Configurationally stable asymmetric nitrogen atom in the palladium(II) aminophosphine complex

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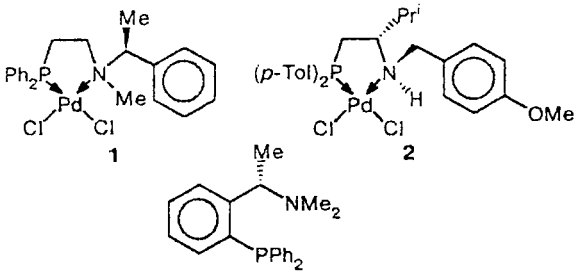
The synthesis of a new optically active aminophosphine ligand *i-Pramphos*, containing a potentially stereogenic nitrogen atom, from (*S*)-*N*-isopropyl-*N*-methyl-α-methylbenzylamine is described; its complex with palladium(II) chloride was obtained. NMR spectroscopy revealed that the coordination of the aminophosphine with the metal resulted in stereospecific locking of the donor nitrogen atom in only one of two possible configurations.

Key words: aminophosphine, *ortho*-lithiation, asymmetric nitrogen atom.

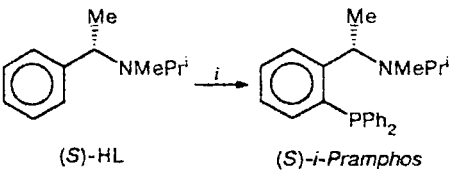
Recently, interest in enantioselective catalysts containing chiral donor atoms has substantially increased.[1—3] The potential of these stereoselectors is due to the possibility of more efficient transfer of chiral information from the catalyst to substrate.[4—6] However, among aminophosphine ligands, whose complexes are widely used in catalysis of cross coupling, hydrosilylation, hydrogenation, and other processes, only a few systems with chiral P*-[7—11] and/or *N**-donor centers[10—15] are known. Presently only two N*-chiral palladium(II) aminophosphine complexes with a five-membered aliphatic metallacycle have been characterized.[12,15]



One of them, complex **1**, additionally contains an exocyclic carbon stereocenter, and is configurationally unstable.[12] The endocyclic arrangement of the C*-stereocenter in complex **2** provides configurational stability of the adjacent asymmetric nitrogen atom, but the palladacycle retains its conformational mobility,[15] which decreases the potential of use of these complexes as stereoselectors.

The configurational stability of the asymmetric donor nitrogen atom in cyclopalladated complexes based on homochiral α-arylalkylamines,* which we established previously,[16—18] and the high contribution of the *N**-stereocenter to processes of chiral recognition[20] stimulated interest in preparing aminophosphine complexes with the same framework. In this work, we present the preliminary results on the synthesis of the first *N**-chiral analog of the known aminophosphine *Amphos* and its complex with palladium(II) containing a configurationally stable *N**-stereocenter.

The new aminophosphine ligand (*S*)-*o*-diphenylphosphino-*N*-isopropyl-*N*-methyl-α-methylbenzylamine (named *i-Pramphos*) was obtained by the classic scheme[21] involving *ortho*-lithiation of the corresponding tertiary amine (*S*)-HL followed by treatment of the Li derivative formed with chlorodiphenylphosphine.



i. 1) BuLi/TMEDA, hexane, 25 °C, 4.5 days; 2) Ph_2PCl, ether

To optimize the conditions of *ortho*-lithiation, we first estimated the effects of the lithiating agent (Bu^nLi or Bu^tLi), the solvent (ether or hexane), the introduction of chelating additives (TMEDA), and the duration of the reaction (1—11 days) on the degree of metallation. The process was monitored by ^1H NMR after quenching of an aliquot of the formed carbanion with excess of Me_3SiCl. It should be mentioned that using this electrophile to estimate the degree of metallation was more efficient than using another electrophile that is often used, D_2O, due to the considerable difference between the chemical shifts of the both methine protons (α-C<u>H</u> and C<u>H</u>Me_2) in the spectra of the initial amine HL and its *ortho*-silylated derivative Me_3SiL (Δδ ~0.2 ppm, see Experimental).

