opening polymerization of cyclic siloxanes); b) K. Landfester, F. Tiarks, H.-P. Hentze, M. Antonietti, *Macromol. Chem. Phys.* **2000**, *201*, 1–5 (polyaddition).

[3] a) *Ziegler Catalysts* (Eds.: G. Fink, R. Mülhaupt, H. H. Brintzinger), Springer, Berlin, **1995**; b) H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, *Angew. Chem.* **1995**, *107*, 1255–83; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143–1170; c) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448–468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428–447; d) W. Kaminsky, M. Arndt, *Adv. Polym. Sci.* **1997**, *127*, 143–187.

[4] a) A. Held, F. M. Bauers, S. Mecking, *Chem. Commun.* **2000**, 301–302; b) F. M. Bauers, S. Mecking, *Macromolecules* **2001**, *34*, 1165–1171.

[5] Shortly after our initial report,[4a] the results of independent investigations by others on Ni^{II}-catalyzed ethylene polymerization in water were published: A. Tomov, J.-P. Broyer, R. Spitz, *Macromol. Symp.* **2000**, *150*, 53–58. See also A. Tomov, R. Spitz, T. Saudemont, X. Drujon (Elf Atochem), WO 00/20464, **2000** [*Chem. Abstr.* **2000**, *132*, 279651a].

[6] For suspension-type polymerization of ethylene to high molecular mass amorphous polyethylene, see a) A. Held, S. Mecking, *Chem. Eur. J.* **2000**, *6*, 4623–4629, and references therein. For a very slow (one turnover per day) suspension-type Rh-catalyzed ethylene polymerization in water, see b) L. Wang, R. S. Lu, R. Bau, T. C. Flood, *J. Am. Chem. Soc.* **1993**, *115*, 6999–7000. Catalytic polymerization of olefinic monomers other than ethylene in water has been described: c) R. E. Rinehart, H. P. Smith, H. S. Witt, H. Romeyn, *J. Am. Chem. Soc.* **1961**, *83*, 4864–4865; d) G. Natta, G. Dall'Asta, L. Porri, *Makromol. Chem.* **1965**, *81*, 253–257; e) R. E. Rinehart, *J. Polym. Sci. C* **1969**, *27*, 7–25; f) B. M. Novak, R. H. Grubbs, *J. Am. Chem. Soc.* **1988**, *110*, 7542–7543; g) D. M. Lynn, B. Mohr, R. H. Grubbs, *J. Am. Chem. Soc.* **1998**, *120*, 1627–1628; h) W. Reppe, A. Magin, US-Pat. 2577208, **1951** [*Chem. Abstr.* **1952**, *46*, 6143b]; i) Z. Jiang, A. Sen, *Macromolecules* **1994**, *27*, 7215–7216; j) G. Verspui, G. Papadogianakis, R. A. Sheldon, *Chem. Commun.* **1998**, 401–402; k) E. Lindner, M. Schmid, J. Wald, J. A. Queisser, M. Geprägs, P. Wegner, C. Nachtigal, *J. Organomet. Chem.* **2000**, *602*, 173–187.

[7] Reviews on late transition metal catalysis for olefin polymerization: a) S. Mecking, *Coord. Chem. Rev.* **2000**, *203*, 325–351; b) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–1204; c) S. Mecking, *Angew. Chem.* **2001**, *113*, 550–557; *Angew. Chem. Int. Ed.* **2001**, *40*, 534–540; d) ref. [3c].

[8] a) K. A. Ostoja-Starzewski, J. Witte, *Angew. Chem.* **1987**, *99*, 76–77; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 63–64; b) U. Klabunde, S. D. Ittel, *J. Mol. Catal.* **1987**, *41*, 123–134.

[9] a) L. K. Johnson, A. M. A. Bennett, S. D. Ittel, L. Wang, A. Parthasarathy, E. Hauptman, R. D. Simpson, J. Feldman, E. B. Coughlin (DuPont), WO 98/30609, **1998** [*Chem. Abstr.* **1998**, *129*, 149362j]; b) C. Wang, S. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs, D. A. Bansleben, M. W. Day, *Organometallics* **1998**, *17*, 3149–3151; c) T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, D. A. Bansleben, *Science* **2000**, *287*, 460–462.

