Chiral Nickel(II) and Palladium(II) NCN-Pincer Complexes Based on Substituted Benzene: Synthesis, Structure, and Lewis Acidity

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Received May 13, 2008

Air- and moisture-stable nickel(II) and palladium(II) complexes from phebox pincer ligands **1**−**5** have been synthesized, and their Lewis activity was investigated. 2,6-Bis(oxazolinyl)phenylnickel halide complexes [NiX(phebox)] and 2,6-bis(oxazolinyl)phenylpalladium halide complexes [PdX(phebox)] were synthesized via oxidative addition with $[Ni(COD)_2]$ or Pd_2dba_3, respectively, followed by halide abstraction using silver(I) salts to form complexes such as $[Ni(phebox)][ClO_4]$ (**41**). Herein, X-ray crystal structures are reported for several pincer complexes having the expected square-planar geometries with the terdentate NCN pincer system. Complexes with general structure [M(phebox)]X where X is a halogen showed no relative Lewis acidity. On the other hand, complexes where X was exchanged for a less coordinating counterion showed increased Lewis acidity. The relative Lewis acidity varies depending on the substituents on the benzene core of the pincer ligands, due to the electronic effects of the ligand on the metal center.

Introduction

The development of chiral Lewis acid catalysts for the formation of carbon−carbon (C−C) bonds is currently a difficult yet attractive undertaking in organic chemistry.[1,2] Chelating aryl ligands have been utilized on metal centers that are catalytically active in a variety of C−C bond forming reactions.[1,3] One such class of chelating ligands is the phebox ligand framework.[4] Phebox ligands have three donor sites, one central C and two flanking N atoms in fixed positions, making them so-called "NCN-pincer" ligands. The chelating sites are bonded to an aryl ring by one sp^2 carbon and two sp^2 nitrogen centers (Figure 1).

This arrangement results in binding to metal centers that is predicted to be less flexible than other aryldiamine ligands.[5,6] An interesting feature of this class of ligands is the ease with which a number of chiral analogues can be synthesized from readily available homochiral amino alcohols.[1,7] Organometallic pincer complexes of the general structure **B** are multipurpose, often air-stable compounds that have attracted interest in catalysis.[8] These pincer ligands can coordinate a variety of transition metals, including Ni,[9,10] Pd,[3,11−13] Pt,[12,14,15] and Rh,[1,7]

Figure 1. General structure of an "NCN-pincer" ligand (**A**) and an M(NCN)-pincer complex (**B**).

to form complexes with C_2-symmetry.[16] The modular nature of these structures allows for straightforward modification of the activity of the metal center via steric and electronic effects. For example, metal complexes of these ligands can be transformed into cationic complexes for use in Lewis acid catalyzed reactions.[4,15]

Here, the synthesis of multiple NCN-pincer ligands and complexation with nickel(II) and palladium(II) to form NCN-pincer complexes are reported, as well as their relative Lewis acidities. Several X-ray crystal structures are reported as well.

Results and Discussion

Ligand Synthesis. Thirteen chiral phebox ligands (**1**−**5**) were synthesized using modified literature procedures.[1,7,17,18] All the chiral phebox ligands were derived from the amino alcohols L-valine, L-phenylalanine, and D-phenylglycine. Synthesis of [(*S*,*S*)-phebox-*i*-Pr]Br (**1a**) was performed via the combination of methodologies reported by Nishiyama[1] in 2001 and Kanazawa[7] in 2006, as shown in Scheme 1. 2-Bromoisophthalic chloride (**7**) was obtained from 2-bromo-*m*-xylene using the

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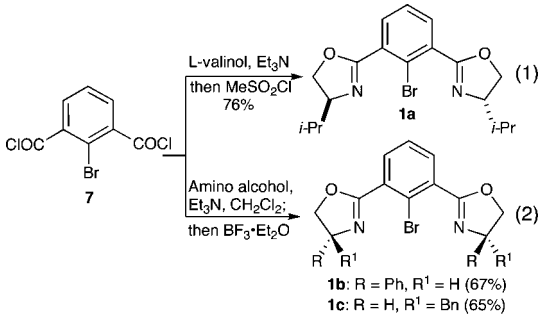
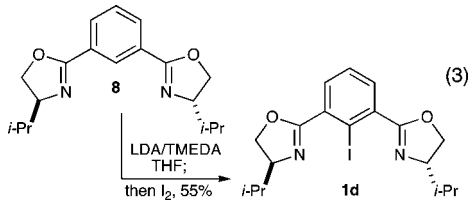
10.1021/om8004367 CCC: $40.75
Publication on Web 08/16/2008

Scheme1. Synthesisof[(*S,S*)-phebox-*i*-Pr]Br(1a),[(*R,R*)-phebox-Ph]Br (1b), and [(*S,S*)-phebox-Bn]Br (1c)



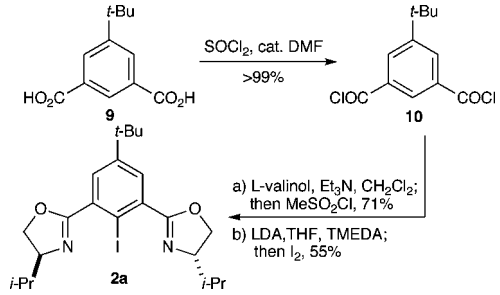
reported protocol[1] and coupled to 2 equiv of L-valinol[19] to form a bis(amide), followed by $MeSO_2Cl/NEt_3$-promoted cyclization[7] to furnish the pincer ligand **1a** in 76% yield.

Pincer ligands [(*R,R*)-phebox-Ph]Br (**1b**) and [(*S,S*)-phebox-Bn]Br (**1c**) were synthesized using a similar procedure from acyl chloride **7** and D-phenylgycinol[19] or L-phenylalaninol,[19] respectively, to give the corresponding bis(amides), from which bis(oxazolines) were formed using methodology reported by Davies et al.,[20] which utilizes $BF_3 \cdot Et_2O$ to induce the cyclization to give **1b** and **1c**, in 67% and 65% yields, respectively (eq 2).



The pincer ligand **1d** was derived form commercially available isophthaloyl dichloride, which was transformed to the known pincer precursor (*S,S*)-phebox-*i*-Pr (**8**) using the known procedure.[7] The resulting pincer ligand **8** was halogenated using the methodology of Richards et al.:[9] (*S,S*)-phebox-*i*-Pr (**8**) by treatment with LDA/TMEDA, followed by the addition of iodine to give [(*S,S*)-phebox-*i*-Pr]I (**1d**) (eq 3). Although bromine was initially employed as the electrophile in this halogenation, iodine resulted in a better yield for this transformation (11% vs 55%, respectively).

Scheme 2. Synthesis of [(S,S)-phebox-*i*-Pr]I (2a)



The pincer ligand **2a** was derived form commercially available 5-*tert*-butylisophthalic acid (**9**), which was transformed to the acyl chloride **10** with $SOCl_2$[21] before condensation with L-valinol. The resulting diamide was cyclized employing $MeSO_2Cl$ to afford (*S,S*)-*t*-Buphebox-*i*-Pr in 71% yield. Halogenation of the bis(oxazoline) was again performed using the methodology of Richards[9] (LDA/TMEDA then I_2) to give [(*S,S*)-*t*-Bu-phebox-*i*-Pr]I (**2a**) in 58% yield (Scheme 2). A single-crystal X-ray structure of **2a** was obtained (Figure 2) to corroborate the identity of this pincer ligand.

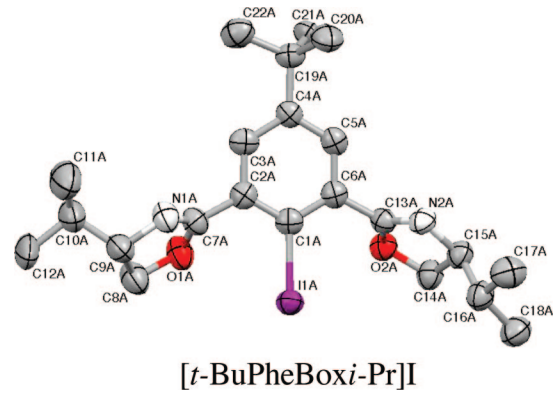
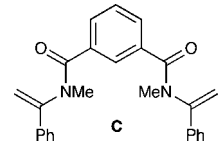
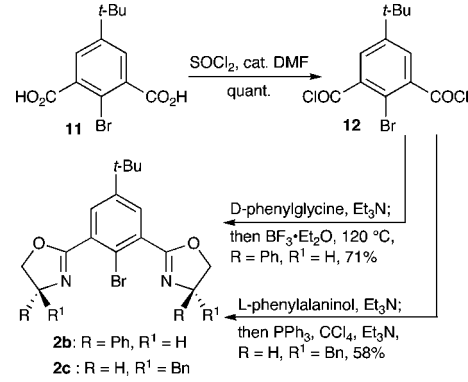


Figure 2. X-ray structure of [(*S,S*)-phebox-*i*-Pr]I (**2a**).



Unfortunately, synthesis of similar pincer ligands **2b** and **2c**, each containing acidic benzylic protons, could not incorporate the same final halogenation as used in the synthesis of **2a** because deprotonation and ring opening of the oxazolines afforded the undesired bis(enamine). Stark et al. in 2000 reported a similar finding, where compound **C** was isolated from the corresponding bis(oxazoline) upon treatment with LDA/TMEDA, then iodomethane.[3] To avoid this problem, we incorporated the halogen at the beginning of the synthesis. We utilized the procedure of Field et al.[22] to synthesize 2-bromo-5-*tert*-butylisophthalic acid (**11**) from 5-*tert*-butyl-*m*-xylene by bromination and then oxidation (Scheme 3). A modified solvent system of 1:1 *t*-BuOH/H_2O was necessary for smooth oxidation of the intermediate 5-*tert*-butyl-2-bromo-*m*-xylene to **11** (see Supporting Information). Diacid **11** was then treated with $SOCl_2$ to obtain **12**, which was condensed independently with two β-amino alcohols (L-phenylalaninol and D-phenylgycinol), to give the corresponding bis(amides). Finally, bis(oxazoline) formation to give **2b** in 71% yield was accomplished using a

Scheme 3. Synthesis of [(*R,R*)-*t*-Buphebox-Ph]Br (2b) and [(*S,S*)-*t*-Buphebox-Bn]Br (2c)



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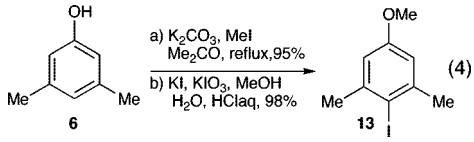
$BF_3 \cdot Et_2O$-promoted cyclization, whereas compound **2c** was most efficiently prepared by utilizing PPh_3/CCl_4, following the procedure of Vorbrüggen, albeit in only 58% yield.[18]

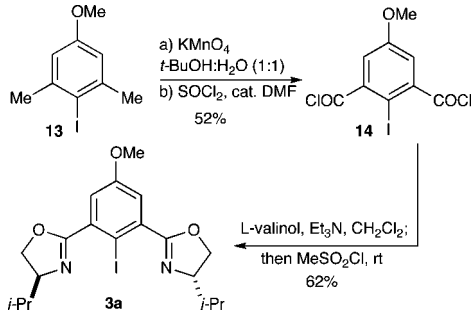
Synthesis of monomethoxy ligand **3a** began with a modification of a U.S. patent procedure[23] (eq 4) used to synthesize 3,5-dimethyl-4-iodoanisole (**13**).



This modification consists of the inversion of the two reaction steps (eq 4), to increase the overall yield from 11% to 93%. In our step 1, the methylation of 3,5-dimethylphenol (**6**) using iodomethane was promoted by potassium carbonate in refluxed acetone to give 3,5-dimethylanisole in 95% yield. Treatment of the latter anisole **6** with potassium iodide and potassium iodate in acidic water gave **13** in 98% yield (eq 4).

The oxidation of the **13** and chlorination of the resultant isophthalic acid proceeded similarly to the procedures describe above to obtain **14** (Scheme 4). An important observation in

Scheme 4. Synthesis of [(*S,S*)-MeO-phebox-*i*-Pr]I (3a)

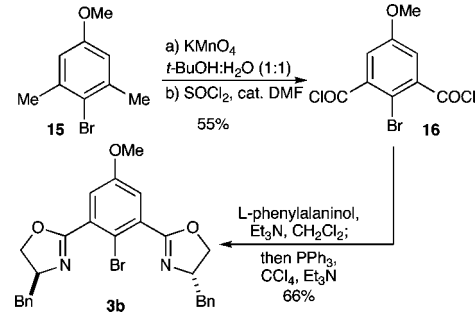


the cyclization step to form **3a** from the uncylclized bis(amide) intermediate is that for compounds possessing a methoxy group in the aryl ring, $BF_3 \cdot Et_2O$ was not tolerated. Demethylation of the phenylmethyl ethers occurs when the bis(amide) is heated in the presence of $BF_3 \cdot Et_2O$.[24−26] For this reason, it was necessary to cyclize using $MeSO_2Cl/Et_3N$, which provided **3a** in 62% yield.

