Combination of Aryl and Carbonyl Ligands in Ruthenium(II) Complexes: A Kinetic Study

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Reactions of diaryl complexes [Ru(CO)$_2$RR'(PMe$_2$Ph)$_2$] with Me$_3$CNC yield the acyl complexes [Ru(CO)(CNCMe$_3$)(COR)R'(PMe$_2$Ph)$_2$]. Rate-determining combination of aryl and carbonyl ligands is followed by rapid attack by isonitrile *trans* to the acyl ligand. In symmetrical diaryl complexes, rates are increased by electron-releasing substituents in the *para* position of the aryl ring. A methyl substituent in the *meta* position has a rather large accelerating effect, presumably for steric reasons. In unsymmetrical diaryl complexes, the aryl ligand bearing the more electron-releasing substituent becomes incorporated in the acyl ligand. Variations in the aryl ligand not directly involved in the reaction have little effect on rate, and solvent effects are relatively small. The fairly large negative entropies of activation are attributed to the formation in the transition state of a three-membered metal–carbonyl–aryl ring, in which the aryl ring has presumably lost its freedom of rotation.

In previous papers, we have shown that methyl complexes of ruthenium(II), [Ru(CO)$_2$(Me)X(PMe$_2$Ph)$_2$] (X = Cl, Br, I, Me, COMe, or Ph), react with CO to form acetyl complexes [Ru(CO)$_2$(COMe)X(PMe$_2$Ph)$_2$].[1,2] The complexes [Ru(CO)$_2$(Me)X(PMe$_2$Ph)$_2$] (X = Cl, Br, or I) also form acetyl complexes, [Ru(CO)(COMe)X(PMe$_2$Ph)$_3$], when treated with PMe$_2$Ph.[1] In contrast, we have found no evidence for the formation of benzoyl complexes when phenyl complexes [Ru(CO)$_2$(Ph)X(PMe$_2$Ph)$_2$] (X = Cl, Br, I, Me, COMe, or Ph) are treated with CO at atmospheric pressure or with PMe$_2$Ph, although Roper and Wright[3] have shown that the related complexes [Ru(CO)$_2$(C$_6$H$_4$Me-4)X(PPh$_3$)$_2$] (X = Cl, Br, or I) are in equilibrium with acyl species [Ru(CO)(CO-C$_6$H$_4$Me-4)X(PPh$_3$)$_2$] in solution.

We now report that all the members of a range of diaryl complexes [Ru(CO)$_2$RR'(PMe$_2$Ph)$_2$] react with the isonitrile Me$_3$CNC to form acyl complexes [Ru(CO)(CNCMe$_3$)(COR)R'(PMe$_2$Ph)$_2$], providing an opportunity to determine how the rate and activation parameters for the formation of the acyl ligand depend both on the aryl ligand directly involved in the reaction and on the ' uninvolved ' aryl ligand R'.

Results and Discussion

Details of the i.r. and ^{1}H n.m.r. spectra of new complexes are given in Table 1, and ^{13}C n.m.r. data are listed in Table 2. A complete list of the complexes and their complex numbers is given in Table 3 together with analytical data for the new compounds.

Preparation and Characterization of Acyl Complexes.— Treatment of the diaryl complexes [Ru(CO)$_2$R$_2$(PMe$_2$Ph)$_2$] [R = Ph (1a), C$_6$H$_4$OMe-4 (1b), C$_6$H$_4$Me-3 (1c), C$_6$H$_4$Me-4 (1d), C$_6$H$_4$F-4 (1e), or C$_6$H$_4$Cl-4 (1f)] with an equimolar quantity of Me$_3$CNC in CHCl$_3$ solution at room temperature resulted in the solution becoming coloured. Removal of the solvent and recrystallization of the residue yielded yellow or orange products (2a)—(2f) for which elemental analysis indicated the formula [Ru(CO)(CNCMe$_3$)(COR)R(PMe$_2$Ph)$_2$].