[10] It should be noted that the different mechanisms of chain initiation, growth, and transfer in free-radical versus coordination polymerization can clearly affect the delicate steps involved in particle nucleation and growth. Nonetheless, the general comparison drawn here is reasonable.

[11] For background information on mini-emulsions and the function of the hydrophobe, see a) E. D. Sudol, M. S. El-Aasser in *Emulsion Polymerization and Emulsion Polymers* (Eds.: P. A. Lovell, M. S. El-Aasser), Wiley, Chichester, **1997** pp. 699–722; b) K. Landfester, N. Bechthold, F. Tiarks, M. Antonietti, *Macromolecules* **1999**, *32*, 5222–5228, and references therein.

[12] In regard to the development of particle numbers during polymerization, a comprehensive interpretation of the data is complicated by the necessity of extensively diluting the turbid emulsion for light-scattering analysis. Deviations from the original state may result in analyses of the catalyst mini-emulsion (liquid/liquid dispersion).

[13] Like the polymers obtained in traditional polymerization in organic media with these catalysts,[9] the polyethylenes prepared in water are moderately branched. For the material isolated from dispersions, about 20 branches/1000 carbon atoms (predominantly methyl branches) were observed by ^{1}H and ^{13}C NMR spectroscopy. By comparison to linear polyethylene, a moderate decrease in crystallinity results.

[14] Note added upon revision of this manuscript (May 23, 2001): after submission of this manuscript, the preparation of latexes of low molecular mass materials by the polymerization of ethylene employing mini-emulsions of water-stable nickel(II) complexes was reported: R. Soula, C. Novat, A. Tomov, R. Spitz, J. Claverie, X. Drujon, J. Malinge, T. Saudemont, *Macromolecules* **2001**, *34*, 2022–2026.

Formal Enantioselective Michael Addition with Umpolung of Reactivity[**]

Eike Hupe and Paul Knochel[*]

Dedicated to Professor Dieter Seebach

The conjugate addition of nucleophiles to unsaturated carbonyl derivatives is an important reaction,[1] and its enantioselective variant has received much attention over the last few years.[2] Several general methods such as copper-catalyzed additions of organolithium or organomagnesium derivatives,[3] or the addition of diorganozinc compounds[4] have been described in detail. Recently, a rhodium-catalyzed addition of boronic acids has also been reported.[5] Although satisfactory results have been obtained in many cases, several classes of organometallic compounds, such as alkynyl,[6] allylic, and allenyl organometallic compounds still cannot be added enantioselectively. Herein, we report a new synthetic approach to conjugate additions in which an umpolung[7] of the Michael acceptor reactivity occurs. Whereas the usual reactivity of an enone of type **1** (a^3-reactivity)[7] requires a reaction with a nucleophile (Nu^-) and leads to the addition product of type **2** (Scheme 1), we envisioned an umpolung of the enone reactivity by successive protection of the carbonyl function and formal hydrometalation, leading to the chiral organometallic species **3**. After the reaction of **3** with an electrophile (E^+) and deprotection, products of type **4** would be produced. If an asymmetric hydrometalation and a stereoselective reaction with the electrophile (E^+) is possible, then this would correspond, after deprotection, to a formal enantioselective Michael addition with umpolung of the normal reactivity pattern (Scheme 1).

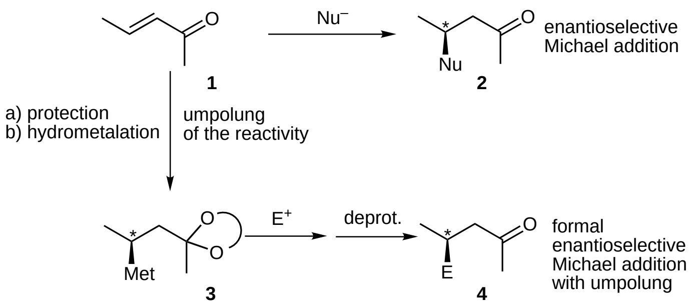
Recently, we developed a reaction sequence involving an asymmetric hydroboration followed by a boron–zinc ex-

