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Mechanisms of Organometallic Substitution Reactions.
Part 3.[a] Kinetics of the Reaction of Organonitriles with Tricarbonyl(cycloheptatriene) Complexes of Metals in Group VI

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A kinetic study of the displacement of cycloheptatriene from $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ *(M = Cr, Mo. W) by benzonitrile shows unusual changes in rate law down the triad. While the chromium complex obeys the second-order rate law Rate =* $k[\text{complex}][RCN]$, *the molybdenum species follows the third-order law Rate =* $k[\text{complex}][RCN]^2$. *With tungsten kinetic behaviour intermediate between these two extremes is observed. These results are rationalised by a general mechanism involving stepwise attack by two benzonitrile nucleophiles via the steady-state intermediate* $[(\eta^4\text{-}C_7H_8)M(CO)_3(RCN)]$. *Attack by a third benzonitrile rapidly leads to the products.*

Analogous kinetic studies of the reaction of $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ *(M = Cr, Mo) with* o*-toluonitrile and 1,3,5-trimethylbenzonitrile give more complex behaviour. While second-order kinetics are uniformly observed with chromium, the rate law with molybdenum varies from third-order at* $[RCN] \leqslant 0.2$ *mol* dm^{-3} *to second-order at higher [RCN]. Electronic factors are seen to be more important than steric considerations in these reactions.*

Introduction

A recent kinetic study [1] of the displacement of the cycloheptatriene ligand from the complex $[(\eta^6\text{-}C_7H_8)Mo(CO)_3]$ by acetonitrile (eqn 1, M = Mo, R = Me) unexpectedly revealed the third-order rate law

$$[(C_7H_8)M(CO)_3] + 3RCN \rightarrow cis\text{-}[(RCN)_3M(CO)_3] + C_7H_8 \qquad (1)$$

(2). This rate order was interpreted in terms of the pre-equilibrium formation of a seven-coordinate intermediate, followed by rate-determining attack by a second acetonitrile molecule. In contrast previous studies of ring displacement reactions by phosphorus nucleophiles on $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ (M = Cr, Mo, W) and related arene systems [2–4] had shown the expected second-order kinetics.

$$\text{Rate} = k[\text{Complex}][CH_3CN]^2 \qquad (2)$$

We have now determined the rate law for reaction (1, RCN = benzonitrile) with each of the metals Cr, Mo, and W. Interestingly, while removal of cycloheptatriene from the Mo complex again follows rate law (2), with the chromium substrate a first-order dependence on [RCN] is observed. Tungsten exhibits a kinetic behaviour intermediate between chromium and molybdenum.

Similar kinetic studies of the analogous reactions of $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ (M = Cr, Mo) with *o*-toluonitrile and 1,3,5-trimethylbenzonitrile throw further light on the factors contributing to this unusual change in rate law down the triad. In particular, the relative importance of steric and electronic effects in reaction (1) is investigated.

Experimental

The complexes $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ (M = Cr, Mo, W) were prepared by published methods [5, 6] and purified by recrystallisation from light petroleum (60–80 °C) (Cr, Mo) or sublimation (W, 60 °C, 0.05 mm). [Calcd. for $C_{10}H_8O_3Cr$: C, 52.7; H, 3.5. Found: C, 52.1; H, 3.4%. Calcd. for $C_{10}H_8O_3Mo$: C, 44.2; H, 3.0. Found: C, 44.0; H, 2.9%. Calcd. for $C_{10}H_8O_3W$: C, 33.3; H, 2.2. Found: C, 33.2; H, 2.4%]. Benzonitrile and *o*-toluonitrile were freshly distilled before use, while the dichloroethane solvent was distilled in bulk and stored over molecular sieves.

Kinetic Procedure

All reactions were studied under pseudo first-order conditions using a large excess of nucleophile. Solution preparation and i.r. sampling techniques have been previously described [7], the reactions being generally monitored by following the decrease of the

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[a] Part 2. K. M. Al-Kathumi and L. A. P. Kane-Maguire, *J. Chem. Soc. Dalton,* 428 (1974).

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TABLE I. Kinetic Results for Reaction of Benzonitrile with $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ Complexes.

