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Synthesis and Characterization of Chiral Bimetallic Complexes Bearing Hard and Soft Lewis Acidic Sites

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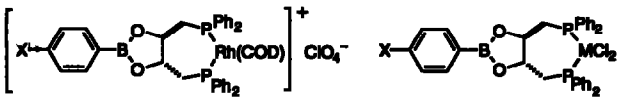
Abstract: A new class of optically active heterobimetallic complexes is described. The complexes L*MCl_2 (M = Pt(II), Pd(II), L* = C_2-symmetric boron-containing bisphosphine ligand) and [Rh(cod)(L*)]ClO_4 (cod = η^2,η^2-1,5-cyclooctadiene) were synthesized as possible templates for asymmetric catalytic reactions that involve substrate precoordination to a Lewis acidic site remote from the transition metal reaction site. Primary amines were found to bind reversibly via a B-N interaction to the free ligands L*. ^{1}H NMR measurements revealed that the binding constant of representative primary amines to L* could be tuned through variation of the electronic properties of the substituents covalently bound to boron.

Asymmetric catalytic processes, whether biological or synthetic, involve multi-step mechanisms that often include reversible substrate precoordination to the catalyst prior to the enantioselectivity-determining transformation. In such processes, the intramolecular nature of the key step reduces the degrees of freedom in the transition state and is thus critical to the achievement of high stereoselectivity. Extremely successful examples of synthetic enantioselective and diastereoselective catalysts for directed group transfer to functionalized substrates have been developed.[3] However, single small molecule catalysts that function on the principle of substrate precoordination are generally restricted with regard to substrate scope if the same metal that catalyzes group transfer to the substrate must also act as the precoordination site.[4] In these cases the types of functionalized substrates capable of binding to the catalyst are narrowly defined by the catalytic reaction.

A related strategy for achieving high stereoselectivity in group transfer to functionalized substrates involves the use of multifunctional catalysts with available sites for substrate precoordination other than the reaction center itself. This approach, which is commonly exploited by enzymes, has also been incorporated into synthetic catalyst design in complexes bearing a chiral bis-phosphinoferrocenyl unit with a pendant amine terminus.[5] In these catalysts, the phosphine groups coordinate to a catalytically active low-valent transition metal, while the amino group is capable of directing approach of the substrate through hydrogen bonding to a functional group. Analogs of this ligand have been applied in highly selective asymmetric hydrogenations,[6]

aldol reactions,[7] and allylic nucleophilic substitution reactions.[8] Although limited to substrates capable of hydrogen bonding, these catalysts provide the first successful examples of synthetic asymmetric catalysts in which selectivity arises as a result of substrate precoordination to a functional group away from the catalytically active metal center. Generalization of this strategy to include other modes of substrate precoordination would clearly be valuable.[9]

In this paper we describe the preparation of chiral heterobimetallic complexes **1-3** from the tartrate-derived chiral diphosphine diop (2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane).[10] Complexes **1-3** incorporate both hard and soft Lewis acidic environments that are chemically isolated in a rigid matrix. They thus serve as possible templates for directed catalytic reactions of alkenes bearing hard Lewis basic functional groups.



1a, X = H
1b, X = Cl
1c, X = CF_3

2, M = Pd **3**, M = Pt
a, X = H
b, X = Cl
c, X = CF_3

Results and Discussion

Ligand Design and Synthesis. The choice of ligands for the chiral heterobimetallic complexes in this study was predicated by the premise that a conformationally rigid dissymmetric bridge would best facilitate cooperation between the two metals. Bisphosphinodiol **5** (eq. 1) fulfills the criterion of rigidity due to its ability to chelate to two different Lewis acidic metals simultaneously, and it also has the appealing characteristic of being readily accessible in either enantiomeric form.[11] The 1,2-diol functionality in **5** is ideally suited for coordination to a variety of early transition metals or highly electropositive main group metals. Several complexes of **5** with titanium, aluminum, and boron were examined, although the latter proved to be the most tractable and kinetically non-labile. In particular, arylboronate esters were selected for further study because of their observed stability and since these Lewis acidic groups are well-precedented to reversibly bind amines.[12,13] Amino olefins might then be targeted as potential substrates for two-point binding to bimetallic derivatives of **5** (e.g. Figure 1). Finally, the acidity at boron could in principle be fine-tuned by appropriate aryl substitution.

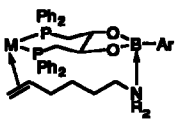


Figure 1. Proposed interaction of alkenamines with transition metal complexes derived from **4**.

The arylboronate bisphosphine ligands **4a-c** were generated in good yield by mixing equimolar amounts of the appropriate arylboric acid or anhydride with **5** (eq. 1). Compounds **4a-c** were isolated as colorless crystalline solids and were found to be stable to the atmosphere for weeks in the solid state.