* The possibility of locking of the configuration of the asymmetric nitrogen atom during cyclopalladation was shown for the first time in Ref. 19 for the prochiral ligand.

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Table 1. Optimization of conditions for *ortho*-lithiation of amine HL

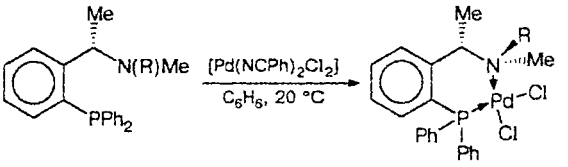
Entry	Metallation conditions				I_{Me_3SiL} : I_{HL}[a]		β[b] (%)
	Reagent	Solvent	Chelating agent	τ /days	α-C<u>H</u>	C<u>H</u>Me$_2$	
1	Bu^{n}Li	Ether—hexane 1 : 1	None	2	16 : 84	16 : 84	16
				4	14 : 86	14.5 : 85.5	14
2	Bu^{n}Li	Hexane	TMEDA	5	49 : 51	49.5 : 50.5	49[c]
				11	43 : 57	45 : 55	44
3	Bu^{t}Li	Pentane	None	1	37 : 63	38 : 62	37.5
				3	51 : 49	52 : 48	51.5
				6	45 : 55	45 : 55	45

[a] The ratio of integral intensities of signals of protons of Me_3SiL and HL. [b] β is the average degree of metallation of the ligand HL. [c] When an aliquot of the reaction mixture is quenched with excess D_2O, the degree of metallation, according to the ^1H NMR data, is equal to 51%.

The results presented in Table 1 show that even when the best systems are used (Bu^{t}Li/pentane or Bu^{n}Li/TMEDA/hexane), the degree of metallation is limited to a value of ~50%. Perhaps this result is caused by steric hindrances created by the bulky *N*-isopropyl substituent and/or the possible formation of specific associates of the lithiated derivatives with the free amine.[22,23] The further decrease in yield (down to ~9%) during isolation and purification of the free aminophosphine is associated with its high susceptibility to oxidation in solutions.

The structure and chemical purity of the free ligand *i-Pramphos* were confirmed by elemental analysis and ^1H and $^{31}P\{^1H\}$ NMR spectra (see Experimental). It is noteworthy that the spin-spin coupling constant of the interaction of the α-methine proton with the phosphorus nucleus in the case of the *i-Pramphos* ligand is somewhat greater ($^4J_{PH}$ = 8.1 Hz) than that of the known *Amphos* analog ($^4J_{PH}$ = 6—6.3 Hz[24,25] or 7.2 Hz according to our data); it approaches that for the *Amphos* chlorohydrate ($^4J_{PH}$ = 8.6 Hz). The introduction of a PPh_2 group to the *o*-position of the phenyl ring of the tertiary benzylamine HL results in a substantial increase in the nonequivalence of the two diastereotopic methyl groups of the *N*-isopropyl substituent: Δδ 0.15 ppm in the spectrum of the aminophosphine *i-Pramphos* and 0.01 ppm in the case of the initial benzylamine.[16]

For the purpose of estimating the stereoselectivity of the formation of a complex between the new *N**-chiral aminophosphine and palladium(II) and the configurational stability of the *N**-stereocenter locked by coordination with the metal, we prepared the monochelate complex [{(S_C)-*i-Pramphos*}$PdCl_2$] (**3a**) by a standard procedure[26,27] including displacement of the labile benzonitrile ligand from the [$Pd(NCPh)_2Cl_2$] complex. The previously described[26—28] analogous complex with the (*S*)-*Amphos* ligand (**3b**) was also obtained as the *N*-achiral model.



3a: R = Pr^i
3b: R = Me

The spectral parameters of complex **3a** suggest that it exists in solutions as only one diastereomer: the $^{31}P\{^1H\}$ NMR spectrum contains only one signal, while the ^1H NMR spectrum exhibits one set of signals. Therefore, the complex formation is stereospecific with locking of the *N**-stereocenter in one of two possible absolute configurations. At this time, it seems impossible to determine the configuration of the nitrogen atom. However, based on steric considerations and the known data for the *N**-chiral cyclopalladated complexes,[16,17] we can propose that the *N**-donor atom should have an absolute configuration opposite to that of the adjacent α-benzyl carbon stereocenter, *i.e.*, (S_CR_N).

