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Hypercoordinate Aryltrialkylsilanes and -stannanes and Their Use in the Synthesis of Homodinuclear Organometallic Complexes with a 1,4-Phenylene Bridge[†]

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New mono- and dinuclear aryltrialkylsilanes and -stannanes [$Me_3M\{C_6H_3(CH_2NMe_2)_2$-2,6}] (M = Si (**5**), Sn (**6**)) and [$(Me_3M)_2$-1,4-{$C_6(CH_2NMe_2)_4$-2,3,5,6}] (M = Si (**9**), Sn (**10**)) have been prepared from transmetalation reactions of dimeric [$Li\{C_6H_3(CH_2NMe_2)_2$-2,6}]$_2$ and new polymeric [Li_2-1,4-{$C_6(CH_2NMe_2)_4$-2,3,5,6}]$_\infty$ with (trimethylsilyl)trifluoromethanesulfonate or trimethyltin chloride. The X-ray crystal structures of dinuclear **9** and **10** have been determined and in the molecular geometries found the central 1,4-phenylene dimetalated aryl ligand system provides bidentate *C,N*-coordination to silicon in **9** and terdentate pseudofacial *N,C,N′*-coordination to tin in **10**. Reactions of the newly prepared silanes **5** and **9** and stannanes **6** and **10** with diverse palladium(II) and platinum(II) substrates afford organometallic products arising from both aryl and methyl group transfer. For example, the reaction of dinuclear stannane **10** (or dinuclear silane **9**) with palladium(II) species gives the bimetallic complex [$(PdCl)_2$-1,4-{$C_6(CH_2NMe_2)_4$-2,3,5,6}] (**15**), whereas its reaction with [$PtCl_2$(COD)] (COD = cycloocta-1,5-diene) or Me_3SnCl gives the ionic tin(IV) species [$(Me_2Sn)_2$-1,4-{$C_6(CH_2NMe_2)_4$-2,3,5,6}]$^{2+}(X^-)_2$ with X being Cl (**18a**) or Me_3SnCl_2 (**18b**). The X-ray crystal structure of **18b** has been determined and the molecular geometry found shows that the central dimetalated aryl ligand system provides terdentate meridional *N,C,N′*-coordination to both tin centers.

Introduction

Organometallic complexes of the group 14 (IVB) metals silicon and tin remain a topic of interest because the formally tetracoordinate species as a class usually have weak Lewis acidic properties, and this provides a potential means of influencing their reactivity when they are used as alkylating or arylating reagents. For example, tetracoordinate mixed aryl/alkylstannanes can selectively transfer their aryl group to a transition metal center, a process that has been used extensively in the Stille reaction.[1] This process involves a transfer of an organyl ligand (usually the aryl group in mixed aryl/alkylstannanes) from tin to palladium. The same process of aryl transfer from a stannane has also been used for the selective synthesis of monoaryl transition metal complexes[2] since aryl transfer from aryllithium, arylzinc, or Grignard reagents often results in mixtures of mono- and diarylated transition metal species. However, intramolecularly coordinated organometallic tin(IV) compounds have, compared to their tetracoordinate analogs,[3,4] different reactivity patterns and different spectroscopic properties. This subject has been reviewed by Jastrzebski and van Koten.[4c]

Similarly, the reactivity and (spectroscopic) properties of silicon(IV) compounds with an expanded silicon coordination sphere differ substantially from the tetracoordinate silanes,[5] and Chuit et al.[5a] have reviewed silanes in which intramolecular oxygen and nitrogen

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[†] We propose to use the term "hypercoordinate" instead of "hypervalent". For example, in the tetraorganotin compounds described in this paper, it is not the formal oxidation state of the tin cation that changes but actually it is its ligand environment, which is extended from the anticipated four to five, six, or seven neutral or anionic donor sites. The ligands each contribute one or a multiple number of electron pairs for binding. Using bidentate monoanionic *C,N*-coordinating ligands the primary Sn−C interaction is complemented by Sn−N binding promoted by entropy effects. In a separate paper we will address this point in more detail.

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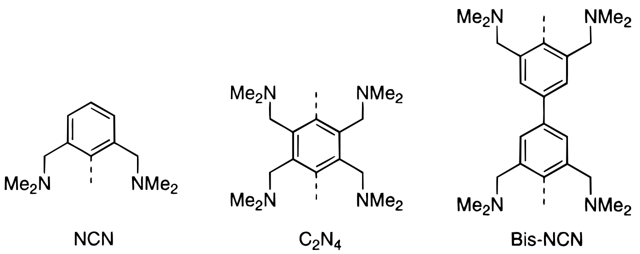


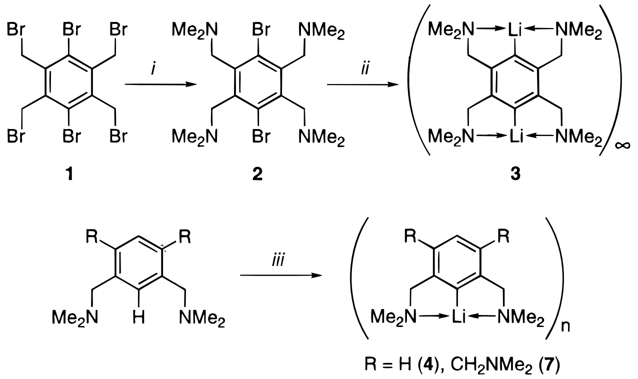
Figure 1. Schematic representation of the mono- and dianionic potentially (bis-) *N,C,N′*-terdentate coordinating aminoaryl ligands NCN, C_2N_4, and bis-NCN.

coordination provide penta-, hexa-, and even heptacoordinate silicon nuclei.

In our group, we have for many years employed aryl ligands with potentially coordinating N-donor substituents for the preparation and study of unusual organometallic species,[6] some of which have been shown to have application in metal-mediated and metal-catalyzed reactions.[7] The most commonly used ligand of this type has been the monoanionic aryldiamine ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (NCN), shown in Figure 1, which often functions as a terdentate *N,C,N′*-coordinating ligand. More recently, we have also employed dianionic arylamine ligands such as $[C_6(CH_2NMe_2)_4\text{-}2,3,5,6]^{2-}$ (C_2N_4) and $[4,4'\text{-}\{C_6H_2(CH_2NMe_2)_2\text{-}2,6\}_2]^{2-}$ (bis-NCN; see Figure 1), for the preparation of dinuclear mono- and biphenylene-bridged organometallic complexes.[8] Such species may have potential in the field of bimetallic catalysis and in the development of organometallic polymers[9] and of molecules with interesting (electronic) properties.

