Synthesis and Structural Characterization of Lithium and Trimethyltin Complexes of 2,6-Bis(oxazolinyl)phenyl

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The treatment of 2,6-bis(oxazolinyl)phenyl bromide (Phebox-Br) with *n*-BuLi affords a Phebox-Li complex. Subsequent transmetalation with [$SnClMe_3$] affords a Phebox-Sn complex. The Phebox ligand can coordinate to a transition metal in various terdentate fashions; both the oxazoline oxygen and the imine nitrogen are perfectly positioned for chelation; "NCN", "OCO", or mixed terdentate coordination modes are theoretically possible using this ligand. The structural properties and NMR spectra of [Sn(Me,Me-Phebox)Me_3] (**2**) and [Li(R,R′-Phebox)] complexes **3a** (R = R′ = Me), **3b** (R = *i*Pr, R′ = H), and **3c** (R = *t*Bu, R′ = H) were investigated. It was found that **2** exhibits no chelation of the Phebox ligand to the Sn center in this case. The [Li(R,R′-Phebox)] complex **3a** has been crystallographically characterized and is in the form of a molecular dimer (i.e. [Li(Phebox)]$_2$), containing two formally three-center−two-electron bonds in a four-membered Li_2C_2 ring. The formal Phebox anion is bonded to the lithium cation via the two ortho imine N centers and the intraannular aromatic C atom. The $^{13}C\{^1H\}$ NMR signal of C_{ipso}, being a seven-line pattern with coupling constant $^1J(^{13}C-^7Li) = 18$ Hz, confirms that the dimeric structure is maintained in solution at room temperature. Variable-temperature (VT) NMR studies of **3a** indicate that a fluxional process is occurring at room temperature, which can be frozen out below −16 °C ($\Delta G^{\ddagger} = 56$ kJ/mol). This fluxional process is not observed in VT-NMR studies on **3b**,**c**. This is likely due to the presence of bulky (*i*Pr or *t*Bu) substituents that effectively shut down the pathways to rapid inversion of the puckering of the five-membered chelate ring.

Introduction

Chelating aryl ligands are an important class of ligands in homogeneous catalysis[1] and also in other fields of interest.[1b,2] One of the classes of chelating ligands which is applied in homogeneous catalysis is the monoanionic bis(oxazolinyl)phenyl or Phebox ligand. An interesting feature of Phebox ligands is the ease of synthesis of a number of chiral analogues. Phebox ligands have been previously shown to coordinate in a terdentate fashion;[3] both the oxazoline oxygen and nitrogen can potentially be positioned for chelation, and hence, "NCN", "OCO", or mixed "NCO" terdentate coordination modes are theoretically possible using this class of metal binding agents. In the terdentate bonding mode, Phebox ligands have three C, and O- or N-donor sites in fixed positions. This is due to the fact that the ortho-chelating ligands are connected to the aryl ring by an sp^2 C and one sp^2 N or sp^3 O center. For this reason, the binding is predicted to be less flexible in comparison to the wide variety of bonding modes encountered in the aryldiamine ligands, the so-called "NCN-pincer" ligands.[1b,4] We were interested in the structural properties, both in the solid state and in solution, and the mode of coordination (C,N- vs C,O-chelation) of the Phebox ligand in simple model complexes incorporating Li or Sn metal.[3e] In a triorganotin

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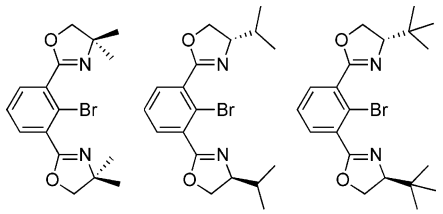


Figure 1. Achiral and chiral Phebox-Br ligands.

Phebox complex, the Phebox fragment will be attached to the Sn nucleus via a direct aryl C−Sn bond. The question then arises as to how the ortho substituents orient themselves relative to the electrophilic Sn center. In an isolated Phebox-Li compound, a dimeric structure is anticipated,[5] although steric constraints could give rise to novel or unusual structural features.

Results and Discussion

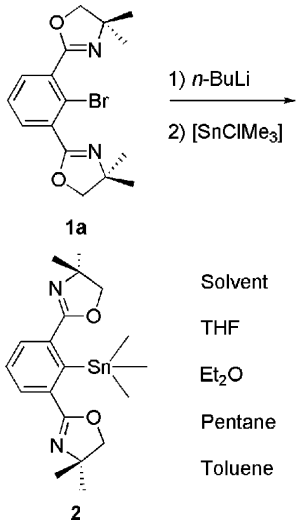
Three different Phebox ligands were synthesized in this work. One achiral Phebox ligand (**1a**) was derived from 2-amino-2-methyl-1-propanol, and two chiral Phebox ligands (**1b**,**c**, respectively; Figure 1) were obtained from L-valinol and L-*tert*-leucinol.

2,6-Bis(4′,4′-dimethyl-2′-oxazolinyl)phenyl bromide ([Me,Me-PheboxBr], **1a**), was synthesized using modified literature procedures.[3e,6] Compound **1a** can be lithiated, via selective Li−Br exchange, with *n*-BuLi in THF solution.[3e] After the product was treated with [$SnClMe_3$], [Sn(Me,Me-Phebox)Me_3] (**2**) was obtained.[3e] To study a possible solvent dependence of this reaction, [Me,Me-PheboxBr] was reacted with *n*-BuLi in both polar coordinating solvents (THF and diethyl ether) and apolar solvents (pentane and toluene) (Scheme 1). The reaction mixture was quenched with [$SnClMe_3$][3e] and the conversion studied by ^{1}H NMR spectroscopy.

