

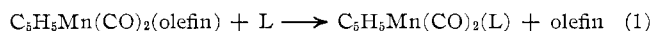
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
IOWA STATE UNIVERSITY, AMES, IOWA 50010Kinetic Studies of Olefin Replacement in  
Cyclopentadienylmanganese–Olefin–Dicarbonyl Complexes<sup>1</sup>

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To determine the relative labilities of olefins in transition metal complexes, a kinetic investigation of the following reaction in methylcyclohexane solvent was undertaken:  $C_5H_5Mn(CO)_2(olefin) + L \longrightarrow C_5H_5Mn(CO)_2L + olefin$  [L = a phosphine, an amine, or  $(C_6H_5)_2S$ ]. The rate of reaction is independent of the concentration of L suggesting a mechanism in which the rate of dissociation of the olefin is the rate-determining step. The high positive entropies of activation support the SN1 mechanism. At 80° in decalin the rates of olefin dissociation increase in the order: ethylene < norbornadiene < norbornylene < cyclooctene < propylene < cyclopentene < pentene-1 ~ cycloheptene. The introduction of a methyl group into the cyclopentadienyl ring as in  $CH_3C_5H_4Mn(CO)_2(C_8H_{14})$  has a very small effect on the rate of olefin replacement. It has also been noted that under the conditions of the above reactions there is no measurable substitution of CO by phosphines in  $C_5H_5Mn(CO)_3$  indicating that CO is far more inert than any of the olefins when bonded to the  $C_5H_5Mn(CO)_2$  moiety.

Although olefin complexes of transition metals have been known for at least a century, accurate kinetic measurements of the relative labilities of various olefins in a given metal complex have not been made. Qualitative rate studies of some ethylene complexes have shown that ethylene exchange occurs very rapidly in square-planar Pt(II) and Rh(I) complexes<sup>2</sup> but that a nonsquare-planar Rh(I) complex,  $C_6H_5Rh(CH_2=CH_2)_2$ ,<sup>3</sup> and some Fe(II) and Hg(II) complexes<sup>4</sup> are inert to exchange even at relatively high temperatures. The purpose of the present work is to compare the labilities of various olefins in the complexes,  $C_5H_5Mn(CO)_2(olefin)$ . This was accomplished by determining the rates of the reaction



where L = a phosphine, an amine, or  $(C_6H_5)_2S$ . The synthetic aspects of this reaction were originally investigated by Fischer and Herberhold,<sup>5</sup> who found that monodentate norbornadiene could be displaced from  $C_5H_5Mn(CO)_2(norbornadiene)$  with  $P(C_6H_5)_3$  to yield  $C_5H_5Mn(CO)_2[P(C_6H_5)_3]$ .

## Experimental Section

**Preparation and Purification of Materials.**—The  $C_5H_5Mn(CO)_2(olefin)$  complexes were prepared according to the method of Fischer and Herberhold<sup>5</sup> by irradiating solutions of 80 ml of hexane containing 2.0 g of  $C_5H_5Mn(CO)_3$  (a gift of the Ethyl Corp.) and a tenfold excess of the desired olefin with a Hanovia ultraviolet lamp. All reactions were carried out in a quartz vessel under a nitrogen atmosphere. Details of the isolation and characterization which were not given in or differ from those in ref 5 are given below.

**$C_5H_5Mn(CO)_2(ethylene)$ .**—The irradiated solution was filtered and evaporated under vacuum to 25 ml. Cooling to  $-78^\circ$  yielded yellow crystals which were sublimed at room temperature for 24 hr under high vacuum to remove unreacted  $C_5H_5Mn(CO)_3$ . The unsublimed solid was dissolved in 20 ml of hexane; the solution was filtered and cooled to  $-78^\circ$ . After drying under

vacuum, the compound gave two C–O stretching absorptions in methylcyclohexane at 1978 and 1919  $cm^{-1}$  in good agreement with those reported by Fischer and Herberhold.