As a complementary aspect of these recent studies, we are interested in preparing mixed aryl/alkylsilane and -stannane complexes based on such arylamine ligands as novel alkylating or arylating reagents for the preparation of multimetallic systems. The present report concentrates on the preparation and characterization of new mono- and dinuclear silicon(IV) and tin(IV) complexes of NCN and C_2N_4 in which N-donor coordination to the metal centers has been established. The application of the silane and stannane complexes of C_2N_4 as reagents for a potential entry into new bimetallic complexes of platinum and palladium is presented, and the reactivity patterns are compared with those of related mononuclear NCN complexes. Some preliminary aspects of this work have recently been communicated.[8b]

Scheme 1. Synthesis of the Tetraaminoaryl Dibromide 2 and of the Dimeric and Polymeric Organolithium Reagents 3, 4 (R = H), and 7 (R = CH_2NMe_2)[a]



[a] Conditions: (i) $HNMe_2$, THF. (ii) *n*-BuLi, Et_2O or THF. (iii) *n*-BuLi, hexane.

Results

The target complexes of this study are the silane and stannane of general formula $[Me_3M\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (M = Si (**5**), Sn (**6**)) and the dinuclear species $[(Me_3M)_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]$ (M = Si (**9**), Sn (**10**)). The synthetic strategy involved in the synthesis of these silanes and stannanes is based on the preparation of the organolithium derivatives of the ligands NCN and C_2N_4 (Scheme 1), followed by transmetalation of these reagents with suitable silicon and tin precursors (Scheme 2).

Synthesis of the Organolithium Species. To prepare the organodilithium derivative of C_2N_4, $[Li_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]_\infty$ (**3**), a two-step procedure was developed (see Scheme 1). In the first step, nucleophilic amination of $Br_2\text{-}1,4\text{-}\{C_6(CH_2Br)_4\text{-}2,3,5,6$ (**1**) with $HNMe_2$ affords $Br_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6$ (**2**). In the second step, a lithium–halogen exchange reaction of dibromide **2** with *n*-BuLi in Et_2O selectively forms the dilithiated species **3**. Complex **3** was identified as the dilithiated species by quenching of samples of the isolated white solid with H_2O and D_2O and subsequent identification of the organic products as $C_6H_2(CH_2NMe_2)_4\text{-}1,2,4,5$[10] and $C_6D_2(CH_2NMe_2)_4\text{-}1,2,4,5$, respectively. The direct precursors of the ligands NCN and C_2N_4 are $C_6H_4(CH_2NMe_2)_2\text{-}1,3$ (1,3-bis[(dimethylamino)methyl]benzene) and $C_6H_2(CH_2NMe_2)_4\text{-}1,2,4,5$ (1,2,4,5-tetrakis[(dimethylamino)methyl]benzene) for which an improved synthetic pathway has been developed. For $C_6H_4(CH_2NMe_2)_2\text{-}1,3$, this pathway proceeds through a Clark–Eschweiler reductive alkylation of α,α′-diamino-*m*-xylene with aqueous formaldehyde and formic acid (see Experimental Section). The known dimeric organolithium derivatives of NCN and C_2N_4, namely, $[LiC_6H_3(CH_2NMe_2)_2\text{-}2,6]_2$ (**4**) and $[Li\{C_6H(CH_2NMe_2)_4\text{-}2,3,5,6\}]_2$ (**7**), were prepared as previously described.[10,11c]

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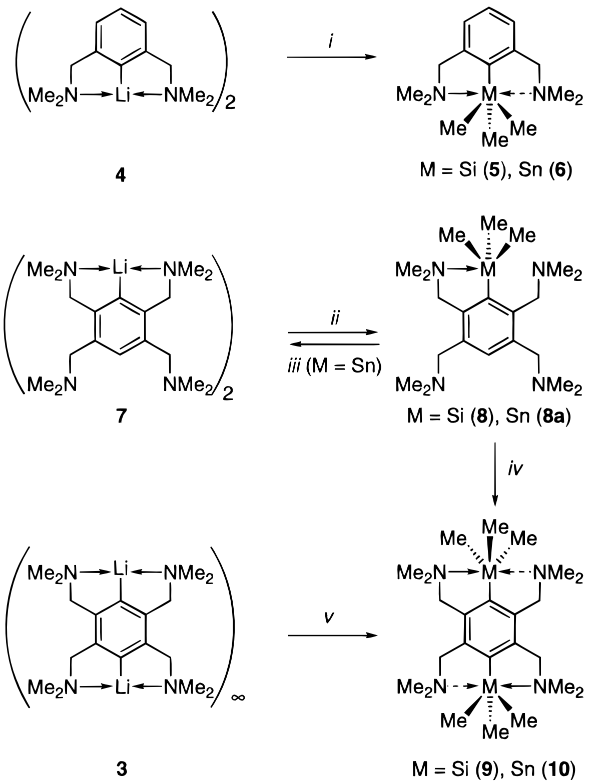
Scheme 2. Synthesis of the New Silanes 5 and 9 (M = Si) and the Stannanes 6 and 10 (M = Sn)[a]



[a] Conditions: (i) Me$_3$SiOTf, hexane/THF or Me$_3$SnCl, THF. (ii) Me$_3$SiOTf, Et$_2$O or Me$_3$SnCl, THF. (iii) *n*-BuLi, hexane, $-$BuSnMe$_3$. (iv) *n*-BuLi, hexane followed by Me$_3$SiOTf, THF. (v) Me$_3$SiOTf, Et$_2$O or Me$_3$SnCl, THF.

Synthesis of Silanes 5 and 9 and Stannanes 6 and 10. The desired monosilane [Me$_3$Si{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}] (**5**) and monostannane [Me$_3$Sn{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}] (**6**) can be prepared from transmetalation reactions of the organolithium species **4** in THF with Me$_3$SiOTf (OTf = OSO$_2$CF$_3$ = triflate) and Me$_3$SnCl, respectively (Scheme 2).