In all cases, selective Li−Br exchange occurred and quantitative formation of **2** was observed. Thus, suppression of the directed ortho metalation of **1a** (i.e. metalation at the aryl C-3 position) is accomplished by these synthetic protocols.[7]

The ^{1}H NMR spectrum of a solution of **2** (C_6D_6, room temperature) reveals singlet resonances for both the oxazoline methyl groups and ring methylene protons (δ 1.17 and 3.70 ppm, respectively). The Sn−Me groups are centered at δ 0.46 ppm, with the diagnostic ^{117}Sn/^{119}Sn satellites ($^2J_{H-Sn}$ = 26.7, 27.8 Hz) confirming the presence of the $SnMe_3$ group. It is known that the magnitude of ^{1}H−Sn spin−spin coupling constants are a function of the coordination number in tin(IV) compounds.[8] The observed $^2J_{H-Sn}$ values indicate that the tin center in **2** is tetracoordinated[9] (i.e. with no significant Sn−O or Sn−N coordination). This conclusion is further corroborated by the molecular structure of **2** in the solid state. Single crystals of **2** were obtained by slow evaporation of a pentane solution of the complex at room temperature. A view of the molecular structure is shown in Figure 2.

Scheme 1. Synthesis of [Sn(Me,Me-Phebox)Me_3] in Apolar and Polar Solvents



Solvent	Temp. (°C)	Time (h)	Conversion
THF	-78	0.17	quant.
Et_2O	-78	1	quant.
Pentane	-78	3	quant.
Toluene	-78	3	quant.

The molecule has an approximate local plane of symmetry containing C(4), C(1), Sn, and C(18) (the torsion angle C(18)−Sn−C(1)−C(6) is 99.63(17)°) (RMS deviation of ideal positions ±0.08 Å). The configuration at tin can be described as a distorted tetrahedron, as is shown by the bond angles around tin, where the angle C(1)−Sn−C(18) is opened to 113.6° and the angle C(17)−Sn−C(19) is compressed to 103.70(8)°. The Sn−Me and Sn−Ar bond lengths correspond well with bond lengths reported in the literature (2.08−2.19 and 2.15−2.18 Å) for similar tin compounds.[10] The oxazoline substituents are rotated with respect to the plane defined by the aryl ring by 27.19(10)° (substituent containing O(1)) and 22.81(10)° (substituent containing O(2)). The absence of additional coordination of the Sn center by the oxazoline moieties is further indicated by the position of the Sn center out of the plane of the aryl ring. The angle C(4)−C(1)−Sn is 164.68(10)° (i.e. the Sn center is "lifted" by ∼0.612(1) Å out of the least-squares aryl plane). These structural features point to steric interaction between the $SnMe_3$ group and the oxazoline ring substituents. There is no evidence of the oxazoline N or O atoms interacting with the Sn center, although this is a feature in other tetravalent Sn compounds.[10a,d] The distances between the oxazoline oxygens and the Sn center are 2.9842(13) and 3.0271(14) Å, respectively. These lengths are distinctively

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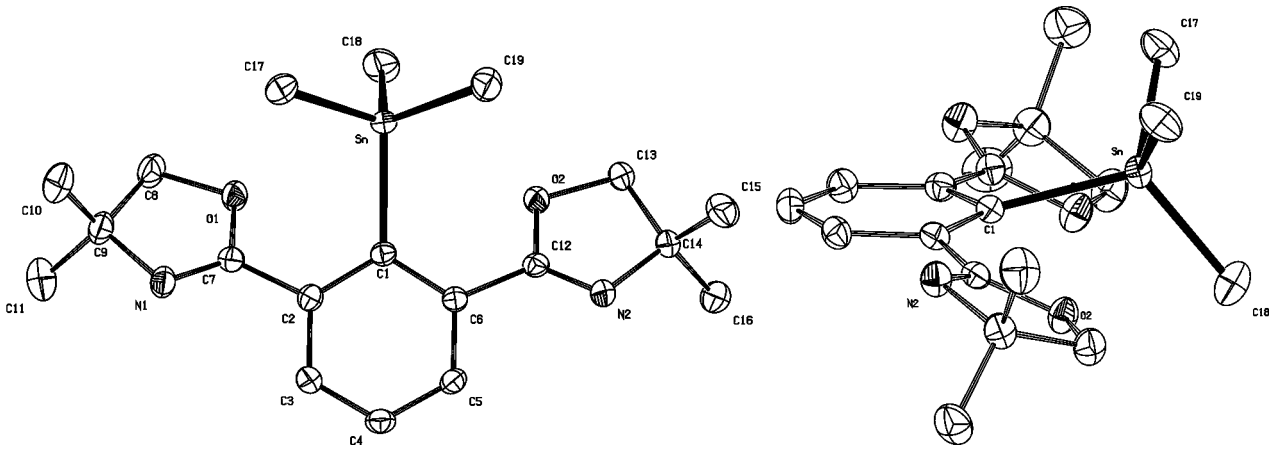
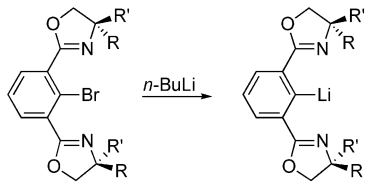


Figure 2. Top and side-on views of the crystal structure of [Sn(Me,Me-Phebox)Me_3]. Hydrogen atoms have been omitted for clarity. Relevant bond distances (Å) and angles (deg): Sn−C(1) = 2.1810(18), Sn−C(17) = 2.150(2), Sn−C(18) = 2.129(3), Sn−C(19) = 2.153(2), Sn−O(1) = 2.9842(13), Sn−O(2) = 3.0271(14); C(1)−Sn−C(17) = 106.03(8), C(1)−Sn−C(18) = 113.64(8), C(1)−Sn−C(19) = 108.45(7), C(17)−Sn−C(18) = 112.18(9), C(17)−Sn−C(19) = 103.70(8), C(18)−Sn−C(19) = 112.18(9).

