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Intramolecular Activation of Metal Carbonyl Cluster Complexes. Kinetics and Mechanism of Ligand Substitution Reactions of $[Os_3(CO)_{10}LX]^-$ (L = PPh_3, CO; X = Cl, Br, I, NCO)

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Kinetic results are reported for ligand substitutions of $[Os_3(CO)_{10}LX]^-$ (L = PPh_3, CO; X = NCO^-, Cl^-, Br^-, I^-). The complexes $[Os_3(CO)_{11}X]^-$ react with PPh_3 at mild conditions to initially yield monosubstituted products $[Os_3(CO)_{10}(PPh_3)X]^-$, which can further react with excess ligand to form the disubstituted complex $[Os_3(CO)_9(PPh_3)_2(NCO)]^-$ and trisubstituted $Os_3(CO)_9(PPh_3)_3$ when X = halide ion. The rate of CO substitution is first-order in complex concentration and independent of ligand concentrations. The rates for the reactions decrease in the order $Cl^- \sim Br^- > I^- > NCO^-$, with $\Delta H^{\ddagger}$ values increasing from 15 to 18 kcal/mol and $\Delta S^{\ddagger}$ values varying from −19 to −13 cal/(mol K). The enhanced reactivities of these complexes as well as the low activation energies and negative $\Delta S^{\ddagger}$ values are discussed in terms of μ-X bridge formation effects on the transition state of the reaction. PPh_3 substitution with the CO ligand in $[Os_3(CO)_{10}(PPh_3)X]^-$ (X = Cl^- and NCO^-) follows a first-order kinetic rate law. Activation parameters are, for the Cl^- complex, $\Delta H^{\ddagger} = 22.3$ kcal/mol and $\Delta S^{\ddagger} = 3.5$ cal/(mol K) and, for the NCO^- complex, $\Delta H^{\ddagger} = 27.3$ kcal/mol, and $\Delta S^{\ddagger} = 15.2$ cal/(mol K). That the μ-X formation effect in the transition state is less significant for PPh_3 substitution than for CO substitution is discussed in terms of the steric and electronic effects of the phosphorus ligand.

Introduction

The kinetics and mechanism of CO substitution reactions of $Mn(CO)_5X$ (X = Cl, Br, I) were first reported in 1961.[1] It was found that the reaction undergoes a dissociative pathway, with the reactivity order Cl > Br > I. This order of reactivity was explained in terms of the polarizability of halide ions increasing from Cl to I, resulting in an increase of Mn–C bond strengths of the compounds in the same order, due to greater π bonding because of increased electron density on the metal. The point was made that the rates decrease with decreasing IR values of ν_{CO} in the ground state of the compounds, but the contribution of the transition state to the rates was not discussed. Brown and Atwood[2] later suggested that the site preference in the five coordinated transition state or active intermediate $M(CO)_4L$ plays a more important role than the ground state in determining the reactivities of the complexes. This suggestion is also supported by molecular orbital calculations.[3] These studies indicated that *cis* labilization and site preference in $M(CO)_5L$ will be greatest when L has potential π-donor character, due to the overlap of a lone pair orbital on the coordinated atom with an appropriate empty metal orbital in the transition state.

More recently, there has been great interest in using nucleophilic anions to activate metal carbonyl clusters.[4] These activated clusters may be used in homogeneous catalysis[5] and in the tailoring of organic substrates.[6] The activation effects of nucleophiles on the reactivities of metal carbonyl clusters was first noticed in 1980 by Kaesz,[7] although it had been known that anionic nucleophiles could readily react with metal carbonyl clusters.[8] Studies[4] show that activation is achieved by using common salts as catalysts. It is believed that activation is due either to a nucleophilic attack of the anion on a carbonyl carbon atom to weaken its M–C bond,[9,10] or to incorporating the anion as an ancillary ligand in the cluster.[11] The latter case is the subject of this report. Although considerable attention has been given to the syntheses and characterizations of these complexes,[11,12] there is a paucity of kinetic information for understanding the mechanism by which the anions activate these clusters. As a parallel study to the earlier investigations on mononuclear metal carbonyl complexes,[1,13] reported are kinetic results for ligand substitutions of $[Os_3(CO)_{11}X^-]$ with PPh_3 (eq 1) and of $[Os_3(CO)_{10}PPh_3X]^-$ with CO (eq 2).

