afforded by xenon, and oxygen was used for reionization. The CA/CA mass spectrum of $[C,Si,Cl]^+$ was obtained by daughter ion selection with B2, and recording the subsequent fragmentations by scanning E(2).[21c] All spectra were accumulated and on-line processed with the AMD/Intectra data system; in general 5 to 50 spectra were averaged to improve the signal-to-noise ratio.

[21] a) R. Srinivas, D. Sülzle, T. Weiske, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 368; b) R. Srinivas, D. Sülzle, W. Koch, C. H. DePuy, H. Schwarz, *J. Am. Chem. Soc.* **1991**, *113*, 5970; c) D. Schröder, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1995**, *146/147*, 183; d) C. A. Schalley, D. Schröder, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1996**, *153*, 173.

[22] A. E. Newkirk, *J. Am. Chem. Soc.* **1946**, *68*, 2736.

[23] In analogy, photolysis of **4** (X = Cl) has been speculated to yield neutral **1c**, see ref. [7].

[24] For a definition and examples for distonic ions: R. L. Smith, P. K. Chou, H. I. Kenttämaa in *The Structure and Dynamics of Organic Ions* (Eds.: T. Baer, C. Y. Ng), Wiley, London, **1996**, p. 197.

[25] According to the experimental data in ref. [19a], the preference for SiF^+ formation is only 16 kcal mol^{-1}. However, we trust our calculated value of 26.9 kcal mol^{-1}. A similar discrepancy between calculated and experimental energetics of SiF^+ was reported earlier, see: E. W. Ignacio, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 7439.

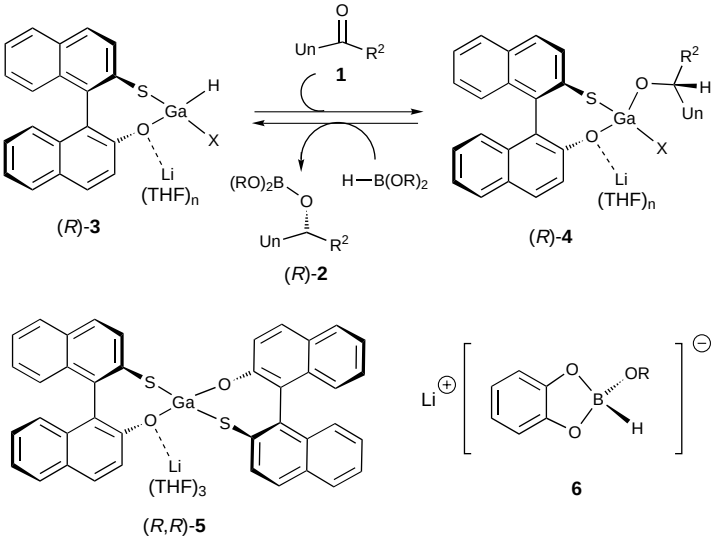
[26] While the fragmentations of $[Si,C,Cl]^+$ leading to $[SiCl^+ + C]$ and to $[Si^+ + CCl]$ may also be attributed to the mere energetic preference of these exit channels ($\Sigma\Delta H_f^0 = 386$ and 388 kcal mol^{-1}, respectively), compared to those for the formation of $[SiC^+ + Cl]$ ($\Sigma\Delta H_f^0 =$ 416 kcal mol^{-1}) or $[Si + CCl^+]$ ($\Sigma\Delta H_f^0 = 405$ kcal mol^{-1}), of the higher energy channels only SiC^+ is observed experimentally, but not the lower energy fragment CCl^+; data taken from refs. [19a,b,27].

[27] A. E. Ketvirtis, D. K. Bohme, A. C. Hopkinson, *J. Phys. Chem.* **1995**, *99*, 16121.

Catalytic Enantioselective Reduction of Ketones by a Chiral Gallium Complex and Catecholborane**

Alan Ford and Simon Woodward*

Practical catalytic reduction of prochiral ketones to secondary alcohols of high enantiopurity is indispensable to many organic preparations. Oxazaborolidine-catalyzed BH_3 reduction[1] and ruthenium-catalyzed transfer hydrogenation[2] are effective for the reduction of $R^1C(O)R^2$ **1** provided an appropriate difference, steric or electronic, exists between the groups. As steric differences cannot always be realized, alternative catalysts that sense electronic differences between the groups in addition to steric requirements are highly desirable. In a seminal paper Noyori described the use of [LiAlH(OEt)(BINOL dianion)] (BINOL = 2,2′dihydroxy-1,1′-binaphthyl) in stoichiometric amounts to effect an electronically controlled hydride addition to **1** (R^1 = unsaturated unit, R^2 = alkyl).[3] We have used the principles of "hard" and "soft"[4] Lewis acids and bases to attempt a catalytic analogue of this reagent. Monothiobinaphthol (MTB)[5] and $LiGaH_4$[6] were selected as the "soft" ligand/catalyst combination and catecholborane as a "hard" terminal hydride source to promote only the removal of alkoxide products and not the chiral ligand from **4** (Scheme 1). While a