The reaction of **4** with Me$_3$SiOTf to form **5** is rapid (complete in 3 min at room temperature) and was shown to be quantitative by ^{1}H NMR spectroscopy. Monosilane **5** has been isolated from the reaction mixture as a colorless oil in 79% yield. Note that Me$_3$SiCl failed to silylate lithium reagent **4**, even after 24 h at room temperature. The reaction of **4** with Me$_3$SnCl in THF affords selectively (as determined by ^{1}H NMR spectroscopy) the tin species [Me$_3$Sn{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}] (**6**). After appropriate workup, complex **6** was isolated from the reaction mixture in 92% yield as a white solid.

The monosilane **5** and monostannane **6** have been characterized by NMR spectroscopy and elemental microanalysis. Some ^{1}H and ^{13}C NMR spectroscopic data relevant to discussion of possible coordination of the N-donor substituents to the group 14 center are summarized in Table 1. A characteristic feature of the ^{1}H and ^{13}C NMR spectra of **6** is the coupling of the ^{117}Sn and ^{119}Sn nuclei (I = $^1/_2$, 7.68 and 8.58% natural abundance, respectively) to the H and C atoms of the organic ligand array. For example, in the ^{1}H NMR spectrum of **6** (CDCl$_3$ solution) the Me$_3$Sn group shows double satellites with coupling constant values of 51 and 53 Hz.

The disilylated complex of C$_2$N$_4$, namely, [(Me$_3$Si)$_2$-1,4-{C$_6$(CH$_2$NMe$_2$)$_4$-2,3,5,6}] (**9**), can be prepared by two different methods (Scheme 2). The first method involves reaction of the polymeric organodilithium species [Li$_2$-1,4-{C$_6$(CH$_2$NMe$_2$)$_4$-2,3,5,6}]$_\infty$ (**3**) with Me$_3$SiOTf in THF. This affords disilylated **9** in 93% yield. The second method for the preparation of **9** employs two successive monolithiation/monosilylation cycles, starting from lithium species **7**.[10] This method, which involves the formation of the monosilylated aryltetramine **8** as an intermediate product, afforded **9** in isolated yields of 59% after chromatographic purification. Earlier we have found that **8** is, through selective C$-$Si bond activation and transmetalation reactions, a very useful precursor to unsymmetrical M$\cdots$M′ heterobimetallic complexes of C$_2$N$_4$.[8b] The characterization of complex **9** as a bis(silane) with a 1,4-phenylene bridge includes characteristic NMR data (see Table 1) and an X-ray crystallographic study (*vide infra*).

The bis(organotin) complex [(Me$_3$Sn)$_2$-1,4-{C$_6$(CH$_2$NMe$_2$)$_4$-2,3,5,6}] (**10**) can be prepared by the reaction of the dilithio species **3** (prepared *in situ* from dibromide **2** with *n*-BuLi in THF) with Me$_3$SnCl. Complex **10** has been isolated as an air-stable white solid in 53% yield. Note that this complex cannot be prepared in a two-cycle process of monolithiation and monostannylation starting from organolithium reagent **7** as described for the bis(silane) **9**. The reaction of the intermediate monoorganotin complex [Me$_3$Sn{C$_6$H(CH$_2$NMe$_2$)$_4$-2,3,5,6}] (**8a**) with *n*-BuLi did not result in aromatic deprotonation, but instead quantitative reformation of the organolithium reagent **7** occurred (Scheme 2 and Experimental Section). This reactivity of organotin(IV) compounds toward organolithium reagents has been described, for example, by Gielen and Tondeur.[12] The characterization of complex **10** as a bis(stannane) with a 1,4-phenylene bridge includes characteristic NMR data (see Table 1) and an X-ray crystallographic study (*vide infra*).

Reactions of 5, 6, 9, and 10 with Pd(II) and Pt(II) Complexes. The reactivity of the new silanes **5** and **9** and the stannanes **6** and **10** as organyl group-transfer reagents has been tested using some divalent platinum group complexes as substrates. The organometallic products of these reactions, which result from both alkyl and aryl transfer, are summarized in Schemes 3 and 4; product characterization and product distributions were determined by ^{1}H and ^{13}C NMR spectroscopy.

The silanes **5** and **9** react rather slowly with Pd(OAc)$_2$ (in MeOH, 10 h). In analogous reactions, the stannanes **6** and **10** react significantly faster and the Pd(OAc)$_2$ was consumed in ~30 min. In all four cases, after addition of excess LiCl and workup, one finds by ^{1}H and ^{13}C NMR spectroscopy quantitative formation of either the mononuclear species [PdCl{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}] (**11**)[13] (from complexes **5** and **6**) or the dinuclear species [(PdCl)$_2$-

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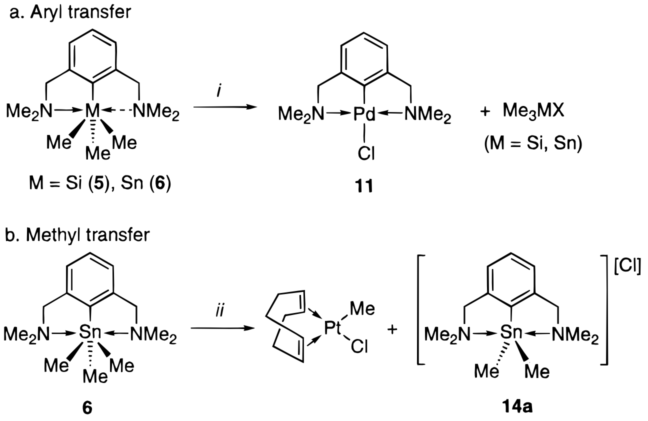
Table 1. Selected ^{1}H and ^{13}C NMR Data[a] of the Silanes 5 and 9 and Stannanes 6 and 10 Together with Those of Their Free Ligand Precursors $C_6H_4(CH_2NMe_2)_2$-1,3 and $C_6X_2(CH_2NMe_2)_4$-1,2,4,5 (X = H, Br)

	^{1}H NMR			^{13}C NMR		
compound	CH_2	NMe_2	Me_3M ($^2J_{SnH}$)[d]	CH_2 ($^3J_{SnH}$)[d]	NMe_2	Me_3M ($^1J_{SnC}$)[d]
(NCN)H[b]	3.12	1.94		64.1	45.2	
[(NCN)$SiMe_3$] (**5**)[b]	3.52	2.14	0.38	64.9	45.3	3.3
[(NCN)$SnMe_3$] (**6**)[b]	3.63	2.22	0.37 (53, 51)	66.1 (21)	44.9	−3.4 (371, 355)
$(C_2N_4)H_2$[b]	3.41	2.14		61.0	45.5	
$(C_2N_4)Br_2$[c]	3.97	2.27		59.7	45.4	
[$(C_2N_4)(SiMe_3)_2$] (**9**)[c]	3.62	2.06	0.28	61.4	44.4	4.1
[$(C_2N_4(SnMe_3)_2$] (**10**)[c]	3.57	2.08	0.12 (42)	60.1 (25)	43.7	−2.2 (356)

