Mechanisms of Organometallic Reactions. Part II.[1] Kinetics of the Reaction of Acetonitrile with Tricarbonyl-(cycloheptatriene) and -(arene) Complexes of Metals in Group VI

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Kinetic studies of the reaction of acetonitrile with $[(C_7H_8)M(CO)_3]$ (M = Cr, Mo, or W) complexes show the third-order rate law, Rate = k[Complex][MeCN]^2. This order is explained in terms of a mechanism involving pre-equilibrium association between the complex and acetonitrile, followed by rate-determining addition of a second molecule of MeCN. The ease of cycloheptatriene displacement varies with the nature of the metal in the order Mo > W > Cr. In contrast, similar studies of the reaction of acetonitrile with the complex $[(C_6H_3Me_3)Mo(CO)_3]$ indicate the second-order rate law, Rate = k[Complex][MeCN]. The change in mechanism is rationalised in steric terms. Comparison with previous data for the corresponding reaction of acetonitrile with the cation $[(C_7H_7)Mo(CO)_3]^+$ suggest the order $C_7H_8 > C_6H_3Me_3 > C_7H_7$ for ease of displacement of π-bonding organic ligands from $[LMo(CO)_3]^{n+}$ (n = 0 or 1) species.

A RECENT study [1] of the kinetics of the reaction of MeCN with the complexes $[(C_7H_7)M(CO)_3]BF_4$ (M = Cr, Mo, or W) indicated displacement of the tropylium ligand *via* S_N2 attack at the metal. These results prompted us to investigate related reactions of acetonitrile with tricarbonyl(cycloheptatriene) complexes of metals in Group VI, which are reported [2] to proceed cleanly according to equation (1). Reaction (1) has been shown

$$[(C_7H_8)M(CO)_3] + 3MeCN \longrightarrow cis\text{-}[(MeCN)_3M(CO)_3] + C_7H_8 \quad (1)$$

to be kinetically third order, allowing an assignment of the reaction mechanism. The corresponding reaction of acetonitrile with some tricarbonyl(arene) metal complexes was also investigated. From these studies it has been possible to determine the relative ease of nucleophilic displacement of tropylium, cycloheptatriene, and arene moieties from metal tricarbonyl units. The results are also compared with recent studies [3,4] of the reaction of the strong nucleophile trimethyl phosphite with cycloheptatriene and arene complexes.

EXPERIMENTAL

The complexes $[(C_7H_8)M(CO)_3]$ (M = Cr, Mo, or W) were prepared from the metal hexacarbonyls or $[(MeCN)_3M(CO)_3]$ using published procedures.[5,6] They were recrystallised from light petroleum (60—80 °C) until analytically pure {Found: C, 52·9; H, 3·6. $[(C_7H_8)Cr(CO)_3]$ requires C, 52·7; H, 3·5. Found: C, 44·6; H, 3·1. $[(C_7H_8)Mo(CO)_3]$ requires C, 44·2; H, 3·0. Found: C, 34·0; H, 2·2. $[(C_7H_8)W(CO)_3]$ requires C, 33·4; H, 2·2%}. The solvents acetonitrile and dichloroethane were distilled and stored over molecular sieves. Benzonitrile was distilled immediately prior to use. All solvents were deoxygenated by passing through a stream of nitrogen for 20 min prior to use.

Kinetic Studies.—All reactions were studied under an atmosphere of nitrogen and in the absence of light. Solution preparation and sampling techniques have been previously

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[1] Part I, K. M. Al-Kathumi and L. A. P. Kane-Maguire, *J.C.S. Dalton*, 1973, 1683.

[2] H. Werner, K. Deckelmann, and U. Schonenberger, *Helv. Chim. Acta*, 1970, **53**, 2002.

[3] A. Pidcock and B. W. Taylor, *J. Chem. Soc. (A)*, 1967, 877.