The results from this study show that the reactivities of these clusters follow the order Cl ~ Br > I > NCO, where the $\Delta H^{\ddagger}$ for CO substitution (eq 1) is very low (15–18 kcal/mol), and $\Delta S^{\ddagger}$ values are negative. These results

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$$[Os_3(CO)_{11}X]^- + PPh_3 \rightarrow [Os_3(CO)_{10}PPh_3X]^- + CO \quad (1)$$

$$X = Cl^-, Br^-, I^-, NCO^-$$

$$[Os_3(CO)_{10}PPh_3(X)]^- + CO \rightarrow [Os_3(CO)_{11}(X)]^- + PPh_3 \quad (2)$$

$$X = Cl^-, NCO^-$$

are not expected on the basis of the *cis* labilization effect of anions in mononuclear metal carbonyls,[2] where $\Delta H^\ddagger$ values are large (30 kcal/mol) and $\Delta S^\ddagger$ values are positive for CO dissociation reactions.[1] Instead, activation parameters for the reaction (eq 1) are similar to that for the intramolecular associative CO substitution of $Os_3(CO)_{11}(\eta^1$-dppm) (dppm = $CH_2(PPh_2)_2$),[14] where it was believed that the chelating effect of dppm is important in the reaction transition state. It is believed the present study demonstrates that the predominant effect of these anions on the reactivities of metal clusters is different from that in mononuclear metal complexes and is the result of intramolecular bridge formation of the anion between two neighboring metal atoms.

Experimental Section

Reagents. PPh_3 was obtained from Aldrich and recrystallized from ethyl alcohol. THF was distilled under N_2 from sodium benzophenone ketyl. PPN[$Os_3(CO)_{11}X$] (X = Cl^-, Br^-, NCO^-) and N(*n*-Bu)$_4$[$Os_3(CO)_{11}X$] (X = Br, I) were synthesized according to the literature method.[15] $Os_3(CO)_{12}$ (90 mg, 0.09 mmol), Me_3NO (12 mg, 1.5 equiv), and 1 equiv of the appropriate salt were placed into a Schlenk tube equipped with a stir bar. Dry THF (15 mL) was added *via* syringe, and the solution was stirred at 0 °C under reduced pressure for 4 h. The solvent was then removed under vacuum, and the residue was washed with CCl_4 (2 × 5 mL). The products were purified from THF–pentane solvents. All the products have their CO stretching frequencies in agreement with that reported in the literature.[15]

CO Substitutions of [$Os_3(CO)_{11}X$]$^-$ (X = Cl^-, Br^-, I^-, NCO^-). All kinetic experiments were run under pseudo-first-order conditions, with the concentration of entering nucleophile in 10-fold excess or more. Kinetic data were obtained by following the disappearances of the CO stretching bands of the reactants. The infrared spectra were obtained on a Nicolet 5PC-FTIR spectrophotometer equipped with a P/N 20.500 variable temperature IR cell with 0.6-mm AgCl windows. Constant temperatures were obtained using a Neslab RTE-S refrigeration circulating bath. In a typical experiment, 0.5 mL of a PPN[$Os_3(CO)_{11}Cl$] THF solution (2 × 10^{-3} M) was mixed with 0.5 mL of a PPh_3 (0.500 M) THF solution in a Schlenk tube which was kept in an ice bath (0 °C). The mixed solution was then diluted with THF to 2 mL. The solution was transferred into the IR cell with a syringe. After a few minutes, when temperature equilibration was reached, the IR spectral changes were recorded (Figure 1). Plots of ln A_t (A_t is the absorbance of ν_{CO} of the substrate) *vs* time were linear over 2 half-lives ($r^2 > 0.995$) for all the reactions. The slopes of these lines yield observed rate constants.

