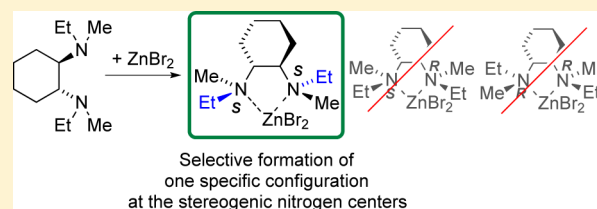


Formation of Specific Configurations at Stereogenic Nitrogen Centers upon Their Coordination to Zinc and Mercury

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S Supporting Information

ABSTRACT: The coordination of (*R,R*)-tetramethylcyclohexane-1,2-diamine derivatives with stereogenic nitrogen centers to zinc and mercury halides is investigated. It is shown that the resulting complexes display one specific configuration at the stereogenic nitrogen centers. This fact is unusual due to the fast inversion of nitrogen centers but highly desirable as the stereoinformation of the ligands is brought closer to the metal centers of the potential catalysts. A combination of NMR studies and quantum chemical calculations gives insight into the selective formation of one specific configuration at the stereogenic nitrogen centers of the zinc complexes.



INTRODUCTION

Coordination compounds containing chiral cyclohexane-1,2-diamine derivatives and transition metals play an active role as catalysts in stereoselective synthesis. The ligand (*R,R*)-tetramethylcyclohexane-1,2-diamine [(*R,R*)-TMCD, **1**] for example, can be coordinated to titanium(II) chloride and cobalt chloride to enhance the stereoselectivity of pinacol coupling and cross-coupling reactions, respectively.¹ As the metal center of such coordination compounds constitutes the active site of the catalyst, the stereoselectivity of a reaction might be even further enhanced if the stereogenic information of the ligand were brought closer to the metal. In the case of (*R,R*)-TMCD (**1**), this would mean that the stereo-information of the (*R*)-configured carbon centers would have to be passed on to the coordinating nitrogen centers. This could be achieved if one of the methyl groups at the nitrogen centers was substituted by a different group. Then, upon coordination of the ligand to a metal, the formation of three (in the case of two stereogenic nitrogen centers containing the same alkyl substituents) or two (in the case of one stereogenic nitrogen center) diastereomers is possible (Figure 1). If one of the diastereomers was formed selectively, its use as a catalyst in preparative synthesis might lead to enhanced stereoselectivity. Achieving this is quite a challenge, however, as nitrogen centers tend to undergo a fast inversion process² which is usually only avoided by using ligands that fix the configuration at the nitrogen centers by enclosing them in rigid carbocycle ring structures (the most commonly employed example for this principle is (–)-sparteine³). If this fast interconversion were slowed down, resulting in a fixed equilibrium of diastereomers, a useful catalyst for preparative synthesis would be formed.

In the past, transition metal coordination compounds of cyclohexane-1,2-diamine derivatives containing one proton and

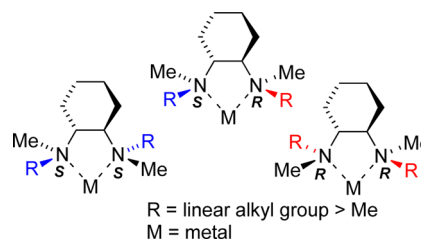


Figure 1. Different diastereomers that can be formed upon coordination of an (*R,R*)-TMCD derivative with two stereogenic nitrogen centers to a transition metal.

one alkyl group at the stereogenic nitrogen centers have already been used in asymmetric synthesis with mixed results.^{4,5} Crystal structure analysis of some compounds revealed nickel, copper, and zinc complexes with (*S*)-configuration at both stereogenic nitrogen centers,^{5,6} while crystal structures of cobalt and palladium compounds displayed (*R*)-configuration at one and (*S*)-configuration at the other stereogenic nitrogen center.^{7,8}

For tertiary bidentate cyclohexane-1,2-diamine derivatives, however, little is known about the configuration of the stereogenic nitrogen centers, although the configuration plays an important role in some proposed reaction mechanisms.⁹ We recently noted the specific formation of (*S*)-configuration at the stereogenic nitrogen center in coordination compounds with silyl substituted TMCD derivatives.¹⁰ Extensive literature research revealed only one additional crystal structure of a copper complex with (*S*)-configuration at all stereogenic nitrogen centers.^{11,12} NMR studies by Rafi et al., however,

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Table 1. Data Collection and Structure Refinement Details for Coordination Compounds 7–10

	7	8	9	10
formula	C ₁₁ H ₂₆ Br ₂ N ₂ Zn	C ₁₂ H ₂₆ Br ₂ N ₂ Zn	C ₁₄ H ₃₀ Cl ₂ N ₂ Zn	C ₁₂ H ₂₆ Br ₂ N ₂ Zn
fw [g·mol ^{−1}]	409.51	423.54	362.67	423.54
temp [K]	173(2)	173(2)	173(2)	173(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
cryst syst	orthorhombic	orthorhombic	monoclinic	orthorhombic
space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁	P2 ₁ 2 ₁ 2 ₁
a [Å]	8.2007(9)	7.8253(4)	12.3903(18)	9.9604(15)
b [Å]	13.2412(14)	12.4256(6)	12.8524(19)	12.2299(18)
c [Å]	14.1628(15)	16.7554(8)	12.6936(19)	13.610(2)
β [deg]			116.785(2)	
vol [Å ³]	1537.9(3)	1629.20(14)	1804.5(5)	1657.9(4)
Z	4	4	4	4
calcd density [Mg·m ^{−3}]	1.769	1.727	1.335	1.697
μ (Mo Kα) [mm ^{−1}]	6.773	6.397	1.648	6.286
F(000)	816	848	768	848
cryst dimensions [mm]	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.30	0.40 × 0.30 × 0.20	0.50 × 0.20 × 0.20
Θ range [deg]	2.11–26.99	2.43–25.00	1.80–27.00	2.24–25.99
index ranges	−10 ≤ h ≤ 10 −16 ≤ k ≤ 16 −18 ≤ l ≤ 18	−9 ≤ h ≤ 9 −14 ≤ k ≤ 14 −19 ≤ l ≤ 19	−15 ≤ h ≤ 15 −16 ≤ k ≤ 16 −16 ≤ l ≤ 16	−12 ≤ h ≤ 12 −15 ≤ k ≤ 15 −16 ≤ l ≤ 16
reflns collected	42365	10634	40541	16054
independent reflns	3353 [R _{int} = 0.0592]	2873 [R _{int} = 0.0487]	7884 [R _{int} = 0.0318]	3268 [R _{int} = 0.1192]
data/restraints/params	3353/0/149	2873/0/158	7884/1/351	3268/0/158
goodness-of-fit on F ²	1.067	0.961	1.026	1.019
final R indices	R1 = 0.0229	R1 = 0.0260	R1 = 0.0251	R1 = 0.0482
[I > 2σ(I)]	wR2 = 0.0557	wR2 = 0.0329	wR2 = 0.0629	wR2 = 0.0898
R indices	R1 = 0.0250	R1 = 0.0356	R1 = 0.0275	R1 = 0.0595
(all data)	wR2 = 0.0568	wR2 = 0.0335	wR2 = 0.0642	wR2 = 0.0925
absolute structure param	−0.004(10)	−0.010(11)	−0.009(6)	0.01(2)
largest diff. peak and hole [e/Å ^{−3}]	0.675, −0.475	0.389, −0.391	0.379, −0.168	0.846, −0.775

indicate that upon coordination of such a tertiary cyclohexane-1,2-diamine derivative to PdCl₂, a mixture of all three possible stereoisomers is formed.⁸ With such little information known about the configuration of the nitrogen centers of tertiary cyclohexane-1,2-diamines in coordination compounds with transition metals and considering the possibility of a broad number of applications if the targeted complexes indeed showed a selective configuration at the coordination sites, we set out to investigate these compounds.

