Pergamon

Tetrahedron Letters 40 (1999) 3547–3548

TETRAHEDRON LETTERS

Transition Metal Complexes in Organic Synthesis, Part 50.[1]

Asymmetric Catalytic Complexation of 1-Methoxycyclohexa-1,3-diene by the Tricarbonyliron Fragment Using Amino Acid-Derived 1-Azabuta-1,3-dienes

Hans-Joachim Knölker* and ***Daniela Herzberg***

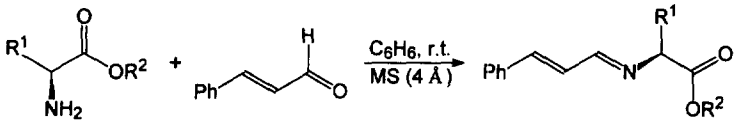
Institut für Organische Chemie, Universität Karlsruhe, Richard-Willstätter-Allee, 76131 Karlsruhe, Germany

Received 3 February 1999; revised 3 March 1999; accepted 10 March 1999

Abstract: L-Amino acid esters as chiral auxiliaries in the asymmetric complexation of 1-methoxycyclohexa-1,3-diene with pentacarbonyliron afford the *R*-enantiomer of the corresponding planar chiral tricarbonyliron complex in up to 24% *ee*.

Tricarbonyliron-cyclohexa-1,3-diene complexes have found versatile applications in organic synthesis.[2] The enantiopure complexes represent useful starting materials for asymmetric synthesis in which the planar chirality of the metal complex is transformed into central chirality at carbon.[3] Optically active tricarbonyliron–diene complexes can be prepared directly by enantioselective complexation of prochiral dienes.[4] We introduced (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes as novel tricarbonyliron transfer reagents.[5] The 1-azabuta-1,3-dienes are highly efficient catalysts for the catalytic complexation of buta-1,3-dienes and cyclohexa-1,3-dienes with pentacarbonyliron.[5] An important application is the asymmetric catalytic complexation of prochiral dienes using chiral 1-azabuta-1,3-dienes as catalysts.[1,6] This reaction represents the first example of an asymmetric catalysis providing planar-chiral transition metal π-complexes.[7]

In our investigation of the asymmetric catalytic complexation of 1-methoxycyclohexa-1,3-diene we found that 1-azadienes prepared from cinnamaldehyde and a simple centrally chiral amine, *e.g.* (*R*)- or (*S*)-phenylethylamine, led only to low asymmetric inductions of 6% *ee*.[6] On the other hand, 2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosylamine and the planar chiral 2-alkoxy-2'-amino-1,1'-binaphthyl as chiral auxiliaries provided up to 28% and 32% *ee*, respectively.[1] Herein we describe the use of amino acid esters as chiral auxiliaries in the asymmetric catalytic complexation of 1-methoxycyclohexa-1,3-diene by the tricarbonyliron fragment.



L-1 2 L-3

Scheme 1

Condensation of L-**1** with cinnamaldehyde **2** in benzene at room temperature in the presence of molecular sieves (4 Å)[8] provided the chiral 1-azadienes L-**3** in most cases quantitatively (Scheme 1, Table 1).

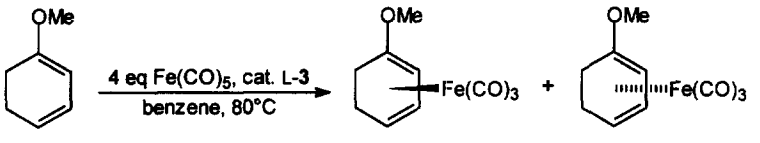
The asymmetric catalytic complexation of 1-methoxycyclohexa-1,3-diene (**4**) was investigated by using the reaction conditions (4 eq. $Fe[CO]_5$, benzene, reflux, 0.25 eq. of catalyst) previously applied (Scheme 2). The *ee* was accurately determined by separation of the two enantiomeric complexes (*R*)-**5** and (*S*)-**5** *via* HPLC on a permethylated β-cyclodextrin column.[9] In all cases the L-amino acid esters as chiral auxiliaries in the catalytic complexation led to an excess of the *R* enantiomer of complex **5**. We could confirm that the *ee* of the planar chiral complex is independent of the turnover of the catalytic complexation. Thus, using a certain catalyst an increase of the reaction time results in a higher yield of the product with the same enantiomeric excess.

0040-4039/99/$ - see front matter
PII: S0040-4039(99)00548-1

Table 1. Synthesis of the amino acid-derived 1-azadienes L-**3** and application to catalytic complexation.

