Intramolecular Lithium Cation Solvation in the "Active Ligand Periphery" of a Tripodal Triaminostannate

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The tris(aminosilyl)methane derivative HC{$SiMe_2NH(2\text{-}MeOC_6H_4)$}$_3$ (**1**) was reacted with three molar equivalents of *n*-butyllithium in pentane to give the solvate-free trilithium triamide HC{$SiMe_2N(Li)(2\text{-}MeOC_6H_4)$}$_3$ (**2**) for which an X-ray diffraction study established the internal solvation of the lithium ions. The trilithium triamide **2** was converted to the triamidostannate [HC{$SiMe_2N(2\text{-}MeOC_6H_4)$}$_3$SnLi] (**3**) by treatment of **2** with one molar equivalent of $SnCl_2$. Both the NMR spectroscopic data obtained in solution and an X-ray structure analysis confirmed the intramolecular coordination of the lithium cation by the peripheral *ortho*-methoxy groups. Reaction of compound **3** with 0.5 molar equivalents of the dinuclear compound $[Rh(COD)Cl]_2$ in toluene afforded the mixed heterodimetallic complex [HC{$SiMe_2N(2\text{-}MeOC_6H_4)$}$_3$Sn(Li)–Rh($\eta^4$-$C_8H_{12}$)(Cl)] (**4**), for which a doublet resonance at high field in the ^{119}Sn NMR spectrum (δ = –196.3; $^1J_{SnRh}$ = 871.6 Hz) confirmed the formation of a Sn–Rh bond. The X-ray structure analysis revealed that the Rh centre in **4** adopts a slightly distorted, square-planar coordination mode, with a tin-rhodium bond length of 2.6048(4) Å, and that the chloro ligand is additionally bonded to the lithium cation.

Introduction

The structural chemistry and reactivity of neutral and anionic tin(II) compounds has attracted much attention in recent years.[1] Group 14 metal-amido and -imido derivatives, in particular, have displayed a great variety of forms of aggregation and reaction patterns.[2,3] The combination of thermodynamic stabilization of the triamidometallates by their integration into a rigid molecular cage structure along with the well-defined orientation and high variability of the peripheral N-substituents has established the tripodal triamidometallates as a versatile new class of ligands in the coordination chemistry of the transition metals.[4] The electronegative N-substituents at the divalent metal atoms render them less oxidizable than would be expected for alkyl- or aryl-substituted derivatives.

An interesting aspect of the structural chemistry of the lithium triamidometallates in solution and in the solid state is the type of interaction between the anionic cage and the countercation (in most cases solvated Li^+). Both solvent-separated salts (**I**) and contact ions have been found (Figure 1).[5] In the latter, the alkali metal ion is either bound directly to the group 14 metal (**II**), in what is thought to be primarily an ionic metal-metal bonding interaction, or attached to the amido-N atoms in a bridging coordination mode (**III**), thus breaking the overall threefold symmetry of the system.

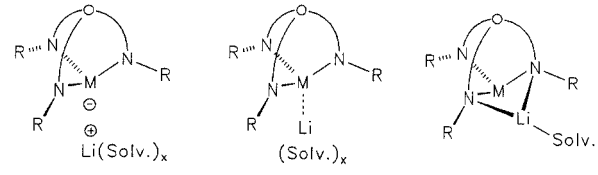

Figure 1. Different modes of cation-anion interactions in triamidostannates and their principal structural types

Which of the structural alternatives discussed above is observed in a given case has been found to be largely unpredictable. It was therefore thought that the design of an amido tripod containing a specific binding site for the metal cation in the ligand periphery would yield "ion pairs" of predefined arrangement.

In an extension of our concept of the "active ligand periphery" in polydentate amides[6,7] containing additional donor functions for cation binding, we synthesised a tripod with peripheral 2-anisyl groups. In this paper we report the

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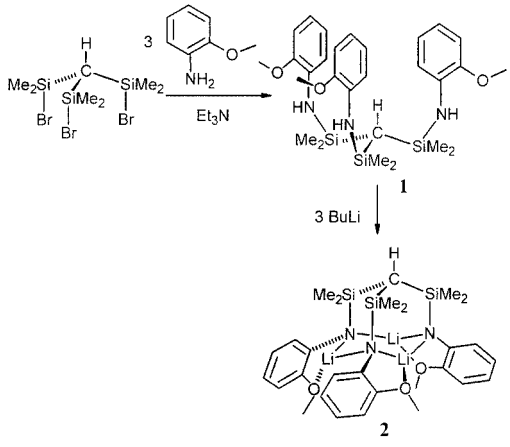
synthesis and crystallographic characterisation of the tripodal triamine, the corresponding trilithium triamide, and its triaminostannate. The "ligand properties" of the latter are demonstrated by the characterisation of a heterobimetallic rhodium complex containing this novel type of stannate fragment.

Results and Discussion

Preparation and Crystallographic Studies of $HC\{SiMe_2NH(2\text{-}MeOC_6H_4)\}_3$ (1) and the Lithium Triamide $HC\{SiMe_2N(Li)(2\text{-}MeOC_6H_4)\}_3$ (2)

Reaction of $HC(SiMe_2Br)_3$ [8] in diethyl ether with three molar equivalents of 2-methoxyaniline in the presence of Et_3N as auxiliary base yielded the triamine $HC\{SiMe_2NH(2\text{-}MeOC_6H_4)\}_3$ (**1**) as a colourless solid (Scheme 1).



