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Reactions of Metal Carbonyl Complexes. II.* Kinetics and Mechanism of *cis*-Cyclooctene Substitution in π-$C_5H_5Mn(CO)(CS)(C_8H_{14})$ by Triphenylphosphine

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Kinetic data have been obtained for the replacement of cis-*cyclooctene in* π–$C_5H_5Mn(CO)(CS)(C_8H_{14})$ *by triphenylphosphine to form* π-$C_5H_5Mn(CO)(CS)PPh_3$. *The observed reaction rates in methylcyclohexane at 50–70°C are first order in substrate and independent of the concentration of* PPh_3 *suggesting a mechanism in which the rate of dissociation of the olefin is the rate-determining step. The high positive entropy of activation is suportive of the proposed* S_N1 *dissociative mechanism. The kinetic results suggest that CS is a better* π*–acceptor ligand than CO, in agrement with other studies on transition metal thiocarbonyl complexes.*

Introduction

In 1967, Angelici and Loewen reported[1] kinetic data for the following substitution reaction in methylcyclohexane solution:

$$\pi\text{-}C_5H_5Mn(CO)_2(C_8H_{14})+PPh_3\rightarrow \pi\text{-}C_5H_5Mn(CO)_2PPh_3+C_8H_{14} \qquad (1)$$

They proposed that the reaction proceeds by an S_N1 dissociative mechanism involving the slow loss of *cis*-cyclooctene in the rate-determining step to form the intermediate, π–$C_5H_5Mn(CO)_2$, followed by rapid entry of PPh_3. Recently, we had occasion to synthesize the *cis*-cyclooctene thiocarbonyl complex, π–$C_5H_5Mn(CO)(CS)(C_8H_{14})$,[2] which is presumably isostructural with π-$C_5H_5Mn(CO)_2(C_8H_{14})$. This thiocarbonyl complex also undergoes *cis*-cyclooctene substitution with PPh_3 in methylcyclohexane solution:[3]

$$\pi\text{-}C_5H_5Mn(CO)(CS)(C_8H_{14})+PPh_3\rightarrow \pi\text{-}C_5H_5Mn(CO)(CS)PPh_3+C_8H_{14} \qquad (2)$$

Owing to the similarity of this reaction to reaction 1, we decided to investigate the kinetics and mechanism of the reaction in an attempt to compare the bonding properties of CO and CS in related transition metal complexes. Prior to this study, no kinetic data for transition metal thiocarbonyl camplexes had been reported in the literature.

Experimental Section

The complex, π-$C_5H_5(CO)(CS)(C_8H_{14})$, was prepared by ultraviolet irradiation of an *n*-hexane solution of π-$C_5H_5Mn(CO)_2CS$ and excess *cis*-cyclooctene. Complete preparative details of this and related reactions of π-cyclopentadienylmanganese thiocarbonyl complexes, including the synthesis of π-$C_5H_5Mn(CO)(CS)$-PPh_3, will be described elsewhere.[3] Methylcyclohexane was dried over P_2O_5 and fractionally distilled before use in the kinetic measurements.

Kinetic data were obtained by monitoring the rate of decrease of the C–O stretching absorption of π–$C_5H_5Mn(CO)(CS)(C_8H_{14})$ at 1958 cm^{-1} using a Perkin-Elmer model 337 grating infrared spectrophotometer. This disappearence was accompanied by the growth of two C–O absorptions at 1928 and 1938 cm^{-1} due to the reaction product, π–$C_5H_5Mn(CO)(CS)PPh_3$.[4] Pseudo-first-order conditions were employed in all cases - the substrate concentration being kept at about $2\times10^{-3}M$. Methylcyclohexane solutions of the substrate and varying concentrations of PPh_3 were prepared in aluminum-foil-wrapped reaction vessels fitted with neoprene serum caps and thermostated in a constant-temperature (±0.1°) oil bath. Samples were withdrawn with a syringe at appropriate intervals and their infrared spectra scanned in the C–O stretching region. Linear first-order plots of $\ln(A-A_\infty)$, where A is the absorbance at time t and A_∞ is the absorbance at infinite time, *vs.* t were obtained. The reactions went to completion and the plots were linear to at least 85% completion. The rate constants for identical kinetic runs were reproducible to within ±6%. All the rate constants were calculated using a least-squares computer program.

