larger steric bulk of tri-*n*-butylphosphane relative to triethylphosphane.

We have demonstrated a novel route to a macrocycle with palladium acetylide units in the backbone. We are currently investigating the extension of this method to the formation of macrocycles with other bridging acetylide ligands.

Experimental Section

1a: A mixture of *o*-diethynylbenzene (126 mg, 1 mmol) and [PdCl$_2$(PEt$_3$)$_2$] (1.034 g, 2.5 mmol) in diethylamine (50 mL) in the presence of CuCl (ca. 2 mol%) was stirred at room temperature for 18 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on alumina with CH$_2$Cl$_2$ as eluent. Recrystallization from CH$_2$Cl$_2$/hexane gave pale yellow crystals (544 mg, 62%). IR (KBr): $\tilde{\nu}$ = 2114 cm^{-1} ($C\equiv C$); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.22$ (dd, $J = 5.8$, 3.5 Hz, 2H), 6.99 (dd, $J = 5.8$, 3.5 Hz, 2H), 2.00–1.93 (m, 24H), 1.19 (dt, $J = 16.6$, 8.0 Hz, 36H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 138.3$, 127.9, 124.9, 107.0 (t, $J_{P,C} = 5.8$ Hz), 98.2 (t, $J_{P,C} = 16.5$ Hz), 15.4 (vt, $N = 14.1$ Hz), 8.43; ^{31}P NMR (162 MHz, CDCl$_3$): $\delta = 18.2$; satisfactory elemental analysis.

2: An equimolar mixture of *o*-diethynylbenzene and [Pd(PEt$_3$)$_2$Cl$_2$] was treated as for **1a** to give pale yellow crystals in 33% yield. IR (KBr): $\tilde{\nu}$ = 2088 cm^{-1} ($C\equiv C$); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.23$ (dd, $J = 5.9$, 3.4 Hz, 8H), 6.99 (dd, $J = 5.9$, 3.4 Hz, 8H), 2.05–2.00 (m, 48H), 1.21 (dt, $J = 16.3$, 8.0 Hz, 72H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 132.4$, 128.6, 124.0, 114.2 (t, $J_{P,C} = 17.4$ Hz), 111.1 (t, $J_{P,C} = 3.7$ Hz), 17.2 (vt, $N = 14.1$ Hz), 8.9; ^{31}P NMR (162 MHz, CDCl$_3$): $\delta = 19.3$; satisfactory elemental analysis.

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Completely Regioselective Synthesis of Directly Linked *meso,meso* and *meso,β* Porphyrin Dimers by One-Pot Electrochemical Oxidation of Metalloporphyrins**

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Porphyrin dimers have been attracting considerable attention as biomimetic models of photosynthetic systems, and as photonic materials and functional molecular devices.[1–7] Since the type of bond connecting the porphyrin rings influences the electronic communication in the dimer, a variety of porphyrin arrays has been explored.[8–10] Directly linked porphyrin arrays are one interesting class of these compounds, because of the strong interaction between the two porphyrin rings.[1, 7, 11–14]

We previously reported that electrochemical oxidation has an advantage over silver salt oxidation for obtaining directly linked *meso,meso* porphyrins, since the former method can be

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author. The following data are available as supporting information: a preliminary X-ray crystal structure of **10**, the ROESY NMR spectrum of **11**, and cyclic and differential-pulse voltammograms of **2**, **4**, **5**, **8**, **10**, **11**, and **13**–**15**.

applied to a wider range of substrates.[15] To determine the scope and limitations of the electrochemical method, we performed the reaction using a variety of metalloporphyrins that were unsubstituted at the *meso* position, and discovered a surprising dependence of the coupling product on the metal incorporated in the porphyrin ring. When electrolyzed, magnesium(II) (**1**) and zinc(II) 5,15-di(3,5-di-*tert*-butylphenyl)porphyrin (**2**) produced the corresponding directly linked *meso,meso* dimers shown in Table 1.[15] In contrast, the copper(II) (**3**), palladium(II) (**4**), and nickel(II) porphyrins (**6**) as well as the free porphyrin base (**5**) produced the corresponding directly linked *meso,β* dimers exclusively (Table 1, Scheme 1). In all the reactions, trace amounts of higher coupling products were detected, although full identifications of these products have not yet been performed. The structures of these unforeseen *meso,β* products were confirmed by FAB mass spectrometry and ^{1}H NMR and ROESY NMR spectroscopy as well as high-resolution FAB-MS of the metal-free dimer (**11**).

