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m-Carborane-Based Chiral NBN Pincer-Metal Complexes: Synthesis, Structure, and Application in Asymmetric Catalysis

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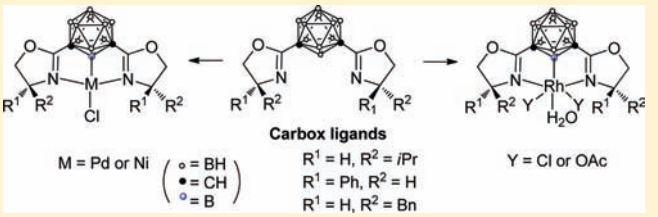
Supporting Information

ABSTRACT: We have succeeded in synthesizing *m*-carborane-based chiral NBN-pincer ligands, 1,7-bis(oxazolinyl)-1,7-dicarba-*closo*-dodecaborane (Carbox) (**7**−**9**). The combination of bis(hydroxyamides) and 3 equiv of diethylaminosulfur trifluoride (DAST) is a key step for cyclization to form oxazoline rings in excellent yields. X-ray crystal structures of these ligands confirmed three donor sites, one central B and two flanking N atoms in fixed positions. The electrophilic halogenation of the Carbox pincer ligands with iodine and a catalytic amount of Lewis acid led to ring-opening of the oxazolines and afforded bis(haloamides) (**13** and **14**). The air- and moisture-stable Carbox pincer complexes of rhodium(III), nickel(II), and palladium(II) were synthesized by the oxidative addition of $RhCl_3 \cdot 3H_2O$, $Ni(COD)_2$, and $Pd(CH_3CN)_4[BF_4]_2$ to the Carbox pincer ligands (**7**−**9**), respectively. The catalytic activity of the rhodium(III) complexes (**18**−**20**) was examined for the asymmetric conjugate reduction of α,β-unsaturated esters and reductive aldol reaction. Among these catalysts, [(*S*,*S*)-Carbox-*i*Pr]$Rh(OAc)_2 \cdot H_2O$ (**18**) showed the highest enantioselective catalytic ability for both asymmetric conjugate reduction and reductive aldol reaction.



INTRODUCTION

An icosahedral carborane framework involves delocalized electron-deficient three-center two-electron bonding, forming trigonal faces and hyperconjugation.[1,2] The carboranes consist of 2 carbon atoms and 10 boron atoms, which result in three isomers: 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaboranes (*o*-, *m*-, and *p*-carboranes) and thus highly tailorable structures.[3,4] Carborane units can be attached to other molecules either via their C or B atoms. While substitution at the carbon atom in carborane derivatives has been extensively studied,[5] alternative routes involving reactions at the boron center are still a challenge.[6]

Transition-metal catalysis is one of the most important subjects in organic synthesis.[7] Especially, the proper choice of ligands for transition-metal-catalyzed reactions is crucial for expanding synthetic applications. Among the various ligand systems that can be found in the literature, pincer-type ligands and their metal complexes have attracted long-lasting interest because of their high stability and activity as catalysts.[8−14] Pincers are a class of the rigid tridentate ligands that are connected to the metals via at least one-metal carbon σ bond. Beside these carbon-based platforms, pincers having amido,[15] silyl,[16] and phosphido[17] units have also been studied extensively.

Recently, the boryl-based pincers were reported by two research groups.[18,19] In general, boryl species are very strong σ donors and exhibit a strong *trans* effect.[20] However, π back-donation is considered to be rather weak in most metal complexes; therefore, the boryl ligands have been considered as reactive ligands.[21] Mirkin and co-workers reported the carborane-based tridentate metal SeBSe and SBS pincers and complexes of these ligands metalated with palladium(II), where a B−Pd bond formation was observed as an analogue of the C−Pd bond (Figure 1).[18] Yamashita and Nozaki reported a similar B−Ir bond formation observed in PBP pincer iridium complexes.[19] Although both findings showed a new aspect of boron-based synthons in organometallic and coordination chemistry,[22] their practical application in organic reactions has not been examined. In this paper, we report the first carborane-based chiral NBN pincers, 1,7-bis(oxazolinyl)-1,7-dicarba-*closo*-dodecaborane (Carbox) and their pincer complexes with rhodium(III), palladium(II), and nickel(II). An interesting feature of the optically active C_2-symmetric NCN pincers (Phebox) is the ease with which a number of chiral analogues can be synthesized from readily available homochiral amino alcohols.[13,14] These pincer ligands can coordinate a variety of transition metals, including Ni,[23−25] Pd,[26−29] Pt,[28,30,31] and Rh,[14,32] to form complexes with C_2-symmetry. Pincer complexes are multipurpose, often air-stable compounds that have attracted interest not only in asymmetric catalysis but also in molecular electronics[33] and medicine.[34] We demonstrate the Carbox-rhodium complexes as suitable catalysts for asymmetric conjugate reduction of α,β-unsaturated esters and the asymmetric reductive aldol reaction of *tert*-butyl acrylate and benzaldehyde using diethoxymethylsilane as a reductant.[14c]

RESULTS AND DISCUSSION

The construction of ligands for transition metal complexes is very important, especially in the field of molecular catalysis and organic synthesis, because ligands can provide appropriate

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stereochemical and electronic environments around active metal centers, thereby controlling catalysis. This fact prompted us to develop new tridentate chiral pincers, 1,7-bis(oxazolinyl)-1,7-dicarba-*closo*-dodecaboranes (Carbox). We adopted a heterocyclic oxazoline skeleton, 4,5-dihydro-1,3-oxazole, as the modular unit of these multidentate ligands because the oxazoline skeleton could supply sufficient substituent diversity, including chiral centers at 4- and 5-positions, using a variety of β-amino alcohols (Scheme 1).[35]

Synthesis of NBN-Pincer (Carbox) Ligands. At the start of our investigations, we synthesized chiral ligands (**7**−**9**) in a similar manner to Phebox ligands via the combination of methodologies described in the literature,[14c,23] as shown in Scheme 1. *m*-Carborane dicarboxylic acid (**2**) was obtained from commercially available *m*-carborane (**1**) using the reported protocol[36] and transformed to the acyl chloride (**3**) with $SOCl_2$. Condensation with 2 equiv of amino alcohols, such as L-valinol, L-phenylalaninol, and D-phenylglycinol, afforded trace amounts of bis(oxazolinyl)-*m*-carboranes (**7**−**9**), and the corresponding uncyclized bis(hydroxyamide)-*m*-carboranes (**4**−**6**) were obtained in 95−98% yields. Treatment of **4**−**6** with $MeSO_2Cl/Et_3N$ led to the formation of 1-(oxazolinyl)-7-(hydroxyamide)-1,7-dicarba-*closo*-dodecaboranes (**10**−**12**) in high yields after 8 h. These incompletely cyclized intermediates were obtained as major products even when the compounds (**4**−**6**) were treated with an excess of $MeSO_2Cl/Et_3N$ reagents for 2 days. We also noted that $BF_3\cdot Et_2O$ and PPh_3/CCl_4[23] were not tolerated during the cyclizations of **4**−**6**. Therefore, we examined the possibility of modifications of these methods with respect to the availability of starting materials, literature knowledge, and ease of synthesis.

By carefully studying the reaction, we discovered that diethylaminosulfur trifluoride (DAST)[37] is an effective reagent for this cyclization process. Bis(hydroxyamide)-*m*-carborane **4** underwent the double cyclization when treated with 3 equiv of DAST to afford [(*S*,*S*)-Carbox-*i*Pr]H (**7**) in a 96% yield. Pincer ligands [(*R*,*R*)-Carbox-Ph]H (**8**) and [(*S*,*S*)-Carbox-Bn]H (**9**) were also synthesized from bis(hydroxyamide)-*m*-carboranes **5** and **6** using the similar procedure in 92% or 94% yields, respectively.

Reaction with Halogens. Introduction of heavy atoms such as iodine and bromine is necessary to confirm the absolute configuration of chiral compounds by X-ray single crystal analysis. Therefore, we performed the reaction of bis(oxazolinyl)-*m*-carboranes (**7** and **9**) with halogens by refluxing carbon tetrachloride in the presence of either ultraviolet radiation (chlorination) or aluminum trichloride (chlorination, bromination, and iodination). Molecular iodine and a Lewis acid catalyst are the reagents most commonly used to achieve B−I formation from the B−H of icosahedral carboranes.[38] However, the halogenation of bis(oxazolinyl)-*m*-carboranes **7** and **9** using the methodology of Andrews et al.[38a] led to the ring-opening of the oxazolines, affording the undesired bis(haloamides) **13** and **14**, respectively (Scheme 2). The type of halogenation depends on the Lewis acid used in the catalysis. Treatment of **7** and **9** with iodine and $AlBr_3$

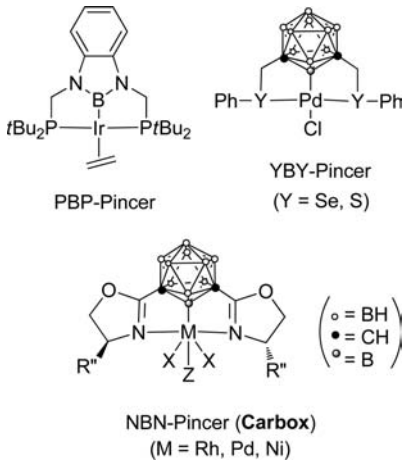
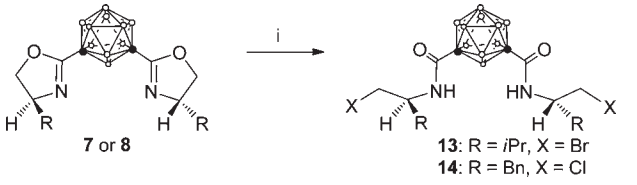


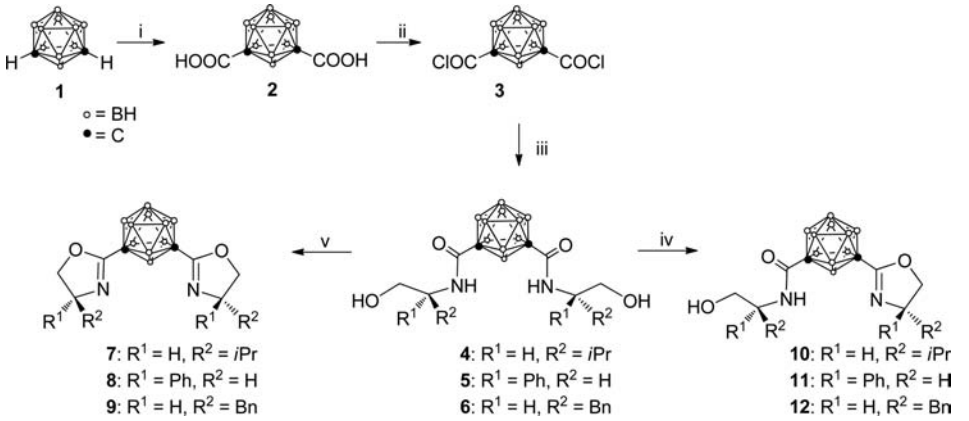
Figure 1. Strucutures of boryl-based pincers.

Scheme 2. Reaction of 7 and 9 with Halogens[a]



[a] (i) CH_2Cl_2, I_2, **7**, $AlBr_3$, reflux, 16.5 h, **13** 98%, or CH_2Cl_2, I_2, **9**, $AlCl_3$, reflux, 16.5 h, **14** 98%.

Scheme 1. Synthesis of Chiral NBN-Pincer Ligands 4−9[a]



[a] (i) *n*-BuLi, ether, CO_2, HCl 95%; (ii) $SOCl_2$, reflux, 24 h, quant.; (iii) amino alcohol, CH_2Cl_2, Et_3N, r.t, 24 h, **4** 98%, **5** 97%, **6** 95%; (iv) CH_2Cl_2, amino alcohol, Et_3N, $MeSO_2Cl$, r.t, 8 h, **10** 72%, **11** 75%, **12** 69%; (v) 3 equiv DAST, CH_2Cl_2, −20 °C, 12 h, **7** 96%, **8** 92%, **9** 94%.

