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Synthesis of a Phosphine-Modified Cyclodextrin and its Rhodium Complex

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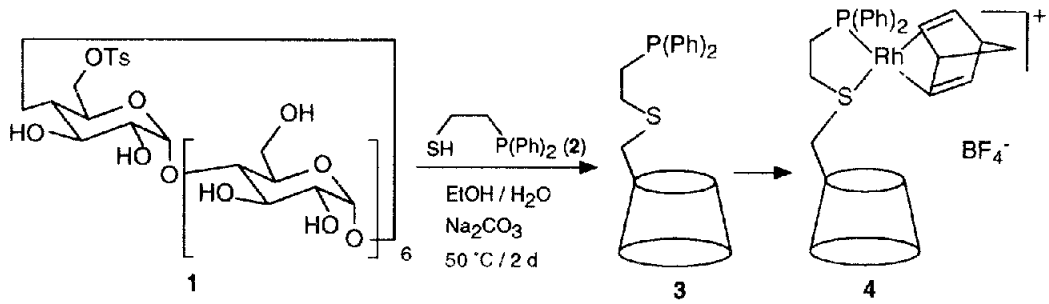
Abstract: A bidentate ligand consisting of a 2-(diphenylphosphinoethyl)-thio moiety was attached to β-cyclodextrin at the 6-position. The corresponding norbornadiene Rh(I) complex in the form of the BF_4^- salt was prepared.

Molecular recognition involving synthetic receptors and organic guests is based on reversible non-covalent interactions such as hydrogen bonding and π-π-interactions[1]. We are interested in expanding the types of reversible interactions to include metal centers with vacant coordination sites which can coordinate to donor positions in guest molecules in such a way as to make synergistic effects via multiple point binding possible, as in boron-containing crown ethers[2]. In order to combine molecular recognition with catalysis, we are now studying receptor molecules which contain transition metals[3]. Phosphine-modified cyclodextrins appeared to be an attractive starting point for the realization of such a strategy. The recent communication by Ito[4] describing a phosphine-substituted ferrocene moiety attached to a β-cyclodextrin derivative prompts us to report our own initial efforts in this interesting new area[3,4].

Purified 6-mono-6-p-toluenesulfonyl-β-CD (**1**)[5,6] was reacted with the thiol (**2**) in the presence of Na_2CO_3 to afford 66% of the desired bidentate ligand **3**[7] which was fully characterized: melting point 302 - 310°C (decomposition); elemental analysis C 49.32 (calc. 49.33), H 6.16 (calc. 6.14), P 2.39 (calc. 2.35), S 2.28 (calc. 2.27); $[\alpha]_D^{22} = +12.0 \pm 0.2$ (c = 2.5, DMF); FAB-MS (diethanolamine as matrix), $[M+H]^+$ = 1363; M = 1362; ^{31}P-NMR (161.3 MHz, d_7-DMF): δ/ppm = -17.2 (rel. to H_3PO_4 ext.); ^{13}C-NMR (100.6 MHz, d_5-pyridine): δ/ppm (δ_C rel. TMS, measured relative to β-C of d_5-pyridine, δ_C = 123.6) = 28.9 (d, $J_{P,C}$ = 15.3 Hz, $\underline{C}H_2$-P), 30.1 (d, $J_{P,C}$ = 20.9 Hz, $\underline{C}H_2$-S), 34.0 (C-6'), 61.4 - 61.6 (C-6), 73.0 (C-5'), 73.7 - 74.6 (C-2, 3, 5), 83.1 - 83.4 (C-4), 85.9 (C-4'), 103.5 - 103.8 (C-1), 128.7, 133.0, 138.8 (m, dd, d, arom.); ^{1}H-NMR (400.13 MHz, d_5-pyridine): δ/ppm (δ_H rel. TMS, measured relative to β-H of solvent, δ_H = 7.38) = 2.76 (m, 2H, $C\underline{H}_2$-P), 3.19 (m, 2H, $C\underline{H}_2$-S), 3.55 (dd, 1H, *J* = 14 Hz, 6 Hz, H-6a'), 3.80 (d, 1H, *J* = 13 Hz, H-6b'), 4.29 - 4.36 (m, 7H, H-2), 4.29 - 4.41 (m, 7H, H-4), 4.54 - 4.68 (m, ~16H, H-5,6, D_2O), 4.80 - 4.91 (m, 7H, H-3), 5.72 - 5.94 (m, 7H, H-1), 7.44 - 7.52, 7.71 - 7.75 (m, m, 10H, arom. H).

