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Chiral *N*-heterocyclic biscarbenes based on 1,2,4-triazole as ligands for metal-catalyzed asymmetric synthesis[†]

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A facile and straightforward synthetic procedure for the preparation of new chiral bis-1,2,4-triazolium salts and their corresponding rhodium(I) biscarbene complexes are reported. It is widely applicable for the synthesis of 1,2,4-triazolium salts. The new chiral biscarbenes represent promising ligands for transition metal-catalyzed asymmetric syntheses. Their first successful application is demonstrated by the rhodium-catalyzed hydrogenation of dimethylitaconate and methyl-2-acetamidoacrylate which yielded enantioselectivities of up to 61% ee.

Chiral *N*-heterocyclic carbene (NHC) ligands are becoming more attractive in asymmetric catalysis since the first systems were developed in 1996.^{1,2} In contrast to the numerous chiral phosphine ligands, NHCs form stronger M–L bonds and hence generate more stable and rigid complexes.³ Particularly chiral C_2 -symmetric bis-NHC ligands are promising for asymmetric applications, however, there exist only a few examples in the literature.⁴⁻⁷ Most are bisbenzylimidazolium-derived ligands based on an axially chiral binaphthyl framework. They show good to excellent results in different catalytic applications such as asymmetric hydrosilylation,⁴ oxidative kinetic resolution,⁵ asymmetric conjugate addition⁶ and asymmetric arylation.⁷ Imidazolium-based systems are also known,⁸⁻¹⁰ whereas triazolium-based systems have not been reported in the literature so far.

Herein a facile synthetic pathway to chiral bistriazolium salts, starting from the easily accessible chiral R,R-(-)-1,2-diaminocyclohexane is reported. Furthermore, two new chiral biscarbene rhodium(1) complexes are presented with the first 1,2,4-triazole-based example.

The synthetic procedure for chiral 1,2,4-triazolium salts is shown in Scheme 1. Triethyl orthoformate and formyl hydrazine readily reacted with chiral R,R-(-)-1,2-diaminocyclohexane to



Scheme 1 Synthesis of the chiral bistriazolium salts.

form the corresponding bistriazole species (1),¹¹ which was converted to the corresponding *N*-substituted bistriazolium salt (2) by reaction with an alkyl halide in acetonitrile. Anion exchange finally led to the bistriazolium salt (3).

The described synthetic method allows further modification by varying of the *N*-substituents and thus changing the steric properties. By applying the method of Köcher and Herrmann as shown in Scheme 2,¹² complexes 4^{Me} and 4^{MN} were obtained in high yields (84–91%).



Scheme 2 Synthesis of chiral rhodium complexes 4^{Me} and 4^{MN} .

In contrast to **3**, the ¹H and ¹³C {¹H} NMR spectra of **4**^{Me} and **4**^{MN} indicate C_1 -symmetry with separate signals for each H and C atom. The molecular structure of the cationic Rh(I) complex **4**^{Me}, as determined by X-ray crystallography,¹³⁻²⁰ confirms the proposed C_1 symmetry (Fig. 1).

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Fig. 1 Molecular structure of the cation in 4^{Me} . The counter ion PF_6^- , and hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.¹³⁻²⁰ Selected bond lengths (Å) and angles (°): Rh1–C9 2.036(7), Rh1–C11 2.042(7), Rh1–Cg 1 2.099, Rh1–Cg2 2.111, Rh1–C1 2.212(6), Rh1–C12 2.200(5), Rh1–C5 2.212(6), Rh1–C6 2.229(7), C9–Rh1–C11 83.2(3), Cg1–Rh1–Cg2 86.4, N1–C9–N2 102.5(5), N2–C9–Rh1 129.7(5), N1–C9–Rh1 127.8(5), N4–C11–N5 104.8(6), N4–C11–Rh1 116.8(5), N5–C11–Rh1 138.3(6).

The metallacycle arranges in a boat conformation and the bite angle of the biscarbene ligand is $83.2(3)^{\circ}$. The Rh–C_{carbene} distances of 2.036(7) Å and 2.042(7) Å are found within the typical range for rhodium NHC complexes based on 1,2,4-triazoles.²¹ More crystallographic details to 4^{Me} are provided in the ESI.[†]

The rhodium(1) complexes 4^{Me} and 4^{MN} were applied as catalysts in the hydrogenation of methyl-2-acetamidoacrylate **5** and dimethylitaconate 7 (Scheme 3). The experiments were carried out in 1,2-dichloroethane at 60 °C in the presence of 1 mol% catalyst.



Scheme 3 Catalytic hydrogenation performed with complexes 4^{Me} and 4^{MN} .

The conversions and enantiomeric excesses were determined after 20 h and are summarized in Table 1.

At a hydrogen pressure of 40 bar **5** was fully converted to **6** by both catalysts, but 4^{MN} led to a slightly higher enantiomeric excess (entry 2). Sterically more demanding groups seem to positively influence the optical induction (entries 1 and 2). At 40 bar 7 was also quantitatively reduced by 4^{Me} and 4^{MN} (entries 4 and 6) while at reduced pressure (25 bar) only 4^{Me} led to full conversion (entry 3). The highest ee value, however, was found for complex 4^{MN} , when the reaction was done at a hydrogen pressure of 25 bar with 61% although the conversion was incomplete (entry 5).