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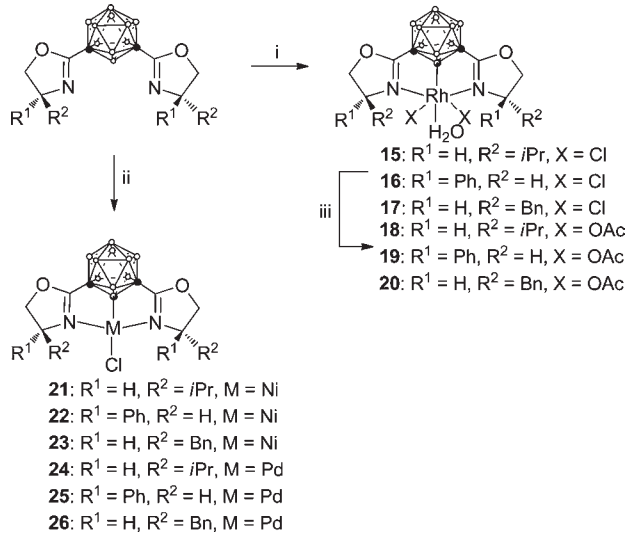
Scheme 3. Synthetic Pathways of NBN-Pincer Complexes[a]



[a] (i) MeOH, $RhCl_3 \cdot 3H_2O$, $NaHCO_3$, H_2O, 60 °C, 6 h, **15**: 79%, **16**: 76%, **17**: 82%; (ii) $Pd(CH_3CN)_4[BF_4]_2$, CH_3CN, reflux, 24 h, then $(n\text{-}Bu)_4NCl$ (2 equiv), **21**: 73%, **22**: 86%, **23**: 82% or $Ni(COD)_2$, CH_3CN, reflux, 24 h, then $(n\text{-}Bu)_4NCl$ (2 equiv), **24**: 76%, **25**: 74%, **26**: 80%; (iii) AgOAc, CH_2CH_2, r.t, 24 h, quant.

or $AlCl_3$ in CH_2Cl_2 gave bis(bromoamide) **13** and bis(chloroamide) **14** in nearly quantitative yields, respectively. Furthermore, the electrophilic halogenations of bis(oxazolinyl)-*m*-carboranes (**7** and **8**) with iodine or LDA/TMEDA, followed by iodine, using the methodology of Harris et al.[39] did not proceed at all. According to the X-ray single crystal analysis of bis(bromoamide) **13**, the absolute configuration was a (*S,S*) isomer, and this result indicates that the current cyclization conditions did not affect the configuration of the starting amino alcohols.

Synthesis of Metal-Carbox Complexes via the *ortho*-Metallative B−H Bond Insertion of Rh(III), Ni(0), and Pd(II). A method similar to that reported by Nishiyama[14c] was used to synthesize Rh(III) pincer complexes of Carbox ligands. Heating a mixture of the pincer ligands (**7**−**9**), $RhCl_3 \cdot 3H_2O$, and $NaHCO_3$ in a cosolvent of methanol/water (10:1) gave the corresponding chloride complexes [(*S,S*)-Carbox-*i*Pr]$RhCl_2 \cdot H_2O$ (**15**, 79%), [(*R,R*)-Carbox-Ph]$RhCl_2 \cdot H_2O$ (**16**, 76%), and [(*S,S*)-Carbox-Bn]$RhCl_2 \cdot H_2O$ (**17**, 82%), respectively (Scheme 3). The chloride complexes could, in turn, be converted to the corresponding acetate complexes **18**−**20** in quantitative yields by treatment with an excess of silver acetate in dichloromethane at room temperature for 24 h.

We next examined the synthesis of nickel complexes, which required a different strategy, as B−Ni derivatives of *m*-carborane are unknown. The reaction of pincer ligands, [(*S,S*)-Carbox-*i*Pr]H, [(*R,R*)-Carbox-Ph]H, and [(*S,S*)-Carbox-Bn]H, with $Ni(COD)_2$ in acetonitrile at reflux temperature resulted in a slow change of the solution color from yellow to orange over 24 h. The treatment of this solution with 2 equiv of $(n\text{-}Bu)_4NCl$ provided the nickel complexes [(*S,S*)-Carbox-*i*Pr]NiCl (**21**), [(*R,R*)-Carbox-Ph]NiCl (**22**), and [(*S,S*)-Carbox-Bn]NiCl (**23**) in 73%, 86%, and 82% yields, respectively.

A similar protocol was employed for the synthesis of palladium complexes. A mixture of the pincer ligands, [(*S,S*)-Carbox-*i*Pr]H, [(*R,R*)-Carbox-Ph]H, and [(*S,S*)-Carbox-Bn]H, and $Pd(CH_3CN)_4[BF_4]_2$ was refluxed in acetonitrile, followed by

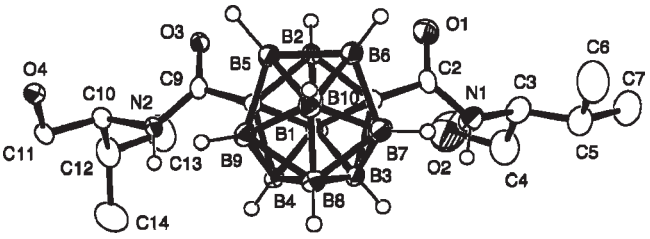


Figure 2. X-ray crystal structure of **4**. Thermal probability ellipsoids are drawn at the 50% probability level (hydrogen atoms are omitted for clarity).

treatment with 2 equiv of $(n\text{-}Bu)_4NCl$, which furnished [(*S,S*)-Carbox-*i*Pr]PdCl (**24**), [(*R,R*)-Carbox-Ph]PdCl (**25**), and [(*S,S*)-Carbox-Bn]PdCl (**26**) in 76%, 74%, and 80% yields, respectively. All resulting complexes were stable and could be stored in air at room temperature for several months without decomposition.

X-ray Structural Analysis. We analyzed the molecular structures of **4**, **7**, **9**, **10**, **13**, and **14** by X-ray crystallography to determine their C_{2v} symmetrical forms (Figures 2−5). Table 1 presents the crystallographic data. Single crystals of compound **4** were grown at room temperature from methanol, and the structure is shown in Figure 2. Compound **4** crystallized in the acentric space group $P2_12_12_1$ retains an *S*-configuration on the α-carbon originated the amino alcohol as a starting material. The *m*-carborane cluster has a slightly distorted icosahedron with typical B−B bond lengths of 1.779(5) Å (average), ranging between 1.767(5) and 1.791(5) Å. The average C−B bond length for **4** was 1.715(5) Å, ranging between 1.698(5) and 1.731(8) Å. The amide carbon C(2) has the longer C−O bond length of 1.267(5) Å and the shorter C−N bond of 1.300(5) Å than that of the other amide carbon (C(9)−O(3) 1.226 Å and C(9)−N(2) 1.341 Å, respectively). The difference arises from an intermolecular hydrogen bond between the carbonyl oxygen of the amide group and the hydroxyl groups of two solvated methanol of which the distances were observed at about 2.76 Å.

Single crystals suitable for X-ray crystallography of pincers **7** and **9** were obtained by slow evaporation from hexane and dichloromethane/hexane solution, respectively. As shown in Figure 3, the carborane clusters were distorted icosahedrons in which the B−B bond lengths (average distance: 1.781(3) Å, range: 1.769(2)−1.795(2) Å) and C−B bond lengths (average distance: 1.726(2) Å, range: 1.701(2)−1.730 (2) Å) were within the expected values. We identified the carbon atoms in the cage by noting the shorter C−B bond lengths relative to the elongated B−B bond distances. The C−N and C−O bond lengths of 2-position carbon on the oxazoline rings in **7** and **9** were unexceptional at about 1.26 and 1.35 Å, respectively.

Single crystals of compound **10** were grown at room temperature from a mixture of dichloromethane/hexane. As shown in Figure 4, compound **10** was also a slightly distorted icosahedron having typical B−B bond lengths (average distance: 1.686(4) Å, range: 1.761(4)−1.795(4) Å). The average C−B bond length for compound **10** was 1.711(4) Å, ranging between 1.694(3) and 1.730(4) Å. The C−N and C−O bond lengths around C(2) were 1.270(4) and 1.349(3) Å, respectively, similar to their of the pincer ligands **7** and **9**.

The crystal structures of **13** and **14** obtained from a mixture of dichloromethane/hexane locate in the acentric space group *P*1 of triclinic system and $P4_32_12$ of tetragonal system, respectively

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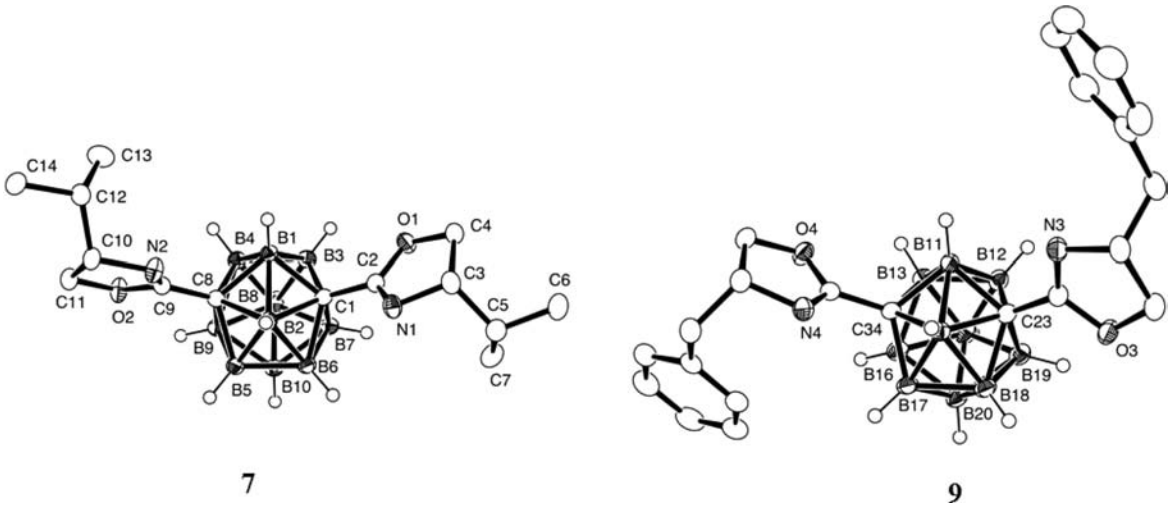

Figure 3. X-ray crystal structures of **7** and **9**. Thermal probability ellipsoids are drawn at the 50% probability level (hydrogen atoms are omitted for clarity).

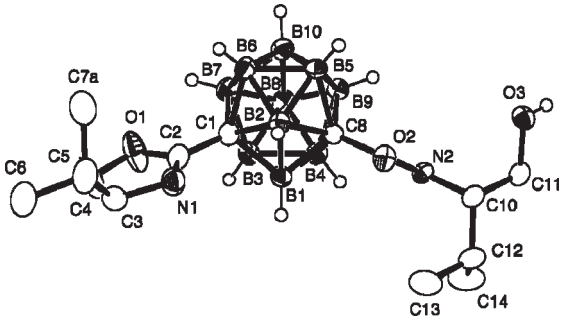

Figure 4. X-ray crystal structure of **10**. Thermal probability ellipsoids are drawn at the 50% probability level (hydrogen atoms are omitted for clarity).

(Table 1). The structures, as shown in Figure 5, confirmed that the oxazoline rings of **7** and **9** were opened and brominated or chlorinated by the presence of $AlBr_3$ or $AlCl_3$ as the reactant, respectively. The α-carbon in **13** including heavier element bromine exhibited a (*S*)-configuration coincident with that of the starting amino alcohol, revealing an evidence of the retention of absolute configuration on the α-carbon under the synthetic condition of pincer ligands. The B−C (1.708(5)∼1.742(5) Å) and B−B bond lengths (1.759(5)∼1.806(5) Å) in **14** did not differ significantly from the corresponding lengths in **13** (B−C, 1.691(3)∼1.734(3); B−B, 1.762(3)∼1.807(4)); hence, the same cage distortions were observed. The average C−Br bond lengths for **13** and the C−Cl bond lengths for **14** were 1.907 Å, ranging between 1.847(4) and 1.964(5) Å, and 1.974(2) Å, ranging between 1.970(2) and 1.978(2), respectively.

Characterization of Carbox-Metal Complexes. Although we tried to confirm the structures of the Carbox-metal complexes by X-ray crystallographic analysis, we did not obtain crystals suitable for X-ray structural analysis. Therefore, we characterized the complexes by spectroscopic analysis. In the ^{1}H NMR spectra of (*S,S*)-Carbox-*i*Pr (**7**), the chemical shifts of the $-CH_2O$ and −CHN groups appeared at 4.26 (2H), 4.06 (2H), and 3.98 (2H) ppm, respectively. In contrast, the chemical shifts of the $-CH_2O$ and −CHN protons in (*S,S*)-PheBox-*i*Pr appeared at 4.09−4.19 (4H) and 4.38−4.48 (2H) ppm,[13] the CHNH proton of **7** shifted at a higher field. The chemical shifts of the $-CH_2O$ and −CHN protons in **8** and **9** were also slightly shifted to a higher field (∼0.2 ppm) than those of (*S,S*)-PheBox-Ph and (*S,S*)-PheBox-Bn, respectively.[14c] The C═N carbon signals of Carbox ligands **7**−**9** also shifted to a higher field (158.29−159.88 ppm) than those of the corresponding PheBox ligands (162.97−163.9 ppm).

