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Design of Transition Metal Complexes with High Quantum Yields for Ligand Substitution: Efficient Photochemical Chelate Ring Closure in Cyclopentadienylmanganese Tricarbonyl Derivatives

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The quantum yields for photosubstitution of $(\eta^5\text{-}C_5H_4R)Mn(CO)_3$ (R = H, $COCH_3$, $COCH_2OCH_3$, $COCH_2SCH_3$, $CO(CH_2)_2SCH_3$, $CH_2CO_2CH_3$, $(CH_2)_2CO_2CH_3$)) in heptane for 337 nm irradiation are 0.67, 0.82, 0.64, 1.00, 0.82, 0.80, and 1.05, respectively. The yields of ring-closed products were determined for the sulfur-containing complexes while the yields of substitution with dispersed ligands were determined for the remaining complexes since the ring-closed products were not stable. In contrast to a previous study for cyclopentadienylmanganese complexes the quantum yields were found to change with the structure of a substituent. The results for R = $COCH_2SCH_3$ and $(CH_2)_2CO_2CH_3$ are apparently the first *bona fide* examples of unit quantum yields for organometallic complexes in solution. It is proposed that after CO dissociation that selected ring substituents can trap the metal center before CO can recombine with the metal.

Introduction

We have studied various organometallic compounds in an effort to understand processes that effect the quantum yields for ligand substitution reactions.[1] A perfectly efficient photochemical reaction would have a unit quantum yield, and while such cases have been reported for the substitution of organometallic complexes in solution, the quantum yields were later found to be less than unity.[1,2] Many of the organometallic complexes that have high quantum yields are carbonyls; nevertheless, the quantum yields vary greatly for these complexes, and what determines which complexes have high quantum yields is not clear.[3] It has been postulated that for some metal carbonyl complexes a competition between the cage recombination and cage escape of photodissociated CO has a role in determining the quantum yield.[1b,2b,4] Hence a ligand that could chelate before CO recombination could increase the net yield of CO substitution. Previous studies of $(Cp)Mn(CO)_2(\eta^1\text{-}Me_2P(CH_2)_nPMe_2)$ ($n = 1-3$) were not encouraging: the quantum yields for the ring closures that follow CO photodissociation do not change with chain length suggesting that ring closure does not compete with the processes that partition CO loss and return to the ground-state complex.[5] We thought that these were unusual results; thus, we investigated the photochemical ring closure of the related $(\eta^5\text{-}C_5H_4R)Mn(CO)_3$ (R = H, $COCH_3$, $COCH_2OCH_3$, $COCH_2SCH_3$, $CO(CH_2)_2SCH_3$, $CH_2CO_2CH_3$, $(CH_2)_2CO_2CH_3$)). In contrast to the previous study, we have obtained quantum yields for chelate ring closure that are highly dependent on R. Two of the complexes are apparently the first reported *bona fide* examples of organometallic complexes that have unit quantum yields for substitution in solution. These results may be of synthetic utility as well. In particular, we found a labile intermediate for R = $(CH_2)_2CO_2CH_3$ (most likely an oxygen chelate)[6] can react further with a dispersed ligand to give a substitution product with a unit quantum yield.

Experimental Section

Materials. All compounds were used as received from Aldrich unless mentioned otherwise. Heptane (HPLC grade) was refluxed with sodium overnight under argon prior to distillation. Toluene was distilled over Na. $CpMn(CO)_3$ was sublimed twice under vacuum before use. Triphenylphosphine was recrystallized from ethanol, and tetrahydrothiophene (THT) was distilled after refluxing over CaH_2 for 6 h. Aberchrome 540 ((*E*)-2-[1-(2,5-dimethyl-3-furanyl)ethylidene]-3-(1-methylethylidene)succinic anhydride, Aberchromics, Ltd., Cardiff, Wales) was stored at −20 °C until used. The synthesis of various $(\eta^5\text{-}C_5H_4R)Mn(CO)_3$ derivatives (including chelates) have been described recently.[6,7]

