Nitroaldol Reaction

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A Heterobimetallic Pd/La/Schiff Base Complex for *anti*-Selective Catalytic Asymmetric Nitroaldol Reactions and Applications to Short Syntheses of β-Adrenoceptor Agonists**

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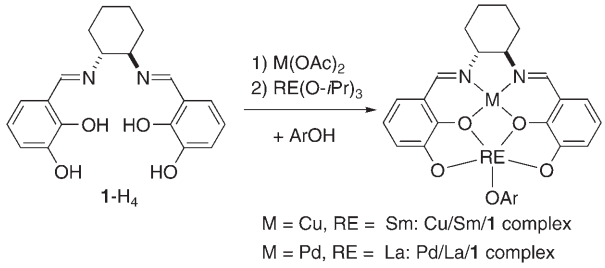
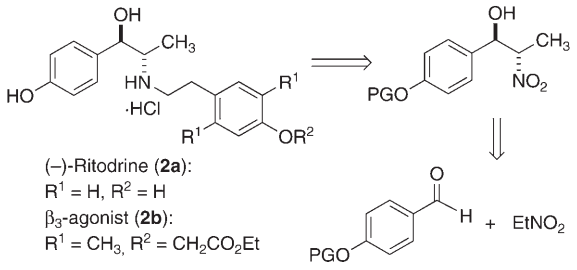
Chiral β-amino alcohols are useful building blocks found in various biologically active natural products, pharmaceuticals, chiral auxiliaries, and chiral ligands.[1] Various methods for catalytic enantioselective synthesis of β-amino alcohols have been developed over the past decade,[2] and the catalytic asymmetric nitroaldol (Henry) reaction is an efficient method for providing β-amino alcohols by reduction of the nitro moiety in nitroaldol adducts.[3] Since our first report of the catalytic asymmetric nitroaldol reaction,[4] various chiral catalysts, which are effective with nitromethane as a donor, have been developed.[5] However, diastereo- and enantioselective nitroaldol reactions that use nitroethane and other nitroalkanes as donors are limited. To realize direct nitroaldol reactions, chiral Brønsted base catalysts could deprotonate the α proton of the nitroalkane to generate a metal nitronate, but epimerization of the products must be prevented to achieve high diastereoselectivity under kinetic control. *Syn*-selective asymmetric reactions have been established by our group and others;[6] but *anti*-selective asymmetric reactions required pre-activation of nitroalkanes to silylnitronates[7] to avoid basic conditions. Therefore, a new catalyst for *anti*-selective asymmetric nitroaldol reactions for direct use with nitroalkanes is needed in terms of atom economy.[8] Quite recently, Ooi and co-workers[9] reported an elegant chiral *P*-spiro triaminoiminophosphorane catalyst for the first direct nitroaldol reaction with excellent *anti* selectivity, enantioselectivity, and broad substrate generality.[10–11] Considering the importance of *anti* amino alcohols as precursors for various important pharmaceuticals such as β-adrenoceptor agonists, additional studies of the *anti*-selective reactions are desirable. Herein, we report a new heterobimetallic Pd/La/**1** complex (Scheme 1) for *anti*-selective nitroaldol reactions, and its application to short syntheses of β-adrenoceptor agonists **2a**·HCl (ritodrine·HCl) and **2b**·HCl.



Scheme 1. Dinucleating (*R*,*R*)-Schiff base ligand **1**-H_4 and the proposed structures of heterobimetallic Cu/Sm/(*R*,*R*)-**1** and Pd/La/(*R*,*R*)-**1** complexes with an ArOH additive.

