Angewandte Chemie

DOI: 10.1002/ange.200801501

Asymmetric Catalysis

$[Ru(phgly)_2(binap)]/Li_2CO_3$: A Highly Active, Robust, and Enantioselective Catalyst for the Cyanosilylation of Aldehydes**

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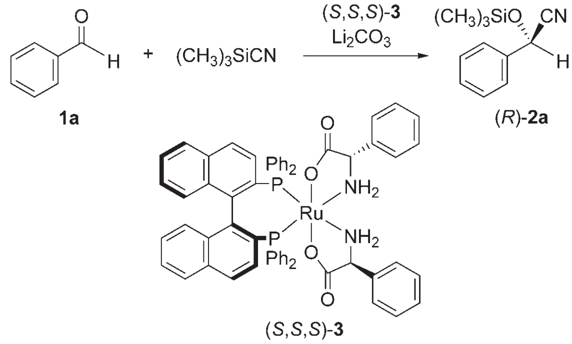
The enantioselective cyanosilylation of aldehydes is one of the most efficient and general methods for producing optically active cyanohydrin derivatives, which can be readily converted into biologically important compounds, including β-amino alcohols and α-hydroxycarboxylic acid derivatives.[1] A variety of chirally modified catalysts have been utilized for this asymmetric transformation, and some of them have achieved high enantioselectivity.[1,2] However, the development of a highly active and robust chiral catalyst for this reaction is challenging.

We and other research groups have reported that simple lithium salts, such as LiCl,[3] $LiClO_4$,[4] and lithium alkoxides,[5] show high catalytic activity for the cyanosilylation of carbonyl compounds. We expected that the combination of a lithium salt and a metal complex with appropriate chiral ligands would form an efficient catalyst system for this asymmetric reaction. Herein we disclose a highly active, robust, and enantioselective catalyst consisting of $[Ru(phgly)_2(binap)]$ (phgly = phenylglycinate, binap = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl) and Li_2CO_3 for the cyanosilylation of aldehydes. The reaction is conducted with a substrate-to-catalyst ratio (S/C) of 10000:1 at −78 to −70 °C, and 100000:1 at −40 °C. A series of aromatic, aliphatic, and α,β-unsaturated aldehydes can be converted into silylated cyanohydrins in up to 98 % *ee* by using this system.

[Ru{(*S*)-PhGly}$_2${(*S*)-binap}] ((*S,S,S*)-**3**; Scheme 1)[6] was isolated in 74 % yield by treatment of [RuCl$_2${(*S*)-binap}(dmf)]$_n$ (oligomeric form)[7] and 3.0 equivalents of the (*S*)-PhGly sodium salt in a DMF/CH_3OH mixed solvent at 25 °C for 12 h (see the Experimental Section). This complex was so robust that it could be purified by chromatography on silica gel in air, and could be stored in a vial at room temperature. The $^{31}P\{^1H\}$ NMR spectrum of (*S,S,S*)-**3** in $CDCl_3$ shows a singlet at $\delta = 52.3$ ppm, which indicates a *trans*-$Ru(OCOR)_2$ geometry.[8,9]



Scheme 1. Asymmetric cyanosilylation of banzaldehyde (**1a**).

