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Kinetics of the Migratory Insertion of Olefins into Rhodium–Hydrogen Bonds. Influence of Electronic Factors

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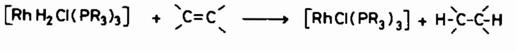
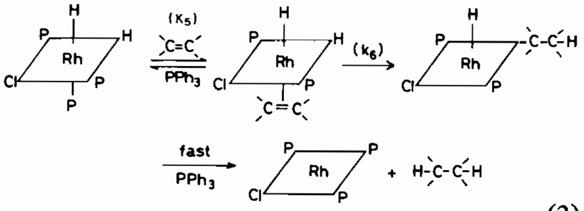
Intramolecular migratory insertion of a coordinated olefin into a transition metal–hydride bond has been widely invoked as a step in catalytic hydrogenation and related reactions such as hydroformylation and hydrosilation and, thus, constitutes a process of great importance and fundamental interest in organometallic chemistry and catalysis [1]. Nevertheless, such migratory insertion reactions have rarely been directly identified and the parameters that influence the kinetics of such reactions have not been extensively elucidated [2].

Previously we have shown [3] that such an intramolecular olefin migratory insertion step can be identified in the stoichiometric reaction of $[RhH_2Cl(PPh_3)_3]$ with cyclohexene (eqn. 1) which proceeds in accord with the mechanistic sequence of eqn. (2).



$$[RhH_2Cl(PR_3)_3] + \mathrm{{>}C{=}C{<}} \longrightarrow [RhCl(PR_3)_3] + \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H}$$

(1)



(2)

We have now extended the study of such reactions to encompass a number of other olefinic substrates, notably styrene and para-substituted styrenes [p-$X{-}C_6H_4CH{=}CH_2$], as well as rhodium complexes containing other phosphine ligands, notably para-substituted triarylphosphines, [$(p$-Y-$C_6H_4)_3P$]. The selection of olefins and phosphines was such that steric factors remained essentially constant, thereby permitting the influence of electronic factors to be elucidated.

TABLE I. Equilibrium and Kinetic Parameters for the Reactions of $[RhH_2Cl(PR_3)_3]$ with Olefins in Benzene at 25 °C.

PR_3	Olefin	$10^3\ K_5$	$k_6\ (s^{-1})$
$P(C_6H_5)_3$	Cyclohexene[a]	0.34	0.20
$P(C_6H_5)_3$	p-Cl-styrene	2.53	0.097
$P(C_6H_5)_3$	Styrene	1.72	0.11
$P(C_6H_5)_3$	p-F-styrene	1.04	0.22
$P(C_6H_5)_3$	p-CH_3-styrene	0.69	0.23
$P(C_6H_5)_3$	p-CH_3O-styrene	0.34	0.50
$P(p$-$Cl{-}C_6H_4)_3$	Styrene	0.47	0.053
$P(p$-$F{-}C_6H_4)_3$	Styrene	0.80	0.067
$P(C_6H_5)_3$	Styrene	1.72	0.11
$P(p$-$Me{-}C_6H_4)_3$	Styrene	0.83	0.50
$P(p$-$MeO{-}C_6H_4)_3$	Styrene	0.57	0.24

[a] From Ref. 2.

Following the procedure previously described for the reaction of $[RhH_2Cl(PPh_3)_3]$ with cyclohexene [3] the kinetics of the other reactions, under pseudo-first order conditions (excess PR_3 and olefin), were monitored spectrophotometrically in benzene at 25 °C and found to conform to the rate-law,

$$-d[RhH_2Cl(PR_3)_2]/dt = k_{obs}[RhH_2Cl(PR_3)_3] \qquad (3)$$

where,

$$k_{obs} = \frac{K_5 k_6 [\mathrm{{>}C{=}C{<}}]}{[PR_3] + K_5 [\mathrm{{>}C{=}C{<}}]} \qquad (4)$$

which yields, upon rearrangement,

$$\frac{1}{k_{obs}} = \frac{1}{k_6} + \frac{[PR_3]}{K_5 k_6 [\mathrm{{>}C{=}C{<}}]} \qquad (5)$$

Values of K_5 and k_6, determined from the slopes and intercepts of linear plots of $(k_{obs})^{-1}$ *vs.* $[PR_3]/[\mathrm{{>}C{=}C{<}}]$, exemplified by Fig. 1, are listed in Table I. The following features are noteworthy.