---

[*] Prof. Dr. P. Knochel, Dipl.-Chem. E. Hupe
Ludwig-Maximilians-Universität München
Department of Chemie
Butenandtstrasse 5–13, 81377 München (Germany)
Fax: (+49) 89-2180-7680
E-mail: Paul.Knochel@cup.uni-muenchen.de

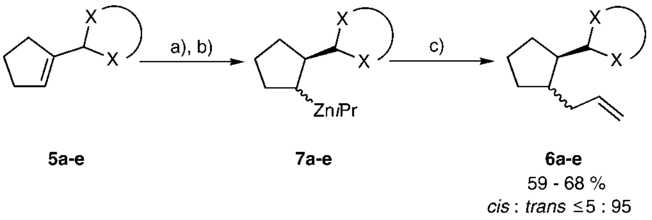
[**] This work was supported by the DFG (Leibniz-Program) and the Fonds der Chemischen Industrie (Kekulé-scholarship to E.H.). We thank D. Renard for preliminary experiments, as well as Chemetall GmbH (Frankfurt), the BASF AG, and the Degussa-Hüls AG (Hanau) for generous gifts of chemicals.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.



Scheme 1. Formal Michael addition with umpolung of reactivity.

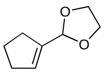
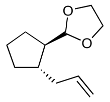
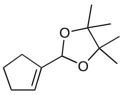
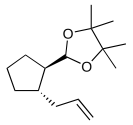
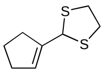
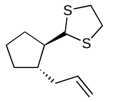
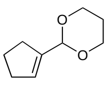
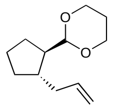
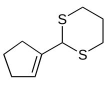
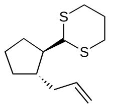
change reaction, which allows a general preparation of secondary, optically active organozinc reagents.[8a,b] Moreover, we showed that their reaction with various electrophiles proceeds with retention of configuration.[8c] Preliminary experiments on protected enone systems revealed that the nature of the protecting group strongly influences the configurational stability of the resulting diorganozinc species, especially in the case of five-membered systems. Thus, the hydroboration of the 1,3-dioxolane **5a** with Et_2BH followed by treatment with iPr_2Zn, $CuCN \cdot 2LiCl$, and allylic bromide provides the desired allylated product **6a** in 68% yield (Scheme 2 and Table 1). However, a 47:53 mixture of *cis* and *trans* isomers was obtained, showing that an epimerization of the intermediate organozinc reagent **7a** had occurred (Scheme 2 and Table 1). A systematic study revealed that this result can be greatly improved by careful choice of the protecting group. The 1,3-dioxane acetal **5d** gives an improved selectivity, but the best result is obtained with the 1,3-dithiane **5e**, leading to a *cis*:*trans* selectivity of 5:95.



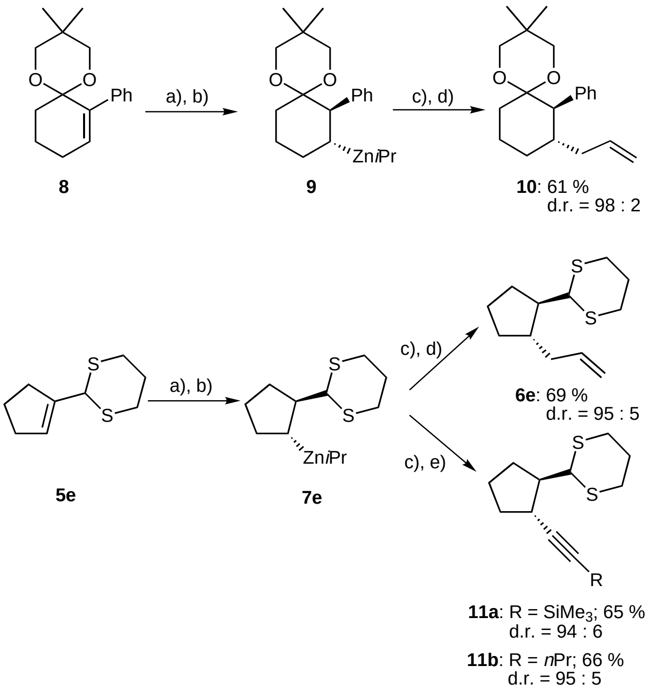
Scheme 2. Optimization of configurational stability of the zinc intermediate **7a–e** by varying the protecting group. a) Et_2BH (3 equiv, 50 °C, 16 h); b) iPr_2Zn (3 equiv, 25 °C, 5 h); c) $CuCN \cdot 2LiCl$ (1 equiv, −78 °C, 0.5 h), then allylic bromide (3 equiv, −78 °C to 25 °C, 10 h).

