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Tetrahedron Letters 47 (2006) 6361–6364
Tetrahedron Letters

Chiral aminoalcohol NOBIN for instantaneous chirality control of racemic but *tropos* BIPHEP–Rh(I)-complexes: highly enantioselective ene-type cyclization of 1,6-enynes catalyzed by the Rh(I)-complexes without use of acid

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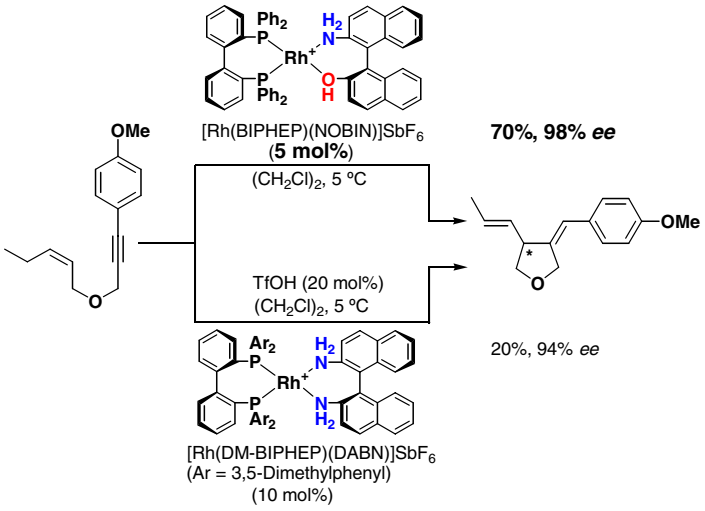
Received 12 June 2006; revised 30 June 2006; accepted 30 June 2006

Abstract—The *tropos* (chirally flexible) or *atropos* (chirally rigid) nature of BIPHEP–Rh complexes critically depends on amines and alcohols complexed. The BIPHEP–Rh complex with aminoalcohol NOBIN is significantly *tropos* and can be chirally controlled by aminoalcohol NOBIN instantaneously even at room temperature. The BIPHEP–Rh/NOBIN complex thus controlled can be used as an asymmetric catalyst to give higher enantioselectivity (up to 98% ee) and yield in ene-type cyclization of 1,6-enynes without use of acid.

In catalytic asymmetric reactions, a variety of enantiopure atropisomeric (originated from Greek *atropos*; *a* = not, *tropos* = turn)[1] ligands are prepared, enantioresolved, and then complexed with metals.[2] In sharp contrast, we have succeeded in asymmetric catalysis using racemic but chirally flexible (*tropos*)[1] bis(phosphanyl)biphenyl (BIPHEP) ligands,[3,4] of which the axial chirality can be controlled by a chiral diamine. It is necessary to cleave the diamine off by acid treatment to open the coordination site for enyne



Scheme 1.

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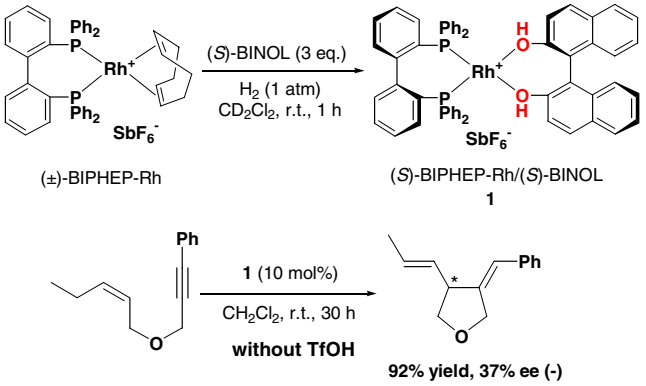
doi:10.1016/j.tetlet.2006.06.179

substrates, so that the diamine-free BIPHEPs–Rh complexes afford high enantioselectivity and yield in asymmetric ene-type cyclization.[4b] However, the presence of acid causes polymerization or decomposition of acid-labile substrates or products. We thus examined to use diols or aminoalcohols instead of diamines, because the weakly coordinating hydroxy portion could be easily dissociated upon association of dienyne or enyne substrates without acid treatment. Herein, we wish to report instantaneous chirality control of *tropos* BIPHEPs–Rh complexes by chiral aminoalcohol NOBIN (2′-amino-1,1′-binaphth-2-ol)[5] at room temperature and their application as highly enantioselective catalysts (Scheme 1). Ene-type cyclization of 1,6-enynes proceeds with higher enantioselectivity at 5 °C even in the absence of acid.