Table 1. Electrochemical reactions of metal 5,15-di(3,5-di-*tert*-butylphenyl)porphyrins.

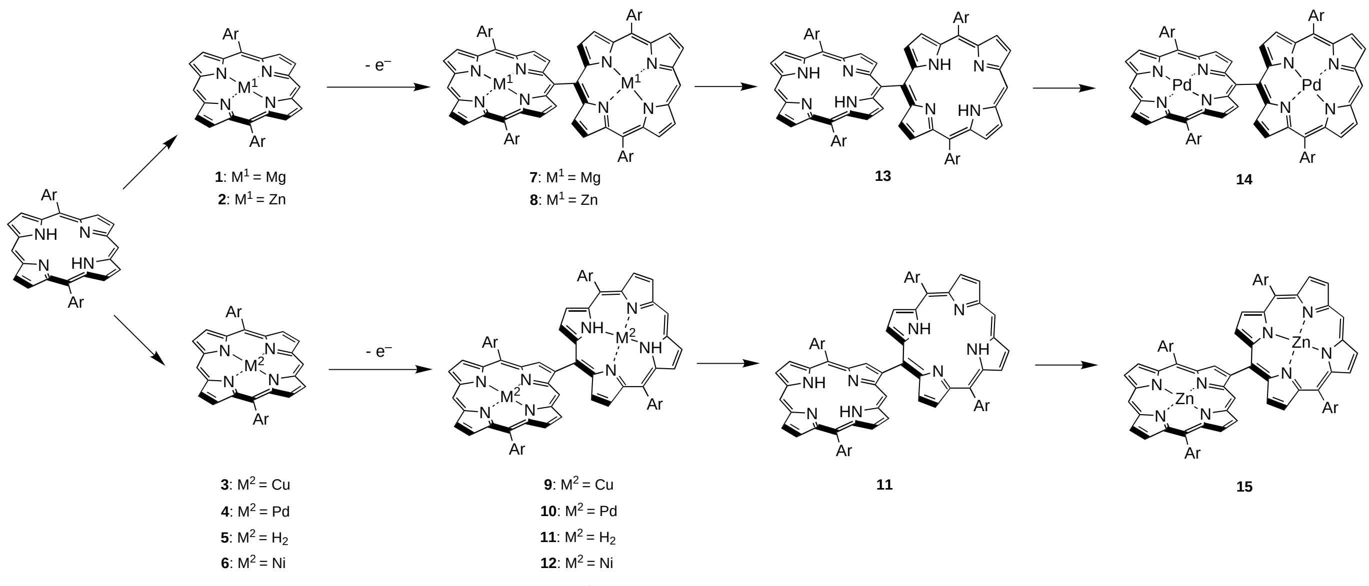
Metal ion	E_{ox} [mV][a] vs. $AgNO_3$/Ag	Yield [%][b]		
		monomer	*meso,meso* dimer	*meso,β* dimer
Mg^{2+}	355	34.4[c]	9.2[c]	0.0
Zn^{2+}[d]	540	44.0	20.7	0.0
Cu^{2+}	716	64.6	trace	4.3
Pd^{2+}	750	60.2	0.0	9.2
$2H^{+}$	765	95.5	trace	2.5
Ni^{2+}	780	70.8	0.0	19.1

[a] The electrochemical reactions were performed in benzonitrile at the first oxidation potentials cited here. [b] Yields given are for isolated products. The electricity passed was roughly 1.7 equiv of that required for the starting porphyrin. [c] The yields of isolated products were relatively low because of the difficult separation of the products from the electrolyte since the products have similar polarity to the electrolyte. [d] Data from ref. [15]; about 2.5 equiv of the electricity were used.

The ^{1}H NMR spectrum of the products clearly indicated a nonsymmetrical structure. The presence of four singlet peaks in the aromatic region is consistent only with the *meso,β* dimer structure. Of the two possible isomers of the *meso,β* dimers, that depicted in Scheme 1 is consistent with the ROESY NMR spectrum.