The ^{1}H and ^{13}C NMR spectra of the Carbox ligand rhodium complexes, such as [(*S,S*)-Carbox]$RhCl_2 \cdot H_2O$ (**15**−**17**) and [(*S,S*)-Carbox]$Rh(OAc)_2 \cdot H_2O$ (**18**−**20**), displayed a similar profile to that of the metal-free Carbox ligands (**7**−**9**), except for the additional peaks of the OAc, which appeared at 1.69−1.75 ppm in the ^{1}H NMR and at 175.11−175.42 (C═O) and 23.72−23.76 ppm (CH_3) in the ^{13}C NMR for the complexes **18**−**20**. Others have reported that the oxazoline protons ($-CH_2O$ and −CHN groups) of the PheBox ligands shifted to a lower field after complexation with rhodium in the range 0.12−0.39 ppm in ^{1}H NMR and 8.3−9.2 ppm in ^{13}C NMR because of the conformational change of the PheBox ligands by the coordination of the oxazoline nitrogen to the metal. Because the chemical shifts of the Carbox ligands did not change significantly, the conformation of the Carbox ligands might be fixed by the unique structure of the *m*-carborane framework (Figure 2).

The ^{11}B NMR resonances of **4**−**14** exhibited a distinctly different pattern from those of the corresponding metalated pincer complexes **15**−**26** (Figures 6 and 7). Although the chemical shifts of the signals due to the boron atoms coupled with hydrogens basically appeared in the same field among the *m*-carboranes (**4**−**26**), the metal-substituted boron atoms were deshielded and produced the most downfield resonances, a typical feature of a boron−metal bond formation, and similar downfield shifts have been reported by Mirkin and co-workers.[18] The metalation of the Carbox ligands **7**−**9** broke the C_{2v} symmetry of its parent *m*-carborane cage, and we observed a larger number of ^{11}B resonances as compared with the spectra of ligands **7**−**9**. The ^{11}B{^{1}H} spectra of **15**−**26** consisted of four overlapping singlet signals (from approximately −10 to −19 ppm) and an isolated signal at approximately +0.92 ppm. Integration of the area under these signals showed a 9:1 ratio. A broad multiplet of the ^{1}H-coupled ^{11}B NMR spectra of complexes **15**−**26** was observed in the −10 to −19 ppm region of the spectra, but the resonance around +0.92 ppm remained a

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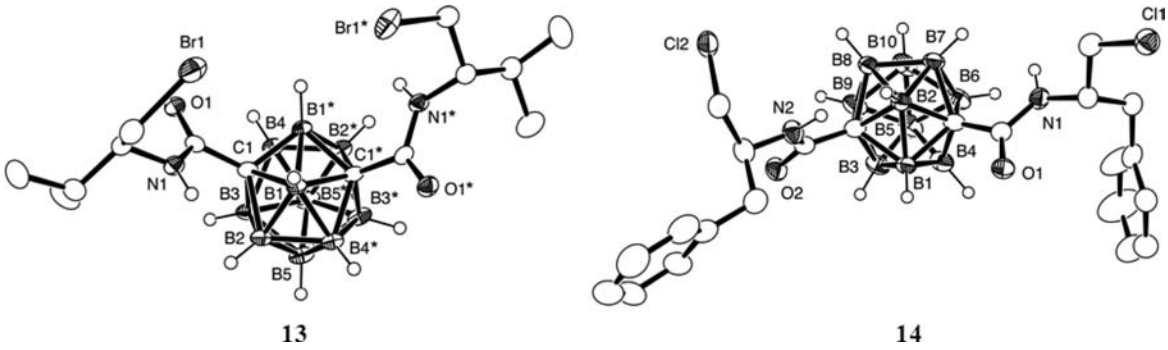

Figure 5. X-ray crystal structures of **13** and **14**. Thermal probability ellipsoids are drawn at the 50% probability level (hydrogen atoms are omitted for clarity).

Table 1. Details of Crystallographic Data Collection for 4, 7, 9, 10, 13, and 14

	4	7	9	10	13	14
formula	$C_{15}H_{38}B_{10}N_2O_5$	$C_{14}H_{30}B_{10}N_2O_2$	$C_{22}H_{30}B_{10}N_2O_2$	$C_{14}H_{32}B_{10}N_2O_3$	$C_{14}H_{32}B_{10}Br_2N_2O_2$	$C_{22}H_{32}B_{10}Cl_2N_2O_2$
Fw	434.57	366.50	462.58	384.52	528.34	535.50
crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic	tetragonal	triclinic
space group	*P*2(1)2(1)2(1)	*P*2(1)2(1)2(1)	*P*2(1)	*C*2	*P*4(3)2(1)2	*P*1
a/Å	6.7826(10)	6.6356(8)	12.2405(10)	33.866(14)	21.6668(17)	9.7591(10)
b/Å	17.136(3)	15.8615(19)	6.6058(5)	6.684(3)	21.6668(17)	10.1277(10)
c/Å	21.403(3)	19.740(2)	31.330(3)	9.784(4)	10.4424(8)	15.0464(15)
α/deg	90.00	90.00	90.00	90.00	90.00	94.2120(10)
β/deg	90.00	90.00	99.5400(10)	92.669(5)	90.00	102.3010(10)
γ/deg	90.00	90.00	90.00	90.00	90.00	94.3040(10)
V/nm^3	2.4876(6)	2.0777(4)	2.4983(3)	2.2124(16)	4.9022(7)	1.4428(3)
Z	4	4	4	4	8	2
D_c/g cm^{-3}	1.118	1.172	1.230	1.154	1.432	1.233
F(000)	896	776	968	816	2128	556
μ/mm^{-1}	0.069	0.067	0.071	0.069	3.321	0.249
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
range (2*θ*) for data collection/deg	1.52−27.48	1.65−27.53	2.64−27.47	2.36−27.33	2.16−26.59	2.29−27.47
GOF	1.155	1.04	0.986	1.025	1.057	1.042
T/K	123	123	123	123	123	123
$R1^a$ ($I > 2\sigma(I)$)	0.0787	0.0398	0.0402	0.0539	0.0259	0.0601
${}_wR_2{}^b$ ($I > 2\sigma(I)$)	0.2159	0.0926	0.0879	0.1472	0.0592	0.1692
$R1^a$ (all data)	0.0900	0.0484	0.0504	0.0630	0.0320	0.0635
${}_wR_2{}^b$ (all data)	0.2239	0.0966	0.0934	0.1537	0.0608	0.1736

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

singlet, consistent with its assignment as the B(2) atom bound to the metals.

The carborane ligands (**7**−**9**) and the metal complexes (**15**−**26**) had characteristic stretching modes that were suitable for study by IR spectroscopy. The vibrational frequencies of the B−H bond (*ν*(B−H)) and the B−B bond (*ν*(B−B)) were not sensitive to the cyclization reactions. The B−H stretching frequencies of **7**−**9** were broad (*ν*(B−H) 2596−2623 cm^{-1}; *ν*(B−B) 1049−1057 cm^{-1}) and within the expected range for related *m*-carborane derivatives, including 1,7-dihydroxycarbonyl-1,7-dicarba-*closo*-dodecaborane reported by Kahl et al.[36] For the pincer complexes **15**−**26**, *ν*(B−H) was observed in the 2622−2625 cm^{-1} region, whereas *ν*(B−B) varied from 1065 to 1052 cm^{-1}. Among the frequencies of the $C_2B_{10}H_{10}$ moiety (*ν*(B−H) 2619−2626 cm^{-1}; *ν*(B−B) 1073−1057 cm^{-1}),[40] we found only slight differences among the compounds, indicating that the substitution of the icosahedron did not perturb the intracluster bonding.

We characterized all synthesized boronated compounds by electrospray ionization mass spectrometry (ESI-MS). The negative-ion ESI-MS of compounds **4**−**12** and **15**−**26** showed only the signal of a singly charged ion, whose mass and typical isotopic pattern of boron isotopes (^{10}B and ^{11}B) suggested a molecular formula at $m/z = [M]^-$ and $[M + Cl]^-$; however, compounds **13** and **14** gave molecular ion peaks corresponding to $[M + Br]^-$ and $[M + I]^-$, respectively. The results of the microanalysis for the Rh(III), Pd(II), and Ni(II) complexes with Carbox ligands (**7**−**9**) were in good agreement with those calculated for the suggested formulas and confirmed the formation of 1:1 (metal:ligand) complexes (for details see the Experimental Section).

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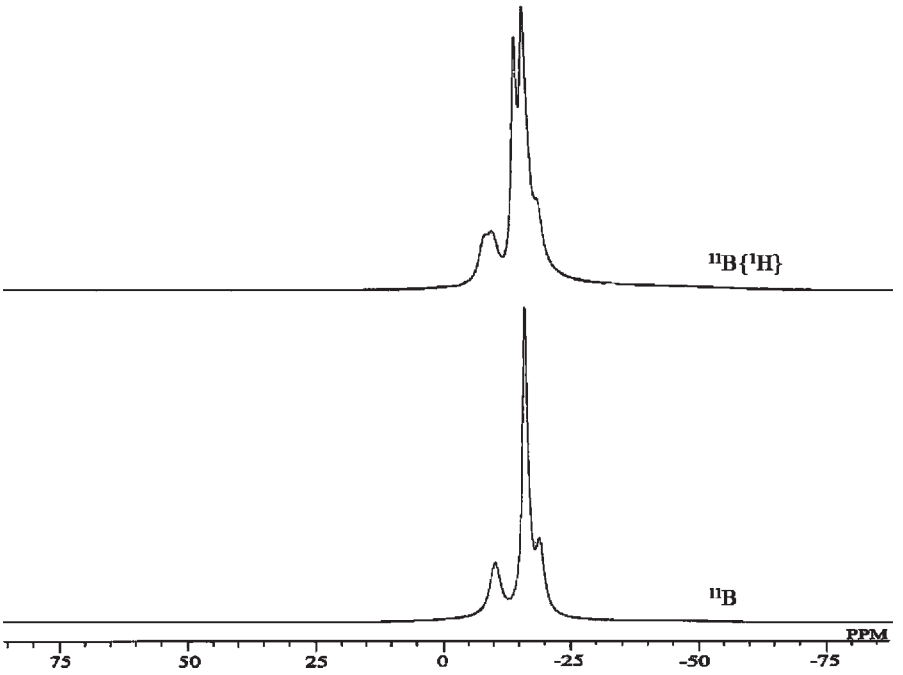

Figure 6. ^{11}B and $^{11}B\{^1H\}$ Spectra of [(*S*,*S*)-Carbox-*i*Pr]H (**7**) in $CDCl_3$.

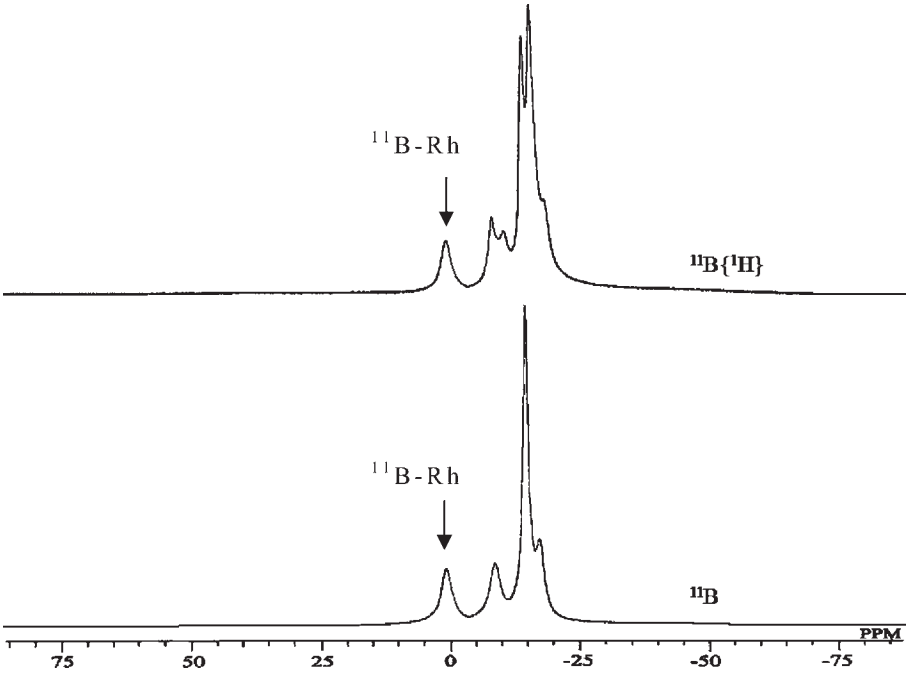

Figure 7. ^{11}B and $^{11}B\{^1H\}$ spectra of [(*S*,*S*)-Carbox-*i*Pr]Rh$(OAc)_2 \cdot H_2O$ (**18**) in $CDCl_3$.