Quantum Yield Determinations. UV−vis absorption coefficients of all complexes were obtained from the slopes of absorbance versus concentration plots. The square of the correlation coefficient (R^2) was greater than 0.998 in all

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Table 1. Molar Absorptions of (η^5-C_5H_4R)Mn(CO)$_3$, Substitution Products, and Ligands in Heptane[a]

(η^5-C_5H_4R)Mn(CO)$_3$			(η^5-C_5H_4R)Mn(CO)$_2$L	
R	ϵ_{337} (M^{-1} cm^{-1})	L (M)	ϵ_{337} (M^{-1} cm^{-1})	ϵl^b (M^{-1})
H	1003	PPh_3 (0.02)[c]	1559	801 (1885)
$COCH_3$	1221	THT (0.0476)[c]	1357	650 (1885)
$COCH_2OCH_3$	1827	THT (0.125)	1362	658 (1887)
$COCH_2SCH_3$	2022		491	761 (1898)
$COCH_2CH_2SCH3$	1377		1370	683 (1894)
$CH_2CO_2CH_3$	915	P(OEt)$_3$ (0.258)	1168	685 (1888)
			955[d]	387 (1868)
$CH_2CH_2CO_2CH_3$	1113	P(OEt)$_3$ (0.100)	1000	640 (1887)
			1024[d]	364 (1867)

[a] Errors are ±3%. [b] $l = 0.2$ mm; values in parentheses are IR peak frequencies in cm^{-1}. [c] The 337 nm extinction coefficients of PPh_3 and THT are 3.03 ± 0.03 and 0.249 ± 0.006, respectively. [d] A disubstituted product.

determinations. The absorbance at 337 nm of solutions containing 10% THT and (η^5-C_5H_4R)Mn(CO)$_3$ (R = H, $COCH_3$, $COCH_2OCH_3$) were investigated. After correction for THT absorbance, the absorbance due to (η^5-C_5H_4R)Mn(CO)$_3$ was found to be the same as solutions containing no THT. Examination of (η^5-$C_5H_4COCH_3$)Mn(CO)$_3$ infrared spectra revealed that CO bands broadened at high THT concentration (0.5 M), but the areas remained constant. No such broadening was observed for the other complexes in the absence added ligand. To simplify measurements, ligand concentrations were kept constant for measurements of all complexes. Photoproduct concentrations were determined from CO stretching frequencies by using calibration plots of absorbance versus concentration. Concentrations were determined from IR absorbances below 0.3 where the R^2 for the calibration plots were greater than 0.998. Molar absorption data for quantum yield determinations are listed in Table 1. The UV−vis spectra of (η^5-C_5H_4R)Mn(CO)$_3$ in cyclohexane, dichloromethane, THF, acetone, and acetonitrile were also obtained. No peak shifts were observed for these solvents, although the magnitude of these peaks changed slightly (5 to 14%).

The actinometry apparatus has been described previously.[1] Light intensities at 337 nm were routinely determined with Aberchrome 540.[8] The accuracy of this chemical actinometer was verified by using azobenzene and Cr(CO)$_6$ as secondary actinometers.[2a,9] The volume of the Aberchrome 540 solution was calculated from its weight and density.[10] The 494 nm absorbance of the Aberchrome 540 solution was measured before and after each irradiation of Aberchrome 540. The average of the light intensities determined before and after sample irradiation was used to calculate the quantum yield for each sample.

