

Contribution from the Institute of Physical Chemistry,
University of Perugia, 06100 Perugia, Italy**Mechanism of Substitution of (π -Monoolefin)iron Tetracarbonyl Complexes by Triphenylphosphine. Effect of Carbon Monoxide**

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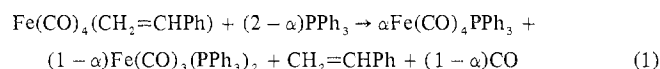
Received March 27, 1974

AIC402021

The reaction between $\text{Fe}(\text{CO})_4(\text{CH}_2=\text{CHPh})$ and PPh_3 is studied in the presence of carbon monoxide (0–22 atm). The effect of carbon monoxide on the rate constants and on the $[\text{Fe}(\text{CO})_4\text{PPh}_3]/[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]$ ratio is observed. The results indicate that the $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ complex is formed by reaction of PPh_3 with the intermediate $\text{Fe}(\text{CO})_3$. This intermediate is obtained by dissociation of $\text{Fe}(\text{CO})_2$, which is the product of the dissociation of the $\text{Fe}(\text{CO})_4(\text{CH}_2=\text{CHPh})$ complex.

Introduction

In a previous paper¹ we reported the results obtained in the mechanistic study of the reaction



in which α is the fraction of monosubstituted complex formed per mole of the starting olefin compound. On the basis of the results available two different reaction mechanisms were suggested to explain the simultaneous formation of monosubstituted and disubstituted complexes. The first assumed that the intermediate, $\text{Fe}(\text{CO})_4$, formed in the first reaction step, was present in two forms in equilibrium, as observed for the $\text{M}(\text{CO})_6$ ($\text{M}=\text{Cr}, \text{Mo}, \text{W}$) complexes² and that these two forms, due to their different reactivity towards PPh_3 , give rise to both monosubstituted and disubstituted complexes. The second mechanism assumed, instead, that the intermediate, $\text{Fe}(\text{CO})_4$, underwent further dissociation to give $\text{Fe}(\text{CO})_3$, which was then responsible for the formation of the bisubstituted complex. In the hope of shedding further light on the mechanism and on the nature of the reaction intermediates, this paper reports results obtained from the study of the effect of carbon monoxide on the kinetics of reaction 1 and on the ratio $\alpha/(1 - \alpha)$.

Experimental Section

$\text{Fe}(\text{CO})_4(\text{CH}_2=\text{CHPh})$ was prepared as in the literature.³ Kinetic runs were carried out at atmospheric pressure (or less) of carbon monoxide in a thermostated vessel⁴ from which aliquots were drawn using a syringe. The solution was saturated with CO, prepared and purified according to ref 5. The reaction vessel was connected to a CO reserve so as to maintain constant CO pressure during the reaction. A CO pressure less than atmospheric was obtained by dilution with nitrogen, and a Mohr vessel was used to measure gas volumes. The solutions were stirred magnetically. The kinetics were followed by observing the intensities of the CO stretching bands both of $\text{Fe}(\text{CO})_4(\text{CH}_2=\text{CHPh})$, at higher frequency, and of the mono- and disubstituted complexes. Measurements were carried out on a Perkin-Elmer IR 257 spectrophotometer.

The reactions at CO pressure greater than atmospheric (1–22 atm) were carried out in a beaker set in a reactor of the bomb calorimeter type. The reactor was thermostated at 50° and the toluene solution stirred magnetically. The carbon monoxide used was of commercial origin and contained small amounts of $\text{Fe}(\text{CO})_5$. The ratio $\alpha/(1 -$

$\alpha)$ was measured spectrophotometrically at the end of reaction. It was not possible to remove intermediate aliquots during the measurements, so reaction rate constants for the reaction could not be determined.

The formation of $\text{Fe}(\text{CO})_5$ in trace amounts ($\sim 1\%$) was ascertained only where the ratio $[\text{CO}]/[\text{PPh}_3] \cong 1$. These values are very low owing to the vigorous stirring and partial temperature evaporation of $\text{Fe}(\text{CO})_5$.

