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CYCLODIOP, AN EXAMPLE OF A NEW CLASS OF CHIRAL DIPHOSPHINES

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Cyclodiop, a chiral diphosphine with an intact P-P bond was prepared and used as a ligand in rhodium complexes. Asymmetric reduction of some prochiral olefins was observed. The nature of the rhodium complexes is discussed in the light of their ^{31}P nmr spectra.

The spectacular progress of homogeneous asymmetric catalysis with transition complexes has been mainly the result of the synthesis of various types of new chiral ligands (1-4). Chiral phosphines and especially chelating diphosphines are particularly useful for asymmetric hydrogenation and enantiomeric excesses close to 100 % can be achieved (1-5).

The various chiral diphosphines which are now routinely used (some of them are commercially available) contain two phosphorus atoms connected by a C_2 to C_4 chain. We were intrigued to see the behaviour of derivatives of diphosphines itself, where there would be a P-P unit. In addition, since the coordination chemistry of this type of ligands is almost unknown (6) it was interesting to investigate the nature and properties of the rhodium complexes.

We wish to report our first results on the synthesis of diphosphine 3 which was named cyclodiop by analogy with diop 4.

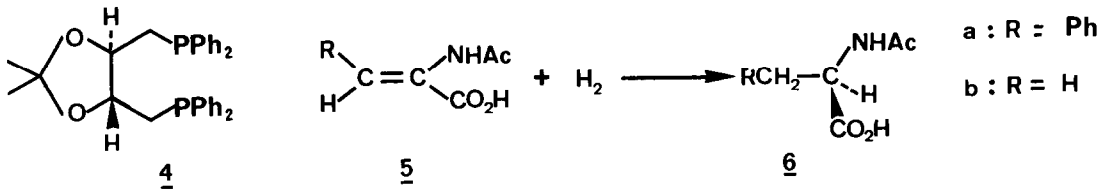
The ditosylate 1, easily prepared (7) from (+)-tartaric acid, was the starting point of the synthesis. The first attempts to obtain 3 by treating 1 with Cl_2PPh and lithium (8) led to irreproductible results. A very reliable method of preparation of 3 was latter found as follows. Cl_2PPh was transformed by magnesium into crystalline pentaphenylcyclopentaphosphine $(PPh)_5$ according to (9) with 85 % yield. The 1,2-dilithiodiphenylphosphine 2 is prepared by the method of Issleib (10), by cleavage of $(PPh)_5$ with lithium in THF under nitrogen. The red solution of 2 is immediately used for the preparation of 3. In a typical experiment, to 4 g (8.5 mmoles) of 1 dissolved in 35 ml THF was slowly added a 35 ml THF solution of 2 (8.5 mmoles). After stirring 17 h at 35°C under nitrogen the solvent was evaporated under vacuum. The residue was dissolved in 150 ml benzene, washed with deoxygenated water, and dried on magnesium sulfate. After evaporation of benzene, a mixture of two diastereomers of 3 was obtained (with an 8/1 ratio as established by ^{31}P nmr) mixed with a few percent of $(PPh)_5$. After crystallisation in ethanol (under nitrogen) the major diastereomer of 3 was obtained stereochemically pure (yield 57 %).

mp = 114-116°C (sealed capillary) ; $(\alpha)_D$ = - 643° (c = 0.2, benzene). Mass spectrum $M^{\cdot+}$ = 344

Analysis : $C_{19}H_{22}O_2P_2$ C% = 66.26 H% = 6.44 ; found C% = 66.20 H% 6.50 .

^{31}P nmr : δ = - 36.5 ppm (singlet) , 85 % H_3PO_4 external standard.

^1H nmr : δ = 1.28 ppm (singlet, 2 CH_3) ; δ = 2.72 (multiplet, 2 $-CH_2-$) ;
δ = 3.53 (multiplet, 2 -CH-) ; δ = 7.3 and 7.6 (aromatic protons).



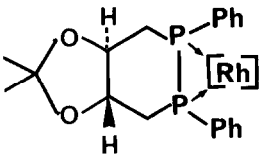
Because of the presence of a singlet in the ^{31}P nmr of 3 it is very likely that the two phenyl rings are in a trans configuration to each other. This relative stereochemistry gives a C_2 symmetry to the molecule. It cannot be easily deduced from nmr data whether the groups on the phosphorus atoms are diequatorial or diaxial.

The ligand was used for the preparation of an *in situ* catalyst $[RhCl(C_2H_4)_2$, (-)-3$]$ by mixing it with 0.5 equivalent of $[RhCl(C_2H_4)_2]_2$ in benzene, according to a classical procedure (7). An isolated cationic complex formulated as $[RhCOD$, (-)-3$]^+ PF_6^-$ was prepared in dichloromethane from $[RhClCOD]_2$ and PF_6NH_4 as described for other ligands (11).

The *in situ* catalyst catalyzes reduction of (Z)-PhCH=C(NHAc)CO_2H 5a into (R)-N-acetylphenylalanine 6a with 71 % e.e. The reaction was performed in a benzene-ethanol medium (1/1) under 10 bars with a catalyst/substrate ratio of 1/100 (yield 79 % after 48 h). Under similar conditions (R)-N-acetylalanine 6b was obtained with 17 % e.e. Under 20 bars of hydrogen we checked that the *in situ* rhodium complex based on 3 is able to catalyze the homogeneous reduction of a wide range of olefins (cyclohexene, 1-methyl cyclohexene, 1-octene).