By applying the results of this study to the protected cyclohexenone **8** and to the 1,3-dithiane **5e**, excellent diastereoselectivities (*trans*:*cis* ratio ≥94:6) can be achieved (Scheme 3). Thus, the allylation of **9**, obtained by the usual sequence from **8**, proceeds with a diastereoselectivity of 98:2 (*trans*:*cis* ratio) and affords product **10** in 61% yield. Similarly, the alkynylation of the unsaturated dithiane **5e** furnishes the akynylated product **11b** in 66% yield (d.r. = 95:5).

Table 1. Hydroboration of the unsaturated acetals and thioacetals **5a–e**, followed by boron–zinc exchange and copper-mediated allylation, leading to products **6a–e**.

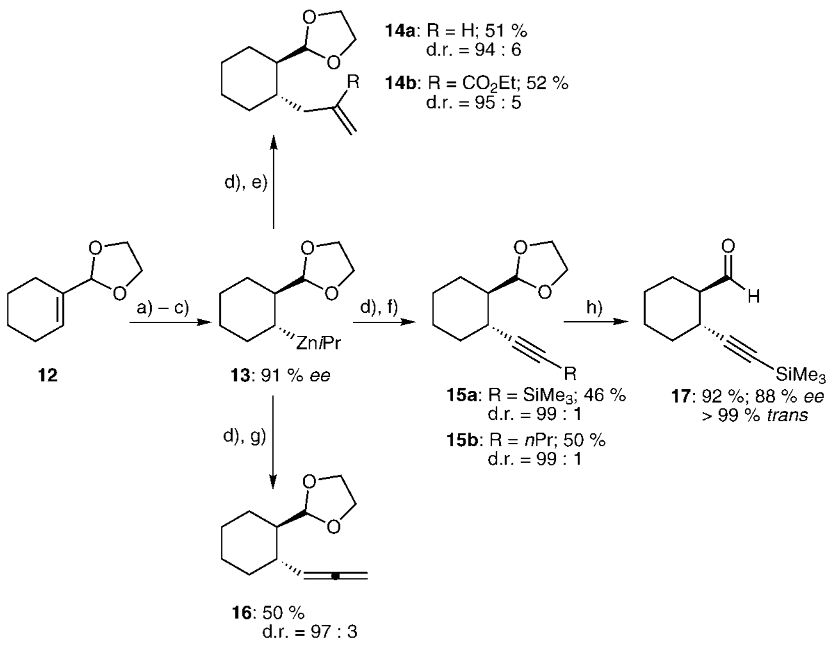
Starting material **5**	Product **6**	*trans*:*cis*	Yield [%][a]
 **5a**	 **6a**	53:47	68
 **5b**	 **6b**	60:40	65
 **5c**	 **6c**	72:28	59
 **5d**	 **6d**	80:20	62
 **5e**	 **6e**	95:5	69

[a] Yield of isolated, analytically pure compound.



Scheme 3. Diastereoselective reactions of the zinc reagents **9** and **7e** obtained by sequential hydroboration and boron–zinc exchange. a) Et_2BH (3 equiv, 50 °C, 16 h); b) iPr_2Zn (3 equiv, 25 °C, 5 h); c) $CuCN \cdot 2LiCl$ (1 equiv, −78 °C, 0.5 h); d) allylic bromide (3 equiv, −78 °C to 25 °C, 10 h); e) alkynyl bromide (3 equiv, −40 °C, 20 h).

