Kinetics and Mechanism of the Addition of Azide Ion to a Carbonyl Ligand of $[Ru_3(CO)_{12}]$: Cluster Activation

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Spectroscopic studies of the reaction of azide ion with the cluster $[Ru_3(CO)_{12}]$ in acetone solvent confirmed the occurrence of process (i) under a CO atmosphere. Kinetic measurements of this rapid

$$[Ru_3(CO)_{12}] + N_3^- \longrightarrow \underset{\mathbf{1}}{[Ru_3(NCO)(CO)_{11}]^-} + N_2 \qquad \text{(i)}$$

reaction revealed the rate law, Rate = $k[Ru][N_3^-]$, and the activation parameters $\Delta H^\ddagger = 61.6 \pm 3.4$ kJ mol^{-1} and $\Delta S^\ddagger = 3.5 \pm 11.8$ J K^{-1} mol^{-1}. These results are consistent with the addition of N_3^- to a CO ligand of $[Ru_3(CO)_{12}]$ to form an intermediate under either steady-state or pre-equilibrium conditions, followed by a Curtius-type rearrangement (k_2) to give the isocyanato complex **1**. In the absence of CO, the product **1** undergoes rapid loss of CO to give the bridged isocyanato complex $[Ru_3(\mu\text{-NCO})(CO)_{10}]^-$. Kinetic studies of reaction (i) in tetrahydrofuran (thf) or thf–MeOH (1:1), in contrast, showed no dependence of rate on azide-ion concentration. This is inconsistent with a steady-state mechanism, but may be rationalised by a pre-equilibrium mechanism provided the condition $K_1[N_3^-] \gg 1$ is met, *i.e.* the pre-equilibrium constant K_1 is large under the kinetic conditions employed.

The use of anionic additives (X^-), including halide, hydroxide, alkoxide and azide ions, to labilise normally inert metal carbonyl clusters such as $[Ru_3(CO)_{12}]$ to carbonyl substitution [equation (1)] has attracted considerable recent interest.[1–9]

$$[Ru_3(CO)_{12}] + L \xrightarrow{X^-} [Ru_3(CO)_{11}L] + CO \qquad (1)$$

This labilisation is significant in several reactions catalysed by metal carbonyl clusters such as the water gas shift reaction and the facile hydrogenation of alkenes using the anionic isocyanato complexes $[M_3(NCO)(CO)_{10}]^-$ (M = Ru or Os).[10] It has been suggested[3,7,10] that metal–carbonyl bond cleavage may be promoted by the formation of intermediate species of the type M–COX. Such species have been characterised spectroscopically for $X^- = MeO^-$ in the reaction of $[M_3(CO)_{12}]$ (M = Ru or Os) with MeO^-, and in the ruthenium case found to undergo subsequent rapid substitution of CO by tertiary phosphites.[11] Alternatively, activation has been ascribed[12] to binding of the anion as an ancillary ligand in the cluster.

A particularly interesting process in this respect is the reaction of azide ion with $[Ru_3(CO)_{12}]$ in tetrahydrofuran (thf) solvent, which has been shown[13] to give the isocyanato complex $[Ru_3(NCO)(CO)_{11}]^-$ **1** in a rapid initial step [equation (2)]. Subsequent CO ligand dissociation led to the

$$[Ru_3(CO)_{12}] + N_3^- \longrightarrow [Ru_3(NCO)(CO)_{11}]^- + N_2 \qquad (2)$$

complex $[Ru_3(\mu\text{-NCO})(CO)_{10}]^-$ **2**, followed by slow (days) conversion into the tetranuclear cluster $[Ru_4(NCO)(CO)_{13}]^-$ **3**. Related reactions have been previously reported[14] between azide ion and mononuclear metal carbonyls to give isocyanato complexes.

In order to throw light on the mechanism of carbonyl-ligand activation in these cluster reactions, we have carried out a detailed kinetic and spectroscopic study of reaction (2) in a range of solvents. The reaction was typically complete in less than 1 min under the conditions employed $\{[N_3^-] = (1\text{–}30) \times 10^{-3}$ mol dm$^{-3}\}$, and under a CO atmosphere no further reaction was observed over several hours. The rate and activation parameters support rapid initial addition of azide to a CO ligand, followed by rate-determining loss of N_2 in a Curtius-type rearrangement to give the $[Ru(NCO)(CO)_{11}]^-$ product.