[4] A. Pidcock, J. D. Smith, and B. W. Taylor, *J. Chem. Soc. (A)*, 1967, 872; 1969, 1604.

[5] R. B. King, 'Organometallic Syntheses,' Academic Press, New York, 1965, vol. 1, p. 123.

[6] R. B. King, *J. Organometallic Chem.*, 1967, **8**, 139.

described.[1,7] The reactions were studied by following the decrease of the strong tricarbonyl(cycloheptatriene)- and arene(tricarbonyl)-metal bands at *ca.* 1 990 and 1 970 cm^{-1}, respectively, using a Perkin-Elmer 257 spectrophotometer. These bands were sufficiently separated from any of the product carbonyl bands as to avoid complications. During the reaction the only product carbonyl bands which appeared were assigned to $[M(CO)_{6-x}(MeCN)_x]$ (x = 1—3) species from their published spectra.[8,9] Blank determinations using only 1,2-dichloroethane as solvent established that no decomposition occurred for the complex $[(C_7H_8)Cr(CO)_3]$ over 1 day at 70 °C. Pseudo-first-order rate constants were obtained from gradients of plots of log A_t against time, where A_t = absorbance at time t of the reaction solution at *ca.* 1 990 cm^{-1} (or *ca.* 1 970 cm^{-1}).

RESULTS

With each of the reactions investigated linear first-order kinetics were generally obeyed for at least two half-lives. Data were obtained for the complexes $[(C_7H_8)M(CO)_3]$ (M = Cr or W) in both pure acetonitrile (19·1M) and mixed acetonitrile–dichloroethane solvents (Table 1). For the complex $[(C_7H_8)Mo(CO)_3]$ reaction with neat MeCN was too rapid to follow by conventional techniques, and all data are for [MeCN] < 0·8M (Table 1). All rate constants are the average of duplicate determinations (reproducibility ±5%).

TABLE 1

k_{obs} Values for reaction of acetonitrile with tricarbonyl(cycloheptatriene)metal complexes. [Complex] = 5 × 10^{3}M

Solvent	[MeCN]/M	t/°C	10k/s^{-1}
	$[(C_7H_8)Cr(CO)_3]$		
$C_2H_2Cl_2$	0·955	51·4	0·144
		59·5	0·440
		70·5	0·980
		80·0	2·47
	7·64	51·4	0·84
	15·3	51·4	2·26
MeCN	19·1	30·2	0·420
		40·2	1·01
		45·0	2·41
		50·1	3·52
	$[(C_7H_8)Mo(CO)_3]$		
$C_2H_2Cl_2$	0·191	21·3	2·10, 2·41 [a]
		30·3	3·54
		40·1	6·37
		50·0	13·1
		21·0	1·38 [b]
	$[(C_7H_8)W(CO)_3]$		
		35·2	0·73
$C_2H_2Cl_2$	0·955	45·0	1·25
		55·2	2·03
		59·0	2·78

[a] Calculated from growth of product peak at 1 790 cm^{-1}. [b] Nucleophile is benzonitrile.

The variation of k_{obs} with [MeCN] for both $[(C_7H_8)Cr(CO)_3]$ (Table 1) and $[(C_7H_8)Mo(CO)_3]$ (Figure 1) is consistent with a third-order rate law. Since plots of k_{obs} against [MeCN] for both the chromium and molybdenum complexes pass through the origin, no first-order term (or decomposition) arises in the rate law. The pseudo-first-order kinetics arise from the large excess of nucleophile employed ([MeCN] ⩾ 0·096M). Table 2 summarises the k_{obs} values and activation parameters for the various cycloheptatriene metal complexes in dichloroethane solvent. $\Delta H_{obs}^{\ddagger}$ Values were obtained from gradients of Arrhenius plots, calculated by a least-squares method. The errors quoted are standard deviations derived from the least-squares analyses. Entropies of activation were calculated after conversion of the observed rate constants to third-order rate constants.