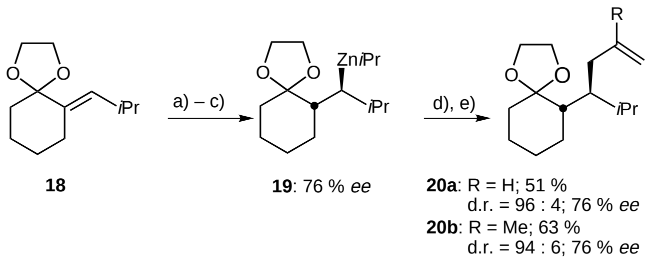
Our method can also be readily performed with enantiomerically enriched organozinc reagents. Thus, the asymmetric hydroboration of **12** with (−)-isopinocampheylborane ((−)-$IpcBH_2$)[9] produces the *trans*-configured, secondary organozinc reagent **13** in 91% *ee* after treatment with Et_2BH[10] and iPr_2Zn (Scheme 4).[11] This organozinc compound reacts with allylic, alkynyl, and propargyl bromides, affording the desired



Scheme 4. Enantioselective conjugate functionalization of the unsaturated acetal **12** by an asymmetric hydroboration and boron–zinc exchange sequence. a) (−)-IpcBH$_2$ (1.1 equiv, −25 °C, 48 h); b) Et$_2$BH (5 equiv, 50 °C, 16 h); c) *i*Pr$_2$Zn (5 equiv, 25 °C, 5 h); d) CuCN·2LiCl (1.5 equiv, −78 °C, 30 min); e) allylic bromide (5 equiv, −78 °C to 25 °C, 10 h for **14a** or 5 equiv, −40 °C, 48 h for **14b**); f) alkynyl bromide (5 equiv, −40 °C, 16 h); g) propargyl bromide (5 equiv, −40 °C, 16 h); h) 5% HCl, 35 °C, 16 h.

allylated products **14a**, **b**, the alkynylated derivatives **15a**, **b** and the allenylated compound **16** in satisfactory overall yields (46–52%).[12] To demonstrate the validity of the umpolung procedure, we have deprotected the product **15a** by treatment with dilute HCl to obtain the desired *trans*-aldehyde **17** in 92% yield and 88% *ee* (42% overall yield starting from the unsaturated acetal **12**; Scheme 4).

Finally, we have extended our method to an exocyclic system. Thus, the protected *exo*-alkylidene enone **18** was hydroborated with (−)-IpcBH$_2$ affording, after further treatment with Et$_2$BH and *i*Pr$_2$Zn, the chiral secondary alkylzinc reagent **19** in 76% *ee* (Scheme 5).[11] Following transmetalation with CuCN·2LiCl and allylation, the desired products **20a**, **b** were obtained with excellent diastereoselectivities (≥94:6), thus allowing the stereocontrol of two contiguous chiral centers.[13]



Scheme 5. Enantioselective conjugate functionalization of the unsaturated acetal **18** by an asymmetric hydroboration and boron–zinc exchange sequence. a) (−)-IpcBH$_2$ (1.1 equiv, −25 °C, 48 h); b) Et$_2$BH (5 equiv, 50 °C, 16 h); c) *i*Pr$_2$Zn (5 equiv, 25 °C, 5 h); d) CuCN·2LiCl (1.5 equiv, −78 °C, 30 min); e) allylic bromide (5 equiv, −78 °C to 25 °C, 10 h for **20a**, or 5 equiv, −40 °C, 48 h for **20b**).

In summary, we have shown that unsaturated acetals and ketals can be stereoselectively hydroborated and converted by a boron–zinc exchange to a secondary alkylzinc reagent with high retention of configuration. These chiral, functionalized diorganozinc reagents react with retention of configuration with allylic bromides, alkynyl halides, and propargyl bromide, affording the products of formal Michael addition. As such, this new method fully complements the existing, traditional conjugate addition protocols, which often encounter problems in the enantioselective conjugate addition of allylic, alkenyl, and allenyl organometallic species.

