DOI: 10.1002/ejoc.200700330

# Asymmetric Catalytic Intramolecular Pauson–Khand Reactions with Ir(phox) Catalysts

**Zhong-Lin Lu,[a] Eva Neumann,[a] and Andreas Pfaltz*[a]**

*Dedicated to Professor Miguel Yus on the occasion of his 60th birthday*

**Keywords:** Pauson–Khand reactions / Asymmetric catalysis / N,P ligands / Phosphane–oxazolines / Iridium

Iridium complexes derived from chiral phosphane–oxazolines (phox ligands) are efficient catalysts for intramolecular Pauson–Khand reactions. Under optimized conditions high yields and enantioselectivities of > 90 % *ee* were obtained with 2 mol-% of catalyst. The influence of the CO pressure and the anion were studied. The structure of a dicarbonyl(phox)iridium complex was determined by X-ray analysis.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

## Introduction

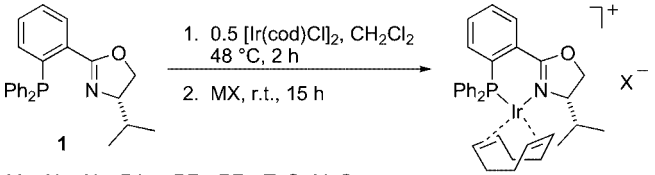
Metal-catalyzed cycloadditions are highly valuable transformations as they allow the construction of complex cyclic structures from simple precursors with perfect atom economy.[1] A particularly attractive example is the Pauson–Khand reaction, a formal [2+2+1] cycloaddition of an alkene, an alkyne and carbon monoxide leading to cyclopentenones, which are versatile synthetic intermediates. The development of intramolecular variants, initiated by the work of Shore and Croudace,[2] considerably enhanced the scope of the Pauson–Khand reaction. In contrast to the intermolecular reaction, strained alkenes are no longer required and the resulting [5.5]- and [5.6]-fused bicycles can be obtained as single regioisomers.

In recent years substantial progress has been made in the development of catalytic and also enantioselective Pauson–Khand reactions.[3] In addition to cobalt complexes,[4] many other types of metal catalysts based on Fe,[5] Ni,[6] Ti,[7] Zr,[8] Ru,[9] Rh,[10] and Ir[11] have been reported. Shibata et al.[11] studied the use of iridium complexes such as $[IrCl(cod)]_2$ in catalytic intramolecular Pauson–Khand reactions and observed that addition of triphenylphosphane as co-ligand improved the reaction yields. When they replaced triphenylphosphane by tolbinap, they obtained high yields and enantiomeric excesses. More recently, they extended the reaction to a wider range of substrates and also employed aldehydes as CO source.[12]

In connection with our work on chiral phosphane–oxazolines (phox ligands) and their use in iridium-catalyzed asymmetric hydrogenation[13] we became interested in evaluating Ir(phox) complexes as catalysts for asymmetric Pauson–Khand reactions. Here we report the results of an initial study, which showed that high enantioselectivities and yields can be obtained in intramolecular reactions of en-ynes using readily available Ir(phox) complexes as catalysts.

## Results and Discussion

The precatalysts **2** were prepared according to standard procedures from $[IrCl(cod)]_2$, phox ligand **2** {2-[2-(diphenylphosphanyl)phenyl]-4,5-dihydro-4-isopropyloxazole} and the respective silver, lithium or sodium salts (Scheme 1).[14] In addition, a series of analogous complexes with differently substituted phox ligands was synthesized.



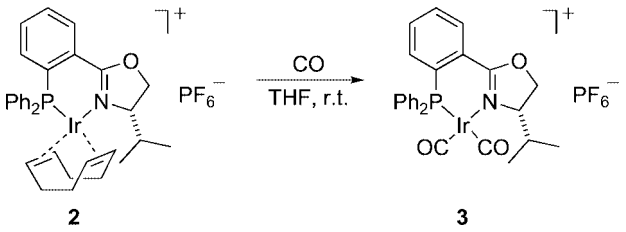

Scheme 1. Preparation of Ir(cod)(phox) complexes **2**; $BAr_F$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

In order to test the reactivity toward carbon monoxide, CO gas was bubbled through a solution of the 1,5-cyclooctadiene complex **2** (X = $PF_6$) at room temperature (Scheme 2). Under these conditions, the dicarbonyl complex **3** was cleanly formed by replacement of the cod ligand by two 2 CO molecules. This implies that under the condi-

