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Homoleptic Complexes of Bisstannylenes with Nickel(0): Synthesis, X-Ray Diffraction Studies, and ^{119}Sn NMR Investigations

Alexander V. Zabula, Tania Pape, Alexander Hepp, and F. Ekkehardt Hahn*

Institut für Anorganische und Analytische Chemie der Westfälischen Wilhelms-Universität Münster, Corrensstrasse 36, D-48149 Münster, Germany

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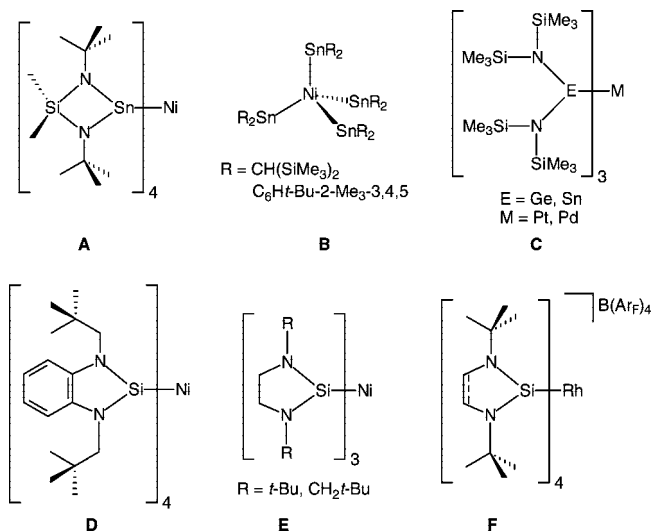
The benzannulated bisstannylenes linked by a $\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2$ (**3**) or 1,3- $(\text{CH}_2)_2\text{C}_6\text{H}_4$ bridging unit (**4**) react with $[\text{Ni}(\text{cod})_2]$ to give the intensely colored homoleptic Ni^0 complexes **5** and **6**. X-ray diffraction and ^{119}Sn NMR studies for the complex of the bisstannylene with the $\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2$ linker **5** reveal the presence of four identical tin atoms. For the nickel complex **6** of the bisstannylene ligand, which contains a 1,3- $(\text{CH}_2)_2\text{C}_6\text{H}_4$ bridging unit, two types of tin atoms with different coordination environments were found both in solution and in the solid state.

Introduction

The coordination chemistry of the heavy analogues of carbenes—silylenes, germynes, and stannylenes—has attracted considerable attention during the last 20 years. Germylenes and stannylenes can potentially act as σ -donor and π -acceptor ligands toward transition metals due to the presence of an unshared electron pair and a vacant p-orbital at the germanium or tin atom. The majority of derivatives of germynes and stannylenes with transition metals are heteroleptic complexes.¹ Homoleptic complexes of the heavier analogues of carbenes are quite rare. The first homoleptic nickel(0) complex of an N-heterocyclic stannylene **A** (Scheme 1)—a stannylene analogue of nickel tetracarbonyl—was prepared in 1990.² Homoleptic complexes with dialkyl stannylene ligands of type **B** (Scheme 1) were first isolated in 1999.³ In complexes of types **A** and **B** four stannylene donors coordinate to a Ni^0 atom in a tetrahedral fashion according to X-ray diffraction analyses and NMR data. Some N-heterocyclic stannylenes prepared by Veith⁴ react with metal salts MX_2 ($\text{M} = \text{Ni}, \text{Pt}, \text{Pd}$; $\text{X} = \text{Cl}, \text{Br}$) under formation of stannylene complexes that exhibit additional bridging halogen atoms between two tin atoms.⁵ Lappert's stannylene and germylene $\text{E}[\text{N}(\text{SiMe}_3)_2]_2$ react with $\text{Pd}(\text{II})$ or $\text{Pt}(\text{II})$ precursors to give neutral homoleptic complexes **C** (Scheme 1) with an E_3M^0 ($\text{E} = \text{Ge}^{\text{II}}, \text{Sn}^{\text{II}}$) core.⁶