Experimental Section

Preparation of **15a**: A flame-dried 25 mL flask equipped with a magnetic stirring bar, an argon inlet, and a septum was cooled to −25 °C and charged with freshly prepared (−)-IpcBH$_2$ (1.1 mL, 1.1 mmol, 1.1 equiv, 1 M solution in THF). The protected olefin **12** (154 mg, 1.0 mmol, 1.0 equiv, 1 M in THF) was added dropwise over a period of 1 h. Stirring at this temperature was continued for 48 h. After pumping off the volatiles (0.1 Torr, 25 °C, 2 h), Et$_2$BH (0.69 mL, 5.0 mmol, 5 equiv, 7.3 M in Me$_2$S,) was added and the resulting mixture was stirred for 16 h at 50 °C. After pumping off the volatiles (0.1 Torr, 25 °C, 2 h), *i*Pr$_2$Zn (1.0 mL, 5.0 mmol, 5 equiv, 5.0 M in Et$_2$O,) was added and the mixture was stirred 5 h at 25 °C. According to GC analysis of an oxidized aliquot (3 M NaOH/30% H$_2$O$_2$) the boron–zinc conversion was >85%. The volatiles were pumped off (0.1 Torr, 25 °C, 0.5 h), and the gray-black residue was diluted with THF (3 mL) and cooled to −78 °C. A freshly prepared solution of CuCN·2LiCl (1.5 mL, 1.5 mmol, 1.5 equiv, 1 M in THF) was slowly added over 40 min by syringe pump and the mixture stirred for 30 min at −78 °C. Then, a solution of 1-bromo-2-trimethylsilylacetylene (885 mg, 5 mmol , 5 equiv) in THF (1 mL) was added slowly (40 min) by syringe pump. After stirring for 30 min at −78 °C, the mixture was allowed to warm to −40 °C and stirred at this temperature for 16 h. The reaction mixture was then poured into a saturated aqueous NH$_4$Cl solution (150 mL) containing NH$_{3(aq)}$ (2 mL, 30% in H$_2$O). After extraction with Et$_2$O (3 × 100 mL) the combined organic phases were dried over MgSO$_4$. The solvent was removed and the crude product purified by column chromatography (SiO$_2$, hexanes/Et$_2$O 19:1) affording **15a** as a colorless oil (116 mg, 0.46 mmol, 46%).

Received: April 4, 2001 [Z16903]

---

[1] P. Perlmutter in *Conjugate Addition Reactions in Organic Synthesis, Vol. 9* (Eds.: J. E. Baldwin, P. D. Magnus), Pergamon, Oxford, **1992** (*Tetrahedron Organic Chemistry Series*).

[2] a) K. Tomioka, Y. Nagaoka in *Comprehensive Asymmetric Catalysis III* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Heidelberg, **1999**, pp. 1105–1120; b) B. L. Feringa, *Acc. Chem. Res.* **2000**, *33*, 346; c) A. Alexakis, *Chimia* **2000**, *54*, 55; d) G. Helmchen, A. Pfaltz, *Acc. Chem. Res.* **2000**, *33*, 336; e) N. Krause, A. Hoffmann-Röder, *Synthesis* **2001**, 171.

[3] a) M. van Klaveren, F. Lambert, D. J. F. M. Eijkelkamp, D. M. Grove, G. van Koten, *Tetrahedron Lett.* **1994**, *35*, 6135; b) G. van Koten, *Pure Appl. Chem.* **1994**, *66*, 1455; c) Y. Nakagawa, K. Matsumoto, K. Tomioka, *Tetrahedron* **2000**, *56*, 2857; d) Y. Nagaoka, K. Tomioka, *Org. Lett.* **1999**, *1*, 1467; e) M. Kanai, Y. Nakagawa, K. Tomioka, *Tetrahedron* **1999**, *55*, 3831; f) Y. Moritani, D. H. Appella, V. Jurkauskas, S. L. Buchwald, *J. Am. Chem. Soc.* **2000**, *122*, 6797.

