Chiral *o*-Methoxyaryldiazaphosphonamides − A New Class of Efficient Lewis Bases in the Catalytic Asymmetric Ring Opening of Cyclooctene Oxide with Silicon Tetrachloride[‡]

Gérard Buono[a]

This paper reported a new class of diastereomerically pure *ortho*-methoxydiazaphosphonamide Lewis bases prepared from the corresponding *o*-hydroxyarylphosphonamides. These bases have been applied to the catalytic asymmetric ring opening of cyclooctene oxide with $SiCl_4$. During the last weeks, I disclosed in a correspondence (corrigenda) to *Angewandte Chemie* that I personally could not reproduce results previously published in this journal about the opening of cyclooctene oxide by such Lewis base catalysts.[1] Instead, I obtained results similar to those reported by Denmark et al. in their rebuttal of our original communication.[2] To date, my co-workers[4] have been unable to provide an appropriate scientific rationale for the non-reproducibility of the former results and several inconsistencies I found in analytical data they provided me with. Consequently, all the material concerning asymmetric catalysis in the paper previously published in this journal should be considered as irrelevant. Therefore, I wish to withdraw this article.

[‡] S. Reymond, O. Legrand, J. M. Brunel, G. Buono, *Eur. J. Org. Chem*. **2001**, 2819−2823.

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[1] G. Buono, *Angew. Chem. Int. Ed.* **2001**, *40*, 6001.
[2] S. E. Denmark, T. Wynn, B. G. Jellerichs, *Angew. Chem.* **2001**, *113*, 2315; *Angew. Chem. Int. Ed.* **2001**, *40*, 2255.
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Chiral *o*-Methoxyaryldiazaphosphonamides − A New Class of Efficient Lewis Bases in the Catalytic Asymmetric Ring Opening of Cyclooctene Oxide with Silicon Tetrachloride

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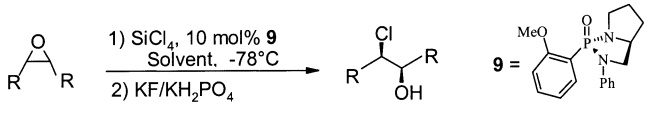
The synthesis of a new class of chiral *o*-methoxydiazaphosphonamides (as Lewis bases) has been investigated, together with their use as catalysts in the asymmetric ring opening (ARO) of cyclooctene oxide with silicon tetrachloride. Enantiomeric excesses varying from 6 to 99% *ee* were observed, depending on the nature of the catalyst examined. On the basis of experimental considerations, a mechanistic rationale involving hexacoordinate silicon species has been proposed.

Introduction

In the last few years, the asymmetric ring opening of epoxides (ARO) has appeared to constitute one of the most efficient methods for the preparation of various complex molecules.[1] Numerous procedures for asymmetrization of *meso* compounds have been developed; these include deprotonation,[2] protonation,[3] esterification,[4] and hydrolysis.[5] Although, in asymmetric synthesis, the use of nucleophiles such as halide ion (Cl, Br, F) is one method of choice for the preparation of valuable intermediates bearing two contiguous stereogenic centers, no efficient, catalytic, enantioselective method has yet been reported. Thus, although the classical addition of hydrogen chloride or hydrogen bromide remains as the simplest, most atom-efficient method, the need to manipulate sensitive polyfunctional intermediates has resulted in the introduction of a variety of new and milder alternatives for this transformation.[6] Only Denmark et al., in 1998, have described the formation of optically active chlorohydrins in moderate enantiomeric excesses (*ee* values of up to 87%), through the use of chiral phosphoramide Lewis bases as catalysts, activating various silylated nucleophiles.[7]

Recently we reported a beneficial secondary ligand interaction effect in the asymmetric ring opening of cyclooctene oxide with $SiCl_4$, catalyzed by a chiral *o*-methoxyphenyldiazaphosphonamide Lewis base **9**, and producing *ee* values of up to 99% (Scheme 1).[8]



Scheme 1. Catalytic asymmetric ring opening of *meso*-epoxides

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In this paper we describe the synthesis of various new organophosphorus Lewis bases and their successful use in the asymmetrization of cyclooctene oxide. We also report evidence in support of a mechanistic hypothesis implying hexacoordinate cationic silicon intermediates.