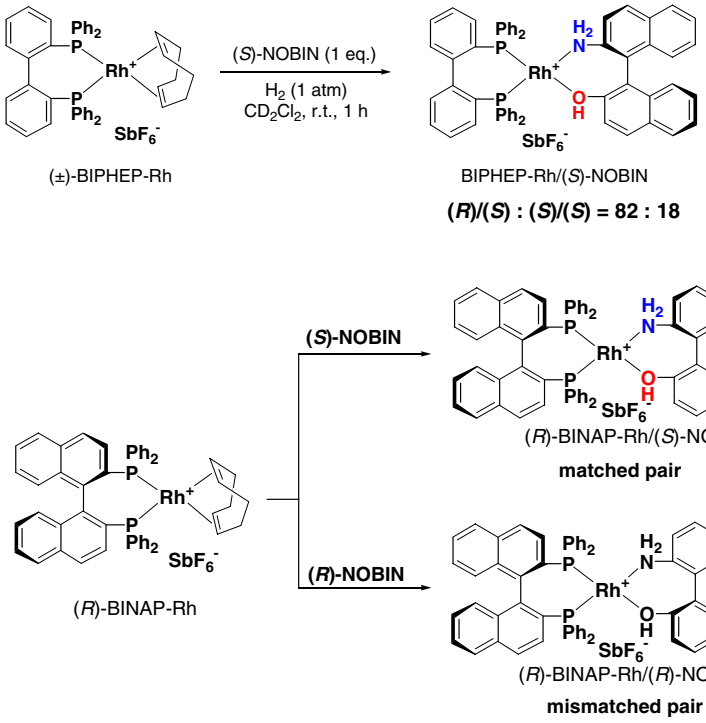


(1)

First, weakly coordinating BINOL (1,1′-bi-2,2′-naphthol) was used to complex the BIPHEP–Rh complex. Unfortunately, 3 equiv of (*S*)-BINOL was necessary to give, however, a single diastereomer[6] instantaneously even at room temperature (Eq. 1). In sharp contrast, the BIPHEP–Rh/DABN (2,2′-diamino-1,1′-binaphthyl) complex isomerized slowly in dichloromethane at room temperature over 17 days (80 °C, 5 h).[4b] The BIPHEP–Rh/BINOL complex thus obtained could be used as a catalyst for ene-type cyclization[7] of 1,6-enyne substrate without TfOH. The BIPHEP–Rh/BINOL complex **1** gave the desired cyclic product in good yield but in only low enantioselectivity.

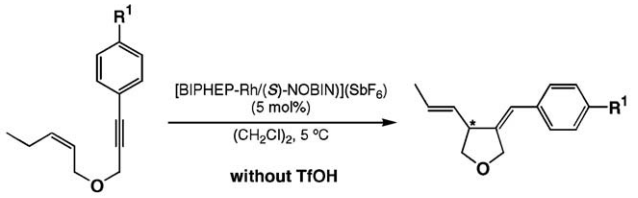
(*S*)-NOBIN was thus examined as a hybrid of DABN and BINOL to give again instantaneously the *R*,*S*-major diastereomer (82% selectivity) at room temperature (Scheme 2). The absolute configuration of the major BIPHEP–Rh/(*S*)-NOBIN[8] complex was deduced in comparison with the enantiopure form of (*R*)-BINAP–Rh/(*S*)-NOBIN complex by ^{31}P NMR (J_{Rh-P}) analyses.[9] (*R*)-BINAP–Rh/(*S*)-NOBIN complex [δ 39.4 (dd, $J_{Rh-P} = 203.6$ Hz, 1P), 40.1 (dd, $J_{Rh-P} = 201.5$ Hz, 1P)] was quite similar to the major diastereomer of (*R*)-BIPHEP–Rh/(*S*)-NOBIN complex [δ 37.9 (dd, $J_{Rh-P} = 198.5$ Hz, 1P), 38.4 (dd, $J_{Rh-P} = 201.4$ Hz, 1P)] in their ^{31}P NMR spectra [cf. (*S*)-BIPHEP–Rh/(*S*)-NOBIN: δ 37.0 (dd, $J_{Rh-P} = 170.4$ Hz, 1P), 38.2 (dd, $J_{Rh-P} = 165.5$ Hz, 1P)].