During the reactions carried out with commercial CO, the formation of $\text{Fe}(\text{CO})_5$ was checked by carrying out blanks under identical conditions and comparing the final concentrations of $\text{Fe}(\text{CO})_5$ obtained with those found during reaction. The concentrations of carbon monoxide present were determined assuming Henry's law was valid and using the solubility data for 1 atm and various temperatures.⁶

Results and Discussion

Table I shows the values of the rate constants measured from the disappearance of $\text{Fe}(\text{CO})_4(\text{CH}_2=\text{CHPh})$ and also those from the appearance of $\text{Fe}(\text{CO})_4\text{PPh}_3$ and $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$, for various concentrations of PPh_3 and carbon monoxide. The values of $\alpha/(1 - \alpha)$ measured under the same experimental conditions are reported. These ratios remain constant as the reaction proceeds. Table II shows the values of $\alpha/(1 - \alpha)$ obtained at high CO pressure (1–22 atm) and at various concentrations of PPh_3 . These reactions were not followed kinetically. The $\alpha/(1 - \alpha)$ values for several reactions, carried in excess of $\text{CH}_2=\text{CHPh}$, are also reported.

The additional points of relevance, considering the results of ref 1, are as follows.

(1) The ratio $\alpha/(1 - \alpha)$ does not vary with the concentration of $\text{CH}_2=\text{CHPh}$.

(2) In the absence of CO, the ratio $\alpha/(1 - \alpha)$ does not depend on the concentration of PPh_3 when $[\text{PPh}_3]/[\text{Fe}(\text{CO})_4(\text{CH}_2=\text{CHPh})] > 5$. For lower values of the latter ratio, $\alpha/(1 - \alpha)$ increases with decrease in the ratio $[\text{PPh}_3]/[\text{Fe}(\text{CO})_4(\text{CH}_2=\text{CHPh})]$.

(3) The ratio $\alpha/(1 - \alpha)$ increases with the CO pressure. At constant CO pressure $\alpha/(1 - \alpha)$ decreases with increase in PPh_3 concentration. Figure 1 shows the $\alpha/(1 - \alpha)$ plots vs. P_{CO} at constant concentration. Figure 2 shows the $\alpha/(1 - \alpha)$ plots vs. $1/[\text{PPh}_3]$ at constant CO pressure. All of the plots are parabolic with nonzero intercepts on the ordinate axis.

(4) The first-order rate constants do not depend on the concentration of CO, and the k values obtained from the $\text{Fe}(\text{CO})_4(\text{CH}_2=\text{CHPh})$ disappearance and from the $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ and $\text{Fe}(\text{CO})_4\text{PPh}_3$ appearance are equal, within the limits of experimental error.

The independence of the rate constants and the change of $\alpha/(1 - \alpha)$ with the CO pressure support the presence of a

(1) G. Cardaci, *Inorg. Chem.*, **13**, 368 (1974).(2) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Amer. Chem. Soc.*, **85**, 1013 (1963); J. Nasielski, P. Kirsh, and L. Wilputte-Steinert, *J. Organometal. Chem.*, **29**, 269 (1971); G. R. Dobson, M. F. A. El-Sayed, I. W. Stolz, and R. K. Sheline, *Inorg. Chem.*, **1**, 526 (1962).(3) E. Koerner von Gustorf, M. C. Henry, and C. Di Pietro, *Z. Naturforsch. B*, **21**, 42 (1966).(4) G. Innorta, G. Reichenbach, and A. Foffani, *J. Organometal. Chem.*, **22**, 731 (1970).(5) W. L. Gilliland and A. R. Blanchard, *Inorg. Syn.*, **2**, 81 (1946).

(6) E. W. Washburn, "International Critical Tables," Vol. 3, McGraw-Hill, New York, N. Y., 1926, p 265.

