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Octahedral Metal Carbonyls. XIX.[1a] Kinetics of the Reactions of Triphenylgermyl- and Triphenylstannylpentacarbonylmanganese(0) with Phosphines

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Triphenylgermylpentacarbonylmanganese(0) and triphenylstannylpentacarbonylmanganese(0) react with phosphines (L) in decalin solvent at 150-190° to give trans*–$(C_6H_5)_3M–Mn(CO)_4(L)$ products according to the rate law, rate$=k_1[(C_6H_5)_3M–Mn(CO)_5]+k_2[(C_6H_5)_3M$-$Mn(CO)_5][L]$. The kinetic data suggest two competing mechanisms in which the rate-determining steps involve slow fission of Mn–CO bonds, and nucleophilic attack of L on the substrate. The mechanism of formation of the* trans *isomers, as observed, and the relationships between the observed reactivity and carbonyl stretching and related data are discussed.*

Introduction

Several kinetic investigations of the substitution reactions of $XMn(CO)_5$ complexes (X=one electron donating group) have been reported.[2-5] It has been found apparently without exception that these reactions.

$$XMn(CO)_5+L \rightarrow XMn(CO)_4L+CO, \qquad (1)$$

proceed *via* ligand-independent rate laws for which a common mechanism involving rate-determining dissociation of CO is probable. Moreover, for X=Cl, Br, and I[2] and CH_3CO,[3] reaction rates are observed to be faster than for the parent $Mn_2(CO)_{10}$ itself.[4,5] However, the reaction conditions employed in the synthesis of substitution products of $(C_6H_5)_3M–Mn(CO)_5$ (M=Ge,[6] Sn[7]) suggested that carbonyl complexes containing Group IVA metal-Mn bonds might be even more inert than is $Mn_2(CO)_{10}$. Thus a kinetic investigation of these reactions might, in addition to providing evidence (albeit indirect) as to the nature of the metal-metal bonds in these complexes, extend the range of reactivity of $XMn(CO)_5$ species which have been investigated in detail. Such an extension would reveal if other reaction paths are available to octahedral manganese carbonyls under these more drastic reaction conditions.

Experimental Section

Reagents. The $(C_6H_5)_3M–Mn(CO)_5$ complexes (M=Si,[8] Ge,[9] Sn,[7] and Pb[7]) were prepared through the published procedures and were identified through elemental analyses, infrared spectra and melting points. Triphenylphosphine was recrystallized from absolute ethanol and was then dried by heating *in vacuo* at its melting point (82°) for three hours. Technical grade decalin was stirred over sulfuric acid, shaken repeatedly with water, dried over anhydrous calcium chloride, and then was fractionally distilled at reduced pressure. Tri(*n*-butyl)phosphine, generously provided by the Carlisle Chemical Works, was fractionally distilled over sodium under reduced.

Kinetics. With exceptions to be noted, kinetic runs were carried out under pseudo first order reaction conditions, employing at least a ten-fold excess of ligand. Decalin was the solvent employed for all runs. Reaction rates were followed by monitoring the decay of the highest energy carbonyl stretching absorption of the substrate (Si, 2098; Ge, 2097; Sn, 2093 cm^{-1}) in 1 mm NaCl cells. Where k_{obsd} values are given (Table I), plots of $\ln(A_t–A_\infty)$ *vs.* t were linear, in most cases, to at least 80% of competition. In a typical run, a weighed amount of ligand was placed in a glass-stoppered 25 ml volumetric flask and was dissolved in about 20 ml of decalin. The flask was then placed in a constant temperature oil bath (±0.05°) and after a period of time the volume of solution was adjusted to the inscribed mark on the flask through dropwise addition of solvent. After the solution had equilibrated it was removed from the oil bath and poured into a foil-wrapped 50 ml volumetric flask

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[1] (a) Part XVIII: R. A. Brown and G. R. Dobson, *J. Inorg. Nucl. Chem.*, in press; presented in part at the C. I. C.-A. C. S. Joint Conference, Toronto, May, 1970. (b) To whom correspondence concerning this work should be addressed at North Texas State University. (c) Taken in part from a dissertation submitted by E. P. R. to the Graduate School of The University of South Dakota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1969.

[2] R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, *84*, 2495 (1962).

[3] F. Calderazzo and F. A. Cotton, *Chim. Ind.* (*Milan*), *46*, 1165 (1964); K. Noack, M. Ruch, and F. Calderazzo, *Inorg. Chem.*, *7*, 345 (1968).

[4] L. I. B. Haines, D. Hopgood, and A. Poë, *J. Chem. Soc.*, *A*, 421 (1968).