The BIPHEP–Rh/NOBIN complex thus obtained could be used as a chiral catalyst for ene-type cyclization of 1,6-enyne substrates without TfOH to protonate NOBIN off from the Rh metal center (Table 1). The BIPHEP–Rh/NOBIN complex gave the desired cyclic product at 5 °C in good yield and with higher enantiose-



Scheme 2.

Table 1. Asymmetric ene-cyclization by BIPHEP–Rh/NOBIN catalyst without TfOH



Entry	R^1	Time (h)	Yield (%)	ee[a] (%)
1	H	3	89	91 (−)
2	OMe	8	70	98 (−)
3	Cl	3	99	92 (−)
4[b]	H	3	77	99 (−)
5[c]	H	3	3	99 (+)
6[d]	H	3	25	92 (−)

[a] Enantiopurity was determined by chiral HPLC (Daicel CHIRALCEL OJ-H) analysis.
[b] (*R*)-BINAP–Rh + (*S*)-NOBIN.
[c] (*S*)-BINAP–Rh + (*S*)-NOBIN.
[d] (±)-BINAP–Rh + (*S*)-NOBIN.

lectivity (Scheme 1), presumably because of the association of the more coordinating amino portion to maximize the steric effect of the BIPHEP–Rh/NOBIN complex. All the reactions were thus shown to be effective by the catalysis of the BIPHEP–Rh/NOBIN complex without TfOH particularly in the case of acid-labile *p*-MeO-substrate.

In order to reconfirm the absolute configuration of the BIPHEP–Rh/NOBIN complex, the use of two enantiopure forms of BINAP was examined (Table 1). The (*R*)-BINAP–Rh/(*S*)-NOBIN complex gave the (−)-ene-product with 99% ee in 77% yield. In sharp contrast, the opposite combination of (*S*)-BINAP–Rh and (*S*)-NOBIN gave only 3% yield but again 99% ee of the enatiomeric (+)-product.[9] These results show the absolute configuration of the major BIPHEP–Rh/NOBIN complex and the reason why the use of a mixture of diastereomeric BIPHEP–Rh/(*S*)-NOBIN complexes provides 91% ee of the ene-type cyclization (−)-product in 89% yield, through chiral poisoning[10] of (*S*)-BIPHEP–Rh enantiomer by (*S*)-NOBIN. Indeed, the use of racemic (±)-BINAP–Rh complexes in association with (*S*)-NOBIN provides 92% ee of the ene-type cyclization (−)-product.

In conclusion, we have reported that 1,6-enyne substrates even with acid-labile *p*-methoxy substituent could be cyclized in high yield and enantioselectivity with BIPHEP–Rh/NOBIN complex without use of acid.

Typical experimental procedure of the enantioselective ene-type cyclization using the BIPHEP–Rh/(S)-NOBIN catalyst: To a mixture of [Rh(biphep)(nbd)]SbF_6 (0.01 mmol) and (*S*)-NOBIN (0.01 mmol) in 10 ml Schlenk tube was added dry dichloroethane (0.60 ml) under Ar atmosphere. A mixture was freezed and charged with hydrogen gas using balloon (1 atm), and then stirred for 30 min at room temperature. After again charged with Ar gas, the mixture was cooled to 5 °C. After the 1,6-enyne substrate (0.2 mmol) was added, the reaction mixture was stirred at 5 °C for 3 h, and then directly loaded on a silica gel chromatography to give the cyclic product as a colorless oil.

Acknowledgements

We are grateful to Professor Kuiling Ding of Shanghai Institute of Organic Chemistry for generous gift of NOBIN.

