[2,2′-Dimethyl-6,6′-bis(diphenylphosphino)biphenyl](triphenylphosphine)-dichlororuthenium(II): an Enantioselective Catalyst for the Hydrogenation of Diketones

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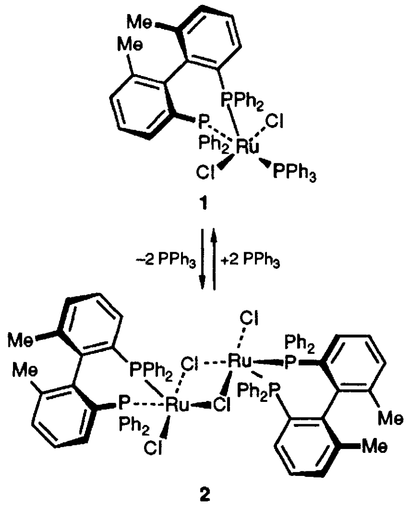
The novel species $[RuCl_2(PPh_3)\{(S)\text{-biphemp}\}]$ **1** and $[RuH(\eta^2\text{-}BH_4)(PPh_3)\{(S)\text{-biphemp}\}]$ **3** [biphemp = 2,2′-dimethyl-6,6′-bis(diphenylphosphino)biphenyl] have been synthesized; **1** has a labile triphenylphosphine ligand and is a very active and enantioselective catalyst for the mono- or bis-hydrogenation of pentane-2,4-dione.

Ruthenium(II) complexes containing chelating tridentate phosphine ligands have shown a very interesting reactivity of relevance to catalytic applications,[1] possibly owing to the easy creation of a vacant site by ligand dissociation. Similar characteristics can be expected in compounds of the type $[RuX_2(L')(L\text{–}L)]$ (L–L = diphosphine ligand) when L′ is a strongly coordinating but potentially labile ligand such as PPh_3. These species appear particularly interesting when the diphosphine is chiral owing to their catalytic potential for asymmetric synthesis.[2] Unsuccessful attempts were indeed

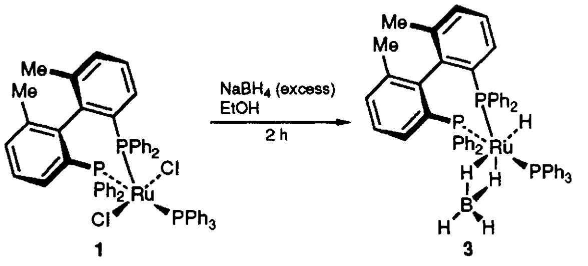


Scheme 1

made to exploit the ligand exchange reaction of $[RuCl_2(PPh_3)_3]$[3] with 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) (binap),[4] though this method had been previously applied to the synthesis of $[RuCl_2(PPh_3)(diop)]$[2] {diop = [(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)]bis-[diphenylphosphine]} and $[RuCl_2(PPh_3)(dppb)]$[4] [dppb = butane-1,4-diylbis(diphenylphosphine)]. In fact, ruthenium(II) complexes containing the chiral diphosphine binap represent the most impressive examples of efficient catalysts for enantioselective hydrogenation reactions.[5] The related axially dissymmetric diphosphines of the biphenyl series have received much less attention, despite the fact that they show comparable and sometimes better asymmetric discrimination in transition metal catalysed enantioselective reactions.[6–8]

By treating $[RuCl_2(PPh_3)_3]$ with the optically pure atropisomeric ligand 2,2′-dimethyl-6,6′-bis(diphenylphosphino)biphenyl [(*S*)-biphemp][6] in toluene at room temperature, a green material analysing as $[RuCl_2(PPh_3)\{(S)\text{-biphemp}\}]$ **1** was obtained (yield >90%).† The IR spectrum (Nujol) exhibits a single band at 330 cm^{-1} suggesting that the compound is monomeric with the chlorine atoms occupying mutually *trans*-positions. As expected for a five-coordinate structure the ^{31}P NMR spectra of **1** are temperature dependent. At room temperature a slightly broadened triplet (δ_A 20.1, J_{PP} 151 Hz) is observed for the coordinated PPh_3, while the biphemp signals are coalesced in a broad hump centred at δ 56. The low-temperature spectra‡ indicate a meridional arrangement of the phosphorus atoms which, together with the IR data, suggest a square-pyramidal structure.