2a·HCl is a selective β_2-adrenoceptor agonist, clinically used for the prevention of pre-term birth (Scheme 2),[12] and related compound **2b**·HCl is a selective β_3-adrenoceptor agonist that provides a new therapeutic for urinary dysfunction.[13] The common chiral *anti* β-amino alcohol unit (4′-hydroxynorephedrine) in both drugs is key for high biological activity, and we anticipated the *anti*-nitroaldol reaction to be one of the most straightforward methods for constructing two contiguous stereocenters in the common unit (Scheme 2). **2a** and **2b** could be synthesized by reduction of the nitro group of the *anti*-nitroaldol adduct with subsequent reductive alkylation of the amine moiety. Initially, we planned to utilize *anti*-selective nitroaldol reactions catalyzed by a Nd/Na/chiral amide complex recently developed by our group,[11] but when used with aldehyde precursors suitable for **2a** and **2b** the reactions resulted in low enantioselectivities of the prod-



Scheme 2. Structures and retrosynthesis of (−)-ritodrine **2a**·HCl and β_3-adrenoceptor agonist **2b**·HCl. PG = protecting group.

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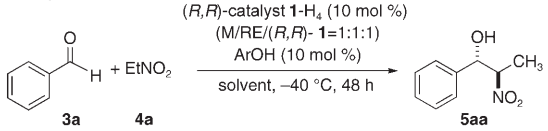
ucts.[14] Therefore, we turned our attention to developing a new catalyst suitable for β-adrenoceptor agonists syntheses.

We recently reported the utility of dinucleating Schiff base **1**-H_4 (Scheme 1) in nitro-Mannich reactions of *N*-Boc imines (Boc = *tert*-butylcarboxy) with nitroethane and nitropropane.[15] Schiff base **1**-H_4 selectively incorporated Cu into the inner N_2O_2 cavity and an oxophilic rare earth metal, having a large ionic radius, into the outer O_4 cavity. The cooperative functions of the two metals[16,17] in the heterobimetallic Cu/Sm/**1** complex (Scheme 1; M = Cu, RE = Sm) were key to achieving high diastereo- and enantioselectivity in the nitro-Mannich reactions. An achiral 4-*tert*-butylphenol additive improved the enantioselectivity by performing as an achiral ligand. We hypothesized that suitable selection of a dinucleating Schiff base, a transition metal (M)/rare earth metal (RE) combination, and a phenolic additive would afford an optimal chiral environment for the *anti*-selective nitroaldol reaction. Thus, we initiated optimization reactions by using Schiff base **1**-H_4, a phenolic additive, aldehyde **3a**, and nitroethane **4a** (Table 1). The Cu/Sm/**1** and 4-*tert*-butylphenol system, which was optimal for the nitro-Mannich reactions, gave poor reactivity and selectivity (Table 1, entry 1). Screening of other rare earth metals (Table 1, entries 1-4) indicated that La(O-*i*Pr)$_3$ had the best reactivity (Table 1, entry 4), and additional optimization with regard to the inner metal (Table 1, entries 4–7) revealed that the best combination was Pd(OAc)$_2$ and La(O-*i*Pr)$_3$. These conditions gave **5aa** in 82% yield, *anti*/*syn* = 5.3:1, and 58% *ee* (Table 1, entry 7). Other metals such as Ni(OAc)$_2$ and Zn(OAc)$_2$ gave less satisfactory results (Table 1, entries 5–6). The phenolic additive also affected both the diastereo- and enantioselectivity (Table 1, entries 7-9), and 4-bromophenol was found to be optimal (Table 1, entry 9). Finally, minor modifications of the solvent and the reaction time gave the optimum results in THF/xylenes, producing **5aa** in 92% yield, *anti*/*syn* = 19:1, and 84% *ee* (Table 1, entry 10).

Table 1: Optimization of the reaction conditions.