[a] Department of Chemistry, University of Basel,
St. Johanns-Ring 19, 4056 Basel, Switzerland
Fax: +41-61-2671103
E-mail: andreas.pfaltz@unibas.ch

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 

tions of the Pauson–Khand reaction, the precatalyst **2** is rapidly converted into the corresponding dicarbonyl complex. The structure of complex **3** was determined by X-ray analysis (Figure 1). As a consequence of the stronger π-acceptor properties of the P atom, the C–O bond *trans* to the phosphanyl group is shorter and the Ir–C bond longer than the corresponding bonds in the Ir–CO fragment *trans* to the oxazoline ring.

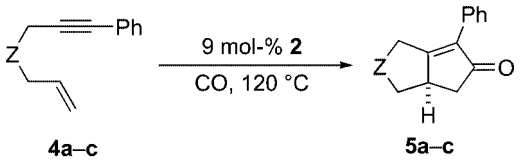



**2** **3**

Scheme 2. Preparation of $Ir(CO)_2$(phox) complex **3**.

Figure 1. Crystal structure of complex **3**. The anion has been omitted for clarity. Selected bond lenghths [Å]: Ir–P 2.3166(7), Ir–N 2.086(2), Ir–C(*trans* to P) 1.915(3), Ir–C(*trans* to N) 1.850(3), O–C(*trans* to P) 1.126(4), O–C(*trans* to N) 1.140(4).

The precatalysts **2** and related complexes with differently substituted phox ligands were tested in the intramolecular Pauson–Khand reaction of en-yne **4a** (Scheme 3). The reaction was carried out in DME or THF in an ampule sealed under 1.4–2.2 bar of carbon monoxide. At 120 °C in the presence of 9 mol-% of iridium complex, a high conversion to the desired cyclization product **5a** was observed. HPLC analysis using a Chiralcel AD column showed that the reaction proceeded in an enantioselective manner. The highest enantiomeric excesses and yields were obtained with the commercially available ligand **1** [91% *ee*, > 90% yield; **2** (X = $PF_6$), 2.2 bar CO, DME, 24 h]. Ligands bearing more bulky substituents such as 2-tolyl at the P atom gave only very low yields. Replacement of the isopropyl substituent at the stereogenic center of the oxazoline ring by a methyl group resulted in a slightly lower enantioselectivity with a similar yield, whereas a *tert*-butyl group at this position gave much lower conversion and only 50% *ee*. Although a large number of other phox derivatives was screened, no ligand was found that was superior to the simple diphenylphosphanyl-isopropyl-substituted phox ligand **1**.




**4a–c** **5a–c**

**a:** Z = O; **b:** Z = NTs; **c:** Z = $C(CO_2Me)_2$

Scheme 3. Enantioselective Pauson–Khand reaction with Ir(phox) catalysts.

The solvents DME and THF proved to be the ones of choice. Reactions in toluene and 1,2-dichloroethane gave slightly inferior enantioselectivities, whereas in acetonitrile and dioxane the yields were very low. The optimal reaction temperature was 120 °C. At 140 °C in toluene much shorter reaction times were necessary (4 h for > 90% conversion), however, the *ee* dropped from 78% at 120 °C to 74%. At 100 °C a modest increase in *ee* was observed, but reaction times became inpractically long.

The concentration of carbon monoxide influences both the enantioselectivity and reaction rate. A linear dependence between yield and CO pressure was observed. When the pressure was increased from 1.4 to 2.2 bar, the yields of isolated product improved from 51% to 85% (Table 1). In contrast, the enantioselectivity dropped from 97% to 91% *ee*. In order to obatin high yields within reasonable reaction times, 2.2 bar was chosen as standard pressure for subsequent reactions.

Table 1. Influence of the CO pressure in the Pauson–Khand reaction of **4a** (Scheme 3).[a]

| Entry | X | Solvent | $p_{CO}$ (bar)[b] | Yield (%)[c] | *ee* (%)[d] |
|---|---|---|---|---|---|
| 1 | TfO | DME | 1.4 | 51 | 97 (*R*) |
| 2 | TfO | DME | 1.6 | 61 | 96 (*R*) |
| 3 | TfO | DME | 1.8 | 71 | 94 (*R*) |
| 4 | TfO | DME | 2.0 | 81 | 92 (*R*) |
| 5 | TfO | DME | 2.2 | 85 | 91 (*R*) |

[a] Reaction time: 24 h. [b] CO pressure in the reaction vessel at room temp. [c] Yield of isolated product after column chromatography (silica gel, hexane/EtOAc, 3:1). [d] Determined by HPLC: Chiralcel AD, 25 × 0.46 cm, heptane/2-propanol (90:10), 1.0 mL/min, 220/254 nm, $t_R$ = 11.1 min (*R*), 14.6 min (*S*).