Table 1. Infrared [a] and ^{1}H n.m.r.[b] spectra of the new complexes

Complex	ν(CN)/cm^{-1}	ν(CO)/cm^{-1}	δ/p.p.m.	Assignment
(2a)	2 134	1 935	1.25 (t, 6)	PMe$_2$Ph
		1 560	1.21 (t, 6)	PMe$_2$Ph
			1.16 (s, 9)	CNCMe$_3$
(3a) [c]	2 145	1 936		
		1 545		
(2b)	2 140	1 933	3.70 (s, 6) [d]	4-OMe
		1 588	1.23 (t, 6)	PMe$_2$Ph
			1.17 (s, 9)	CNCMe$_3$
			1.14 (t, 6)	PMe$_2$Ph
(2c)	2 142	1 935	2.20 (s, 3)	3-Me
		1 540	2.10 (s, 3)	3-Me
			1.27 (t, 6)	PMe$_2$Ph
			1.21 (t, 6)	PMe$_2$Ph
			1.18 (s, 9)	CNCMe$_3$
(2d)	2 130	1 949	2.28 (s, 3)	4-Me
		1 550	2.26 (s, 3)	4-Me
			1.28 (t, 6)	PMe$_2$Ph
			1.21 (t, 6)	PMe$_2$Ph
			1.17 (s, 9)	CNCMe$_3$
(2e)	2 145	1 938	1.27 (t, 6)	PMe$_2$Ph
		1 590	1.19 (s, 9)	CNCMe$_3$
			1.18 (t, 6)	PMe$_2$Ph
(2f)	2 145	1 942	1.32 (t, 6)	PMe$_2$Ph
		1 578	1.20 (t, 6)	PMe$_2$Ph
			1.18 (s, 9)	CNCMe$_3$
(2g)	2 145	1 942	2.28 (s, 3)	4-Me
		1 550	1.32 (t, 6)	PMe$_2$Ph
			1.21 (t, 6)	PMe$_2$Ph
			1.18 (s, 9)	CNCMe$_3$
(1h)		2 020	2.19 (s, 3)	3-Me
		1 955	1.38 (t, 12) [d]	PMe$_2$Ph
(2h)	2 140	1 940	2.14 (s, 3)	3-Me
		1 545	1.19 (t, 6)	PMe$_2$Ph
			1.16 (t, 6)	PMe$_2$Ph
			1.13 (s, 9)	CNCMe$_3$

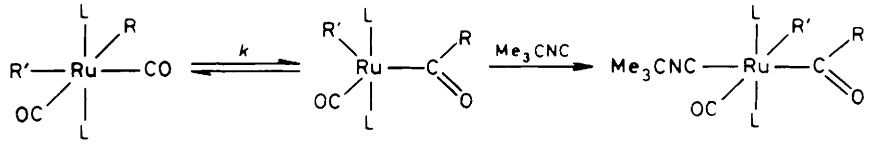
[a] In CHCl$_3$ solution. Only nitrile, carbonyl, and acyl resonances are listed. [b] In CDCl$_3$ solution. Only methyl proton resonances are listed. Multiplicities and relative areas are given after the chemical shift values. For PMe$_2$Ph methyl protons, $|^2J(P-H) + ^4J(P-H)|$ = *ca.* 7 Hz. [c] Proton n.m.r. spectrum uninformative owing to overlapping resonances. [d] Accidental superimposition of two resonances.

The i.r. spectra of complexes (2a)—(2f) contained the expected bands due to the stretching modes of the cyano-group (2 130—2 145 cm^{-1}), the carbonyl ligand (1 935—1 949 cm^{-1}), and the carbonyl group within the acyl ligand (1 540—1 590 cm^{-1}). The n.m.r. spectra of the complexes included triplet resonances at *ca.* δ 200 and 270 for the carbon atoms in the carbonyl ligand and the carbonyl group of the acyl ligand. Resonances for the carbon and hydrogen atoms in the Me$_3$CNC ligand were all identified, although that for the carbon atom directly attached to the metal (at *ca.* δ 153) was always weak and broad. From the observation of triplet resonances for the methyl carbon and hydrogen atoms in the