Results and Discussion

The synthesis of various diastereomerically pure *o*-methoxydiazaphosphonamides Lewis bases has been achieved by methylation of the corresponding *o*-hydroxyarylphosphonamides, easily prepared by a stereospecific and regioselective 1,3 migration rearrangement reaction as outlined in Scheme 2.[9,10] Methylation of these compounds produced the expected pure *o*-methoxydiazaphosphonamides Lewis bases, obtained in diastereomerically pure form and in high chemical yields, varying from 84 to 91% (Scheme 3). These Lewis bases have been successfully employed in the catalytic asymmetric ring opening of cyclooctene oxide as test substrate, with freshly distilled $SiCl_4$ in CH_2Cl_2 at −78 °C (Table 1).[11]

In all cases, the chlorohydrin was obtained in good yields, varying from 60 to 83%, but the enantioselectivity of the reaction was highly dependent on the catalyst structure. Thus, depending on the nature of the substituent on the aryl group, a significant decrease in the *ee* was sometimes encountered, values varying from 99 to 6%. Moreover, the lower *ee* values were observed when using catalyst **13** and **15**, affording the expected chlorohydrin with only 20 and 6% *ee*, respectively. In the case of catalyst **13**, this important lack of enantioselectivity can be explained by a decrease in the donor character of the methoxy group, and consequently by a weak coordination of this latter with the silicon atom. An interesting point to mention is that the use of diastereomers *anti*-**9** and *syn*-**10** produced the same results in terms of enantioselectivities and that the chlorohydrins in both cases possess the same absolute configuration (1*R*,2*R*).[12]

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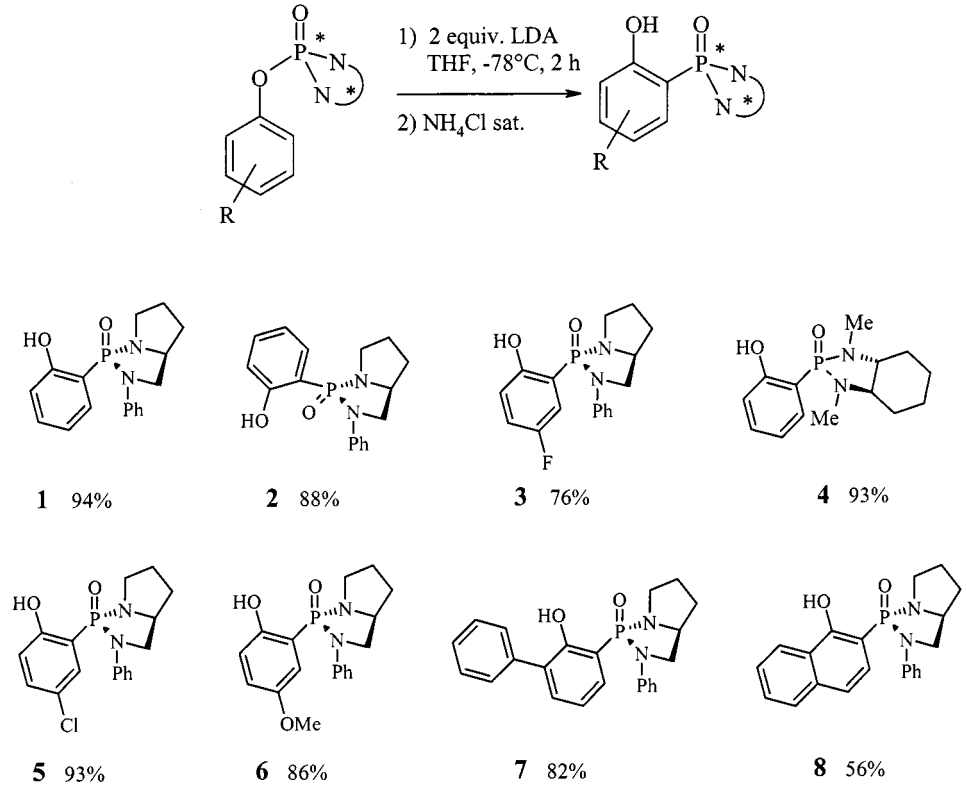
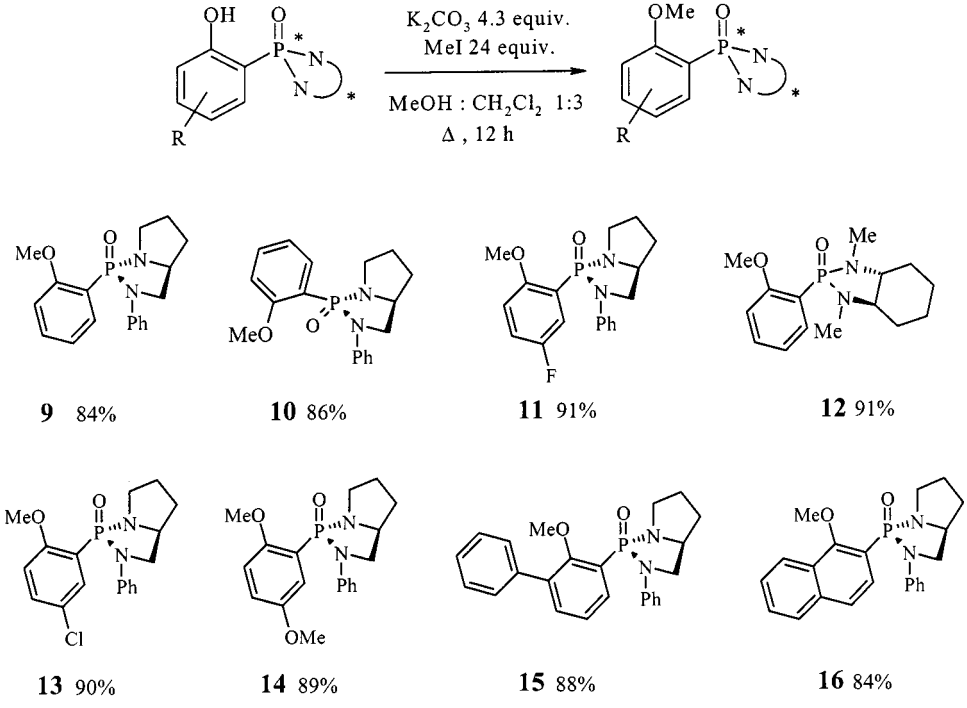


