High Selectivity in the Homogeneous Hydrogenation of 1-Alkynes to 1-Alkenes by Rhodium(I) Carboxylato-Complexes

By Robert H. Crabtree
(*Institut de Chimie des Substances Naturelles, C.N.R.S.,* 91190 *Gif-sur-Yvette, France*)

Summary $[Rh(cod)(PPh_3)(C_5H_5N)]^+PF_6^-$ or $[RhOCOPh(cod)(PPh_3)]$ (cod = cyclo-octa-1,5-diene) in benzene containing $PhCO_2H$ and NEt_3 under H_2, reduce a variety of 1-alkynes with high selectivity to the corresponding 1-alkenes.

Complexes of the type $[Rh(cod)L_2]^+PF_6^-$ (L = $PMePh_2$ or PMe_2Ph) in ethanol or acetone under H_2 are known[1a] to give the cations $[RhH_2L_2(solvent)_2]^+$ which are capable of reducing certain ketones to alcohols and alkynes or alkenes to the corresponding alkanes. Activity is lost on deprotonation. Internal alkynes are reduced to the *cis*-alkenes by a related system.[1b]

The complexes $[Rh(cod)L^1L^2]^+PF_6^-\{L^1 = PPh_3,\ L^2 = C_5H_5N$ (**1**) or PPh_3 (**2**)$\}$ are now found to dissolve in benzene under H_2, only in the presence of at least 1 equiv. of a base, such as NEt_3, to give highly active hydrogenation catalysts. Hex-1-ene, for example, is reduced at a rate of 1500 (expressed in mol H_2 uptake per mol of catalyst per h) compared to 130 measured for $[RhCl(PPh_3)_3]$[2] under the same conditions (catalyst 5 mM, H_2 60 cm Hg, 25 °C). Other unsaturated substances are reduced much more slowly, *e.g.* cyclohexene (rate 10), and benzophenone (rate 7). Phenylacetylene is polymerised.

The selectivity of these systems can be profoundly modified by the presence of an anionic ligand. For example, the complex (**1**) (5 mM) dissolves in benzene (25 °C) containing $PhCO_2H$ (25 mM) and NEt_3 (100 mM) under H_2 (60 cm Hg) to give a yellow solution which becomes dark red or orange on the addition of a 1-alkyne substrate (0·5 M). Hex-1-yne, phenylacetylene, prop-2-ynyl alcohol, 2-ethynylbutan-2-ol, and 1-ethynylcyclohexanol were all smoothly reduced to the corresponding vinyl derivatives at a rate of 2—6 mol H_2 {mol Rh}$^{-1}$ h^{-1}.

The course of the reduction was followed by ^1H n.m.r. spectroscopy, v.p.c., and manometrically. The colour of the solutions lightened and the absorption rate fell as the H_2 uptake approached 1 mol per mol of subtrate. Beyond this point further reduction to the alkyl derivative occurred more slowly (rate 0·2—1). Nitriles, ketones, and internal alkynes were not reduced and complex (**2**) gave only inactive solutions. Cinnamate or crotonate, but not hydrocinnamate or acetate, can replace the benzoate to give an active system.

Complex [$RhOCOPh(cod)PPh_3$] was prepared by metathesis of the corresponding chloride[3] with TlOCOPh; the i.r. spectrum suggests[4] that the carboxylate ligand is monodentate. This complex can replace the complex salt (**1**) in the catalyst system described above. Excess of $PhCO_2H$ and NEt_3 must, however, still be present, probably to suppress dissociation of the carboxylate ligand as otherwise the substrate polymerises.

No crystalline complexes could be isolated from the active solutions but their i.r. spectra show that decarbonylation of the carboxylate to give carbonyl complexes does not occur.

The reduction of phenylacetylene with D_2 and the catalyst derived from the complex (**1**) gave a dideuteriostyrene consisting of $\geqslant 95\%$ *cis* PhDC=CDH, having a triplet at τ 4·1 with $^3J_{HD}$ 2·7 Hz for the vinyl proton. This reduction therefore occurs *via* a π-bonded intermediate.[2]

I thank Dr. H. Felkin for helpful discussions, the Compagnie des Métaux Précieux for the loan of rhodium, and the C.N.R.S. and D.G.R.S.T. for financial support.

(*Received, 2nd June* 1975; *Com.* 609.)

[1] R. R. Schrock and J. A. Osborn, (a) *J.C.S. Chem. Comm.*, 1970, 567; (b) *J. Amer. Chem. Soc.*, 1971, **93**, 3089.

[2] F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 1574.

[3] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 4735.

[4] S. D. Robinson and M. F. Uttley, *J.C.S. Dalton*, 1973, 1912.