The configurational stability of the *N**-stereocenter, which is stereochemically supported by the adjacent endocyclic carbon stereocenter, is a substantial advantage of the new complex **3a**. It should be mentioned for comparison that when the arrangement is exocyclic, the similar α-methylbenzylic stereocenter in the previously described complex **1** does not provide configurational stability to the nitrogen atom: this complex is epimerized in solutions to a mixture of diastereomers (3 : 1) in 30 min.[12]

A previous study[26] of the temperature dependence of the ^1H NMR spectra of the [(*Amphos*)Pd(Me)Br] complex showed restricted conformational mobility of the metallacycle formed by the aminophosphine ligand. Unlike the known complex **3b**, whose ^1H NMR spectrum (recorded at room temperature) contains strongly broadened signals of the protons of the α-CH- and

NMe_2-groups, all aliphatic protons appear in the spectrum of complex **3a** as narrow well resolved signals. This suggests that one of the possible conformations is strongly predominant, although fast exchange between several conformations cannot be ruled out at the moment.

Experimental

^1H NMR spectra were recorded on a Varian VXR-400 spectrometer at ~20 °C in $CDCl_3$ or CD_3OD using $SiMe_4$ as the internal standard; signals were assigned on the basis of double homonuclear resonance. $^{31}P\{^1H\}$ spectra were recorded on an FT-80A spectrometer with a working frequency of 32.2 MHz in dichloromethane, diethyl ether, or methanol using 85% H_3PO_4 as the external standard. The specific rotation was measured at the D-line of Na on an A1-EPO automated polarimeter (VNIEKIProdmash).

All experiments with free aminophosphines were carried out in an atmosphere of purified argon in anhydrous deoxygenated solvents. The following reagents were used: Me_3SiCl (chemically pure grade) degassed by bubbling argon for 2 h and distilled in the presence of 5 vol.% quinoline in an argon atmosphere; diamine TMEDA refluxed and distilled over solid KOH; and Ph_2PCl obtained by the described procedure.[29]

The starting tertiary amines (*S*)-(−)-α,*N*,*N*-trimethylbenzylamine[30] and (*S*)-(−)-*N*-isopropyl-α,*N*-dimethylbenzylamine[16] were obtained by the previously described methods; racemic *N*-isopropyl-α,*N*-dimethylbenzylamine was synthesized similarly to the (*S*)-enantiomer.[16]

(*S*)-*o*-Diphenylphosphino-α,*N*,*N*-trimethylbenzylamine (Amphos) was obtained in 33% yield by a modified method including synthesis according to Horner[21] and purification through the hydrochloride according to Payne[25] followed by recrystallization of the free aminophosphine from pentane.

(*S*)-*o*-Diphenylphosphino-α,*N*,*N*-trimethylbenzylamine hydrochloride. $^{31}P\{^1H\}$ NMR (MeOH), δ: −17.9. ^1H NMR (CD_3OD), δ: 1.49 (d, 3 H, α-Me, $^3J_{HH}$ = 6.8 Hz); 2.66 (s, 3 H, NMe); 3.00 (s, 3 H, NMe); 5.21 (d.q, 1 H, α-CH, $^3J_{HH}$ = 6.7 Hz, $^4J_{PH}$ = 8.6 Hz); 7.0—7.9 (m, 14 H, aromatic protons). The $^{31}P\{^1H\}$ NMR spectra of the unpurified samples contain an additional signal of *P*-oxide hydrochloride at 36.5 ppm (MeOH).

(*S*)-*o*-Diphenylphosphino-α,*N*,*N*-trimethylbenzylamine. $^{31}P\{^1H\}$ NMR (CH_2Cl_2), δ: −17.1. ^1H NMR ($CDCl_3$), δ: 1.22 (d, 3 H, α-Me, $^3J_{HH}$ = 7.2 Hz); 2.04 (s, 6 H, NMe_2); 4.17 (d.q, 1 H, α-CH, $^3J_{HH}$ = 7.2 Hz, $^4J_{PH}$ = 7.2 Hz); 6.9—7.9 (m, 14 H, aromatic protons). The $^{31}P\{^1H\}$ NMR spectra of unpurified samples of the aminophosphine contain a signal of the corresponding *P*-oxide at 29.5 ppm (CH_2Cl_2).