Only one example of a homoleptic complex with N-heterocyclic germylene ligands is known. In this complex the nickel(0) atom is coordinated by four equivalent N-heterocyclic germylene moieties derived from 1,8-di(isopropylamino)naphthalene.⁷ The X-ray diffraction study showed nickel(0) complex

Scheme 1. Homoleptic Complexes of Heavy Carbene Analogues



D (Scheme 1) with four benzannulated N-heterocyclic silylene ligands to be built in a tetrahedral fashion.⁸ A different situation was found for saturated N-heterocyclic silylenes. The nickel(0) complex contains only three ligands, which are arranged in a trigonal fashion around the metal center (**E**, Scheme 1).^{9a} Four saturated or three unsaturated N-heterocyclic silylene ligands were found to coordinate to the palladium atom in some palladium(0) complexes.^{9b} Some rhodium(I) complexes with saturated or unsaturated N-heterocyclic silylene ligands **F** exhibit a square-planar coordination geometry of the $\text{Rh}^{\text{I}}\text{Si}_4$ core.¹⁰

We have described the preparation of benzannulated bisgermylenes¹¹ and bisstannylenes¹² with different bridging groups and some heteroleptic complexes with these ligands. Stannylenes containing a divalent tin atom can be considered as heavier

* Corresponding author. E-mail: fehahn@uni-muenster.de.

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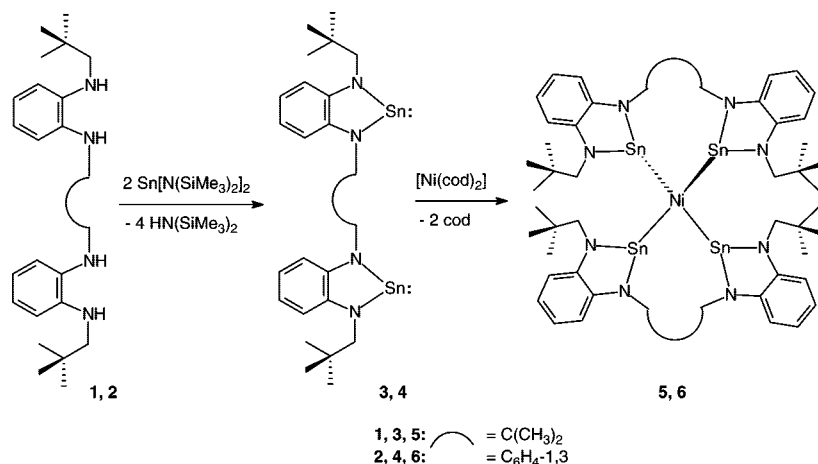
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Scheme 2. Preparation of the Bisstannylenes **3** and **4** and Their Homoleptic Complexes **5** and **6**

analogues of the carbon(II) ligands CO, RNC, or NHC (NHC = N-heterocyclic carbene). The tetrahedral nickel(0) complexes of these carbon(II) ligands have been described.¹³ We describe here the reaction of bisstannylenes with Ni^0 precursors that lead to homoleptic complexes of type $[\text{Ni}(\text{Sn}-\text{Sn})_2]$ ($\text{Sn}-\text{Sn}$ = chelating bisstannylene ligand) and the solvent-dependent ^{119}Sn NMR spectra of these complexes. Some nonchelating^{14a} and chelating bisstannylenes^{14b} have meanwhile been described.

Results and Discussion

The bisstannylenes **3** and **4** have been synthesized by the transamination reaction between the tetraamine **1** or **2**, respectively, and $\text{Sn[N(SiMe}_3)_2]_2$ according to the known procedure for the preparation of the benzannulated mono-^{15,16} and bisstannylenes.¹² The bisstannylenes are bright yellow solids that are moderately soluble in THF. They react with $[\text{Ni(cod)}_2]$ to give the moisture- and air-sensitive homoleptic tetrakis-stannylene complexes **5** and **6** (Scheme 2) in yields of 56–80%. The dark red complex **6** can be purified by recrystallization from a toluene or THF solution, while the purple complex **5** is soluble in various organic solvents including hexane.