3a 4a 5aa

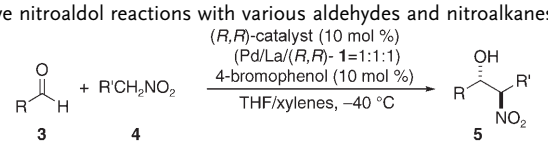
Entry	M[a]	RE[b]	ArOH	Solvent	Yield [%]	d.r. *anti*/*syn*[c]	*ee* [%][f]
1	Cu	Sm	4-*t*BuC_6H_4OH	THF	33	2.3:1	1[d]
2	Cu	Gd	4-*t*BuC_6H_4OH	THF	26	2.3:1	4[d]
3	Cu	Dy	4-*t*BuC_6H_4OH	THF	25	2.8:1	3
4	Cu	La	4-*t*BuC_6H_4OH	THF	73	2:1	28
5	Ni	La	4-*t*BuC_6H_4OH	THF	61	2:1	12
6	Zn	La	4-*t*BuC_6H_4OH	THF	30	1:2	2
7	Pd	La	4-*t*BuC_6H_4OH	THF	82	5.3:1	58
8	Pd	La	4-MeO-C_6H_4OH	THF	65	3.3:1	49
9	Pd	La	4-BrC_6H_4OH	THF	77	12:1	77
10[e]	Pd	La	4-BrC_6H_4OH	THF/xylenes	92	19:1	84

[a] M(OAc)$_2$ was used. [b] RE(O-*i*Pr)$_3$ was used. [c] Determined by ^{1}H NMR analysis. [d] *ent*-**5aa** was the major product. [e] Reaction time was 69 h. [f] Values determined for the *anti* product.

The substrate scope and limitations are shown in Table 2. Aromatic aldehydes with electron-donating substituents at the *para*-, *meta*-, or *ortho*-position gave products with high *anti* selectivity and good enantioselectivity (Table 2, entries 2–7). For the less reactive aldehyde **3e**, the reaction at −30°C was required for good conversion (Table 2, entry 6 versus entry 7), and aldehyde **3f** having an electron-withdrawing substituent resulted in a slightly lower stereoselectivity (Table 2, entry 8). Heteroaromatic aldehyde **3g** gave product **5ga** with good d.r. and *ee* values (Table 2, entry 9). The present system is also applicable to both α,β-unsaturated and aliphatic aldehydes, which delivered products in 92–77% *ee*, albeit with modest *anti* selectivity (Table 2, entries 10–12). The reaction with nitropropane (**4b**) as a donor proceeded smoothly to give product **5ab** in *anti*/*syn* = 19:1 and 85% *ee* (Table 2, entry 13). By using a 5 mol% catalyst loading, good *anti* selectivity and enantioselectivity were maintained, but a long reaction time was required (Table 2, entry 14).

4-benzyloxybenzaldehyde **3k** was selected for the synthesis of **2a** and **2b**. A catalytic asymmetric nitroaldol

Table 2: *anti*-Selective nitroaldol reactions with various aldehydes and nitroalkanes.[a]

