

DOI:10.1002/ejic.201300151

Zinc Complexes of Bipyrrolidine-Based Diamine-Diphenolato and Diamine-Diolato Ligands: Predetermination of Helical Chirality Around Tetrahedral Centres

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Keywords: Zinc / Chirality / Tetradentate dianionic ligands / {ONNO} ligands / Salan ligands

The coordination chemistry of chiral tetradentate dianionic ligands of the diamine-diphenolato and diamine-diolato families having the (*R*,*R*)-2,2'-bipyrrolidine core around Zn^{II} was investigated. Reactions with diethylzinc led to complexes of the type [{ONNO}Zn] for most ligands and to bridging dinuclear complexes of the type [μ -Lig⁴(ZnEt)₂] for one of the diamine-diolato ligands. Reactions with bis(hexamethyldisilaz-ide)zinc led to complete conversions. Most complexes were obtained as mononuclear complexes. The least bulky Salan ligand, Lig³, led to an equilibrium between mononuclear and dinuclear complexes in noncoordinating solvents. All ligands

Introduction

The synthesis of enantiomerically pure "chiral-at-metal" complexes is a topic of major current interest with implications in the fields of asymmetric catalysis, materials science and pharmacology.^[1–5] For relatively labile metals, the most general approach for attaining chirality at the metal relies on the helical wrapping of a chelating ligand (or chelating ligands). Helically wrapping achiral ligands lead to racemic chiral complexes which need to be resolved should they be required in their enantiomerically pure form.^[6-8] A more efficient method relies on chiral chelating ligands that are able to wrap around the metal in a highly diastereoselective manner and which should be available in their enantiomerically pure form.^[9-12] However, such high chiral induction from ligand backbone to the helical sense of ligand wrapping depends on the design of selective chiral cores and is still scarce. For example, trans-1,2-diaminocyclohexane, which is a successful chiral core for nonhelically wrapping ligands like the {ONNO}-type Salens,^[13] has led to unpredictable and diverse diastereoselectivities in helically wrapping ligands like the {ONNO}-type Salans.^[14] Herein, we

[a] School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Ramat Aviv, Tel Aviv 69978, Israel Fax: +972-3-6409293 E-mail: moshekol@post.tau.ac.il Homepage: http://tau.ac.il/chemistry/kol/ were found to wrap around the tetrahedral zinc with very high diastereoselectivities supporting predetermined chiral induction from the bipyrrolidine core to the helical ligand wrapping. Molecular structures determined by single-crystal X-ray diffraction for two complexes of the type [{ONNO}Zn] substantiated the predicted Δ wrapping of the (*R*,*R*)-based ligands. In contrast, representative Salan and diamine-diolato ligands assembled around the *trans*-1,2-diaminocyclohexane core led to diastereomer mixtures of the corresponding complexes.

demonstrate for the first time that tetradentate dianionic {ONNO}-type ligands assembled around the 2,2'-bipyrrolidine core wrap in a highly diastereoselective helical manner around tetrahedral centres, zinc being a representative metal, to give enantiomerically pure chiral-at-metal complexes.

Chiral 2,2'-bipyrrolidine and its derivatives have been investigated in organocatalysis^[15] and as chiral cores for neutral ligands^[16-18] and yet the unique ability of 2,2'-bipyrrolidine to direct a diastereoselective helical wrapping of multidentate ligands has been somewhat overlooked. A simple "ball-and-stick" model shows that converging of the electron pairs of the two nitrogen atoms (namely, chelating to a metal) requires that they emerge from specific faces of the pyrrolidine rings. Arms that lead to the peripheral donors of the multidentate ligands should emerge from the opposite faces of the pyrrolidine rings, thus favouring a specific helical wrapping around a metal. Recently, we introduced the first two families of tetradentate dianionic {ONNO}-type ligands that feature the chiral bipyrrolidine backbone: the diamine-diphenolato (Salans)^[19] and the diamine-diolato families.^[20] When such ligands chelate to an octahedral metal centre in a *fac-fac* helical mode,^[21] the bipyrrolidine motif exhibits a dramatic preference for formation of one of the possible diastereomers: an (R,R) tetradentate ligand wraps in a Δ manner whereas an (S,S) ligand wraps in a Λ manner as can be readily predicted by the





molecular models and supported by molecular structures determined by X-ray diffraction. In the current work, we set out to explore the coordination chemistry of these two ligand families around zinc(II). Specifically, we wished to explore whether the same high degree of (predictable) diastereoselectivity in helical ligand wrapping found for octahedral complexes would also be found for tetrahedral complexes of the [{ONNO}Zn]-type, despite the difference in helical pitch in these two geometries.

The coordination chemistry of tetradentate dianionic {ONNO}-type ligands around zinc is well-developed and revolves mostly around Salen ligands. Salen zinc complexes have found various applications including CO₂ fixation,^[22] asymmetric catalysis,^[23] supramolecular assemblies^[24] and fluorescence-based detection.^[25] The tendency of the (twocarbon bridge) Salen ligands to wrap in a planar form conflicts with the tendency of the closed shell Zn^{II} to adopt a tetrahedral geometry. Therefore, Salen-Zn complexes are often found to increase their coordination number by either O-bridging or binding of an additional ligand.^[26] Salan zinc complexes have been explored to a lesser extent.^[27] Nonbulky Salans tend to adopt a bridging dinuclear structure^[28] but adding a bulky substituent at the ortho-position of the phenolato group leads to mononuclear tetrahedral complexes.^[27a,29] Relevant to the present work, enantioselective aryl transfer to aldehydes with catalytic bipyrrolidine-based Salans^[19] in the presence of a large excess of diethylzinc was recently reported.^[30] However, no description of a presumably formed zinc complex was given.

