2414 J. Am. Chem. Soc. 1988, 110, 2414-2418

Oxygen Atom Transfer Reactions to Metal Carbonyls. Kinetics and Mechanism of CO Substitution Reactions of $M_3(CO)_{12}$ (M = Fe, Ru, Os) in the Presence of $(CH_3)_3NO$

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Received August 25, 1987

Abstract: Reported are the rates of reaction and activation parameters for CO substitution reactions of $M_3(CO)_{12}$ (M = Fe, Ru, Os) with L (L = PPh_3, $P(OPh)_3$, $AsPh_3$) in the presence of $(CH_3)_3NO$. In aprotic solvents the reactions are too fast to follow by conventional spectroscopy, but the rates decrease with added protonic solvents. Reactions are readily monitored at room temperature in the mixed solvent $CHCl_3$–C_2H_5OH (v/v, 2:1), and the rates of reaction are inversely proportional to the concentration of C_2H_5OH. It is suggested that this is due to hydrogen bonding to give $(CH_3)_3NO\cdots HOC_2H_5$, which is unreactive compared with the very reactive free $(CH_3)_3NO$ at these reaction conditions. The rates of formation of $M_3(CO)_{11}L$ are first-order in concentrations of metal cluster and of $(CH_3)_3NO$ but zero-order in concentration of L. This suggests a mechanism that involves a nucleophilic attack of the O atom of $(CH_3)_3NO$ on the C atom of a CO, accompanied by oxidation of CO to CO_2. Since CO_2 is a good leaving group, its departure from the metal clusters affords the active intermediates $M_3(CO)_{11}$. These then rapidly react with entering ligands to form the monosubstituted products $M_3(CO)_{11}L$. The rates of reaction decrease in the order $F_3(CO)_{12} > Ru_3(CO)_{12} > Os_3(CO)_{12}$, and an attempt is made to account for the observed relative rates.

Oxygen atom transfer reagents have been widely used[1] to facilitate CO release from metal carbonyls in the syntheses and reactions of metal carbonyls. Recently, we reported[2] on a kinetic study of the reactions of $M(CO)_6$ (M = Cr, Mo, W) with phosphine and phosphite ligands in the presence of Me_3NO (eq 1). The rates of reaction decrease in the order W > Mo $\gtrsim$ Cr,

$$M(CO)_6 + L + Me_3NO \rightarrow M(CO)_5L + Me_3N + CO_2 \quad (1)$$

and the rates are first order in concentrations of $M(CO)_6$ and Me_3NO but zero order in entering ligand. It appears the rate-determining step involves attack by the oxygen atom of Me_3NO on the carbon of a CO, converting it to CO_2, which is a good leaving group. This then generates the reactive coordinatively unsaturated intermediate $M(CO)_5$, and it rapidly reacts with the entering phosphine or phosphite ligands.

Since it appears no kinetic study has been made of such reactions with metal carbonyl clusters, we decided to investigate the CO substitution reactions of $M_3(CO)_{12}$ and $M_3(CO)_{11}L$ in the presence of Me_3NO. It is known[3] that mechanisms of thermal and photochemical CO substitution reactions of metal carbonyl clusters may differ from corresponding reactions of monomeric metal carbonyls. Furthermore, there is considerable interest in the use of metal carbonyl clusters as homogeneous catalysts[4] so that a detailed study of the kinetics and mechanism of the use of oxygen atom transfer reagents to generate active intermediates for possible catalysis could be helpful.

Reported here are the results of our kinetic study of the reactions represented by eq 2. The reactions of $M_3(CO)_{12}$ are much faster

$$M_3(CO)_{12} + Me_3NO + L \rightarrow M_3(CO)_{11}L + Me_3N + CO_2 \quad (2)$$

$$M = Fe, Ru, Os;\ L = PPh_3, AsPh_3, P(OPh)_3$$

than corresponding reactions of $M(CO)_6$, yet it appears the same type of mechanism is involved for both series of compounds.

Experimental Section

Compounds and Solvents. Manipulations involving $Fe_3(CO)_{12}$ were routinely carried out under an Ar atmosphere with standard Schlenk techniques. $CHCl_3$ and C_2H_5OH were dried with P_2O_5 and $Mg(OC_2H_5)_2$, respectively, and distilled under Ar atmosphere prior to use. $M_3(CO)_{12}$ (M = Fe, Ru, Os) were obtained from Aldrich Chemical Co. and used without further purification. Trimethylamine *N*-oxide (Me_3NO) was synthesized and purified by the literature method.[5] PPh_3 and $AsPh_3$ were purified by recrystallization from anhydrous alcohol. $P(OPh)_3$ was purified by vacuum distillation [~170 °C (0.4 mmHg)].