When benzaldehyde (**1a**; 1.05 g, 9.9 mmol) and $(CH_3)_3SiCN$ (1.19 g, 12.0 mmol) were treated with (*S,S,S*)-**3** (20 mM in THF, 50 μL, 1.0 μmol, S/C 10000:1) and aqueous Li_2CO_3 (0.10 M, 10 μL, 1.0 μmol) at −78 °C in $(C_2H_5)_2O$ (10 mL) for 12 h, the *R* cyanation product (*R*)-**2a** was obtained quantitatively with 97 % *ee* (Scheme 1 and Table 1, entry 1). A 1:1 ratio of complex **3** and Li_2CO_3 gave the best catalyst performance. The enantioselectivity was slightly lower when the reaction was conducted with a **3**/Li_2CO_3 ratio of 1:2 (Table 1, entry 2). The reaction rate was slower when the proportion of Li_2CO_3 was reduced (Table 1, entries 3 and 4). The Ru complex **3** alone was a poor catalyst for the reaction under the standard conditions (Table 1, entry 5), while Li_2CO_3 showed medium catalytic activity and gave racemic **2a** (Table 1, entry 6).[10] When the less Lewis basic salt LiCl or LiOTf was used instead of Li_2CO_3 (**1a**/**3**/Li salt 10000:1:1 or 10000:1:2), **2a** was obtained in less than 3 %

Table 1: Asymmetric cyanosilylation of benzaldehyde (**1a**).[a]

Entry	**1a**/**3**/Li_2CO_3	Solvent	Yield [%][b]	*ee* [%][b]
1	10000:1:1	Et_2O	> 99	97
2	10000:1:2	Et_2O	> 99	95
3	10000:1:0.5	Et_2O	98	97
4	10000:1:0.2	Et_2O	9	98
5	10000:1:0	Et_2O	< 1	n.d.[c]
6	10000:0:1	Et_2O	47	–
7	10000:1:1	*t*BuOMe	> 99	94
8	10000:1:1	THF	38	39
9	10000:1:1	toluene	84	88
10	10000:1:1	CH_2Cl_2	84	88

[a] Unless otherwise stated, reactions were conducted using **1a** (9.9–10.0 mmol) and $(CH_3)_3SiCN$ (12.0 mmol) in solvent (10 mL) with (*S,S,S*)-**3** (20 mM in THF) and aqueous Li_2CO_3 (0.1 M) at −78 °C for 12 h. [b] Data for (*R*)-**2a** were determined by GC analysis on a chiral stationary phase. [c] Not determined.

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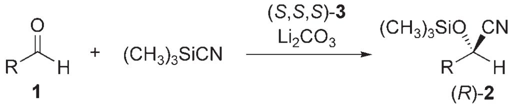
[**] This work was supported by Grants-in-Aid from the Japan Society for the Promotion of Science (JSPS) (No. 18350046) and the Innovation Plaza Hokkaido in the Japan Science and Technology Agency (JST). phgly = phenylglycinate, binap = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200801501.

yield. These results clearly indicate that the combination of **3** and Li_2CO_3 generates a new highly active catalyst for this asymmetric transformation. Similarly reactivity was observed on using $tC_4H_9OCH_3$ as the solvent under conditions otherwise identical to those shown in Table 1, entry 1, and afforded (*R*)-**2a** in 94 % *ee* (Table 1, entry 7). Interestingly, both the reactivity and the enantioselectivity were significantly lower in THF (Table 1, entry 8). The use of toluene or dichloromethane, which are typical solvents for cyanosilylations,[1,2] gave lower yields and enantioselectivities than reactions in $(C_2H_5)_2O$ (Table 1, entries 9 and 10).