Homoleptic complexes $[\text{NiL}_4]$ of nickel(0) normally are colorless or yellow. However, it was noted previously^{2,3} that the stannylene complexes of types **A** and **B** are intensely colored. This was attributed to π -interactions of the tin(II) atom with the nickel(0) atom. We have recently presented data indicating that benzannulated bisstannylenes may indeed not act exclusively as σ -donors but also function as π -acceptor ligands.¹²

The ^{119}Sn NMR spectra of the nickel-stannylene complexes **5** and **6** exhibit different chemical shifts for the tin atoms depending on the solvent used for recording the spectra (THF-

d_8 or toluene- d_8). Only one ^{119}Sn resonance was recorded for **5** at $\delta = 492.3$ ppm in toluene- d_8 and at $\delta = 440.1$ ppm in THF- d_8 (Figure 1, left). The ^{119}Sn resonance is shifted significantly upfield in THF- d_8 . These observations are consistent with the presence of four identical tin(II) atoms in **5**, with the upfield shift in THF- d_8 caused by coordination of THF to the tin atoms. The upfield shift of the tin resonance in coordinating solvents is typical for benzannulated mono- and bisstannylenes and their complexes.^{12,16}

Surprisingly, two only slightly separated resonances ($\delta = 439.0$ and 434.0 ppm) with a relative intensity of 1:1 were observed in the ^{119}Sn NMR spectrum of **6** measured in toluene- d_8 at 300 K (Figure 1, right). One of these ^{119}Sn resonances is significantly shifted upfield in THF- d_8 at 200 K to $\delta = 390.0$ ppm, whereas the other one shows an almost unchanged chemical shift compared to the one observed in toluene ($\delta = 441.5$ ppm). The separation between the ^{119}Sn resonances in THF- d_8 increases when the temperature is lowered to 200 K (Figure 1, right).

The observation of two ^{119}Sn resonances indicates the presence of two different types of tin atoms in complex **6** with a significantly different coordination environment in THF- d_8 . The tin atom that does not show a dependence of the ^{119}Sn resonance signal from the solvent does not coordinate THF molecules, while the other one does, causing the observed highfield shift. In addition, the ^1H NMR spectrum of **6** shows broad signals for the $\text{C(CH}_3)_3$ and NCH_2 groups at ambient temperature. These resonances become sharper at elevated temperature (350 K). The resonance signal for the $\text{C(CH}_3)_3$ protons is split into two signals with a relative intensity of 1:1 at 200 K.

The observation of four identical (in **5**) and two different tin atoms (in **6**) was further investigated by X-ray crystallography. Crystals of **5** suitable for an X-ray diffraction study were grown from a toluene/hexane solution. Complex **5** crystallizes together with one molecule of toluene and 1.5 molecules of hexane in the asymmetric unit. The X-ray structure analysis of **5** (Figure 2) shows a nickel atom surrounded by four stannylene donors in a tetrahedral fashion. The Ni–Sn distances fall in the range 2.3724(15)–2.4007(15) Å, which are typical values for $\text{Sn}_{\text{stannylene}}-\text{Ni}^0$ bond distances.² Small N–Sn–N angles (range 80.2(3)–80.7(3)°) compared to the analogous N–E–N angles in N-heterocyclic carbenes^{15,17} and germylenes¹¹ are found in **5**. The conformations of two eight-membered chelate rings in **5** are similar to those observed for heteroleptic complexes of a similar bisgermylene with molybdenum tetracarbonyl.^{11a} A