Estimation of the degree of metallation of amine HL. Racemic *N*-isopropyl-α,*N*-dimethylbenzylamine (1.1 mL, 0.9679 g, 5.4 mmol) and TMEDA ((0.82 mL, 0.6314 g, 5.4 mmol) were placed in a two-neck flask with a vacuum stop-cock and a rubber septum. After degassing of the mixture of amines *in vacuo*, pre-degassed anhydrous hexane (5 mL) was frozen through the vacuum line into the reaction flask, the flask was filled with deoxygenated argon, and a 1.49 *M* solution (3.7 mL) of BuLi in hexane was injected by a syringe through the septum. Five days after, an aliquot (1 mL) of the reaction mixture was taken by a syringe through the septum and introduced into a solution of Me_3SiCl (0.6 mL) in pentane (2 mL) in a Shlenk flask in an atmosphere of argon at 0 °C. The mixture was stirred with cooling for 10 min. After the addition of water (3 mL) and treatment with solid NaOH, the organic layer was separated and dried over 4 Å molecular sieves, and the solvent was distilled off. The ratio of the Me_3SiL and HL amines in the reaction mixture was determined by the ^1H NMR spectra from the integral intensities of the signals of the α-benzyl and *N*-isopropyl methine protons.

(*R*,*S*)-*N*-Isopropyl-α,*N*-dimethyl-*o*-trimethylsilylbenzylamine (Me_3SiL). ^1H NMR ($CDCl_3$), δ: 0.35 (s, 9 H, Me_3Si); 0.95 (d, 3 H, $CH\underline{Me}_2$, ^3J = 6.8 Hz); 1.03 (d, 3 H, $CH\underline{Me}_2$, ^3J = 6.6 Hz); 1.25 (d, 3 H, α-Me, ^3J = 6.4 Hz); 2.06 (s, 3 H, N<u>Me</u>); 3.16 (m, 1 H, $C\underline{H}Me_2$, ^3J = 6.6 Hz); 3.79 (q, 1 H, α-CH, ^3J = 6.4 Hz); 7.45 (m, 1 H, C(3)H or C(6)H, ^3J = 7.4 Hz); 7.70 (d, 1 H, C(6)H or C(3)H, ^3J = 7.8 Hz); signals of other aromatic protons overlap with the corresponding signals of the initial amine.

(*R*,*S*)-*N*-Isopropyl-α,*N*-dimethylbenzylamine. ^1H NMR ($CDCl_3$), δ: 0.97 (d, 3 H, $CH\underline{Me}_2$, ^3J = 6.8 Hz); 0.93 (d, 3 H, $CH\underline{Me}_2$, ^3J = 6.6 Hz); 1.32 (d, 3 H, α-Me, ^3J = 6.8 Hz); 2.13 (s, 3 H, N<u>Me</u>); 2.95 (m, 1 H, $C\underline{H}Me_2$, ^3J = 6.6 Hz); 3.60 (q, 1 H, α-CH, ^3J = 6.8 Hz); 7.2—7.4 (m, 5 H, Ph).