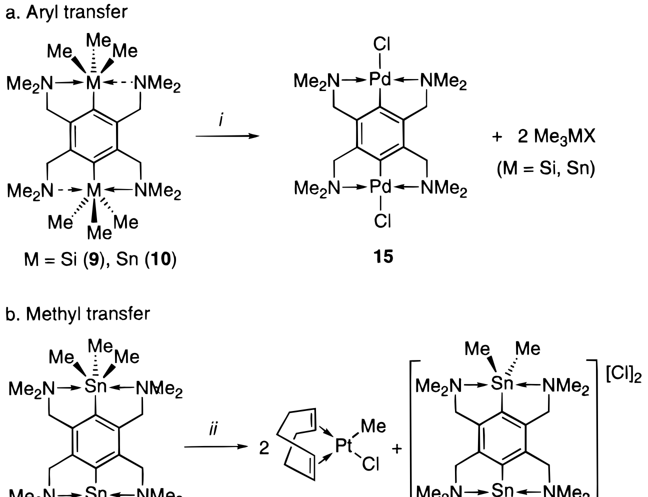
[a] In $CDCl_3$ at 298 K. [b] NCN = $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$. [c] C_2N_4 = $[C_6(CH_2NMe_2)_2\text{-}2,3,5,6]^{2-}$. [d] Coupling in hertz.

Scheme 3. Reactivity of Silane 5 and Stannane 6 toward $Pd(OAc)_2$ and [$M'Cl_2(COD)$] (M′ = Pd, Pt)[a]



[a] Conditions: (i) $Pd(OAc)_2$, MeOH followed by LiCl, MeOH or [$PdCl_2(COD)$], CH_2Cl_2. (ii) [$PtCl_2(COD)$], CH_2Cl_2.

Scheme 4. Reactivity of Silane 9 and Stannane 10 toward $Pd(OAc)_2$ and [$M'Cl_2(COD)$] (M′ = Pd, Pt)[a]



[a] Conditions: (i) 2 equiv of $Pd(OAc)_2$, MeOH followed by LiCl, MeOH or 2 equiv [$PdCl_2(COD)$], CH_2Cl_2. (ii) 2 equiv [$PtCl_2(COD)$], CH_2Cl_2.

1,4-{$C_6(CH_2NMe_2)_4$-2,3,5,6}] (**15**)[8b] (from complexes **9** and **10**). These products result from aryl transfer from the silane or stannane to palladium, and since there is no formation of products resulting from C−H activation, one can conclude that the Me_3M group (M = Si, Sn) has a strong directing effect in these reactions.[14]

Similar reactions of silanes **5** and **9** and stannanes **6** and **10** with the palladium(II) substrate [$PdCl_2(COD)$] (COD = cycloocta-1,5-diene) (instead of $Pd(OAc)_2$) are in all cases slow and substrate conversion is only complete after ~10 h. The tin species **6** and **10** give rise, via aryl transfer, to aryl palladium complexes **11** and **15**, respectively, together with traces of the methyl transfer product [PdClMe(COD)].[15] Interestingly, also minor amounts of the ionic tin-containing compounds **14a**[16] and **18a** (*vide infra*) are formed, the nature of which is discussed below in detail. The products of the reactions of silanes **5** and **9** with [$PdCl_2(COD)$] appear to be coordination complexes, but the identity of these materials has not been established; species resulting from C−Si bond cleavage were not detected.

The silanes **5** and **9** did not react with the Pt(II) halide complex [$PtCl_2(COD)$]. However, there is a slow reaction of this Pt(II) substrate with stannanes **6** and **10**, and in both cases, after 48 h a white precipitate had formed. The ready solubility of these precipitates in water point to materials that probably have an ionic formulation. The NMR spectra of solutions of these precipitates in D_2O show signals of the arylamine ligands NCN and C_2N_4 for the products derived from **6** and **10**, respectively, and of methyl groups bonded to tin. The ^{1}H NMR integral data and elemental microanalysis data are in accordance with these materials being ionic stannanes $[Me_2Sn\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]^+Cl^-$ (**14a**)[16] and $[(Me_2Sn)_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]^{2+}(Cl^-)_2$ (**18a**) (see Schemes 3 and 4). These reactions of **6** and **10** with [$PtCl_2(COD)$] also afforded organoplatinum(II) species which remain dissolved in the reaction mixture. After workup we identified small amounts (<5%) of products arising from aryl transfer, i.e., [PtCl-{$C_6H_3(CH_2NMe_2)_2$-2,6}] (**12**)[13,17] (from stannane **6**) and [$(PtCl)_2$-1,4-{$C_6(CH_2NMe_2)_4$-2,3,5,6}] (**16**)[8c] (from **10**). However, the principal Pt(II) species obtained with both **6** and **10** is [PtCl(Me)(COD)],[18] which is the product of methyl group transfer to platinum.

For identification purposes, the ionic complexes $[Me_2Sn\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]^+X^-$ (**14**) and $[(Me_2Sn)_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]^{2+}(X^-)_2$ (**18**) were independently synthesized (see Scheme 5). Reaction of the neutral stannanes **6** and **10** with excess of Me_3SnCl in CH_2Cl_2

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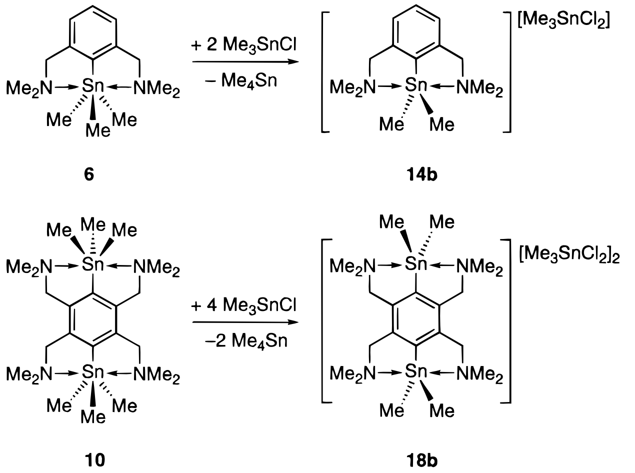
Scheme 5. Independent Synthesis of the Novel Ionic Species 14b and 18b



afforded, in a redistribution reaction, the complexes **14b** (95% yield) and **18b** (59% yield), with X = $[Me_3SnCl_2]^-$ (*vide infra*). Complexes **14b** and **18b** are white solid hygroscopic complexes which readily crystallize from mixtures of MeOH and dibutyl ether.