Experimental

The complex $[Ru_3(CO)_{12}]$ was obtained from Strem Chemicals and used as such, $[N(PPh_3)_2][N_3]$ from Aldrich. AnalaR acetone solvent was used, while thf and methanol were distilled from benzophenone and calcium hydride, respectively. Immediately prior to use, the solvents were deoxygenated by passing through a stream of either carbon monoxide or dinitrogen. Infrared spectra were recorded on a Biorad FTS-7 Fourier-transform spectrophotometer using a calcium fluoride liquid cell with a 0.5 mm path.

Kinetic Studies.—Reaction (2) was studied using a thermostatted (±0.1 °C) stopped-flow spectrophotometer, by monitoring the large increase in absorbance at 370 nm. Each of the reactions was studied under pseudo-first-order conditions by employing a large excess of the N_3^- nucleophile $\{[Ru_3(CO)_{12}] = (2.0\text{–}2.5) \times 10^{-4}$ mol dm^{-3}; $[N_3^-] = (1.0\text{–}30) \times 10^{-3}$ mol dm$^{-3}\}$. In the majority of reactions the reagent solutions were saturated with CO prior to mixing, while in the remainder a dinitrogen atmosphere was employed.

Pseudo-first order rate constants, k_{obs}, were calculated from the slopes of plots of $\log(A_\infty - A_t)$ *vs.* time using a least-squares program. These plots were generally linear for at least two half-lives. Each k_{obs} quoted is the average from at least three separate runs, with an average reproducibility of ±6%. Least-squares analyses of plots of k_{obs} *vs.* $[N_3^-]$ were used to obtain the second-order rate constants, k. The activation parameters for reaction (2) in acetone were calculated from a least-squares analysis of the Eyring equation using the second-order rate constants (k).

Results and Discussion

Nature of the Reactions.—Infrared spectroscopic studies of the reaction of $[N(PPh_3)_2][N_3]$ with $[Ru_3(CO)_{12}]$ in CO-saturated solvent $\{[Ru_3(CO)_{12}] = [N_3^-] = (0.5$ or $1.0) \times 10^{-3}$ mol dm$^{-3}\}$ confirm the rapid formation of the isocyanato complex $[Ru_3(NCO)(CO)_{11}]^-$ **1**. A typical IR spectrum recorded after 1 min at room temperature showed ν(CO) bands at 2100w, 2061m, 2028vs, 2014 (sh) and 1968m cm^{-1}, which are almost identical to those previously reported[13] for $[Ru_3(NCO)(CO)_{11}]^-$ in thf solvent (Table 1). No other ν(CO) bands were noted, indicating a clean reaction as shown in equation (2). In addition, the medium-intensity, broad band at 2230 cm^{-1} confirms the presence of the linear terminally bonded NCO ligand.

No further change occurred in the IR spectrum of this reaction mixture in CO-saturated acetone over another 30 min, confirming that the reaction monitored under the stopped-flow kinetic conditions $\{[Ru_3(CO)_{12}] = 2.5 \times 10^{-4}$ mol dm^{-3}, $[N_3^-] = (2.5–30) \times 10^{-3}$ mol dm$^{-3}\}$ is indeed as in equation (2). However, if argon is bubbled through the above acetone solution of **1** for 5 min the IR spectrum changes rapidly to give bands at 2209ms (sharp), 2230w, 2060s, 2027s, 1996m, 1979m and 1920m cm^{-1}. These spectral changes indicate the partial conversion of **1** into the species $[Ru_3(\mu\text{-}NCO)(CO)_{10}]^-$ **2** (see Table 1 for assignments). Particularly significant is the decrease in the broad terminal ν(NCO) band of **1** at 2230 cm^{-1}, and the appearance of the sharp ν(NCO) band at 2209 cm^{-1} characteristic of the bridging μ-NCO ligand.

This latter conversion **1** $\longrightarrow$ **2**, which involves loss of a CO ligand, can be readily reversed by bubbling CO gas through the reaction mixture for 5 min. The sharp ν(NCO) band of complex **2** disappears together with its ν(CO) bands at 1996, 1979 and 1920 cm^{-1}, and the original spectrum of $[Ru_3(NCO)(CO)_{11}]^-$ **1** is quantitatively regenerated. These overall changes are summarised in Scheme 1.

