Chiral Boron-Bridged Bisoxazoline (Borabox) Ligands: Structures and Reactivities of Pd and Cu Complexes

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Abstract: Anionic boron-bridged bisoxazolines (borabox ligands) have been synthesized and characterized in their protonated forms. The ligands are tuneable over a wide range, allowing either alkyl or aryl substituents at the oxazoline rings and the central bridging boron atom. The structural parameters of this new ligand type have been investigated by X-ray analyses of palladium and copper complexes. Electronic properties have been studied by ^{13}C NMR spectroscopy and by DFT calculations on palladium allyl complexes and compared to those of analogous bisoxazoline (box) complexes.
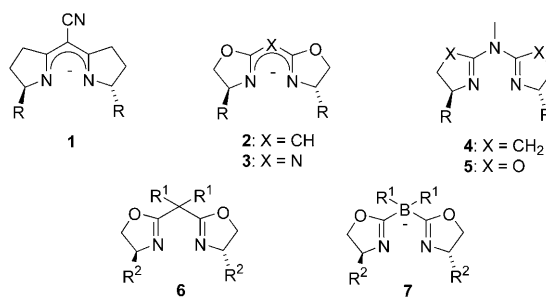
Borabox complexes are more electron-rich at the metal center than their neutral box congeners, and as a consequence of the longer bonds between the bridging atom and the oxazoline rings, their bite angles are larger. Palladium(II) complexes bearing an unsubstituted allyl ligand and homoleptic copper(II) complexes each possess an almost flat chelate ring. NMR analysis of a (1,3-diphenylallyl)(borabox)palladium complex showed a 92:8 mixture of (syn,syn) and (anti,syn) allyl isomers, in contrast with a previously reported box analogue that existed exclusively in the (syn,syn) form. Comparison of the corresponding crystal structures revealed that the distance between the bisoxazoline and the allyl ligand in the borabox complex is shorter. In the copper-catalyzed allylic oxidation of cyclohexene and cyclopentene with tert-butyl perbenzoate, borabox ligands gave results similar—and in some cases superior—to those obtained with analogous box ligands.

Keywords: asymmetric catalysis · copper · N ligands · oxazolines · palladium

Introduction

The structural motif of the semicorrin ligands **1** has inspired the development of a variety of related neutral and anionic N,N ligands such as **2–6**.[1–3] C_2-Symmetric bisoxazolines of this type are particularly attractive because they are readily assembled from commercially available enantiopure amino alcohols. Among them, the neutral bisoxazoline (box) ligands **6** have emerged as the most versatile representatives of this ligand class, as can be seen in the impressive range of applications they have found in asymmetric catalysis.[3] As a further variant of this structure we have recently introduced anionic bisoxazolines **7** (borabox ligands) with a tetrasubsti-

tuted boron atom connecting the two oxazoline rings.[4] The borabox ligands would be expected to be weaker electron donors towards a coordinated metal center than other structurally related anionic ligands such as **1–3**, which each possess an electron-rich π-system with high electron density at the coordinating N atoms, and in this respect to resemble more closely the neutral box ligands **6**.

The geometrical properties of borabox and box ligands **6** are very similar, as each possesses a tetrahedral bridging

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atom, in contrast to ligands **1–5** with their rigid, planar π systems. The anionic charges of borabox ligands could offer advantages—by enforcing the binding of a metal cation due to Coulomb attraction, for example, or by increasing the solubilities of metal-borabox complexes in apolar solvents— relative to complexes derived from neutral ligands, which are more polar, due to the higher charge of the complex and the additional external anion.[5] The absence of an additional external anion that might interfere with catalysis through coordination could also prove beneficial for certain reactions. We therefore thought that borabox ligands would be a useful addition to the bisoxazoline ligand family.

Results and Discussion

Synthesis of the ligands: Borabox ligands were assembled in a one-step procedure through coupling of 2H-oxazolines **8a–f** with dialkyl- or diarylhaloboranes **9w–z** (Scheme 1).[4a]
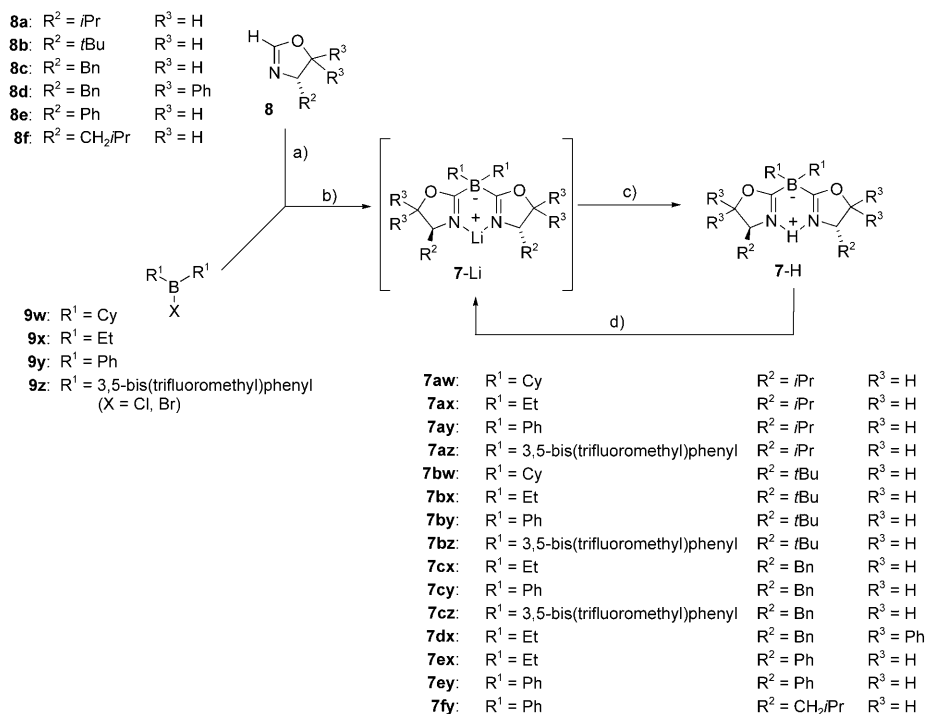
A library of 15 different ligands was prepared by this approach. Lithiation of oxazolines **8a–f**[6] and subsequent treatment with the appropriate haloborane (0.5 equiv) at low temperature in THF led to the lithium salts **7-Li**. In general, these compounds could be isolated in high purity according to NMR spectroscopy (^{1}H, ^{13}C, ^{11}B), as highly hygroscopic, white powders in moderate to excellent yields. In general, for practical reasons, the lithium salts were converted into the air-stable protonated ligands **7-H** by simple chromatographic workup on silica gel with mixtures of hexane,

ethyl acetate and triethylamine as eluents. When necessary, the lithium salts **7-Li** could be quantitatively regenerated by treatment of compounds **7-H** with *n*-butyllithium (1 mol equiv) in diethyl ether or THF at 0 °C.

Synthesis of palladium complexes: Protonated borabox ligands **7ax–az** were converted into the corresponding lithium salts by slow addition at 0 °C of *n*BuLi (1 equiv) in THF (Scheme 2). Subsequent treatment with a solution of [Pd-(C₃H₅)Cl]₂ (0.5 equiv) in THF at room temperature led to the desired palladium complexes **10ax–az**, which were isolated after removal of lithium chloride by filtration. In the cases of **10ay** and **10az**, recrystallization from EtOH/H₂O gave colorless crystals suitable for X-ray analysis. Similarly, complex **11cx** was obtained by treatment of [Pd(1,3-diphenylallyl)Cl]₂ (0.5 equiv) with **7cx**-H (1 equiv) and K₂CO₃ in a CH₂Cl₂/THF/methanol mixture[7] at 50 °C. Crystallization from EtOH/H₂O gave single crystals suitable for X-ray analysis. Crystalline borabox palladium complexes can be handled under air, although they were usually stored under N₂ either at room temperature (**11cx**) or at −20 °C (**10ax–az**). The analogous box palladium complexes **12a** and **12b** were prepared by published procedures.[7]

NMR studies and DFT calculations of Pd–borabox complexes: Palladium box and aza-semicorrin complexes catalyze the allylic alkylation of *rac*-(*E*)-1,3-diphenylpropenyl acetate with dimethyl malonate with high efficiency (2 mol % catalyst precursor, 23 °C, 48 h, 94–99 % yield) and high enantiomeric excesses (88–97 %).[7] In contrast, borabox complex **10az** does not induce any reaction between *rac*-(*E*)-1,3-diphenylprop-2-enyl 1-acetate and dimethyl malonate. Furthermore, complex **11cx**, which is structurally very similar to the box complex **13**, did not show any decomposition, nor was any product formation observed when it was treated with stoichiometric amounts of dimethyl malonate/BSA/ [Bu₄N]OAc.