Application to Asymmetric Catalysis. The structural rigidity of the carborane cage and its unique spatial and chemical features might be beneficial in chemical catalysis. To apply NBN-pincer complexes in a more general sense and to find the optimal catalyst for a respective transformation, we were interested in systematic variations of the steric and electronic parameters of the corresponding ligands. Therefore, we demonstrated the following two types of reactions: (i) an asymmetric conjugate reduction of α,β-unsaturated esters and (ii) an asymmetric reductive aldol reaction, using [(*S*,*S*)-Carbox-*i*Pr]Rh$(OAc)_2 \cdot H_2O$ (**18**) as a chiral catalyst.[14c]

(i). Catalytic Asymmetric Conjugate Reduction of α,β-Unsaturated Esters. The enantioselective transfer of hydrogen to prochiral carbon−carbon double bonds is one of the most important catalytic asymmetric processes to date. In this context, the conjugate reduction of α,β-unsaturated carbonyl compounds offers a valuable method for the construction of building blocks with a β-stereogenic center found in many natural products.[41]

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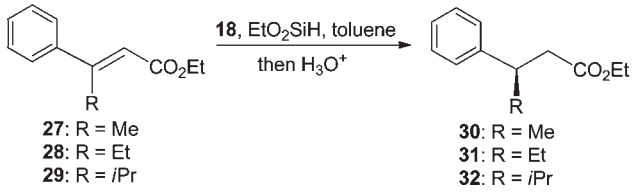
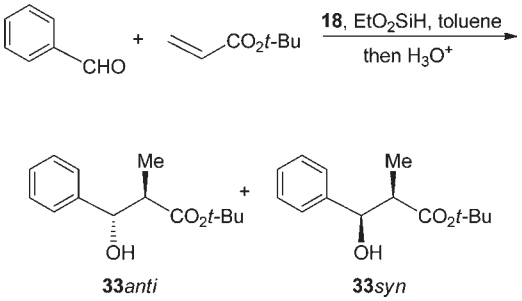
Scheme 4. Asymmetric Conjugate Reduction of α,β-Unsaturated Esters 27−29 with [(*S*,*S*)-Carbox-*i*Pr]Rh(OAc)$_2$·H$_2$O (18) Catalyst



Scheme 5. Asymmetric Reductive Aldol Reaction of *tert*-Butyl Acrylate and Benzaldehyde with [(*S*,*S*)-Carbox-*i*Pr]Rh(OAc)$_2$·H$_2$O (18) Catalyst



There are few catalysts that can reduce carbon−carbon double bonds to generate products with β-stereocenters from carbonyls with high enantiomeric excess (ee). We used [(*S*,*S*)-Carbox-*i*Pr]Rh(OAc)$_2$·H$_2$O (**18**) as a chiral pincer catalyst for the asymmetric conjugate reduction of α,β-unsaturated esters (**27**−**29**). The reaction of **27** with (EtO)$_2$MeSiH proceeded smoothly at 60 °C in the presence of **18** (1 mol %) in toluene, giving the corresponding conjugated reduction products **30** in a 92% yield with 94% ee (Scheme 4).[42−44] When we reduced the amount of the catalyst to 0.5 mol %, a longer reaction time was needed to complete the reaction, but the ee of the product was not affected. Moreover, a lower temperature resulted in substantial decreases in both yield and selectivity. The chloride form **15** was also effective for the asymmetric conjugate reduction, and the corresponding conjugated reduction product **30** was obtained with 93% ee. However, the other Carbox catalysts (**19** and **20**) decreased the ee to 27% and 82%, respectively. A bulky substituent at the β-position of the α,β-unsaturated esters, such as an ethyl (**28**) or an *iso*-propyl (**29**) group, resulted in higher enantioselectivity, and the corresponding reduction products **31** and **32** were obtained in 89% and 96% yields with 97% and 98% ee, respectively. These enantioselectivities are similar to those obtained from the use of Phebox ligands.[14c]

(ii). Catalytic Asymmetric Reductive Aldol Reaction. We also examined the asymmetric reductive aldol reaction of benzaldehyde, *tert*-butyl acrylate, and (EtO)$_2$MeSiH with Carbox-Rh complexes **18**, **19**, and **20** (Scheme 5). The reaction proceeded in the presence of [(*S*,*S*)-Carbox-*i*Pr]Rh(OAc)$_2$·H$_2$O (**18**) (1 mol %) and (EtO)$_2$MeSiH (1.5 equiv) in toluene at 60 °C to give the corresponding reductive aldol product **33**[25] in a 98% yield with a 9:1 ratio of anti:syn. The ee of the major product **33** (*anti*) was 91%. It was reported that the reductive aldol reaction of benzaldehyde, *tert*-butyl acrylate, and (EtO)$_2$MeSiH with Phebox-Rh complex gave **33** with a 87:13 ratio of anti:syn, and the ee of the major product **33** (*anti*) was 83%. 4-NO$_2$-substituted Phebox-Rh complex exhibited higher enantioselectivity (87% ee), and use of 4-MeO-substituted Phebox-Rh complex decreased the enantioselectivity to 77%. These results suggested that electron deficient Phebox ligands were preferable in the catalytic asymmetric reductive aldol reaction.[14a] In this regard, the current Carbox-Rh complex resulted in the production of **33** (*anti*) with higher enentioselectivity presumably because of the electron deficient property of an icosahedral dicarba-*closo*-dodecaborane framework.

CONCLUSIONS

We have succeeded in synthesizing Carbox ligands **7**−**9** as the first chiral NBN pincer ligands. The combination of bis(hydroxyamides) and 3 equiv of DAST is a key step for cyclization to form oxazoline rings in excellent yields. We clarified the structures of the Carbox ligands (**7** and **9**) as well as the intermediates (**4** and **10**) by X-ray analysis. The electrophilic halogenation of the Carbox pincer ligands with iodine and a catalytic amount of Lewis acid led to the ring-opening of the oxazolines and afforded bis(haloamides) (**13** and **14**). The Carbox pincer complexes of rhodium(III), nickel(II), and palladium(II) were synthesized by the oxidative addition of RhCl$_3$·3H$_2$O, Ni(COD)$_2$, and Pd(CH$_3$CN)$_4$[BF$_4$]$_2$ to the Carbox pincer ligands (**7**−**9**), respectively. The Carbox-Rh complexes (**15**−**17**) were transformed into their acetate complexes (**18**−**20**) by acetate abstraction using AgOAc. These rhodium complexes **18**−**20** were examined as chiral catalysts for the asymmetric conjugate reduction of α,β-unsaturated esters and the reductive aldol reaction. Among these catalysts, [(*S*,*S*)-Carbox-*i*Pr]Rh(OAc)$_2$·H$_2$O (**18**) showed the highest enantioselective catalytic ability for both asymmetric conjugate reduction and reductive aldol reaction. The versatile coordination ability of the Carbox structures to various transition metals and their rigidity as coplanar NBN-tridentate ligands make them an excellent chiral induction environment for the transition metals. We previously found that the electron-deficient feature of carboranes is effective in a certain catalytic reaction;[45] therefore, we believe that the chiral Carbox ligands have a great potential for development of transition metal-catalyzed asymmetric synthesis.

EXPERIMENTAL SECTION

Materials and Methods. Most chemicals were of analytical grade and used without further purification. The substrates **2**, **28**, and **29** were prepared according to a previously reported literature procedure.[24,31] ^{1}H NMR and ^{13}C NMR spectra were measured on a JEOL JNM-AL 300 (300 MHz) and VARIAN UNITY−INOVA 400 and 500 (400 and 500 MHz) spectrometers. Chemical shifts of ^{1}H NMR and ^{13}C NMR were expressed in parts per million (ppm, δ units), and coupling constant (*J*) values were expressed in units of hertz (Hz). ^{11}B NMR spectra were recorded on a JEOL JNM−AL 300 spectrometer (96.3 MHz), and the chemical shifts were reported in δ units relative to external BF$_3$·Et$_2$O in CDCl$_3$. IR (cm^{-1}) spectra were determined as KBr disk on a Shimadzu FTIR−8600PC spectrometer. Electron spray ionization (ESI) mass spectra were recorded on a Shimadzu LCMS−2010 eV spectrometer or Bruker Daltonics micro TOF−15 focus. Elemental analyses were performed by a CE instrument EA1110 CHNS−O automatic elemental analyzer. All compounds gave elemental analysis within ±0.4% of the theoretical values. Analytical thin layer chromatography (TLC) was performed

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on a glass plates of silica gel 60 GF_{254} (Merck). Visualization was accompanied by UV light (254 nm), I_2, $KMnO_4$, or $PdCl_2$. Column chromatography was conducted on silica gel (Merck Kieselgel 70−230 mesh).

General Synthesis of NBN-Pincer Ligands (4−6). *m*-Carborane dicarboxylic acid (**2**) (1.0 g, 4.3 mmol) and $SOCl_2$ (50 mL) were placed under nitrogen atmosphere into a three neck 100 mL round-bottom flask equipped with a condenser, and the mixture was refluxed for 24 h. Excess $SOCl_2$ was then removed under reduced pressure to give the diacid chloride (**3**) as a colorless oil in quantitative yield. A solution of the acid dichloride (3) (1.15 g, 4.27 mmol) in dichloromethane (20 mL) was slowly added via cannula to a solution of amino alcohol (9.4 mmol) in dichloromethane (20 mL) cooled to 0 °C under nitrogen. Then a solution of triethylamine (4.5 mL, 3.24 g, 32.0 mmol) in dichloromethane (20 mL) was added slowly, and the mixture was stirred at room temperature for 24 h. Formation of the intermediate diamide/dialcohol was monitored by TLC. After completion, the mixture was washed with NH_4Cl and dried with sodium sulfate. The solution was concentrated under reduced pressure to give the corresponding crude bis(amide), which was purified by column chromatography (EtOAc:hexane, 2:1), affording a white solid of analytically pure bis(amide)-*m*-carboranes.

*(S,S)-1,7-Bis(1-hydroxy-3-methylbutanamide-2-yl)-1,7-dicarba-closo-dodecaborane (**4**).* This compound was prepared from L-valinol (969 mg, 9.4 mmol) to give **4** (1.68 g, 98%) as a white solid. A sample suitable for X-ray analysis was prepared by slow evaporation of a methanol solution in air to give colorless needle crystals. $[\alpha]^{25}_D = -3.43$ (*c* 1 in $CHCl_3$), R_f = 0.55, Mp: 120−122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.07 (d, J_{CH} = 10.0 Hz, 2H, NH), 3.75−1.52 (bm, 10H, B−H), 3.65 (m, 4H, CH_2OH), 3.61 (m, 2H, CHNH), 1.87 (hept, 2H, *i*Pr−CH), 0.95, 0.87 (dd, 12H, *J* = 8.8 Hz, *J* = 10.0 Hz, *i*Pr−CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.37 (2C, CONH), 72.4 (2C, CHNH), 71.52 (2C, CH_2OH), 66.75 (2C, cluster−C), 32.11 (2C, *i*Pr−CH), 18.17, 17.29 (4C, *i*Pr−CH_3). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ −9.84 to −18.56 (bm, 10B). IR (KBr, cm^{-1}): ν(OH) 3413 (S), ν(NH) 3286 (S), ν(CH) 2962 (S), 2896 (W), ν(BH) 2596 (S), ν(C═O) 1658 (S), ν(NH) 1531 (S), ν(CH) 1470 (m), ν(C−O) 1288 (m), ν(B−B) 1056 (m), ν(CH) 829 (m), 732 (m). MS (ESI, negative): *m*/*z* 402.4 (M^-). Elemental analysis calcd for $C_{14}H_{34}B_{10}N_2O_4$: C, 51.05; H, 6.43; N, 5.95%. Found: C, 50.92; H, 6.31; N, 5.86%.