Scheme 1

The spectroscopic and analytical data are consistent with an effective threefold symmetry of **1** in solution. The low-field shift of the apical C−H proton resonance (δ = 0.93 ppm in C_6D_6) which we observed previously for aryl-substituted tris(aminosilyl)methane derivatives[9] indicated a preferred conformation of the molecule in solution that is inverted with respect to the adamantane-related arrangement found for the corresponding alkyl-substituted derivatives.[10] The peripheral groups of the ligand precursor are thus effectively turned "inside-out". This type of molecular structure is also prevalent in the solid state as was found in an X-ray diffraction study of the compound. The molecular structure of **1** is depicted in Figure 2 along with the principal bond lengths and interbond angles. The main structural features resemble those of the previously characterised triamine $HC\{SiMe_2NH(4\text{-}CH_3C_6H_4)\}_3$, the three *ortho*-anisyl groups being very regularly arranged with the aromatic rings in the same plane as the quasi-planar amine units and the methoxy groups pointing outwards.

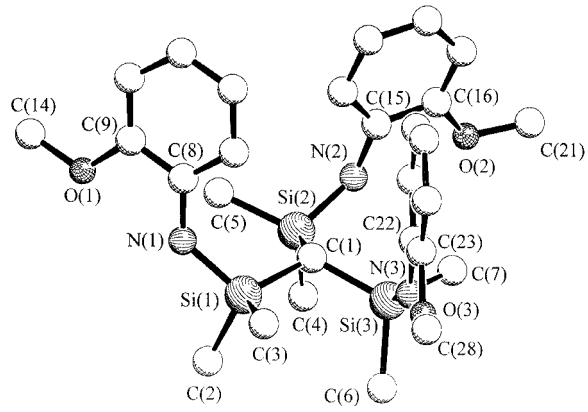


Figure 2. View of the molecular structure of **1**; principal bond lengths (Å) and angles (°): C(1)−Si(1) 1.8829(17), C(1)−Si(2) 1.8825(16), C(1)−Si(3) 1.8867(17), N(1)−Si(1) 1.7358(16), N(2)−Si(2) 1.7439(14), N(3)−Si(3) 1.7395(15), N(1)−C(8) 1.394(2), N(2)−C(15) 1.390(2), N(3)−C(22) 1.394(2); N(1)−Si(1)−C(1) 110.75(7), N(2)−Si(2)−C(1) 109.97(7), N(3)−Si(3)−C(1) 109.73(8), C(8)−N(1)−Si(1) 129.96(14), C(15)−N(2)−Si(2) 129.48(12), C(22)−N(3)−Si(3) 131.19(13)

Upon reaction of **1** with three molar equivalents of *n*-butyllithium in pentane, the solvent-free trilithium triamide $HC\{SiMe_2N(Li)(2\text{-}MeOC_6H_4)\}_3$ (**2**) was obtained as an extremely air- and moisture-sensitive compound (Scheme 1). The signal patterns in the ^1H, ^{13}C, ^{29}Si and ^7Li NMR spectra indicate a threefold symmetrical structure in solution which does not appear to undergo dynamic processes on the NMR time scale. The high molecular symmetry of the trilithium salt **2** was also found in the single crystal X-ray structure. The molecular structure is shown in Figure 3 along with the principal metric parameters.

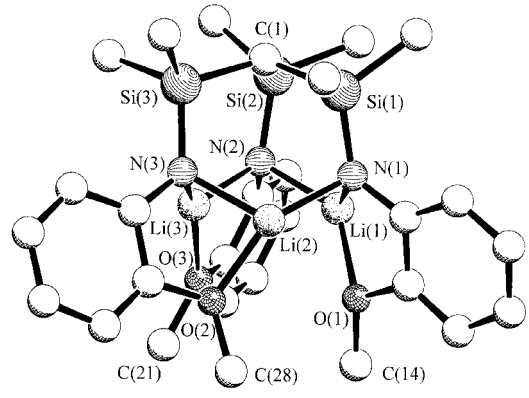
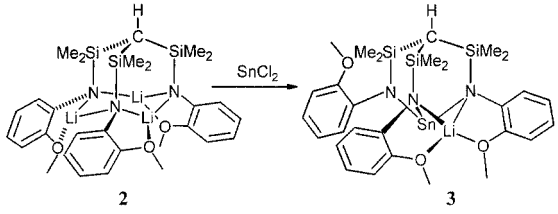