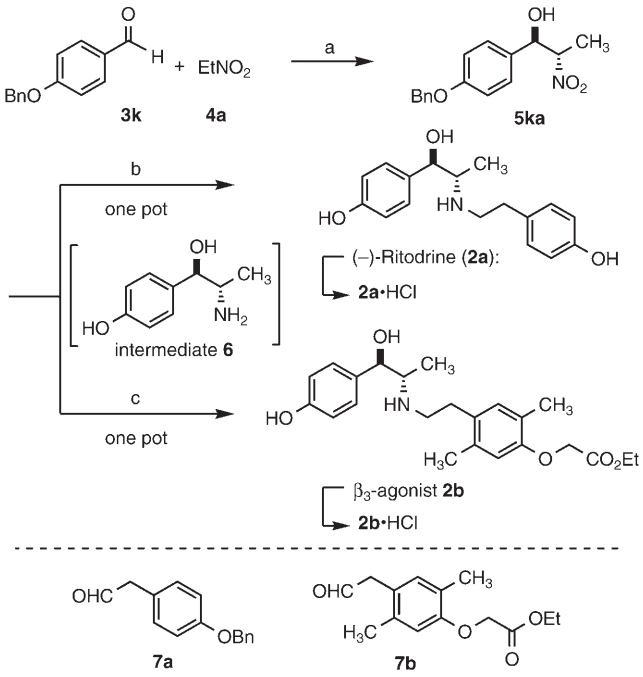


3 4 5

Entry	R	3	R′	4	Product	*t* [h]	Yield[b] [%]	d.r. *anti*/*syn*[c]	*ee* [%][f]
1	C_6H_5	**3a**	CH_3	**4a**	**5aa**	69	92	19:1	84
2	4-$CH_3C_6H_4$	**3b**	CH_3	**4a**	**5ba**	72	80	19:1	87
3[d]	4-$CH_3C_6H_4$	**3b**	CH_3	**4a**	**5ba**	72	97	15:1	83
4	3-$CH_3C_6H_4$	**3c**	CH_3	**4a**	**5ca**	72	81	13:1	83
5	2-$CH_3C_6H_4$	**3d**	CH_3	**4a**	**5da**	72	83	21:1	81
6	4-$CH_3OC_6H_4$	**3e**	CH_3	**4a**	**5ea**	72	47	22:1	88
7[d]	4-$CH_3OC_6H_4$	**3e**	CH_3	**4a**	**5ea**	72	78	15:1	83
8	4-ClC_6H_4	**3f**	CH_3	**4a**	**5fa**	72	87	8:1	72
9	2-furyl	**3g**	CH_3	**4a**	**5ga**	72	80	12:1	80
10	*E*-cinnamyl	**3h**	CH_3	**4a**	**5ha**	85	70	5:1	80
11	$Ph(CH_2)_2$	**3i**	CH_3	**4a**	**5ia**	85	75	3:1	77
12[d]	Cy	**3j**	CH_3	**4a**	**5ja**	72	65	4:1	92
13	C_6H_5	**3a**	CH_3CH_2	**4b**	**5ab**	85	67	19:1	85
14[e]	C_6H_5	**3a**	CH_3	**4a**	**5aa**	120	82	16:1	85

[a] The reaction was run with 10 mol% of Pd/La/**1** complex and 4-bromophenol at −40°C unless otherwise noted. Cy = cyclohexyl. [b] Yield of product isolated after column chromatography. [c] Determined by ^{1}H NMR analysis of the crude reaction mixture. [d] Reaction was run at −30°C. [e] Reaction was performed with 5 mol% of Pd/La/**1** complex and 4-bromophenol. [f] Determined for *anti*-**5**.

reaction run with the Pd/La/(*S*,*S*)-**1** complex and 4-bromophenol afforded *anti*-adduct **5ka** in 85% yield, *anti*/*syn* = 14:1, and 83% *ee* on a 1.0-mmol scale.[18] Salt-free ritodrine (**2a**) was obtained in a one-flask operation from **5ka** (Scheme 3). Treatment of **5ka** in ethyl acetate with Pd/C under H_2 (1 atm) at room temperature for 12 h gave



Scheme 3. Syntheses of β_2-adrenoceptor agonist (−)-ritodrine **2a**·HCl and β_3-adrenoceptor agonist **2b**·HCl; Reagents and conditions: a) Pd/La/(*S*,*S*)-**1** (10 mol%), 4-bromophenol (10 mol%), THF/xylenes, −30°C, 85 h, 85%, *anti*/*syn* = 14:1, 83% *ee*; b) 1. Pd/C, H_2, EtOAc, RT, 12 h; 2. **7a**, 60°C, 24 h; then HCl in CH_3OH, 93%; c) 1. Pd/C, H_2, EtOAc, RT, 12 h; 2. **7b**, 60°C, 24 h; then HCl in CH_3OH, 73%.

intermediate **6** without epimerization. Completion of the conversion of **5ka** into **6** was verified by TLC analysis, and then aldehyde **7a**[19] was added to the reaction mixture. The reaction mixture was heated at 60°C under H_2 (1 atm) for 24 hours to facilitate the reductive alkylation to afford salt-free ritodrine (**2a**). After treating **2a** with HCl in methanol **2a**·HCl was obtained in 93% yield. Both the use of ethyl acetate as the solvent, instead of methanol, and the addition of aldehyde **7a** after the formation of intermediate **6** were important in achieving the one-pot process to transform **5ka** into **2a**. Under similar conditions **2b**·HCl was obtained from **5ka** and aldehyde **7b**[13c] in 73% yield by the one-pot process to convert **5ka** into **2b**.