Complex	[PhCN] /mol dm^{-3}	Temp./°C	10^5 k_{obs}/s^{-1}
$[(\eta^6\text{-}C_7H_8)Cr(CO)_3]$	0.50	70.0	2.54
	1.00	70.0	6.45
	1.50	70.0	8.55
	2.00	70.0	12.8
	2.00	59.4	5.70
	2.00	63.7	7.76
	2.00	78.0	24.9
	1.00	45.0	0.68
$[(\eta^6\text{-}C_7H_8)Mo(CO)_3]$	0.10	21.3	4.50
	0.20	21.3	19.9
	0.30	21.3	40.1
	0.35	21.3	57.5
	0.40	21.3	79.2
	0.10	30.1	9.94
	0.10	35.1	13.6
	0.10	40.1	19.5
	0.10	46.0	26.8
$[(\eta^6\text{-}C_7H_8)W(CO)_3]$	0.30	44.8	4.19
	0.50	44.8	9.75
	0.80	44.8	20.8
	1.00	44.8	32.2

strong tricarbonyl(cycloheptatriene)metal band at *ca.* 1990 cm^{-1} using a Perkin-Elmer 257 spectrophotometer. Pseudo first-order rate constants were calculated from the slopes of plots of log A_t *versus* time, where A_t = absorbance at time t of the reaction solution at 1990 cm^{-1}.

However, the reactions of $[(\eta^6\text{-}C_7H_8)Mo(CO)_3]$ with *o*-toluonitrile and 1,3,5-trimethylbenzonitrile when [RCN] $\geqslant$ 0.4 mol dm^{-3} were too rapid to follow by the above i.r. sampling technique. Instead they were monitored using a Beckman DK2A spectrophotometer fitted with a thermostatted cell block. The solvent and *o*-toluonitrile were thoroughly degassed under vacuum (10^{-3} torr) prior to use, since the presence of small amounts of oxygen was shown to lead to irreproducible results. Reaction solutions ([Mo] = 1×10^{-4} mol dm^{-3}) were prepared and placed in a stoppered 1 cm quartz cell under an atmosphere of nitrogen. The cell was then rapidly transferred to the thermostatted block and the decrease of the original complex band at 325 nm followed. Pseudo first-order rate constants were calculated from the slopes of plots of log $(A_t - A_\infty)$ *versus* time.

Activation parameters were calculated by a least squares fit to the Arrhenius equation. The errors quoted are the standard deviations obtained from the least squares analyses. Entropies of activation were calculated after conversion of the observed rate constants to the appropriate second- or third-order rate constants.

Results and Discussion

Nature of the Reactions

While the stoichiometry of reaction (1) is well-established [8, 9], it should be noted that during some kinetic runs with each of the nitriles i.r. peaks due to $[(RCN)_2M(CO)_4]$ and $[(RCN)M(CO)_5]$ were also observed. In our earlier study [1] of the analogous acetonitrile reactions, these tetra- and penta-carbonyl species were shown to arise from disproportionation of the initial $[(RCN)_3M(CO)_3]$ product in the presence of traces of oxygen. Such disproportionation of the tricarbonyl product is the probable cause of the negative deviation from first-order kinetics sometimes observed here after *ca.* 50–60% of reaction for attack of nitriles on $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ (M = Cr, Mo). At long reaction times the subsequent growth of the $[(RCN)M(CO)_5]$ band at *ca.* 1945 cm^{-1} will partly mask the disappearance of the starting material peak at *ca.* 1990 cm^{-1}, which was used to monitor the reactions. Support for this explanation comes from the reaction of benzonitrile on $[(\eta^6\text{-}C_7H_8)W(CO)_3]$ where good first-order kinetics were obtained for at least 75% of reaction. Here, only minor amounts of $[(PhCN)_2W(CO)_4]$ and $[(PhCN)W(CO)_5]$ were observed at long reaction times, which is consistent with independent experiments showing $[(RCN)_3W(CO)_3]$ species to be much more stable towards oxygen than their chromium and molybdenum analogues.