The proposed mechanism for the reaction involves the loss of a single electron by the metalloporphyrin followed by nucleophilic attack by a neutral metalloporphyrin. According to the four-orbital model,[16] when a porphyrin is oxidized to its radical cation, one of the closer orbitals, either A_{1u} or A_{2u}, becomes the magnetic orbital. The orbital involved depends on both the substrates and the central metals.[17] Gouterman et al. reported that Pd^{II}–TPP and Cu^{II}–TPP (TPP = tetraphenylporphyrin) favor A_{1u} cation radicals, while Zn^{II}–TPP and H_2–TPP favor A_{2u} cation radicals.[18] Cation radicals in the A_{1u} state will attack the neutral porphyrin at *meso* positions, which are the most nucleophilic carbon atoms, through their *β* positions. This leads to the formation of *meso,β* porphyrin dimers. Similarly, cation radicals in the A_{2u} state produce *meso,meso* porphyrin dimers. This mechanism is consistent with our results, except for the reaction of **5**. It is worthy to note that the regioselectivity is nearly complete and quite contrasting (*meso,meso* coupling for **1** and **2** and *meso,β* coupling for **4** and **6**). According to Gouterman, the free porphyrin base should favor the A_{2u} cation radical state (*meso*-dominant) over the zinc porphyrin. However, **5** produced *meso,β* dimer **11**, while **2** produced *meso,meso* dimer **8**. A possible interpretation of this result is that the cation radical of the free porphyrin base rapidly loses a proton from an NH group, giving rise to a neutral radical with A_{2u} symmetry. The radical either picks up one hydrogen atom to reform the original porphyrin, or attacks another neutral porphyrin to produce a directly linked *meso,β* dimer. The observed low efficiency of **5** (Table 1) seems to be consistent with this mechanism.

The absorption and fluorescence spectra of the zinc diporphyrins **8** and **15** are shown in Figure 1. The *meso,β*-



Scheme 1. Electrochemical syntheses of the *meso,meso*- and *meso,β*-linked porphyrin dimers **7**–**15**. Ar = 3,5-di-*tert*-butylphenyl.

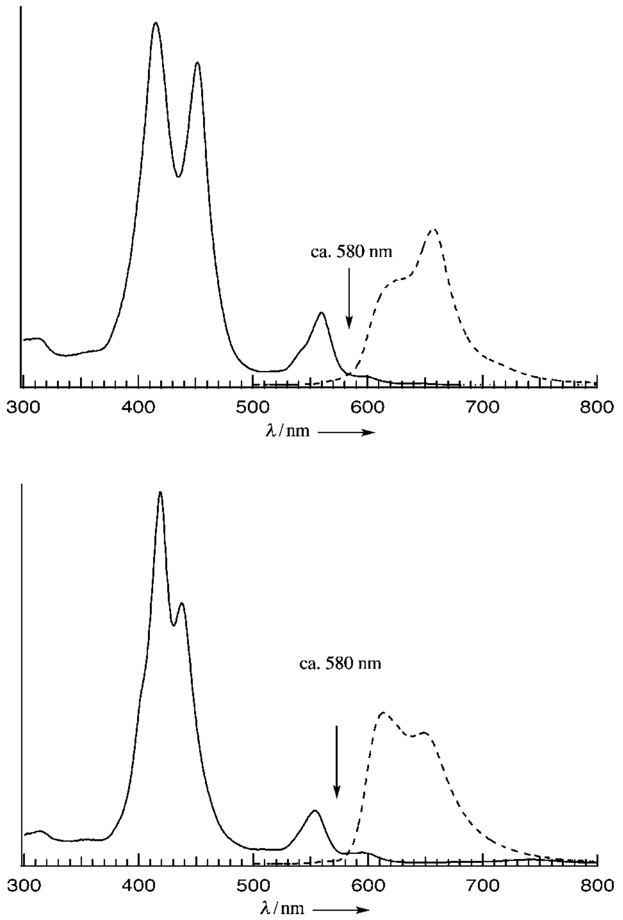


Figure 1. The electronic absorption (——) and emission spectra (----) of the *meso,β* dimer–Zn complex **15** (bottom) and the *meso,meso* dimer–Zn complex **8** (top).