Scheme 1. Reduction of ketone **1** with a complex of MTB and LiGaH4 (Un = unsaturated unit) as well as with the complex **5** and the borate **6**.

range of spectator ligands gave moderate selectivities (X = OMe (72% *ee*), 2-S-$C_{10}H_7$ (72% *ee*), 1,2-$HOCH_2CH_2SH$ (24% *ee*)), a mixture of $LiGaH_4$ and two MTB ligands proved particularly effective for a range of ketones (Table 1); the mixture was characterized in the solid state as **5**, which is isostructural with the gallium–BINOL catalysts of Shibasaki.[7]

These reactions are technically simple, stirring the reaction is not essential and any cryostat or even a domestic freezer suffices for cooling. At catalyst loadings below 2.5 mol% the enantioselectivity falls: At 1 mol% (−25 °C) **1a** is reduced in 86% *ee* and with 0.5 mol% (0 °C) in 72% *ee*. Pre-storage of solutions of $LiGaH_4$/2MTB at ambient temperature for two

Table 1. Enantioselective reduction of ketones **1** by **5** (2.5 mol%) and catecholborane (1.1 equiv) by method B (see experimental section, unless otherwise stated).

Ketone	R^1	R^2	Yield [%]	*ee* [%]
a	Ph	Me	89–95[a]	89–91[a]
b	Ph	Et	96	93
c	Ph	*n*Bu	80	92
d	Ph	*i*Bu	65	92
e	4-BrPh	Me	80	87
f	4-MePh	Me	95	87
g	2-furyl	*n*-C_6H_{13}	76	81
h	PhCH=CH	Me	70	75
i	EtC≡C	Me	60	63

[a] Using methods A–C.

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

weeks did not affect the *ee* value for the reduction of **1a**, neither did deliberate addition of water to the reaction (one equivalent per Ga, to simulate impure "wet" ketones).

The enantioselectivity in the reduction of **1a** shows an unusual temperature dependence: a maximum *ee* value is attained at -20 to $-15\,^{\circ}C$, both the chemical yield and *ee* value decrease steadily at temperatures below this range. At $-78\,^{\circ}C$ an 18% yield of racemic alcohol is realized. One explanation of this behavior is that transmetalation of **4** to **3** (X = MTB dianion) is slow below $-20\,^{\circ}C$ and that an achiral catalytic process begins to compete. Support for this hypothesis comes from the observation that added lithium alkoxides do catalyze catecholborane reduction of **1a** via the borate **6**.[8] The use of the MTB ligand is vital to the reaction; $LiGaH_4$ with either 1,1′-bi(2-naphthol) or 1,1′-bi(2-thionaphthol) leads to low selectivities (3–34% *ee*). The probable causes are decomplexation of the chiral ligand by catecholborane and poor lithium coordination. Both the presence of **6** and removal of the chiral ligand may account, in part, for the lower enantioselectivities encountered in some recent titanium work.[9]

The solid-state structure of the pre-catalyst **5**[7] is not retained in solution during the catalysis. The new species formed are currently still under investigation. However, the absence of a nonlinear effect[10] in the reduction of **1a** by **5** suggests that a mononuclear catalyst with a single active MTB ligand is responsible for the enantioselection. In Noyori's BINAL reagent[3] the (R_a)-ligand gives the (*R*)-alcohol because of repulsion between the n electrons of the reagent and the π electrons of the substrate. The similarity in the *ee* value for the reduction of **1a–d** suggests a related electronic control with **5**, but steric factors cannot be ruled out.