In summary, we developed an *anti*-selective catalytic asymmetric nitroaldol reaction utilizing a newly tuned Pd/La/**1** complex with 4-bromophenol as an additive. *anti*-Nitroaldol adducts were obtained in up to 97% yield, *anti*/*syn* = 22:1–3:1, and 92–72% *ee*. We also demonstrated the utility of the reaction in the short syntheses of clinically important β-adrenoceptor agonists **2a**·HCl and **2b**·HCl. Investigations into improving the stereoselectivity and reactivity of the reaction, and mechanistic studies to elucidate the precise roles of the two metals[20,21] are ongoing.

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[1] a) D. J. Ager, I. Prakash, D. R. Schaad, *Chem. Rev.* **1996**, *96*, 835; b) *Comprehensive Asymmetric Catalysis*, 1st ed. (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, **1999**; c) *Catalytic Asymmetric Synthesis*, 2nd ed. (Ed.: I. Ojima), Wiley-VCH, New York, **2000**.

[2] For reviews on asymmetric synthesis of vicinal amino alcohols, see: a) S. C. Bergmeier, *Tetrahedron* **2000**, *56*, 2561; b) M. T. Reetz, *Chem. Rev.* **1999**, *99*, 1121; c) H. C. Kolb, K. B. Sharpless in *Transition Metals for Organic Synthesis* (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **1998**, pp. 243.

[3] For recent reviews see, a) C. Palomo, M. Oiarbide, A. Laso, *Eur. J. Org. Chem.* **2007**, 2561; b) J. Boruwa, N. Gogoi, P. P. Saikia, N. C. Barua, *Tetrahedron: Asymmetry* **2006**, *17*, 3315, and references therein.

[4] a) H. Sasai, T. Suzuki, S. Arai, T. Arai, M. Shibasaki, *J. Am. Chem. Soc.* **1992**, *114*, 4418; For reviews, see: b) M. Shibasaki, H. Sasai, T. Arai, *Angew. Chem.* **1997**, *109*, 1290; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1236; c) M. Shibasaki, N. Yoshikawa, *Chem. Rev.* **2002**, *102*, 2187; For recent related works, see: d) S.-y. Tosaki, K. Hara, V. Gnanadesikan, H. Morimoto, S. Harada, M. Sugita, N. Yamagiwa, S. Matsunaga, M. Shibasaki, *J. Am. Chem. Soc.* **2006**, *128*, 11776.