*(R,R)-1,7-Bis(1-hydroxy-2-phenylacetamide-2-yl)-1,7-dicarba-closo-dodecaborane (**5**).* This compound was prepared from D-phenylglycinol (1.28 g, 9.4 mmol) to give **5** (1.95 g, 97%) as a white solid. $[\alpha]^{25}_D$ = +2.68 (*c* 1.04 in $CHCl_3$), R_f = 0.59, Mp: 71−73 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38−7.18 (m, 10H, aromatic−CH), 6.67 (d, *J* = 6.4 Hz, 2H, NH), 3.82−1.55 (bm, 10H, B−H), 4.9 (m, 2H, CHNH), 3.84 (m, 4H, CH_2OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.68 (2C, CONH), 137.93, 128.66, 127.77, 126.05 (10C, aromatic CH), 72.82 (2C, CHNH), 65.68 (2C, cluster−C), 56.14 (2C, CH_2OH). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ −9.92 to −18.54 (bm, 10B). IR (KBr, cm^{-1}): ν(OH) 3417 (S), ν(NH) 3400 (S), ν(CH) 2935 (W), 3031 (W), ν(BH) 2603 (S), ν(C═O) 1678 (S), ν(NH) 1556 (S), ν(CH) 1454 (m), ν(C−O) 1280 (m), ν(B−B) 1068 (S), ν(CH) 837 (m), 759 (m). MS (ESI, negative): *m*/*z* 472.4 (M^-). Elemental analysis calcd for $C_{20}H_{30}B_{10}N_2O_4$: C, 51.05; H, 6.43; N, 5.95%. Found: C, 50.98; H, 6.39; N, 5.87%.

*(S,S)-1,7-Bis(1-hydroxy-3-phenylpropanamide-2-yl)-1,7-dicarba-closo-dodecaborane (**6**).* This compound was prepared from L-phenylalaninol (1.42 g, 9.4 mmol) to give **6** (2.02 g, 95%) as a white solid. $[\alpha]^{25}_D = -2.48$ (*c* 1.3 in $CHCl_3$), R_f = 0.53, Mp: 72−74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.14 (m, 10H, aromatic−CH), 6.13 (d, *J* = 7.6 Hz, 2H, NH), 4.12 (m, 2H, CHNH), 3.75−1.62 (bm, 10H, B−H), 3.6 (m, 4H, CH_2OH), 2.86 (m, 4H, Bn−CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.34 (2C, CONH), 136.48, 129.43, 128.46, 126.64 (10C, aromatic CH), 73.02 (2C, CHNH), 67.56 (2C, cluster−C), 54.63 (2C, CH_2OH), 40.5 (2C, Bn−CH_2). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ −9.84 to −18.38 (bm, 10B). IR (KBr, cm^{-1}): ν(OH) 3421 (S), ν(NH) 3294 (S), ν(CH) 3058 (m), 3024 (m), ν(BH) 2607 (S), ν(C═O) 1654 (S), ν(NH) 1539 (S), ν(CH) 1473 (m), ν(C−O) 1288 (m), ν(B−B) 1041 (S), ν(CH) 835 (m), 744 (m). MS (ESI, negative): *m*/*z* 534.4 $(M+Cl)^-$. Elemental analysis calcd for $C_{22}H_{34}B_{10}N_2O_4$: C, 52.99; H, 6.87; N, 5.62%. Found: C, 52.92; H, 6.85; N, 5.59%.

General Synthesis of Carboxes (7−9). DAST (396 μL, 3.0 mmol) was slowly added to a solution of bis(hydroxyamide)-*m*-carborane (1.0 mmol) in CH_2Cl_2 (5 mL) at −20 °C under nitrogen atmosphere. After 12 h stirring at −20 °C, ammonium hydroxide solution (1 mL) was added slowly. Subsequently the cooling bath was removed and water (20 mL) was added. When the reaction mixture had reached room temperature, two layers were separated and the aqueous layers were extracted with CH_2Cl_2 (20 mL × 2). The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/hexane, 1:3) to give bis(oxazolines)-*m*-carboranes as analytically pure white solids.

*[(S,S)-Carbox-iPr]H (**7**).* This compound was prepared from **4** (402 mg, 1.0 mmol) to give **7** (353 mg, 96%) as a white solid. Colorless needle crystals suitable for X-ray analysis were obtained by recrystallization from a hexane solution. $[\alpha]^{25}_D = -1.14$ (*c* 1.0 in $CHCl_3$), R_f = 0.38, Mp: 43−45 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.26 (dd, *J* = 9.2, 8.4 Hz, 2H, oxazoline−CH), 4.06 (t, *J* = 8.4 Hz, 2H, oxazoline−CH_2), 3.98 (m, 2H, oxazoline−CH_2), 3.25−1.22 (bm, 10H, B−H), 1.79 (m, 2H, *i*Pr−CH), 0.88 (d, *J* = 6.8 Hz, 6H, *i*Pr−CH_3), 0.82 (d, *J* = 6.8 Hz, 6H, *i*Pr−CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.29 (2C, C═N), 72.4 (2C, CHN), 71.52 (2C, CH_2−O), 66.87 (2C, cluster−C), 32.1 (2C, *i*Pr−CH), 18.1, 17.32 (4C, *i*Pr−CH_3). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ −9.33 to −19.37 (bm, 10B). IR (KBr, cm^{-1}): ν(CH) 2962 (m), 2927 (m), ν(BH) 2623 (S), ν(C═N) 1666 (S), ν(CH) 1465 (m), ν(C−O) 1284 (m), ν(C−N) 1107 (m), ν(B−B) 1055 (S), ν(CH) 806 (m), 736 (m). MS (ESI, negative): *m*/*z* 368.3 (M^-). Elemental analysis calcd for $C_{14}H_{30}B_{10}N_2O_2$: C, 45.88; H, 8.25; N, 7.64%. Found: C, 45.72; H, 8.19; N, 7.58%.

*[(R,R)-Carbox-Ph]H (**8**).* This compound was prepared from **5** (472 mg, 1.0 mmol) to give **8** (399 mg, 92%) as a white solid. $[\alpha]^{25}_D$ = +1.64 (*c* 1.04 in $CHCl_3$), R_f = 0.38, Mp: 118−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.12 (m, 10H, aromatic−CH), 5.19 (dd, *J* = 10.4, 8.0 Hz, 2H, oxazoline−CH), 4.65 (dd, *J* = 10.4, 8.4 Hz, 2H, oxazoline−CH_2), 4.14 (t, *J* = 8.4 Hz, 2H, oxazoline−CH_2), 3.95−1.56 (bm, 10H, B−H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.88 (2C, C═N), 140.99, 128.77, 127.84, 126.26 (10C, aromatic−CH), 76.67 (2C, CHN), 70.1 (2C, CH_2−O), 66.66 (2C, cluster−C). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ −10.51 to −19.97 (bm, 10B). IR (KBr, cm^{-1}): ν(CH) 2973 (m), 2932 (m), ν(BH) 2620 (S), ν(C═N) 1657 (S), ν(CH) 1486 (m), ν(C−O) 1282 (m), ν(C−N) 1115 (m), ν(B−B) 1052 (S), ν(CH) 968 (m), 745 (m). MS (ESI, negative): *m*/*z* 436.2 (M^-). Elemental analysis calcd for $C_{20}H_{26}B_{10}N_2O_2$: C, 55.28; H, 6.03; N, 6.45%. Found: C, 55.21; H, 5.98; N, 6.39%.

*[(S,S)-Carbox-Bn]H (**9**).* This compound was prepared from **6** (499 mg, 1.0 mmol) to give **9** (434 mg, 94%) as a white solid. A sample suitable for X-ray analysis was prepared by slow evaporation of a mixture of dichloromethane/hexane solution in air to give colorless needle crystals. $[\alpha]^{25}_D = -2.85$ (*c* 1.1 in $CHCl_3$), R_f = 0.42, Mp: 108−110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.13 (m, 10H, aromatic−CH), 4.40 (m, 2H, oxazoline−CH), 4.20 (dd, *J* = 9.6, 8.8 Hz, 2H, oxazoline−CH_2), 4.03 (dd, *J* = 8.8, 6.8 Hz, 2H, oxazoline−CH_2), 3.65−1.62 (bm, 10H, B−H), 2.98 (dd, *J* = 14.0, 4.8 Hz, 2H, Bn−CH_2), 2.70 (dd, *J* = 14.0, 8.0 Hz, 2H, Bn−CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.34 (2C, C═N), 136.48, 129.43, 128.46, 126.64 (10C, aromatic−CH), 73.02 (2C, CHN), 67.56 (2C, cluster−C), 54.62 (2C,

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CH_2-O), 40.5 (2C, Bn$-CH_2$). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ −9.76 to −20.03 (bm, 10B). IR (KBr, cm^{-1}): ν(CH) 2986 (m), 2908 (m), ν(BH) 2619 (S), ν(C=N) 1658 (S), ν(CH) 1492 (m), ν(C−O) 1261 (m), ν(C−N) 1114 (m), ν(B−B) 1055 (S), ν(CH) 950 (m), 748 (m). MS (ESI, negative): m/z 464.4 $(M)^-$. Elemental analysis calcd for $C_{22}H_{30}B_{10}N_2O_2$: C, 57.12; H, 6.54; N, 6.06%. Found: C, 57.09; H, 6.51; N, 6.02%.

General Synthesis of 10−12. A solution of **3** (1.15 g, 4.27 mmol) in dichloromethane (20 mL) was slowly added via cannula to a solution of amino alcohols (9.39 mmol) and triethylamine (4.5 mL, 3.24 g, 32.0 mmol) in dichloromethane (40 mL) at 0 °C. The mixture was stirred at room temperature for 24 h. Formation of the intermediate diamide/dialcohol was monitored by TLC. Then, methanesulfonyl chloride (1.07 g, 9.39 mmol) was added at 0 °C, and the mixture was stirred at room temperature for 8 h. Formation of the product (**10−12**) was monitored by TLC. At 0 °C, aqueous potassium carbonate (1 N, ca. 30 mL) was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with saturated brine, dried over magnesium sulfate, and concentrated. The crude product was purified by column chromatography using EtOAc:hexane (1:1) as eluent.

*(S,S)-1-(4-Isopropyl-4,5-dihydrooxazol-2-yl)-7-(1-hydroxy-3-methylbutanamide-2-yl)-1,7-dicarba-closo-dodecaborane (**10**).* This compound was prepared from L-valinol (969 mg, 9.4 mmol) to give **10** (1.18 g, 72%) as a white solid. Colorless needle crystals suitable for X-ray analysis were obtained by recrystallization from a dichloromethane/hexane solution. $[\alpha]^{25}_D$ = +1.08 (*c* 1.2 in $CHCl_3$), R_f = 0.47, Mp: 100−102 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 6.16 (d, *J* = 8.4 Hz, 1H, NH), 4.27 (t, *J* = 9.2 Hz, 1H, oxazoline−CH), 4.08 (t, *J* = 7.8 Hz, 2H, oxazoline−CH_2), 3.99 (m, 1H, CHNH), 3.62 (m, 2H, CH_2OH), 3.25−1.22 (bm, 10H, B−H), 1.87 (m, 1H, *i*Pr−CH), 1.78 (m, 1H, *i*Pr−CH), 0.93 (d, *J* = 7.2 Hz, 3H, *i*Pr−CH_3), 0.88 (d, *J* = 6.8 Hz, 3H, *i*Pr−CH_3), 0.87 (d, *J* = 6.8 Hz, 3H, *i*Pr−CH_3), 0.83 (d, *J* = 7.2 Hz, 3H, *i*Pr−CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.15 (1C, CONH), 158.37 (1C, C=N), 75.19 (1C, cluster−C), 72.31 (1C, CHN), 71.59 (1C, CH_2-O), 67.04 (1C, cluster−C), 62.35 (1C, CH_2-O), 57.85 (1C, CHN), 32.06, 28.92 (2C, *i*Pr−CH), 19.43, 18.5, 18.05, 17.26 (4C, *i*Pr−CH_3). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ −10.75 to −18.54 (bm, 10B). IR (KBr, cm^{-1}): ν(OH) 3417, ν(NH) 3282, ν(CH) 2962 (S), 2931 (m), ν(BH) 2600 (S), ν(C=N) 1665 (S), ν(C=N) 1625 (S), ν(CH) 1469 (m), ν(C−O) 1288 (m), ν(C−N) 11026 (m), ν(B−B) 1052 (S), ν(CH) 960 (m), 825(m), 759 (m). MS (ESI, negative): m/z 384.4 $(M)^-$. Elemental analysis calcd for $C_{14}H_{32}B_{10}N_2O_3$: C, 43.73; H, 8.39; N, 7.29%. Found: C, 43.62; H, 8.25; N, 7.05%.

