electrical effect acts principally through the π bond. This might occur either because the π bond is the stronger bond or because it is more susceptible to inductive effects.[13]

If the enthalpy data of Table III are accepted as significant, they can be interpreted as tending to reinforce the proposed importance of the π bond in electronic effects.[14] Displacements of ethylene by alkylated olefins have a positive enthalpy increment because a weaker coordination bond is formed through a combination of steric and electronic factors.

Conversely, in displacement of ethylene by vinyl fluoride enthalpy decreases because of stronger π bonding. The entropy increment is apparently large enough to overcome a negative enthalpy change giving a positive free-energy change for displacement of ethylene by vinyl fluoride.

In accounting for the relative stabilities of silver(I)-olefin complexes most authors,[2a,3a,15] although recognizing the possible importance of electronic factors, have been concerned with steric effects. However, the greater stability of 3-methylcyclopentene as compared with 4-methylcyclopentene was attributed to electronic effects,[16] and this is supported by molecular orbital calculations[17] which indicate that the increased stability of 3-methylcyclopentene complex is due to the higher donor power of the double bond leading to a stronger σ bond.

Quinn and co-workers,[2b,13a] in precise measurements involving solid olefin complexes of $AgBF_4$ and $AgClO_4$, have demonstrated a progressive *enthalpy change favoring coordination as ethylene hydrogen is replaced by methyl.* This is in contrast to results reported here for rhodium complexes. They found that the amount of perturbation of the olefin double-bond stretch frequency as a consequence of complex formation ($\nu_{\text{uncomplexed}} - \nu_{\text{complexed}}$) was linearly related to the olefin ionization potential (equivalent to olefin basicity) and to the enthalpy change accompanying complex formation. These results indicate that in formation of silver complexes, olefin substituents affect the σ bond primarily.

Kinetics. It has been estimated that the half-life of coordinated ethylene in $acacRh(C_2H_4)_2$ is less than 10^{-4} sec at 25°.[10,18] Although displacement of ethylene by C_2F_4 is thermodynamically favored ($K = 59$), the rate is less than 10^{-6} that of ethylene exchange. This behavior conforms with a mechanism in which the rate-determining step is the nucleophilic addition of the olefin to a d^8 square-planar rhodium(I) complex. It further suggests that development of the σ bond (and not the π bond) is of critical importance in the formation of the activated complex.[19]

Acknowledgment. Dr. C. A. Tolman made important suggestions relating to the calculation of equilibrium constants.

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[13] The much stronger coordination of 1,2-dihaloethylene as compared with 1,1-dihalides may be a consequence of the symmetrical development of both lobes of the π bond: (a) H. W. Quinn, J. S. McIntyre, and D. J. Peterson, *Can. J. Chem.*, **43**, 2897 (1965); (b) J. R. Holden and N. C. Baenziger, *J. Am. Chem. Soc.*, **77**, 4987 (1955).

[14] Another reasonable interpretation is that the entropy and enthalpy changes reflect differences in the solvation of either the olefins or their complexes. The possibility of measuring a series of equilibrium constants for eq 1 in ethylene glycol, the solvent generally used with silver complexes, has been explored. $acacRh(C_2H_4)_2$ is so sparingly soluble in this liquid that the concentration must be reduced by a factor of 10. The solubility of ethylene is also lower in glycol than in toluene. Because of dilution and the high viscosity of the solutions, equilibration is inconveniently slow. A few measurements with propene gave a value for K_E of 0.06.

[15] M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962); I. Jardine and F. J. McQuillin, *J. Chem. Soc., Sect. C*, 458 (1966).

[16] E. Gil-Av and J. Herling, *J. Phys. Chem.*, **66**, 1208 (1962).

[17] W. H. Prichard and W. J. Orville-Thomas, *Theoret. Chim. Acta*, **3**, 426 (1965).

[18] R. Cramer, *Inorg. Chem.*, **4**, 445 (1965).

[19] In a related reaction, H. G. Schuster-Woldan and F. Basolo (*J. Am. Chem. Soc.*, **88**, 1657 (1966)) noted the importance of σ-bond formation. They found phosphines (better σ donors) displaced CO from π-$C_5H_5Rh(CO)_2$ faster than phosphites (better π acceptors).

