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THE MECHANISM OF ASYMMETRIC HYDROGENATION CATALYSED BY RHODIUM (I) DIPAMP COMPLEXES.

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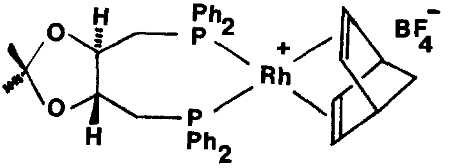
Asymmetric homogeneous hydrogenation of dehydroamino acid derivatives may be effected in high optical yield by several rhodium complexes of chelating biphosphines[1]. We have recently reported n.m.r. evidence[2] on the mechanism of reactions catalysed by 2,3-isopropylidene-2,3-*trans* dihydroxy-1,4-*bis*(diphenylphosphino)butane norbornadiene rhodium (I) tetrafluoroborate 1 in methanol, where the olefinic ligand is first hydrogenated and replaced by solvent in the coordination sphere. Addition of excess Z-benzamidocinnamic acid 2 to this solution gives a complex whose phosphorus-31 n.m.r. spectrum is a sharp rhodium-coupled AX quartet at 275 K but exchange-broadened at higher temperatures. The corresponding experiment with E-benzamidocinnamic acid 3 gives rise to two diastereomeric species differentiated by coordination of opposite enantiotopic olefin faces to the metal, there being no exchange broadening up to 300 K.



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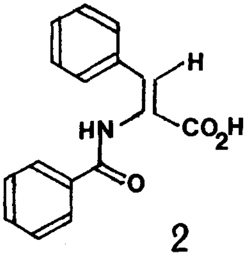

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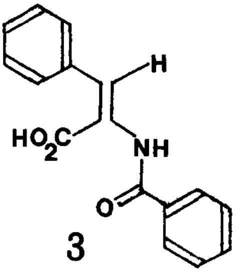

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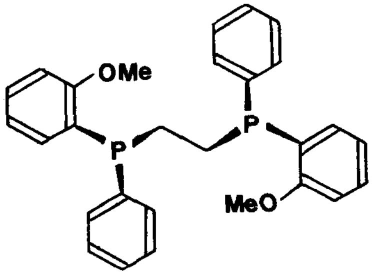
Complexes of DIOP are conformationally labile[3] and their efficiency as asymmetric catalysts is exceeded by complexes based on 4 (DIPAMP)[4] or 5 (CHIRAPHOS)[5] which both form 5-membered chelate rings. It was therefore of interest to carry out related experiments with one of these ligands. The rhodium (I) cyclooctadiene complex of 4 is reported to give a 94% optical yield on hydrogenation of 2 and an optical yield of 47% on hydrogenation of 3, both under somewhat forcing conditions, (323 K, 3 atm H_2).



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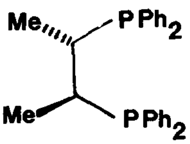

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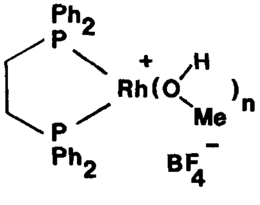

