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Solvent and Structural Effects in Substitution Reactions of Metal Carbonyl Halides

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Received August 11, 1970

A comparison of the kinetics of substitution by phosphite ligands of cyclopentadienyl iron and ruthenium carbonyl halides is reported and in all cases a dissociative mechanism indicated. The ruthenium compounds are much less reactive than their iron analogues. Detailed solvent studies of the reactions of these compounds and of the manganese pentacarbonyl halides indicate that substitution proceeds via a transition state which is less polar than the ground state. The special role of coordinating solvents is discussed.

Introduction

This paper is a continuation of our previous studies[1] of the kinetics of substitution reactions of various metal carbonyl halides. In particular, we have compared the nature and ease of carbonyl-substitution reactions of compounds containing *a* first and *b* second-row transition metals. Detailed studies of the effect of solvent on the rates of substitution of both cyclopentadienyl metal carbonyl halides and metal carbonyl halides by triphenylphosphite and triphenylphosphine have also been made.

The substitution of the manganese pentacarbonyl halides by a variety of nucleophiles has been shown[2] to proceed by a simple dissociative mechanism:

$$\mathrm{Mn(CO)_5X + L \longrightarrow Mn(CO)_4LX + CO}$$

and a similar dissociative mechansm holds for the π-cyclopentadienyl iron carbonyl halides:[1]

$$\pi\mathrm{-CpFe(CO)_2X + L \longrightarrow \pi\!-\!CpFe(CO)LX + CO}$$

although in this latter case, substitution by PPh_3 in arene solvents gives a mixture of ionic and covalent products:[3]

$$\mathrm{2\pi\!-\!CpFe(CO)_2X + 2L \longrightarrow}$$
$$\mathrm{[\pi CpFe(CO)_2L]^+X^- + \pi CpFe(CO)LX + CO}$$

Experimental Section

The solvents, n-octane, di-n-butyl ether, were purified as described previously.[1] Xylene was dried over sodium and distilled under nitrogen from calcium hydride. Nitrobenzene was distilled under nitrogen at 209°C.

Ligand purification was as described previously.

Preparative Reactions

Hydrated $RuCl_3$ (Johnson, Matthey Ltd) was converted to $[Ru(CO)_3Cl_2]_2$ by the method of Cleare and Griffith.[4]

$[\pi\text{--}C_5H_5Ru(CO)_2]_2$ was prepared by treatment of $[Ru(CO)_3Cl_2]_2$ with an eight-fold molar excess of NaC_5H_5 in T.H.F. at room temperature. Evaporation of the solvent followed by extraction of the solid residue with benzene gave the dimer in 40-50% yield.

$\pi\text{--}C_5H_5Ru(CO)_2X$ ($X = I$, Br, Cl). These compounds were obtained from $[\pi\text{--}C_5H_5Ru(CO)_2]_2$ as described in the literature.[5,6,7]

$\pi\text{--}C_5H_5Ru(CO)(L)X$. The complexes listed in Table I were prepared by refluxing $\pi\text{--}C_5H_5Ru(CO)_2X$ and a slight molar excess of the phosphine or phosphite ligand in xylene. The time required for complete reaction was two hours for the chloride, four hours for the bromide and eight hours for the iodide compounds. In each case the cooled reaction mixture was filtered, and on removal of the solvent by evaporation a yellow to orange solid was obtained. Products were purified by recrystallization from hexane for the $P(OCH_3)_3$ and $P(C_4H_9)_3$ derivatives and methylene chloride-hexane mixture for the $P(OPh)_3$ and PPh_3 compounds until good analytical results were obtained.

85-95% Yields were recorded.

The pure products were reasonably stable in air over a period of two to three weeks.

There was no evidence for the formation of ionic products, $[\pi\text{--}C_5H_5Ru(CO)_2PR_3]^+X^-$.