Figure 3. View of the molecular structure of **2**; principal bond lengths (Å) and angles (°): C(1)−Si(1) 1.904(2), C(1)−Si(2) 1.8902(19), C(1)−Si(3) 1.895(2), N(1)−Si(1) 1.7197(16), N(2)−Si(2) 1.7189(16), N(3)−Si(3) 1.7205(17), Li(1)−O(1) 1.963(4), Li(1)−N(1) 1.973(4), Li(1)−N(2) 1.997(4), Li(2)−O(3) 1.938(4), Li(2)−N(3) 2.000(4), Li(2)−N(1) 2.011(4), Li(3)−O(2) 1.915(4), Li(3)−N(2) 1.976(4), Li(3)−N(3) 1.992(4); N(1)−Si(1)−C(1) 107.00(8), N(2)−Si(2)−C(1) 106.40(8), N(1)−Si(1)−C(1) 106.39(8), Li(1)−N(1)−Li(2) 93.98(17), Li(3)−N(2)−Li(1) 92.76(17), Li(3)−N(3)−Li(2) 85.70(18), O(1)−Li(1)−N(1) 83.59(15), O(3)−Li(2)−N(3) 83.54(15), O(2)−Li(3)−N(2) 84.94(16)

The structural centrepiece is an adamantane-related heteroatom cage comprising three Li, N and Si atoms as well as the carbon atom C(1) at the apex of the trisilylmethane unit. This type of structural motif has been reported previously for a series of achiral[8,10] and C_3-chiral[11] tripodal lithium amides. The most remarkable feature is the internal solvation of the lithium ions which generates a rare tris-solvated lithium amide ring structure. The lithium atoms themselves attain a highly nonsymmetrical coordination geometry that is closer to a T-arrangement than to the conventional trigonal structure. In spite of this unequal distribution of the donor atoms, the lithium atoms are very symmetrically disposed vis-à-vis the negatively charged amido functions, as is evident from the approximately equal Li−N distances [overall variation: Li(1)−N(1)/N(2) 1.963(4)/1.973; Li(2)−N(1)/N(3) 2.000(4)/2.011(4); Li(3)−N(2)/N(3) 1.976(4)/1.992(4) Å]. The lithium atoms are not located within the planes defined by the two amido-N atoms they bridge and the oxygen atom of the solvating ether function but are rather displaced outside the cage structure. Due to the Li coordination, the aryl rings of the anisyl groups adopt a symmetrical propeller arrangement.

Synthesis and Structures of the Lithium Triamidostannate(II) HC{SiMe$_2$N(2-MeOC$_6$H$_4$)}$_3$SnLi (3) and the Rh−Sn Heterodimetallic Complex HC{SiMe$_2$N(2-MeOC$_6$H$_4$)}$_3$Sn(Li)−Rh(η^4-C$_8$H$_{12}$)(Cl) (4)

The trilithium triamide **2** was converted into the triamidostannate [HC{SiMe$_2$N(2-MeOC$_6$H$_4$)}$_3$SnLi] (**3**) by treatment of **2** with one molar equivalent of $SnCl_2$ in toluene at elevated temperature in an ultrasound bath. The reaction product crystallised as a colourless solid and was isolated in 63% yield (Scheme 2).



Scheme 2

The observation of three ^{1}H and ^{13}C NMR resonances for the $SiMe_2$ groups (^{1}H: δ = 0.14, 0.59, 0.62 ppm; ^{13}C: δ = 4.9, 5.6, 6.6 ppm) and two NMR resonances for the MeO groups (^{1}H: δ = 3.04, 3.34 ppm; ^{13}C: δ = 55.0, 55.6 ppm) as well as the detection of two ^{29}Si NMR signals for the $SiMe_2$ groups (δ = −1.9, −1.2 ppm) indicate a reduction of the effective symmetry in solution from C_3 to C_S. These spectral patterns are consistent with the coordination of the lithium cation to two amido N-atoms and its internal "solvation" by two of the *ortho*-anisyl groups. In order to establish the details of the molecular structure of this new type of lithium stannate(II), an X-ray diffraction study was carried out (Figure 4).

Figure 4a

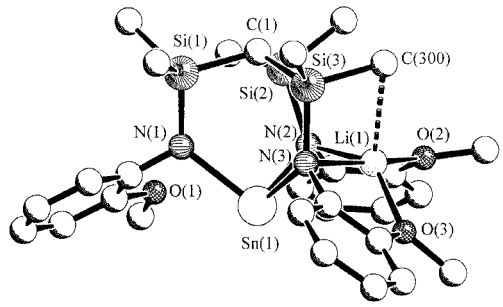


Figure 4b

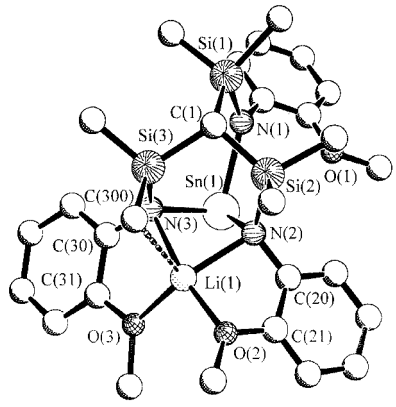


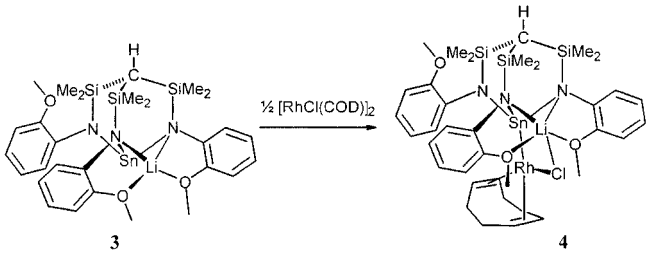
Figure 4. View of the molecular structure of **3**; principal bond lengths (Å) and angles (°): Sn(1)−N(1) 2.255(2), Sn(1)−N(2) 2.2235(19), Sn(1)−N(3) 2.096(2), Sn(1)−Li(1) 2.931(4), Li(1)−N(2) 2.039(5), Li(1)−N(3) 2.139(5), Li(1)−O(2) 1.908(5), Li(1)−O(3) 2.044(5); N(1)−Sn(1)−N(2) 94.20(7), N(1)−Sn(1)−N(3) 96.55(7), N(2)−Sn(1)−N(3) 77.84(7), N(3)−Li(1)−N(2) 81.03(17), N(2)−Li(1)−O(2) 88.2(2), N(3)−Li(1)−O(3) 85.39(18)