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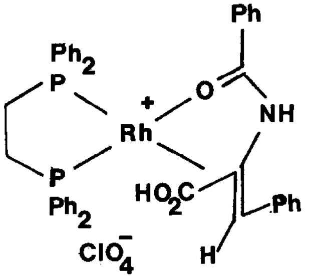
Initial experiments were conducted with bis-diphenylphosphinoethane norbornadiene rhodium (I) perchlorate which took up hydrogen rapidly at atmospheric pressure (43 μM, 0.5 ml. MeOH, $t_{\frac{1}{2}}$ 100 s.) giving the methanol complex 6 (δ = 81.2 ppm, J_{Rh-P} = 206 Hz)[6,7]. Addition of 2 in methanol at 195 K (150 μM, 0.5 ml.) under argon gave rise to a red solution of the enamide complex 7 whose phosphorus-31 n.m.r. spectrum at 301 K showed a rhodium coupled AX quartet (δ_A = 60.5 ppm, J_{Rh-P} = 158 Hz; δ_X = 72.2 ppm, J_{Rh-P} = 162 Hz, J_{P-P} = 39 Hz). In a similar experiment with 3, a broad spectrum was initially obtained which changed with time ($t_{\frac{1}{2}}$ = 3000 s.) giving 7 as the only observable species.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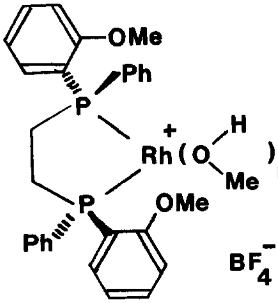
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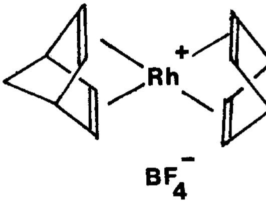
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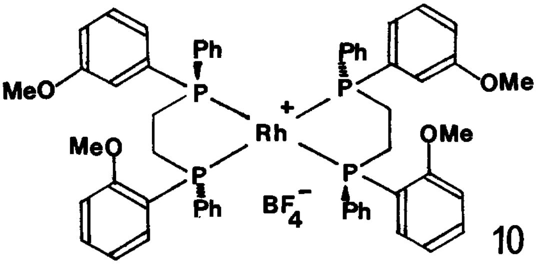
No success was derived from attempts to prehydrogenate the rhodium (I) cyclooctadiene complex of 4 which either resisted reaction, or decomposed under forcing conditions. The methanol complex 8 was obtained, however, by hydrogenating ($t_{\frac{1}{2}}$ ∿ 100 s.) a solution of 4 (33 μM, 0.5 ml. MeOH) and bis-norbornadiene rhodium (I) tetrafluoroborate 9 (92 μM)[8]. Excess of the latter avoids the formation (<5%) of 10, but leads to the deposition of metallic rhodium on hydrogenation. This may be removed by filtration, giving a clear yellow solution of 8 (δ = 80.8 ppm, J_{Rh-P} = 209 Hz). Addition of 2 in methanol at 195 K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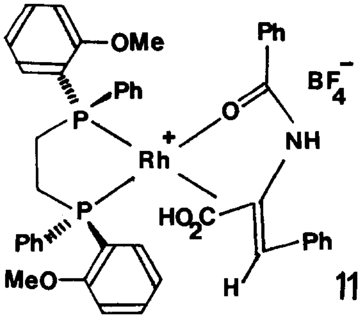

11

under argon gave 11 whose n.m.r. spectrum at 301 K resembled that of 7 (δ_A = 49.5 ppm, J_{Rh-P} = 154 Hz; δ_X = 70.8 ppm, J_{Rh-P} = 161 Hz, J_{P-P} = 41 Hz) but showing a minor amount of a second, partially obscured rhodium coupled AX quartet. The nature of the species present is made clearer from a related experiment with the corresponding Z-ester whose complexed n.m.r. clearly shows the presence of two diastereomers in the ratio 91:9 at 301 K (FIGURE). This is consistent with structures 12a and 12b respectively related to the major and minor enantiomers obtained on hydrogenation. The diastereomer ratio observed represents a stereoselectivity in binding of 5.9 kJ mol^{-1}, which compares with a value of 9.2 kJ mol^{-1} derived from the enantiomer ratio reported[4] for hydrogenation of the same ester. It is thus clear that the major part of the observed asymmetric induction arises from stereoselectivity in the binding step, rather than the relative rates of formation or hydrogenation of the diastereomeric complexes. In a similar experiment using the E-acid 3 a broad spectrum centred at 72 ppm was obtained which rapidly ($t_{\frac{1}{2}}$ ∿ 500 s.) changed to the spectrum of 11.