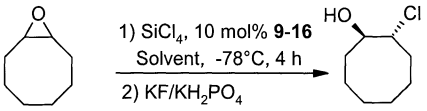
Scheme 2. Synthesis of chiral *o*-hydroxyaryldiazaphosphonamides **1**–**8**



Scheme 3. Synthesis of chiral *o*-methoxyaryldiazaphosphonamides **9**–**16**

In order to explain all the experimental results, a mechanistic rationale involving hexacoordinate silicon species has been proposed.[13] Thus, as a test of this assumption, nonlinear effect (NLE) studies were performed. Indeed, it is now well known that NLE represents an important tool for the explanation of mechanisms, providing useful insights both into the behavior of enantioselective catalytic systems and into the mechanisms of the processes they mediate.[14]

Table 1. Catalytic asymmetric ring opening of cyclooctene oxide with $SiCl_4$



Entry[a]	Lewis base	Solvent	Yield (%)[c]	*ee* (%)[d]
1	**9**	CH_2Cl_2	77	> 99
2[b]	**9**	CH_2Cl_2	60	34
3	**10**	CH_2Cl_2	75	> 99
4	**11**	CH_2Cl_2	70	88
5	**12**	CH_2Cl_2	83	> 99
6	**13**	CH_2Cl_2	72	20
7	**14**	CH_2Cl_2	77	95
8	**15**	CH_2Cl_2	65	6
9	**16**	THF	69	> 99

[a] Reactions performed on 1.2 mmol scale at − 78 °C over 4 h, using freshly distilled $SiCl_4$. − [b] Reaction performed using commercial $SiCl_4$ without any purification. − [c] Isolated yield after flash chromatography. − [d] *ee* values determined by GC analysis, using a LIPODEX E column, the major enantiomer possessing (1*R*,2*R*) absolute configuration.

Consequently, experiments were performed to determine whether NLEs were operative in the enantioselective catalyzed ring opening of *meso*-epoxides with $SiCl_4$. A strong positive NLE was encountered, suggesting the existence of various catalytic species (Figure 1).