The lithium stannate **3** crystallises in the centrosymmetrical space group $P2_1/n$, and possesses a molecular structure in the solid which, albeit distorted, is consistent with the C_s-symmetry derived from the NMR spectroscopic data recorded in solution. The most characteristic structural feature of **3** is undoubtedly the intramolecular coordination of the lithium cation by the peripheral *ortho*-methoxy groups. The Li−O bond lengths found in **3** [1.908(5) Å and 2.044(5) Å] are similar to those found in structurally related solvated metallates, such as HC{SiMe$_2$N[(*S*)-CH(Me)Ph]}$_3$SnLi(THF) [1.95(1) Å][13b] and MeSi{SiMe$_2$N(*t*Bu)}$_3$Pb-Li(THF) [2.11(7) Å].[5b] Significantly, the lithium cation is placed above the plane, which is spanned by the atoms O2, N2, N3 and O3. This exposed position of the lithium leads to a very close contact with the adjacent methyl group C300 [*d*(Li1−C300) = 2.603(2) Å] which effectively occupies the vacant coordination site of the lithium centre. Such "agostic" interactions with hydrocarbon fragments are quite common in lithium amides provided that the coordination numbers of the lithium centres are low.[12] It is therefore surprising to observe this structural feature for four-coordinate lithium, which is probably due to the unusual coordination geometry (distorted square

planar instead of tetrahedral) imposed by the rigid caged structure of the triamidostannate(II).

It is noteworthy that compound **3** is also formed in an in situ reaction of $[HC\{SiMe_2NH(2\text{-}MeOC_6H_4)\}_3]$ (**1**) with *n*-butyllithium and $SnCl_2$ in diethyl ether, and therefore no indication for a competitive coordination of the anisyl groups vs. diethyl ether has been found. However, the formation of **3** using diethyl ether as a reaction medium is accompanied by a redox process (formation of the free ligand) and is therefore unsuitable for a high yield synthetic protocol.

Due to the efficient intramolecular cation solvation, the lithium stannate **3** can be viewed as a neutral compound. In reactions of **3** with transition metal complexes it was therefore expected to act as a neutral "ligand" and thus display a behaviour that differs from the anionic stannates we studied recently.[5,13] Reaction of compound **3** with 0.5 molar equivalents of the dinuclear compound $[Rh(COD)Cl]_2$ in toluene afforded the mixed heterodimetallic complex $[HC\{SiMe_2N(2\text{-}MeOC_6H_4)\}_3Sn(Li)-Rh(\eta^4\text{-}C_8H_{12})(Cl)]$ (**4**) in high yield (Scheme 3).



Scheme 3

The observation of a doublet resonance at high field in the ^{119}Sn NMR spectrum ($\delta = -196.3$; $^1J_{SnRh} = 871.6$ Hz) confirms the formation of a Sn−Rh bond and the elemental analysis the formulation given above. The resonance patterns attributable to the stannate fragment in the ^1H, ^{13}C, and ^{29}Si NMR spectra are very similar to those of **3** indicating the retention of the local C_S symmetry. This is consistent with the anticipated nature of the tin cage as a formally neutral ligand at the rhodium, which retains its square planar coordination geometry due to the presence of the chloro ligand and the chelating COD ligand. In order to obtain a detailed insight into the relative arrangement of the two metal complex fragments a single crystal X-ray structure analysis of complex **4** was carried out. Its molecular structure is depicted in Figure 5 along with the principal bond lengths and angles.

As can be seen in Figure 5, the overall structure of the stannate fragment in the heterodimetallic complex is the same as in the noncoordinated compound **3**. A structural effect of the transition metal coordination of the tin in **4** is the slight contraction of the Sn−N bonds relative to those in **3** [average Sn−N distance in **4** is 2.136(2) Å compared to 2.192(2) Å in **3**] which we observed in all the structurally characterised transition metal-stannate complexes. The Rh centre in **4** adopts a slightly distorted, square-planar coordination mode and the tin-rhodium bond length of