EXPERIMENTAL SECTION

Instruments, Measurements, and Chemicals. Melting points: Büchi B-545. GC-MS, gas chromatography: HP 6890 [column: J. & W. Scientific, 25 m length, ID 0.2; gas: helium, 2.06 bar; temperature program: 50 °C (1 min) −40 °C/min −300 °C (5 min)]. EI-MS: HP Selective Detector 5973 (70 eV). The selected *m/z* values refer to the isotopes ¹H, ¹²C, and ¹⁴N. Elemental analysis: Leco Instrument CHNS-932. Powder diffraction data: Siemens D5005, Cu tube, λ = 1.54178 Å, 1.00 kV, 40 mA, steps 0.02°. Measuring time: 1 s per step. X-ray structure determination: (1) Bruker APEX-CCD, T = 173 K. Programs used for data collection: Smart V. 5622, SaintPlus V. 6.02, Sadabs V. 2.01. (2) Oxford Diffraction Xcalibur S, T = 173 K. Programs used for data collection: CrysAlis (Oxford, 2008), CrysAlis RED (Oxford, 2008). The structures were solved using direct methods (SHELXS90); structural refinement was done with SHELXL97. The H atoms were refined on a riding model in their ideal geometric positions. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 873207 (7), 873208 (8), 873209 (9), 873210 (10), 873203 (11), 873204 (12), 873205 (13), 873206 (14a), and 880491 (14b). Data collection and structure refinement

details are shown in Tables 1 and 2. Quantum chemical calculations were carried out using the programs Gaussian 03, revision E.01¹³ and Turbomole V6.3.¹⁴ The synthesis of (R,R)-TMCD (1), (R,R)-dimethylcyclohexane-1,2-diamine (2), and *N*-ethyl-*N,N'*-trimethyl-(1*R*,2*R*)-cyclohexane-1,2-diamine (3) has already been reported.^{12,15} The lithiation step in the synthesis of the ligands **5a** and **5b** required an inert argon atmosphere, dry solvents, and the use of standard Schlenk techniques.

***N*-Propyl-*N,N'*-trimethyl-(1*R*,2*R*)-cyclohexane-1,2-diamine (5a).** To a solution of **1** (3.0 g, 17.6 mmol) in pentane (10 mL) was added *tert*-butyllithium (14 mL, 26.4 mmol, 1.9 M solution in pentane) at −55 °C. The solution was stirred at room temperature for 6 h, and 1-bromoethane (2.7 mL, 36.3 mmol, dried over calcium hydride and freshly distilled) was then added at −65 °C. After stirring for 12 h at room temperature, sodium hydroxide solution (13 mL, 2 M solution) was added until the reaction mixture was basic. The mixture was then extracted with diethylether (five 20 mL portions). The combined organic phases were dried over sodium sulfate and filtered, and the solvent was removed. Subsequent Kugelrohr distillation (80 °C, 3.7 × 10^{−1} mbar) yielded the pure ligand **5a** as a clear liquid. Yield: 39% (1.35 g, 6.81 mmol). ¹H NMR (CDCl₃): δ 0.87 (t, ³J_{HH} = 7.5 Hz, 3H; C₂H₄CH₃), 1.05–1.19 (m, 4H; CH₂), 1.42–1.51 (m, 2H; CH₂CH₂CH₃), 1.69–1.82 (m, 4H; CH₂), 2.19 (s, 3H; NCH₃), 2.29 [s, 6H; N(CH₃)₂], 2.38–2.48 (m, 4H; C₂H₄CH₃ + CHN). ¹³C NMR (CDCl₃): δ 12.2 (C₂H₄CH₃), 21.6 (CH₂CH₂CH₃), 24.0, 24.7, 25.9 (CH₂), 36.2 (NCH₃), 40.5 [N(CH₃)₂], 57.0 (NCH₂C₂H₅), 62.7, 63.8 (CHN). GC(+)-MS: *t*_R = 4.93 min; *m/z* 198 (100) [M⁺], 127 (57) [C₆H₁₁N(CH₃)₂]⁺, 112 (90) [C₆H₁₁NHCH₂]⁺, 84 (76) [CH₂CHCHN(CH₃)₂]⁺, 72 (48) [CH₃CHN(CH₃)₂]⁺, 58 (48) [CH₂N(CH₃)₂]⁺. Anal. Calcd: C, 72.66; H, 13.21; N, 14.12. Found: C, 72.7; H, 13.0; N, 13.9.

***N*-Pentyl-*N,N'*-trimethyl-(1*R*,2*R*)-cyclohexane-1,2-diamine (5b).** To a solution of **1** (6.0 g, 35.2 mmol) in pentane (20 mL) was

Table 2. Data Collection and Structure Refinement Details for Coordination Compounds 11–14