Table I. Observed Rate Constants for Reaction (Eq 2) Where M= Fe and L = $AsPh_3$

$[AsPh_3]$, M	k_{obsd},^{a} s^{-1}	$[AsPh_3]$, M	k_{obsd},^{a} s^{-1}
2.08×10^{-3}	5.00×10^{-3}	6.24×10^{-3}	5.05×10^{-3}
4.16×10^{-3}	4.85×10^{-3}	8.32×10^{-3}	5.10×10^{-3}

^{a}At 13.1 °C, in $CHCl_3$–C_2H_5OH (v/v, 2:1) and with $[Me_3NO] = 2.95 \times 10^{-3}$ M.

Kinetic Measurements. Infrared spectra were recorded on a Nicolet-5DX FT IR with a 0.5-mm NaCl cell. Ultraviolet–visible spectral measurements were obtained on a Shimadzu UV-240 spectrophotometer with 1-cm quartz cells.

The reaction of $M_3(CO)_{12}$ with Me_3NO in the presence of phosphorus ligands (or $AsPh_3$) was studied at temperatures between 5 and 33 °C. All reactions were performed under pseudo-first-order conditions, with the concentration of Me_3NO and of ligand being at least greater than 10 times that of $M_3(CO)_{12}$. Rate data were obtained by monitoring UV–vis spectral changes. In a typical experiment with a UV spectrophotometer, a solution of Me_3NO in C_2H_5OH and a solution of PPh_3 in $CHCl_3$ were mixed in a cuvette and the cuvette was placed in a temperature-regulated jacket. Constant temperature was maintained by the internal circulating bath of the Shimadzu UV-240. After 30 min of temperature equilibration, a solution of $M_3(CO)_{12}$ in $CHCl_3$ was syringed into the cuvette, the cuvette was removed, rigorously shaken, and replaced in the light beam, and the resultant spectral changes were monitored. The products were characterized by their IR spectra.

Plots of ln $(A_\infty - A_t)$ vs time for appearance of products were linear over 2–3 half-lives (linear correlation coefficient >0.999). The slope of these lines gave values of k_{obsd}.

Results

The rates of reaction (eq 2) of $M_3(CO)_{12}$ in $CHCl_3$–C_2H_5OH (v/v, 2:1) mixed solvent with entering ligand in the presence of Me_3NO were monitored by following changes in UV–visible absorption spectra with time. Spectral changes of reaction mixtures show good isosbestic points (Figures 1–4), which suggest good stoichiometric reactions affording monosubstituted products.

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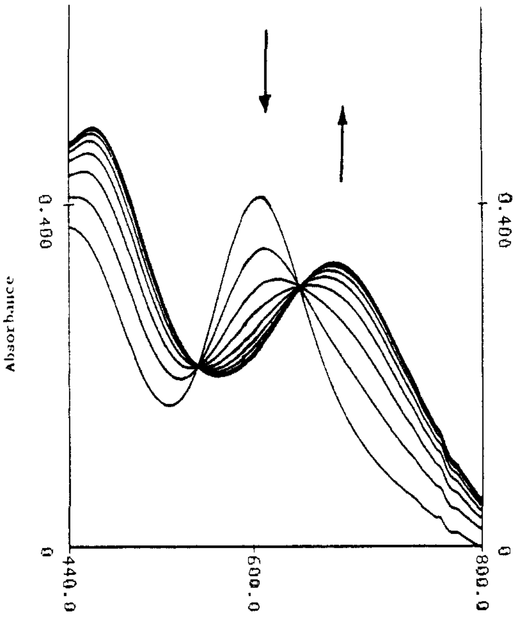

Figure 1. UV–vis absorbance changes vs time for the reaction $Fe_3(CO)_{12} + Me_3NO + AsPh_3 \rightarrow Fe_3(CO)_{11}AsPh_3 + Me_3N + CO_2$ in $CHCl_3$–C_2H_5OH (v/v, 2:1) at room temperature.