Scheme 2. Synthesis of [Li(R,R′-Phebox)] Complexes



1a R = R' = Me
1b R = *i*Pr, R' = H
1c R = *t*Bu, R' = H

3a R = R' = Me (66%)
3b R = *i*Pr, R' = H (quant.)
3c R = *t*Bu, R' = H (42%)

longer than corresponding Sn−O distances reported previously for tetraorganotin compounds, where weak Sn−O interactions (2.770, 2.781 Å)[11] are inferred. The oxazoline N is most likely too sterically hindered to approach the tin center, by virtue of the adjacent Me groups in the ring, while the oxazoline O donor site is probably too weak a donor for coordination.

For the structural characterization of [Li(R,R′-Phebox)]$_2$ complexes, **3a** (R = R′ = Me), **3b** (R = *i*Pr, R′ = H), and **3c** (R = *t*Bu, R′ = H) were synthesized and isolated (Scheme 2).

To address the structural motif(s) of these organolithium species, single crystals were obtained from a saturated solution of **3a** (Et_2O, −30 °C). The molecular structure, depicted in Figure 3, confirms the anticipated dimeric form and shows distinct NCN chelation (cf. **2**) of the Phebox ligand.

Both aryl groups bridge the two lithium atoms via a three-center−two-electron $C_{ipso}Li_2$ bonding interaction. Both lithium atoms have distorted-tetrahedral geometries, and the two Phebox ligands are almost perpendicular to each other (angle beween the least-squares planes through the ring atoms is 84.67(7)°) with the two Li atoms above and below the plane of the aryl rings. This type of structure can be in the form of three different modes of chelation (Figure 4) with two different donor atoms (O, N).

From the crystal structure data, it is clear that [Me,Me-PheboxLi]$_2$ (**3a**) is present as aggregate type **A** in the solid state. In the related compound [$(Et_2O)LiC_6H_4C(O)N(iPr)_2$]$_2$,[12] C=O donation is preferred over iPr_2N donation. In our case, imine N coordination is preferred over O donation, which is, to our knowledge, the first crystallographically characterized organolithium compound with intramolecular C=N chelates present in the structure.[13] Synthetically, it also appears that Li−Br exchange is favored over *n*-BuLi addition to the C=N double bond.[14] In addition, the product ArLi species are obviously also unreactive toward the imine functionalities. The C_{ipso}−Li bond lengths (2.25−2.30 Å) are slightly longer than in comparable structures with two donating amine arms (2.19−2.24 Å).[5] The opposite trend is observed for the Li−N bond lengths. These are somewhat shorter (1.99−2.01 Å) than distances found in the literature for amine donor systems (2.07−2.13 Å).[5] The Li···Li distance (2.333(4) Å) is also shorter than in the bis(amino)aryl systems (2.40−2.48 Å).[5] The angles between the nonplanar C_2Li_2 rhombus and the aryl planes (42.39(11) and 42.74(11)°) are smaller than found in other NCN chelating systems (56−59°).[5] Elongation of the C_{ipso}−Li bond distances and shortening of the Li−N and Li···Li distances may be the result of a stronger interaction of the Li centers with the imine groups as opposed to the interaction with tertiary amines. The acute angle Li−C_{ipso}−Li (62°) is smaller than comparable literature values (66−68°),[5] as a result of reduced repulsion between the Li atoms.

The ^{1}H and $^{13}C\{^1H\}$ NMR spectra (room temperature) of **3a**−**c** suggest that all three [Li(R,R′-Phebox)]$_n$ complexes have distinct dimeric structures in solution. The $^{13}C\{^1H\}$ NMR signal for C_{ipso} is observed as a seven-line pattern (intensities 1:2:3:4:3:2:1) and a coupling constant $^1J(^{13}C-^7Li)$ of 18 Hz. This pattern, as well as the magnitude of $^1J_{C-Li}$, is direct proof that C_{ipso} is bonded to two Li atoms. The above coupling constant is similar to the value found for dimeric [Li(C_6H_3(CH_2-

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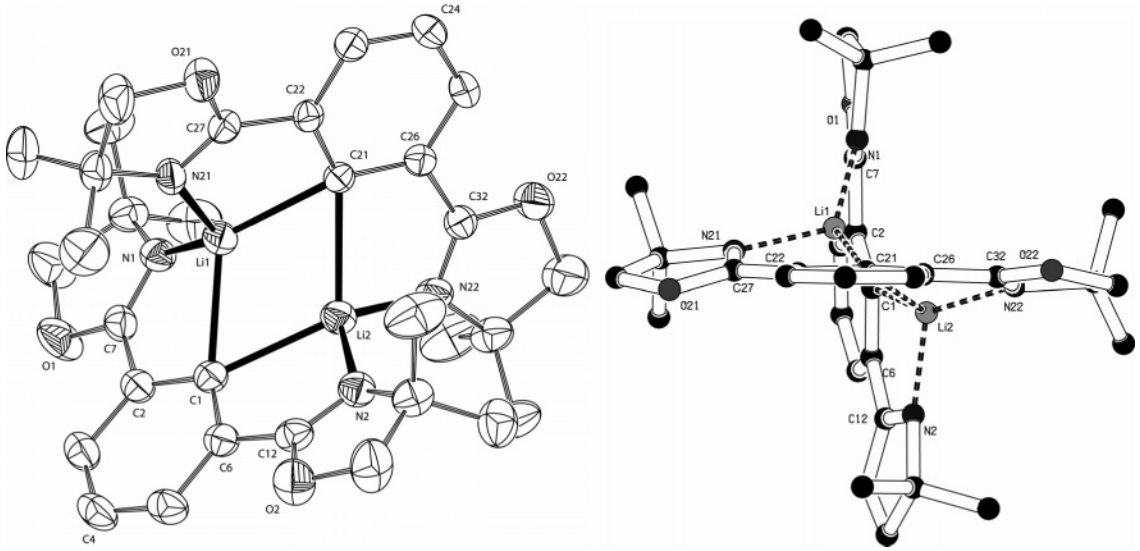

