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Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsrt19</u>

Oxygen Atom Transfer Reactions to Metal Carbonyls: Kinetics and Mechanism of CO Substitution Reactions of $M_2(CO)_9L$ (M = Re, L = PPh₃, PMePh₂, PMe₂Ph, C_5H_5N , or M = Mn, L = C_5H_5N) in the Presence of (CH₃)₃NO

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To cite this article: Li Peng & Yi-Ci Gao (2004) Oxygen Atom Transfer Reactions to Metal Carbonyls: Kinetics and Mechanism of CO Substitution Reactions of $M_2(CO)_9L$ (M = Re, L = PPh₃, PMePh₂, PMe₂Ph, C₅H₅N, or M = Mn, L = C₅H₅N) in the Presence of (CH₃)₃NO, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 34:7, 1181-1190, DOI: 10.1081/SIM-120039265

To link to this article: <u>http://dx.doi.org/10.1081/SIM-120039265</u>

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SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY Vol. 34, No. 7, pp. 1181–1190, 2004

Oxygen Atom Transfer Reactions to Metal Carbonyls: Kinetics and Mechanism of CO Substitution Reactions of M₂(CO)₉L (M=Re, L=PPh₃, PMePh₂, PMe₂Ph, C₅H₅N, or M=Mn, L=C₅H₅N) in the Presence of (CH₃)₃NO

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ABSTRACT

Rates for the reactions of $M_2(CO)_9L$ (M = Re, L = PPh₃, PMePh₂, PMe₂Ph, C₅H₅N or M = Mn, L = C₅H₅N) with L in the presence of (CH₃)₃NO as O-atom transfer reagent and CHCl₃ as solvent are reported. The reaction rates suggest a pathway of association (k_2). The reaction rate order of Re₂(CO)₉L with the four ligands is as follows: PPh₃ > PMePh₂ > PMe₂Ph > C₅H₅N.

Key Words: Manganese; Rhenium; Metal carbonyls; Oxygen atom transfer; Amine N-oxide.

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INTRODUCTION

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Hieber and Lipp^[1] first reported the use of pyridine N-oxide to facilitate CO release from Fe(CO)₅. Since that time, such reactions have played an important role in organometallic chemistry, particularly in the syntheses of metal carbonyl derivatives.^[2,3] The conditions for these reactions are very mild, usually proceeding at room temperature. In 1975, Shvo and Hazum^[4] presented a convenient and effective approach for the syntheses of olefin derivatives of metal carbonyls by using amine N-oxide. In spite of the extensive applications of these reactions, the first detailed kinetic study of the reaction was only reported^[5] in 1987. The reaction mechanism seems to involve attack of an oxygen atom transfer reagent to a CO group of the metal carbonyls. This results in the conversion of a good ligand (CO) into a poor ligand (CO₂) and formation of an active, coordinative unsaturated intermediate, which then readily reacts with an added-entering ligand to afford the expected substituted product.

Earlier kinetics studies of O-atom transfer reactions have been made on mononuclear metal carbonyls $M(CO)_6^{[5]}$ (M = Cr, Mo, W), with the rates of reaction increasing in the order Cr < Mo < W, whereas for metal carbonyl clusters such as $M_3(CO)_{12}^{[6]}$ and $M_3(CO)_{11}L^{[7]}$ (M = Fe, Ru, Os), the rates vary in the opposite order Fe > Ru > Os. Suggestions were made that for the Cr-molecular triad the order of reactivity is attributed to steric factors, but for the Fe-cluster triad the order of reactivity decreases with the tendency to form bridging carbonyl groups in the transition state for the reaction. Usually, one thinks that a bridging carbonyl attracts electrons more strongly than a terminal carbonyl; therefore, it can disperse and accept more negative electric charge from the oxygen atom transfer reagent and stabilize the intermediate better.