(*S*)-*o*-Diphenylphosphino-*N*-isopropyl-α,*N*-dimethylbenzylamine (*i*-*Pramphos*). The device described by Horner[31] was evacuated and filled with argon. Freshly distilled (*S*)-*N*-isopropyl-α,*N*-dimethylbenzylamine (8.7 mL, 45.0 mmol) and TMEDA (6.9 mL, 45.8 mmol) were placed in a flask, and the mixture of the amines was degassed *in vacuo*. Then absolute hexane (30 mL) was frozen *in vacuo* into the reaction flask, and the device was filled with argon. A 1.46 *M* solution of BuLi (34 mL, 49.5 mmol) in hexane was placed in a dropping funnel in an argon back-flow and added dropwise to the reaction mixture, which was left for 4.5 days. A solution of Ph_2PCl (8.89 mL, 49.5 mmol) in absolute ether (25 mL) was placed in a dropping funnel in an argon back-flow; the dropwise addition of this solution is accompanied by heating of the reaction mixture and the formation of a precipitate. After the reaction mixture attained room temperature, the stirring was continued for 30 min. The reaction mixture was transferred into a separating funnel pre-filled with argon and containing water (70 mL) that had been distilled in an argon flow and additionally deoxygenated by successive evacuation on a water aspirator pump and saturation with argon. The aqueous layer was separated, and the organic layer was extracted with a mixture of water (70 mL) and 6 *N* HCl (25 mL) that had been distilled and deaerated by a procedure similar to that used for water. The aqueous layer was treated with solid NaOH, the aminophosphine that separated was extracted with ether (2×40 mL) and dried with Na_2SO_4, and the solvent was removed on a rotary evaporator. At this stage, the content of the target product in the extract was not less than 75% according to the data of ^{31}P NMR spectroscopy. Then the aminophosphine was extracted with hexane. The yield of the analytically pure ligand was 1.365 g (9.2%), m.p. 74 °C (from hexane), R_f 0.6 (Silufol, MeOH/NH_3(aq), 100 : 1); $[\alpha]_D$ −109° (*c* 1.1, C_6H_6). Found (%): C, 79.84; H, 7.64; N, 3.46. $C_{24}H_{28}NP$. Calculated (%): C, 79.75; H, 7.81; N, 3.87.

$^{31}P\{^1H\}$ NMR (Et_2O), δ: −18.7. ^1H NMR ($CDCl_3$), δ: 0.77 (d, 3 H, $CH\underline{Me}_2$, $^3J_{HH}$ = 6.6 Hz); 0.92 (d, 3 H, $CH\underline{Me}_2$, $^3J_{HH}$ = 6.6 Hz); 1.16 (d, 3 H, α-Me, $^3J_{HH}$ = 6.5 Hz); 2.06 (s, 3 H, NMe); 2.87 (septet, 1 H, $C\underline{H}Me_2$, $^3J_{HH}$ = 6.6 Hz); 4.51 (d.q, 1 H, α-CH, $^3J_{HH}$ = 6.6 Hz, $^4J_{PH}$ = 8.1 Hz); 6.9—7.8 (m, 14 H, aromatic protons).

Synthesis of palladium(II) complexes with aminophosphines

Dichloro{(*S*)-*o*-diphenylphosphino-α,*N*,*N*-trimethylbenzylamine-*N*,*P*}palladium (3b). (*S*)-*o*-Diphenylphosphino-α,*N*,*N*-trimethylbenzylamine (0.372 g, 1.115 mmol) was placed in a flask filled with argon, anhydrous benzene (45 mL) was frozen into the flask *in vacuo*, and the flask was again filled with

argon. Then dichlorobis(benzonitrile)palladium(II) (0.420 g, 1.093 mmol) was added, and the mixture was stirred with a magnetic stirrer for 2 days. The precipitated yellow residue was filtered off in an argon atmosphere, washed with hot absolute benzene, and dried *in vacuo*. The yield was 0.52 g (86%); R_f 0.52 (C_6H_6/Me_2CO, 2 : 1, Silufol); $[\alpha]_D$ 283° (*c* 1.1, CH_2Cl_2). Found (%): C, 54.61; H, 4.93; N, 2.33. $H_{22}H_{24}Cl_2NPPd \cdot 0.5C_6H_6$. Calculated (%): C, 54.61; H, 4.95; N, 2.55. The presence of the benzene molecule of solvation is confirmed by the singlet at 7.37 ppm with an integral intensity of 3 H in the ^1H NMR spectrum of the complex. $^{31}P\{^1H\}$ NMR (CH_2Cl_2), δ: 14.9. ^1H NMR ($CDCl_3$), δ: 1.37 (d, 3 H, α-Me, $^3J_{HH}$ = 6.7 Hz); 2.84, 3.24 (both br.s, 3 H, NMe); 3.28 (br.m, 1 H, α-CH); 7.00—8.10 (m, 14 H, aromatic protons); 7.37 (s, 3 H, 0.5 C_6H_6).

