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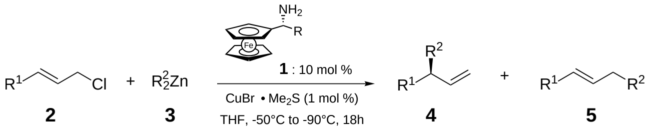
Copper(I)-Catalyzed Enantioselective Substitution of Allyl Chlorides with Diorganozinc Compounds**

Frank Dübner and Paul Knochel*

Catalytic asymmetric allylic substitutions are potentially useful methods for the preparation of a wide range of chiral molecules. Several highly enantioselective palladium(0)-catalyzed allylic substitutions have been described in recent years;[1] however, these reactions are generally limited to symmetrical substrates. Only recently, several regioselective palladium(0)-catalyzed asymmetric allylation reactions have been reported.[2] Alternatively, copper(I)-catalyzed asymmetric allylations can be performed. These reactions proceed with high S_N2' regioselectivity and therefore accommodate unsymmetrical allylic substrates as starting materials. A further advantage is that a broad range of organometallic compounds (organolithium, Grignard, and organozinc reagents) can be used in these allylic substitutions.[3] Unfortunately, only moderate enantioselectivities are usually obtained in these copper(I)-catalyzed allylations.[4] To develop such an asymmetric reaction, we have screened a broad range of ligands (amines, diamines, phosphanes, phosphites, sulfur derivatives) and have observed that primary amines show the highest catalytic activity. Further fine-tuning of chiral primary amines indicated that chiral ferrocenyl amines of type **1** are highly effective ligands. Thus, the substitution of various unsymmetrical allyl chlorides of type **2** with diorganozinc reagents **3** in the presence of $CuBr \cdot Me_2S$ (1 mol%) and **1** (10 mol%) as catalyst leads to the desired allylated products **4**. The reaction is highly regioselective (ratio **4**:**5** > 90:10) and affords products **4** with up to 87% *ee* (Scheme 1 and Table 1).



Scheme 1. Copper(I)-catalyzed enantioselective allylation. The groups R^1 and R^2 are given in Table 1, and the group R is defined in Scheme 2.

The ligands **1** are readily prepared from the ferrocenyl ketones **6** by Corey–Bakshi–Shibata (CBS) reduction, leading to the ferrocenyl alcohols **8** with high enantioselectivity (>99% *ee*).[5] Acylation of alcohols **8a–d** with acetic anhydride furnishes in quantitative yield the intermediate ferrocenyl acetates **9a–d**. Treatment with an aqueous NH_3 solution in CH_3CN provides the desired ferrocenyl amines **1a–d** in 44–66% yield (Scheme 2).

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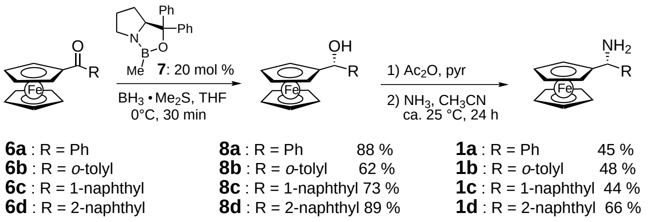
[*] Prof. Dr. P. Knochel, Dipl.-Chem. F. Dübner
Fachbereich Chemie der Universität
Hans-Meerwein-Strasse, D-35032 Marburg (Germany)
Fax: (+49)6421-28-21-89
E-mail: knochel@ps1515.chemie.uni-marburg.de

[**] F.D. thanks Zeneca Ltd. for a fellowship and the Fonds der Chemischen Industrie for generous support. We thank the BASF AG, Degussa AG, Bayer AG, and Chemetall GmbH for generous gift of chemicals.

Table 1. Copper(I)-catalyzed substitutions of allyl chlorides **2** with diorganozinc compounds **3** in the presence of the ferrocenyl amine **1d** at −90 °C.