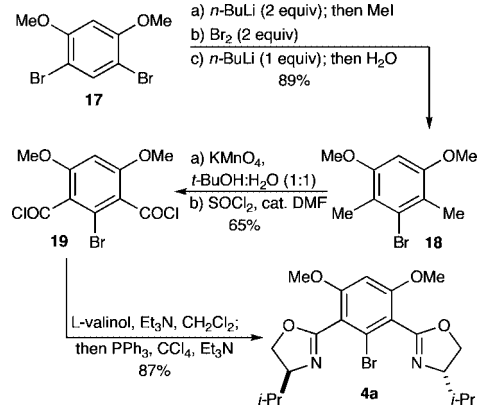
A method analogous to the synthesis of ligand **3a** was employed to synthesize **3b**. Bromination of 3,5-dimethylanisole gave **15** in 66% yield.[27] The oxidation of **15** with $KMnO_4$ followed by chlorination of the resulting isophthalic acid with $SOCl_2$ gave bis(acyl chloride) **16** in 55% yield (Scheme 5). Condensation to provide the bis(amide) was uneventful. However, we again noted that $BF_3 \cdot Et_2O$ was not tolerated for the cyclization of this oxygenated bis(amide).[24−26] Unfortunately, treatment with $MeSO_2Cl/Et_3N$ was also unable to induce the desired cyclization to provide product **3b**. However, we were able to cyclize the bis(amide) using PPh_3/CCl_4, which furnished [(*S,S*)-MeO-phebox-Bn]Br (**3b**) in 62% yield.[18]

The synthesis of pentasubstituted benzene ligand precursor **4a** was challenging due to the regiochemistry of the methoxy

Scheme 5. Synthesis of [(*S,S*)-MeO-phebox-Bn]Br (3b)



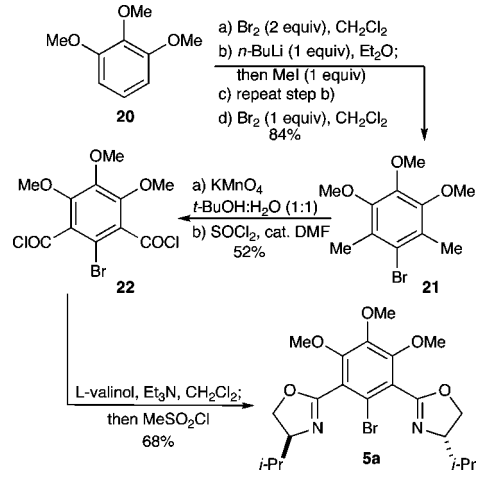
Scheme 6. Synthesis of [(*S,S*)-(MeO)$_2$-phebox-*i*-Pr]Br (4a)



groups and the halogen on the benzene ring. Several routes toward this compound were attempted, but the following synthesis proved to be the most viable. The sequence started with treatment of 1,3-dimethoxybenzene with 2 equiv of Br_2 to afford dibromide **17** (Scheme 6).[28] Metal−halogen exchange of **17** with *n*-BuLi followed by MeI delivered 1,3-dimethoxy-4,6-dimethylbenzene. An additional 2 equiv of Br_2 provided the fully substituted 2,5-dibromo-1,3-dimethoxy-4,6-dimethylbenzene. Site-selective debromination via metal−halogen exchange with *n*-BuLi afforded **18** in 89% yield for the three steps. Oxidation of **18** with $KMnO_4$ in *t*-BuOH/water gave 2-bromo-4,6-dimethoxyisophthalic acid, which was then treated with $SOCl_2$ to obtain bis(acyl chloride) **19** in 65% yield. This acid chloride was treated with L-valinol, and the resulting bis(amide) was cyclized with PPh_3/CCl_4 to give [(*S,S*)-(MeO)$_2$-phebox-*i*-Pr]Br (**4a**) in 87% yield for the two steps.

The synthesis of fully substituted aryl pincer ligand **5a** was similar to the dimethoxy pincer ligand **4a** synthesis (Scheme 7).

Scheme 7. Synthesis of [(*S,S*)-(MeO)$_3$-phebox-*i*-Pr]Br (5a)



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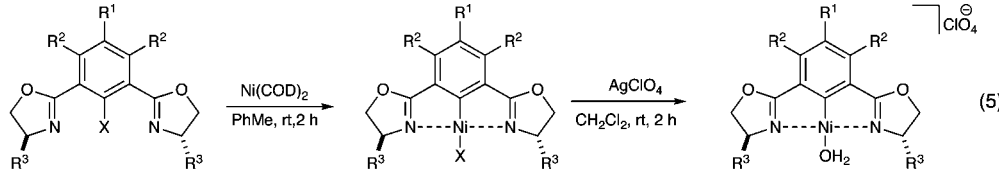
Scheme 8. General Procedure for the Synthesis of Neutral and Cationic Nickel NCN-Pincer Complexes

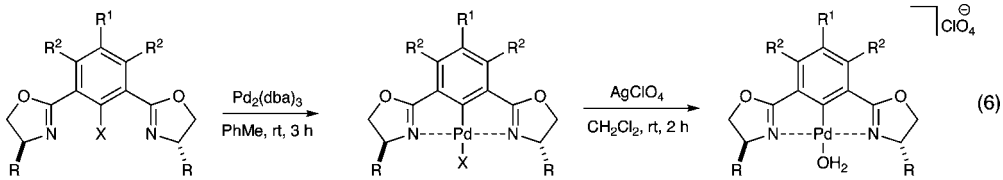


1a: $R^1 = R^2 = H$, $R^3 = i$-Pr, X = Br
1b: $R^1 = R^2 = H$, R^3 = Ph, X = Br
1c: $R^1 = R^2 = H$, R^3 = Bn, X = Br
2a: $R^1 = t$-Bu, $R^2 = H$, $R^3 = i$-Pr, X = I
2b: $R^1 = t$-Bu, $R^2 = H$, R^3 = Ph, X = Br
2c: $R^1 = t$-Bu, $R^2 = H$, R^3 = Bn, X = Br
3a: R^1 = OMe, $R^2 = H$, $R^3 = i$-Pr, X = I
4a: $R^1 = H$, R^2 = OMe, $R^3 = i$-Pr, X = Br
5a: $R^1 = R^2$ = OMe, $R^3 = i$-Pr, X = Br

23: $R^1 = R^2 = H$, $R^3 = i$-Pr, X = Br
24: $R^1 = R^2 = H$, R^3 = Ph, X = Br
25: $R^1 = R^2 = H$, R^3 = Bn, X = Br
26: $R^1 = t$-Bu, $R^2 = H$, $R^3 = i$-Pr, X = I
27: $R^1 = t$-Bu, $R^2 = H$, R^3 = Ph, X = Br
28: $R^1 = t$-Bu, $R^2 = H$, R^3 = Bn, X = Br
29: R^1 = OMe, $R^2 = H$, $R^3 = i$-Pr, X = I
30: $R^1 = H$, R^2 = OMe, $R^3 = i$-Pr, X = Br
31: $R^1 = R^2$ = OMe, $R^3 = i$-Pr, X = Br

41: $R^1 = R^2 = H$, $R^3 = i$-Pr
42: $R^1 = R^2 = H$, R^3 = Ph
43: $R^1 = R^2 = H$, R^3 = Bn
44: $R^1 = t$-Bu, $R^2 = H$, $R^3 = i$-Pr
45: $R^1 = t$-Bu, $R^2 = H$, R^3 = Ph
46: $R^1 = t$-Bu, $R^2 = H$, R^3 = Bn
47: R^1 = OMe, $R^2 = H$, $R^3 = i$-Pr
48: $R^1 = H$, R^2 = OMe, $R^3 = i$-Pr
49: $R^1 = R^2$ = OMe, $R^3 = i$-Pr

Scheme 9. General Procedure for the Synthesis of Neutral and Cationic Palladium NCN-Pincer Complexes



1a: $R^1 = R^2 = H$, $R^3 = i$-Pr, X = Br
1b: $R^1 = R^2 = H$, R^3 = Ph, X = Br
1c: $R^1 = R^2 = H$, R^3 = Bn, X = Br
2a: $R^1 = t$-Bu, $R^2 = H$, $R^3 = i$-Pr, X = I
2b: $R^1 = t$-Bu, $R^2 = H$, R^3 = Ph, X = Br
2c: $R^1 = t$-Bu, $R^2 = H$, R^3 = Bn, X = Br
3a: R^1 = OMe, $R^2 = H$, $R^3 = i$-Pr, X = I
4a: $R^1 = H$, R^2 = OMe, $R^3 = i$-Pr, X = Br
5a: $R^1 = R^2$ = OMe, $R^3 = i$-Pr, X = Br

32: $R^1 = R^2 = H$, $R^3 = i$-Pr, X = Br
33: $R^1 = R^2 = H$, R^3 = Ph, X = Br
34: $R^1 = R^2 = H$, R^3 = Bn, X = Br
35: $R^1 = t$-Bu, $R^2 = H$, $R^3 = i$-Pr, X = I
36: $R^1 = t$-Bu, $R^2 = H$, R^3 = Ph, X = Br
37: $R^1 = t$-Bu, $R^2 = H$, R^3 = Bn, X = Br
38: R^1 = OMe, $R^2 = H$, $R^3 = i$-Pr, X = I
39: $R^1 = H$, R^2 = OMe, $R^3 = i$-Pr, X = Br
40: $R^1 = R^2$ = OMe, $R^3 = i$-Pr, X = Br

50: $R^1 = R^2 = H$, $R^3 = i$-Pr
51: $R^1 = R^2 = H$, R^3 = Ph
52: $R^1 = R^2 = H$, R^3 = Bn
53: $R^1 = t$-Bu, $R^2 = H$, $R^3 = i$-Pr
54: $R^1 = t$-Bu, $R^2 = H$, R^3 = Ph
55: $R^1 = t$-Bu, $R^2 = H$, R^3 = Bn
56: R^1 = OMe, $R^2 = H$, $R^3 = i$-Pr
57: $R^1 = H$, R^2 = OMe, $R^3 = i$-Pr
58: $R^1 = R^2$ = OMe, $R^3 = i$-Pr

The reaction of 1,2,3-trimethoxybenzene **20** with 2 equiv of Br_2 afforded 4,6-dibromo-1,2,3-trimethoxybenzene. This dibromide, in one reaction flask, was treated sequentially with 1 equiv of *n*-BuLi followed by 1 equiv of MeI and then again with 1 equiv of *n*-BuLi followed by 1 equiv of MeI to give 4,5,6-trimethoxy-*m*-xylene. Treatment of the *m*-xylene with 1 equiv of Br_2 afforded the fully substituted benzene **21** in 84% yield. Oxidation of **21** with $KMnO_4$ followed by chlorination with $SOCl_2$ gave **22** in 52% yield. Bis(acid chloride) **22** was treated with L-valinol to give the corresponding bis(amide), followed by $MeSO_2Cl/NEt_3$ to give [(*S,S*)-(MeO)$_3$-phebox-*i*-Pr]Br (**5a**) in 68% yield.

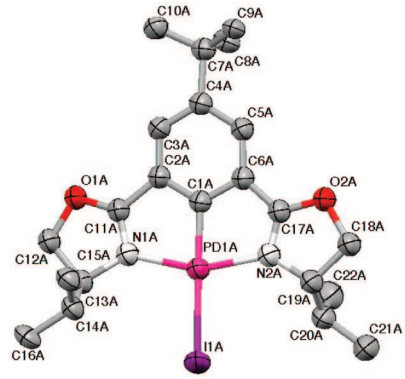
A method similar to that reported by Richards[9] was used to synthesize Ni(II) and Pd(II) pincer complexes of these ligands. Treatment of pincer ligand [PheBox-Ph]Br (**1b**), [*t*-BuPheBox-Ph]Br (**2b**), or [*t*-BuPheBox-*i*-Pr]I (**2a**) with $Ni(COD)_2$ in PhMe at rt resulted in a slow change of the color of the solution from yellow to orange over 2 h and provided the nickel complexes [PheBox-Ph]NiBr (**24**), [*t*-BuPheBox-Ph]NiBr (**27**), and [*t*-BuPheBox-*i*-Pr]NiI (**26**), respectively. The identity of each of these nickel compounds was confirmed by X-ray structure analysis of a crystal obtained by slow evaporation from a CH_2Cl_2 solution in air. The resulting bright orange crystals have been stored in air at room temperature for several months without decomposition. Anion exchange was accomplished by treatment of the (phebox)NiX complexes **23**−**31** with $AgClO_4$. After filtering and concentration in vacuo, the cationic complexes were obtained in quantitative yield. The X-ray structure of the nickel complex [PheBox-*i*-Pr]$NiClO_4 \cdot H_2O$ (**41**) is shown in Figure 3.