Figure 3. Top and side-on views of the crystal structure of [Li(Me,Me-Phebox)]$_2$. Hydrogen atoms have been omitted for clarity. Relevant bond distances (Å) and angles (deg): C(1)−Li(1) = 2.268(3), C(1)−Li(2) = 2.289(3), C(21)−Li(1) = 2.247(3), C(21)−Li(2) = 2.299(3), Li(1)−N(1) = 2.004(3), Li(1)−N(21) = 1.987(3), Li(2)−N(2) = 1.989(3), Li(2)−N(22) = 2.006(3); Li(1)−C(1)−Li(2) = 61.61(10), Li(1)−C(21)−Li(2) = 61.74(10), C(1)−Li(1)−C(21) = 117.99(13), C(1)−Li(1)−N(1) = 84.46(10), C(1)−Li(1)−N(21) = 114.11(14), N(1)−Li(1)−N(21) = 121.39(14), N(21)−Li(1)−C(21) = 85.76(11), N(1)−Li(1)−C(21) = 135.61(15), C(1)−Li(2)−C(21) = 115.03(12), C(1)−Li(2)−N(2) = 84.78(11), C(1)−Li(2)−N(22) = 139.79(14), N(2)−Li(2)−N(22) = 118.46(14), N(22)−Li(2)−C(21) = 84.24(11), N(2)−Li(2)−C(21) = 117.84(13).

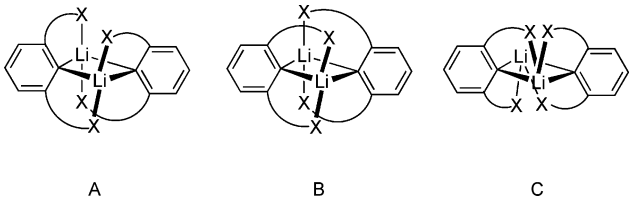

Figure 4. Possible modes of chelation.

$NMe_2)_2$-2,6)]$_2$ (20.5 Hz).[15] Moreover, these features are temperature independent, indicating that the dimeric structure is apparently preserved over the temperature range −60 to 25 °C. Hence, the three-center−two-electron C−Li bonding motif (cf. X-ray data of **3a**) is also retained in solution.

The remaining resonances in the ^{1}H and ^{13}C{^{1}H} NMR spectra of **3a** (toluene-d_8), however, exhibit temperature *dependence*. At 25 °C, the methylene protons and methyl protons appear as singlets in the ^{1}H NMR spectrum; the ^{13}C{^{1}H} NMR spectrum also has two singlet signals for the methylene carbon and methyl substituents, respectively. At −50 °C, the CH_2 grouping now appears (^{1}H NMR) as an AB pattern (δ_A 3.55 ppm, δ_B 3.58 ppm, J_{AB} = 8.6 Hz) and the CMe_2 groups are separated into two singlets (at 0.73 and 0.83 ppm, respectively). This aspect is also apparent in the ^{13}C{^{1}H} NMR spectrum (−60 °C), where two signals at 28.3 and 28.2 ppm are found for the CMe_2 groups.

The described observations can be explained by considering the ring puckering present in the four five-membered chelate rings, as demonstrated by the structure in the solid state. The ring puckering of the four chelate rings is coupled, and all have either the Λ or the Δ configuration. As a result, **3a** exists in the slow-exchange limit as a 1:1 mixture of two enantiomers. In the fast-exchange limit rapid inversion of the ring puckering by rotation (wagging) about the C(4)−C_{ipso}−C'_{ipso}−C(24) axis provides **3a** with an apparent molecular symmetry plane containing the methylene and the C(Me_2) carbon centers. Consequently, this inversion process renders the CH_2 protons and CMe_2 methyl groupings enantiotopic. This view is corroborated by the observation that the CH_2 resonances coalesce (^{1}H NMR) at −16 °C, which corresponds to $\Delta G^{\ddagger}$ = 57 kJ/mol,[16] while the related CMe_2 resonances coalesce at −14 °C and hence a $\Delta G^{\ddagger}$ value of 55 kJ/mol is calculated.[16] The ^{1}H and ^{13}C{^{1}H} NMR spectra of **3b**,**c** (toluene-d_8) do not exhibit the above-mentioned temperature dependence for **3a** at the temperatures studied (−60 to 25 °C). On the basis of the above discussion of **3a** compounds **3b**,**c** are expected to exist in solution as Λ *SS* or the Δ *SS* diastereoisomers (see Figure 5), i.e. exhibiting two ^{1}H and ^{13}C NMR resonance patterns. Most interestingly, only one resonance pattern is observed, which suggests that only one diastereoisomer is present in solution over a wide temperature range: i.e., the inversion process, operative in **3a**, is blocked in **3b**,**c**, resulting in the presence of either the Λ *SS* or the Δ *SS* diastereoisomer. It is conceivable that steric interference between the bulky ring substituents *i*Pr (**3b**) and *t*Bu (**3c**) lock the wagging process about the C(4)−C_{ipso}−C'_{ipso}−C(24) axis, leading to the stabilization of one diastereoisomer over the other.