Rates and Mechanism of Substitution Reactions of Nitrosyltetracarbonylmanganese(0) and Trinitrosylcarbonylmanganese(0)

Henning Wawersik[1] and Fred Basolo

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received April 3, 1967*

Abstract: Kinetic studies for substitution reactions of the five-coordinated compound $MnNO(CO)_4$ and some of its derivatives are reported. The parent compound reacts by a second-order process, whereas the replacement of CO from $MnNO(CO)_3L$ is largely a first-order reaction. Investigations on the last known member of the pseudonickel carbonyl series, $Mn(NO)_3CO$, show it to be very reactive. Its rate of reaction depends on the nature and concentration of the reagent.

The compound $MnNO(CO)_4$[2] is isoelectronic and presumably isostructural with $Fe(CO)_5$ which has a trigonal bipyramidal structure.[3] Several five-coordinated metal complexes are known,[4] but the kinetics and mechanism of substitution reactions of these systems have not been extensively examined. Three such studies have been reported. One deals with the reactions of $RCOCo(CO)_4$ with $P(C_6H_5)_3$,[5] another with

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[1] Exchange graduate student from the Technischen Hochschule, München, Germany.

[2] P. M. Treichel, E. Pitcher, R. B. King, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 2593 (1961).

[3] J. Donohue and A. Caron, *Acta Cryst.*, **17**, 663 (1964).

[4] E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

the acid-induced carbon monoxide exchange with $Fe(CO)_5$,[6] and the most recent with the reaction of $Fe(CO)_4P(C_6H_5)_3$ with $P(C_6H_5)_3$.[7] In all of these cases the reactions take place by a dissociation (SN1) mechanism. Data are reported in this paper in support of a displacement (SN2) mechanism for substitution reactions of $MnNO(CO)_4$.

Also reported here are the few results obtained on substitution reactions of $Mn(NO)_3CO$.[8] This compound is the last known member of the pseudo-nickel carbonyl series $Ni(CO)_4$, $CoNO(CO)_3$, $Fe(NO)_2(CO)_2$, $Mn(NO)_3CO$, and $Cr(NO)_4$. The results obtained are compared with those made on the corresponding nickel,[9] cobalt,[10] and iron[11] compounds.

Experimental Section

Compounds and Solvents. The solvents used were purified by distillation and carefully dried. The reagents $P(C_6H_5)_3$, $As(C_6H_5)_3$, and $P(OC_6H_5)_3$ were Eastman Organic Chemicals. The first two compounds were purified by recrystallization from absolute methanol, and $P(OC_6H_5)_3$ was distilled over sodium. Aldrich Chemical Co. was the source of $P(n\text{-}C_4H_9)_3$ which was distilled at reduced pressures and under nitrogen before use.

The compounds $MnNO(CO)_4$ and $Mn(NO)_3CO$ were prepared by the methods described earlier.[12] Preparations of derivatives for $MnNO(CO)_4$ not previously reported are described here. The mono[13] and bis[14] $P(C_6H_5)_3$ derivatives were prepared as described in the literature. Compounds of the type $Mn(NO)_3L$ were not isolated but were demonstrated to be present in solution by comparing their infrared spectra with that for $Mn(NO)_3P(C_6H_5)_3$.[8] The infrared spectra in the C-O and N-O stretching regions for $MnNO(CO)_4$ and its derivatives are shown in Table I, and Table II gives this information for $Mn(NO)_3CO$ and its derivatives.

Table I. Infrared Spectra in C–O and N–O Regions for $MnNO(CO)_4$ and Its Derivatives in *p*-Xylene (cm^{-1})

	ν_{CO}			ν_{NO}
$MnNO(CO)_4$	2106 w,	2034 s,	1979 s	1763 s
$MnNO(CO)_3P(C_6H_5)_3$	2034 s,	1972 m,	1925 s	1712 s
$MnNO(CO)_2[P(C_6H_5)_3]_2$		1952 m,	1868 ss	1662 s
$MnNO(CO_3)P(n\text{-}C_4H_9)_3$	2034 s,	1964 m,	1912 s	1702 s
$MnNO(CO)_2[P(n\text{-}C_4H_9)_3]_2$[a]		1937 m,	1854 ss	1657 s
$MnNO(CO)_3P(OC_6H_5)_3$	2050 s,	1987 m,	1940 s	1731 s
$MnNO(CO)_2[P(OC_6H_5)_3]_2$		1985 m,	1881 ss	1702 s
$MnNO(CO)_3As(C_6H_5)_3$	2036 s,	1968 m,	1925 s	1712 s

[a] In Nujol since bands overlap with *p*-xylene absorptions.