Rapid apparent allyl rotation was observed by 1D ^{1}H NMR spectroscopy after the preparation of box complex **12a** by a published procedure[7] that involves washing of the filtered reaction mixture with NaCl solution. Since the promoting effects of halides on apparent allyl rotation of Pd complexes are known,[8] we investigated the influence of chloride ions on box complex **12b**, prepared
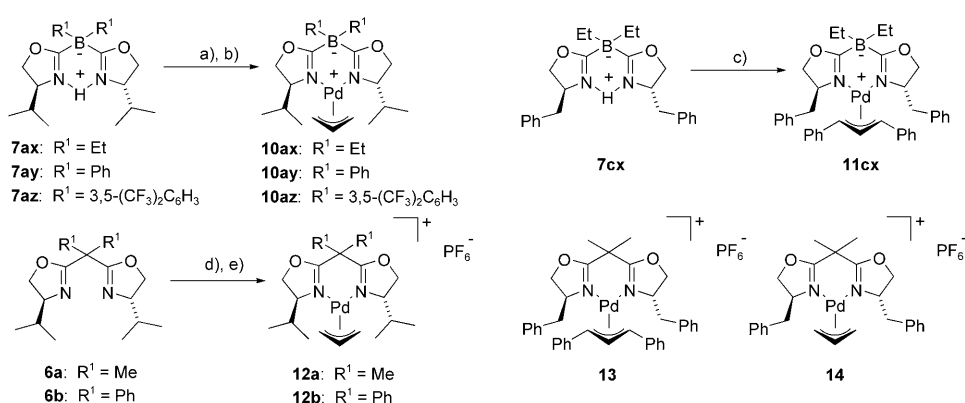

8a: R² = *i*Pr R³ = H
8b: R² = *t*Bu R³ = H
8c: R² = Bn R³ = H
8d: R² = Bn R³ = Ph
8e: R² = Ph R³ = H
8f: R² = CH₂*i*Pr R³ = H

9w: R¹ = Cy
9x: R¹ = Et
9y: R¹ = Ph
9z: R¹ = 3,5-bis(trifluoromethyl)phenyl
(X = Cl, Br)

7aw:	R¹ = Cy	R² = *i*Pr	R³ = H
7ax:	R¹ = Et	R² = *i*Pr	R³ = H
7ay:	R¹ = Ph	R² = *i*Pr	R³ = H
7az:	R¹ = 3,5-bis(trifluoromethyl)phenyl	R² = *i*Pr	R³ = H
7bw:	R¹ = Cy	R² = *t*Bu	R³ = H
7bx:	R¹ = Et	R² = *t*Bu	R³ = H
7by:	R¹ = Ph	R² = *t*Bu	R³ = H
7bz:	R¹ = 3,5-bis(trifluoromethyl)phenyl	R² = *t*Bu	R³ = H
7cx:	R¹ = Et	R² = Bn	R³ = H
7cy:	R¹ = Ph	R² = Bn	R³ = H
7cz:	R¹ = 3,5-bis(trifluoromethyl)phenyl	R² = Bn	R³ = H
7dx:	R¹ = Et	R² = Bn	R³ = Ph
7ex:	R¹ = Et	R² = Ph	R³ = H
7ey:	R¹ = Ph	R² = Ph	R³ = H
7fy:	R¹ = Ph	R² = CH₂*i*Pr	R³ = H

Scheme 1. Synthesis of borabox ligands in their lithiated (**7-Li**; 34–98 %) or protonated (**7-H**; 5–89 %) forms. a) *t*BuLi, −78 °C (−100 °C for **7ex**, **7ey**), THF; b) (R¹)₂BX (X = Cl, Br), toluene, −78 °C (−100 °C for **7ex**, **7ey**); c) hexane/ethyl acetate/Et₃N, silica gel; d) *n*BuLi, Et₂O or THF, 0 °C.

with omission of the NaCl washing step, and its borabox analogue **10ay** in a NMR titration experiment. In the absence of chloride the spectrum shows the signals of a C_1-symmetric complex, with separate signals for the four methyl groups. Upon addition of [Bu$_4$N]Cl (8 mol%), the signal sets of the two oxazoline rings and of each pair of methyl groups in complex **12b** merged, whereas the five protons of the allyl fragment remained distinguishable (Figure 1). The observed dynamic effect was clearly caused by the presence of chloride ions, since addition of excess AgPF$_6$ reversed the effect. In contrast, similar apparent rotation of the allyl fragment could not be detected when a solution of the analogous borabox complex **10ay** was treated with [Bu$_4$N]Cl, even when one equivalent of chloride was added.

To investigate whether this contrasting behavior of complexes **12b** and **10ay** was due to stronger binding of the anionic borabox ligand to the cationic palladium center, a ligand-exchange reaction with dppp [1,3-bis(diphenylphosphino)propane] was performed. In both complexes the N,N ligands were displaced upon addition of diphosphine (1 mol equiv), leading in the case of complex **10ay** to a dppp palladium-allyl complex with the borabox ligand **7ay** as counter-ion. The most

Scheme 2. Synthesis of box and borabox palladium complexes. a) *n*BuLi, THF, 0°C; b) [Pd(C$_3$H$_5$)Cl]$_2$, THF, RT; c) K$_2$CO$_3$, [Pd(C$_{13}$H$_{15}$)Cl]$_2$, CH$_2$Cl$_2$/THF/methanol, 50°C; d) [Pd(C$_3$H$_5$)Cl]$_2$, CH$_2$Cl$_2$, RT; e) AgPF$_6$, THF, RT. Complexes **13**, **14**: ref. [7].
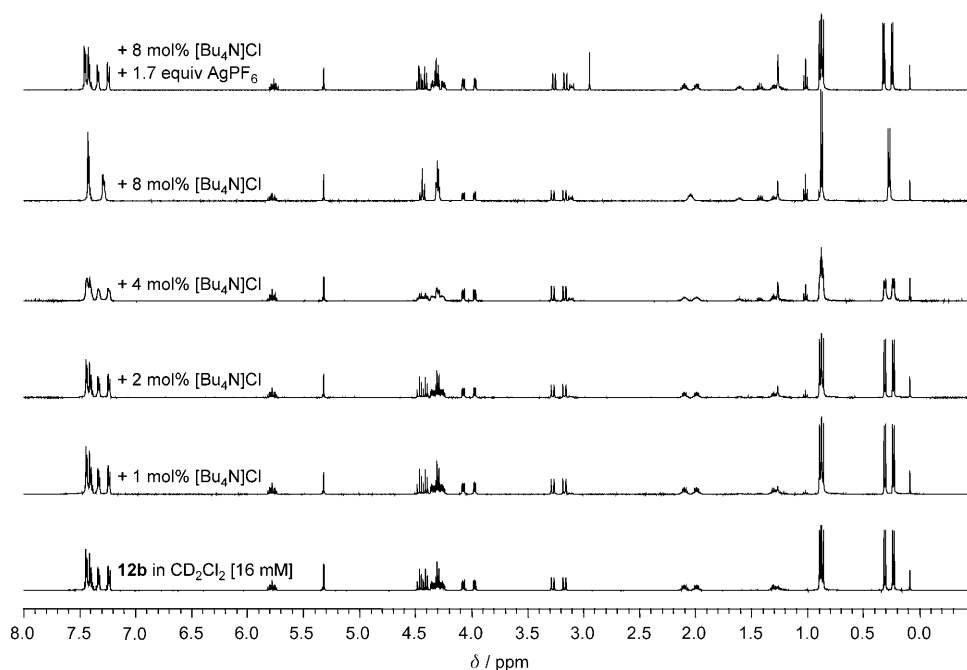

Figure 1. ^{1}H NMR spectra (500 MHz, CD$_2$Cl$_2$, 295 K) showing a titration experiment of complex **12b** (16 mM) with a solution of [Bu$_4$N]Cl (10 mM in CD$_2$Cl$_2$). Spectrum at top: addition of [Bu$_4$N]Cl (8 mol%) and AgPF$_6$ (1.7 equiv).

likely explanation for the different behavior of the two complexes upon addition of chloride is the lower electrophilicity of the palladium atom in **10ay**, which therefore has a weaker tendency to coordinate a chloride ion.