Kinetic Studies

An I.R. sampling method was used as described

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Table I. Analytical data for the ruthenium complexes

Compound	M.Pt.(°C)[a]	Found % C	Found % H	Found % X	Required % C	Required % H	Required % X
$\pi{-}C_5H_5Ru(CO)[P(OC_6H_5)_3]I$	170-172°	46.0	3.5	20.5	45.6	3.2	20.1
$\pi{-}C_5H_5Ru(CO)[P(OCH_3)_3]I$	77-78°	24.7	3.4	28.2	24.3	3.2	28.5
$\pi{-}C_5H_5Ru(CO)[P(C_6H_5)_3]I$	190-194°(d)	49.0	3.6	29.9	49.4	3.4	21.7
$\pi{-}C_5H_5Ru(CO)[P(n{-}C_4H_9)_3]I$	78-80°	41.2	6.2	24.4	41.3	6.1	24.3
$\pi{-}C_5H_5Ru(CO)[P(OC_6H_5)_3]Br$	125-127°(d)	49.1	3.6	13.4	49.3	3.4	13.7
$\pi{-}C_5H_5Ru(CO)[P(OCH_3)_3]Br$	65-67°	27.3	3.7	20.1	27.1	3.5	20.1
$\pi{-}C_5H_5Ru(CO)[P(C_6H_5)_3]Br$	236-238°	53.5	3.9	—	53.7	3.7	—
$\pi{-}C_5H_5Ru(CO)[P(n{-}C_4H_9)_3]Br$	77-79°	45.3	6.7	16.6	45.4	6.7	16.8
$\pi{-}C_5H_5Ru(CO)[P(OC_6H_5)_3]Cl$	147-149°	53.1	4.2	6.5	53.3	3.7	6.6
$\pi{-}C_5H_5Ru(CO)[P(OCH_3)_3]Cl$	91-98°	30.4	4.0	10.3	30.5	4.0	10.0
$\pi{-}C_5H_5Ru(CO)[P(C_6H_5)_3]Cl$	249-252°(d)	58.5	4.0	7.7	58.6	4.0	7.8
$\pi{-}C_5H_5Ru(CO)[P(n{-}C_4H_9)_3]Cl$	82-84°(d)	50.3	7.7	8.0	50.1	7.4	8.2

[a] (d) ≡ melts with decomposition.

Table II. CO Stretching Frequencies (cm^{-1}) of $C_5H_5Ru(CO)_2X$ and its derivatives

Compound	Absorption Bands			
$\pi{-}C_5H_5Ru(CO)_2I$	2051(7.8)		2005(10)	[b]
$\pi{-}C_5H_5Ru(CO)_2Br$	2054(7.8)		2009(10)	[b]
$\pi{-}C_5H_5Ru(CO)_2Cl$	2058(7.4)		2010(10)	[b]
$\pi{-}C_5H_5Ru(CO)[P(OC_6H_5)_3]I$		1989		[a]
$\pi{-}C_5H_5Ru(CO)[P(OCH_3)_3]I$	1985(7.3)		1974(10)	[b]
$\pi{-}C_5H_5Ru(CO)[P(C_6H_5)_3]I$		1962		[a]
$\pi{-}C_5H_5Ru(CO)[P(n{-}C_4H_9)_3]I$		1959		[b]
$\pi{-}C_5H_5Ru(CO)[P(OC_6H_5)_3]Br$		1990		[a]
$\pi{-}C_5H_5Ru(CO)[P(OCH_3)_3]Br$	1986(7.5)		1975(10)	[b]
$\pi{-}C_5H_5Ru(CO)[P(C_6H_5)_3]Br$		1962		[a]
$\pi{-}C_5H_5Ru(CO)[P(n{-}C_4H_9)_3]Br$		1959		[b]
$\pi{-}C_5H_5Ru(CO)[P(OC_6H_5)_3]Cl$		1989		[a]
$\pi{-}C_5H_5Ru(CO)[P(OCH_3)_3]Cl$	1986(7.5)		1976(10)	[b]
$\pi{-}C_5H_5Ru(CO)[P(C_6H_5)_3]Cl$		1960		[a]
$\pi{-}C_5H_5Ru(CO)[P(n{-}C_4H_9)_3]Cl$		1957		[b]

[a] Solvent carbon disulphide. [b] Solvent n-heptane.

in the previous paper.[1] The results reported in Table III are the mean of at least three kinetic runs and in all cases the variation of rate with [ligand]/[substrate] ratios of 2 to 50 were made in order to check whether there was any second-order contribution to the overall rate; in no case was this observed. In the case of reactions with $P(OPh)_3$ in nitrobenzene at elevated temperatures (>70°C) direct reaction between the ligand and solvent was observed, presumably analogous to that reported by Cadogan and co-workers[8] for the reaction between $P(OEt)_3$ and nitrobenzene. However, this side reaction had only a small effect on the rate of substitution so we regard these rates as valid although the experimental error in rate constant is about 10% in these cases whereas in all other cases rate constants are reproducible to 5%. Errors in activation parameters are estimated as ± 1 K.cal/mole^{-1} for E_a and ± 2 e.u. for ΔS^*. Kinetic studies of the ruthenium compounds were limited to the chloride and bromide because the iodide was so unreactive that reaction temperatures above the boiling points of usual solvents are required.