**$C_5H_5Mn(CO)_2(propylene)$ .**—A hexane solution of  $C_5H_5Mn(CO)_3$  was irradiated for 0.5 hr while propylene was bubbled through it. The resulting solution was filtered, concentrated to 10 ml, and chromatographed on an alumina column using hexane as the eluent. The hexane was removed under vacuum from the  $C_5H_5Mn(CO)_2(propylene)$  fraction which followed the unreacted  $C_5H_5Mn(CO)_3$  off the column. The compound decomposes significantly faster in solution than the ethylene analog. In methylcyclohexane,  $C_5H_5Mn(CO)_2(propylene)$  exhibits two C–O stretching absorptions at 1978 and 1920  $cm^{-1}$ . Its proton nmr spectrum in  $CDCl_3$  gave the proton resonances shown in Table I, which are downfield relative to tetramethylsilane.

TABLE I

Ppm	Integration	Assignment	Multiplicity
1.50	3	CH <sub>3</sub>	Broad doublet
1.8–3.5	3	Olefinic H's	Complex
4.45	5	C <sub>5</sub> H <sub>5</sub>	Singlet

**$C_5H_5Mn(CO)_2(pentene-1)$ .**—While it was evident from the two characteristic C–O stretching absorptions at 1978 and 1920  $cm^{-1}$  that the desired complex was formed during the irradiation of a hexane solution of  $C_5H_5Mn(CO)_3$  and pentene-1, its extreme air sensitivity precluded isolation and thorough characterization of the complex. Kinetic studies of the complex were carried out by filtering the irradiated solutions and adding a given amount of  $P(C_6H_5)_3$ . The rate of olefin replacement was then followed in the hexane solution which also contained substantial amounts of unreacted  $C_5H_5Mn(CO)_3$ . The addition of more  $C_5H_5Mn(CO)_3$  did not change the rate of reaction of  $C_5H_5Mn(CO)_2(pentene-1)$ .

**$C_5H_5Mn(CO)_2(cyclopentene)$ .**—This compound was prepared and isolated in the same manner indicated for  $C_5H_5Mn(CO)_2(ethylene)$ . It was identified by its C–O stretching absorptions at 1976 and 1911  $cm^{-1}$ , in good agreement with those found by Fischer and Herberhold<sup>5</sup> for the same complex. In solution it decomposes moderately rapidly when exposed to air.

**$C_5H_5Mn(CO)_2(cycloheptene)$ .**—The irradiated solution of  $C_5H_5Mn(CO)_3$  and cycloheptene was concentrated to 25 ml and cooled to  $-78^\circ$ . From the resulting solid,  $C_5H_5Mn(CO)_3$  was removed by sublimation at 50°. The unsublimed residue was recrystallized from hexane at  $-78^\circ$ . The two C–O absorptions at 1968 and 1919  $cm^{-1}$  in methylcyclohexane are in good agreement with those given in the literature.<sup>5</sup> The compound in solution is significantly more stable than any of the noncyclic olefinic complexes.

(1) Presented at the 9th International Conference on Coordination Chemistry, St. Moritz, Switzerland, Sept 5, 1966.

(2) R. Cramer, *Inorg. Chem.*, **4**, 445 (1965).

(3) R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964).

(4) G. Pajara and A. Panunzi, *Ricerca Sci. Rend.*, **4** (A), 601 (1964).

(5) E. O. Fischer and M. Herberhold in "Essays in Coordination Chemistry," Birkhäuser Verlag, Basel, Switzerland, 1965, pp 259–305.

$C_5H_5Mn(CO)_2$ (*cis*-cyclooctene).—The irradiated solution was evaporated to dryness, and the  $C_5H_5Mn(CO)_3$  was removed under high vacuum at 50°. The product was then sublimed at 65°. *Anal.* Calcd for  $C_5H_5Mn(CO)_2(C_8H_{14})$ : C, 62.93; H, 6.65. Found: C, 62.83; H, 6.69.

Two C—O absorptions at 1968 and 1894  $cm^{-1}$  in methylcyclohexane were observed. The nmr spectrum in  $CDCl_3$  gave absorptions at 1.40 (broad), 2.50 (broad), 3.10 (broad), and 3.95 ppm (singlet,  $C_5H_5$ ) with relative intensities of 10, 2, 2, and 5, respectively. The solution stability of the compound is similar to that of the cycloheptene derivative.