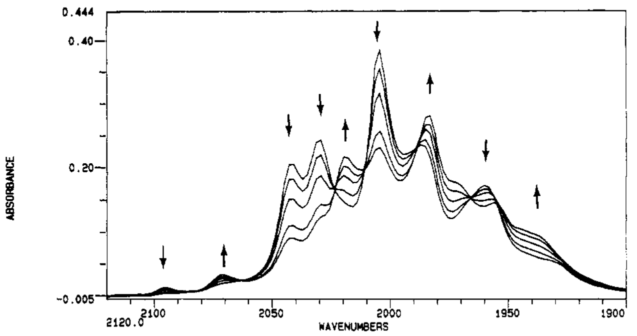

Figure 1. Infrared ν_{CO} absorbance changes *vs* time for CO substitution (eq 1) of PPN[$Os_3(CO)_{11}Br$] with PPh_3 in THF at 15 °C.

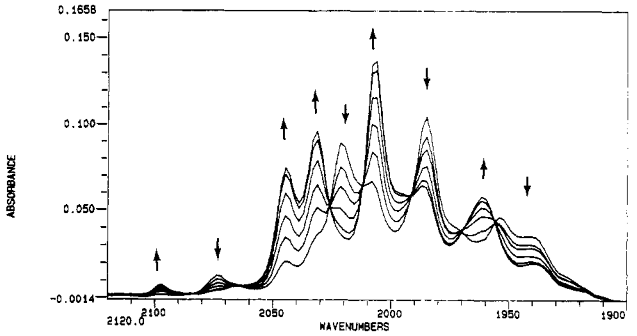

Figure 2. Infrared ν_{CO} absorbance changes *vs* time for PPh_3 substitution (eq 2) of PPN[$Os_3(CO)_{10}(NCO)PPh_3$)] with CO in THF at 31.5 °C.

PPN[$Os_3(CO)_{10}(NCO)PPh_3$]. The reaction of PPN[$Os_3(CO)_{10}(\mu$-NCO)][16] with an equal amount of PPh_3 at 0 °C immediately affords this addition product. The solvent was then removed under vacuum. The residue was washed with pentane and dried under reduced pressure. The compound was obtained as a yellow-orange powder. The complex can also be made from the reaction between PPN[$Os_3(CO)_{11}(NCO)$] and PPh_3 (1/1.5) at room temperature. The reaction was followed with an IR spectrophotometer. When all of the reactant was converted to products (monosubstituted with a small amount of disubstituted complex), the solution was exposed to CO for 1–2 min to convert the disubstituted complex to PPN[$Os_3(CO)_{10}(NCO)PPh_3$]. The product was obtained upon adding pentane to the solution. The compound was purified from THF–pentane at 0 °C. It slowly decomposes at room temperature in solution and in the solid state even under N_2. The compound can be converted to its parent compound under CO at mild conditions. Spectral changes during the reaction (Figure 2) show good isosbestic points for this conversion, suggesting a good stoichiometric reaction affording [$Os_3(CO)_{11}(NCO)$]$^-$. IR (cm^{-1}, THF): 2073 (w), 2020 (s), 1985 (s), 1953 (m), 1939 (m). Anal. Calcd for $C_{65}H_{45}N_2O_{11}Os_3P_3$: C, 46.11; H, 2.66; N, 1.65. Found: C, 46.91; H, 2.96; N, 1.60.

The analogous Cl^- complex was made *in situ* using the same method as that used for making PPN[$Os_3(CO)_{10}(NCO)PPh_3$]. The chloro cluster product has IR ν_{CO} values the same as those for the NCO^- compound and can also be converted to its parent complex under CO atmosphere.