Results and Discussion

The values of the observed first-order rate constants, k_{obs} 10^4 sec^{-1}, are given in Table III for a range of substrates and ligands in a number of solvents. The corresponding activation parameters are given in Table IV. In all cases rigorous first-order kinetics were observed and concentration-dependence studies gave no evidence for any second-order contribution. It is concludd that all the metal carbonyl halides studied in this work react by a first-order dissociative mechanism.

Effective of replacing the central metal by a congener. In this work we have prepared a series of monosubstituted π-cyclopentadienyl ruthenium carbonyl halides by direct substitution of the halide with either a phosphine or phosphite. The compounds so prepared are listed in Table I and their infra-red CO stretching frequencies given in Table II. In general, the parent halides, $\pi{-}CpRu(CO)_2X$ ($X = Cl, Br, I$), are much more stable than the analogous iron compounds as evidenced by the higher temperatures required for reaction with phosphine and phosphite ligands. Similarly, the monosubstituted complexes, $\pi{-}CpRu(CO)LX$, are also more stable than their iron analogues and less soluble in organic solvents. The CO frequencies generally lie about 3-4 wavenumebrs higher than the corresponding iron compounds which suggests a slightly weaker M–CO bond for the ruthenium series although in the absence of a full vibrational analysis such comparisons remain speculative. It is interesting that in all the preparative

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Table III. Substrate + L ⟶ Product + CO

Substrate	Solvent	ε^{20}	Temp. (°C)	Ligand (L)	$10^4 k_{obs}$ (sec^{-1})
$Mn(CO)_5Br$	n—Octane	1.96 [a]	30	$P(C_6H_5)_3$	2.49
$Mn(CO)_5Br$	n—Octane		36	$P(C_6H_5)_3$	5.19
$Mn(CO)_5Br$	n—Octane		41.5	$P(C_6H_5)_3$	12.01
$Mn(CO)_5I$	n—Octane		50	$P(C_6H_5)_3$	2.89
$Mn(CO)_5I$	n—Octane		53	$P(C_6H_5)_3$	4.12
$Mn(CO)_5I$	n—Octane		56	$P(C_6H_5)_3$	6.36
π—$C_5H_5Ru(CO)_2Cl$	n—Octane		99.7	$P(OC_6H_5)_3$	0.48
π—$C_5H_5Ru(CO)_2Cl$	n—Octane		104.7	$P(OC_6H_5)_3$	0.75
π—$C_5H_5Ru(CO)_2Cl$	n—Octane		110.0	$P(OC_6H_5)_3$	1.46
$Mn(CO)_5Br$	Xylene	2.3 [a]	35	$P(C_6H_5)_3$	2.39
$Mn(CO)_5Br$	Xylene		40.3	$P(C_6H_5)_3$	4.90
$Mn(CO)_5Br$	Xylene		45.0	$P(C_6H_5)_3$	10.94
$Mn(CO)_5I$	Xylene		50.1	$P(C_6H_5)_3$	1.68
$Mn(CO)_5I$	Xylene		55.2	$P(C_6H_5)_3$	3.42
$Mn(CO)_5I$	Xylene		60.2	$P(C_6H_5)_3$	6.72
π—$C_5H_5Fe(CO)_2Br$	Xylene		72	$P(OC_6H_5)_3$	1.43
π—$C_5H_5Fe(CO)_2Br$	Xylene		76.7	$P(OC_6H_5)_3$	2.86
π—$C_5H_5Fe(CO)_2Br$	Xylene		82.4	$P(OC_6H_5)_3$	5.50
π—$C_5H_5Fe(CO)_2I$	Xylene		91.8	$P(OC_6H_5)_3$	0.81
π—$C_5H_5Fe(CO)_2I$	Xylene		97.2	$P(OC_6H_5)_3$	1.59
π—$C_5H_5Fe(CO)_2I$	Xylene		102.2	$P(OC_6H_5)_3$	2.91
π—$C_5H_5Ru(CO)_2Cl$	Xylene		110.0	$P(OC_6H_5)_3$	1.05
π—$C_5H_5Ru(CO)_2Cl$	Xylene		115.4	$P(OC_6H_5)_3$	1.75
π—$C_5H_5Ru(CO)_2Cl$	Xylene		120.4	$P(OC_6H_5)_3$	2.87
π—$C_5H_5Ru(CO)_2Br$	Xylene		125.4	$P(OC_6H_5)_3$	1.01
π—$C_5H_5Ru(CO)_2Br$	Xylene		130.4	$P(OC_6H_5)_3$	1.47
π—$C_5H_5Ru(CO)_2Br$	Xylene		135.4	$P(OC_6H_5)_3$	2.33
$Mn(CO)_5Br$	di-n-butyl ether	3.08 [b]	30.3	$P(C_6H_5)_3$	2.17
$Mn(CO)_5Br$	di-n-butyl ether		35.0	$P(C_6H_5)_3$	4.07
$Mn(CO)_5Br$	di-n-butyl ether		40.2	$P(C_6H_5)_3$	8.67
π—$C_5H_5Ru(CO)_2Br$	di-n-butyl ether		120.4	$P(OC_6H_5)_3$	1.30
π—$C_5H_5Ru(CO)_2Br$	di-n-butyl ether		125.4	$P(OC_6H_5)_3$	2.01
π—$C_5H_5Ru(CO)_2Br$	di-n-butyl ether		130.4	$P(OC_6H_5)_3$	3.59
π—$C_5H_5Fe(CO)_2Br$	nitrobenzene	34.8 [a]	80.2	$P(OC_6H_5)_3$	1.87
π—$C_5H_5Fe(CO)_2Br$	nitrobenzene		84.2	$P(OC_6H_5)_3$	3.37
π—$C_5H_5Fe(CO)_2Br$	nitrobenzene		88.8	$P(OC_6H_5)_3$	5.79
π—$C_5H_5Fe(CO)_2I$	nitrobenzene		106.9	$P(OC_6H_5)_3$	2.11
π—$C_5H_5Fe(CO)_2I$	nitrobenzene		112.2	$P(OC_6H_5)_3$	3.92
π—$C_5H_5Fe(CO)_2I$	nitrobenzene		116.7	$P(OC_6H_5)_3$	6.43