Further information about the electronic properties of the borabox-palladium complexes, as well as their differences from analogous box complexes, was obtained from ^{13}C NMR spectra and density functional theory (DFT) calculations. The ^{13}C chemical shifts of the carbon atoms of the allyl fragment are known to reflect the electronic properties of the complex.[7,9] Comparison of the ^{13}C NMR spectra of complexes **12a**, **12b** and **10ax–az** revealed that allyl C

atoms of the borabox complexes resonate at higher field, consistent with more electron-rich allyl moieties.

This conclusion was corroborated by DFT calculations. Natural population analyses (NPA) at the B3LYP level of theory were carried out for all five palladium complexes.[10] A correlation between the net atomic charges of the allyl C atoms and the ^{13}C NMR chemical shifts is given in Figure 2.

The allyl systems in the box-complexes **12a** and **12b** were found to be less electron-rich than those in their borabox congeners **10ax–az**. The relative charges on the three carbon atoms were clearly related to the natures of the substituents at boron. Electron-withdrawing 3,5-(CF$_3$)$_2$C$_6$H$_3$-groups resulted in lower electron densities at the allyl frag-
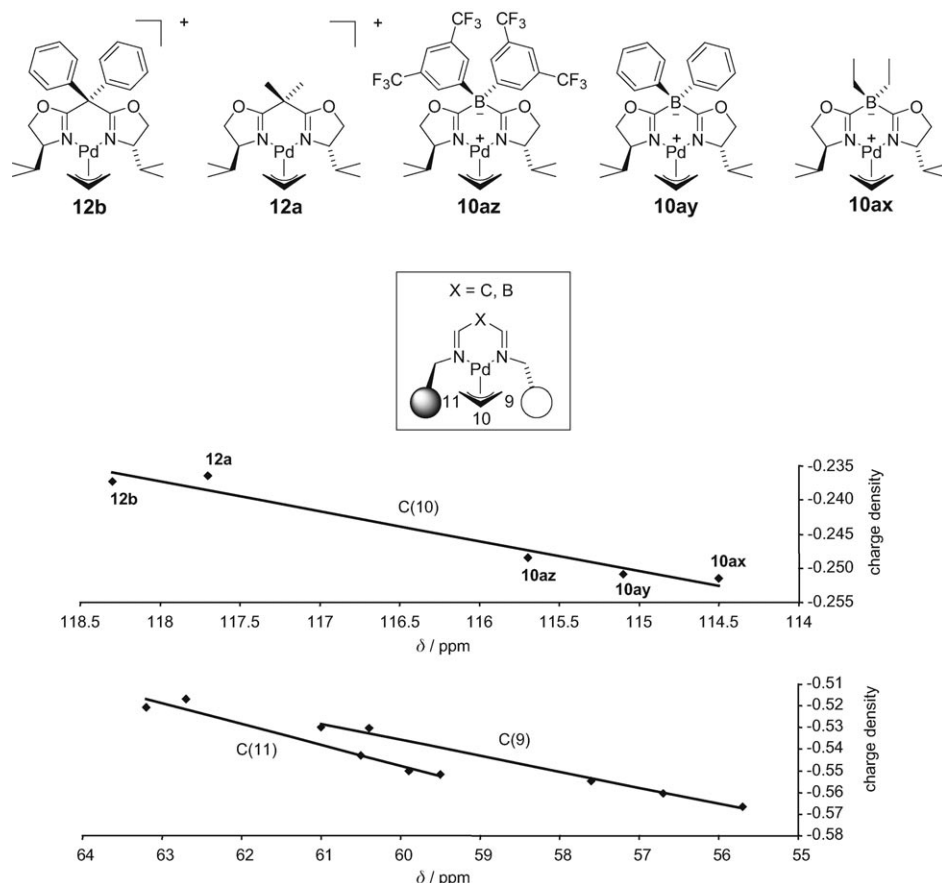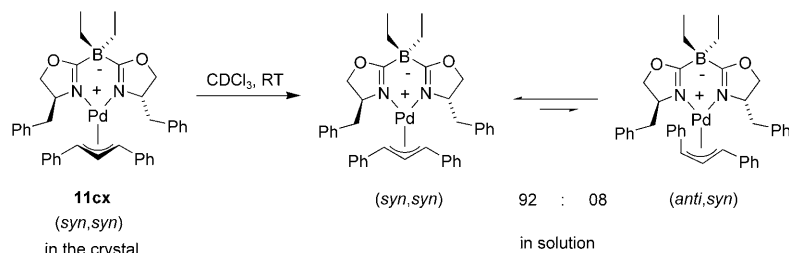
Figure 2. Correlation between ^{13}C NMR chemical shifts (500 MHz) and charge densities (DFT, B3LYP, NPA) of the C atoms of the allyl fragments for box and borabox palladium complexes.

and 7.7 Hz were observed for the (*anti*, *syn*) isomer. The latter value is clearly indicative of a *cis* relationship of the central proton of the allyl system with one of the protons at the allyl termini.

In contrast, the analogous box complex **13** exists exclusively in the (*syn*,*syn*) form.[7] On the other hand, partial *syn–anti* isomerization of a 1,3-diphenylallyl ligand in palladium–box complexes bearing phenyl substituents at C(4) and C(4′) of the oxazoline rings and additional substituents at C(5) and C(5′) has been described by Pericàs et al.[11]

Assignment of the NMR signals for complexes 10 ax, 10 ay, 12 a and 12 b: In order to allow comparison of the ^{13}C shifts of the terminal carbon atoms of the allylic fragments of complexes **10 ax**, **10 ay**, **12 a** and **12 b**, the relative positions of the allyl termini with regard to the oxazoline ligands were determined by 2D-NOE spectroscopy (Figure 3).

ment (charge = −0.543, −0.249 and −0.555 e at C(9), C(10) and C(11), respectively) than ethyl groups did (charge = −0.552, −0.251 and −0.567 e at C(9), C(10) and C(11), respectively).

In addition, complex **11 cx** exhibited unexpected behavior in solution. When single crystals of the pure (*syn*, *syn*) isomer were dissolved in CDCl$_3$, partial isomerization of the 1,3-diphenylallyl ligand to form an (*anti*, *syn*) isomer was observed by NMR spectroscopy (Scheme 3). The isomers of **11 cx** were distinguished by the different $^3J_{H,H}$ coupling constants in the allyl system. The two $^3J_{H,H}$ coupling constants of the two terminal allyl protons are 11.4 Hz and 10.7 Hz in the (*syn*, *syn*) isomer, whereas coupling constants of 11.5 Hz

The C(6)−H bond preferentially points toward the allyl ligand and is oriented parallel to the C(4)−C(5) bond, as shown by the sizes of 3 Hz of the coupling constants between HC(4) and HC(6) in complexes **10 ax**, **10 ay**, **10 az**, **12 a** and **12 b**, the strong NOEs between HC(4) and HC(6), the strong differences in intensities of the NOEs of the spectroscopically distinguishable methyl groups
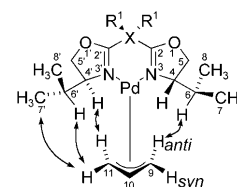

Figure 3. Relevant NOEs for the determination of the relative positions of the allyl termini in complexes **10 ax**, **10 ay**, **12 a** and **12 b**. X = C, B.

and HC(4), and the weak—or complete absence of—NOE signals between HC(6) and the protons at C(5). The same orientation is also found for the C(6′)−H bonds. Although the analyses were hampered by overlapping oxazoline signals for some of the complexes, and additionally, in the case of complex **12 b**, by dynamic processes

Scheme 3. *syn–anti* Isomerization of complex **11 cx**.

(see below), overall the data confirmed the conformation of the *i*Pr groups depicted in Figure 3 for all complexes.

The NOEs between HC(4′) and H_{anti}C(11) and between HC(6) and H_{anti}C(9) allowed unambiguous assignment of the relative positions of C(9) and C(11). Complex **10ax** showed additional signals between HC(6′) and H_{syn}C(11) and between H_3C(7′) and H_{syn}C(11) (Figure 3). Dynamic behavior was found for bisoxazoline complex **12b**,[12] in which exchange peaks were observed between HC(6) and HC(6′) and between H_3C(8) and H_3C(8′). A combination of exchange peaks and NOE signals between HC(6′) and H_{anti}C(9) and between HC(6) and H_{syn}C(11) indicated rapid apparent allyl rotation on the timescale of the NOE experiment. Nevertheless, assignment of the two sets of ^{13}C and ^{1}H NMR signals for the spectroscopically distinguishable oxazoline rings was also possible in this case by consideration of all observed NOE signals between the bisoxazoline ligand and the allyl fragment.