1. The values of K_5 for the styrenes, corresponding to the equilibrium constants for binding to Rh in competition with PPh_3, range from 3.4×10^{-4} for p-$CH_3O{-}C_6H_4CH{=}CH_2$ to 2.53×10^{-3} for p-$Cl{-}C_6H_4CH{=}CH_2$. The trend is for K_5 to increase with the electron withdrawing power of the para-substituent X, as measured by the substituent constant σ^+ (values in parentheses) *i.e.*, CH_3O (−0.76) < CH_3 (−0.31) < F (−0.07) < H(0) < Cl (+0.11). The correlation of log K_5 with σ^+ corresponds to ρ_x^+

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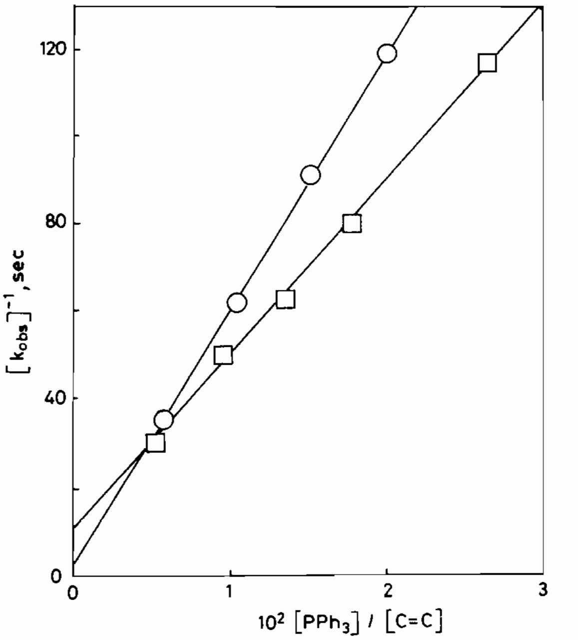

Fig. 1. Representative plots of $(k_{obs})^{-1}$ *vs.* $[PPh_3]\,[{>}C{=}C{<}]$ for the reactions of $[RhH_2Cl(PPh_3)_3]$ with p-$CH_3O-C_6H_4CH{=}CH_2$ (○) and p-$Cl-C_6H_4CH{=}CH_2$ (□).

≈ +1. This is consistent with a predominant role of π-electron back-donation (*i.e.*, from Rh to the olefin) in binding of the olefin to the rhodium. Also consistent with this is the observation that the values of K_5 for the styrenes are generally higher than that for cyclohexene (3.4×10^{-4}).

2. The values of the intramolecular migratory insertion rate constant, k_6, follow the reverse trend and increase with the electron donating power of the para-substituent, X, ranging from 0.097 s^{-1} for p-$Cl-C_6H_4CH{=}CH_2$ to 0.50 s^{-1} for p-$CH_3O-C_6H_4CH{=}CH_2$. The dependence of k_6 on σ_x^+ corresponds to $\rho_x^+ \approx -0.9$. Thus, not unexpectedly, the reactivity of the coordinated olefin with respect to the π- to σ-migratory insertion rerrangement exhibits an inverse dependence on the stability of the initial π-bonded adduct. The trend of k_6 values is qualitatively similar to that found for the migratory insertion of coordinated styrenes into Nb–H bonds [2d].

3. Because of the opposing trends of K_5 and k_6, the influences of these two parameters tend to cancel and the overall rates of the bimolecular reactions depicted by eqn. (1) do not vary greatly for the different styrenes. This is reflected in Fig. 1 which depicts plots of $(k_{obs})^{-1}$ *vs.* $[PPh_3]/[{>}C{=}C{<}]$ for the two limiting members of the series of styrenes examined. The plots for p-$Cl-C_6H_4CH{=}CH_2$ and p-$CH_3O-C_6H_4CH{=}CH_2$ actually cross at $[PPh_3]/[{>}C{=}C{<}] \approx 10^{-2}$. Thus, at low olefin concentration, where binding of the olefin to Rh exerts a dominant influence, the overall rate of olefin insertion (k_{obs}) is higher for the more strongly bound p-$Cl-C_6H_4$-$CH{=}CH_2$ ($K_6 = 2.53 \times 10^{-3}$ *vs.* 3.4×10^{-4} for p-$CH_3O-C_6H_4CH{=}CH_2$). However, at higher olefin concentrations, when binding approaches saturation, the relative rates are determined by the intramolecular migratory insertion rate constant (*i.e.*, $k_{obs} \approx k_6$), which is higher for p-$CH_3O-C_6H_4CH{=}CH_2$ (0.50 s^{-1} *vs.* 0.097 s^{-1}). This inversion of the relative rates emphasizes the unreliability of inferring the relative activities of a given catalyst for different substrates by comparing catalytic rates at a fixed single substrate concentration.

4. For rhodium complexes containing different phosphine ligands, $(p$-$Y-C_6H_4)_3P$, the value of the migratory insertion rate constant k_6 tends to increase with increasing electron donor power of the substituent Y ($Cl < F < H < CH_3O < CH_3$). The trend of k_6 values is irregular and does not exhibit a good correlation with either σ_Y or σ_Y^+. One possible explanation for the direction of the trend is that electron donating ligands, by stabilizing the electron deficient (16 electron) coordinately unsaturated product of the migratory insertion step, *i.e.*, of $[RhH({-}{>}C{-}C{<}{-}H)Cl(PR_3)_2]$, increase the driving force, and hence the rate constant (k_6), for this step. For the same series, the dependence of the equilibrium constant, K_5, on Y does not exhibit a clear pattern, K_5 being a maximum for $P(C_6H_5)_3$ and decreasing both with electron donating and electron withdrawing substituents. Since this comparison involves simultaneous variation both of the phosphine being replaced and of the two residual phosphine ligands, the biphasic character of the resulting trend is not altogether unexpected.

Acknowledgement

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