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(81 MHz, CD_2Cl_2, ppm): 11.98 (s).

10: *trans*-Pd[(η^6-C_6H_5CO)Cr$(CO)_3$]Cl(dpph). IR (KBr): ν(CO) 1967, 1890 cm^{-1}; ν(C═O) 1639 cm^{-1}. $^{31}P\{^1H\}$ NMR (81 MHz, CD_2Cl_2, ppm): 14.64 (s).

11: $Pd_2[(\eta^6\text{-}C_6H_5CO)Cr(CO)_3]_2(\mu\text{-}Cl)_2(PPh_3)_2$. Anal. Calcd for $C_{56}H_{40}Cl_2Cr_2O_8P_2Pd_2$: C, 52.12; H, 3.12; Cl, 5.49; Cr, 8.06; O, 9.92; P, 4.80; Pd, 16.49. Found: C, 52.61; H, 3.42; Cl, 5.07; Cr, 7.44; O, 9.38; P, 4.45; Pd, 16.75. IR (KBr): ν(CO) 1980, 1925, 1890 cm^{-1}; ν(C═O) 1657 cm^{-1}; ν(C═C) 1480, 1438 cm^{-1}. $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6, ppm): 27.06 (s).

Preparation of $Pd_2[(\eta^6\text{-}C_6H_5CO)Cr(CO)_3]_2(\mu\text{-}Cl)_2(PCy_3)_2$ (12). A solution of $Pd_2[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2(\mu\text{-}Cl)_2(PCy_3)_2$ (**3**) (508 mg, 0.4 mmol) in benzene (7 mL) was charged in a stainless steel reactor under 5 bar of CO and stirred overnight at room temperature. The green-brown solid formed was filtered, washed with hexane (5 mL), and dried in vacuo: 530 mg, 100%.

Anal. Calcd for $C_{56}H_{76}Cl_2Cr_2O_8P_2Pd_2$: C, 50.67; H, 5.73; Cr, 7.84; Pd, 16.04. Found: C, 50.28; H, 5.89; Cr, 7.42; Pd, 16.59. IR (KBr): ν(CO) 1980, 1922, 1907 cm^{-1}; ν(C═O), 1650 cm^{-1}. $^{13}C\{^1H\}$ NMR (25 MHz, CD_2Cl_2, ppm): 10.2–35.76 ($P(C_6H_{11})_3$, m), 90–103 ((η^6-C_6H_5)Cr, m), 217.35 (C═O acyl, s), 232 ($Cr(CO)_3$, s). $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6, ppm): 39.76 (s).

Preparation of *cis*-Pd[(η^6-C_6H_5CO)Cr$(CO)_3$]Cl(dppe) (13). A dark green solution of $Pd_2[(\eta^6\text{-}C_6H_5CO)Cr(CO)_3]_2(\mu\text{-}Cl)_2(PPh_3)_2$ (516 mg, 0.4 mmol) and dppe (350 mg, 0.88 mmol) in benzene (5 ml) was stirred at room temperature for 1 h. A light green solid was precipitated by hexane (10 mL), filtered off, washed further with hexane (5 mL), and dried in vacuo: 610 mg, 97%.

Anal. Calcd for $C_{36}H_{29}ClCrO_4P_2Pd$: C, 55.32; H, 3.71; Cr, 6.65; Pd, 13.62. Found: C, 55.69; H, 3.98; Cr, 6.18; Pd, 14.02. IR (KBr): ν(CO) 1960, 1900, 1870 cm^{-1}; ν(C═O) 1462 cm^{-1}; ν(C═C) 1480, 1440 cm^{-1}. ^1H NMR (100 MHz, CD_2Cl_2, ppm): 1.93–2.85 (CH_2, m, 4 H), 4.61–5.87 ((η^6-C_6H_5)Cr$(CO)_3$, m, 5 H), 7.03–8.02 ($P(C_6H_5)_2$, m, 20 H). $^{13}C\{^1H\}$ NMR (25 MHz, CD_2Cl_2, ppm) 20–30 (CH_2, m), 89.9–108.6 (η^6-C_6H_5)Cr, m), 128.2–139.3 ($P(C_6H_5)_2$, m), 232.45 ($Cr(CO)_3$, s), 233.9 (C═O acyl, s). $^{31}P\{^1H\}$ NMR (81 MHz, CD_2Cl_2, ppm): 42.8 (d, $^2J_{P-P} = 42$ Hz), 26.37 (d, $^2J_{P-P} = 42$ Hz).

Reaction of Complexes 8 and 11 with Methanol and Triethylamine. Triethylamine (140 μL, 1 mmol) was added dropwise to a stirred solution of **8** (363 mg, 0.4 mmol) or **11** (258 mg, 0.2 mmol) in chlorobenzene (19 mL), methanol (1 mL), and dodecane (500 μL, internal standard for GLC). The clear solution darkened instantaneously. The products were analyzed by GLC on a 25 m Cp sil 5 capillary column.

Registry No. 1, 136805-06-6; 2, 136827-07-1; 3, 136805-07-7; 4, 136805-08-8; 5, 136805-09-9; 6, 136805-10-2; 7, 136827-08-2; 8, 136805-11-3; 9, 136805-12-4; 10, 136805-13-5; 11, 136805-14-6; 12, 136805-15-7; 13, 136805-16-8; (η^6-C_6H_5Cl)Cr$(CO)_3$, 12082-03-0; $Pd(PPh_3)_4$, 14221-01-3.

