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Kinetics and Mechanism of Oxidative Addition Reactions. I. Reactions of Methyl Iodide and Ethyl Iodide with π-Cyclopentadienylcarbonylphosphine Complexes of Cobalt, Rhodium, and Iridium

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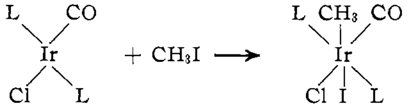
A kinetic study of the oxidative addition reaction of π-$C_5H_5M(CO)L$ (where M = Co, Rh, Ir and L = tertiary phosphine) with CH_3I and C_2H_5I has been carried out. The reactions are first order in both metal complex and alkyl iodide. Rates are slightly greater for M = Ir than for M = Co or Rh, are much greater for CH_3I than for C_2H_5I, and increase with increasing solvent polarity. The reactions are discussed in terms of the nucleophilicity of the metal atom.

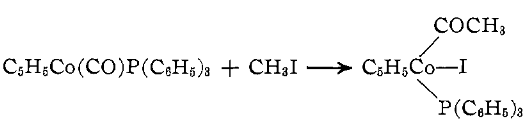
Introduction

Many reactions are known in which a molecule X–Y adds to a transition metal carbonyl compound in such a way that the metal becomes bonded to both X and Y and its formal oxidation state is increased by 2. In the case of coordinatively unsaturated compounds, such as square-planar complexes of Ir(I)[1,2] and Rh(I),[3,4] addition of X–Y makes up the full complement of 18 electrons in the valence shell of the metal, *e.g.*, for L = $PC_6H_5(CH_3)_2$[1]

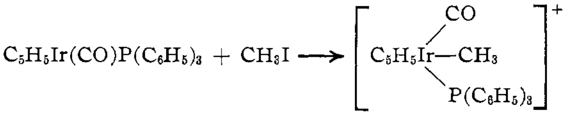


In most other cases addition of X–Y is accompanied by elimination of a ligand such as a molecule of carbon monoxide,[5] *e.g.*, $C_5H_5Co(CO)P(C_6H_5)_3 + I_2 \rightarrow C_5H_5CoI_2P(C_6H_5)_3 + CO$.

The recently reported reactions between alkyl halides and the compounds $C_5H_5M(CO)L$ (L = phosphine, M = Co, Rh,[6a] and Ir[6b]), however, are oxidative additions which do not cause elimination of a ligand, although the starting materials are coordinatively saturated. In the case of cobalt and rhodium the products are acylmetal complexes, while with iridium ionic products are formed



$$C_5H_5Co(CO)P(C_6H_5)_3 + CH_3I \longrightarrow C_5H_5Co(COCH_3)(I)P(C_6H_5)_3$$



$$C_5H_5Ir(CO)P(C_6H_5)_3 + CH_3I \longrightarrow \left[C_5H_5Ir(CO)(CH_3)P(C_6H_5)_3\right]^+ I^-$$

We are investigating the kinetic, mechanistic, and preparative possibilities of these reactions. This paper describes the effects of varying the metal, the phosphine, and the solvent on the rates of reaction with methyl iodide and ethyl iodide.

Experimental Section

All operations were performed under an atmosphere of dry nitrogen. The cobalt complexes are particularly sensitive to air in solution.

Solvents were fractionated twice under nitrogen before use. Tetrahydrofuran (THF) was dried over sodium and benzophenone, toluene was dried over sodium, and acetone was dried over Drierite. Methyl iodide and ethyl iodide were fractionated under nitrogen before use. The phosphines were obtained from Strem Chemicals, Inc., Danvers, Mass., and from Alfa Inorganics, Inc., Beverley, Mass.

Infrared data were obtained with a Perkin-Elmer Model 337 spectrophotometer, equipped with a Hewlett-Packard Model 7127A external recorder. The positions of the carbonyl stretching bands were determined by calibration with carbon monoxide in the terminal region and polystyrene in the acyl region and are probably accurate to within ±2 cm^{-1}. Nmr spectra were recorded on a Varian A56/60A instrument. Analytical data were obtained by the microanalytical laboratory of this department.

Preparation of Starting Materials.—Preparation of $C_5H_5Ir(CO)P(C_6H_5)_3$ has been described.[6b] The complexes $C_5H_5M(CO)PR_3$ (M = Co, Rh) were prepared by the following general method.[7] $C_5H_5M(CO)_2$ (1–3 g) and phosphine (1.0 mol per metal atom) were refluxed in hexane (40–80 ml) for a suitable period of time (see Table I). On cooling the reaction mixture to 0° (room temperature for the $P(C_6H_5)_3$ complexes) the product separated, generally as large prisms. These were washed with hexane and recrystallized, when necessary, from CH_2Cl_2–hexane. Some of the cobalt complexes (notably $C_5H_5Co(CO)P(C_6H_{11})_3$) crystallized from the reaction mixture in an analytically pure state.