The relative chemical shifts of the ^{13}C signals of the allyl termini are in agreement with the results of a previous study of the analogous box complex **14** (see Scheme 2): the allyl terminus of which the *syn* proton points toward the substituent of the oxazoline ring resonates at lower field.[7]

Crystal structures of complexes 10ay, 10az and 11cx:[13] The bonds between the bridging atom and the oxazoline rings are approximately 0.1 Å longer in the borabox complexes **10ay** and **10az** than in the reported analogous box complex **14**[14] (Figure 4, Table 1), in accordance with the bond lengths measured in analogous borabox copper complexes.[4a] The bite angles of the ligand are very close to 90°, as expected for square planar metal complexes (90.8° for **10ay** and **10az**). The C_{oxa}-B-C_{oxa} angle is close to the ideal tetrahedral angle in both structures (110.7° for **10ay** and 111.2° for **10az**).

Although the allyl fragments were disordered in both complexes, analysis of the residual electron density allowed

the refinement for complex **10ay**. Distances between the Pd center and the allyl termini are very similar: 2.12 Å for Pd−C(9) and 2.11 Å for Pd−C(11). Likewise, the angles between the carbon atoms of the allyl termini and the neighbouring nitrogen atoms at the palladium center differ only marginally (101.2° for N-Pd-C(9) and 99.7° for N′-Pd-C(11)). The Pd−N bonds have nearly the same lengths (**10az** = 2.0846(18) and 2.070(2) Å; **10ay** = 2.0753(16) and 2.0746(17) Å). Both complexes form flat chelate rings (Figure 4).

Borabox complex **11cx** has shorter Pd−N bonds than box analogue **13**, and the benzylic C atoms of the ligand are noticeably closer to the *ipso* carbon atoms of the 1,3-diphenylallyl fragment in the former (closest distance: 3.32 Å for **11cx**, 3.67 Å for **13**). The resulting larger strain in the borabox complex, which destabilizes the (*syn*, *syn*) arrangement, provides an explanation for the observed *syn–anti* isomerization in complex **11cx** in solution.

Although the deviation from the ideal planar coordination geometry is small in both complexes, the allyl fragment of the borabox complex **11cx** is bent in the opposite direction relative to the ligand, compared to the box complex **13**. As a consequence, the dihedral angles between the plane formed by the N atoms of the ligand and the Pd atom and the plane formed by the allyl termini and the Pd atom are of opposite sign in the two complexes (+4°, −4°).[15]

Synthesis and x-ray analysis of copper complexes 15ax–az and 15cx: Copper(II) complexes of borabox ligands were prepared either by treating the lithium salts (**7-Li**) of the ligands (**7ax**, **7ay**, **7cx**) with $CuSO_4 \cdot H_2O$ (1.0 equiv) in a biphasic mixture of water and CH_2Cl_2, or by treating the protonated ligand **7az**-H with $Cu(OAc)_2$ (1.0 equiv) in MeOH.[16] Crystallization was achieved by layering concentrated solutions of the complexes in CH_2Cl_2 or Et_2O with hexane or pentane. Complex **15ax** crystallized upon slow evaporation of a CH_2Cl_2 solution (Scheme 4).

Single homoleptic copper complexes were found in the asymmetric units for **15ax** and **15cx**, whereas two complexes, with slightly different geometries, occupied the asymmetric unit in the case of **15az**. The structure of complex **15ay** has an additional C_2 axis that allows superposition of the two ligand fragments as depicted in Figure 5. For conciseness, averaged angles and bond lengths are used in the following discussion.

All complexes adopt a distorted tetrahedral geometry, and the geometric parameters of the four complexes are very similar, the C_{oxa}-B-C_{oxa} angles

Table 1. Selected interatomic distances [Å] and angles [°] in palladium complexes.

	10ay[a]	10az[a,b]	14[c]	11cx[d]	13[c]
C(2)−X[e]	1.614(3)	1.619(3)	1.499	1.644(3)	1.504
C(2′)−X[e]	1.612(3)	1.618(4)	1.501	1.635(3)	1.510
Pd−C(9)	2.124(2)	–	2.110(4)	2.1360(18)	2.118(3)
Pd−C(10)	2.109(2)	–	2.108	2.1119(17)	2.100
Pd−C(11)	2.114(2)	–	2.117(4)	2.1621(17)	2.169(3)
N−Pd	2.0753(16)	2.070(2)	2.075(3)	2.0837(15)	2.105(3)
N′−Pd	2.0746(17)	2.0846(18)	2.099(3)	2.0966(16)	2.130(3)
C(2)=N	1.287(4)	1.290(3)	1.266	1.289(2)	1.272
C(2′)=N′	1.282(3)	1.286(3)	1.267	1.293(2)	1.268
N′-Pd-N	90.85(11)	90.76(7)	87.6(1)	86.22(6)	84.5(1)
C(2′)-X-C(2)[e]	110.71(17)	111.19(18)	113.48	102.60(15)	105.98
N-Pd-C(9)	101.20(12)	–	101.3(1)	99.19(7)	99.3(1)
N′-Pd-C(11)	99.71(12)	–	102.8(1)	106.17(7)	108.0(1)
C(11)-Pd-C(9)	68.17(14)	–	68.2(2)	68.55(7)	68.3(1)

[a] Data were collected at 173 K. [b] The allyl ligand was disordered and its position relative to the oxazoline rings could not be determined. Distinctions made between the left and right half of the molecule are therefore arbitrary. [c] Interatomic distances and angles for these compounds were taken from reference [7] or calculated with ORTEP-3 (Version 1.08) from the fractional coordinates deposited in the CCDC. Data for these compounds were collected at 250 K. [d] Data for this compound were collected at 123 K. [e] X = B, C.
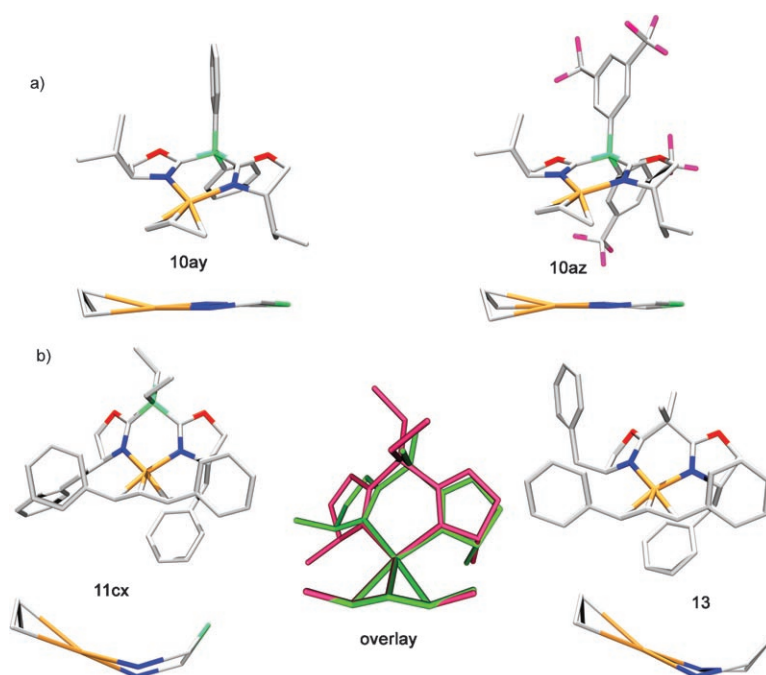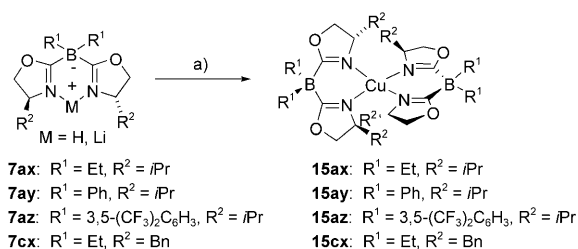
Figure 4. a) Crystal structures of complexes **10 ay** and **10 az** (allyl fragment and one CF_3 group are disordered); side view of the chelate rings. b) Comparison between complexes **11 cx** and **13**; side view of the chelate rings and superposition of relevant fragments (middle). Data for complex **13** are taken from ref. [7].