TABLE 2

k_{obs} Values ([MeCN] = 0·955M) and activation parameters for the reaction of acetonitrile with the complexes $[(C_7H_8)M(CO)_3]$ in dichloroethane

M	10^4k_{obs} (45 °C) / s^{-1}	$\Delta H_{obs}^{\ddagger}$ / kcal mol^{-1}	$\Delta S_{obs}^{\ddagger}$ / cal K^{-1} mol^{-1}
Cr	0·09 [a]	21·6 ± 1·0 (20·4 ± 1·3)	−15 (−23) [c]
Mo	154 [a,b]	11·3 ± 0·6	−31
W	1·25	10·4 ± 0·6	−43

1 cal = 4·184 J.

[a] Extrapolated from Arrhenius plot. [b] Extrapolated from Figure 1. [c] Value in parentheses for MeCN as solvent.

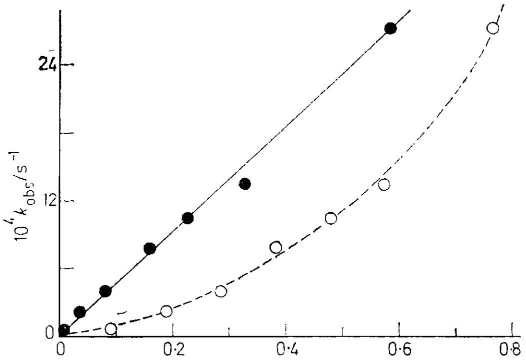

FIGURE 1 Variation of k_{obs} for the complex $[(C_7H_8)Mo(CO)_3]$ with (○), [MeCN] and (●), [MeCN]^2 at 23·1 °C in dichloroethane as solvent

TABLE 3

k_{obs} Values for reaction of acetonitrile with tricarbonyl(mesitylene)molybdenum. [Complex] = 5 × 10^{-3}M

Solvent	[MeCN]/M	t/°C	10^4/s^{-1}
$C_2H_2Cl_2$	0·096	24·1	0·64
	0·191	24·1	1·22
	0·382	24·1	1·50
	0·573	24·1	2·65
	0·764	24·1	3·14
	1·14	24·1	4·42
	0·382	16·4	0·675
	0·382	23·9	1·37
	0·382	28·3	1·98
	0·382	33·2	2·70
	0·382	50·0	11·5 [a]

[a] Extrapolated from Arrhenius plot.

The kinetic data obtained for the corresponding reaction of acetonitrile with tricarbonyl(mesitylene)molybdenum at various temperatures and nucleophile concentrations are collected in Table 3. Unlike the above reaction with the

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[7] L. A. P. Kane-Maguire, *J. Chem. Soc.* (*A*), 1971, 1602.

[8] G. B. Dobson, M. F. Amr El Sayed, I. W. Stolz, and R K. Sheline, *Inorg. Chem.*, 1962, **1**, 526.

[9] I. W. Stolz, G. R. Dobson, and R. K. Sheline, *Inorg. Chem.*, 1963, **2**, 323.

cycloheptatriene complexes, the variation of k_{obs} with [MeCN] is consistent with the second-order rate law (2).

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

Table 4 summarises the kinetic data and activation parameters for the reaction of acetonitrile with each of the substrates $[(C_7H_8)M(CO)_3]$, $[(C_7H_7)M(CO)_3]BF_4$, and [(arene)-$M(CO)_3$], permitting a comparison of the ease of removal of cycloheptatriene, tropylium, and arene ligands from the $[LM(CO)_3]^{n+}$ (n = 0 or 1) complexes.