Table 2. Carbon-13 n.m.r. spectra of new complexes in $CDCl_3$ solution

			C_6H_4X [c]					
Complex	CO [a]	$CNCMe_3$ [b]	C^1	C^2, C^6	C^3, C^5	C^4	X	PMe_2Ph [d]
(2a)	202.7 *	153.6	155.9	127.5	125.8	128.2		15.7
	273.1 †	56.4	166.4	143.5	125.8	121.4		15.0
		30.1						
(3a)	202.6 *	154.8	156.5	127.6	125.9	128.1		15.4
	273.9 †		166.3	143.6	125.6	121.5		14.9
(2b)	202.7 *	153.8	148.7	128.2	112.4	159.9	55.2	15.8
	270.1 †	56.3	154.3	143.6	112.0	155.8	54.8	15.0
		30.1						
(2c)	202.8 *	153.4	156.2	127.4,	136.8,	122.9	21.3	15.9
	272.9 †	56.3	165.9	128.8	126.9			15.0
		30.1		140.6,	133.7,	122.1	21.7	
				144.7	125.5			
(2d)	202.7 *	154.0	153.2	128.0	126.4	138.1	21.2	15.8
	272.2 †	56.3	161.0	143.4	126.9	130.4	21.0	15.1
		30.1						
(2e)	202.3 *	153.1	151.7	128.0	113.9	162.9		15.6
	270.3 †	56.6	158.6	143.9	112.6	160.8		15.1
		30.1						
(2f)	202.3 *	152.7	153.4	127.4	127.4	134.2		15.6
	270.5 †	56.6	163.8	144.3	125.7	128.4		15.2
		30.1						
(2g)	202.6 *	153.0	152.8	128.0	126.2	138.2	21.1	15.5
	271.3 †	56.4	164.5	144.4	125.7	128.2		15.2
		30.1						
(1h)	198.2 *		161.7	144.6,	134.7,	122.8	21.7	14.3 [e]
	197.8 *			140.6	126.0			
			160.5	144.6	126.0	128.3		
(2h)	202.6 *	152.9	155.7	127.4,	136.8,	122.8	21.3	15.7
	273.6 †	56.6		129.1	126.9			15.0
		30.1	164.4	144.5	125.6	128.2		

[a] Triplet resonances: for carbonyl ligands (*) $|^2J(P-C)|$ = *ca.* 9.5 Hz; for acyl ligands (†) $|^2J(P-C)|$ = *ca.* 11.5 Hz. [b] Resonances are listed in the order $\mathit{C}NCMe_3$, $CN\mathit{C}Me_3$, $CNC\mathit{Me}_3$. Resonances for $\mathit{C}NCMe_3$ were weak and broad; others were sharp singlets. For (3a), only $\mathit{C}NC_6H_{11}$ is listed. [c] For (2a)—(2h) and (3a), upper and lower entries are for acyl and aryl ligands respectively. For (1h) upper and lower entries are for 3-methylphenyl and 4-chlorophenyl ligands respectively. Aryl ligand C^1, C^2, and C^6 resonances showed triplet splittings due to phosphorus: $|^2J(P-C)|$ = *ca.* 16.0, $|^3J(P-C)|$ = *ca.* 2.5 Hz. Other resonances showed no clear phosphorus splittings. For (2e) all resonances exhibited doublet splittings due to fluorine. [d] Only methyl resonances are listed. These are triplets: $|^1J(P-C) + {}^3J(P-C)|$ = *ca.* 31.5 Hz. [e] Accidental superimposition of two resonances.



