A First Example of the Faster Migration of Phenyl over Methyl: Kinetics of the Reaction of Triphenylphosphine with Organo-carbonyl-iodo-rhodium(III) Complexes

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The reactions of PPh_3 with $[C_5Me_5RhR(CO)I]$ to yield $[C_5Me_5Rh(COR)(PPh_3)I]$, proceed by a 'direct attack' mechanism in less-polar solvents; the migrations are favoured by electron releasing R, but follow organic rearrangements in that phenyl migrates more rapidly than methyl.

Although a variety of 'carbonyl insertion' (alkyl migration) reactions have been studied,[1—3] surprisingly few involve rhodium, one of the most important metals in catalytic carbonylation. We report that reactions of the organo-carbonyl-iodo Rh^{III} complexes (**1a**—**g**) with triphenylphosphine occur smoothly (toluene; 20 °C) to give the corresponding acyls (**2a**—**g**) in high yields [reaction (i)].

$$\underset{(1)}{[C_5Me_5Rh(CO)I(R)]} + PPh_3 \rightarrow \underset{(2)}{[C_5Me_5Rh(PPh_3)I(COR)]} \quad \text{(i)}$$

a; R = Me **b**; R = Ph
c; R = p-MeC_6H_4 **d**; R = p-ClC_6H_4
e; R = p-$OHCC_6H_4$ **f**; R = p-NCC_6H_4
g; R = p-$O_2NC_6H_4$

The kinetics of reaction (i) under pseudo-first-order conditions, with a ten-fold or greater excess of triphenylphosphine, have been studied by monitoring (a) the disappearance of ν(CO) of (**1**) in the infrared, and (b) the changes in the absorbance in the visible region between 500 and 400 nm. The results from the two methods showed excellent agreement; this allowed a wide range of concentrations to be used.

The data obtained showed a clean first-order dependence on the Rh^{III} complexes in all solvents, and also a first-order dependence on PPh_3 in toluene, dichloromethane, and tetrahydrofuran (concentrations of PPh_3 in the range 9×10^{-2} to 9×10^{-4} M). This indicated an overall second-order process corresponding to a 'direct attack' of nucleophile on the complex [equation (ii)].

$$\text{rate} = k_2\,[(\mathbf{1})][PPh_3] \qquad \text{(ii)}$$

The measured reactivity of the phenyl complex (**1b**) is about four times that of the methyl analogue (**1a**); this is the first kinetic evidence of higher migratory ability for the phenyl group in a direct and quantitative M(CO)R → M(COR) transformation. No change in rate for the phenyl complex (**1b**), and little for the methyl complex (**1b**), was observed on changing from toluene to dichloromethane (which has weak acceptor properties) or tetrahydrofuran (THF) (which is a donor solvent) (Table 1).[4] This excludes any contribution from solvent acting as nucleophile to the migratory insertion process.

The p-substituted phenyl complexes (**1c**—**g**) reacted similarly, but a competitive substitution process also occurred for (**1e**—**g**) (which also react the slowest) giving $[C_5Me_5Rh(R)I(PPh_3)]$ (**3**) as well as $[C_5Me_5Rh(COR)I(PPh_3)]$ (**2**).

A Hammett plot of the rate constants for the reactions of complexes (**1b**—**f**) exhibited good linearity, indicating no change in the migration mechanism from the most to the least reactive substrate. The value of ρ (−3.1) is similar to that of −3.6 for aryl migration in aryl(iodo)bis(triphenylphosphine)platinum(II) complexes.[5] The sign and the absolute value of ρ indicate that the migrating group bears negative charge which is being localized in the formation of the carbon–carbon bond, and that the CO migratory insertion occurs during the rate-limiting step. This interpretation is also

Table 1. Second-order rate constants for the reaction of $[(C_5Me_5)Rh(R)I(CO)]$ with triphenylphosphine (25 °C).

Solvent	$[C_5Me_5Rh(C_6H_5)I(CO)]$ $k_2/dm^3\,mol^{-1}\,s^{-1}$	$[C_5Me_5Rh(CH_3)I(CO)]$ $k_2/dm^3\,mol^{-1}\,s^{-1}$
Toluene	0.35 ± 0.03	0.092 ± 0.003
CH_2Cl_2	0.35 ± 0.02	0.15 ± 0.02
THF	0.25 ± 0.03	0.064 ± 0.004

Table 2. Activation parameters for the reaction of [$C_5Me_5Rh(R)(I)(CO)$] with PPh_3 in toluene (286—343 K).

Complex	$\Delta H^\ddagger$ kJ mol^{-1}	$\Delta S^\ddagger$ J K^{-1} mol^{-1}
(**1a**)	55.6 ± 0.5	−79 ± 2
(**1b**)	62.3 ± 1.3	−43 ± 4
(**1c**)	48.5 ± 0.8	−82 ± 3
(**1d**)	59.0 ± 1.7	−66 ± 6

supported by the similarities in migratory aptitude between this reaction and the pinacol rearrangement. In both cases, phenyl migrates faster than methyl and the relative migratory aptitude decreases with increasing electron-withdrawing ability of substituents.[6]

Both the enthalpy ($\Delta H^\ddagger$) and the entropy ($\Delta S^\ddagger$) of activation for the complexes (**1a** and **b**) [toluene; 13—70 °C] are typical of bimolecular associative processes (Table 2). The entropy is less negative for the complex (**1b**) and this factor is responsible for the higher reactivity exhibited by this compound.

Little quantitative information is available on relative migratory abilities,[1d] but it has been reported that methyl migrates onto CO faster than phenyl, by a factor of 8 in the reaction of [$RMn(CO)_5$] with CO in 2,2-diethoxydiethyl ether,[1b] and from CO onto rhenium by a factor of 30 in [$Re(COMe)(COPh)(CO)_4]^-$.[2] Other, qualitative data, have generally supported this conclusion for organometallic complexes.

Reaction (i) in acetonitrile and nitromethane showed enhanced reactivity [6—10 fold higher values of k_{obs} with respect to the reaction in toluene, at comparable PPh_3 concentrations, for both (**1a** and **b**)]. The kinetic pattern is characterised by a saturation effect with increasing nucleophile concentration, typical of a reaction proceeding with substantial accumulation of an intermediate. Work is in progress to elucidate the mechanism in these solvents.

Although a direct comparison with migrations found in other metal-methyl complexes is difficult, the complex (**1a**) appears to react several orders of magnitude faster than other systems reported in the literature.[3b,c,e] This is in agreement with the qualitative observation of the high migration rates for rhodium(III); for example, in the reaction of MeI with [$Rh(CO)_2I_2]^-$ the only product seen is the acyl, [$MeCORh(CO)I_3]_n^-$.[7]

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