Binuclear metal complexes represent the simplest class of cluster complexes. Our previous investigation on the kinetics for reaction of $M_2(CO)_{10}$ with PPh₃ or C₅H₅N in the presence of (CH₃)₃NO shows that the rates of the reaction vary in the order Mn > Re.^[8] This result is in accord with the above metal carbonyl clusters. For the purpose of getting more information about the presumed effect on the rates of reaction due to CO bridging, it was decided to investigate the second substitution reactions of M₂(CO)₉L, and this paper reports the kinetic data of the O-atom transfer reactions of M₂(CO)₉L with different entering ligands L.

RESULTS AND DISCUSSION

Rates for the reaction of Eq. (1) of $M_2(CO)_9L$ in CHCl₃ with an entering ligand (M = Re, L = PPh₃, PMePh₂, PMe₂Ph, C₅H₅N or M = Mn, L = C₅H₅N) in the presence of (CH₃)₃NO were monitored by following changes





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in the IR spectra (or UV-Visible absorption spectra) in the $2120-1880 \text{ cm}^{-1}$ range with time.

$$\begin{split} M_2(CO)_9L + (CH_3)_3NO + L &\longrightarrow M_2(CO)_8L_2 + (CH_3)_3N + CO_2 \qquad (1) \\ (M = \text{Re}, \ L = \text{PPh}_3, \ \text{PMePh}_2, \ \text{PMe}_2\text{Ph}, C_5\text{H}_5\text{N} \text{ or } M = \text{Mn}, \\ L = C_5\text{H}_5\text{N}) \end{split}$$

The reactants $M_2(CO)_9L$ were generated by reactions of $M_2(CO)_{10}$ with the entering ligand L in the presence of $(CH_3)_3NO$, and studied *in situ*. All spectral changes for two typical reaction examples display good isosbestic points (Figs. 1 and 2), which suggest stoichiometric reactions yielding disubstituted products.

This was confirmed by the fact that the IR spectra of the reactants and products in the CO stretching region (Table 1) are in good agreement with data reported^[9-11] for the known compounds.

Plots of $-\ln A$ (where A represents the value of absorbance) vs. time for the reaction of Eq. (1) were linear over 2–3 half-lives. As is well known, carbonyls are very sensitive to air and easily undergo changes in longer reaction time reactions. Thus, longer reaction times are not necessarily suitable in this case. They may even provide flawed results, especially, for the second substitution reactions of the carbonyls. The validity of the kinetic data is not only dependent on the experimental methods (such as UV, IR, or



Figure 1. IR absorbance changes of ν (CO) vs. time for the reaction Mn₂(CO)₉-(C₅H₅N) + (CH₃)₃NO + C₅H₅N \rightarrow Mn₂(CO)₈(C₅H₅N)₂ + (CH₃)₃N + CO₂ in CHCl₃ at room temperature.



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Figure 2. UV-VIS absorbance changes vs. time for the reaction $\text{Re}_2(\text{CO})_9$ (PMe₂Ph) + (CH₃)₃NO + PMe₂Ph \rightarrow Re₂(CO)₈(PMe₂Ph)₂ + (CH₃)₃N + CO₂ in CHCl₃ at room temperature.

NMR), but is also dependent on reaction rates. Many reports^[5-8,12,13] show that kinetic data of 2–3 half-live reactions are reliable, as concluded by Basolo and his group.^[14,15] We also calculated the half-lives for some of the reactions in this communication. For the fastest reaction, the reaction of rhenium carbonyl with the ligand PPh₃, the half-life is only about 19 min, and the actual reaction time for which data were collected was about 5 half-lives; however, the rate is only linear over 2–3 half-lives. The same procedure has been adopted by the authors of the above-cited references.

Table 1. The CO stretching frequencies of $M_2(CO)_{10-n}L_n$ (M = Mn, Re; n = 1, 2).

