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Metal Carbonyls. V. Kinetics of the Reaction of Monosubstituted Manganese Pentacarbonyl Bromides with a Variety of Reagents

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The rates of reaction of $\text{Mn}(\text{CO})_5\text{LX}$ with a variety of reagents L' to form $\text{Mn}(\text{CO})_5\text{LL}'\text{X}$ were found to be independent of the nature and concentration of L' , but to decrease with increasing atomic number of X and also to decrease with changes in L in the following order: $\text{P}(\text{C}_6\text{H}_5)_3 > \text{As}(\text{C}_6\text{H}_5)_3 > \text{P}(\text{C}_4\text{H}_9)_3 \sim \text{P}(\text{C}_6\text{H}_5)_2\text{Cl} > \text{P}(\text{OC}_6\text{H}_5)_3 \sim \text{Sb}(\text{C}_6\text{H}_5)_3 > \text{P}(\text{C}_6\text{H}_5)\text{Cl}_2 \sim \text{P}(\text{OC}_4\text{H}_9)_3 > \text{P}(\text{OCH}_2)_3\text{CCH}_3$ (the group C_4H_9 is *n*-butyl). These results have been interpreted as indicating a dissociation mechanism in which the bulkiness of L determines the rate of CO dissociation. The absorption maxima of several $\text{Mn}(\text{CO})_5\text{LBr}$ complexes in the near-ultraviolet region also are reported.

Recently the kinetics and mechanism of the reaction of the manganese pentacarbonyl halides with various ligands to form the *cis*-substituted compounds, $\text{Mn}(\text{CO})_5\text{LX}$, were investigated.^{1,2} The results suggested a dissociative mechanism, and the rates were observed to depend upon the Mn-CO bond strength. The present work considers the kinetics and mechanism of the formation of $\text{Mn}(\text{CO})_5\text{LL}'\text{X}$ by the reaction between $\text{Mn}(\text{CO})_5\text{LX}$ and L' .



Experimental

Preparation and Purification of Materials.—1-Methyl-phospha-3,5,8-trioxabicyclo[2.2.2]octane, $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, was a gift from Dr. J. G. Verkade, diphenylchlorophosphine a gift from the Victor Chemical Works, and $\text{Mn}_2(\text{CO})_{10}$ a gift from the Ethyl Corporation. *s*-Tetrachloroethane (TCE) was shaken with concentrated sulfuric acid, washed with water, dried over calcium chloride, and distilled. Other compounds and solvents used in this study were prepared and purified as previously reported.¹

Solutions of the $\text{Mn}(\text{CO})_5\text{LBr}$ complexes were prepared by the direct reaction of $\text{Mn}(\text{CO})_5\text{Br}$ and L in TCE and identified by their infrared spectra.¹ The experimental conditions for the

in situ preparations of the $\text{Mn}(\text{CO})_5\text{LBr}$ compounds are given in Table I. In every case the infrared spectrum of the reaction mixture was that of the desired monosubstituted compound, and the solution was used directly for the kinetic studies of reaction 1.

TABLE I
CONDITIONS FOR THE *In Situ* PREPARATION OF $\text{Mn}(\text{CO})_5\text{LBr}$ IN
s-TETRACHLOROETHANE (TCE)

$\text{Mn}(\text{CO})_5\text{Br}$, g.	L, g.		TCE, ml. ^a	Temp., °C.	Time, hr.
0.057	0.055	$\text{P}(\text{C}_6\text{H}_5)_3$	3	55	16
.057	.064	$\text{As}(\text{C}_6\text{H}_5)_3$	3	55	16
.054	.069	$\text{Sb}(\text{C}_6\text{H}_5)_3$	3	55	16
.040	.083	$\text{P}(\text{C}_4\text{H}_9)_3$	15	55	16
.069	.078	$\text{P}(\text{OC}_6\text{H}_5)_3$	5	40	16
.044	.066	$\text{P}(\text{OC}_4\text{H}_9)_3$	1	55	16
.042	.063	$\text{P}(\text{C}_6\text{H}_5)_2\text{Cl}$	2	50	16
.049	.053	$\text{P}(\text{C}_6\text{H}_5)\text{Cl}_2$	20	60	1 ^b
.0764	.21	$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	5	40	10

^a For reactions in chloroform, toluene, and nitrobenzene, these solvents were used instead of TCE. ^b These reaction conditions yielded the monosubstituted product and a small amount of the disubstituted compound, $\text{Mn}(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)\text{Cl}_2]_2\text{Br}$, as shown by the infrared spectrum. This solution then was thermostated at 40.0° and the rate of reaction to form the disubstituted product was followed.