As already found for $[RuCl_2(PPh_3)(dppb)]$,[9] dissociation of triphenylphosphine (about 20%) is indicated by a sharp signal at δ −5, which is present in the spectra both at room and at low temperature. Moreover, as for analogous compounds,[10] two low-intensity AX systems§ of equal intensity in the δ 50–60 region suggest the formation of the dimeric species $[RuCl_2\{(S)\text{-biphemp}\}]_2$ **2**. In fact, when **1** is refluxed in hexane a mixture of products is formed whose ^{31}P NMR spectrum consists mainly of the two doublets of doublets also present as minor signals in the spectrum of **1**, together with signals due to small amounts of unreacted **1** and $[RuCl_2(PPh_3)_2]_2$. We formulate the main product as the dimer **2** on the basis of both NMR evidence and reactivity (see below).



Scheme 2

Evidence for a dynamic interchange between free and complexed triphenylphosphine in **1** at room temperature was obtained by a magnetization transfer experiment performed *via* selective excitation of free PPh_3 with a DANTE pulse sequence.[11] A rate constant of about 10 s^{-1} can be evaluated for the dissociation of PPh_3 from **1**. Moreover, at 100 °C the signals of both free and coordinated PPh_3 in the ^{31}P NMR spectrum are strongly broadened as the scrambling process becomes fast on the NMR timescale. Dissociation amounts to *ca.* 50%. The low-intensity signals of **2** broaden and eventually disappear upon raising the temperature, suggesting that this species also is involved in a dynamic process. These data strongly support the equilibrium in Scheme 1 taking place in solution. This equilibrium is also established in the solutions containing **2** and PPh_3 in a 1 : 2 molar ratio.

Preliminary experiments show that complex **1** is able to display very large steric discrimination in stoichiometric as well as in catalytic reactions. In fact, as for $[RuCl_2\{PhP(CH_2CH_2CH_2PPh_2)_2\}]$,[1e] **1** reacts with $NaBH_4$ in ethanol to give $[RuH(\eta^2\text{-}BH_4)(PPh_3)\{(S)\text{-biphemp}\}]$ **3** (Scheme 2). Interestingly, the ^1H and ^{31}P NMR spectra indicate that **3** is formed as a single diastereoisomer.¶

Furthermore, **1** behaves as a very effective hydrogenation catalyst.[8] Pentane-2,4-dione in ethanol solution (c = 50%) is rapidly (100% conversion in 15 h) hydrogenated to pentane-2,4-diol in the presence of 0.05% of **1** under 100 bar of hydrogen at 50°C. A diastereoisomeric ratio of *ca.* 94:6 (*lk* : *ul*) of the two possible diols is obtained,|| the *lk*-diastereoisomer being essentially enantiomerically pure (*S,S*, e.e. >99%).** A higher *lk* : *ul* ratio of 98:2 is achieved at 40°C under the same conditions at the cost of a slower reaction rate (100% conversion in 60 h, e.e. of *lk* isomer >99%). Remarkably, the mono-hydrogenated product (*S*)-4-hydroxypentan-2-one can be isolated in 86% yield after 10 h reaction time at 40 °C (80% conversion). This selectivity can be improved (90% yield of 4-hydroxypentane-2-one at 85% conversion) by running the reaction at 50°C for 10 h in the presence of a slight excess of triphenylphosphine (**1** : PPh_3 molar ratio 1 : 1). It is worth mentioning that on using '$RuCl_2[(R)\text{-(binap)}]$'[12,13] as the catalyst precursor, the mono-hydrogenation product was obtained only at very low conversion (*ca.* 10%). Complex **1** displays catalytic activity also under hydrogen transfer conditions (in refluxing propan-2-ol under argon) both in the presence and in the absence of base.

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† All new compounds gave satisfactory elemental analysis.

‡ ^{31}P NMR (81.0 MHz, ppm from ext. 85% H_3PO_4, CD_2Cl_2, 193 K) ABX pattern, δ_A 20.8 (J_{AB} 323, J_{AX} 23 Hz), δ_B 29.5 (J_{BX} 40 Hz), δ_X 85.2.

§ ^{31}P NMR (CD_2Cl_2, 298 K) δ_A 40.2, δ_X 45.7 (J_{AB} 28.3 Hz); $\delta_{A'}$ 43.6, $\delta_{X'}$ 49.2 ($J_{A'X'}$ 30.5 Hz).

