New Type of π-Allyl Isomerisation: Conversion of 1,1- into 1,2-Dimethylallyl Complexes of Cobalt and Rhodium

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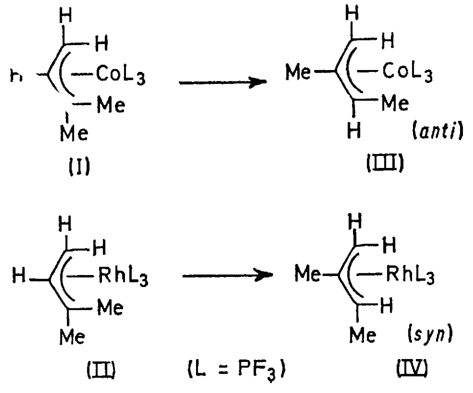
Summary The first examples of isomerisation of 1,1-dimethyl-π-allyl metal complexes to the corresponding 1,2-dimethyl-π-allyl compounds are described.

The fluxional behaviour of π-allyl metal complexes is well known.[1] As part of a general study of group migration within π-allylic transition-metal complexes,[2] we report the first examples of a new type of allyl isomerisation, namely the conversion of 1,1-dimethyl-π-allyl complexes of cobalt(I) (I) and rhodium(I) (II) into the corresponding 1,2-dimethyl-π-allyl metal compounds (III) and (IV) (Scheme 1).

The isomerisations, which were essentially quantitative, were effected by heating solutions of 1,1-dimethyl-π-allyltris(trifluorophosphine)cobalt (I),[3] and 1,1-dimethyl-π-allyltris(trifluorophosphine)rhodium (II),[4] at 60° in sealed tubes, the rate of isomerisation being much faster for the rhodium complex than for the cobalt compound. The *anti* isomer was obtained in the cobalt case whereas the *syn* isomer was found exclusively for rhodium.

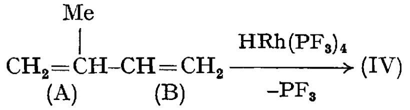
Since compound (IV) is the sole product[4] from the reaction between isoprene and $HRh(PF_3)_4$, the mechanism of the π-allyl isomerisation process most likely involves a 1,4-hydrogen shift (Scheme 2) with intermediate formation of a diolefin metal hydride (V).

Our results support previous suggestions[5] that 1-phenacyl-π-allyltetracarbonylmanganese (not isolated) is the first product of the reaction between butadiene and $PhMn(CO)_5$, and subsequently isomerises by a similar mechanism to afford 3-benzoyl-1-methyl-π-allyltetracarbonylmanganese.



Scheme 1.

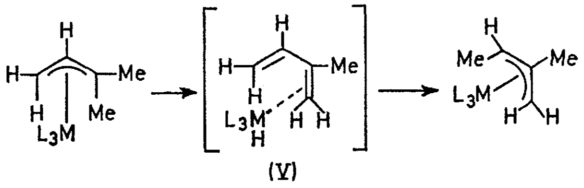
It is noteworthy that addition of $HRh(PF_3)_4$ to isoprene only occurs at the least basic double bond (B) of the diene to yield initially equal amounts of (IV) and its *anti* isomer



$$\underset{(A)}{CH_2{=}\overset{\overset{\textstyle Me}{|}}{C}H}{-}\underset{(B)}{CH{=}CH_2} \xrightarrow[-PF_3]{HRh(PF_3)_4} (IV)$$

which on heating isomerises to (IV). This contrasts with the known behaviour of isoprene with $HCo(CO)_4$, where addition occurs exclusively at (A) producing 1,1-dimethyl-π-allyltricarbonylcobalt, (VI).[6]

It has been suggested[7] that the acidity of the hydrogen of a transition metal hydride determines the direction of addition to an unsymmetrical conjugated diene. However, the different behaviour of the strongly acidic $HCo(CO)_4$ and $HRh(PF)_3)_4$[8] complexes towards isoprene is not compatible with this proposal. Compound (VI) shows no tendency to undergo isomerisation to 1,2-dimethyl-π-allyltricarbonylcobalt on heating.



SCHEME 2.

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