Supplementary Material Available: Tables of crystal data, hydrogen fractional coordinates and thermal parameters, anisotropic thermal parameters, and bond lengths and bond angles for **3** and **6** (10 pages); listings of structure factors for **3** and **6** (31 pages). Ordering information is given on any current masthead page.

Ligand Effects on the Rates of the Migratory Insertion in Rhodium(III) Methyl Carbonyl Complexes

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The complexes (η^5-C_5Me_5)Rh(CO)(X)(Me) (X = I, Br, Cl, $MeCO_2$, CF_3CO_2) react readily with triphenylphosphine in toluene at 25 °C to yield quantitatively the corresponding acyl species (η^5-C_5Me_5)-Rh(COMe)(X)(PPh_3). The reactions of the halide complexes are first order in both the substrate and the phosphine. The rate increases in the order I < Br < Cl, following the increasing electronegativity of the halogen atoms. The activation parameters ($\Delta H^\ddagger = 56 \pm 2$ (I), 46 ± 3 (Br), 36 ± 2 (Cl) kJ mol^{-1}; $\Delta S^\ddagger = -79 \pm 4$ (I), -93 ± 5 (Br), -122 ± 3 (Cl) J K^{-1} mol^{-1}) indicate that the order of reactivity is dominated by changes in $\Delta H^\ddagger$. The carboxylate complexes exhibit saturation kinetics, typical of the formation of an intermediate and unprecedented for migratory insertion in a nonpolar solvent. It is proposed that the intermediate is (η^5-C_5Me_5)Rh(η^2-O_2CR)(COMe) (R = Me, CF_3), where the carboxylate moiety acts as a bidentate ligand to stabilize the otherwise unsaturated species. The rate constant for the formation of the intermediate, determined from the reactions with different nucleophiles, is somewhat larger for X = CF_3CO_2 ($k_1 = 0.16$ s^{-1}) than for X = $MeCO_2$ ($k_1 = 0.105$ s^{-1}).

Introduction

The migratory insertion of carbon monoxide into metal–alkyl bonds is a reaction of fundamental importance in organometallic chemistry and has extensive application in catalysis.[1] Many features of this reaction, including kinetics and mechanism,[2] stereochemistry,[3] migratory aptitudes of alkyl and aryl groups,[4,5] the influence of solvents

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Table I. ^1H NMR[a] and IR[b] Data for $(C_5Me_5)Rh(CO)(X)(Me)$ and $(C_5Me_5)Rh(COMe)(X)(L)$ Complexes

complex	X	L	δ, ppm[c]		ν_{CO}, cm^{-1}
			C_5Me_5	Me	
1a	I		1.48 [0.4]	1.16 [2.2]	2034
1b	Br		1.38 [0.4]	1.21 [2.2]	2038
1c	Cl		1.34 [0.4]	1.22 [2.1]	2041
1d	$MeCO_2$		1.32 [0.4]	1.11 [2.0]	2046
				2.16 ($MeCO_2$)	1630 ($MeCO_2$)
1e	CF_3CO_2		1.20 [0.4]	1.07 [1.9]	2057
					1700 (CF_3CO_2)
2a	I	PPh_3	1.46 [0.5] {2.7}	2.90 {0.7}	1658, 1640
2b	Br	PPh_3	1.35 [0.5] {2.6}	2.75 {0.6}	1661, 1654, 1646
2c	Cl	PPh_3	1.29 [0.5] {2.7}	2.64 {0.6}	1660, 1644
2d	$MeCO_2$	PPh_3	1.41 [0.5] {2.8}	2.48	1666
				1.89 ($MeCO_2$)	1635 ($MeCO_2$)
3d	$MeCO_2$	$P(OPh)_3$	1.53 [0.4] {4.7}	2.34 {0.5}	1680
				2.11 ($MeCO_2$)	1628 ($MeCO_2$)
4d	$MeCO_2$	$PMePh_2$	1.40 [0.5] {2.7}	2.34	1600 (broad)
				1.98 ($MeCO_2$)	
				1.93 [1.0] {10.3} (PMe)	
2e	CF_3CO_2	PPh_3	1.29 {2.8}	2.39	1668
					1711 (CF_3CO_2)
3e	CF_3CO_2	$P(OPh)_3$	1.41 [0.5] {4.7}	2.21	1678[d]
					1696 (CF_3CO_2)
4e	CF_3CO_2	$PMePh_2$	1.29 [0.55] {2.7}	2.28	1666, 1645
				1.84 [1.1] {10.0} (PMe)	1711, 1695 (CF_3CO_2)

[a] All spectra measured in toluene-d_8, with tetramethylsilane (TMS) as internal standard. [b] In hexane. [c] J_{Rh-H} values are given in brackets and J_{P-H} in braces (±0.2 Hz). [d] In toluene.

and incoming ligands,[6] acceleration by Lewis acids,[7] oxidation–reduction effects,[8] and the characterization of intermediates formed on migration,[9] have been investigated in great detail. However, few studies have been reported on the influence of ligands which are not part of the migration step,[10] and none has dealt with the effect of halide or carboxylate ligands. The ancillary ligands extensively change the electronic and steric environment at the metal and will therefore affect the reactivity.

