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Preparation and X-ray Structure of a Rhodium(III)-(S)- 6,6'-dimethyl-2,2'-diamino-biphenyl Complex

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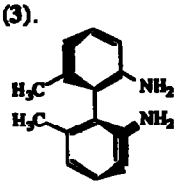
Abstract: trans-Dichlorobis[(S)-6,6'-dimethyl-2,2'-diaminobiphenyl]rhodium(III) chloride was prepared, and its structure was determined by X-ray diffraction.

Chiral chelating bidentate nitrogen ligands have found wide-spread application in asymmetric homogeneous catalysis by transition metal complexes .[1] We are currently investigating the reaction of asymmetric hydrogen transfer to ketones from 2-propanol under mild conditions using complexes of rhodium containing chiral diaminobiphenyl derivatives (e.g. 1) as ligands. These complexes were found to be efficient catalysts at low temperatures in the hydrogen transfer reaction to various ketones using 2-propanol as the hydrogen donor. We propose that in the catalytic cycle the first catalytic precursor is 2 (DH_2= 2-propanol), which in 2-propanol will convert to [bis(S)-6,6'-dimethyl-2,2'-diamino-biphenylrhodium(III)L_2]$^{+3}$ $3Cl^-$ (L = 2-propanol). In this paper we report the preparation and crystal structure of trans-dichlorobis[(S)-6,6'-dimethyl-2,2'-diamino- biphenyl]-rhodium(III) chloride (3).



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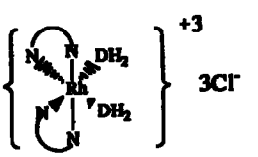

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A suspension of 0.5-0.75 mmol of (S)-6,6'-dimethyl-2,2'-diaminobiphenyl,[2] and 0.25 mmol of $RhCl_3.3H_2O$ in ethanol under N_2 or Ar was heated to 80°C for 3 h. During this period a yellow solid separated out. The yellow solid was filtered off and washed with ethanol (70% yield). The solubility of the complex in common solvents such as ethanol, methanol, acetone, acetonitrile, chloroform and methylene chloride was very low. Dimethylformamide and dimethylsulfoxide were the only solvents that dissolved appreciable amounts of the material. The complex was not stable in the solid state and did not gave a satisfactory microanalysis. Recrystallysation from ethanol or 2-propanol gave yellow needles, which broke when separated from the solvent. ^{1}H-NMR of the vacuum-dried complex in DMSO-d_6 indicated the presence of a molecule of solvent in addition of the proton signals of the diamino ligand.[3] The specific rotation of the complex 3 in DMSO was found to be high ($[\alpha]^{20}_D$ -1162±3), in keeping with the high optical rotation found in similar complexes.[5]

Recrystallisation of the complex 3 (which was separated from ethanol as the reaction solvent) from acetonitrile gave a cubic orange crystals which were more stable than those crystallised from ethanol. Single crystal X-ray diffraction showed complex 3 to be trans-dichlorobis[(S)-6,6'-dimethyl-2,2'-diaminobiphenyl] rhodium(III) chloride.CH_3CN (Fig. 1).[4] The structure shows two ligands of (S)-2,2'-diamino-6,6-dimethyl-biphenyl co-ordinated to the Rh(III) with the four nitrogens forming a square-planar geometry around the metal.

Two trans chlorine atoms form an octahedral geometry around the Rh(III) center. The angles between the planes of the two phenyl groups in the ligands are 66.17° and 65.03°. The complex is ionic and crystallises with one molecule of solvent (CH_3CN), with the methyl group pointed towards the complex. As expected from the chiral ligands, the complex crystallises in the space group $P2_12_12_1$.