TABLE 4

Comparison of k_{obs} and $\Delta H^\ddagger$ values for the reaction of acetonitrile with $[LM(CO)_3]^{n+}$ complexes

Complex	t/°C	[MeCN]/ M	10^4k_{obs}/s^{-1}	$\Delta H^\ddagger$/kcal mol^{-1}
$[(C_7H_8)Mo(CO)_3]$	16·4	0·38	5·00 [a]	10·3
$[(C_6H_3Me_3)Mo(CO)_3]$	16·4	0·38	0·70	14·9
$[(C_7H_7)Mo(CO)_3]BF_4$	16·4	0·38	0·0056 [b]	10·5
$[(C_7H_8)Cr(CO)_3]$	70·5	19·1	25·5	18·1
$[(C_6H_6)Cr(CO)_3]$	70·5	19·1	<0·05 [c]	
$[(C_7H_7)Cr(CO)_3]BF_4$	70·5	19·1	0·64 [b]	24·2

[a] Extrapolated from Figure 1 and Arrhenius plot. [b] From data in ref. 1. [c] No observable reaction after 4 h.

DISCUSSION

Cycloheptatriene Complexes.—Only two product carbonyl bands (1 920 and 1 800 cm^{-1}) were observed during the action of acetonitrile on the complexes $[(C_7H_8)M(CO)_3]$ (M = Cr, Mo, or W), confirming that reaction (1) proceeds cleanly to completion in both acetonitrile and dichloromethane as solvent. Further support for the stoicheiometry (1) is the equivalence of k_{obs} values calculated following either the disappearance of the complexes $[(C_7H_8)M(CO)_3]$ or the growth of the product carbonyl bands (Table 1). However, in close analogy with the behaviour of the corresponding tropylium systems,[1] the primary products $[(MeCN)_3M(CO)_3]$ were in some instances observed to undergo subsequent equilibration to mixtures of $[(MeCN)_2M(CO)_4]$ and $[(MeCN)M(CO)_5]$. This has been explained[1] as arising from slow ingress of oxygen through the Suba seals of the reaction vessels. These small amounts of oxygen have no effect on the observed kinetics, since runs carried out under strictly oxygen-free conditions in a Schlenk tube gave k_{obs} values identical to those obtained from runs in which tetra- and penta-carbonyl products were observed.

The most striking feature of the kinetic behaviour of reaction (1) is the third-order rate law (3) observed.

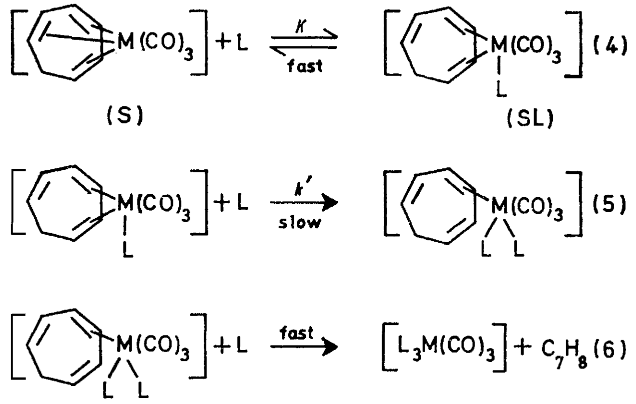
$$\begin{aligned} \text{Rate} &= k[\text{Complex}][\text{MeCN}]^2 \\ &= k_{obs}[\text{Complex}] \qquad (3) \\ \text{where} \quad k_{obs} &= k[\text{MeCN}]^2 \end{aligned}$$

From Figure 1, experimental agreement with this rate law is seen to be excellent for the complex $[(C_7H_8]Mo(CO)_3]$ in dichloroethane solvent. The data in Table 1 indicate the same rate law for the complex $[(C_7H_8)Cr(CO)_3]$, and a similar dependence on $[MeCN]^2$ may be assumed for the tungsten analogue. This behaviour contrasts sharply with the second-order kinetics (Rate = k[Complex][N]) previously observed for the action of phosphorus nucleophiles on $[(C_7H_8)M(CO)_3]$ and related arene systems.[3,4,10] It also differs from recent data[1] for the displacement of the tropylium ligand from $[(C_7H_7)M(CO)_3]BF_4$ complexes, which show a linear dependence of k_{obs} on [MeCN] for up to 4·5M-acetonitrile in dichloroethane. This latter observation rules out speculation that the present third-order kinetics may arise fortuitously because of rate variations with solvent composition, since the $[(C_7H_8)Mo(CO)_3]$ data involve a smaller solvent variation (maximum [MeCN] = 0·764M, 4% by volume) than that employed in the $[(C_7H_7)M(CO)_3]BF_4$ study (up to 24% MeCN).