Analogous IR spectroscopic studies of the reaction between $[N(PPh_3)_2][N_3]$ and $[Ru_3(CO)_{12}]$ in N_2-saturated acetone reveal a more complex situation, with ν(NCO) and ν(CO) bands associated with the previously reported[13] tetrameric cluster $[Ru_4(NCO)(CO)_{13}]^-$ **3** appearing gradually over several hours [2189s, 2030s, 2007s and 1974m (br) cm^{-1}]. A similar, but slower, formation of $[Ru_4(NCO)(CO)_{13}]^-$ from the reaction between azide ion and $[Ru_3(CO)_{12}]$ has been previously described[13] in thf solvent in the absence of a CO atmosphere.

Kinetics and Mechanism.—Kinetic data for reaction (2) in CO-saturated acetone at various temperatures and azide-ion concentrations are summarised in Table 2 and Fig. 1. These data conform to rate law (3) where $k_{obs} = k[N_3^-]$. This rate law

$$\text{Rate} = k_{obs}[Ru_3(CO)_{12}] \quad (3)$$

is also followed for the corresponding reaction in N_2-saturated acetone (Table 2). The similarity of the rate constants obtained at 24.9 °C under both CO and N_2 suggests that the subsequent transformations of the initial $[Ru_3(NCO)(CO)_{11}]^-$ product observed under N_2 do not interfere with the stopped-flow monitoring of reaction (2).

The observed rate law is consistent with the mechanism outlined in Scheme 2, involving initial addition of azide ion to the CO ligand of $[Ru_3(CO)_{12}]$ followed by a Curtius-type rearrangement of the intermediate **4**. Assuming a steady-state concentration for intermediate **4**, the general expression (4) is derived for this scheme. Provided that $k_2 \gg k_{-1}$, equation (4) reduces to (5), consistent with the observed rate law (3). In this case the calculated second-order rate constants, k, in Table 2 refer to the bimolecular addition (k_1) of N_3^- to a CO ligand. In contrast, if $k_{-1} \gg k_2$, equation (4)

$$k_{obs} = \frac{k_1 k_2 [N_3^-]}{k_{-1} + k_2} \quad (4)$$

$$k_{obs} = k_1[N_3^-] \quad (5)$$

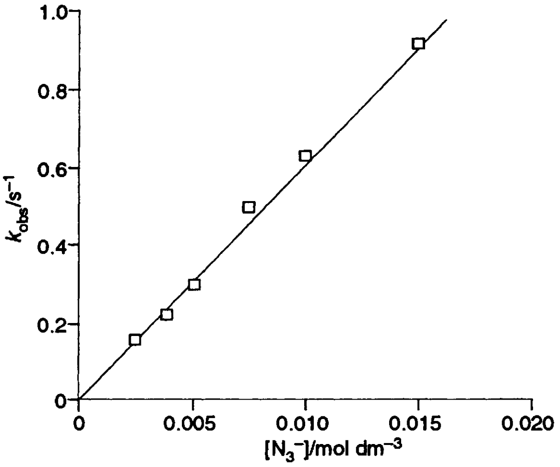
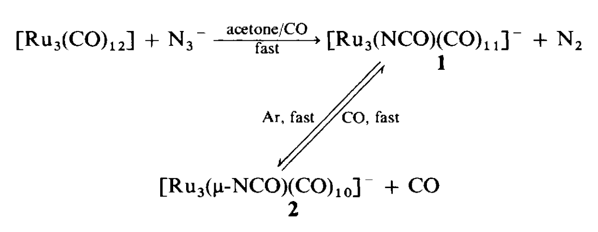
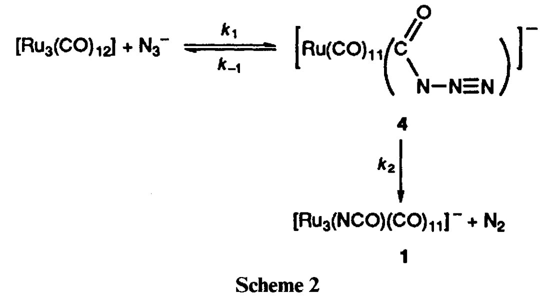


Fig. 1 Dependence of k_{obs} on $[N_3^-]$ for the reaction of $[Ru_3(CO)_{12}]$ with $[N(PPh_3)_2][N_3]$ in CO-saturated acetone at 11.7 °C