References and notes

1. Mikami, K.; Aikawa, K.; Yusa, Y.; Jodry, J. J.; Yamanaka, M. *Synlett* **2002**, *10*, 1561–1578.
2. Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H. In *Comprehensive Asymmetric Catalysis*; Springer: Berlin, 1999; Vols. 1–3.
3. The activation barrier to axial torsion in selectivity deuterated BIPHEP is measured to be only (22±1) kcal, which suggests that axial rotation takes place at room temperature or above: Desponds, O.; Schlosser, M. *Tetrahedron Lett.* **1996**, *37*, 47–48.
4. For the BIPHEP–Ru complex: (a) Mikami, K.; Korenaga, T.; Terada, M.; Ohkuma, T.; Pham, T.; Noyori, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 495–497; For the BIPHEP–Rh complex: (b) Mikami, K.; Kataoka, S.; Yusa, Y.; Aikawa, K. *Org. Lett.* **2004**, *6*, 3699–3701; For the BIPHEP–Pd complex: (c) Mikami, K.; Aikawa, K.; Yusa, Y.; Hatano, M. *Org. Lett.* **2002**, *4*, 91–94; (d) Mikami, K.; Aikawa, K.; Yusa, Y. *Org. Lett.* **2002**, *4*, 95–97; For the BIPHEP–Pt complex, see: (e) Tudor, M. D.; Becker, J. J.; White, P. S.; Gagné, M. R. *Organometallics* **2000**, *19*, 4376–4484; (f) Becker, J. J.; White, P. S.; Gagné, M. R. *J. Am. Chem. Soc.* **2001**, *123*, 9478–9479; (g) Mikami, K.; Kakuno, H.; Aikawa, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 7257–7260.
5. (a) Smrcina, M.; Lorenc, M.; Hanus, V.; Kocovsky, P. *Synlett* **1991**, 231–232; (b) Smrcina, M.; Lorenc, M.; Hanus, V.; Sedmera, P.; Kocovsky, P. *J. Org. Chem.* **1992**, *57*, 1917–1920; (c) Ding, K.; Wang, Y.; Yun, H.; Liu, J.; Wu, Y.; Terada, M.; Okubo, Y.; Mikami, K. *Chem. Eur. J.* **1999**, *5*, 1734–1737.
6. ^{31}P NMR of BIPHEP–Rh/(*S*)-BINOL (162 MHz, CD_2Cl_2) δ 35.4 (d, $J_{Rh-P} = 147.7$ Hz).
7. For reviews on ene-type cycloisomerization: (a) Trost, B. M. *Acc. Chem. Res.* **1990**, *23*, 34–42; (b) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635–662; (c) Trost, B. M. *Chem. Eur. J.* **1998**, *4*, 2405–2412; (d) Trost, B. M.; Krische, M. J. *Synlett* **1998**, 1–16; (e) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813–834; (f) Mendez, M.; Victor, M.; Fürstner, A. *Chemtracts Org. Chem.* **2003**, *16*, 397–425; (g) Lei, A.; He, M.; Zhang, X. *J. Am. Chem. Soc.* **2002**, *124*, 8198–8199; (h) Lei, A.; He, M.; Wu, S.; Zhang, X. *Angew. Chem., Int. Ed.* **2002**, *41*, 3457–3460; (i) Lei, A.; Waldkirch, J. P.; He, M.; Zhang, X. *Angew. Chem., Int. Ed.* **2002**, *41*, 4526–4529; (j) Mikami, K.; Hatano, M. *PNAS* **2004**, *20*, 5767–5769; (k) Hatano, M.; Mikami, K. *J. Am. Chem. Soc.* **2003**, *125*, 4704–4705; (l) Mikami, K.; Yusa, Y.; Hatano, M.; Wakabayashi, K.; Aikawa, K. *Chem. Commun.* **2004**, 98–99; (m) Mikami, K.; Hatano, M.; Akiyama, K. In *Topics in Organometallic Chemistry*; Tsuji, J., Ed.; Springer: Berlin, 2005.
8. ^{31}P NMR of (*R*)-BIPHEP–Rh/(*S*)-NOBIN (162 MHz, CD_2Cl_2): δ 37.9 (dd, $J_{Rh-P} = 198.5$, $J_{P-P} = 50.4$ Hz, 1P), 38.4 (dd, $J_{Rh-P} = 201.4$, $J_{P-P} = 50.4$ Hz, 1P);

(*S*)-BIPHEP–Rh/(*S*)-NOBIN (162 MHz, CD_2Cl_2): δ 37.0 (dd, $J_{Rh-P} =$ 170.4, $J_{P-P} = 51.4$ Hz, 1P), 38.2 (dd, $J_{Rh-P} = 165.5$, $J_{P-P} = 49.4$ Hz, 1P).

9. ^{31}P NMR of (*R*)-BINAP–Rh/(*S*)-NOBIN (162 MHz, CD_2Cl_2): δ 39.4 (dd, $J_{Rh-P} = 203.6$, $J_{P-P} = 89.3$ Hz, 1P), 40.1 (dd, $J_{Rh-P} = 201.46$, $J_{P-P} = 89.3$ Hz, 1P). Unfavorable mismatched combination of (*S*)-BINAP–Rh and (*S*)-NOBIN did not provide the (*S*)-BINAP–Rh/(*S*)-NOBIN complex, presumably because of the chirally rigid nature of BINAP.
10. Faller, J. W.; Lavoie, A. R.; Parr, J. *Chem. Rev.* **2003**, *103*, 3345–3367.