In a typical irradiation experiment, 0.0260 g of (η^5-$C_5H_4CH_2CO_2CH_3$)Mn(CO)$_3$ was weighed in a 10-mL volumetric flask. The flask was moved into a drybox, filled to the mark with 0.258 M P(OEt)$_3$ in heptane, and sealed with a rubber septum. After stirring, the absorbance of this solution was greater than 3.5 at 337 nm. The solution was cannula transferred to an argon-filled septum-sealed quartz cuvette, kept in the dark, and stirred with a micro stir bar for 0.5 h before use. Two matched quartz cuvettes were used: one was filled with actinometer solution (65 mg of Aberchrome 540 dissolved in 50 mL of toluene), and the other was filled with the (η^5-$C_5H_4CH_2CO_2CH_3$)Mn(CO)$_3$ stock solution. At least three different concentrations of each (η^5-C_5H_4R)Mn(CO)$_3$ were prepared, and the concentration of trapping ligand was the same as that used in molar absorption determinations. Since the chelate products were stable for R = $COCH_2SCH_3$ and $COCH_2CH_2SCH_3$, no trapping ligand was required.[6] The measurement for each (η^5-C_5H_4R)Mn(CO)$_3$ concentration was the average of at least 4 determinations where the irradiation time was varied for each determination. The quantum yield was found to be independent of concentration of (η^5-C_5H_4R)Mn(CO)$_3$ and irradiation time. The conversion to photoproducts was limited to 1−4%. Quantum yields were corrected for the inner-filter effect.[2b]

Table 2. Quantum Yields for 337 nm Photosubstitution of (η^5-C_5H_4R)Mn(CO)$_3$

R (10^{-3}M)	L (M)	n^a	λ_{max} (ϵ)	Φ (1σ)^b
H (14−21)	PPh_3 (0.02−0.1)	4	330 (1410)	0.67 (±0.04)
$COCH_3$ (9−12)	THT (0.0476)	3	338 (1360)	0.82 (±0.05)
$COCH_2OCH_3$ (8−33)	THT (0.125)	6	338 (120)	0.64 (±0.05)
$COCH_2SCH_3$ (3.4−12)		4	336 (2020)	1.00 (±0.06)
$COCH_2CH_2SCH_3$ (12−15)		4	338 (1380)	0.82 (±0.05)
$CH_2CO_2CH_3$ (9−19)	P(OEt)$_3$ (0.258)	3	332 (920)	0.80 (±0.05)
$CH_2CH_2CO_2CH_3$ (2−19)	P(OEt)$_3$ (0.100)	4	330	1.05 (±0.06)

[a] Number of independent stock solutions of (η^5-C_5H_4R)Mn(CO). [b] Propagated errors.

Results

The values of the quantum yields for monosubstitution of (η^5-C_5H_4R)Mn(CO)$_3$ are reported in Table 2. The literature value of the quantum yield for CpMn(CO)$_3$ photosubstitution (0.65) was confirmed by using the same conditions.[11] Photolysis of (η^5-$C_5H_4CH_2CO_2CH_3$)Mn(CO)$_3$ resulted in the formation of a disubstituted and a monosubstituted product. The quantum yield of the disubstituted product was 0.14. No disubstituted photoproducts were found for the other derivatives. To further establish the differences in the quantum yields (η^5-$C_5H_4COCH_2CH_2SCH_3$)Mn(CO)$_3$ (1.23×10^{-2} M in heptane) and (η^5-$C_5H_4COCH_2OCH_3$)Mn(CO)$_3$ (1.37×10^{-2} M in 0.125 M THT heptane solution) were alternatively irradiated, and the Aberchrome 540 was only used at the beginning and the end of the experiment to verify the magnitude of the light intensity. The ratio of the yields for (η^5-$C_5H_4COCH_2CH_2SCH_3$)Mn(CO)$_3$ and (η^5-$C_5H_4COCH_2OCH_3$)Mn(CO)$_3$ was 1.25, and this agrees with the ratio of 1.28 obtained from Table 2. The quantum yields were independent of the ratio of the metal-to-ligand concentrations used. The λ_{max} in Table 2 corresponds to lowest energy band for each complex.

Discussion

The lowest electronic transition for (η^5-C_5H_4R)Mn(CO)$_3$ is populated by 337 nm irradiation and has been assigned to Mn → η^5-C_5H_4R CT with lesser contributions from LF and Mn−CO π*CT.[3] The proposal that the absorption is dominated largely by Mn → η^5-C_5H_4R CT is consistent with our results where small but significant wavelength increases are observed for electron-withdrawing substituents on the cyclopentadienyl ring. While absorption is dominated by the more intense Mn → η^5-C_5H_4R CT transition, the photochemistry is most likely to occur by population of LF excited states which are σ antibonding.[3] The changes in the electronic spectra with R are small and show no correlation with the changes in the quantum yields; thus, we propose that the same excited state is accessed in each case. No luminescence[12] or side products were observed. For such cases the quantum yield for product formation is determined by the competition between the forward and