Results and Discussion

The six chiral {ONNO}H₂ ligand precursors employed in this study are outlined in Scheme 1. All ligands are based on the (R,R)-2,2'-bipyrrolidine backbone and are C_2 -symmetric having identical anionic phenolato or alcoholato arms. Lig^2H_2 is described herein for the first time while the other ligands have been described previously in coordination chemistry of group 4 metals.^[19,20] Ligand precursors Lig¹⁻³H₂ are diamine-diphenolato(Salan) type ligands which may form 6-5-6 chelate arrays if all donor atoms bind to a given metal atom. $Lig^{1}H_{2}$ and $Lig^{2}H_{2}$ bear bulky alkyl substituents *ortho* to the phenolato oxygen. $Lig^{3}H_{2}$ includes small electron-withdrawing chloro substituents in the ortho positions. Ligand precursors $Lig^{4-6}H_2$ are diamine-diolato type ligands, featuring two phenyl, methyl or trifluoromethyl groups α to the oxygen donors, respectively, thus exhibiting different steric and electronic properties. They may form 5–5-5 chelate arrays when all donor atoms bind to a given metal atom. The two families of ligands were synthesised by S_N -type reactions from (R,R)-bipyrrolidine and the corresponding substituted bromomethyl phenols or substituted oxiranes, respectively.

The coordination chemistry of the chiral diamine-diphenolato ligands around zinc was first explored by treating the ligand precursors (R,R)-Lig¹⁻³H₂ with diethylzinc as outlined in Scheme 2. Conducting these reactions for 2 h at



Scheme 1. Bipyrrolidine-based {ONNO}-type diamine-diphenolato and diamine-diolato ligand precursors described in this work, and their respective syntheses.

room temp. resulted in the formation of undefined products, according to ¹H NMR spectroscopy. However, extending the reaction time to 24 h resulted in selective formation of complexes of the form [{ONNO}Zn] for the bulky ligands Lig¹ and Lig². The ¹H NMR spectra supported the formation of single diastereomers of C_2 symmetry: two narrow doublets in the aromatic region and a single AB system at $\delta \approx 3.8$ and ≈ 2.7 ppm for the enantiotopic protons of the methylene groups of these two complexes. This is consistent with perfect chiral induction from ligand to metal. Single crystals of the complex [Lig¹Zn] were obtained from diethyl ether at -35 °C and the molecular structure was determined by X-ray diffraction. The ORTEP representation and selected bond lengths and angles are outlined in Figure 1. The structure reveals a tetracoordinate mononuclear zinc complex having crystallographic C_2 symmetry. The (R,R)-configuration of the bipyrrolidine core was established and the helical screw-sense of the {ONNO} ligand around the zinc centre was found to be Δ . This is equivalent to the screw sense that was found for wrapping the bipyrrolidine-based Salan ligands around octahedral group 4 metals [(S,S)-bipyrrolidine based Salans were found to wrap in a Λ helical sense in that report].^[19] Hence, the formation of a chelate



Scheme 2. Coordination tendencies of bipyrrolidine-based Salan ligands around zinc.



ring that includes the two nitrogen donors of the bipyrrolidine motif around a given metal atom determines the chirality at the metal irrespective of the coordination number.



Figure 1. ORTEP representation of complex [Lig¹Zn] with 50% probability ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn–O2, 1.879(2); Zn–N3, 2.076(2); O2–Zn–O2ⁱ, 118.0(1); N3–Zn–N3ⁱ, 84.97(9).

Employing the same reaction conditions for $Lig^{3}H_{2}$ resulted in the formation of a mixture of two or more complexes that could not be identified by ¹H NMR spectroscopy and extending the reaction time to several days did not lead to a well-defined complex (Scheme 2). To try to carry the reaction with zinc to completion, we treated the ligand precursor Lig³H₂ with Zn(HMDS)₂ which includes labile amido groups. Indeed, the amine elimination reaction proceeded more smoothly to give a complex of the type [Lig³Zn] as evident from the disappearance of the trimethylsilylamide peaks in the ¹H NMR spectrum. The sharp peaks observed for [Lig¹Zn] and [Lig²Zn] were not observed in the ¹H NMR spectrum of [Lig³Zn] which consisted of broad humps in the aliphatic region. VT-NMR experiments in $[D_8]$ toluene revealed that heating the sample up to 358 K led to a spectrum with sharp peaks consistent with a practically single diastereomer of [Lig³Zn] (accompanied by some impurities) while cooling the sample to 218 K led to sharpening and doubling of the number of peaks. We propose that [Lig³Zn] is in equilibrium between a C_2 -symmetric mononuclear complex (dominant at high temperature) and a C_1 -symmetric dinuclear Zn complex (dominant at low temperature). Zn complexes of achiral and nonbulky Salan ligands were reported by Atwood and coworkers, and were found by X-ray crystallography to be dinuclear with one of the phenolato oxygens of each Salan bridging between two zinc atoms.^[28] The low steric bulk of Lig³ may lead to formation of dinuclear complexes having a similar structure.^[29,31]

To see whether similar diastereoselectivity in ligand wrapping could also be achieved with chiral Salans assembled around the common trans-1,2-diaminocyclohexane core, we prepared the Salan ligand featuring that core and ortho-tert-butyl *para*-chloro phenolato substituents (Scheme 3). Its reaction with diethylzinc led to a mixture of products but its reaction with Zn(HMDS)₂ led to a product of the form [{ONNO}Zn] as was found for the bipyrrolidine based Salans. However, this complex was obtained as a 1:0.4 mixture of C_2 symmetric diastereomers indicating a very low induction from the diaminocyclohexane backbone to the helicity in ligand wrapping, as previously found for octahedral titanium complexes.^[14a,14b] This further supports the uniqueness of the bipyrrolidine core in inducing a specific screw-sense of helical ligand wrapping.