Determination of Rates.—The stock solutions prepared as shown in Table I were diluted to the desired concentrations with solutions of the reagent L' (Table II). The rate of reaction 1 then was determined by following the disappearance of the highest frequency carbonyl stretching absorption of the monosubstituted complexes. A Baird-Associates Model 4-55 double beam recording spectrophotometer with NaCl optics was used to follow the reactions. The reaction flask was wrapped with aluminum foil and thermostated in a constant temperature bath. At various times a sample of the reaction solution was withdrawn and placed in an infrared cell. The spectrum of this sample then was taken in the carbonyl region using the solvent as a reference. A typical series of spectra taken during the reaction is shown in Fig. 1. The data were plotted as for a first order reaction, *viz.*, $\ln(A - A_\infty)$ vs. *t*, time, and the rate constants calculated from the slopes of these lines. Here *A* is the absorbance at time *t*. The absorbance at infinite time, A_∞ , was taken as zero in all cases, since the absorption band being followed disappeared at the completion of the reaction. All reactions proceeded to completion, except those of $\text{Mn}(\text{CO})_5\text{I}$.¹

This same procedure was used for solvents other than TCE. The *in situ* preparation of $\text{Mn}(\text{CO})_5\text{LBr}$ was carried out in the new solvent which also is used to dissolve the reagent, L' . The effect of solvent was small. However, the reaction of $\text{Mn}(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)\text{Cl}_2]_2\text{Br}$ was not followed.

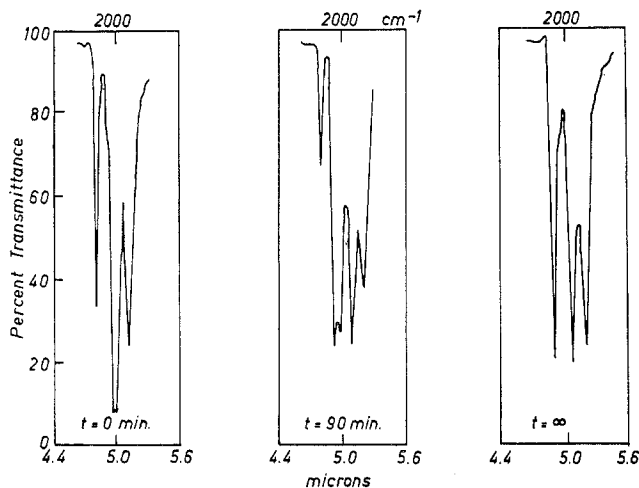


Figure 1.

(1) R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, **84**, 2495 (1962).(2) W. Hieber, G. Faulhaber, and F. Theubert, *Z. anorg. allgem. Chem.*, **314**, 125 (1962).

TABLE II

RATES OF THE REACTION $\text{Mn}(\text{CO})_4\text{LBr} + \text{L}' \longrightarrow \text{Mn}(\text{CO})_3\text{LL}'\text{Br} + \text{CO}$ IN TCE AT 40.0°