$C_5H_5Mn(CO)_2$ (norbornadiene).—This compound was a gift of Herberhold.<sup>5</sup>

$C_5H_5Mn(CO)_2$ (norbornylene).—Preparation and purification was carried out in the same manner used for the cyclooctene complex. The product was sublimed at 75°. *Anal.* Calcd for  $C_5H_5Mn(CO)_2(C_7H_{10})$ : C, 62.17; H, 5.60. Found: C, 62.23; H, 5.69.

The C—O stretching absorptions occurred at 1973 and 1915  $cm^{-1}$ . The proton nmr in  $CDCl_3$  gave relatively broad absorptions which have been assigned to protons A, B, C, etc. The designations for these protons are the same as those used by Fritz and Keller,<sup>6</sup> who analyzed the nmr spectrum of  $C_5H_5Mn(CO)_2$ (norbornadiene) on the basis of a structure in which the bridging methylene group is adjacent to the Mn atom causing the methylene protons to absorb at unusually high field. This structure has been confirmed by an X-ray structural determination.<sup>7</sup> The nmr absorptions of the norbornylene compound in  $CDCl_3$  are given in Table II.

TABLE II

Ppm	Integration	Assignment	Multiplicity
4.46	5	H <sub>B</sub> , C <sub>5</sub> H <sub>5</sub>	Singlet
3.39	2	H <sub>C</sub> , olefinic H's	Singlet
2.55	2	H <sub>D</sub> , bridgehead H's	Singlet
1.33	4	H <sub>A</sub> , CH <sub>2</sub> CH <sub>2</sub>	Two doublets
0.28	1	H <sub>E</sub> , methylene H directed away from Mn	Doublet
-0.25	1	H <sub>F</sub> , methylene H directed toward Mn	Doublet

In solution  $C_5H_5Mn(CO)_2$ (norbornylene) decomposes slowly but is definitely more stable than the complexes of either the noncyclic or monocyclic olefins.

$C_5H_5Mn(CO)_2$ (*endic anhydride*).—A solution of 1.0 g of  $C_5H_5Mn(CO)_3$  and 6.6 g of *endic anhydride* (*endo-cis*-bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride,  $C_9H_8O_3$ ) in 40 ml of benzene was irradiated for 12 hr. After filtering, the benzene was removed under vacuum. The resulting solid was washed with hexane to remove unreacted  $C_5H_5Mn(CO)_3$ . Excess *endic anhydride* was removed by washing with methanol yielding pale yellow crystals of the product. *Anal.* Calcd for  $C_5H_5Mn(CO)_2(C_9H_8O_3)$ : C, 56.50; H, 4.12. Found: C, 56.67; H, 3.89.

The metal carbonyl C—O absorptions occur at 1968 (vs) and 1899 (vs)  $cm^{-1}$  while the anhydride group gives absorptions at 1850 (w) and 1777 (vs)  $cm^{-1}$ . The proton nmr spectrum in  $CDCl_3$  shows the resonances given in Table III.

The above assignments were made on the basis of the spectrum of *endic anhydride* itself in  $CDCl_3$  (see Table IV).

Because of its insolubility in methylcyclohexane,  $C_5H_5Mn(CO)_2$ (*endic anhydride*) was not investigated kinetically.

**Other Complexes.**— $C_5H_5Mn(CO)_2P(C_6H_5)_3$ , the product of the kinetic studies, was prepared by the ultraviolet irradiation method.<sup>8</sup> Owing to the instability of  $C_5H_5Mn(CO)_2$ (diphenylacetylene) in solvents, kinetic studies on it were not possible.

**Determination of Rates of Reaction.**—The rate of reaction 1,

TABLE III

Ppm	Integration	Assignment	Multiplicity
4.57	5	C <sub>5</sub> H <sub>5</sub>	Singlet
3.55	4	Remaining H's	Broad singlet
3.20	2	Olefinic H's	Singlet
0.69	1	Bridging methylene H directed away from Mn	Doublet
0.15	1	Bridging methylene H directed toward Mn	Doublet