[5] H. Wawersik and F. Basolo, *Inorg. Chim. Acta*, *3*, 113 (1969).

[6] A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. B. Antonova, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 139 (1966).

[7] R. D. Gorsich, *J. Am. Chem. Soc.*, *84*, 2486 (1962).

[8] W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, *5*, 2217 (1966).

[9] D. Seyferth, H. P Hofman, R. Burton, and J. F. Helling, *Inorg. Chem.*, *1*, 227 (1962).

which contained a preweighed amount (*ca.* 40 mg) of the appropriate substrate. The reaction flask was then quickly flushed with nitrogen, sealed with a rubber septum and allowed to re-equilibrate. At appropriate time intervals nitrogen was injected into the flask by means of a syringe and a sample (*ca.* 0.5 ml) of egual volume was withdrawn. Absorbance were measured on a Beckman IR-12 infrared spectrophotometer immediately, or samples were collected for later absorbance measurements depending upon circumstances (see below). For runs carried out under CO, nitrogen was replaced by carbon monoxide in all appropriate operations.

Initial studies of the feasibility of kinetic studies of reactions of $(C_6H_5)_3M{-}Mn(CO)_5$ (M = Si, Ge, Sn, Pb) with phosphines and phosphites were made. Although it proved possible to prepare the product of the reaction of triphenylphosphine with $(C_6H_6)_3Si{-}Mn(CO)_5$ *trans*–$(C_6H_5)_3Si{-}(CO)_4[P(C_6H_5)_3]$,[10] it was not possible to obtain linear pseudo first order kinetic plots since the reaction was found to be autocatalytic as indicated by negative deviations from linearity of the plots with increased reaction time. Consequently the data obtained could be employed only to establish roughly the upper limits of reaction rates at given temperatures.

Autocatalysis was also noted for reactions of $(C_6H_5)_3Ge{-}Mn(CO)_5$ with triphenylphosphine at lower reaction temperatures and at high ($>0.4\,M$) ligand concentrations. The observed reaction behavior necessitated the use of reaction temperatures which procuced greater rates than for the analogous Sn complex (discussed below). Consequently samples as removed from the reaction vessel were stored in evacuated tubes sealed with rubber septa for later absorbance measurements.

Reactions of $(C_6H_5)_3Si{-}Mn(CO)_5$ with phosphites, $P(OR)_3$, were found to yield *trans*–$RCOMn(CO)_3[P(OR)_3]_2$ products;[10] these and other preparative results obtained for reactions of $(C_6H_5)_3M{-}Mn(CO)_5$ complexes (M = Si, Ge, Sn) with both mono- and bidentate Lewis bases are the subject of a separate report.[11]

For M = Pb, decomposition of the substrate with the formation of a finely divided black precipitate was observed under appropriate reaction conditions even in the presence of a large excess of L. No substitution products, $(C_6M_5)_3Pb{-}Mn(CO)_4(L)$, were ever obtained, either through reaction in solution or through direct combination of substrate and ligand in the absence of solvent in sealed tubes.

It proved possible to study the kinetics of the reactions of $(C_6H_5)_3Ge{-}Mn(CO)_5$ and $(C_6H_5)_3Sn{-}Mn(CO)_5$ with triphenylphosphine (and in some cases with tri(*n*-butyl)phosphine) in decalin solvent. These reactions proceeded at elevated temperatures (Ge, 150-170°; Sn, 170-190°) according to the equation.

$$(C_6H_5)_3M{-}Mn(CO)_5 + L \rightarrow \text{trans}{-}(C_6H_5)_3M{-}Mn(CO)_4L + CO. \qquad \text{(II)}$$

Both reaction products (for $L = (C_6H_5)_3P$) had previously been prepared[6,7] and were identified by elemental analysis and infrared spectrum. The *trans*-product for M = Sn, $L = P(n{-}C_4H_9)_3$ is also known,[12] and was identified through its infrared spectrum.

Results and Discussion

Rate (k_{obsd}) data for the reactions (according to Eq. (II)) of $(C_6H_5)_3M{-}Mn(CO)_5$ (M = Ge, Sn) with triphenylphosphine in decalin solvent are given in Table I. Plots of k_{obsd} *vs.* [L] are exhibited in Figures 1 and 2. These plots are consistent with a rate law,

$$\text{rate} = k_1[(C_6H_5)_3M{-}Mn(CO)_5] + k_2[C_6H_5)_3M{-}Mn(CO)_5][L], \qquad \text{(III)}$$

suggestive of two competing mechanisms. The ligand-independent term is best ascribable to rate-determining fission of Mn–C bonds to yield a five-coordinate intermediate which can then react with L to give the observed product. This mechanism is the most com-