L-**1**	R^1	R^2	L-**3**, Yield [%]	$[\alpha]_D^{20}$ (*c*, solvent)	reaction conditions	**5**, Yield [%]	*ee* [%] [a]
–	—	—	—	—	no catalyst, 9 d	2	0
a	CH_2Ph	*t*-Bu	90	−249.8 (0.53, $CHCl_3$)	0.25 eq L-**3a**, 67 h	36	4 (*R*)
b	*i*-Pr	Me	99	−119.4 (0.50, $CHCl_3$)	0.25 eq L-**3b**, 88 h	91	12 (*R*)
c	(*S*)-*s*-Bu	Me	97	−123.6 (0.82, $CHCl_3$)	0.25 eq L-**3c**, 67 h	72	8 (*R*)
d	*t*-Bu	Me	97	−96.2 (0.58, $CHCl_3$)	0.25 eq L-**3d**, 67 h	61	15 (*R*)
e	*t*-Bu	*t*-Bu	96	−86.1 (0.65, C_6H_6)	0.25 eq L-**3e**, 67 h	45	15 (*R*)
e	*t*-Bu	*t*-Bu	96	−86.1 (0.65, C_6H_6)	1.00 eq L-**3e**, 67 h	97	24 (*R*)

[a] *ee* values as determined by chiral HPLC (absolute configuration of the excess enantiomer).[9]



4 (*R*)-**5** (*S*)-**5**

Scheme 2

The azadiene L-**3a** provided complex **5** with 4% *ee* of the *R* enantiomer. Catalyst L-**3b** afforded complex (*R*)-**5** in 91% yield and 12% *ee*. Catalyst L-**3c** with isoleucine methyl ester as chiral auxiliary gave an induction of 8% *ee* and L-**3d** resulting from *tert*-leucine methyl ester provided 15% *ee*. The corresponding *tert*-butyl ester L-**3e** afforded the same asymmetric induction. Finally, complexation of the prochiral diene **4** with pentacarbonyliron in the presence of 1 eq. of L-**3g** led to a further increase of the asymmetric induction and provided the tricarbonyliron complex (*R*)-**5** in 97% yield with 24% *ee* of the *R* enantiomer.[10] The blank experiment (2% yield after 9 d at reflux in benzene) indicates that this additional increase of asymmetric induction compared to the result of the catalytic complexation is not due to a competing uncatalyzed complexation of the diene.

Acknowledgements: This work was supported by the *Deutsche Forschungsgemeinschaft* (Kn 240/5-3) and the *Fonds der Chemischen Industrie*. We are grateful to Professor K. Drauz (Degussa AG, Hanau) for a generous gift of L-*tert*-leucine and the BASF AG, Ludwigshafen, for a constant supply of pentacarbonyliron.

References and Notes

1. Part 49: H.-J. Knölker, H. Goesmann, H. Hermann, D. Herzberg, G. Rohde, *Synlett* **1999**, in print.
2. A. J. Pearson, *Iron Compounds in Organic Synthesis*; Academic Press: London, **1994**; Chap. 4 and 5. H.-J. Knölker in *Transition Metals for Organic Synthesis*; M. Beller, C. Bolm, Eds.; Wiley-VCH: Weinheim, **1998**; Vol. 1, Chap. 3.13, p. 534. H.-J. Knölker, *Chem. Soc. Rev.* **1999**, *28*, in print.
3. See for example: A. J. Birch, L. F. Kelly, D. V. Weerasuria, *J. Org. Chem.* **1988**, *53*, 278.
4. A. J. Birch, W. D. Raverty, G. R. Stephenson, *Organometallics* **1984**, *3*, 1075.
5. H.-J. Knölker, G. Baum, N. Foitzik, H. Goesmann, P. Gonser, P. G. Jones, H. Röttele, *Eur. J. Inorg. Chem.* **1998**, 993. H.-J. Knölker, E. Baum, P. Gonser, G. Rohde, H. Röttele, *Organometallics* **1998**, *17*, 3916.
6. H.-J. Knölker, H. Hermann, *Angew. Chem.* **1996**, *108*, 363; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 341.
7. For some leading references, see: *Catalytic Asymmetric Synthesis*; I. Ojima, Ed.; VCH: Weinheim, **1993**.
8. S. Hashimoto, S. Yamada, K. Koga, *Chem. Pharm. Bull.* **1979**, *27*, 771.
9. H.-J. Knölker, P. Gonser, T. Koegler, *Tetrahedron Lett.* **1996**, *37*, 2405.
10. (*R*)-**5**: A solution of **4** (110 mg, 1.00 mmol), pentacarbonyliron (526 µl, 784 mg, 4.00 mmol), and L-**3e** (301 mg, 1.00 mmol) in dry, degassed benzene (15 ml) was heated at reflux for 67 h under argon (exclusion of light). The cold reaction mixture was filtered through a short path of Celite and the solvent was evaporated in vacuum. Flash chromatography (pentane) of the residue on silica gel provided (*R*)-**5** (243 mg, 97%) as a yellow oil; $[\alpha]_D^{20} = -32.2$ (*c* = 1.37 in $CHCl_3$).