Table I. Pseudo-First-Order Rate Constants (k) at 50° for the Reaction $\text{Fe}(\text{CO})_4(\text{CH}_2=\text{CHPh}) + (2 - \alpha)\text{PPh}_3 \rightarrow \alpha\text{Fe}(\text{CO})_4\text{PPh}_3 + (1 - \alpha)\text{Fe}(\text{CO})_3(\text{PPh}_3)_2 + (1 - \alpha)\text{CO} + \text{CH}_2=\text{CHPh}$ at Various CO Pressures and PPh_3 Concentrations in Toluene

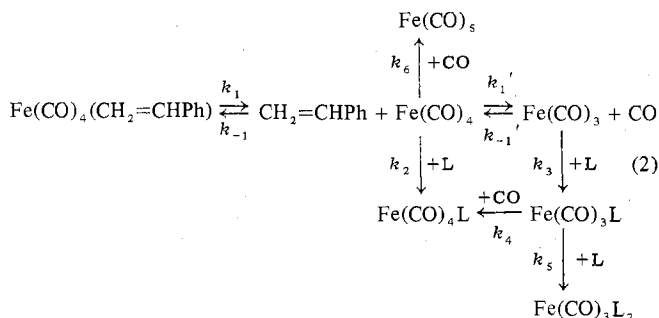
[PPh_3], M	P_{CO} , atm	[CO], M	$10^4 k$, sec^{-1}			$\alpha/(1 - \alpha)$
			a	b	c	
5.16×10^{-1}	1	5.76×10^{-3}	3.87	3.91	3.91	2.7
5.73×10^{-2}	1	5.76×10^{-3}	3.92	3.85	3.64	3.0
2.13×10^{-2}	1	5.76×10^{-3}	3.75	3.80	3.55	3.3
1.08×10^{-2}	1	5.76×10^{-3}	3.73	3.64	3.64	6.2
6.57×10^{-3}	1	5.76×10^{-3}	3.93	3.83	3.71	9.0
4.81×10^{-3}	1	5.76×10^{-3}	3.66	3.60	3.51	14.5
4.92×10^{-3}	0.75	4.32×10^{-3}	3.53	3.54	3.52	9.3
4.77×10^{-3}	0.50	2.88×10^{-3}	3.61	3.52	3.48	7.2
4.81×10^{-3}	0.25	1.44×10^{-3}	3.70	3.51	3.59	4.9
4.92×10^{-3}	0	0	3.52	3.69	3.50	4.4

^a Rate constants based on olefinic complex disappearance. ^b Rate constants based on monosubstituted complex appearance. ^c Rate constants based on disubstituted complex appearance.

Table II. Values of $\alpha/(1 - \alpha)$ at Various PPh_3 , $\text{CH}_2=\text{CHPh}$, and CO Concentrations in Toluene at 50°

[PPh_3], M	P_{CO} , atm	[CO], M	[$\text{CH}_2=\text{CHPh}$], M	$\alpha/(1 - \alpha)$
[$\text{Fe}(\text{CO})_4(\text{CH}_2=\text{CHPh})$] = 1×10^{-2} , M				
5.00×10^{-2}	1	5.76×10^{-3}	0	2.9
5.00×10^{-2}	3.8	2.19×10^{-2}	0	5.9
5.00×10^{-2}	5.5	3.17×10^{-2}	0	8.3
5.00×10^{-2}	8.3	4.79×10^{-2}	0	12.5
5.00×10^{-2}	11	6.34×10^{-2}	0	18.2
5.00×10^{-2}	22	1.27×10^{-1}	0	∞
6.64×10^{-2}	5.5	3.17×10^{-2}	0	6.1
1.04×10^{-1}	5.5	3.17×10^{-2}	0	4.7
2.02×10^{-1}	5.5	3.17×10^{-2}	0	3.5
2.97×10^{-1}	5.5	3.17×10^{-2}	0	3.3
5.10×10^{-1}	5.5	3.17×10^{-2}	0	3.0
5.00×10^{-2}	0	0	0	2.7
5.00×10^{-2}	0	0	0	2.6
[$\text{Fe}(\text{CO})_4(\text{CH}_2=\text{CHPh})$] = 2×10^{-3} , M				
5.00×10^{-2}	0	0	0	2.9
5.00×10^{-2}	0	0	0	2.7
1.00×10^{-2}	0	0	0	2.8
1.00×10^{-1}	0	0	0	2.8
5.00×10^{-1}	0	0	0	2.5
1.10×10^{-2}	0	0	5.95×10^{-2}	2.8
1.03×10^{-2}	0	0	1.26×10^{-1}	2.9
1.22×10^{-2}	0	0	3.23×10^{-1}	2.7
1.10×10^{-2}	0	0	9.13×10^{-1}	2.5

dissociative step of $\text{Fe}(\text{CO})_4$ to $\text{Fe}(\text{CO})_3$ in the mechanism. On the basis of these results, the following reaction mechanism of eq 2 is proposed.