[a] CRC Handbook of Chemistry and Physics, 48th. Edition. [b] R. Mecke, R. Joeckle, and G. Klingenberg, *Z. Electrochem.*, *66*, 239 (1962).

Table IV. Activation Parameters

Complex	Solvent	ε^{20}	$10^5 k_T$ [a]	E_a Kcal/mole	ΔS^*, e.u.	Reference
$Mn(CO)_5Br$	n-Octane	1.96	99	26.4	10.1	
	Xylene	2.3	49	29.3	17.9	
	Di-n-butyl ether	3.08	87	25.3	7.5	
	Chloroform	4.8	33	29.8	18.9	2
	Nitrobenzene	34.8	10.7	30.9	22.1	2
$Mn(CO)_5I$	n-Octane		8.3	28.6	10.8	
	Xylene		1.1	29.8	14.3	
	Chloroform		1.7	32.2	20.7	2
π—$C_5H_5Fe(CO)_2Br$	n-Octane		27.6	31.2	14.1	1
	Xylene		10.8	34.6	21.5	
	Di-n-butyl ether		23.4	26.4	−0.5	1
	Nitrobenzene		4.4	33.7	17.5	
π—$C_5H_5Fe(CO)_2I$	n-Octane		1.04	26.8	−4.2	1
	Xylene		0.44	33.2	11.6	
	Di-n-butyl ether		0.9	23.8	−12.5	1
	Nitrobenzene		0.17	33.5	10.5	
π—$C_5H_5Ru(CO)_2Cl$	Xylene		0.15	29.9	−1.0	
π—$C_5H_5Ru(CO)_2Br$	Xylene		0.015	31.1	−1.4	
	Di-n-butyl ether		0.04	30.1	−2.1	

[a] The rate constants for $Mn(CO)_5X$ refer to 40°C and for π—Cp $M(CO)_2X$ to 70°C.