	11	12	13	14a	14b
formula	C ₁₂ H ₂₆ Cl ₂ N ₂ Zn	C ₁₀ H ₂₂ Br ₂ HgN ₂	C ₁₂ H ₂₆ Br ₂ HgN ₂	C ₁₄ H ₃₀ Br ₂ HgN ₂	C ₁₄ H ₃₀ Br ₂ HgN ₂
fw [g·mol ^{−1}]	334.62	530.71	558.76	586.81	586.81
temp [K]	173(2)	173(2)	173(2)	173(2)	173(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁	P2 ₁
a [Å]	10.2752(11)	9.9374(6)	8.6139(4)	12.0059(11)	8.7499(6)
b [Å]	14.4299(16)	11.5949(6)	13.1839(7)	8.2368(5)	15.8447(9)
c [Å]	21.668(3)	12.8313(6)	14.3439(8)	19.3045(10)	13.4635(11)
β [deg]				99.499(7)	92.018(8)
vol [Å ³]	3212.8(6)	1478.46(14)	1628.96(15)	1882.9(2)	1865.4(2)
Z	8	4	4	4	4
calcd density [Mg·m ^{−3}]	1.384	2.384	2.278	2.070	2.089
μ (Mo Kα) [mm ^{−1}]	1.845	15.792	14.339	12.411	12.527
F(000)	1408	984	1048	1112	1112
cryst dimensions [mm]	0.50 × 0.50 × 0.30	0.50 × 0.20 × 0.20	0.50 × 0.20 × 0.10	0.40 × 0.30 × 0.20	0.30 × 0.10 × 0.10
Θ range [deg]	1.70–27.00	2.37–25.00	2.76–26.00	2.14–25.00	2.33–27.00
index ranges	−13 ≤ h ≤ 12 −18 ≤ k ≤ 18 −27 ≤ l ≤ 27	−12 ≤ h ≤ 12 −13 ≤ k ≤ 14 −15 ≤ l ≤ 15	−10 ≤ h ≤ 10 −16 ≤ k ≤ 13 −17 ≤ l ≤ 16	−14 ≤ h ≤ 14 −9 ≤ k ≤ 9 −22 ≤ l ≤ 22	−11 ≤ h ≤ 11 −20 ≤ k ≤ 20 −14 ≤ h ≤ 17
reflns collected	33644	8698	8125	20225	15591
independent reflns	7008 [R _{int} = 0.0524]	2912 [R _{int} = 0.0323]	3207 [R _{int} = 0.0337]	6620 [R _{int} = 0.0389]	8041 [R _{int} = 0.0496]
data/restraints/params	7008/0/315	2912/0/140	3207/0/158	6620/1/351	8036/1/342
goodness-of-fit on F ²	1.041	1.027	1.057	1.013	1.030
final R indices	R1 = 0.0272	R1 = 0.0644	R1 = 0.0676	R1 = 0.0314	R1 = 0.0563
[I > 2σ(I)]	wR2 = 0.0504	wR2 = 0.1522	wR2 = 0.1551	wR2 = 0.0493	wR2 = 0.1060
R indices	R1 = 0.0310	R1 = 0.0706	R1 = 0.0779	R1 = 0.0417	R1 = 0.0909
(all data)	wR2 = 0.0513	wR2 = 0.1540	wR2 = 0.1576	wR2 = 0.0501	wR2 = 0.1106
absolute structure param	0.005(7)	−0.01(4)	0.01(3)	−0.005(9)	0.010(14)
largest diff. peak and hole [e/Å ^{−3}]	0.353, −0.347	3.678, −0.707	2.797, −0.727	1.758, −2.130	3.307, −1.562

added *tert*-butyllithium (28 mL, 47.6 mmol, 1.9 M solution in pentane) at −50 °C. The solution was stirred at room temperature for 22 h, and then 1-chlorobutane (7.4 mL, 71.3 mmol, 6.6 g) was added at −50 °C. After stirring for 22 h at room temperature, sodium hydroxide solution (25 mL, 2 M solution) was added until the reaction mixture was basic. The mixture was then extracted with diethylether (five 20 mL portions). The combined organic phases were dried over sodium sulfate and filtered, and the solvent was removed. Subsequent Kugelrohr distillation (95 °C, 4 × 10^{−1} mbar) yielded the pure ligand **5b** as a clear liquid. Yield: 47% (3.74 g, 16.5 mmol). ¹H NMR (CDCl₃): δ 0.88 (t, ³J_{HH} = 8.00 Hz, 3H; C₄H₈CH₃), 1.06–1.17 (m, 4H; C₄H₈CH₃ + CH₂), 1.24–1.34 (m, 4H; C₃H₆CH₂CH₃ + CH₂), 1.42–1.48, 1.70–1.72, 1.76–1.82 (m, 2H; CH₂), 2.20 (s, 3H; NCH₃), 2.30 [s, 6H; N(CH₃)₂], 2.39–2.50 (m, 4H; CHN + CH₂C₄H₁₁). ¹³C NMR (CDCl₃): δ 14.3 (C₄H₈CH₃), 22.9 (C₄H₈CH₃), 24.1, 24.6, 25.9 (CH₂), 28.3, 30.1 (C₄H₈CH₃), 36.3 (NCH₃), 40.5 [N(CH₃)₂], 55.0 (C₄H₈CH₃), 62.7, 63.8 (CHN). GC(+)-MS: *t*_R = 5.52 min; *m/z* 226 (10) [M⁺], 169 (71) [M⁺−C₄H₉], 124 (100) [CH₂(CH)₅N(CH₃)₂H⁺], 84 (24) [CH₂CHCHN(CH₃)₂], 58 (43) [CH₂N(CH₃)₂]. Anal. Calcd: C, 74.27; H, 13.36; N, 12.37. Found: C, 74.2; H, 13.2; N, 12.3.

N,N'-Diethyl-N,N'-dimethyl-(1*R*,2*R*)-cyclohexane-1,2-diamine (6). To a solution of (*R,R*)-dimethylcyclohexane-1,2-diamine (**2**; 2.5 g, 17.6 mmol) in toluene (25 mL) were added triethylamine (5.4 mL, 3.94 g, 38.7 mmol) and bromoethane (2.9 mL, 4.22 g, 38.7 mmol). The reaction mixture was refluxed for 14 h. Then, hydrochloric acid (3 M solution) was added until the mixture was acidic. The aqueous phase was separated, and the organic phase was washed with water (25 mL). To the combined aqueous phases was added sodium hydroxide until the reaction mixture was basic. The reaction mixture was then extracted with diethyl ether (four 50 mL portions). The combined organic phases were dried over sodium sulfate, and the solvent was

removed. Subsequent Kugelrohr distillation (74 °C, 4 × 10^{−1} mbar) yielded the pure ligand **6** as a clear liquid. Yield: 76% (2.65 g, 13.4 mmol). ¹H NMR (CDCl₃): δ 0.96–1.24 (m, 4H; CH₂), 1.05 (t, ³J_{HH} = 7.20 Hz, 6H; CH₂CH₃), 1.62–1.73 (m, 2H; CH₂), 1.76–1.83 (m, 2H; CH₂), 2.24 (s, 6H; NCH₃), 2.47–2.66 (m, 6H; CHN + CH₂CH₃). ¹³C NMR (CDCl₃): δ 13.7 (CH₂CH₃), 25.1, 25.8 (CH₂), 36.3 (NCH₃), 48.0 (CH₂CH₃), 61.9 (CHN). GC(+)-MS: *t*_R = 4.84 min; *m/z* 198 (90) [M⁺], 169 (14) [M⁺−CH₃−CH₂], 138 (33) [C₆H₁₁N(CH₂)−CHCH₂], 114 (43) [C₄H₉CHN(CH₃)₂], 98 (100) [CH₃(CH)₃N(CH₃)₂], 72 (71) [CH₃CHN(CH₃)₂]. Anal. Calcd: C, 72.66; H, 13.21; N, 14.12. Found: C, 72.5; H, 13.2; N, 14.2.

Zinc Coordination Compounds (General Procedure). The zinc halide was diluted in acetone and 1 equivalent of ligand was added. The solvent was allowed to evaporate slowly, and the resulting colorless crystals were washed with cold acetone.

(S_N)-[ZnBr₂3] (7). Yield: 86%; mp: 221 °C. ¹H NMR (CDCl₃): δ 1.13–1.50 (m, 4H; CH₂), 1.38 (t, ³J_{HH} = 7.5 Hz, 3H; NC₂CH₃), 1.87–1.95, 2.00–2.14 (m, 2H; CH₂), 2.40, 2.47, 2.66 (s, 3H; NCH₃), 2.56–2.91 (m, 3H; CHN + NCH₂CH₃), 2.95–3.11 (m, 1H; NCH₂CH₃). ¹³C NMR (CDCl₃): δ 13.3 (NCH₂CH₃), 23.0, 23.1, 24.5, 24.6 (CH₂), 36.7, 42.3, 47.8 (NCH₃), 52.3 (NCH₂CH₃), 64.7, 65.1 (CHN). Anal. Calcd: C, 32.26; H, 5.91; N, 6.84. Found: C, 32.4; H, 5.9; N, 6.7.