Preparation of Reaction Products.—The products of the oxidative addition reactions were prepared by the following general method. $C_5H_5M(CO)L$ (100–500 mg) and RI (2 ml) were dissolved in CH_2Cl_2 (3 ml) and kept at room temperature for a suitable period of time (see Table I). Excess alkyl iodide and solvent were removed under vacuum and the product was recrystallized from CH_2Cl_2–hexane. This method gave good yields with CH_3I of all products except $C_5H_5CoI(COCH_3)P(C_6H_{11})_3$, which we were unable even to observe in solution. The ethyl iodide products $C_5H_5MI(COC_2H_5)P(C_6H_5)_3$ (M = Co, Rh) were obtained with some difficulty, especially the cobalt compound, which decomposes almost as fast as it is formed. The analytical sample was obtained by three recrystallizations and hand picking of the best crystals. The ionic iridium products were produced in very high yield.[6b]

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TABLE I

PREPARATION, PROPERTIES, AND ANALYTICAL DATA

Compound	Color	Reaction time, hr	Yield, %	Mp,[a] °C	ν_{CO},[b] cm^{-1}	% calcd C	% calcd H	% found C	% found H
$C_5H_5Co(CO)P(C_6H_5)_3$	Dark red	24	86		1937 h[c]	69.6	4.9	69.3	5.0
$C_5H_5Co(CO)P(C_6H_5)_2CH_3$	Dark red	2	65		1934 h	64.8	5.2	64.8	5.3
$C_5H_5Co(CO)PC_6H_5(CH_3)_2$	Dark red	1	60		1934 h	57.9	5.6	58.1	5.5
$C_5H_5Co(CO)P(C_6H_{11})_3$	Dark red	48	62		1920 h	66.6	8.9	66.6	8.9
$C_5H_5Rh(CO)P(C_6H_5)_3$	Orange	24	88	153–156	1957 h	62.9	4.4	63.0	4.6
$C_5H_5Ir(CO)P(C_6H_5)_3$	Yellow	*f*			1947 h				
$C_5H_5CoI(COCH_3)P(C_6H_5)_3$[d]	Dark red	1	83	100–110	1655, 1628 sh	54.0	4.2	53.8	4.2
$C_5H_5CoI(COCH_3)P(C_6H_5)_2CH_3$	Dark red	0.3	60		1651, 1627 sh	48.6	4.3	48.8	4.2
$C_5H_5CoI(COCH_3)PC_6H_5(CH_3)_2$	Dark red	0.3	80		1650, 1629 sh	41.7	4.4	41.6	4.3
$C_5H_5RhI(COCH_3)P(C_6H_5)_3$[e]	Red-brown	1	70	170–175	1666, 1643 sh	50.0	3.9	50.0	4.1
$[C_5H_5IrCH_3(CO)P(C_6H_5)_3]^+I^-$	Yellow	*f*			2050				
$C_5H_5CoI(COC_2H_5)P(C_6H_5)_3$	Dark red	48	Low		1646	54.8	4.4	54.0	4.5
$C_5H_5CoI(COC_2H_5)P(C_6H_5)_2CH_3$	Dark red	...	...		1644	...	...	...	...
$C_5H_5RhI(COC_2H_5)P(C_6H_5)_3$	Red-brown	66	56	167–171	1660–1654	50.8	4.1	50.5	4.3
$[C_5H_5IrC_2H_5(CO)P(C_6H_5)_3]^+I^-$	Yellow	*f*			2043				

[a] Obtained on Kofler hot stage. Rhodium compounds melted with decomposition. Cobalt compounds decomposed over a wide temperature range. [b] h = hexane. Other spectra taken in CH_2Cl_2. [c] 1919 cm^{-1} in CH_2Cl_2; 1918 cm^{-1} in Nujol. [d] Nmr in $CDCl_3$, τ values: C_6H_5, 2.5 (multiplet); C_5H_5, 5.23 (singlet); CH_3, 6.63 (singlet). [e] Nmr in $CDCl_3$, τ values: C_6H_5, 2.5 (multiplet); C_5H_5, 4.76 (singlet); CH_3, 7.08 (singlet). [f] See ref 6b.