(1) (3) (2)

Scheme. Proposed mechanism for the reactions of $[Ru(CO)_2RR'L_2]$ with Me_3CNC

PMe_2Ph ligands, it was evident that these ligands were mutually *trans*.* No attempt was made to analyse the jumble of resonances for the arene ring hydrogens in the aryl, acyl, and PMe_2Ph ligands, but, with the help of spectra recorded under conditions of weak noise decoupling and by comparison with the spectra of the parent diaryl complexes, it was possible to assign nearly all the resonances for the ring carbon atoms in the aryl and acyl ligands with reasonable certainty. Where the substituent in the ring contained carbon and hydrogen atoms, the resonances for these atoms were also identified.

Unfortunately none of the spectroscopic data helped to indicate the relative positions of the four carbon-bonded ligands in the complex. *X*-Ray investigation [6] of complex (2a) showed it to possess the structure (2) in the Scheme, where L = PMe_2Ph and R = R' = Ph. Comparing this structure with that of complexes (1a)—(1f), structure (1) in the Scheme, it can be seen that the isonitrile ligand has entered *trans* to the newly formed acyl ligand. This stereochemistry matches that of the reactions of the methyl complexes $[Ru(CO)_2(Me)X(PMe_2Ph)_2]$ mentioned above.[1]

For the purposes of the kinetic study, one complex, $[Ru(CO)(CNC_6H_{11})(COPh)Ph(PMe_2Ph)_2]$ (3a), was prepared using cyclohexyl isonitrile in place of Me_3CNC. Reactions were also carried out between Me_3CNC and two complexes

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* The ways in which phosphorus ligands can be used as stereochemical probes in ruthenium(II) complexes have been described by Shaw and co-workers.[4,5]

Table 3. Formulae of complexes and analytical data for new complexes

	Found (%)			Calculated (%)		
Complex	C	H	N	C	H	N
$[Ru(CO)_2Ph_2(PMe_2Ph)_2]$ (1a)						
$[Ru(CO)(CNCMe_3)(COPh)Ph(PMe_2Ph)_2]$ (2a)	62.5	6.25	2.10	62.65	6.15	2.10
$[Ru(CO)(CNC_6H_{11})(COPh)Ph(PMe_2Ph)_2]$ (3a)	63.65	6.30	2.05	63.8	6.20	2.00
$[Ru(CO)_2(C_6H_4OMe\text{-}4)_2(PMe_2Ph)_2]$ (1b)						
$[Ru(CO)(CNCMe_3)(COC_6H_4OMe\text{-}4)(C_6H_4OMe\text{-}4)(PMe_2Ph)_2]$ (2b)	60.9	6.35	2.00	60.8	6.20	1.90
$[Ru(CO)_2(C_6H_4Me\text{-}3)_2(PMe_2Ph)_2]$ (1c)						
$[Ru(CO)(CNCMe_3)(COC_6H_4Me\text{-}3)(C_6H_4Me\text{-}3)(PMe_2Ph)_2]$ (2c)	63.45	6.55	2.05	63.6	6.50	2.00
$[Ru(CO)_2(C_6H_4Me\text{-}4)_2(PMe_2Ph)_2]$ (1d)						
$[Ru(CO)(CNCMe_3)(COC_6H_4Me\text{-}4)(C_6H_4Me\text{-}4)(PMe_2Ph)_2]$ (2d)	63.45	6.45	1.95	63.6	6.50	2.00
$[Ru(CO)_2(C_6H_4F\text{-}4)_2(PMe_2Ph)_2]$ (1e)						
$[Ru(CO)(CNCMe_3)(COC_6H_4F\text{-}4)(C_6H_4F\text{-}4)(PMe_2Ph)_2]$ (2e)	59.2	5.55	2.15	59.5	5.55	2.00
$[Ru(CO)_2(C_6H_4Cl\text{-}4)_2(PMe_2Ph)_2]$ (1f)						
$[Ru(CO)(CNCMe_3)(COC_6H_4Cl\text{-}4)(C_6H_4Cl\text{-}4)(PMe_2Ph)_2]$ (2f)	56.85	5.45	2.15	56.85	5.30	1.90
$[Ru(CO)_2(C_6H_4Cl\text{-}4)(C_6H_4Me\text{-}4)(PMe_2Ph)_2]$ (1g)						
$[Ru(CO)(CNCMe_3)(COC_6H_4Me\text{-}4)(C_6H_4Cl\text{-}4)(PMe_2Ph)_2]$ (2g)	60.2	5.95	2.10	60.1	5.90	1.95
$[Ru(CO)_2(C_6H_4Cl\text{-}4)(C_6H_4Me\text{-}3)(PMe_2Ph)_2]$ (1h)	58.45	5.00		58.55	5.25	
$[Ru(CO)(CNCMe_3)(COC_6H_4Me\text{-}3)(C_6H_4Cl\text{-}4)(PMe_2Ph)_2]$ (2h)						