The NMR spectra of **14b** and **18b** (D_2O) are similar to those of the chloro analogs **14a**[16] and **18a**, respectively, with the exception that they also contain the extra resonance due to the $[Me_3SnCl_2]^-$ counteranion. This anion affords a ^{1}H NMR signal at ~0.5 ppm ($^2J_{SnH}$ = 66 and 69 Hz) and a ^{13}C NMR signal at ~1.5 ppm ($^1J_{SnC}$ = 478 and 499 Hz). Prolonged drying of **14b** *in vacuo* resulted in partial (~15 mol %) elimination of volatile Me_3SnCl, as deduced from a lower than expected intensity for the $[Me_3SnCl_2]^-$ resonances in its ^{1}H NMR spectrum. This also hindered elemental microanalysis of this compound. An interesting aspect of complexes **14** and **18** is that the CH_2NMe_2 groups afford two singlet resonances in both the ^{1}H and ^{13}C NMR spectra. This equivalence of the CH_2NMe_2 groups is associated with chemical shifts and coupling data with ^{119,117}Sn that indicate meridional *N,C,N′*-coordination of the NCN and C_2N_4 ligands, whereby the tin(IV) centers are pentacoordinate (*vide infra*).[16]

Spectroscopic Aspects of Silanes 5 and 9 and Stannanes 6 and 10. The overall composition of the new organometallic silicon(IV) and tin(IV) species $[Me_3M\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (M = Si (**5**), Sn (**6**)) and $[(Me_3M)_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]$ (M = Si (**9**), Sn (**10**)) could be readily established by standard spectroscopic and microanalytical techniques (see Experimental Section and above). However, because of the presence of potentially coordinating N-donor centers in the CH_2NMe_2 substituents of the NCN and C_2N_4 ligands, we have examined the ^{1}H and ^{13}C NMR data carefully for evidence of possible N → M interactions. Data that allow direct comparison of complexes **5**, **6**, **9**, and **10** with the arylamines $C_6H_4(CH_2NMe_2)_2$-1,3 and $C_6H_2(CH_2NMe_2)_4$-1,2,4,5, i.e., the precursors of the NCN and C_2N_4 ligands, are collected in Table 1.

Compared to the free arylamines, the data for complexes **5**, **6**, **9**, and **10** show that introduction of a silicon or a tin center into the organic cleft of NCN or C_2N_4 provides in general a downfield shift of the ^{1}H and ^{13}C NMR resonances of the CH_2NMe_2 substituents. For example, the ^{1}H NMR resonances the CH_2 groups in the silicon and tin complexes **5** and **6** are ~0.5 ppm downfield to those of the free arylamine $C_6H_4(CH_2NMe_2)_2$-1,3, and a somewhat smaller downfield shift of ~0.3 ppm is found for the NMe_2 resonances. Although the ^{13}C NMR data of **5** and **6** show a similar downfield trend for the CH_2 resonances, it is interesting to see that the chemical shifts of the NMe_2 resonances are virtually identical to those of the free arylamines. As a general observation, one also sees from Table 1 that the downfield shifts are more pronounced for the tin complexes **6** and **10** than for the analogous silicon species **5** and **9**. Furthermore, relative to the free arylamines these downfield shifts arising from metal coordination are smaller for the dinuclear C_2N_4 complexes of silicon (**9**) and tin (**10**) than for the mononuclear NCN complexes **5** and **6**.

The solution NMR shift data in Table 1 for complexes **5**, **6**, **9**, and **10** are consistent with some degree of intramolecular N → M interaction from the CH_2NMe_2 groups with the incorporated metal centers but in themselves are not particularly conclusive. Direct evidence of such coordination is in theory possible through observation of satellites arising from coupling to ^{29}Si ($I = {}^1/_2$, 4.67% natural abundance) and ^{117}Sn ($I = {}^1/_2$, 7.68% natural abundance) and ^{119}Sn ($I = {}^1/_2$, 8.58% natural abundance) in both ^{1}H and ^{13}C NMR spectra. However, the only coupling observed was of tin to the CH_2 resonances (^{1}H and ^{13}C NMR) in complexes **6** and **10**; since this coupling could arise from a coupling pathway through the aromatic skeleton,[4d] these data are also not conclusive for N → M coordination. Variable-temperature ^{1}H and ^{13}C NMR spectra of the new silanes **5** and **9** and stannanes **6** and **10** also did not afford any further evidence for N → M coordination.

To further investigate N → M coordination, we have also measured ^{29}Si NMR spectra of **5** and **9** and ^{119}Sn NMR spectra of complexes **6** and **10**. Silanes **5** and **9** show in their ^{29}Si NMR spectra (C_6D_6) resonances at −7.7 and −11.2 ppm, respectively, that are significantly more highfield than those of silanes $SiMe_3(C_6H_5)$[19] and $[SiMe_3\{C_6H_4(CH_2NMe_2)\text{-}2\}]$[20] (see Table 2). These highfield shifts point to increased electron density at the silicon centers. Since it is known that substitution of the aromatic ring of aryltrimethylsilanes with alkyl donor groups only leads to minor changes in ^{29}Si NMR chemical shifts (up to ~1 ppm),[19] it can be concluded that **5** and **9** do have some inteaction of one (or two) CH_2NMe_2 donor substituent(s) with the silicon center. Although the highfield shifts for **5** and **9** are small, they are consistent with the trend found in ^{29}Si NMR data for hypercoordinate silicon complexes.[5a] From the fact that the ^{1}H and ^{13}C NMR data of silanes **5** and **9** show the complexes to be symmetrical with equivalent CH_2NMe_2 donor substituents, it is likely that there is a fast equilibrium involving coordination and decoordination of one or both of the N-donor groups to silicon in these species.