(1)

Binding Studies with 4. Reversible binding between various Lewis bases and the free ligands 4a-c was probed by ^{1}H NMR spectroscopy. Dilute $CDCl_3$ solutions (0.04 M) of ligand were titrated with aliquots of 1-hexanol, 2-pentanone, *N,N*-dimethylhexylamine, *N*-acetylhexylamine and hexylamine. Of these, only addition of hexylamine resulted in significant changes in the spectrum of 4. The chemical shift of the resonance due to the methine protons of 4 was monitored as a function of Lewis base concentration. Titration with hexylamine induced an incremental upfield shift in this resonance, indicating a rapid, reversible association between boron and nitrogen. Titration of diop with hexylamine produced no corresponding upfield shift, thus showing that the interaction between the amine and 4 indeed involved coordination to the boron center.

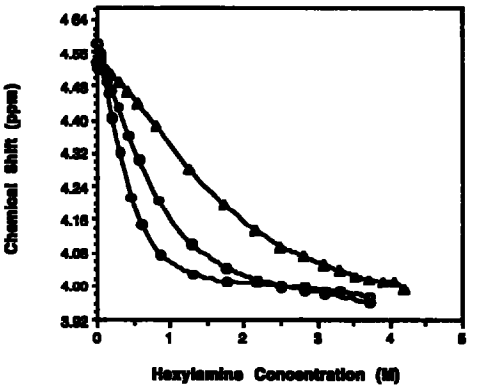
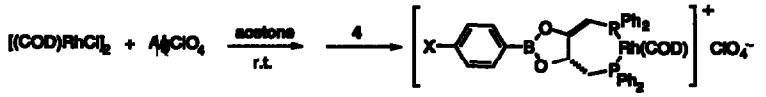


Figure 2. Chemical shift of the methine proton in 4 (0.3 M) vs. hexylamine concentration at 19° C in $CDCl_3$. 4a Δ; 4b ●; 4c ○.

Binding constants were calculated using the method of Higuchi[14] from data in Figure 2 where [amine] ≥ 10 x [ligand]. For 4a, 4b, and 4c the calculated K_{eq} values were 0.5, 1.5, and 3 M^{-1}, respectively. Thus, although binding was found to be rather weak in all cases, it correlated well with the electronic properties of the arylboronate group.

Rhodium Complexes. On the basis of the observed binding between 4 and primary amines, cationic Rh(I) complexes of 4 were prepared as possible catalysts for asymmetric transformations of prochiral olefins which bear remote (separated by > 3 carbons) amine functionality. The synthesis of complexes 1a-c was carried out from $[RhCl(cod)]_2$[15] by applying a modification of the method described by Tani et al. for the synthesis of the corresponding (binap)Rh complex.[16] (eq. 2). Complexes 1a-c were isolated as orange-yellow powders in high

yield after precipitation from acetone solution with diethyl ether. The complexes slowly decomposed upon standing in air and were thus manipulated under a nitrogen atmosphere using dry solvents.



1a, X = H, 80%
1b, X = Cl, 98%
1c, X = CF_3, 80%

(2)

The interaction between rhodium complex **1** and model substrates was monitored by ^1H NMR spectroscopy. Simple molecular modeling analysis indicated that in order to bridge the two metals, a substrate should contain at least 3-4 methylene groups separating the amine from the alkene group (Figure 3); in order to guarantee enough flexibility in the bridging unit, 5-hexen-1-amine **6**[17] was selected as a model substrate.

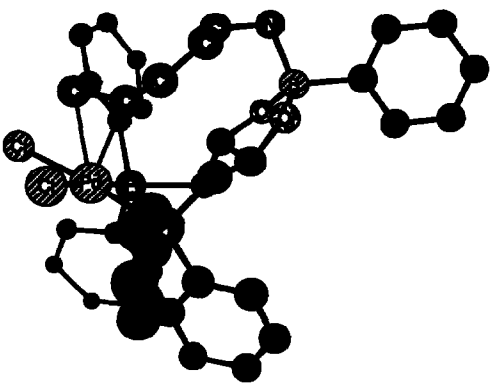


Figure 3. Chem 3D model of a proposed chelating interaction between 4-penten-1-amine and **2a** (hydrogens omitted for clarity). The coordinates for **2a** were derived from those of the corresponding DIOP complex.[20]

Titrations were carried out with [**1b**] = 0.04 M and the chemical shift of the internal vinylic proton of the aminoalkene was monitored as a function of concentration of **6** (Figure 4). The methine resonances of the ligand were obscured by the vinylic cod resonances, so these could not be monitored accurately. A strong upfield shift was observed in the alkene resonances of **6** as the concentration approached that of **1b**. As excess alkene was added, the chemical shift re-approached that of free **6**. Titration of Rh(cod)(diop)ClO_4 with **6** resulted in similar behavior, except that the observed upfield shift of the vinylic protons of **6** was significantly smaller (Figure 4). The nature of the olefin-rhodium interaction is expected to be very similar in **1b** as in Rh(cod)(diop)ClO_4. Thus, although the magnitude of chemical shift does not reflect the binding strength directly, binding between **6** and the cationic rhodium complex **1b** appears to be enhanced by the presence of the Lewis acidic boron center. Given that 1-hexene exhibited no measurable binding to either Rh complex, the interaction of **6** and Rh(cod)(diop)ClO_4 appears to involve chelation of the amine and the double bond to

Rh. While a similar interaction may be taking place in binding to 1b, the apparently enhanced binding to the boron-containing complex strongly suggests that a direct B-N interaction is involved.

