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Reactions of Tricarbonyl-π-cyclopentadienylhalomolybdenum(II) Complexes with Phosphorus(III) Ligands: A Kinetic Study

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The reactions of the complexes $\pi\text{–}C_5H_5Mo(CO)_3X$ *(X = Cl, Br and I) with phosphorus(III) ligands (L) to give* $\pi\text{–}C_5H_5Mo(CO)_2LX$ *are shown to have a dissociative mechanism similar to that for* $Mn(CO)_5X$*, except for certain reactions of the bromo- and iodo-complexes which appear to have a radical mechanism. The rates of the dissociative processes decrease in the order Cl>Br>I, as* ΔH^* *increases. The reaction of* $\pi\text{–}C_5H_5Mo(CO)_3Cl$ *with* $L = PBu^n{}_2Ph$ *and* $PBu^n{}_3$ *also yields fac–*$Mo(CO)_3L_3$ *and cis–*$Mo(CO)_4L_2$ *in amounts which vary according to the solvent used and the temperature. The rate of formation of these complexes is first order in both* $\pi\text{–}C_5H_5Mo(CO)_3Cl$ *and L. Two alternative mechanisms are suggested for the reaction.*

Introduction

The most common mechanism for carbon monoxide replacement reactions of the type

$$\pi\text{–}C_5H_5M(CO)L_n + L' \longrightarrow \pi\text{–}C_5H_5ML'L_n + CO$$

(where M represents a transition metal, L_n are other ligands bonded to the metal and L′ is a nucleophile) is an associative one. It has been suggested[1] that this may be due to the presence of the π–cyclopentadienyl ligand, since similar reactions for metal carbonyl complexes which do not contain the π-cyclopentadienyl ligand often take place by a dissociative mechanism.[2] Schuster-Woldan and Basolo suggested[1] that the π-cyclopentadienyl ligand was able to stabilize the transition state for the associative process by removing negative charge from the metal during attack by the incoming nucleophile.

This paper describes a study of the reactions

$$\pi\text{–}C_5H_5Mo(CO)_3X + L \longrightarrow \pi\text{–}C_5H_5Mo(CO)_2LX + CO \quad (1)$$

where X = Cl, Br and I, and L is one of a range of ligands containing a phosphorus donor atom. If one regards the π-cyclopentadienyl group as a tridentate ligand, these complexes are seven-coordinate. An associative mechanism for reaction (1) would involve an eight-coordinate transition state, and hence would involve considerable crowding round the molybdenum atom. The aim of the study was to determine whether, under these circumstances, the mechanism of CO replacement reactions would revert to the dissociative type common for metal carbonyl complexes lacking a π-cyclopentadienyl ligand.

Experimental Section

All reactions and distillations were carried out under nitrogen except where otherwise stated. Solvents used for kinetic studies were purified by standard methods and distilled shortly before use. Petroleum ether, wherever used for preparative work, had a 40-60°C boiling range.

Ligands. $P(C_6H_5)_3$, obtained from B.D.H., was recrystallized from CH_2Cl_2/hexane. PBu^nPh_2, $PBu^n{}_2Ph$ and $PBu^n{}_3$ were prepared by a standard technique[3] from Bu^nMgBr and Ph_2PCl, $PhPCl_2$ and PCl_3 respectively. All were distilled at reduced pressure shortly before use. $P(OMe)_3$ and $P(OPh)_3$, obtained from B.D.H., were distilled at reduced pressure shortly before use.

Preparation of Complexes. $[\pi\text{–}C_5H_5Mo(CO)_3]_2$ was prepared as described by King and Stone.[4]

$\pi\text{–}C_5H_5Mo(CO)_3Cl$. A solution of $[\pi\text{–}C_5H_5Mo(CO)_3]_2$ (3.0 g) in $CHCl_3$ (100 ml) was irradiated with two 60 w light bulbs for 10 hr. After removal of the solvent under vacuum, the residue was purified by chromatography on silica gel, using CH_2Cl_2/petroleum ether mixtures as eluent. Yield 2.3 g, 67%. $\pi\text{–}C_5H_5Mo(CO)_3Br$ was prepared in the same way using $CHBr_3$ and a reaction time of 24 hr. Yield 70%. $\pi\text{–}C_5H_5Mo(CO)_3I$ was prepared as described by Abel *et al.*[5]

$\pi\text{–}C_5H_5Mo(CO)_2LX$. These complexes (X = halogen; L = phosphorus ligand) were prepared by mixing $\pi\text{–}C_5H_5Mo(CO)_3X$ with a slight excess of the ligand in tetrahydrofuran (benzene for the iodo-complexes). Typical reaction conditions were 18 hr at 40°C for chloro-complexes, 8 hr under reflux for bromo-complexes and 12 hr under reflux for iodo-complexes. Products were purified in the same way as $\pi\text{–}C_5H_5Mo(CO)_3Cl$, followed by recrystallisation from CH_2Cl_2/hexane.