PPh_3 Substitutions of [$Os_3(CO)_{10}(X)PPh_3$]$^-$ (X = Cl^-, NCO^-). The reaction of [$Os_3(CO)_{10}(X)PPh_3$]$^-$ with CO yields [$Os_3(CO)_{11}(X)$]$^-$ (X = Cl^-, NCO^-) in THF solution. In a typical experiment, 3 mL of a THF solution of [$Os_3(CO)_{10}(NCO)PPh_3$]$^-$ was syringed into a 100-mL flask equipped with stir bar under CO atmosphere. The flask was maintained in a Neslab RTE-8 refrigeration circulating bath. IR spectra were recorded with a 0.2-mm NaCl IR cell. Rate constants were obtained by following the increase of CO stretching bands of the product (Figure 2), using $\ln(A_\infty - A_t) = k_{obsd}t$ + constant. Plots of $\ln(A_\infty - A_t)$ *vs* time are linear over 3–4 half-lives ($r^2 > 0.995$).

$Os_3(CO)_9[PPh_3]_3$. The compounds PPN[$Os_3(CO)_{11}X$] (X = Cl, Br, I) were allowed to react with an excess of PPh_3 in THF at room temperature for 2 h. Then THF was removed under vacuum and the residue was extracted with toluene. $Os_3(CO)_9$-

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Table I. Observed Rate Constants for CO Substitution (Eq 1) of $[Os_3(CO)_{11}(NCO)]^-$ with Phosphorus Ligands in THF

ligand	T, °C	[L], M	10^4k_{obsd}, s^{-1}
PPh_3	29.5	0.050	7.20
		0.125	7.40
		0.250	7.10
$P(OMe)_3$	30.0	0.0706	10.3
		0.353	9.84
$P(n\text{-}Bu)_3$	30.0	0.0402	10.2
		0.0804	9.51
		0.209	9.72

Table II. Rate Constants and Activation Parameters for CO Substitution (Eq 1) of $[Os_3(CO)_{11}X]^-$ with PPh_3 in THF

X	T, °C	10^3k_1, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol K)
Cl^-	8.5	0.262		
	19.7	0.823		
	28.8	1.86	15.7 ± 0.4	−19.1 ± 1.4
Br^-	9.1	0.270		
	18.2	0.710		
	30.2	2.27	16.6 ± 0.2	−15.8 ± 0.4
I^-	9.3	0.200		
	19.0	0.570		
	31.0	1.88	17.1 ± 0.1	−14.9 ± 0.2
NCO^-	8.9	0.0807		
	18.3	0.244		
	29.5	0.722		
	39.0	2.04	18.1 ± 1.2	−13.0 ± 2.0

Table III. Rate Constants and Activation Parameters for PPh_3 Substitution (Eq 2) of $[Os_3(CO)_{10}XPPh_3]^-$ with CO in THF

X	T, °C	10^3k_1, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol K)
NCO^-	21.0	0.0685		
	31.5	0.371		
	42.0	1.66	27.3 ± 0.5	15.2 ± 1.5
Cl^-	9.8	0.184		
	19.0	0.666		
	30.0	2.77	22.3 ± 0.1	3.5 ± 0.2