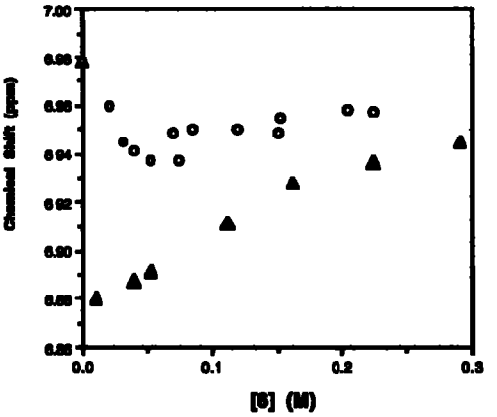
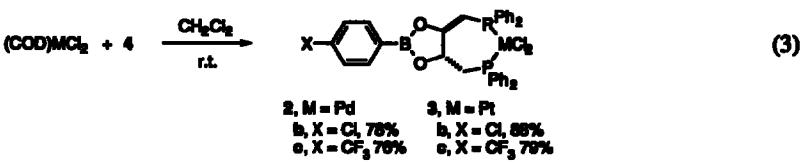


Figure 4. Chemical shift of the internal vinylic proton of 5-hexen-1-amine vs. concentration in the presence of 0.04 M of rhodium complex. 1b ▲; Rh(cod)(diop)ClO_4 O.

Platinum and Palladium Complexes. The most efficient method for preparing the Pd(II) and Pt(II) dichlorides 2 and 3 was found to be by ligand exchange of the cod complex (eq. 3). Alternatively, the dichloroplatinum complex of 4a was prepared in 52% yield directly from K_2PtCl_4 and the ligand by refluxing in xylenes overnight.[18] The palladium complexes 2a and 2b were also prepared from $PdCl_2(PhCN)_2$[19] in 65 % yield and 39% yields, respectively, according to the method of Consiglio.[20]



(3)

The platinum complexes are colorless, air stable solids, and the corresponding palladium complexes are pale yellow and also air stable. In general the platinum complexes are more soluble in polar aprotic solvents than the palladium complexes, and for a given metal solubility decreases as the boron acidity increases. The solubility of complexes 2c and 3c was less than 1 mg/mL in chloroform at room temperature.

The ^{31}P NMR chemical shifts of complexes 1-3 provide compelling evidence that the two Lewis acidic sites in each complex are well separated and do not interact. Thus, for a given metal, the ^{31}P NMR chemical shifts are essentially unaffected by the aryl substituents on the arylboronate group (Table 1).

Table 1. ^{31}P NMR chemical shifts of complexes 1-4[a]

	metal			
Ligand	none	Rh (*J*)	Pd	Pt (*J*)
4a	–24.4	14.0 (144)	19.2	0.8 (3527)
4b	–24.2	13.8 (145)	19.0	0.8 (3527)
4c	–24.3	14.0 (144)	19.0	0.8 (3527)

[a] Spectra of complexes 1-3 measured in CD_2Cl_2. Spectra of free ligands 4 measured in $CDCl_3$.

The most soluble of these complexes, **3a**, was selected for binding studies, and ^{31}P NMR was used to monitor its interaction with selected amines. The unsaturated amine 6-hepten-1-amine **9**, was prepared from the corresponding nitrile **10**, and was used to titrate a 0.02 M solution of **3a** in CD_2Cl_2 at room temperature. Although binding between **3a** and **9** was observed, it appeared to involve only interaction of the amine group with platinum. This was deduced from the observation that titration of **3a** with hexylamine resulted in identical chemical shift differences. Thus, the cooperative binding effect of unsaturated amines that was apparent with rhodium complex **1b** does not seem to extend to the analogous platinum series.

Conclusion

This work demonstrates that transition metal complexes derived from **4** are capable of binding amino olefins in which the two functionalities are >3 methylene groups apart. Evidence has been obtained for a cooperative effect between boron and rhodium in the binding of **6** by complex **1b**. Our current efforts are directed toward taking advantage of such long-range directing effects to enhance selectivity in asymmetric transformations.

Experimental Section

General Aspects. Melting points were obtained with a Mel-Temp II equipped with a digital thermometer and are uncorrected. for air-sensitive rhodium complexes were obtained under N_2 in sealed capillaries. The ^1H NMR spectra were obtained at the University of Illinois on a Varian XL-200 (200 MHz), a General Electric QE-300 (300 MHz), or a Nicolet NT-360 Fourier Transform spectrometer. The ^{13}C NMR spectra were obtained on a General Electric QE-300 (75 MHz) or a General Electric GN300NB (75.44 MHz) spectrometer. The ^{31}P NMR spectra were obtained on the General Electric GN300NB at 121.6 MHz. Chemical shifts for ^1H NMR and ^{13}C NMR are reported in ppm downfield from tetramethylsilane (TMS). ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 (capillary tube insert). Elemental analyses were performed at the Microanalytical Laboratory at the University of Illinois. The mass spectrum was recorded by the Mass Spectrometry Laboratory Staff at the University of Illinois on a VG70-SE-4F tandem mass spectrometer. Optical rotations were measured on a Jasco DIP-360 digital polarimeter. Flash chromatography was performed using E.M. 32-63 μ silica packed in glass columns at a silica:compound weight ratio of approximately 200. Analytical thin layer chromatography (TLC) was performed on alumina-coated glass plates with uv light or iodine as a visualization technique. Manipulations of air-sensitive compounds were carried out under nitrogen in a Vacuum Atmospheres drybox equipped with a MO 40-2 Dri-Train or by using