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(1) H. G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.*, *88*, 1657 (1966).
(2) R. J. Angelici, *Organometallic Chem. Rev.*, 3, 173 (1968).
(3) D. M. Adams and J. B. Raynor, « Advanced Practical Inorganic Chemistry », Wiley, London, 1965.
(4) R. B. King and F. G. A. Stone, *Inorg. Synth.*, 7, 99 (1963).
(5) E. W. Abel, A. Singh and G. Wilkinson, *J. Chem. Soc.*, 1960, 1321.

Table I. Analytical Data

	Colour	M.Pt. °C	Found %C	Found %H	Found %X	Calculated %C	Calculated %H	Calculated %X
π—$C_5H_5Mo(CO)_3Cl$	red	118 ^{d}	34.5	2.1	12.6 ^{a}	34.3	1.8	12.6 ^{a}
π—$C_5H_5Mo(CO)_3Br$	red	123 ^{d}	29.4	1.6	24.6 ^{a}	29.6	1.6	24.6 ^{a}
π—$C_5H_5Mo(CO)_3I$	maroon	120 ^{d}	25.9	1.4		25.8	1.4	
π—$C_5H_5Mo(CO)_2(PPh_3)Cl$	orange	171 ^{d}	58.3	3.8		58.3	3.9	
π—$C_5H_5Mo(CO)_2(P\{OMe\}_3)Cl$	red	112	31.8	3.7	9.6 ^{a}	31.9	3.7	9.4 ^{a}
π—$C_5H_5Mo(CO)_2(PBu^nPh_2)Cl$	orange	150-2	56.0	4.9	7.1 ^{a}	55.8	4.9	7.2 ^{a}
π—$C_5H_5Mo(CO)_2(PBu^n_2Ph)Cl$	red	102-3	52.9	6.0	8.0 ^{a}	53.1	5.9	7.4 ^{a}
π—$C_5H_5Mo(CO)_2(PBu^n_3)Cl$	red	89-90	49.8	6.9	6.3 ^{b}	50.2	7.1	6.8 ^{b}
π—$C_5H_5Mo(CO)_2(PPh_3)Br$	orange	166	53.1	3.9		53.7	3.6	
π—$C_5H_5Mo(CO)_2(P\{OMe\}_3)Br$	orange	96	28.4	3.4		28.5	3.3	
π—$C_5H_5Mo(CO)_2(PPh_3)I$	orange	223 ^{d}	49.9	3.6		49.5	3.3	
fac—$Mo(CO)_3(PBu^n_2Ph)_3$	white	119	64.3	8.3	11.3 ^{b}	63.8	8.2	11.0 ^{b}
cis—$Mo(CO)_4(PBu^n_2Ph)_2$	white	98-9	59.6	7.1	9.8 ^{b}	58.9	7.1	9.5 ^{b}
$[C_5H_5PBu^n_3]PF_6$	white	124	49.6	7.8	14.9 ^{b}	49.5	7.8	15.0 ^{b}

^{a} X = halogen; ^{b} X = phosphorus; ^{d} melts with decomposition.

Table II. Infrared Spectra ^{a} in the C—O Stretching Region Region for Complexes $Mo(CO)_3L_3$ and $Mo(CO)_4L_2$

	cm^{-1}
fac—$Mo(CO)_3(PBu^n_2Ph)_3$	1945, 1854
cis—$Mo(CO)_4(PBu^n_2Ph)_2$	2018, 1920, 1904, 1898
fac—$Mo(CO)_3(PBu^n_3)_3$ ^{b}	1939, 1845
cis—$Mo(CO)_4(PBu^n_3)_2$ ^{b}	2015, 1918, 1903, 1892

^{a} All spectra were recorded in n-pentane solution. ^{b} Obtained as an inseparable mixture.