Table 4. Kinetic data for reactions of complexes (1a)—(1h) with isonitriles [a]

Complex (λ nm)	10^3[complex]/ mol dm^{-3}	T/K	$10^5k_{\text{obs.}}$ [b]/s^{-1}	$10^5k_{\text{obs.}}$ [c]/s^{-1}	$10^5k_{\text{obs.}}$ [d]/s^{-1}
(1a)	2.01	293.2	4.18(2)	4.18(2)	4.19(2)
(392)	2.28	298.3	7.61(8)	7.75(3)	7.69(2)
	2.08	304.3	13.3(1)	13.5(1)	13.4(1)
	2.01	309.1	19.1(2)	18.4(2)	18.9(2)
(1b)	2.70	293.9	30.4(2)	30.8(5)	30.4(2)
(385)	2.32	298.5	50.2(6)	49.0(5)	49.7(5)
	2.70	303.5	77.5(8)	78.8(8)	77.8(7)
	2.47	308.9	139(2)	135(2)	141(2)
(1c)	2.19	289.7	10.0(1)	10.3(1)	10.3(1)
(390)	2.18	298.3	28.1(1)	27.9(1)	27.8(2)
	2.11	303.4	43.2(1)	44.4(2)	45.0(1)
	2.11	309.1	70.5(11)	72.4(5)	71.3(11)
(1d)	2.40	289.3	7.58(2)	7.62(3)	7.64(4)
(389)	2.24	298.3	20.2(1)	20.2(1)	20.4(1)
	2.34	304.1	37.9(2)	38.2(2)	38.1(2)
	2.45	310.0	66.2(8)	66.7(3)	66.3(5)
(1e)	1.67	295.3	2.55(1)	2.40(3)	2.51(4)
(390)	1.76	298.3	3.81(1)	3.75(2)	3.70(3)
	1.51	303.7	7.12(5)	7.02(6)	7.10(8)
	1.72	308.7	11.4(1)	11.4(1)	11.2(1)
(1f)	2.02	298.9	0.650(3)	0.664(4)	0.645(4)
(390)	2.22	303.5	1.11(1)	1.10(1)	1.18(1)
	2.32	308.5	2.12(1)	2.20(1)	2.04(1)
	2.02	314.5	3.59(2)	3.60(1)	3.56(8)
(1g)	2.06	294.4	8.82(4)	8.53(11)	8.69(2)
(392)	2.31	298.3	11.9(1)	12.2(1)	12.1(1)
	1.92	302.8	17.2(2)	17.4(2)	18.0(1)
	1.92	308.9	36.5(2)	36.1(2)	36.7(4)
(1h)	2.04	298.3	13.2(1)	13.5(1)	12.7(1)
(390)					
(1a) [e]	2.84	298.3	7.49(6)	7.52(4)	7.49(5)
(400)					
(1a) [f]	1.96	290.7	1.43(3)	1.48(5)	1.52(4)
(393)	2.08	298.1	4.17(3)	4.18(2)	4.21(4)
	2.04	304.3	6.48(2)	6.47(3)	6.49(3)
	1.87	309.1	10.5(1)	10.5(1)	10.8(1)
(1a) [g]	1.76	293.1	2.49(1)	2.52(1)	2.50(1)
(393)	1.74	298.3	4.52(4)	4.48(4)	4.48(3)
	1.81	303.3	7.06(4)	7.02(8)	6.97(4)
	2.31	308.7	13.3(1)	13.0(1)	12.2(1)