Scheme 3. Low diastereoselectivity in wrapping around zinc for *trans*-diaminocyclohexane based Salan ligands.

Different reactivity was observed during the attempted complexation of the diamine-diolato ligand precursor Lig⁴H₂ with Et₂Zn. Using diethyl ether as a solvent and stirring the reaction for 2, 24 and even 48 h did not show formation of any single well-defined product according to ¹H NMR spectroscopy. However, following storage of an NMR-tube with the reaction product dissolved in C_6D_6 at -18 °C for 24 h, the formation of a defined complex was evident by ¹H NMR spectroscopy (taken at r.t.). While the exact structure could not be deciphered, high field peaks supported the presence of CH_3CH_2 -Zn groups signifying an incomplete reaction and possible formation of a dinuclear complex. This complex was crystallised from diethyl ether at -35 °C and its molecular structure was determined by Xray diffraction. The asymmetric unit was found to contain two independent molecules each having the same constitution and connectivity and very similar bond lengths and angles. The ORTEP representation of one of these molecules is outlined in Figure 2. The structure reveals a dinuclear complex of the form $[\mu-Lig^4(ZnEt)_2(OEt_2)]$ in which each zinc atom still carries an ethyl group and resides in a different environment (Scheme 4, top). Zn1 (internal) is pentacoordinate, binding to all nitrogen and oxygen donors



and to an ethyl group. Its geometry is best described as square-pyramidal with the ethyl ligand occupying the apical position. Atypically, the diamine-diolato ligand does not wrap around the metal in a helical manner in this complex. This is evident in opposite configurations of the two tetrahedral N-donors. Zn2 (external) binds to the two O-donors of the ligand and to a second ethyl group and its tetrahedral coordination sphere is completed by an ether molecule. The Zn-O and Zn-C bonds around Zn2 are shorter than the corresponding bonds around Zn1 in accordance with the lower coordination number. The Zn…Zn distance is short^[32] (3.061 and 3.065 Å in the two molecules) and may indicate a metal-metal interaction. A possible explanation for the incomplete reaction in this diamine-diolato ligand is the lower acidity of the OH groups relative to that of the diamine-diphenolato ligands.



Figure 2. ORTEP representation of [μ-Lig⁴(ZnEt)₂(OEt₂)] with 50% probability ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1-··Zn2, 3.061; Zn1-O3, 2.079(6); Zn1-O4, 2.148(6); Zn1-N6, 2.379(8); Zn1-N7, 2.257(8); Zn2-O3, 1.967(6); Zn2-O4, 1.989(6); O3–Zn1-O4, 78.5(3); N6–Zn1–N7, 78.2(3); O4–Zn1–O3, 77.1(3); Zn1–O3–Zn2, 98.3(3); Zn1–O4–Zn2, 95.4(3); O3–Zn2–O4, 85.1(3).



Scheme 4. Coordination tendencies of bipyrrolidine-based diaminediolato ligands around zinc.

To investigate the possible influence of the coordinating solvent on product formation, we repeated the crystallisation but this time employing noncoordinating toluene as solvent. Suitable crystals were obtained at -35 °C but the molecular structure was of lower quality and, except for the zinc atoms, could only be refined isotropically. Two molecules were found in the asymmetric unit and the ORTEP representation of one of them is outlined in Figure 3. In line with the previous structure, the current complex was also found to be dinuclear. However, the diamine-diolato ligand was now bound to the zinc atoms symmetrically creating two tetracoordinate metal centres: each zinc atom binds to a different N-donor, to the two (bridging) O-donors, and to an ethyl group (Scheme 4, middle). An even tighter Zn…Zn distance of 2.93 Å is consistent with a binding interaction. Since each metal atom binds to only three donors of the {ONNO} ligand, the sense of chiral helicity is irrelevant but the stereogenic nature of the two N-donors is still valid. These were found to be of identical configuration, equivalent to that found in [Lig¹Zn]. We repeated the reaction using toluene as a solvent. The ¹H NMR spectrum taken after 48 h in toluene was consistent with that obtained when using diethyl ether, indicating the formation of an undefined product at room temperature that converted to a single well defined product after cooling the solution. Based on the ¹H NMR spectra and molecular structures we assume that these two dinuclear complexes may interconvert and the preference for the former may result from the presence of the coordinating ether.



Figure 3. ORTEP representation of $[\mu$ -Lig⁴(ZnEt)₂] in which only the Zn atoms were refined anisotropically. Zn1…Zn2, 2.927 Å.

