Oxidative-addition of Tertiary Phosphine–Ruthenium Complexes to Allylic Carbon–Hydrogen Bonds

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Summary Reaction of tertiary phosphine complexes of ruthenium(0) with allylic olefins produces isolable hydrido-π-allylruthenium(II) compounds which have been characterized.

The oxidative-addition of a transition metal complex to an allylic carbon–hydrogen bond has been frequently invoked in the mechanism for the catalytic isomerization of olefins under hydride-free conditions.[1] Previously Bönnemann[2] has detected at low temperatures the insertion of a trifluorophosphine-stabilized nickel(0) species into the carbon–hydrogen bond of co-ordinated propene but isolation of the resulting π-allyl complex was not possible. More recently Byrne et al.[3] have observed exchange between the hydride ligand and the terminal hydrogen atoms of the π-allylic ligand in the complex [HMo(π-C_3H_5)($Ph_2PCH_2CH_2PPh_2$)$_2$]. We report that reaction of tertiary phosphine complexes of ruthenium(0) with simple allylic olefins leads to isolable hydrido π-allyl ruthenium(II) species.

When an acetonitrile slurry of [(Ph_3P)$_4$Ru(π-MeCN)]·MeCN[4] is treated in a stainless steel autoclave with an excess of propene (185 lb in^{-2}) for 20 h at 50 °C, a pale yellow solid, which is sparingly soluble in aromatic solvents, m.p. 193 °C (decomp.), separates from the reaction mixture. Elemental analysis of this product is in accord with the formula [(Ph_3P)$_2$Ru(C_3H_6)(MeCN)] (1). In addition to the expected triphenylphosphine bands, the i.r. spectrum of (1) (Nujol) exhibits characteristic bands at 2267, 1958, and 582 cm^{-1}. The band at 2267 cm^{-1} is readily assigned to ν(CN) of the acetonitrile ligand which is co-ordinated to the metal through the nitrogen lone pair of electrons.[5] The band at 1958 cm^{-1} is assigned to a ruthenium–hydride stretching vibration. This assignment is supported by the almost quantitative formation of chloroform (identified by g.l.c. and mass spectrometry) upon reaction of (1) with carbon tetrachloride.
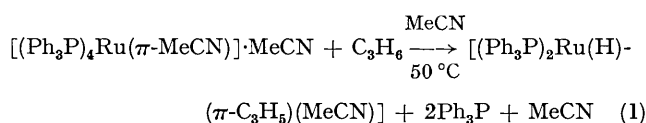
The perdeuteriopropene analogue of (1), [(Ph_3P)$_2$-Ru(C_3D_6)(MeCN)], was synthesized by reaction of C_3D_6 with

[(Ph$_3$P)$_4$Ru(π-MeCN)]·MeCN under conditions identical to those described previously. Satisfactory elemental analysis has been obtained for the indicated formula of the per-deuteriopropene derivative. In the i.r. spectrum of the perdeuteriopropene complex (Nujol) ν(CN) occurs at 2273 cm^{-1} and a band at 1409 cm^{-1} which is assigned to ν(RuD) is also observed. No bands are detected in the 1900—2000 cm^{-1} region for [(Ph$_3$P)$_2$Ru(C$_3$D$_6$)(MeCN)]. The measured ratio of 1·39:1 for ν(RuH):ν(RuD) is in good agreement with the expected value of 1·41:1 and confirms the initial assignment of the metal–hydride vibration in (1). Furthermore, these data unequivocally demonstrate that propene is the sole source of the hydrido-ligand in (1).

Absorption bands at 1006 and 582 cm^{-1} in the i.r. spectrum of (1), which are tentatively assigned to the carbon-skeletal symmetric stretching and in-plane deformation modes of the allyl fragment, respectively, suggest that the allyl ligand is π-bonded to the metal centre. The i.r. spectrum of [{(p-MeC$_6$H$_4$)$_3$P}$_2$Ru(π-C$_3$H$_5$)$_2$] exhibits bands in the same spectral regions and supports this conclusion. The low solubility of [(Ph$_3$P)$_2$Ru(C$_3$H$_6$)(MeCN)] in most solvents has prevented confirmation of π-bonding of the allyl ligand by n.m.r. spectroscopy. The presence of a π-allyl ligand in (1) is in accord with the expected octahedral co-ordination for a formally ruthenium(II) complex.
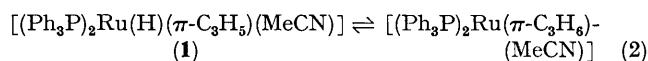
The available data suggest that reaction of the ruthenium-(0) compound with propene leads to oxidative-addition of the metal to the allylic carbon–hydrogen bond and the formation of a hydrido-π-allyl complex [equation (1)].