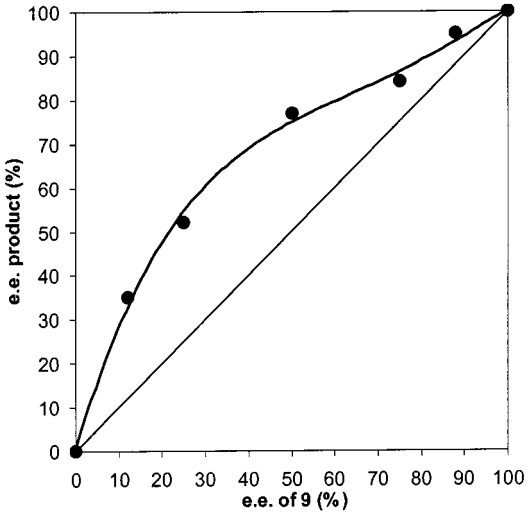
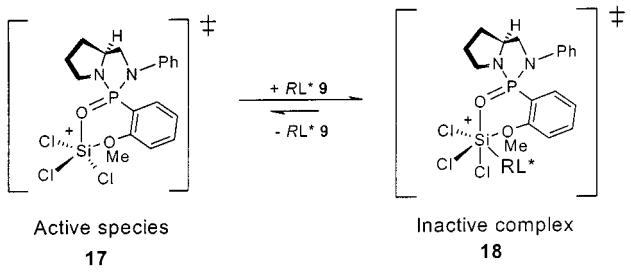


Figure 1. NLEs observed in the asymmetric ring opening of cyclooctene oxide with $SiCl_4$ using catalyst **9**

Moreover, on the basis of these results we may postulate that catalyst disproportionation had occurred and that the formation of a stable [Cl_3Si(*R*L*)(*S*L*)] cationic complex **18** results in a catalytically inactive reservoir for the minor (*R*L*) ligand, in equilibrium with the active species [Cl_3Si(*S*L*)] (Scheme 4).[13a,15]



Scheme 4. Catalyst disproportionation

Conclusion

In conclusion, we have developed the synthesis of a new class of diastereomerically pure *o*-methoxydiazaphosphonamides Lewis bases and their successful use in the enantioselective, catalytic ring opening of cyclooctene oxide with $SiCl_4$, with *ee* values of up to 99% in numerous cases. Further studies dealing with application of these catalysts in other asymmetric reactions are currently under investigation.

Experimental Section

Materials and Methods: ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded with Bruker AC 100 and AC 200 spectrometers, in $CDCl_3$ as solvent. The chemical shifts (ppm) were determined relative to Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). − Optical rotations were measured with a Perkin−Elmer 241 MC polarimeter. − Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl immediately prior to use. Dichloromethane was distilled from P_2O_5. Silicon tetrachloride was distilled under argon immediately prior to use. Ethyl acetate and petroleum ether (35−60 °C) were purchased from SDS and used without any previous purification. − Column chromatography was performed on SDS silica gel (70−230 mesh). − Enantiomeric excesses of the chlorohydrin were determined by GC analysis after derivatization of the chlorohydrin using trifluoroacetic anhydride (Lipodex E, 30 KPa, isothermal). − Precursors **1**−**8** were prepared as previously described.[9]

General Procedure for the Preparation of Catalysts 9−16: K_2CO_3 (400 mg, 2.9 mmol) was added at 25 °C under argon to a solution of precursor **1**−**8** (0.67 mmol) in CH_2Cl_2 (30 mL) and MeOH (10 mL), followed by dropwise addition of MeI (1 mL, 16 mmol). The mixture was stirred under reflux for 12 h. After removal of the solvent in vacuo, CH_2Cl_2 (20 mL) was added to the residue, and the mixture was filtered through a small pad of silica gel and concentrated in vacuo. Purification by silica gel chromatography yielded the desired compounds **9**−**16**.

(2*S*,5*S*)-2-(2-Anisyl)-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]octane 2-Oxide (9): This compound was obtained by following the general procedure with precursor **1** {(2*S*,5*S*)-2-(2-hydroxyphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane 2-oxide} (210 mg, 0.67 mmol). Purification by silica gel chromatography (ethyl acetate) afforded 185 mg (84%) of compound **9** as a white solid, m.p. 144 °C. − $[\alpha]_D^{20} = -28.9$ (c = 1.0, CH_2Cl_2). − ^{31}P NMR (40.5 MHz, $CDCl_3$): δ = 24.4. − ^1H NMR (200 MHz, $CDCl_3$): δ = 8.06 (ddd, J = 14.9, 7.4, 2.2 Hz, 1 H), 7.38−7.32 (m, 1 H),