(S_N)-[ZnBr₂5a] (8). Yield: 91%; mp: 188 °C. ¹H NMR (CDCl₃): δ 0.93 (t, ³J_{HH} = 12.0 Hz, 6H; NC₂H₄CH₃), 1.12–1.23, 1.28–1.39 (m, 2H; CH₂), 1.57–1.69 (m, 1H; CH₂), 1.82–2.00 (m, 3H; CH₂), 2.03–2.11 (m, 2H; CH₂), 2.40, 2.46 (s, 3H; NCH₃), 2.60–2.73 (m, 3H; CH₂ + CHN), 2.65 (s, 3H; NCH₃), 2.77–2.84 (m, 1H; CHN). ¹³C NMR (CDCl₃): δ 11.6 (NCH₂CH₃), 21.5, 23.0, 23.1, 24.5, 24.6 (NCH₂), 37.3, 42.3, 47.8 (NCH₃), 59.7 (CH₂), 64.5, 65.1 (CHN). Anal. Calcd: C, 34.03; H, 6.19; N, 6.61. Found: C, 33.8; H, 6.2; N, 6.5.

(S_N)-[ZnCl₂5b] (9). Yield: 40%; mp: 124 °C. ¹H NMR (CDCl₃): δ 0.89 (t, ³J_{HH} = 8.0 Hz, 3H; NC₄H₈CH₃), 1.10–1.44 (m, 8H; NCH₂),

1.56–1.70 (m, 1H; NCH₂), 1.81–1.95 (m, 3H; NCH₂), 2.01–2.11 (m, 2H; NCH₂), 2.37, 2.43 (s, 3H; NCH₃), 2.54–2.84 (m, 4H; CHN + CH₂), 2.64 (s, 3H; NCH₃). ¹³C NMR (CDCl₃): δ 14.2 (NC₄H₈CH₃), 22.5, 22.9, 23.1, 24.5, 24.6, 27.6, 29.7 (CH₂), 36.7, 41.1, 47.1 (NCH₃), 58.1 (CH₂), 64.6, 65.3 (CHN). Anal. Calcd: C, 46.36; H, 8.34; N, 7.72. Found: C, 46.0; H, 8.4; N, 7.6.

(S_NS_N)-[ZnBr₂6] (10). Yield: 63%; mp: 185 °C. ¹H NMR (CDCl₃): δ 1.12–1.26, 1.32–1.43 (m, 2H; CH₂), 1.37 (t, ³J_{HH} = 10.0 Hz, 6H; NCH₂CH₃), 1.83–1.94, 2.02–2.10 (m, 2H; CH₂), 2.42 (s, 6H; NCH₃), 2.69–2.77 (m, 2H; CHN), 2.79–2.87, 2.97–3.06 (m, 2H; CH₂). ¹³C NMR (CDCl₃): δ 13.1 (NCH₂CH₃), 23.6, 24.6 (CH₂), 37.5 (NCH₃), 52.7 (NCH₂CH₃), 64.7 (CHN). Anal. Calcd: C, 34.03; H, 6.19; N, 6.61. Found: C, 34.1; H, 6.1; N, 6.5.

(S_NS_N)-[ZnCl₂7] (11). Yield: 40%; mp: 157 °C. ¹H NMR (CDCl₃): δ 1.11–1.27, 1.30–1.44 (m, 2H; CH₂), 1.36 (t, ³J_{HH} = 6.0 Hz, 6H; NCH₂CH₃), 1.82–1.94, 2.00–2.09 (m, 2H; CH₂), 2.38 (s, 6H; NCH₃), 2.52–3.01 (m, 6H; CHN + NCH₂CH₃). ¹³C NMR (CDCl₃): δ 12.9 (NCH₂CH₃), 23.1, 24.4 (CH₂), 36.3 (NCH₃), 52.1 (NCH₂CH₃), 64.4 (CHN). Anal. Calcd: C, 34.07; H, 7.83; N, 8.37. Found: C, 34.0; H, 8.0; N, 8.4.

Mercury Coordination Compounds (General Procedure). A total of 1–1.2 equivalents of ligand were added to a suspension of mercury bromide in toluene. The mixture was stirred for 1 min, and the solution was then decanted from the remaining mercury salt. The solvent was allowed to evaporate slowly, and the resulting colorless crystals were washed with diethyl ether.

(S_N)-[HgBr₂1] (12). Yield: 97%; mp: 131 °C. ¹H NMR (CDCl₃): δ 0.35–0.49, 1.05–1.21 (m, 4H; CH₂), 1.79 (s, ³J_{HHg} = 30 Hz, 8H; CH₃ + CHN), 1.95 (s, 6H, ³J_{HHg} = 30 Hz; CH₃). ¹³C NMR (CDCl₃): δ 22.0, 24.5 (CH₂), 40.2, 64.1 [N(CH₃)₂], 63.0 (CHN).

(S_N)-[HgBr₂4] (13). Yield: 64%; mp: 142 °C. ¹H NMR (CDCl₃): δ 0.74–0.99 (b, 3H; C₂H₄CH₃), 1.02–1.55, 1.59–2.05 (m, 5H; CH₂), 2.12–2.81 (m, 4H; CH₂ + CHN), 2.31, 2.34, 2.53 (s, 3H; NCH₃). ¹³C NMR (CDCl₃): δ 11.7 (C₂H₄CH₃), 22.9, 23.5, 24.8, 24.9 (CH₂), 27.3, 41.3, 47.2 (NCH₃), 59.6 (NCH₂), 63.4, 64.2 (CHN).

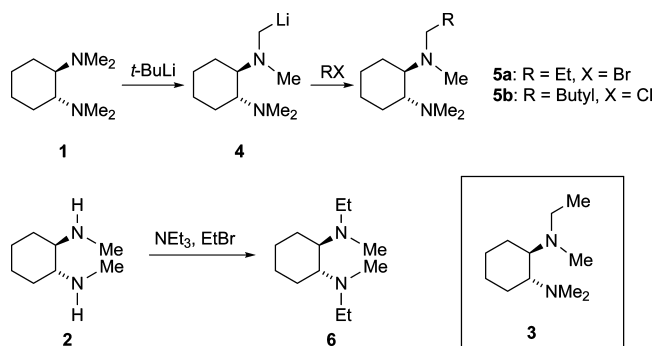
(S_N)-[HgBr₂5] (14). Yield: 38%; mp: 127 °C. ¹H NMR (CDCl₃): δ 0.88 (t, ³J_{HH} = 15.0 Hz, 3H; C₄H₈CH₃), 1.00–2.94 (m, 18H; CH₂ + CHN), 2.13, 2.34, 2.53 (s, 3H; NCH₃). ¹³C NMR (CDCl₃): δ 14.2 (C₄H₈CH₃), 22.5 (C₄H₈CH₃), 22.9, 23.5, 24.9 (CH₂), 29.2, 29.6 (C₄H₈CH₃), 37.3, 41.2, 47.2 (NCH₃), 58.0 (C₄H₈CH₃), 63.4, 64.2 (CHN).