Both complexes of the type $[\mu$ -Lig⁴(ZnEt)₂] represent an incomplete reaction of Et₂Zn. Attempting to drive the reaction to completion by prolonging it at elevated temperature did not lead to a mononuclear complex of the [{ONNO}Zn] type. However, starting from Zn(HMDS)₂ did yield a mononuclear complex of the [Lig⁴Zn]form. ¹H

NMR spectroscopic analysis indicated the formation of a single diastereomer of C_2 symmetry, consistent with a specific helical ligand wrapping.^[33] We propose that this (R,R)-diamine-diolato ligand wraps in the Δ form around Zn as previously found for the Salan ligands Lig^{1–3}. Reaction between Lig⁵H₂ and diethyl zinc for 24 h resulted in formation of an undefined product. However, leaving the compound in toluene solution for a week resulted in formation of a single well-defined complex having the empirical formula of [Lig⁵Zn], the NMR spectrum of which was consistent with a mononuclear complex of C_2 symmetry. Based on the predictable wrapping of these bipyrrolidine-based {ONNO} ligands, we propose that the sense of helical chirality around the zinc metal in Lig⁵Zn is identical to that found for [(R,R)-Lig²Zn], i.e. Δ .

When Lig⁶H₂ was treated with Et₂Zn, the ¹H NMR and ¹⁹F NMR spectra showed the formation of several products. Following cooling of a C₆D₆ solution of this mixture to –18 °C, a single product of empirical formula Lig⁶Zn was formed according to ¹H and ¹⁹F NMR spectra taken at room temp. Single crystals suitable for X-ray diffraction analysis were grown from diethyl ether at –35 °C and the structure was solved confirming the formation of a mononuclear complex of tetracoordinate zinc. The ORTEP representation and selected bond lengths and angles for [Lig⁶Zn] are outlined in Figure 4. The Zn-N and Zn–O bond lengths and N–Zn–N and O–Zn–O angles are similar to those found for [Lig¹Zn]. Again, the (*R*,*R*)-chirality of the bipyrrolidine skeleton was translated to a Δ helical screw-sense



Figure 4. ORTEP representation of complex [Lig⁶Zn] with 50% probability ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn–O2, 1.866(3); Zn–O3, 1.875(4); Zn–N4, 2.077(4); Zn–N5, 2.090(4); O2–Zn–O3, 129.9(2); N4–Zn–N5, 87.0(2).

wrapping of the {ONNO} ligand around the zinc. However, the smaller 5-5-5 chelate array leads to a shallower helix relative to the 6-5-6 helix observed for [Lig¹Zn].

Conclusions

The chiral tetradentate bipyrrolidine-based {ONNO} ligands of the diamine-diphenolato and diamine-diolato families featuring different steric bulk and electronic character were found to exhibit rich coordination chemistry around zinc, depending on the zinc precursor. The reactions of all ligand precursors with diethylzinc were sluggish. Longer reaction times were typically required for the diamine-diolato ligands to form the final product of the [{ONNO}Zn]-type, possibly due to their reduced acidity. For Lig⁴, this product could not be formed and "arrested" dinuclear complexes amenable to connectivity manipulation by coordinating solvents were the end-products. Zn(HMDS)₂ reacted more readily with the ligand precursors and so [{ONNO}Zn]type complexes could be obtained for all ligands. Except for [Lig³Zn] which includes nonbulky phenol arms and tends to form dinuclear complexes in noncoordinating solvents at room temp., all complexes were found to form as single C_2 symmetric chiral-at-metal diastereomers attesting to a very high induction from bipyrrolidine backbone chirality to helical-sense wrapping around the tetrahedral zinc centre. Simple "ball-and-stick" molecular models predict a Δ helical chirality for these (R,R)-bipyrrolidine ligands and in the two cases where crystallographic data was available ([Lig¹Zn] and [Lig⁶Zn]), this prediction was validated. These results stand in sharp contrast to those obtained with the {ONNO} ligands based on the common chiral trans-1,2-diaminocyclohexane core that led to mixtures of diastereomers. We are currently broadening the scope of pyrrolidine-based chiral ligands and exploring the reactivity of their resultant complexes.

Experimental Section

General: All experiments employing zinc complexes were performed under an atmosphere of dry nitrogen in a nitrogen-filled glovebox. Ether was purified by reflux and distillation under a dry argon atmosphere from Na/benzophenone. Pentane was washed with HNO₃/H₂SO₄ prior to distillation from Na/benzophenone/tetraglyme. Toluene was heated to reflux over Na and distilled. (R,R)bipyrrolidine was purchased from OBITER. The ligand precursors Lig^{2,3}H₂ were prepared according to previously published procedures from (R,R)-bipyrrolidine and the corresponding disubstituted bromomethylphenols.^[19] The ligand precursors Lig⁴⁻⁶H₂ were prepared according to previously published procedures from (R,R)bipyrrolidine and the corresponding disubstituted oxiranes.^[20] NMR spectroscopic data were recorded on Bruker Avance 400 and Avance 500 spectrometers. CDCl₃ was used as NMR solvent for the ligands (chemical shift of TMS at $\delta = 0.00$, and ¹³C chemical shift of the solvent at δ = 77.16 were used as reference) and C₆D₆ was used as an NMR solvent for the metal complexes (referenced to proton impurities at δ = 7.15, and to the ¹³C chemical shift at δ = 128.7 ppm of benzene). Diffraction measurements were performed on a Nonius Kappa CCD diffractometer system using Mo-



 K_{α} ($\lambda = 0.7107$ Å) radiation. The analysed crystals grown from diethyl ether or toluene solutions at -35 °C were embedded within a drop of viscous oil and freeze-cooled to ca. 110 K. The structures were solved by a combination of direct methods and Fourier techniques using SIR-97^[34] software and were refined by full-matrix least-squares methods with SHELXL-97.^[35] Elemental analyses were performed in the microanalytical laboratory in the Hebrew University of Jerusalem.