*(R,R)-1-(4-phenyl-4,5-dihydrooxazol-2-yl)-7-(1-hydroxy-2-phenylacetamide-2-yl)-1,7-dicarba-closo-dodecaborane (**11**).* This compound was prepared from D-phenylglycinol (1.28 g, 9.4 mmol) to give **11** (1.45 g, 75%) as a white solid. $[\alpha]^{25}_D$ = +3.15 (*c* 1.0 in $CHCl_3$), R_f = 0.5, Mp: 85−87 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.32−7.11 (m, 10H, aromatic−CH), 6.71 (d, *J* = 5.0 Hz, 1H, NH), 5.19 (t, *J* = 10.0 Hz, 1H), 4.92 (m, 1H), 4.65 (t, *J* = 13.0 Hz, 1H), 4.17 (t, *J* = 11.5 Hz, 1H), 3.84 (m, 2H), 3.75−1.52 (bm, 10H, B−H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.89 (1C, CONH), 158.06 (1C, C=N), 140.99, 137.94, 128.78, 127.84, 126.27 (10C, aromatic−CH), 76.56(1C, CHN), 75.83 (1C, cluster−CHN), 70.13 (1C, CH_2O), 66.66 (2C, cluster−C), 56.32 (1C, CH_2-O). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ −10.58 to −18.12 (bm, 10B). IR (KBr, cm^{-1}): ν(OH) 3421, ν(NH) 3288, ν(CH) 2965 (S), 2945 (m), ν(BH) 2612 (S), ν(C=N) 1667 (S), ν(C=N) 1631 (S), ν(CH) 1471 (m), ν(C−O) 1287 (m), ν(C−N) 11025 (m), ν(B−B) 1054 (S), ν(CH) 827(m), 747 (m). MS (ESI, negative): m/z 452.5 $(M)^-$. Elemental analysis calcd for $C_{20}H_{28}B_{10}N_2O_3$: C, 53.08; H, 6.24; N, 6.19%. Found: C, 52.91; H, 6.05; N, 6.01%.

*(S,S)-1-(4-Benzyl-4,5-dihydrooxazol-2-yl)-7-(1-hydroxy-3-phenylpropanamide-2-yl)-1,7-dicarba-closo-dodecaborane (**12**).* This compound was prepared from L-phenylalaninol (1.42 g, 9.4 mmol) to give **12** (1.41 g, 69%) as a white solid. $[\alpha]^{25}_D$ = −1.95 (*c* 1.0 in $CHCl_3$), R_f = 0.53, Mp: 103−105 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.31−7.13 (m, 10H, aromatic−CH), 6.13 (d, *J* = 9.5 Hz, 1H, NH), 4.41 (m, 1H, oxazoline−CH), 4.20 (t, *J* = 12 Hz, 2H, oxazoline−CH_2), 4.05 (m, 1H, CHNH), 3.93 (m, 2H, CH_2-OH), 3.75−1.59 (bm, 10H, B−H), 3.58 (m, 2H, CH_2-OH), 3.0 (m, 2H, Bn−CH_2), 2.71 (m, 2H, Bn−CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.34 (1C, CONH), 157.62 (1C, C=N), 139.76, 136.48, 129.62, 128.5, 126.68 (10C, aromatic−CH), 73.03 (2C, CHN), 67.59 (2C, cluster−C), 54.66 (2C, CH_2-O), 40.51 (2C, Bn−CH_2). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ −10.55 to −18.72 (bm, 10B). IR (KBr, cm^{-1}): ν(OH) 3434, ν(NH) 3291, ν(CH) 2961 (S), 2935 (m), ν(BH) 2615 (S), ν(C=N) 1667 (S), ν(C=N) 1629 (S), ν(CH) 1469 (m), ν(C−O) 1287 (m), ν(C−N) 11025 (m), ν(B−B) 1054 (S), ν(CH) 968 (m), 827(m), 752 (m). MS (ESI, negative): m/z 480.3 $(M)^-$. Elemental analysis calcd for $C_{22}H_{32}B_{10}N_2O_3$: C, 54.98; H, 6.71; N, 5.83%. Found: C, 54.83; H, 6.59; N, 5.72%.

*Synthesis of (S,S)-1,7-Bis(1-bromo-3-methylbutanamide-2-yl)-1,7-dicarba-closo-dodecaborane (**13**).* A mixture of **7** (500 mg, 1.36 mmol), iodine (344 mg, 2.72 mmol), and $AlBr_3$ (100 mg, 0.37 mmol) in 10 mL of dry CH_2Cl_2 was refluxed for 16.5 h under nitrogen. The reaction mixture was poured into 100 mL of ice-cold distilled water, and the organic phase was separated from the mixture. The aqueous layer was then extracted with diethyl ether (20 mL). The combined organic phase was washed with dilute $Na_2S_2O_3$ solution followed by water and dried over $MgSO_4$. After removal of the solvent, the residue was purified by recrystallization from hexane to yield **13** (703 mg, 98%) as colorless needle crystals. $[\alpha]^{25}_D$ = −63.4 (*c* 1.06 in $CHCl_3$), Mp: 138−140 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 5.89 (d, *J* = 8.8 Hz, 2H, NH), 3.75−1.58 (bm, 10H, B−H), 3.66 (m, 2H, CHNH), 3.45 (m, 2H, CH_2Br), 1.81 (m, 2H, *i*Pr−CH), 0.88 (d, 6H, *J* = 6.8 Hz, *i*Pr−CH_3), 0.83 (d, 6H, *J* = 6.8 Hz, *i*Pr−CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.73 (2C, CONH), 75.05 (1C, cluster−C), 55.91 (2C, CHNH), 55.75 (1C, cluster−C), 35.5 (2C, CH_2Br), 30.41 (2C, *i*Pr−CH), 19.08, 18.52 (4C, *i*Pr−CH_3). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ −11.29 to −19.12 (bm, 10B). IR (KBr, cm^{-1}): ν(NH) 3344 (S), ν(CH) 2966 (m), 2873 (W), ν(BH) 2605 (S), ν(C=O) 1670 (S), ν(NH) 1535 (S), ν(CH) 1470 (m), ν(C−O) 1296 (m), ν(B−B) 1060 (m), ν(CH) 745 (m). MS (ESI, negative): m/z 608.1 $(M+Br)^-$. Elemental analysis calcd for $C_{14}H_{32}B_{10}Br_2N_2O_2$: C, 31.83; H, 6.1; N, 5.3%. Found: C, 31.8; H, 6.07; N, 5.28%.

*(S,S)-1,7-Bis(1-chloro-3-phenylpropanamide-2-yl)-1,7-dicarba-closo-dodecaborane (**14**).* This compound was prepared from **9** (500 mg, 1.08 mmol), I_2 (274 mg, 2.16 mmol), and $AlCl_3$ (100 mg, 0.75 mmol) by the procedure described for **13** to yield **14** (567 mg, 98%) as colorless needle crystals. $[\alpha]^{25}_D$ = −47.4 (*c* 1.03 in $CHCl_3$), Mp: 147−149 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34−7.16 (m, 10H, aromatic−CH), 6.0 (d, *J* = 8.0 Hz, 2H, NH), 4.3 (m, 2H, CHNH), 3.85−1.61 (bm, 10H, B−H), 3.61 (dd, *J* = 11.6, 4.0 Hz, 2H, CH_2Cl), 3.48 (dd, *J* = 11.6, 4.0 Hz, 2H, CH_2Cl), 2.89 (d, *J* = 7.6 Hz, 4H, Bn−CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.14 (2C, CONH), 135.89, 129.13, 129.1, 128.87 (10C, aromatic CH), 74.83 (1C, cluster−C), 52.11 (2C, CHNH), 51.22 (1C, cluster−C), 45.81 (2C, Bn−CH_2), 37.06 (2C, CH_2Cl). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ −11.29 to −19.12 (bm, 10B). IR (KBr, cm^{-1}): ν(NH) 3348 (S), ν(CH) 3062 (W), 3028 (W), ν(BH) 2619 (S), ν(C=O) 1666 (S), ν(NH) 1523 (S), ν(CH) 1472 (m), ν(C−O) 1303 (m), ν(B−B) 1087 (S), ν(CH) 767 (m), 740 (m). MS (ESI, negative): m/z 662.3 $(M+I)^-$. Elemental analysis calcd for $C_{22}H_{32}B_{10}Cl_2N_2O_2$: C, 49.34; H, 6.02; N, 5.23%. Found: C, 49.29; H, 5.99; N, 5.21%.

*Synthesis of [(S,S)-Carbox-iPr]RhCl$_2$·H$_2$O (**15**).* A mixture of $RhCl_3 \cdot 3H_2O$ (289 mg, 1.1 mmol), **7** (368 mg, 1.0 mmol), and sodium bicarbonate (84 mg, 1.0 mmol) were placed in a 30 mL flask. After addition of methanol (10 mL) and water (1 mL), the mixture was heated at 60 °C for 5 h. The concentrated residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1:1) as eluent

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to give **15** in 79% yield (440 mg, 0.79 mmol) as a yellow solid. R_f = 0.34, Mp: 252−254 °C (decomp). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.29 (m, 2H, oxazoline−CH), 4.1 (t, J = 9 Hz, 2H, oxazoline−CH_2), 3.99 (m, 2H, oxazoline−CH_2), 3.73−1.52 (bm, 9H, B−H), 3.46 (bs, 2H, H_2O), 1.81 (m, 2H, *i*Pr−CH), 0.88 (d, J = 5.5 Hz, 6H, *i*Pr−CH_3), 0.83 (d, J = 8.5 Hz, 6H, *i*Pr−CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.21 (2C, C═N), 74.00 (2C, CHN), 71.80 (2C, CH_2−O), 67.57 (2C, cluster−C), 33.24 (2C, *i*Pr−CH), 19.96, 19.09 (2C, *i*Pr−CH_3). ^{11}B-{^{1}H} NMR (96.3 MHz; $CDCl_3$): δ 0.77 (s, 1B), −9.56 to −18.61 (bm, 9B). IR (KBr, cm^{-1}): ν(H_2O) 3421 (m), ν(CH) 3031 (m), 2927 (m), ν(BH) 2607 (S), ν(C═N) 1624 (S), ν(CH) 1470 (m), ν(C−O) 1288 (m), ν(C−N) 1105 (m), ν(B−B) 1052 (S), ν(CH) 806 (m), 736 (m). MS (ESI, negative): m/z 592.8 (M+Cl)$^-$. Elemental analysis calcd for $C_{14}H_{31}B_{10}Cl_2N_2O_3Rh$: C, 30.17; H, 5.61; N, 5.03%. Found: C, 30.04; H, 5.52; N, 4.93%.

[(R,R)-Carbox-Ph]RhCl$_2$·H$_2$O (***16***). This compound was prepared from **8** (434 mg, 1.0 mmol) by the procedure described for **15** to give **16** in 76% yield (475 mg, 0.76 mmol) as a yellow solid. R_f = 0.34, Mp: 240−242 °C (decomp). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29−7.14 (m, 10H, aromatic−CH), 5.26 (dd, J = 12.0, 10.2 Hz, 2H, oxazoline−CH), 4.69 (dd, J = 15.0, 11.5 Hz, 2H, oxazoline−CH_2), 4.18 (dd, J = 16, 12.6 Hz, 2H, oxazoline−CH_2), 3.79−1.58 (bm, 9H, B−H), 3.58 (bs, 2H, H_2O), ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.67 (2C, C═N), 141.02, 129.68, 129.03, 126.08 (10C, aromatic CH), 76.68 (2C, CHN), 70.13 (2C, CH_2−O), 66.32 (2C, cluster−C). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ 0.82 (s, 1B), −9.65 to −19.35 (bm, 9B). IR (KBr, cm^{-1}): ν(H_2O) 3421 (m), ν(CH) 2972 (m), 2935 (m), ν(BH) 2624 (S), ν(C═N) 1658 (S), ν(CH) 1485 (m), ν(C−O) 1288 (m), ν(C−N) 1112 (m), ν(B−B) 1049 (S), ν(CH) 967 (m), 745 (m). MS (ESI, negative): m/z 660.8 (M+Cl)$^-$. Elemental analysis calcd for $C_{20}H_{27}B_{10}Cl_2N_2O_3Rh$: C, 38.41; H, 4.35; N, 4.48%. Found: C, 38.32; H, 4.27; N, 4.33%.