Table 1	Enantioselective	hydrogenation	catalyzed by 4 ^{Ma}	and 4 ^m
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Entry	Complex	Substrate	p (bar)	conversion (%	b) ee (%)
1	4 ^{Me}	5	40	100	49
2	4 ^{MN}	5	40	100	53
3	4 ^{Me}	7	25	100	32
4	4 ^{Me}	7	40	100	14
5	4 ^{MN}	7	25	65	61
6	4 ^{MN}	7	40	100	53
Conver	sion was de	termined by	¹ H NMR	spectroscopy	enantiomeric

Conversion was determined by 'H NMR spectroscopy, enantiomeric excesses were extracted from chiral GC.

In conclusion, a straightforward synthesis for new chiral bis-1,2,4-triazolium salts and their corresponding rhodium(I) complexes was presented. The latter were successfully applied as enantioselective catalysts for the hydrogenation of prochiral olefins that yielded moderate to good ee values. The potential of the new chiral ligands is currently being investigated for a variety of other catalytic applications.

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Notes and references

- (a) W. A. Herrmann, L. J. Gooßen, C. Köcher and G. R. J. Artus, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2805–2807; (b) D. Enders, K. Breuer and J. H. Teles, *Helv. Chim. Acta*, 1996, **79**, 1217–1221; (c) D. Enders, K. Breuer, J. Runsink and J. H. Teles, *Helv. Chim. Acta*, 1996, **79**, 1899–1902.
- 2 (a) V. Cesar, S. Bellemin-Laponnaz and L. H. Gade, *Chem. Soc. Rev.*, 2004, 33, 619–636; (b) L. Gade and S. Bellemin-Laponnaz, in *N-Heterocyclic Carbenes in Transition Metal Catalysis*, 2007, pp. 117– 157; (c) M. C. Perry and K. Burgess, *Tetrahedron: Asymmetry*, 2003, 14, 951–961.
- 3 (a) F. E. Hahn and M. C. Jahnke, Angew. Chem., Int. Ed., 2008, 47, 3122–3172; (b) W. A. Herrmann, Angew. Chem., Int. Ed., 2002, 41, 1290–1309.
- 4 (*a*) W.-L. Duan, M. Shi and G.-B. Rong, *Chem. Commun.*, 2003, 2916–2917; (*b*) Q. Xu, X. Gu, S. Liu, Q. Dou and M. Shi, *J. Org. Chem.*, 2007, **72**, 2240–2242; (*c*) L.-j. Liu, F. Wang and M. Shi, *Organometallics*, 2009, **28**, 4416–4420.
- 5 (a) T. Chen, J.-J. Jiang, Q. Xu and M. Shi, Org. Lett., 2007, 9, 865–868; (b) S.-J. Liu, L.-j. Liu and M. Shi, Appl. Organomet. Chem., 2009, 23, 183–190.
- 6 (a) T. Zhang and M. Shi, *Chem.-Eur. J.*, 2008, **14**, 3759–3764; (b) H. Clavier, J.-C. Guillemin and M. Mauduit, *Chirality*, 2007, **19**, 471–476.
- 7 G.-N. Ma, T. Zhang and M. Shi, Org. Lett., 2009, 11, 875-878.
- 8 (a) D. S. Clyne, J. Jin, E. Genest, J. C. Gallucci and T. V. RajanBabu, Org. Lett., 2000, 2, 1125–1128; (b) A. R. Chianese and R. H. Crabtree, Organometallics, 2005, 24, 4432–4436; (c) A. Arnanz, C. Gonzalez-Arellano, A. Juan, G. Villaverde, A. Corma, M. Iglesias and F. Sanchez, Chem. Commun., 2010, 46, 3001–3003.
- 9 M. C. Perry, X. Cui and K. Burgess, *Tetrahedron: Asymmetry*, 2002, 13, 1969–1972.
- 10 L. G. Bonnet, R. E. Douthwaite and R. Hodgson, Organometallics, 2003, 22, 4384–4386.
- 11 Y. Garcia, G. Bravic, C. Gieck, D. Chasseau, W. Tremel and P. Gutlich, *Inorg. Chem.*, 2005, 44, 9723–9730.
- 12 C. Köcher and W. A. Herrmann, J. Organomet. Chem., 1997, 532, 261–265.
- 13 K. Brandenburg, DIAMOND Version 3.1, Crystal and Molecular Structure Visualization, 2005, Bonn.

- 14 APEX suite of crystallographic software, APEX 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA, 2008.
- 15 SAINT, Version 7.56a and SADABS Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA (2008).
- 16 International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Wilson, A. J. C., Ed., Kluwer Academic, Publishers, Dordrecht, The Netherlands, 1992.
- 17 G. M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Germany, (1998).
- 18 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, (2010).
- 19 L. J. Farrugia, WinGX (Version 1.70.01 January 2005), J. Appl. Crystallogr., 1999, **32**, 837–838.
- 20 (a) F. H Allen, The Cambridge Structural Database: a quarter of a million crystal structures and rising, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 380–388; (b) I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson and R. Taylor, New Software for searching the Cambridge Structural Database and visualizing crystal structures, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 389–397.
- 21 S. K. U. Riederer, P. Gigler, M. P. Högerl, E. Herdtweck, B. Bechlars, W. A. Herrmann and F. E. Kühn, *Organometallics*, 2010, DOI: 10.1021/om1005897.