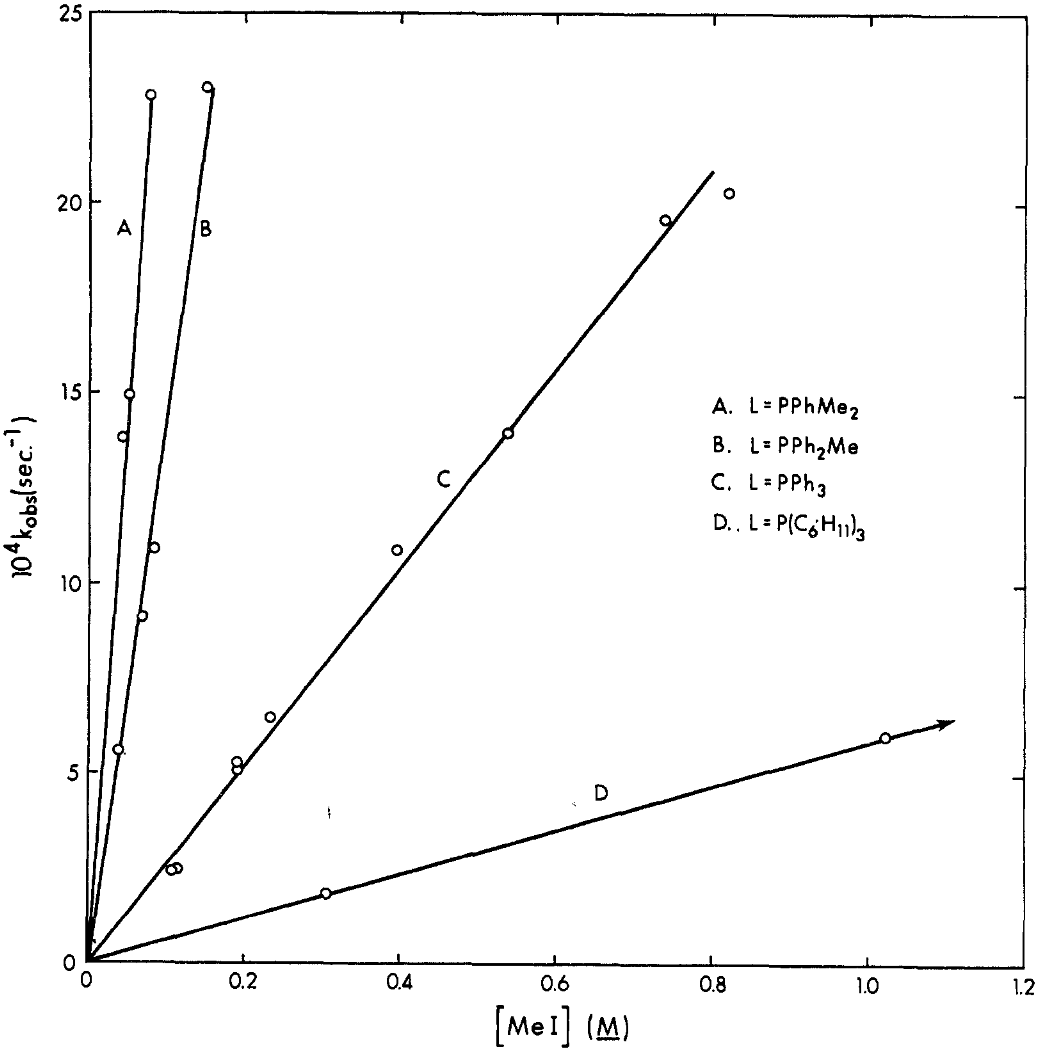


Figure 1.—Second-order rate plots for the reactions of $C_5H_5Co(CO)L$ with CH_3I in dichloromethane at 25°, showing the effect of different phosphines.

Kinetic Measurements.—The observed rate constants recorded below refer to the rate of disappearance of starting material, as determined by the intensity of its carbonyl stretching band in the infrared spectrum. All reactions were carried out under pseudo-first-order conditions, using at least a tenfold excess of alkyl iodide. Concentrations of metal complexes from 0.003 *M* (0.5-mm ir cells) up to an optimum of 0.03 *M* (0.2-mm ir cells) were used in such a way as to maintain the necessary excess of alkyl iodide. All reactions went to completion. Beer's law was shown to be obeyed over the concentration range used for $C_5H_5Rh(CO)P(C_6H_5)_3$ in CH_2Cl_2 and was assumed to be obeyed by the other complex–solvent combinations studied.

Reaction flasks were kept in a constant-temperature bath and small samples were withdrawn at suitable intervals for infrared measurement. Between 13 and 20 readings were generally taken over a period of about 3 half-lives of the reaction.

Plots were drawn of ln log (T_0/T), where T is the transmittance of the peak being followed and T_0 is the transmittance of the base line at that point, determined at "infinite" time. The linearity of these plots demonstrates that the reactions are first order with respect to the metal complex, the pseudo-first-order rate constants being given by the negative gradients. The rate constants were evaluated by a least-squares method and generally showed standard errors of 1–2%.

TABLE II

RATES OF REACTIONS OF $C_5H_5Co(CO)P(C_6H_5)_3$ WITH CH_3I IN CH_2Cl_2

[CH$_3$I], *M*	10^4k_{obsd}, sec^{-1}	10^3k_2, M^{-1} sec^{-1}	[CH$_3$I], *M*	10^4k_{obsd}, sec^{-1}	10^3k_2, M^{-1} sec^{-1}
	15°			25°	
0.378	5.3 (4.7^a)	1.4	0.114	2.50	2.2^b
0.424	6.2	1.5	0.190	5.30	2.8
0.806	11.6	1.4	0.191	5.08 (5.5^a)	2.7
1.397	18.4	1.3	0.233	6.48	2.8
			0.396	10.9	2.8
	20°		0.539	14.0	2.6
0.333	6.9	2.1	0.738	19.6	2.7
0.403	8.2	2.0	0.820	20.3	2.5
0.863	16.3	1.9		30°	
1.047	19.9	1.9	0.190	8.4	4.4
	25°		0.228	9.2	4.0
0.0	0.007	...	0.462	18.2	3.9
0.107	2.41	2.3^b	0.482	19.1	4.0

[a] Rate of growth of product acyl band. [b] Low results for k_2 were generally obtained at low [CH$_3$I], which probably reflects evaporation of CH$_3$I from the reaction mixtures.

