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SHORT COMMUNICATIONS

New P-Chiral Polyfluoroalkyl Phosphorodiamidite Ligand in Asymmetric Transformations Catalyzed by Palladium and Copper Complexes

E. B. Benetskii[a], V. A. Davankov[a], P. V. Petrovskii[a], E. A. Rastorguev[a], T. B. Grishina[b], K. N. Gavrilov[b], S. Rosset[c], G. Bailat[c], and A. Alexakis[c]

[a] *Nesmeyanov Institute of Organometallic Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia*
e-mail: eduardben@mail.ru

[b] *Esenin Ryazan State University, Ryazan, Russia*

[c] *Departement de Chimie Organique, Universite de Geneve, Suisse*

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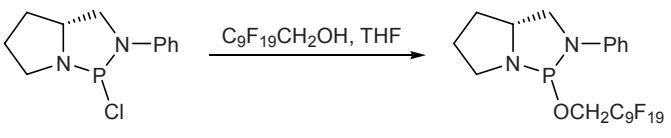
Chiral phosphorus-containing ligands having polyfloroalkyl substituents may be used for the preparation of metal complex catalysts which could be recycled via phase separation [1]. Following the approach proposed by us previously [2], we synthesized a new P-chiral polyfluoroalkyl phosphorodiamidite **L** as shown in Scheme 1. The product was stable on storage and readily soluble in organic solvents. It was tested as chiral auxiliary in palladium-catalyzed enantioselective amination of 1,3-diphenylprop-2-en-1-yl acetate (**I**) with dipropylamine according to the procedure described in [3] (Scheme 2). In all experiments, a steadily high enantioselectivity level was reached (*ee* 91–95%), regardless of the **L**/Pd molar ratio (1:1 or 2:1) and reaction medium. However, the substrate conversion turned out to be quite sensitive to the solvent nature: it did not exceed 32% in tetrahydrofuran but was almost complete in methylene chloride.

Ligand **L** was also used in copper-catalyzed conjugate addition of diethylzinc to cyclohex-2-en-1-one (**III**) [4] (Scheme 3). The reaction was carried out in diethyl ether in the presence of copper thiophenecarboxylate as pre-catalyst, and the molar ratio **L**–Cu was 2:1 (–30°C, 3 h). The optical yield of 3-ethylcyclohexanone (**IV**) was 70% (*ee*), the substrate conversion being higher than 99%.

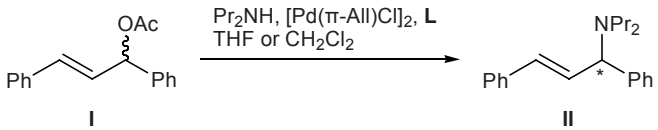
Compound **L** is a fairly effective stereoinductor. It is inferior to phosphoramidites based on biphenyl-2,2′-diol and BINOL (1,1′-binaphthalene-2,2′-diol) in Cu-catalyzed conjugate addition reactions [4], but it ensures higher enantioselectivity in Pd-catalyzed allyla-

Scheme 1.



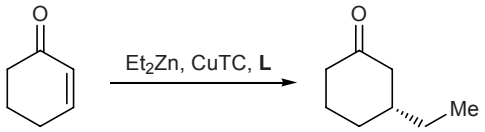
L

Scheme 2.



I **II**

Scheme 3.



III IV

tion of 1,3-diphenylprop-2-en-1-yl acetate [5, 6]. On the other hand, ligand **L** was much more effective than its analogs having a 3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane skeleton in Cu-catalyzed conjugate addition of Et_2Zn to cyclohex-2-en-1-one. The corresponding π*,N-bidentate phosphorodiamidites ensured enantiomeric excess of no higher than 55% [7], while π*-monodentate, only *ee* 10–20% [8].

