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R - PHENYL BIS DIPHENYLPHOSPHINOETHANE; STRUCTURAL STUDIES PERTAINING TO RHODIUM - CATALYSED ASYMMETRIC HYDROGENATION

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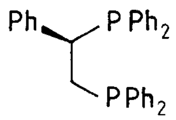
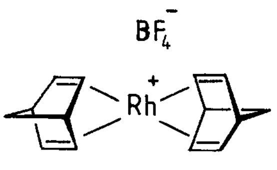
Summary: Intermediates in asymmetric hydrogenation by the title phosphine are defined by NMR techniques.

The mechanism of homogeneous hydrogenation by Wilkinson's catalyst, $(PPh_3)_3RhCl$, is now established and with simple olefins hydrogen addition to rhodium precedes olefin co-ordination[1] although the reverse is true for acrylonitrile and other electrophilic olefins.[2] Cationic rhodium complexes derived from monophosphines normally form stable dihydrides on hydrogenation in protic solvents,[3] but cis-chelating diphosphine-derived complexes give rise to solvent adducts with no affinity for hydrogen under normal conditions.[4] We present experiments which provide insight into the structure of these adducts and on selectivity in substrate complexation.



1a
(1b, CD_2 analogue)



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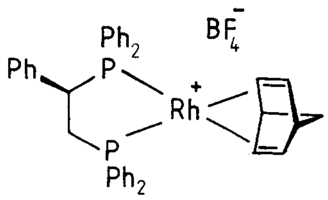

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R - Phenylbisdiphenylphosphinoethane (1a) which has recently been synthesised independently[5] was prepared from S-mandelic acid via the dimesylate of S-phenylethanediol in 53% overall yield. (Lit[5] 20%). It differs from the majority of chiral biphosphines in having inequivalent phosphorus atoms, giving considerable additional structural information by NMR. Mixing (1a) with bis(norbornadiene)rhodium tetrafluoroborate (2)[6] gives the mixed complex (3a)(δ_{P1} = 70.6, δ_{P2} = 43.9 p.p.m.; J_{P_1Rh} = 158, J_{P_2Rh} = 154, J_{PP} = 37 Hz) Hydrogenation of this solution (0.04M, 1 ml, 5 min.) gives rise to the 24-line NMR spectrum of Figure 1a. The major species is a monomeric solvent adduct of the conventional type (4) and the two minor species are stereoisomeric dimers (5) and (6). Thus (4) predominates in dilute solution (0.02M) but is the minor component at higher concentration (0.08M). Furthermore, hydrogenation of the complex(3b) prepared from racemic(1) gives two new species

(7) and (8) at the same concentration as (5) and (6), the total concentration of dimers[7] being unchanged (Figure 1b). This is precisely the result which would be expected on simple symmetry considerations, since there are two possible optically active dimers and two racemic (meso) dimers, each giving rise to an eight line spectrum. The bridging unit is most probably two or three solvent molecules[8] and not an arene, the high values of J_{PRh} (197 - 210 Hz) being inconsistent with the latter.[9] In 2-methoxyethanol the analogue of monomer (4) is strongly favoured over dimers.

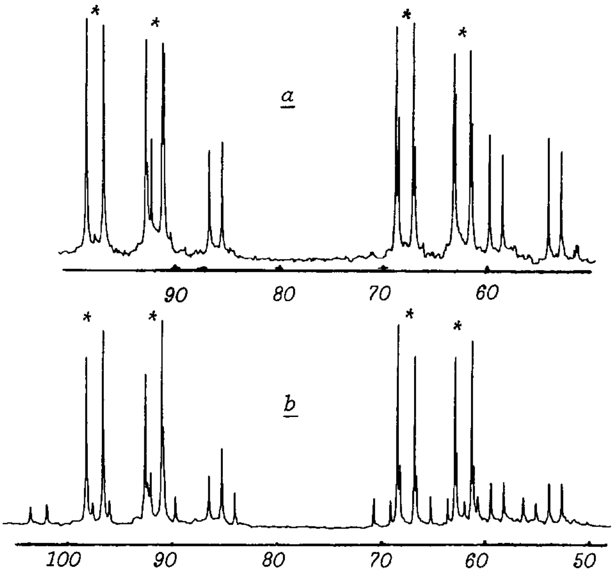
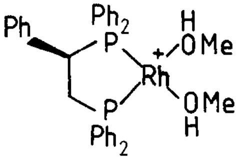


FIGURE 1. Methanol complexes derived from 1a. *Starred resonances are due to* 4.