Reduction of the catalyst loading from 9 mol-% to 1 mol-% had no apparent influence on the enantioselectivity (Table 2). The yields of isolated product after a reaction

Table 2. Influence of the catalyst loading on the Pauson–Khand reaction of **4a** (Scheme 3).[a]

| Entry | X | mol-% cat. | Yield (%)[b] | *ee* (%)[c] |
|---|---|---|---|---|
| 1 | $BF_4$ | 9 | 89 | 91 (*R*) |
| 2 | $BF_4$ | 5 | 84 | 91 (*R*) |
| 3 | $BF_4$ | 2 | 88 | 91 (*R*) |
| 4 | $BF_4$ | 1 | 59 | 91 (*R*) |

[a] Reaction time: 24 h; CO pressure in the reaction vessel at room temp.: 2.2 bar. [b] Yield of isolated product after column chromatography (silica gel, hexane/EtOAc, 3:1). [c] Determined by HPLC (see Table 1).

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 

Table 3. Influence of the anion in the Pauson–Khand reaction of substrates **4a**–**c** (Scheme 3).[a]

| Entry | Substrate | Solvent | mol-% cat. | Time (h) | $p_{CO}$ (bar)[b] | X | Yield (%)[c] | *ee* (%)[d] |
|---|---|---|---|---|---|---|---|---|
| 1 | **4a** | DME | 9 | 24 | 2.0 | $BAr_F$ | 63 | 85 (*R*) |
| 2 | **4a** | DME | 9 | 24 | 2.2 | $BAr_F$ | 69 | 85 (*R*) |
| 3 | **4a** | DME | 9 | 24 | 2.0 | $Al[OC(CF_3)_3]_4$ | 55 | 85 (*R*) |
| 4 | **4a** | DME | 9 | 24 | 2.2 | $Al[OC(CF_3)_3]_4$ | 78 | 85 (*R*) |
| 5 | **4a** | DME | 9 | 24 | 2.2 | OTf | 85 | 91 (*R*) |
| 6 | **4a** | DME | 9 | 24 | 2.2 | $BF_4$ | 89 | 91 (*R*) |
| 7 | **4a** | DME | 9 | 24 | 2.2 | $PF_6$ | 93 | 91 (*R*) |
| 8 | **4a** | DME | 9 | 24 | 2.2 | $SbF_6$ | 96 | 91 (*R*) |
| 9 | **4a** | DME | 9 | 24 | 2.2 | MsO | traces | nd |
| 10 | **4a** | DME | 9 | 24 | 2.2 | TsO | traces | nd |
| 11 | **4a** | DME | 9 | 24 | 2.2 | $CF_3COO$ | traces | nd |
| 12 | **4b** | DME | 9 | 24 | 2.2 | $BAr_F$ | 96 | 50 |
| 13 | **4b** | DME | 9 | 24 | 2.2 | $Al[OC(CF_3)_3]_4$ | 96 | 56 |
| 14 | **4b** | DME | 9 | 24 | 2.2 | OTf | 93 | 81 |
| 15 | **4b** | DME | 9 | 24 | 2.2 | $BF_4$ | 98 | 80 |
| 16 | **4b** | DME | 9 | 24 | 2.2 | $PF_6$ | 95 | 77 |
| 17 | **4b** | DME | 9 | 24 | 2.2 | $SbF_6$ | 95 | 71 |
| 18 | **4c** | THF | 5 | 24 | 2.2 | $BAr_F$ | 46 | 71 |
| 19 | **4c** | THF | 5 | 48 | 2.2 | $Al[OC(CF_3)_3]_4$ | 62 | 72 |
| 20 | **4c** | THF | 9 | 48 | 2.2 | OTf | 75 | 85 |
| 21 | **4c** | THF | 5 | 48 | 2.2 | OTf | 48 | 94 |
| 22 | **4c** | THF | 9 | 48 | 2.2 | $BF_4$ | 76 | 91 |
| 23 | **4c** | THF | 5 | 48 | 2.2 | $BF_4$ | 57 | 94 |
| 24 | **4c** | THF | 5 | 48 | 2.2 | $PF_6$ | 71 | 91 |
| 25 | **4c** | THF | 9 | 48 | 2.2 | $SbF_6$ | 80 | 82 |
| 26 | **4c** | THF | 5 | 48 | 2.2 | $SbF_6$ | 76 | 86 |