A similar protocol for the synthesis of cationic palladium complexes was employed. A mixture of the pincer ligands [*t*-BuPheBox*i*-Pr]I (**2a**) or [*t*-BuPheBoxBn]Br (**2d**) and $Pd_2(dba)_3$ was combined in PhMe. The reaction mixture was filtered through silica gel, eluting with toluene to remove the dba. The silica gel was then washed separately with ethyl acetate to give a yellow solution, which was collected, and the solvent was removed under reduced pressure to give the pincer complex as a yellow solid. Column chromatography was employed to purify the palladium complexes [*t*-BuPheBox*i*-Pr]PdI (**35**) and [*t*-BuPheBoxBn]PdBr (**37**). Samples suitable for X-ray analysis of [*t*-BuPheBox*i*-Pr]PdI (**35**) and [*t*-BuPheBoxBn]PdBr (**37**) were prepared by slow evaporation of a dichloromethane solution in air to give light yellow crystals. Their X-ray structure is shown in Figure 3. The resulting light yellow crystals have been stored in air at room temperature for several months without decomposition.

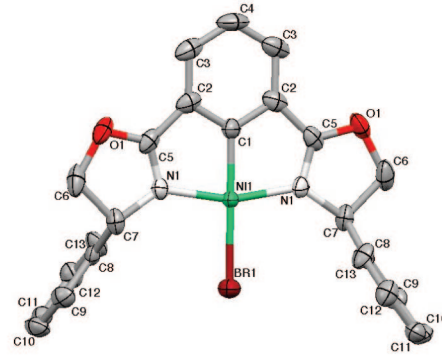
Structure Properties. Single crystals, suitable for X-ray crystallography, were obtained by slow evaporation from dichloromethane (Figure 3).

The structure of nickel pincer complexes [PheBox-Ph]NiBr (**24**), [*t*-BuPheBox-Ph]NiBr (**27**), and [*t*-BuPheBox-*i*-Pr]NiI (**26**) is correlated to the previously reported structures of (PheBox-Me_2)NiI[9] and [(*S,S*)-PheBox-*i*-Pr]NiBr.[10] The square-planar Ni(II) center in these new pincer complexes is four-coordinate, NCN and halogen.

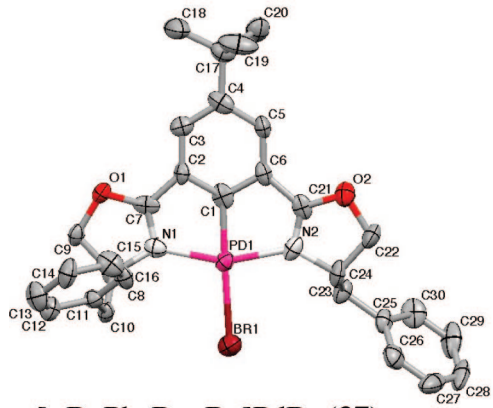
The M−C bond length in [PheBox-Ph]NiBr (**24**), [*t*-BuPheBox-Ph]NiBr (**27**), [*t*-BuPheBox-*i*-Pr]NiI (**26**), [PheBox-*i*-Pr]$NiClO_4 \cdot H_2O$ (**41**), [*t*-BuPheBox*i*-Pr]PdI (**35**), and [*t*-BuPheBoxBn]PdBr (**37**) follows the general trend as expected (Ni−C < Pd−C) (Table 1). For example, complex [(*S,S*)-*t*-BuPheBox-*i*-Pr]NiI (**26**) has a Ni−C bond length of 1.841 Å, where its congener [(*S,S*)-*t*-BuPheBox-*i*-Pr]PdI (**35**) has a Pd−C bond length of 1.944 Å. Another structure feature is the effect of the electron-donating groups on the benzene core; it is observed that [(*R,R*)-*t*-BuPheBoxPh]NiBr (**27**) has a Ni−C bond length of 1.835 Å, whereas [(*R,R*)-PheBoxPh]NiBr (**24**) has a Ni−C bond length of 1.844 Å. The *tert*-butyl group shortens the distance between the aryl group and the metal center by electron



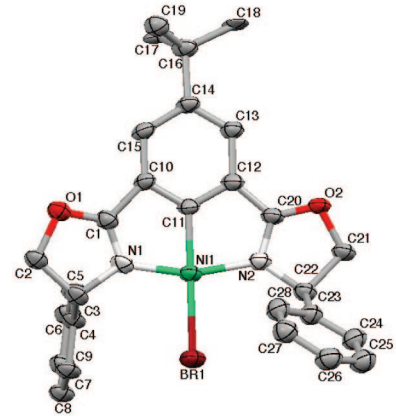
[*t*-BuPheBox*i*-Pr]PdI (**35**)



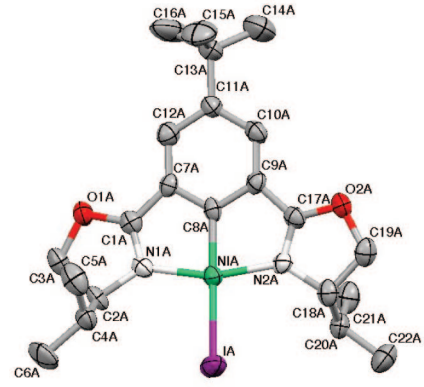
[PheBoxPh]NiBr (**24**)



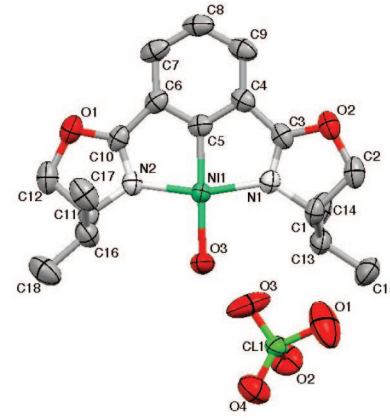
[*t*-BuPheBoxBn]PdBr (**37**)



[*t*-BuPheBoxPh]NiBr (**27**)



[*t*-BuPheBox*i*-Pr]NiI (**26**)



[PheBox*i*-Pr]NiClO$_4$•H$_2$O (**41**)

Figure 3. Crystal structures of M(NCN)-pincer complexes.

donation. The trans influence,[29] or lengthening of the bonds trans to each other, can be seen by comparing the complex [(*R,R*)-*t*-BuPheBoxPh]NiBr (**27**), with a Ni−Br bond length of 2.3443 Å, versus [(*R,R*)-PheBoxPh]NiBr (**24**), with a Ni−Br bond length of 2.3164 Å. Is noticeable that the Ni−Br bond is longer for the complex with an electron-donating group in the benzene core. The relative importance of the trans influences depends on the formal electron configuration of the metal center,[29] proving our hypothesis that electron donation to the metal center is possible by incorporation of electron-donating groups in the benzene core of the pincer complex, resulting in more electron-rich complexes. Complex [(*S,S*)-PheBox-*i*-Pr]NiClO$_4$ • H$_2$O (**30**) also has differences from its precursor [(*S,S*)-PheBox-*i*-Pr]NiBr (**23**); some of the differences are the Ni−C bond length, being shorter for the aqueous complex **30** and vice versa for the Ni−X bond length, being longer for the halogenated complex **23**. These bond length variations are explained by the trans effect as well.

Figure 4 shows how the Lewis acidity of the pincer complexes can be tailored by incorporating substituents on the aryl group. Electron-withdrawing groups will increase the Lewis acidity of the complex due to the electron-deficient metal center (Figure 4, left). On the other hand, the new complexes with an electron-donating group on the aryl ring will increase electron density

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(29) Anderson, K. M.; Orpen, A. G. *Chem. Commun.* **2001**, 2682–2683.

Table 1. Selected Bond Lengths and Bond Angles of the Nickel and Palladium Pincer Complexes

entry	M(NCN) complex	M−N(1)	M−C	M−N(2)	M−X	angle C−M−X
1	[*t*-BuPheBox*i*-Pr]PdI (**35**)	2.073(11)	1.944(12)	2.077(1 1)	2.6846(18)	178.5(4)
2	[*t*-BuPheBoxBn]PdBr (**37**)	2.071(7)	1.951(8)	2.074(7)	2.5226(10)	178.2(2)
3	[*t*-BuPheBox*i*-Pr]NiI (**26**)	1.946(5)	1.841(6)	1.929(5)	2.5301(16)	177.25(19)
4	[*t*-BuPheBoxPh]NiBr (**27**)	1.896(8)	1.835(10)	1.929(8)	2.3443(18)	178.4(3)
5	[PheBoxPh]NiBr (**24**)	1.9371(19)	1.844(3)	1.9371(19)	2.3164(5)	180.0
6	[PheBox*i*-Pr]NiBr[a] (**23**)	1.908(2)	1.841(19)	1.910(2)	2.3572(4)	178.10(6)
7	[PheBox*i*-Pr]$NiClO_4 \cdot H_2O$ (**41**)	1.9195(13)	1.8333(4)	1.9101(13)	1.9403(12)	177.35(6)

[a] Previously reported by Van Koten in 2007.

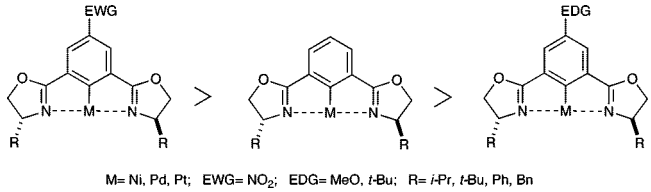

Figure 4. Decreasing Lewis acidity of pincer complexes.

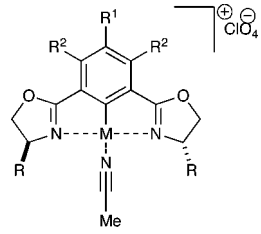

Figure 5. MeCN complexation by the cationic pincer complexes.

at the metal center, thus presumably decreasing the Lewis acidity of the complex (Figure 4, right).

The relative Lewis acidity of these pincer complexes can be measured by how tightly a Lewis base, such as MeCN, coordinates to the metal center (Figure 5). This electron donation from MeCN to the metal can be indirectly measured by a shift in the ^{1}H NMR of the methyl group of the MeCN. The downfield shift in the signal, relative to free MeCN, will be proportional to the Lewis acidity of the pincer complexes. According to the procedure of Richards,[15] 1.0 equiv of pincer complex was combined with 0.9 equiv of MeCN in $CDCl_3$ (approximately 0.013 M), and the resulting solutions were analyzed by 300 MHz ^{1}H NMR. Pincer complexes where X was a nondissociating anion (Br and I) showed no Lewis acidity (Table 2, entries 2, 3, 14, and 15). On the other hand, complexes where X was exchanged for a less coordinating counterion (ClO_4) showed increased Lewis acidity. For example, [*t*-BuPheBox-*i*-Pr]$NiClO_4$ (**44**) shows a shift at 2.381 ppm, 0.024 smaller than [PheBox-*i*-Pr]$NiClO_4$ (**41**). [$(MeO)_3$PheBox-*i*-Pr]$NiClO_4$ (**49**) shows a shift at 2.362, 0.043 smaller than [PheBox-*i*-Pr]$NiClO_4$ (**41**). Although the palladium pincer complexes show less Lewis acidity than the Ni(II) complexes, due to the greater inherent electronegativity of Ni(II) vs Pd(II),[30−32] these complexes follow the same general pattern of electronegativity that the Ni(II) pincer complexes show, that is, decreasing Lewis acidity as the number of electron-donating group on the ligand is increased. For example, the nickel complex [PheBox-*i*-Pr]$NiClO_4$ (**41**) has a shift of 2.405, and palladium complex [PheBox-*i*-Pr]$PdClO_4$ (**50**) has a shift at 2.138 ppm.

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In summary, 13 PheBox(NCN) pincer ligands were synthesized, varying the electronics of the basic backbone structure, from readily available enantiomeric pure amino alcohols and aromatic compounds. Air- and moisture-sensitive nickel(II) and palladium(II) bis(oxazoline) pincer complexes were synthesized via oxidation addition of $Ni(COD)_2$ or $Pd_2(dba)_3$ to PheBox pincer ligands. These pincer complexes were transformed into cationic complexes by halide abstraction using $AgClO_4$. Their relative Lewis acidity was measured and reported. The identity of several neutral and cationic complexes was confirmed by X-ray crystal structure analysis.

Experimental Section

All reactions were carried out under an argon atmosphere in oven-dried glassware with magnetic stirring. Dry solvents were obtained from a solvent purification system (neutral alumina, copper(II) oxide). All commercially obtained reagents were used as received. Heating was accomplished by a silicone oil bath. The temperature was controlled with a digital temperature controller. Purification of reaction products was carried out by flash column chromatography using silica gel 60 (230−400 mash). Visualization was accompanied with UV light and ceric ammonium molybdate staining. Concentration in vacuo refers to the removal of volatile solvent using a rotory evaporator attached to a dry diaphragm pump (10−15 mmHg) followed by pumping to a constant weight with an oil pump (<300 mTorr). ^{1}H NMR spectra were recorded at 300 MHz relative to $CDCl_3$ (δ 7.27). ^{1}H NMR coupling constants (J) are reported in hertz (Hz), and multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), m (multiplet). Proton-decoupled ^{13}C NMR spectra were recorded at 75 MHz and are reported relative to $CDCl_3$ (δ 77). Infrared spectra were recorded as a thin film on NaCl plates.