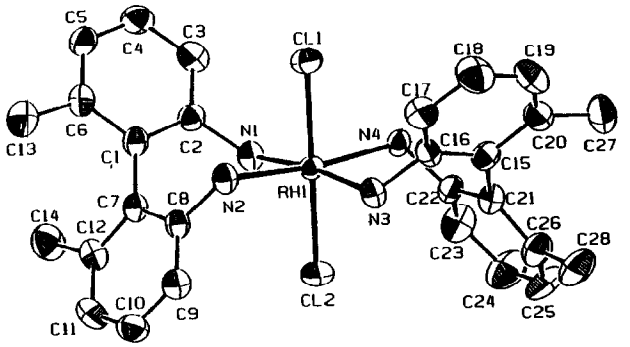

Figure1. ORTEP diagram of the cation of trans-dichlorobis[(S)-6,6'-dimethyl-2,2'-diaminobiphenyl]-rhodium(III) .CH_3CN. Selected interatomic distances and angles are as follows : Rh-N(1) 2.112(4), Rh-N(2) 2.102(4), Rh-N(3) 2.087(4), Rh-N(4) 2.091(4), Rh-Cl(1) 2.336(1), Rh-Cl(2) 2.332(1), Cl(1)-Rh-Cl(2) 179.49(6), Cl(1)-Rh-N(1) 94.1(1), Cl(1)-Rh-N(2) 86.2(1), Cl(1)-Rh-N(3) 93.8(1), Cl(1)-Rh-N(4) 86.4(1), N(1)-Rh-N(2) 87.3(2), N(1)-Rh-N(3) 172.1(2), N(1)-Rh-N(4) 93.2(2), N(3)-Rh-N(4) 88.0(2).

References.

1. a) G. Mestroni, A. Camus and G. Zassinovich in R. Ugo (Ed.), *Aspects of Homogeneous Catalysis;* Vol. 4, D. Reidel Publishing Co., Dordrecht, 1981, p.71; b) C. Botteghi, A. Schionato, G. Chelucci, H. Brunner, A. Kürzinger and U. Obermann, *J.Organometal. Chem.*,**1989**, 370, 17 and references therein; c) H. Brunner and U. Obermann, *Chem. Ber.*, **1989**,122,499 ; d) G. Zassinovich, G. Mestroni, *Chem. Rev.* **1992**, 92, 1051.
2. Prepared from 2,2'-dinitro-6,6-dimethylbiphenyl by reduction in the presence of Pd/C and 50 psi of H2 and then chiral separation with *l*-tartaric acid. T.L. Marxen, B.J. Johnson, P.V. Nilsson, L.H. Pignolet, *Inorg. Chem.*, **1984**, 23, 4663.
3. Spectral data and elemental analyses of the complex **3** : ^{1}H NMR : (DMSO-d_6, ppm); 7.471(bd, NH2), 6.720 (m,4H), 6.581 (m, 2H), 5.048 (bd, $N\underline{H}_2$), 2.046 (bs,6H);13C NMR : (DMSO-d6, ppm); 142.63, 137.56, 136.24,125.35(b), 125.16, 119.8, 17.48; IR(cm^{-1}): 3490, 3253, 3080, 1582, 1458, 1119, 786, 734, 475, 456.
   Analysis of **3.isopropanol**; Calcd. for $C_{31}H_{40}Cl_3N_4ORh$: C, 53.68; H, 5.77; Cl, 15.29. Found: C, 53.26; H, 5.50; Cl, 15.80.
4. Crystal data: **3**,{$(C_{14}H_{16}N_2)_2RhCl_2]^+Cl^-.CH_3CN$, space group $P2_12_12_1$, a=14.403(3),b= 15.944(4), c= 13.704(3) Å, V= 3147(1) $Å^3$, Z= 4, Dc= 1.42 g cm^{-3}, m (MoKa)= 8.17 cm^{-1}, no. of unique reflections = 3114, no. of reflections with I≥2s(I)= 2797 (Philips PW 1100/20 diffractometer) R = 0.032, Rw = 0.037. The R,R-isomer gives : R = 0.034, Rw = 0.040. The position of the hydrogen of the amino groups was found in the difference Fourier map.
5. T. Hayashi, A. Yamamoto, M. Hojo, K. Kishi, Y. Ito, E. Nishioka, H. Miura, K. Yanagi, *J. Organomet. Chem.*, **1989**, 370, 129.