$$[(Ph_3P)_4Ru(\pi\text{-MeCN})]\cdot MeCN + C_3H_6 \xrightarrow[50\,°C]{MeCN} [(Ph_3P)_2Ru(H)-$$

$$(\pi\text{-}C_3H_5)(MeCN)] + 2Ph_3P + MeCN \quad (1)$$

Presumably co-ordination of the olefin precedes the oxida-tive-addition reaction although the co-ordinated olefin intermediate has not been detected. The yield of (1) is 98%.

Reaction of [(Ph$_3$P)$_4$Ru(π-MeCN)]·MeCN with isobutene under conditions similar to those employed with propene produced oils from which no crystalline product has been obtained. However, reaction of (1) at 50 °C with an excess of isobutene in acetonitrile for 48 h yields a yellow solid, m.p. 177—179 °C. Elemental analyses are in accord with the formula [(Ph$_3$P)$_2$Ru(C$_4$H$_8$)(MeCN)] (2). Thermal decom-position of (2) and mass spectral analysis of the volatile

decomposition products confirm the presence of a single mole of isobutene per mole of ruthenium. The i.r. spectrum (Nujol) of (2) exhibits characteristic bands at 2268, 1975, and 578 cm^{-1}. By analogy with the i.r. spectrum of [(Ph$_3$P)$_2$Ru(H)(π-C$_3$H$_5$)(MeCN)] these bands are tentatively assigned to ν(CN), ν(RuH), and δ(CCC) of acetonitrile, hydride, and π-methylallyl ligands, respectively. Compound (2) is, therefore, formulated as [(Ph$_3$P)$_2$Ru(H)(π-C$_4$H$_7$)(MeCN)]. The conversion of (1) into (2) most probably proceeds through a ruthenium(0) complex which is in tautometric equilibrium with (1) [equation (2)]. Similar

$$[(Ph_3P)_2Ru(H)(\pi\text{-}C_3H_5)(MeCN)] \rightleftharpoons [(Ph_3P)_2Ru(\pi\text{-}C_3H_6)-$$
$$\text{(1)} \hspace{5.5cm} (MeCN)] \quad (2)$$

equilibria between hydrido-aryl–ruthenium species and their corresponding arene complexes have been reported.[6] Subsequent exchange of propene by isobutene in [(Ph$_3$P)$_2$Ru-(π-C$_3$H$_6$)(MeCN)] followed by oxidative-addition of ruthen-ium to an allylic carbon–hydrogen bond of isobutene would lead to the isolated product (2).

At room temperature metathesis of (1) with a four-fold amount of diphenylphosphine in acetonitrile under propene (185 lb in^{-2}) produces (Ph$_2$PMe)$_3$Ru(H)(π-C$_3$H$_5$)] (3). Com-pound (3) is an off-white solid, m.p. 164 °C (decomp.), and has been identified by elemental analyses and i.r. spectro-scopy [ν(RuH), 1932; δ(CCC), 585 cm^{-1}]. Treatment of [(Ph$_2$PMe)$_3$Ru(H){C$_6$H$_4$P(Me)Ph}][4] with propene at 50 °C in acetonitrile also affords (3). In this latter case co-ordinatively unsaturated tetrakis(diphenylmethylphos-phine)ruthenium(0), which is in equilibrium with the ortho-metallated complex, may be postulated as the intermediate which yields (3) upon propene co-ordination and oxidative-addition to the allylic carbon–hydrogen bond.

The ready isolation of hydrido-π-allylruthenium(II) com-plexes from the reaction of allylic olefins with ruthenium(0) complexes provides a unique opportunity to study the electronic and co-ordination requirements of this novel oxidative-addition reaction. To this end we are currently determining the effect of other ligands and substituted allylic olefins on the course of this reaction. Also it should be noted that the catalytic activity of [(Ph$_3$P)$_4$Ru(π-MeNC)]·MeCN in benzene solution in the isomerization of olefins such as hex-1-ene suggests that this isomerization occurs through a π-allyl mechanism in accord with the reactions observed for more simple allylic olefins.

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