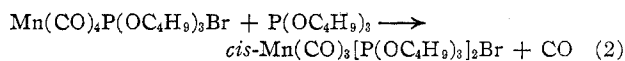
$10^3[\text{complex}]$ M	L	L'	[L'] M	10^3k , sec. ⁻¹
3.77	$\text{P}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	0.318	77
4.16	$\text{P}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.639	78
4.14	$\text{P}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.639	81
0.593	$\text{As}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.0992	21
0.767	$\text{As}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.202	21
3.72	$\text{As}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.326	22
4.19	$\text{As}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.535	21
6.81	$\text{As}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.200	4.1 ^a
6.73	$\text{As}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.399	4.1 ^a
6.51	$\text{As}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.205	58 ^b
6.78	$\text{As}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.398	66 ^b
6.53	$\text{As}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.203	43 ^c
6.27	$\text{As}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.201	28 ^d
0.572	$\text{P}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.286	12
0.578	$\text{P}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.880	11
4.55	$\text{P}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	1.59	11
0.909	$\text{P}(\text{C}_6\text{H}_5)_2\text{Cl}$	$\text{P}(\text{OC}_4\text{H}_9)_3$	0.193	10
1.00	$\text{P}(\text{C}_6\text{H}_5)_2\text{Cl}$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.404	12
0.755	$\text{P}(\text{C}_6\text{H}_5)_2\text{Cl}$	$\text{P}(\text{C}_6\text{H}_5)_2\text{Cl}$	.0680	8.6
0.633	$\text{P}(\text{OC}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.322	5.7
0.574	$\text{P}(\text{OC}_6\text{H}_5)_3$	$\text{P}(\text{OC}_6\text{H}_5)_3$	.275	4.8
3.90	$\text{Sb}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.326	5.0
4.93	$\text{Sb}(\text{C}_6\text{H}_5)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.804	5.3
0.894	$\text{P}(\text{C}_6\text{H}_5)\text{Cl}_2$	$\text{P}(\text{C}_6\text{H}_5)\text{Cl}_2$	.147	3.5
0.900	$\text{P}(\text{C}_6\text{H}_5)\text{Cl}_2$	$\text{P}(\text{C}_6\text{H}_5)\text{Cl}_2$	.441	4.0
0.504	$\text{P}(\text{OC}_4\text{H}_9)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.0470	3.6
0.514	$\text{P}(\text{OC}_4\text{H}_9)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.238	3.5
4.31	$\text{P}(\text{OC}_4\text{H}_9)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.324	3.1
4.10	$\text{P}(\text{OC}_4\text{H}_9)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.640	3.4
5.05	$\text{P}(\text{OC}_4\text{H}_9)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	.513	5.1 ^e
5.56	$\text{P}(\text{OC}_4\text{H}_9)_3$	$\text{P}(\text{OC}_4\text{H}_9)_3$	1.46	5.5 ^e
5.17	$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	0.232	0.49 ^e
5.71	$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	.639	0.40 ^e
1.22	CO	$\text{As}(\text{C}_6\text{H}_5)_3$	.0695	19
1.23	CO	$\text{P}(\text{OC}_4\text{H}_9)_3$	.164	18

^a 30°. ^b 48°. ^c Toluene as the solvent. ^d Nitrobenzene as the solvent. ^e Chloroform as the solvent.

$(\text{OCH}_2)_3\text{CCH}_3\text{Br}$ with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ was studied in chloroform, because in TCE at 40° no reaction occurred. At higher temperatures (55°), however, the desired reaction also took place in TCE. During the reaction in chloroform, the disubstituted product precipitated, and after rinsing with small amounts of chloroform and drying at room temperature, gave the expected analysis.

Product Identification.—During the reaction of $\text{Mn}(\text{CO})_4\text{LBr}$ with $\text{P}(\text{OC}_4\text{H}_9)_3$, 1 mole of CO per mole of complex was evolved. The reaction products were not isolated but were identified by their spectral similarities to $\text{cis-Mn}(\text{CO})_3\text{L}_2\text{Br}$, where the L groups are *cis* to each other as well as to Br.³ Hence, products in which L and L' are the same ligands were readily identified by a comparison of the final reaction spectrum with that of the known $\text{Mn}(\text{CO})_3\text{L}_2\text{Br}$ compounds. Attempts to isolate mixed ligand products, $\text{Mn}(\text{CO})_3\text{LL}'\text{X}$, where $\text{L}' = \text{P}(\text{OC}_4\text{H}_9)_3$, from excess $\text{P}(\text{OC}_4\text{H}_9)_3$ by precipitation on the addition of various solvents to the reaction mixture and by chromatography on silica gel were not successful. In each case a $\text{P}(\text{OC}_4\text{H}_9)_3$ solution of the complex was obtained; an excess of $\text{P}(\text{OC}_4\text{H}_9)_3$ was necessitated by the slightly unfavorable equilibrium. It also is possible that these complexes are oils as is true of $\text{Ni}(\text{CO})_2[\text{P}(\text{OC}_4\text{H}_9)_3]_2$.⁴