7.16−6.93 (m, 5 H), 6.84−6.71 (m, 2 H), 4.14−3.72 (m, 6 H), 3.47 (td, J = 8.2, 3.3 Hz, 1 H), 3.04−2.87 (m, 1 H), 2.17−1.73 (m, 4 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 160.5, 142.1 (d, J = 6.6 Hz), 136.6 (d, J = 7.3 Hz), 133.5, 128.8 (2 C), 120.6, 120.3, 120.0 (d, J = 163.0 Hz), 115.8 (d, J = 4.4 Hz), 111.0, 110.9, 59.3 (d, J = 6.2 Hz), 55.8, 48.8 (d, J = 15.9 Hz), 45.1, 33.4, 26.5 (d, J = 2.5 Hz). − $C_{18}H_{21}N_2O_2P$ (328.35): calcd. C 65.8, H 6.5, N 8.5, P 9.4; found C 65.5, H 6.6, N 8.4, P 9.5.

(2*R*,5*S*)-2-(2-Anisyl)-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]octane 2-Oxide (10): This compound was obtained by following the general procedure with precursor **2** {(2*R*,5*S*)-2-(2-hydroxyphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane 2-oxide} (210 mg, 0.67 mmol). Purification by silica gel chromatography (ethyl acetate) afforded 189 mg (86%) of compound **10** as a white solid, m.p. 198 °C. − $[\alpha]_D^{20}$ = +108.7 (c = 1.15, CH_2Cl_2). − ^{31}P NMR (40.5 MHz, $CDCl_3$): δ = 18.9. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.13 (ddd, J = 14.9, 7.4, 2.2 Hz, 1 H), 7.40−7.32 (m, 1 H), 7.09−6.95 (m, 5 H), 6.75−6.66 (m, 2 H), 4.28−4.18 (m, 1 H), 3.85−3.65 (m, 1 H), 3.62 (s, 3 H), 3.55−3.47 (m, 1 H), 3.06−2.93 (m, 1 H), 2.79−2.64 (m, 1 H), 2.16−2.05 (m, 1 H), 2.01−1.81 (m, 2 H), 1.67−1.54 (m, 1 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 159.9 (d, J = 2.4 Hz), 142.6 (d, J = 5.9 Hz), 138.9 (d, J = 4.8 Hz), 134.2, 128.6 (2 C), 120.9, 120.6, 120.0, 115.1 (d, J = 118 Hz), 110.3 (d, J = 6.2 Hz), 58.4 (d, J = 9.1 Hz), 53.5 (d, J = 9.4 Hz), 50.0, 44.7 (d, J = 6.4 Hz), 31.5 (d, J = 3.7 Hz), 27.7 (d, J = 5.4 Hz). − $C_{18}H_{21}N_2O_2P$ (328.35): calcd. C 65.8, H 6.5, N 8.5, P 9.4; found C 65.6, H 6.8, N 8.6, P 9.4.

(2*S*,5*S*)-2-(5-Fluoro-2-methoxyphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane 2-Oxide (11): This compound was obtained by following the general procedure from precursor **3** {(2*S*,5*S*)-2-(5-fluoro-2-hydroxyphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane 2-oxide} (222.4 mg, 0.67 mmol). Purification by silica gel chromatography (ethyl acetate/petroleum ether, 80:20) afforded 211 mg (91%) of compound **11** as a white solid, m.p. 160 °C. − $[\alpha]_D^{20}$ = −64.3 (c = 0.375, CH_2Cl_2). − ^{19}F NMR (94.2 MHz, $CDCl_3$): δ = −68.5. − ^{31}P NMR (40.5 MHz, $CDCl_3$): δ = 24.0. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.91 (ddd, J = 15.6, 8.4, 2.3 Hz, 1 H), 7.28−7.09 (m, 5 H), 6.96−6.89 (m, 1 H), 6.80−6.72 (m, 1 H), 4.20−3.87 (m, 3 H), 3.79 (s, 3 H), 3.64−3.53 (m, 1 H), 3.00−3.16 (m, 1 H), 2.26−2.13 (m, 2 H), 2.10−1.82 (m, 2 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 156.7 (dd, J = 240.6, 19.8 Hz), 156.5, 141.7 (d, J = 7.2 Hz), 128.9 (2 C), 122.9 (dd, J = 24.5, 8.6 Hz), 120.9, 119.6 (d, J = 23.3 Hz), 115.8, 115.9, 112.1 (dd, J = 10.0, 7.3 Hz), 122.1 (dd, J = 163, 5.7 Hz), 59.3 (d, J = 5.9 Hz), 56.4, 48.8 (d, J = 15.9 Hz), 45.0, 33.3, 26.4. − $C_{18}H_{20}FN_2O_2P$ (346.34): calcd. C 62.4, H 5.8, N 8.1, P 8.9; found C 62.0, H 5.7, N 8.1, P 9.0.