Table I. Kinetic and Activation Data for Reactions of Triphenylgermyl- and Triphenylstannylpentacarbonylmanganese Complexes with Triphenylphosphine

Metal (T, °C)	$[P(C_6H_5)_3]$ (*M*)	10^4k_{obsd} (sec^{-1}) ^{a}	10^4k_1 (sec^{-1}) ^{a}	10^4k_2 (M^{-1}sec^{-1}) ^{a}
Ge (150.15)	0.024	1.37		
	0.074	1.42		
	0.140	1.47	1.24	2.24
	0.248	1.74		
	0.348	1.97		
	0.398	2.24		
(160.15)	0.025	4.00		
	0.077	4.11		
	0.157	4.24	3.93	2.08
	0.220	4.28		
	0.277	4.55		
	0.346	4.67		
(170.05)	0.076	10.99		
	0.159	11.18	10.70	3.32
	0.350	11.88		
Sn (168.65)	0.027	0.50		
	0.101	0.66	0.52	0.86
	0.201	0.68		
	0.337	0.80		
(178.75)	0.019	1.43		
	0.037	1.50		
	0.056	1.64	1.46	1.21
	0.195	1.61		
	0.317	1.88		
(188.75)	0.027	4.25		
	0.091	4.50		
	0.179	4.54	4.21	2.21
	0.251	4.73		
	0.326	4.98		

	ΔH_1^* (kcal/mole)^b	ΔS_1^* (e u) ^{b}	ΔH_2^* (kcal/mole) ^{b}	ΔS_2^* (e u) ^{b}
Ge	39.4 ± 1.6	16.1 ± 3.8	6.7 ± 10.5	60.2 ± 20.4
Sn	41.4 ± 1.3	14.8 ± 3.0	18.3 ± 4.7	36.7 ± 10.4

^{a} Values obtained through linear least squares analysis of data. ^{b} Limits of error: one standard deviation.

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[10] E. P. Ross and G. R. Dobson, *J. Chem. Soc., D,* 1229 (1969).

[11] G. R. Dobson, R. T. Jernigan, and E. P. Ross, *J. Inorg. Nucl. Chem.,* in press.

[12] L. M. Bower and M. H. B. Stiddard, *J. Chem. Soc., A,* 706 (1968).

mon one observed for substitution reactions of metal carbonyls[13] and is supported by the calculated positive entropies of activation (Table I) observed for the ligand-independent paths for both $(C_6H_5)_3M{-}Mn(CO)_5$ substrates. That the reaction is reversible was demonstrated through studies employing conditions (CO atmosphere, low $(C_6H_5)_3P$ concentration) under which both CO and $(C_6H_5)_3P$ can compete for the postulated intermediate: under such conditions decreased reaction rates are observed.

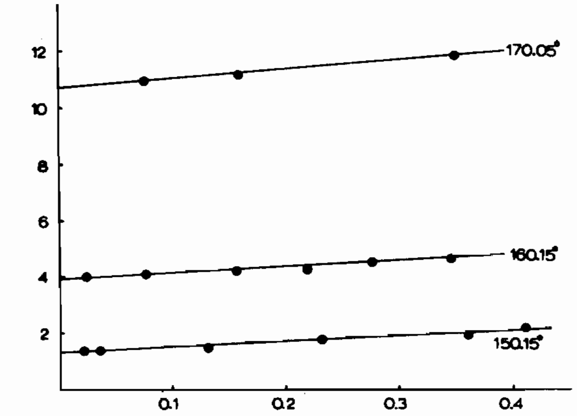

Figure 1. Plots of k_{obsd} *vs.* Ligand Concentration for the Reaction of Triphenylgermylpentacarbonylmanganese(0) with Triphenylphosphine at Various Temperatures.
Ordinate: 10^4 k_{obsd} (sec^{-1})
Abscissa: Triphenylphosphine Concentration (*M*).

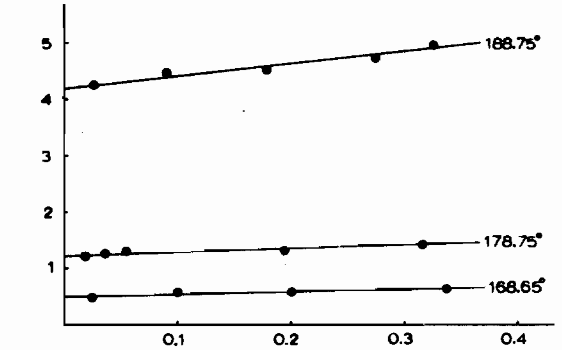

Figure 2. Plots of k_{obsd} *vs.* Ligand Concentration of the Reaction of Triphenylstannylpentacarbonylmanganese(0) with Triphenylphosphine at Various Temperatures.
Ordinate: 10^4 k_{obsd} (sec^{-1})
Abscissa: Triphenylphosphine Concentration (*M*).