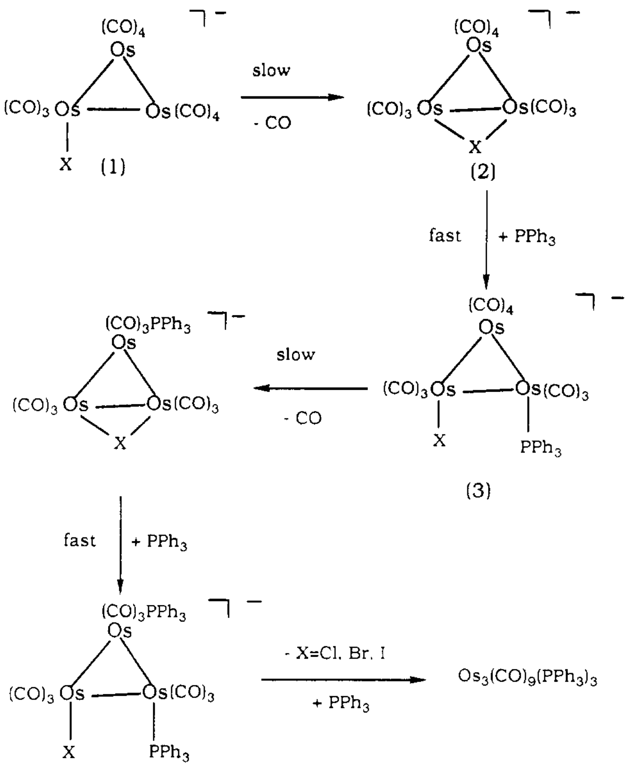
$[PPh_3]_3$[17] was obtained upon adding pentane to the solution. The compound was recrystallized from THF–pentane solution. IR (THF, cm^{-1}): 1943 (s), 1972 (s), 1987 (s). IR (CCl_4, cm^{-1}): 2053 (w), 1999 (sh), 1990 (m), 1976 (s), 1944 (m).[17]

Results

The solid product $PPN[Os_3(CO)_{10}(NCO)PPh_3]$ was isolated from the reaction of $[Os_3(CO)_{11}(NCO)]^-$ with PPh_3. The product reacts further with excess ligand to form $[Os_3(CO)_9(NCO)(PPh_3)_2]^-$, which is returned to the monosubstituted product under CO atmosphere. Reactions of $[Os_3(CO)_{11}X]^-$ (X = Cl, Br, I) with PPh_3 all yield the same final product $Os_3(CO)_9[PPh_3]_3$.[17] Although intermediates observed during the reactions have IR spectra similar to that of $[Os_3(CO)_{10}(NCO)PPh_3]^-$ in the CO stretching vibration range, isolation and purification of these halogen compounds were not successful. The rates of disappearance of the substrates (eq 1) are first-order in complex concentrations but zero-order in ligand concentrations (Table I). Rate constants at different temperatures and the activation parameters for the reaction are included in Table II.

The rates for PPh_3 substitution (eq 2) were measured under different CO pressures (1–3 atm) at temperatures from 20 to 40 °C. The rate is first-order in complex concentration and independent of CO pressure. First-order rate constants and activation parameters for the reaction are included in Table III.

Scheme I



Discussion

The rates of CO substitution (eq 1) are first-order in complex and zero-order in ligand concentrations. This rate law is typical for a dissociative mechanism, but the activation parameters of small $\Delta H^{\ddagger}$ and negative $\Delta S^{\ddagger}$ (Table II) are typical of an associative pathway. This seemingly anomalous kinetic result can be explained by assuming the halide ligand makes use of its nonbonding electron pair to attack a neighboring metal and displace CO (see Scheme I). Thus, the slow rate-determining step is first-order in cluster concentration only and the active intermediate (**2**) is a bridged complex. There are ample examples of such bridged complexes, which are also known to labilize ligand substitution. The pseudohalide complex $[Os_3(\mu\text{-}NCO)(CO)_{10}]^-$ was shown[16] by IR spectrophotometry to have a bridged structure. Other examples which show the stabilization of active species by bridging ligands in such clusters include $[Ru_3(CO)_{10}(\mu\text{-}Cl)]^-$ [18] and alkoxo, amido, and thiolato groups in triruthenium carbonyl clusters.[11] These active species readily react with entering ligands to form substituted products. Attempts to measure the rate constants for the addition of PPh_3 to $[Os_3(\mu\text{-}NCO)(CO)_{10}]^-$ were not successful, because the reaction was complete within the time of mixing even at low temperatures (~−20 °C). However, the addition product from $[Os_3(\mu\text{-}NCO)(CO)_{10}]^-$ and PPh_3 has the same ν_{CO} bands as that obtained from the substitution reaction of $[Os_3(NCO)(CO)_{11}]^-$, both forming $[Os_3(CO)_{10}(NCO)PPh_3]^-$. As expected, further CO substitution to form $[Os_3(CO)_9(NCO)(PPh_3)_2]^-$ (at 40 °C, $k_1 = 3.62 \times 10^{-4}$ s^{-1}) is