(R,R)-Lig²H₂: Et₃N (1.2 mL, 2 equiv.) was added dropwise to a solution of (R,R)-bipyrrolidine (0.60 g, 4.27 mmol) and 2-adamantyl-4-methyl-6-bromomethylphenol^[36] (2.86 g, 8.54 mmol) in THF (50 mL). The mixture was stirred for 24 h at room temp. producing a white precipitate of Et₃N·HBr which was filtered off and extracted with cold THF. The filtrate was washed twice with water and dried under vacuum. The resultant solid was recrystallised from a mixture of pentane and methanol, yielding 1.9 g (69%) of (R,R)-Lig²H₂. MS (DCI): $m/z = [MH^+] 647.5$. ¹H NMR (400 MHz, $CDCl_3$): $\delta = 6.92$ (d, J = 1.6 Hz, 2 H), 6.62 (d, J = 1.6 Hz, 2 H), 3.92 (d, J = 13.6 Hz, 2 H, AB system), 3.38 (d, J = 13.6 Hz, 2 H, AB system), 3.01 (m, 2 H), 2.78 (m, 2 H), 2.24 (s, 3 H), 2.14 (br. s, 6 H), 2.06 (br. s, 3 H), 1.78 (br. s, 6 H) ppm. ¹³C NMR (100.66 MHz, $CDCl_3$): $\delta = 155.1$ (C), 137.1 (C), 127.8 (C), 127.1 (CH), 127.0 (CH), 123.6 (C), 66.3 (CH₂), 59.7 (CH₂), 55.6 (CH), 41.1 (CH), 37.9 (CH₂), 29.9 (CH₃), 26.3 (C), 24.5 (CH₂), 21.5 (CH₂) ppm. C44H60N2O2 (648.97): calcd. C 81.43, H 9.32, N 4.32; found C 80.73, H 9.02, N 4.14.

(*R*,*R*)-Lig⁷H₂: A mixture of 2-*tert*-butyl-4-chlorophenol (1.1 g, 6.0 mmol), *rac-trans-N,N'*-dimethylcyclohexane-1,2-diamine (0.4 g, 3.0 mmol) and paraformaldehyde (0.3 g, 8.3 mmol) in methanol (1 mL) was heated in a pressure glass vessel to 90–95 °C overnight. The solution was cooled to room temp. and the white solid that had formed was collected by filtration and washed several times with cold methanol yielding 1.1 g of *rac*-Lig⁷H₂ (40% yield). ¹H NMR (CDCl₃, 400 MHz): $\delta = 10.70$ (br. s, 2 H, ArH), 7.13 (d, *J* = 2.5 Hz, 2 H, ArH), 6.81 (d, *J* = 2.5 Hz, 2 H, ArH), 3.73 (s, 4 H, CH₂), 2.64 (m, 2 H, CH), 2.16 (s, 6 H, CH₃), 1.95 (m, 2 H, CH), 1.82 (m, 2 H, CH), 1.33 [s, 18 H, (CH₃)₃], 1.16 (m, 4 H, CH) ppm. ¹³C NMR (CDCl₃, 100.67 MHz): $\delta = 155.8$ (C), 138.7 (C), 126.3 (CH), 123.7 (C), 122.9 (C), 61.2 (CH), 58.0 (CH₂), 35.0 (CH₃), 29.4 (CH₃), 25.3 (CH₂), 22.1 (CH₂) ppm. C₃₀H₄₄Cl₂N₂O₂ (535.60): calcd. C 67.28, H 8.28, N 5.23; found C 67.58, H 8.33, N 5.23.

Complex [Lig¹Zn]: (R,R)-Lig¹H₂ (14.2 mg, 0.025 mmol) was dissolved in ether (ca. 2 mL) and cooled to -35 °C. A solution of Et₂Zn in hexane (1.0 M, 0.02 mL) was added dropwise. The mixture was warmed to room temp. and stirred for 24 h. The solvent was removed under reduced pressure to give the product as a white solid (12.5 mg, 79%). ¹H NMR (400 MHz, C_6D_6): δ = 7.58 (d, J = 2.5 Hz, 2 H), 6.71 (d, J = 2.5 Hz, 2 H), 3.80 (d, J = 9.4 Hz, 2 H, AB system), 2.78 (d, J = 9.4 Hz, 2 H, AB system), 2.53 (m, 2 H), 2.25 (m, 4 H), 1.82 (s, 18 H), 1.26 (s, 18 H), 1.24 (m, 4 H), 0.82 (m, 2 H), 0.58 (m, 2 H) ppm. ¹³C NMR (100.66 MHz, C₆D₆): δ = 164.9 (C), 139.6 (C), 129.6 (C), 126.4 (CH), 125.2 (CH), 122.4 (C), 64.2 (CH), 61.1 (CH₂), 52.9 (CH₂), 36.3 [C(CH₃)₃], 34.5 [C(CH₃)₃], 32.5 [C(CH₃)₃], 30.6 [C(CH₃)₃], 24.6 (CH₂), 22.1 (CH₂) ppm. Single crystals of the complex were grown from cold diethyl ether. Crystal data for $C_{38}H_{58}ZnN_2O_2$; M = 640.23; orthorhombic; space group $P2_12_12$; a = 11.2070(4), b = 21.8553(10), c =8.4109(3) Å; V = 2060.1 Å³; Z = 2; $D_c = 1.032$ g cm⁻³; μ (Mo– K_a) = 0.625 mm⁻¹; T = 110(2) K; No. of data collected 4636; R_1 = 0.0471 and $wR_2 = 0.1059$ for 3130 reflections with $I > 2\sigma(I)$; R_1 = 0.0846 and wR_2 = 0.1178 for all 4636 reflections. C42H68N2O3Zn·Et2O (714.39): calcd. C 70.61, H 9.59, N 3.92; found C 70.06, H 9.64, N 3.77.