A reasonable explanation for our observed kinetics is a mechanism [reactions (4)—(6)] involving rapid pre-equilibrium between the complexes $[(C_7H_8)M(CO)_3]$ (S) and acetonitrile (L) to form an activated complex (SL), which is then attacked by a further acetonitrile molecule in a rate-determining step (5) leading to the product. Assuming a genuine pre-equilibrium, one expects the rate law (7) for this mechanism, which agrees with the experimental

$$\text{Rate} = k'K[S][L]^2 \qquad (7)$$

observations. Also consistent with this mechanism are the large negative $\Delta S_{obs}^\ddagger$ values obtained, since negative contributions are expected from both ΔS^0 for pre-equilibrium (4) and $\Delta S^\ddagger$ for step (5).



Intermediates of the type (SL) have been previously proposed in the reaction of phosphines with arenetricarbonylmolybdenum complexes,[10] and recently for the reaction of acetonitrile with $[(C_7H_7)M(CO)_3]^+$ (M = Cr, Mo, or W) cations.[1] However, the present studies provide the first experimental evidence for the formation of such intermediates. Unfortunately no supporting spectroscopic evidence could be obtained for the existence of (SL). This may be associated with a low value of the equilibrium constant K, causing the concentration of the intermediate to be too small to permit its detection. It

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[10] F. Zingales, A. Chiesa, and F. Basolo, *J. Amer. Chem. Soc.*, 1966, **88**, 2707.

is interesting that a similar mechanism to reactions (4)—(6) was recently suggested[11] for the reaction of triethyl phosphite with nickelocene, which also showed third-order kinetics.

The reaction represented by equation (4) is a genuine equilibration since if steady-state conditions existed one would expect the rate law (8) which predicts second-

$$\text{Rate} = k'K[\text{S}][\text{L}]^2/(1 + K[\text{L}]) \qquad (8)$$

order kinetics at high [L]. Our observation of a strict third-order rate law for up to $0{\cdot}764\text{M}$-acetonitrile (Figure 1) therefore argues against a steady-state mechanism. Attempts to extend the range of [MeCN] to higher concentrations have been prevented by the speed of the reaction. An alternative mechanism consistent with rate law (3) is of course a termolecular reaction. However, the simultaneous attack of two ligands on the substrate seems improbable on statistical grounds.

The case of displacement of cycloheptatriene by acetonitrile from the species $[(C_7H_8)M(CO)_3]$ decreases sharply in the order Mo > W > Cr (1 700 : 14 : 1), which is the usual order found[1,3,12,13] for bimolecular displacement at Group VI metal centres. The slow rate for the chromium complex is obviously due to its high $\Delta H^{\ddagger}$ value, despite the relatively favourable entropy of activation (Table 2). On the other hand, for the molybdenum and tungsten complexes which have similar $\Delta H^{\ddagger}$ values, the much greater rate for molybdenum is associated with its less negative $\Delta S^{\ddagger}$ value. In view of the additive nature of the contributions to the $\Delta H_{\text{obs}}^{\ddagger}$ values ($= \Delta H_4^0 + \Delta H_5^{\ddagger}$), and the absence of any general clear-cut correlation between them and the rates, it is not possible to make deductions concerning the relative $M-C_7H_8$ bond strengths from the present data. The similarity of the activation parameters (Table 2) and rate constants (Table 1) for the reaction of the complex $[(C_7H_8)Cr(CO)_3]$ in 1,2-dichloroethane and acetonitrile as solvents confirms the independence of solvent character expected for a reaction between two neutral species.