Preparation of Compounds. All operations were carried out using anhydrous solvents and under nitrogen with the careful exclusion of oxygen.

The compounds $MnNO(CO)_3P(OC_6H_5)_3$ and $MnNO(CO)_2[P(OC_6H_5)_3]_2$ were prepared by the reaction of $MnNO(CO)_4$ with $P(OC_6H_5)_3$ in *p*-xylene solution. A reaction mixture containing 150 mg of $MnNO(CO)_4$ and 0.5 ml of $P(OC_6H_5)_3$ in 50 ml of *p*-xylene was heated for 2 hr at 120°. After cooling the solution to room temperature, the solvent was removed at reduced pressure. The residue was dissolved in 5 ml of hexane and the solution passed through a filter. Upon standing in an ice bath for 3 days, red crystals of $MnNO(CO)_2[P(OC_6H_5)_3]_2$ separated from solution, mp 95–97°.

Table II. The N-O Stretching Frequencies (cm^{-1}) of $Mn(NO)_3CO$ and Its Derivatives in *p*-Xylene

	ν_{NO}	
$Mn(NO)_3CO$[a]	1824 m,	1731 ss
$Mn(NO)_3P(C_6H_5)_3$	1780 w,	1690 ss
$Mn(NO)_3P(n\text{-}C_4H_9)_3$	1774 w,	1680 ss
$Mn(NO)_3P(OC_6H_5)_3$	1788 w,	1705 ss
$Mn(NO)_3As(C_6H_5)_3$	1792 w,	1692 ss

[a] ν_{CO}, 2095 cm^{-1}.

Anal. Calcd for $MnNO(CO)_2[P(OC_6H_5)_3]_2$: C, 59.93; H, 3.97; N, 1.84. Found: C, 58.66; H, 3.71; N, 1.89.

The mother liquor from this low yield of the bis compound was chromatographed on alumina with hexane. Concentration of the eluent did not yield a product so that the solvent was removed at reduced pressure. The resulting oil was kept under high vacuum for 18 hr. With considerable difficulty the oil was caused to crystallize, giving 230 mg (63% yield) of monosubstituted product, mp 42–46°.

Anal. Calcd for $MnNO(CO)_3P(OC_6H_5)_3$: C, 52.63; H, 3.15; N, 2.92. Found: C, 51.88; H, 3.08; N, 3.02.

The synthesis of $MnNO(CO)_2[P(n\text{-}C_4H_9)_3]_2$ was achieved by heating at 120° for ~100 hr 50 ml of a *p*-xylene solution containing 170 mg of $MnNO(CO)_4$ and 1.3 ml of $P(n\text{-}C_4H_9)_3$. After concentration to dryness at reduced pressure, the residue was dissolved in 30 ml of methanol and filtered. The filtrate was kept at −78° for 24 hr during which time yellow crystals of the product separated from solution. These were recrystallized from methanol, collected on a filter, and dried at room temperature under vacuum. A yield of 360 mg (83%) of the bis compound, mp 50–51°, was obtained which is very soluble in organic solvents.

Anal. Calcd for $MnNO(CO)_2[P(n\text{-}C_4H_9)_3]_2$: C, 57.24; H, 9.28; N, 2.57; mol wt, 545.6. Found: C, 56.43; H, 9.72; N, 2.53; mol wt, 528.

Kinetic Studies. Purified anhydrous *p*-xylene was used as the solvent in all of the experiments. The reaction mixtures were kept at constant (±0.1°) temperature, in the dark, and under an atmosphere of nitrogen during the kinetic runs. All of the kinetics were carried out under pseudo-first-order conditions, using at least a tenfold excess of reagent. The rates of reaction were followed spectrophotometrically as described below. Measurements were usually made over a period of three half-lives. All reactions went to completion. The data gave good linear plots of log $(A - A_\infty)$ *vs.* t, where t is time, A is the absorption at time t, and A_∞ is the absorption at infinite time. Estimated rate constants were reproducible to within 10% or better.

The rates of reaction of $MnNO(CO)_4$ and its derivatives were followed by monitoring changes in the infrared spectra of the reaction mixtures. This was done by observing changes in the C-O and N-O stretching regions of the spectra to record the disappearance of starting material and/or appearance of product. The reaction flasks were kept under a slight positive N_2 pressure in order to avoid the introduction of O_2 when samples were removed for infrared measurements by means of a syringe.