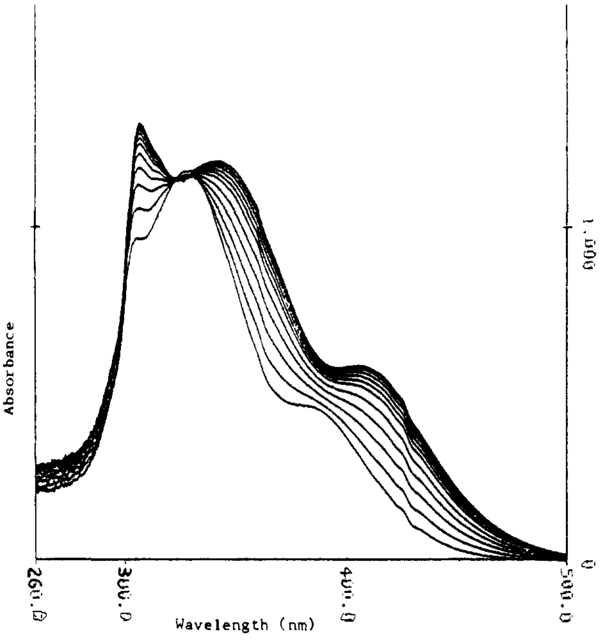

Figure 2. UV–vis absorbance changes vs time for the reaction $Os_3(CO)_{12} + Me_3NO + PPh_3 \rightarrow Os_3(CO)_{11}PPh_3 + Me_3N + CO_2$ in $CHCl_3$–C_2H_5OH (v/v, 2:1) at room temperature.

On longer standing, disubstituted products appear and fragmentation occurs for M = Fe. In all cases, the initial reaction products had IR spectra in agreement with reported spectra of the known compounds.[6]

Plots of k_{obsd} vs [Me_3NO] show a first-order dependence on trimethylamine *N*-oxide (Figure 5). Rates of the reactions are zero order in [L], as shown in Table I. So the reactions obey the second-order rate law given by eq 3. Rate constants for all

$$-d[M_3(CO)_{12}]/dt = k_2[M_3(CO)_{12}][Me_3NO] \qquad (3)$$

the reactions at different temperature are given in Table II. Eyring plots provide activation parameters, ΔH^* and ΔS^*, for the three clusters, which are shown in Table II. The rates of reaction show an inverse dependence on the concentration of C_2H_5OH (Table III, Figure 6).

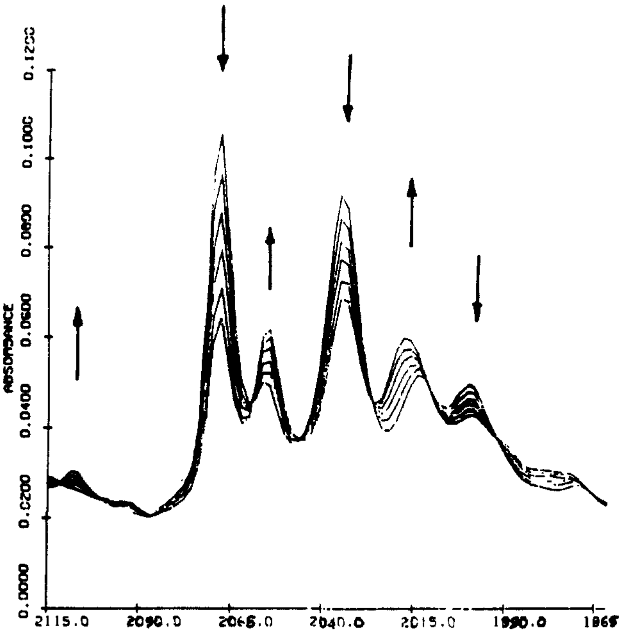

Figure 3. IR absorbance changes of ν_{CO} vs time for the reaction $Os_3(CO)_{12} + Me_3NO + PPh_3 \rightarrow Os_3(CO)_{11}PPh_3 + Me_3N + CO_2$ in $CHCl_3$–C_2H_5OH (v/v, 2:1) at room temperature.