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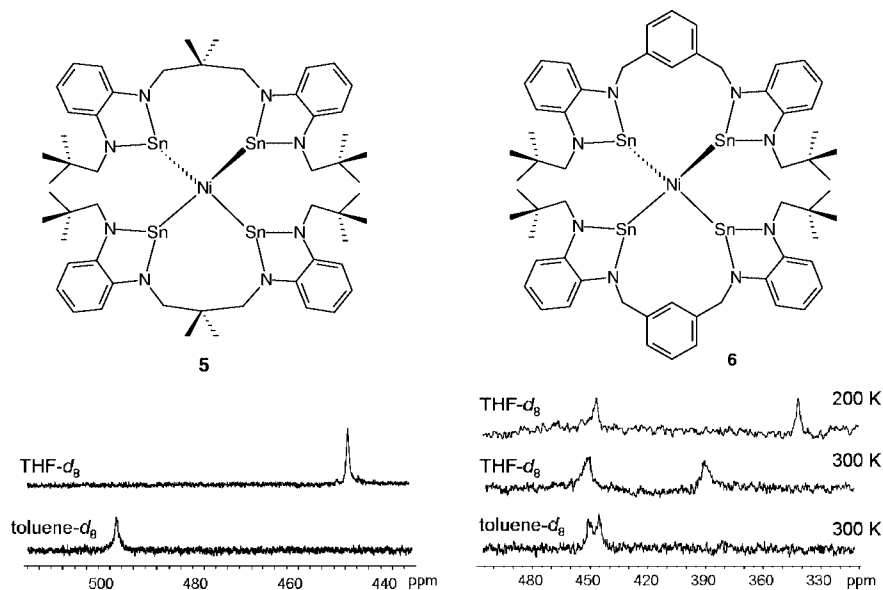


Figure 1. ^{119}Sn NMR spectra of complexes **5** and **6** measured in different solvents and at different temperatures.

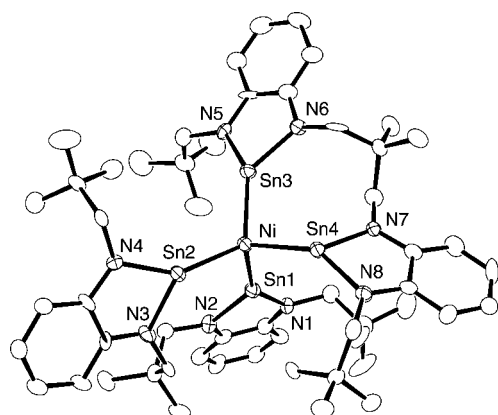


Figure 2. Molecular structure of complex **5**. Selected bond lengths (Å) and angles (deg): Ni–Sn1 2.3724(15), Ni–Sn2 2.3891(15), Ni–Sn3 2.3773(15), Ni–Sn4 2.4007(15), Sn1–N1 2.020(7), Sn1–N2 2.036(8), Sn2–N3 2.050(7), Sn2–N4 2.038(7), Sn3–N5 2.041(8), Sn3–N6 2.050(8), Sn4–N7 2.023(8), Sn4–N8 2.029(8); Sn1–Ni–Sn2 102.14(5), Sn1–Ni–Sn3 105.75(5), Sn1–Ni–Sn4 103.18(5), Sn2–Ni–Sn3 121.58(6), Sn2–Ni–Sn4 121.05(6), Sn3–Ni–Sn4 100.03(5), N1–Sn1–N2 80.7(3), N3–Sn2–N4 80.2(3), N5–Sn3–N6 80.4(3), N7–Sn4–N8 80.6(3).

2-fold noncrystallographic symmetry axis passes through the central carbon atoms of the bridging units $\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2$ and the nickel atom. The structure analysis confirms the presence of four essentially equivalent stannylene donors, all of which are easily accessible for coordination of donor solvents such as THF. This situation is responsible for the observation of only one ^{119}Sn resonance in both toluene- d_8 and THF- d_8 and for the highfield shift of this resonance in THF- d_8 owing to THF coordination to the stannylene centers.