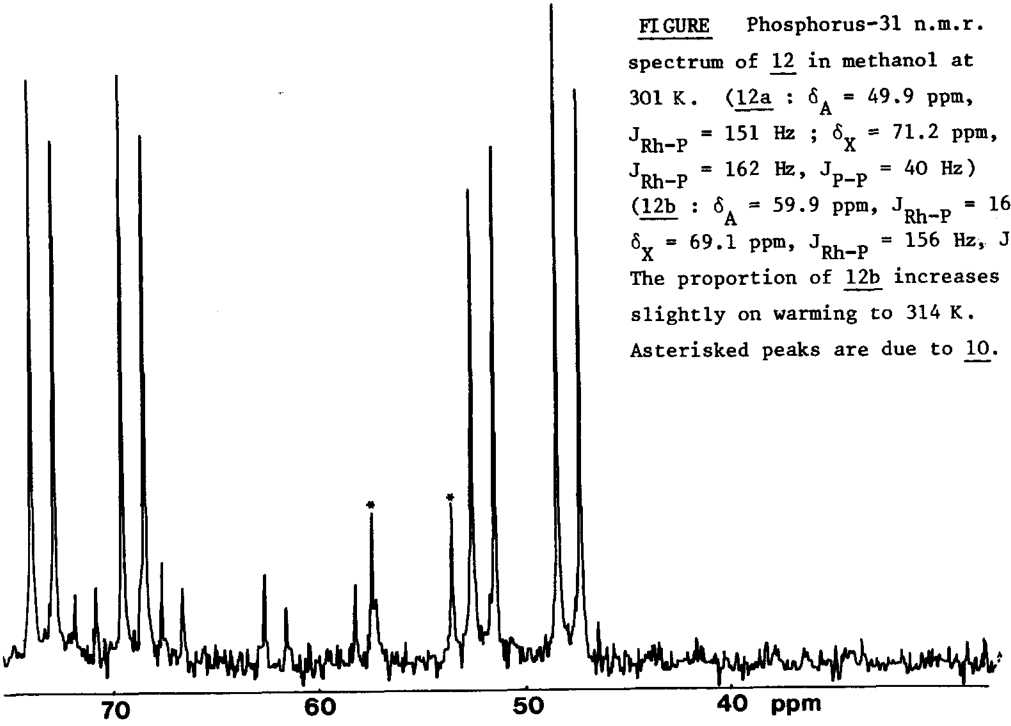
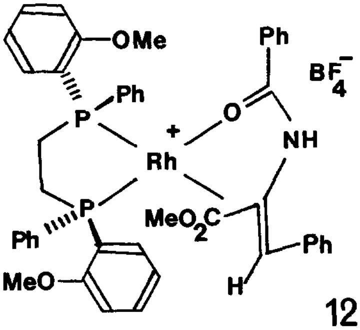
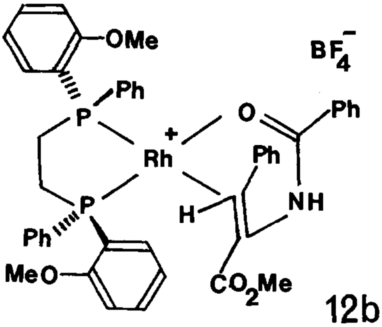


FIGURE Phosphorus-31 n.m.r. spectrum of 12 in methanol at 301 K. (12a : δ_A = 49.9 ppm, J_{Rh-P} = 151 Hz ; δ_X = 71.2 ppm, J_{Rh-P} = 162 Hz, J_{P-P} = 40 Hz) (12b : δ_A = 59.9 ppm, J_{Rh-P} = 160 Hz ; δ_X = 69.1 ppm, J_{Rh-P} = 156 Hz, J_{P-P}= 36 Hz The proportion of 12b increases slightly on warming to 314 K. Asterisked peaks are due to 10.


12a


12b

Enamide complexes of DIPAMP are different from those of DIOP in two ways. Firstly the Z-acid and ester complex of 4 show no exchange broadening in their phosphorus n.m.r. spectrum at 301 K, whilst in the DIOP series the spectra are only sharp below 275 K at which temperature one diastereomer is observed. Secondly the E- acid 3 (but not its methyl ester) binds strongly to rhodium DIOP without isomerisation , but binds weakly to rhodium DIPAMP and isomerises rapidly.

The simplicity and informative nature of these experiments suggests their application to catalyst design since diastereospecificity in binding may be studied by n.m.r. without the necessity for resolution of the chiral phosphine.

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