Scheme 4. Synthesis of the homoleptic borabox copper complexes **7**₂Cu. a) Cu(SO₄), H₂O/CH₂Cl₂ for **15 ax**, **15 ay** and **15 cx**; Cu(OAc)₂, MeOH for **15 az**.

being close to the ideal tetrahedral angle, with values between 108.8° (**15 ax**) and 110.4° (**15 az**). Bond lengths between boron and the quaternary carbon atoms of the oxazoline rings vary from 1.61 Å (**15 ay**, **15 cx**) to 1.62 Å (**15 ax**, **15 az**), whereas C=N bond lengths are in the range from 1.28 Å (**15 ax**) to 1.30 Å (**15 cx**). These values are in good agreement with the corresponding interatomic distances and angles in the Pd complexes **10 ay** and **10 az** discussed above.[17]

Allylic oxidation of cycloalkenes: Borabox ligands were evaluated in Cu-catalyzed asymmetric allylic oxidations of cyclohexene and cyclopentene (Table 2). Initial investigations showed that enantioselectivities were significantly higher when the protonated borabox ligands **7**-H and K₂CO₃ were used for catalyst preparation instead of the lithium salts **7**-Li. A direct comparison with box ligand **6b** re-

vealed that borabox ligand **7 ay** with the same substitution pattern gives higher enantioselectivity in the oxidation of cyclohexene. In contrast with box ligands,[18] *tert*-butyl substituents at the stereogenic centers were not suitable for this reaction when borabox ligands were used.

The observed enantioselectivities compare well with the best results obtained with box ligands.[19] Cyclohexene reacted with 79% *ee* at room temperature (Table 2) and cyclopentene with 86% *ee* at −15°C (Table 3) when ligand **7 cx** (R¹ = Et, R² = Bn) was employed. Ligand **7 dx**, bearing two additional phenyl substituents at the 5-positions of the oxazoline rings, allowed the oxidation of cyclopentene in 86% *ee* even at room temperature (Table 2).[20, 21]

The reaction of cyclopentene in the presence of the catalyst derived from borabox ligand **7 cx** showed only a weak temperature dependence of the *ee*, in contrast with the oxidation of cyclohexene (Table 3 and Figure 6). Thus, at 80°C cyclopentene could be fully converted into the benzoate within 1 hour and with a respectable *ee* of 76%. The *ee* values obtained in the oxidation of cyclopentene are among the best results reported to date for this reaction.[18,19,22] As with other ligands, relatively high catalyst loadings and long reaction times are required. In this respect, further studies of borabox ligands might be rewarding, in view of the fast rates combined with relatively high enantioselectivities observed with ligand **7 cx** at elevated temperatures (Figure 6).

Conclusion

Borabox ligands are readily prepared in a modular fashion from chiral oxazolines and diaryl- or dialkylhaloboranes. Variation of the substituents in the oxazoline rings and at boron allows steric and electronic fine-tuning of the corresponding metal complexes. Borabox ligands are stronger electron donors than their neutral box counterparts, as shown by NMR data and DFT calculations. As a consequence of the longer bonds between the bridging atom and the adjacent oxazoline rings, the C_{oxa}-B-C_{oxa} angles in metal complexes are smaller, whereas the bite angles are wider than the corresponding angles in box complexes. With the exception of sterically overcrowded derivatives (**11 cx**), borabox complexes form almost flat chelate rings.
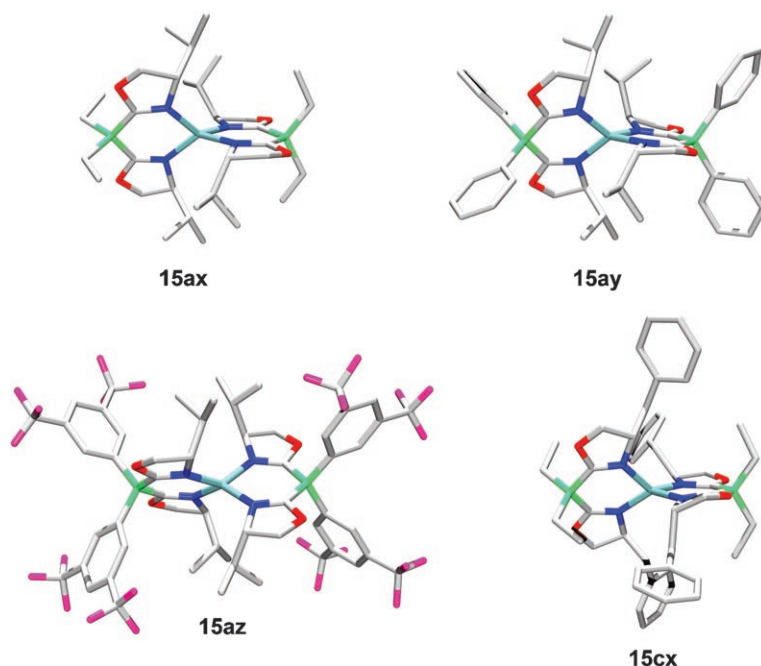
Figure 5. Crystal structures of four different homoleptic borabox copper complexes. CF$_3$ groups in **15az** were disordered.

allyl fragments. Borabox ligands, on the other hand, are well suited for copper-catalyzed allylic oxidation reactions. The results described here, together with previous work on enantioselective cyclopropanation[4a] and acylation of 1,2-diols and pyridyl alcohols,[4a,b] demonstrate that borabox ligands are a useful addition to the previously developed bisoxazolines, with different electronic and geometric properties. Further applications of borabox ligands in asymmetric catalysis are currently under investigation.

Experimental Section

General: All reactions were carried out under argon or nitrogen unless otherwise noted. Solvents were purified by standard procedures or were used as purchased from FLUKA (puriss., absolute, over molecular sieves). NMR spectra were recorded on 400 and 500 Bruker Avance spectrometers at 295 K, if not otherwise noted. NOE spectra for **10ax–z** and **11cx** were acquired at 295 K with use of a mixing time of 350 ms and 256 points in the F1 dimension and 2048 points in the F2 dimension with corresponding acquisition times of 26 and 205 ms. In the case of **12a**, two NOE spectra were acquired at 275 K and 295 K, with use of a mixing time of 1 s and 128 and 2048 points with acquisition times of 13 ms and 205 ms in the F1 and F2 dimensions, respectively. Infrared spectra were obtained on a Shimadzu FTIR-8400S spectrometer fitted with a Specac Golden Gate Mk II ATR unit, with use of neat samples. Optical rotations were measured on a Perkin–Elmer 341 polarimeter fitted with a Na lamp. Elemental analyses were obtained from the Micro-Analytical Laboratory of the Department of Chemistry of the University of Basel. Ph$_2$BCl,[23a] Et$_2$BBr,[23] bis-[3,5-bis(trifluoromethyl)phenyl]boron chloride,[5d,23c,24] oxazolines **8a–c**, **8e** and **8f**,[25] box ligands **6a** and **6b** (R^1= Ph, R^2=iPr[4a,23c] and R^1=Me, R$_2$= iPr[26]) and [Pd(1,3-diphenylallyl)Cl]$_2$[7] were prepared by literature procedures. All other reagents were available from commercial suppliers and were used without further purification. For conciseness the abbreviation "oxa" has been used for "oxazoline".

Table 2. Allylic oxidation of cyclopentene and cyclohexene in the presence of different Cu catalysts.[a]

| L*	R^1	R^2	R^3	n	t [d]	Yield [%][b]	ee [%][c]
7ay-Li	Ph	iPr	H	2	19	59	60
7aw-Li	Cy	iPr	H	2	18	56	31
7bw-Li	Cy	tBu	H	2	19	63	rac.
7az-Li	3,5-(CF$_3$)$_2$C$_6$H$_3$	iPr	H	2	24	78	71
7ay-Li	Ph	iPr	H	1	34	53	71
7ay-H	Ph	iPr	H	2	8	53	74
7ax-H	Et	iPr	H	2	2–3	71[d]	64
7cy-H	Ph	Bn	H	2	5	69[d]	78
7cx-H	Et	Bn	H	2	10	69[d]	79
7cz-H	3,5-(CF$_3$)$_2$C$_6$H$_3$	Bn	H	2	14	76	70
7dx-H	Et	Bn	Ph	2	5	20[d]	78
7ey-H	Ph	Ph	H	2	2	80	65
7fy-H	Ph	CH$_2$$i$Pr	H	2	4	77	72
7ay-H	Ph	iPr	H	1	2	70	75
7bx-H	Et	tBu	H	1	1.5	65	8
7cx-H	Et	Bn	H	1	2	79	82
7dx-H	Et	Bn	Ph	1	3	87	86
7ey-H	Ph	Ph	H	1	2	75	78
6b	Ph	iPr	H	2	19	75	48
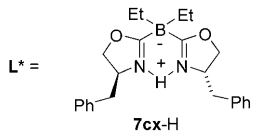
[a] Reactions were performed on a 0.5 mmol scale with [Cu(CH$_3$CN)$_4$][PF$_6$] (5 mol%), ligand (7.5 mol%) and K$_2$CO$_3$ (M=H, 15 mol%). [b] After column chromatography. [c] ee and absolute configuration determined by HPLC by literature procedures; see Experimental Section. [d] Reaction performed on a 0.25 mmol scale.