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Table IV. Rate Constants for CO Substitution (Eq 1) of $[Os_3(CO)_{11}Br]^-$ with PPh_3 at 30.2 °C

cation	solvent	ϵ	10^3k_1, s^{-1}
PPN^+	THF	7.32	2.22
	CH_2Cl_2	8.9	1.86
	CH_3CN	36.2	2.07
$(n\text{-}Bu)_4N^+$	THF	7.32	2.27

slower than the first CO substitution. For halide complexes, the anions finally are also replaced to form the trisubstituted compound $Os_3(CO)_9(PPh_3)_3$.

The reaction (eq 1, $X = Br^-$) was investigated in different solvents and with different cations, in order to test the ionic effect on the rate of the reaction. The results (Table IV) show that the rates are about the same in the three solvents used for this study. This indicates that solvent stabilization effects are about the same on the ground state as on the transition state, suggesting no significant charge redistribution takes place in the transition state. Also the two different countercations in THF solution have no effect. This is consistent with the proposed reaction mechanism (Scheme I).

The $\Delta H^\ddagger$ values for the reaction (eq 1) vary from 15 to 18 kcal/mol with $\Delta S^\ddagger$ values changing between −19 and −13 kcal/(mol K) for all four complexes (Table II). This is unusual for CO dissociative reactions, which are known to have $\Delta H^\ddagger$ values of about 30 kcal/mol and positive $\Delta S^\ddagger$ values.[19] These low $\Delta H^\ddagger$ values and negative $\Delta S^\ddagger$ values suggest that there is considerable intramolecular reorganization in the reaction transition state, which energetically favors CO dissociation from the metal center. For mononuclear complexes $M(CO)_5X$, where it is believed[2,3] that the overlap of a lone pair orbital with an appropriate empty metal orbital stabilizes the reaction transition state, M–X bond order and geometrical relaxation may also occur, but these reactions all have large $\Delta H^\ddagger$ values and very positive $\Delta S^\ddagger$ values.[1,13] The differences in activation parameters suggest that the halide ligands play a different role in activating CO in mononuclear complexes from that in metal cluster complexes. Similar activation parameters were reported[20] for CO substitution of $[Ru_3(CO)_{11}(CO_2CH_3)]^-$ with $P(OMe)_3$, for which the rate-determining step is CO dissociation from the metal complex. Although it was speculated that the enhanced reactivity of the metal cluster methoxycarbonyl adduct perhaps results from *cis* labilization of the methoxycarbonyl group, the structure of the active intermediate remains unknown. Intramolecular CO substitution of $Os_3(CO)_{11}$dppm was studied.[14] The reaction is much faster than that of $Os_3(CO)_{11}L$ (L = phosphorus ligands), having values of $\Delta H^\ddagger = 22$ kcal/mol and $\Delta S^\ddagger = -9.6$ cal/(mol K). The enhanced reactivity and negative $\Delta S^\ddagger$ value are believed due to the attack of the free P atom on an adjacent Os atom in the transition state of the reaction.

These results and the isolation[16] of $[Os_3(\mu\text{-}NCO)(CO)_{10}]^-$ and other similar species[11,18] suggest that anions can activate CO dissociation from metal clusters by stabilizing the reaction transition state through bridging X^- formation, since this bonding transformation would coordinatively saturate the reaction transition state. Kinetic results presented in this report are consistent with this interpretation. The small $\Delta H^\ddagger$ values and the very negative $\Delta S^\ddagger$ values for the reactions indicate a great extent of X–Os bond formation in the transition state.