Synthesis of 2-Bromoisophthalyl Dichloride (7). To a suspension of 2-bromoisophthalic acid (1 g, 4 mmol) in benzene (40 mL) and a drop of DMF was added $SOCl_2$ (9 mL, 61 mmol) at 0 °C. After the mixture was refluxed for 3 h, excess $SOCl_2$ was removed by distillation, which gave **7** in 99% yield (1.1 g): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, 2H), 7.62 (t, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 139.1, 134.5, 127.9, 117.3; MS (CI) LRMS calcd for $C_8H_3BrCl_2O_2$ + H requires m/z 280.87, found 280.9 and 282.9.

Synthesis of [(*S,S*)-Phebox-*i*-Pr]Br (1a).[1] A solution of 2-bromoisophthaloyl dichloride (**7**) (1.02 g, 4.0 mmol) in dichloromethane (20 mL) was slowly added to a solution of L-valinol (907 mg, 8.8 mmol) and triethylamine (8.1 mL, 60 mmol) in dichloromethane (20 mL) at 0 °C. The mixture was stirred at room temperature for 5 h. Formation of the intermediate diamide/dialcohol was monitored by TLC examination; R_f = 0.4 (ethyl acetate/methanol = 10:1). Then, methanesulfonyl chloride (1.003 g, 8.8 mmol) was added at 0 °C, and the mixture was stirred at room temperature for 16 h. Formation of the product **1a** was monitored by TLC examination; R_f = 0.8 (ethyl acetate/hexane = 3:1). 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 sodium sulfate, and concentrated under reduced pressure. The crude product was purified

Table 2. Relative Lewis Acidity of Ni(II) and Pd(II) Pincer Complexes

entry	Ni(NCN) complex	^{1}H NMR of $NCCH_3$[a]	entry	Pd(NCN) complex	^{1}H NMR of $NCCH_3$[a]
1	none	2.020	13	none	2.020
2	[PheBoxPh]NiBr (**24**)	2.021	14	[PheBoxPh]PdBr (**33**)	2.020
3	[*t*-BuPheBox*i*-Pr]NiI (**26**)	2.020	15	[*t*-BuPheBox*i*-Pr]PdI (**35**)	2.019
4	[PheBox*i*-Pr]$NiClO_4$ (**41**)	2.405	16	[PheBox*i*-Pr]$PdClO_4$ (**50**)	2.138
5	[PheBoxPh]$NiClO_4$ (**42**)	2.381	17	[PheBoxPh]$PdC10_4$ (**51**)	2.184
6	[PheBoxBn]$NiClO_4$ (**43**)	2.385	18	[PheBoxBn]$PdClO_4$ (**52**)	2.207
7	[*t*-BuPheBox*i*-Pr]$NiClO_4$ (**44**)	2.381	19	[*t*-BuPheBox*i*-Pr]$PdClO_4$ (**53**)	2.053
8	[*t*-BuPheBoxPh]$NiClO_4$ (**45**)	2.350	20	[*t*-BuPheBoxPh]$PdClO_4$ (**54**)	2.166
9	[*t*-BuPheBoxBn]$NiClO_4$ (**46**)	2.354	21	[*t*-BuPheBoxBn]$PdClO_4$ (**55**)	2.165
10	[(MeO)PheBox*i*-Pr]$NiClO_4$ (**47**)	2.379	2°	[(MeO)PheBox*i*-Pr]$PdClO_4$ (**56**)	2.135
11	[$(MeO)_2$PheBox*i*-Pr]$NiClO_4$ (**48**)	2.366	23	[$(MeO)_2$PheBox*i*-Pr]$PdClO_4$ (**57**)	2.133
12	[$(MeO)_3$PheBox*i*-Pr]$NiClO_4$ (**49**)	2.362	24	[$(MeO)_3$PheBox*i*-Pr]$PdClO_4$ (**58**)	2.130

[a] Broad singlet.

by column chromatography (20% EtOAc/hexanes) to give **1a** in 76% yield (1.27 g, 2.71 mmol) as a colorless solid: $[\alpha]^{19}_D = -56.62$ (*c* 1 in $CHCl_3$); IR (thin film) 1628 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, $J = 8.3$ Hz, 2H), 7.37 (t, $J = 8.3$ Hz, 1H), 4.42 (m, 2H), 4.18 (m, 4H), 1.92(m, 2H), 1.05 (d, $J = 6.8$ Hz, 6H), 0.99 (d, $J = 6.8$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.03, 144.1, 132.57, 132.23, 126.93, 72.85, 70.53, 32.58, 18.75, 18.25; MS (ESI) LRMS calcd for $C_{18}H_{23}BrN_2O_2$ + H requires *m*/*z* 379.09, found 379.26 and 381.18.

Synthesis of [(*R,R*)-Phebox-Ph]Br (1b). A procedure analogous to the synthesis of **1a** was employed using 2-bromoisophthalic acid chloride (**7**) (1.02 g, 4.0 mmol) and D-phenylglycinol (1.07 g, 7.8 mmol), to yield the uncyclized oxazoline (bis(amide)) as a white solid. A suspension of the crude bis(amide) in $BF_3 \cdot Et_2O$ (10 mL) was heated to 120 °C (the mixture became homogeneous at 75 °C) for 4 h. The solution was allowed to cool, diluted with dichloromethane (50 mL), and poured into ice-cold 2 N NaOH (50 mL). The phases were separated and dried with sodium sulfate. Concentration of this solution gave [(*R,R*)-Phebox-Ph]Br (**1b**), which was purified by column chromatography (20% EtOAc/hexanes). Yield: 1.06 g (67% after two steps) of **1b** as a white solid; $[\alpha]^{19}_D = +67.98$ (*c* 1 in $CHCl_3$); IR (thin film) 1651 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, $J = 8.3$ Hz, 2H), 7.44 (t, $J = 8.3$ Hz, 1H), 7.31−7.40(m, 10H), 5.45(t, $J = 5.6$ Hz, 2H), 4.85 (t, $J = 6.6$ Hz, 2H), 4.32(t, $J = 5.6$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.25, 141.72, 132.93, 131.81, 128.6, 127.5, 127.0, 126.6, 121.4, 75.09, 70.25; MS (ESI) LRMS calcd for $C_{24}H_{19}BrN_2O_2$ + H requires *m*/*z* 447.06, found 447.05 and 449.05.

Synthesis of [(*S,S*)-Phebox-Bn]Br (1c).[1] A procedure analogous to the synthesis of **1b** was employed using 2-bromoisophthalic acid chloride (**7**) (1.02 g, 4.0 mmol) and L-phenylalaninol (1.238 g, 8.2 mmol), to yield 1.09 g (65% after two steps) of **1c**: $[\alpha]^{19}_D = -50.21$ (*c* 1 in $CHCl_3$); IR (thin film) 1649 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, $J = 8.3$ Hz, 2H), 7.38 (t, $J = 8.3$ Hz, 1H), 7.22−7.33(m, 10H), 4.64−4.67 (m, 2H), 4.41(t, $J = 5.6$ Hz, 2H), 4.20 (t, $J = 6.6$ Hz, 2H), 3.24(dd, $J = 5.6$ Hz, 6.8 Hz, 2H). 2.85(dd, $J = 5.8$ Hz, 4.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 137.5, 132.5, 131.8, 129.2, 128.4, 126.8, 126.4, 121.2, 72.0, 67.9, 41.3; MS (ESI) LRMS calcd for $C_{26}H_{23}BrN_2O_2$ + H requires *m*/*z* 475.09, found 475.10 and 477.09.

Synthesis of [(*S,S*)-Phebox-*i*-Pr]I (1d). To a solution of diisopropylamine (0.34 g, 3.36 mmol) in THF (2 mL), cooled to −78 °C, was added *n*BuLi in hexanes (3.7 mmol), and the resulting mixture stirred at room temperature for XXXXX min. After recooling to −78 °C this was added via cannula to a separate flask, also cooled to −78 °C, containing (*S,S*)-Phebox-*i*-Pr (**8**) (0.39 g, 1.12 mmol) and TMEDA (0.43 g, 3.7 mmol) in THF (10 mL). After the addition, the resulting deep red solution was stirred at room temperature for 5 h prior to the addition of iodine (1.22 g, 4.8 mmol). The solvent was removed in vacuo and the crude product dissolved in CH_2Cl_2 (50 mL). After washing with aqueous sodium thiosulfate solution (50 mL), the organic phase was dried ($MgSO_4$) and filtered and the solvent removed in vacuo. Column chromatography of the residue (20% EtOAc/hexanes) gave [(*S,S*)-Phebox-*i*-Pr]I (**1d**) as a pale yellow oil (0.303 g, 55%): $[\alpha]^{19}_D = -58.32$ (*c* 1 in $CHCl_3$); IR (thin film) 1628 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, $J = 8.3$ Hz, 2H), 7.39 (t, $J = 8.1$ Hz, 1H), 4.46 (m, 2H), 4.16 (m, 4H), 1.93(m, 2H), 1.07 (d, $J = 6.8$ Hz, 6H), 1.00 (d, $J = 6.8$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.48, 142.12, 136.63, 131.64, 127.77, 73.03, 70.69, 32.67, 18.96, 18.45; MS (ESI) LRMS calcd for $C_{18}H_{23}IN_2O_2$ + H requires *m*/*z* 427.08, found 427.079.

Synthesis of Isophthaloyl Dichloride (10). To a suspension of 5-*tert*-butylisophthalic acid (**9**) (10 g, 56 mmol) in benzene (40 mL) and a drop of DMF was added $SOCl_2$ (30 mL, excess) at 0 °C. After the mixture was refluxed for 5 h, excess $SOCl_2$ was removed by distillation, which gave **10** in 99% yield (11.63 g): IR (thin film) 1761 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.41 (s, 2H), 1.42 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 153.9, 134.2, 134.0, 131.6, 35.2, 30.9; MS (CI) LRMS calcd for $C_{12}H_{12}Cl_2O_2$ + H requires *m*/*z* 259.02, found 259.0.

Synthesis of (*S,S*)-*t*-BuPhebox-*i*-Pr (S-1). A solution of isophthaloyl dichloride (**10**) (1.55 g, 6.0 mmol) in dichloromethane (20 mL) was slowly added to a solution of L-valinol (1.36 g, 13.2 mmol) and triethylamine (12.5 mL, 90 mmol) in dichloromethane (20 mL) at 0 °C. The mixture was stirred at room temperature for 5 h. Formation of the intermediate diamide/dialcohol was monitored by TLC examination; $R_f = 0.5$ (ethyl acetate/methanol = 10:1). Then, methanesulfonyl chloride (1.25 mL, 13.2 mmol) was added at 0 °C, and the mixture was stirred at room temperature for 16 h. Formation of the product **S-1** was monitored by TLC examination; $R_f = 0.8$ (ethyl acetate/hexane = 3:1). At 0 °C, aqueous potassium carbonate (1 N, ca. 50 mL) was added and the mixture was extracted with ethyl acetate. The organic layer was washed with saturated brine, dried over sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography (20% EtOAc/hexanes) to give (*S,S*)-*t*-BuPhebox-*i*-Pr (**S-1**) in 71% yield (1.5 g, 4.2 mmol) as a white solid: $[\alpha]^{19}_D = -72.56$ (*c* 1 in $CHCl_3$); IR (thin film) 1648 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.11 (s, 2H), 4.42 (m, 2H), 4.15 (m, 4H), 1.88 (m, 2H), 1.38 (s, 3H), 1.04 (d, $J = 5.8$ Hz, 6H), 0.94 (d, $J = 5.8$ Hz, 6H); MS (ESI) LRMS calcd for $C_{22}H_{32}N_2O_2$ + H requires *m*/*z* 357.25, found 357.2.