The choice of $\text{P}(\text{OC}_4\text{H}_9)_3$ as L' in most of these reactions was made because reaction 2 is very slow. Thus if in reaction 1 L



were first displaced by $\text{P}(\text{OC}_4\text{H}_9)_3$, then the rate of formation of $\text{cis-Mn}(\text{CO})_3[\text{P}(\text{OC}_4\text{H}_9)_3]_2\text{Br}$ would be slow and have the same rate as that determined for reaction 2. Also if L is displaced first, one would expect to see a small shift in the infrared spectrum as $\text{Mn}(\text{CO})_4\text{LBr}$ forms $\text{Mn}(\text{CO})_4\text{P}(\text{OC}_4\text{H}_9)_3\text{Br}$. This was not observed. It is therefore certain that CO is first displaced by $\text{P}(\text{OC}_4\text{H}_9)_3$ to give $\text{Mn}(\text{CO})_3\text{L}[\text{P}(\text{OC}_4\text{H}_9)_3]\text{Br}$, and that this is the reaction followed by measuring the disappearance of the $\text{Mn}(\text{CO})_4\text{LBr}$ high frequency carbonyl absorption. However, $\text{cis-Mn}(\text{CO})_3\text{L}[\text{P}(\text{OC}_4\text{H}_9)_3]\text{Br}$ then reacts further to form $\text{cis-Mn}(\text{CO})_3[\text{P}(\text{OC}_4\text{H}_9)_3]_2\text{Br}$. The subsequent isomerization to $\text{trans-Mn}(\text{CO})_3[\text{P}(\text{OC}_4\text{H}_9)_3]_2\text{Br}$ also has been noted.³

Near-Ultraviolet Absorption Spectra.—The spectra of $\text{Mn}(\text{CO})_4\text{LBr}$ complexes in TCE were taken with a Beckman DK-2 double beam recording spectrophotometer. The instrument was carefully set for all compounds such that the error in λ_{max} was less than $\pm 1 \text{ m}\mu$. The solutions were prepared as shown in Table I.

Results

The rates of reaction 1 were followed by recording the disappearance of the highest frequency carbonyl stretching absorption as shown in Fig. 1. The kinetic data obtained are summarized in Table II. These show that the rate of reaction is first order in carbonyl and zero order in the entering reagent. Solvent has only a slight effect on the rate of reaction, which decreases for $\text{Mn}(\text{CO})_4\text{LX}$ with changes in X in the order $\text{Cl} > \text{Br} > \text{I}$. The near-ultraviolet absorption maxima of some of the monosubstituted compounds are reported in Table III.

TABLE III

NEAR-ULTRAVIOLET ABSORPTION SPECTRA OF $\text{Mn}(\text{CO})_4\text{LBr}$ IN TCE

L	λ_{max} , $\text{m}\mu$ ^a	ϵ , l./mole-cm.
$\text{P}(\text{OC}_4\text{H}_9)_3$	382	640
$\text{P}(\text{C}_6\text{H}_5)_3$	385	410
CO	386	340
$\text{P}(\text{OC}_6\text{H}_5)_3$	386	680
$\text{P}(\text{C}_6\text{H}_5)\text{Cl}_2$	392	730
$\text{P}(\text{C}_6\text{H}_5)_3$	396	640
$\text{As}(\text{C}_6\text{H}_5)_3$	403	710
$\text{Sb}(\text{C}_6\text{H}_5)_3$	409	710

^a $\pm 1 \text{ m}\mu$.

Discussion

The kinetic results for reaction 1 in TCE given in Table II show that the rates are independent of the nature and concentration of L' and are first order in complex concentration. This suggests that the reaction involves a dissociative mechanism in which the dissociation of CO from the complex is the rate determining process (3).



Because of the known relative inertness of the CO

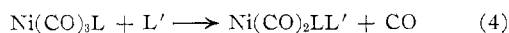
(3) R. J. Angelici, F. Basolo, and A. J. Poë, *Nature*, **195**, 993 (1962).