(S_NS_N)-[HgBr₂6] (15). Yield: 44%; mp: 154 °C. ¹H NMR (CDCl₃): δ 1.09–1.27 (m, 4H; CH₂), 1.36 (t, ³J_{HH} = 8.0 Hz, 6H; CH₂CH₃), 1.77–1.89, 1.94–2.09 (m, 2H; CH₂), 2.33 (s, 6H; NCH₃), 2.49–3.07 (m, 6H; CHN + CH₂CH₃). ¹³C NMR (CDCl₃): δ 14.2 (CH₂CH₃), 23.8, 25.0 (CH₂), 37.3 (NCH₃), 52.3 (CH₂CH₃), 63.8 (CHN).

RESULTS AND DISCUSSION

Ligand Synthesis. We synthesized four (*R,R*)-tetramethylcyclohexane-1,2-diamine [(*R,R*)-TMCD] derivatives (3, 5a, 5b, 6) containing one or two stereogenic nitrogen centers (Scheme 1). The synthesis of ligand 3 is described in the literature.¹² For the synthesis of the derivatives 5a and 5b containing one stereogenic nitrogen center, (*R,R*)-TMCD (1) was deprotonated with *tert*-butyllithium according to literature methods.¹⁶ The resulting lithiated product 4 was then reacted with bromoethane and 1-chlorobutane, resulting in the asymmetric ligands 5a and 5b, respectively. The known synthesis of ligand 6 starts from the primary cyclohexane-1,2-diamine to which the ethyl groups are added in a two-step procedure first, while the methyl groups are added afterward.¹² We decided to synthesize ligand 6 by reacting the more widely used secondary (*R,R*)-dimethylcyclohexane-1,2-diamine with 2.2 equivalents of bromoethane in the presence of triethylamine. All ligands were subsequently coordinated to transition metal halides.

Scheme 1. Synthesis of (*R,R*)-TMCD Derivatives with One (3, 5a,5b) or Two (6) Stereogenic Nitrogen Centers



Coordination Compounds. To examine the coordination behavior of the ligands and the configuration of the stereogenic nitrogen centers, we chose the transition metals zinc (a harder Lewis acid) and mercury (a soft Lewis acid),¹⁷ as complexes with these metals were expected to be stable in the air and solution as well as diamagnetic, thereby allowing for a broad variety of characterization techniques. As coordination compounds with tertiary diamines and zinc halides can be used as catalysts for lactide polymerization,^{18,19} we decided to employ both zinc chloride and zinc bromide for a wider variety. Crystals of the coordination compounds with zinc chloride and zinc bromide were grown from acetone solutions.

With the ligands 3 and 5a, coordination compounds 7 and 8 were obtained with zinc bromide. Both coordination compounds crystallize in the orthorhombic crystal system, space group *P*₂₁₂₁₂₁. In both monomeric structures, the zinc center displays a distorted tetrahedral coordination sphere with N1–Zn–N2 angles of only 87.93(9)° in 7 and 86.95(14)° in 8. The angle Br1–Zn1–Br2 is significantly larger [116.49(2)° in 7 and 117.60(3)° in 8] (Figure 2). This distortion of the tetrahedral environment at the zinc center has already been reported for [ZnBr₂(tmeda)].²⁰ While the chelating bond lengths are quite similar in 7 [2.081(2) Å (N1–Zn1), 2.087(2) Å (N2–Zn1)], they differ significantly in 8 [2.102(3) Å (N1–Zn1), 2.069(3) Å (N2–Zn1)]. The coordination compounds 7 and 8 display only one diastereomer with (*S*)-configuration at the stereogenic nitrogen center: In each complex, the alkyl group avoids the sterical demand of the cyclohexane backbone. This is also made clear by comparing the distance of the α -carbon atom of the alkyl group and the carbon atom of the methyl group to the sterically closest carbon atom of the cyclohexane ring (Figure 3): In 7, C9–C7 is shorter [2.850(4) Å] than C10–C7 [3.185(4) Å], and in 8, C9–C7 is shorter [2.988(5) Å] than C10–C7 [3.022(5) Å]. For all zinc complexes, powder diffraction data were collected to ascertain that all crystals contain complexes with (*S*)-configuration at the stereogenic nitrogen center exclusively. This is explained at the end of the section. We were pleasantly surprised that even with ligand 3, (*S*)-configuration is formed selectively upon coordination to zinc bromide, although the ethyl group at the stereogenic nitrogen center is only slightly longer than the original methyl group.

By reacting ligand 5b with zinc chloride, the coordination compound 9 was obtained. It crystallizes in the monoclinic crystal system, space group *P*₂₁. The asymmetric unit contains two molecules of 9 which are so similar that only one of them is discussed and displayed in Figure 4. Similar to the coordination compounds [ZnCl₂(tmeda)]²¹ and [ZnCl₂(tmcd)],²² the zinc

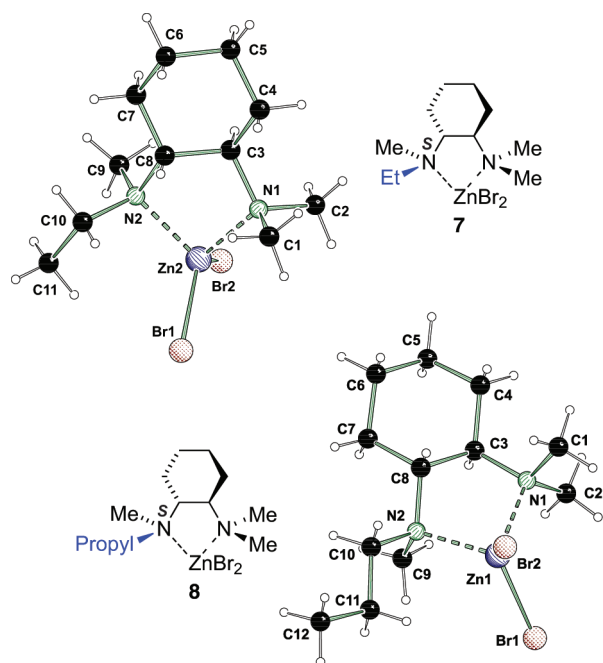


Figure 2. Molecular structures and numbering scheme of the coordination compounds **7** and **8**. Selected angles [deg] and bond lengths [Å] of **7**: N1–Zn1–N2 87.93(9), Br1–Zn1–Br2 116.49(2), N1–Zn1 2.081(2), N2–Zn1 2.087(2), C9–C7 2.850(4), C10–C7 3.185(4). Selected angles [deg] and bond lengths [Å] of **8**: N1–Zn1–N2 86.95(14), Br1–Zn1–Br2 117.60(3), N1–Zn1 2.102(3), N2–Zn1 2.069(3), C9–C7 2.988(5), C10–C7 3.022(5).

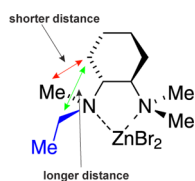


Figure 3. The sterically more demanding alkyl group evades the steric demand of the cyclohexane ring.

