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Preliminary communication

Homogeneous asymmetric catalysis by means of chiral metal complexes of 1-dimenthylphosphino-3-dimethylamines

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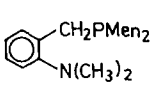
Abstract

o-(Dimenthylphosphinomethyl)-*N*,*N*-dimethylaniline (**1**), *o*-(dimenthylphosphino)-*N*,*N*-dimethylbenzylamine (**2**) and 3-dimenthylphosphino-*N*,*N*-dimethylamino-n-propylamine (**3**) have been used as ligands for Rh and Pt complexes in asymmetric hydrosilylation. Ni and Pd complexes of these ligands were tested in the Grignard cross-coupling reaction. The hydrosilylation of acetophenone led to 20% e.e., attempts to asymmetric cross-coupling reactions resulted in low enantiomeric excess up to 11%.

During the last years various types of chiral metal complexes, of which the most preferable were those with bidentate N/N, P/N and P/P ligands, have been synthesized as catalysts for the asymmetric hydrosilylation and Grignard cross-coupling reactions. In 1989 we reported such reactions catalyzed by metal complexes with the P/P-ligands 2,3-bis(dimenthylphosphino)-*N*-phenylmaleic anhydride and 2,3-bis(dimenthylphosphino)-*N*-phenylmaleimide [1]. In continuation of our studies on the efficiency of chiral catalysts with dimenthylphosphino groups we investigated the 1-dimenthylphosphino-3-dimethylamines **1**, **2** and **3** as ligands for control of enantioselectivity in rhodium and platinum catalyzed hydrosilylation of ketones and in nickel and palladium catalyzed cross-coupling reactions, respectively.



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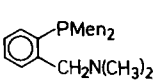

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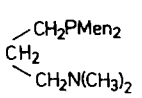

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[Men = (−)−(1R, 3R, 4S)−menthyl]

Previously, we have shown that the similar structured P/N-ligand AMPHOS is an effective ligand in both these reactions [2,3]. The (−)-ligands **1**–**3** were prepared in a similar way as AMPHOS [4] by reaction of the appropriate lithium compounds with dimenthylchlorophosphine [5].

Crystalline palladium chloride complexes (lig)$PdCl_2$ of the ligands **1** and **2** were prepared by ligand exchange in benzene solution with $Pd(COD)Cl_2$ as starting

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Table 1

Asymmetric Grignard cross-coupling of 1-phenylethylmagnesium chloride with (*E*)-β-bromostyrene at room temperature, time 20 h

Catalyst [a]	Chemical yield (%)	Optical yield (% e.e.)	Catalyst [a,c]	Chemical yield (%)	Optical yield (% e.e.)
1-$PdCl_2$	65	11 (*R*)	**1**+$NiCl_2$	45	–
2-$PdCl_2$	60	5 (*R*)	**2**+$NiCl_2$	40	–
3-$PdCl_2$ [b]	70	7 (*R*)	**3**+$NiCl_2$	45	–

[a] Catalyst/bromostyrene/Grignard reagent = 1/200/300, mixing in 12 ml ether under argon at −45 °C. [b] Prepared by reaction of Pd(COD)Cl_2 and **3** in benzene. After 10 h stirring at room temperature benzene was evaporated. [c] Prepared in situ, Ni/L = 1/1.

compound. We tried to prepare the crystalline complex (lig **3**)$PdCl_2$ but failed to isolate it. In this case the complex was preformed in benzene solution. These compounds and the Ni complexes prepared in situ were used as catalysts in the asymmetric Grignard cross-coupling between (*E*)-β-bromostyrene and 1-phenylethylmagnesium chloride. Details of the analysis of the reaction products have been published previously [2].

The values given in Table 1 represent the calculated averages of four independent runs in each case. It was found that all complexes are active, the Pd system more so than Ni, contrary to the inactive "in situ" Ni-AMPHOS system [2]. However, only in the Pd catalyzed cross-coupling reaction the menthyl groups show an asymmetric induction, the different structure of the ligands having no significant influence with respect to their optical induction.