[4] a) A. Alexakis, J. Vastra, J. Burton, P. Mangeney, *Tetrahedron: Asymmetry* **1997**, *8*, 3193; b) A. Alexakis, J. Vastra, J. Burton, C. Benhaim, P. Mangeney, *Tetrahedron Lett*. **1998**, *39*, 7869; c) A. Alexakis, C. Benhaim, X. Founioux, A. van den Heuvel, J.-M. Leveque, S. March, S. Rosset, *Synlett* **1999**, 1811; d) A. Alexakis, C. Benhaim, *Org. Lett*. **2000**, *2*, 2579; e) A. Alexakis, J. Burton, J. Vastra, C. Benhaim, X. Fournioux, A. van den Heuvel, J.-M. Leveque, F. Maze, S. Rosset, *Eur. J. Org. Chem*. **2000**, *24*, 4011; f) X. Hu, H. Chen, X. Zhang, *Angew. Chem*. **1999**, *111*, 3720; *Angew. Chem. Int. Ed*. **1999**, *38*, 3518; g) B. L. Feringa, M. Pineschi, L. A. Arnold, R. Imbos, A. H. M. De Vries, *Angew. Chem*. **1997**, *109*, 2733; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 2620; h) R. Naasz, L. A. Arnold, M. Pineschi, E. Keller, B. L. Feringa, *J. Am. Chem. Soc*. **1999**, *121*, 1104; i) R. Imbos, M. H. G. Brilman, M. Pineschi, B. L. Feringa, *Org. Lett*. **1999**, *1*, 623; j) J. P. G. Versleijen, A. M. van Leusen, B. L. Feringa, *Tetrahedron Lett*. **1999**, *40*, 5803; k) L. A. Arnold, R. Imbos, A. Mandolini, A. H. M. de Vries, R. Naasz, B. L. Feringa, *Tetrahedron* **2000**, *56*, 2865; l) I. Chataigner, C. Gennari, U. Piarulli, S. Ceccarelli, *Angew. Chem*. **2000**, *112*, 953; *Angew. Chem. Int. Ed*. **2000**, *39*, 916; m) A. K. H. Knoebel, I. H. Escher, A. Pfaltz, *Synlett* **1997**, 1429; n) I. H. Escher, A. Pfaltz, *Tetrahedron* **2000**, *56*, 2879.

[5] a) Y. Takaya, M. Ogasawara, T. Hayashi, M. Sakai, N. Miyaura, *J. Am. Chem. Soc*. **1998**, *120*, 5579; b) Y. Takaya, M. Ogasawara, T. Hayashi, *Tetrahedron Lett*. **1998**, *39*, 8479; c) Y. Takaya, M. Ogasawara, T. Hayashi, *Tetrahedron Lett*. **1999**, *40*, 6957; d) T. Hayashi, T. Senda, Y. Takaya, M. Ogasawara, *J. Am. Chem. Soc*. **1999**, *121*, 11591; e) Y. Takaya, T. Senda, K. Hiroaki, M. Ogasawara, T. Hayashi, *Tetrahedron: Asymmetry* **1999**, *10*, 4047; f) Y. Takaya, M. Ogasawara, T. Hayashi, *Chirality* **2000**, *12*, 469; g) T. Hayashi, T. Senda, M. Ogasawara, *J. Am. Chem. Soc*. **2000**, *122*, 10716.

[6] J. M. Chong, L. Shen, N. J. Taylor, *J. Am. Chem. Soc*. **2000**, *122*, 1822.

[7] D. Seebach, *Angew. Chem*. **1979**, *91*, 259; *Angew. Chem. Int. Ed. Engl*. **1979**, *18*, 239.

[8] a) A. Boudier, C. Darcel, F. Flachsmann, L. Micouin, M. Oestreich, P. Knochel, *Chem. Eur. J*. **2000**, *6*, 2748; b) A. Boudier, E. Hupe, P. Knochel, *Angew. Chem*. **2000**, *112*, 2396; *Angew. Chem. Int. Ed*. **2000**, *39*, 2294; c) E. Hupe, P. Knochel, *Org. Lett*. **2001**, *3*, 127.

[9] H. C. Brown, A. K. Mandal, N. M. Yoon, B. Singaram, J. R. Schwier, P. K. Jadhav, *J. Org. Chem*. **1982**, *47*, 5069.