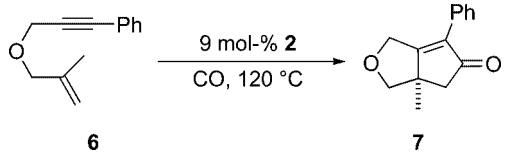
[a] Reaction time: 24 h. [b] CO pressure in the reaction vessel at room temp. [c] Yield of isolated product after column chromatography [silica gel, hexane/EtOAc (3:1) for **5a**, hexane/EtOAc (2:1) for **5b** and **5c**]. [d] Determined by HPLC: **5a**: see Table 1; **5b**: Chiralcel AD, 25 × 0.46 cm, 220/254 nm, heptane/2-propanol 80:20, 0.9 mL/min, $t_R$ = 19.6 min (major), 23.4 min (minor); **5c**: Chiralcel AS, 25 × 0.46 cm, heptane/2-propanol (90:10), 1.0 mL/min, $t_R$ = 15.1 (minor), 24.1 (major).

time of 24 h remained between 84–89% when the catalyst loading was lowered to 2 mol-%, whereas with 1 mol-% of catalyst the yield decreased to 59%.

The anion was found to have a surprisingly strong influence on the enantioselectivity and yield, as shown in Table 3 for the reactions of substrates **4a**–**c**. With the allyl ether **4a** the best results were obtained with relatively small, weakly coordinating anions such as tetrafluoroborate, hexafluorophosphate and hexafluoroantimonate (Entries 6–8). Triflate gave approximately the same results (Entry 5), whereas the larger non-coordinating anions $BAr_F^-$ and $[Al\{OC(CF_3)_3\}_4]^-$[15] caused a drop in yield and enantioselectivity (Entries 1–4). Tosylate, mesylate, and trifluoroacetate salts showed almost no catalytic activity (Entries 9–11).

For reactions with substrates **4b** and **4c** tetrafluoroborate and triflate gave the highest enantioselectivities with up to 81% *ee* for product **5b** and 94% *ee* for **5c**. Substrate **4c** was less reactive and required longer reaction times. In this case THF proved to be the best solvent. Interestingly, the enantioselectivity increased when the catalyst loading was reduced from 9 mol-% to 5 mol-%.

Finally, substrate **6** with a 2,2-disubstituted vinyl group was tested (Scheme 4 and Table 4). The additional methyl group at the C=C bond reduced the reactivity significantly compared to the analogous substrate **4a** and, therefore, only low to moderate yields were obtained, with enantioselectivities ranging between 58% and 71%.




Scheme 4. Pauson–Khand reaction of substrate **6**.

Table 4. Pauson–Khand reaction of substrate **6** (Scheme 4).[a]

| Entry | X | Solvent | Yield (%) | *ee* (%)[b] |
|---|---|---|---|---|
| 1 | TfO | DME | 9 | 58 (*R*) |
| 2 | $BAr_F$ | DME | traces | n.d. |
| 3 | TfO | THF | 10 | 71 (*R*) |
| 4 | $BAr_F$ | THF | 28 | 64 (*R*) |
| 5 | $Al[OC(CF_3)_3]_4$ | THF | 15 | 61 (*R*) |
| 6 | $BF_4$ | THF | 6 | 64 (*R*) |

[a] CO pressure in the reaction vessel at room temp. was 2.2 bar; reaction time: 24 h. [b] Determined by HPLC: Chiralcel AD, 25 × 0.46 cm, heptane/2-propanol (90:10), 1.0 mL/min, 220/254 nm, $t_R$ = 8.3 min (*R*), 17.7 min (*S*).