TABLE III

RATES OF REACTION OF $C_5H_5Co(CO)L$ WITH CH_3I AT 25°. EFFECTS OF VARIATION IN PHOSPHINE AND SOLVENT

L = $P(C_6H_5)_3$, solvent THF

[CH$_3$I], *M*	10^4k_{obsd}, sec^{-1}	10^4k_2, M^{-1} sec^{-1}
0.574	3.09	5.4
1.434	8.0	5.6
1.971	12.5	6.3

L = $P(C_6H_5)_2CH_2$, solvent CH_2Cl_2

[CH$_3$I], *M*	10^4k_{obsd}, sec^{-1}	10^2k_2, M^{-1} sec^{-1}
0.038	5.6	1.5
0.068	9.1	1.3
0.084	10.9	1.3
0.150	23.0	1.5

L = $P(C_6H_5)_3$, solvent $(CH_3)_2CO$

[CH$_3$I], *M*	10^4k_{obsd}, sec^{-1}	10^3k_2, M^{-1} sec^{-1}
0.188	4.3	2.3
0.324	7.3	2.3
0.500	10.9	2.2
0.769	17.1	2.2

L = $P(C_6H_5)(CH_3)_2$, solvent CH_2Cl_2

[CH$_3$I], *M*	10^4k_{obsd}, sec^{-1}	10^2k_2, M^{-1} sec^{-1}
0.042	13.8	3.3
0.050	14.9	3.0
0.076	22.8	3.0

L = $P(C_6H_5)_3$, solvent CH_3CN

[CH$_3$I], *M*	10^4k_{obsd}, sec^{-1}	10^3k_2, M^{-1} sec^{-1}
0.163	*Ca.* 13^a	*Ca.* 8
0.344	*Ca.* 19^a	*Ca.* 6
0.498	*Ca.* 32^a	*Ca.* 6

L = $P(C_6H_{11})_3$, solvent CH_2Cl_2

[CH$_3$I], *M*	10^4k_{obsd}, sec^{-1}	10^4k_2, M^{-1} sec^{-1}
0.0	0.005	...
0.306	1.87	6.1
1.022	6.06	5.9
2.810	14.3	5.1

[a] Decomposition caused poor kinetics in CH$_3$CN.

TABLE IV

RATES OF REACTION OF $C_5H_5Rh(CO)P(C_6H_5)_3$ AND $C_5H_5Ir(CO)P(C_6H_5)_3$ with CH_3I

$C_5H_5Rh(CO)P(C_6H_5)_3$, CH_2Cl_2, 25°

[CH$_3$I], *M*	10^4k_{obsd}, sec^{-1}	10^3k_2, M^{-1} sec^{-1}
0.0	0.0004	...
0.164	5.3	3.3
0.310	10.8	3.5
0.428	14.8	3.5
0.522	18.2	3.5

$C_5H_5Ir(CO)P(C_6H_5)_3$, CH_2Cl_2, 25°

[CH$_3$I], *M*	10^4k_{obsd}, sec^{-1}	10^2k_2, M^{-1} sec^{-1}
0.057	8.1	1.4^c
0.070	12.6 (11.7^a)	1.8^c
0.096	25	2.6
0.164	37	2.3

$C_5H_5Rh(CO)P(C_6H_5)_3$, CH_2Cl_2, 10°

[CH$_3$I], *M*	10^4k_{obsd}, sec^{-1}	10^3k_2, M^{-1} sec^{-1}
0.227	3.0	1.3
0.366	4.8	1.3
0.656	8.8	1.3
0.795	10.6	1.3

$C_5H_5Ir(CO)P(C_6H_5)_3$, CH_2Cl_2, 10°

[CH$_3$I], *M*	10^4k_{obsd}, sec^{-1}	10^2k_2, M^{-1} sec^{-1}
0.063	5.7 (5.9^a)	0.91
0.098	9.8	0.99
0.142	14.6	1.02

$C_5H_5Rh(CO)P(C_6H_5)_3$, toluene, 25°

[CH$_3$I], *M*	10^4k_{obsd}, sec^{-1}	10^5k_2, M^{-1} sec^{-1}
0.285	0.22	7.1^b
1.212	1.27	
1.705	1.90	
3.283	5.1	

[a] Rate of growth of product band (2050 cm^{-1}). [b] See text and Figure 2. [c] See footnote *b*, Table II. These reactions are too fast to obtain precise kinetic data by our method.

TABLE V

RATES OF REACTION WITH C_2H_5I IN CH_2Cl_2 AT 25°

$C_5H_5Co(CO)P(C_6H_5)_3$

[C$_2$H$_5$I], *M*	10^6k_{obsd}, sec^{-1}	10^6k_2, M^{-1} sec^{-1}
1.21	7.5	6.2
2.38	14.5	6.1

$C_5H_5Co(CO)P(C_6H_5)_2CH_3$

[C$_2$H$_5$I], *M*	10^5k_{obsd}, sec^{-1}	10^5k_2, M^{-1} sec^{-1}
0.703	2.3	3.3
0.716	2.3 (2.3^a)	3.3
1.084	3.1	2.8
1.262	3.5 (3.2^a)	2.8
1.603	4.8	3.0
2.399	7.0	2.9

$C_5H_5Rh(CO)P(C_6H_5)_3$

[C$_2$H$_5$I], *M*	10^6k_{obsd}, sec^{-1}	10^6k_2, M^{-1} sec^{-1}
0.778	2.6	3.4
1.562	4.9	3.1
2.162	7.7	3.6
3.048	8.7	2.8

$C_5H_5Ir(CO)P(C_6H_5)_3$

[C$_2$H$_5$I], *M*	10^5k_{obsd}, sec^{-1}	10^5k_2, M^{-1} sec^{-1}
0.386	0.86	2.2
0.890	1.84	2.1
3.765	6.5	1.7

[a] Rate of growth of product band.