In a similar way, stannanes **6** and **10** show in their ^{119}Sn NMR spectra (C_6D_6) resonances at −86.9 and −107.0 ppm, respectively, that are significantly more highfield than those of stannanes $SnMe_3(C_6H_5)$[21] and

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Table 2. ^{29}**Si (59.6 MHz) and** ^{119}**Sn NMR (75 MHz) Data for Some Aryl/alkylsilanes**

compound	$\delta(^{29}Si)$	solvent
$SiMe_3(C_6H_5)$	−4.5	C_6D_6
$SiMe_3(C_6H_5)$	−4.1	$CDCl_3$
$[SiMe_3\{C_6H_4(CH_2NMe_2)\text{-}2\}]$	−4.9	$CDCl_3$
$[SiMe_3\{C_6H_3(CH_2NMe_2)\text{-}2,6\}]$ (**5**)	−7.7	C_6D_6
$[(SiMe_3)_2\{C_6(CH_2NMe_2)\text{-}2,3,5,6\}]$ (**9**)	−11.2	C_6D_6

compound	$\delta(^{119}Sn)$	solvent
$SnMe_3(C_6H_5)$	−24.1	C_6D_6
$[SnMe_3\{C_{10}H_6NMe_2\text{-}8\}]$	−46.7	$C_6D_5CD_3$
$[SnMe_3\{C_6H_4(CH_2NMe_2)\text{-}2\}]$	−50.0	$C_6D_5CD_3$
$[SnMe_2C_6H_4(CH_2NMe_2)\text{-}2]Br$	−50.0	$C_6D_5CD_3$
$[SnMe_3\{C_6H_3(CH_2NMe_2)\text{-}2,6\}]$ (**6**)	−86.9	C_6D_6
$[(SnMe_3)_2\{C_6(CH_2NMe_2)\text{-}2,3,5,6\}]$ (**10**)	−107.0	C_6D_6
$[SnMe_2\{C_6H_3(CH_2NMe_2)\text{-}2,6\}][Me_3SnCl_2]$ (**14b**)	72.0 (br)[a] and 34.1[b]	CD_3OD
$[(SnMe_2)_2\{C_6(CH_2NMe_2)\text{-}2,3,5,6\}][Me_3SnCl_2]_2$ (**18b**)	53.6 (br)[a] and 35.2[b]	CD_3OD

[a] Chemical shift of the cation. [b] Chemical shift of the anion, $[Me_3SnCl_2]^-$.

$[SnMe_3\{C_6H_4(CH_2NMe_2)\text{-}2\}]$[22] (see Table 2) and that clearly indicate the presence of N-donor coordination of the CH_2NMe_2 groups to the metal center in these new stannanes. From examination of ^{119}Sn NMR data for the series $SnMe_3(C_6H_5)$,[21] $[SnMe_3\{C_{10}H_6NMe_2\text{-}8\}]$ ($C_{10}H_6\text{-}NMe_2$ = 8-(dimethylamino)-1-naphthyl),[23] $[SnMe_3\{C_6H_4(CH_2NMe_2)\text{-}2\}]$,[22] $[SnMe_3\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (**6**), and $[(SnMe_3)_2\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]$ (**10**), in which the resonance of the tin nucleus shifts upfield from −24.1 to −107.0 ppm (Table 2), we conclude that in complexes **6** and **10** the tin(IV) centers are likely to be six-coordinate, rather than five-coordinate, with both CH_2NMe_2 donor substituents involved in N → Sn interactions on the NMR time scale. It has been proposed that the enhanced reactivity of Sn−C bonds in tetraorganotin compounds containing *C*,*N*-chelating ligands is a result of this type of intramolecular N → Sn coordination.[22,23]

Solid-State Structures of 9, 10, and 18b. As shown above, the NMR data of silanes **5** and **9** and stannanes **6** and **10** are indicative of various degrees of intramolecular N → M coordination in solution. To further investigate the nature of such interactions in the solid state, X-ray crystal structures of representative complexes, namely, the bis(silane) $[(SiMe_3)_2\text{-}1,4\text{-}C_6(CH_2NMe_2)_4\text{-}2,3,5,6]$ (**9**), the bis(stannane) $[(SnMe_3)_2\text{-}1,4\text{-}C_6(CH_2NMe_2)_4\text{-}2,3,5,6]$ (**10**), and the ionic bis(stannane) $[(Me_2Sn)_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]^{2+}([Me_3SnCl_2]^-)_2$ (**18b**), have been carried out (Figures 2−4, respectively). Selected geometrical details of complexes **9**, **10**, and **18b** are collected in Table 3. Crystal data of these complexes are collected in Table 4.

The molecular geometry of bis(silane) **9** (Figure 2) shows the C_2N_4 ligand functioning as a bridge between two $SiMe_3$ groups. The two silicon centers have identical coordination spheres as a result of a crystallographic center of symmetry positioned at the center of the aromatic ring and the intramolecular Si(1)···Si(1)A distance is 6.6403(6) Å. The silicon(IV) center forms four σ-bonds with the three methyl groups and a C_{ipso} atom (C(1)) of the bridging C_2N_4 ligand. Furthermore, the silicon center has an interaction with one of the two available *o*-CH_2NMe_2 groups with the N(2)−Si(1) bond distance being 3.0403(12) Å, and this is substantially smaller then the sum of the van der Waals radii of nitrogen and silicon (3.65 Å). As a consequence of this

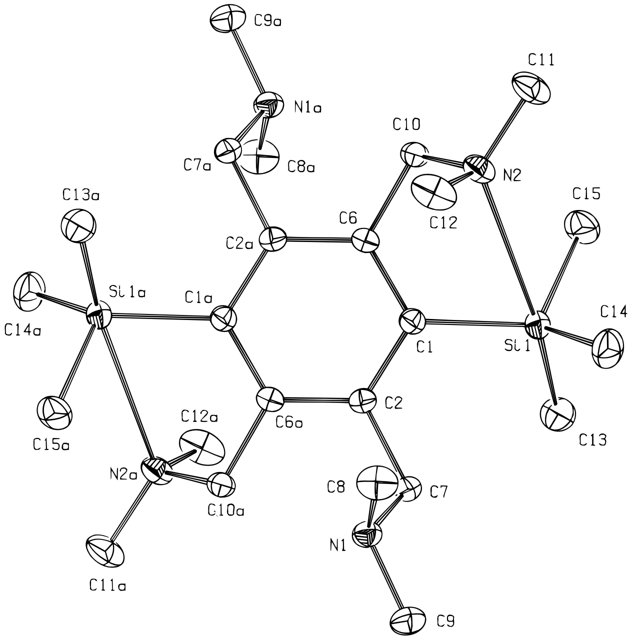

Figure 2. ORTEP drawing (50% probability atomic displacement ellipsoids) of $[(Me_3Si)_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]$ (**9**). Hydrogen atoms have been omitted for clarity.