Reaction of π—$C_5H_5Mo(CO)_3Cl$ with PBu^n_3. π—$C_5H_5Mo(CO)_3Cl$ (0.5 g) in MeOH (20 ml) was added dropwise, over 30 min., to a stirred solution of PBu^n_3 (1.48 g) in MeOH (5 ml). After stirring for a further 10 min., the mixture was cooled to 0°C. An aqueous solution of NH_4PF_6 was added dropwise until precipitation ceased. The white precipitate was removed by filtration*, washed twice with a little cold water and recrystallized twice from MeOH/Et_2O/hexane. White crystals of $[C_5H_5PBu^n_3]PF_6$ (0.35 g) were obtained.

The filtrate* was evaporated to dryness and subjected to silica gel chromatography. Elution with petroleum ether gave an inseparable mixture of two compounds which (on the basis of the similarity of their infra-red spectra — see Table II — with the corresponding products of the reaction between π—$C_5H_5Mo(CO)_3Cl$ and PBu^n_2Ph) were assigned the formulae *fac*—$Mo(CO)_3(PBu^n_3)_3$ and *cis*—$Mo(CO)_4(PBu^n_3)_2$. Elution with CH_2Cl_2/petroleum ether yielded π—$C_5H_5Mo(CO)_2(PBu^n_3)Cl$, obtainable in much greater yield by performing the reaction in C_6H_6/hexane rather than MeOH.

Reaction of π—$C_5H_5Mo(CO)_3Cl$ *with* PBu^n_2Ph. PBu^n_2Ph (1.40 g) was added to a solution of π—$C_5H_5Mo(CO)_3Cl$ (0.41 g) in tetrahydrofuran (2 ml). After 24 hr, the mixture was subjected to chromatography on silica gel. Elution with petroleum ether gave a mixture of *fac*—$Mo(CO)_3(PBu^n_2Ph)_3$ and *cis*—$Mo(CO)_4(PBu^n_2Ph)_2$, which were separated by repeated fractional crystallization from hexane, in which the former compound is the more soluble of the two. Elution with CH_2Cl_2/hexane yielded π—$C_5H_5Mo(CO)_2(PBu^n_2Ph)Cl$.

$[\pi$—$C_5H_5Mo(CO)_3NH_3]BPh_4$. This was prepared as described by Fischer and Moser.[6]

Attempted preparation of $[\pi$—$C_5H_5Mo(CO)_3(PBu^n_3)]PF_6$. π—$C_5H_5Mo(CO)_2(PBu^n_3)Cl$ (0.7 g) and $AlCl_3$ (0.3 g) were heated in benzene (60 ml) at 70°C for 16 hr under 1200 p.s.i. CO in a glass-lined autoclave. After cooling to 0°C, aqueous NH_4PF_6 solution was added. No precipitate was obtained. On removing the solvent, the black residue showed no evidence of the presence of any carbonyl complexes of molybdenum.

Analytical data for complexes are given in Table I. In order to save space, infra-red data are given only for the complexes *fac*—$Mo(CO)_3L_3$ and *cis*—$Mo(CO)_4L_2$ (see Table II), and no N.M.R. data are given. The authors will supply the remaining data on request.

Kinetic Studies. In most cases, reactions were followed by monitoring the disappearance of the highest frequency carbonyl stretching band in the infra-red spectra of the complexes π—$C_5H_5Mo(CO)_3X$. The procedure used, and the method of treating the data to obtain rate constants have been described in an earlier paper.[7] Concentrations of the complexes π—$C_5H_5Mo(CO)_3X$ were about 0.01 *M*, except where limited solubility in certain solvents made the use of lower concentrations necessary. Ligand concentration was always at least ten times greater than the concentration of molybdenum complex. A Perkin-Elmer 257 spectrophotometer was used, with KBr cells, except for reactions in MeOH, where CaF_2 cells were employed.

In certain cases reactions were also followed by other methods, for example (i) the rate of appearance of a band in the infrared spectrum of a product, (ii) the rate of carbon monoxide evolution (using an apparatus similar to that described by Calderazzo and Cotton[8]), or (iii) (where there was no evidence of light catalysis of a reaction) the rate of change of absorbance at a particular wavelength in the visible/near ultra-violet spectrum of a reaction mixture. In all

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(6) E. O. Fischer and E. Moser, *J. Organometallic Chem.*, *2*, 230 (1964).
(7) A. J. Hart-Davis and R. J. Mawby, *J. Chem. Soc. (A)*, 1969, 2403
(8) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, *1*, 30 (1962).

such cases, rate constants obtained by the various different methods agreed well with one another.