This procedure could not be used for the much faster reactions of $Mn(NO)_3CO$. The rates of reaction were decreased by using lower concentrations of reactants, and this required that the rates be followed by recording changes in optical densities at 480 mμ. This was done using a Cary 14 equipped with a thermostated cell compartment and a quartz cell of 10-cm length. This was flushed with N_2, and then 25 ml of a freshly prepared solution of $Mn(NO)_3CO$ in *p*-xylene was introduced using a gas-tight syringe. After a few minutes the solution was at constant temperature and 1 ml of a *p*-xylene solution of the reagent was added by means of a syringe. The solutions were rapidly mixed by shaking the cell and the change in absorbance was recorded.

Results

The infrared spectra in the C–O and N–O stretching regions for $MnNO(CO)_4$ and its derivatives are given in Table I, and the same is shown for $Mn(NO)_3CO$ in Table II.

The experimental rate constants, k_{obsd}, and the estimated second-order rate constants, k_2, are collected in

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Table III. Rate Constants for Reaction 1 in *p*-Xylene at 50° ($[MnNO(CO)_4] = 0.0012\ M$)

L	[L], *M*	k_{obsd}, sec^{-1}	k_2, M^{-1} sec^{-1}
$P(C_6H_5)_3$[a]	6.55×10^{-3}	1.6×10^{-5}	2.5×10^{-3}
$P(C_6H_5)_3$	3.25×10^{-2}	7.1×10^{-5}	2.2×10^{-3}
$P(C_6H_5)_3$	1.34×10^{-1}	3.1×10^{-4}	2.3×10^{-3}
$P(C_6H_5)_3$[b]	...	...	4.4×10^{-3}
$P(C_6H_5)_3$[c]	...	...	1.1×10^{-2}
$P(OC_6H_5)_3$	5.02×10^{-2}	8.7×10^{-6}	1.7×10^{-4}
$P(OC_6H_5)_3$	8.05×10^{-2}	1.4×10^{-5}	1.7×10^{-4}
$P(n\text{-}C_4H_9)_3$	1.06×10^{-2}	9.4×10^{-4}	8.9×10^{-2}
$As(C_6H_5)_3$	8.3×10^{-2}	3.0×10^{-6}	3.6×10^{-5}
$As(C_6H_5)_3$	1.5×10^{-1}	4.5×10^{-6}	3.0×10^{-5}

[a] $[MnNO(CO)_4] = 0.0004\ M$. [b] 60°. [c] 70°; values of k_2 for *b* and *c* estimated from three runs each. $\Delta H^{\ddagger} = 19 \pm 1$ kcal/mole; $\Delta S^{\ddagger} = -11 \pm 3$ eu.

Table IV. Rate Constants for Reaction 2 in *p*-Xylene at 120° ($[MnNO(CO)_3L] = 0.0012\ M$)

L	[L], *M*	k_{obsd}, sec^{-1}	k_1, sec^{-1} [a]	k_2, M^{-1} sec^{-1} [a]
$P(C_6H_5)_3$	8.07×10^{-3}	12.7×10^{-6}	1.3×10^{-5}	1.2×10^{-5}
$P(C_6H_5)_3$	3.89×10^{-2}	13.1×10^{-6}	...	...
$P(C_6H_5)_3$	1.52×10^{-1}	14.4×10^{-6}	...	...
$P(n\text{-}C_4H_9)_3$	1.31×10^{-2}	5.3×10^{-6}	4.7×10^{-6}	4.1×10^{-5}
$P(n\text{-}C_4H_9)_3$	6.35×10^{-2}	7.3×10^{-6}	...	...
$P(n\text{-}C_4H_9)_3$	1.94×10^{-1}	12.7×10^{-6}	...	...
$P(OC_6H_5)_3$	8.25×10^{-3}	4.9×10^{-6}	4.0×10^{-6}	...
$P(OC_6H_5)_3$	6.32×10^{-2}	3.5×10^{-6}	...	...
$P(OC_6H_5)_3$	1.54×10^{-1}	4.2×10^{-6}	...	...

[a] See eq 3 for meaning of k_1 and k_2. Values of k_1 are the nonzero intercepts of the plots of k_{obsd} *vs.* [L], and values of k_2 are obtained from the slope of the lines.