(1*R*,6*R*)-8-(2-Anisyl)-7,9-dimethyl-7,9-diaza-8-phosphabicyclo[4.3.0]nonane 8-Oxide (12): This compound was obtained by following the general procedure from precursor **4** {(1*R*,6*R*)-8-(2-hydroxyphenyl)-7,9-dimethyl-7,9-diaza-8-phosphabicyclo-[4.3.0]-nonane 8-oxide} (188 mg, 0.67 mmol). Purification by silica gel chromatography (ethyl acetate) afforded 179 mg (91%) of compound **12** as a white solid, m.p. 115 °C. − $[\alpha]_D^{20}$ = −28.3 (c = 1.0, CH_2Cl_2). − ^{31}P NMR (40.5 MHz, $CDCl_3$): δ = 32.2. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.00 (ddd, J = 13.9, 7.6, 1.8 Hz, 1 H), 7.49−7.37 (m, 1 H), 6.98 (td, J = 7.4, 2.6 Hz, 1 H), 6.87 (dd, J = 8.2, 6.0 Hz, 1 H), 3.89 (s, 3 H), 2.80−3.00 (m, 2 H), 2.45 (d, J = 12 Hz, 2 H), 2.35 (d, J = 11.6 Hz, 2 H), 2.10−1.85 (m, 4 H), 1.5−1.2 (m, 4 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 160.9, 138.0 (d, J = 5.9 Hz), 133.7, 120.5 (d, J = 12.9 Hz), 118.0 (d, J = 152.0 Hz), 111.0 (d, J = 7.7 Hz), 64.8 (d, J = 5.8 Hz), 64.0 (d, J = 8.7 Hz), 55.5, 29.6, 28.9 (d, J = 11.0 Hz), 28.5 (d, J = 8.3), 28.3 (d, J = 5.8), 24.8, 24.7. − $C_{15}H_{23}N_2O_2P$ (294.33): calcd. C 61.2, H 7.9, N 9.5, P 10.5; found C 61.5, H 7.7, N 9.4, P 10.6.

(2*S*,5*S*)-2-(5-Chloro-2-methoxyphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane 2-Oxide (13): This compound was obtained by following the general procedure from precursor **5** {(2*S*,5*S*)-2-(5-chloro-2-hydroxyphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]-octane 2-oxide} (348.5 mg, 0.67 mmol). Purification by silica gel chromatography (ethyl acetate/petroleum ether, 80:20) afforded 219 mg (90%) of compound **13** as a white solid, m.p. 171 °C. − $[\alpha]_D^{20}$ = −9.5 (c = 0.105, CH_2Cl_2). − ^{31}P NMR (40.5 MHz, $CDCl_3$): δ = 22.4. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.07 (dd, J = 15.1, 2.8 Hz, 1 H), 7.29 (dd, J = 15.1, 2.8 Hz, 1 H), 7.14 (dd, J = 7.1, 7.6 Hz, 2 H), 7.02 (d, J = 7.6 Hz, 2 H), 6.83 (t, J = 7.1 Hz, 1 H), 6.65 (dd, J = 8.8, 6.9 Hz, 1 H), 3.96−3.75 (m, 3 H), 3.69 (s, 3 H), 3.52−3.42 (m, 1 H), 3.00−2.87 (m, 1 H), 2.15−1.67 (m, 4 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 158.9, 141.6 (d, J = 6.7 Hz), 136.1 (d, J = 8.7 Hz), 133.1, 129.0, 125.6 (d, J = 17.9 Hz), 122.3 (d, J = 162.6 Hz), 121.0, 115.8 (d, J = 4.4 Hz), 112.3 (d, J = 9.8 Hz), 59.3 (d, J = 6.2 Hz), 56.2, 48.7 (d, J = 15.9 Hz), 44.9, 33.3, 26.4. − $C_{18}H_{20}ClN_2O_2P$ (362.79): calcd. C 59.6, H 5.6, N 7.7, P 8.5; found C 59.7, H 5.6, N 7.4, P 8.9.

