Interactions of Alkenes with Hydridotriphenylphosphine Complexes of Ruthenium†

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Summary Study of the interaction of tetrahydridotris(triphenylphosphine)ruthenium or of dihydridotetrakis(triphenylphosphine)ruthenium with various alkenes shows that in most cases the product is a ruthenium(II) complex; for buta-1,3-diene, pent-1-ene, and but-1-ene, ruthenium(0) complexes are obtained.

We have shown[1] that hydridoalkyl tris(triphenylphosphine) complexes of ruthenium(II) eliminate alkane to form not a ruthenium(0) complex but the orthometallated ruthenium(II) species, $RuH(C_6H_4PPh_2)(PPh_3)_2(S)$ ($S = Et_2O$ or tetrahydrofuran).

The interaction of $RuH_2(PPh_3)_4$ or $RuH_4(PPh_3)_3$ with alkenes could have been expected to proceed *via* hydridoalkyl intermediates in a similar manner. The claims[2,3] that such reactions produce ruthenium(0) species cannot be fully substantiated. In most cases ruthenium(II) species are formed that have (a) a hydride and an orthometallated

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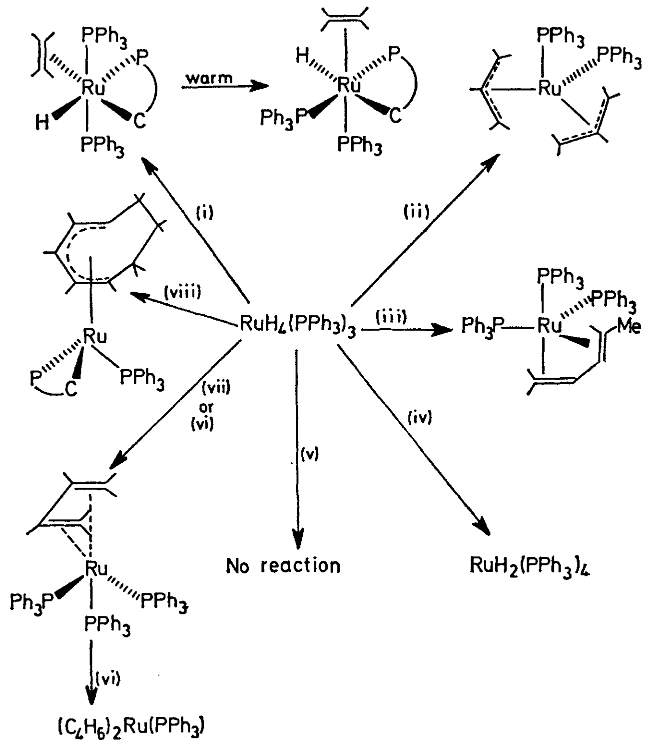
† No reprints available.

phosphine, (b) two π-allyl groups, or (c) one π-allyl group plus a Ru–C σ-bond. The exceptions are butadiene and terminal olefins with more than four carbon atoms, which do give ruthenium(0) species.



Scheme. Interaction of $RuH_4(PPh_3)_3$ or of $RuH_2(PPh_3)_4$ with alkenes:
(i) ethylene, (ii) propene, (iii) pent-1-ene, (iv) *cis*-pent-2-ene, (v) isobutene or cyclohexene, (vi) buta-1,3-diene, (vii) but-1-ene, (viii) cyclo-octa-1,5-diene. P–C = o-$C_6H_4PPh_2$.

It may be noted that (a) the apparent absence of an Ru–H bond[3–5] is not necessarily evidence for the presence of a ruthenium(0) species; (b) much of the work[2–7] on the use of $RuH_2(PPh_3)_4$ in reactions involving alkenes and other unsaturated substrates is either in error‡ or in need of re-interpretation; and (c) isolation of complexes by evaporation of reaction solutions or suspensions to dryness[3–5] may well lead to mixtures of products which do not analyse correctly[4] and which lead to erroneous structural assignments on the basis of spectroscopic data.[3–5,7] For the reactions summarised in the Scheme, all compounds have been characterised by i.r. and ^1H and ^{31}P n.m.r. spectra and analysis. The previously best characterised compound, said[2] to be $Ru(C_2H_4)(PPh_3)_3$, has peaks at 1552 and 1414 cm^{-1} characteristic of an o-$C_6H_4PPh_2$ group, while the presence of the Ru–H bond is shown by a doublet of triplets centred at τ 16·5. The compound formed thus is the isomer shown in the Scheme; it is converted on warming into a second, more stable isomer.

The broad quartet observed near τ 20 in the ^1H n.m.r. spectrum of the product from the reaction of pent-2-ene or a small excess of pent-1-ene and $RuH_4(PPh_3)_3$, and attributed[3,7] to $RuH_2(PPh_3)_3(C_5H_{10})$, is due to $RuH_2(PPh_3)_4$. Not only can this complex be identified in the solution by its ^{31}P n.m.r. spectrum but it can also be isolated from the solutions. Also, the product from the reaction of $RuH_4(PPh_3)_3$ with a large excess of pent-1-ene is not $Ru(C_5H_{10})(PPh_3)_3$ as claimed[3] but is the penta-1,3-diene complex $Ru(C_5H_8)(PPh_3)_3$.

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‡ In ref. 4 reactions are carried out in chloroform which reacts with $RuH_2(PPh_3)_4$ to give $RuHCl(PPh_3)_3$.

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