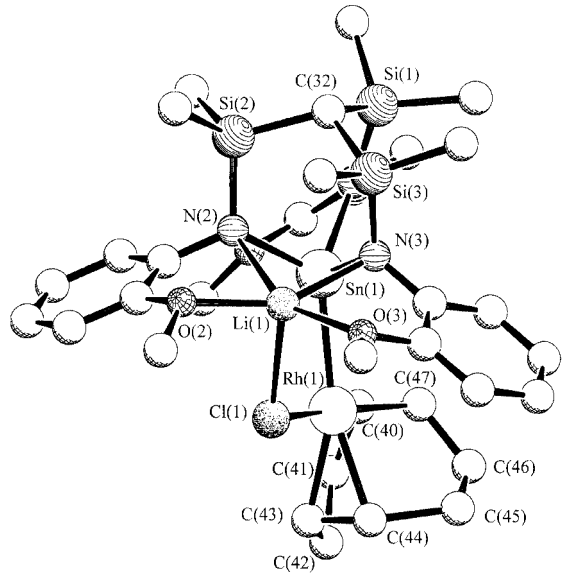


Figure 5. View of the molecular structure of **4**; principal bond lengths (Å) and angles (°): Sn(1)−N(1) 2.108(2), Sn(1)−N(2) 2.137(19), Sn(1)−N(3) 2.164(2), Sn(1)−Li(1) 2.891(5), Sn(1)−Rh(1) 2.6048(3), Rh(1)−C(43) 2.163(4), Rh(1)−C(44) 2.169(4), Rh(1)−C(40) 2.114(3), Rh(1)−C(47) 2.106(3), Li(1)−N(2) 2.371(6), Li(1)−N(3) 2.167(6), Li(1)−O(2) 1.976(5), Li(1)−O(3) 2.115(6), Li(1)−Cl(1) 2.426(5), Rh(1)−Cl(1) 2.3721(7); N(1)−Sn(1)−N(2) 99.80(9), N(1)−Sn(1)−N(3) 98.77(9), N(2)−Sn(1)−N(3) 83.35(8), N(3)−Li(1)−N(2) 77.96(18), N(2)−Li(1)−O(2) 76.76(19), N(3)−Li(1)−O(3) 77.97(19), Cl(1)−Rh(1)−Sn(1) 83.017(19), Cl(1)−Li(1)−Sn(1) 76.26(14), Rh(1)−Sn(1)−Li(1) 89.04(11), Rh(1)−Cl(1)−Li(1) 107.07(12)

2.6048(4) Å is within the range of previously characterised Rh−Sn complexes.[14] The chloro ligand is additionally bonded to the lithium cation of the stannate unit. Although the Li(1)−Cl(1) distance of 2.426(5) Å is ca. 0.2 Å greater than the Li−Cl bond length found in $[HC\{SiMe_2N(Li)[(S)\text{-}3,3\text{-dimethyl-2-butyl}]\}_3\text{-}LiCl(Et_2O)_3]$[11a] it is similar to those previously characterised in a series of Li−Cl complexes.[15]

The lithium stannate ligand has a stronger *trans* influence than the chloro ligand as is evident from the metal-carbon distances to the COD ligand [Rh(1)−C(43) 2.163(4), Rh(1)-2.169(4) Å *trans* to Sn(1) in comparison to Rh(1)−C(40) 2.114(3), Rh(1)−C(47) 2.106(3) *cis* to Sn(1)]. As a neutral ligating unit it therefore resembles the ubiquitous group 15 donor ligands.[16] The *trans* influence of the lithium stannate ligand in **4** is similar to that previously found in square-planar $[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}P,Sb\text{-}i\text{Pr}_2\text{PCH}_2\text{Sb}t\text{Bu}_2)]\text{-}PF_6$.[16a]

Conclusion

We have shown in this first study of the tin(II) chemistry of a new tripodal amido ligand containing an "active ligand periphery" that the type of lithium-stannate interaction may be controlled by secondary coordinating functions in the ligand. The stannates thus obtained can be viewed as neutral species that may serve as neutral Sn-donor "ligands" in transition metal chemistry. The scope of this ap-

proach, in particular the application of monodentate ligands with extremely large cone angles in transition metal complexes, is currently being studied in our laboratories.