Complex	ν (CO) (cm ⁻¹)		
$Mn_2(CO)_9(C_5H_5N)^{[9]}$	2,089 w, 2,016 s, 2,005 m, 1,980 vs, 1,962 m, 1,943 m		
$Mn_2(CO)_8(C_5H_5N)_2^{[9]}$	2,035 s, 1,954 vs, 1,917 m		
$\text{Re}_{2}(\text{CO})_{9}(\text{PPh}_{3})^{[10]}$	2,113 w, 2,040 w, 1,998 vs, 1,964 (sh), 1,940 m		
$\text{Re}_{2}(\text{CO})_{8}(\text{PPh}_{3})_{2}^{[10]}$	2,000 (sh), 1,958 vs		
$\operatorname{Re}_2(\operatorname{CO})_9(\operatorname{PMePh}_2)^{[10]}$	2,111 w, 2,040 w, 1,995 vs, 1,962 (sh), 1,938 m		
$\operatorname{Re}_2(\operatorname{CO})_8(\operatorname{PMePh}_2)_2^{[10]}$	2,015 w, 1,954 vs		
$\operatorname{Re}_2(\operatorname{CO})_9(\operatorname{PMe}_2\operatorname{Ph})^{[10]}$	2,108 w, 2,038 m, 1,990 vs, 1,960 (sh), 1,932 m		
$\text{Re}_{2}(\text{CO})_{8}(\text{PMe}_{2}\text{Ph})_{2}^{[10]}$	2,010 w, 1,949 vs		
$\text{Re}_2(\text{CO})_9(\text{C}_5\text{H}_5\text{N})^{[11]}$	2,099 w, 2,039 m, 2,011 s, 1,985 vs, 1,960 m		
$\text{Re}_{2}(\text{CO})_{8}(\text{C}_{5}\text{H}_{5}\text{N})_{2}^{[11]}$	2,006 w, 1,950 vs, 1,917 m		



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The reaction rates are zero-order in PPh₃ concentration (Table 2), and the same rates are obtained for corresponding reactions of this type using other entering ligands.

The plots of k_{obsd} vs. the (CH₃)₃NO concentration show a first-order dependence on the trimethylamine N-oxide concentration (Fig. 3). Thus, CO substitution obeys the second-order rate law given by Eq. (2), and the second-order rate constants for the reaction of Eq. (1) are given in Table 3.

$$-\frac{d[M_2(CO)_9L]}{dt} = k_2[M_2(CO)_9L][(CH_3)_3NO][L]^0$$
(2)

This rate law and kinetic behavior are the same as those reported earlier for the corresponding reactions of mononuclear metal carbonyls and metal cluster,^[5–8,12] suggesting that the same associative mechanism is involved for these second substitution reactions, where both bond making by attack of the (CH₃)₃NO nucleophile and bond breaking of the M–C bond contribute to the energetics of the rate-determining step, which is supported by the experimental activation parameters: lower ΔH^{\neq} and negative ΔS^{\neq} .^[5–8,12] This then permits the oxidation of a CO group to the poor ligand and good leaving group CO₂, resulting in the formation of the active, coordinative unsaturated intermediate "M₂(CO)₈L," which then rapidly reacts with an entering ligand to give the product M₂(CO)₈L₂ (scheme in Fig. 4).

The second substitution reaction rates of $M_2(CO)_9L$ were slower than the first substitute reaction rates of $M_2(CO)_{10}$ (Table 4). This is so because the substituted ligand L is a stronger σ donor and a weaker π acceptor than a CO group. When L substitutes a carbonyl, the positive charges on the other carbonyl carbons decrease, which makes the nucleophilic attack slower. The IR spectra of all reaction products show that the second substitutions occur on the unsubstituted metal, which is in good agreement with earlier reports.^[9-11]

Previous studies^[9,10] suggest that the ease of nucleophilic attack on the carbon of a metal carbonyl correlates with the C–O stretching frequencies of the carbonyl. The higher the value of ν (CO), the greater the ease of attack on the