The rates of the reactions were not noticeably affected by wrapping the flasks in aluminum foil.

Plots of observed rate constants against alkyl iodide concentrations gave good straight lines with near-zero intercepts (Figure 1). Second-order rate constants were evaluated from the gradients of these lines and are collected in Table VI. "Individual" second-order rate constants (k_{obsd}/[RI]) are listed in Tables II–V. The reactions of $C_5H_5Rh(CO)P(C_6H_5)_3$ with CH$_3$I in toluene are exceptional and are discussed below.

The cobalt starting materials used were unstable.[5] The solids darkened with time, and solutions, while remaining clear, showed growth of bands corresponding in position and relative intensity to those of $C_5H_5Co(CO)_2$. This reaction was rapid for a few minutes, during which time some 3% of the starting material disappeared, and then became very slow. Kinetic

TABLE VI

SECOND-ORDER RATE CONSTANTS (AT 25°) FOR THE REACTIONS OF $C_5H_5M(CO)L$ WITH CH_3I AND $C_2H_5I^a$

		M = Co				L = $P(C_6H_5)_3$, M	
	Solvent	$P(C_6H_5)_3$	$P(C_6H_5)_2CH_3$	$PC_6H_5(CH_3)_2$	$P(C_6H_{11})_3$	Rh	Ir
CH_3I	CH_2Cl_2	25.7	150	300	5.5	35	210
C_2H_5I	CH_2Cl_2	0.061	0.28	...	...	0.030	0.20
CH_3I	$C_6H_5CH_3$	...	...	...	...	0.71	...
CH_3I	THF	6					
CH_3I	$(CH_3)_2CO$	22.2					
CH_3I	CH_3CN	*Ca.* 60					

[a] All values are quoted as 10^4k^2 (M^{-1} sec^{-1}).

studies in the case of the $P(C_6H_5)_3$ and $P(C_6H_{11})_3$ complexes showed the rate of this reaction to be negligible compared with the rates of all but the slowest of the oxidative additions studied. Further it was found that in the case of $C_5H_5Co(CO)P(C_6H_5)_3$ the side reaction could be suppressed by the addition of triphenylphosphine (1 mol per Co atom) and that this added $P(C_6H_5)_3$ had no appreciable effect on the observed rate constant of the CH_3I addition. Thus the occurrence of the side reactions cannot seriously interfere with the kinetic studies.

The side reactions of $C_5H_5Co(CO)L$ were increasingly extensive in the order L = $P(C_6H_{11})_3$ < $PC_6H_5(CH_3)_2$ < $P(C_6H_5)_2CH_3$ < $P(C_6H_5)_3$ and in the solvents CH_3CN < $(CH_3)_2CO$ < THF < CH_2Cl_2 < toluene < hexane, suggesting that an initial equilibrium dissociation of phosphine was involved. The compounds $C_5H_5Rh(CO)P(C_6H_5)_3$ and $C_5H_5Ir(CO)P(C_6H_5)_3$ were much more stable, the rhodium compound decomposing at least 10 times more slowly than the cobalt analog.

The cobalt–acyl products were somewhat unstable in coordinating solvents. Thus in THF the acyl CO band grew and then decayed again, and greenish yellow crystals of an apparently ionic product were formed. In CH_3CN no acyl band could even be observed in solution, while the expected product $C_5H_5CoI(COCH_3)P(C_6H_{11})_3$ seemed to be unstable even in CH_2Cl_2.

Results

Most of the kinetic reaction products were prepared and characterized by means of analysis (Table I). The positions of the carbonyl infrared bands of these compounds correspond closely to those of the kinetic reaction mixtures at infinite time.

The observed rate constants (k_{obsd}) and the second-order rate constants derived from them (k_2) are listed in Tables II–V and k_2 values are collected in Table VI. Activation parameters are listed in Table VII.

TABLE VII

ACTIVATION PARAMETERS FOR REACTIONS WITH CH_3I IN CH_2Cl_2

	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$C_5H_5Co(CO)P(C_6H_5)_3$	12 (±1)	−31 (±3)
$C_5H_5Rh(CO)P(C_6H_5)_3$	10 (±1)	−36 (±3)
$C_5H_5Ir(CO)P(C_6H_5)_3$	*Ca.* 8–9^a	−(35–40)^a

[a] Approximate values.