The ligand-dependent term of the observed rate law is most probably attributable to nucleophilic attack of triphenylphosphine on the substrate. The term is relatively small, and thus it is not surprising that large uncertainties in the calculated activation parameters are observed. The calculated entropies of activation are, however, highly negative, and are thus consistent with an associative mechanism. Also consistent with this mechanism was the greater ligand-dependent rate observed for reaction of the strong nucleophile tri(*n*-butyl)phosphine with $(C_6H_5)_3Sn{-}Mn(CO)_5$ at 178.75° ($4.88 \times 10^{-4}\ M^{-1}$ sec^{-1} *vs.* $1.21 \times 10^{-4}\ M^{-1}$ sec^{-1} for $(C_6H_5)_3P$ under the same reaction conditions). Kinetic plots for tri(*n*-butyl)phosphine, after initial linearity, exhibited curvature attributable to autocatalysis. Autocaalytic behavior, as has been noted, was also observed for some Ge systems, and prevented a detailed kinetic investigation of triphenylsilylpentacarbonylmanganese(0) in its reactions with phosphines. Similar autocatalytic behavior has been observed by Wawersik and Basolo for reactions of strong nucleophiles with $Mn_2(CO)_{10}$.[5]

Under the reaction conditions of the kinetic runs for M = Ge (and thus, presumably, for Sn) there was no evidence for the formation of the *cis*-isomer—as determined from periodic scans of the carbonyl stretching region of the infrared during the course of the reaction. The fact that only a single isomer is observed indicates formation of the *trans*-isomer *via* the associative process as expected on steric grounds. However, it has been observed for the non-bulky dipy (= 2,2′-dipyridyl) ligand that *cis*-$(C_6H_5)_3M{-}Mn(CO)_3$(dipy) products (M = Si, Ge, Sn) are obtained.[11] In these cases also, only one isomer is found. These observations are consistent with the overall mechanism as shown in Figure 3. For the dissociative path it is suggested that rate-determining fission of a Mn–C bond yields the *cis*-intermediate. The reaction can then proceed, depending upon the nature of the attacking ligand, through a *trans*-intermediate, or *via* attack of L on the *cis*-intermediate. In this view, for the reaction of a sterically demanding ligand such as triphenylphosphine, formation of the *trans*-intermediate and its subsequent attack by L would be energetically less unfavorable than direct attack on the *cis*-intermediate by L. The fact that there must be greater steric discrimination for the *cis*-intermediate would indicate that the *cis*-intermediate is first formed.

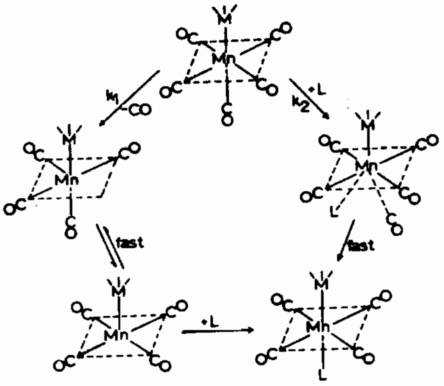

Figure 3. Proposed Mechanism.

Stereochemical non-rigidity of the type envisioned in the *cis-trans* isomerism of the intermediate is not without precedent in octahedral metal carbonyl complexes. For example, Harrill and Kaesz in a study of the replacement of olefins from carbonyl complexes of molybdenum by ^{13}CO, have found that the stereochemistry of the carbonyl groups is not preserved during the olefin replacement:[14] it is highly probable that

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(13) See, *e.g.*, R. J. Angelici, *Organometal. Chem. Rev.*, 3, 173 (1968).

(14) R. W Harrill and H. D. Kaesz, *J. Am. Chem. Soc.*, 90, 1449 (1968).

these reactions proceed through rate-determining dissociation of the olefinic ligands.

It should also be pointed out that a mechanism in which *cis*–$(C_6H_5)_3M–Mn(CO)_4(L)$ is rapidly converted to the corresponding *trans*-isomer *via* dissociation of L is in violation of the principle of microscopic reversibility.[15] Under the pseudo first order conditions employed, were isomerism of *cis*–$(C_6H_5)_3M–Mn(CO)_4(L)$ to involve carbonyl dissociation, a trisubstituted product, rather than the observed *trans*-disubstituted complex would be expected.