All reactions for which rate constants are listed were found to be first order in molybdenum complex, and reliable kinetic data could be obtained from at least the first 2½ half lives. Rate constants were found to be reproducible to, at the worst, 4%.

Results

The course and rate of many of the reactions of the complexes π–$C_5H_5Mo(CO)_3X$ (X = Cl, Br and I) were affected by light. In all such cases, kinetic studies were carried out in the absence of light. Under these conditions, all three complexes reacted with the ligands L = PPh_3, PBu^nPh_2, $P(OPh)_3$ and $P(OMe)_3$ in accordance with equation (1). In some cases, this was followed by a much slower reaction to give π–$C_5H_5Mo(CO)L_2X$, but this did not interfere with the study of reaction (1).

Reproducible kinetic data were obtained for the reaction of all four ligands with π–$C_5H_5Mo(CO)_3Cl$. Rate constants in tetrahydrofuran are listed in Table III, while Table IV illustrates the effect on reaction rate of changes in solvent. The reactions of π–$C_5H_5Mo(CO)_3Br$ and π–$C_5H_5Mo(CO)_3I$ with PPh_3 and $P(OPh)_3$ also gave rise to reproducible kinetic data: rate constants for these reactions are compared with the corresponding data for π–$C_5H_5Mo(CO)_3Cl$ in Table V.

Table III. Observed Rate Constants for the Reactions of π–$C_5H_5Mo(CO)_3Cl$ with Various Ligands in Tetrahydrofuran

Temperature (°C)	Ligand	Ligand Concentration (*M*)	10^5 k_{obs} (sec^{-1})
40	PPh_3	0.089	10.7
		0.209	10.8
		0.343	10.5
		0.664	10.6
40	$P(OPh)_3$	0.134	10.3
		0.322	10.3
40	$P(OMe)_3$	0.096	10.7
		0.109	10.9
		0.302	11.1
		0.488	11.3
40	PBu^nPh_2	0.200	11.2
		0.372	10.8
		0.563	11.0
35	PPh_3	0.115	5.40
30	PPh_3	0.115	2.48
25	PPh_3	0.114	1.22
		0.301	1.23

Table IV. Observed Pate Constants for the Reaction of π–$C_5H_5Mo(CO)_3Cl$ with PPh_3 in Various Solvents at 40°C

Solvent	Dielectric Constant	Ligand Concentration (*M*)	10^5 k_{obs} (sec^{-1})
Heptane	1.89	0.023	15.5
		0.056	15.2
C_6H_6	2.24	0.114	9.0
		0.215	8.8
$CHCl_3$	4.46	0.114	6.2
		0.280	6.2
Diglyme	6.3	0.096	10.2
		0.159	10.2
Tetrahydrofuran	7.7	0.089	10.7
		0.664	10.6
$MeNO_2$	34.4	0.114	6.9
		0.135	7.2

Table V. Comparison of Rate Constants for the Reactions of the Complexes π–$C_5H_5Mo(CO)_3X$ (X = Cl, Br, I) with PPh_3 and $P(OPh)_3$ in Diglyme

Complex	Temperature (°C)	Ligand Concentration [a] (*M*)	10^5 k_{obs} (sec^{-1})
π–$C_5H_5Mo(CO)_3Cl$	35.0	0.111	47.98
		0.306	4.4
	40.0	0.096	10.2
		0.159	10.2
	50.0	0.122	37.5
		0.355	37.7
	55.0	0.192	70.5
		0.283	71.6
π–$C_5H_5Mo(CO)_3Br$	45.0	0.132	1.33
		0.264	1.36
	50.0	0.127	2.81
		0.387	2.88
	60.0	0.196	10.9
		0.335	11.0
	70.0	0.114	39.3
		0.277	41.5
		0.401	41.9
π–$C_5H_5Mo(CO)_3I$	70.0	0.114	2.14
		0.271	2.14
	80.0	0.101	7.8
		0.233	7.8
		0.304*	7.4
	87.0	0.108	16.6

[a] Ligand is PPh_3, except where asterisked, when it is $P(OPh)_3$

The reactions of π–$C_5H_5Mo(CO)_3Br$ and π–$C_5H_5Mo(CO)_3I$ with $P(OMe)_3$, although following the course of equation (1), were extremely complicated from a kinetic viewpoint. An initial induction period was followed by a very rapid reaction: this then gave way to a much slower reaction. These reaction mixtures, unlike those for the corresponding reaction of π–$C_5H_5Mo(CO)_3Cl$, exhibited electron spin resonance spectra. The individual reactants and products did not give rise to such spectra.. It seems clear that a free radical mechanism, possibly involving homolytic cleavage of the metal-halogen bond (as has been suggested[9] for reactions of the complexes $Fe(CO)_4X_2$, where X = Cl, Br and I), is operating in these cases. No reproducible kinetic data could be obtained, and the reactions will not be further discussed in this paper.