linked diporphyrin **15** displays split Soret bands due to the exciton coupling, but its exciton coupling energy (ca. 1265 cm^{-1}) is smaller than that of the *meso*,meso-linked diporphyrin **8** (2100 cm^{-1}). In the both cases, the two porphyrin rings are nearly orthogonal, leading to relatively small exciton coupling energies regardless of the direct linkage of the porphyrin. The spectral changes in the Q-band region are also weaker for **15** than for **8**. The energies of the S$_1$ state estimated on the basis of the absorption and fluorescence spectra are 2.03 and 2.05 eV for **8** and **15**, respectively, and thus smaller than that of reference monomer **2** (2.13 eV). The fluorescence spectra of **8** and **15** are both red-shifted compared with that of **2**, and the shape of the spectra of **15** is more similar to that of **2**. The fluorescence quantum yields of **8** and **15** determined in THF relative to Zn–TPP (0.030) are 0.025 and 0.043, respectively, and the fluorescence lifetime determined by the single photon counting technique are 1.92 and 1.97 ns for **8** and **15**, respectively. Therefore, it may be concluded that the S$_1$ state of the these directly linked diporphyrins are not so strongly perturbed.

Cyclic and differential-pulse voltammograms have been measured for the monomer porphyrins as well as the *meso,meso*-, and *meso,β*-linked diporphyrins to clarify the electronic communications between the two porphyrin rings. For both the free porphyrin base and the palladium porphyrins, the first oxidation potential of the monomeric porphyrins split into two separate waves in the dimeric porphyrins. The separation of the peaks is larger in the *meso,meso* dimers than those in the *meso,β* dimers (**5**: 760 mV, **11**: 760 and 800 mV, **13**: 780 and 930 mV, **4**: 800 mV, **10**: 860 and 980 mV, **14**: 860 and 1040 mV). Although the zinc dimers **8** and **15** do not show apparent separation of the oxidation waves, the peaks of the *meso,meso* dimer **8** at 560 and 910 mV are broader than the corresponding peaks of **15**.

Since the splitting is caused by the Coulomb interaction between the positive charge in one porphyrin ring of the monocation radical generated in the first oxidation and the electron to be extracted from another porphyrin ring in the second oxidation,[11] it will depend both on the distance between the two porphyrin rings and on the molecular orbital distribution in each of the rings. The distance between the centers of the porphyrin rings in the *meso,β* dimer was determined to be 8.74 Å from a preliminary X-ray crystallographic analysis, and that of the *meso,meso* dimer was estimated to be about 8.34 Å from a semiempirical molecular orbital optimization. Thus in all cases the splitting of the *meso,meso* dimers with shorter distances between the two rings was larger than that of the *meso,β* dimers. The dependence of the splittings on the central metals may be ascribed to the different distribution of the molecular orbitals.

This electrochemical method is a new, simple way to produce directly linked *meso,meso* and *meso,β* porphyrin arrays, which should permit control of the electronic interactions and thus physical properties of multiporphyrin assemblies. Incorporation of these directly linked diporphyrin units into more elaborate photosynthetic models is our next target.

Experimental Section

Typical procedure for the electrochemical dimerization: Porphyrin **6** (200 mg, 0.27 mmol) was electrolyzed in dry benzonitrile (200 mL) in a single cell with tetrabutylammonium perchlorate (0.05 M) as the electrolyte, a platinum net (1.8 × 2.4 cm) as the counter electrode, and a platinum net (3 × 4 cm) as the working electrode; the electricity used was 0.55 mF. The porphyrin products were purified by being passed through an alumina and then a silica gel chromatography column, and isolated by preparative-scale HPLC with a gel-permeation chromatography column (GPC-HPLC) to give the *meso,β*-linked dimer **12** and the recovered monomer **6** in yields of 19.1 and 70.8%, respectively. It was possible to utilize open-column gel-permeation chromatography with Bio-Beads S-X1 (BIO-RAD) and chloroform as the eluent instead of GPC-HPLC in the final separation.