reactions carried out in xylene no evidence was obtained for the formation of ionic derivatives such as $[\pi\text{—}CpRu(CO)_2L]^+X^-$ even in the case when X=Cl; this result suggests a much lower tendency for the ruthenium compounds to react by any S_N2 associative process than for the corresponding iron series where reaction in arene solvents leads to appreciable yields of the ionic compound especially for π—CpFe-

(CO)$_2$Cl although in this case it is possible that the reaction may proceed, at least partially, *via* an S$_N$1 halide dissociative mechanism.[3]

It will be noted from Table II that the I.R. spectra of π–CpRu(CO)P(OMe)$_3$X, X = Cl, Br and I, show CO bands, measured in n-heptane solution, with a separation of about 10 wavenumbers. A similar effect was reported for the corresponding iron compounds in the previous paper.[1] In a separate communication,[9] we have suggested that the doubling of the number of CO frequencies in these compounds arises from rotational isomerism due either to restricted rotation about the M–P bond or, more probably, to conformational isomerism within the P(OR)$_3$ ligand. In the case of the ruthenium compounds the ratio of the intensities of the two peaks is closer to unity than for the iron compounds suggesting a more equal participation of the two isomers in the former case.

Relative reactivity of iron and ruthenium compounds. The results in Tables III and IV show clearly that in all cases the π-cyclopentadienyl ruthenium carbonyl halides are much less reactive than the corresponding iron compounds, the rate of substitution generally being about 700 times slower. The rate sequence with variation in halogen is the same as for the iron compounds (and the manganese pentacarbonyl halides), namely:

$$\mathrm{Cl} > \mathrm{Br} > \mathrm{I}$$

The lower reactivity of the ruthenium series is in contrast to the enhanced reactivity of some complexes of second-row elements; for example, the more rapid substitution of π–CpRh(CO)$_2$ by phosphines and phosphites compared to the corresponding Co and Ir compounds.[10b] It has been suggested that the occurrence of such bimolecular reactions may be due to presence of π^* orbitals which can accommodate excess electron-density of an approaching nucleophile thereby promoting an S$_N$2 reaction;[10a] however, in the present work no such tendency is found and the contrary effect on reactivity occurs. The activation parameters for π-cyclopentadienyl ruthenium carbonyl bromide may be compared with those for its iron analogue for a given solvent from Table IV. In xylene the activation energy of the ruthenium compound is actually 3.5 K.cals/mole *less* than that of the iron compound so that the decrease in rate is due to the much lower ΔS^* value. However, in di-n-butyl ether, the activation energy is higher but ΔS^* lower for the ruthenium compound. These results suggest that xylene has a much greater solvating effect on the ruthenium compound than on the iron compound but we can offer no obvious explanation for this difference.

Solvents effects. There have been few detailed studies of solvent effects on substitution reactions of metal carbonyl complexes possibly because since these reactions generally involve the displacement of one neutral molecule (CO) by another (*e.g.* PR$_3$) any effect is likely to be small.[11,12] Previous studies include CO insertion reactions of CH$_3$Mn(CO)$_5$,[13] CO substitution reactions of Mo(CO)$_6$,[14] Ni(CO)$_4$,[15] Co(CO)$_3$NO[16] and CO exchange reactions of Fe$_3$(CO)$_9$Te$_2$.[17] As expected above, the effect of varying solvent polarity is generally small except in the case of the CO insertion reaction but the recent studies of Foffani and coworkers[16] confirm that solvents of reasonable coordinating ability exert a proportionately greater effect than that expected on purely electrostatic solvation by stabilizing the transition state by weak coordination thereby giving rise to the so-called « solvent-assisted » dissociative mechanism. In the case of the substitution of Ni(CO)$_4$ by PPh$_3$ which proceeds by a first-order dissociative mechanism,[15] arene solvents were shown to accelerate the reaction even more than simple coordinating solvnts such as tetrahydrofuran or acetonitrile; it was suggested that for such solvents the transition state was stabilized by some form of interaction with the π-electrons of the arene. The much lower ΔH^* value for toluene of 20.4 K.cal/mole compared to ΔH^* for cyclohexane of 26.6 K.cal/mole supports this suggestion.[15] In the case of the manganese pentacarbonyl halides, Basolo and coworkers[2] found that the reaction rate in a polar solvent such as nitrobenzene was lower than that in chloroform and concluded that the transition state was less polar than the ground state.

