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Preliminary communication

On the π-allylmetal hydride mechanism for the isomerisation of olefins catalysed by transition metal complexes

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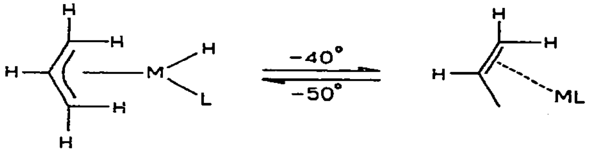
SUMMARY

Migration of hydrogen from the metal to the coordinated π-allyl group has been demonstrated for π-allylrhodium(III) hydrides, which are shown to be stable at low temperatures.

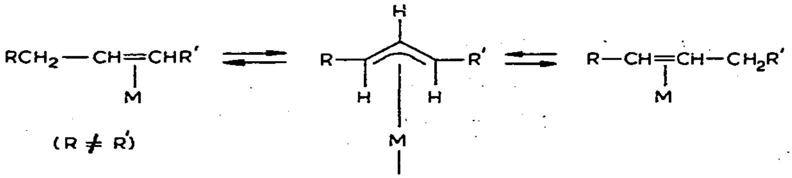
Several mechanisms have been considered for the transition metal-catalysed isomerisation of olefins[1-7]. Metal–alkyl[8], metal–carbene[9], and π-allylmetal hydride[10-18] complexes have been postulated as reaction intermediates.

Although there is indirect evidence for participation of a π-allylmetal hydride in certain systems[16-17] only in one case has an equilibrium been established between a π-allylmetal hydride complex and the corresponding olefin metal(0) complex[19], *viz.*



(M = Ni ; L = PF_3)

In transition metal hydride complexes containing a symmetric π-allyl group, migration of hydrogen from the metal atom to either terminal carbon atom can afford only one olefin, and the isomerisation process requires that the hydrogen atom move to both ends of an asymmetrically coordinated π-allylic group, *e.g.*:



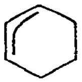
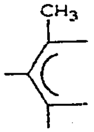
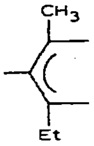
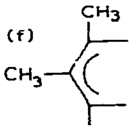
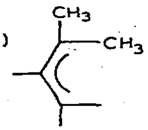
(R ≠ R′)

We have tested the feasibility of such a migration by studying the addition of hydrogen chloride to a series of π-allylic rhodium trifluorophosphine complexes[20,21]. The overall reactions (which are complete in several hours at room temperature) are represented by eqn.1 (see Table 1).

TABLE 1

ADDITION OF HCl to π-ALLYLIC $Rh(PF_3)_3$ COMPLEXES

$$\underset{\text{(I)}}{\pi\text{-allylic–}Rh(PF_3)_3} + HCl \xrightarrow{-PF_3} \text{olefin} + \underset{\text{(II)}}{\tfrac{1}{2}[(PF_3)_2RhCl]_2} \quad (1)$$

Allylic group		*Olefin products*
(a)	C_3H_5	$CH_3CH{=}CH_2$
(b)	1,3-dimethylallyl	$CH_3CH{=}CHEt$
(c)		cyclohexene
(d)		(i) $CH_3CH{=}CHCH_3$ (ii) $EtCH{=}CH_2$
(e)		(i) $CH_3CH{=}CHPr$ (ii) $EtCH{=}CHEt$
(f)		$CH_3CH{=}C(CH_3)_2$ and/or $Et(CH_3)C{=}CH_2$ [a]
(g)		(i) $(CH_3)_2C{=}CH(CH_3)$ (ii) $(CH_3)_2CHCH{=}CH_2$

[a] See text.