Scheme 1



Scheme 2

Table 1 Infrared spectra of cluster complexes

Complex	Solvent	ν̃(NCO)/cm^{-1}	ν̃(CO)/cm^{-1}	Ref.
1 $[Ru_3(NCO)(CO)_{11}]^-$	Acetone	2230m (br)	2100w, 2061m, 2028vs, 2014 (sh), 1968m	This work
	thf	2230m (br)	2098vw, 2060m, 2028vs, 2011s, 1963m	11
2 $[Ru_3(\mu\text{-}NCO)(CO)_{10}]^-$	Acetone	2209ms	2060s, 2027s, 1996m, 1979m, 1920m	This work
	thf	2209s	2068m, 2025s, 1985s (br), 1910m	11
3 $[Ru_4(NCO)(CO)_{13}]^-$	Acetone	2189s	2030s, 2007s, 1974m (br)	This work
	thf	2189s	2061vw, 2028s, 2004vs, 1970m (br), 1945 (sh)	11

Table 2 Kinetic results for the reaction of $[Ru_3(CO)_{12}]$ with $[N(PPh_3)_2][N_3^-]$ in acetone; $[Ru] = 2.5 \times 10^{-4}$ mol dm^{-3}

T/°C	$10^3[N_3^-]$/ mol dm^{-3}	k_{obs}/s^{-1}	k*/dm^3 mol^{-1} s^{-1}
CO-Saturated solvent			
0.8	5.0	0.085	
4.8	5.0	0.092	
7.6	5.0	0.129	
8.3	5.0	0.142	
11.7	2.5	0.157	62.2 (1.9)
	3.75	0.215	
	5.0	0.298	
	7.5	0.494	
	10.0	0.630	
	15.0	0.917	
18.2	5.0	0.357	
19.2	5.0	0.430	
22.5	5.0	0.640	
24.9	5.0	0.730	
26.9	5.0	0.824	
28.5	5.0	0.945	
N_2-Saturated solvent			
24.9	2.5	0.280	141 (9)
	5.0	0.690	
	7.5	0.964	
	11.0	1.70	
	12.5	1.98	
	16.0	2.61	
	25.0	3.16	
	30.0	4.42	

* Values in brackets are the standard deviations derived from least-squares analyses.

simplifies to (6), in which the calculated second-order rate

$$k_{obs} = K_1k_2[N_3^-] \qquad (6)$$

constants, k, equate to K_1k_2, *i.e.* the product of the equilibrium constant (K_1) for formation of intermediate **4** and its unimolecular rearrangement (k_2).

The transition state for the rearrangement process, $k_2(\mathbf{4} \longrightarrow \mathbf{1})$, cannot be unambiguously assigned, but may involve a structure such as **5**. This involves partial cleavage of the Ru–C(O)N_3 bond and dissociative release of N_2, together with bond formation between the nascent NCO ligand and an adjacent ruthenium atom and concomitant movement of a CO ligand on this Ru atom to a bridging position. One further terminal-to-bridging CO rearrangement is needed to give the final product $[Ru(NCO)(\mu\text{-}CO)_2(CO)_9]^-$ **1**, for which the structure shown has been previously proposed.[13]

The relatively low enthalpy of activation, $\Delta H^\ddagger$, of 61.6 ± 3.4 kJ mol^{-1} calculated for reaction (2) in CO-saturated acetone is consistent with bimolecular nucleophilic addition at a CO ligand. However, the $\Delta S^\ddagger$ value of 3.5 ± 11.8 J K^{-1} mol^{-1} is not as negative as might be expected for a simple bimolecular addition, k_1. This may arise from a positive contribution from desolvation of the azide ion in achieving the transition state. Alternatively, it may be rationalised in terms of the limiting situation (6), where $k = K_1k_2$, and the observed entropy of activation, $\Delta S^\ddagger$, is given by equation (7); $\Delta S^\ddagger$ would be expected

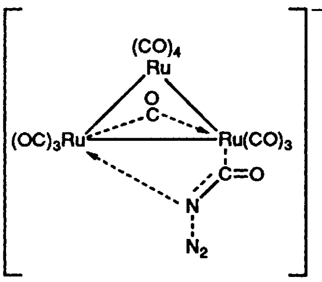
$$\Delta S^\ddagger = \Delta S^\circ_1 + \Delta S^\ddagger_2 \qquad (7)$$

to include a significant positive contribution from $\Delta S^\ddagger_2$ for the step k_2 if Ru–C and N–N bond cleavage in transition state **5** are more advanced than formation of the bond between Ru and the nascent NCO ligand. Interestingly, we have also recently obtained[15] a small positive $\Delta S^\ddagger$ value for the addition of azide ion to a CO ligand of the complex $[Fe(\eta\text{-}C_5H_5)(CO)_3]^+$ in acetone–methanol (1 : 1) solvent.