[a] Reactions were with Me_3CNC and in $CHCl_3$ solution except where stated otherwise. Standard deviations, given in parentheses, refer to the final figure(s) of the values given for the rate constants. [b] Molar ratio isonitrile : complex, 10 : 1. [c] Molar ratio isonitrile : complex, 20 : 1. [d] Molar ratio isonitrile : complex, 30 : 1. [e] Reaction with $C_6H_{11}NC$ in $CHCl_3$ solution. [f] Reaction with Me_3CNC in benzene solution. [g] Reaction with Me_3CNC in ethyl acetate solution.

containing two different aryl ligands, $[Ru(CO)_2(C_6H_4Cl\text{-}4)(C_6H_4Me\text{-}4)(PMe_2Ph)_2]$ (1g) and $[Ru(CO)_2(C_6H_4Cl\text{-}4)(C_6H_4\text{-}Me\text{-}3)(PMe_2Ph)_2]$ (1h). From spectroscopic data it was clear that each reaction yielded a single product, of the type $[Ru(CO)(CNCMe_3)(COR)R'(PMe_2Ph)_2]$. Evidence as to which aryl ligands in (1g) and (1h) had been incorporated into the acyl ligands in the products, (2g) and (2h), came from the ^{13}C n.m.r. spectra of the products and, in particular, from spectra run under conditions of weak noise decoupling, in which the resonances for the ring carbon atoms bearing substituents could readily be identified. Thus the resonances for the two C^4 atoms in (2g) were at δ 128.2 and 138.2. Typical chemical shift values for C^4 in a 4-chlorophenyl ligand are δ 128.7, 128.4, and 128.8 [in complexes (1f), (2f), and (1g), respectively], whereas the value for C^4 in the 4-chlorobenzoyl ligand in (2f) is δ 134.2. For C^4 in a 4-methylphenyl ligand the values are δ 131.0, 130.4, and 131.2 [in complexes (1d), (2d), and (1g), respectively], as opposed to δ 138.1 for C^4 in the 4-methylbenzoyl ligand in (2d). Hence we concluded that (2g) was $[Ru(CO)(CNCMe_3)(COC_6H_4Me\text{-}4)(C_6H_4Cl\text{-}4)(PMe_2Ph)_2]$, and a similar approach led to the formulation of (2h) as $[Ru(CO)(CNCMe_3)(COC_6H_4Me\text{-}3)(C_6H_4Cl\text{-}4)(PMe_2Ph)_2]$.

Kinetic Studies.—Since the colourless diaryl complexes (1a)—(1h) reacted with Me_3CNC to give products (2a)—(2h) with absorption bands centred in the region 385—400 nm, these reactions could be monitored by visible spectroscopy. The solvent used was normally $CHCl_3$, since this was the solvent employed for the preparative work. All the kinetic studies were carried out with the isonitrile ligand in large excess, so that its concentration could be regarded as remaining constant throughout a given run. The spectra of the solutions at the end of the kinetic runs were checked against those of the isolated products (2a)—(2h) in $CHCl_3$ solution.

Preliminary studies established that the reactions were first order in ruthenium complex, and that rate constants were unaffected by variation in the initial concentration of ruthenium complex. As a check on the reproducibility of rate constant values, sets of five supposedly identical kinetic runs were carried out for the reaction of complex (1a) with Me_3CNC at 298.3 K at three different isonitrile concentrations. In the set showing the greatest variation in values, all five were still within ±2.5% of the mean.