Results and Discussion

The observed pseudo-first-order rate constants (k_{obsd}) for reaction 2 given in Table I are independent

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(*) For Part 1 of this series see: I.S. Butler, N.J. Coville, and H.K. Spendjian, *J. Organometal. Chem.*, *43*, 185 (1972).
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(2) A.E. Fenster and I.S. Butler, *Can. J. Chem.*, *50*, 598 (1972).
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Table I. Rates of reaction of π-$C_5H_5Mn(CO)(CS)(C_8H_{14})$ with PPh_3 in methylcyclohexane.[a]

Temp. (°C)	$[PPh_3]$ (*M*)	$10^5 k_{obsd}$ (sec^{-1})
50.0	0.015	9.43
	0.025	9.82
	0.05	9.03
60.0	0.05	38.8
	0.1	38.9
	0.2	38.3
65.0	0.025	76.2
	0.05	80.2
70.0	0.025	165
	0.05	166

[a] Averages of several kinetic runs.

Table II. Comparison of kinetic data for the reactions of π-$C_5H_5Mn(CO)(CS)(C_8H_{14})$ and π-$C_5H_5Mn(CO)_2(C_8H_{14})$ with PPh_3 in methylcyclohexane.[a]

Complex	$10^5 k_{obsd}$ (sec^{-1}) 60.0°C	70.0°C	ΔH^* (kcal $mole^{-1}$)	ΔS^* (e.u.)
π-$C_5H_5Mn(CO)(CS)(C_8H_{14})$	38.7	165	30.6±0.9	19.7±2.7
π-$C_5H_5Mn(CO)_2(C_8H_{14})$[b]	9.25	46.9	34.9±0.7	27.5±2.0

[a] The rate constants listed are averages of several kinetic runs at different concentrations of PPh_3. The limits of error on the activation parameters are 1 standard deviation. [b] Data from ref. 1.

of the concentration of PPh_3 over the temperature range investigated (50–70°). The associated activation entropy (19.7 ± 2.7e.u.) is in the range expected for an S_N1 dissociative mechanism.[5] These data are in accord with the mechanism shown in Eq. 3 and 4 involving the rupture of the manganese-olefin bond as the slow rate-determining step *i.e.*, a similar mechanism to that proposed for reaction 1 by Angelici and Loewen.[1]

$$\pi\text{-}C_5H_5Mn(CO)(CS)(C_8H_{14}) \xrightarrow[-C_8H_{14}]{slow} \pi\text{-}C_5H_5Mn(CO)CS \qquad (3)$$

$$\pi\text{-}C_5H_5Mn(CO)CS \xrightarrow[+PPh_3]{fast} \pi\text{-}C_5H_5Mn(CO)(CS)PPh_3 \qquad (4)$$

Some of the kinetic data for the replacement of *cis*-cyclooctene in π–$C_5H_5Mn(CO)(CS)(C_8H_{14})$ and π–$C_5H_5Mn(CO)_2(C_8H_{14})$ by PPh_3 in methylcyclohexane solution are compared in Table II. It is immediately evident that at 60.0 and 70.0° the reaction rates for the thiocarbonyl complex are about four times faster than those for the dicarbonyl complex. Furthermore, the activation parameters suggest that the increased reaction rate for the thiocarbonyl complex arises mainly because of a decrease in enthalpy of activation.

The increased lability of the olefin in the thiocarbonyl complex can be readily explained if CS is a better π–acceptor than CO. When one CO group in π–$C_5H_5Mn(CO)_2(C_8H_{14})$ is replaced by a CS group there will be a resultant lowering of electron density available on the manganese atom for backbonding to the olefin. Consequently, the manganese-olefin bond in π–$C_5H_5Mn(CO)(CS)(C_8H_{14})$ should be weaker than that in π–$C_5H_5Mn(CO)_2(C_8H_{14})$ and thus be broken more easily, as is observed. This explanation receives some suport from a molecular orbital treatment of the CS molecule in which it was shown that back-donation from a metal to CS should be easier than to CO.[6] Furthermore, Mössbauer data for the π–cyclopentadienyliron cationic complexes, $[\pi\text{–}C_5H_5Fe(CO)_2CS]^+$ and $[\pi\text{–}C_5H_5Fe(CO)_3]^+$, also suggest that CS is a more effective π–acceptor than CO.[7]

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(4) The appearence of *two* C-O stretching absorptions for this monocarbonyl complex is attributed to conformational isomerism due to restricted rotation of the phenyl groups within the PPh_3 ligand [c.f. D.A. Brown, H.J. Lyons, and A.R. Mannin, *Inorg. Chim. Acta*, 4, 428 (1970)].

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