Table 3 Kinetic results for the reaction of $[Ru_3(CO)_{12}]$ with NaN_3 in various solvents; $[Ru] = 2.0 \times 10^{-4}$ mol dm^{-3}

Solvent	T/°C	$10^3[N_3^-]$/ mol dm^{-3}	k_{obs}/s^{-1}
thf[a]	25.2	1.02[b]	0.350
		3.00	0.259
		4.00	0.249
thf–MeOH (1:1)	0.0	1.0	0.191
		2.0	0.208
		10.0	0.183
		30.0	0.214
	25.0	5.0	2.03
MeOH	25.0	1.0	8.8
		2.0	10.1
		4.0	8.9
		6.0	10.8

[a] Solvent CO-saturated. [b] $[Ru] = 1.5 \times 10^{-4}$ mol dm^{-3}.



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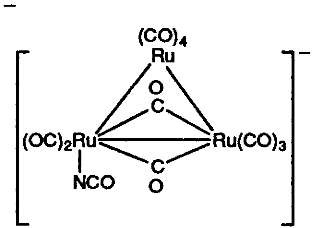

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An alternative mechanism involving the rapid pre-equilibrium formation of intermediate **4**, followed by a slow rearrangement to product **1**, would give rise to the general rate equation (8).

$$k_{obs} = \frac{K_1k_2[N_3^-]}{1 + K_1[N_3^-]} \qquad (8)$$

Providing $K_1[N_3^-] \ll 1$ (*i.e.* $K_1 \leqslant 0.3$ dm^3 mol^{-1}) this again reduces to the observed form (3). However, if $K_1[N_3^-] \gg 1$ then $k_{obs} = k_2$, and no dependence of k_{obs} on $[N_3^-]$ is anticipated. This latter condition clearly does not hold for reaction (2) in acetone solvent.

In marked contrast to the above results in acetone, kinetic data summarised in Table 3 for reaction (2) in thf or thf–MeOH (1 : 1) as solvent reveal no dependence of k_{obs} on $[N_3^-]$. This cannot be explained by a steady-state mechanism, but is consistent with a pre-equilibrium mechanism where $K_1[N_3^-] \gg 1$, *i.e.* $K_1 > 10^3$ dm^3 mol^{-1}. The observed rate constants would consequently refer to the unimolecular rearrangement, k_2. In earlier studies[11] of the related addition of methoxide ion to $[Ru_3(CO)_{12}]$, a large equilibrium constant K_1 of *ca.* 5×10^3 dm^3 mol^{-1} was in fact observed for the formation of the relatively stable intermediate species $[Ru_3(CO)_{11}(CO_2Me)]^-$. Unfortunately, extension of our kinetic studies of reaction (2) to considerably lower $[N_3^-]$ values [where the general pre-equilibrium rate equation (8) might reduce to the form (6)] were hampered by the small absorbance changes observed using the lower $[Ru_3(CO)_{12}]$ concentrations required for pseudo-first-order conditions.

The results in Table 3 reveal a significant dependence of the rearrangement rate constant, k_2, on the nature of the solvent (MeOH > thf–MeOH(1 : 1) > thf; 37 : 7 : 1). The order parallels the Gutmann acceptor numbers[16] for these solvents (MeOH 41.3, thf 8), and is the reverse of that expected on solvation grounds for the preceding azide addition step (k_1).

Finally, the rapid (< 5 min) room-temperature conversion of complex **1** into **2** observed here upon passing a stream of argon through an acetone solution of $[Ru_3(NCO)(CO)_{11}]^-$ **1** confirms the marked activation of the ruthenium cluster towards CO ligand loss achieved *via* initial addition of N_3^-. The initial activation step in equation (2) has a low enthalpy of activation ($\Delta H^\ddagger = 61.6$ kJ mol^{-1}), which contrasts with the high activation energies and temperatures generally required[17,18] for CO substitution with unactivated $[Ru_3(CO)_{12}]$.

Detailed kinetic studies of the subsequent facile CO substitution reactions of the anion $[Ru_3(NCO)(CO)_{11}]^-$ {*e.g.* $\mathbf{1} \longrightarrow [Ru_3(\mu\text{-NCO})(CO)_{10}]^-$} are planned in order to provide further light on the activation process. Recent kinetic studies by Shen and Basolo[9] on the substitution reactions of the related osmium complexes $[Os_3X(CO)_{11}]^-$ ($X^- = Cl^-$, Br^-, I^- or NCO^-) suggest that CO labilisation is achieved by the formation of reactive μ-X intermediates rather than *via cis* labilisation by the anions X^-.

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