We have recently investigated the migratory insertion in some alkyl- and aryliodocarbonylrhodium(III) complexes $(C_5Me_5)Rh(CO)(I)(R)$ (R = Me (**1a**), aryls) induced by triphenylphosphine and reported the first detailed kinetic study of the reaction at a rhodium center.[5]

We now report on the effects of different X groups on the kinetics and mechanism of related new rhodium(III) complexes $(C_5Me_5)Rh(CO)(X)(Me)$ (X = Br, Cl, $MeCO_2$, CF_3CO_2; **1b–e**).

Table II. Observed Rate Constants for the Reactions of $(C_5Me_5)Rh(CO)(X)(Me)$ (1a–c) with Triphenylphosphine in Toluene at 25.0 °C

X	$[PPh_3]$, M	K_{obs}, s^{-1}
I[a]	8.75×10^{-2}	8.4×10^{-3}
	1.88×10^{-2}[b]	1.9×10^{-3}
	1.75×10^{-2}	1.7×10^{-3}
	9.15×10^{-3}	8.0×10^{-4}
Br[c]	0.104	5.48×10^{-2}
	3.2×10^{-2}	1.74×10^{-2}
	1.96×10^{-2}	1.12×10^{-2}[d]
	1.96×10^{-2}	9.45×10^{-3}[e]
	8.40×10^{-3}	4.76×10^{-3}
	2.85×10^{-3}	1.58×10^{-3}
Cl[f]	3.27×10^{-2}	4.84×10^{-2}
	1.88×10^{-2}	2.95×10^{-2}
	8.00×10^{-3}	1.26×10^{-2}

[a] Reference 5a; [**1a**] = 5.1×10^{-4} M. [b] IR at 2027 cm^{-1}; [**1a**] = 7.3×10^{-4} M. [c] λ = 360–380 nm; [**1b**] = $(2.7–1.4) \times 10^{-4}$ M. [d] [**1c**] = 2.5×10^{-4} M. [e] [**1c**] = 2.5×10^{-5} M. [f] λ = 360 nm; [**1c**] = $(4.7–1.6) \times 10^{-4}$ M.

Results

In order to study the effect of changes in the coligand on the migratory insertion, several new complexes were synthesized. The bromo and chloro complexes **1b,c** were obtained by the reactions of $(C_5Me_5)Rh(Me)_2(CO)$ with HX, while the carboxylates **1d,e** were prepared by the reaction of the bromide **1b** or the iodide **1a** with the appropriate silver carboxylate. The new compounds were characterized by microanalysis and spectroscopy.

The reactions of complexes **1a–e** with triphenylphosphine occur smoothly, in toluene at 25 °C, to yield the corresponding acyls (**2a–e**) quantitatively (eq 1). This was

$$\underset{\mathbf{1a{-}e}}{(C_5Me_5)Rh(CO)(X)(Me)} + PPh_3 \xrightarrow[25\ ^\circ C]{toluene} \underset{\mathbf{2a{-}e}}{(C_5Me_5)Rh(COMe)(X)(PPh_3)} \quad (1)$$

X = I (**a**), Br (**b**), Cl (**c**), $MeCO_2$ (**d**), CF_3CO_2 (**e**)

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Table III. Second-Order Rate Constants and Activation Parameters for the Reaction of $(C_5Me_5)Rh(CO)(X)(Me)$ (1a–c) with Triphenylphosphine in Toluene

complex	X	T, °C	k, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}
1a[a]	I	13.0	0.034	55.6 (±2)	−78.6 (±4)
		25.0	0.093		
		40.0	0.295		
		56.0	0.82		
		70.0	2.0		
1b	Br	15.0	0.274	46.4 (±3)	−93.3 (±5)
		25.0	0.525		
		40.0	1.52		
		55.0	3.22		
1c	Cl	15.0	0.89	35.6 (±2)	−122.2 (±3)
		25.0	1.53		
		35.0	2.50		
		45.0	3.99		

[a] Reference 5a.

shown by following the reaction by ^1H NMR spectroscopy in toluene-d_8. IR and ^1H NMR data for the new complexes are reported in Table I.

The kinetics of reaction 1, carried out under pseudo-first-order conditions using a large excess of phosphine, were followed by monitoring the increase of absorbance due to product formation in the visible region between 350 and 420 nm and the disappearance of the ν(CO) band of 1 in the infrared region. The two methods showed satisfactory agreement. The solutions of complexes **1d**,**e** in toluene were stable, whereas those of complexes **1a**–**c** decomposed irreversibly, at a rate increasing in the order I < Br < Cl. The decomposition involved loss of CO, and the rate was much slower (**1b**, $t_{1/2} \simeq 2$ h; **1c**, $t_{1/2} \simeq 1$ h) than that of reaction 1 and did not affect the kinetic measurements. All runs were carried out with freshly prepared solutions of complexes **1a**–**c**. A steady absorbance at infinite time was observed with all substrates.

The reactivity of the halide complexes **1a**–**c** decreased in the order Cl > Br > I. The observed rate constants are reported in Table II. The reactions showed second-order behavior, first order in substrate and first order in nucleophile, up to the highest concentration of triphenylphosphine (0.1 M) compatible with measurements carried out by standard UV–visible spectroscopy. Plots of k_{obs} vs $[PPh_3]$ were linear with a zero intercept. The observed rate constants were the same, within experimental error, when the concentration of the rhodium complex **1b** was changed by a factor of 10 (2.5×10^{-4}–2.5×10^{-5} M), at the same concentration of phosphine (1.96×10^{-2} M). Rates were measured at different temperatures, between 13 and 70 °C (**1a**),[5] 15 and 55 °C (**1b**), and 15 and 45 °C (**1c**). Second-order behavior was observed in all cases, but a PPh_3 concentration range as large as that used at 25 °C was not accessible at the higher temperatures. The second-order rate constants and the activation parameters are reported in Table III.