standard Schlenk line techniques. Solvents used for oxygen- or moisture-sensitive procedures were dried and distilled under a nitrogen atmosphere using standard techniques. Chloroform-*d* was dried over 4Å molecular sieves and degassed by 3 freeze-pump-thaw cycles, and stored over 4Å molecular sieves. d_2-Dichloromethane was dried over CaH_2, degassed by 3 freeze-pump-thaw cycles, and stored over 4Å sieves. Reagents were prepared according to standard procedures or were obtained from commercial sources and used as received.

(4*R*)-*trans*-2-Phenyl-4,5-bis(diphenylphosphinomethyl)-1,3,2-dioxaborolane [(+)-4a]. A solution of phenylboric acid (0.698 g, 5.71 mmol) in THF (5 mL) was added to a solution of (2*R*, 3*R*)-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane 5[11] (2.62 g, 5.71 mmol) in 25 mL THF. After stirring ca. one minute the solid was completely dissolved and TLC analysis indicated complete disappearance of 5. Volatile materials were removed in vacuo and the resulting solid was recrystallized from dichloromethane/heptane to afford **4a** as a colorless crystalline solid (2.61 g, 4.79 mmol, 84%). Mp 120.9-121.1 °C; ^{1}H NMR ($CDCl_3$): δ 2.38 (dd, J = 13.5 Hz, 6.1 Hz, 2 H), 2.54 (dd, J = 13.6 Hz, 5.6 Hz, 2 H), 4.5-4.6 (m, 2 H), 7.1-7.6 (m, 25 H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 36.0 (d, J_P = 15 Hz), 81.7 (dd, J_P = 17 Hz, 8 Hz), 127.6 , 127.9, 128.5 (d, J_P = 6 Hz), 128.7 (d, J_P = 7 Hz), 131.3, 132.7 (d, J_P = 18 Hz), 132.9 (d, J_P = 19 Hz), 134.9, 135.6, 137.8 (d, J_P = 12 Hz), 138.1 (d, J_P = 12 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$): δ –24.4; $[\alpha]_D$ +4.0 (*c*1.16, $CHCl_3$). Anal. Calcd for $C_{34}H_{31}BO_2P_2$: C, 75.02; H, 5.74; P, 11.38; B, 1.98. Found: C, 74.83; H, 5.76; P, 11.22; B, 1.88.

4-Chlorophenylboric acid. This procedure is a modification of the method of Washburn[21] for the preparation of phenylboric acid. With mechanical stirring, trimethyl borate (5.6 mL, 50.5 mmol) and then 4-chlorophenylmagnesium bromide (50 mmol as a 1M ether solution) were added sequentially by syringe in approximately 10 mmol aliquots to 25 mL of anhydrous ether cooled to –60 °C under nitrogen. After addition of both reagents was complete, the solution was stirred for 25 minutes at –60 °C. Distilled water (5 mL) was added by syringe over six minutes, followed by addition of 30 mL of a 1.7 N H_2SO_4 solution over 12 minutes. The layers were separated and the aqueous layer was extracted with ether (3 x 20 mL). The combined ether extracts were dried over $MgSO_4$ and the solvent was removed in vacuo. The remaining solids were washed with petroleum ether (2 x 10 mL) and recrystallized twice from boiling water. The isolated crystals were composed of a mixture of the acid and anhydride, yield 2.98 g (19.0 mmol, 38% calcd. as the acid). The anhydride was formed upon heating the crystals under vacuum. Mp > 255 °C; ^{1}H NMR (d_6-acetone): δ 7.56 (d, J = 8.0 Hz, 2 H), 8.24 (d, J = 7.9 Hz, 2 H). Anal. Calcd for C_6H_4BClO: C, 52.08; H, 2.91. Found: C, 52.09; H, 2.82.

(4*R*)-*trans*-2-(4-Chlorophenyl)-4,5-bis(diphenylphosphinomethyl)-1,3,2-dioxaborolane [(+)-4b]. Compound **4b** was prepared from 4-chlorophenylboric acid as described above for **4a**. Recrystallization of the crude product mixture from dichloromethane/heptane afforded **4b** as colorless crystals in 88% yield (0.973 g, 1.68 mmol) which contained 6 mol% phosphine oxide impurity by ^{1}H NMR. The ligand was further purified by flash chromatography (eluted with hexane/ethyl acetate 4:1), and the residue recrystallized from methanol in 62% overall recovery. Mp 117.8-118.2 °C; ^{1}H NMR ($CDCl_3$): δ 2.43 (dd, J = 13.9 Hz, 6.2 Hz, 2 H), 2.56 (dd, J = 14.0 Hz, 5.8 Hz, 2 H), 4.55 (dd, J = 11.1 Hz, 5.2 Hz, 2 H), 7.2-7.5 (m, 24 H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 35.9 (d, J_P =15 Hz), 81.8 (d/d, J_P = 18 Hz, 8 Hz), 127.8, 128.5 (s), 128.5 (d, J_P =8 Hz), 128.7 (d,

J_P = 8 Hz), 132.6 (d, J_P = 17 Hz), 132.9 (d, J_P = 18 Hz), 136.2, 137.6, 137.7 (d, J_P = 12 Hz), 138.0 (J_P = 12 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ –24.2; $[\alpha]_D$ +6.1 (*c*1.20, $CHCl_3$). Anal. Calcd for $C_{34}H_{30}BClO_2P_2$: C, 70.55; H, 5.22; Cl, 6.12. Found: C, 70.59; H, 5.25; Cl, 6.03.