TABLE IV

Ppm	Integration	Assignment	Multiplicity
6.30	2	Olefinic H's	Doublet
3.60	4	Remaining H's	Multiplet
1.69	2	Bridging methylene	Two doublets

where  $L = P(C_6H_5)_3$ , was followed by noting the decrease in intensity of the high-frequency C—O stretching absorption of the  $C_5H_5Mn(CO)_2$ (olefin) complexes at about 1975  $cm^{-1}$ . This disappearance was accompanied by the growth of the two absorptions of  $C_5H_5Mn(CO)_2P(C_6H_5)_3$  at 1948 and 1878  $cm^{-1}$ . The reactions were carried out under nitrogen in an aluminum-foil-wrapped vessel fitted with a serum cap. Reaction solutions of  $2.5 \times 10^{-3} M$  complex and varying concentrations of L in 10 ml of methylcyclohexane were thermostated to  $\pm 0.1^\circ$  in an oil bath for 15 min. At appropriate time intervals samples were withdrawn with a syringe and the intensity of the 1975- $cm^{-1}$  absorption was determined. First-order rate constants were determined from the absorbance measurements by plotting  $\ln(A - A_\infty)$  vs. time. Such plots were linear to at least 75% completion, and the average deviation for identical runs was less than  $\pm 6\%$ . A general nonlinear least-squares program was used to calculate the activation parameters and their standard deviations.<sup>9</sup>

If  $C_5H_5Mn(CO)_2$ (norbornylene) is allowed to stand in methylcyclohexane in the absence of a reacting ligand, L, the compound is observed to decompose at a rate which is about 40% that of its reaction with L. This decomposition is accompanied by the formation of a brown precipitate and  $C_5H_5Mn(CO)_3$  as identified from its infrared spectrum. If, however, L is present in a concentration of 5 times that of the complex or more, the decomposition products are not observed. This suggests that an intermediate in the reaction mechanism at least partially decomposes in the absence of L but reacts with L to form a stable product if L is present.

The solvent, methylcyclohexane, was dried over  $P_2O_5$  and fractionally distilled before use in the kinetic studies.

**Spectra.**—All infrared spectra were recorded using a Beckman IR-8 infrared spectrophotometer. The instrument was calibrated with a polystyrene standard giving frequency measurements accurate to  $\pm 5 cm^{-1}$ . Proton nmr spectra were determined with Varian A-60 and HR-60 spectrometers.

## Results

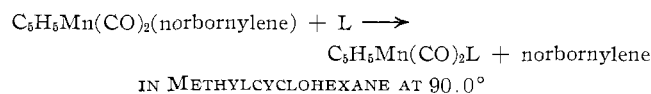
Reaction 1 has been shown to yield  $C_5H_5Mn(CO)_2L$  without additional products. The rate of the reaction is independent of the concentration of L but does to a relatively small extent depend on the nature of L as shown in Table V. The rate increases slightly from sulfur to phosphorus to nitrogen donors but there are no obvious trends within a given group of ligands. That the dependence on the nature of L is so small suggests that solvation of the complex by the ligand may be responsible for the slight differences in rate. In an attempt to find evidence for solvation, a differential

(9) R. H. Moore, based on a report from Los Alamos Scientific Laboratory, LA2367 plus addenda. We thank Mr. J. P. Birk for modification of this program for use on the present problem and computer facilities.

(6) H. P. Fritz and H. J. Keller, *Chem. Ber.*, **96**, 1676 (1963).

(7) R. A. Jacobson and B. Granoff, private communication.

(8) R. S. Nyholm, S. S. Sandhu, and M. H. B. Stiddard, *J. Chem. Soc.*, 5916 (1963).

TABLE V  
RATES OF THE REACTION

L	[L], M	$10^4 k_{\text{obsd}}$ , sec <sup>-1</sup>
S(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	0.05	4.72
	0.10	4.96
	0.10	5.06
	0.20	4.94
P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	0.05	5.06
	0.10	5.05
	0.20	5.21
P( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	0.05	5.51
	0.10	5.74
	0.20	5.25
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	0.05	5.80
	0.10	5.90
	0.20	5.68
Pyrrolidine	0.05	6.57
	0.10	6.34
	0.20	6.12
Quinuclidene	0.05	6.46
	0.10	6.21

infrared spectrum of the complex and the complex plus P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub> was measured in the C–O stretching region. There was complete cancellation and no evidence for solvation by P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>. The slight rate differences, however, must be due to some small interaction between the complex and L. Basically, however, the reaction proceeds according to a first-order rate law: rate =  $k[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{olefin})]$ . To minimize solvation effects by L, the broad study of reaction 1 was carried out only with L = P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>.