After recrystallization from a benzene—dichloromethane mixture and then from a chloroform—hexane mixture, the solvated complex crystallized as light-yellow needle-like crystals with m.p. 253—256 °C (with decomp.); $[\alpha]_D$ 239° (*c* 1.0, CH_2Cl_2). Found (%): C, 47.91; H, 4.50; N, 2.17; Cl, 19.47. $C_{22}H_{24}NPPdCl_2 \cdot 0.4CHCl_3$. Calculated (%): C, 48.17; H, 4.40; N, 2.51; Cl, 20.31. ^1H NMR ($CDCl_3$), δ: 1.37 (d, 3 H, α-Me, $^3J_{HH}$ = 6.8 Hz); 2.84, 3.24 (both br.s, 3 H, NMe); 3.28 (m, 1 H, α-CH); 7.05 (m, 1 H, H(3)); 8.02 (m, 2 H, *o*-PPh); 7.25—7.59 (group of m, 11 H, other aromatic protons).

The presence of a chloroform molecule of solvation is confirmed by the signal at 7.76 ppm with an integral intensity of ~0.5 H in the ^1H NMR spectrum of the complex recorded in the CD_3OD/CD_3CN mixture; its intensity increases after addition of $CHCl_3$. ^1H NMR (CD_3OD/CD_3CN), δ: 1.40 (d, 3 H, α-Me, $^3J_{HH}$ = 6.6 Hz); 2.82 (br.s, 3 H, NMe); 3.09 (br.s, 3 H, NMe); 8.05 (m, 2 H, *o*-PPh); 7.12 (m, 1 H, H(3)); 7.4—7.7 (group of m, 11 H, other aromatic protons).

Dichloro{(*S*)-*o*-diphenylphosphino-*N*-isopropyl-α,*N*-dimethylbenzylamine-*N*,*P*}palladium (3a) was obtained similarly from (*S*)-*o*-diphenylphosphino-*N*-isopropyl-α,*N*-dimethylbenzylamine (0.39 g, 1.07 mmol) and dichlorobis(benzonitrile)palladium(II) (0.40 g, 1.05 mmol) in 86% yield (0.52 g). The complex was purified by column chromatography on Silpearl (*h* 155 mm, *d* 17 mm) using a benzene—methanol (8 : 1) mixture as eluent. After recrystallization from the benzene—methanol mixture and drying *in vacuo* over P_2O_5 and paraffin, the solvated complex was obtained as light-yellow crystals with m.p. 185—186 °C (with decomp.); R_f 0.41 (C_6H_6/Me_2CO 2 : 1, Silufol); $[\alpha]_D$ 99.4° (*c* 1.0, CH_2Cl_2). Found (%): C, 56.55; H, 5.58; N, 2.16. $C_{24}H_{28}Cl_2NPPd \cdot 0.5C_6H_6$. Calculated (%): C, 56.12; H, 5.41; N, 2.42.

$^{31}P\{^1H\}$ NMR (CH_2Cl_2), δ: 13.3. ^1H NMR ($CDCl_3$), δ: 0.99 (d, 3 H, $CH\underline{Me}_2$, $^3J_{HH}$ = 6.5 Hz); 1.90 (d, 6 H, $CH\underline{Me}_2$ + α-Me, $^3J_{HH}$ = 6.7 Hz); 3.05 (s, 3 H, NMe); 3.39 (d.q, 1 H, $C\underline{H}Me_2$, $^3J_{HH}$ = 6.5 and 6.7 Hz); 3.67 (d.q, 1 H, α-CH, $^3J_{HH}$ = 6.7 Hz, $^4J_{PH}$ = 2.7 Hz); 7.90 (m, 2 H, o-PPh, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 1.4 Hz, $^3J_{PH}$ = 12.0 Hz); 7.62 (m, 2 H, *o*-PPh, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.4 Hz, $^3J_{PH}$ = 12.2 Hz); 7.20—7.64 (m, 10 H, other aromatic protons); 7.36 (s, 3 H, 0.5 C_6H_6).

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