Entry		R^1		R^2	Product	S_N2':S_N2	*ee* [%][a]	Yield [%][b]
1	**2a**	Ph	**3a**	neopentyl	**4a**	95:5	82	68
2	**2b**	4-$CF_3C_6H_4$	**3a**	neopentyl	**4b**	97:3	87	72
3	**2c**	1-naphthyl	**3a**	neopentyl	**4c**	94:6	71	65
4	**2d**	2-naphthyl	**3a**	neopentyl	**4d**	91:9	70	60
5	**2e**	*c*-C_6H_{11}	**3a**	neopentyl	**4e**	98:2	76	67
6	**2f**	3-thienyl	**3a**	neopentyl	**4f**	94:6	63	70
7	**2g**	(*Z*)-$TIPSOCH_2$[c]	**3a**	neopentyl	**4g**	>99:1	64	45
8	**2a**	Ph	**3b**	$PhMe_2SiCH_2$	**4h**	90:10	42	50[d]
9	**2a**	Ph	**3c**	Me_3SiCH_2	**4i**	94:6	67	52[d]
10	**2a**	Ph	**3d**	(+)-myrtanyl	**4j**	97:3	41	65[d]
11	**2a**	Ph	**3e**	(−)-myrtanyl	**4k**	98:2	37	60[d]

[a] Enantiomeric excess determined by gas chromatography (CP-Chirasil-Dex CB, 40→80 °C at 2–4 °C min^{-1}). [b] Yield of isolated products **4**+**5**. [c] TIPS = triisopropylsilyl. [d] The reaction was performed at −50 °C.



Scheme 2. Synthesis of the ferrocenyl ligands **1a–d**.

The nature of the group R in the ligand is essential for obtaining a high level of enantioselectivity. Therefore, under standard reactions conditions (5 mol% of CuBr · Me_2S, 5 mol% of **1a–d**), the reaction of cinnamyl chloride (**2a**, 1.0 equiv) with dineopentylzinc (**3a**, 1.2 equiv) affords (+)-(*S*)-5,5-dimethyl-3-phenyl-1-hexene (**4a**) with 32 % *ee* for **1a**, 16 % *ee* for **1b**, 33 % *ee* for **1c**, and 42 % *ee* for **1d**. When the optimum ratio of 1:10 between CuBr · Me_2S and the amine is used, the enantioselectivity can be increased to 67 % *ee* with the ligand **1d.** This ligand was used in all further experiments.

A short screening of the leaving group (Cl, Br, carbonate, xanthate, phosphate) showed that cinnamyl chloride was the best substrate. Likewise, investigations into the nature of the zinc reagent showed that no enantioselectivity was observed when RZnCl or RZnI was used instead of R_2Zn. Finally, there was an almost linear dependence of the enantioselectivity with the temperature. Thus, the reaction of **1a** with **3a** affords the product **4a** with 82 % *ee* at −90 °C (bath temperature), whereas an enantioselectivity of only 25 % *ee* was observed at +25 °C (Figure 1)!

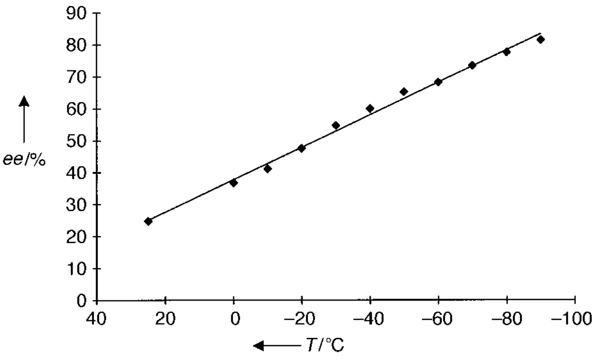


Figure 1. Dependence of the enantioselectivity on the temperature.