In contrast with Pd–box complexes, Pd–borabox complexes do not catalyze allylic substitution reactions, which can be explained by the higher electron densities in their

Table 3. Temperature effect on the allylic oxidation in the presence of catalyst Cu(**7**cx).[a]

7cx-H

n	T [°C]	t [h]	Yield [%][b]	ee [%][c]
1	−15	360	30	86
1	5	141	80	82
1	25	48	79	82
1	40	8	78	81
1	60	2	70	78
1	80	1	69	76
2	25	219	69	79
2	60	86	72	68
2	80	11	61	65

[a] Reactions were performed on a 0.5 mmol scale in the presence of [Cu-(CH$_3$CN)$_4$][PF$_6$] (5 mol%), (**7**cx)-H (7.5 mol%) and K$_2$CO$_3$ (15 mol%). [b] After column chromatography. [c] ee and absolute configuration determined by HPLC by literature procedures; see Experimental Section.
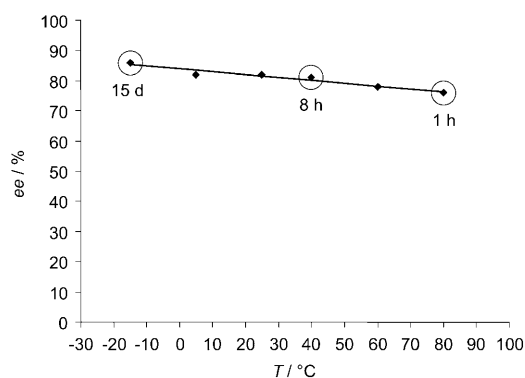
Figure 6. Temperature dependence of ee in the copper-catalyzed allylic oxidation of cyclopentene (conditions, see Table 2).

Synthesis of protonated borabox ligands 7-H: tBuLi (1.7 M in hexane, 1.78 mL, 3.03 mmol) was added at −78 °C over a 10 min period to a solution of oxazoline (2.75 mmol) in THF (100 mL), resulting in a pale yellow solution. After the system had been stirred for 30 min at this temperature, a solution of R$_2$BCl (1.38 mmol) in toluene (5 mL) was added by cannula, and the cooling bath was removed immediately after addition. After 4 to 12 h, the reaction was complete, and volatile compounds were removed under vacuum. The remaining foamy residue was redissolved in benzene and filtered to remove LiCl, and the solvent was evaporated again. The crude product was washed with pentane (3× 20 mL) and dried. The lithium salt **7**-Li was then dissolved in the minimum possible amount of the eluent mixture (typically: hexane/ethyl acetate/Et$_3$N 10:1:0.5 unless otherwise mentioned) and directly transferred to a silica gel column (h = 10–12 cm; ⌀ = 2 cm). After elution and evaporation of the solvents, the product was isolated in its protonated form.

Lithium salts **7**ax-Li and **7**bx-Li were extracted from the crude product with dichloromethane instead of benzene. Lithium salts of entirely alkyl-substituted ligands (**7**aw-Li, **7**ax-Li, **7**bw-Li, **7**bx-Li) are soluble in alkanes, and the amount of pentane used to wash the crude products should be reduced in these cases to avoid loss of product.

Note: Although the lithium salts **7**-Li can be isolated as highly hygroscopic white solids, it was generally preferable to convert them directly into the protonated ligands, which are less hygroscopic, easier to handle and

purifiable by chromatography. If necessary, the lithium salts can be readily prepared from the protonated derivatives (see below).

Compound 7aw-H: Yield: 70%; R$_f$ = 0.30 (hexane/ethyl acetate/Et$_3$N 10:1:0.5); [α]$_D^{20}$ = −63 (c = 0.11 in CH$_2$Cl$_2$); ^{1}H NMR (500 MHz, CDCl$_3$): δ = 13.09 (br s, 1 H; NHN), 4.37 (m, 2 H; oxa), 4.00 (m, 2 H; oxa), 3.75 (m, 2 H; oxa), 1.61–1.48 (m, 6 H; Cy), 1.43 (br d, $^3J_{H,H}$ = 9.5 Hz, 4 H; Cy), 1.21–0.28 (m, 12 H; Cy), 1.15 (m, 2 H; CH(CH$_3$)$_2$), 0.98 (d, $^3J_{H,H}$ = 7.0 Hz, 6 H; CH$_3$), 0.92 ppm (d, $^3J_{H,H}$ = 7.0 Hz, 6 H; CH$_3$); ^{13}C NMR (126 MHz, CDCl$_3$): δ = 197.5 (N=C), 71.3 (oxa), 67.1 (oxa), 32.9 (CH(CH$_3$)$_2$), 31.5 (Cy), 31.3 (Cy), 29.1 (Cy), 27.9 (Cy), 19.1 (CH$_3$), 18.9 ppm (CH$_3$); ^{11}B NMR (161 MHz, CDCl$_3$): δ = −12.9 ppm (s); IR: $\tilde{\nu}$ = 2962, 2908, 2839, 1573, 1465, 1442, 1411, 1311, 1203, 1018, 956, 933, 864 cm^{-1}; MS (FAB): m/z (%): 403 [M+H]$^+$ (100), 208 [M−oxa−Cy+H]$^+$ (18); elemental analysis calcd (%) for C$_{24}$H$_{43}$BN$_2$O$_2$ (402.43): C 71.63, H 10.77, N 6.96; found: C 71.53, H 10.75, N 6.90.

Conversion of the protonated ligands into their lithium salts: nBuLi (0.14 mL, 0.23 mmol) was added at 0 °C to a solution of **7**ay-H (84 mg, 0.22 mmol) in THF (10 mL). After 2 h of additional stirring at room temperature, the volatiles were removed under reduced pressure and **7**ay-Li was isolated as a white solid (82.0 mg, 0.207 mmol, 96%). [α]$_D^{20}$ = −49 (c = 0.11 in CH$_2$Cl$_2$); ^{1}H NMR (500 MHz, (CD$_3$)$_2$CO): δ = 7.31 (br d, $^3J_{H,H}$ = 6.9 Hz, 4 H; arom CH ortho), 6.98 (m, 4 H; arom CH meta), 6.90 (m, 2 H; arom CH para), 3.86–3.73 (m, 4 H; oxa), 3.64 ("t", J$_{H,H}$ = 7–8 Hz, 2 H; oxa), 1.79 (m, 2 H; CH(CH$_3$)$_2$), 0.85 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H; CH$_3$), 0.73 ppm (d, $^3J_{H,H}$ = 6.9 Hz, 6 H; CH$_3$); ^{13}C NMR (126 MHz, (CD$_3$)$_2$CO): arom C ipso to B: not detected, δ = 209.4 (N=C), 134.5 (arom CH), 125.7 (arom CH ortho), 123.1 (arom CH para), 71.1 (oxa), 65.4 (oxa), 31.6 (CH(CH$_3$)$_2$), 18.9 (CH$_3$), 16.3 ppm (CH$_3$); ^{11}B NMR (160 MHz, (CD$_3$)$_2$CO): δ = −12.7 ppm (s); IR: $\tilde{\nu}$ = 2962, 2877, 2360, 1635, 1589, 1465, 1388, 1265, 1157, 1103, 1033, 964, 864, 732 cm^{-1}.

For analytical data for ligands **7**aw-Li, **7**bw-Li, **7**bx-Li, **7**by-Li, **7**bz-Li, see Supporting Information of reference [4a].

General procedure for the synthesis of palladium complexes 10 ax–az: A solution of **7**ay-H (54 mg, 0.14 mmol) in THF (2 mL) was cooled to 0 °C, and nBuLi (1.6 M in hexane, 95 μL, 0.15 mmol) was slowly added with stirring. After 30 min the reaction mixture was allowed to warm up to room temperature, and a solution of [Pd(C$_3$H$_5$)Cl]$_2$ (25.3 mg, 69.2 μmol) in THF (1 mL) was slowly added. After a further 20 minutes, the volatiles were removed in vacuo, benzene (5 mL) was added, and the turbid solution was filtered. After removal of volatiles, the solid was redissolved in hot EtOH, and the minimum possible amount of water was added. Upon cooling to room temperature and standing overnight the product recrystallized as colorless needles, which were suitable for X-ray analysis. Crystallization was repeated twice from the mother liquors (65 mg, 88%).