Both ^{1}H and ^{7}Li NMR signals of **3a** are insensitive to the addition of 1 equiv of diethyl ether, THF, or triethylamine. This suggests that the dimeric structure is not disrupted by these simple bases, and hence, stronger coordination of the bis(oxazoline) substituents is implied.

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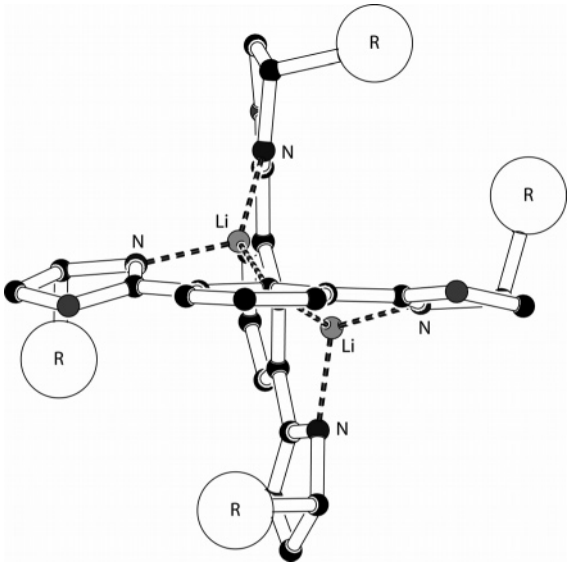

Figure 5. Schematic representation of the structure of one of the proposed diastereoisomers (Λ *SS*) of **3b**,**c**.

Conclusions

The synthesis and structural features of [Sn(Me,Me-Phebox)Me_3] (**2**) and [Li(R,R′-Phebox)] complexes **3a** (R = R′ = Me), **3b** (R = *i*Pr, R′ = H), and **3c** (R = *t*Bu, R′ = H) were investigated. It was found that the Phebox ligand in **2** is η^1(C)-bonded to the Sn center: i.e., no chelation of the bis(oxazoline) substituents occurs. The [Li(R,R′-Phebox)] complex **3a** (R = R′ = Me) exists both in solution (^{13}C NMR) and in the solid state (X-ray) as a dimer containing formal three-center−two-electron bonds in a Li_2C_2 central ring. The Phebox ligand is η^3-(N,C,N)-bonded to the lithium centers, presenting the first structurally characterized aryllithium complex containing intramolecular imine N−lithium coordination. The [Li(R,R′-Phebox)] complexes can be prepared in high yield and are excellent starting materials for the preparation of R,R′-Phebox−metal complexes which can be used as transmetalating reagents ([Au(Me,Me-Phebox)(PPh_3)],[17a] [(Au(Me,Me-Phebox))$_2$(dppbp)])[17b] and as homogeneous catalysts (R,R′-Phebox−Pd,[3b,d,g,i] −Pt,[3c,g,i] −Rh[3e,f,h]).

Experimental Section

All experiments were carried out under a dry, oxygen-free nitrogen atmosphere, using standard Schlenk techniques. Solvents were dried and distilled from sodium (pentane, toluene), Na/benzophenone (diethyl ether, tetrahydrofuran), CaH_2 (CH_2Cl_2, CH_3CN), or KOH (Et_3N) prior to use. *n*-BuLi (1.6 M in hexanes) was supplied by Acros and used as received. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Inova 300 spectrometer. ^{7}Li NMR (5 mm tube) and NMR experiments with diethyl ether, tetrahydrofuran, and triethylamine (10 mm tube) were recorded on a Varian Mercury 200 spectrometer. Benzene-d_6 and toluene-d_8 were purchased from Cambridge Isotope Laboratories, distilled from Na, and stored in a nitrogen-filled M. Braun glovebox. Other NMR solvents (acetone-d_6, $CDCl_3$) were used as received. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal as an internal standard. The ^{7}Li NMR spectra are referenced to LiCl (1.0 M) in D_2O as an external standard. 2-Bromoisophthalic acid,[6a] L-valinol, and L-*tert*-leucinol[18] were synthesized according to literature procedures. (R,R′-Phebox)Br was synthesized according to a combination of literature procedures.[3e,6] All other chemicals were purchased from either Acros or Aldrich and used as received. Elemental analysis were performed by Kolbe, Mikroanalytisches Laboratorium, Mülheim/Ruhr, Germany.