Experimental Section

All manipulations were performed under nitrogen (desiccant P_4O_{10}, Granusic®, J.T. Baker) on a high vacuum line using standard Schlenk techniques, or in a glovebox. All reaction flasks were heated prior to use during three evacuation-refill cycles. Solvents and solutions were transferred by needle-septa techniques. Solvents were dried according to standard methods and saturated with nitrogen. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and stored over 4 Å molecular sieves. Solids were separated from suspensions by filtration through dried Celite. The ^{1}H, ^{7}Li, ^{13}C, ^{19}F, ^{29}Si and ^{119}Sn NMR spectra were recorded on Bruker AC 200, Bruker Avance 250 and Bruker AMX 400 FT NMR spectrometers. ^{1}H and ^{13}C data are listed in parts per million [ppm] relative to tetramethylsilane and are referenced using the residual protonated solvent peak (^{1}H) or the carbon resonance (^{13}C). ^{7}Li data are listed in ppm relative to LiCl/D_2O (1 M, external). ^{29}Si data are listed in ppm relative to tetramethylsilane as an external standard. ^{119}Sn data are listed in ppm relative to tetramethyltin as an external standard. Infrared spectra were recorded on a Nicolet Magna IRTM 750 spectrometer. Elemental analyses were carried out with a Leco CHNS-932 microanalyzer and a CE-instruments EA 1110 CHNS-O microanalyzer, respectively. $[Rh(COD)Cl]_2$,[17] and $[HC(SiMe_2Br)_3]$[8] were prepared according to published procedures. *o*-Methoxyaniline employed in the ligand synthesis was distilled prior to use. All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of Compounds. $[HC\{SiMe_2NH(2\text{-}MeOC_6H_4)\}_3]$ (1): At 0 °C a solution of $[HC(SiMe_2Br)_3]$ (5.22 g, 12.2 mmol) in diethyl ether (20 mL) was added dropwise to a vigorously stirred solution of 2-methoxyaniline (4.51 g, 36.7 mmol) and triethylamine (3.71 g, 36.7 mmol) in diethyl ether (50 mL). After the addition was completed the reaction mixture was stirred for another 12 h at room temperature. The solution was filtered through Celite and the residue was extracted with diethyl ether (3 × 20 mL). The solvent was removed in vacuo and the pale yellow crude product was recrystallized from diethyl ether (10 mL) at −35 °C to yield 5.61 g (83%) of a colourless powder. ^{1}H NMR (200.13 MHz, C_6D_6, 295 K): δ = 0.43 [s, 18 H, $Si(CH_3)_2$], 0.93 [s, 1 H, $HC(SiMe_2)_3$], 3.27 (s, 9 H, OCH_3), 4.60 (s, 3 H, N*H*), 6.54−6.87 (m, 12 H, aryl hydrogens) ppm. ^{13}C{^{1}H} NMR (50.32 MHz, C_6D_6, 295 K): δ = 2.9 [$Si(CH_3)_2$], 4.6 [$HC(SiMe_2)_3$], 55.1 (OCH_3), 110.6, 115.2, 117.7, 121.8, 137.4, 148.6 (aryl carbons) ppm. ^{29}Si{^{1}H} NMR (39.76 MHz, C_6D_6, 295 K): δ = 1.6 [$Si(CH_3)_2$] ppm. IR (KBr): $\tilde{\nu}$ = 3373 cm^{-1} vs, 3060 w, 2958 m, 2894 w, 2843 w, 2830 w, 1602 vs, 1519 vs, 1909 ww, 1858 ww, 1449 m, 1398 s, 1329 m, 1301 m, 1261 w, 1244 w, 1219 w, 1179 m, 1111 s, 1054 w, 1037 m, 1000 s, 900 vs, 846 vs, 767 w, 744 m, 738 m, 687 vw. $C_{28}H_{43}N_3O_3Si_3$ (553.92): calcd. C 60.71, H 7.82, N 7.59; found C 60.55, H 7.93, N 7.56.

$[HC\{SiMe_2N(Li)(2\text{-}MeOC_6H_4)\}_3]$ (2): *n*-Butyllithium (14 mL, 22.4 mmol of a 1.6 mol/L solution in hexane) was added to a slurry of $[HC\{SiMe_2NH(2\text{-}MeOC_6H_4)\}_3]$ **(1)** (4.13 g, 7.45 mmol) in pentane (50 mL) at −20 °C. The reaction mixture was slowly warmed up to ambient temperature and stirring at room temperature was continued for 2 h. The off white slurry was subsequently refluxed for 15 min and stirred for a further 12 h at room temperature. The reaction mixture was filtered through a G3 frit, washed with pentane (3 × 10 mL) and dried under vacuum to yield 4.00 g (94%) of a colourless, microcrystalline powder. ^{1}H NMR (250.13 MHz, C_6D_6, 295 K): δ = −0.59 [s, 1 H, $HC(SiMe_2)_3$], 0.61 [s, 18 H, $Si(CH_3)_2$], 3.00 (s, 9 H, OCH_3), 6.44 (dd, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.3 Hz, 3 H), 6.58 (dt, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.3 Hz, 3 H), 6.94 (dt, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.3 Hz, 3 H), 7.07 (dd, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.3 Hz, 3 H) ppm. ^{7}Li{^{1}H} NMR (97.21 MHz, C_6D_6, 295 K): δ = −0.4 ppm. ^{13}C{^{1}H} NMR (62.89 MHz, C_6D_6, 295 K): δ = 6.2 [$Si(CH_3)_2$], 12.4 [$HC(SiMe_2)_3$], 54.5 (OCH_3), 109.1, 113.7, 123.2, 123.4, 149.6, 152.8 (aryl carbons) ppm. ^{29}Si{^{1}H} NMR (49.69 MHz, C_6D_6, 295 K): δ = −1.9 [$Si(CH_3)_2$] ppm. $C_{28}H_{40}Li_3N_3O_3Si_3$ (571.72): calcd. C 58.82, H 7.05, N 7.35; found C 58.65, H 6.93, N 7.42.