Table IV. Observed Rate Constants for the Reaction of $(C_5Me_5)Rh(CO)(MeCO_2)(Me)$ (1d)[a] with Methyldiphenylphosphine, Triphenylphosphine, and Triphenyl Phosphite in Toluene at 25.0 °C

methyldiphenylphosphine[b]		triphenylphosphine[b]		triphenyl phosphite[c]	
$[PMePh_2]$, M	k_{obs}, s^{-1}	$[PPh_3]$, M	k_{obs}, s^{-1}	$[P(OPh)_3]$, M	k_{obs}, s^{-1}
0.371	0.120	0.354	0.0899	0.0394	0.0349
0.253	0.111	0.238	0.0819	0.0298	0.0295
0.180	0.119	0.165	0.0776	0.0199	0.0222
0.130	0.113	0.105	0.0654	0.0125	0.0154
0.0785	0.114	0.0663	0.0542	0.0095	0.0118
0.0526	0.108	0.0531	0.0502	0.0027	0.00376
0.0264	0.0990	0.0422	0.0416		
0.0133	0.0656	0.0337	0.0370		
		0.0294	0.0336		
		0.0219	0.0274		
		0.0139	0.0190		
		0.00697	0.0104		
		0.00219	0.0035		

[a] [**1d**] = $(3.3\text{–}1.8) \times 10^{-4}$ M. [b] λ = 350 nm. [c] λ = 324 nm.

Table V. Observed Rate Constants for the Reaction of $(C_5Me_5)Rh(CO)(CF_3CO_2)(Me)$ (1e)[a] with Methyldiphenylphosphine, Triphenylphosphine, and Triphenyl Phosphite in Toluene at 25.0 °C

methyldiphenylphosphine[b]		triphenylphosphine[c]		triphenyl phosphite[d]	
$[PMePh_2]$, M	k_{obs}, s^{-1}	$[PPh_3]$, M	k_{obs}, s^{-1}	$[P(OPh)_3]$, M	k_{obs}, s^{-1}
0.371	0.127	0.422	0.0826	0.148	0.0407
0.313	0.121	0.349	0.0757	0.114	0.0327
0.253	0.113	0.260	0.0620	0.0599	0.0186
0.159	0.0924	0.193	0.0495	0.0182	0.0062
0.0531	0.0530	0.0928	0.0288		
0.0265	0.0318	0.0442	0.0152		
0.0133	0.0179	0.0177	0.0065		
0.0053	0.0075	0.0093	0.0037		
		0.0040	0.0017		

[a] [**1e**] = $(4.8\text{–}1.6) \times 10^{-4}$ M. [b] λ = 345 nm. [c] λ = 354 nm. [d] λ = 334 nm.

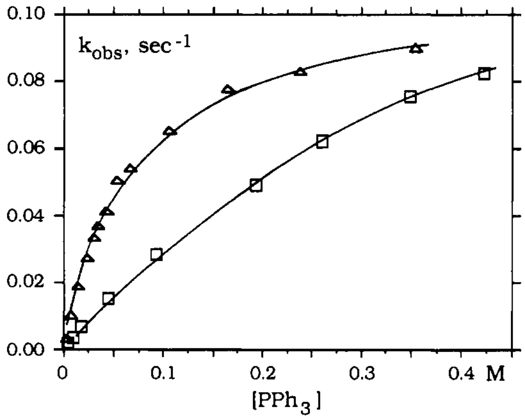

Figure 1. Plot of k_{obs} vs PPh_3 concentration for the reactions of $(C_5Me_5)Rh(CO)(X)(Me)$: (△) X = $MeCO_2$ (**1d**); (□) X = CF_3CO_2 (**1e**).

The reactions of the carboxylate complexes were not first order in nucleophile. The observed rate constants are reported in Tables IV and V for the reactions with triphenylphosphine, triphenyl phosphite ($P(OPh)_3$), and methyldiphenylphosphine ($PMePh_2$). A plot of the observed rate constants for **1d**,**e** vs triphenylphosphine concentrations tended toward saturation at high nucleophile concentration (Figure 1). In the reactions with $PMePh_2$, the acetate complex **1d** had reached a constant reactivity above 0.08 M concentration of nucleophile, whereas the trifluoroacetate complex **1e** was still rising toward a limiting value at 0.4 M nucleophile (Figure 2). This is modeled by the mechanism in Scheme I, described by eq 2, which is obtained by applying the steady-state approximation for intermediate A.

Scheme I

$$\underset{\mathbf{1}}{(C_5Me_5)Rh(CO)(X)(Me)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A \xrightarrow{k_2,\ L} \underset{\mathbf{2}}{(C_5Me_5)Rh(COMe)(X)(L)}$$

$$k_{\mathrm{obs}} = \frac{k_1 k_2[\mathrm{L}]}{k_{-1} + k_2[\mathrm{L}]} \qquad (2)$$

Equation 2 requires that plots of the reciprocal of the observed rate constants vs the reciprocal of the nucleophile (L) concentrations are linear with a positive intercept, according to eq 3.

$$\frac{1}{k_{\mathrm{obs}}} = \frac{k_{-1}}{k_1 k_2[\mathrm{L}]} + \frac{1}{k_1} \qquad (3)$$

Linear plots of $1/k_{\mathrm{obs}}$ vs $1/[\mathrm{L}]$, as shown in Figure 3 for the reactions of complex **1e**, were obtained for the reactions in the region where saturation effects were becoming significant. The *y* intercepts in the graph give the reciprocals of the reactivity at infinite concentration of the nucleophile, when eq 2 reduces to $k_{\mathrm{obs}} = k_1$. The rate constants k_1, obtained from the *y* intercept (or from the linear portion of the graph in the case of **1d** with $PMePh_2$), and the ratios k_{-1}/k_2, from the slopes, are reported in Table VI, for the reactions of **1d**,**e** with different phosphines.

