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A Chiral Aminophosphine Ligand: Improved Synthesis, and Coordination Properties

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Chiral ligands attract considerable attention [1], commensurate to their role in asymmetric catalysis promoted by complexes of transition metals. In a preliminary study from our laboratory [2] we obtained the synthesis of the new ligand (S)2-diphenylphosphino-N-methyl,N(1-phenyl-ethyl)-ethanamine (dmpe), by reaction of (S)-2-bromo-N-methyl,N(1-phenyl-ethyl)ethanamine with $(C_6H_5)_2PLi$.

The recent report [3] of a synthesis of dmpe from diphenylvinylphosphine prompted us to describe our findings on the preparation, and on the ligand properties of dmpe. We found that the reaction* between (S)-2-chloro-N-methyl,N(1-phenyl-ethyl)-ethanamine hydrochloride and diphenylphosphine in presence of potassium tert-butoxide (Scheme 1) is a more convenient method for the preparation of dmpe than both our first approach and the procedure by Märkl and Merkl [3].

The ^1H NMR spectrum of the crude dmpe, which is obtained in good yield from an easily available phosphine, does not show a significant amount of impurities.

The coordination properties of dmpe toward d^8 ions have been also explored. Pt(II) and Pd(II) complexes of the type $(dmpe)MCl_2$ were obtained and characterized. A rhodium complex, most probably $Rh(dmpe)_2Cl$, was also prepared.

Noticeably, the ^1H NMR spectra show that in the case of the platinum complex, the same diastereoisomer is always obtained, *i.e.* the prochiral nitrogen has only one configuration, no matter which solvent is used for its recrystallization. In addition, the ^1H NMR spectra and optical activity of the dissolved complex did not change even after several hours. The Pd complex similarly cyrstallizes as a single diastereoisomer, but the coordinated nitrogen epimerizes, till a 3:1 ratio between the starting isomer and the epimerization product is reached. According to the optical activity measurements the epimerization half-life is about 30 minutes.

These data point to a relevant effect of asymmetric induction on the coordination of the prochiral nitrogen atom.

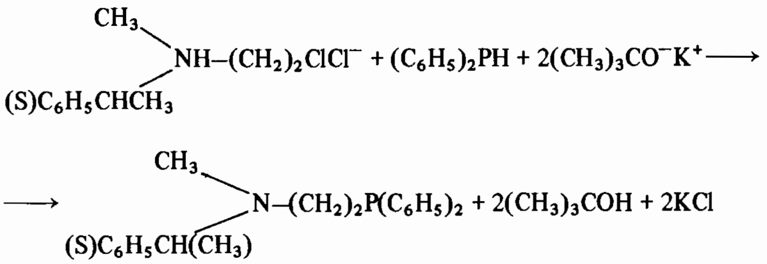
We are at present investigating on the catalytic properties of dmpe complexes of d^8 ions.

Experimental

All manipulations were carried out under nitrogen or argon. ^1H NMR spectra were obtained on a Varian T-60A and a Bruker WH270 spectrometer using TMS as internal standard. Solvents were dried with usual methods and stored in argon after distillation.

Preparation of dmpe

A solution of 10.7 g (95.5 mmol) of potassium terbutilate in 300 ml of dry THF, to which diphenylphosphine (10.7 ml, 61.5 mmol) was added, was stirred for about 5 min. To the deep red solution 14.4 g of (S)-2-chloro N-methyl,N(1-phenyl-ethyl)-ethanamine hydrochloride** (61.5 mmol) was added



$$\begin{matrix}CH_3 \\ (S)C_6H_5CHCH_3\end{matrix}\!\!>\!NH\text{–}(CH_2)_2Cl\,Cl^- + (C_6H_5)_2PH + 2(CH_3)_3CO^-K^+ \longrightarrow$$

$$\longrightarrow \begin{matrix}CH_3 \\ (S)C_6H_5CH(CH_3)\end{matrix}\!\!>\!N\text{–}(CH_2)_2P(C_6H_5)_2 + 2(CH_3)_3COH + 2KCl$$

Scheme 1

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*This type of procedure proved to be quite useful in the preparation of bis-phosphino-amines: M. E. Wilson, R. G. Nuzzo and G. M. Whiteside, *J. Amer. Chem. Soc., 100,* 2269 (1978).