Table II. Second-Order Rate Constants and Activation Parameters for Reactions of Eq 2

$M_3(CO)_{12}$	L	*T*, °C	k_2,[a] M^{-1} s^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal mol^{-1} K^{-1}
$Fe_3(CO)_{12}$	PPh_3	0.56	0.854	12.49 ± 0.61	−13.95 ± 2.10
		13.1	1.53		
		17.3	2.02		
		25.6	4.18		
	$P(OPh)_3$	5.6	0.852	12.34 ± 0.55	−14.51 ± 1.90
		13.1	1.50		
		17.3	2.01		
		25.6	4.08		
	$AsPh_3$	5.6	0.805	13.84 ± 0.19	−9.18 ± 0.67
		13.1	1.63		
		17.3	2.27		
		25.2	4.62		
$Ru_3(CO)_{12}$	PPh_3	14.1	0.350	12.11 ± 0.16	−18.40 ± 0.54
		20.1	0.538		
		25.6	0.822		
		33.4	1.41		
$Os_3(CO)_{12}$	PPh_3	14.1	0.0307	17.08 ± 0.29	−5.92 ± 0.97
		20.2	0.0575		
		25.6	0.104		
		33.4	0.213		

[a] Solvent $CHCl_3$–C_2H_5OH (v/v, 2:1).

Table III. Solvent Effect on Rates of Reaction (Eq 2), Where L = PPh_3

$M_3(CO)_{12}$	solvent (v/v)	k_2, M^{-1} s^{-1}
$Ru_3(CO)_{12}$[a]	$CHCl_3$–C_2H_5OH (2:1)	0.54
	CH_2Cl_2–C_2H_5OH (2:1)	1.32
$Os_3(CO)_{12}$[b]	CH_2Cl_2–C_2H_5OH (9:1)	0.67
	CH_2Cl_2–C_2H_5OH (7:1)	0.48
	CH_2Cl_2–C_2H_5OH (5:1)	0.37
	CH_2Cl_2–C_2H_5OH (4:1)	0.33

[a] At 20.1 °C. [b] At 24.7 °C.

Discussion

The reactions of $M_3(CO)_{12}$ (M = Fe, Ru, Os) with phosphorus and arsenic ligands in the presence of Me_3NO afford the mono-

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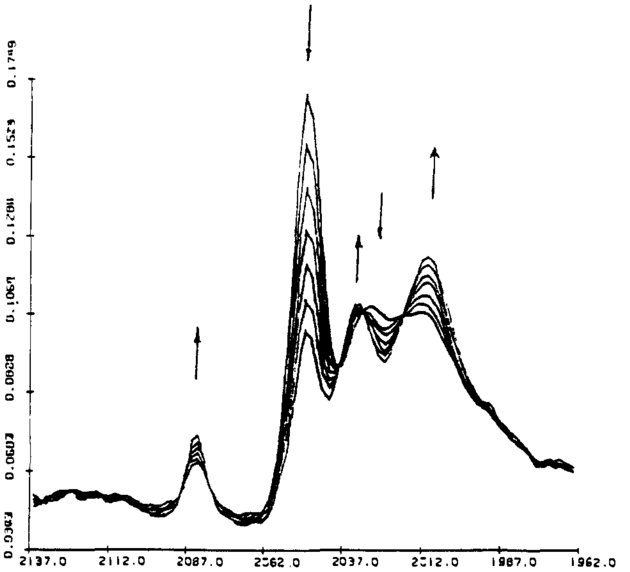


Figure 4. IR absorbance changes of ν_{CO} vs time for the reaction $Fe_3(CO)_{12} + Me_3NO + PPh_3 \rightarrow Fe_3(CO)_{11}PPh_3 + Me_3N + CO_2$ in $CHCl_3$–C_2H_5OH (v/v, 2:1) at room temperature.

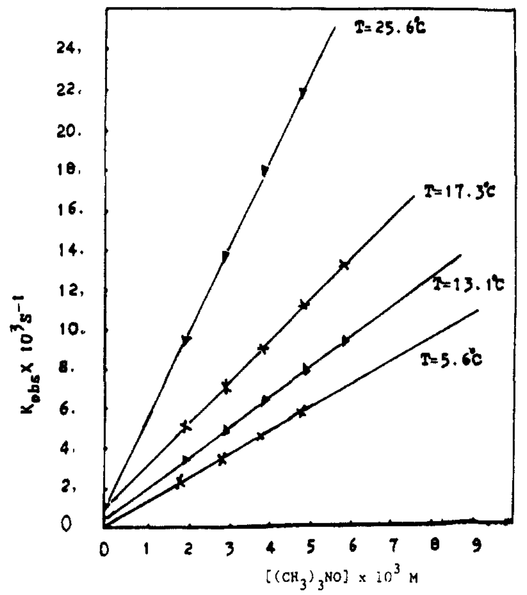


Figure 5. Plot of k_{obsd} vs Me_3NO concentration for the reaction $Fe_3(CO)_{12} + Me_3NO + PPh_3 \rightarrow Fe_3(CO)_{11}PPh_3 + Me_3N + CO_2$ in $CHCl_3$–C_2H_5OH (v/v, 2:1) at room temperature.