A series of aromatic, aliphatic, and α,β-unsaturated aldehydes were converted quantitatively into the cyanohydrin silyl ethers in high enantioselectivity with an S/C ratio of 10000:1 (Scheme 2). The reaction of benzaldehyde (**1a**) and 1.2 equivalents of $(CH_3)_3SiCN$ in $(C_2H_5)_2O$ at −78 °C in the presence of (*S*,*S*,*S*)-**3** and Li_2CO_3 (**3**/Li_2CO_3 1:1) was complete in 12 h. The silylated cyanohydrin (*R*)-**2a** was readily isolated in 98 % yield and 97 % *ee*, without aqueous workup, simply by concentration of the mixture and a short-path distillation (Table 2; see the Experimental Section). The high catalytic activity of the (*S*,*S*,*S*)-**3**/Li_2CO_3 system resulted in complete conversion when an S/C ratio of 100000:1 was used at −40 °C over 24 h, and gave the *R* product with 90 % *ee*. The reaction of 2-methylbenzaldehyde (**1b**) gave a comparable enantioselectivity of 96 %. Substitution at the C2-position of the aldehydes with F or Cl atoms (**1c** and **1d**) did not significantly affect the enantioselectivity. The cyanation of 3-methylbenzaldehyde (**1e**) was conducted at −70 °C because of its low reactivity, but the desired product (*R*)-**2e** was obtained in high enantioselectivity. A high *ee* value of 98 % was achieved in the cyanation of substrates with Cl or Br atoms at the C3-position (**1f** and **1g**). The reaction of a benzaldehyde with an electron-donating methoxy group at the C3-position (**1h**) at −70 °C and an S/C ratio of 10000:1 required 24 hours for completion, and afforded (*R*)-**2h** with 95 % *ee*. 4-Methyl- and 4-chloro-substituted aldehydes **1i** and **1j** were converted into the *R* products with 97 % *ee*. The electron-deficient 4-CF_3-substituted aldehyde **1k** showed high reactivity, although the enantioselectivity was somewhat lower. A substrate with an electron-donating methoxy group at the C4-position (**1l**) was converted at −70 °C quantitatively into (*R*)-**2l** with 96 % *ee* after 24 hours. 1-Naphthaldehyde (**1m**) was also a good substrate, and afforded (*R*)-**2m** with 95 % *ee*. The cyanation was applicable to heteroaromatic aldehydes: 2-furancarbaldehyde (**1n**) and 3-pyridinecarbaldehyde (**1o**) were converted into the *R* products with 93 % *ee*.



a: R = C_6H_5	**k**: R = 4-$CF_3C_6H_4$
b: R = 2-$CH_3C_6H_4$	**l**: R = 4-$CH_3OC_6H_4$
c: R = 2-FC_6H_4	**m**: R = 1-naphthyl
d: R = 2-ClC_6H_4	**n**: R = 2-furyl
e: R = 3-$CH_3C_6H_4$	**o**: R = 3-pyridyl
f: R = 3-ClC_6H_4	**p**: R = tC_4H_9
g: R = 3-BrC_6H_4	**q**: R = cyclo-C_6H_{11}
h: R = 3-$CH_3OC_6H_4$	**r**: R = nC_6H_{13}
i: R = 4-$CH_3C_6H_4$	**s**: R = (*E*)-$C_6H_5CH_2$=CH
j: R = 4-ClC_6H_4	**t**: R = 1-cyclohexenyl

Scheme 2. Asymmetric cyanosilylation of aldehydes **1**.

Table 2: Asymmetric cyanosilylation of aldehydes.[a]

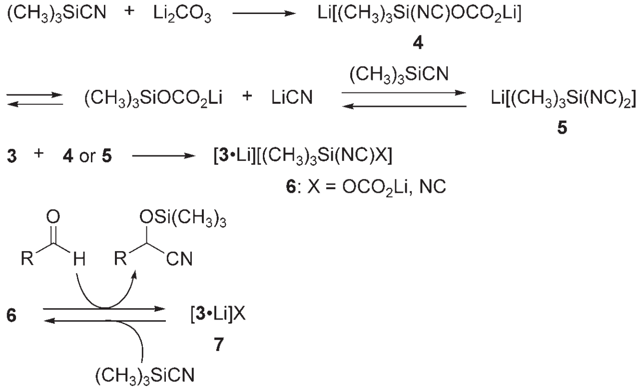
1	Solvent	S/C[b]	*T* [°C]	*t* [h]	Yield [%][c]	*ee* [%][d]
1a	Et_2O	10000:1	−78	12	98	97
1a[e]	Et_2O	100000:1	−40	24	94	90
1b	Et_2O	10000:1	−78	18	99	96
1c[f]	Et_2O	10000:1	−78	12	97	96
1d[f]	Et_2O	10000:1	−78	12	97	94
1e	Et_2O	10000:1	−70	12	99	97
1f[f]	Et_2O	10000:1	−78	12	98	98
1g[f]	Et_2O	10000:1	−78	12	98	98
1h	Et_2O	10000:1	−70	24	97	95
1i	Et_2O	10000:1	−70	24	95	97
1j[f]	Et_2O	10000:1	−70	12	96	97
1k[f]	Et_2O	10000:1	−78	12	98	94
1l	Et_2O	10000:1	−70	24	99	96
1m	Et_2O	10000:1	−70	18	97	95
1n	Et_2O	10000:1	−70	18	97	93
1o	Et_2O	10000:1	−78	18	91[g]	93
1p	Et_2O	10000:1	−78	18	94	93
1p	*t*BuOMe	10000:1	−78	18	92	95
1q	*t*BuOMe	10000:1	−78	18	97	88
1r	*t*BuOMe	10000:1	−78	18	98	70
1s	*t*BuOMe	10000:1	−78	18	93	91
1t	*t*BuOMe	10000:1	−70	18	92	93