[(S,S)-Carbox-Bn]RhCl$_2$·H$_2$O (***17***). A procedure analogous to the synthesis of **15** was employed using **9** (464 mg, 1.0 mmol) to give **17** as a yellow solid in 82% yield (553 mg, 0.82 mmol). R_f = 0.32, Mp: 215−217 °C (decomp). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32−7.14 (m, 10H, aromatic−CH), 4.45 (m, 2H, oxazoline−CH), 4.21 (t, J_{CH} = 12.5 Hz, 2H, oxazoline−CH_2), 4.06 (t, J_{CH} = 9.5 Hz, 2H, oxazoline−CH_2), 3.65−1.55 (bm, 9H, B−H), 3.58, (bs, 2H, H_2O), 3.04, 2.98 (dd, J_{CH} = 11.5 Hz, J_{CH} = 11.5 Hz, 2H, Bn−CH_2), 2.75, 2.67 (dd, J_{CH} 9.5 Hz, J_{CH} = 13.0 Hz, 2H, Bn−CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.15 (2C, C═N), 135.89, 129.99, 129.37, 126.23 (10C, aromatic CH), 71.99 (2C, CHN), 66.68 (2C, CH_2−O), 54.68 (2C, cluster−C), 40.81 (2C, Bn−CH_2). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ 0.89 (s, 1B), −9.55 to −18.87 (bm, 9B). IR (KBr, cm^{-1}): ν(H_2O) 3429 (m), ν(CH) 2989 (m), 2905 (m), ν(BH) 2622 (S), ν(C═N) 1657 (S), ν(CH) 1495 (m), ν(C−O) 1266 (m), ν(C−N) 1112 (m), ν(B−B) 1057 (S), ν(CH) 955 (m), 745 (m). MS (ESI, negative): m/z 687.9 (M+Cl)$^-$. Elemental analysis calcd for $C_{22}H_{31}B_{10}Cl_2N_2O_3Rh$: C, 40.44; H, 4.78; N, 4.24%. Found: C, 40.3; H, 4.59; N, 3.99%.

Synthesis of [(S,S)-Carbox-iPr]Rh(OAc)$_2$·H$_2$O (***18***). A solution of **15** (278 mg, 0.50 mmol) and silver acetate (166 mg, 2.0 mmol) in dry dichloromethane (10 mL) was stirred for 24 h at room temperature under nitrogen and wrapped in aluminum foil to protect the reaction mixture from light, and the reaction was monitored by TLC (EtOAc/methanol, 10:1). The reaction mixture was filtered through Celite eluting with dichloromethane. The solvent was removed under reduced pressure, and the concentrated residue was purified by column chromatography on silica gel with ethyl acetate/methanol (10:1) to give **18** as an orange solid (301 mg, 0.5 mmol, >99%). R_f = 0.47, Mp: 241−243 °C (decomp). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.88 (bs, 2H, H_2O), 4.26 (t, J = 9.0 Hz, 2H, oxazoline−CH), 4.09 (t, J = 7.8 Hz, 2H, oxazoline−CH_2), 3.99 (m, 2H, oxazoline−CH_2), 3.76−1.55 (bm, 9H, B−H), 1.82 (m, 2H, *i*Pr−CH), 1.69 (s, 6H, acetate−CH_3), 0.87 (d, J = 8.5 Hz, 6H, *i*Pr−CH_3), 0.82 (d, J = 8.5 Hz, 6H, *i*Pr−CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.11 (2C, CO), 160.11 (2C, C═N), 72.41 (2C, CHN), 71.52 (2C, CH_2−O), 66.85 (2C, cluster−C), 32.22 (2C, *i*Pr−CH), 23.72 (2C, acetate−CH_3), 18.15, 17.39 (4C, *i*Pr−CH_3). ^{11}B{^{1}H} NMR (96.3 MHz; $CDCl_3$): δ 0.92 (s, 1B), −9.49 to −18.54 (bm, 9B). IR (KBr, cm^{-1}): ν(H_2O) 3422 (m), ν(CH) 3032 (m), 2925 (m), ν(BH) 2611 (S), ν(C═O) 1747 (S), ν(C═N) 1625 (S), ν(CH) 1472 (m), ν(C−O) 1287 (m), ν(C−N) 1105 (m), ν(B−B) 1049 (S), ν(CH) 748 (m). MS (ESI, negative): m/z 604.4 (M)$^-$. Elemental analysis calcd for $C_{18}H_{37}B_{10}N_2O_7Rh$: C, 35.76; H, 6.17; N, 4.63%. Found: C, 35.68; H, 6.07; N, 4.51%.

[(R,R)-Carbox-Ph]Rh(OAc)$_2$·H$_2$O (***19***). This compound was prepared from **16** (312 mg, 0.5 mmol) by the procedure described for **18** to give **19** (336 mg, 0.5 mmol, >99%) as an orange solid. R_f = 0.49, Mp: 233−235 °C (decomp). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35−7.12 (m, 10H, aromatic−CH), 5.19 (dd, J = 10.0, 9.5 Hz, 2H, oxazoline−CH), 4.99 (bs, 2H, H_2O), 4.63 (dd, J = 15.0, 10.0 Hz, 2H, oxazoline−CH_2), 4.14 (t, J = 10.0 Hz, 2H, oxazoline−CH_2), 3.79−1.58 (bm, 9H, B−H), 1.67 (s, 6H, acetate−CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.69 (2C, CO), 160.00 (2C, C═N), 140.49, 129.14, 126.65, 125.23 (10C, aromatic−CH), 75.56 (2C, CHN), 69.56 (2C, CH_2−O), 67.53 (2C, cluster−C), 23.53 (2C, acetate−CH_3). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ 0.86 (s, 1B), −9.69 to −19.24 (bm, 9B). IR (KBr, cm^{-1}): ν(H_2O) 3425 (m), ν(CH) 2974 (m), 2930 (m), ν(BH) 2622 (S), ν(C═O) 1745 (S), ν(C═N) 1657 (S), ν(CH) 1482 (m), ν(C−O) 1286 (m), ν-(C−N) 1111 (m), ν(B−B) 1045 (S), ν(CH) 968 (m), 743 (m). MS (ESI, negative): m/z 672.5 (M)$^-$. Elemental analysis calcd for $C_{24}H_{33}B_{10}N_2O_7Rh$: C, 42.86; H, 4.95; N, 4.17%. Found: C, 42.62; H, 4.76; N, 4.01%.

[(S,S)-Carbox-Bn]Rh(OAc)$_2$·H$_2$O (***20***). A procedure analogous to the synthesis of **18** was employed using **17** (326 mg, 0.5 mmol) to give **20** as a yellowish−orange solid (35 mg, 0.5 mmol) in quantitative yield. R_f = 0.44, Mp: 246−248 °C (decomp). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28−7.14 (m, 10H, aromatic−CH), 5.05 (bs, 2H, H_2O), 4.41 (m, 2H, oxazoline−CH), 4.23 (m, 2H, oxazoline−CH_2), 4.05 (m, 2H, oxazoline−CH_2), 3.71−1.55 (bm, 9H, B−H), 3.01 (dd, J_{CH} = 5.0 Hz, J_{CH} = 10.0 Hz, 2H, Bn−CH_2), 2.73 (dd, J_{CH} = 10.0 Hz, J_{CH} = 10.0 Hz, 2H, Bn−CH_2), 1.67 (s, 6H, acetate−CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.84 (2C, CO), 159.89 (2C, C═N), 138.07, 130.09, 128.88, 127.23 (10C, aromatic−CH), 73.09 (2C, CHN), 67.56 (2C, CH_2−O), 54.62 (2C, cluster−C), 40.51 (2C, Bn−CH_2), 23.06 (2C, acetate−CH_3). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ 0.88 (s, 1B), −9.53 to −18.85 (bm, 9B). IR (KBr, cm^{-1}): ν(H_2O) 3427 (m), ν(CH) 2990 (m), 2902 (m), ν(BH) 2625 (S), ν(C═O) 1751 (S), ν(C═N) 1663 (S), ν(CH) 1492 (m), ν(C−O) 1286 (m), ν(C−N) 1113 (m), ν(B−B) 1052 (S), ν(CH) 968 (m), 745 (m). MS (ESI, negative): m/z 700.5 (M)$^-$. Elemental analysis calcd for $C_{26}H_{37}B_{10}N_2O_7Rh$: C, 44.57; H, 5.32; N, 4.0%. Found: C, 44.39; H, 5.26; N, 3.84%.

Synthesis of [(S,S)-Carbox-iPr]NiCl (***21***). A mixture of **7** (368 mg, 1.0 mmol) and Ni(COD)$_2$ (275 mg, 1.0 mmol) in 3 mL of dry CH_3CN was refluxed under nitrogen for 24 h, by which time the reaction was deemed complete by TLC (EtOAc/methanol 10:1). The resulting yellowish reaction mixture was cooled to room temperature, and 2 equiv of (n-Bu)$_4$NCl dissolved in 2 mL of dry CH3CN was added to this mixture via syringe. After 1 h, the solution was filtered through a layer of Celite, and the organic filtrate was evaporated in vacuo to yield crude product. Recrystallization from the dichloromethane/pentane mixture yielded analytically pure **21** as a yellow solid in 73% yield (335 mg, 0.73 mmol). Mp: 203−205 °C (decomp). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.28 (m, 2H, oxazoline−CH), 4.05 (m, 2H, oxazoline−CH_2), 3.96 (m, 4H, oxazoline−CH_2), 3.73−1.55 (bm, 9H, B−H), 1.78 (m, 2H, *i*Pr−CH), 0.89, 0.85 (dd, J_{CH} = 7.0 Hz, J_{CH} = 7.0 Hz, 12H, *i*Pr−CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.77 (2C, C═N), 72.88 (2C, CHN), 70.74 (2C, CH_2−O), 65.96 (2C, cluster−C), 32.99 (2C, *i*Pr−CH), 18.84, 17.27 (4C, *i*Pr−CH_3). ^{11}B{^{1}H} NMR (96.3 MHz; $CDCl_3$): δ 0.93 (s,

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1B), −9.32 to −18.55 (bm, 9B). IR (KBr, cm^{-1}): ν(CH) 3035 (m), 2930 (m), ν(BH) 2619 (S), ν(C=N) 1652 (S), ν(CH) 1471 (m), ν(C−O) 1287 (m), ν(C−N) 1104 (m), ν(B−B) 1055 (S), ν(CH) 862 (m), 745 (m). MS (ESI, negative): m/z 494.6 $(M+Cl)^-$. Elemental analysis calcd for $C_{14}H_{29}B_{10}ClN_2NiO_2$: C, 36.58; H, 6.36; N, 6.09%. Found: C, 36.42; H, 6.29; N, 5.94%.

*[(R,R)-Carbox-Ph]NiCl (**22**).* A procedure analogous to the synthesis of **21** was employed using pincer ligand **8** (434 mg, 1.0 mmol) to give **22** as a yellow solid in 86% yield (453 mg, 0.86 mmol). Mp: 196−198 °C (decomp). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35−7.11 (m, 10H, aromatic−CH), 5.21 (t, J_{CH} = 10 Hz, 2H, oxazoline−CH), 4.68 (t, J_{CH} = 10.5 Hz, 2H, oxazoline−CH_2), 4.16 (t, J_{CH} = 5.5 Hz, 2H, oxazoline−CH_2), 3.85−1.58 (bm, 9H, B−H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.89 (2C, C=N), 140.99, 128.78, 127.85, 126.27 (10C, aromatic−CH), 75.06 (2C, CHN), 70.74 (2C, CH_2−O), 65.96 (2C, cluster−C). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ 0.72 (s, 1B), −9.52 to −19.16 (bm, 9B). IR (KBr, cm^{-1}): ν(CH) 2975 (m), 2939 (m), ν(BH) 2621 (S), ν(C=N) 1662 (S), ν(CH) 1487 (m), ν(C−O) 1285 (m), ν(C−N) 1114 (m), ν(B−B) 1045 (S), ν(CH) 962 (m), 745 (m). MS (ESI, negative): m/z 563.18 $(M+Cl)^-$. Elemental analysis calcd for $C_{20}H_{25}B_{10}ClN_2NiO_2$: C, 45.52; H, 4.78; N, 5.31%. Found: C, 45.39; H, 4.61; N, 5.22%.