Synthesis of [(*S,S*)-*t*-BuPhebox-*i*-Pr]I (2a). To a solution of diisopropylamine (0.34 g, 3.36 mmol) in THF (2 mL), cooled to −78 °C, was added *n*-BuLi in hexanes (3.7 mmol) and the resulting mixture stirred at −78 °C for 30 min, followed by a further 30 min at room temperature. After recooling to −78 °C this was added via cannula to a separate flask, also cooled to

−78 °C, with (*S*,*S*)-*t*-BuPhebox-*i*-Pr (**S-1**) (0.4 g, 1.12 mmol) and TMEDA (0.43 g, 3.7mmol) in THF (10 mL). After the addition, the resulting deep red solution was stirred at room temperature for 5 h prior to the addition of iodine (1.22 g, 4.8 mmol). The solvent was removed in vacuo and the crude product dissolved in CH_2Cl_2 (50 mL). After washing with aqueous sodium thiosulfate solution (50 mL), this was dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo. Column chromatography of the residue (20% EtOAc/hexanes) gave [(*S*,*S*)-*t*-BuPhebox-*i*-Pr]I (**2a**) as a pale brown crystalline solid (0.313 g, 58%): $[\alpha]^{19}_D = -63.99$ (*c* 1 in $CHCl_3$); IR (thin film) 1658 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 (s, 2H), 4.44 (m, 2H), 4.13 (m, 2H), 1.94 (m, 2H), 1.28 (s, 9H), 1.03 (d, J = 6.8 Hz, 6H), 0.98 (d, J = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.78, 151.2, 136.1, 128.9, 92.0, 73.0, 70.5, 34.5, 32.6, 30.8, 19.0, 18.4; MS (ESI) LRMS calcd for $C_{22}H_{31}IN_2O_2$ + H requires *m*/*z* 483.14, found 483.31.

X-ray Crystal Structure Determination of [(*S*,*S*)-*t*-BuPhebox-*i*-Pr]I (**2a**): $C_{22}H_{31}IN_2O_2$, M = 482.39, orange needle, 0.40 × 0.10 × 0.10 mm^3, monoclinic, space group $P2_1$ (No. 4), a = 9.478(6) Å, b = 21.389(13) Å, c = 11.315(7) Å, β = 95.246(8)°, V = 2284(2) $Å^3$, Z = 4, D_c = 1.403 g/cm^3, F_{000} = 984, Bruker APEX-II CCD, Mo Kα radiation, λ = 0.71073 Å, T = 163(2) K, $2\theta_{max}$ = 50.0°, 18 541 reflections collected, 7590 unique (R_{int} = 0.0729). Final GooF = 1.019, R1 = 0.0461, wR2 = 0.0862, R indices based on 6256 reflections with $I > 2\sigma(I)$ (refinement on F^2), 487 parameters, 424 restraints. *Lp* and absorption corrections applied, μ = 1.420 mm^{-1}. Absolute structure parameter = −0.03(2). Displacement ellipsoid plot (50% probability) of **2a** is shown in Figure 2 with full numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): I(1)−C(1A) 2.115(6), N(1A)−C(7A) 1.270(9), C(7A)−O(1A) 1.365(8), N(2A)−C(13A) 1.270(9), C(13A)−O(2A) 1.362(8), I(1A)−C(1A)−C(2A) 119.6(4), I(1A)−C(1A)−C(6A) 120.5(4), N(1A)−C(7A)−O(1A) 116.7(6), N(2A)−C(13A)−O(2A) 119.5(6), N(1A)−C(7A)−C(2A) 126.7(6), O(1A)−C(7A)−C(2A) 116.6(6).

Synthesis of 2-Bromo-5-*tert*-butylisophthaloyl Dichloride (12). To a suspension of 2-bromo-5-*tert*-butylisophthalic acid (**11**) (5 g, 15 mmol), in benzene (25 mL) and a drop of DMF, was added $SOCl_2$ (25 mL, excess) at 0 °C. After the mixture was refluxed for 3 h, excess $SOCl_2$ was removed by distillation to give 5.55 g of **12** in 99% yield as a white solid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (s, 2H), 1.39 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 152.0, 138.5, 131.3, 113.7, 35.12, 30.7; MS (CI) LRMS calcd for $C_{12}H_{11}BrCl_2O_2$ + H requires *m*/*z* 336.93, found 336.9 and 338.9.

Synthesis of [(*R*,*R*)-*t*-BuPhebox-Ph]Br (2b). A solution of isophthaloyl dichloride (**12**) (1 g, 3 mmol) in dichloromethane (10 mL) was slowly added to a solution of D-phenylglycinol (856 mg, 6.25 mmol) in dichloromethane (10 mL). Then a solution of triethylamine (2.06 mL, 15 mmol) in dichloromethane (10 mL) was added slowly at 0 °C under argon. The mixture was stirred at room temperature for 8 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). MS (ESI) LRMS calcd for $C_{29}H_{31}BrN_2O_4$ + H requires *m*/*z* 539.15, found 539.14 and 541.14. A suspension of the crude bis(amide) (1 g, 2 mmol) in $BF_3 \cdot Et_2O$ (10 mL) was heated to 120 °C (the mixture became homogeneous at 75 °C) for 4 h. The solution was allowed to cool, diluted with dichloromethane (50 mL), and poured into ice-cold 2 N NaOH (50 mL). The phases were separated and dried with sodium sulfate. Concentration of this solution gave [(*R*,*R*)-*t*-BuPhebox-Ph]Br (**2b**), which was purified by column chromatography (20% EtOAc/hexanes), affording a white solid, 1.06 g (71% yield after two steps): $[\alpha]^{19}_D = +46.91$ (*c* 1 in $CHCl_3$); IR (thin film) 1650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.81 (s, 2H), 7.31−7.42 (m, 10H), 5.47 (t, J = 8.3 Hz 2H), 4.87 (t, J = 5.6 Hz, 2H), 4.33 (t, J = 6.6 Hz, 2H), 1.37(s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 150.5, 141.7, 131.3, 130.1, 128.6, 127.5, 126.7, 118.1, 70.3, 34.6, 30.8; MS (ESI) LRMS calcd for $C_{28}H_{27}BrN_2O_2$ + H requires *m*/*z* 503.13, found 503.1 and 505.1.

Synthesis of [(*S*,*S*)-*t*-BuPhebox-Bn]Br (2c). A procedure analogous to the synthesis of **2b** was employed using 2-bromo-5-*tert*-butylisophthalic acid chloride (**12**) (600 mg, 1.78 mmol) and L-phenylalaninol (593 mg, 3.93 mmol), to yield the crude uncyclized oxazoline (bis(amide)) as a white solid after removal of volatiles under reduced pressure. Acetonitrile (10 mL), PPh_3 (981 mg, 3.7 mmol), and triethylamine (0.512 mL, 3.7 mmol) were added to the crude bis(amide). The temperature was reduced to 0 °C, after which CCl_4 (0.37 mL, 3.7 mmol) was slowly added via syringe. The reaction mixture was warmed to room temperature overnight, after which the mixture was quenched with H_2O (10 mL) and the volatiles were removed under vacuum. The residue was dissolved in H_2O (50 mL) and dichloromethane (100 mL). After separation of the layers, the organic layer was washed with H_2O (30 mL) and brine (30 mL). The combined aqueous layers were extracted with dichloromethane (100 mL). The combined organic layers were dried on Na_2SO_4 and filtered. After the solvent was removed under vacuum, the crude product was purified by silica gel column chromatography (20% EtOAc/hexanes) to afford **2c** as a white solid, 549 mg (58% yield after two steps): $[\alpha]^{19}_D = -52.15$ (*c* 1 in $CHCl_3$); IR (thin film) 1658 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.60 (s, 2H), 7.25−7.38 (m, 10H), 4.65 (m, 2H), 4.38 (t, J = 6.6 Hz, 2H), 4.22 (t, J = 5.6 Hz, 2H), 3.25(dd, J = 5.6 Hz, 6.8 Hz, 2H). 2.88 (dd, J = 5.8 Hz, 4.2 Hz, 2H), 1.33 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 150.24, 137.4, 131.3, 129.7, 129.3, 128.3, 126.4, 117.8, 71.8, 67.8, 41.2, 34.5, 30.8; MS (ESI) LRMS calcd for $C_{30}H_{31}BrN_2O_2$ + H requires *m*/*z* 531.16, found 531.16 and 533.16.

Synthesis of 3,5-Dimethylanisole (S-2). To a solution of 3,5-dimethylphenol (**6**) (30 g, 246 mmol) in acetone (200 mL) were added anhydrous K_2CO_3 (51 g, 369 mmol) and iodomethane (52.4 g, 369 mmol). The mixture was heated at reflux under argon for 24 h. After cooling the reaction to room temperature, the solution was filtrated with Celite, washed with acetone, and concentrated under reduced pressure. The residue was dissolved in dichloromethane and washed with 2 N NaOH. Further simple distillation afforded pure 3,5-dimethylanisole (**S-2**) as a colorless liquid in 95% yield: ^1H NMR (300 MHz, $CDCl_3$) δ 6.99 (s, 1H), 6.63 (s, 2H), 3.85 (s, 3H), 2.38 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 139.9, 122.3, 54.9, 21.3; MS (CI) LRMS calcd for $C_9H_{12}O$ + H requires *m*/*z* 137.09, found 137.1.

Synthesis of 3,5-Dimethyl-4-iodoanisole (13). To a solution of 3,5-dimethylanisole (**S-2**) (4 g, 30 mmol) in 40 mL of methanol was added 20 mL of 36% hydrochloric acid, with occasional cooling to maintain the temperature at 20−30 °C. To the resulting solution was then added a solution of 3.2 g (20 mmol) of potassium iodide and 2.1 g (10 mmol) of potassium iodate in 25 mL of water over a 10 min period. The solution color changed from colorless to brown and cloudy. After stirring at room temperature overnight, the reaction mixture was extracted with dichloromethane and washed with saturated $Na_2S_2O_3$ and NaOH; then the organic phase was dried with Na_2SO_4. The solvent was removed under reduced pressure. The resulting tan solid was recrystallized several times from hot methanol by cooling to −4 °C to yield 7.7 g (98% yield) of white crystals, which were identified as 3,5-dimethyl-4-iodoanisole (**13**): ^1H NMR (300 MHz, $CDCl_3$) δ 6.67 (s, 2H), 3.78 (s, 3H), 2.45 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 142.8,

112.8, 96.9. 55.2, 29.7; MS (CI) LRMS calcd for $C_9H_{11}IO$ + H requires *m/z* 262.99, found 263.1.

Synthesis of 2-Iodo-5-methoxyisophthaloyl Dichloride (14). In a 250 mL three-necked round-bottom flask equipped with a mechanical stirrer and a reflux condenser was added 2-iodo-5-methoxy-1,3-dimethylbenzene (**13**) (2 g, 8 mmol), dispersed in 30 mL of water and NaOH (1.3 g, 32 mmol). A hot solution of $KMnO_4$ (10.8 g, 72 mmol) in 100 mL of water was added at 100 °C, and the reaction mixture was heated to reflux for 8 h. After the mixture was cooled to room temperature, the reaction was filtered using vacuum filtration. The solution was acidified with concentrated HCl. The resulting white precipitate was collected by vacuum filtration and oven-dried (<80 °C) overnight to give 1.3 g (53% yield) of 2-iodo-5-methoxyisophthalic acid. To a suspension of 2-iodo-5-methoxyisophthalic acid (0.7 g, 2.2 mmol) in benzene (50 mL) and a drop of DMF was added $SOCl_2$ (11 mL, 150 mmol) at 0 °C. After the mixture was refluxed for 5 h, excess $SOCl_2$ was removed by distillation to give 772 mg (99% yield) of 2-iodo-5-methoxyisophthalic acid chloride (**14**) as a pale yellow liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.4 (s, 2H), 3.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 158.9, 139.5, 119.3, 106.8, 56.3; MS (CI) LRMS calcd for $C_9H_5Cl_2IO_3$ + H requires *m/z* 358.87, found 358.9.

Synthesis of [(*S,S*)-MeOPhebox-*i*-Pr]I (3a). A solution of 2-iodo-5-methoxyisophthaloyl dichloride (**14**) (750 mg, 2.09 mmol) in dichloromethane (10 mL) was slowly added to a solution of L-valinol (474 mg, 4.6 mmol) in dichloromethane (10 mL) and triethylamine (4.25 mL, 31 mmol) in dichloromethane (10 mL) at 0 °C. The mixture was stirred at room temperature for 5 h. Formation of the intermediate diamide/dialcohol was monitored by TLC. Then methanesulfonyl chloride (524.4 mg, 4.6 mmol) was added at 0 °C, and the mixture was stirred at room temperature for 8 h. Formation of the product **3a** was monitored by TLC examination; R_f = 0.4 (60% ethyl acetate/hexane). 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 sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography (20% EtOAc/hexanes) to give **3a** in 62% yield after two steps (580 mg, 1.27 mmol) as a colorless oil: $[\alpha]^{19}_D = -62.42°$ (*c* 1 in $CHCl_3$); IR (thin film) 1650 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (s, 2H), 4.47 (m, 2H), 4.14 (m, 4H), 3.79 (s, 3H), 1.89 (m, 2H), 1.04 (d, J = 6.8 Hz, 6H), 0.96 (d, J = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 159.0, 137.8, 117.7, 84.0, 72.3, 70.6, 55.0, 32.6, 18.9, 18.4; MS (ESI) LRMS calcd for $C_{19}H_{25}IN_2O_3$ + H requires *m/z* 457.091, found 457.085.