[a] Unless otherwise stated, reactions were conducted using **1** (9.7–10.6 mmol) and $(CH_3)_3SiCN$ (12.0 mmol) in solvent (10 mL) with (*S*,*S*,*S*)-**3** (20 mM in THF) and aqueous Li_2CO_3 (0.1 M); **3**/Li_2CO_3 1:1. [b] Substrate-to-catalyst (**3**) ratio. [c] Yield of isolated (*R*)-**2**. Yields determined by GC analysis were >99 % in all cases. [d] Data for (*R*)-**2** were determined by GC analysis on a chiral stationary phase. [e] Reaction using 50.7 mmol (5.38 g) **1a** in 50 mL of $(C_2H_5)_2O$. [f] Reaction in 20 mL of solvent. [g] Yield after deprotection.

Interestingly, the cyanation of aliphatic aldehydes showed higher enantioselectivity in $tC_4H_9OCH_3$ than in $(C_2H_5)_2O$. Thus, pivalaldehyde (**1p**), a tertiary alkyl aldehyde, was converted into (*R*)-**2p** with 95 % *ee* in $tC_4H_9OCH_3$, and with 93 % *ee* in $(C_2H_5)_2O$ (Table 2). The sense of enantioselection was the same as that of the reaction of **1a**. The reaction of cyclohexanecarbaldehyde (**1q**) gave a high enantioselectivity of 88 %, although *n*-heptanal (**1r**) was converted into **2r** in only 70 % *ee*.[11] The cyanation of cinnamaldehyde (**1s**) afforded the 1,2-adduct (*R*)-**2s** in 93 % yield and 91 % *ee*. An even better enantioselectivity of 93 % *ee* was achieved in the reaction of 1-cyclohexenecarbaldehyde (**1t**).

ESI mass-spectrometric analysis of a mixture of the Ru complex **3** (*m*/*z* 1024), aqueous Li_2CO_3 (0.1 M; **3**/Li_2CO_3 1:1), and an excess amount of $(CH_3)_3SiCN$ showed prominent signals centered at *m*/*z* 1031, which correspond to the Ru-Li bimetallic species $[\mathbf{3}\cdot Li]^+$, and a decrease in the intensity of the signals of **3** (see the Supporting Information). ^1H NMR analysis ($[D_8]$THF) of this mixture also suggested the formation of the $[\mathbf{3}\cdot Li]^+$ species. The signal for the PhGly benzylic protons of **3**, which appear at $\delta = 3.94$ ppm in the absence of Li_2CO_3, was shifted to $\delta = 4.15$ ppm. A Li cation might be held between two PhGly phenyl rings of **3** through a cation–π interaction.[12]