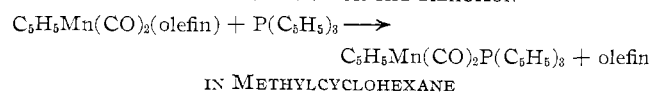
The reaction of C<sub>5</sub>H<sub>5</sub>Mn(CO)<sub>2</sub>(cyclooctene) and P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> at 80.0° proceeded with a first-order rate constant of  $1.92 \times 10^{-4} \text{ sec}^{-1}$  in methylcyclohexane and  $1.41 \times 10^{-4} \text{ sec}^{-1}$  in the much more polar nitromethane. Although the dielectric constants of these solvents at 20° are 2 and 36, respectively, the difference in polarity has only a very small effect on the rate of reaction.

Table VI shows the rate constants for reaction 1 with L = P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> using a variety of olefins. All rates of reaction were found to be independent of the concentration of P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>. The first-order rate constants given in Table VI are averages of several runs at different concentrations of P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>.<sup>10</sup> Also given in the table are the rate constants for olefin replacement in the methylcyclopentadienyl complex, CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>Mn(CO)<sub>2</sub>(cyclooctene).

Rate constants evaluated at 80.0° and values of the enthalpy and entropy of activation for olefin replacement by P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> in C<sub>5</sub>H<sub>5</sub>Mn(CO)<sub>2</sub>(olefin) are reported in Table VII. The limits of error given in the table are 1 standard deviation. At 80° the rate of replacement of the olefin in C<sub>5</sub>H<sub>5</sub>Mn(CO)<sub>2</sub>(olefin) increases in the order: ethylene < norbornadiene < norbornylene < cyclooctene < propylene < cyclopentene < pentene-1 ~ cycloheptene.

TABLE VI

RATE CONSTANTS FOR THE REACTION

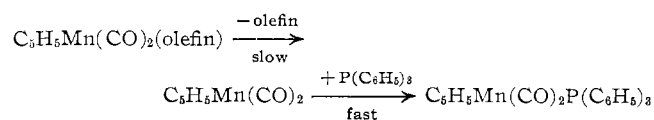


Complex	Temp, °C	$10^6 k_{\text{obsd}}$ , sec <sup>-1</sup>
C <sub>5</sub> H <sub>5</sub> Mn(CO) <sub>2</sub> (ethylene)	75.0	1.99
	80.0	4.80
	85.0	8.30
	90.0	16.5
	95.0	33.7
	70.0	2.34
	75.0	6.53
C <sub>5</sub> H <sub>5</sub> Mn(CO) <sub>2</sub> (norbornadiene)	80.0	12.9
	85.0	24.6
	90.0	51.4
	92.5	83.0
	70.0	2.46
	80.0	18.5
	85.0	39.5
C <sub>5</sub> H <sub>5</sub> Mn(CO) <sub>2</sub> (norbornylene)	90.0	57.5
	92.5	98.1
	70.0	9.25
	80.0	18.5
	85.0	39.5
	90.0	57.5
	92.5	98.1
C <sub>5</sub> H <sub>5</sub> Mn(CO) <sub>2</sub> (cyclooctene)	60.0	9.25
	70.0	46.9
	72.5	60.6
	75.0	99.5
	77.5	126.
	80.0	193.
	80.0	193.
C <sub>5</sub> H <sub>5</sub> Mn(CO) <sub>2</sub> (propylene)	55.0	6.43
	70.0	75.3
	72.5	92.5
	75.0	130.0
	55.0	11.2
	65.0	51.4
	67.5	78.4
C <sub>5</sub> H <sub>5</sub> Mn(CO) <sub>2</sub> (cyclopentene)	70.0	113.
	72.5	155.
	47.4	4.35
	54.8	19.4
	61.8	39.2
	69.8	148.
	69.8	148.
C <sub>5</sub> H <sub>5</sub> Mn(CO) <sub>2</sub> (cycloheptene)	55.0	26.6
	67.5	125.
	70.0	175.
	72.5	263.
	75.0	349.
	55.0	5.19
	65.0	27.5
CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> Mn(CO) <sub>2</sub> (cyclooctene)	72.5	71.0
	75.0	96.2
	77.5	166.
	80.0	179.
	80.0	179.