Synthesis of [R,R′-PheboxBr] Compounds. (a) [Me,Me-PheboxBr] (1a). Thionyl chloride (12 mL, 164 mmol) was added to 2-bromoisophthalic acid (9.8 g, 40 mmol). The mixture was refluxed overnight, and the residual $SOCl_2$ was removed in vacuo. A portion of the resulting 2-bromoisophthalic acid chloride (6.9 g, 25 mmol) was weighed into a 500 mL one-necked round-bottom flask, equipped with a nitrogen inlet. The acid was dissolved in CH_2Cl_2 (25 mL), and the temperature of the flask was reduced to 0 °C (ice/water bath). In a separate Schlenk vessel, 2-amino-2-methyl-1-propanol (5.07 g, 56.3 mmol) and NEt_3 (13.9 mL, 100 mmol) were dissolved in CH_2Cl_2 (35 mL) and slowly added by syringe to the cooled 2-bromoisophthalic acid chloride solution. The reaction mixture was stirred overnight, after which time the solvent was removed in vacuo. Acetonitrile (200 mL), PPh_3 (23.7 g, 90.6 mmol), and Et_3N (15.0 mL, 108 mmol) were added to the residue. The temperature was reduced to 0 °C, after which time CCl_4 (20.7 mL, 215 mmol) was slowly added via a syringe. After it was stirred overnight, the mixture was quenched with H_2O (10 mL) and the volatiles were removed in vacuo. The residue was dissolved in H_2O (200 mL) and ethyl acetate (200 mL). After separation of the layers, the organic layer was washed with H_2O (100 mL). The combined aqueous layers were extracted with ethyl acetate (3 × 100 mL), dried ($MgSO_4$), and filtered. After the solvent was removed in vacuo, the residue was stirred for 3 h in Et_2O (250 mL). The suspension was filtered, the residue was washed with additional Et_2O (200 mL), and the filtrate was dried in vacuo. The crude product was filtered over alumina (neutral Merck 90: Et_2O; R_f 0.25), resulting in the recovery of 6.95 g (20 mmol, 81%) of the white solid product. ^{1}H NMR (300 MHz, acetone-d_6): δ 1.35 (s, 12 H, CMe_2), 4.14 (s, 4H, CH_2), 7.52 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, Ar *H*), 7.67 (d, 2H, $^3J_{H-H}$ = 7.5 Hz, Ar *H*). ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 28.4 (CMe_2), 69.1 (*C*Me$_2$), 79.9 (O*C*H$_2$), 121.7 (Ar *C*), 128.1 (Ar *C*), 133.2 (Ar *C*), 133.7 (Ar *C*), 161.7 (O*C*N). Anal. Calcd for $C_{16}H_{19}BrN_2O_2$: C, 54.71; H, 5.45; N, 7.98. Found: C, 54.63; H, 5.38; N, 7.96.

Synthesis of [(*S*,*S*)-*i*Pr,H-PheboxBr] (1b). A procedure analogous to the synthesis of **1a** was employed using 2-bromoisophthalic acid (5.05 g, 21 mmol) and L-valinol (4.91 g, 48 mmol), giving a light yellow oil. Yield: 5.16 g (67%). R_f value (Et_2O): 0.28. $[\alpha]^{20}_D = -63.2°$ (c = 0.10 g/mL, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.98 (d, 6H, $^3J_{H-H}$ = 6.6 Hz, CHMe_2), 1.04 (d, 6H, $^3J_{H-H}$ = 6.6 Hz, CHMe_2), 1.91 (septet, 2H, $^3J_{H-H}$ = 6.6 Hz, C*H*Me$_2$), 4.18 (m, 4H, OCH_2), 4.45 (m, 2H, C*H*N), 7.37 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, Ar *H*), 7.65 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, Ar *H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 32.3 (CMe_2), 60.0 (*C*Me$_2$), 70.2 (*C*HN), 72.6 (O*C*H$_2$), 121.0 (Ar *C*), 126.6 (Ar *C*), 132.0 (Ar *C*), 132.2 (Ar *C*), 162.6 (O*C*N). Anal. Calcd for $C_{18}H_{23}BrN_2O_2$: C, 57.00; H, 6.11; N, 7.39. Found: C, 56.88; H, 6.07; N, 7.26.

Synthesis of [(*S*,*S*) *t*Bu,H−PheboxBr] (1c). A procedure analogous to the synthesis of **1a** was employed using 2-bromoisophthalic acid (4.1 g, 15 mmol) and L-*tert*-leucinol (3.5 g, 30 mmol), giving a colorless oil. Yield: 4.31 g (73%). R_f value (1:1 diethyl ether/ethyl acetate): 0.71. $[\alpha]^{20}_D = -60.2°$ (c = 0.11 g/mL, EtOH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (s, 18H, CMe_3), 4.06 (dd, 2H, $^3J_{H-H}$ = 10.1 Hz, $^3J_{H-H}$ = 8.3 Hz, OCH_2), 4.22 (t, 2H, $^3J_{H-H}$ = 8.7 Hz, C*H*N), 4.37 (dd, 1H, $^3J_{H-H}$ = 10.1 Hz, $^3J_{H-H}$ = 8.9 Hz, OCH_2), 7.33 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, Ar

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H), 7.60 (d, 2H, $^3J_{H-H}$ = 7.2 Hz, Ar *H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 26.1 (C*Me*$_3$), 34.0 (*C*Me$_3$), 69.2 (*C*HN), 76.7 (O*C*H$_2$), 121.4 (Ar *C*), 127.0 (Ar *C*), 132.4 (Ar *C*), 132.6 (Ar *C*), 163.0 (O*C*N). Anal. Calcd for $C_{20}H_{27}BrN_2O_2$: C, 58.97; H, 6.68; N, 6.88. Found: C, 59.10; H, 6.74; N, 6.76.