Ketones remain unchanged, but the Schiff base PhCH=NPh is reduced, which is unusual for most rhodium catalysts. Curiously, the complex $[RhCOD$, (-)-3$]^+ PF_6^-$ gave aminoacids of racemic composition by hydrogenation under the same conditions used with the *in situ* catalyst. We did some nmr experiments in order to have a model to try to understand the nature of the unprecedented rhodium complexes of diphosphines containing a P-P bond.

^{31}P nmr of the *in situ* complex (in $CDCl_3$) obtained from $[RhClCOD]_2$ and 3 (ratio 0.5/1) shows one doublet at 0.06 ppm (J = 288 Hz) and two doublets at - 1.9 ppm (J = 188 Hz and J = 144 Hz). The spectrum is in favour of a monodentate structure 8 and has some similarities to those of independently prepared cyclodiop monosulfide 9 (see figure). After hydrogen admission there is only a broad signal at 57 ppm, indicating that both the phosphorus atoms are now bound to rhodium, either as in chelate 7, or intermolecularly. ^{31}P nmr of $[RhCOD$, (-)-3$]^+ PF_6^-$ shows a spectra similar to that of the *in situ* catalyst with an additional four lines signal between 35.5 and 46.2 ppm. This signal could be assigned to chemically equivalent phosphorus atoms coordinated to rhodium as in partial formula 10. The cationic complex appears to be a mixture of the two complexes, one having cyclodiop as a monodentate ligand.



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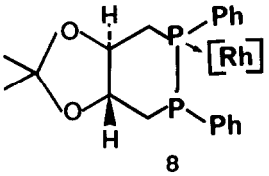

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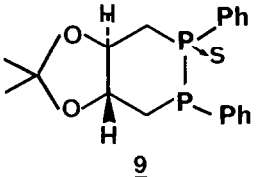

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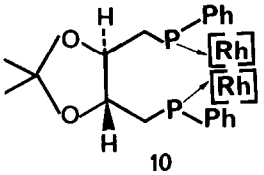

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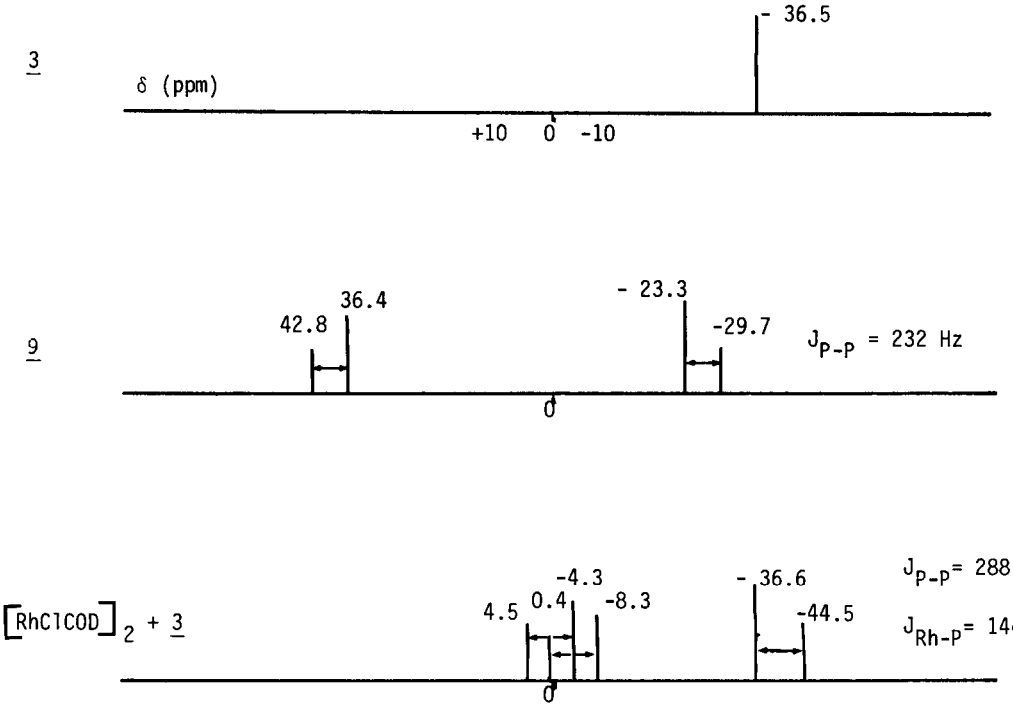

^{31}P nmr spectra of cyclodiop 3, cyclodiop monosulfide 7, and the in situ rhodium complex based on 3 (in $CDCl_3$, with H_3PO_4 85 % as external standard).

Proton decoupling for cationic or in situ rhodium complexes of 3 under hydrogen shows an absence of P-H coupling, which establishes that the P-P bond is not cleaved into PH moieties. Nmr experiments are in progress in order to define better the properties of cyclodiop in various rhodium complexes. Many chiral diphosphines with two asymmetric phosphorus atoms could be prepared by the method used for synthesis of cyclodiop, by simply treating chiral ditosylates by 2 and separating the diastereomers. We are currently checking this route as well as the properties of the chiral ligands thus obtained.

Acknowledgments

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