[10] The purpose of the treatment with Et_2BH is to replace the bulky isopinocampheyl ligand by an ethyl group or a hydrogen atom.

[11] The enantiomeric excess was determined by chiral GC analysis of the alcohol obtained from oxidation with aqueous H_2O_2 after the asymmetric hydroboration step.

[12] The absolute configuration of **14**–**17** was determined by deprotection and reduction of the corresponding *trans*-alcohol, obtained after asymmetric hydroboration and oxidative workup, to *trans*-2-(hydroxymethyl)cyclohexanol. The $[\alpha]_D^{20}$ values were compared with those reported in the literature. See: L. J. Dolby, F. A. Meneghini, T. Koizumi, *J. Org. Chem*. **1968**, *33*, 3060.

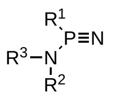
[13] The absolute configuration of **20a** and **20b** was determined according to method applied by: K. Ishihara, S. Kondo, H. Yamamoto, *J. Org. Chem*. **2000**, *65*, 9128.

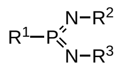
Reversible Tautomeric Transformation between a Bis(amino)cyclodiphosph(V)azene and a Bis(imino)cyclodiphosph(V)azane[**]

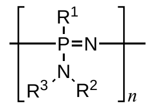
Jürgen Tirreé, Dietrich Gudat, Martin Nieger, and Edgar Niecke[*]

Dedicated to Professor Rolf Appel
on the occacion of his 80th birthday

Amino-substituted phosphinonitrenes (**I**) with suitable substitution patterns can be rearranged to tautomeric bis(imino)phosphoranes (**II**).[1] In the absence of the possibility to rearrange, oligo- and polyphosphazenes (**III**) are formed.[2] Whereas in general the formation of tri- and tetramers appears to be thermodynamically favored,[2] a sterically overcrowded bisamino-substituted phosphinonitrene (**I**, $R^1 = NR^2R^3$, $R^2,R^3 = i\mathrm{Pr}_2N$) was noted to undergo instead an unusual cyclodimerization to give a cyclodiphosph(v)azene.[3] In connection with studies on NH-functionalized bis(imino)phosphoranes and the anions derived therefrom[4] we also became interested in [2+2] cycloadditions of these species which yielded as yet unknown bis(imino)diphosph(v)azanes. Herein, we report on the synthesis of a cyclodiphosph(v)azane as well as on its reversible conversion into a tautomeric cyclodiphosph(v)azene.


I


II


III

Treatment of the azidophosphane **2**,[6] which is accessible from reaction of pentamethylcyclopentadienyl-(2,4,6-tri-*tert*-butylphenyl)iminophosphane, Cp*P=NMes* (**1**),[5] with hydrogen azide under dry pyrolysis (pure substance, 130 °C) conditions produced a mixture of the tautomeric four-membered-ring P–N heterocycles **5** and **7** in 1:9 ratio (Scheme 1). Colorless crystals of the bis(amino)cyclodiphosp(v)azene **7** were isolated by crystallization of the mixture from a little toluene.[7] Probable intermediates during the elimination of nitrogen from **2** are the phosphinonitrene **3** and the bis(imino)phosphorane **4**, which is formed from **3** by subsequent 1,3-H shift.[8] Metalation of **7** (MeLi, 0 °C) to the dilithiated complex **8**[9] and subsequent protonation with *t*BuOH gave a quantitative yield of the tautomeric bis(imino)cyclodiphosph(v)azane **5**, which was likewise isolated in crystalline form.[10]

---

[*] Prof. Dr. E. Niecke, Dr. J. Tirreé, Priv.-Doz. Dr. D. Gudat, Dr. M. Nieger
Anorganisch-chemisches Institut der Universität
Gerhard-Domagk-Strasse 1, 53121 Bonn (Germany)
Fax: (+49) 228-73-5327
E-mail: e.niecke@uni-bonn.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Part of this work was presented at the International Conference on Inorganic Ring Systems (IRIS-IX), Saarbrücken, Germany, 24–28 July 2000, Abstr. Nr. P-22.

1433-7851/01/4016-3025 $ 17.50+.50/0