Table V. Rate Constants for Reaction 4 in *p*-Xylene ($[MnNO(CO)_3P(OC_6H_5)_3] = 0.001\ M$)

Temp, °C	L	[L], *M*	k_{obsd}, sec^{-1}	k_2, M^{-1} sec^{-1}
50	$P(n\text{-}C_4H_9)_3$	2.17×10^{-2}	1.0×10^{-6}	4.6×10^{-5}
50	$P(n\text{-}C_4H_9)_3$	1.57×10^{-1}	6.8×10^{-6}	4.3×10^{-5}
50	$P(n\text{-}C_4H_9)_3$	4.18×10^{-1}	1.8×10^{-5}	4.3×10^{-5}
80	$P(n\text{-}C_4H_9)_3$[a]	2.27×10^{-2}	8.3×10^{-6}	3.6×10^{-4}
80	$P(n\text{-}C_4H_9)_3$	1.71×10^{-1}	6.2×10^{-5}	3.6×10^{-4}
80	$P(n\text{-}C_4H_9)_3$	4.13×10^{-1}	1.5×10^{-4}	3.6×10^{-4}
80	$P(C_6H_5)_3$	4.46×10^{-2}	Too slow	...
80	$P(C_6H_5)_3$	1.32×10^{-1}	5.2×10^{-7}	3.9×10^{-6}
80	$P(C_6H_5)_3$	4.3×10^{-1}	1.8×10^{-6}	4.2×10^{-6}

[a] $\Delta H^{\ddagger} = 15 \pm 2$ kcal/mole; $\Delta S^{\ddagger} = -30 \pm 5$ eu.

Table VI. Rate Constants for Reaction 5 in *p*-Xylene at 22° ($[Mn(NO)_3CO] = 5 \times 10^{-5}\ M$)

L	[L], *M*	k_{obsd}, sec^{-1}	k_2, M^{-1} sec^{-1}
$As(C_6H_5)_3$	6.4×10^{-4}	7.3×10^{-3}	5.6[a]
$As(C_6H_5)_3$	1.9×10^{-3}	1.4×10^{-2}	...
$As(C_6H_5)_3$	3.8×10^{-3}	2.5×10^{-2}	...
$P(C_6H_5)_3$	5.9×10^{-4}	3.2×10^{-2}	54[b]
$P(n\text{-}C_4H_9)_3$	5.5×10^{-4}	$>10^{-1}$	>200[b]

[a] Estimated from slope of line of plot of k_{obsd} *vs.* $[As(C_6H_5)_3]$. [b] Estimated assuming first-order dependence on reagent.

Table III for the reaction of $MnNO(CO)_4$ with various reagents. Also included are rates at different temperatures and activation parameters for its reaction with $P(C_6H_5)_3$.

Rate constants for the formation of the bis compounds $MnNO(CO)_2L_2$ are given in Table IV, and Table V contains data on the ligand exchange reactions of $MnNO(CO)_3L$.

Table VI contains the rate constants for the reactions of $Mn(NO)_3CO$ with different reagents.

Discussion

Extensive investigations have been made of the kinetics and mechanism of substitution reactions of metal complexes having either octahedral or square-planar structures. These studies show that the coordination number and the geometry of the metal complex play a major role in its mechanism of reaction. Thus octahedral substitution appears to involve primarily a dissociative process, whereas square-planar substitution takes place by an associative process.[15] In both cases a five-coordinated active intermediate or activated complex is involved. This then adds a ligand in octahedral substitutions and loses a ligand in square-planar substitutions in order to form products.

Stable five-coordinated metal complexes are known[4] and afford one an opportunity to investigate substitution reactions in some of these systems. Quantitative studies on such metal compounds containing unidentate ligands are not extensive, but the results obtained support trigonal bipyramidal substitution by a dissociation mechanism.[5-7] However, the data in Table III clearly show that the rate of reaction 1 is second order, being

$$MnNO(CO)_4 + L \longrightarrow MnNO(CO)_3L + CO \qquad (1)$$

first order in the concentrations of both the substrate and the reagent. This suggests that reaction takes place by an SN2 displacement process. Additional support is afforded this mechanism by the observation that the reaction between $Mn(NO)(CO)_4$ and $P(C_6H_5)_3$ has a negative entropy of activation. Such a result implies there is a net increase in bonding in the formation of the transition state, and negative entropies of activation are often observed for displacement reactions.[16] For poor nucleophiles a dissociative reaction path may contribute to the total rate, and this appears to be true for the reagent $As(C_6H_5)_3$ as it was for its reaction with $CoNO(CO)_3$.[10]