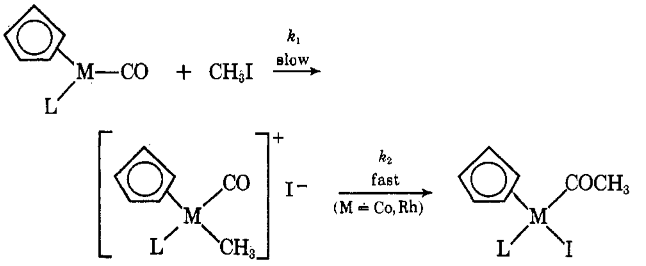
Discussion

The second-order nature of these reactions and the observed negative entropies of activation are consistent with a bimolecular mechanism. The acceptable agreement between the rate of disappearance of starting material and the rate of formation of product shows that there is only one rate-determining step in each reaction.

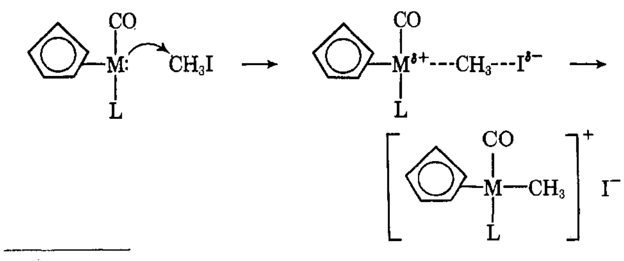
The marked effect of solvent on the reaction rate suggests that there is considerable charge separation in the activated complex. In fact the pattern of the kinetics is similar to that found for the addition of methyl iodide to square-planar Rh(I)[3,4] and Ir(I)[2] complexes and for Menschutkin reactions between amines and alkyl halides.[8,9]

The reaction at the alkyl iodide is most probably a nucleophilic attack on the α carbon or an electrophilic attack on iodine. Since the carbon atom in carbonyl ligands is often reactive toward base,[10] it seems unlikely that in this case it should act as a nucleophile. Furthermore the electron density at the metal atom is high in these $C_5H_5M(CO)L$ complexes, as shown by the low frequency of the carbonyl stretching band. It seems likely that the metal atoms have some nucleophilic power; the Lewis basicity of transition metals has recently been reviewed.[11]

We therefore propose that the rate-determining step in these reactions is a nucleophilic attack by the metal atom on the α carbon of the alkyl iodide. This produces an ionic species,[6a] which is stable in the case of iridium. With cobalt and rhodium, however, the ionic species is only an intermediate which collapses in a rapid second step involving coordination of iodide ion and migration of the alkyl group to the carbonyl ligand (carbon monoxide "insertion").



The proposed first step may be represented as



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[11] J. C. Kotz and D. G. Pedrotty, *Organometal. Chem. Rev., Sect. A*, **4**, 479 (1969).

The "latent" lone pair of electrons in the starting material is intended to have a nucleophilic but not a stereochemical significance.

Similar nucleophilic attacks by the metal atoms have been proposed in the oxidative additions of methyl iodide to complexes $(Ar_3P)_2M(CO)X$ (M = Rh,[3] Ir[2]) and $(C_6H_5)_3PRh(CO)_2Cl$.[4] Furthermore in the latter cases the rhodium but not the iridium complexes undergo methyl migration to the carbonyl ligand. There is clearly much similarity between these systems and our own.

There is also a close relationship between the proposed stages of this reaction and related reactions of species with one more negative charge,[6a] *e.g.*, $Mn(CO)_5^- + CH_3I \rightarrow CH_3Mn(CO)_5 + I^-$ and $CH_3Mn(CO)_5 + I^- \rightarrow IMn(CO)_4COCH_3^-$.

Support for our proposed mechanism comes from isolation of one of the ionic intermediates. The compound $C_5H_5RhBr(COCH_3)PC_6H_5(CH_3)_2$ reacts rapidly with $NaB(C_6H_5)_4$ in methanol to give a high yield of the white ionic product $[C_5H_5Rh(CH_3)COPC_6H_5(CH_3)_2]^+B(C_6H_5)_4^-$ (ν_{CO} 2068 cm^{-1}).[6a] The reaction between $C_5H_5RhI(COCH_3)P(C_6H_5)_3$ and $NaB(C_6H_5)_4$ is complicated by the low solubility of the former in methanol, but by using a CH_2Cl_2–CH_3OH mixture about 3–4 mg of pale yellow crystalline product was isolated. This had ν_{CO} 2070 cm^{-1} in CH_2Cl_2. On addition of $(CH_3)_4NI$ this band disappeared rapidly and was replaced by the expected bands[12] at 1666 and 1643 cm^{-1} of the product $C_5H_5RhI(COCH_3)P(C_6H_5)_3$.

Effect of Solvent.—The reaction rates are strongly dependent on the solvent. The reaction between $C_5H_5Co(CO)P(C_6H_5)_3$ and CH_3I can only be studied in a limited range of solvents because of the instability of starting materials and products, but relative rates at 25° were found: THF, 0.2; $(CH_3)_2CO$, 0.9; CH_2Cl_2, 1.0; CH_3CN, 2–3 (approximate). Study of the reaction between $C_5H_5Rh(CO)P(C_6H_5)_3$ and CH_3I in toluene was complicated by the coincidence of the carbonyl stretching band with a toluene mode and by slow crystallization of the product. The second-order rate plot (Figure 2a) shows an upward curvature which is probably a medium effect; at high concentrations of methyl iodide (up to 0.3 mol fraction) the polarity of the medium is much greater than that of pure toluene. A plot of $k_{obsd}/[CH_3I]$ against $[CH_3I]$ (Figure 2b) was extrapolated back to obtain the second-order rate constant in pure toluene. This is the value recorded in Table IV and is 50 times smaller than the corresponding rate constant for CH_2Cl_2.