The competition between SbPh_3 or AsPh_3 and CO for the $\text{Fe}(\text{CO})_4$ intermediate can be calculated from the results of ref 1, 7, and 8. The values obtained at 50° in toluene are

(7) G. Cardaci and V. Narciso, *J. Chem. Soc., Dalton Trans.*, 2289 (1972).
 (8) G. Cardaci, *Int. J. Chem. Kinet.*, 5, 805 (1973).

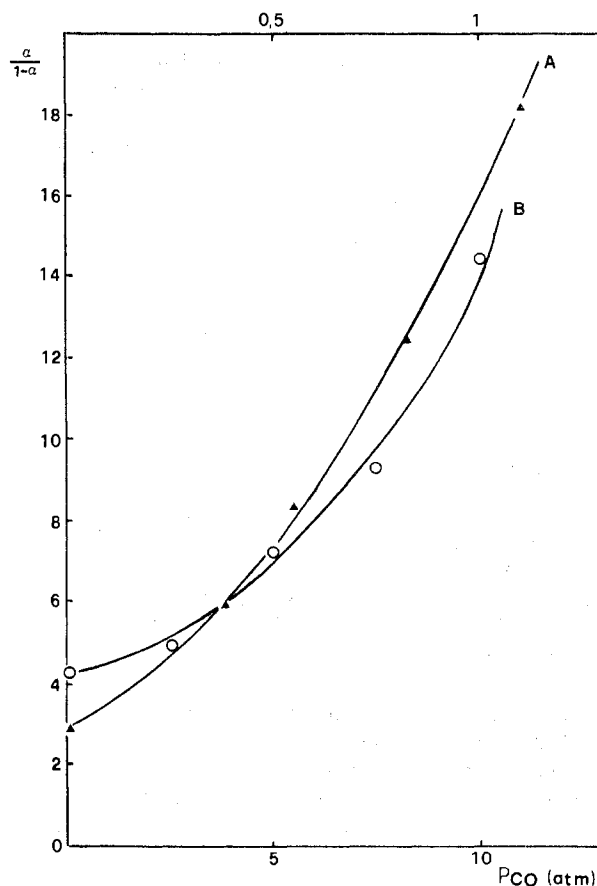


Figure 1. $\alpha/(1 - \alpha)$ vs. P_{CO} plots at 50° in toluene: curve A, [PPh_3] = 5×10^{-2} M , lower abscissa scale; curve B, [PPh_3] = 5×10^{-3} M , upper abscissa scale.

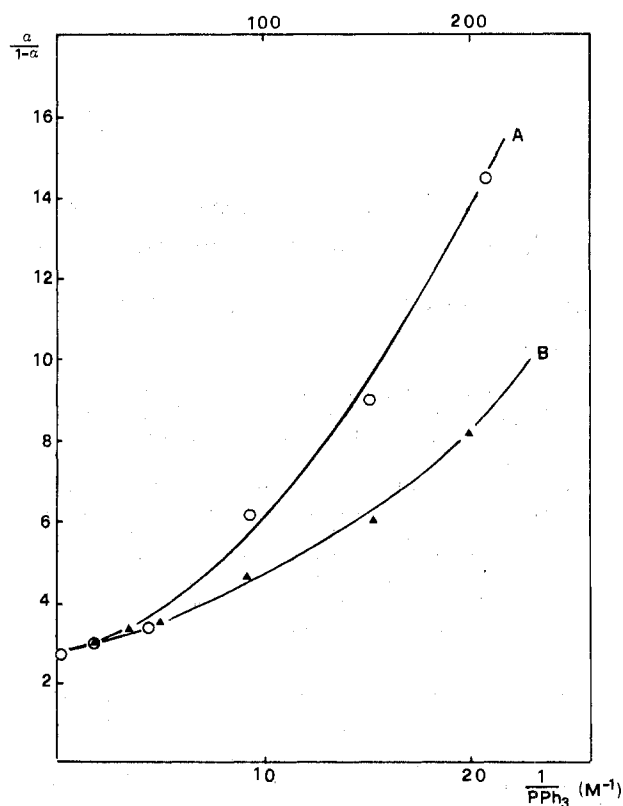


Figure 2. $\alpha/(1 - \alpha)$ vs. $1/[\text{PPh}_3]$ plots at 50° in toluene: curve A, $P_{\text{CO}} = 1$ atm, upper abscissa scale; curve B, $P_{\text{CO}} = 5.5$ atm, lower abscissa scale.