Complex [Lig²Zn]: (*R*,*R*)-Lig²H₂ (37.5 mg, 0.058 mmol) was dissolved in toluene (*ca.* 2 mL) and cooled to -35 °C. A solution of Et₂Zn in hexane (1.0 M, 0.06 mL) was added dropwise. The mixture was warmed to room temp. and stirred for 24 h. The solvent was removed under reduced pressure to give the product as a white solid (40.3 mg, 96%). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.25$ (d, *J* = 2.4 Hz, 2 H), 6.44 (d, *J* = 2.4 Hz, 2 H), 3.80 (d, *J* = 12.2 Hz, 2 H, AB system), 2.73 (d, *J* = 12.2 Hz, 2 H, AB system), 2.64 (m, 6 H), 2.51 (m, 2 H), 2.37 (m, 2 H), 2.32 (s, 3 H), 2.19 (s, 3 H), 2.96 (m, 6 H), 1.82 (m, 6 H), 1.24 (m, 2 H), 0.79 (m, 2 H), 0.53 (m, 2 H) ppm. ¹³C NMR (100.66 MHz, C₆D₆): $\delta = 165.2$ (*C*), 140.5 (*C*), 130.2 (*C*H), 129.6 (*C*H), 122.9 (*C*), 122.8 (*C*), 64.1 (*C*H), 60.5 (*C*H₂), 52.9 (*C*H₂), 41.5 (*C*H₂), 38.2 (*C*H₂), 30.5 (*C*H₂), 24.4 (*C*H₃), 21.9 (*C*H₂), 21.5 (*C*H₂) ppm. C₄₄H₅₈N₂O₂Zn (712.33): calcd. C 74.19, H 8.21, N 3.93; found C 74.50, H 8.52, N 2.86.

Complex [Lig³Zn]: Lig³H₂ (117 mg, 0.24 mmol) was dissolved in toluene (ca. 1 mL) and added dropwise to a solution of Zn-(HMDS)₂ (92 mg, 0.24 mmol) in toluene (ca. 1 mL). The mixture was stirred for 10 h and the solvent removed under reduced pressure to give the product as a white solid which was washed with cold pentane to remove traces of HMDS-containing compounds (118 mg, 89%). ¹H NMR ([D₈]toluene, 500 MHz, 358 K): $\delta = 7.30$ (s, 2 H, ArH), 6.56 (s, 2 H, ArH), 3.53 (d, J = 15.0 Hz, 1 H, AB system), 3.25 (d, J = 15.0 Hz, 1 H, AB system), 2.59–2.54 (m, 2 H, CH), 1.42-1.35 (m, 3 H, CH), 1.10 (m, 1 H, CH), 0.82 (m, 1 H, CH) ppm. ¹H NMR ([D₈]toluene, 500 MHz, 218 K): δ = 7.51 (s, 2 H, ArH), 7.46 (s, 2 H, ArH), 6.62 (s, 2 H, ArH), 6.49 (s, 2 H, ArH), 5.33 (d, J = 18.0 Hz, 1 H, AB system), 4.81 (d, J = 12.5 Hz, 1 H, AB system), 4.53 (m, 1 H, CH), 3.69 (d, J = 12.5 Hz, 1 H, AB system), 3.58 (m, 1 H, CH), 3.39 (m, 1 H, CH), 3.26 (m, 1 H, CH), 2.86 (d, J = 18.0 Hz, 1 H, AB system), 1.97 (m, 1 H, CH), 1.88 (m, 1 H, CH), 1.71 (m, 3 H, CH), 1.40-1.01 (m, 3 H, CH), 0.76 (m, 2 H, CH) ppm. ¹H NMR ([D₈]THF, 400 MHz, 298 K): δ = 7.18 (d, J = 2.4 Hz, 1 H), 6.81 (d, J = 2.4 Hz, 1 H), 4.05 (d, J = 11.2 Hz, 1 H, AB system), 3.41 (d, J = 11.2 Hz, 1 H, AB system), 2.79–2.74 (m, 2 H, CH), 2.01-1.98 (m, 3 H, CH), 1.56 (m, 1 H, CH), 1.47 (m, 1 H, CH) ppm. C₂₂H₂₂Cl₄N₂O₂Zn (553.62): calcd. C 47.73, H 4.01, N 5.06; found C 48.29, H 4.53, N 4.03.