Table IV. C–O Stretching Frequencies of $M_3(CO)_{12}$ and Their Rates of Reaction (Eq 2)

$M_3(CO)_{12}$	ν_{CO},[a] cm^{-1}	k_2,[b] M^{-1} s^{-1}
$Fe_3(CO)_{12}$	2045 (vs) 2015 (m) 1850 (vw br)	4.18
$Ru_3(CO)_{12}$	2061 (vs) 2031 (s) 2012 (m)	0.822
$Os_3(CO)_{12}$	2069 (vs) 2036 (vs) 2015 (m) 2004 (m)	0.104

[a] Reference 20. [b] At 25.6 °C in solvent $CHCl_3$–C_2H_5OH (v/v, 2:1).

substituted products $M_3(CO)_{12}L$ (eq 2). This was confirmed by the fact that the IR spectra of all reaction products in the CO stretching region (Table IV) were in good agreement with reported[6] spectra for the known compounds. On prolonged reaction times, disubstituted products appear and $Fe_3(CO)_{12}$ even undergoes cluster fragmentation. Formation of $M_3(CO)_{11}L$ (eq 2) follows a second-order rate law (eq 3), with the rates of reaction being first order in concentrations of metal cluster and Me_3NO (Figure 5) but zero order in entering ligand (Table I). This rate law is identical with that observed[2] for corresponding reactions (eq 1) of $M(CO)_6$ (M = Cr, Mo, W), and it is believed the mechanisms of reaction are the same.

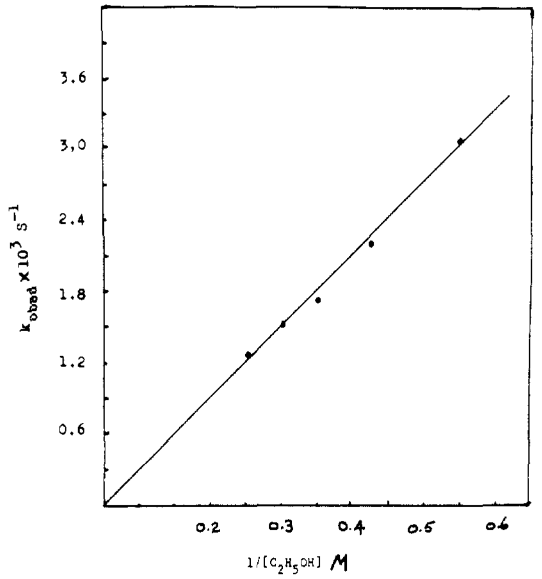
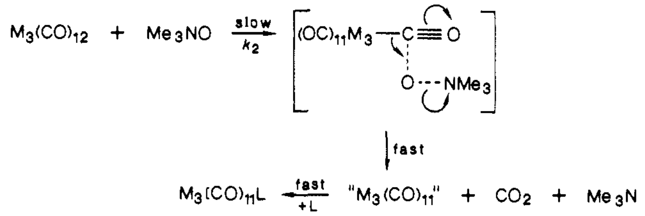


Figure 6. Plot of k_{obsd} vs $1/[C_2H_5OH]$ for the reaction $Os_3(CO)_{12} + Me_3NO + PPh_3 \rightarrow Os_3(CO)_{11}PPh_3 + Me_3N + CO_2$ in the solvent mixture $CHCl_3$–C_2H_5OH at 24.7 °C and $[Me_3NO] = 4.60 \times 10^{-3}$ M.

Scheme I



The rate-determining step of the oxygen atom transfer reactions is believed to involve an intersphere electron-transfer process, preceded by a nucleophilic attack of the oxygen atom of Me_3NO on a carbon atom of a CO (Scheme I). This results in the oxidation of CO to CO_2, which is a good leaving group and its departure from the cluster generates the coordinatively unsaturated active intermediate "$M_3(CO)_{11}$". This then readily reacts with the entering ligand to afford the monosubstituted product $M_3(CO)_{11}L$.

