$ as the only product, confirming that $Mn(CO)_4L\cdot$ is produced under these conditions.

One consequence of the slower rates of recombination for the $Mn(CO)_4PR_3\cdot$ radicals is that they are long-lived in solution, insofar as their lifetimes are limited by formation of the dinuclear species. This means that there will be, in general, longer time available for other chemical processes, notably substitution, atom transfer, or electron transfer, to occur. Where the steric requirements of ligands on the metal are sufficiently large, the radicals cannot assume a configuration that permits a stable metal–metal bond, so the radicals persist in solution. This occurs for the disubstituted species, $Mn(CO)_3(PR_3)_2\cdot$. In this limiting case it is possible to directly measure the rates of substitution[10] or atom transfer.[9] The results to date show that the disubstituted species are much less labile toward substitution than $Mn(CO)_5\cdot$ and that substitution proceeds by an associative route. That this is the case, even with bulky phosphines on the metal, indicates that dissociative loss of ligands from $Mn(CO)_3(PR_3)_2\cdot$ radicals is slow. There is reason also to believe that monosubstituted radicals, $Mn(CO)_4PR_3\cdot$, are less labile than $Mn(CO)_5\cdot$. We are currently examining the reactivities of the $Mn(CO)_4PR_3\cdot$ radicals toward atom-transfer agents. We have also recently completed a study of the formation of $Mn_2(CO)_7L_2$ by flash photolysis and measured the rates of back-reaction with CO.[24]

Registry No. $Mn_2(CO)_{10}$, 10170-69-1; $Mn_2(CO)_8(P(n\text{-}Bu)_3)_2$, 15609-33-3; $Mn_2(CO)_8(P(i\text{-}Bu)_3)_2$, 83634-21-3; $Mn_2(CO)_8(P(i\text{-}Pr)_3)_2$, 75847-41-5; $Mn_2(CO)_8(PPh_3)_2$, 15279-67-1; $Mn_2(CO)_8(P(OPh)_3)_2$, 15228-70-3; $Mn_2(CO)_8(dppe)$, 75847-46-0; $Mn(CO)_5\cdot$, 54832-42-7; $Mn(CO)_4P(n\text{-}Bu)_3\cdot$, 45264-38-8; $Mn(CO)_4P(i\text{-}Bu)_3\cdot$, 92186-52-2; $Mn(CO)_4P(i\text{-}Pr)_3\cdot$, 92186-53-3; $Mn(CO)_4P(OPh)_3\cdot$, 47670-58-6; $Mn(CO)_4PPh_3\cdot$, 14971-47-2.

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Optical and ESR Studies for the Reaction of Molybdenum Tetraphenylporphyrins in γ-Ray-Irradiated 2-Methyltetrahydrofuran

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The molybdenum(V) tetraphenylporphyrins, $Mo^{V}O(TPP)X$ (X = NCS, F, Cl, Br), in the glassy matrix of 2-methyltetrahydrofuran (MeTHF) at 77 K are reduced by γ-ray irradiation to form the constrained complexes, $[Mo^{IV}O(TPP)X]^-$, in which the ligand X is forced to be coordinated to the central molybdenum. When the solution is warmed, $Mo^{IV}O(TPP)$ is formed by release of the ligand X. The bands of the visible absorption spectra of $[Mo^{IV}O(TPP)X]^-$ formed in the rigid matrix depend on the ligand X and shift to longer wavelengths in the order of X = F < NCS < Cl < Br. The formation of the complex of MeTHF, $Mo^{IV}O(TPP)MeTHF$, was also detected as the temperature of the solution of $Mo^{IV}O(TPP)$ was lowered to −72 °C. The velocity of the backward reaction of $Mo^{IV}O(TPP)$ to form $Mo^{V}O(TPP)X$ is dependent on the ligand X.

Introduction

Molybdenum porphyrin complexes have been widely studied in the last several years because of the versatility of their reactions in organic solvents. The molybdenum(V) tetraphenylporphyrin complexes, $Mo^{V}O(TPP)X$ (X = NCS, Br), are reduced by superoxide ion to form the molybdenum(IV) tetraphenylporphyrin complex, $Mo^{IV}O(TPP)$, via an intermediate that is suggested to be the dioxygen complex.[1] The methoxo complex, $Mo^{V}O(TPP)OCH_3$, is also reduced photochemically to the Mo(IV) complex in benzene solution.[2] In the course of the photochemical reaction of the *trans*-diperoxo complex, $Mo^{VI}(O_2)_2(TTP)$ (TTP = tetra-*p*-tolylporphinato), to form *cis*-dioxo complex, $Mo^{VI}(O)_2(TTP)$, a change in the oxidation state of the central molybdenum of the complexes was suggested.[3,4] Thus, these reaction processes may include transient reaction intermediates in which the oxidation state of the central molybdenum is different from that of the starting materials. Detection and characterization of the intermediates have significance for the elucidation of the mechanisms of electron-transfer and photochemical reactions, so we were motivated to study the reaction of $Mo^{V}O(TPP)X$ by γ-irradiation, which is considered to cause simple oxidation–reduction reactions of the complex.

The Soret bands, the α bands, and the β bands of the spectra of these complexes, $Mo^{V}O(TPP)X$, shift to longer wavelength in the order X = F < Cl < Br, which was ascribed to the electronegativity of the ligand X.[5] Thus, we were also interested in a spectroscopic study of the intermediate, which might be observed as a constrained complex in which the ligand X was forced to be coordinated to the central molybdenum, owing to the rigidity of the solvent matrix at 77 K.[6]

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