2.8, and 2.9, respectively. Probably the value for PPh_3 is not very different, as found for various other complexes.⁹ For this reason, in eq 2 is inserted also the reaction of $\text{Fe}(\text{CO})_3\text{L}$ with CO.

Given eq 2 and assuming the steady-state approximation is valid for the intermediates $\text{Fe}(\text{CO})_4$, $\text{Fe}(\text{CO})_3$, and $\text{Fe}(\text{CO})_3\text{L}$, expression 3 is obtained for the ratio $\alpha/(1-\alpha)$.

$$\frac{\alpha}{1-\alpha} = \frac{v_M}{v_D} = \frac{k_2}{k_5} \frac{[\text{Fe}(\text{CO})_4]}{[\text{Fe}(\text{CO})_3\text{L}]} + \frac{k_4}{k_5} \frac{[\text{CO}]}{[\text{L}]} = \frac{k_2 k_{-1}' k_4 [\text{CO}]^2}{k_1' k_5 k_3 [\text{L}]} + \left[\frac{k_2 k_{-1}'}{k_3 k_1'} + \frac{k_2 k_4}{k_1' k_5} \right] [\text{CO}] + \frac{k_4}{k_5} \frac{[\text{CO}]}{[\text{L}]} + \frac{k_2}{k_1'} [\text{L}] \quad (3)$$

The values of v_M and v_D correspond to the rates of formation of $\text{Fe}(\text{CO})_4\text{L}$ and $\text{Fe}(\text{CO})_3\text{L}_2$, respectively. All the rate constants refer to reaction mechanism 2 and L indicates the phosphine ligand. Expression 3 indicates a parabolic dependence of $\alpha/(1-\alpha)$ on both $[\text{CO}]$ and $1/[\text{PPh}_3]$ variation. Curve A of Figure 1 fits better than curve B to a parabolic dependence: owing to the low CO pressure value for the measurements of curve B, the CO developed during the reaction changes the CO total pressure. For this reason the intercept of curve B is higher than that of curve A. Both curves are consistent with a parabolic dependence. The coefficients of the parabolic plots give the following very rough

(9) J. P. Day, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **90**, 6927 (1968); C. Hyde and D. J. Darensbourg, *Inorg. Chem.*, **12**, 1286 (1973); M. Basato and A. Poe, *J. Chem. Soc., Dalton Trans.*, 456 (1974); W. D. Covey and T. L. Brown, *Inorg. Chem.*, **12**, 2820 (1973).

values: $k_2 k_{-1}' k_4 / k_1' k_5 k_3 \approx (1-2) \times 10^2$, $k_4 / k_5 \approx 5-7$, and $k_2 k_{-1}' / k_3 k_1' + k_2 k_4 / k_1' k_5$ negligible compared to $k_4 / k_5 [\text{L}]$.

The fact that the ratio $\alpha/(1-\alpha)$ is not zero for zero concentration of CO and for very low concentration of PPh_3 may be due to the development of CO during the reaction 1. The amount given off is sufficient to influence the dissociative step of $\text{Fe}(\text{CO})_4$ to $\text{Fe}(\text{CO})_3$ and to favor the formation of $\text{Fe}(\text{CO})_4\text{PPh}_3$.

The formation of the $\text{Fe}(\text{CO})_3$ is not unreasonable; in fact other carbonyl complexes¹⁰ undergo step dissociation, and recently experimental evidence of the formation of $\text{Fe}(\text{CO})_3$ in the photolysis of $\text{Fe}(\text{CO})_5$ in matrix¹¹ was obtained.