Complex **6** crystallizes from a THF solution together with four solvent molecules. The structure analysis (Figure 3) also shows a tetrahedral nickel(0) atom surrounded by four stan-

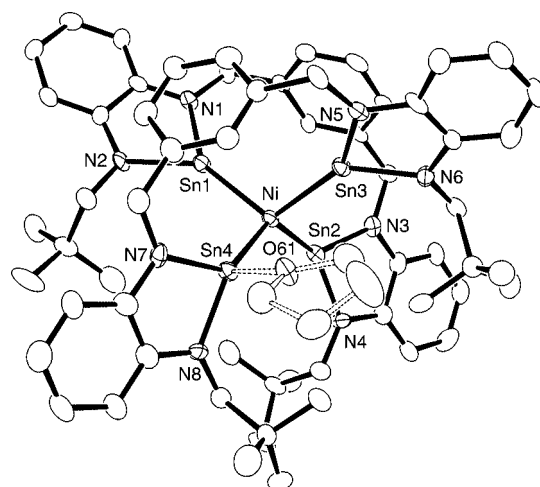


Figure 3. Molecular structure of complex **6**. Selected bond lengths (Å) and angles (deg): Ni–Sn1 2.3667(14), Ni–Sn2 2.3654(15), Ni–Sn3 2.3683(14), Ni–Sn4 2.3827(14), Sn1–N1 2.040(8), Sn1–N2 2.033(8), Sn2–N3 2.040(8), Sn2–N4 2.042(8), Sn3–N5 2.044(8), Sn3–N6 2.056(8), Sn4–N7 2.052(8), Sn4–N8 2.053(8); Sn4–O61 2.537(7); Sn1–Ni–Sn2 108.86(5), Sn1–Ni–Sn3 111.76(5), Sn1–Ni–Sn4 104.28(5), Sn2–Ni–Sn3 100.04(5), Sn2–Ni–Sn4 125.58(6), Sn3–Ni–Sn4 106.18(5), N1–Sn1–N2 79.9(3), N3–Sn2–N4 80.5(3), N5–Sn3–N6 80.1(3), N7–Sn4–N8 80.2(3), O61–Sn4–N7 85.2(3), O61–Sn4–N8 95.1(3).

nylene donors exhibiting unspectacular Sn–Ni bond distances (range 2.3654(15)–2.3827(14) Å) and N–Sn–N angles. No symmetry relation exists between the two 10-membered chelate rings in **6**. Complex **6** possesses two different types of tin(II) atoms. One type (Sn1, Sn3) is sterically protected by the phenylene bridges between the stannylene units; the other type (Sn2, Sn4) is sterically much less shielded. In noncoordinating toluene- d_8 , this leads to two almost identical ^{119}Sn resonances around $\delta = 450$ ppm (Figure 1, right). In THF- d_8 solution the sterically unprotected tin atoms (Sn2 and Sn4) are coordinated by solvent molecules, causing the upfield shift to $\delta = 390$ ppm, while the other two tin atoms (Sn1 and Sn3) are inaccessible for solvent coordination and thus still exhibit a ^{119}Sn resonance at around $\delta = 450$ ppm.

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Table 1. Crystallographic Data for the Complexes 5·toluene·1.5hexane and 6·4THF

parameter	5·C ₇ H ₈ ·1.5C ₆ H ₁₄	6·4THF
formula	C ₇₀ H ₁₀₉ N ₈ NiSn ₄	C ₇₆ H ₁₀₈ N ₈ NiO ₄ Sn ₄
cryst size [mm]	0.17 × 0.07 × 0.02	0.08 × 0.08 × 0.03
<i>M</i> _r	1596.12	11731.19
<i>a</i> [Å]	18.149(5)	13.673(4)
<i>b</i> [Å]	12.499(4)	15.729(4)
<i>c</i> [Å]	32.399(10)	18.926(5)
α [deg]	90	113.997(5)
β [deg]	101.773(7)	90.057(5)
γ [deg]	90	94.065(5)
<i>V</i> [Å ³]	7195(4)	3707(2)
<i>Z</i>	4	2
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1̄
ρ _{calcd} [g cm ^{−3}]	1.473	1.551
μ [mm ^{−1}]	1.670	1.631
2θ range [deg]	2.3–50.0	4.4–50.0
no. of data collected	48 656	29 791
no. unique data, <i>R</i> _{int}	12 638, 0.1664	13 071, 0.0756
no. obsd data [<i>I</i> ≥ 2σ(<i>I</i>)]	7019	8874
<i>R</i>	0.0707	0.0725
<i>wR</i>	0.1044	0.1720
no. of variables	692	850
peak/hole [e Å ^{−3}]	1.134/−0.896	4.519/−1.41