$[HC\{SiMe_2N(2\text{-}MeOC_6H_4)\}_3SnLi]$ (3): Toluene (30 mL) was added to a mixture of $[HC\{SiMe_2N(2\text{-}MeOC_6H_4)\}_3Li_3]$ **(2)** (1.00 g, 1.75 mmol) and $SnCl_2$ (332 mg, 1.75 mmol) at room temperature. The resulting mixture was sonicated for 6 h at 60 °C and subsequently filtered through Celite. The residue was extracted with hot toluene (2 × 10 mL) and the solvent of the filtrate was evaporated under vacuum. The obtained off white residue was washed with diethyl ether (10 mL) and pentane (2 × 10 mL) and dried under vacuum to give 746 mg (63%) of a colourless, microcrystalline powder. ^{1}H NMR (400.13 MHz, C_6D_6, 295 K): δ = −0.49 [s, 1 H, $HC(SiMe_2)_3$], 0.14, 0.59, 0.62 [s, 18 H, $Si(CH_3)_2$], 3.04, 3.34 (s, 9 H, OCH_3), 6.52 (dd, $^3J_{H,H}$ = 7.9, $^4J_{H,H}$ = 1.2 Hz, 2 H), 6.67 (dd, $^3J_{H,H}$ = 9.7, $^4J_{H,H}$ = 1.5 Hz, 1 H), 6.82 (dt, $^3J_{H,H}$ = 7.9, $^4J_{H,H}$ = 1.8 Hz, 2 H), 6.85 (dt, $^3J_{H,H}$ = 7.9, $^4J_{H,H}$ = 1.4 Hz, 1 H), 6.93 (dt, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.5 Hz, 2 H), 7.01 (dt, $^3J_{H,H}$ = 7.3, $^4J_{H,H}$ = 1.5 Hz, 1 H), 7.34 (dd, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.8 Hz, 2 H), 7.42 (dd, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.5 Hz, 1 H) ppm. ^{7}Li{^{1}H} NMR (77.77 MHz, C_6D_6, 295 K): δ = −0.3 ppm. ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 295 K): δ = 4.9, 5.6, 6.6 [$Si(CH_3)_2$], 8.2 [$HC(SiMe_2)_3$], 55.0, 55.6 (OCH_3), 111.0, 111.6, 120.0, 121.2, 121.6, 123.4, 130.3, 142.5, 143.0, 154.7, 155.1 (aryl carbons) ppm. ^{29}Si{^{1}H} NMR (39.76 MHz, C_6D_6, 295 K): δ = −1.9, −1.2 [$Si(CH_3)_2$] ppm. ^{119}Sn{^{1}H} NMR (93.28 MHz, C_6D_6, 291 K): δ = −96.5 ppm. $C_{28}H_{40}LiN_3O_3Si_3Sn$ (676.53): calcd. C 49.71, H 5.96, N 6.21; found C 49.84, H 5.90, N 5.94.

$[HC\{SiMe_2N(2\text{-}MeOC_6H_4)\}_3Sn(Li)-Rh(\eta^4\text{-}C_8H_{12})(Cl)]$ (4): Toluene (10 mL) was added to a solid mixture of $[HC\{SiMe_2N(2\text{-}MeOC_6H_4)\}_3SnLi]$ **(3)** (380 mg, 0.56 mmol) and $[Rh(COD)Cl]_2$ (139 mg, 0.28 mmol) at room temperature. The orange solution was stirred for a further 12 h at room temperature and subsequently filtered through Celite. The residue was extracted with toluene (10 mL) and the filtrate was dried under vacuum. The obtained yellow residue was washed with pentane (10 mL) and diethyl ether (5 mL) and dried under vacuum to yield 410 mg (79%) of a yellow, microcrystalline powder. ^{1}H NMR (250.13 MHz, C_6D_6, 323 K): δ = −0.51 [s, 1 H, $HC(SiMe_2)_3$], 0.30, 0.40, 0.45 [s, 18 H, $Si(CH_3)_2$], 1.09−1.86 (m, 8 H, allylic hydrogens), 3.51 (s, 6 H, OCH_3), 3.78 (s, 3 H, OCH_3), 3.98 (d, $^3J_{H,H}$ = 2.8 Hz, 2 H, olefinic hydrogens), 4.33 (d, $^3J_{H,H}$ = 2.5 Hz, 2 H, olefinic hydrogens), 6.61−7.41 (m, 12 H, aryl hydrogens) ppm. ^{7}Li{^{1}H} NMR (97.21 MHz, C_6D_6, 295 K): δ = 1.5 ppm. ^{13}C{^{1}H} NMR (62.89 MHz, C_6D_6, 323 K): δ = 5.0 [$Si(CH_3)_2$], 5.6 [br, $Si(CH_3)_2$], 8.1 [$HC(SiMe_2)_3$], 28.0, 33.7 (allylic carbons), 55.0, 55.2 (OCH_3), 63.8 (d, $^1J_{RhC}$ = 13.3 Hz, olefinic carbons), 94.5 (d, $^1J_{RhC}$ = 8.3 Hz, olefinic carbons), 110.7, 110.9, 121.3, 121.8, 122.2, 122.8, 128.1, 130.9, 141.6, 141.8, 155.6, 155.9 (aryl carbons) ppm. ^{29}Si{^{1}H} NMR (49.69 MHz, C_6D_6, 295 K): δ = 1.4, 2.0 [$Si(CH_3)_2$] ppm. ^{119}Sn{^{1}H} NMR (149.19 MHz, C_6D_6, 291 K): δ = −196.3 (d, $^1J_{RhSn}$ = 871.6 Hz, N_3Sn−Rh) ppm. IR (KBr): $\tilde{\nu}$ = 3379 cm^{-1} s, 3068 vw, 2961m, 2834 vw, 2289 vw, 2019