[5] For selected examples using nitromethane as a donor, see: a) C. Christensen, K. Juhl, R. G. Hazell, K. A. Jørgensen, *J. Org. Chem.* **2002**, *67*, 4875; b) B. M. Trost, V. S. C. Yeh, *Angew. Chem.* **2002**, *114*, 889; *Angew. Chem. Int. Ed.* **2002**, *41*, 861; c) D. A. Evans, D. Seidel, M. Rueping, H. W. Lam, J. T. Shaw, C. W. Dowey, *J. Am. Chem. Soc.* **2003**, *125*, 12692; d) Y. Kogami, T. Nakajima, T. Ashizawa, S. Kezuka, T. Ikeno, T. Yamada, *Chem. Lett.* **2004**, *33*, 614; e) C. Palomo, M. Oiarbide, A. Laso, *Angew. Chem.* **2005**, *117*, 3949; *Angew. Chem. Int. Ed.* **2005**, *44*, 3881; f) Y. Sohtome, Y. Hashimoto, K. Nagasawa, *Adv. Synth. Catal.* **2005**, *347*, 1643; g) D.-M. Du, S.-F. Lu, T. Fang, J. Xu, *J. Org. Chem.* **2005**, *70*, 3712; h) B. M. Choudary, K. V. S. Ranganath, U. Pal, M. L. Kantam, B. Sreedhar, *J. Am. Chem. Soc.* **2005**, *127*, 13167; i) H. Li, B. Wang, L. Deng, *J. Am. Chem. Soc.* **2006**, *128*, 732; j) T. Marcelli, R. N. S. van der Haas, J. H. van Maarseveen, H. Hiemstra, *Angew. Chem.* **2006**, *118*, 943; *Angew. Chem. Int. Ed.* **2006**, *45*, 929; k) T. Arai, M. Watanabe, A. Fujiwara, N. Yokoyama, A. Yanagisawa, *Angew. Chem.* **2006**, *118*, 6124; *Angew. Chem. Int. Ed.* **2006**, *45*, 5978; l) Y. Xiong, F. Wanng, X. Huang, Y. Wen, X. Feng, *Chem. Eur. J.* **2007**, *13*, 829; m) M. Bandini, F. Piccinelli, S. Tommasi, A. Umani-Ronchi, C. Ventrici, *Chem. Commun.* **2007**, 616; n) K. Ma, J. You, *Chem. Eur. J.* **2007**, *13*, 1863; o) T. Mandal, S. Samanta, C.-G. Zhao, *Org. Lett.* **2007**, *9*, 943; p) M. Bandini, M. Benaglia, R. Sinisi, S. Tommasi, A. Umani-Ronchi, *Org. Lett.* **2007**, *9*, 2151; q) F. Tur, J. M. Saá, *Org. Lett.* **2007**, *9*, 5079, and references therein. For other examples, see reviews in reference [3].

[6] a) H. Sasai, T. Tokunaga, S. Watanabe, T. Suzuki, N. Itoh, M. Shibasaki, *J. Org. Chem.* **1995**, *60*, 7388; b) Y. Sohtome, Y. Hashimoto, K. Nagasawa, *Eur. J. Org. Chem.* **2006**, 2894; c) Y. Sohtome, N. Takemura, K. Takada, R. Takagi, T. Iguchi, K. Nagasawa, *Chem. Asian J.* **2007**, *2*, 1150; d) T. Arai, M. Watanabe, A. Yanagisawa, *Org. Lett.* **2007**, *9*, 3595.

[7] a) T. Ooi, K. Doda, K. Maruoka, *J. Am. Chem. Soc.* **2003**, *125*, 2054; b) T. Risgaard, K. V. Gothelf, K. A. Jørgensen, *Org. Biomol. Chem.* **2003**, *1*, 153.

[8] B. M. Trost, *Science* **1991**, *254*, 1471.

[9] D. Uraguchi, S. Sakaki, T. Ooi, *J. Am. Chem. Soc.* **2007**, *129*, 12392.

[10] For an *anti*-selective asymmetric nitroaldol reaction of benzaldehyde and nitroethane catalyzed by hydroxynitrile lyase, see: a) T. Purkarthofer, K. Gruber, M. Gruber-Khadjawi, K. Waich, W. Skranc, D. Mink, H. Griengl, *Angew. Chem.* **2006**, *118*, 3532; *Angew. Chem. Int. Ed.* **2006**, *45*, 3454; b) M. Gruber-Khadjawi, T. Purkarthofer, W. Skranc, H. Griengl, *Adv. Synth. Catal.* **2007**, *349*, 1445.

[11] T. Nitabaru, N. Kumagai, M. Shibasaki, *Tetrahedron Lett.* **2008**, *49*, 272.