¶ **2**: ^{31}P NMR (C_6D_6, 298 K) ABX pattern, δ_A 44.8 (J_{AB} 279, J_{AX} 26 Hz), δ_B 49.3 (J_{BX} 33 Hz), δ_X 70.4; ^1H NMR (200 MHz): δ_A −13.4 (q, J_{PH} 25 Hz), δ_B −9.4 (br d, J_{PH} 54 Hz), δ_C −4.2 (br s) and δ_D 4.9 (br s). IR, ν/cm^{-1} (Nujol) 2403 m, 2333 m ($\nu_{B\text{-}H}$); 1966 w, br, 1331 m, br ($\nu_{B\text{-}H\text{-}M}$); 1178 s ($\delta_{BH_2}$).

|| Diastereoisomers not separated, ratios determined by ^1H NMR.

** Enantiomeric excesses (e.e.) determined by polarimetry.

At variance with **1**, **3** is totally ineffective for the hydrogenation of pentane-2,4-dione under analogous conditions (ethanol solution, 100 bar H_2, 50 °C), even in the presence of an excess of acid (HBF_4) or base (NEt_3). This may be not unexpected, since it was reported that other Ru–binap complexes which do not contain chloro ligands failed to catalyse the reduction of β-keto carboxylic esters to the corresponding alcohol.[14] Further applications of **1** and **3** as well as of derivatives thereof as enantioselective catalysts for the reduction of a number of diketones are in progress.

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References

1 (*a*) R. R. Guimerans, E. C. Hernandez, M. M. Olmstead and A. L. Balch, *Inorg. Chim. Acta*, 1989, **165**, 45; (*b*) G. Jia, A. L. Rheingold and D. W. Meek, *Organometallics*, 1989, **8**, 1378; (*c*) G. Jia and D. W. Meek, *J. Am. Chem. Soc.*, 1989, **111**, 757; (*d*) J. B. Letts, T. J. Mazanec and D. W. Meek, *Organometallics*, 1983, **2**, 695; (*e*) J. B. Letts, T. J. Mazanec and D. W. Meek, *J. Am. Chem. Soc.*, 1982, **104**, 3898; (*f*) G. Jia, I. Lee, D. W. Meek and J. C. Gallucci, *Inorg. Chim. Acta*, 1990, **177**, 81; (*g*) A. Nann, T. Ward and L. M. Venanzi, *Abstracts of the Autumn Meeting of the Swiss Chemical Society*, 1990, p. 108.

2 G. E. Rodgers, W. R. Cullen and B. R. James, *Can. J. Chem.*, 1983, **61**, 1314.

3 P. S. Hallman, T. A. Stephenson and G. Wilkinson, *Inorg. Synth.*, 1972, **12**, 237.

4 T. Ikariya, Y. Ishii, H. Kawano, T. Arai, M. Saburi, S. Yoshikawa and S. Akutagawa, *J. Chem. Soc., Chem. Commun.*, 1985, 922.

5 R. Noyori and H. Takaya, *Acc. Chem. Res.*, 1990, **23**, 345.

6 R. Schmid, M. Cereghetti, B. Heiser, P. Schönholzer and H.-J. Hansen, *Helv. Chim. Acta*, 1988, **71**, 897.

7 T. Frejd and T. Klingstedt, *Acta Chem. Scand.*, 1989, **43**, 670.

8 (*a*) B. Heiser, E. Broger, Y. Crameri, P. Schönholzer and R. Schmid, *Abstracts of the Autumn Meeting of the Swiss Chemical Society*, 1990, p. 98; (*b*) R. Schmid, J. Foricher, M. Cereghetti and P. Schönholzer, *Helv. Chim. Acta*, 1991, **74**, 370; (*c*) B. Heiser, E. Broger and Y. Crameri, *Tetrahedron: Asymmetry*, 1991, **2**, 51.

9 C. W. Jung, P. E. Garrou, P. R. Hoffman and K. G. Caulton, *Inorg. Chem.*, 1984, **23**, 726.

10 B. R. James, A. Pacheco, S. J. Rettig, I. S. Thorburn, R. G. Ball and J. A. Ibers, *J. Mol. Catal.*, 1987, **41**, 147.

11 For the application of the DANTE technique to similar exchange processes: J. M. Brown, P. L. Evans and A. R. Lucy, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1589 and references therein.

12 M. Kitamura, T. Ohkuma, S. Inoue, N. Sayo, H. Kumobayashi, S. Akutagawa, T. Ohta, H. Takaya and R. Noyori, *J. Am. Chem. Soc.*, 1988, **110**, 629.

13 H. Kawano, Y. Ishii, M. Saburi and Y. Uchida, *J. Chem. Soc., Chem. Commun.*, 1988, 87.

14 R. Noyori, T. Ohkuma, M. Kitamura, H. Takaya, N. Sayo, H. Kumobayashi and S. Akutagawa, *J. Am. Chem. Soc.*, 1987, **109**, 5856.