The change in mechanism from direct S_N2 displacement of C_7H_8 using trimethyl phosphite to reactions (4)—(6) for acetonitrile is somewhat surprising in view of the similar nucleophilic reactivities reported[13] for such ligands on $M(CO)_6$ (M = Cr, Mo, or W) substrates. Perhaps formation of a stable seven-co-ordinate intermediate (SL) is more favoured with acetonitrile because of its smaller steric requirements than the bulky trimethyl phosphite. Similar steric arguments may explain the absence of a kinetic intermediate in the corresponding reaction of acetonitrile with $[(C_7H_7)M(CO)_3]^+$ (M = Cr, Mo, or W) systems.[1] Recent *X*-ray data[14] show that in the salt $[(C_7H_7)Mo(CO)_3]BF_4$ each of the seven ring carbon atoms are $2{\cdot}31 \pm 0{\cdot}02$ Å from the molybdenum, which is almost identical with Mo–C(ring) distances for C(2)—C(5) in the corresponding cycloheptatriene complex[15] (Figure 2). However, not only does the methylene group in the complex $[(C_7H_8)Mo(CO)_3]$ lie above the ring plane [Mo–C(7) = 2·96 Å], but also the adjacent C(1) and C(6) atoms are appreciably further from the molybdenum (2·45 ± 0·02 Å). Thus the approach of a nucleophile towards the metal to form a seven-co-ordinate intermediate is more favoured for the $[(C_7H_8)M(CO)_3]$ complexes.

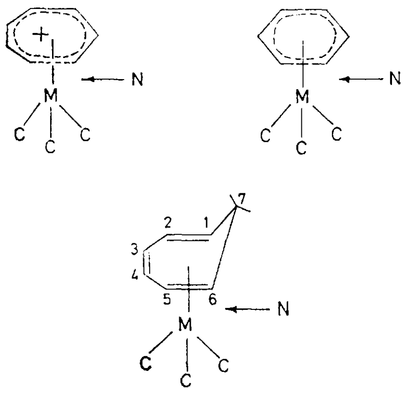

FIGURE 2 Schematic approach of a nucleophile (N) towards $[LM(CO)_3]^{n+}$ species

Tricarbonyl(mesitylene)molybdenum.—Reaction of the complex $[(C_6H_3Me_3)Mo(CO)_3]$ with acetonitrile in dichloroethane was also observed (i.r.) to yield only $[(MeCN)_3Mo(CO)_3]$ [equation (9)], provided oxygen was

$$[(C_6H_3Me_3)Mo(CO)_3] + 3MeCN \longrightarrow [(MeCN)_3Mo(CO)_3] + C_6H_3Me_3 \qquad (9)$$

strictly excluded. However, the kinetic data in Table 3 indicate the second-order rate law (2), which contrasts with the third-order kinetics described above for the reaction with the complex $[(C_7H_8)Mo(CO)_3]$. This change in mechanism may also be rationalised in steric terms. Comparative *X*-ray studies are not available for cycloheptatriene and arene molybdenum tricarbonyl complexes. However, data for the corresponding chromium complexes[16,17] have shown that while four of the ring carbon atoms on bonded cycloheptatriene are almost the same distance (*ca.* 2·2 Å) from the chromium as the six carbon atoms in arene complexes, C(1) and C(6) (Figure 2) are *ca.* 0·1 Å further away. Thus formation of a stable seven-co-ordinate intermediate is sterically more feasible for the cycloheptatriene complexes. In addition, Pidcock *et al.*[4] have suggested that cycloheptatriene may be more capable than arenes of functioning as a bidentate ligand as required in the intermediate (SL).

[11] H. Werner, V. Harder, and E. Deckelmann, *Helv. Chim. Acta*, 1969, **52**, 1081.