Kinetic studies of CO substitution of $Os_3(CO)_{12}$[21] are orders of magnitude slower than are corresponding reactions of $[Os_3(CO)_{11}X]^-$. Furthermore the reactions of $Os_3(CO)_{12}$ undergo a dissociative pathway with values of $\Delta H^\ddagger = 38.6$ kcal/mol and $\Delta S^\ddagger = 24.2$ cal/(mol K). Qualitative observations[21] indicate that $Os_3(CO)_{11}L$ (L = phosphorus ligands) compounds react at about the same rates as the parent cluster. These results show that replacement of CO with a stronger σ-donor phosphorus ligand does not affect the reactivity of the cluster significantly. It was concluded that the Os–CO bonds in these anion complexes were not disturbed considerably, on the basis of X-ray structure studies on $[Os_3(CO)_{11}X]^-$ (X = Br, I).[15] That replacement of CO with a halide ion has a dramatic effect on the rate of CO substitution whereas PR_3 does not is believed due to the fact that the P atom does not possess a pair of electrons to interact with a neighboring Os and assist CO displacement.

The results show that the rates of reaction (eq 1) decrease in the order Cl ~ Br > I > NCO, although the difference is small (Table II). This reactivity order also indicates that the origin of cluster activation is not *cis* labilization of the anions, since it was indicated[2] that the *cis* labilization order follows NCO, Cl > Br > I. Activation parameters (Table I) for the reaction further show that the activation energies increase from Cl to NCO, while $\Delta S^\ddagger$ values decrease in the same order. It is expected that the formation of bridge halide ligands would result in low $\Delta H^\ddagger$ and more negative $\Delta S^\ddagger$ values. Although X-ray structures show that the iodide ion is coordinated in the equatorial plane and the bromide ion is located in an axial position,[15] ^{13}C NMR dynamic studies show that all these ionic ligands undergo rapid fluxional change between axial and equatorial positions through a trigonal-twist mechanism in solution at room temperature.[15] Thus, the location of anion ligands in the solid state seems not to be a factor influencing the reactivities of the complexes. Another factor that needs to be considered is the metal–metal bond distance in the cluster. Results show that the average Os–Os distances in $[Os_3(CO)_{11}X]^-$ (X = Br, I) are similar.[15] The reactivity order may suggest that the ability to form a bridge over Os–Os may decrease in the order Cl > Br > I > NCO. The same reactivity order was reported[18] for halide ion promoted CO substitution of $Ru_3(CO)_{12}$, where it was suggested that complexes $[Ru_3(CO)_{11}X]^-$ might be the reaction intermediates. Although equilibrium studies[22] on $Ru_3(CO)_{12}$/halide ion systems indicated that the iodide anion forms the strongest bridge bond between a Ru–Ru bond, no quantitative thermodynamic information is available regarding the ability of halide ions to form a bridge between an Os–Os bond. It should be pointed out that $[Os_3(CO)_{10}(\mu\text{-}I)]^-$ is readily converted to $[Os_3(CO)_{11}I]^-$ [23] under a diluted CO atmosphere ($CO/N_2 = 1/9$), whereas the Ru complex does not react with CO (1 atm).[22]

It is of interest to note that $[Os_3(CO)_{10}(NCO)(PPh_3)]^-$ reacts with CO at mild experimental conditions to form $[Os_3(CO)_{11}(NCO)]^-$. Qualitative observations indicate

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(23) Compound $N(n\text{-}Bu)_4[Os_3(CO)_{10}(\mu\text{-}I)]$ was made *in situ* by refluxing the THF solution of $N(n\text{-}Bu)_4[Os_3(CO)_{11}(I)]$ under N_2 for 4 h. It has a ν_{co} similar to that of $PPN[Os_3(CO)_{10}(\mu\text{-}NCO)]$.[16] IR (THF, cm^{-1}): 2073 (w), 2015 (s), 2002 (s), 1984 (s), 1942 (m), 1929 (sh).