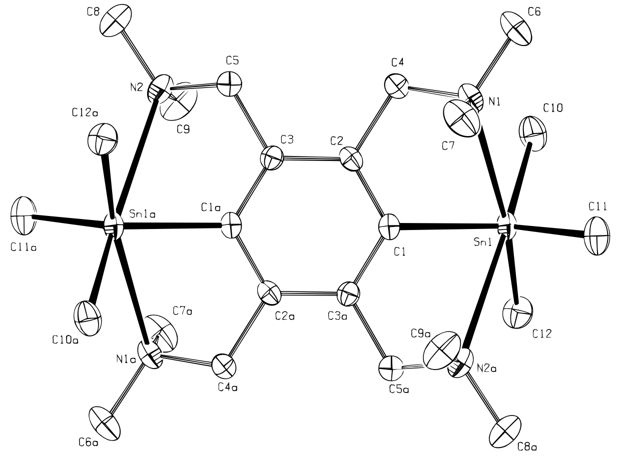

Figure 3. ORTEP drawing (50% probability atomic displacement ellipsoids) of $[(Me_3Sn)_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]$ (**10**). Hydrogen atoms have been omitted for clarity.

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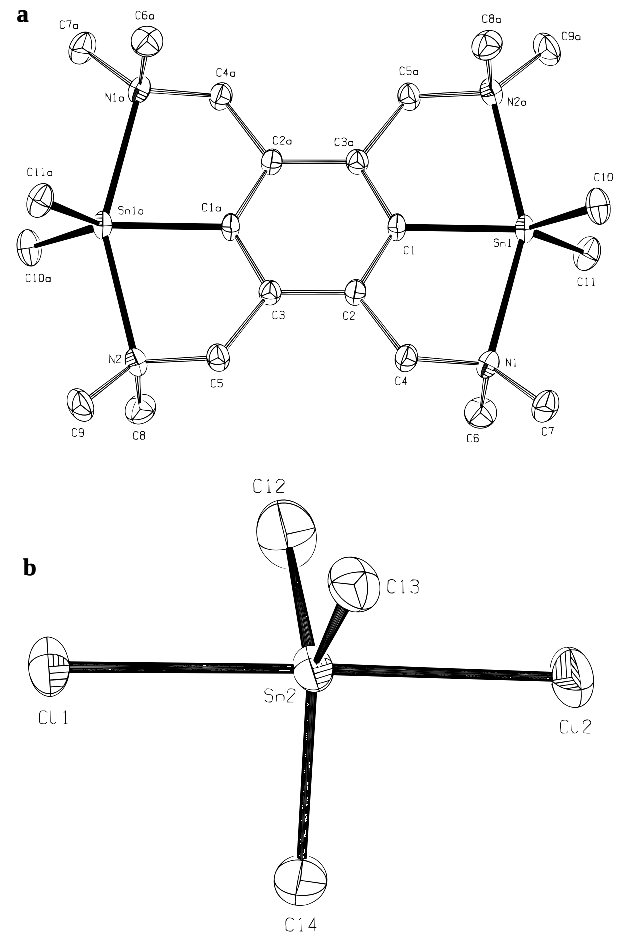

Figure 4. ORTEP drawing (50% probability atomic displacement ellipsoids) of the complex cation of bis(stannane) **18b**, $[(Me_2Sn)_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]^{2+}$ (a) and of the complex counterion, $[Me_3SnCl_2]^-$ (b). Hydrogen atoms and one symmetry-related anion have been omitted for clarity.

interaction, the organyl groups on silicon are moved away from a true tetrahedral geometry (see Table 3) and the Si−Me bond Si(1)−C(13) is slightly longer than the other Si−Me bonds Si(1)−C(14) and Si(1)−C(15). These parameters indicate that the silicon center may be regarded as being pentacoordinate[4c,5] with the geometry being best described as capped tetrahedral with the N-donor atom capping a face defined by C(1) and the two methyl groups bonded by C(14) and C(15). As a result of the N-donor coordination, the silicon center can be seen to participate in a puckered five-membered chelate ring. This ring has an overall envelope form with the N-donor atom positioned out of the plane defined by the aromatic ring. Furthermore, there are slight distortions involving the central aromatic ring, which can be considered to have a twisted chair conformation. This is reflected in the individual deviations (± 0.021(1) Å) of the ring atoms from the least-squares plane of the aromatic ring and the out of plane angle of the C_{ipso}−Si bond in **9** (12.94(5)°) with this least-squares plane.

The molecular geometry of **10**, depicted in Figure 3, shows this complex to be a bis(stannane) in which, as a consequence of a crystallographic center of inversion at the center of the bridging aromatic ring, there are two identical six-coordinate tin(IV) centers separated by an intramolecular distance (Sn(1)···Sn(1)A) of 7.1659(11) Å. Each tin center has a distorted octahedral ligand array that arises from bonding interactions with the C_{ipso} atom (C(1)) of the bridging phenylene group, the three methyl groups and the N-donor atoms of two (*ortho*) CH_2NMe_2 substituents. The N-donor groups are bonded in a *cis* fashion, which results in a pseudofacial *N,C,N′*-coordination mode of the aromatic ligand system. Probably as a result of the *trans*-coordinated CH_2NMe_2 groups, the Sn(1)−C(10) and Sn(1)−C(12) bonds are slightly longer than the Sn(1)−C(11) bond. Due to the pseudofacial coordination mode of each *N,C,N′*-coordination moiety, there is a slight distortion of the planarity of the central aromatic ring in the direction of a chair conformation. This is illustrated by the individual deviations (± 0.014(3) Å) of the ring C atoms from the least-squares plane of the aromatic ring. Furthermore, the angle between the C_{ipso}−Sn bond and this plane is 9.15(9)°. The interbond angles involving tin (see Table 3) show that the coordination geometry of the hexacoordinate tin(IV) center is probably not well suited for a description based on a distorted octahedral geometry but, in fact, may be better described as bicapped tetrahedral with the N-donor atoms of two CH_2NMe_2 groups capping the two trigonal faces defined by C(1), C(10), and C(11) and by C(1), C(11), and C(12).