 $\begin{array}{c|cccc} \hline T(^{\circ}\mathrm{C}) & [(\mathrm{CH}_{3})_{3}\mathrm{NO}]\,(\mathrm{mol}\,\mathrm{L}^{-1}) & [\mathrm{PPh}_{3}]\,(\mathrm{mol}\,\mathrm{L}^{-1}) & k_{\mathrm{obsd}}\,(\mathrm{sec}^{-1}) \\ \hline 44.0 & 5.20\times10^{-3} & 1.58\times10^{-3} & 1.14\times10^{-3} \\ & 4.75\times10^{-3} & 1.06\times10^{-3} \\ & 7.92\times10^{-3} & 1.07\times10^{-3} \\ & 11.08\times10^{-3} & 1.06\times10^{-3} \end{array}$

Table 2. Observed rate constants for the reaction of $\text{Re}_2(\text{CO})_9\text{PPh}_3$ with PPh₃ of Eq. (1) in CHCl₃.



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Figure 3. Plots of k_{obsd} vs. (CH₃)₃NO concentration for the reaction of Eq. (1) in CHCl₃ at 44.0 °C (M = Re; 1, PPh₃; 2, PMePh₂; 3, PMe₂Ph; 4, C₅H₅N).

more positive carbon that results from less π back-bonding from the metal. The experimental results show that the rates of reaction of Re₂(CO)₉L decrease in the order PPh₃ > PMePh₂ > PMe₂Ph > C₅H₅N, which is in accord with the consequence of their IR values of ν (CO) and consistent with what was observed in M₃(CO)₁₁L^[7] and M₄(CO)₁₁L.^[13] It is noteworthy that Re₂(CO)₉PPh₃, Re₂(CO)₉(PMePh₂), and Re₂(CO)₉(PMe₂Ph) in CHCl₃ have nearly the same ν (CO) values. These similar values of ν (CO) suggest that the respective carbon atoms have similar charges, and they should respond to nucleophilic attack on CO group based on the ground state at about the same rate, but the reaction rate

M ₂ (CO) ₉ L	L	$\frac{k_2^{a}}{[mol(L \sec)^{-1}]}$
Re ₂ (CO) ₉ L	PPh ₃ PMePh ₂	1.28×10^{-1} 3.27×10^{-2}
	PMe ₂ Ph C ₅ H ₅ N	3.36×10^{-2} 2.15×10^{-2}
Mn ₂ (CO) ₉ L	C ₅ H ₅ N	3.52×10^{-2}

Table 3. Second-order rate constants for the reaction of Eq. (1) in CHCl₃ at 44.0 $^{\circ}$ C.

^aAt fixed concentrations of the ligand, plots of k_{obsd} vs. [(CH₃)₃NO] provide the second-order rate constant k_2 at the fixed temperature.

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$$M_{2}(CO)_{9}L + (CH_{3})_{3}NO \xrightarrow{k_{2}} \begin{bmatrix} L(CO)_{8}M_{2} \xrightarrow{C} C \stackrel{\frown}{=} O \\ O \xrightarrow{N}(CH_{3})_{3} \end{bmatrix}$$

$$\xrightarrow{\text{fast}} "M_{2}(CO)_{8}L" + N(CH_{3})_{3} + CO_{2} \xrightarrow{\text{fast}} M_{2}(CO)_{8}L_{2}$$

Figure 4. The proposed scheme for the associative mechanism of the second substitution reactions of Eq. (1).