Effect of Alkyl Group and Phosphine.—Ethyl iodide reacts 400–1200 times more slowly than methyl iodide with the $C_5H_5M(CO)L$ compounds investigated. This large rate difference and also the rate differences produced by different phosphines in the $C_5H_5Co(CO)L$ compounds are probably caused mainly by steric effects.

Ingold has surveyed[13] an extensive series of nucleophilic displacements on alkyl halides by halide ions (Finkelstein reactions) in acetone at 25°. The slower rates of all the ethyl halides than those of their methyl analogs are shown to be predominantly a steric rather than an electronic effect, and this steric effect is further shown to be largely ponderal in origin.

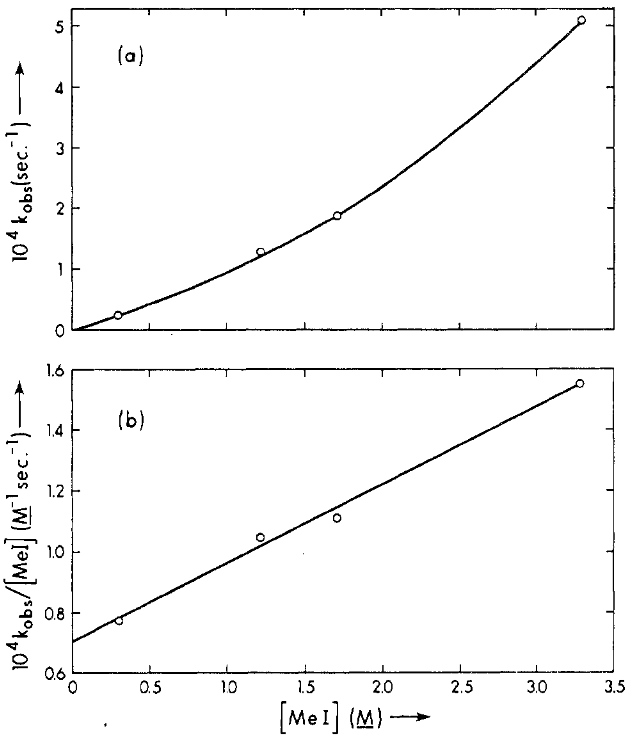
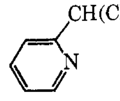
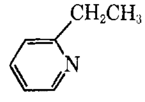
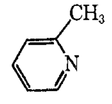


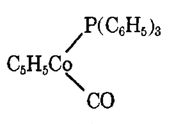
Figure 2.—Reactions of $C_5H_5Rh(CO)P(C_6H_5)_3$ with CH_3I in toluene, showing the effect of increased polarity caused by high CH_3I concentrations.

Brown has studied the effect of steric hindrance on nucleophilic displacements on alkyl halides, and we may compare some of his results[14] on substituted pyridines with our data on $C_5H_5Co(CO)L$ nucleophiles. Relative rates at 25° for nucleophilic displacements on methyl iodide are as follows[15]

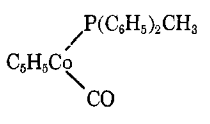

1.0[16]


3.2

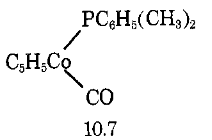

6.7


$C_5H_5Co(P(C_6H_5)_3)(CO)$

1.0


$C_5H_5Co(P(C_6H_5)_2CH_3)(CO)$

6.1


$C_5H_5Co(PC_6H_5(CH_3)_2)(CO)$

10.7

In both series of nucleophiles changes are being made in the bulkiness of the groups some three atoms removed from the reaction site, and the effects on the rate are of the same order of magnitude in both cases.

The increasingly basic $P(C_6H_5)_2CH_3$ and $PC_6H_5(CH_3)_2$ ligands might be expected to make the corresponding $C_5H_5Co(CO)L$ complexes increasingly nucleo-

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[12] The occurrence of two acyl bands in molecules of this type has been noted previously and ascribed to a conformational effect.[6a]

[13] C. K. Ingold, *Quart. Rev., Chem. Soc.*, **11**, 1 (1957).

[14] H. C. Brown, *J. Chem. Soc.*, 1249 (1956).

[15] Nitrobenzene was the solvent for the pyridine reactions and dichloromethane for those of the cobalt compound.

[16] Actual value of $k_2 = 2.45 \times 10^{-5}\ M^{-1}\ sec^{-1}$.[14]

philic with respect to $C_5H_5Co(CO)P(C_6H_5)_3$.[17] The tricyclohexylphosphine complex, however, shows that the steric effect is important, since $P(C_6H_{11})_3$ is one of the most basic but also one of the bulkiest phosphines.[7] As expected, the CO stretching band in $C_5H_5Co(CO)P(C_6H_{11})_3$ is appreciably lower in frequency than those of the other complexes used (Table I). We were unable to isolate any acyl product, but the rate of disappearance of $C_5H_5Co(CO)P(C_6H_{11})_3$ with CH_3I was one-fifth as large as that of $C_5H_5Co(CO)P(C_6H_5)_3$, so that in this case at least the steric effect predominates.