4-(Trifluoromethyl)phenylboric acid. A round bottom flask containing 2.95 g (0.121 mol) Mg turnings was flame dried under N_2 and THF (25 mL) was added. 4-Bromobenzotrifluoride (25.5 g, 0.113 mol) in 50 mL THF was added dropwise over one hour, maintaining a steady reflux. The mixture was refluxed an additional hour with external heating. After cooling to 0 °C, an aliquot removed for titration[22] was determined to contain the corresponding Grignard reagent in a concentration of 1.6 M. The substituted boric acid was prepared in THF at –45 °C, using the same procedure described above for the preparation of 4-chlorophenylboric acid. The acid was heated under vacuum to yield a mixture of 2 oligomeric anhydrides anhydrides (3.95 g, 2310 mmol, 29%): Mp > 240 °C. ^1H NMR (d_6-acetone) δ 7.5 (s, 2 H, major anhydride), 7.79 (d, J = 7.8 Hz, minor anhydride), 7.88 (d, J = 7.9 Hz, 2 H, major anhydride), 8.19 (d, J = 7.8 Hz, 2 H, minor anhydride), 8.47 (d, J = 7.7 Hz, 2 H, major anhydride); $^{13}C\{^1H\}$ NMR of major anhydride (d_6-acetone): δ 123.3 (q, J_F = 4 Hz), 123.9 (d, J_F = 272 Hz), 130.6 (d, J_F = 32 Hz), 134.0 (s), ring carbon ipso to CF_3 not detected). Anal. Calcd for $C_7H_4BF_3O$: C, 48.91; H, 2.34. Found: C, 48.88; H, 2.22.

(4*R*)-*trans*-2-(4-(Trifluoromethyl)phenyl)-4,5-bis(diphenylphosphinomethyl)-1,3,2-dioxaborolane [(+)-4c]. A procedure analogous to the one used to prepare **4a** was followed, with 4-(trifluoromethyl)phenylboric acid used as the arylboric acid source. The product was crystallized from benzene/heptane to afford **4c** as a colorless powder (0.997 g, 1.63 mmol, 79%) judged to be >95% pure by ^1H NMR. Analytically pure material was obtained by flash chromatography followed by recrystallization from methanol. Mp 120.8-121.2 °C; ^1H NMR ($CDCl_3$): δ 2.45 (dd, J = 13.9 Hz, 6.1 Hz, 2 H), 2.57 (dd, J = 14.0 Hz, 5.7 Hz, 2 H), 4.59 (dd, J = 11.3 Hz, 5.3 Hz, 2 H), 7.3 - 7.5 (m, 20 H), 7.52 (d, J = 8.1 Hz, 2 H), 7.63 (d, J = 7.9 Hz, 2 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 35.9 (dd, J_P = 16 Hz, 1 Hz), 82.0 (dd, J_P = 17 Hz, 8 Hz), 124.1 (d, J_F = 272 Hz), 124.2 (q, J_F = 4 Hz), 128.5 (dd, J_P = 7 Hz, 1 Hz), 128.8 (d, J_P = 9 Hz), 132.7 (d, J_P = 20 Hz) 133.0 (d, J_P = 20 Hz), 135.1, 137.7 (d, J_P = 12 Hz), 137.9 (d, J_P = 12 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ –24.3; $[\alpha]_D$ +5.3 (*c*1.23, $CHCl_3$); Anal. Calcd for $C_{35}H_{30}BF_3O_2P_2$: C, 68.65; H, 4.94; P, 10.12; B, 1.76. Found: C, 68.53; H, 4.96; P, 10.00; B. 1.56.

η^2,η^2-(1,5-Cyclooctadiene)-*P*,*P*'-[(4*R*)-*trans*-2-phenyl-4,5-bis(diphenylphosphinomethyl)-1,3,2-dioxaborolane]rhodium(I) perchlorate (1a). [WARNING: *Perchlorate salts may be explosive when dry and in general the use of alternative counterions is recommended.*] The procedure of Tani et al.[16] for the preparation of [(binap)Rh(cod)]ClO_4 was followed using ligand **4a** in place of binap. Compound **1a** was isolated as a yellow-orange powder by precipitation from acetone-ether (80% yield). Mp >150 °C dec.; ^1H NMR (CD_2Cl_2): δ 2.1-2.2 (m, 2 H), 2.3-2.4 (m, 4 H), 2.4-2.5 (m, 2 H), 2.66 (dd, J = 14.5 Hz, 9.6 Hz, 2 H), 3.19 (br t, 2 H), 4.2-4.3 (m, 2 H), 4.4-4.6 (m, 2 H), 4.57 (br s, 2 H), 7.3-7.8 (m, 25 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 14.0 (d, J = 144 Hz). Anal. Calcd for $C_{42}H_{43}BClO_6P_2Rh$: C, 59.01; H, 5.07; B, 1.26; P, 7.25; Rh, 12.04. Found: C, 58.42; H, 5.29; B, 1.06; P, 7.02; Rh, 11.83. HRMS calcd for $[C_{42}H_{43}{}^{11}BO_2P_2Rh]^+$: 755.1886. Found, 755.1904.