M.p. 164 °C; [α]$_D^{20}$ = −24 (c = 0.42 in CH$_2$Cl$_2$); ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ = 7.25 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H; arom CH), 7.16–7.01 (m, 8 H; arom CH), 5.54 ("ddt", $^3J_{H,H}$ = 12.4, 12.0, 6.9 Hz, 1 H; HC(10)), 4.07 (dd, $^2J_{H,H}$ = 9.0 Hz, $^3J_{H,H}$ = 4.3 Hz, 1 H; HC(5) trans to HC(4)), 4.05 (m, 2 H;

H$_2$C(5′)), 3.99 (dd, $^3J_{H,H}$ = 9.6 Hz, ^2J = 9.0 Hz, 1 H; HC(5) cis to HC(4)), 3.94 (td, $^3J_{H,H}$ = 6.9, 3.1 Hz, 1 H; HC(4′)), 3.83 (ddd, $^3J_{H,H}$ = 9.6, 4.3, 3.1 Hz, 1 H; HC(4)), 3.74 ("dd", $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 2.2 Hz, 1 H; HC(11) syn), 3.57 ("dd", $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 2.2 Hz, 1 H; HC(9) syn), 2.93 (m, $^3J_{H,H}$ = 12.4 Hz, 1 H; HC(11) anti), 2.85 (m, $^3J_{H,H}$ = 12.0 Hz, 1 H; HC(9) anti), 2.01 (qqd, $^3J_{H,H}$ = 7.1, 6.9, 3.1 Hz, 1 H; HC(6)), 1.89 (qqd, $^3J_{H,H}$ = 7.1, 6.9, 3.1 Hz, 1 H; HC(6′)), 0.86 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H; H$_3$C(7)), 0.85 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H; H$_3$C(7′)), 0.49 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H; H$_3$C(8)), 0.44 ppm (d, $^3J_{H,H}$ = 6.9 Hz, 3 H; H$_3$C(8′)); ^{13}C NMR (126 MHz, CD$_2$Cl$_2$): δ = 193.2 (br, 2 C; C(2), C(2′)), 152.2 (br, 2 C; arom C ipso), 134.6, 127.2, 127.1, 125.1, 125.0 (10 C; arom CH), 115.1 (C(10)), 74.5 (2 C; C(4), C(4′)), 67.1, 67.0 (C(5), C(5′)), 59.9 (C(11)), 56.7 (C(9)), 31.3 (2 C; C(6), C(6′)), 19.6, 19.5 (C(7), C(7′)), 14.3 (H$_3$C(8′)), 14.2 ppm (H$_3$C(8));
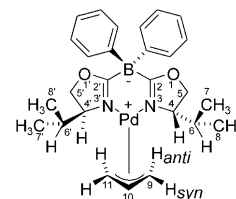
^{11}B NMR (161 MHz, CD$_2$Cl$_2$): $\delta = -12.8$ ppm (s); IR: $\tilde{v} = 3070$, 3058, 3041, 2989, 2954, 2923, 1577, 1558, 1481, 1188, 1172, 1114, 974, 960, 948, 788, 742, 727, 700 cm^{-1}; MS (FAB): m/z (%): 536 [M]$^+$ (22), 495 [$M-$C$_3$H$_5$]$^+$ (13), 459 [$M-$C$_6$H$_5$]$^+$ (58), 391 [$M-$Pd(C$_3$H$_5$)+2H]$^+$ (30), 278 [$M-$Pd(C$_3$H$_5$)$-$oxa+H]$^+$ (27), 41 (100); elemental analysis calcd (%) for C$_{27}$H$_{35}$N$_2$O$_2$B$_1$Pd$_1$ (536.8): C 60.41, H 6.57, N 5.22; found: C 60.59, H 6.56, N 5.23.

Synthesis of palladium complex 11cx: Ligand **7cx**-H (230 mg, 589 µmol), (1,3-diphenylallyl)palladium chloride dimer (196 mg, 292 µmol)[7] and K$_2$CO$_3$ (81.6 mg, 590 µmol) were stirred at 50 °C for 80 min in a mixture of CH$_2$Cl$_2$ (12 mL), THF (10 mL) and methanol (10 mL) in a sealed Schlenk flask. After the system had cooled to room temperature, the solution was filtered, and the volatiles were removed. The residue was dissolved in CH$_2$Cl$_2$ (50 mL) and washed with water (2×20 mL). The organic phase was separated and dried over Na$_2$SO$_4$. After removal of volatiles the remaining solid was recrystallized from hot EtOH/H$_2$O by slow cooling to room temperature. During the first crystallization the formation of a black precipitate was observed, which made another filtration and evaporation of solvents necessary. The product finallyrecrystallized as yellow blocks (179 mg), which were washed with a small amount of MeOH. Another batch (49 mg) was obtained by crystallization from the mother liquor. The crystals obtained were suitable for x-ray diffraction (228 mg, 56 %); m.p. 156–158 °C.

NMR data for the (syn,syn)-isomer: The ratio of (*syn*, *syn*) to (*anti*, *syn*) isomer in the sample was 91:9.

(syn,syn)
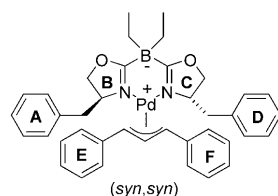
^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 275 K): $\delta = 7.53$–7.48 (m, 2H; arom CH (E) *ortho*), 7.46–7.41 (m, 4H; arom CH (F) *ortho*, arom CH (D) *meta*), 7.36–7.20 (m, 10H; arom CH), 7.16 (m, 2H; arom CH (D) *ortho*), 6.87 (m, 2H; arom CH (A) *ortho*), 5.86 (dd, $^3J_{H,Ph(E)CH} = 11.3$ Hz, $^3J_{H,Ph(F)CH} = 10.7$ Hz, 1H; (PhCH)$_2$CH), 4.01 (d, $^3J_{H,H} = 10.7$ Hz, 1H; Ph(F)CH), 3.90 (m, overlaid signal, 1H; oxa CH (B)), 3.86 ("t", $^2J_{H,H} = 8.0$ Hz, $^3J_{H,H} = 8.0$ Hz, 1H; oxa CHH (B)), 3.75 (dd, $^2J_{H,H} = 8.5$ Hz, $^3J_{H,H} = 4.1$ Hz, 1H; oxa CHH (C)), 3.50 ("t", $^2J_{H,H} = 9$ Hz, $^3J_{H,H} = 9$ Hz, 1H; oxa CHH (C)), 3.46 ("t", $J_{H,H} = 8.0$ Hz, 1H; oxa CHH (B)), 3.01 (d, $^3J_{H,H} = 11.3$ Hz, 1H; Ph(E)CH), 2.81 ("tdd", $^3J_{H,H} = 9.3$, 5.5, 4.1 Hz, 1H; oxa CH (C)), 2.68 (dd, $^2J_{H,H} = 13.8$ Hz, $^3J_{H,H} = 4.1$ Hz, 1H; Ph(A)CHH), 2.53 (dd, $^2J_{H,H} = 13.1$ Hz, $^3J_{H,H} = 5.5$ Hz, 1H; Ph(D)CHH), 2.45 (dd, $^2J_{H,H} = 13.1$ Hz, $^3J_{H,H} = 9.3$ Hz, 1H; Ph(D)CHH), 1.35 (dd, $^2J_{H,H} = 13.8$ Hz, $^3J_{H,H} = 10.3$ Hz, 1H; Ph(A)CHH), 0.78 (m, 6H; CH$_3$), 0.77 (m, 2H; CH_2CH$_3$), 0.33 ppm (m, 2H; CH_2CH$_3$); ^{13}C NMR (126 MHz, CD$_2$Cl$_2$, 275 K): $\delta = 196.9$ (b, N=C), 140.9 (arom C (E) *ipso*), 140.2 (arom C (F) *ipso*), 139.1 (arom C (D) *ipso*), 138.5 (arom C (A) *ipso*), 130.1 (2C; arom CH (D) *ortho*), 129.4 (2C; arom CH), 129.3 (2C; arom CH), 129.2 (2C; arom CH), 128.7 (2C; arom CH), 128.6 (2C; arom CH), 128.3 (4C, arom CH (E+F) *ortho*), 127.7 (2C; arom CH (E+F) *para*), 126.8 (arom CH (D) *para*), 126.6 (arom CH (A) *para*), 109.2 ((PhCH)$_2$CH), 74.1 (Ph(E)CH), 72.1 (oxa CH$_2$ (C)), 71.3 (oxa CH$_2$ (B)), 71.1 (Ph(F)CH), 66.9 (oxa CH (B)), 63.8 (oxa CH (C)), 43.4 (Ph(D)CH$_2$), 41.2 (Ph(A)CH$_2$), 18.8, 12.3 (b, CH$_2$CH$_3$), 12.1, 11.7 ppm (CH$_3$).
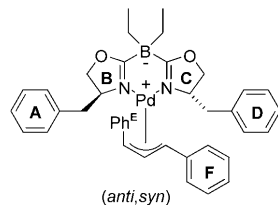
NMR data for the (anti,syn) isomer