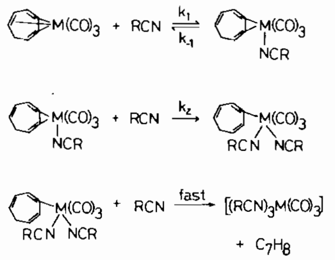
Kinetics and Mechanism

The kinetic results in Table I for the reaction of benzonitrile with $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ (M = Cr, Mo, W) reveal an interesting dependence of the rate law on the nature of the metal. The molybdenum complex obeys the third-order rate law (2) previously found [1] for the analogous reaction with acetonitrile. In contrast, the simple second-order rate law (3) is followed by chromium. With the tungsten compound a nucleophile dependence intermediate between eqns. (2) and (3) is indicated.

$$\text{Rate} = k[\text{complex}][\text{RCN}] \qquad (3)$$

An explanation for this unusual change in rate law may be sought in terms of the general mechanism (Scheme 1) previously proposed [1] for the acetonitrile reaction. If one assumes the rapid pre-equilibrium formation of intermediate (I) followed by rate-determining attack of a second nitrile ligand, the rate law (4) is derived (where $K_1 = k_1/k_{-1}$). Alternatively, the assumption of a steady-state concentration for the intermediate (I) leads to the rate expression (5):

$$k_{obs} = \frac{k_1k_2[\text{RCN}]^2}{k_{-1} + k_2[\text{RCN}]} \qquad (5)$$



(I)

Scheme 1.

$$k_{obs} = \frac{k_2K_1[\text{RCN}]^2}{1 + K_1[\text{RCN}]} \qquad (4)$$

Either mechanism can explain the first-order dependence of k_{obs} on [PhCN] observed for chromium. Thus, provided $K_1[\text{RCN}] \gg 1$, eqn. (4) simplifies to rate law (6). Similarly, the steady-state expression (5) collapses to eqn. (7) under the limiting condition $k_2[\text{RCN}] \gg k_{-1}$. However, in order for the pre-equilibrium mechanism to obey eqn. (6) over the [PhCN] range studied (0.50–2.0 mol dm^{-3}) it is necessary that $K_1 \gg 2$ mol^{-1} dm^3. Under the conditions employed in Table I, the intermediate (I) will therefore predominate in the pre-equilibrium. Since no spectroscopic evidence has been found for this intermediate, the steady-state mechanism seems more reasonable.

$$k_{obs} = k_2[\text{RCN}] \qquad (6)$$

$$k_{obs} = k_1[\text{RCN}] \qquad (7)$$

The steady-state approach also provides a more plausible rationale for the more complex kinetic behaviour of the related molybdenum and tungsten complexes. The second-order dependence of k_{obs} on [PhCN] observed for the molybdenum complex (Table I) is explained provided $k_2[\text{RCN}] \ll k_{-1}$, which causes the general expression (5) to simplify to eqn. (8). On the other hand, the intermediate behaviour of the tungsten compound indicates that here $k_2[\text{RCN}]$ and k_{-1} are of similar magnitude, *i.e.* the general rate law (5) is followed.

$$k_{obs} = \frac{k_1k_2[\text{RCN}]^2}{k_{-1}} \qquad (8)$$

Inverting and rearranging eqn. (5) leads to expression (9). Thus a plot of $[\text{RCN}]/k_{obs}$ *versus* $1/[\text{RCN}]$ should be linear with an intercept equal to $1/k_1$. The kinetic results in Table I for tungsten give a reasonable fit to eqn. (9), from which a value for k_1 of *ca.* 6.7×10^{-4} mol^{-1} dm^3 s^{-1} is estimated at 44.8 °C. This compares with a k_1 of 6.8×10^{-4} mol^{-1} dm^3 s^{-1} calculated for the analogous chromium reaction assuming the steady-state rate law (7). Similar k_1 values for the chromium and tungsten complexes are compatible with previous data [2, 7] showing that substitution rates at the Group VI metals usually decrease in the order Mo ≫ Cr ~ W.

$$\frac{[\text{RCN}]}{k_{obs}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_2[\text{RCN}]} \qquad (9)$$

Although the pre-equilibrium mechanism would also predict such an inverse plot for the tungsten complex $\{[\text{RCN}]/k_{obs} = 1/k_2 + 1/(k_2K_1[\text{RCN}])\}$, combination of the intercept and gradient values leads to a K_1 value of *ca.* 0.83 mol^{-1} dm^3, which seems inconsistent with the lack of spectroscopic evidence for (I).

