Catalytic Asymmetric Hydrogenation Using Ruthenium(II) Chiral Phosphine Complexes

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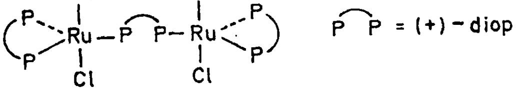
Summary The ruthenium(II) complexes $[Ru_2X_4\{(+)\text{-}(diop)\}_3]$[X = Cl, Br; diop = 2,2-dimethyl-1,3-dioxolan-4,5-bis(methylene)bis(diphenylphosphine)], which contain a bridging bidentate phosphine ligand, catalyse under mild conditions the hydrogenation of unsaturated carboxylic acids and can give products of high optical yields (*ca.* 60%).

Asymmetric hydrogenation using rhodium(I) complexes containing chiral tertiary phosphine ligands, including diop, is well documented,[1] but corresponding ruthenium(II) systems have not been reported, in spite of the high catalytic hydrogenating activity of the $[RuCl_2L_3]$-$[HRuClL_3]$ ($L = PPh_3$) system.[2] We have now synthesised both mononuclear and bi-nuclear ruthenium(II) complexes containing chiral phosphine ligands, and interestingly only a binuclear species containing a bridging (+)-diop ligand has been found effective for catalytic hydrogenation under mild conditions.



(1)

The complexes $[RuCl_2(PRPh_2)_n]$, [n = 3 or 4; R = Me or $MeCH_2CH(Ph)CH_2$] were made from $[RuCl_2(PPh_3)_3]$ using the phosphine exchange method.[3] However, these complexes under H_2 are not very efficient for catalytic hydrogenation of olefinic substrates in toluene containing triethylamine, which is added to promote formation of a hydride.[2] More basic solvents such as *NN*-dimethylacetamide (DMA) were also not effective, although an added problem here is the production of ionic dimers $[Ru_2Cl_3L_6]^+Cl^-$ in the polar media.[3]

A phosphine exchange synthesis using diop {$[RuCl_2(PPh_3)_3]$: (+)-diop = 1 : 2·5} readily yields a green compound, which we formulate as (**1**). The complex is a non-electrolyte and analyses correctly, the Cl content ruling out the expected $[RuCl_2(diop)_2]$ product. The single ν(Ru–Cl) at 310 cm^{-1} is consistent with *trans* chloro-ligands,[4] and the electronic spectrum with maxima at 455 and 700 nm closely resembles that of the five-co-ordinate $[RuCl_2(PPh_3)_3]$ complex.[5] Toluene–ethanol or DMA solutions of (**1**) (or the bromide) catalyse the hydrogenation of αβ-unsaturated carboxylic acids at 30 °C and 1 atm H_2; the prochiral substrate α-acetamidoacrylic acid (0·1M) is converted quantitatively in 1 day with 10^{-3}M catalyst into a product with *ca.* 60% optical yield with respect to optically pure *N*-acetyl-(*S*)-alanine. The optical purity is similar to that obtained using $[HRh(diop)_2]$[6] or *in situ* 1 : 1 Rh–diop complexes;[7] again use of (+)-diop gives the *S*-conformer, and *vice versa*.[1]

Of note is that a phosphine exchange reaction using diphos ($Ph_2PCH_2CH_2PPh_2$) yields the well-characterized *trans*-$[RuCl_2(diphos)_2]$ complex and this co-ordinatively saturated species, unlike (**1**) is ineffective for hydrogenation under similar conditions. The diop ligand with four C atoms between the P donors does not give rise to the usual d^6 octahedral structure, presumably because of steric problems. Bridging bidentate phosphine ligands are not uncommon.[9] Consistent with unsaturated character, solutions of (**1**) readily react with small gas molecules such as CO, H_2, and O_2.

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