<sup>a</sup> In hexane solvent.

### Discussion

The experimental results show that all of the C<sub>5</sub>H<sub>5</sub>Mn(CO)<sub>2</sub>(olefin) complexes undergo substitution according to a first-order rate law. This suggests an S<sub>N</sub>1 mechanism for the reaction



The observed high positive entropies of activation support this dissociative mechanism as does the small solvent effect which would be expected for the dissociation of a neutral olefin in the rate-determining step.

TABLE VII  
ACTIVATION PARAMETERS FOR THE REACTION  
 $C_5H_5Mn(CO)_2(olefin) + P(C_6H_5)_3 \rightarrow C_5H_5Mn(CO)_2P(C_6H_5)_3 + olefin$   
IN METHYLCYCLOHEXANE

Complex	$10^6 k_{obsd}$ , sec <sup>-1</sup> at 80.0°	$\Delta H^*$ , kcal/mole	$\Delta S^*$ , eu
$C_5H_5Mn(CO)_2$ (ethylene)	4.80	$34.6 \pm 1.0$	$+19.1 \pm 2.9$
$C_5H_5Mn(CO)_2$ - (norbornadiene)	12.9	$37.2 \pm 0.7$	$+28.7 \pm 2.0$
$C_5H_5Mn(CO)_2$ - (norbornylene)	18.5	$38.8 \pm 1.2$	$+33.5 \pm 3.5$
$C_5H_5Mn(CO)_2$ (cyclooctene)	193	$34.9 \pm 0.7$	$+27.5 \pm 2.0$
$C_5H_5Mn(CO)_2$ (propylene)	263 <sup>b</sup>	$33.8 \pm 0.7$	$+25.1 \pm 2.1$
$C_5H_5Mn(CO)_2$ - (cyclopentene)	408 <sup>b</sup>	$33.5 \pm 0.4$	$+25.1 \pm 1.3$
$C_5H_5Mn(CO)_2$ - (pentene-1) <sup>a</sup>	580 <sup>b</sup>	$33.2 \pm 1.4$	$+24.3 \pm 4.3$
$C_5H_5Mn(CO)_2$ - (cycloheptene)	584 <sup>b</sup>	$28.5 \pm 0.8$	$+11.6 \pm 2.3$
$CH_3C_6H_4Mn(CO)_2$ - (cyclooctene)	179	$32.3 \pm 0.7$	$+20.3 \pm 2.1$

<sup>a</sup> In hexane solvent. <sup>b</sup> Obtained by extrapolation.

Similar solvent effects are observed in SN1 mechanisms involving the dissociation of a carbon monoxide group.<sup>11</sup>

Some of the factors which appear to determine the lability of the olefin in these complexes are more obvious if the complexes of noncyclic and cyclic olefins are discussed separately. In the noncyclic category, the rate of olefin dissociation increases in the order: ethylene  $\ll$  propylene  $<$  pentene 1. Although the enthalpies of activation are all very similar, they appear to decrease in the same order. The relatively small rate enhancement in going from propylene to pentene-1 suggests that the larger steric requirements of pentene-1 increase its rate of dissociation. This effect is relatively small, however, compared to the difference in rates of dissociation between the ethylene and propylene compounds. This difference could be accounted for in terms of the steric effect of the methyl group as compared to that of the hydrogen atom. On the other hand, the electron-releasing nature of the methyl group would also decrease the amount of  $\pi$  bonding<sup>12</sup> from the Mn to the olefin resulting in a much weaker manganese-olefin bond with propylene. Whether one or the other or both of these factors is of significant importance is not known. Attempts to study olefinic complexes of 2-methylpentene-1 and 2,3-dimethylbutene-2 were precluded by our inability to prepare the complexes. Presumably the introduction of more than one alkyl group on the olefinic carbons allows the olefin to complex with the metal only very weakly. An equilibrium study<sup>13</sup> of  $Ag(olefin)^+$  gives formation constants for these complexes which decrease with the olefin as follows: ethylene  $>$  propylene  $>$  pentene-1  $>$  2-methylpentene-1  $>$  2,3-dimethylbutene-2, a trend observed in the present kinetic studies. Since the relative thermodynamic stabilities of the various  $Ag(olefin)^+$