Synthesis of 2-Bromo-5-methoxy-1,3-dimethylbenzene (15). To a stirred solution of 3,5-dimethylanisole (**S-2**) (8.2 g, 60 mmol) in CH_2Cl_2 (100 mL) was added dropwise a 1.0 M solution of bromine in CH_2Cl_2 (9.95 g, 63 mmol) at 0 °C via cannula over a 2 min period under argon. The reaction was stirred for 1 h at room temperature; progress was monitored by TLC analysis. The product was washed with saturated sodium thiosulfate until the organic phase became colorless, dried with sodium sulfate and concentrated under reduced pressure. The residue was purified by simple distillation to give 10.88 g (66%) of pure 2-bromo-5-methoxy-1,3-dimethylbenzene (**15**) as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.56 (s, 2H), 3.78 (s, 3H), 2.40(s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 138.8, 118.8, 113.9, 55.6, 24.2; MS (CI) LRMS calcd for $C_9H_{11}BrO$ + H requires *m/z* 215.0, found 215.1 and 217.1.

Synthesis of 2-Bromo-5-methoxyisophthaloyl dichloride (16). In a 250 mL three-necked round-bottom flask equipped with a mechanical stirrer and a reflux condenser was added 2-bromo-5-methoxy-1,3-dimethylbenzene (**15**) (2.5 g, 9.1 mmol), dissolved in 300 mL of *t*-BuOH−water (1:1) and $KMnO_4$ (3.1 g, 19.1 mmol). The reacation was set to reflux for 2 h and cooled to room temperature; then more $KMnO_4$ (3.1 g, 19.1 mmol) was added. The reaction mixture was refluxed for another 16 h. After the mixture was cooled to room temperature and filtered using vacuum filtration, the *t*-BuOH was removed under reduced pressure. The solution was acidified with concentrated HCl. The resulting white precipitate was collected by vacuum filtration and oven-dried (<80 °C) overnight to give 1.79 g (56% yield) of 2-bromo-5-methoxyisophthalic acid. To a suspension of 2-bromo-5-methoxyisophthalic acid (1 g, 3.7 mmol) in benzene (50 mL) and a drop of DMF was added $SOCl_2$ (11 mL, 150 mmol) at 0 °C. After the mixture was refluxed for 5 h, excess $SOCl_2$ was removed by distillation to give 1.12 g (99% yield) of the 2-bromo-5-methoxyisophthaloyl dichloride (**16**) as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (s, 2H), 3.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 158.9, 139.5, 119.3, 106.8, 56.3; MS (CI, CH_4) LRMS calcd for $C_9H_5BrCl_2O_3$ + H requires *m/z* 310.88, found 310.9 and 312.9.

Synthesis of [(*S,S*)-MeOPhebox-Bn]Br (3b). A solution of 2-bromo-5-methoxyisophthaloyl dichloride (**16**) (806 mg, 2.6 mmol) in dichloromethane (10 mL) was slowly added to a solution of L-phenylalaninol (824 mg, 5.4 mmol) in dichloromethane (10 mL) and triethylamine (1.6 mL, 11.25 mmol) in dichloromethane (10 mL) at 0 °C. The mixture was stirred at room temperature for 5 h. The volatiles were removed under reduced pressure to afford the crude bis(amide), which was used without further purification. Acetonitrile (10 mL), PPh_3 (1.52 g, 5.7 mmol), and triethylamine (551 mg, 5.46 mmol) were added to the crude bis(amide). The temperature was reduced to 0 °C, after which CCl_4 (840 mg, 5.46 mmol) was slowly added via syringe. The reaction mixture was warmed to room temperature overnight, after which the mixture was quenched with H_2O (10 mL) and the volatiles were removed in vacuo. The residue was dissolved in H_2O (50 mL) and dichloromethane (100 mL). After separation of the layers, the organic layer was washed with H_2O (30 mL) and brine (30 mL). The combined aqueous layers were extracted with dichloromethane (100 mL). The combined organic layers were dried on Na_2SO_4 and filtered. After the solvent was removed under reduced pressure, the crude product was purified by silica gel column chromatography (20% EtOAc/hexanes) to afford **3b** as a colorless oil: 858 mg (66% after two steps); $[\alpha]^{19}_D = -55.68$ (*c* 1 in $CHCl_3$); IR (thin film) 1645 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24−7.35 (m, 10H), 7.17 (s, 2H), 4.63 (m, 2H), 4.40 (t, J = 7.6 Hz, 2H), 4.20 (t, J = 5.6 Hz, 2H), 3.81 (s, 3H), 3.23 (dd, J = 5.6 Hz, 6.8 Hz, 2H). 2.86 (dd, J = 5.8 Hz, 4.2 Hz, 2H), 1.33 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 157.8, 137.4, 132.4, 129.2, 128.5, 128.3, 126.3, 126.4, 118.2, 111.35, 71.9, 67.8, 55.64, 41.2; MS (ESI) LRMS calcd for $C_{27}H_{25}BrN_2O_3$ + H requires *m/z* 505.10, found 505.10 and 507.10.

Synthesis of 1,5-Dibromo-2,4-dimethoxybenzene (17). To a stirred solution of 1,3-dimethoxybenzene (15 g, 108 mmol) in CH_2Cl_2 (100 mL) was added dropwise a 1.0 M solution of bromine in CH_2Cl_2 (36 g, 230 mmol) at 0 °C via cannula over a 2 min period under argon. The reaction was stirred for 30 min, and progress was monitored by TLC analysis. The product was washed with saturated sodium thiosulfate until the organic phase became colorless, dried with sodium sulfate and concentrated under reduced pressure to give 32 g (99%) of pure 1,5-dibromo-2,4-dimethoxybenzene (**17**) as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 1H), 6.48 (s, 1H), 3.9 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 135.8, 102.3, 97.3, 56.4; MS (CI, CH_4) LRMS calcd for $C_8H_8Br_2O_2$ + H requires *m/z* 293.89, found 294.0, 295.0, 297.0, and 299.0.

Synthesis of 1,5-Dimethoxy-2,4-dimethylbenzene (S-3). A *n*-BuLi (2.39 g, 37.4 mmol) solution was added to a solution of 1,5-dibromo-2,4-dimethoxybenzene (**17**) (5 g, 17 mmol) in 100

mL of ether at −78 °C under argon. The colorless solution was stirred at −78 °C for 30 min. Iodomethane (4.7 mL, 74.8 mmol) was added slowly at −78 °C under argon via syringe. The mixture was allowed to warm to room temperature and stirred for 1 h. The mixture was quenched with NH_4Cl, washed with aqueous NaOH, water, and brine, dried with sodium sulfate, and concentrated under reduced pressure to give 2.8 g (99%) of pure 1,5-dimethoxy-2,4-dimethylbenzene (**S-3**) as white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.43 (s, 1H), 3.83 (s, 6H), 2.13 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 132.3, 117.6, 95.3, 55.69, 15.14; MS (CI, CH_4) LRMS calcd for $C_{10}H_{14}O_2$ + H requires *m/z* 167.10, found 167.10.

Synthesis of 1,4-Dibromo-2,6-dimethoxy-3,5-dimethylbenzene (S-4). To a stirred solution of 1,5-dimethoxy-2,4-dimethylbenzene (**S-3**) (2.8 g, 17 mmol) in CH_2Cl_2 (70 mL) was added dropwise a 1.0 M solution of bromine (6.7 g, 42 mmol) in CH_2Cl_2 (30 mL) at 0 °C via cannula over a 2 min period under argon. The reaction was stirred for 16 h at room temperature; progress was monitored by TLC analysis. The product was washed with saturated sodium thiosulfate until the organic phase became colorless, dried with sodium sulfate and concentrated under reduced pressure to give 5.02 g (93%) of pure 1,4-dibromo-2,6-dimethoxy-3,5-dimethylbenzene (**S-4**) as white solid after recrystallization from ether: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 6H), 2.4 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 129.3, 127.7, 112.2, 60.6, 17.3; MS (CI, CH_4) LRMS calcd for $C_{10}H_{12}Br_2O_2$ + H requires *m/z* 322.92, found 323.1, 325.1, and 327.1.

Synthesis of 3-Bromo-1,5-dimethoxy-2,4-dimethylbenzene (18). A *n*-BuLi (795 mg, 12.4 mmol) solution was added to a solution of 1,4-dibromo-2,6-dimethoxy-3,5-dimethylbenzene (**S-4**) (4 g, 12.4 mmol) in 100 mL of ether at −78 °C under argon, and the colorless solution was stirred at −78 °C for 1 h. H_2O (50 mg, 25 mmol) in 5 mL of THF was added slowly at −78 °C under argon. The mixture was allowed to warm to room temperature and stirred for 1 h. The mixture was quenched with saturated NH_4Cl, washed with NH_4OH, water, and brine, dried with sodium sulfate, and concentrated under reduced pressure to give 3.04 g (98%) of pure 3-bromo-1,5-dimethoxy-2,4-dimethylbenzene (**18**) as white solid after recrystallization from ether: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.44 (s, 1H), 3.83 (s, 6H), 2.28 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 129.2, 118.8, 94.7, 56.0, 15.7; MS (CI, CH_4) LRMS calcd for $C_{10}H_{13}BrO_2$ + H requires *m/z* 245.0, found 245.1, and 247.1.

Synthesis of 2-Bromo-4,6-dimethoxyisophthaloyl Dichloride (19). In a 250 mL three-necked round-bottom flask equipped with a mechanical stirrer and a reflux condenser was added 3-bromo-1,5-dimethoxy-2,4-dimethylbenzene (**18**) (2.85 g, 12 mmol), dispersed in 100 mL of a 1:1 mixture of *tert*-butyl alcohol and water. $KMnO_4$ (11.4 g, 72 mmol) was added, and the reaction mixture was heated to reflux for 2 h. After the mixture was cooled to room temperature, more $KMnO_4$ (11.4 g, 72 mmol) was added and the reaction mixture was refluxed for an additional 16 h. After the mixture was cooled to room temperature, the reaction was filtered through Celite and the filtrate was reduced by one-third. The solution was acidified with concentrated HCl. The resulting white precipitate was collected by vacuum filtration and oven-dried (<80 °C) overnight to give 2.30 g (65% yield) of 2-bromo-4,6-dimethoxyisophthalic acid as a pale yellow solid: IR (thin film) 3463, 1663 cm^{-1}. To a suspension of 2-bromo-4,6-dimethoxyisophthalic acid (1.5 g, 5 mmol) in benzene (40 mL) and a drop of DMF was added $SOCl_2$ (9 mL, 61 mmol) at 0 °C. After the mixture was refluxed for 3 h, excess $SOCl_2$ was removed by distillation, which gave 2-bromo-4,6-dimethoxyisophthaloyl dichloride (**19**) in 99% yield (1.6 g) as a pale yellow solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.49 (s, 1H), 3.97 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 158.3, 123.0, 114.2, 94.6, 56.7; MS (CI, CH_4) LRMS calcd for $C_{10}H_7BrCl_2O_4$ + H requires *m/z* 340.89, found 340.9 and 342.9.

Synthesis of [(*S,S*)-(MeO)$_2$Phebox-*i*-Pr]Br (4a). A solution of 2-bromo-4,6-dimethoxyisophthaloyl dichloride (**19**) (110 mg, 0.324 mmol) in dichloromethane (5 mL) was slowly added to a solution of L-valinol (70 mg, 0.679 mmol) and triethylamine (0.2 mL, 1.4 mmol) in dichloromethane (5 mL) at 0 °C. The mixture was stirred at room temperature for 5 h. Formation of the intermediate diamide/dialcohol was monitored by TLC. The volatiles were removed under reduced pressure to afford the crude bis(amide), which was used without further purification. Acetonitrile (5 mL), PPh_3 (254.6 mg, 0.972 mmol), and triethylamine (98 mg, 0.972 mmol) were added to the crude bis(amide). The temperature was reduced to 0 °C, after which CCl_4 (150 mg, 0.972 mmol) was slowly added via syringe. The reaction mixture was warmed to room temperature overnight, after which the mixture was quenched with H_2O (10 mL) and the volatiles were removed in vacuo. The residue was dissolved in H_2O (50 mL) and dichloromethane (100 mL). After separation of the layers, the organic layer was washed with H_2O (30 mL) and brine (30 mL). The combined aqueous layers were extracted with dichloromethane (100 mL). The combined organic layers were dried on Na_2SO_4 and filtered. After the solvent was removed in vacuo, the crude product was purified by silica gel column chromatography (20% EtOAc/hexanes) to afford **4a** as a colorless oil: 123 mg (87% after two steps); $[\alpha]^{19}_D = -64.75$ (*c* 1 in $CHCl_3$); IR (thin film) 1652 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.39 (s, 1H), 4.39 (m, 2H), 4.14 (m, 4H), 3.82 (s, 6H), 1.93(m, 2H), 1.02 (d, J = 6.5 Hz, 6H), 0.92 (d, J = 6.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6, 160.3, 124.2, 113.5, 94.0, 72.4, 70.1, 56.1, 32.2, 18.74, 18.19; MS (ESI) LRMS calcd for $C_{20}H_{27}BrN_2O_4$ + H requires *m/z* 439.11, found 439.12 and 441.11.