The reagent reactivity toward $MnNO(CO)_4$ is seen to decrease in the order $P(n\text{-}C_4H_9)_3$ (40) > $P(C_6H_5)_3$ (1) > $P(OC_6H_5)_3$ (0.08) > $As(C_6H_5)_3$ (0.015). The numbers in parentheses are the relative rates of reaction at 50° assigning a rate of one to $P(C_6H_5)_3$. This order qualitatively parallels that reported earlier[10] for the nucleophilic strengths at 25° toward $CoNO(CO)_3$: $P(n\text{-}C_4H_9)_3$ (90) > $P(C_6H_5)_3$ (1) > $P(OC_6H_5)_3$ (0.03) > $As(C_6H_5)_3$ (0.002). Therefore, it appears that manganese, like cobalt, in the nitrosyl carbonyl is a class

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(15) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965.

(16) U. Belluco, R. Ettore, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **5**, 591 (1966).

(b)[17] metal or soft acid[18] and reacts preferentially with soft bases.

That the isoelectronic and isostructural compounds $Fe(CO)_5$ and $MnNO(CO)_4$ react by different mechanisms is similar to the behavior of the corresponding compounds $Ni(CO)_4$[9] and $CoNO(CO)_3$.[10] The metal carbonyls tend to react by a first-order process, whereas the corresponding metal nitrosyl carbonyls tend to react by a second-order process. This was explained[11] on the basis of the localization of a pair of electrons on the nitrosyl group in the transition state, thus permitting the addition of a pair of electrons by the nucleophile to the system. Such a process would be more difficult for a carbonyl group because carbon is less electronegative than nitrogen and because nitrogen is believed to have a formal positive charge in the metal nitrosyl carbonyls.

It is of interest to briefly comment on the stereochemistry of the displacement reactions of $MnNO(CO)_4$. An examination of molecular models shows that the reaction paths represented in Figure 1 are possible. From this it is apparent that the assumed six-coordinated species II may readily yield products with different structures. In addition this may be further complicated by the fact that five-coordinated systems often have nonrigid structures.[4] For example, ^{13}C nmr shows that all of the carbonyls in $Fe(CO)_5$ are equivalent.[19] If this also is true for $MnNO(CO)_4$ and its derivatives, then it is clear that rearrangements will occur readily to produce the more stable isomers. Structure IV has been assigned[14] $MnNO(CO)_3P(C_6H_5)_3$ on the basis of its dipole moment compared to that for $Fe(CO)_4P(C_6H_5)_3$.

Data in Table IV show that the rates of reaction 2 are much slower than are the rates of reaction 1. This is the usual behavior of metal carbonyls;[20] that is, the

$$MnNO(CO)_3L + L \longrightarrow MnNO(CO)_2L_2 + CO \qquad (2)$$

replacement of the first CO with phosphines or phosphites takes place more readily than do additional replacements. It appears that the remaining CO's become more firmly held because of increased metal-to-carbon π bonding.

In addition to this normal behavior, the data in Table IV show an unexpected result. Except for the best nucleophile, $P(n\text{-}C_4H_9)_3$, the rates of reaction are almost independent of reagent concentration.

For $P(n\text{-}C_4H_9)_3$ the experimentally observed rate constant increases with increasing reagent concentration and appears to follow the two-term rate law given by eq 3. The reagent-independent path, k_1, is believed to

$$k_{\text{obsd}} = k_1 + k_2[L] \qquad (3)$$

take place by a dissociation mechanism, whereas the k_2 path is the direct reagent displacement path. Except for steric factors, the contribution of the k_2 path to the observed rate of reaction will be greater for the better nucleophiles. We see this to be true in that of the reagents used the largest contribution to the total rate is made by the best nucleophile, $P(n\text{-}C_4H_9)_3$, and the poorest, $P(OC_6H_5)_3$, has no effect up to a concentration of 0.15 *M*.