The kinetic results in Table II for reaction (1; RCN = *o*-toluonitrile and 1,3,5-trimethylbenzonitrile; M = Cr, Mo) throw further light on the factors contributing to this unusual change in rate law down the triad. Each increase in steric bulk in these methyl-substituted benzonitriles is accompanied by an increase in electron density at the donor nitrogen atom. As expected for chromium, the rate law (7)

TABLE II. Kinetic Results for Reactions of *o*-Toluonitrile and 1,3,5-Trimethylbenzonitrile with $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ Complexes.

Complex	Nitrile	[RCN]/mol dm^{-3}	Temp./°C	10^5 k$_{obs}$/s^{-1}
$[(\eta^6\text{-}C_7H_8)Cr(CO)_3]$	*o*-$CH_3C_6H_4CN$	0.5	70.0	3.44
		1.00	70.0	7.21
		1.50	70.0	11.0
		2.00	70.0	14.9
		1.00	45.0	0.76
		2.00	45.0	1.50
	$(CH_3)_3C_6H_2CN$	1.00	45.0	1.21
		2.00	45.0	2.49
$[(\eta^6\text{-}C_7H_8)Mo(CO)_3]$	*o*-$CH_3C_6H_4CN$	0.05	23.4	3.00
		0.10	23.4	7.90
		0.15	23.4	16.8
		0.20	23.4	23.8
		0.30	23.4	66.0
		0.60	23.4	174[a]
		1.00	23.4	232[a]
		0.10	25.0	11.2
		0.10	30.0	16.3
		0.10	35.0	23.1
		0.10	40.0	28.7
		0.10	45.0	39.4
	$(CH_3)_3C_6H_2CN$	0.05	30.0	8.27
		0.10	30.0	34.9
		0.15	30.0	59.4
		0.20	30.0	95.5
		0.40	30.0	240[a]
		0.70	30.0	470[a]
		0.05	45.0	22.6
		0.10	45.0	76.5

[a] Determined by u.v.–visible spectroscopy.

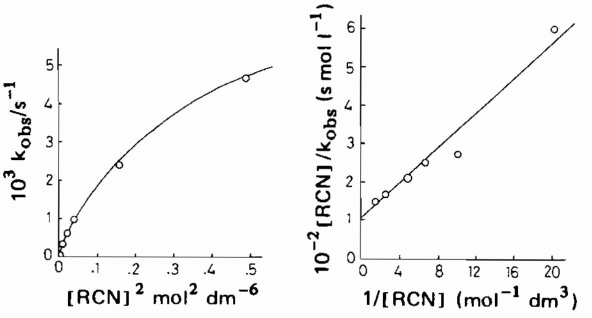


Fig. 1. Reaction of 1,3,5-trimethylbenzonitrile with $[(\eta^6\text{-}C_7H_8)Mo(CO)_3]$ in dichloroethane at 30.0 °C. (a) Plot of k$_{obs}$ *versus* $[RCN]_2$, (b) plot of [RCN]/k$_{obs}$ *versus* 1/[RCN].

was again observed with each of these more sterically demanding nitriles (with [RCN] as high as 2.0 mol dm^{-3}). In the molybdenum case the situation is more complex (*e.g.* Fig. 1a). For [RCN] $\leqslant$ 0.2 mol dm^{-3} these bulky nitriles approximate the second-order dependence on [RCN] found above with benzonitrile. However, at higher [RCN] the rate law tends towards the simple first-order dependence (7). This behaviour indicates the general rate law (5), which is confirmed by the linearity of plots of [RCN]/k$_{obs}$ *versus* 1/[RCN] (*e.g.* Fig. 1b). From the intercepts of these inverse plots for molybdenum a k_1 value of 3.6×10^{-3} mol^{-1} dm^3 s^{-1} is estimated at 23.4 °C for *o*-toluonitrile, and a k_1 of 9.8×10^{-3} mol^{-1} dm^3 s^{-1} at 30.0 °C for 1,3,5-trimethylbenzonitrile.

This variation in rate law for molybdenum with the nature of the nitrile nucleophile may be rationalised in terms of the steady-state mechanism in Scheme 1. Whereas the condition $k_2[RCN] \ll k_{-1}$ must hold over the entire concentration range studied for benzonitrile ([PhCN] as high as 0.4 mol dm^{-3}), with the methyl-substituted benzonitriles $k_2[RCN] \gg k_{-1}$ at [RCN] values larger than 0.2 mol dm^{-3}. This difference would not be anticipated on steric grounds, since k_{-1} would be expected to be larger and k_2 smaller with the bulkier nitriles. On the other hand, it is consistent with the greater basicity of the methyl-substituted nitriles.