When (I) (allylic = C_3H_5) reacts with HCl at −75° in CCl_3F solution the ^{19}F NMR spectrum shows an additional resonance centred at 13.9 ppm (rel. CCl_3F) [Fig. 1(a)] to those known for compounds (I) and (II)[20,22]. The new resonance consists

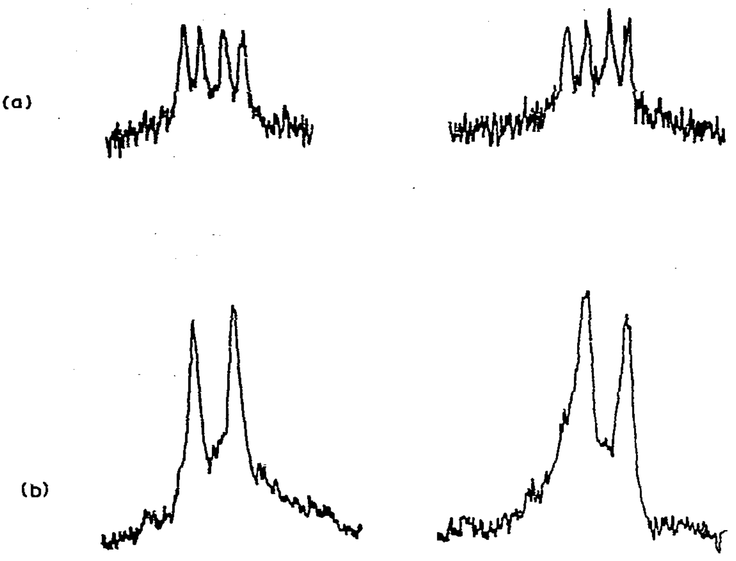
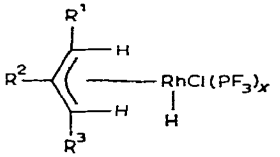


Fig.1. ^{19}F NMR spectrum of the product obtained from π-$C_3H_5Rh(PF_3)_3$ and (a) HCl, (b) DCl at −75° (see text).

of eight lines of equal intensity and is attributed to the intermediate π-allylrhodium(III) hydrido complex (III) ($R^1 = R^2 = R^3 = H$) (x is probably 2) formed by oxidative addition to the rhodium(I) compound. The eight line pattern arises from spin coupling between fluorine and phosphorus (^1J(PF) ≈ 1391 Hz), rhodium (^2J(RhF) 20.0 Hz), and hydrogen (^2J(FH) 8.0 Hz). A similar resonance is observed for (III) (R^1 = Me, $R^2 = R^3 = H$).



(III)

Confirmation of the assignment of (III), ($R^1 = R^2 = R^3 = H$), comes from the observation of a broad resonance at τ 28.8 in the ^{1}H NMR spectrum, furthermore when DCl is added to (I) (allylic = C_3H_5) at −75° the eight line pattern in the ^{19}F NMR spectrum as expected simplifies to four lines of equal intensity [Fig. 1(b)]. When the solution of (I) and HCl is warmed from −75° to room temperature, the ^{19}F resonance of (III) diminishes in intensity as olefin formation occurs while the ^{19}F resonance of (II) increases in intensity. ^{1}H NMR studies show that when DCl reacts with (I), (allylic = C_3H_5), the C-1 and C-3 atoms of the resulting propene are deuterated exclusively.

In systems containing symmetrically bonded π-allylic groups *e.g.*, (allylic = allyl, 1,3-dimethylallyl, cyclohexenyl) as expected only one olefin product is obtained in each case (see Table 1). In the asymmetrically bonded allylic rhodium complexes (allylic = 1-methylallyl and 1-methyl-3-ethylallyl) an almost 1/1 mixture of isomeric olefins is formed, indicating hydrogen migration from rhodium to both terminal carbon atoms has occurred about equally. The 1,1-dimethylallyl compound affords 2-methyl-2-butene and 3-methyl-1-butene in an approximately 2/1 ratio, indicating some preference for hydrogen migration to the least hindered carbon atom. In the 1,2-dimethylallyl complex the direction of hydrogen migration is not certain at present since the observed product $Et(CH_3)_2CCl$ could arise from rapid Markownikoff addition of HCl to either of the possible olefins.

Although it has not yet been possible to identify intermediates of type (III) from the reaction between olefins and $[(PF_3)_2RhCl]_2$, (II) does act as a catalyst for the isomerisation of 1-decene to *cis*- and *trans*-2-decene under mild conditions.

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