We have seen no IR or NMR spectroscopic evidence for the intermediate A. This is as expected if A is only formed in kinetically significant amounts, as occurs under the conditions of the steady-state approximation.

Discussion

Reactions of Complexes 1a–c with PPh_3. We have previously noted that the reactions of $(C_5Me_5)Rh(CO)(I)(R)$ (R = Me (**1a**), aryls) with PPh_3 in toluene to give $(C_5Me_5)Rh(COR)(I)(PPh_3)$ show clean second-order behavior and very fast rates compared to those of other uncatalyzed migratory insertions.[5] The data were interpreted in terms of a direct attack by PPh_3 on the complex, with simultaneous migration of R, via the transition state $[(C_5Me_5)Rh(CO)I(R)(PPh_3)]^{\ddagger}$.

The bromo and chloro complexes **1b**,**c** also reacted with PPh_3 to give $(C_5Me_5)Rh(COMe)(X)(PPh_3)$ (**2b**,**c**). The kinetics of these reactions in toluene solution follow the pattern observed for the iodo methyl complex **1a** and show clean first-order behavior with respect to both reactants. At 25 °C, the second-order rate constant, k_2, for the chloride (**1c**) is 16 times faster than for the iodide (**1a**) and 3 times faster than for the bromide (**1b**). The rate constants of the halide complexes **1a**–**c** increase with increasing electron-withdrawing ability of the halogen atoms (I < Br < Cl). They correlate well with the electronegativity values of the Mulliken–Jaffé scale, whereas a more scattered trend is observed using other electronegativity scales.[11]

The second-order behavior exhibited by the halide complexes **1a**–**c** is in agreement with an associative mechanism, in which attack by the phosphine and methyl migration may occur in a concerted manner.[1a,5]

The activation parameters (Table III) clearly indicate that the order of reactivity is primarily determined by the $\Delta H^{\ddagger}$ terms, which decrease from 55.6 (I, **1a**) to 46.4 (Br, **1b**) to 35.6 (Cl, **1c**) kJ mol^{-1}. The entropies of activation, $\Delta S^{\ddagger}$, are negative, as expected for a reaction where the rate-determining step is associative, and become larger and more negative in the same direction (−79 (I), −93 (Br), −122 (Cl) J K^{-1} mol^{-1}); this to some extent cancels out the effect of $\Delta H^{\ddagger}$. The reason for the more negative $\Delta S^{\ddagger}$ found for Br and Cl compared to that for I may arise from a closer approach of the PPh_3 to the metal in the transition state for the smaller and more electronegative halides, which leads to a more ordered transition state.

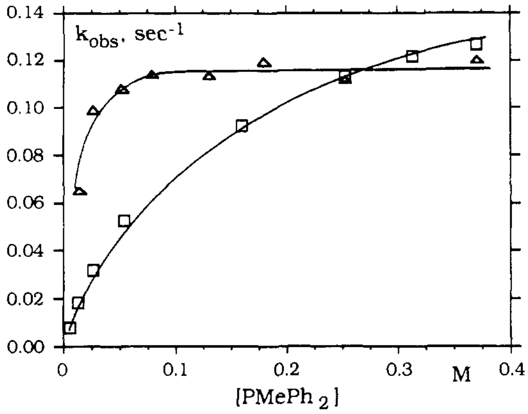

Figure 2. Plot of k_{obs} vs $PMePh_2$ concentration for the reactions of $(C_5Me_5)Rh(CO)(X)(Me)$: (△) X = $MeCO_2$ (**1d**); (□) X = CF_3CO_2 (**1e**).

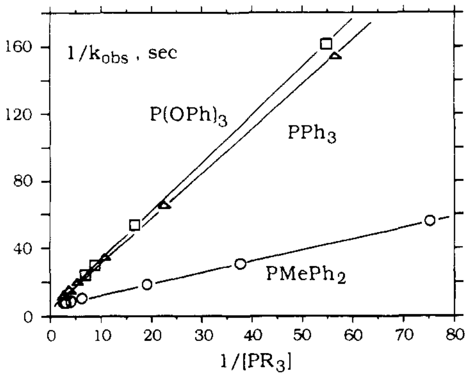

Figure 3. Plot of $1/k_{\mathrm{obs}}$ vs 1/[nucleophile] for the reactions of $(C_5Me_5)Rh(CO)(CF_3CO_2)(Me)$ (**1e**).

Table VI. Kinetic Data for the Reactions of $(C_5Me_5)Rh(CO)(X)(Me)$ (X = $MeCO_2$ (1d), CF_3CO_2 (1e)) with Different Nucleophiles in Toluene at 25.0 °C

	1d		1e	
nucleophile	k_1,[a] s^{-1}	k_{-1}/k_2, M	k_1,[a] s^{-1}	k_{-1}/k_2, M
$PMePh_2$	0.115		0.16	0.10
PPh_3	0.106	0.064	0.16	0.42
$P(OPh)_3$	0.096	0.067	0.17	0.48

[a] All values ±0.01.