of PPh3 is greater than that of PMePh2 and PMe2Ph. An earlier investigation^[16] of the reaction of Fe(CO)₄L complexes with PhCH₂MgBr showed that the rates of nucleophilic attack on CO group by the benzyl nucleophile are controlled by electronic factors. The electronic character of L controls the amount of electron density transferred to the carbonyls by Fe \rightarrow CO π backbonding. As the amount of back-bonding increases, the electron density on the carbon atoms increase, and the carbon atoms become less susceptible to nucleophilic attack. The addition of electron donating methyl groups, not only increased electron density on the phosphorous atom of L, but also decreased the p- π conjugation ability inner phosphorous atom and benzene ring, and the ability to disperse and accept the increasing negative charges in the intermediates. As the electron density can be transferred through the chemical bonds between the L-M-M-CO groups of the clusters,^[7] this also increases the negative charges on the CO group sitting on the unsubstituted metal, which results in a decrease of stability of the coordinative unsaturated intermediates and makes the rates of the reaction slower.

Table 4. Second-order rate constants for the first-substitution reactions and the second-substitution reactions of the binuclear metal carbonyls with $(CH_3)_3NO$ and an entering ligand L in $CHCl_3$ at 44.0 °C.

Complex	L	k_2 [mol (L sec) ⁻¹]
$Mn_2(CO)_{10}^{[8]}$	PPh ₃	1.73
$\text{Re}_2(\text{CO})_{10}^{[8]}$	PPh ₃	1.11
Re ₂ (CO) ₉ PPh ₃	PPh ₃	0.128
$\operatorname{Re}_2(\operatorname{CO})_9(\operatorname{C}_5\operatorname{H}_5\operatorname{N})$	C ₅ H ₅ N	0.022
$Mn_2(CO)_9(C_5H_5N)$	C ₅ H ₅ N	0.035

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EXPERIMENTAL

Materials and Methods

 $Mn_2(CO)_{10}$, PMePh₂, and PMe₂Ph were purchased from Strem Chemicals Co., and $Re_2(CO)_{10}$ was obtained from Aldrich. Trimethylamine N-oxide, $(CH_3)_3NO$ was synthesized by a literature method^[17] and purified by sublimation in our laboratory. CHCl₃ was dried over P₂O₅ and distilled under N₂ atmosphere before use. PPh₃ was purified by recrystallization from anhydrous ethanol. C₅H₅N (Strem) was distilled over CaH₂ under N₂ atmosphere before use.

Instrumentation

Infrared spectra were recorded on a Nicolet-5DX FT-IR spectrophotometer. UV-Visible measurements were done on a Shimadzu UV-240 spectrophotometer. Constant temperature was maintained by the internal circulating bath of the Shimadzu UV-240 in the range ± 0.2 °C.

Kinetic Measurements

The reactions were detected on a Nicolet 5-DX Fourier transfer infrared spectrometer. Kinetic data were obtained by monitoring both the UV-Visible and IR spectral changes. All reactions were carried out using oxygen-free $CHCl_3$ solutions. Phosphine and $(CH_3)_3NO$ concentrations were at least 10 times greater than that of $M_2(CO)_9L$ for pseudo-first-order conditions. In a typical experiment, a solution (~3 mL) of (CH₃)₃NO and the appropriate nucleophile L ($\sim 5 \times 10^{-3}$ M) in CHCl₃ was mixed in a measuring flask previously filled with N2. After 15 min of temperature equilibration, a solution of $M_2(CO)_{10}$ (~3 × 10⁻⁴ M) in CHCl₃ was syringed into the flask, which was shaken vigorously, and then the liquid was introduced into special temperature-constant IR cells and sealed with rubber septa. The resulting spectral changes were monitored, and the products were characterized by their IR spectra. Plots of $-\ln A$ vs. time for the disappearance of reactant and plots of $\ln(A_t - A_{\infty})$, where A_t represents the value of absorbance at different times t and A_{∞} represents the value of absorbance when the reaction is over, vs. time for the appearance of product were linear over 2-3 half-lives (linear correlation coefficients >0.995). The slopes of these lines gave k_{obsd} values. Both methods for monitoring the reaction rates yielded similar k_{obsd} values for a given reaction.

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Received July 8, 2003 Accepted March 7, 2004

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