Mechanism 2 also suggests that the formation of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$, observed during the reaction between several carbonyl complexes of Fe and PPh_3 , is due to the formation of the intermediate $\text{Fe}(\text{CO})_4$ in the first step of the reaction. If this mechanism does indeed occur, then the ratio $\alpha/(1-\alpha)$ should be the same. This has been observed for all the $(\text{CH}_2=\text{CHX})\text{Fe}(\text{CO})_4$ and $\text{Fe}_2(\text{CO})_9$ complexes.¹ For $\text{Fe}_3(\text{CO})_{12}$, however, this ratio is very different and changes with the concentration of PPh_3 . In fact, a different reaction mechanism for this complex was suggested.¹² According to this mechanism $\text{Fe}_3(\text{CO})_{12}$ reacts with PPh_3 , giving $\text{Fe}_3(\text{CO})_{11}-\text{PPh}_3$, which on further reaction with PPh_3 leads to $\text{Fe}(\text{CO})_4-\text{PPh}_3$ and $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$.

Acknowledgment. This work was supported in part by the Italian National Research Council.

Registry No. $\text{Fe}(\text{CO})_4(\text{CH}_2=\text{CHPh})$, 12193-57-6; PPh_3 , 603-35-0; CO, 630-08-0.

(10) J. P. Day, R. G. Pearson, and F. Basolo, *J. Amer. Chem. Soc.*, **90**, 6933 (1968).

(11) M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1351 (1973); M. Poliakoff, *ibid.*, 210 (1974).

(12) R. J. Angelici and E. E. Siefert, *Inorg. Chem.*, **5**, 1457 (1966).

Contribution from the Laboratorio di Fotochimica e Radiazioni d'Alta Energia del CNR and the Istituto Chimico "G. Ciamician," Universita di Bologna, Bologna 40126, Italy

Reduction by the Triplet Charge-Transfer State of Tris(bipyridyl)ruthenium(II). Photochemical Reaction between Tris(bipyridyl)ruthenium(II) and Thallium(III)¹

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Received May 7, 1974

AIC40291Z

Phosphorescent emission from the ^3CT state of $\text{Ru}(\text{bipy})_3^{2+}$ is quenched by Fe^{3+} , Fe^{2+} , and Tl^{3+} ions in aqueous solution with quenching rate constants of 1.9×10^9 , 1.6×10^7 , and $1.1 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$, respectively at room temperature (*ca.* 20°), $\mu = 0.5 \text{ M}$. Irradiation of solutions containing $\text{Ru}(\text{bipy})_3^{2+}$ and Tl^{3+} in the singlet charge-transfer absorption band of $\text{Ru}(\text{bipy})_3^{2+}$ causes oxidation of the ruthenium(II) complex to $\text{Ru}(\text{bipy})_3^{3+}$. The limiting quantum yield for the loss of $\text{Ru}(\text{bipy})_3^{2+}$ at infinite thallium(III) concentration is 2.0 ± 0.4 . The rate constant for the photochemical reduction of Tl^{3+} determined from the dependence of the quantum yield upon thallium(III) concentration is the same as the rate constant for the quenching of the $\text{Ru}(\text{bipy})_3^{2+}$ phosphorescence by thallium(III). Tl^{2+} ions are produced as intermediates in the photochemical reaction and can oxidize $\text{Ru}(\text{bipy})_3^{2+}$ and reduce $\text{Ru}(\text{bipy})_3^{3+}$. The quantum yield is unchanged in the presence of methanol. The quenching of the $\text{Ru}(\text{bipy})_3^{2+}$ phosphorescence cannot take place by an energy-transfer mechanism and electron transfer from $^3\text{CT } \text{Ru}(\text{bipy})_3^{2+}$ to Tl^{3+} is responsible for the phosphorescence quenching and the initial step in the photochemical reaction.

In recent years $\text{Ru}(\text{bipy})_3^{2+}$ has been widely used in quenching and photosensitization experiments with transition metal

(1) This paper was presented in part at the symposium on Mechanistic Aspects of Inorganic Photochemistry, Mulheim, March, 1974.

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complex acceptors. The lowest charge-transfer triplet state (17.1 kK above the ground state³) which is involved in these processes emits phosphorescence (λ 620 nm, lifetime 0.65 μsec ⁴) even in fluid solution at room temperature and is ex-

(3) R. J. Watts and G. A. Crosby, *J. Amer. Chem. Soc.*, **93**, 3184 (1971).