 $[\mu-\text{Lig}^4(\text{ZnEt})_2(\text{OEt}_2)]$: (R,R)-Lig⁴H₂ Complex (36.2 mg, 0.068 mmol) was dissolved in ether (ca. 2 mL) and cooled to -35 °C. A solution of Et₂Zn in hexane (1.0 м, 0.07 mL) was added dropwise. The mixture was warmed to room temp. stirred for 48 h and then returned to -35 °C for 24 h. The solvent was removed under reduced pressure to give the product as a white solid (47.8 mg). ¹H NMR (400 MHz, C_6D_6): $\delta = 7.61$ (d, J = 8.4 Hz, 4 H), 7.58 (d, J = 8.4 Hz, 4 H), 7.25 (m, 4 H), 7.11 (m, 4 H), 7.04 (m, 2 H), 6.99 (m, 2 H), 3.31 (d, J = 12.5 Hz, 2 H, AB system), 2.96 (d, J = 12.5 Hz, 2 H, AB system), 2.24 (m, 2 H), 1.49 (t, J =7.9 Hz, 6 H), 1.21 (m, 4 H), 0.79 (m, 4 H), 0.54 (m, 4 H), 0.18 (m, 4 H) ppm. ¹³C NMR (100.66 MHz, C₆D₆): δ = 153.3 (C), 153.2 (C), 129.6 (CH), 128.9 (CH), 127.2 (CH), 126.9 (CH), 126.4 (CH), 126.0 (CH), 80.4 (C), 78.4 (CH), 70.3 (CH₂), 69.2 (CH₂), 55.9 (CH₂), 26.0 (CH₂), 23.6 (CH₂), 21.7 (CH₃) ppm. Single crystals of the complex were grown from cold diethyl ether. Crystal data for $C_{44}H_{58}Zn_2N_2O_3$; M = 793.66; triclinic; space group P1; a =9.7241(3), b = 10.5708(4), c = 19.2159(8) Å; a = 94.7256(14), β = 94.2445(16), γ = 100.360(3)°; V = 1928.46(12) Å³; Z = 2; D_{c} = 1.367 g cm⁻³; μ (Mo– K_a) = 1.286 mm⁻¹; T = 110(2) K; No. of data collected 12512; $R_1 = 0.0619$ and $wR_2 = 0.1304$ for 8224 reflections with $I > 2\sigma$ (I); $R_1 = 0.1128$ and $wR_2 = 0.1568$ for all 12512 reflections. C44H58N2O3Zn2 (793.71): calcd. C 66.58, H 7.37, N 3.53; found C 65.14, H 6.50, N 3.63.



Complex [μ -Lig⁴(ZnEt)₂]: This complex was prepared in an analogous way as [μ -Lig⁴(ZnEt)₂(OEt₂)] in 89% yield, using toluene as a solvent. The NMR measurements in C₆D₆ showed only broad humps. Single crystals of the complex were grown from cold toluene. *Crystal data* for C₄₃H₄₆Zn₂N₂O₂; M = 753.56; monoclinic; space group P_{21} ; a = 13.1330(2), b = 15.4570(3), c = 20.3670(4) Å; $\beta = 108.700(8)^{\circ}$; V = 3916.18(12) Å³; Z = 4; $D_c = 1.278$ gcm⁻³; μ (Mo- K_a) = 1.261 mm⁻¹; T = 110(2) K; No. of data collected 15937; $R_1 = 0.1325$ and $wR_2 = 0.3384$ for 13440 reflections with $I > 2\sigma$ (I); $R_1 = 0.1483$ and $wR_2 = 0.3384$ for all 15937 reflections. C₄₇H₅₆N₂O₂Zn₂·C₇H₈: C 69.54, H 6.95, N 3.45; found C 70.02, H 6.97; N 3.37.

Complex Lig⁴Zn: (R,R)-Lig⁴H₂ (35 mg, 0.06 mmol) was dissolved in toluene (ca. 1 mL) and added dropwise to a solution of Zn(HMDS)₂ (25 mg, 0.06 mmol) in toluene (ca. 1 mL). The mixture was stirred for 10 h and the solvent was removed under reduced pressure to give the product as a white solid (36 mg, 92%). ¹H NMR (C₆D₆, 400 MHz): δ = 8.02 (d, J = 6.0 Hz, 2 H, ArH), 7.85 (d, J = 6.0 Hz, 2 H, ArH), 7.26 (t, J = 6.0 Hz, 2 H, ArH), 7.12 (t, J = 6.0 Hz, 2 H, ArH), 7.07 (t, J = 6.0 Hz, 2 H, ArH), 6.98 (t, J = 6.0 Hz, 2 H, ArH), 3.25 (d, J = 10.0 Hz, 1 H, AB system), 2.81 (d, J = 10.0 Hz, 1 H, AB system), 2.26 (m, 1 H, CH), 2.10 (m, 1 H, CH), 1.82 (m, 1 H, CH), 1.21 (m, 1 H, CH), 1.12 (m, 1 H, CH), 0.82 (m, 1 H, CH), 0.55 (m, 1 H, CH) ppm. ¹³C NMR (C₆D₆, 100.67 MHz): δ = 153.1 (C), 152.9 (C), 126.9 (CH), 126.6 (CH), 126.2 (CH), 126.1 (CH), 78.3 (C), 70.0 (CH₂), 68.8 (CH₂), 55.6 (CH), 25.6 (CH₂), 23.3 (CH₂) ppm. $C_{41}H_{50}N_2O_2Zn \cdot C_5H_{12}$: C 73.69, H 7.54, N 4.19; found C 73.81, H 6.69, N 4.10.