In comparison with the AMPHOS ligand we can state that significantly higher stereoselectivity was observed in the Pd-AMPHOS catalyzed reaction. This indicates that a ligand with a chiral carbon center at the dimethylamino group is more effective than one with a chiral center at the phosphino group.

The rhodium and platinum complexes, active in the asymmetric hydrosilylation following a standard procedure [1], were generated from [Rh(COD)Cl]$_2$ and Pt(COD)Cl_2 and the appropriate ligand. The results obtained are shown in Table 2 and 3. All ligands catalyze the hydrosilylation of acetophenone in good chemical yields but the optical yields were lower than with AMPHOS. Difference in the position of the asymmetric center and the sterically hindered menthyl group might cause the lower optical yield. As expected, the variation of the ligand to metal ratio

Table 2

Asymmetric hydrosilylation of acetophenone with diphenylsilane at room temperature in toluene, $p(H_2)$ 0.1 MPa, time 24 h, substrate/metal = 250

Run	Catalyst [a]	L/Rh	Conversion (%)	Optical [b] yield (% e.e.)	Configuration
1	**1**+[Rh(COD)Cl]$_2$	5/1	75	20	*R*
2	**2**+[Rh(COD)Cl]$_2$	5/1	90	13	*R*
3	**3**+[Rh(COD)Cl]$_2$	5/1	94	21	*R*

[a] Prepared in situ. [b] Chemical and optical yields for 1-phenylethanol were determined by GLC [3].

Table 3
Asymmetric hydrosilylation of acetophenone with diphenylsilane at room temperature in toluene, $p(H_2)$ 0.1 MPa, time 7 h, substrate/metal = 250

Run	Catalyst	M/L	Conversion (%)	Optical yield (% e.e.)	Configuration
1	**1** + $[Rh(COD)Cl]_2$	1/1	56	4	*R*
2		1/2	56	11	*R*
3		1/3	72	14	*R*
4		1/5	73	20	*R*
5	**1** + $Pt(COD)Cl_2$	1/5	76	8	*S*

(Table 3, runs 1–4) shows that the chemical and optical yield increases when the ratio L/Rh is changed from 1 to 5. If the ligand excess is ten-fold, optical induction changes insignificantly.

In the case of AMPHOS the platinum complex catalyzed the hydrosilylation with conversions as high as those of rhodium, but the optical induction was reduced and accompanied by opposite configuration [2]. This effect was observed also in the case of ligand **1** (Table 3, run 5).

Experimental

Dichloro-[o-(dimenthylphosphinomethyl)-N,N-dimethylaniline]palladium(II),1-$PdCl_2$. To a suspension of 86 mg (0.3 mmol) $Pd(COD)Cl_2$ in 4 ml of dry benzene under argon, a solution of 133 mg (0.3 mmol) of (−)-*o*-(dimenthylphosphinomethyl)-*N*,*N*-dimethylaniline (**1**) in 5 ml of benzene was added with stirring. After 24 h stirring at room temperature the solution was concentrated to a volume of 3 ml and 15 ml hexane was added. The precipitate was filtered, washed with hexane and dried in vacuum giving 142 mg (75%) of yellow complex.

Anal. Found: C, 56.14; H, 7.88; N, 2.08; Cl, 11.65; P, 4.79; Pd, 17.34%. $C_{29}H_{50}Cl_2NPPd$ (621.01) calcd.: C, 56.09; H, 8.11; N, 2.26; Cl, 11.42; P, 4.99; Pd, 17.13%.

Dichloro-[o-(dimenthylphosphino)-N,N-dimethylbenzylamine]palladium (II), 2-$PdCl_2$. **2**-$PdCl_2$ was prepared as described above for **1**-$PdCl_2$. Yellow complex, 150 mg (79%).

Anal. Found: C, 56.14; H, 8.21; N, 2.06; Cl, 11.40; P, 4.70; Pd, 17.42%.

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