Synthesis of 1,5-Dibromo-2,3,4-trimethoxybenzene (S-5). To a stirred solution of 1,2,3-trimethoxybenzene (**20**) (4 g, 24 mmol) in CH_2Cl_2 (40 mL) was added dropwise a 1.0 M solution of bromine in CH_2Cl_2 (8.4 g, 53 mmol) at 0 °C via cannula over a 2 min period under argon. The reaction was stirred for 1 h at room temperature; progress was monitored by TLC analysis. The product was washed with saturated sodium thiosulfate until the organic phase became colorless, dried with sodium sulfate and concentrated under reduced pressure to give 7.4 g (97%) of pure 1,5-dibromo-2,3,4-trimethoxybenzene (**S-5**) as a colorless liquid after simple distillation: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 1H), 3.94 (s, 3H), 3.9 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.8, 148.2, 129.7, 112.2, 61.2, 60.9; MS (CI, CH_4) LRMS calcd for $C_9H_{10}Br_2O_3$ + H requires *m/z* 324.9, found 324.9, 235.9, and 237.9.

Synthesis of 2,3,4-Trimethoxy-1,5-dimethylbenzene (S-6). A *n*-BuLi (1.66 g, 26 mmol) solution was added to a solution of 1,5-dibromo-2,3,4-trimethoxybenzene (**S-5**) (7 g, 22 mmol) in 100 mL of ether at −78 °C under argon, and the cloudy solution was stirred at −78 °C for 30 min. Iodomethane (3.3 mL, 52.8 mmol) was added slowly at −78 °C under argon via syringe. The mixture was allowed to warm to room temperature and stirred for 1 h; the mixture became clear. A second addition of *n*-BuLi (1.66 g, 26 mmol) was added at −78 °C under argon and stirred at −78 °C for 30 min. Iodomethane (3.3 mL, 52.8 mmol) was added again slowly at −78 °C under argon via syringe. The mixture was allowed to warm to room temperature and stirred for 1 h. The mixture was diluted with ether, quenched with aqueous NH_4Cl, washed with 1 N NaOH, water, and brine, dried with sodium sulfate, and concentrated under reduced pressure to give 4.2 g (99%) of pure 2,3,4-trimethoxy-1,5-dimethylbenzene (**S-6**) as a colorless liquid after distillation under reduced pressure: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.70 (s, 1H), 3.92 (s, 3H), 3.84 (s, 6H), 2.20 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 146.1, 126.3, 126.1, 60.5, 60.3, 15.3; MS (CI, CH_4) LRMS calcd for $C_{11}H_{16}O_3$ + H requires *m/z* 197.11, found 197.1.

Synthesis of 1-Bromo-3,4,5-trimethoxy-2,6-dimethylbenzene (21). To a stirred solution of 2,3,4-trimethoxy-1,5-dimethylbenzene (**S-6**) (2 g, 10 mmol) in CH_2Cl_2 (20 mL) was added dropwise a 1.0 M solution of bromine (3.18 g, 11 mmol) in CH_2Cl_2 (10 mL) at 0 °C via cannula over a 2 min period under argon. The reaction was stirred for 2 h at room temperature; progress was monitored by TLC analysis. The product was washed with saturated sodium thiosulfate until the organic phase became colorless, dried with sodium sulfate and concentrated under reduced pressure to give 2.4 g (86%) of pure 1-bromo-3,4,5-trimethoxy-2,6-dimethylbenzene (**21**) as colorless oil after silica gel column chromatography: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.90 (s, 3H), 3.81 (s, 6H), 2.32 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 145.6, 127.7, 121.8, 60.8, 60.7, 16.47; MS (CI, CH_4) LRMS calcd for $C_{11}H_{15}BrO_3$ + H requires *m*/*z* 275.02, found 275.0 and 277.0.

Synthesis of 2-Bromo-4,5,6-trimethoxyisophthaloyl dichloride (22). In a 250 mL three-necked round-bottom flask equipped with a mechanical stirrer and a reflux condenser was added 1-bromo-3,4,5-trimethoxy-2,6-dimethylbenzene (**21**) (2 g, 7.3 mmol), dispersed in 30 mL of water and NaOH (2.34 g, 58.4 mmol). The mixture was heated to 100 °C. A hot solution of $KMnO_4$ (6.95 g, 44 mmol) in 100 mL of water was added, and the reaction mixture was stirred at 100 °C for 8 h. After the mixture was cooled to room temperature, the reaction was filtered through Celite and the filtrate was reduced by one-third. The solution was acidified with concentrated HCl. The resulting white precipitate was collected by vacuum filtration and the precipitate collected and oven-dried (<80 °C) overnight to give 1.42 g (52% yield) of 2-bromo-4,5,6-trimethoxyisophthalic acid as a white solid: IR (thin film) 3460, 1675 cm^{-1}. To a suspension of 2-bromo-4,5,6-trimethoxyisophthalic acid (1 g, 3 mmol) in benzene (40 mL) and a drop of DMF was added $SOCl_2$ (9 mL, 61 mmol) at 0 °C. After the mixture was refluxed for 3 h, excess $SOCl_2$ was removed by distillation, which gave 2-bromo-4,5,6-trimethoxyisophthaloyl dichloride (**22**) in 99% yield (1.1 g) as a pale yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (s, 6H), 3.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.04, 152.34, 145.2, 130.8, 105.7, 62.07, 61.13; MS (CI, CH_4) LRMS calcd for $C_{11}H_9BrCl_2O_5$ + H requires *m*/*z* 370.9, found 370.9 and 372.9.

Synthesis of [(*S*,*S*)-(MeO)$_3$Phebox-*i*-Pr]Br (5a). A solution of 2-bromo-4,5,6-trimethoxyisophthaloyl dichloride **22** (1 g, 2.7 mmol) in dichloromethane (10 mL) was slowly added to a solution of L-valinol (1.114 mg, 11 mmol) and triethylamine (6.3 mL, 45 mmol) in dichloromethane (20 mL) at 0 °C. The mixture was stirred at room temperature for 5 h. Formation of the intermediate diamide/dialcohol was monitored by TLC. Then, methanesulfonyl chloride (1.5 g, 13.2 mmol) was added at 0 °C, and the mixture was stirred at room temperature for 16 h. Formation of the product **5a** 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 sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography (20% EtOAc/hexanes) to give [(*S*,*S*)-(MeO)$_3$Phebox-*i*-Pr]Br (**5a**) in 68% yield after two steps (862 mg, 1.83 mmol) as a white solid: $[\alpha]^{19}_D$ = −67.86 (*c* 1 in $CHCl_3$); IR (thin film) 1650 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.41 (t, J = 8.8 Hz, 2H), 4.16 (m, 4H), 3.88 (s, 6H), 3.84 (s, 3H), 1.87 (m, 2H), 1.03 (d, J = 4.5 Hz, 6H), 0.98 (d, J = 4.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0, 154.2, 145.5, 122.9, 116.3, 72.8, 70.3, 61.6, 60.8, 32.4, 18.7, 18.39; MS (ESI) LRMS calcd for $C_{21}H_{29}BrN_2O_5$ + H requires *m*/*z* 469.12, found 469.11 and 471.11.

Typical Procedure for the Synthesis of (NCN)MX Pincer Complexes. A mixture of (NCN)X (**1**−**5**) (1 equiv) and $Ni(COD)_2$ (1.1 equiv) or Pd_2dba_3 (1.1 equiv) was stirred in dry toluene at room temperature, by which time the reaction was deemed complete by TLC (60% EtOAc/hexanes) in 2 or 3 h. The reaction mixture was filtered through silica eluting with toluene followed by ethyl acetate. The yellow band was collected and the solvent was removed under reduced pressure to give (NCN)MX (**23**−**40**). A sample suitable for X-ray analysis was prepared by slow evaporation of dichloromethane solution in air.

Typical Procedure for the Synthesis of (NCN)MClO$_4$ Pincer Complexes. A mixture of (NCN)MX (**23**−**40**) (1 equiv) and $AgClO_4$ (1.2 equiv) was stirred in dry dichloromethane for 2 h at room temperature, under argon and wrapped in aluminum foil to protect the reaction mixture from light, and the reaction was monitored by TLC (60% EtOAc/hexanes). The reaction mixture was filtered through Celite eluting with dichloromethane. The solvent was removed under reduced pressure to give **41**−**58**. A sample of **41** suitable for X-ray analysis was prepared by slow evaporation of a dichloromethane solution in air.

Synthesis of [(*R*,*R*)-Phebox-Ph]NiBr (24). A mixture of [(*R*,*R*)-Phebox-Ph]Br (**1b**) (171 mg, 0.385 mmol) and $Ni(COD)_2$ (115.2 mg, 0.424 mmol) was stirred in dry toluene (9 mL) for 2 h at room temperature, by which time the reaction was deemed complete by TLC (60% EtOAc/hexanes). The reaction mixture was filtered through silica eluting with ethyl acetate. The yellow band was collected and the solvent was removed under reduced pressure to give **24** as a yellow solid (160 mg, 0.32 mmol) in 76% yield. A sample suitable for X-ray analysis was prepared by slow evaporation of dichloromethane solution in air to give bright yellow crystals: IR (thin film) 1650 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.27 (m, 12H), 7.20 (t, J = 5.6 Hz, 1H), 5.09 (dd, J = 4.1 Hz, 2H), 4.94 (t, J = 8.6 Hz, 2H), 4.68 (dd, J = 4.3 Hz, 2H).

Synthesis of [(*R*,*R*)-*t*-BuPhebox-Ph]NiBr (27). A mixture of [(*R*,*R*)-*t*-BuPhebox-Ph]Br (**2b**) (193 mg, 0.385 mmol) and $Ni(COD)_2$ (115.2 mg, 0.424 mmol) was stirred in dry toluene (9 mL) for 2 h at room temperature, by which time the reaction was deemed complete by TLC (60% EtOAc/hexanes). The reaction mixture was filtered through silica eluting with ethyl acetate. The yellow band was collected and the solvent was removed under reduced pressure to give **27** as a yellow solid (207 mg, 0.37 mmol) in 96% yield. A sample suitable for X-ray analysis was prepared by slow evaporation of a dichloromethane solution in air to give bright yellow crystals: IR (thin film) 1650 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (s, 2H), 7.28−7.34 (m, 10H), 5.07 (dd, J = 4.3 Hz, 2H), 4.96 (t, J = 8.6 Hz, 2H), 4.68 (dd, J = 4.3 Hz, 2H), 1.36 (s, 9H).

Synthesis of [(*S*,*S*)-*t*-BuPhebox-*i*-Pr]PdI (35). A mixture of [(*S*,*S*)-*t*-BuPhebox-*i*-Pr]I (**2a**) (48.2 mg, 0.1 mmol) and $Pd_2(dba)_3$ (50 mg, 0.11 mmol) was stirred in dry toluene (5 mL) for 3 h at room temperature, by which time the reaction was deemed complete by TLC (60% EtOAc/hexanes). The reaction mixture was filtered through silica eluting with toluene to remove dba. The silica gel was then washed and separated with ethyl acetate to give a yellow solution, which was collected, and the solvent was removed under reduced pressure to give **35** as a yellow solid (52.5 mg, 0.095 mmol) in 95% yield. A sample suitable for X-ray analysis was prepared by slow evaporation of a dichloromethane solution in air to give light yellow crystals: IR (thin film) 1633 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (s, 2H), 4.73 (dd, J = 4.3 Hz, 2.5 Hz, 2H), 4.60 (t, J = 5.4 Hz, 2H), 4.38 (m, 2H), 2.96 (m, 2H), 1.33 (s, 9H), 0.95 (d, J = 6.3 Hz, 6H), 0.79 (d, J = 6.3 Hz, 6H).

Synthesis of [(*R*,*R*)-*t*-BuPhebox-Ph]PdBr (36). A mixture of [(*R*,*R*)-*t*-BuPhebox-Ph]Br (**2b**) (50.2 mg, 0.1 mmol) and $Pd_2(dba)_3$ (50 mg, 0.11 mmol) was stirred in dry toluene (5 mL) for 3 h at room temperature, by which time the reaction was deemed complete by TLC (60% EtOAc/hexanes). The reaction mixture was filtered through silica eluting with toluene to remove dba. The silica gel was then washed and separated with ethyl acetate to give a yellow solution, which was collected, and the solvent was removed under reduced pressure to give **36** as a yellow solid (44 mg, 0.08 mmol) in 88% yield. A sample suitable for X-ray analysis was prepared by slow evaporation of a dichloromethane solution in air to give

light yellow crystals: IR (thin film) 1635 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (s, 2H), 7.29−7.35 (m, 10H), 5.38 (q, J = 4.3 Hz, 2H), 5.03 (t, J = 5.6 Hz, 2H), 4.77 (q, J = 4.3 Hz, 2H), 1.37(s, 9H).