Table 1. Crystal data and structure refinement for **1**, **2**, **3** and **4**

	1	**2**	**3**	**4**
Molecular formula	$C_{28}H_{43}N_3O_3Si_3{\cdot}C_6D_6$	$C_{28}H_{40}Li_3N_3O_3Si_3Sn{\cdot}2.5C_6D_6$	$C_{28}H_{40}LiN_3O_3Si_3Sn$	$C_{36}H_{49}ClLiN_3O_3RhSi_3Sn{\cdot}C_6D_6$
M_r	638.07	782.08	676.53	1004.19
Temperature	150(2) K	150(2) K	173(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/c$	$P2_1/c$
Z	4	8	4	4
Unit cell dimensions	a = 14.03350(10) Å	a = 24.5027(3) Å	a = 9.1341(18) Å	a = 12.13230(10) Å
	b = 15.1319(2) Å	b = 15.8137(3) Å	b = 14.172(3) Å	b = 19.5031(2) Å
	c = 17.0806(2) Å	c = 24.7797(4) Å	c = 24.977(5) Å	c = 18.7930(2) Å
	α = 90°	α = 90°	α = 90°	α = 90°
	β = 99.5400(6)°	β = 116.6346(6)°	β = 94.57(3)°	β = 92.2699(4)°
	γ = 90°	γ = 90°	γ = 90°	γ = 90°
Volume	3576.96(7) Å^3	8582.7(2) Å^3	3222.9(11) Å^3	4443.26(8) Å^3
$D_{calcd.}$	1.185 g cm^{-1}	1.211 g cm^{-1}	1.394 g cm^{-1}	1.501 g cm^{-1}
Absorption coefficient	0.169 mm^{-1}	0.151 mm^{-1}	0.936 mm^{-1}	1.115 mm^{-1}
F(000)	1360	3272	1392	2036
Crytal size [mm]	0.30 × 0.30 × 0.30	0.30 × 0.30 × 0.10	0.35 × 0.25 × 0.15	0.30 × 0.30 × 0.30
θ range for data collection	3.92 to 27.45°	2.58 to 27.48°	2.32 to 25.0°	3.41 to 26.37°
Limiting indices	$-18 \le h \le 18$	$-31 \le h \le 31$	$-10 \le h \le 10$	$-15 \le h \le 15$
	$-19 \le k \le 19$	$-20 \le k \le 20$	$-16 \le k \le 16$	$-24 \le k \le 24$
	$-22 \le l \le 22$	$-32 \le l \le 32$	$-29 \le l \le 29$	$-23 \le l \le 23$
Reflections collected	15821	18820	30955	53620
Independent reflections ($R_{int.}$)	8128 (0.0231)	9714 (0.0390)	5666 (0.0401)	9064 (0.0479)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8128/0/397	9714/0/505	5666/0/361	9064/0/524
Goodness-of-fit on F^2	1.043	1.022	1.030	1.082
Final R indices	R_1 = 0.0429	R_1 = 0.0484	R_1 = 0.0268	R_1 = 0.0298
[$I > 2\sigma(I)$]	wR_2 = 0.1086	wR_2 = 0.1060	wR_2 = 0.0679	wR_2 = 0.0676
R indices (all data)	R_1 = 0.0604	R_1 = 0.0853	R_1 = 0.0335	R_1 = 0.0410
	wR_2 = 0.1212	wR_2 = 0.1209	wR_2 = 0.0698	wR_2 = 0.0725
Largest diff. peak and hole	0.298 and −0.290 e·Å^{-3}	0.249 and −0.290 e·Å^{-3}	0.659 and −0.498 e·Å^{-3}	0.676 and −0.647 e·Å^{-3}

vw, 1602 s, 1515 vs, 1444 m, 1393 m, 1332 s, 1301 s, 1240 vs, 1179 w, 1113 s, 1052 w, 1042 m, 1006 m, 904 s, 843 s, 772 w, 746 m, 690 vw. $C_{36}H_{52}ClLiN_3O_3RhSi_3Sn$ (923.07): calcd. C 46.84, H 5.68, N 4.55; found C 47.13, H 5.80, N 4.24.

X-ray Crystallographic Study of Compounds 1−4

The X-ray diffraction data were collected on a Nonius KappaCCD diffractometer (**1**, **2**, and **4**) or on an IPDS (STOE) diffractometer (**3**) using Mo-K_α radiation (λ = 0.71073 Å). The Denzo-Scalepack[18] program package or IPDS programs were used for cell refinements and data reduction. A multi-scan absorption correction, based on equivalent reflections (XPREP in SHELXTL v5.1),[19] was applied to the data of **4** (T_{max}/T_{min} 0.26648/0.21770). Structures were solved by direct methods using the SHELXS-97[20] (**1**, **3** and **4**) or SIR-97[21] (**2**) program. All structures were refined with the SHELXL-97[22] program. In **3** hydrogens were located from a difference Fourier map and refined isotropically. In **1**, **2** and **4** hydrogens were placed on an idealized position and constrained to ride on their parent atom. The crystallographic data are summarised in Table 1. The molecular structures of the complexes along with principal bond lengths and angles are presented in Figure 2−5.

CCDC-178729 (**1**), -178730 (**2**), -178731 (**3**) and -178732 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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