The rates of reaction (eq 2) of the metal carbonyl cluster in CH_2Cl_2 or $CHCl_3$ solvent are too fast to follow by ordinary spectral techniques. Deactivation of Me_3NO by hydrogen bonding was successful, and all the kinetic studies were done in either mixed solvents of CH_2Cl_2–C_2H_5OH or $CHCl_3$–C_2H_5OH. A quantitative study of the effect of added ethanol shows the rates of reaction are inversely proportional to the concentration of C_2H_5OH in the solvent (Table III, Figure 6). This appears to be due to the rapid hydrogen-bonding equilibrium (eq 4), which decreases the concentration of the active free Me_3NO in the reaction mixture. That the hydrogen-bonded species $Me_3NO \cdots HOC_2H_5$ is not reactive is shown (Figure 6) by extrapolation of the plot of k_{obsd} versus $1/[C_2H_5OH]$. Within experimental error, the value of k_{obsd} is zero at the extrapolated value of zero for $1/[C_2H_5OH]$, which means infinite concentration of C_2H_5OH or total formation of $Me_3NO \cdots HOC_2H_5$. This is in accord with the rate-determining step involving a nucleophilic attack on the cluster, since $Me_3NO \cdots HOC_2H_5$ is a poor nucleophile whereas Me_3NO is a good nucleophile.[2]

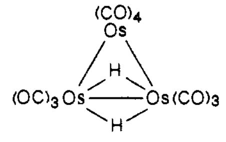
$$Me_3NO + C_2H_5OH \rightleftharpoons Me_3NO \cdots HOC_2H_5 \qquad (4)$$

Although the CO-substitution reactions of $M_3(CO)_{12}$ in the presence of Me_3NO are too fast to measure by conventional methods in aprotic solvents, analogous reactions of $M(CO)_6$ can be followed in such solvents. Unfortunately it was not possible to make a quantitative comparison between the rates of reaction of $M_3(CO)_{12}$ and of $M(CO)_6$, which shows no reaction even after days with the same mixed solvents and temperatures that result in the rapid reactions of $M_3(CO)_{12}$. Note that the rates of reaction of $M_3(CO)_{12}$ are orders of magnitude larger than the rates of corresponding reactions of $M(CO)_6$. This is in agreement with previous studies[7] that show that rates of nucleophilic attack on carbon in metal carbonyls increase with increasing CO stretching frequencies. The very strong bands in the CO stretching region of the IR for $M_3(CO)_{12}$ are at about 2050 cm^{-1} (Table IV) compared with an approximate value of 1980 for the $M(CO)_6$ compounds. The higher ν_{CO} values indicate less metal to carbon π back-bonding, giving rise to a more positive carbon in $M_3(CO)_{12}$ than in $M(CO)_6$. For example, calculations estimate the positive charge on carbon in $Cr(CO)_6$ to be +0.20[8] and in $Ru_3(CO)_{12}$ for the axial carbon to be +0.34.[9]

In spite of the general correlation between increasing rates of nucleophilic attack on carbon in metal carbonyls with increasing values of ν_{CO}, kinetic date in Table IV show exactly the opposite trend, Thus, the rates of reaction decrease in the order $Fe_3(CO)_{12} > Ru_3(CO)_{12} > Os_3(CO)_{12}$, although the ν_{CO} values increase in this order. Since the ground-state positive charge on carbon does not appear to control the relative rates of reaction, it is necessary to consider factors that can affect the stabilities of the transition states. Gross and Ford[10] report the same rate order for the reactions of $M_3(CO)_{12}$ with CH_3O^- to form $[M_3(CO)_{11}C(O)CH_3]^-$. This reaction also involves attack of CH_3O^- on a carbon atom, and it was suggested that rates decrease in the order Fe > Ru > Os because the stability of the transition state for reaction decreases in this same order. The reason given for such an order of transition-state stability is that bridging carbonyls are more electron withdrawing[11] and can better accommodate the developing negative charge on the metal cluster as CH_3O^- attacks a carbonyl carbon in the transition state. The ground-state structure of $Fe_3(CO)_{12}$ in solid and solution contains two bridging carbonyls, whereas $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ contain only terminal carbonyls.[12] Because of the longer M–M bond distances going down the iron triad, it becomes increasingly difficult to form bridging carbonyls to delocalize negative charge accumulating in the transition state. For example, the mechanism proposed[13] for the intramolecular fluxional scrambling of COs in $M_3(CO)_{12}$ is believed to involve bridging carbonyls, and the rates of CO scramble decrease in the order Fe > Ru > Os. A more specific example[14] of a third-row transition-metal carbonyl with only terminal carbonyls, which forms bridging carbonyls to accommodate negative charge, is provided by $Ir_4(CO)_{12}$ and $[Ir_4(CO)_{11}C(O)OCH_3]^-$, respectively.