The rate difference between CH_3I and C_2H_5I is surprisingly large. Hine stated that "in SN2 reactions methyl halides are usually found to be 4–150 times as reactive as the corresponding ethyl halides."[18] The absolute values of our rate constants, however, are not unlike those reported for well-known systems.[13,14] The complexes under investigation behave therefore as nucleophiles of moderate reactivity but unusual steric selectivity.

Effect of Metal.—The initial nucleophilic attack on methyl and ethyl iodides seems to be an essentially similar process for the three metals Co, Rh, and Ir in the compounds $C_5H_5M(CO)P(C_6H_5)_3$. The kinetic patterns and activation parameters (for CH_3I) are all of the same kind. The failure of the iridium reaction to undergo the second stage is interesting; a related case has been discussed.[3]

The relative rates of reaction of the complexes with different metals are as follows: CH_3I: Co, 1.0; Rh, 1.4; Ir, *ca.* 8; C_2H_5I: Co, 2; Rh, 1; Ir, 6. Thus the expected[9] increase in nucleophilicity on descending the group is apparent in the reaction with methyl iodide but is outweighed in the ethyl iodide case by the alternating effect so common in this triad.[7] $C_5H_5Rh(CO)P(C_6H_5)_3$ has a higher CO stretching frequency than either the Co or the Ir analogs, which suggests that the electron density at the metal atom is relatively low and may be related to its low nucleophilicity. Similar trends in reactivity have been noted for metal carbonyl anions.[19]

In order to gain further insight into these systems we have studied the reactions of $C_5H_5Rh(CO)P(C_6H_5)_3$ with benzyl and allyl halides. These results will be reported in a subsequent paper.

Acknowledgment.—We thank the National Research Council of Canada for financial support.

[17] A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1802 (1969).

[18] J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1956.

[19] R. E. Dessy, R. L. Pohl, and R. B. King, *J. Amer. Chem. Soc.*, **88**, 5121 (1966).

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Preparation, Stereochemistry, and Conformational Analysis of Cobalt(III)–Triethylenetetramine-*N*-methyl-(*S*)-alaninato Complexes

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The preparations and structural assignments of some β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ ions are described; the $\Lambda(+)_{589}$-β_2-(*SSR*)-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$, $\Delta(-)_{589}$-β_2-(*RSS*)-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$, $\Delta(-)_{589}$-β_2-(*RRS*)-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$, and $\Delta(-)_{589}$-β_2-(*RRS*)-Co(trien)(*N*-Me-(*R*)-ala)$^{2+}$ diastereoisomers have been separated by fractional crystallization and resolution methods or observed following mutarotation at pH 7 or 12. Under equilibrium conditions, pH 6.5 (25°), the Δ-*RRS*(*S*) and Δ-*RSS*(*S*) isomers exist in approximately equal amounts; at pH 12 (25°) the equilibrated solution contains Δ-*RRS*(*R*) (~60%), Δ-*RRS*(*S*) (~20%), and Δ-*RSS*(*S*) (~20%). Strain energy minimization calculations support the structural assignments and predict that significant angular deformations will occur in the molecular ions to relieve steric crowding.

Introduction

Previous experiments have shown that the reaction of β-Co(trien)(OH)(H$_2$O)$^{2+}$ (trien = triethylenetetramine) with (*S*)-proline is kinetically controlled and that equal amounts of the diastereoisomers Δ-β_2-(*RRS*)-Co(trien)((*S*)-pro)$^{2+}$ and Λ-β_2-(*SSS*)-Co(trien)((*S*)-pro)$^{2+}$ are formed.[1,2] However, it was not possible to measure the relative stabilities of the Δ-β_2-(*RRS*)-Co(trien)((*S*)-pro)$^{2+}$ and Δ-β_2-(*RRR*)-Co(trien)((*R*)-pro)$^{2+}$ ions, since base-catalyzed dissociation of the amino acid moiety preceded mutarotation. The slow rate of mutarotation compared to other chelated amino acids[3] was attributed to the requirement that protons

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(1) D. A. Buckingham, L. G. Marzilli, I. E. Maxwell, A. M. Sargeson, and H. C. Freeman, *Chem. Commun.*, 583 (1969).

(2) Nomenclature: *R* and *S* designate the asymmetry about the "angular" and "planar" asymmetric N atoms of triethylenetetramine and the secondary N atom of the amino acid in that order and follow the rules suggested by C. K. Ingold, V. Prelog, and R. S. Cahn, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966), and accepted by the IUPAC. For consistency we have also used this nomenclature to specify the configuration of the α-C atom of the amino acid (*e.g.*, (*S*)-proline = L-proline). The use of β, β_1, and β_2 follows that used by L. G. Marzilli and D. A. Buckingham, *Inorg. Chem.*, **6**, 1042 (1967). The absolute configuration about the cobalt center is indicated by the prefix Δ or Λ: *ibid.*, **9**, 1 (1970).

(3) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **89**, 5133 (1967).