The work reported here has allowed us to ascertain the effects of different anionic coligands, a topic rather neglected in the literature. So far as we are aware, the only other kinetic investigations of the effect of changing a halide coligand in carbonyl reactions are those of CO substitution in $W(CO)_4(NO)X$, $Re(CO)_5X$, $Mn(CO)_5X$, and $(C_5H_5)Mo(CO)_3X$ complexes.[12] In all cases the rates decrease in the order Cl > Br > I and $\Delta H^{\ddagger}$ increases in the same order and dominates the reaction. This effect was explained as due to the polarizabilities (I > Br > Cl). The most polarizable and least electronegative ligand (iodide) results in a greater electron density on the metal, more back-donation of electron density leading to a greater M–CO strength, and hence a slower reaction. Although these reactions are not strictly comparable to the one described here since they all involve dissociation of CO in the rate-determining step of the substitution, a similar

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explanation can also account for the order of $\Delta H^{\ddagger}$ observed in the reactions of **1a–c**, and again the chloride complex should give the fastest migration. The activation enthalpies for the substitution reactions are around 120 kJ mol^{-1},[12] about 3 times that found here for complexes **1a–c**. However, in all cases the difference between chloride and iodide is about 20 kJ/mol. It is also noteworthy that the observed electronic effect, where the reactivity increases with increasing electron-withdrawing ability of the halide, is in the opposite direction from those within the migrating alkyl ligands.[4,5]

It has been speculated that complexes of the second- or third-row transition metals having halogens as ligands may stabilize acetyl intermediates by dinuclear halide bridges.[10f] Such dimers with bridging halides and terminal acetyl ligands have been reported for platinum and rhodium and proposed in migration reactions of iridium.[13] For the reactions discussed here, that would imply an intermediate of the form $[\{(C_5Me_5)Rh(COMe)(L)(\mu\text{-}X)\}_2]$ and, hence, an effect of the rhodium concentration on the rate. Since the kinetic experiments carried out at different concentrations of the rhodium complex **1b** gave similar observed rate constants (Table II), this rules out a significant contribution from such dimers.

Reactions of Complexes 1d,e. The carboxylate complexes **1d,e**, prepared by the reaction of the bromide **1b** with the appropriate silver carboxylate, also reacted readily with PPh_3 to give the acyl complexes **2d,e**. However, in contrast with the complexes **1a–c**, the reactions of the carboxylates **1d,e** showed quite different kinetic behavior. The observed rate constants, k_{obs}, tended toward a limiting value at high concentrations of triphenylphosphine (Figure 1). This is typical of a reaction proceeding through formation of a kinetically detectable intermediate,[1a,2a,b] which can either regenerate the starting complex or react with the nucleophile to give the product, for example A in Scheme I. A "solvent assisted" methyl migration[2,6a] is unlikely because of the poor donicity of toluene and because of the clean second-order behavior exhibited by the halide complexes **1a–c**.

However, since we have previously found that carboxylates on $(C_5Me_5)Rh$ can either chelate or act as monodentate ligands,[14] for example

$$(C_5Me_5)Rh(PMe_3)(\eta^1\text{-}OCOMe)_2 \rightleftarrows [(C_5Me_5)Rh(PMe_3)(\eta^2\text{-}OCOMe)]^+MeCO_2^-$$

we suggest that a similar process can occur for **1d,e** and that the intermediate A in Scheme I is the acyl η^2-carboxylate:

$$(C_5Me_5)Rh(COMe)(\eta^2\text{-}O_2CR)$$

A

$$R = Me, CF_3$$

The carbonyl oxygen of the CO_2 group may induce the migration step by an internal nucleophilic attack and then stabilize the otherwise unsaturated 16-electron intermediate by acting as a bidentate ligand.

If this is indeed the case, then the rate constant k_1 in Scheme I ought to be independent of the nucleophile. This proposal was tested by reacting **1d,e** with a range of nucleophiles, including $P(OPh)_3$ and $PMePh_2$, as well as PPh_3. These measurements indicated that the rates extrapolated to infinite concentration, where $k_{obs} = k_1$, were the same within experimental error for each complex (Table VI and Figure 3). For the reaction of **1d** with $PMePh_2$, the reactivity reached an average value of 0.115 s^{-1} (at 0.08 M $PMePh_2$), in good agreement with the value of 0.106 s^{-1} extrapolated from the reaction with PPh_3. Moreover, Figure 2 shows that the reactivity of **1e** toward $PMePh_2$ becomes larger than that of **1d** in the high concentration range, a point which one could previously only predict from the reactions involving PPh_3.

The averaged values of reactivity are $k_1 = 0.105 \pm 0.01$ s^{-1} for **1d** and $k_1 = 0.16 \pm 0.01$ s^{-1} for **1e**, implying a slightly faster migration for the trifluoroacetate than for the acetate. This is quite a small difference, although well off the experimental error, and is probably the result of two effects going in opposite directions, the larger electronegativity effect of the trifluoroacetate group, consistent with the trend observed in the halide complexes **1a–c**, and the larger nucleophilicity of the acetate ligand.