Although the addition of Me_3NO to $M_3(CO)_{12}$ in the transition state does not develop a negative charge on the cluster, as does the addition of CH_3O^-, attack by the negative oxygen of $Me_3N^{\delta+}$–$O^{\delta-}$ does increase the electron density in the cluster. This may be sufficient to require carbonyl bridge formation in the transition state for reaction and to account for the relative rates observed. However, it should be noted that reaction of $M_3(CO)_{12}$ with Me_3NO requires breaking a M–C bond, but reaction with CH_3O^- does not involve M–C bond cleavage. Reactions that do require M–C bond cleavage are thermal CO substitution or exchange reactions of $M_3(CO)_{12}$, which also decrease in rate[15] in the order Fe > Ru > Os. These observations are consistent with the relative rates found for the reactions of $M_3(CO)_{12}$ with Me_3NO, which are believed to involve both O–C bond making and M–C bond breaking.

The structure of the presumed coordinatively unsaturated active intermediate $M_3(CO)_{11}$ is not known, but the formation of such species finds support in the existence of the stable isoelectronic compound $Os(CO)_{10}(H)_2$. X-ray studies show[16] this compound has the structure represented by I. The hydrogen-bridged Os–Os bond distance is 2.670 Å, the nonbridged Os–Os bond distances are 2.814 Å, and for $Os_3(CO)_{12}$, the Os–Os bond distances are 2.85 Å. This suggests that even in the osmium intermediate $Os_3(CO)_{11}$, which has the least tendency relative to the corresponding iron or ruthenium intermediates to form bridging carbonyls, it should be possible to form carbonyl bridges. Sonnenberger and Atwood[17] have invoked carbonyl bridge formation for the thermal dissociation CO substitution reactions of $MnRe(CO)_{10}$, and CO bridging for coordinatively unsaturated cluster intermediates were suggested[18] for thermal dissociation CO substitution reactions of $M_3(CO)_{12}$. Possible structures of $M_3(CO)_{11}$ intermediates are given by II–V. The electron count for each metal is given for each structure. Regardless of structure, the intermediates are all expected to readily react with entering ligands. The most direct reactions would involve structures II and III, which have a 16-electron metal site that would quickly add a pair of electrons of the entering ligand to form the stable 18-electron product. Structures IV and V would require a more involved reaction pathway but would also be expected to take place rapidly. It is well-known[19] that 17-electron organometallic compounds are substitution labile and that the reactions take place via a 19-electron active intermediate. This suggests that for structures IV and V the entering ligand would readily add to a 17-electron metal to form a 19-electron metal, but a bridging CO with the second 17-electron metal would become terminal on that metal in order to convert both 17-electron metals into stable



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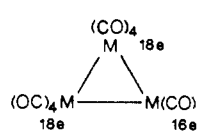

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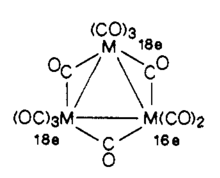

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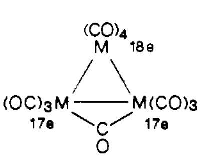

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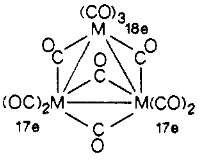

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18-electron metals of the monosubstituted products.

One of the reviewers makes the point that the activation parameters in Table II support our contention that bridging carbonyls are progressively less stabilizing in the transition state in the order $Fe_3(CO)_{12} > Ru_3(CO)_{12} > Os_3(CO)_{12}$. It is suggested that the similarity of $\Delta H^{\ddagger}$ for the reaction of either $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$ with PPh_3 reflects a similar attack by Me_3NO in both cases, but the more negative value of $\Delta S^{\ddagger}$ for the Ru system reflects the need for steric reorganization (perhaps, terminal CO → bridging CO). However, the larger $\Delta H^{\ddagger}$ and less negative $\Delta S^{\ddagger}$ for the reaction of $Os_3(CO)_{12}$ with PPh_3 may indicate that CO bridging is not important in the Os system.