A plausible mechanism is shown in Scheme 3 (nonproductive and minor pathways are not considered). The reaction of $(CH_3)_3SiCN$ and Li_2CO_3 is expected to give the pentacoordinated Si species **4**, since the less Lewis basic salts LiCl and LiOTf promote the cyanation only to a small extent. In the presence of an excess amount of $(CH_3)_3SiCN$, the formation of another pentavalent Si compound **5** is possible from the reaction of $(CH_3)_3SiCN$ with LiCN; **5** is reversibly released from the **4**. The Ru complex **3** and the Li salt **4** or **5** then form a chiral [**3**·Li] species **6**. The $[\mathbf{3}\cdot Li]^+$ ion acts as an efficient chiral Lewis acid, while the nucleophilic $[(CH_3)_3Si(NC)X]^-$ ion ($X = OCO_2Li$, NC) donates CN^- ions effectively.[13] Thus, the chiral compound **6** reacts smoothly with an aldehyde to afford a cyanohydrin silyl ether and a chiral salt **7**,[14] which readily reacts with $(CH_3)_3SiCN$ to regenerate **6**.



Scheme 3. Plausible mechanism for the cycnosilylation of aldehydes.

In summary, we have reported the highly reactive and enantioselective cyanosilylation of aldehydes that is catalyzed by a new $[Ru(phgly)_2(binap)]/Li_2CO_3$ system. The combination of a chiral Ru complex and the Li salt is crucial to achieve high catalytic activity. The reaction can be carried out with an S/C ratio as high as 100000:1. A series of aromatic, aliphatic, and α,β-unsaturated aldehydes were converted into the silylated cyanohydrins with up to 98% *ee*. The high activity and robustness of the catalyst system are notable, although the low reaction temperature (−78 to −70 °C) is a disadvan tage from a practical viewpoint. The ESIMS and NMR measurements suggest the formation of an active chiral Ru-Li bimetallic complex in the reaction system. The detailed reaction mechanism is currently being studied.

Experimental Section

Preparation of (*S,S,S*)-**3**: $[\{RuCl_2(benzene)\}_2]$ (258 mg, 0.52 mmol) and (*S*)-binap (661 mg, 1.06 mmol) were placed in a 100 mL Schlenk flask. After replacing the air in the flask with argon, degassed DMF (15 mL) was added, and the mixture was heated at 100 °C for 10 min with stirring to give a reddish brown solution.[7] After the solution had cooled to 25 °C, a degassed solution of sodium (*S*)-phenylglycinate (533 mg, 3.08 mmol) in CH_3OH (30 mL) was added and the mixture was stirred for 12 h. Water (50 mL) was added to the solution to precipitate a yellowish orange solid. The collected precipitates were dissolved in CH_2Cl_2 (40 mL), washed with water (50 mL × 3), and dried over $MgSO_4$. After filtration and removal of the solvent, the residue was purified by preparative TLC (silica gel, eluent: ethyl acetate, $R_f = 0.45$–0.61). A further precipitation with a mixture of CH_2Cl_2 (10 mL) and pentane (100 mL) afforded (*S,S,S*)-**3** (light yellow powder, 787 mg, 74%). M.p 223 °C (decomp); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.45$ (brs, 2H, N*H*H), 3.23 (brs, 2H, NH*H*), 3.63 (t, 2H, $J = 8.3$ Hz, 2PhC*H*), 6.24 (d, 2H, $J = 9.3$ Hz, ArH), 6.50 (m, 6H, ArH), 6.71 (m, 6H, ArH), 7.07–7.67 (m, 24H, ArH), 8.06 ppm (m, 4H, ArH); ^{31}P NMR (161.7 MHz, $CDCl_3$): $\delta = 52.3$ ppm (s); HRMS (ESI): *m/z* calcd for $C_{60}H_{48}N_2O_4P_2Ru$: 1024.21494 $[M]^+$; found: 1024.21231.