Synthesis of [(*S,S*)-Phebox-*i*-Pr]NiClO$_4$·H$_2$O (41). A mixture of [(*S,S*)-Phebox-*i*-Pr]NiBr (**23**)[10] (207 mg, 0.37 mmol) and $AgClO_4$ (82 mg, 0.42 mmol) was stirred in dry dichloromethane (10 mL) for 2 h at room temperature, under argon and wrapped in aluminum foil to protect the reaction mixture from light, and the reaction was monitored by TLC (60% EtOAc/hexanes). The reaction mixture was filtered through Celite eluting with dichloromethane. The solvent was removed under reduced pressure to give **41** as a red solid (211 mg, 0.37 mmol) in quantitative yield. A sample suitable for X-ray analysis was prepared by slow evaporation of a dichloromethane solution in air to give a greenish-yellow crystal.

Synthesis of [(*R,R*)-*t*-BuPhebox-Ph]PdClO$_4$·H$_2$O (54). A mixture of [(*R,R*)-*t*-BuPhebox-Ph]PdBr (**36**) (20 mg, 0.03 mmol) and $AgClO_4$ (10.3 mg, 0.05 mmol) was stirred in dry dichloromethane (10 mL) for 2 h at room temperature, under argon and wrapped in aluminum foil to protect the reaction mixture from light, and the reaction was monitored by TLC (60% EtOAc/hexanes). The reaction mixture was filtered through Celite eluting with dichloromethane. The solvent was removed under reduced pressure to give **54** as a yellow solid (19 mg, 0.03 mmol) in quantitative yield: IR (thin film) 1645 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 (s, 2H), 7.32−7.42 (m, 10H), 5.43 (t, J = 6.3 Hz, 2H), 5.25 (t, J = 8.6 Hz, 2H), 4.64 (t, J = 6.3 Hz, 2H), 1.75 (s, 2H), 1.38 (s, 9H).

X-ray Crystal Structure Determination of [(*R,R*)-Phebox-Ph]NiBr (24): $C_{24}H_{19}BrN_2NiO_2$, M = 506.03, yellow needle, 0.09 × 0.06 × 0.01 mm^3, orthorhombic, space group $P2_12_12$ (No. 18), a = 13.1670(9) Å, b = 5.8235(4) Å, c = 13.0951(8) Å, V = 1004.11(12) Å^3, Z = 2, D_c = 1.674 g/cm^3, F_{000} = 512, MWPC area detector, Cu Kα radiation, λ = 1.54178 Å, T = 110(2) K, $2\theta_{max}$ = 120.0°, 7380 reflections collected, 1406 unique (R_{int} = 0.0339). Final GooF = 1.035, R1 = 0.0196, wR2 = 0.0474, R indices based on 1344 reflections with $I > 2\sigma(I)$ (refinement on F^2), 138 parameters, 0 restraints. *Lp* and absorption corrections applied, μ = 3.921 mm^{-1}. Absolute structure parameter = −0.019(19). Displacement ellipsoid plot (50% probability) of **24** is shown in Figure 3 with full numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)−C(1) 1.844(3), Ni(1)−Br(1) 2.3164(5), Ni(1)−N(1) 1.9371(19), N(1)−C(5) 1.301(3), C(1)−Ni(1)−Br(1) 180.0, N(1)−Ni(1)−N(2) 162.27(11), C(1)−Ni(1)−N(1) 81.13(6), Br(1)−Ni(1)−N(1) 98.87(6).

X-ray Crystal Structure Determination of [(*S,S*)-*t*-BuPhebox-*i*-Pr]NiI (26): $C_{33}H_{46.50}I_{1.50}N_3Ni_{1.50}O_3$, M = 811.65, yellow needle, 0.50 × 0.10 × 0.10 mm^3, monoclinic, space group $P2_1$ (No. 4), a = 5.901(3) Å, b = 32.739(19) Å, c = 18.306(10) Å, β = 95.539(9)°, V = 3520(3) Å^3, Z = 4, D_c = 1.532 g/cm^3, F_{000} = 1644, CCD area detector, Mo Kα radiation, λ = 0.71073 Å, T = 60(2) K, $2\theta_{max}$ = 50.0°, 33 048 reflections collected, 12 179 unique (R_{int} = 0.0575). Final GooF = 1.029, R1 = 0.0413, wR2 = 0.0761, R indices based on 9396 reflections with $I > 2\sigma(I)$ (refinement on F^2), 813 parameters, 133 restraints. *Lp* and absorption corrections applied, μ = 2.161 mm^{-1}. Absolute structure parameter = −0.005(14). Displacement ellipsoid plot (50% probability) of **26** is shown in Figure 3) with full numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(A)−C(8A) 1.841(6), Ni(A)−I(A) 2.5301(16), Ni(A)−N(1A) 1.946(5), Ni(A)−N(2A) 1.929(5), N(1A)−C(1A) 1.291(8), N(2A)−C(17A) 1.295(7), C(8A)−Ni(A)−I(A) 177.25(19), N(1A)−Ni(A)−N(2A) 162.0(2), C(8A)−Ni(A)−N(1A) 81.2(2), C(8A)−Ni(A)−N(2A) 80.9(2), I(A)−Ni(A)−N(1A) 99.60(15), I(A)−Ni(A)−N(2A) 98.36(15).

X-ray Crystal Structure Determination of [(*R,R*)-*t*-BuPhebox-Ph]NiBr (27): $C_{112}H_{108}Br_4N_8Ni_4O_8$, M = 2248.54, colorless needle, 0.12 × 0.01 × 0.01 mm^3, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 6.2679(8) Å, b = 10.9501(13) Å, c = 35.488(5) Å, V = 2435.7(5) Å^3, Z = 1, D_c = 1.533 g/cm^3, F_{000} = 1152, MWPC area detector, Cu Kα radiation, λ = 1.54178 Å, T = 293(2) K, $2\theta_{max}$ = 120.0°, 17 814 reflections collected, 3349 unique (R_{int} = 0.1626). Final GooF = 1.035, R1 = 0.0720, wR2 = 0.1645, R indices based on 2845 reflections with $I > 2\sigma(I)$ (refinement on F^2), 307 parameters, 326 restraints. *Lp* and absorption corrections applied, μ = 3.293 mm^{-1}. Absolute structure parameter = 0.02(5). Displacement ellipsoid plot (50% probability) of **27** is shown in Figure 3 with full numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)−C(11) 1.835(10), Ni(1)−Br(1) 2.3443(18), Ni(1)−N(1) 1.896(8), Ni(1)−N(2) 1.929(8), N(1)−C(1) 1.279(13), N(2)−C(20) 1.292(12), C(11)−Ni(1)−Br(1) 178.4(3), N(1)−Ni(1)−N(2) 161.9(3), C(11)−Ni(1)−N(1) 80.2(4), C(11)−Ni(1)−N(2) 81.8(4), Br(1)−Ni(1)−N(1) 99.4(3), Br(1)−Ni(1)−N(2) 98.6(2).

X-ray Crystal Structure Determination of [(*S,S*)-*t*-BuPhebox-*i*-Pr]PdI (35): $C_{22}H_{31}IN_2O_2Pd$, M = 588.79, colorless needle, 0.20 × 0.02 × 0.02 mm^3, monoclinic, space group $P2_1$ (No. 4), a = 6.0186(12) Å, b = 32.173(6) Å, c = 12.237(3) Å, β = 94.131(9)°, V = 2363.3(8) Å^3, Z = 4, D_c = 1.655 g/cm^3, F_{000} = 1168, MWPC area detector, Cu Kα radiation, λ = 1.54184 Å, T = 110(2) K, $2\theta_{max}$ = 119.9°, 18 046 reflections collected, 6390 unique (R_{int} = 0.1589). Final GooF = 1.015, R1 = 0.0784, wR2 = 0.1515, R indices based on 4041 reflections with $I > 2\sigma(I)$ (refinement on F^2), 505 parameters, 601 restraints. *Lp* and absorption corrections applied, μ = 16.731 mm^{-1}. Absolute structure parameter = 0.013(15). Displacement ellipsoid plot (50% probability) of **35** is shown in Figure 3 with full numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1A)−C(1A) 1.944(12), Pd(1A)−I(1A) 2.6846(18), Pd(1A)−N(1A) 2.073(11), Pd(1A)−N(2A) 2.077(11), N(1A)−C(11A) 1.306(17), N(2A)−C(17A) 1.296(17), C(1A)−Pd(1A)−I(1A) 178.5(4), N(1A)−Pd(1A)−N(2A) 157.1(4), C(1A)−Pd(1A)−N(1A) 79.2(4), C(1A)−Pd(1A)−N(2A) 79.9(4), I(1A)−Pd(1A)−N(1A) 102.2(3), I(1A)−Pd(1A)−N(2A) 100.7(3).

X-ray Crystal Structure Determination of [(*S,S*)-*t*-BuPhebox-Bn]PdI (37): $C_{30}H_{31}BrN_2O_2Pd$, M = 637.88, yellow needle, 0.10 × 0.01 × 0.01 mm^3, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 6.6808(7) Å, b = 19.625(2) Å, c = 20.422(2) Å, V = 2677.6(5) Å^3, Z = 4, D_c = 1.582 g/cm^3, F_{000} = 1288, MWPC area detector, Cu Kα radiation, λ = 1.54178 Å, T = 110(2) K, $2\theta_{max}$ = 120.0°, 19 307 reflections collected, 3920 unique (R_{int} = 0.0846). Final GooF = 1.005, R1 = 0.0453, wR2 = 0.1079, R indices based on 3494 reflections with $I > 2\sigma(I)$ (refinement on F^2), 326 parameters, 0 restraints. *Lp* and absorption corrections applied, μ = 7.570 mm^{-1}. Absolute structure parameter = 0.000(14). Displacement ellipsoid plot (50% probability) of **37** is shown in Figure 3 with full numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)−C(1) 1.951(8), Pd(1)−Br(1) 2.5226(10), Pd(1)−N(1) 2.071(7), Pd(1)−N(2) 2.074(7), N(1)−C(7) 1.294(10), N(2)−C(21) 1.276(10), C(1)−Pd(1)−Br(1) 178.2(2), N(1)−Pd(1)−N(2) 157.7(3), C(1)−Pd(1)−N(1) 78.3(3), C(1)−Pd(1)−N(2) 79.3(3), Br(1)−Pd(1)−N(1) 103.39(17), Br(1)−Pd(1)−N(2) 98.93(19).

X-ray Crystal Structure Determination of [(*S,S*)-Phebox-*i*-Pr]NiClO$_4$·H$_2$O (41): $C_{18}H_{25}ClN_2NiO_7$, fw = 475.56, yellow plate, 0.26 × 0.12 × 0.12 mm^3, orthorhombic, $P2_12_12_1$ (No. 19), a = 6.1341(6) Å, b = 11.6353(10) Å, c = 29.016(3) Å, β = 90°, V = 2070.9(3) Å^3, T = 90(2) K, λ = 0.71073 Å, Z = 4, D(calcd) = 1.25 Mg/m^3, F(000) = 992, μ(Mo KR)) 1.108 mm^{-1}. 23 472 reflections were collected on a Bruker APEX II diffractometer with CCD area detector at a temperature of 90(2) K. Maximum theta was 28.73. The *hkl* ranges were −8/8, −15/15, −39/38; 4942 unique reflections measured [R_{int} = 0.0277]. Semiempirical absorption correction from equivalents; maximum and minimum correction

factors: 0.8785; 0.7615. The structure was solved with automated direct methods and refined with SHELXL-97 with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H atom is attached. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0339P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Goodness-of-fit on F^2 was 1.041, R1 [for 4685 reflections with $I > 2\sigma(I)$] = 0.0224, wR2 = 0.00539. Data/restraints/ parameters: 4942/48/314. Largest difference Fourier peak and hole: 0.341 and −0.171 e/Å^3. Displacement ellipsoid plot (50% probability) of **41** is shown in Figure 3 with full numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)−C(5) 1.8333(14), Ni(1)−O(3) 1.9403(12), Ni(1)−N(1) 1.9195(13), Ni(1)−N(2) 1.9101(13), Cl(1)−O(3) 1.366(9), N(1)−C(3) 1.296(2), N(2)−C(10) 1.292(2), C(5)−Ni(1)−O(3) 177.35(6), N(1)−Ni(1)−N(2) 163.31(6), C(5)−Ni(1)−N(1) 81.69(6), C(5)−Ni(1)−N(2) 81.67(6), O(3)−Ni(1)−N(1) 98.09(5), O(3)−Ni(1)−N(2) 98.59(5).

Acknowledgment. We are grateful to Texas A&M University and the Robert Welch Foundation for financial support. Dr. Joseph H. Reibenspies obtained the X-ray crystal structure data, and Dr. Shane Tichy provided MS services.

Supporting Information Available: Experimental details and spectra for all new compounds and cif X-ray structure data for **2a**, **24**, **26**, **27**, **35**, **37**, and **41**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8004367