Synthesis of [Sn(Me,Me-Phebox)Me$_3$] (2). A portion of *n*-BuLi (0.70 mL, 1.1 mmol, 1.6 M solution in hexanes) was added to a solution of **1a** (0.35 g, 1.0 mmol) in an appropriate solvent (20 mL, THF, diethyl ether, pentane, or toluene; Scheme 1) at −78 °C. After the solution was stirred and slowly warmed to room temperature, $SnClMe_3$ (2.8 mL, 1.0 mmol, 0.36 M solution in pentane) was added, and the resulting mixture was stirred for 1 h. The mixture was then quenched with water (10 mL) and the layers separated. The organic layer was washed with H_2O (10 mL), dried (Na_2SO_4), and filtered, and the solvent was removed in vacuo. A yellow oil was obtained, which crystallized rapidly. The yields in the following solvents were as follows: THF (97%), diethyl ether (97%), pentane (98%), toluene (99%). ^1H NMR (300 MHz, C_6D_6): δ 0.46 (s, 9H, ^{117}Sn (7.7%) and ^{119}Sn (8.4%) satellites, ^2J = 26.7 Hz, 27.8 Hz, Sn*Me*$_3$), 1.17 (s, 12H, C*Me*$_2$), 3.67 (s, 4H, O*CH*$_2$), 8.11 (t, 1H, $^3J_{H-H}$ = 7.8 Hz, Ar *H*), 7.96 (d, 2H, $^3J_{H-H}$ = 7.5 Hz, Ar *H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ −2.0 ($^1J(^{117,119}Sn-^{13}C)$ = 190 Hz, Sn*Me*$_3$), 28.6 (C*Me*$_2$), 68.1 (*C*Me$_2$), 79.2 (O*C*H$_2$), 128.0 (Ar *C*), 131.3 ($^1J(^{117,119}Sn-^{13}C)$ = 16 Hz, Ar *C*), 137.0 (Ar *C*), 148.2 (Ar *C*), 163.6 (O*C*N). Anal. Calcd for $C_{19}H_{28}N_2O_2Sn$: C, 52.44; H, 6.49; N, 6.44. Found: C, 52.53; H, 6.57; N, 6.37.

Synthesis of [Li(Me,Me-Phebox)]$_2$ (3a). To a solution of **1a** (1.01 g, 2.89 mmol) in pentane (50 mL) was added *n*-BuLi (1.8 mL, 2.9 mmol, 1.6 M in hexane) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 3 h, after which the volatile components were removed in vacuo. The residue was washed twice with pentane (4 mL), which afforded an off-white solid product (yield: 531 mg, 66%). ^1H NMR (300 MHz, C_6D_6): δ 0.92 (s, 12H, C*Me*$_2$), 3.76 (s, 4H, O*CH*$_2$), 7.20 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, Ar *H*), 8.09 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, Ar *H*). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 28.4 (C*Me*$_2$), 65.6 (*C*Me$_2$), 79.9 (O*C*H$_2$), 124.0 (Ar *C*), 127.7 (Ar *C*), 139.7 (Ar *C*), 172.2 (O*C*N), 199.4 (septet, $^1J(^{13}C,^7Li)$ = 17.7 Hz, Ar *C*). ^7Li NMR (78 MHz, toluene-d_8): δ 1.50. Anal. Calcd for $C_{16}H_{19}LiN_2O_2$: C, 69.06; H, 6.88; N, 10.07. Found: C, 68.83; H, 6.95; N, 9.83.

Synthesis of [Li(*i*Pr,H-Phebox)]$_2$ (3b). To a solution of **1b** (0.47 g, 1.24 mmol) in pentane (25 mL) was added *n*-BuLi (0.9 mL, 1.44 mmol, 1.6 M in hexane) at a temperature of −78 °C. The reaction mixture was warmed to room temperature and stirred for 4 h, after which the suspension was decanted after centrifugation. The residue was washed with pentane (10 mL), which afforded a white solid product (yield: 370 mg, 98%). ^1H NMR (300 MHz, toluene-d_8): δ 0.63 (d, 6H, $^3J_{H-H}$ = 6.6 Hz, CH*Me*$_2$), 0.70 (d, $^3J_{H-H}$ = 6.6 Hz, CH*Me*$_2$), 1.41 (sp, 2H, $^3J_{H-H}$ = 6.6 Hz, C*H*Me$_2$), 3.76, 4.02, 4.06 (ABX pattern, 6H, $^2J_{H-H}$(AB) = 8.4 Hz, $^3J_{H-H}$(AX + BX) = 15.8 Hz, O*CH*$_2$, NC*H*) 7.21 (t, 1H, $^3J_{H-H}$ = 7.8 Hz, Ar *H*), 8.04 (d, $^3J_{H-H}$ = 7.8 Hz, Ar *H*). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 18.5 (CH*Me*$_2$), 18.9 (CH*Me*$_2$), 33.4 (*C*HMe$_2$), 71.4 (N*C*H), 71.6 (O*C*H$_2$), 124.2 (Ar *C*), 128.6 (Ar *C*), 139.7 (Ar *C*), 173.9 (O*C*N), 198.8 (sp, $^1J(^{13}C,^7Li)$ = 17.6 Hz, Ar *C*).). ^7Li NMR (78 MHz, toluene-d_8): δ 1.64. Anal. Calcd for $C_{19}H_{23}LiN_2O_2$: C, 70.58; H, 7.57; N, 9.14. Found: C, 70.15; H, 7.49; N, 8.86.