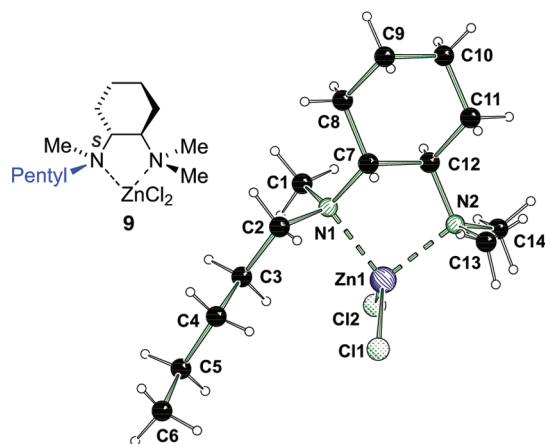


Figure 4. Molecular structure and numbering scheme of the coordination compound **9**. Selected angles [deg] and bond lengths [Å]: N1–Zn1–N2 87.95(7), Cl1–Zn1–Cl2 120.18(3), N1–Zn1 2.086(2), N2–Zn1 2.076(2), C1–C8 2.898(3), C2–C8 3.181(3).

center displays a pseudotetrahedral environment with a small N1–Zn1–N2 angle [87.95(7)°] and a large Cl1–Zn1–Cl2 angle [120.18(3)°]. The coordinating bond lengths are quite

similar to 2.086(2) Å (N1–Zn1) and 2.076(2) Å (N2–Zn1). As observed in complexes **7** and **8**, the sterically more demanding pentyl group evades the cyclohexane backbone, resulting in (*S*)-configuration of the stereogenic nitrogen center. Therefore, the C1–C8 distance is shorter than the C2–C8 distance [2.898(3) Å compared to 3.181(3) Å].

Finally, the coordination compounds **10** and **11** were obtained by reacting ligand **6** with zinc bromide and zinc chloride. Both complexes crystallize in the orthorhombic crystal system, space group $P2_12_12_1$. The asymmetric unit of **11** contains two molecules which are so similar that only one of them is discussed and displayed in Figure 5. Both coordination

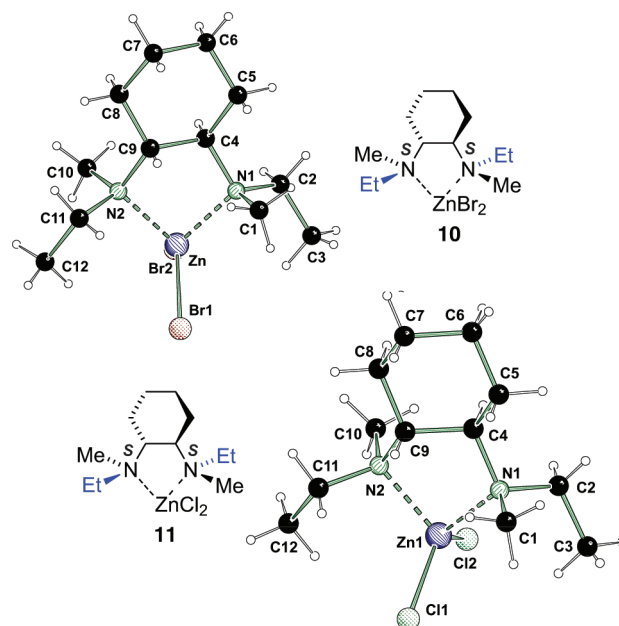


Figure 5. Molecular structures and numbering scheme of the coordination compounds **10** and **11**. Selected angles [deg] and bond lengths [Å] of **10**: N1–Zn1–N2 88.03(19), Br1–Zn1–Br2 117.10(4), N1–Zn1 2.081(5), N2–Zn1 2.085(5), C10–C8 2.893(10), C1–C5 2.892(11), C11–C8 3.110(10), C2–C5 3.201(12). Selected angles [deg] and bond lengths [Å] of **11**: N1–Zn1–N2 88.03(7), Cl1–Zn1–Cl2 118.33(3), N1–Zn1 2.085(2), N2–Zn1 2.088(2), C10–C8 2.865(4), C1–C5 2.888(4), C11–C8 3.194(4), C2–C5 3.144(4).

compounds display a pseudotetrahedral surrounding of the zinc center. As in **7**, the angle N1–Zn1–N2 is small [88.03(19)° in **10** and 88.03(7)° in **11**] while the angle comprising the two halide groups is significantly larger [**10**, 117.10(4)° (Br1–Zn1–Br2); **11**, 118.33(3)° (Cl1–Zn1–Cl2)]. The N–Zn bond lengths are also quite similar [**10**, 2.081(5) Å (N1–Zn1), 2.085(5) Å (N2–Zn1); **11**, 2.085(2) Å (N1–Zn1), 2.088(2) Å (N2–Zn1)]. As in the other coordination compounds with zinc halides and the copper coordination compound with ligand **6**,^{11,12} the stereogenic nitrogen center is (*S*)-configured, and the ethyl groups evade the steric demand of the cyclohexane backbone. This can also be shown by comparing the distances C10–C8 [**10**, 2.893(10) Å; **11**, 2.865(4) Å] and C1–C5 [**10**, 2.892(11) Å; **11**, 2.888(4) Å] to the distances C11–C8 [**10**, 3.110(11) Å; **11**, 3.194(4) Å] and C2–C5 [**10**, 3.201(12) Å; **11**, 3.144(4) Å]. Again, the α -carbon atom of the ethyl group is further away from the sterically demanding cyclohexane backbone than the carbon atom of the methyl group.

Coordination compounds with mercury bromide were obtained from toluene solutions. The reaction was first tested with the parent compound (*R,R*)-TMCDA (**1**) to give crystals of complex **12** and then used for the other ligands. Complexes **13** and **14** with the ligands **5a** and **5b** were obtained as crystals, while the reaction with ligand **3** yielded no product, and crystals of the coordination compound **15** obtained with ligand **6** were of very poor quality.

Complex **12** crystallizes in the orthorhombic crystal system, space group $P2_12_12_1$. The mercury center of the coordination compound displays a distorted tetrahedral environment with a N1-Hg-N2 angle [$76.3(4)^\circ$] that is smaller than the corresponding angles in the zinc complexes. The Br1-Hg1-Br2 angle is very large, amounting to $134.05(6)^\circ$. As expected, the N-Hg bond lengths N1-Hg1 [$2.406(14)$ Å] and N2-Hg1 [$2.381(15)$ Å] are distinctly longer than the coordinating bonds in the zinc complexes (Figure 6).

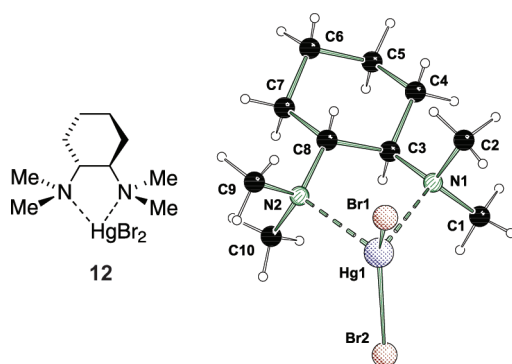


Figure 6. Molecular structures of the coordination compounds **12**. Selected angles [deg] and bond lengths [Å]: N1-Hg1-N2 $76.3(4)$, Br1-Hg1-Br2 $134.05(6)$, N1-Hg1 $2.406(14)$, N2-Hg1 $2.381(15)$.