For the compounds studied in this paper and from previous work, it can be seen from Tables III and IV that for Mn(CO)$_5$X, π–CpFe(CO)$_2$X and π–CpRu(CO)$_2$X the following rate sequence is observed, independent of solvent:

$$k_{\mathrm{Cl}} > k_{\mathrm{Br}} > k_{\mathrm{I}}$$

In all cases this rate sequence parallels the observed CO stretching frequencies (Table II of this paper and references 1-2). Where available, the variation of rate constants for Mn(CO)$_5$Br, π–CpFe(CO)$_2$Br with solvent polarity follow the sequence:

$$\begin{array}{lllll} k_{\mathrm{octane}} > & k_{\mathrm{DNB}} > & k_{\mathrm{xylene}} > & k_{\mathrm{CHCl_3}} > & k_{\mathrm{PhNO_2}} \\ [\varepsilon = 1.96, & 3.08, & 2.3, & 4.8 & 34.8] \end{array}$$

with dielectric constants given in brackets below. With the exception of di-n-butyl ether (DNB), a general decrease in rate with increasing solvent polarity occurs. Again, with the exception of DNB, the above rate sequence is generally paralleled by the sequences in E$_a$ and ΔS^*:

$$(E_a)\mathrm{octane} < (E_a)\mathrm{xylene} < (E_a)\mathrm{nitrobenzene}$$

$$(\Delta S^*)\mathrm{octane} < (\Delta S^*)\mathrm{xylene} < (\Delta S^*)\mathrm{nitrobenzene}$$

although there are a few exceptions to this sequence.

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[9] D. A. Brown, H. J. Lyons, and A. R. Manning, *Inorg. Chim. Acta, 4,* 428 (1970)
(10a) A. Wojcicki and F. Basolo, *J. Inorg. Nucl. Chem., 17,* 77 (1961).
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It follows that for the three metal carbonyl bromides described above the transition state is less polar than the ground state; we are presently carrying out some SCCC molecular orbital calculations for these systems to find an explanation for this difference in polarity. However, it is interesting to note that the difference in polarity between transition state and ground state is larger for the manganese compound, as evidenced by the quantity

$$(E_a)_{PhNO_2}-(E_a)_{octane} = 4.5 \text{ K.cal/mole}$$

whereas for π–CpFe(CO)$_2$Br it is only 2.5 K.cal/mole which is close to experimental error. This lower difference in polarity is probably related to the presence of the π-orbitals of the cyclopentadienyl ring whose electrons can be involved in some form of conjugation in the transition state as postulated in our previous paper[1] although in that case we had interpreted the increased solvation by di-n-butyl ether as a polarity effect and that the transition state was therefore more polar than the ground state. It is now obvious from the present extensive solvent studies that DNB acts as a coordinating solvent since for the three bromides, its position is anomalous in the solvent-rate sequence; for example, it causes an increase in rate relative to xylene despite its higher dielectric constant and, moreover, it always gives the lowest E$_a$ value for a given bromide for any of the above solvents. This effect is similar to that found by Foffani and coworkers[16] for the substitution of Co(CO)$_3$NO by AsPh$_3$ where in strongly coordinating solvents such as acetonitrile the E$_a$ values for the first-order dissociative mechanism are nearly 12 K.cal/mole lower than the corresponding value in cyclohexane.

Finally, in contrast to the accelerating effect of arene solvents on the substitution of Ni(CO)$_4$ by PPh$_3$,[15] the results in Tables III and IV show clearly that xylene exerts a normal effect on the substitution of the metal carbonyl bromides consistent with its dielectric constant; for example, it retards the rate of the bromides with respect to octane and the corresponding activation energies are about 2-3 K.cals/mole higher. Clearly the effect of arene solvents such as xylene upon two simple dissociative processes as the substitution of Ni(CO)$_4$ and of Mn(CO)$_5$Br (and CpFe(CO)$_2$Br) is completely different. Moreover, substitution reactions of the isoelectronic Co(CO)$_3$NO show a solvent effect due to toluene[16] which is similar to that observed for the bromides in this work. It is difficult to offer any simple explanation of the anomalous effect for Ni(CO)$_4$ but it is possible that the Ni(CO)$_3$ intermediate may interact more strongly with the π-electrons of an arene molecule than the more bulky CpFe(CO)X group.