Synthesis of [Li(*t*Bu,H-Phebox)]$_2$ (3c). To a solution of **1c** (0.24 g, 0.59 mmol) in diethyl ether (20 mL) was added *n*-BuLi (0.5 mL, 0.8 mmol, 1.6 M in hexane) at −78 °C. The reaction mixture was stirred at this temperature for 45 min, after which time it was warmed to room temperature and stirred for another 3 h. The volatile components of the mixture were then removed in vacuo. The residue was washed with pentane (2 × 5 mL), which afforded a white solid product (yield: 83 mg, 42%). ^1H NMR (300 MHz, toluene-d_8): δ 0.67 (s, 18H, C*Me*$_3$), 3.79, 4.067, 4.116 (ABX pattern, 6H, $^2J_{H-H}$(AB) = 8.4 Hz, $^3J_{H-H}$(AX + BX) = 19.8 Hz, O*CH*$_2$, NC*H*), 7.23 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, Ar *H*), 8.14 (2H, $^3J_{H-H}$ = 7.8 Hz, Ar *H*). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 26.0 (C*Me*$_3$), 33.4 (*C*Me$_3$), 69.4 (N*C*H), 75.4 (O*C*H$_2$), 124.1 (Ar *C*), 128.4 (Ar *C*), 139.7 (Ar *C*), 173.8 (O*C*N), 198.1 (sp, $^1J(^{13}C,^7Li)$ = 17.8 Hz, Ar *C*). ^7Li NMR (78 MHz, toluene-d_8): δ 1.74. Anal. Calcd for $C_{20}H_{27}LiN_2O_2$: C, 71.84; H, 8.14; N, 8.38. Found: C, 71.64; H, 8.02; N, 8.22.

Table 1. Crystallographic Data for Crystal Structure Determinations of 2 and 3a

	2	**3a**
formula	$C_{19}H_{28}N_2O_2Sn$	$C_{32}H_{38}Li_2N_4O_4$
mol wt	435.15	556.54
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	11.1077(10)	11.4446(10)
b (Å)	11.3324(10)	17.530(2)
c (Å)	18.4916(19)	17.622(3)
β (deg)	121.130(6)	115.945(11)
V (Å^3)	1992.5(3)	3179.1(7)
D_{calcd} (g cm^{-3})	1.4506(2)	1.1628(3)
Z	4	4
F(000)	888	1184
μ(Mo Kα) (mm^{-1})	1.295	0.076
cryst color	colorless	pale yellow
cryst size (mm)	0.15 × 0.30 × 0.30	0.2 × 0.3 × 0.3
θ_{min}, θ_{max} (deg)	1.0, 27.6	1.0, 27.5
dist from cryst to detector (mm)	50	40
data set (hkl)	−14 to +14, −14 to +14, −24 to +23	−14 to +14, −22 to +22, −22 to +22
abs cor range	0.596−0.875	
total no. of data, no. of unique data	39 706, 4589	82 804, 7294
R_{int}	0.1012	0.1016
no. of refined params	224	387
final R1[a]	0.0242 (4199, $I > 2\sigma(I)$)	0.0493 (5095, $I > 2\sigma(I)$)
final wR2[b]	0.0627	0.1275
goodness of fit	1.029	1.034
w^{-1} [c]	$\sigma^2(F_o^2) + (0.0313P)^2 + 0.89P$	$\sigma^2(F_o^2) + (0.0506P)^2 + 1.00P$
min, max residual density (e Å^{-3})	−1.14, 0.93 (near Sn)	−0.24, 0.22

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$.

NMR Experiments of 3a with Subsequent Addition of Diethyl Ether, Tetrahydrofuran, and Triethylamine. In a nitrogen-filled glovebox, **3a** (128 mg, 0.46 mmol) was weighed in a 10 mm NMR tube and dissolved in toluene-d_8. After the NMR spectra were recorded without additional coordinating solvents present, the NMR tube was placed under nitrogen in a modified Schlenk tube and Et_2O (45 μL, 0.46 mmol) was added. ^1H, $^7Li\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded at room temperature and ^1H and $^7Li\{^1H\}$ NMR spectra at −60 °C. The NMR tube was again placed under nitrogen before adding THF (40 μL, 0.49 mmol) to the mixture. ^1H and ^7Li NMR spectra were again recorded at −60 °C and at room temperature. Following the same procedure, Et_3N (65 μL, 0.47 mmol) was added to the mixture and ^1H and $^7Li\{^1H\}$ spectra were recorded of the mixture at room temperature. No change was observed in the chemical shift of the ^7Li signal for **3a**. $^7Li\{^1H\}$ NMR (78 MHz, toluene-d_8, Et_2O): 298 K, δ 1.48; 213 K, δ 1.50. $^7Li\{^1H\}$ NMR (78 MHz, toluene-d_8, Et_2O, THF): 298 K, δ 1.48; 213 K, δ 1.48. $^7Li\{^1H\}$ NMR (78 MHz, toluene-d_8, Et_2O, THF, Et_3N, 298 K): δ 1.46.

X-ray Crystal Structure Analyses. Pertinent data for the structure determinations are given in Table 1. Data were collected at 150 K on a Nonius KappaCCD diffractometer on a rotating anode (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å). The unit-cell parameters were checked for

the presence of higher lattice symmetry.[19] The intensity data of **2** were corrected for absorption using an algorithm based on multiple measurements of symmetry-related reflections incorporated in Platon.[20] The structures were solved with direct methods using SHELXS86[21] and refined on F^2 using SHELXL-97[22] (no observance criterion was applied during refinement). Hydrogen atoms were included on calculated positions riding on their carrier atoms. The methyl groups were allowed to rotate along the $X-CH_3$ bond. Non-hydrogen atoms were refined with anisotropic displacement parameters. The isotropic displacement parameters of the hydrogen atoms were linked to the value of the equivalent isotropic displacement parameters of their carrier atoms. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 23. Validation, geometrical calculations, and illustrations were performed with PLATON.[20]

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Supporting Information Available: Further details on the crystal structures of complexes **2** and **3a**, including tables of atomic coordinates, displacement parameters, bond lengths, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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