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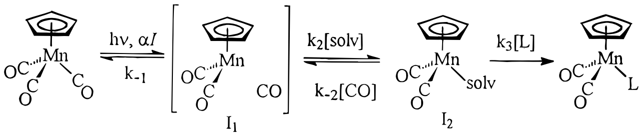
Scheme 1



reverse processes for each step in a photoreaction. Scheme 1 shows possible steps in the photosubstitution of CpMn(CO)$_3$ that could account for a quantum yield of less than unity, where α is the fraction of excited state that undergoes CO dissociation and *I* is the light intensity. Upon application of the steady-state assumption to I$_1$ and I$_2$, eq 1 is obtained. Every I$_2$ is converted

$$\Phi = \frac{d[\mathrm{CpMn(CO)_2L}]/dt}{I} = \frac{\alpha k_2[\mathrm{solv}]\dfrac{k_3[\mathrm{L}]}{k_{-2}[\mathrm{CO}] + k_3[\mathrm{L}]}}{k_{-1} + k_2[\mathrm{solv}]\dfrac{k_3[\mathrm{L}]}{k_{-2}[\mathrm{CO}] + k_3[\mathrm{L}]}} \qquad (1)$$

to product if k_3[L] ≫ k_{-2}[CO], and an examination of our data and the literature indicates this is the case. Specifically, k_3 and k_{-2} for the addition of PPh$_3$ and CO to CpMn(CO)$_2$(cyclohexane) are 5.3×10^6 and 3.4×10^5 L mol^{-1} s^{-1}, respectively, and the rate constants in heptane are greater by a factor of 2−3 for each ligand that was investigated.[13] The upper limit of the CO produced from CpMn(CO)$_3$ in our experiments is 9×10^{-4} M, while the lowest concentration of added PPh$_3$ was 1.36×10^{-2} M. Thus k_3[L] ≫ k_{-2}[CO], and eq 1 simplifies to eq 2. According to this expression the

$$\Phi = \alpha\frac{k_2[\mathrm{solv}]}{k_{-1} + k_2[\mathrm{solv}]} \qquad (2)$$

nonunit quantum yield is due to either deactivation of the excited state of (Cp)Mn(CO)$_3$ ($\alpha < 1$), cage recombination with CO (k_2[solv]/(k_{-1} + k_2[solv] < 1), or both. A similar mechanism is proposed in Scheme 2 for the photosubstitution of (η^5-C$_5$H$_4$R)Mn(CO)$_3$ (excluding perhaps R = COCH$_3$) where I$_3$ is either a stable product or is an intermediate that is converted completely to a stable product. The steady-state assumption applied to I$_1$ and I$_2$ yields eq 3. If direct addition of L to I$_2$ (not shown) is faster than CO addition (as it is for CpMn(CO)$_3$) or if k_3 ≫ k_{-2}[CO] (even more likely), then the quantum yield can be expressed as eq 4. If Schemes 1 and 2 are correct, an analysis of the structures and quantum yields suggests that ring closure in certain cases can compete with geminate CO recombination (*vide infra*).

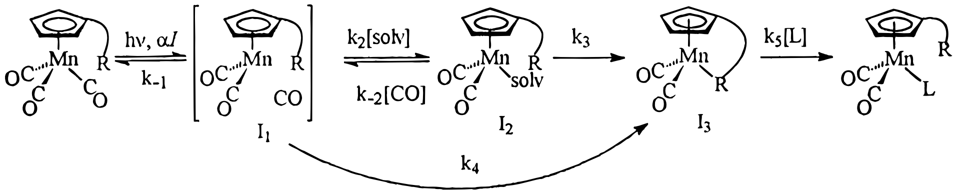
$$\Phi = \frac{d[(\eta^6\text{-}\mathrm{C_5H_4R})\mathrm{Mn(CO)_2}]/dt}{I} = \frac{\alpha k_4 + \alpha k_2[\mathrm{solv}]\dfrac{k_3}{k_{-2}[\mathrm{CO}] + k_3}}{k_{-1} + k_4 + k_2[\mathrm{solv}]\dfrac{k_3}{k_{-2}[\mathrm{CO}] + k_3}} \qquad (3)$$

$$\Phi = \frac{\alpha(k_4 + k_2[\mathrm{solv}])}{k_{-1} + k_4 + k_2[\mathrm{solv}]} \qquad (4)$$