General procedure for the cyanosilylation of aldehydes: **Caution**: $(CH_3)_3SiCN$ must be used in a well-ventilated hood because of its high toxicity. $(CH_3)_3SiCN$ (1.19 g, 12.0 mmol) and aqueous Li_2CO_3 (0.10 M, 10 μL, 1.0 μmol) were placed in a 40 mL Schlenk flask in an Ar atmosphere, and the mixture was stirred for 20 min at 25 °C. $(C_2H_5)_2O$ (10 mL) and (*S,S,S*)-**3** (20 mM in THF, 50 μL, 1.0 μmol) were added to the pale yellow solution, and the mixture was stirred for 30 min. The resulting yellow solution was cooled down to −78 °C, and then **1a** (1.05 g, 9.9 mmol) was added, and the mixture was stirred for 12 h. After evaporation of the solvent and the volatile compounds under reduced pressure at ambient temperature, the residue was purified by a short-path distillation to give (*R*)-**2a** (colorless oil, 1.99 g, 98%, 97% *ee*). B.p. 68 °C/0.08 mmHg; $[\alpha]_D^{23} = +28.4\ \mathrm{deg\,cm^3\,g^{-1}\,dm^{-1}}$ ($c = 1.12\ \mathrm{g\,cm^{-3}}$, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.23$ (s, 9H, $Si(CH_3)_3$), 5.50 (s, 1H, CHCN), 7.37–7.50 ppm (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -0.3$, 63.9, 119.2, 126.3, 128.9, 129.3, 136.2 ppm; HRMS (EI): *m/z* calcd for $C_{11}H_{15}NOSi$: 205.0923 $[M]^+$; found: 205.0931. The *ee* value of **2a** was determined by GC analysis: column, CP-Chirasil-Dex (0.32 mm × 25 m, depth of film = 0.25 μm, Varian); carrier gas: helium (72.0 kPa); column temp.: 110 °C; injection temp.: 220 °C; retention time (t_R) of (*R*)-**2a**: 14.7 min (98.4%), t_R of (*S*)-**2a**: 14.3 min (1.6%). The absolute configuration was determined after conversion into 2-hydroxy-2-phenylacetonitrile. $[\alpha]_D^{25} = +45.4\ \mathrm{deg\,cm^3\,g^{-1}\,dm^{-1}}$ ($c = 1.40\ \mathrm{g\,cm^{-3}}$, $CHCl_3$); lit.[2c] $[\alpha]_D^{24} = +36.8\ \mathrm{deg\,cm^3\,g^{-1}\,dm^{-1}}$ ($c = 2.0\ \mathrm{g\,cm^{-3}}$, $CHCl_3$), 85% *ee* (*R*).

Received: March 31, 2008

Keywords: aldehydes · asymmetric catalysis · cyanosilylation · lithium · ruthenium

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[13] [(CH$_3$)$_3$Si(NC)$_2$]$^-$ is known as an efficient CN$^-$ donor, see: a) D. A. Dixon, W. R. Hertler, D. B. Chase, W. B. Farnham, F. Davidson, *Inorg. Chem.* **1988**, *27*, 4012 – 4018; b) M. B. Sassaman, G. K. S. Prakash, G. A. Olah, *J. Org. Chem.* **1990**, *55*, 2016 – 2018.

[14] The catalyst system showed a tendency to give high enantioselectivity at lower concentrations (higher S/C ratios; see the Supporting Information). Weak positive nonlinear effects were also observed. These observations suggest that the catalytic species is monomeric, although weakly interacting dimeric or oligomeric structures also exist. For nonlinear effects, see: a) C. Girard, H. B. Kagan, *Angew. Chem.* **1998**, *110*, 3088 – 3127; *Angew. Chem. Int. Ed.* **1998**, *37*, 2922 – 2959; b) D. R. Fenwick, H. B. Kagan, *Top. Stereochem.* **1999**, *22*, 257 – 296.