The asymmetric reaction was performed with various allylic chlorides **2** and various diorganozinc reagents **3** (Table 1). The reaction of **2b** (entry 2), which contains the electron-withdrawing 4-trifluoromethylphenyl substituent, with **3a** furnishes **4b** with the best enantioselectivity of 87 % *ee* and in 72 % yield. Naphthyl-substituted substrates give a lower stereoselectivity than those with a phenyl group, and provide the products **4c** and **4d** with 70–71 % *ee* (entries 3 and 4). The allyl halide with a cyclohexyl substituent (**2e**) gives the substitution compound **4e** with a similar enantioselectivity as **2a** (entries 1 and 5). The presence of functional groups such as a 3-thienyl ring or a silyl ether at R^1 lowers the enantioselectivity somewhat to 63 and 64 % *ee* (entries 6 and 7). Finally, it was observed that the use of sterically demanding diorganozinc compounds is important for obtaining good asymmetric inductions. Thus, the less reactive bis(trialkylsilylmethyl)zinc compounds **3b** and **3c** give the desired substitution products of **2a** with 42–67 % *ee.* A matched and mismatched stereoselectivity is observed for the reaction of bis(myrtanyl)zinc, which is prepared by hydroboration with Et_2BH[6] of (+)- or (−)-*β*-pinene,[7] leading to two diastereomeric products **4j** and **4k** with 41 and 37 % *ee*, respectively.

We have reported a new copper(I)-catalyzed substitution of unsymmetrical allyl chlorides with diorganozinc compounds using the novel ferrocenyl amine **1d** as chiral ligand. The allylated products are obtained with moderate to good enantioselectivities (up to 87 % *ee*) and excellent S_N2' regioselectivities. We are currently studying the scope of the reaction and further improving the activity of the catalyst.[8]

Experimental Section

1d: A solution of **6d** (4.5 g, 13.2 mmol) in THF (30 mL) and $BH_3 \cdot Me_2S$ (1.4 mL, 14 mmol) were added simultaneously over a period of 30 min to a solution of the CBS catalyst **7** (0.7 g, 2.5 mmol) in THF (80 mL) at 0 °C under argon. After the mixture was stirred for an additional 30 min, it was quenched with aqueous ammonium chloride solution (70 mL). The organic layer was separated, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with pentane/diethyl ether (1/1) as eluent to afford **8d** (4.0 g, 89 %, 99.5% *ee*) as an orange solid (m.p. 117 °C). The ferrocenyl alcohol **8d** (4.0 g, 11.6 mmol) was dissolved in dry pyridine (30 mL) and acetic anhydride (20 mL) at room temperature. After the mixture had been stirred for 18 h at room temperature, all volatile components were removed under high vacuum at 50 °C to furnish the pure acetate **9a** (4.5 g, 100 %) as a red "glue", which crystallized on standing to yield a red solid (m.p. 127 °C). This acetate (3.0 g, 8 mmol) was dissolved in acetonitrile (200 mL) and 37 %

aqueous ammonia solution (40 mL). After the mixture was stirred for 24 h at room temperature, it was poured into 10% aqueous hydrochloric acid (200 mL). The resulting precipitate was removed by filtration and washed with diethyl ether (4 × 20 mL). The residue was dissolved in 20% aqueous sodium hydroxide solution (200 mL), and the desired product was extracted with diethyl ether (3 × 50 mL). After the solution was dried over $MgSO_4$, the solvent was removed under reduced pressure and pure **1d** (1.8 g, 66%) was obtained as an orange solid (m.p. 97 °C).