Complex **13** crystallizes in the orthorhombic crystal system, space group $P2_12_12_1$. Complex **14** forms two different crystals (**a** and **b**) (Figure 7). Both times, it crystallizes in the monoclinic crystal system, space group $P2_1$. In both crystal structures **a** and **b**, the asymmetric unit contains two molecules of **14** which differ in the geometry of the pentyl group. The carbon atoms of this group are eclipsed in **14a** and one molecule in **14b** and stacked in the second molecule of **14b**. Additionally, the second molecule in **14a** displays a disorder at the terminal methyl moiety of the pentyl group.

In both coordination compounds, **13** and **14**, the N-Hg-N angle is very small [**13**, $76.3(5)^\circ$ (N1-Hg1-N2); **14a**, $77.1(2)^\circ$ (N1-Hg1-N2), $76.1(3)^\circ$ (N3-Hg2-N4); **14b**, $76.8(5)^\circ$ (N1-Hg1-N2), $78.2(4)^\circ$ (N3-Hg2-N4)] while the angle Br-Hg-Br is quite large [**13**, $127.56(8)^\circ$ (Br1-Hg1-Br2); **14a**, $135.45(3)^\circ$ (Br1-Hg1-Br2), $127.84(4)^\circ$ (Br3-Hg2-Br4); **14b**, $132.77(6)^\circ$ (Br1-Hg1-Br2), $131.08(7)^\circ$ (Br3-Hg2-Br4)]. Not only the angles surrounding the mercury center but also the N-Hg bond lengths are comparable to those in complex **12** [**13**, $2.393(16)$ Å (N1-Hg1), $2.406(14)$ Å (N2-Hg1); **14a**, $2.399(5)$ Å (N1-Hg1), $2.391(6)$ Å (N2-Hg1), $2.404(5)$ Å (N3-Hg2), $2.367(7)$ Å (N4-Hg2); **14b**, $2.386(14)$ Å (N1-Hg1), $2.351(11)$ Å (N2-Hg1), $2.275(15)$ Å (N3-Hg2), $2.416(11)$ Å (N4-Hg2)]. As in the zinc complexes with stereogenic nitrogen centers, the alkyl groups in **13** and **14** evade the sterical demand of the cyclohexane ring, resulting in (*S*)-configuration at the stereogenic nitrogen centers. In **13**, the distance between the methyl

group and the cyclohexane ring (C9-C7) is shorter [$2.923(32)$ Å] than the distance between the α -carbon atom of the propyl group and the cyclohexane ring [C10-C7 , $3.198(32)$ Å]. Similarly, C9-C7 [$2.832(10)$ Å] and C23-C21 [$2.541(26)$ Å] in **14a** are shorter than C10-C7 [$3.110(25)$ Å] and C24-C21 [$3.134(28)$ Å], and C9-C7 [$2.964(23)$ Å] and C23-C21 [$2.917(27)$ Å] in **14b** are shorter than C10-C7 [$3.183(40)$ Å] and C24-C21 [$3.138(24)$ Å].

In conclusion, both the zinc and the mercury complexes with ligands **3**, **5a**, **5b**, and **6** display (*S*)-configuration selectively. To ascertain that all crystals obtained from the reaction mixtures exhibit the same configuration at the stereogenic nitrogen centers, powder diffractograms of all the crystals obtained from the reaction mixture were measured and compared to the patterns calculated from the crystal structures (this was not possible for complex **14** as the compound formed two different kinds of crystals). As can be seen from the data included in the Supporting Information, both patterns overlap.

NMR Studies. NMR spectra of the zinc and mercury coordination compounds showed only one set of signals, even after heating or cooling to -50°C , another indication that only one diastereomer is formed selectively. In a first attempt to better understand this selective formation of one specific configuration, further NMR studies were carried out to determine whether the complexes are kinetic or thermodynamic products: To the solution of the zinc compound **11**, the free ligand **5b** was added. After 10 min, NMR spectra revealed a slow equilibrium of both possible coordination compounds and both free ligands, which had formed a stable ratio after 1 h. This indicates that the zinc coordination compounds are thermodynamic products. The same experiment with the mercury complexes did not show any exchange, not even after heating the sample. However, when adding an excess of ligand **6** to a solution of complex **14**, the products **15** and **5b** were formed after 10 min, and no signals of complex **14** remained. An equilibrium was formed in solution, which in this case was shifted completely toward the products (Scheme 2). The experiment indicates that the mercury coordination compounds are thermodynamic products, and therefore an equilibrium between the different configurations at the stereogenic nitrogen centers must exist and seems to be shifted toward the (*S*) or (*S,S*)-configured isomer.

Quantum Chemical Calculations. The NMR studies have shown thermodynamic equilibria between complexes with different ligands in solution. Therefore, a thermodynamic equilibrium between the different configurations of the stereogenic nitrogen center must exist as well and be shifted to the thermodynamically most stable compound with (*S*)-configuration at the nitrogen centers. To confirm this assumption, DFT studies can be performed to calculate the energies of all possible isomers. These calculations were only carried out for the zinc complexes though, as the many electrons of the mercury atoms make calculations difficult and time-consuming.

Initial gas phase calculations with the B3LYP/6-31+G(d) method provided by the program Gaussian 03 of the zinc compound **7** showed great deviations in the geometries of the calculated compound and crystal structure. The Br-Zn-Br angle, especially, was too large [128.84° compared to $116.36(2)^\circ$ in the crystal structure]. An extensive evaluation of several different methods and basis sets showed that the combination of BP86/def-TZVP and the additional use of dispersion and the COSMO solvation model provided by the