η^2,η^2-(1,5-Cyclooctadiene)-*P,P'*-[(4*R*)-*trans*-2-(4-chlorophenyl)-4,5-bis(diphenylphosphinomethyl)-1,3,2-dioxaborolane]rhodium(I) perchlorate (1b). The same procedure used for the preparation of **1a** was followed using 4-chlorophenylboric acid in place of phenylboric acid. Compound **1b** was isolated by precipitation from acetone-diethyl ether as a yellow powder (98% yield). Mp >150°C dec.; ^{1}H NMR ($CDCl_3$): δ 2.08-2.13 (m, 2 H), 2.22-2.27 (m, 2 H), 2.37-2.53 (m, 4 H), 2.74 (dd, J = 14.2 Hz, 9.4 Hz, 2 H), 3.12 (t, J = 12.1 Hz, 2 H), 4.20 (br s, 2 H), 4.54 (br s, 4 H), 7.25 (d, J = 8.2 Hz, 2 H), 7.44-7.67 (m, 18 H), 8.04 (br s, 4 H); ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 13.8 (d, J = 145 Hz). Anal. Calcd for $C_{42}H_{42}BCl_2O_6P_2Rh$: C, 56.72; H, 4.76. Found: C, 56.42; H, 5.02.

η^2,η^2-(1,5-Cyclooctadiene)-*P,P'*-[(4*R*)-*trans*-2-(4-(trifluoromethyl)phenyl)-4,5-bis(diphenylphosphinomethyl)-1,3,2-dioxaborolane]rhodium(I) perchlorate [(+)-1c]. The same procedure used for the preparation of **1a** was followed using 4-(trifluoromethyl)phenylboric acid in place of phenylboric acid. Compound **1c** was isolated as an orange-yellow powder in 80% yield by precipitation from acetone-diethyl ether, and was determined to be ca. 95% pure by ^{1}H NMR. Mp >160 °C dec.; ^{1}H NMR (CD_2Cl_2): δ 2.17 (t, J = 7 Hz, 2 H), 2.29-2.35 (m, 4 H), 2.4-2.5 (m, 2 H), 2.69 (dd, J = 14 Hz, 9.0 Hz, 2 H), 3.19 (t, J = 12 Hz, 2 H), 4.25 (t, J = 4 Hz, 2 H), 4.46 (br s, 2 H), 4.58 (br s, 2 H), 7.4-7.8 (m, 20 H), 8.00 (t, J = 8 Hz, 4 H); ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 14.0 (d, J = 144 Hz); $[\alpha]_D$ +1.8 (*c*1.10, CH_2Cl_2). Anal. Calcd for $C_{43}H_{42}BClF_3O_6P_2Rh$: C, 55.96; H, 4.59; B, 1.17; Cl, 3.84; P, 6.71, Rh, 11.15. Found: C, 55.61, H, 4.74; B, 1.22, Cl, 3.91; P, 6.59; Rh, 10.98.

***P,P'*-[(4*R*)-*trans*-2-Phenyl-4,5-bis(diphenylphosphinomethyl)-1,3,2-dioxaborolane]dichloropalladium(II) (2a). Method A.** Compound **2a** was prepared according to the method of Consiglio for the synthesis of the analogous diop complex.[20] Ligand **4a** (0.129 g, 0.238 mmol) was added as a solid to a stirred suspension of $PdCl_2(PhCN)_2$ (0.0912 g, 0.238 mmol) in ether (10 mL) and the resulting mixture was stirred 36 h at room temperature. The resulting precipitate was isolated by vacuum filtration and washed with ether (8 mL) to afford a pale yellow solid (0.112 g, 0.155 mmol, 65%). Mp >200 °C dec.; ^{1}H NMR($CDCl_3$): δ 2.6-2.8 (m, 2 H), 3.1-3.3 (m, 2 H), 4.31 (t, J = 6.0 Hz, 2 H), 7.32 (t, J = 7.5 Hz, 2 H), 7.4-7.7 (m, 19 H), 8.11 (dd, J = 12.0 Hz, 7.2 Hz, 4 H); ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 19.2. Anal. Calcd for $C_{34}H_{31}BCl_2O_2P_2Pd$: C, 56.59; H, 4.33; Cl, 9.82; P, 8.58, Pd, 14.74; B, 1.50. Found: C, 56.54; H, 4.42; Cl, 9.82; P, 8.69; Pd, 14.99; B, 1.42.