First-order rate constants for all the reactions studied are listed in Table 4. Each complex (1a)—(1h) reacted with Me_3CNC at a rate that was essentially independent of the concentration of isonitrile, indicating that the rate-determining step under the conditions used did not involve the isonitrile. In addition, comparison of the rate constants for the reactions of complex (1a) with Me_3CNC and with $C_6H_{11}NC$ at 298.3 K revealed that the rate was not significantly affected by the choice of isonitrile. These findings were compatible with the mechanism shown in the Scheme, in which the rate-determining step (rate constant k) involved the combination of aryl and carbonyl ligands. The species (3) thus formed was then attacked by isonitrile *trans* to the newly formed acyl ligand, and the simple kinetic behaviour indicated that this step must be appreciably faster than either the formation of (3) or its reconversion to (1).

A check on the extent of involvement of the solvent in the rate-determining step was carried out by varying the solvent for the reaction of (1a) with Me_3CNC. The choice of solvent was limited by the lack of solubility of (1a) in many (particularly the more polar) solvents, but the reaction was successfully studied in benzene and in ethyl acetate. In both cases the product was again (2a) (this was shown by elemental analysis and i.r. and n.m.r. spectroscopy). Comparison of the data for the reaction of (1a) in the three solvents indicated little variation of rate with the nature of the solvent.

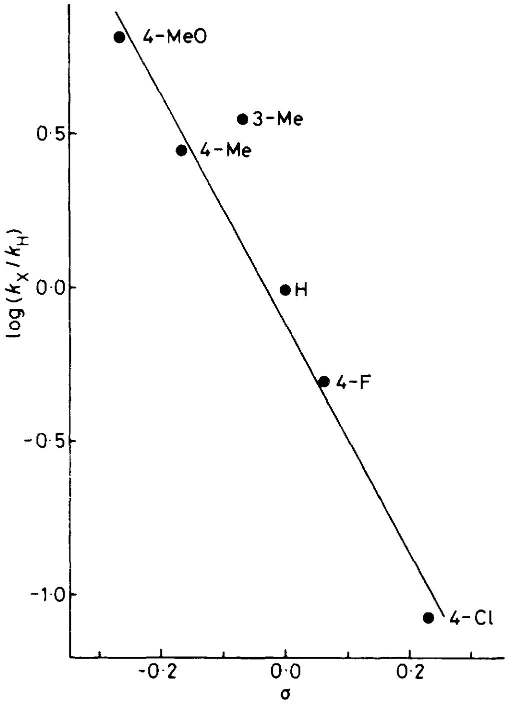

Figure. Hammett plot for the reaction of complexes (1a)—(1f) with Me_3CNC in $CHCl_3$ at 298.3 K

Plots of ln k against T^{-1} were used both to determine rate constants at a common temperature, 298.3 K, and to obtain activation parameters for the reactions (see Table 5). The rate constants for the reactions of the *para*-substituted symmetrical diaryl complexes were used to construct a Hammett plot [7] (see Figure), which indicated that the combination of aryl and carbonyl ligands was accelerated by electron-releasing substituents and retarded by electron-withdrawing substituents [a similar effect has been noted by Cross and Gemmill [8] for the *equilibrium* constants for the reversible combination of aryl and carbonyl ligands in platinum(II) complexes]. As Cross and Gemmill pointed out, such variations could reflect changes in the strength of the metal-aryl bond, since the extent of back-donation from metal to ring must vary according to the nature of the *para* substituent. An alternative approach would be to treat the combination of aryl and carbonyl ligands as a nucleophilic attack on the carbon atom of the carbonyl ligand, with the substituents altering the nucleophilicity of the aryl ligand. Craig and Green,[9] however, have claimed that little charge separation occurs during the conversion of alkyl complexes $[Mo(\eta\text{-}C_5H_5)(CO)_3R]$ into acyl complexes, and the absence of a marked dependence of rate on solvent for the reaction of complex (1a) with Me_3CNC seemed to indicate that the same was true for our ruthenium complexes.

Also included in the Figure is the value for $[Ru(CO)_2(C_6H_4Me\text{-}3)_2(PMe_2Ph)_2]$ (1c). This complex reacted more rapidly than expected from the Hammett plot, presumably because the crowding resulting from the presence of a substituent in the *meta* position was to some extent relieved as aryl and carbonyl ligands combined.

