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Preliminary Communication

A Chiral Phosphine (CRC-PHOS) Derived from (+)-Champhanic Acid. A New Ligand for Homogeneous Asymmetric Hydrogenation

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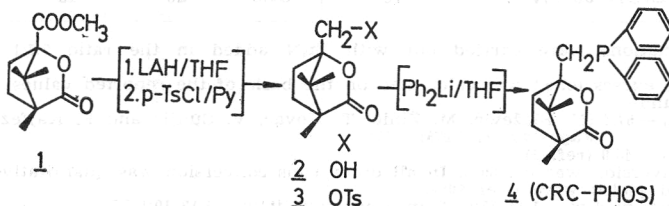
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The lactone of 1S,3S-1-hydroxy-1-diphenylphosphinomethyl-2,2,3-tri-methyl-cyclopentan-3-carboxylic acid (**4**, CRC-PHOS) was prepared from (+)-camphanic acid methylester **1**, and its complex salt $[\text{Rh}(\text{CRC-PHOS})_2\text{NBD}] \cdot \text{ClO}_4 \cdot \text{THF}$ (**5**) was isolated. The latter exhibited rather a high rate, but low enantioselectivity in the first attempt at asymmetric hydrogenation.

Recently, Bosnich rationalized¹ the existing knowledge in the field of »tailoring« of chiral phosphine ligands in transition metal complexes as homogeneous catalysts for asymmetric hydrogenation. Among specific features required of chiral *monophosphines* to achieve high enantioselectivity, the presence of an additional coordination site, usually an oxygen atom, is the most important^{2,3}. The »lock and key« relation between catalytic complex and substrate still deserves general full attention in this field, however. Thus we have directed our attention to the preparation of a new chiral phosphine coded CRC-PHOS, and its catalytic activity and conformation in solution⁴.

Camphanic acid methyl ester⁵ was reduced with complete site-selectivity to the alcohol **2** (88,9%, m.p. 179—180 °C, $[\alpha]_D + 1.85^\circ$ ($c = 1.90$ in CHCl_3)), the lactonic group remaining unaffected. Tosylation in pyridine afforded **3** (93%, m.p. 116—117 °C, $[\alpha]_D + 16,3$ ($c = 2.12$ in CHCl_3)), which was reacted with diphenylphosphine lithium in THF at -10°C to afford **4** (53,4%, colourless oil after chromatography on silica with *n*-hexane/acetone (7 : 3) as eluant, $[\alpha]_D - 11.2^\circ$ ($c = 1.93$ in CHCl_3)).⁷

A cationic complex $[\text{Rh}(\text{CRC-PHOS})_2\text{NBD}] \cdot \text{ClO}_4$ (**5**, NBD-norbornadiene) was prepared by the reaction of **4** with $[(\text{NBD})_2\text{Rh}] \cdot \text{ClO}_4$ in THF for 1 h at room temperature. It precipitated from THF on slow addition of *n*-hexane as a fine orange-red powder which contained one mole of THF and exhibited amorphous structure, as ascertained by X-ray diffraction⁸.



REFERENCES AND NOTES

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4. LIS-NMR measurements and computer assisted data evaluation were performed for CRC-PHOS and some related model compounds in order to determine conformation of the lanthanide complexes in solution — manuscript in preparation.
5. Prepared from (+)-camphanic acid, lit.⁶ mp. 108—109 °C. $[\alpha]_D^{25}$ -22.8 °C. (c = 3.25 in CHCl₃). (+)-Camphanic acid (now available commercially from Fluka) is a well established chiral resolving agent, see e.g. H. Gerlach and W. Müller, *Helv. Chim. Acta* **55** (1972) 2277; V. Šunjić, F. Kajfež, D. Kolbah, and N. Blažević, *Croat. Chem. Acta* **43** (1971) 205; A. Konoval, Y. Yurczak, and A. Zamojski, *Tetrahedron* **32** (1976) 2957.
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10. It is interesting to note that complex 5 exhibited high diastereoselectivity in hydrogenation of metacycline-hydrochloride into 6- α -methyl-6-deoxy-tetracycline. At 14 atm and 100 °C the 6-epimer was quantitatively formed after 4 h., diastereomeric purity being over 95%.
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12. The S-configuration has been recently determined by chemical and spectroscopic correlation, for (+)- α -(3-benzoyl)-phenyl propionic acid, which was obtained in 66% e.e. by asymmetric hydrogenation of 6 with (—)-DIOP.¹³
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SAŽETAK

Kiralni fosfin (CRC-PHOS) izveden od (+)-kamfan-kiseline. Novi ligand za homogenu asimetričnu hidrogenaciju

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Lakton 1S,3S-1-hidroksi-1-difenilfosfometil-2,2,3-trimetil-ciklopentan-3-karbo-ksilne kiseline (4, CRC-PHOS), pripremljen je pošavši od metilnog estera (+)-kamfan-kiseline, i izolirana je njegova kompleksna sol [Rh(CRC-PHOS)₂NBD] · ClO₄ · THF (5). Taj je katalitički kompleks pokazao visoku reaktivnost, ali nisku enantio-selektivnost u prvim pokušajima asimetričnih hidrogenacija.

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