Enantioselective allylation of **2b** to **4b** (Table 1, entry 2): The ligand **1d** (70 mg, 0.2 mmol) and $CuBr \cdot Me_2S$ (3 mg, 0.02 mmol) were dissolved in THF (5 mL). After the clear solution was cooled to −90 °C, **3a** (0.3 mL, 2.4 mmol) and **2b** (440 mg, 2.0 mmol) were added successively. The reaction mixture was stirred for 18 h at −90 °C and then worked up as usual. The crude residue obtained after evaporation of the solvents was purified by flash chromatography (diethyl ether/pentane 1/50) to provide the desired product **4b** (370 mg, 72% yield; S_N2':S_N2 ratio = 97:3). The enantiomerical excess of the chiral product was determined by gas chromatography (Chiraldex capillary column) to be 87%.

Received: August 27, 1998 [Z12344IE]
German version: *Angew. Chem.* **1999**, *111*, 391–393

Keywords: asymmetric catalysis · copper · ferrocenes · substitutions

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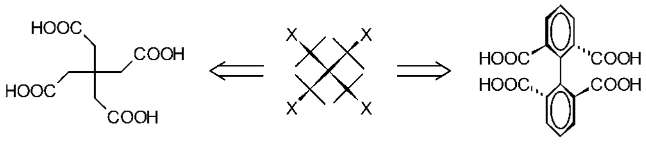
Self-Assembly of 1,1′-Biphenyl-2,2′,6,6′-tetracarboxylic Acid: Formation of an Achiral Grid with Chiral Compartments**

Petr Holý, Jiří Závada,* Ivana Císařová, and
Jaroslav Podlaha

Supramolecular self-assembly is the spontaneous association of molecular subunits (tectons) into structurally well-defined aggregates, which are organized by noncovalent interactions (synthons).[1, 2] The most versatile synthons for the self-assembly of organic tectons are intermolecular hydrogen bonds. Tetrafunctional molecules with tetrahedrally arranged substituents have been investigated in this context and have shown to be endowed with the fascinating faculty of building diamond-like networks,[3] with methanetetraacetic acid **1** being a prototypal example.[4] We are interested in the hydrogen bond driven self-assembly of 2,2′,6,6′-tetrasubstituted biaryls[5, 6] that are topologically related to the tetrasubstituted methanes. For example, if we stretch the D_{2d} symmetry conformer of the tecton **1** along its axis a framework of 1,1′-biphenyl-2,2′,6,6′-tetracarboxylic acid (**2**) gradually (on further elaboration) emerges (Scheme 1).



1 **2**

Scheme 1. Stereochemical correlation of tectons **1** and **2.**

Consideration of models that use a double hydrogen bond as the synthon suggests that the self-assembling properties of the two topologically related tectons **1** and **2** should be entirely different. In contrast to the intrinsic propensity of the tetrahedral tecton **1** to form chairlike distorted cyclohexamers that underlie the three-dimensional diamondoid network,[3, 4] the biaryl tecton **2** should prefer to undergo cyclotetramerization and result ultimately in a unilayered "square" grid (Figure 1).

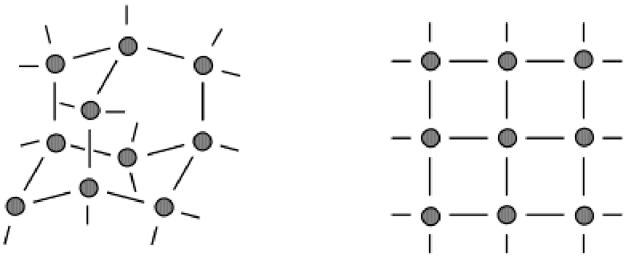


Figure 1. Schematic representation of diamondoid and square grids.

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[*] Dr. J. Závada, P. Holý
Institute of Organic Chemistry and Biochemistry
Academy of Sciences of the Czech Republic
16610 Prague 6 (Czech Republic)
Fax: (+420)2-3111733
E-mail: zavada@uochb.cas.cz

I. Císařová, J. Podlaha
Charles-University, Department of Inorganic Chemistry
12840 Prague 2 (Czech Republic)

[**] The financial support by the Grant Agency of the Czech Republic (grants no. 203/97/0025 and 203/96/0111) is gratefully acknowledged.