(2*S*,5*S*)-2-(2,5-Dimethoxyphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane 2-Oxide (14): This compound was obtained by following the general procedure from precursor **6** {(2*S*,5*S*)-2-(2-hydroxy-5-methoxyphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]octane 2-oxide} (230.5 mg, 0.67 mmol). Purification by silica gel chromatography (ethyl acetate/petroleum ether, 80:20) afforded 214 mg (89%) of compound **14** as a white solid, m.p. 164 °C. − $[\alpha]_D^{20}$ = −28.7 (c = 0.115, CH_2Cl_2). − ^{31}P NMR (40.5 MHz, $CDCl_3$): δ = 24.0. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.62 (dd, J = 16.0, 3.2 Hz, 1 H), 7.01 (d, J = 8.0 Hz, 1 H), 7.09 (dd, J = 8.8, 8.0 Hz, 1 H), 6.89 (dd, J = 8.9, 3.2 Hz, 1 H), 6.79 (t, J = 7.0 Hz, 1 H), 6.66 (t, J = 8.8 Hz, 1 H), 4.0−3.69 (m, 6 H), 3.64 (s, 3 H), 3.45 (td, J = 8.3, 3.2 Hz, 1 H), 3.01−2.90 (m, 1 H), 2.15−1.67 (m, 4 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 154.7, 153.2 (d, J = 17.2 Hz), 141.9 (d, J = 7.2 Hz), 128.8 (2 C), 121.1 (d, J = 152.9 Hz), 120.6, 120.5, 119.4, 115.8, 115.7, 112.4 (d, J = 10.2 Hz), 59.2 (d, J = 5.8 Hz), 56.4, 55.9, 48.9, 48.6, 45.0, 33.3, 26.4 (d, J = 3.2 Hz). − $C_{19}H_{23}N_2O_3P$ (358.37): calcd. C 63.7, H 6.5, N 7.8, P 8.6; found C 64.0, H 6.6, N 7.6, P 8.6.

(2*S*,5*S*)-2-(2-Methoxybiphenyl-3-yl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane 2-Oxide (15): This compound was obtained by following the general procedure from precursor **7** {(2*S*,5*S*)-2-(2-hydroxybiphenyl-3-yl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane 2-oxide} (261.3 mg, 0.67 mmol). Purification by silica gel chromatography (ethyl acetate) afforded 238 mg (88%) of compound **15** as a white solid, m.p. 112 °C. − $[\alpha]_D^{20}$ = −33.0 (c = 0.225, CH_2Cl_2). − ^{31}P NMR (40.5 MHz, $CDCl_3$): δ = 24.4. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.01 (ddd, J = 14.7, 7.2, 2.4 Hz, 1 H), 7.48−7.09 (m, 11 H), 6.87−6.80 (m, 1 H), 4.04−3.86 (m, 3 H), 3.52−3.44 (m, 1 H), 3.24 (s, 3 H), 3.15−2.85 (m, 1 H), 2.13−1.75 (m, 4 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 159.3, 142.1 (d, J = 5.7 Hz), 138.0, 133.5, 135.1, 135.0, 134.7 (d, J = 7.1 Hz), 129.0−128.4 (m, 5 C), 127.4, 126.4 (d, J = 132.4 Hz), 123.9, 123.6, 120.7, 115.9 (d, J = 4.1 Hz), 60.3, 58.9 (d, J = 6.2 Hz), 48.8 (d, J = 15.8 Hz), 45.0, 32.9, 26.4. − $C_{24}H_{25}N_2O_2P$ (404.44): calcd. C 71.3, H 6.2, N 6.9, P 7.7; found C 71.4, H 6.5, N 6.8, P 7.9.