The THF coordination to the sterically less protected tin atoms is detectable in the solid state structure, where one of the four THF molecules in the asymmetric unit coordinates to Sn4. The plane of the THF molecule is oriented perpendicular to the stannylene plane, as would be expected for coordination into the p-orbital of an sp²-hybridized stannylene center. The Sn4–O61 distance of 2.537(7) Å is typical for coordinative Sn–O bonds.¹⁸ This weak coordination does not lead to a significant elongation of the Ni1–Sn4 bond (2.3827(14) Å) compared to the three other Ni–Sn bond lengths (2.3654(15)–2.3683(14) Å). The distances between the tin atoms Sn1 and Sn3 and the centroids of the benzene rings in their vicinity (3.507 and 3.620 Å) are indicative of a weak intramolecular interaction. Similar interactions of this type have been observed previously for *N,N'*-dineopentylbenzimidazoline-2-stannylene, with the corresponding separation measuring 3.23 Å,¹⁹ and for benzannulated plumbylenes.²⁰

We have shown that the empty p-orbital at free N-heterocyclic stannylenes¹⁶ is much more Lewis acidic than the equivalent orbital at analogous carbenes^{15,17} and germylenes.¹¹ We have demonstrated that this strong Lewis acidity prevails in tetrahedral Ni⁰ complexes of N-heterocyclic stannylenes and leads to coordination of THF to the tin centers of the coordinated stannylenes.

Experimental Section

General Comments. All manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques. Solvents were dried over sodium/benzophenone under argon and were freshly distilled prior to use. Toluene-*d*₈ and THF-*d*₈ were dried over Na/K alloy. The tetraamines **1** and **2** were prepared as we have described previously.^{11a} [Ni(cod)₂] was synthesized as described in the literature.²¹ ¹H, ¹³C, and ¹¹⁹Sn NMR spectra were measured on a Bruker AC-400 spectrometer at 400 MHz for ¹H,

100.6 MHz for ¹³C, and 149.2 MHz for ¹¹⁹Sn and are reported relative to TMS or Me₄Sn.

General Procedure for the Synthesis of the Bisstannylenes 3 and 4. A solution of the tetraamine **1** or **2** (0.22 mmol) in THF (10 mL) was treated with Sn[N(SiMe₃)₂]₂ (202 mg, 0.46 mmol). The reaction mixture was stirred for 2 days at ambient temperature. Subsequently the solvent and volatile products were removed *in vacuo*. The colored residue was washed with hexane and dried *in vacuo* to give analytically pure **3** or **4**.

1,3-Bis(*N*-neopentylbenzimidazoline-2-stannylene)-2,2-dimethylpropane (3). Yield: 90% of a bright yellow solid. ¹H NMR (400 MHz, THF-*d*₈): δ 6.81 (m, 4H, Ar–H), 6.51 (m, 4H, Ar–H), 4.14 (s, 4H, CH₂–C(CH₃)₂–CH₂), 3.89 (s, 4H, CH₂–C(CH₃)₃), 1.17 (s, 6H, C(CH₃)₂), 0.98 (s, 18H, C(CH₃)₃). ¹³C NMR (100.6 MHz, THF-*d*₈): δ 147.6, 147.5 (Ar–C_{ipso}), 116.2, 116.0 (Ar–C_{meta}), 110.2, 110.0 (Ar–C_{ortho}), 58.7 (CH₂–C(CH₃)₃), 57.3 (CH₂–C(CH₃)₂–CH₂), 39.2 (C(CH₃)₂), 33.9 (C(CH₃)₃), 29.1 (C(CH₃)₃), 27.0 (C(CH₃)₂). ¹¹⁹Sn NMR (149.2 MHz, THF-*d*₈): δ 178.0. ¹¹⁹Sn NMR (149.2 MHz, THF-*d*₈ + toluene, ν/ν = 1:1): δ 200.9. MS (EI, 70 eV): *m/z* (%) 658 (31) [M]⁺, 601 (33) [M – *t*-Bu]⁺, 540 (100) [M – Sn]⁺, 483 (55) [M – *t*-Bu – Sn]⁺. Anal. Calcd: C, 49.28; H, 6.13; N, 8.51. Found: C, 49.24; H, 6.45; N, 8.26.