The analysis begins with (η^5-C$_5$H$_4$CH$_2$CH$_2$CO$_2$CH$_3$)Mn(CO)$_3$ for which the quantum yield is unity. This requires that α is also unity and k_4 + k_2[solv] ≫ k_{-1}. The electronic spectra of the complexes do not change with the polarity of solvent, and this indicates a charge transfer with R in the excited state is unlikely. The metal-centered electronic structure of (η^5-C$_5$H$_4$CH$_2$CH$_2$CO$_2$CH$_3$)Mn(CO)$_3$ and CpMn(CO)$_3$ should be nearly identical (see Table 2); thus, we conclude that α is also unity for CpMn(CO)$_3$. It follows that the quantum yield for CpMn(CO)$_3$ is determined by the competition between CO recombination and solvent addition and that k_2[solv] and k_{-1} are of comparable magnitude. Since k_2[solv] or k_{-1} are not expected to be different for (η^5-C$_5$H$_4$CH$_2$CH$_2$CO$_2$CH$_3$)Mn(CO)$_3$ and CpMn(CO)$_3$, the unit quantum yield for the former must be due to k_4 being greater than k_{-1} (eq 4). This analysis suggests we have created compounds that have substituents that can compete with CO cage recombination. Indeed ring closure must be much faster than CO recombination.

Our results suggest that subtle changes in R dramatically effect k_4. For example, substitution of sulfur for the ether oxygen in (η^5-C$_5$H$_4$COCH$_2$OCH$_3$)Mn(CO)$_3$ increases the quantum yield to unity, or increasing the chain length in (η^5-C$_5$H$_4$COCH$_2$SCH$_3$)Mn(CO)$_3$ decreases the quantum yield. Such a ring closure would have to be extraordinarily fast since recent studies have reported that cage CO recombination can occur within 200−300 fs.[14] Extremely rapid ring closures have been reported in studies of Mn$_2$CO$_{10}$ and spiropyrans.[14a,15,16] In both these examples ring closure was for geminate reaction sites generated with no intervening solvent molecules. As a consequence, the recombinations are not diffusive. For R = COCH$_2$SCH$_3$ a five-membered ring must close, and if the most stable conformation of R extends into the solvent, ring closure will be >100 ps and will not compete with solvent coordination or CO recombination.[17] A very rapid ring closure could be explained by an association between the metal center and R prior to photolysis, but an examination of the UV−vis, IR, and NMR spectra shows no evidence of such an association.[7] Among the various confirmations available to R, one having a reactive site in the proximity of the metal center needs to be favored by only 2−3 kcal/mol. Such a conformation could be assisted by a

Scheme 2



weak dipole–dipole interaction, which might go undetected by routine spectroscopic examination. In contrast, it might be argued that association of R should have no effect on the quantum yield since a solvent molecule is always available after CO dissociation and would eventually be displaced by R; however, this neglects the importance of bond strengths in overcoming the excess vibrational energy of the excited complex. Upon CO dissociation, the complex is vibrationally excited and, by analogy to $M(CO)_5$, will relax in 100 ps.[18] While CO can coordinate 300 fs after photolysis, a hydrocarbon solvent does not coordinate until about 10 ps.[14,19] This difference can be attributed to the excess vibrational energy that breaks the weak metal–solvent bond until the complex has relaxed sufficiently. Finally it should be pointed out that subtle changes in solvent can have significant effects on quantum yields.[1b] For example the quantum yield for substitution on $Cr(CO)_6$ is 0.73 ± 0.01 in *n*-heptane and 0.66 ± 0.1 in *n*-octane, and the authors concluded that the quantum yield is not a simple function of viscosity.[20] These results and other suggest that molecular properties (such as shape) that are not directly related to bulk viscosity can effect dissociation quantum yields. Thus, given the right circumstances we propose R can be more efficient than solvent in trapping the metal center.