12: ^{1}H NMR (500 MHz, [D$_6$]acetone): $\delta = 1.51$ (m, 72H, *t*Bu-H), 7.35 (d, $J = 2.0$ Hz, 4H, Ar-2,6-H), 7.87 (m, 4H, Ar-2,6-H), 7.95 (d, $J = 1.5$ Hz, 2H, Ar-4-H), 8.34 (d, $J = 1.5$ Hz, 2H, Ar-4-H), 8.75 (d, $J = 5.0$ Hz, 1H, *β*-H), 8.77 (d, $J = 5.0$ Hz, 2H, *β*-H), 8.80 (d, $J = 5.0$ Hz, 1H, *β*-H), 8.96 (d, $J = 4.5$ Hz, 2H, *β*-H), 8.99 (d, $J = 5.0$ Hz, 1H, *β*-H), 9.01 (d, $J = 5.0$ Hz, 2H, *β*-H), 9.20 (d, $J = 4.5$ Hz, 1H, *β*-H), 9.43 (m, 4H, *β*-H), 9.50 (d, $J = 5.0$ Hz, 1H, *β*-H), 9.79 (s, 1H, *meso*-H), 10.25 (s, 1H, *meso*-H), 10.32 (s, 1H, *meso*-H); FAB MS: *m/z*: 1485.6 (calcd for $C_{96}H_{102}N_8Ni_2$: 1484.7); UV/Vis (CHCl$_3$): $\lambda_{max} = 410.8$, 525.0 nm.

9: An NMR spectrum could not be measured because of the paramagnetism of Cu^{II}. FAB MS: *m/z*: 1494.8 (calcd for $C_{96}H_{102}N_8Cu_2$: 1494.7); UV/Vis (CHCl$_3$): $\lambda_{max} = 412.0$, 493.0, 538.4 nm. The dimer was demetalated with 10% H$_2$SO$_4$/CF$_3$COOH[7] to give the free base meso,*β* dimer **11** in a yield of 65%.

10: ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 1.48$ (s, 18H, *t*Bu-H), 1.49 (s, 18H, *t*Bu-H), 1.494 (s, 18H, *t*Bu-H), 1.495 (s, 18H, *t*Bu-H), 7.75 (m, 4H, Ar-2,6-H), 8.03 (d, $J=2.0$ Hz, 4H, Ar-2,6-H), 8.17 (t, $J=1.8$ Hz, 2H, Ar-4-H), 8.37 (d, $J=1.5$ Hz, 2H, Ar-4-H), 8.62 (d, $J=4.5$ Hz, 1H, β-H), 8.81 (d, $J=5.0$ Hz, 2H, β-H), 8.82 (d, $J=4.5$ Hz, 1H, β-H), 8.96 (d, $J=5.0$ Hz, 2H, β-H), 9.08 (d, $J=5.0$ Hz, 3H, β-H), 9.25 (d, $J=5.0$ Hz, 1H, β-H), 9.33 (d, $J=4.5$ Hz, 2H, β-H), 9.34 (d, $J=4.5$ Hz, 1H, β-H), 9.40 (d, $J=5.0$ Hz, 1H, β-H), 9.78 (s, 1H, *meso*-H), 9.88 (s, 1H, *meso*-H), 10.31 (s, 1H, *meso*-H), 10.35 (s, 1H, *meso*-H); FAB MS: m/z: 1581.1 (calcd for $C_{96}H_{102}N_8Pd_2$: 1580.6); UV/Vis ($CHCl_3$): $\lambda_{max}=414.0$, 522.2, 549.2, 681.2 nm.

11: ^1H NMR (500 MHz, $CDCl_3$): $\delta=-2.69$ (s, 1H, N-H), -2.53 (s, 1H, N-H), -2.50 (s, 2H, N-H), 1.49 (s, 18H, *t*Bu-H), 1.50 (s, 18H, *t*Bu-H), 1.506 (s, 18H, *t*Bu-H), 1.512 (s, 18H, *t*Bu-H), 7.76 (m, 4H, Ar-2,6-H), 8.07 (d, $J=2.0$ Hz, 2H, Ar-2,6-H), 8.09 (t, $J=1.5$ Hz, 2H, Ar-2,6-H), 8.19 (t, $J=1.5$ Hz, 2H, Ar-4-H), 8.44 (d, $J=2.0$ Hz, 2H, Ar-4-H), 8.66 (d, $J=4.5$ Hz, 1H, β-H), 8.84 (d, $J=4.5$ Hz, 2H, β-H), 8.88 (d, $J=4.5$ Hz, 1H, β-H), 8.98 (d, $J=5.0$ Hz, 2H, β-H), 9.11 (d, $J=4.5$ Hz, 1H, β-H), 9.13 (d, $J=4.5$ Hz, 2H, β-H), 9.36 (d, $J=4.5$ Hz, 1H, β-H), 9.41 (d, $J=4.5$ Hz, 1H, β-H), 9.42 (d, $J=4.5$ Hz, 2H, β-H), 9.55 (d, $J=4.5$ Hz, 1H, β-H), 9.81 (s, 1H, *meso*-H), 9.96 (s, 1H, *meso*-H), 10.33 (s, 1H, *meso*-H), 10.40 (s, 1H, *meso*-H); HR FAB MS: m/z: 1371.8608 (calcd for $C_{96}H_{107}N_8$: 1371.8619); UV/Vis ($CHCl_3$): $\lambda_{max}=414.8$, 431.6, 514.4, 545.6, 583.6 nm.