The other reactions for which kinetic data are given are those between π–$C_5H_5Mo(CO)_3Cl$ and the ligands L = $PBu^n{}_2Ph$ and $PBu^n{}_3$. In these cases, reaction (1) was accompanied by a more complicated reaction, which was shown (by isolating and characterizing the products) to be:

$$\pi\text{–}C_5H_5Mo(CO)_3Cl + 4L \longrightarrow [C_5H_5L]^+ + Mo(CO)_3L_3 + Cl^- \quad (2)$$

In tetrahydrofuran, the concentration of $Mo(CO)_3L_3$ increased steadily in the early part of the reaction,

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(9) I. A. Cohen and F. Basolo, *J. Inorg. Nuclear Chem.*, *28*, 511 (1966).

Table VI. Rate Constants for the Reaction of π–$C_5H_5Mo(CO)_3Cl$ with $PBu^n{}_2Ph$ and $PBu^n{}_3$

Solvent	Temperature (°C)	Ligand	Ligand Concentration (M)	10^4 k_{obs} (sec^{-1})
Tetrahydrofuran	25.0	$PBu^n{}_3$	0.075	1.85
			0.137	3.07
			0.190	3.69
			0.230	4.53
			0.332	6.13
			0.396	7.54
	30.0	$PBu^n{}_2Ph$	0.154	0.31
			0.318	0.37
			0.422	0.42
	35.0	$PBu^n{}_2Ph$	0.260	0.68
			0.430	0.77
	40.0	$PBu^n{}_2Ph$	0.137	1.24
			0.291	1.33
			0.331	1.34
			0.421	1.41
			0.501	1.42
		$PBu^n{}_3$	0.079	5.42
			0.184	10.0
			0.196	11.1
			0.313	16.9
Methanol	12.4	$PBu^n{}_3$	0.131	7.16
			0.169	8.55
			0.231	11.9
			0.321	15.7
	18.0	$PBu^n{}_3$	0.111	7.10
			0.157	10.8
			0.190	14.4
			0.401	29.1
	19.6	$PBu^n{}_3$	0.124	12.0
			0.206	19.2
			0.240	22.1
	28.3	$PBu^n{}_3$	0.124	20.8
			0.234	38.0
			0.317	50.8
			0.344	55.8

then reached a maximum and finally diminished, owing to the reaction

$$Mo(CO)_3L_3 + CO \longrightarrow Mo(CO)_4L_2 + L \qquad (3)$$

caused by the CO liberated during the course of reaction (1). That the complexes $Mo(CO)_4L_2$ were not formed directly from π–$C_5H_5Mo(CO)_3Cl$ was suggested by the fact that they were not observed at all in the early stages of the reactions. Separate experiments confirmed that $Mo(CO)_3L_3$ could be converted to $Mo(CO)_4L_2$ by reaction with CO under the conditions used. It was also established that $Mo(CO)_3L_3$ could not be formed from the product of reaction (1), π–$C_5H_5Mo(CO)_2LCl$, and hence must be formed directly from π–$C_5H_5Mo(CO)_3Cl$.

Observed overall rate constants for the reaction of π–$C_5H_5Mo(CO)_3Cl$ with $PBu^n{}_2Ph$ and $PBu^n{}_3$ are listed in Table VI.