Our results seem to contradict those reported for $(Cp)Mn(CO)_2(\eta^1\text{-}Me_2P(CH_2)_nPMe_2)$ ($n = 1-3$) where the quantum yields were independent of *n* and less than unity (0.61).[5] These results indicate that ring closure in the phosphine complexes did not occur on the same time scale as CO recombination; either the ring closures must be much faster than the CO recombination or much slower. If the ring closures are faster, then the low quantum yield would have to be due to a partitioning of competing processes at an earlier stage of the reaction. These processes would be CO dissociation and the return of the excited state back to the ground state. In analogy to Schemes 1 and 2, this would mean α for $(Cp)Mn(CO)_2(\eta^1\text{-}Me_2P(CH_2)_nPMe_2)$ is 0.61 in contrast to the 1.0 observed for the tricarbonyl complexes. Previous studies indicate that the LF transitions for $(Cp)Mn(CO)_2L$ are at lower energy than for $(Cp)Mn(CO)_3$, but for 337 nm excitation the ligand dissociation still occurs from the excited LF state.[21] Interestingly, phosphines are the only ligands known where CO not L is observed to substitute.[22] In contrast, when L is an amine, only the amine substitutes and not CO.[21] This is presumably due to the fact that the weakest metal–ligand bond dissociates. With the current data we cannot predict how the relative rates of the excited-state decay pathways may differ for $(Cp)Mn(CO)_2L$ and $(Cp)Mn(CO)_3$. Thus we cannot rule out that the changes favor the return of the excited state to the ground state, in which case $(Cp)Mn(CO)_2(PR_3)$ could have an α of 0.61. Interestingly the quantum yield at 366 nm for CO substitution of $(Cp)Mn(CO)_2(PPh_3)$ is 0.59 ± 0.05. If α is 0.61 for $(Cp)Mn(CO)_2(PPh_3)$, then this leads to the unlikely conclusion that no significant cage CO recombination occurs; otherwise the quantum yield would be lower than 0.61. The alternative conclusion is that all the ring closures for $(Cp)Mn(CO)_2(\eta^1\text{-}Me_2P(CH_2)_nPMe_2)$ is much slower than the CO recombination and that the low quantum yield is due to CO cage recombination. If this is the case, it is curious that at least one $(Cp)Mn(CO)_2(\eta^1\text{-}Me_2P(CH_2)_nPMe_2)$ does not have a higher quantum yield; nevertheless, these compounds are fundamentally different than those in our study in that the ring terminates at a phosphine instead of the C_5H_4 ring and the electron density of the metal center is greater. Both steric effects and electronic effects could conspire to inhibit rapid ring formation. The approach of a phosphine will be sterically inhibited more by $Mn(CO)PR_3$ than by $Mn(CO)_2$, and the noncovalent attraction with the electron-rich $Mn(CO)PR_3$ will be weaker that with $Mn(CO)_2$.

In summary, we have reported the first documented examples of an organometallic photosubstitution in solution with a unit quantum yield. The magnitudes of the quantum yields show no simple correlation with chain length or coordinating atom of R. By analogy with other metal carbonyls geminate CO recombination is expected to be a major pathway for decay of $(\eta^5\text{-}C_5H_4R)Mn(CO)_2$. Thus the unit quantum yields observed for two of the complexes indicates a change in relative rates of very rapid processes. Ring closure for R = $COCH_2SCH_3$ and $(CH_2)_2CO_2CH_3$ could be very rapid if a favorable conformation brings the side chain sulfur or oxygen in close proximity to the metal center. Upon CO dissociation, the sulfur or oxygen would combine with the metal center in an extremely rapid nondiffusive process. Time-resolved and molecular mechanics studies will be undertaken to study these processes in further detail.

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