As a solid the compound is fairly stable to air oxidation. In solution air oxidation is faster, yielding the corresponding phosphine oxide (^{31}P-NMR: δ = +31.0 ppm; FAB-MS: $[M+H]^+$ = 1379; M = 1378). Compounds of the type $(Ph)_2PCH_2CH_2SPh$ have been used previously as bidentate ligands for catalytically active metals such as rhodium and iridium[8]. We therefore synthesized the rhodium complex **4**[9].



NMR spectroscopic and mass spectrometric investigations support the proposed structure of **4**. FAB-MS (diethanolamine as matrix), $[M]^+$ = 1558 (representing the cationic part of the compound); ^{31}P-NMR (161.3 MHz, d_7-DMF): δ/ppm = 53.7 (d, $J_{Rh,P}$ = 153 Hz) (rel. to H_3PO_4 ext.); ^{1}H-NMR (400.13 MHz, d_7-DMF): δ/ppm (δ_H rel. TMS, measured relative to solvent signal at δ_H = 2.74): 1.25 (s, 2H, nbd-C<u>H</u>$_2$), 3.08 - 4.29 (m, ~54H, H-2-6, SC<u>H</u>$_2$C<u>H</u>$_2$P, nbd-C<u>H</u>), 4.60 - 4.77 (m, 6H, 6-O<u>H</u>), 5.01 - 5.18 (m, 7H, H-1), 5.88 - 6.10 (m, 14H, 2-O<u>H</u>, 3-O<u>H</u>), 7.30 - 7.76 (m, 10H, arom. H). Of particular interest in the characterization of **4** is its ^{31}P-NMR spectrum which is typical for Rh complexes involving bidentate sulfur/phosphorus ligands of the type $RSCH_2CH_2P(Ph)_2$[8]. Efforts are under way to study catalytic properties of **4** and to prepare other transition metal complexes of bidentate ligands of the type **3**.

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This work was supported by the Deutsche Forschungsgemeinschaft (Leibniz Program). We are also grateful to the chromatography, mass spectrometry and NMR departments of the Max-Planck-Institut für Kohlenforschung for help in the purification and characterization of cyclodextrin derivatives.

References and Notes

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6. Purification of **1** could only be attained by HPLC. We thank A. Deege for carrying this out.
7. Preparation of **3**: 2.0 g (1.55 mmol) of **1** was added to a solution of 100 ml water, 25 ml ethanol, Na_2CO_3 (to give a pH of 12). 2.0 g of **2** (8.1 mmol, excess) was given to this solution, and the mixture was stirred for 2 d at 50°C. Cooling, neutralisation with diluted HCl and perforation with ether (3 d) led to an aqueous solution of the product with only inorganic impurities which are finally removed by recrystallisation from water. Drying *in vacuo* yielded 1.4 g (66%) of HPLC-pure **3** (Rudolph, J. Diplomarbeit, Universität Bonn, May 1993).
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9. Preparation of **4**: 290 mg (0.21 mmol) of **3** was added to a hot solution of 30 ml H_2O/EtOH (1:1). This mixture was dropped into a solution of 49 mg (0.11 mmol) $[Rh(nbd)Cl]_2$ and 84 mg (0.25 mmol) Bu_4NBF_4 in 40 ml H_2O/EtOH (1:1). After stirring for 3 h the solvent was vaporized *in vacuo*. Bu_4N^+-salts and other impurities were removed by several washings of the crude product with THF. Yield of **4** after drying *in vacuo*: 293 mg (84%). (All preparations were done under an inert atmosphere with degassed solvents).