complexes parallel the rates of olefin dissociation from  $C_5H_5Mn(CO)_2(olefin)$ , whatever factors are responsible for the thermodynamic properties are probably also of prime importance in determining the rates of these reactions.

For the cyclic olefins, the rate of olefin dissociation increases in the order: norbornadiene  $<$  norbornylene  $\ll$  cyclooctene  $<$  cyclopentene  $<$  cycloheptene. Except for the reversal of norbornadiene and norbornylene, the enthalpies of activation decrease in the same order. Attempted preparations of the cyclohexene complex did not even give spectroscopic evidence for the formation of a complex, as was also observed by Fischer and Herberhold.<sup>5</sup> If cyclohexene is included last in the above trend, the ordering generally, although not exactly, parallels that of decreasing formation constants<sup>13,14</sup> of these olefins with  $Ag^+$ . The observed formation constants were correlated by these workers with the relative strain energies of the free olefin as evaluated from heat of formation data (for cyclopentene, cycloheptene, and cyclohexene),<sup>14</sup> comparison with strain energies in cycloalkanes,<sup>13</sup> and heats of hydrogenation<sup>15</sup> of norbornylene. The over-all estimated trend<sup>13</sup> of strain energies of the free olefins decreases from norbornadiene to cyclohexene in exactly the same order observed above for the increasing rate of olefin dissociation in  $C_5H_5Mn(CO)_2(olefin)$ . That the trend in rate of olefin dissociation again generally parallels the equilibrium results suggests that the manganese-olefin bond strength is of major importance in determining the rate of olefin dissociation and that the strength of the manganese-olefin bond increases as the strain within the free olefin increases. The strength of the manganese-olefin bond is apparently owing to a relief of strain (as a result of partial rehybridization) within the olefin as it complexes with the metal.<sup>13,14</sup> Thus, the greater the strain initially present in the olefin, the greater the relief upon complexation and the more energy required for dissociation of the olefin from the metal. From the standpoint of the number of alkyl groups substituted on the olefinic carbons, it would be expected that the disubstitution present in all of the cyclic olefins would make cyclic olefin replacement exceedingly rapid. Strain within the ring apparently enhances the manganese-olefin bond strength to such an extent that stability results. In cyclohexene, however, where the strain energy is small, this disubstitution yields a very weak Mn-C<sub>6</sub>H<sub>10</sub> bond.

Since the amount of alkyl substitution at the olefinic carbons was of great importance in determining the lability of the olefin, it was of interest to examine the effect of alkyl substitution in the cyclopentadienyl ring. Therefore the rates of olefin substitution in  $C_5H_5Mn(CO)_2$ (cyclooctene) and  $CH_3C_6H_4Mn(CO)_2$ (cyclooctene) are compared in Table VI. The comparison suggests that the rates of cyclooctene disso-

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ciation in the two compounds are virtually the same with the methylcyclopentadienyl derivative perhaps being slightly faster. The enthalpy of activation of the methylcyclopentadienyl complex also borders on being significantly lower than that for the cyclopentadienyl compound.

In an attempt to compare the relative labilities of CO and olefins when bonded to the  $C_5H_5Mn(CO)_2$  moiety, the rate of CO replacement in  $C_5H_5Mn(CO)_3$  was studied. In the nonpolar solvent, decalin, its reaction with  $P(C_6H_5)_3$  was immeasurably slow even at

temperatures as high as  $140^\circ$ . This unreactivity of  $C_5H_5Mn(CO)_3$  is not due to its relatively high stability compared to  $C_5H_5Mn(CO)_2P(C_6H_5)_3$  since the latter compound can be readily prepared by ultraviolet irradiation of a solution of  $C_5H_5Mn(CO)_3$  and  $P(C_6H_5)_3$ . It therefore appears that CO is far more inert than any olefin in this system.