13: ^1H NMR (500 MHz, $CDCl_3$): $\delta=-2.31$ (s, 4H, N-H), 1.46 (s, 72H, *t*Bu-H), 7.72 (t, $J=1.8$ Hz, 4H, Ar-4-H), 8.08 (d, $J=5.0$ Hz, 4H, β-H), 8.10 (d, $J=1.8$ Hz, 8H, Ar-2,6-H), 8.66 (d, $J=5.0$ Hz, 4H, β-H), 9.10 (d, $J=5.0$ Hz, 4H, β-H), 9.42 (d, $J=5.0$ Hz, 4H, β-H), 10.34 (s, 2H, *meso*-H); HR FAB MS: m/z: 1370.8542 (calcd for $C_{96}H_{106}N_8$: 1370.8540); UV/Vis ($CHCl_3$): $\lambda_{max}=412.6$, 446.6, 520.0, 589.8, 647.0 nm.

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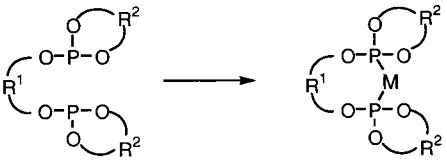
New Diphosphite Ligands for Catalytic Asymmetric Hydrogenation: The Crucial Role of Conformationally Enantiomeric Diols

Manfred T. Reetz* and Torsten Neugebauer

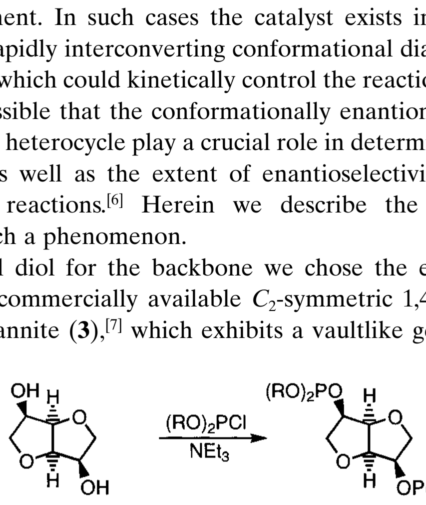
*Dedicated to Reinhard W. Hoffman
on the occasion of his 65th birthday*

Many chiral diphosphanes[1] and diphosphinites[2] have been synthesized as ligands for enantioselective transition metal catalyzed hydrogenations. On the other hand, little is known about chelating, chiral diphosphites as ligands in asymmetric hydrogenations,[3] although such ligands are increasingly being used in other transition metal catalyzed reactions such as hydrocyanations, hydroformylations, and hydrosilylations.[4] The availability of many enantiomerically pure diols allows the production of electron-deficient, bidentate phosphite ligands. Topologically different possibilities arise, for example the use of chiral or achiral diols HO−R^1−OH and HO−R^2−OH as the backbone or as a component of two P/O heterocycles, as is schematically represented in **1** and **2**. If the backbone is chiral, defined local chirality in the P/O heterocycle of the transition metal catalyst **2** may be possible even when seemingly achiral diols such as *meso*-1,2-cyclohexanediol[5] or diphenol serve as the second component. In such cases the catalyst exists in the form of three rapidly interconverting conformational diastereomers, one of which could kinetically control the reaction. It is therefore possible that the conformationally enantiomeric diols in the P/O heterocycle play a crucial role in determining the direction as well as the extent of enantioselectivity in hydrogenation reactions.[6] Herein we describe the first examples of such a phenomenon.



1 **2**

As the chiral diol for the backbone we chose the easily accessible and commercially available C_2-symmetric 1,4:3,6-dianhydro-D-mannite (**3**),[7] which exhibits a vaultlike geom-



3 **4**

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