***P,P'*-[(4*R*)-*trans*-2-(4-Chlorophenyl)-4,5-bis(diphenylphosphinomethyl)-1,3,2-dioxaborolane]-dichloropalladium(II) (2b). Method B.** Solutions of η^2,η^2-(1,5-cyclooctadiene)dichloropalladium(II) ($PdCl_2$(cod))[23] (0.0571 g, 0.200 mmol) and **4b** (0.116 g, 0.200 mmol) in CH_2Cl_2 (10 mL each) were combined at room temperature. TLC analysis indicated immediate and complete disappearance of **4b**. Hexane (10 mL) was layered on the solution and pale yellow crystals precipitated after 2 d. These were filtered, washed with pentane (4 x 5 mL), and dried under vacuum to yield 0.119 g (0.157 mmol, 78%) of **2b**, judged to by >95% pure by ^{1}H NMR. Mp >149° dec.; ^{1}H NMR ($CDCl_3$): δ 2.6-2.7 (m, 2 H), 3.1-3.2 (m, 2 H), 4.31 (t, J = 6.2 Hz, 2 H), 7.29 (d, J = 8.2 Hz, 2 H), 7.4 - 7.7 (m, 18 H), 8.10 (dd, J = 11.7 Hz, 7.4 Hz, 4 H);

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 19.0. Anal. Calcd for $C_{34}H_{30}BCl_3P_2O_2Pd$: C, 54.01; H, 4.00. Pd, 14.07; Cl, 14.07; P, 8.19; B, 1.43. Found: C, 54.15; H, 4.05; Pd, 13.99; Cl, 14.37; P, 8.30; B, 1.46.

***P,P'*-[(4*R*)-*trans*-2-(4-(Trifluoromethyl)phenyl)-4,5-bis(diphenylphosphinomethyl)-1,3,2-dioxaborolane]dichloropalladium(II) (2c).** Method B was used to prepare compound **2c**, with the exception that the non-crystalline powdery product was precipitated by addition of hexane to the CH_2Cl_2 solution and removal of the more volatile CH_2Cl_2 under vacuum. The pale yellow solid proved to be only slightly soluble in most solvents. Yield 0.242 g (0.306 mmol, 76%) of a compound judged to be >95% pure by ^1H NMR: Mp >130° dec.; ^1H NMR ($CDCl_3$): δ 2.6-2.8 (m, 2 H), 3.1-3.3 (m, 2 H), 4.35 (br t, J = 6.0 Hz, 2 H), 7.4-7.7 (m, 20 H), 8.12 (m, 4 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 19.0. Anal. Calcd for $C_{35}H_{30}BCl_2F_3O_2P_2Pd$: C, 53.23; H, 3.83; Pd, 13.47; Cl, 8.98; P, 7.84; B, 1.37. Found: C, 53.33; H, 3.83; Pd, 13.61; Cl, 9.33; P, 7.86; B, 1.25.

***P*, *P'*-[(4*R*)-*trans*-2-Phenyl-4,5-bis(diphenylphosphinomethyl)-1,3,2-dioxaborolane]dichloroplatinum(II) (3a). Method C.** This was prepared according to a modified procedure of Malatesta et al.[18] K_2PtCl_4 (0.148 g, 0.357 mmol) and **4a** (0.204 g, 0.375 mmol) were suspended in xylenes (10 mL) and the mixture was refluxed 21 h under nitrogen. The colorless solids that were formed were removed by filtration of the cooled reaction mixture. The filter cake was washed with 10 mL CH_2Cl_2 and solvents were removed from the filtrate by vacuum transfer to yield a colorless solid which was recrystallized from CH_2Cl_2/hexane. Yield 0.149 g (0.184 mmol, 52%): Mp > 270 °C dec.; ^1H NMR (CD_2Cl_2): δ 2.7-2.8 (m, 2 H), 3.47 (t, J = 14.4 Hz, J_{Pt} 102 Hz, 2 H), 4.37 (t, J = 5.7 Hz, 2 H), 7.32 (t, J = 7.4 Hz, 2 H), 7.4-7.6 (m, 19 H), 8.02 (m, 4 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 0.8 (J_{Pt} = 3527 Hz). Anal. Calcd for $C_{34}H_{31}BCl_2O_2P_2Pt$: C, 50.39; H, 3.86; B, 1.33; Cl, 8.75; P, 7.64; Pt, 24.07. Found: C, 50.03; H, 3.81; B, 1.17; Cl, 8.86; P, 7.49; Pt, 23.86.

***P,P'*-[(4*R*)-*trans*-2-(4-Chlorophenyl)-4,5-bis(diphenylphosphinomethyl)-1,3,2-dioxaborolane]dichloroplatinum(II) (3b). Method D.** A solution of **4b** (0.293 g, 0.506 mmol) in CH_2Cl_2 (6 mL) was added to a solution of η^2,η^2-(1,5-cyclooctadiene)dichloroplatinum(II), $PtCl_2(cod)$[24] in CH_2Cl_2 (40 mL). After 10 min hexane (20 mL) was added. A colorless microcrystalline solid formed upon solvent evaporation. This material was washed with pentane (10 mL) and dried under vacuum (0.378 g, 0.447 mmol, 88%), and was determined to be >95% pure by ^1H NMR. Mp >170 °C dec.; ^1H NMR ($CDCl_3$): δ 2.7-2.8 (m, 2 H), 3.45 (t, J = 14.2 Hz, J_{Pt} = 99.2 Hz, 2 H), 4.37 (t, J = 5.6 Hz, 2 H), 7.29 (d, J = 8.3. Hz, 2 H), 7.4-7.6 (m, 18 H), 8.01 (m, 4 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 0.8 (J_{Pt} = 3527 Hz). Anal. Calcd for $C_{34}H_{30}BCl_3O_2P_2Pt$: C, 48.34; H, 3.58; Pt, 23.09; Cl, 12.59; P, 7.33; B, 1.28. Found: C, 48.56; H, 3.66; Pt, 23.47; Cl, 12.82; P, 7.22; B, 1.39.