(4) L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959).

trans to X in $\text{Mn}(\text{CO})_5\text{X}$,⁵ it is assumed that the CO *trans* to X also does not dissociate in these $\text{Mn}(\text{CO})_4\text{LX}$ compounds. Since the product of the reaction has a structure where the L groups are *cis* to each other as well as to Br,³ the dissociation of a CO *cis* to L and Br is reasonable. Likewise kinetic studies of the replacement of $\text{P}(\text{OC}_6\text{H}_5)_3$ by $\text{P}(\text{OC}_4\text{H}_9)_3$ and $\text{P}(\text{C}_6\text{H}_5)_3$ in *cis* and *trans*- $\text{Mn}(\text{CO})_3[\text{P}(\text{OC}_6\text{H}_5)_3]_2\text{Br}$ show that $\text{P}(\text{OC}_6\text{H}_5)_3$ is replaced approximately seven times faster when it is *trans* to CO than when *trans* to $\text{P}(\text{OC}_6\text{H}_5)_3$.⁶ This result then indicates that in $\text{Mn}(\text{CO})_4\text{LX}$, the CO groups *trans* to each other are more labile than the CO *trans* to L.

Table II summarizes the rate constants for the dissociation of CO from a variety of $\text{Mn}(\text{CO})_4\text{LBr}$ complexes. These data show a decrease in the rates of reaction with changes in L in the order: $\text{P}(\text{C}_6\text{H}_5)_3 > \text{As}(\text{C}_6\text{H}_5)_3 > \text{P}(\text{C}_4\text{H}_9)_3 \sim \text{P}(\text{C}_6\text{H}_5)_2\text{Cl} > \text{P}(\text{OC}_6\text{H}_5)_3 \sim \text{Sb}(\text{C}_6\text{H}_5)_3 > \text{P}(\text{C}_6\text{H}_5)\text{Cl}_2 \sim \text{P}(\text{OC}_4\text{H}_9)_3 > \text{P}(\text{OCH}_2)_3\text{-CCH}_3$. This trend cannot be explained on the basis of the π -bonding ability of the ligands or the Mn-C bond strength as inferred from infrared studies.^{1,7} However, a consideration of molecular models of the $\text{Mn}(\text{CO})_4\text{LBr}$ compounds shows a good correlation between the decreasing bulkiness of L and the decreasing rates of CO dissociation. For the series of complexes, $\text{Mn}(\text{CO})_4[\text{M}(\text{C}_6\text{H}_5)_3]\text{Br}$, where M = P, As, or Sb, the steric interactions of the phenyl rings are reduced by an increase in the size of M. It thus appears that energy changes resulting from steric interactions are more important than changes in Mn-C bond energies.

This same trend was observed for some related nickel carbonyl reactions.⁴ Here the rates



were independent of L' and varied with L in the complex in the following manner: $\text{P}(\text{C}_6\text{H}_5)_3$ (8.23×10^{-4} sec.⁻¹) $>$ $\text{P}(\eta\text{-C}_4\text{H}_9)_3$ (5.99×10^{-4}) $>$ $\text{P}(\text{OC}_2\text{H}_5)_3$ (2.76×10^{-4}). Again the dissociation of CO from the complex appears to be a result of steric factors, but it should be noted that the difference in rates for complexes containing different ligands is greater in the Mn system than in the Ni compounds. This is expected for the more sterically crowded octahedral structure. Steric acceleration also has been reported for dissociation reactions of certain octahedral cobalt(III) complexes.⁸

Data in Table II show that the rates of CO dissociation from $\text{Mn}(\text{CO})_5\text{Br}$ and $\text{Mn}(\text{CO})_4\text{As}(\text{C}_6\text{H}_5)_3\text{Br}$ are very nearly the same. Since these complexes are quite different, a comparison of their activation parameters is of interest. Temperature dependence studies permit calculations of the activation parameters for the dissociation of CO from $\text{Mn}(\text{CO})_4\text{As}(\text{C}_6\text{H}_5)_3\text{Br}$: $E_a = 29.8 \pm 0.6$ kcal./mole; $\Delta S^\ddagger = 17.8$ e.u. These values compare with $E_a = 29.8 \pm 0.4$ kcal./mole and $\Delta S^\ddagger =$

18.9 e.u. for the dissociation of CO from $\text{Mn}(\text{CO})_5\text{Br}$ in chloroform.¹ Thus it appears that the activation parameters for the dissociation of CO from both $\text{Mn}(\text{CO})_4\text{As}(\text{C}_6\text{H}_5)_3\text{Br}$ and $\text{Mn}(\text{CO})_5\text{Br}$ are essentially the same. This result is surprising and not understood. It does suggest that because of the various factors which may contribute to the reactivities of these systems, there can be compensating effects giving analogous results for rather different compounds.