Discussion

Reference to the data in Tables III and V shows that the reactions of π–$C_5H_5Mo(CO)_3X$ ($X = Cl$, Br and I) with PPh_3 and $P(OPh)_3$, and of π–$C_5H_5Mo(CO)_3Cl$ with $P(OMe)_3$ and PBu^nPh_2, proceed at a rate which is virtually independent of both the nature and the concentration of the ligand. The absence of any marked effect of solvent on reaction rate (Table IV) and the positive entropies of activation (Table VII) are consistent with a dissociative mechanism similar to that postulated for the reactions of the compounds $Mn(CO)_5X$ ($X = Cl$, Br and I).[10]

$$\pi\text{–}C_5H_5Mo(CO)_3X \xrightarrow[-CO]{\text{slow}}$$

$$\pi\text{–}C_5H_5Mo(CO)_2X \xrightarrow[+L]{\text{fast}} \pi\text{–}C_5H_5Mo(CO)_2XL \qquad (4)$$

The close similarity in behaviour of the two classes of compound suggests that the π–cyclopentadienyl ligand plays very little part in the reaction. Clearly the high coordination numbers of the complexes π–$C_5H_5Mo(CO)_3X$ make a dissociative mechanism the most favourable one. The decrease in rate of reaction down the series $Cl > Br > I$ is common to both $Mn(CO)_5X$ and π–$C_5H_5Mo(CO)_3X$. Since bond-breaking forms the most important part of a dissociative reaction mechanism, the increase in ΔH^* down the series (Table VII) could be taken to indicate a strengthening of the Mo–CO bond in the ground state. This is in line with the decrease in C–O stretching frequencies for the compounds π–$C_5H_5Mo(CO)_3X$ down the series $Cl > Br > I$ (highest frequency C–O stretching band at 2062, 2056 and 2049 cm^{-1} respectively in pentane solution).

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(10) R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, *84*, 2495 (1962).

Table VII. Activation Parameters for the Reactions of π–$C_5H_5Mo(CO)_3X$ (X = Cl, Br, I) with PPh_3

Compound	Solvent	ΔH* (kcal. mole^{-1})	ΔS* (e.u.)
π–$C_5H_5Mo(CO)_3Cl$	Tetrahydrofuran	26.7(±0.4)	+8.7(±0.5)
	Diglyme	26.6(±0.2)	+7.9(±0.4)
π–$C_5H_5Mo(CO)_3Br$	Diglyme	28.9(±0.2)	+10.0(±0.4)
π–$C_5H_5Mo(CO)_3I$	Diglyme	29.6(±0.6)	+6.0(±0.6)

Table VIII. Computed Values of k_A and k_B, where $k_{obs} = k_A + k_B[L]$, for the Reactions of π–$C_5H_5Mo(CO)_3Cl$ with L (L = $PBu^n{}_2Ph$ and $PBu^n{}_3$)

Solvent	Ligand	Temperature (°C)	10^4 k_A (sec^{-1})	10^4 k_B (M^{-1} sec^{-1})
Tetrahydrofuran	$PBu^n{}_2Ph$	30.0	0.25(±0.01)	0.39(±0.02)
		35.0	0.54(±0.02)	0.53(±0.03)
		40.0	1.13(±0.05)	0.75(±0.07)
Tetrahydrofuran	$PBu^n{}_3$	25.0	0.28(±0.1)	18.2(±0.5)
		40.0	1.23(±0.2)	49.3(±0.7)
Methanol	$PBu^n{}_3$	12.4	1.0(±0.6)	45.8(±1.9)
		18.0	−0.1(±0.8)	75.0(±3.4)
		19.6	1.2(±0.6)	87.2(±0.9)
		28.3	1.1(±0.6)	157.8(±2.2)

Table IX. Activation Parameters for the Second-Order Part of the Reaction of π–$C_5H_5Mo(CO)_3Cl$ with $PBu^n{}_2Ph$ and $PBu^n{}_3$

Solvent	Ligand	ΔH* (kcal.mole^{-1})	ΔS* (e.u.)
Tetrahydrofuran	$PBu^n{}_2Ph$	11.3(±0.4)	−41.3(±0.5)
Tetrahydrofuran	$PBu^n{}_3$	11.7	−32
Methanol	$PBu^n{}_3$	12.7(±0.6)	−24.8(±0.8)

The reactions of π–$C_5H_5Mo(CO)_3Cl$ with $PBu^n{}_2Ph$ and $PBu^n{}_3$ deviate from this simple pattern. Here the rate of disappearance of π–$C_5H_5Mo(CO)_3Cl$ depends on ligand concentration, is appreciably greater for $PBu^n{}_3$ than for $PBu^n{}_2Ph$, and depends sharply on the solvent. In each solvent the observed rate constants could be fitted to the relationship