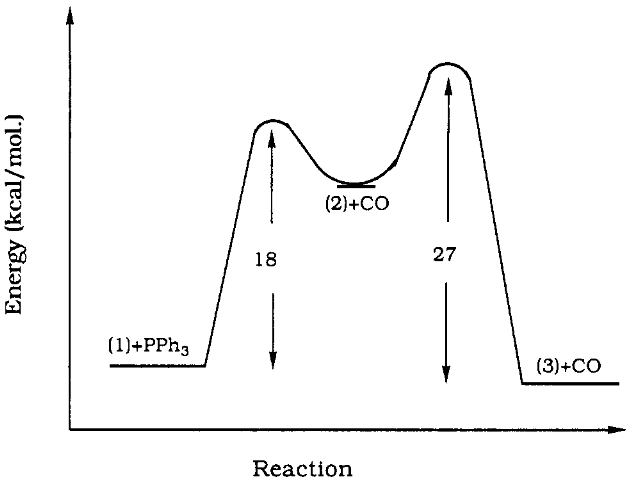

Figure 3. Energy reaction diagram for the reaction of PPN[$Os_3(CO)_{11}(NCO)$] with PPh$_3$. See Scheme I for notations of the cluster and Tables II and III for values of $\Delta H^\ddagger$.

that the corresponding P(OMe)$_3$ complex does not react with CO at these conditions. The relatively large size of the PPh$_3$ ligand and a negative charge on the complex may be the reason for the weak P–Os bond in this cluster. The rate of reaction (eq 2) is first-order in complex but zero-order in CO concentration. The reaction undergoes a dissociative pathway, as is supported by the relatively high $\Delta H^\ddagger$ value and positive $\Delta S^\ddagger$ value for the reaction (Table III). The normal activation parameters for a dissociative reaction suggest that NCO$^-$ does not contribute to the energetics of the reaction transition state as it does in the CO substitution reaction (eq 1), although the two reactions may involve the same active intermediate [$Os_3(\mu\text{-}NCO)(CO)_{10}$]$^-$ (Figure 3). The formation of a bridging μ-NCO$^-$ bond in the transition state for PPh$_3$ substitution requires that the terminally bonded NCO$^-$ ligand attack at the metal which is coordinated with the phosphorus ligand. It is expected that the phosphorus ligand would both sterically and electronically retard such a pathway. Therefore, it appears that in the transition state the Os–P bond is largely broken before the μ-NCO$^-$ bridge forms.

The rate of PPh$_3$ substitution of the chloride ion cluster [$Os_3(CO)_{10}(Cl)(PPh_3)$]$^-$ is much faster than that of [$Os_3(CO)_{10}(NCO)(PPh_3)$]$^-$ (Table III). This parallels the reactivity order for CO displacement of the clusters (Table II). Being a better bridging group than NCO$^-$, the Cl$^-$ ligand makes considerable contribution to the energetics of the transition state of PPh$_3$ substitution. As a result of the μ-Cl$^-$ bridging effect on the transition state, the $\Delta H^\ddagger$ value is 5 kcal/mol lower than that for the NCO$^-$ cluster, and the $\Delta S^\ddagger$ value is nearly zero (Table III).

It should also be noted that apart from the metal atoms, the carbon atoms of the carbonyls are also vulnerable to nucleophilic attack. It was reported[10] that the rates of nucleophilic attack of the halide ions at the C atom of a carbonyl group in metal carbonyl complexes decrease in the order Cl > Br > I. The observed reactivity order of [$Os_3(CO)_{11}X$]$^-$ parallels this order of nucleophilicity of halide ions toward attack on a carbonyl carbon. Intramolecular nucleophilic attack on a carbonyl carbon was suggested[24] for the formation of isocyanate from the cross-link reaction of a μ_2-nitrene with a coordinated carbonyl group. The results of this study do not permit one to say if the X ligand first attacks the C atom of an adjacent CO before migrating to the metal to form the active μ-X bridged intermediate (**2**) (Scheme I). Kinetic data for PPh$_3$ substitutions show that direct attack on the metal is a feasible pathway. It can be concluded that *cis* labilization is not responsible for anion catalysis of CO substitution in such metal carbonyl clusters, and it appears catalysis involves an intramolecular displacement process via formation of an intermediate bridged complex.

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