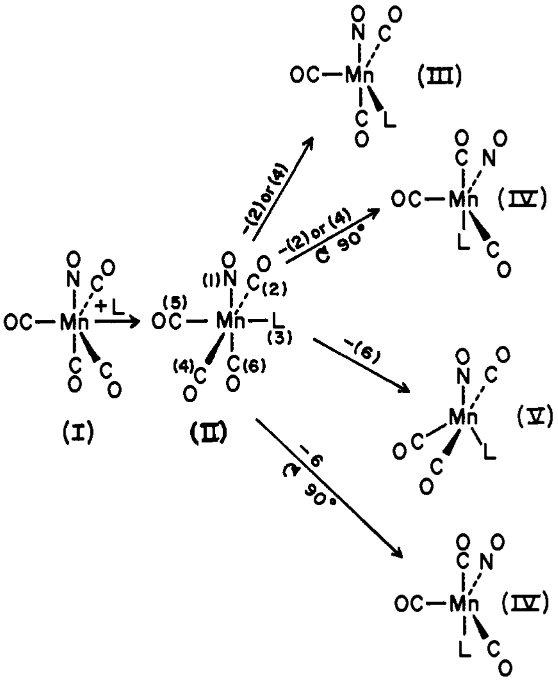

Figure 1. Possible stereochemistry of the reaction of $MnNO(CO)_4$ to yield $MnNO(CO)_3L$. This assumes that CO(5) in II is not replaced because it is *trans* to L and presumably is less reactive than the other CO's: F. Basolo and A. Wojcicki, *J. Am. Chem. Soc.*, **83**, 520 (1961); see also J. Lewis, J. R. Miller, B. H. Robinson, P. W. Robinson, and A. Wojcicki, *Chem. Commun.*, 379 (1967); H. D. Kaez, R. Bow, D. Hendrickson, and J. M. Smith, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

What was unexpected is that a major portion of the reaction of $MnNO(CO)_3L$ takes place by a dissociation process. All previous observations[10] were that, except for very poor nucleophiles, metal nitrosyl carbonyls react primarily by a displacement process. However, these observations were made only on four-coordinated systems. It seems reasonable that steric retardation of bimolecular displacement reactions would increase with increasing coordination number of the metal. This is perhaps what is responsible for the smaller contribution of the k_2 path of the rate of reaction of the five-coordinated compound $MnNO(CO)_3L$ to give $MnNO(CO)_2L_2$. Alternatively, it may be that for some electronic reason the presence of ligand L in the compound stabilizes a four-coordinated transition state of the type $MnNO(CO)_2L$ and permits reaction by a dissociation process.

The rates of dissociation of $MnNO(CO)_3L$ with changes in L decrease in the order $P(C_6H_5)_3 > P(n\text{-}C_4H_9)_3 > P(OC_6H_5)_3$, which corresponds to that found for the reactions of $Ni(CO)_3L$[21] and of $Mn(CO)_4LBr$.[22] Another comparison is that $MnNO(CO)_3P(C_6H_5)_3$ reacts with $P(C_6H_5)_3$ at 120° at a rate approximately 100 times faster than that estimated for the same reaction of its isoelectronic and isostructural compound $Fe(CO)_4P(C_6H_5)_3$.[7] This is somewhat surprising because the Mn–C bond strength is expected to be greater than

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Table VII. Stretching Force Constants for C–O and N–O in Pseudo-Nickel Carbonyl Series and Rates of Reaction

	$Ni(CO)_4$	$CoNO(CO)_3$	$Fe(NO)_2(CO)_2$	$Mn(NO)_3CO$
F_{CO}, 10^5 dynes/cm [a]	17.23	17.04	17.06	17.43
F_{NO}, 10^5 dynes/cm [a]	. . .	14.44	14.12	13.75
k_1, sec^{-1}	1.5×10^{-2} [b]	$\sim 10^{-7}$ [c]	$\sim 10^{-7}$ [c]	$\sim 4 \times 10^{-3}$ [c]
k_2, M^{-1} sec^{-1} [d]	. . .	1×10^{-3}	1×10^{-3}	54

[a] From G. R. Van Hecke and W. D. Horrocks, Jr., *Inorg. Chem.*, **5**, 1960 (1966). [b] Reaction with $P(C_6H_5)_3$ from ref 9. [c] Extrapolated nonzero intercept for reaction with $As(C_6H_5)_3$ from ref 10, 11, and Table VI. [d] Second-order rate constants for reactions with $P(C_6H_5)_3$ from ref 10, 11, and Table VI.

that of Fe–C because of the smaller nuclear charge on manganese permitting more metal-to-carbon π bonding. Relative to CO, the greater activating influence of NO may, therefore, be related largely to its influence on stabilizing the transition state for reaction. The product $MnNO(CO)_2[P(C_6H_5)_3]_2$ has a trigonal bipyramidal structure with the phosphines in axial positions.[14,23] Unfortunately, as stated above, the structures of these reaction products cannot be used to assign mechanisms of reaction.