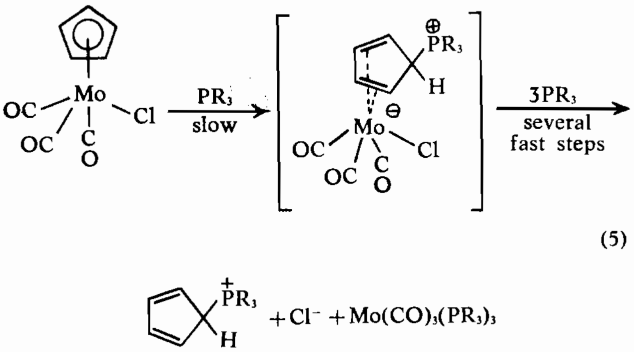
$$k_{obs} = k_A + k_B[L]$$

and computed « best-fit » values of k_A and k_B for each solvent and temperature are given in Table VIII. Although exact product ratios are difficult to determine because of the overlapping of bands in the infra-red spectrum of reaction mixtures, it was possible to show that (to within experimental error) k_A represented the rate of formation of the « normal » product π–$C_5H_5Mo(CO)_2LCl$ *via* reaction (1), while the rate of formation of $Mo(CO)_3L_3$ (and subsequently $Mo(CO)_4L_2$) by reaction (2) was represented by $k_B[L]$.

For the reaction of π–$C_5H_5Mo(CO)_3Cl$ with $PBu^n{}_3$, k_A is so small compared with k_B that one can place little reliance on the k_A values obtained. The more accurate k_A values obtained for the reaction with $PBu^n{}_2Ph$ are very close to the observed rate constants obtained at the same temperature and in the same solvent with ligands which formed π–$C_5H_5Mo(CO)_2LCl$ only. It seems clear, therefore, that the mechanism of formation of π–$C_5H_5Mo(CO)_2(PBu^n{}_2Ph)Cl$, and presumably also π–$C_5H_5Mo(CO)_2(PBu^n{}_3)Cl$, is the same as that for all the other ligands studied, namely equation (4).

In contrast, the rate determining step of reaction (2) must be first order both in π–$C_5H_5Mo(CO)_3Cl$ and in ligand. The data in Table VIII show that this reaction is considerably slower in tetrahydrofuran than in methanol, and we have observed qualitatively that the reaction is much slower still in n-heptane. Table IX shows that ΔH* is much lower for these reactions than for reaction (1), which results in an appreciable variation in the proportions of products formed as the temperature is varied. It is also noticeable that the reactions have remarkably large negative values for ΔS*.

The evidence suggests that the activated state for the rate-determining step of reaction (2) may be much more polar than the ground state. Two mechanims would appear possible. One involves nucleophilic attack on the π–cyclopentadienyl ligand.



(5)

Nucleophilic attack on « aromatic » ligands coordinate to transition metals is a well-documented process.[11] Clearly the reaction involves considerable charge separation in the transition state. Subsequent displacement of the cyclopentadienyl system would be expected to be rapid since it is now coordinated merely as a diene.

An alternative mechanism would involve nucleophilic attack on the metal, with displacement of chloride ion.

$$\pi\text{–}C_5H_5Mo(CO)_3Cl \underset{\text{slow}}{\xrightarrow[-Cl^-]{+PR_3}} [\pi\text{–}C_5H_5Mo(CO)_3PR_3]^+ \xrightarrow[\text{fast}]{\textit{etc.}} \quad (6)$$

Subsequent nucleophilic attack on the π-cyclopentadienyl ligand would be encouraged by the overall positive charge on the intermediate. Attempts to prepare the postulated intermediate $[\pi\text{–}C_5H_5Mo(CO)_3\text{-}PR_3]^+$, in order to study its properties, were unsuccessful. We found, however, that the analogous cation $[\pi\text{–}C_5H_5Mo(CO)_3NH_3]^+$ did react rapidly with PBu^n_3 in methanol with displacement of the π-cyclopentadienyl ligand.

The rate of formation of $Mo(CO)_3(PBu^n_3)_3$ from $\pi\text{–}C_5H_5Mo(CO)_3Cl$ was not reduced by adding chloride ion, as would be expected for mechanism (6) if the rate-determining step was reversible.

It is not possible to decide unambiguously between mechanisms (5) and (6). We feel that (5) is the more likely to be correct, although the possibility of initial attack on molybdenum followed by a rapid intramolecular shift of PR_3 on to the cyclopentadienyl ligand cannot be ruled out.

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