The consistency observed indicates that the intermediate A does not involve a coordinated phosphine complex which collapses to product in the rate-determining step. Such a mechanism would show identical kinetic behavior, but a dependence on the nature of the nucleophile would be expected.[15]

The intermediate A from **1d** ($X = MeCO_2$) reacted comparably with PPh_3 and $P(OPh)_3$, k_{-1}/k_2 being similar in both cases (0.064 M for PPh_3, 0.067 M for $P(OPh)_3$). However, k_{-1}/k_2 for the reaction of the presumed intermediate from **1e**, $(C_5Me_5)Rh(COMe)(CF_3CO_2)$, varied from 0.10 for $PMePh_2$ to 0.42 for PPh_3 and 0.48 M for $P(OPh)_3$. This variation agrees with the expected reactivities of the nucleophiles $PMePh_2 > PPh_3 > P(OPh)_3$[2b,16] and indicates that the nature of the entering ligand plays some role there as well. Preliminary results for the reactions of $(C_5Me_5)Rh(CO)I(Me)$ (**1a**) with different nucleophiles indicate a similar order of reactivity, the second-order rate constants being $k_2 = 0.45$ ($PMePh_2$), 0.093 (PPh_3), and 0.075 s^{-1} M^{-1} ($P(OPh)_3$).[17]

These reactions of complexes **1d,e** appear to be the first examples of the stabilization of an intermediate in a *nonpolar* solvent, in the migratory insertion of carbon monoxide. Nucleophilic neighboring-group participation by acetates is well documented for the solvolysis of organic esters,[18] and a rhodacarborane with a bidentate acetate has also been observed as an intermediate in the hydrosilanolysis of isopropenyl acetate.[19]

Conclusions

Methyl complexes of the type $(C_5Me_5)Rh(CO)(X)(Me)$ (**1a–c**; X = I, Br, Cl) react with triphenylphosphine to give the acetyls $(C_5Me_5)Rh(COMe)(X)(PPh_3)$ in clean bimolecular reactions, the rates of which decrease in the order X = Cl > Br > I, via the transition state $[(C_5Me_5)Rh(CO)X(Me)(PPh_3)]^{\ddagger}$. Evaluation of the activation parameters shows that the reaction is dominated by $\Delta H^{\ddagger}$. In contrast, rate studies on the complexes $(C_5Me_5)Rh$-

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(CO)(X)(Me) (**1d**,**e**; X = $MeCO_2$, CF_3CO_2), which also react with a variety of phosphines and phosphites to give the acetyls $(C_5Me_5)Rh(COMe)(X)(PR_3)$, show that the reaction proceeds via an intermediate (A). It is suggested that A has a bidentate carboxylate which stabilizes it as an 18-electron species.

Experimental Section

General Data. ^1H NMR spectra were recorded on a Bruker WP-80 spectrometer with toluene-d_8 as solvent (Table I); ^{13}C NMR spectra were run on Varian XL-300 and Bruker AM-250 spectrometers, in toluene-d_8. Chemical shifts (ppm) are relative to tetramethylsilane. IR spectra were measured with a Nicolet 510 FT-IR spectrophotometer in the solvent subtraction mode, using 0.1-mm CaF_2 cells. Kinetic measurements were obtained with Varian Cary 219 and diode array HP 8452 instruments. Elemental analyses were performed by the Sheffield University Microanalysis Service.

Unless otherwise indicated, all reactions were carried out under nitrogen or argon using standard Schlenk-line techniques. Solvents were thoroughly degassed before use; toluene was distilled under nitrogen from sodium-benzophenone. Alumina (neutral, activated Brockman 1) was used for chromatography. Chemicals and solvents were reagent grade. Triphenylphosphine was crystallized from ethanol. Triphenyl phosphite and methyldiphenylphosphine were of the highest grade available and were used as received.

Preparation of Compounds. (η^5-C_5Me_5)Rh(CO)(Cl)(Me) (1c). Dichloromethane (20 mL) saturated with HCl gas was added in increments (1 mL) to a solution of $(C_5Me_5)Rh(Me)_2(CO)$[20] (0.20 g, 0.675 mmol) in dichloromethane (40 mL). When the conversion of the starting material (ν_{CO} = 1985 cm^{-1}) into product (2037 cm^{-1}) was complete, the solution was washed with water (3 × 50 mL), dried with anhydrous Na_2SO_4, and filtered. After addition of hexane (20 mL), the volume was reduced to about 25 mL and then the solution was chromatographed with hexane/diethyl ether as eluant. Removing the solvent in vacuo yielded yellow crystals of (η^5-C_5Me_5)Rh(CO)(Cl)(Me) (0.11 g, 50%). Anal. Calcd for $C_{12}H_{18}OClRh$: C, 45.5; H, 5.7; Cl, 11.2. Found: C, 45.6; H, 5.6; Cl, 11.3.

(η^5-C_5Me_5)Rh(CO)(Br)(Me) (1b). The method described for **1c** was used for the synthesis of **1b** as well, using dibromomethane and HBr, and gave 78% of product. ^{13}C NMR: δ 190.8 (d, J_{Rh-C} = 76 Hz, CO), 103.1 (d, J_{Rh-C} = 4 Hz, C_5Me_5), 9.0 (C_5Me_5), −1.85 (d, J_{Rh-C} = 19 Hz, Me). Anal. Calcd for $C_{12}H_{18}OBrRh$: C, 39.9; H, 5.0; Br, 22.1. Found: C, 40.1; H, 5.9; Br, 22.1.