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## Infrared Spectra and Structure of Silicon Cobalt Tetracarbonyls

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The high-resolution gas-phase infrared spectra of  $Cl_3SiCo(CO)_4$  and of the new compounds  $F_3SiCo(CO)_4$ ,  $(CH_3)_3SiCo(CO)_4$ , and  $H_3CSiH_2Co(CO)_4$  have been examined in the CO stretching region. The spectra are consistent with trigonal-bipyramidal type molecular structures in which the silicon substituent occupies an axial position. The data obtained suggest that there may be significant ( $d \rightarrow d$ )- $\pi$  double-bond character in the silicon-cobalt bond in silicon cobalt tetracarbonyls.

A number of silicon cobalt tetracarbonyls of general formula  $R_3SiCo(CO)_4$  ( $R = H, Cl, C_2H_5, H_3CO$ ) have recently been reported in the literature.<sup>3,4</sup> The present investigation was carried out in order to gain further information concerning the structure of and the nature of bonding in substituted silyl cobalt tetracarbonyls. For this purpose the new compounds  $F_3SiCo(CO)_4$ ,  $H_3CSiH_2Co(CO)_4$ , and  $(H_3C)_3SiCo(CO)_4$  were synthesized.<sup>5</sup> It was considered particularly desirable to examine  $F_3SiCo(CO)_4$  since, apart from the recently reported  $H_3SiCo(CO)_4$ ,<sup>4</sup> it is the only silyl cobalt carbonyl for which there is an analogous carbon cobalt carbonyl, *viz.*,  $F_3CCo(CO)_4$ , whose structure has been examined by infrared techniques.

### Experimental Section

The silyl derivatives were prepared from the corresponding silane and  $Co_2(CO)_8$ , according to the method of Chalk and Harrod.<sup>3</sup> High-resolution infrared spectra were obtained with a double-beam Perkin-Elmer 521 spectrophotometer (spectral slit width of approximately  $1\text{ cm}^{-1}$  in the carbonyl stretching region, near  $2000\text{ cm}^{-1}$ ).

The samples were contained in gas cells having a 10-cm path length fitted with NaCl or KBr windows. In the high-resolution spectra in the carbonyl stretching region gas pressures ( $\leq 1\text{ mm}$ ) were adjusted so that the maximum absorption had a transmit-

tance of approximately 20–30%. Absorption maxima were located with a reproducibility of  $1\text{ cm}^{-1}$ .

### Results

The infrared CO stretching vibrations observed in this investigation for  $F_3SiCo(CO)_4$ ,  $(CH_3)_3SiCo(CO)_4$ ,  $H_3CSiH_2Co(CO)_4$ , and  $Cl_3SiCo(CO)_4$  are listed in Table I together with the previously reported values for  $Cl_3SiCo(CO)_4$  (heptane solution) and  $H_3CCo(CO)_4$ . Not unexpectedly, some variation between the solution and gas-phase spectra of  $Cl_3SiCo(CO)_4$  are observed. Values for compounds such as  $F_3CCo(CO)_4$  which have not been examined in the gas phase are not included.

The  $^{13}C$ O stretching vibrations were assigned on the basis of their relative intensities and their separation from the strongest, [E], band, in accordance with the Teller-Redlich rule and the natural abundance of the isotopes.<sup>7</sup> Using values of  $^{12}C$ O and  $^{13}C$ O vibrations given in the literature<sup>8</sup> for a number of transition metal carbonyl derivatives, a value of 0.9811 was calculated for the  $\nu_{^{13}C}O/\nu_{^{12}C}O$  ratio. The  $\nu_{^{13}C}O$  values given in Table I for the compounds studied in this investigation do not differ by more than  $2\text{ cm}^{-1}$  from the values calculated using this ratio.

The infrared spectra of  $Cl_3SiCo(CO)_4$ ,  $F_3SiCo(CO)_4$ , and  $(CH_3)_3SiCo(CO)_4$  showed the presence of three  $^{12}C$ O stretching bands in the carbonyl region. A spectrum of  $Cl_3SiCo(CO)_4$ , which is typical, is given in

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