In the case of the reactions of the mixed diaryl complexes (1g) and (1h), it was the methyl-substituted phenyl ligand rather than the 4-chlorophenyl ligand which became incorporated in the acyl ligand. This result was consistent with the

Table 5. Activation data at 298.3 K [a]

Complex	10^5k/s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta G^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
(1a)	7.23	69(2)	97	−92
(1b)	48.0	73(1)	92	−64
(1c)	26.1	72(2)	94	−71
(1d)	20.4	76(1)	94	−61
(1e)	3.66	83(2)	98	−51
(1f)	0.624	84(2)	103	−64
(1g)	12.3	72(3)	95	−79
(1h) [b]	13.1			

[a] For reactions with Me_3CNC in $CHCl_3$ solution. Standard deviations, given in parentheses, refer to the final figure of the values given for the enthalpies of activation. Errors in values of k and $\Delta G^\ddagger$ reflect those listed in Table 4. [b] Activation parameters not determined.

kinetic studies, since the reaction of the 4-chlorophenyl complex (1f) was much slower than those of the 3- and 4-methylphenyl complexes (1c) and (1d). Comparison of the rate constants listed for (1d) and (1g) in Table 5, making the statistical allowance for the presence of two 4-methylphenyl ligands in (1d) as opposed to one in (1g), revealed that the ' uninvolved ' aryl ligand had virtually no effect on reaction rate. Comparison of the values for (1c) and (1h) led to the same conclusion.

All the reactions were characterized by fairly large negative values for $\Delta S^\ddagger$. One possible explanation for this would be an increased degree of solvation of the complexes in the transition state, but no clear evidence for this emerged from our study of the reaction of (1a) in different solvents. An alternative explanation would be that the negative $\Delta S^\ddagger$ values reflect the ordering imposed on the molecule by the formation of a three-membered ring involving metal, carbonyl, and aryl ligands, as a result of which the aryl ring would presumably lose its freedom of rotation.

Experimental

Preparation of Ruthenium Complexes.—Analytical data for the new complexes are given in Table 3. Details of the preparation of complexes (1a)—(1g) have been given elsewhere.[2] Complex (1h) was prepared from $[Ru(CO)_2(C_6H_4Me\text{-}3)Cl(PMe_2Ph)_2]$ and $Li(C_6H_4Cl\text{-}4)$, using the technique previously described for (1g).[2]

Since the complexes (2a)—(2h) and (3a) were all prepared by the same method, only the preparation of (2d) will be described in detail. Complex (1d) (0.100 g) was dissolved in $CHCl_3$ (8 cm^3), and treated with an equimolar quantity of Me_3CNC (0.014 g). An i.r. spectrum recorded after 6 h revealed that the reaction was complete. The solvent was removed under reduced pressure, and the yellow residue was recrystallized from a mixture of $CHCl_3$ and EtOH and then washed with a mixture of EtOH and light petroleum (b.p. 40—60 °C).

Reaction times for the preparations of the other complexes were as follows: (2a), 10 h; (3a), 8 h; (2b), 1.5 h; (2c), 4 h; (2e), 72 h; (2f), 200 h; (2g), 12 h; (2h), 12 h. Yields of crude product were essentially quantitative. Complex (2h) could not be induced to crystallize, but all other complexes were obtained in a crystalline state.

Spectroscopic and Kinetic Studies.—Details of the instruments used to obtain i.r. and n.m.r. spectra have been given elsewhere.[2] For the kinetic studies, a Pye-Unicam SP8-500 spectrophotometer with a thermostatically controlled cell block was used. Solutions for the kinetic runs were made up under nitrogen (using solvents which had been dried and distilled under nitrogen before use) and transferred to nitrogen-filled cells. Absorbance measurements were made at the wavelengths indicated in Table 4, and data were collected for between 2.5 and 3.0 half-lives. Rate constants were obtained by least-mean-squares treatment of values for $\ln(A_\infty - A)$ and time.

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