(2*S*,5*R*)-2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Nonadecafluorodecyloxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (L). 2,2,3,3,4,4,5,5,6,6,-7,7,8,8,9,9,10,10,10-Nonadecafluorodecan-1-ol, 0.785 g (1.57 mmol), was added under vigorous stirring at 20°C to a solution of 0.378 g (1.57 mmol) of (2*S*,5*R*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane and 0.22 ml (1.57 mmol) of triethylamine in 12 ml of THF. The resulting solution was stirred for 30 min at 20°C, heated to the boiling point, and kept boiling for 2 h. It was then cooled to 20°C, the precipitate of triethylamine hydrochloride was filtered off, the filtrate was evaporated under reduced pressure (40 mm), and the residue was extracted with hexane (3×15 ml). The extracts were combined, filtered, and evaporated under reduced pressure (40 mm), and the residue was evacuated for 2 h at a residual pressure of 1 mm. Yield 0.896 g (81%), light yellow oily substance which solidified on storage, mp 62–63°C. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 145.1 d (C_{arom}, ^2J = 16.8 Hz), 129.2 s (CH_{arom}), 119.7 s (CH_{arom}), 115.0 d (CH_{arom}, ^3J = 11.7 Hz), 109.4 br.m ($C^{2'}$–$C^{10'}$), 63.2 d (C^5, ^2J = 8.8 Hz), 58.6 m (OCH_2, ^2J = 5.3 Hz), 54.9 d (C^4, ^2J = 6.6 Hz), 48.3 d (C^8, ^2J = 37.2 Hz), 31.8 s (C^6), 26.4 d (C^7, ^3J = 3.7 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 124.1 ppm. ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –79.1 to –79.35 m (3F), –117.92 s (2F), –120.25 s (8F), –121.15 s (2F), –121.4 s (2F), –124.55 s (2F). Mass spectrum (electron impact, 70 eV), *m*/*z* (I_{rel}, %): 704 $[M]^+$ (3), 484 $[C_{10}H_2F_{19} + H]^+$ (8), 222 $[M - C_{10}H_2F_{19} + H]^+$ (100), 205 $[M - C_{10}H_2F_{19}O]^+$ (82). Found, %: C 36.04; H 2.37; N 3.79. $C_{21}H_{16}F_{19}N_2OP$. Calculated, %: C 35.81; H 2.29; N 3.98.

Palladium-catalyzed allylic amination of 1,3-diphenylprop-2-en-1-yl acetate (I) with dipropylamine. A solution of 3.7 mg (0.01 mmol) of $[Pd(\pi\text{-All})Cl]_2$ and 7.04–14.08 mg (0.01–0.02 mmol) of ligand **L** in 5 ml of THF or methylene chloride was stirred for 10 min. Compound **I**, 0.1 ml (0.5 mmol), was then added, the mixture was stirred for 15 min, 0.2 ml (1.5 mmol) of freshly distilled dipropylamine was added, and the mixture was stirred for 48 h and passed through a layer of silica gel. The solvent was removed under reduced pressure (40 mm), and the residue was kept for 1 h at a residual pressure of 1 mm. The *ee* value was determined by HPLC (Daicel Chiralcel OD-H; C_6H_{14}–*i*-PrOH–$HNEt_2$, 1000:1:1, 0.5 ml/min; λ 254 nm) as described in [9].

Copper-catalyzed conjugate addition of diethylzinc to 2-cyclohexen-1-one (III). Ligand **L**, 0.04 mmol, was added at 20°C under argon to a solution of 0.02 mmol of copper thiophenecarboxylate in 2.5 ml of diethyl ether. The mixture was stirred for 30 min, cooled to –30°C, and kept for 30 min at that temperature. A 1 M solution of diethylzinc in hexane, 2.4 mmol, was added, the mixture was stirred for 20 min, and a solution of 2 mmol of compound **III** in 0.5 ml of diethyl ether was added. The mixture was stirred for 3 h, allowed to warm up to room temperature, diluted with 20 ml of diethyl ether, and extracted with 2 N hydrochloric acid. The organic phase was then washed with a concentrated solution of sodium chloride, dried over sodium sulfate, and evaporated under reduced pressure (40 mm). The residue was purified by flash chromatography on silica gel using cyclohexane–ethyl acetate (1:1) as eluent. The *ee* value was determined by HPLC as described in [4].

All reactions were carried out under dry argon in thoroughly dehydrated solvents. The ^{31}P, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker Avance-400 spectrometer at 161.98, 100.61, and 282.4 MHz, respectively, using 85% H_3PO_4 in D_2O, $CDCl_3$ (δ_C 76.91 ppm), and CCl_3F as references. Signals in the ^{13}C NMR spectrum of ligand **L** were assigned using DEPT pulse sequence. The mass spectrum was obtained on a Varian MAT-311 spectrometer. Elemental analysis was performed at the Organic Microanalysis Laboratory, Nesmeyanov Institute of Organometallic Compounds, Russian Academy of Sciences.

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