Acknowledgment. We thank the United States-China Cooperative Science Program for the support of this collaborative research. The program is funded by the U.S. National Science Foundation and the PRC National Natural Science Foundation.

Registry No. $Fe_3(CO)_{12}$, 17685-52-8; $Ru_3(CO)_{12}$, 15243-33-1; $Os_3(CO)_{12}$, 15696-40-9; PPh_3, 603-35-0; $P(OPh)_3$, 101-02-0; $AsPh_3$, 603-32-7; $(CH_3)_3NO$, 1184-78-7.

Supplementary Material Available: Additional values are given of k_{obsd} for reactions (eq 2) at different concentrations of Me_3NO and different temperatures (Table S2) (3 pages). Ordering information is given on any current masthead page.

Intrinsic Barriers to Proton Exchange between Transition-Metal Centers: Application of a Weak-Interaction Model

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Abstract: A weak-interaction model for proton self-exchange between transition-metal centers is considered. The rate constant obtained from the Fermi golden-rule expression of radiationless transition theory is a product of terms for assembling acid and base reactants at the correct orientation and distance, a classical reaction frequency, an electron-proton reaction probability, and classical nuclear factors deriving from the requirement for reorganization of ancillary ligands and solvent modes. It is found that such a model yields calculated rate constants and activation parameters in reasonable agreement with the experimental data, provided that the fluxionality of certain metal centers is taken into account.

Because proton transfer fulfills a central role in many processes, understanding and modeling of proton-transfer rates is an important challenge. Proton transfer between strongly electronegative centers such as oxygen or nitrogen is generally extremely rapid in solution[1] and proceeds via hydrogen-bonded "dimers" for which solid-state[2] and gas-phase species provide useful models. Recent ab initio calculations[3] accurately reproduce the properties of the gaseous ions and so provide a point of departure for modeling the dynamics of the proton transfer in this strong interaction limit. By contrast, although slow proton transfer to carbon centers has stimulated considerable experimental and theoretical activity,[4-6] there appears to be no consensus as to whether these reactions are better treated in terms of an adiabatic (strong-interaction)[5] or a nonadiabatic (weak-interaction) model.[6-9] Recent measurements of proton self-exchange rates[10] (eq 1) between transition-metal complexes in acetonitrile provide a basis for a critical

$$ML_nH + ML_n^- \rightarrow ML_n^- + ML_nH \qquad (1)$$

Table I. Proton Self-Exchange Rates at 20–30 °C

	solvent	pK_a	k_{ex}, M^{-1} s^{-1}
$NH_4^+ + NH_3$	H_2O, 30 °C	9.1	1.3×10^{9} [a]
$CH_3NH_3^+ + CH_3NH_2$	H_2O, 30 °C	10.5	0.4×10^{9} [a]
$PhNH_3^+ + PhNH_2$	CH_3CN, 25 °C	10.5	$\geq 10^{8}$ [c]
$HFl + Fl^-$	Et_2O, 25 °C	--	2×10^{-5} [b]
$HM(cp)(CO)_3 + M(cp)(CO)_3^-$	CH_3CN, 25 °C		
M = Cr		13.3	1.8×10^{4} [c]
M = Mo		13.9	2.5×10^{3} [c]
M = W		16.1	6.5×10^{2} [c]
$H_2Fe(CO)_4 + HFe(CO)_4^-$	CH_3CN, 25 °C	11.4	10^{3} [c]
$H_2Os(CO)_4 + HOs(CO)_4^-$	CH_3CN, 25 °C	20.8	10^{-1} [c]

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Table II. Properties of R-H Bonds

R-H	D_0, kcal mol^{-1}	ν_{R-H}, cm^{-1}	δ_{R-H}, cm^{-1}	$d°_{R-H}$, Å
M-H	50-75[a]	1600-2300[b]	600-900[b]	1.6-1.5[c,d] 1.7-1.6[d,e] 1.8-1.7[d,g]
N-H	80-100[f]	~3000[f]	~1500[f]	~1.0[f]
O-H	~110[f]	~3600[f]	~1300[f]	~1.1[f]
C-H	~100[f]	~3000[f]	~1300[f]	~0.98[f]

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