***P,P'*-[(4*R*)-*trans*-2-(4-(Trifluoromethyl)phenyl)-4,5-bis(diphenylphosphinomethyl)-1,3,2-dioxaborolane]dichloroplatinum(II) (3c).** Complex **3c** was prepared according to Method D, and was isolated a colorless crystalline solid in 79% yield. Mp >250 °C dec.; ^1H NMR ($CDCl_3$): δ 2.7-2.8 (m, 2 H), 3.47 (t, J = 14.3 Hz, J_{Pt} = 98.7 Hz, 2 H), 4.41 (br t, J = 5.5 Hz, 2 H), 7.4-7.6 (m, 18 H), 7.73 (d, J = 7.8 Hz, 2 H), 8.02 (m, 4 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 0.8 (J_{Pt} = 3527 Hz). Anal. Calcd for $C_{35}H_{30}BCl_2F_3O_2P_2Pt$:

C, 47.86; H, 3.44, B, 1.23; Cl, 8.07; P, 7.05; Pt, 22.21. Found: C, 47.60; H, 3.42; B, 0.98; Cl, 8.21; P, 7.09; Pt, 22.04.

6-Heptenenitrile (10). The method of Bartlett[25] for the preparation of 5-hexenenitrile was followed using 1-bromo-5-hexene[26] in place of 1-bromo-4-pentene. The product was distilled to yield a clear colorless liquid (5.72 g, 52.4 mmol, 76%). Bp 82 °C/7.5 Torr; ^{1}H NMR ($CDCl_3$): δ 1.5-1.6 (m, 2 H), 1.6-1.7 (m, 2 H), 2.10 (dt, J = 13.8 Hz, 6.6 Hz, 2 H), 2.35 (t, J = 6.9 Hz, 2 H), 5.0-5.1 (m, 2 H), 5.7-5.8 (m, 1 H); IR (NaCl, neat): 3532 (w), 3077 (m), 2936 (s), 2863 (s), 2245 (m), 1833 (w), 1640 (s), 1460 (m), 1427 (m), 995 (s), 914 (s) cm^{-1}.

6-Hepten-1-amine (9). Nitrile **10** (5.69 g, 52.1 mmol) was dissolved in 200 mL dry ether at 0 °C and $LiAlH_4$ (2.07 g, 54.5 mmol) was added as a solid portionwise over 15-20 minutes. The reaction mixture was stirred for 1 h as it was allowed to warm to room temperature. Inorganic materials were separated according to the Fieser method,[27] and solvents were carefully removed from the product under water aspirator pressure at 0 °C. Purification of the crude product mixture by sequential distillations afford a clear colorless liquid (1.64 g, 14.5 mmol, 28%) judged to be 97% pure by GC. Bp 151-152 °C; ^{1}H NMR ($CDCl_3$): δ 1.08 (br s, 2 H), 1.3-1.5 (m, 6 H), 2.04 (dt, J = 13.7 Hz, 6.7 Hz, 2 H), 2.67 (t, J = 7.3 Hz, 2 H), 4.9-5.0 (m, 2 H), 5.7-5.9 (m, 1 H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 26.2, 28.6, 33.6 (2 C), 42.1, 114.2, 138.8; IR (NaCl, neat) 3368 (m), 3293 (m), 3077 (m), 2976 (m), 2921 (s), 2853 (s), 1823 (w), 1640 (s), 1460 (m), 1439 (m), 1073 (m), 994 (s), 966 (m), 909 (s), 816 (s) cm^{-1}; ρ = 0.787 g/mL. Anal. Calcd for $C_7H_{15}N$: C, 74.27; H, 13.36; N, 12.37. Found: C, 73.90; H, 13.48; N, 12.34.

Titration experiments. Titrations were monitored by ^{1}H NMR either at constant temperature or at room temperature (18-22 °C). Water contamination and small variations in probe temperature were found to have no measurable effects on the chemical shifts that were monitored. Chemical shifts were measured in Hz relative to an internal TMS standard (for ^{1}H NMR studies) or to an external (capillary) solution of 85% H_3PO_4 (for ^{31}P NMR studies). Chemical shifts were found to be reproducible to within ±0.5 Hz.

In a typical experiment, a measured amount of ligand or complex was dissolved in $CDCl_3$ and the solution was diluted to 1 mL in a volumetric flask. An aliquot (0.65 to 0.80 mL) was transferred to a 5 mm NMR tube by glass syringe. After an initial NMR spectrum was taken of this solution, the sample was titrated with neat Lewis base.

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