[12] Ritodrine (**2a**) is clinically utilized as a racemate, but (−)-Ritodrine is 40 to 90-fold more active than (+)-Ritodrine in several biological assays, and is supposed to be the actual active species. See, N. Yamazaki, Y. Fukuda, Y. Shibazaki, T. Niizato, I. Kosugi, S. Yoshioka, US Patent 5,449,694, **1995**, and references therein.

[13] a) N. Tanaka, T. Tamai, H. Mukaiyama, A. Hirabayashi, H. Muranaka, M. Sato, M. Akahane, Patent WO00/02846, **1999**; For related studies, see b) N. Tanaka, T. Tamai, H. Mukaiyama, A. Hirabayashi, H. Muranaka, T. Ishikawa, J. Kobayashi, S. Akahane, M. Akahane, *J. Med. Chem.* **2003**, *46*, 105; Synthesis of **2b** and related compounds: c) N. Tanaka, T. Tamai, JP Patent JP2002-64840.

[14] *p*-Alkoxybenzaldehydes, such as *p*-anisaldehyde, are much less reactive than other aldehydes in *anti*-selective nitroaldol reaction. *p*-Anisaldehyde was previously utilized by Jørgensen and co-workers, see reference [7b], resulting in less satisfactory yield and *anti*-selectivity than with other aldehydes.

[15] S. Handa, V. Gnanadesikan, S. Matsunaga, M. Shibasaki, *J. Am. Chem. Soc.* **2007**, *129*, 4900.

[16] For reviews on bimetallic cooperative catalysis, see a) (Eds.: M. Shibasaki, Y. Yamamoto *Multimetallic Catalysts in Organic Synthesis*, Wiley-VCH, Weinheim, **2004**; b) M. Shibasaki, S. Matsunaga, *Chem. Soc. Rev.* **2006**, *35*, 269; c) M. Shibasaki, M. Kanai, *Org. Biomol. Chem.* **2007**, *5*, 2027.

[17] For related attempts to develop bifunctional asymmetric catalysts by using heterobimetallic Schiff base complexes, see a) V. Annamalai, E. F. DiMauro, P. J. Carroll, M. C. Kozlowski, *J. Org. Chem.* **2003**, *68*, 1973, and references therein; b) G. M. Sammis, H. Danjo, E. N. Jacobsen, *J. Am. Chem. Soc.* **2004**, *126*, 9928; c) W. Li, S. S. Thakur, S.-W. Chen, C.-K. Shin, R. B. Kawthekar, G.-J. Kim, *Tetrahedron Lett.* **2006**, *47*, 3453, and references therein.

[18] On a 0.2-mmol scale, **5ka** was isolated in 78% yield, *anti*/*syn* = 16:1, and 85% *ee* by using 10 mol% catalyst.

[19] Aldehyde synthesis: **7a**, N. Aberle, J. Catimel, E. C. Nice, K. G. Watson, *Bioorg. Med. Chem. Lett.* **2007**, *17*, 3741. For aldehyde **7b**, see reference [13c].

[20] The control experiments suggested that both $Pd(OAc)_2$ and $La(O\text{-}iPr)_3$ were essential in the present reaction. We assume that cooperative functions of Pd and La metal centers are important for good *anti*-selectivity and enantioselectivity. For results and discussion, see the Supporting Information.

[21] One of the possible reaction mechanisms is as follows; the La–OAr moiety could function as a Brønsted base to deprotonate α proton of the nitroalkane. The La–nitronate would then react with the aldehyde, which is coordinated to the Pd metal center, from TS-A rather than TS-B (see scheme below) to avoid steric repulsion between the R′ group and the Pd/La catalyst, preferentially giving *anti*-adducts. However, other reaction mechanisms cannot be ruled out at this stage. Detailed mechanistic studies will be reported in due course as a full article. For a recent example utilizing the Brønsted basic property of La–OAr moiety in asymmetric catalysis, see: H. Morimoto, G. Lu, N. Aoyama, S. Matsunaga, M. Shibasaki, *J. Am. Chem. Soc.* **2007**, *129*, 9588, and references therein.