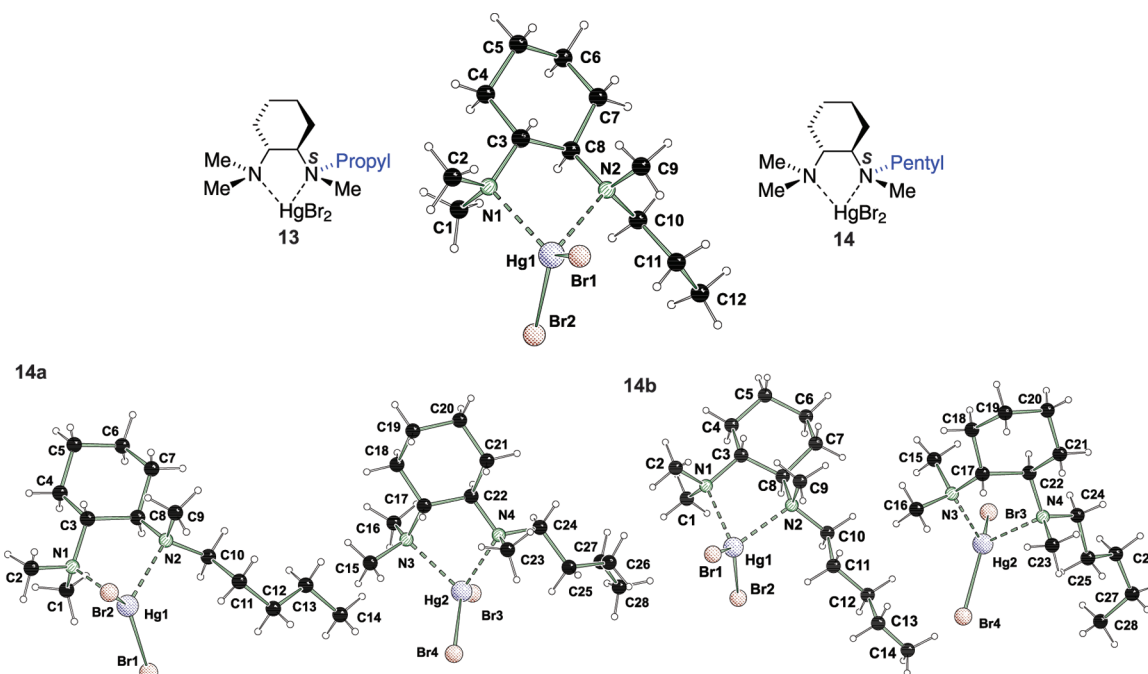
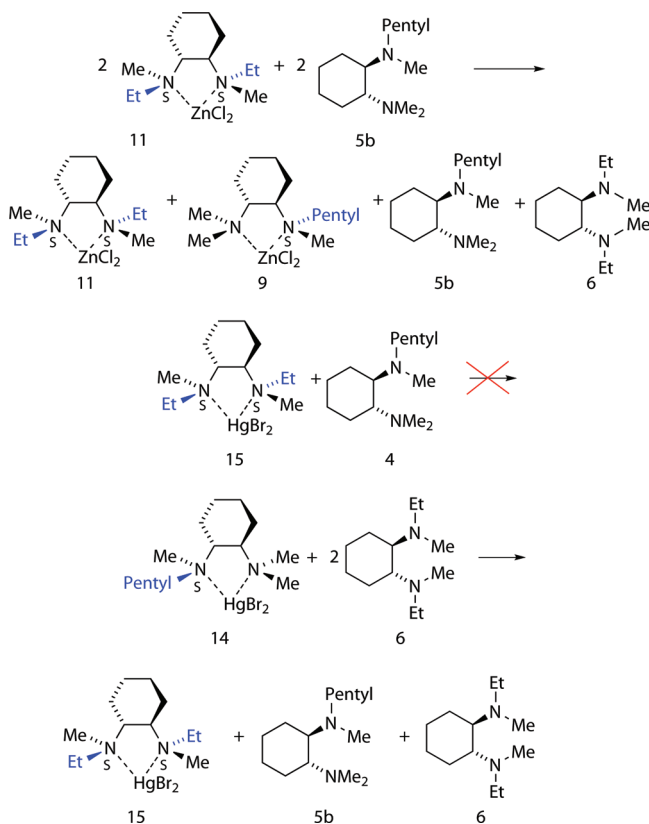


Figure 7. Molecular structures and numbering scheme of the coordination compounds **13** and **14** (with the crystal structures **14a** and **14b**). The asymmetric units of **14a** and **14b** contain two molecules which are placed next to each other. Selected angles [deg] and bond lengths [Å] of **13**: N1–Hg1–N2 76.3(5), Br1–Hg1–Br2 127.56(8), N1–Hg1 2.393(16), N2–Hg1 2.406(14), C9–C7 2.923(32), C10–C7 3.198(32). Selected angles [deg] and bond lengths [Å] of **14a**: N1–Hg1–N2 77.1(2), N3–Hg2–N4 76.1(3), Br1–Hg1–Br2 135.45(3), Br3–Hg2–Br4 127.84(4), N1–Hg1 2.399(5), N2–Hg1 2.391(6), N3–Hg2 2.404(5), N4–Hg2 2.367(7), C9–C7 2.832(10), C24–C21 3.100(13), C10–C7 3.197(9), C23–C21 2.871(10). Selected angles [deg] and bond lengths [Å] of **14b**: N1–Hg1–N2 76.8(5), N3–Hg2–N4 78.2(4), Br1–Hg1–Br2 132.77(6), Br3–Hg2–Br4 131.08(7), N1–Hg1 2.386(14), N2–Hg1 2.351(11), N3–Hg2 2.275(15), N4–Hg2 2.416(11), C9–C7 2.964(23), C23–C21 2.917(27), C10–C7 3.110(25), C24–C21 3.134(28).

Scheme 2. NMR Studies Showing That the Zinc and Mercury Complexes Are Thermodynamic Products



program Turbomole V6.3 is much better suited for calculations of the zinc complexes. This can be seen not only from the Br–Zn–Br angle (116.58°) but also from the RMSD values of the whole molecule, which amount to 0.2 Å in the second calculation method compared to 0.4 Å in the “standard” method B3LYP/6-31+G(d).

Using this method, the different isomers of all coordination compounds were calculated. A comparison of selected bond lengths and angles of the crystal structures as well as the calculated values of the diastereomers are presented in the Supporting Information. The calculated bond lengths and angles fit nicely. A comparison of the calculated energies shows that the (*S*)- or (*S,S*)-configured isomer is indeed the thermodynamically most stable structure, while the other isomers are considerably higher in energy. Therefore, the calculations explain the experimentally observed specific configuration at the stereogenic nitrogen center(s) (Table 3).

Table 3. Calculated Energies [kJ/mol] Using the Method BP86/def-TZVP/COSMO/Dispersion of the Different Possible Diastereomers of Compounds 7–11 in Relation to the Most Stable Isomer

	(S)-isomer	(R)-isomer	
7	0	8	
8	0	7	
9	0	7	
	(S,S)-isomer	(R,S)-isomer	(R,R)-isomer
10	0	8	16
11	0	8	15

CONCLUSION

In this paper, we present a series of zinc and mercury complexes that display a specific configuration at the stereogenic nitrogen center(s). In all cases, the sterically more demanding alkyl group at the nitrogen center evades the sterical demand of the cyclohexane backbone and is found in a pseudoequatorial position in the five-membered ring formed by the coordination of both nitrogen centers to the metal center. We were able to show, both by NMR spectra and by combined single crystal and powder diffractometry, that indeed only one of the possible diastereomers is formed upon coordination to the transition metal halide. Therefore, the complexes are interesting as catalysts for asymmetric reactions or lactide polymerization.^{18,19}

NMR studies indicate that the zinc and mercury compounds are the result of a thermodynamically controlled reaction. By employing quantum chemical calculations including a solvent model, we were able to explain the formation of only one specific diastereomer in the zinc complexes by comparing the energies of the different isomers. Future studies will focus on the question, whether the highly desired selective formation of only one diastereomer is also found in coordination compounds with transition metals that are more widely used in catalysis, such as diethyl zinc and copper chloride.

ASSOCIATED CONTENT

Supporting Information

ORTEP²³ plots with thermal ellipsoids of the crystal structures of complexes **7–14**, powder diffractograms of complexes **7–11** and **13**, MOLEKEL²⁴ plots, input coordinates and output coordinates of the calculated complexes, and an overview of the quantum chemical calculations. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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