For the substitution reactions of $\text{Mn}(\text{CO})_5\text{X}$, the rates of reaction decreased with changes in X in the order: $\text{Cl} > \text{Br} > \text{I}$.¹ The following first order rate constants show a similar effect for the reactions of $\text{Mn}(\text{CO})_4\text{As}(\text{C}_6\text{H}_5)_3\text{X}$ with $\text{P}(\text{OC}_4\text{H}_9)_3$ in TCE at 40.0°: Cl (1.3×10^{-3} sec.⁻¹) $>$ Br (2.1×10^{-4}) $>$ I (1.4×10^{-5}). The relative rates for different halogens are approximately the same for this monosubstituted system as for the parent $\text{Mn}(\text{CO})_5\text{X}$ compounds. Hence the influence of the halogen on the rates of CO dissociation may not be drastically altered by substitution in the complex.

Substitution reactions of $\text{Mn}(\text{CO})_5\text{Br}$ in a variety of solvents show slower rates in the more polar solvents.¹ This was interpreted as indicating a decrease in polarity as $\text{Mn}(\text{CO})_5\text{Br}$ passes into the transition state. A similar study of the reaction of $\text{Mn}(\text{CO})_4\text{As}(\text{C}_6\text{H}_5)_3\text{Br}$ with $\text{P}(\text{OC}_4\text{H}_9)_3$ in toluene, TCE, and nitrobenzene (Table II) indicates a much smaller solvent effect. Since the activation parameters for the $\text{Mn}(\text{CO})_4\text{As}(\text{C}_6\text{H}_5)_3\text{Br}$ and $\text{Mn}(\text{CO})_5\text{Br}$ reactions are essentially the same, one might expect similar solvent effects. Perhaps in the activated complex the bulky $\text{As}(\text{C}_6\text{H}_5)_3$ group prevents contraction of the Mn-Br bond, which may be responsible for the solvent effect in the substitution reactions of $\text{Mn}(\text{CO})_5\text{Br}$.

The near-ultraviolet spectra of various $\text{Mn}(\text{CO})_4\text{LBr}$ compounds consist of one broad absorption band slightly shifted depending on L in the complex (Table III). The absorption maximum moves toward lower energies with changes in L in the order: $\text{P}(\text{OC}_4\text{H}_9)_3 > \text{P}(\text{C}_4\text{H}_9)_3 \sim \text{CO} \sim \text{P}(\text{OC}_6\text{H}_5)_3 > \text{P}(\text{C}_6\text{H}_5)_2\text{Cl}_2 > \text{P}(\text{C}_6\text{H}_5)_3 > \text{As}(\text{C}_6\text{H}_5)_3 > \text{Sb}(\text{C}_6\text{H}_5)_3$. Recently the $\text{Mn}(\text{CO})_5\text{Br}$ absorption was assigned to a charge transfer transition from the $b_2(d_{xy})$ molecular orbital, primarily located on the metal, to the $e(\pi^*)$, which is essentially localized on the CO *trans* to Br.⁹ If in *cis*- $\text{Mn}(\text{CO})_4\text{LBr}$ the d_{xy} orbital is partially stabilized by π -bonding to L, the magnitude of this charge transfer transition may well be determined by the π -bonding ability of L. Thus in the series where $\text{L} = \text{M}(\text{C}_6\text{H}_5)_3$ and $\text{M} = \text{P}, \text{As},$ and Sb , the π -bonding ability can be inferred as decreasing in the order: $\text{P}(\text{C}_6\text{H}_5)_3 > \text{As}(\text{C}_6\text{H}_5)_3 > \text{Sb}(\text{C}_6\text{H}_5)_3$. Similar observations were made in studies of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition in *trans*- $[\text{Pt}(\text{piperidine})\text{LCl}_2]$.¹⁰ Phosphites are observed to be better π -bonding ligands than their corresponding phosphines, which is in agreement with infrared studies.⁷ Not in agreement with previous

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studies⁷ is the position of $P(C_4H_9)_3$, which these results suggest is a stronger π -bonding agent than $P(OC_4H_9)_3$ or $P(C_6H_5)_3$. Likewise the absorption position of $Mn(CO)_5Br$ cannot be reconciled with this interpretation. These discrepancies indicate that other parameters are important in determining the positions of these absorption bands.