[12] H. Werner and R. Prinz, *J. Organometallic Chem.*, 1966, **5**, 79.

[13] K. M. Al-Kathumi and L. A. P. Kane-Maguire, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3759.

[14] G. R. Clark and G. J. Palenik, *Chem. Comm.*, 1969, 667.

[15] J. D. Dunitz and P. Pauling, *Helv. Chim. Acta*, 1960, **43**, 2188.

[16] P. E. Blakie and O. S. Mills, *J. Chem. Soc.* (*A*), 1968, 2704.

[17] G. A. Sim, *Ann. Rev. Phys. Chem.*, 1967, **18**, 57.

It should be noted that the k_{obs} value of $11{\cdot}5 \times 10^{-4}$ s^{-1} in Table 3 for the reaction of 0·38M-acetonitrile with $[(C_6H_3Me_3)Mo(CO)_3]$ at 50 °C is considerably lower than a previous value ($28{\cdot}9 \times 10^{-4}$ s^{-1}) reported by Pidcock *et al.*[18] No explanation is apparent for the differences in rates, except that the previous authors followed the reaction *via* u.v.-visible rather than i.r. spectral changes.

Comparison of Cycloheptatriene, Arene, and Tropylium Complexes.—From Table 4 it is seen that the ease of displacement of π-bonding organic ligands from $[LMo(CO)_3]^{n+}$ ($n = 0$ or 1) systems by acetonitrile varies in the order $C_7H_8 > C_6H_3Me_3 > C_7H_7$ (890 : 125 : 1). Since methyl ring substitution is known [4,10] to retard nucleophilic attack at the metal only slightly, the order $C_7H_8 > C_6H_6 > C_7H_7$ may therefore be assumed for the parent π-bonding ligands. However, the rate order depends to some extent on the nature of the metal, since the rates for the corresponding reactions with $[LCr(CO)_3]^{n+}$ ($n = 0$ or 1) decrease along the series $C_7H_8 > C_7H_7 > C_6H_6$. Nevertheless, the rate trend $C_7H_8 >$ arene is general for acetonitrile, and is similar to that previously reported[4] using phosphines or phosphites as nucleophiles. The present report is the first time that the tropylium ligand has been placed in such a sequence, and shows that it is also more difficult to remove than a cycloheptatriene moiety.

The faster displacement rate for cycloheptatriene compared with arenes is explicable on both steric and electronic grounds. Not only does the greater distance (0·1 Å) of C(1) and C(6) from the metal (Figure 2) suggest a weaker M–ring bond, but it also leaves more room for nucleophilic approach. Similarly, dipole-moment measurements[19] clearly show a greater pull of electrons by $M(CO)_3$ units from co-ordinated arene rings than from cycloheptatriene. This results in a higher effective positive charge on the metal in the cycloheptatriene complexes, facilitating nucleophilic attack. Consistent with this rate order is the significantly lower (*ca.* 5 kcal mol^{-1}) * enthalpy of activation for the cycloheptatriene complex (Table 4).

The slow rate for the $[(C_7H_7)M(CO)_3]^+$ complexes compared to $[(C_7H_8)M(CO)_3]$ can similarly be explained in steric terms (see above). On the other hand, electronically one might have anticipated a significantly faster displacement rate for the tropylium complexes in view of their overall positive charge. However, other factors such as the solvation of the liberated $C_7H_7^+$ species have to be considered in any comparisons. Unfortunately, the present kinetic data cannot be used to obtain a quantitative estimate of the relative $M-C_7H_8$, $M-C_6H_3Me_3$, and $M-C_7H_7$ bond strengths because of the different mechanisms operating in each case.

[3/1745 *Received, 20th August,* 1973]

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* 1 cal = 4·184 J.

[18] A. Pidcock, J. D. Smith, and B. W. Taylor, *Inorg. Chem.*, 1970, **9**, 638.

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