Trichlorotris-(4-biphenyl-1-naphthylphenylphosphine)rhodium(III), a New Homogeneous Hydrogenation Catalyst

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Summary A new saturated Rh^{III} complex has been used to effect the homogeneous hydrogenation of $\alpha\beta$-unsaturated carboxylic acids.

WE report on a new homogeneous hydrogenation catalyst, trichlorotris-(4-biphenylyl-1-naphthylphenylphosphine) rhodium(III) (**1**). The most widely studied homogeneous hydrogenation catalyst thus far has been chlorotris-(triphenylphosphine)rhodium(I) (**2**), first reported by Wilkinson *et al.* in 1965.[1] It has been established that this co-ordinatively unsaturated square-planar complex activates molecular hydrogen by the oxidative addition of hydrogen to form a solvated octahedral dihydrido-species (**3**).[2] The application of some octahedral complexes as homogeneous hydrogenation catalysts has recently been reported by several authors.[3]

The complex (**1**) was prepared in 90% yield by the reaction of 4-biphenylyl-1-naphthylphenylphosphine[4] (**3** mmoles) (**4**) with rhodium trichloride trihydrate (1 mmole) in deoxygenated ethanol. It has m.p. 185—186°, and analyses satisfactorily for $C_{86}H_{63}Cl_3P_3Rh$. The effectiveness of this new complex as a homogeneous hydrogenation catalyst can be illustrated by the quantitative reduction of some internal and highly substituted carbon–carbon double bonds in $\alpha\beta$-unsaturated carboxylic acids that are otherwise difficult to reduce. Under identical reaction conditions (temperature 50°, hydrogen gas pressure 80 lb./in.^{2}, and reaction time 8 hr.), the catalyst (**1**) was found to

Hydrogenation of αβ-unsaturated carboxylic acids

Reactant	Product	Reduction (%)[a]		Yield (%)	
α-Acetamidocinnamic acid ..	*N*-Acetyl-β-phenylalanine	100[b]	100[c]	75[b]	83[c]
Atropic acid	Hydrotropic acid	100	100	90	87
Cinnamic acid	Hydrocinnamic acid	100	80	85	85
Itaconic acid	α-Methylsuccinic acid	100	100	70	92
p-Methylcinnamic acid ..	*p*-Methylhydrocinnamic acid ..	100	100	80	85

[a] Based on n.m.r. and i.r. spectral analyses.
[b] Using Wilkinson's catalyst (**2**).
[c] Using compound (**1**) as the catalyst.

be as effective as the well known Wilkinson's catalyst, (**2**). The results are summarized in the Table. The hydrogenations were conducted by stirring a solution of the unsaturated acid (12·0 mmole) and the complex (0·3 mmole) in benzene–ethanol (1 : 1) in a pressure hydrogenation apparatus. The reaction mixture was evaporated to dryness, treated with 1N-NaOH, filtered, and reacidified with dilute HCl to give the saturated acid whose identity was confirmed by m.p. and spectral (n.m.r. and i.r.) analyses.

Interest in the complex (**1**) as a homogeneous hydrogenation catalyst stems from the fact that it is a saturated complex and still an effective catalyst, although not as easy to prepare as the complex (**2**). The mode of activation of molecular hydrogen by compound (**1**) has not been established so far. However, in our opinion it is more reasonable to assume that the complex (**1**) activates molecular hydrogen through the mechanism suggested by Horner *et al.*[5]

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