The decrease in k_1 for the $[(\eta^6\text{-}C_7H_8)Cr(CO)_3]$ complex down the series 1,3,5-$(CH_3)_3C_6H_2CN$ >

TABLE III. Comparison of Rate and Activation Parameters for Reactions of Nitriles ([RCN] = 1 mol dm^{-3}) with $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ Complexes.

Complex	Nucleophile	$10^4\ k_{obs}/s^{-1}$ (45 °C)	$\Delta H^{\ddagger}_{obs}$/kJ mol^{-1}	$\Delta S^{\ddagger}_{obs}$/J K^{-1} mol^{-1}
$[(\eta^6\text{-}C_7H_8)Cr(CO)_3]$	CH_3CN^a	0.09	90.2 ± 4.1	−63 ± 13
	C_6H_5CN	0.068	74.8 ± 2.1	−109 ± 6
	$o\text{-}CH_3C_6H_4CN$	0.076		
	$(CH_3)_3C_6H_2CN$	0.12		
$[(\eta^6\text{-}C_7H_8)Mo(CO)_3]$	CH_3CN^a	154	47.3 ± 2.5	−130 ± 8
	C_6H_5CN	245^b	53.4 ± 2.9	−109 ± 8
	$o\text{-}CH_3C_6H_4CN$	394	46.0 ± 2.1	−130 ± 6
	$(CH_3)_3C_6H_2CN$	765		
$[(\eta^6\text{-}C_7H_8)W(CO)_3]$	CH_3CN^a	1.25	43.5 ± 2.5	−181 ± 8
	C_6H_5CN	3.22		

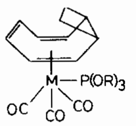
[a] Ref. 1. [b] Extrapolated from results in Table I.

$o\text{-}CH_3C_6H_4CN \geqslant C_6H_5CN$ (1.8:1.1:1; Table III) is also inconsistent with steric control of reactions (1), which would have predicted the reverse order. However, although the observed order is that expected on electronic grounds, the rather small variation with the nature of the nitrile suggests some balancing of steric and electronic factors.

Table III summarises the rate and activation parameters for the reactions of each of the nitriles [(RCN] = 1 mol dm^{-3}) with the $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ (M = Cr, Mo, W) complexes. Direct comparisons between the various metals are not possible because of the different rate laws involved. However, the relatively slow rates for chromium (where k_{obs} refers to k_1) are consistent with the high enthalpies of activation, while the large negative $\Delta S^{\ddagger}_{obs}$ values are as expected for an associative process. Similarly, the large negative entropies of activation observed for the molybdenum and tungsten complexes are consistent with the general mechanism in Scheme 1.

While all of the above observations may thus be accomodated by the general mechanism in Scheme 1, it is not immediately clear why the k_2/k_{-1} ratios vary down the triad in the manner described. Predictions are difficult since each of the primary processes k_1, k_{-1}, and k_2 in Scheme 1 involve both formation of a metal–nitrile bond and cleavage of a metal–olefin bond (or *vice versa*). The k_2/k_{-1} ratio for each metal will be dependent on the relative importance of bond-making or -breaking in each primary process.

Finally, the present results contrast sharply with previous kinetic studies [2, 3] of the corresponding reactions of trimethylphosphite with $[(\eta^6\text{-}C_7H_8)M(CO)_3]$ (M = Cr, Mo, W), which showed $k_{obs} \propto [P(OMe)_3]$ for all the metals over a wide range of phosphite concentrations. It has been suggested [1] that these differences may arise from steric difficulty in forming intermediates of the type (I) with trimethylphosphite. However, very similar species of the type (II; M = Mo, W) have recently been isolated [10]. It therefore seems likely that the phosphite reactions also proceed via a mechanism analogous to Scheme 1, where $k_{-1} \ll k_2[P(OMe)_3]$ for all metals. Failure to fulfil this latter condition in the present study except with chromium probably reflects the poorer nucleophilicity of nitriles compared with trimethylphosphite.



(II)

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