(2*S*,5*S*)-2-(1-Methoxynaphth-2-yl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane 2-Oxide (16): This compound was obtained by following the general procedure from precursor **8** {(2*S*,5*S*)-2-(1-hy-

droxynaphth-2-yl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane 2-oxide} (245.2 mg, 0.67 mmol). Purification by silica gel chromatography (ethyl acetate) afforded 213 mg (84%) of compound **16** as a white solid, m.p. 92 °C. − $[\alpha]_D^{20}$ = −165 (*c* = 0.3, CH_2Cl_2). − ^{31}P NMR (40.5 MHz, $CDCl_3$): δ = 23.9. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.99−7.93 (m, 2 H), 7.77−7.72 (m, 1 H), 7.59−7.53 (m, 1 H), 7.46−7.35 (m, 2 H), 7.09−6.97 (m, 4 H), 6.76−6.68 (m, 1 H); 4.09−3.74 (m, 6 H), 3.53−3.43 (m, 1 H), 2.98−2.82 (m, 1 H), 2.11−1.69 (m, 4 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 159.5, 142.0, 141.8, 137.1, 130.2 (d, *J* = 8.4 Hz), 128.2 (2 C), 127.9 (d, *J* = 12.2 Hz), 127.3 (d, *J* = 3.8 Hz), 126.0, 123.8, 123.6, 122.9, 121.6 (d, *J* = 164.9 Hz), 120.6, 115.7 (d, *J* = 4.6 Hz), 62.7, 59.1 (d, *J* = 6.2 Hz), 48.8 (d, *J* = 15.9 Hz), 44.82, 32.7, 26.4. − $C_{22}H_{23}N_2O_2P$ (378.40): calcd. C 69.8, H 6.1, N 7.4, P 8.2; found C 69.7, H 6.4, N 7.3, P 9.0.

General Procedure for the Catalytic Asymmetric Ring Opening of Cyclooctene Oxide (Table 1, Entry 1): $SiCl_4$ (140 μL, 1.22 mmol) was added at −78 °C under argon to a stirred solution of catalyst **9** (0.122 mmol) in CH_2Cl_2 or THF (6 mL). After 5 min, cyclooctene oxide (154 mg, 1.22 mmol) was added. After the addition was complete, the mixture was stirred at −78 °C for 4 h and then quenched by pouring into cold (−78 °C), rapidly stirred saturated KF/KH_2PO_4 (1:1) (15 mL). It was then allowed to warm to room temperature. The resulting mixture was extracted with CH_2Cl_2 (2 × 15 mL) and the combined organic fractions were washed with water (10 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (petroleum ether/diethyl ether, 90:10), affording (1*R*,2*R*)-2-chlorocyclooctan-1-ol in 77% yield. − $[\alpha]_{365}^{20}$ = −1.4 (*c* = 1.0, CH_2Cl_2); *ee* > 99% (determined by GC analysis after derivatization of the chlorohydrin using trifluoroacetic anhydride), t_R(1*R*,2*R*) = 31.4 min (> 99%), t_R(1*S*,2*S*) = 51.2 min (< 1%) (Lipodex E, 30 KPa, isothermal 120 °C, 0.1 μL). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.11 (ddd, *J* = 9.2, 7.3, 2.8 Hz, 1 H), 3.86 (ddd, *J* = 9.2, 6.9, 2.1 Hz, 1 H), 2.63 (br s, 1 H), 2.29−2.13 (m, 1 H), 2.07−1.30 (m, 11 H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 76.2, 71.2, 32.3, 32.0, 25.7, 25.7, 24.9, 24.1. − $C_8H_{15}ClO$ (162.66): calcd. C 59.1, H 9.3; found C 58.9, H 9.2.

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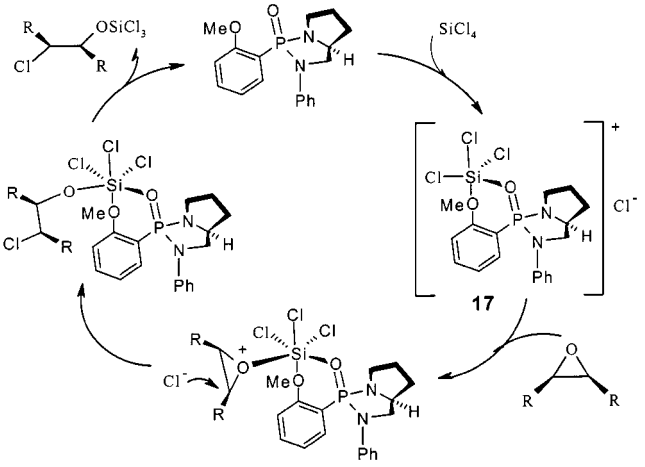

Scheme 5. Proposed mechanistic rationale for the enantioselective ring opening of cyclooctene oxide

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