If the mechanistic interpretation presented above is correct, the ligand-dependent terms observed represent the first example of nucleophilic attack in an octahedral metal carbonyl complex of manganese. If carbonyl stretching force constants[16] can be taken as roughly indicative of the electronic distribution in octahedral metal carbonyl complexes, $(C_6H_5)_3M–Mn(CO)_5$ and $Cr(CO)_6$ should exhibit approximately the same susceptibility to nucleophilic attack. However, it has been estimated[17] that the covalent radius of Mn^0 is *ca.* 0.09 A smaller than for Cr^0, and thus nucleophilic attack at Mn is less probable on steric grounds. Relevant kinetic data for $Cr(CO)_6$,[18] $Mn_2(CO)_{10}$[4,5] and from the present investigation are consistent with such an interpretation. The failure previously to observe ligand-dependent behavior for reactions of $XMn(CO)_5$ is attributable to the relatively labilizing nature of each X as compared to $(C_6H_5)_3Ge$ and $(C_6H_5)_3Sn$. In general, and supported by the activation data presented in Table I, preference for a dissociative mechanism is expected on the basis of the great differences in entropies of activation between the dissociative and associative paths,[19] with the consequent requirement of a much lower ΔH^* for the associative mechanism if the two are to compete.

The ligand-independent path as observed is indicative of the non-labilizing nature of the $(C_6H_5)_3M$ substituents. Thus the ill-uderstood empirical relationship between substituent «hardness» and its effect in labilizing carbonyls[20] is obeyed here, as is shown in Table II. A consideration of carbonyl stretching or force constant data show them to bear no obvious relationship to the observed complex reactivity. Further, Graham parameters[21] for $(C_6H_5)_3M–Mn(CO)_5$ complexes indicate the $(C_6H_5)_3M$–groups to be good σ-donors as well as good π-acceptors. Each of these bonding characteristics would be predicted to result in decreased Mn–C bond strengths, and thus, if it is presumed that the energy of the $XMn(CO)_5$ ground state has an important influence on reactivity, the Graham parameters fail completely to predict complex reactivity. Trends in Graham parameters and reactivities would also indicate this to be true for substituted Group VIB metal carbonyl complexes.

Table II. Bonding *vs.* Reactivity for Reactions of $X\text{-}Mn(CO)_5$ Complexes with Lewis Bases (Dissociative Path)

X	Graham Parameters [a] σ	 π	Approx. T (°C) for Comparable Reaction Rates
Cl	1.25	–0.57	30[2]
Br	1.03	–0.44	45[2]
I	0.73	–0.27	55[2]
CH_3CO	–0.08	0.09 [b]	50[3]
$(C_6H_5)_3Si$	–0.55	0.40	140
$(C_6H_5)_3Ge$	–0.46	0.34 [c]	155
$(C_6H_5)_3Sn$	–0.59	0.41 [c]	185

[a] Values of σ and π parameters given, except as noted, in Ref. 21. [b] Calculated from frequencies given by K. Noack, *J. Organometal. Chim.*, *12*, 181(1968). [c] The carbonyl stretching force constants for these complexes have been revised in light of ^{13}Co stretching data (R.S. Gay and W.A.G. Graham, *Inorg. Chem.* *8*, 1561 (1969)). However, it would not appear that this revision would alter the qualitative conclusions drawn here.

Under such circumstances it is difficult to draw conclusions as to the changes in bonding properties along the series of complexes containing Si, Ge, Sn, and Pb bonded to Mn, although the observed decomposition of $(C_6H_5)_3Pb–Mn(CO)_5$ and the failure to obtain a $(C_6H_5)_3Pb–Mn(CO)_4(L)$ product would suggest the Pb–Mn bond to be relatively weak.

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(15) T. L. Brown, *Inorg. Chem.*, *7*, 2673 (1968).

(16) For $Cr(CO)_6$, k_1 = 16.49 md/A (F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, *84*, 4432 (1962); For $(C_6H_5)_3Ge\text{-}Mn(CO)_5$, k_1 = 16.33, k_2 = 16.70 md/A; For $(C_6H_5)_3Sn\text{-}Mn(CO)_5$, k_1 = 16.34, k_2 = 16 64 md/A (Ref. 21).

(17) F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, *5*, 1851 (1966).

(18) J. R. Graham and R. J. Angelici, *Inorg. Chem.*, *6*, 2082 (1967).

(19) R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, *88*, 3658 (1966).

(20) R. J. Angelici and J. R. Graham, *Inorg. Chem.*, *6*, 988 (1967).

(21) W. A. G. Graham, *Inorg. Chem.*, *7*, 315 (1968).