**This compound was prepared from commercially available materials according to a procedure previously quoted for similar compounds: F. L. Bach, H. J. Brabander and S. Kushner, *J. Amer. Chem. Soc., 79,* 2221 (1957).

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as a powder. The mixture was refluxed for 16 hr, cooled, and transferred to a separation funnel. Hexane (400 ml) and 150 ml of 10% aqueous NaOH were added. The hexane layer was separated, washed with 150 ml of saturated aqueous NaCl, and stirred with 150 ml of 2N aqueous HCl. The oily precipitate was separated and stirred with 50 ml of 10% aqueous NaOH. The mixture was extracted with five 20-ml portions of ether. The ethereal solution was dried and concentrated *in vacuo* to give dmpe as an oil (17.1 g, 80% yield). Optical activity: $\alpha_{20}^{D} = -31.2$ (neat, l = 1 dm). ^{1}H NMR (δ). 7.3 (m) [15H], 3.5 (q) [1H], 2.4 (m) [4H], 2.20 (s) [3H], 1.35 (d) [3H] ($CDCl_3$).

Preparation of (dmpe)PtCl$_2$

A solution of 0.236 g (0.68 mmol) of dmpe in 5ml of methanol was added to a solution of 0.250 g (0.68 mmol) of $K[PtCl_3(C_2H_4)]\cdot H_2O$ in 6 ml of CH_3OH. The reaction mixture was refluxed for 5 minutes, filtered whilst hot, and stored in a refrigerator for a few hours. The light-yellow crystals were filtered and dried. Recrystallization from methylene chloride/n-butanol gave 0.192 g (46% yield) of product. M.P. (dec): 233 °C. *Anal.*. Found (Calcd) %: Pt 31.8 (31.9%). ^{1}H NMR (δ) 7.7 (m) [15H], 5.45 (q) [1H], 3.12 (s) (30 hz) [3H], 2.5 (m) [4H], 1.93 (d) [3H]. $[\alpha]_{20}^{D} = +48$ (c = 0.6, $CHCl_3$). CD spectrum ($CHCl_3$): $\Delta\epsilon = +0.35$ (27.000 cm^{-1}) $\Delta\epsilon = +0.80$ (33.000 cm^{-1}) IR spectrum: Pt–Cl str. 330,290 cm^{-1}.

The same complex was also obtained in low yield by reacting Na_2PtCl_4 in ethanol solution with an equimolar amount of dmpe, according to a procedure quoted for similar complexes [4].

Preparation of (dmpe)PdCl$_2$

A solution of 0.347 g (1.0 mmol) of dmpe in 5 ml of ethanol was added to a solution of Na_2PdCl_4 (0.300 g, 1.0 mmol) in 7 ml of ethanol. A brown precipitate was formed. The reaction mixture was refluxed for 10 minutes. The resulting yellow solution was cooled, filtered, and stored in refrigerator. The yellow crystals were filtered and dried. Recrystallization from n-butanol gave 0.431 g (82% yield) of the product M.P. (dec.) 162 °C. *Anal.* Found (Calcd) %: Pd 19.6 (20.3). ^{1}H NMR (δ): 7.6 (m) [15H], 5.30 (q) [1H], 3.03 (s) [3H], 2.5 (m) [4H], 1.96 (d) [3H]. After epimerization three additional signals were observed: 5.56 (q) [1H], 3.37 (s) [3H], 1.46 (d)]3H]. $[\alpha]_{20}^{D} = +110$ (c 0.5, CH_2Cl_2). After epimerization: $[\alpha]_{20}^{D} = +55$.

CD spectrum (CH_2Cl_2) $\Delta\epsilon = +1.1$ (27.000 cm^{-1}); $\Delta\epsilon = -0.5$ (31.200 cm^{-1}); $\Delta\epsilon = +1.4$ (33.000 cm^{-1}).

IR spectrum: Pd–Cl str. 335,280 cm^{-1}.

Preparation of a Rhodium Complex

According to a known procedure [5] for similar complexes, dmpe and $Rh_2Cl_2(C_2H_4)_4$ were reacted in ether in a 2:1 molar ratio. Workup as quoted gave a yellow product. Attempts to recrystallize the crude product were unsuccessful. On the ground of the analysis and conductivity measurements the formula $Rh(dmpe)_2Cl$ was tentatively assigned.

Acknowledgement

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