(anti,syn)

^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 275 K): $\delta = 7.51$ (m, overlaid signal, 2H; arom CH (F)), 7.40–7.36 (m, 6H; arom CH), 7.31 (fully overlaid signal, assigned by 2D-NMR, arom CH (A) *ortho*), 7.12–7.09 (m, 3H; arom CH), 6.61 (m, 2H; arom CH (D) *ortho*), 5.62 (d, $^3J_{H,H} = 7.7$ Hz, 1H; Ph(E)CH), 5.48 (dd, $^3J_{H,H} = 11.5$, 7.7 Hz, 1H; (PhCH)$_2$CH), 4.56 (d, $^3J_{H,H} = 11.5$ Hz, 1H; Ph(F)CH), 4.44 ("tdd", $^3J_{H,H} = 8.8$, 5.5, 3.3 Hz, 1H; oxa CH (B)), 4.16 (dd, $^2J_{H,H} = 8.8$ Hz, $^3J_{H,H} = 3.3$ Hz, 1H; oxa CHH (B)), 4.08 ("t",

$^2J_{H,H} = 8.8$ Hz, $^3J_{H,H} = 8.8$ Hz, 1H; oxa CHH (B)), 3.70 (dd, $^2J_{H,H} = 8.5$ Hz, $^3J_{H,H} = 3.3$ Hz, 1H; oxa CHH (C)), 3.52 (overlaid signal, $J_{H,H} = 8$–9 Hz, 1H; oxa CHH (C)), 3.13 (dddd, $^3J_{H,H} = 9.8$, 8.8, 4.2, 3.3 Hz, 1H; oxa CH (C)), 3.07 (dd, $^2J_{H,H} = 13.6$ Hz, $^3J_{H,H} = 5.5$ Hz, 1H; Ph(A)CHH), 2.70 (overlaid signal, 1H; Ph(D)CHH), 2.68 (overlaid signal, 1H; Ph(A)CHH), 2.24 (dd, $^2J_{H,H} = 14.2$ Hz, $^3J_{H,H} = 9.8$ Hz, 1H; Ph(D)CHH), 0.63 (t, $^3J_{H,H} = 7.6$ Hz, 3H; CH$_3$), 0.54 (t, $^3J_{H,H} = 7.7$ Hz, 3H; CH$_3$), ≈ 0.32, ≈ 0.26 ppm (overlaid signals, assignment by HMQC, CH_2CH$_3$); the remaining aromatic proton signals of the (*anti, syn*) isomer were overlaid by the signals of the (*syn, syn*) isomer and were not assigned; ^{13}C NMR (126 MHz, CD$_2$Cl$_2$, 275 K): $\delta = 138.2$, 137.6, 137.5 (arom C *ipso*), 130.0, 129.6, 129.6, 126.5, 129.3, 129.1, 128.8, 128.4, 128.2, 127.8, 127.1 (arom CH), 106.7 ((PhCH)$_2$CH), 78.7 (Ph(E)CH), 71.4 (Ph(F)CH), 70.6 (oxa CH$_2$ (B)), 70.2 (oxa CH (B)), 69.3 (oxa CH$_2$ (C)), 64.2 (oxa CH (C)), 43.1 (Ph(A)CH$_2$), 41.3 (Ph(D)CH$_2$), 17.0, 16.7 (assignment by HMQC, CH$_2$CH$_3$), 12.6, 12.4 ppm (CH$_3$); no further signals were detected; ^{11}B NMR (161 MHz, CD$_2$Cl$_2$): $\delta = -15.9$ ppm (s); only one signal was detected, although both isomers were present according to ^{1}H NMR; IR: $\tilde{v} = 3060$, 3027, 2934, 2894, 2872, 2857, 1600, 1568, 1497, 1489, 1453, 1190, 1182, 1171, 1074, 1035, 1028, 948, 942, 836, 756, 735, 694 cm^{-1}; MS (FAB): m/z (%): 689 [M+H]$^+$ (10), 659 [$M-$C$_2$H$_5$]$^+$ (42), 528 [$M-$oxa]$^+$ (6), 299 [Pd(C$_3$H$_3$Ph$_2$)]$^+$ (33); elemental analysis calcd (%) for C$_{39}$H$_{43}$BN$_2$O$_2$Pd (689.0): C 67.98, H 6.29, N 4.07; found: C 68.14, H 6.39, N 4.09.

Synthesis of copper complexes: CuSO$_4$·H$_2$O (21.0 mg, 0.132 mmol) in H$_2$O (10 mL) was combined with a solution of **7ay**-Li (105 mg, 0.265 mmol) in CH$_2$Cl$_2$ (20 mL) with vigorous stirring at room temperature. After 25 minutes a saturated aqueous solution of NaHCO$_3$ (5 mL) was added. Stirring was continued for an additional 25 minutes, during which the organic phase changed from blue to green. The organic phase was separated and filtered through a plug of Celite®, and volatiles were evaporated. The remaining green crystalline solid was dissolved in the minimum possible amount of CH$_2$Cl$_2$/Et$_2$O (1 mL) and layered with hexane. After 2 days, blue-green plates had started to grow. They were collected and subjected to single-crystal analysis. Compound **15ay**: $[\alpha]_D^{20} = -931$ ($c = 0.11$ in CH$_2$Cl$_2$); MS (MALDI-TOF, 2,5-dihydrobenzoic acid): m/z: 842 [M+H]$^+$; elemental analysis calcd (%) for C$_{48}$H$_{60}$B$_2$CuN$_4$O$_4$ (842.19): C 68.46, H 7.18, N 6.65; found: C 68.78, H 7.23, N 6.60.

Copper-catalyzed allylic oxidation of alkenes—Procedure A with Li salts 7-Li: In a glovebox, a ligand **7**-Li (37.6 µmol) and [Cu(CH$_3$CN)$_4$]PF$_6$ (9.3 mg, 25 µmol) were placed in a 10 mL Young® tube, fitted with a magnetic stirring bar. CH$_3$CN (2 mL) was added, and the tube was sealed and removed from the glovebox. The mixture was stirred for 1 h at room temperature. The olefin (2.0 mmol) was then added, followed by *tert*-butyl perbenzoate (95 µL, 0.50 mmol) under a stream of argon. The flask was sealed, and stirring was continued at the desired temperature. Reaction progress was monitored by TLC (hexane/Et$_2$O 15:1; $R_f = 0.30$ (*tert*-butyl peroxybenzoate) and either 0.41 (cyclohex-2-enyl benzoate) or 0.50 (cyclopent-2-enyl benzoate). When the reaction was complete, volatiles were removed in vacuo, and the crude product was purified by column chromatography (SiO$_2$, $\varnothing = 2$ cm, $h = 14$ cm, hexane/Et$_2$O 15:1) to give a colorless oil.

Procedure B with protonated ligands 7-H: In a glovebox, a ligand **7**-H (37.6 µmol), [Cu(CH$_3$CN)$_4$]PF$_6$ (9.1 mg, 24 µmol) and K$_2$CO$_3$ (10.7 mg, 77.4 µmol) were mixed in a 10 mL Young® tube, fitted with a magnetic stirring bar. CH$_3$CN (2 mL) was added, and the tube was sealed and removed from the glovebox. The mixture was stirred for 1 hour at room temperature. The reaction and workup were carried out as described in procedure A.

The complexation reaction with ligand **7dx**-H was performed at 86 °C to circumvent solubility problems.

HPLC conditions

Cyclohex-2-enyl benzoate: Chiracel OD-H; heptane/*i*PrOH 99.8:0.2; 20 °C; 0.5 mL min^{-1}; $\lambda_1 = 210$, $\lambda_2 = 230$ nm; retention time (minutes): 17.7 (major, *S*), 19.2 min (minor, *R*).

Cyclopent-2-enyl benzoate: Chiracel OD-H; heptane/*i*PrOH 99.8:0.2; 20°C; 0.5 mL min^{-1}; $\lambda_1 = 210$, $\lambda_2 = 230$ nm; retention time (minutes): 17.2 (major, *S*), 20.4 min (minor, *R*).

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[13] CCDC 664549 (**15ax**), 664550 (**15cx**), 664551 (**15az**), 664552 (**11cx**), 664553 (**10ay**) and 664554 (**10az**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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