In the ultraviolet region, the monosubstituted com-

pounds investigated ($L = P(C_6H_5)_3$, $P(C_4H_9)_3$, and $P(OCH_2)_3CCH_3$) showed intense absorptions at 254 $m\mu$, whereas $Mn(CO)_5Br$ absorbs at 241 $m\mu$.

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Vinyl Derivatives of Metals. XVI. Addition of Silicon and Tin Hydrides to B-Trivinyl-N-triphenylborazine¹

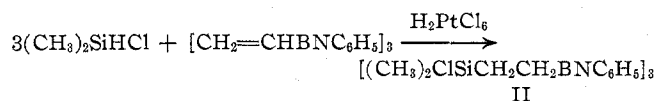
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The addition of CH_3SiHCl_2 , $(CH_3)_2SiHCl$, $(CH_3)_3SiOSi(CH_3)_2H$, and $(CH_3)_3SiOSi(CH_3)HOSi(CH_3)_3$ to $[CH_2=CHBNC_6H_5]_3$ gave the respective B-tris-(β -silylethyl)-N-triphenylborazines. The reactions of those borazines containing Si-Cl bonds with water and with $(CH_3)_3SiOLi$ are described. The reaction of triphenyl- and triethyltin hydrides with $[CH_2=CHBNC_6H_5]_3$ gave $[R_3SnCH_2CH_2BNC_6H_5]_3$ ($R = C_6H_5$ and C_2H_5).

B-Trivinyl-N-triphenylborazine (I) was prepared recently by Pellon, *et al.*,⁴ and the radical-initiated polymerization and copolymerization of this new monomer were studied by these authors. Our interest in organofunctional, and especially in organosilicon-substituted, borazines has prompted this investigation of the addition of a number of silicon and tin hydrides to the vinyl groups of I.

Silicon Hydrides.—Although hydrogen chlorosilanes such as $HSiCl_3$ and CH_3SiHCl_2 did not react with I in the presence of radical initiators, they did add very readily to I in the presence of Speier's⁵ chloroplatinic acid catalyst.



The direction of addition of the Si-H bond to the vinyl side groups was determined by oxidation with alkaline hydrogen peroxide of the completely methylated borazine, $[(CH_3)_3SiCH_2CH_2BNC_6H_5]_3$, derived from II. Cleavage of the B-C bonds gave *only* β -trimethylsilylethanol, establishing the direction of addition as that given in the equation above. Had any $(CH_3)_3SiCH(CH_3)$ side groups been present in

the borazine, oxidation would have given α -trimethylsilylethanol as well, and the latter would have been detected in the gas chromatographic analysis of the alcohols produced.⁶

The availability of II and of $[CH_3Cl_2SiCH_2CH_2BNC_6H_5]_3$ (III) in principle made possible the preparation of β -siloxanylethylborazines. However, neither of the two procedures tried gave wholly satisfactory results. Attempted cohydrolysis of trimethylchlorosilane and II in an ether-water system gave hexamethyldisiloxane and a white solid. This solid, m.p. 137°, also was obtained when II alone was hydrolyzed and was identified as the silanol, $[(CH_3)_2(OH)SiCH_2CH_2BNC_6H_5]_3$ (IV). Cohydrolysis of II with trimethylchlorosilane in an ether-15% HCl mixture gave an oil, which, however, still showed the presence of Si-OH linkages in its infrared spectrum. Most likely steric hindrance, probably due to the other ring substituents, serves to explain this rather difficultly effected condensation of IV. Cohydrolysis of III with trimethylchlorosilane gave a yellow, resinous solid, rather than the expected $\{[(CH_3)_3SiO]_2Si(CH_3)CH_2CH_2BNC_6H_5\}_3$. This is an indication that the borazinylsilanediol condenses at a much slower rate than trimethylsilanol. Hydrolysis of III alone in an aqueous sodium bicarbonate-ether system produced a white, crystalline solid, which appeared to be the silanediol, $[CH_3(OH)_2SiCH_2CH_2BNC_6H_5]_3$, although a satisfactory analysis could not be obtained. Treatment of II and III with lithium trimethylsilanolate resulted in poor yields of products.

The best route to the desired siloxanylethylbor-

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