(η^5-C_5Me_5)Rh(CO)($MeCO_2$)(Me) (1d). Silver acetate (Ag($MeCO_2$); 0.030 g, 0.18 mmol) was added to a solution of (η^5-C_5Me_5)Rh(I)CO(Me) (**1a**;[5a] 0.040 g, 0.09 mmol) in toluene (20 mL), in a round-bottomed flask covered in metal foil; the solution was stirred (3 h). After filtration, the solvent was removed in vacuo and the solid crystallized from pentane at −20 °C, yielding yellow crystals of **1d** (0.010 g, 40%). Anal. Calcd for $C_{14}H_{21}O_3Rh$: C, 49.4; H, 6.2. Found: C, 49.3; H, 6.0.

(η^5-C_5Me_5)Rh(CO)(CF_3CO_2)(Me) (1e). The compound (80–90%) was prepared by the method described for **1d**, by starting from (η^5-C_5Me_5)Rh(CO)(Br)(Me) and silver trifluoroacetate (1.1 molar excess). Anal. Calcd for $C_{14}H_{18}O_3F_3Rh$: C, 42.6; H, 4.6. Found: C, 42.6; H, 4.6. ^{13}C NMR: δ 191.4 (d, J_{Rh-C} = 78 Hz, CO), 162.0 (q, J_{F-C} = 35 Hz, CO_2), 115.9 (quartet of doublets, J_{C-F} = 290 Hz, J_{Rh-C} = 2.5 Hz, CF_3), 102.6 (d, J_{Rh-C} = 5 Hz, C_5Me_5), 8.4 (C_5Me_5), 3.18 (d, J_{Rh-C} = 19.5 Hz, Me).

Reactions of 1b–e with Triphenylphosphine. The reactions were carried out in 5-mm NMR tubes, with the methyl complex (5–10 mg) and a slight excess of PPh_3 being mixed in toluene-d_8 (1 mL). The reactions were completed and were quantitative within 10 min from mixing, yielding the corresponding acyl complexes **2b–e**. After removal of the solvent under vacuum, the IR spectra of the crude products were obtained in hexane (Table I).

(η^5-C_5Me_5)Rh(COMe)(Br)(PPh_3) (2b). **1b** (0.15 g, 0.41 mmol) and PPh_3 (0.12 g, 0.45 mmol) were stirred (1 h) in toluene (10 mL). The solvent was removed in vacuo, and the residue was chromatographed (silica gel) first with hexane and then with hexane/THF (1:1) as eluent to give an orange-red solid (0.25 g, 0.40 mmol, 97%). ^{13}C NMR: δ 246.0 (dd, J_{Rh-C} = 14 Hz, J_{C-P} = 27 Hz, COMe), 102.3 (d, J_{Rh-C} = 3 Hz, C_5Me_5), 46.8 (CO*Me*), 9.2 (C_5Me_5). Crystallization from CH_2Cl_2/hexane yielded red crystals of **2b**. Anal. Calcd for $C_{30}H_{33}OBrPRh$: C, 57.8; H, 5.34. Found: C, 58.0; H, 5.32.

(η^5-C_5Me_5)Rh(COMe)(CF_3CO_2)(PPh_3) (2e). **1e** (12.6 mg, 0.032 mmol) and PPh_3 (9.8 mg, 0.036 mmol) were dissolved in toluene (2 mL). After 10 min, the solution was concentrated under vacuum. Slow vapor diffusion of pentane into the toluene solution, at −20 °C, afforded red crystals of **2e** (19.6 mg, 0.030 mmol, 93%). Anal. Calcd for $C_{32}H_{33}O_3F_3PRh$: C, 58.5; H, 5.07. Found: C, 59.5; H, 5.16.

Kinetic Measurements. Kinetic experiments were carried out under pseudo-first-order conditions in toluene, using a 10-fold or larger excess of the phosphines, by UV–visible spectroscopy. The two compartments of a 1-cm quartz cell with an internal septum were filled with 1 mL each of a phosphine solution and a solution of rhodium complex. The cell was flushed with argon, sealed, and placed in the thermostated cell holder of the spectrophotometer. After thermal equilibrium, the cell was rapidly shaken to ensure mixing, and the increase of absorbance associated with the product formation was followed with time. The experimental details are reported in Tables II, IV, and V. Plots of $-\ln (A_\infty - A_t)$ vs time were linear over 4 half-lives. Kinetic experiments were also carried out by IR spectroscopy, by monitoring the disappearance of the carbonyl stretching band of complexes **1b–e**. This method yielded half-life times similar to those obtained by the UV–visible experiments. All runs were duplicated and were reproducible within 5%.

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Registry No. **1a**, 116351-76-9; **1b**, 136736-81-7; **1c**, 136736-82-8; **1d**, 136736-83-9; **1e**, 136736-84-0; **2a**, 120840-22-4; **2b**, 136736-85-1; **2c**, 136736-86-2; **2d**, 136736-87-3; **2e**, 136736-88-4; **3d**, 136736-89-5; **3e**, 136736-91-9; **4d**, 136736-90-8; **4e**, 136736-92-0; $(C_5Me_5)Rh(Me)_2(CO)$, 103731-64-2; Ag($MeCO_2$), 563-63-3; PPh_3, 603-35-0; $PMePh_2$, 1486-28-8; $P(OPh)_3$, 101-02-0; silver trifluoroacetate, 2966-50-9.

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