The rates of reaction 4, where L is $P(n\text{-}C_4H_9)_3$ or $P(C_6H_5)_3$, are given in Table V. The rates of reaction depend on L, and again it is seen that $P(n\text{-}C_4H_9)_3$ is a

$$MnNO(CO)_3P(OC_6H_5)_3 + L \longrightarrow MnNO(CO)_3L + P(OC_6H_5)_3 \quad (4)$$

better reagent than is $P(C_6H_5)_3$. The observed second-order kinetics suggests that the reactions take place by an SN2 process. That reaction takes place with a negative entropy of activation also lends support to such a mechanism.[16]

Thus, it is of interest to note that reaction 2 takes place largely by a dissociation mechanism and reaction 4 by a displacement process. It was suggested that steric retardation in reaction 2 may be involved to such an extent that the reaction proceeds by dissociation. The results show that such an argument cannot apply to reaction 4. Perhaps here the steric retardation is less, because the leaving group is the bulky phosphite. Assuming it is only weakly bonded to manganese in the transition state, this provides room for attack by the entering nucleophile. Less room would be available when the smaller CO is the leaving group, as per reaction 2. Another factor may be that CO is more firmly bonded to Mn in $MnNO(CO)_3L$ than is L. This means that more drastic conditions are needed to replace CO, and at these higher temperatures the dissociation process predominates.

Finally, a few kinetic studies (Table VI) were made of reaction 5, where L is $As(C_6H_5)_3$, $P(C_6H_5)_3$, or $P(n\text{-}C_4H_9)_3$. The experiments were difficult to perform be-

$$Mn(NO)_3CO + L \longrightarrow Mn(NO)_3L + CO \quad (5)$$

cause of the extreme sensitivity of $Mn(NO)_3CO$ and its rapid rate of reaction, However, the results leave no doubt that the rate of reaction depends on the nature and concentration of the reagent. On the basis of the limited data available, it appears that the reaction of $Mn(NO)_3CO$ with $As(C_6H_5)_3$ follows a two-term rate law of the type shown by eq 3. The same result was found for its reaction with $CoNO(CO)_3$.[10] It is assumed that the phosphines, which are better nucleophiles, react primarly by the k_2 path.

Kinetic investigations have now been made for reactions of all the known compounds of the pseudo-nickel carbonyl series. Some of the data obtained are collected in Table VII along with the estimated C–O and N–O stretching force constants. The stereochemistries of these compounds are the same, but the formal charges on the metals decrease in the order Ni(0), Co(−I), Fe(−II), Mn(−III). On this basis one might expect a continuous increase in metal-to-carbon π bonding across the series to parallel the increase in formal negative charge. However, the C–O force constants suggest that this happens only on the addition of the first NO in going from $Ni(CO)_4$ to $CoNO(CO)_3$. Further addition of NO is accompanied by an increase in the C–O force constant, implying a decrease in metal-to-carbon π bonding. It appears that the reason for this is that NO is a better π bonder than CO. Thus the extent of metal-to-carbon π bonding decreases with added NO, in spite of the increase in negative formal charge. This is supported by the continuous decrease observed in the NO force constants with added NO in the series.

These results suggest that the metal-to-carbon π bonding and presumably M–C bond strength in the series of compounds vary in the order Ni $<$ Co $\sim$ Fe $>$ Mn. It is to be expected that for first-order processes, k_1 in Table VII, where the M–C bond is of major importance, the rates of reaction should parallel their bond strengths. A quantitative comparison is not possible because the estimated data are not sufficiently reliable. However, a good qualitative correspondence is found with the reactions of the Ni and Mn compounds being fast and those of Co and Fe slow.

No second-order path has been observed for reactions of $Ni(CO)_4$ with a variety of reagents.[9] Although a similar low-energy first-order path is available for reactions of $Mn(NO)_3CO$, it also reacts readily by a second-order path. As mentioned above the presence of NO in place of CO in these systems markedly enhances the tendency for reaction by means of a displacement process. This and the weaker M–C bond strength can account for the much larger value of k_2 for $Mn(NO)_3CO$ relative to $CoNO(CO)_3$. What is not clear is that the second-order rates of reaction of the cobalt and the iron compounds are about the same. It might be expected that because the iron compound contains two NO's this would induce a more facile displacement process relative to the cobalt system with only one NO.

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