*[(S,S)-Carbox-Bn]NiCl (**23**).* A procedure analogous to the synthesis of **21** was employed using **9** (464 mg, 1.0 mmol) to give **23** as a yellow solid in 82% yield (455 mg, 0.82 mmol). Mp: 214−216 °C (decomp). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30−7.13 (m, 10H, aromatic−CH), 4.61 (m, 2H, oxazoline−CH), 4.23 (t, J_{CH} = 8.5 Hz, 2H, oxazoline−CH_2), 4.03 (t, J_{CH} = 8.0 Hz, 2H, oxazoline−CH_2), 3.85−1.56 (bm, 9H, B−H), 3.02, 2.98 (dd, J_{CH} = 7.5 Hz, J_{CH} = 8.0 Hz, 2H, Bn−CH_2), 2.75, 2.61 (dd, J_{CH} = 7.5 Hz, J_{CH} = 7.5 Hz, 2H, Bn−CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.03 (2C, C=N), 137.86, 129.69, 128.56, 126.25 (10C, aromatic−CH), 74.00 (2C, CHN), 67.44 (2C, CH_2−O), 54.32 (2C, cluster−C), 40.65 (2C, Bn−CH_2). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ 0.73 (s, 1B), −9.57 to −18.85 (bm, 9B). IR (KBr, cm^{-1}): ν(CH) 2969 (m), 2907 (m), ν(BH) 2623 (S), ν(C=N) 1659 (S), ν(CH) 1494 (m), ν(C−O) 1286 (m), ν(C−N) 1115 (m), ν(B−B) 1052 (S), ν(CH) 968 (m), 747 (m). MS (ESI, negative): m/z 591.2 $(M+ Cl)^-$. Elemental analysis calcd for $C_{22}H_{29}B_{10}ClN_2NiO_2$: C, 47.55; H, 5.26; N, 6.38%. Found: C, 47.34; H, 5.17; N, 6.26%.

*Synthesis of [(S,S)-Carbox-iPr]PdCl (**24**).* A mixture of **7** (368 mg, 1.0 mmol) and $Pd(CH_3CN)_4[BF_4]_2$ (444 mg, 1.0 mmol) in 3 mL of dry CH_3CN was refluxed under nitrogen for 24 h, by which time the reaction was deemed complete by TLC (EtOAc/methanol 10:1). The resulting yellowish compound was cooled to room temperature, and 2 equiv of $(n\text{-}Bu)_4NCl$ in 2 mL of dry CH_3CN was added via syringe. After 1 h, the solution was filtered through a layer of Celite, and the organic filtrate was evaporated in vacuo to yield a crude product. Recrystallization from the dichloromethane/pentane mixture yielded analytically pure **24** as a yellow solid in 76% yield (385 mg, 0.76 mmol). Mp: 224−226 °C (decomp). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.28 (t, J_{CH} = 8.0 Hz, 2H, oxazoline−CH), 4.08 (m, 2H, oxazoline−CH_2), 3.98 (m, 4H, oxazoline−CH_2), 3.76−1.55 (bm, 9H, B−H), 1.77 (m, 2H, *i*Pr−CH), 0.88, 0.82 (dd, J_{CH} = 6.5 Hz, J_{CH} = 8.5 Hz, 12H, *i*Pr−CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.26 (2C, C=N), 73.08 (2C, CHN), 70.13 (2C, CH_2−O), 66.02 (2C, cluster−C), 32.03 (2C, *i*Pr−CH), 19.07, 18.52 (4C, *i*Pr−CH_3). ^{11}B{^{1}H} NMR (96.3 MHz; $CDCl_3$): δ 0.92 (s, 1B), −9.59 to −18.57 (bm, 9B). IR (KBr, cm^{-1}): ν(CH) 3035 (m), 2929 (m), ν(BH) 2615 (S), ν(C=N) 1625 (S), ν(CH) 1471 (m), ν(C−O) 1287 (m), ν(C−N) 1104 (m), ν(B−B) 1050 (S), ν(CH) 845 (m), 742 (m). MS (ESI, negative): m/z 542.8 $(M+Cl)^-$. Elemental analysis calcd for $C_{14}H_{29}B_{10}ClN_2O_2Pd$: C, 33.14; H, 5.76; N, 5.52%. Found: C, 33.07; H, 5.62; N, 5.45%.

*[(R,R)-Carbox-Ph]PdCl (**25**).* A procedure analogous to the synthesis of **24** was employed using pincer ligand **8** (434 mg, 1.0 mmol) to give **25** as a yellow solid in 74% yield (425 mg, 0.74 mmol). Mp: 229−231 °C (decomp). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36−7.18 (m, 10H, aromatic−CH), 5.27 (t, J_{CH} = 15.5 Hz, 2H, oxazoline−CH), 4.65 (t, J_{CH} = 10.5 Hz, 2H, oxazoline−CH_2), 4.16 (t, J_{CH} = 11.0 Hz, 2H, oxazoline−CH_2), 3.82−1.57 (bm, 9H, B−H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.27 (2C, C=N), 141.14, 128.89, 128.37, 126.27 (10C, aromatic−CH), 76.68 (2C, CHN), 70.04 (2C, CH_2−O), 66.27 (2C, cluster−C). ^{11}B NMR (96.3 MHz; $CDCl_3$): δ 0.87 (s, 1B), −9.52 to −19.24 (bm, 9B). IR (KBr, cm^{-1}): ν(CH) 2974 (m), 2936 (m), ν(BH) 2623 (S), ν(C=N) 1662 (S), ν(CH) 1487 (m), ν(C−O) 1287 (m), ν(C−N) 1115 (m), ν(B−B) 1049 (S), ν(CH) 968 (m), 749 (m). MS (ESI, negative): m/z 610.9 $(M+Cl)^-$. Elemental analysis calcd for $C_{20}H_{25}B_{10}ClN_2O_2Pd$: C, 41.75; H, 4.38; N, 4.87%. Found: C, 41.66; H, 4.21; N, 4.72%.

*[(S,S)-Carbox-Bn]PdCl (**26**).* A procedure analogous to the synthesis of **24** was employed using **9** (464 mg, 1.0 mmol) to give **26** as a yellow solid in 80% yield (482 mg, 0.8 mmol). Mp: 242−244 °C (decomp). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32−7.10 (m, 10H, aromatic−CH), 4.45 (m, 2H, oxazoline−CH), 4.21 (t, J_{CH} = 15.5 Hz, 2H, oxazoline−CH_2), 4.05 (t, J_{CH} = 9.5 Hz, 2H, oxazoline−CH_2), 3.79−1.56 (bm, 9H, B−H), 3.07, 2.97 (dd, J_{CH} = 10.5 Hz, J_{CH} = 9.5 Hz, 2H, Bn−CH_2), 2.73, 2.69 (dd, J_{CH} = 8.5 Hz, J_{CH} = 10.0 Hz, 2H, Bn−CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.17 (2C, C=N), 136.56, 130.00, 129.10, 126.32 (10C, aromatic−CH), 71.98 (2C, CHN), 67.68 (2C, CH_2−O), 45.32 (2C, cluster−C), 40.68 (2C, Bn−CH_2). IR (KBr, cm^{-1}): ν(CH) 2993 (m), 2907 (m), ν(BH) 2620 (S), ν(C=N) 1659 (S), ν(CH) 1492 (m), ν(C−O) 1284 (m), ν(C−N) 1114 (m), ν(B−B) 1053 (S), ν(CH) 962 (m), 749 (m). MS (ESI, negative): m/z 638.9 $(M+Cl)^-$. Elemental analysis calcd for $C_{22}H_{29}B_{10}ClN_2O_2Pd$: C, 43.79; H, 4.84; N, 4.64%. Found: C, 43.65; H, 4.71; N, 4.52%.

Conjugate Reduction of α,β-Unsaturated Esters. *Typical Procedure for Synthesis of Ethyl (R)-3-Phenylbutyrate (**30**).* Methyldiethoxysilane (201 mg, 1.5 mmol) was slowly added to a mixture of ethyl *trans*-β-methylcinnamate **27** (190 mg, 1.0 mmol) and the catalyst **18** (6.04 mg, 0.01 mmol) in toluene (1.0 mL) at 60 °C. The mixture was stirred for 1.5 h and then treated with hydrochloric acid (1 N, 1 mL). After extraction with ethyl acetate, the solvents removed under reduced pressure, and the residue was purified by column chromatography on silica gel with diethyl ether/hexane (1:20) to give **30** (176 mg, 0.92 mmol, 92%) as a colorless oil. $[\alpha]^{25}_D$ = −17.9 (c 1.1 in $CHCl_3$); lit.[35] $[\alpha]^{26}_D$ = +19.0 (c 1.1 in $CHCl_3$), 94% ee for R. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.14 (m, 5H), 4.07 (q, J = 7.6 Hz, 2H), 3.28 (m, 1H), 2.61 (dd, J = 15.0, 8.2 Hz, 1H), 2.53 (dd, J = 15.0, 8.0 Hz, 1H), 1.30 (d, J = 7.6 Hz, 3H), 1.18 (t, J = 7.2 Hz, 3H). The ^{1}H NMR spectra were consistent with previously reported literature data.[25]

*Ethyl (R)-3-Phenylpentanoate (**31**).* Following the procedure for synthesis of **30**, compound **28** (204 mg, 1.0 mmol) was converted to **31** as a colorless oil in 89% yield (183 mg, 0.89 mmol). $[\alpha]^{25}_D$ = −17.5 (c 1.1 in $CHCl_3$); lit.[31] $[\alpha]^{25}_D$ = +18 (c 1.1 in $CHCl_3$). 97% ee for R. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.15 (m, 5H), 4.03 (q, J = 8.0 Hz, 2H), 3.02 (m, 1H), 2.57 (dd, J = 15.2, 7.6 Hz, 2H), 1.72−1.53 (m, 2H), 1.15 (t, J = 7.5 Hz, 3H), 0.76 (t, J = 6.8 Hz, 3H). The ^{1}H NMR spectra were consistent with previously reported literature data.[31]

*Ethyl (S)-4-Methyl-3-phenylpentanoate (**32**).* A procedure analogous to the synthesis of **30** was employed for 1 h using substrate **29** (218 mg, 1.0 mmol) to give **32** as a colorless oil in 96% yield (211 mg, 0.96 mmol), $[\alpha]^{25}_D$ = −25 (c 1.1 in $CHCl_3$); lit.[14c] $[\alpha]^{26}_D$ = −25.4 (c 1.0 in $CHCl_3$). 98% ee for S. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.16 (m, 5H), 4.03 (q, J = 8.2 Hz, 2H), 3.05 (m, 1H), 2.51 (m, 1H), 1.75−1.55 (m, 2H), 1.16 (t, J = 7.6 Hz, 3H), 1.02 (d, J = 7.0 Hz, 6H). The ^{1}H NMR spectra were consistent with previously reported literature data.[14c]

Reductive Aldol Reaction. *Synthesis of tert-Butyl-3-hydroxy-2-methyl-3-phenylpropanoate (**33**).* To a mixture of the rhodium complex **18** (6.04 mg, 0.01 mmol) and benzaldehyde (106 mg, 1.0 mmol) in

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toluene (3.0 mL), *tert*-butyl acrylate (192 mg, 1.5 mmol) was added at 50 °C. Methyldiethoxysilane (215 mg, 1.6 mmol) was slowly added, and the mixture was stirred at 50 °C for 0.5 h. The reaction was quenched by addition of aqueous HCl (4 N, 1 mL), MeOH (1 mL), and tetrahydrofuran (THF, 1 mL) at 0 °C. After stirring for 30 min, the mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic layer was washed with aqueous $NaHCO_3$ (2 × 10 mL), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel with hexane−ethyl acetate (20:1) as eluent to give a mixture of the desired products **33anti** and **33syn** (224 mg, 0.95 mmol, 95%). The anti/syn ratio was determined by ^{1}H NMR to be 90:10. **33anti** (major): $[\alpha]^{25}_D$ = −33.5 (c 1.0 in EtOH), 91% ee; lit.[25] $[\alpha]^{26}_D$ = 36.7 (c 1.0 in EtOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (m, 5H), 5.12 (d, J = 6.2 Hz, 1H), 3.02 (m, 1H), 1.45 (m, 9H), 1.2 (m, 3H). The ^{1}H NMR spectra were consistent with previously reported literature data.[25]

Crystal Structure Determination of ***4***, ***7***, ***9***, ***10***, ***13***, *and* ***14***. Each crystal was mounted on a glass fiber, and the diffraction data of all the complexes were collected on a Bruker−AXS APEX II CCD detector using graphite monochromated Mo Kα radiation at 123 K. The crystal data and experimental details are listed in Table 1. All the structures were solved by the combination of the direct method and Fourier techniques, and all the non-hydrogen atoms were anisotropically refined by full-matrix least-squares calculations. The atomic scattering factors and anomalous dispersion terms were obtained from the International Tables for X-ray Crystallography IV.[46] The hydrogen atoms of the boron cluster were obtained from difference Fourier maps.

■ ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic files for **4**, **7**, **9**, **10**, **13**, and **14** in CIF format. ^{1}H and ^{13}C NMR spectra of compounds **4**−**26** and ^{11}B NMR spectra of compounds **4**, **7**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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