1,3-Bis(*N*-neopentyl-*N'*-methylenebenzimidazoline-2-stannylene)benzene (4). Yield: 90% of a bright yellow solid. ¹H NMR (400 MHz, THF-*d*₈): δ 7.68 (s, 1H, Ar–H, NCH₂–C₆H₄), 7.47–7.45 (m, 2H, Ar–H, NCH₂–C₆H₄), 6.80–6.78 (m, 2H, Ar–H, N₂C₆H₄), 6.72–6.71 (m, 2H, Ar–H, N₂C₆H₄), 6.61–6.49 (m, 5H, Ar–H, N₂C₆H₄ and NCH₂–C₆H₄), 5.00 (s, 4H, NCH₂–C₆H₄), 3.83 (s, 4H, NCH₂–C(CH₃)₃), 0.96 (s, 18H, C(CH₃)₃). ¹³C NMR (100.6 MHz, THF-*d*₈): δ 149.2, 146.8 (Ar–C_{ipso}, N₂C₆H₄), 144.0 (Ar–C_{ipso}, NCH₂–C₆H₄), 131.0, 129.9, 129.4 (Ar–C, NCH₂–C₆H₄), 117.0, 115.9 (Ar–C_{meta}, N₂C₆H₄), 110.0, 109.2 (Ar–C_{ortho}, N₂C₆H₄), 59.0 (NCH₂–C(CH₃)₃), 53.7 (NCH₂–C₆H₄), 34.1 (C(CH₃)₃), 29.2 (C(CH₃)₃). ¹¹⁹Sn NMR (149.2 MHz, THF-*d*₈): δ 148.3. MS (EI, 70 eV): *m/z* (%) 692 (64) [M]⁺, 635 (100) [M – *t*-Bu]⁺. Anal. Calcd: C, 52.06; H, 5.53; N, 8.10. Found: C, 52.11; H, 5.86; N, 8.05.

General Procedure for the Synthesis of Complexes 5 and 6. Solid [Ni(cod)₂] (20 mg, 0.072 mmol) was added to a solution of one of the bisstannylenes **3** or **4** (0.145 mmol) in THF (10 mL). The reaction mixture was stirred for 2 days at ambient temperature. Then the mixture was filtered and the solvent and cod were removed *in vacuo*. Complex **5** is soluble in hexane and can be recrystallized from this solvent. X-ray quality crystals of **5** were obtained from a toluene/hexane mixture at –45 °C. Complex **6** is insoluble in hexane. It can be crystallized from toluene or THF at ambient temperature. Satisfactory microanalytical data for **5** and **6** were difficult to obtain owing to the high sensitivity of the compounds toward moisture and air. In addition to the ¹H and ¹³C NMR spectral data reported here, the ¹H and ¹³C spectra of **5** and **6** (measured in toluene-*d*₈) are depicted in the Supporting Information, clearly demonstrating the bulk purity of the substances.