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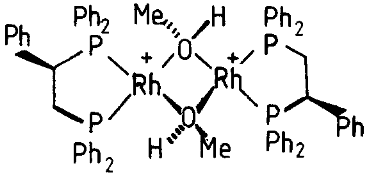

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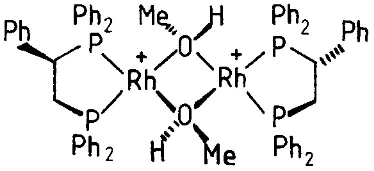

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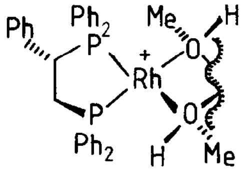


7, *RH chelate as* 5

8, *RH chelate as* 6

Complex (3a) is an effective catalyst for hydrogenation of a range of dehydroamino acids (optical yields typically 85%) and our results are in accord with those previously reported.[5] Since the ligand lacks C_2 symmetry there are four possible rhodium enamide complexes.[10] With (9a), two of these are formed (Figure 2) and it proved possible to demonstrate that these are regioisomers rather than stereoisomers by two further experiments. Dideuterated phosphine (1b) showed little broadening (<3Hz) of its ^{31}P NMR resonances. The corresponding norbornadiene rhodium complex (3b) shows selective broadening of about 8 Hz in its low-field resonance, reflecting a substantial vicinal coupling to the equatorial β-deuterium, as in (10).[11] It has been shown elsewhere[10] that complexation of the carbon-13 enriched enamide (9b) causes an 8 Hz splitting in the cis-phosphine resonance. In the present case, coupling to the two phosphorus nuclei at 74.5 and 41.8 p.p.m. is observed on complexation of (9b). Taken together these experiments demonstrate that the two enamide complexes are regioisomers, presumed to be (11a) and (11b) to accord with the optical course of hydrogenation. The fact that racemic (1a) gives identical enamide complexes to the optically pure phosphine proves the 1:1 stoichiometry.

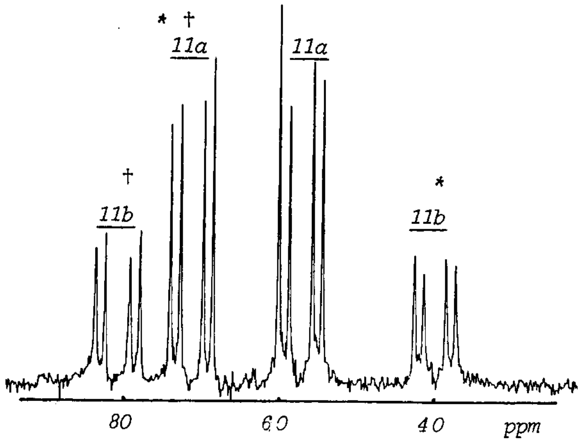
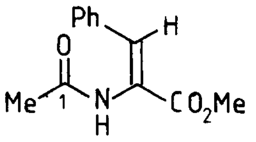


FIGURE 2. ^{31}P *NMR spectrum of* 11.

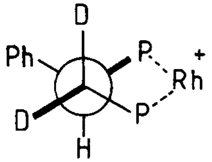
* ^{13}C *coupled in* 9b*-derived complex.*

† *Broadened in* 1b*-derived complex.*



9a

(9b, $^{13}C1$ *enriched benzamide*



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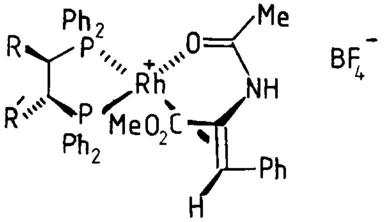

11 *a) R = Ph, R' = H*

b) R = H, R' = Ph

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5) R.B. King, J. Bakos, C.D. Hoff and L. Markó, J. Org. Chem. 1979, 44, 1729. These authors report optical yields of 76-88% in the hydrogenation of four Z-dehydrophenylalanine derivatives. In addition we find similar optical yields with Z-dehydroalanine derivatives.

6) M. Green, T.A. Kuc and S.H. Taylor, J. Chem. Soc, A 1971, 2334.

7) The low solubility of the *bis*-diphenylphosphinoethane analogue of (4) may mean that dimeric species are disfavoured in solution and were therefore not observed in earlier work.[4] On addition of NEt_3, both racemic and R(1a) derived solvent adducts give rise to an identical 32 line NMR spectrum (stereospecific formation of chiral dimers or trimers?) and the structure of this product is under investigation.

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9) For example, J_{PRh} = 153, 156 Hz in the η^6-(phenyl)triphenyl borate rhodium complex derived from (1a); B.A. Murrer, unpublished work; c.f. Y Chauvin, D. Commereuc and R. Stern, J. Organometal Chem, 1978, 146, 311.

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