## Conclusions

Cationic iridium complexes derived from chiral phox ligands proved to be efficient catalysts for intramolecular Pauson–Khand reactions. For optimal results the various reaction parameters had to be carefully adjusted. The nature of the anion also proved to be important, as it had a

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 

significant influence on the enantioselectivity and yield. High enantioselectivities were achieved with substrates **4a** and **4c**, which were comparable to those reported for Ir catalysts derived from tolbinap.[11,12] With substrates **4b** and **6**, on the other hand, tolbinap gives higher enantioselectivities. As with (diphosphane)iridium catalysts, relatively long reaction times are required. However, the fact that high yields could be obtained at catalyst loadings of only 2 mol-% is encouraging. Our results indicate that Ir(phox) complexes are a promising new class of catalysts for asymmetric Pauson–Khand reactions.

## Experimental Section

**Iridium Complexes 2**: Complexes with X = $BAr_F$, $BF_4$, $PF_6$, TsO, MsO, and Al{OC$(CF_3)_3\}_4$ were prepared according to published procedures.[13a,14] Complexes **2** (X = $SbF_6$, OTf, $CF_3CO_2$): A 0.03 M solution of 1.0 equiv. of $[IrCl(cod)]_2$ and 2 equiv. of ligand in dichloromethane was stirred in an ampule, sealed under Ar with a Teflon screw cap, at 48 °C for 2 h. The respective silver salt (1.2 equiv.) was added and the suspension stirred at room temperature overnight. Filtration through Celite and evaporation of the volatiles provided complex **2**.

Enynes **4a**–**c** and **6** were prepared according to published procedures.[16] Spectroscopic data and rotation values of products **5a**–**c** and **7** have been reported in the literature.[4–12]

**General Procedure for the Pauson–Khand Reaction:** In a glove-box a flame-dried Young tube with a Teflon screw cap was charged with substrate (0.22 mmol), catalyst (2.2–20.0 μmol) and solvent (5 mL). The mixture was degassed with three freeze-pump cycles, the ampule filled with 2.2 bar of CO and sealed. After reaction at 120 °C under the conditions specified in Tables 1–4, the reaction mixture was concentrated and purified by column chromatography on silica gel. Product analysis: see footnotes in Tables 1–4.

**Praparation of Complex 3:** Carbon monoxide was bubbled through a solution of complex **2** (X = $PF_6$; 26 mg, 32 μmol) in 5 mL of THF at room temp. under argon. The reaction was accompanied by a color change from red to yellow. After 30 min, the solvent was removed and the residue washed with pentane (75% yield). Crystals suited for X-ray analysis were obtained by slow diffusion of pentane into a solution of **3** in dichloromethane.

**X-ray Analysis of Complex 3:** A crystal of **3** was mounted on a KappaCCD diffractometer using the oil drop method. Data were collected at 173 K using the Collect suite (Nonius BV, 2002). The structure was solved by direct methods using SIR92.[17] All non-hydrogen atoms were refined anisotropically using CRYSTALS.[18] Hydrogen atoms were placed in calculated positions. CCDC-643785 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## Acknowledgments

We thank Markus Neuburger for recording the diffraction data and his help with the refinement of the crystal structure of **3**. We thank Prof. Ingo Krossing for a gift of lithium tetrakis(perfluoro-*tert*-butoxy)aluminate. Financial support by the Swiss National Science Foundation is gratefully acknowledged.