[1,3-Bis(*N*-neopentylbenzimidazoline-2-stannylene)-2,2-dimethylpropane]nickel(0) (5). Yield: 56% of black-purple crystals. ¹H NMR (400 MHz, THF-*d*₈): δ 7.18–6.55 (m, 16H, Ar–H), 4.00 (s, 8H, CH₂–C(CH₃)₂–CH₂), 3.82 (s, 8H, CH₂–C(CH₃)₃), 1.05 (s, 12H, C(CH₃)₂), 0.92 (s, 36H, C(CH₃)₃). ¹³C NMR (100.6 MHz, THF-*d*₈): δ 147.3, 147.3 (Ar–C_{ipso}), 116.0, 115.9 (Ar–C_{meta}), 110.6, 109.7 (Ar–C_{ortho}), 59.1 (NCH₂–C(CH₃)₃), 51.9 (NCH₂–C(CH₃)₂), 40.1 (C(CH₃)₂), 35.0 (C(CH₃)₃), 29.5 (C(CH₃)₃), 25.8 (C(CH₃)₂). ¹¹⁹Sn NMR (149.2 MHz, toluene-*d*₈): δ 492.3. ¹¹⁹Sn NMR (149.2 MHz, THF-*d*₈): δ 440.1.

[1,3-Bis(*N*-neopentyl-*N'*-methylenebenzimidazoline-2-stannylene)benzene]nickel(0) (6). Yield: 80% of dark red crystals. ¹H NMR (400 MHz, toluene-*d*₈, 298 K): δ 7.91 (s, 2H, CH₂–C₆H₄), 7.23 (m, 4H, CH₂–C₆H₄), 6.95–6.93 (m, 8H, N₂C₆H₄), 6.73–6.60

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(m, 10H, $\text{N}_2\text{C}_6\text{H}_4$ and $\text{CH}_2\text{-C}_6\text{H}_4$), 4.87 (s, 8H, $\text{NCH}_2\text{-C}_6\text{H}_4$), 3.84 (br s, 8H, $\text{CH}_2\text{-C}(\text{CH}_3)_3$), 0.75 (br s, 36H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (100.6 MHz, $\text{THF-}d_8$, 298 K): δ 146.9, 145.4 ($\text{Ar-C}_{\text{ipso}}$, $\text{N}_2\text{C}_6\text{H}_4$), 142.2 ($\text{Ar-C}_{\text{ipso}}$, $\text{CH}_2\text{-C}_6\text{H}_4$), 135.0, 132.2, 128.1 ($\text{NCH}_2\text{-C}_6\text{H}_4$), 117.3, 116.3 ($\text{Ar-C}_{\text{meta}}$, $\text{N}_2\text{C}_6\text{H}_4$), 110.2, 108.3 ($\text{Ar-C}_{\text{ortho}}$, $\text{N}_2\text{C}_6\text{H}_4$), 57.0 ($\text{CH}_2\text{-C}(\text{CH}_3)_3$), 55.1 ($\text{NCH}_2\text{-C}_6\text{H}_4$), 34.9 ($\text{C}(\text{CH}_3)_3$), 29.8 ($\text{C}(\text{CH}_3)_3$). ^{119}Sn NMR (149.2 MHz, toluene- d_8 , 300 K): δ 439.0, 434.0. ^{119}Sn NMR (149.2 MHz, $\text{THF-}d_8$, 300 K): δ 441.5, 390.0. ^{119}Sn NMR (149.2 MHz, $\text{THF-}d_8$, 200 K): δ 444.5, 328.4.

X-Ray Diffraction Studies. X-ray diffraction data for **5** and **6** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART²² program package. For further crystal and data collection details see Table 1. Structure solutions were found with the SHELXS-97²³ package using the heavy-atom method and were refined with SHELXL-97²⁴ against F^2 using first isotropic and later

anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions. Complex **5** crystallizes together with one molecule of toluene and 1.5 molecules of hexane in the asymmetric unit, while the asymmetric unit of **6** contains four molecules of THF, one of which is coordinated to one tin atom of the complex. Some large but chemically meaningless electron density was found in close proximity to the heavy atoms of **6**.

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Supporting Information Available: X-ray crystallographic files for the complexes **5** • toluene • 1.5hexane and **6** • 4THF in CIF format and NMR spectra (^1H and ^{13}C for **5** and **6** in toluene- d_8). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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