Experimental Section

All operations were performed under argon. A solution of MTB (15 mg, 0.05 mmol) in THF (5 mL) was treated with $LiGaH_4$ (100 μL of a 0.25 M solution in Et_2O) and the mixture stirred (20 °C, 25 min). The reaction was cooled to $-20\,^{\circ}C$ and catecholborane (1.1 mL of a 1 M THF solution, 1.1 mmol) and ketone (1.0 mmol) were added. The solution was stirred at $-20\,^{\circ}C$ for 18 h (method A), or sealed and stored at $-20\,^{\circ}C$ (method B; $-15\,^{\circ}C$ and 4 mol% catalyst for **1d**). Alternatively, the catecholborane and ketone were added at $-78\,^{\circ}C$ and the reaction mixture stirred as it warmed to room temperature overnight (method C). Normal workup procedures afforded the alcohols **2** as essentially single products (the *ee* values were determined by gas chromatography on a chiral column (LIPODEX A or CYCLODEX B) or the α-methoxy-α-(trifluoromethyl)phenyl acetate analyzed for the alcohol of **1h**).

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[1] a) Review: E. J. Corey, C. J. Helal, *Angew. Chem.* **1998**, *110*, 2092–2118; *Angew. Chem. Int. Ed.* **1998**, *37*, 1987–2012; b) E. J. Corey, R. K. Bakshi, S. Shibata, C.-P. Chen, V. K. Singh, *J. Am. Chem. Soc.* **1987**, *109*, 7925–7926.
[2] Review: R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97–102.
[3] R. Noyori, I. Tomino, Y. Tanimoto, M. Nishizawa, *J. Am. Chem. Soc.* **1984**, *106*, 6709–6716.
[4] R. G. Pearson, *Coord. Chem. Rev.* **1990**, *100*, 403–425.
[5] S. M. Azad, S. M. W. Bennett, S. M. Brown, J. Green, E. Sinn, C. M. Topping, S. Woodward, *J. Chem. Soc. Perkin Trans 1* **1997**, 687–694.
[6] A. E. Shirk, D. F. Shriver, *Inorg. Synth.* **1977**, *17*, 45–47.
[7] Data for structure **5** are given in the supporting information. BINOL analogues are known, see a) M. Shibasaki, H. Sasai, T. Arai, *Angew. Chem.* **1997**, *109*, 1290–1310; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1237–1256; b) T. Iida, N. Yamamoto, H. Sasai, M. Shibasaki, *J. Am. Chem. Soc.* **1997**, *119*, 4783–84; c) T. Iida, N. Yamamoto, S. Matsunaga, H.-G. Woo, M. Shibasaki, *Angew. Chem.* **1998**, *110*, 2383–2386; *Angew. Chem. Int. Ed.* **1998**, *37*, 2223–2226.
[8] For related chemistry, see a) C. W. Lindsley, M. DiMare, *Tetrahedron Lett.* **1994**, *35*, 5141–5144; b) A. Arase, M. Hoshi, T. Yamaki, H. Nakanishi, *J. Chem. Soc. Chem. Commun.* **1994**, 855–856.
[9] a) G. Giffels, C. Dreisbach, U. Kragl, M. Weigerding, H. Waldmann, C. Wandrey, *Angew. Chem.* **1995**, *107*, 2165–2166; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2005–2006; b) F. Almqvist, L. Torstensson, A. Gudmundsson, T. Frejd, *Angew. Chem.* **1997**, *109*, 388–389; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 376–377.
[10] a) Review: C. Girard, H. B. Kagan, *Angew. Chem.* **1998**, *110*, 3088–3127; *Angew. Chem. Int. Ed.* **1998**, *37*, 2922–2959; b) D. G. Blackmond, *J. Am. Chem. Soc.* **1997**, *119*, 12934–12937; c) D. Guillaneux, S. H. Zhao, O. Samuel, D. Rainford, H. B. Kagan, *J. Am. Chem. Soc.* **1994**, *116*, 9430–9439.

Hydroformylation of Internal Olefins to Linear Aldehydes with Novel Rhodium Catalysts**

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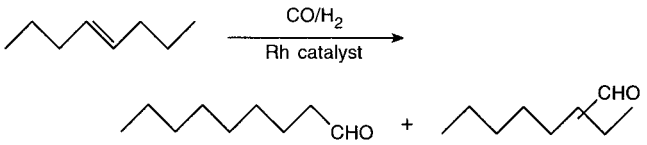
Hydroformylation is one of the world's largest homogeneously catalyzed processes in industry, which produces more than six million tons of aldehydes and alcohols annually.[1] Since linear aldehydes are the most desired products a key issue in this process is the control of regiochemistry. High selectivities in the hydroformylation of terminal alkenes have been reported for both diphosphites and diphosphanes.[2] Selective hydroformylation of internal alkenes, which is of great interest in industry and in synthetic organic chemistry, on the other hand is still a relatively unexplored terrain (Scheme 1).



Scheme 1. The hydroformylation of *trans*-4-octene to linear and branched aldehydes.

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