Complex [Lig⁵Zn]: (*R*,*R*)-Lig⁵H₂ (24.5 mg, 0.086 mmol) was dissolved in toluene (ca. 2 mL) and cooled to -35 °C and a solution of Et₂Zn in hexane (1.0 M, 0.086 mL) was then added dropwise. The mixture was warmed to room temp. stirred for 4 h and then returned to -35 °C for 2 weeks. The solvent was removed under reduced pressure to give the product as a white solid (28.7 mg, 96%). ¹H NMR (500 MHz, C₇D₈): $\delta = 3.11$ (m, 2 H), 2.70 (m, 2 H), 2.52 (d, *J* = 13.2 Hz, 2 H, AB system), 2.27 (m, 6 H), 2.20 (d, *J* = 13.2 Hz, 2 H, AB system), 1.65 (m, 4 H), 1.52 (m, 4 H), 1.30 (s, 6 H), 1.23 (s, 6 H) ppm. ¹³C NMR (100.66 MHz, C₆D₆): $\delta = 70.8$ (*C*H), 70.5 (*C*H₂), 69.5 (*C*H₂), 57.6 (*C*), 32.1 (*C*H₃), 30.5 (*C*H₃), 23.0 (*C*H₂), 22.0 (*C*H₂) ppm. C₁₆H₃₀N₂O₂Zn (347.81): calcd. C 55.25, H 8.69, N 8.05; found C 55.37, H 8.76, N 8.37.

Complex [Lig⁶Zn]: (R,R)-Lig⁶H₂ (29.0 mg, 0.058 mmol) was dissolved in toluene (ca. 2 mL) and cooled to -35 °C and a solution of Et₂Zn in hexane (1.0 M, 0.06 mL) was then added dropwise. The mixture was warmed to room temp. stirred for 4 h and then returned to -35 °C for 2 weeks. The solvent was removed under reduced pressure to give the product as a white solid (30.4 mg, 93%). ¹H NMR (400 MHz, C₆D₆): δ = 2.58 (m, 2 H), 3.57 (d, J = Hz, 2 H, AB system), 2.35 (d, J = 14.9 Hz, 2 H, AB system), 2.19 (m, 2 H), 2.01 (m, 2 H), 1.55 (m, 2 H), 1.16 (m, 2 H), 0.52 (m, 2 H) ppm. ¹³C NMR (100.66 MHz, C₆D₆): δ = 125.8 (*C*F₃), 123.5 (*C*F₃), 74.1 (CH), 68.3 [C(CF₃)₂], 59.8 (CH₂), 55.6 (C), 25.5 (CH₂), 22.9 (*C*H₂) ppm. ¹⁹F NMR (188.16 MHz, C₆D₆): $\delta = -78.5$ [s, (C*F*₃)₂], -78.8 [s, $(CF_3)_2$] ppm. Single crystals of the complex were grown from diethyl ether at -35 °C. Crystal data for C₁₆H₁₈F₁₂ZnN₂O₂; M = 563.39; orthorhombic; space group $P2_12_12_1$; a = 7.9713(2), b = 11.9870(4), c = 21.2891(8) Å; V = 2034.22(11) Å³; Z = 4; $D_c =$ 1.841 g cm⁻³; μ (Mo– K_{α}) = 1.333 mm⁻¹; T = 110(2) K; No. of data collected 3993; $R_1 = 0.0516$ and $wR_2 = 0.0998$ for 3101 reflections with $I > 2\sigma$ (*I*); $R_1 = 0.0774$ and $wR_2 = 0.1114$ for all 3993 reflections. C₁₆H₁₈F₁₂N₂O₂Zn (563.69): calcd. C 34.09, H 3.22, N 4.97; found C 33.57, H 3.51, N 4.09.

Complex [Lig⁷Zn]: rac-Lig⁷H₂ (39 mg, 0.07 mmol) was dissolved in toluene (ca. 1 mL) and added dropwise to a solution of Zn-(HMDS)₂ (28 mg, 0.07 mmol) in toluene (ca. 1 mL). The mixture was stirred for 10 h and the solvent removed under reduced pressure to give the product as a mixture of two diastereomers of C_2 symmetry in a ratio of 1:0.4 and quantitative yield. Major diastereomer: ¹H NMR (400 MHz, C_6D_6): $\delta = 7.51$ (d, J = 2.4 Hz, 2 H, ArH), 6.71 (d, J = 2.4 Hz, 2 H, ArH), 3.45 (d, J = 12.4 Hz, 2 H, AB system), 2.59 (d, J = 12.4 Hz, 2 H, AB system), 2.01 (m, 2 H, CH), 1.57 [s, 18 H, (CH₃)₃], 1.40 (s, 6 H, NCH₃), 1.23-1.18 (m, 4 H, CH), 1.03–0.95 (m, 4 H, CH) ppm. Minor diastereomer: ¹H NMR (400 MHz, C_6D_6): δ = 7.55 (d, J = 2.8 Hz, 2 H, ArH), 6.78 (d, J = 2.8 Hz, 2 H, ArH), 3.14 (d, J = 12.4 Hz, 2 H, AB system),2.39 (d, J = 12.4 Hz, 2 H, AB system), 1.73 (s, 6 H, NCH₃), 1.59 [s, 18 H, (CH₃)₃], 1.23–1.01 (m, 10 H, CH) ppm. C₃₃H₄₂Cl₂N₂O₂Zn (634.99): calcd. C 60.16, H 7.07, N 4.68; found C 61.47, H 6.92, N 4.10.

CCDC-920515 (for [Lig¹Zn]), -920516 {for [μ -Lig⁴(ZnEt)₂-(OEt₂)]}, -920517 (for [μ -Lig⁴(ZnEt)₂]) and -920518 (for [Lig⁶Zn]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

The authors thank the Israel Science Foundation for support.

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Received: January 30, 2013 Published Online: May 21, 2013