[1] B. M. Trost, *Science* **1991**, *254*, 1471–1477.
[2] N. E. Schore, M. C. Croudace, *J. Org. Chem.* **1981**, *46*, 5436–5438.
[3] a) K. M. Brummond, J. L. Kent, *Tetrahedron* **2000**, *56*, 3263–3283; b) S. E. Gibson, A. Stevenazzi, *Angew. Chem. Int. Ed.* **2003**, *42*, 1800–1810; c) J. Blanco-Urgoiti, L. Anorbe, L. Perez-Serrano, G. Dominguez, J. Perez-Castells, *Chem. Soc. Rev.* **2004**, *33*, 32–42; d) S. E. Gibson, S. E. Lewis, N. Mainolfi, *J. Organomet. Chem.* **2004**, *689*, 3873–3890.
[4] a) N. Jeong, S. H. Hwang, Y. Lee, Y. K. Chung, *J. Am. Chem. Soc.* **1994**, *116*, 3159–3160; b) B. Y. Lee, Y. K. Chung, N. Jeong, Y. Lee, S. H. Hwang, *J. Am. Chem. Soc.* **1994**, *116*, 8793–8794; c) B. L. Pagenkopf, T. Livinghouse, *J. Am. Chem. Soc.* **1996**, *118*, 2285–2286; d) N. Y. Lee, Y. K. Chung, *Tetrahedron Lett.* **1996**, *37*, 3145–3148; e) J. W. Kim, Y. K. Chung, *Synthesis* **1998**, 142–144; f) D. B. Belanger, D. J. R. O'Mahony, T. Livinghouse, *Tetrahedron Lett.* **1998**, *39*, 7637–7640; g) D. B. Belanger, T. Livinghouse, *Tetrahedron Lett.* **1998**, *39*, 7641–7644; h) T. Sugihara, M. Yamaguchi, *Synlett* **1998**, 1384–1386; i) T. Sugihara, M. Yamaguchi, *J. Am. Chem. Soc.* **1998**, *120*, 10782–10783; j) M. Hayashi, Y. Hashimoto, Y. Yamamoto, J. Usuki, K. Saigo, *Angew. Chem. Int. Ed.* **2000**, *39*, 631–633.
[5] A. J. Pearson, R. A. Dubbert, *Organometallics* **1994**, *13*, 1656–1661.
[6] M. Zhang, S. L. Buchwald, *J. Org. Chem.* **1996**, *61*, 4498–4499.
[7] a) F. A. Hicks, N. M. Kablaoui, S. L. Buchwald, *J. Am. Chem. Soc.* **1996**, *118*, 9450–9451; b) F. A. Hicks, N. M. Kablaoui, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 5881–5898; c) F. A. Hicks, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 7026–7033.
[8] a) E. Negishi, S. J. Holmes, J. M. Tour, J. A. Miller, *J. Am. Chem. Soc.* **1985**, *107*, 2568–2569; b) E. Negishi, S. J. Holmes, J. M. Tour, J. A. Miller, F. E. Cederbaum, D. R. Swanson, T. Takahashi, *J. Am. Chem. Soc.* **1989**, *111*, 3336–3346.
[9] a) T. Morimoto, N. Chatani, Y. Fukumoto, S. Murai, *J. Org. Chem.* **1997**, *62*, 3762–3765; b) T. Kondo, N. Suzuki, T. Okada, T.-A. Mitsudo, *J. Am. Chem. Soc.* **1997**, *119*, 6187–6188.
[10] a) Y. Koga, T. Kobayashi, K. Narasaka, *Chem. Lett.* **1998**, 249–250; b) N. Jeong, *Organometallics* **1998**, *17*, 3642–3644.
[11] T. Shibata, K. Takagi, *J. Am. Chem. Soc.* **2000**, *122*, 9852–9853.
[12] T. Shibata, N. Toshida, M. Yamasaki, S. Maekawa, K. Takagi, *Tetrahedron* **2005**, *61*, 9974–9979.
[13] a) A. Lightfoot, P. Schnider, A. Pfaltz, *Angew. Chem. Int. Ed.* **1998**, *37*, 2897–2899; b) G. Helmchen, A. Pfaltz, *Acc. Chem. Res.* **2000**, *33*, 336–345; c) S. Bell, B. Wüstenberg, S. Kaiser, F. Menges, T. Netscher, A. Pfaltz, *Science* **2006**, *311*, 642–644.
[14] a) D. G. Blackmond, A. Lightfoot, A. Pfaltz, T. Rosner, P. Schnider, N. Zimmermann, *Chirality* **2000**, *12*, 442–449; b) P. Schnider, G. Koch, R. Prétôt, G. Wang, F. M. Bohnen, C. Krüger, A. Pfaltz, *Chem. Eur. J.* **1997**, *3*, 887–8892.
[15] a) H. Nöth, A. Schlegel, J. Knizek, I. Krossing, W. Ponikwar, T. Seifert, *Chem. Eur. J.* **1998**, *4*, 2191–2203; b) S. M. Ivanova, B. G. Nolan, Y. Kobayashi, S. M. Miller, O. P. Anderson, S. H. Strauss, *Chem. Eur. J.* **2001**, *7*, 503–510.
[16] T. Kobayashi, Y. Koga, K. Narasaka, *J. Organomet. Chem.* **2001**, *624*, 73–87.
[17] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350.
[18] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, D. J. Watkin, *J. Appl. Crystallogr.* **2003**, *36*, 1487–1487.

Received: April 26, 2007
Published Online: May 25, 2007

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 