The molecular geometry of **18b**, depicted in Figure 4, shows it to be an ionic species based on two $[Me_3SnCl_2]^-$ anions and a separate complex dication that contains a central bimetalated aromatic ring with two tin(IV) centers at an intramolecular Sn(1)···Sn(1)A distance of 6.9281(10) Å. The tin atoms are identical and have a trigonal-bipyramidal ligand array arising from meridional *N,C,N′*-coordination of the aryl ligand in combination with two mutually *trans* bonded methyl groups. The two N-donor groups coordinated to each tin center afford a N−Sn−N bond angle of 152.05(7)°. Unlike the situation in complexes **9** and **10**, the central aromatic ring of **18b** is planar within the standard deviation (individual deviations of the ring C atoms from the least-squares plane of the aromatic ring: ±0.000(3) Å) and the Sn atoms are located in the plane of this bridging phenylene moiety. The anion of the ionic species **18b**, $[Me_3SnCl_2]^-$, also has a tin(IV) atom with a trigonal-bipyramidal coordination geometry. Here the methyl groups are in the meridional plane with interbond angles lying close to 120°, and the Cl−Sn−Cl bond angle is close to 180°.

Discussion

We have shown that arylsilanes and -stannanes with potentially coordinating CH_2NMe_2 substituents are synthetically accessible through transmetalation reactions of the corresponding aryllithium reagents with suitable trimethyl chloride (Sn) and triflate (Si) derivatives of the group 14 (IVB) metals silicon and tin.

Organolithium Compounds. In our group, we have a general interest in the structure and reactivity of aryllithium compounds in which the lithium atoms are coordinated intramolecularly by suitable donor substituents, *ortho* positioned on the aromatic ring. In many previous studies of metal NCN complexes, the organolithium derivative **4** was prepared by a lithium−halogen exchange reaction of $C_6H_3Br(CH_2NMe_2)_2\text{-}2,6$ with metallic lithium in Et_2O and isolated as the pure solvent-free material by extraction and recrystallization from alkane solvents. In this study, we present an

Table 3. Selected Bond Distances (Å) and Interbond and Dihedral Angles (deg) for 9, 10, and 18b[a]

bond distances		bond angles		dihedral angles	
		Compound **9**[b]			
Si(1)−C(1)	1.9079(12)	C(1)−Si(1)−C(13)	107.27(7)	C(1)−C(2)−C(6)A−C(1)A	−6.14(19)
Si(1)−C(13)	1.8891(19)	C(1)−Si(1)−C(14)	114.81(7)	C(2)−C(1)−C(6)−C(2)A	−5.94(18)
Si(1)−C(14)	1.8723(14)	C(1)−Si(1)−C(15)	114.45(7)	C(6)−C(1)−C(2)−C(6)A	5.96(18)
Si(1)−C(15)	1.8722(19)	C(13)−Si(1)−C(14)	109.04(8)	Si(1)−C(1)−C(2)−C(6)A	−162.96(10)
Si(1)−N(2)	3.0403(12)	C(13)−Si(1)−C(15)	99.20(8)	Si(1)−C(1)−C(6)−C(2)A	162.80(10)
Si(1)···Si(1)A	6.6403(6)	C(14)−Si(1)−C(15)	110.73(8)	C(1)−C(6)−C(10)−N(2)	−40.48(16)
				C(2)A−C(6)−C(10)−N(2)	132.50(12)
		Compound **10**[c]			
Sn(1)−C(1)	2.178(2)	C(1)−Sn(1)−C(10)	113.36(11)	C(1)−C(2)−C(3)−C(1)A	4.0(3)
Sn(1)−C(10)	2.171(3)	C(1)−Sn(1)−C(11)	120.51(9)	C(2)−C(1)−C(3)A−C(2)A	3.9(3)
Sn(1)−C(11)	2.139(3)	C(1)−Sn(1)−C(12)	107.27(9)	C(3)A−C(1)−C(2)−C(3)	−3.9(3)
Sn(1)−C(12)	2.176(3)	C(10)−Sn(1)−C(11)	108.45(13)	Sn(1)−C(1)−C(2)−C(3)	168.11(16)
Sn(1)−N(1)	2.857(2)	C(10)−Sn(1)−C(12)	94.85(11)	Sn(1)−C(1)−C(3)A−C(2)A	−168.05(16)
Sn(1)−N(2)A	2.999(2)	C(11)−Sn(1)−C(12)	109.28(11)	C(1)−C(2)−C(4)−N(1)	−33.7(3)
Sn(1)···Sn(1)A	7.1659(11)	N(1)−Sn(1)−N(2)A	107.07(5)	C(3)−C(2)−C(4)−N(1)	142.6(2)
				C(1)A−C(3)−C(5)−N(2)	−39.4(3)
				C(2)−C(3)−C(5)−N(2)	134.9(2)
		Compound **18b**[d]			
cationic fragment					
Sn(1)−C(1)	2.105(2)	C(1)−Sn(1)−C(10)	123.43(10)	C(1)−C(2)−C(3)−C(1)A	0.0(9)
Sn(1)−C(10)	2.116(2)	C(1)−Sn(1)−C(11)	120.81(10)	C(2)−C(1)−C(3)A−C(2)A	0.0(15)
Sn(1)−C(11)	2.111(2)	C(10)−Sn(1)−C(11)	115.76(11)	C(3)A−C(1)−C(2)−C(3)	0.0(15)
Sn(1)−N(1)	2.395(2)	N(1)−Sn(1)−N(2)A	152.05(7)	Sn(1)−C(1)−C(2)−C(3)	−177.07(17)
Sn(1)−N(2)A	2.392(2)			Sn(1)−C(1)−C(3)A−C(2)A	177.10(17)
Sn(1)···Sn(1)A	6.9281(10)			C(1)−C(2)−C(4)−N(1)	−29.7(3)
				C(3)−C(2)−C(4)−N(1)	153.2(2)
				C(1)A−C(3)−C(5)−N(2)	27.2(3)
				C(2)−C(3)−C(5)−N(2)	−156.7(2)
anionic fragment					
Sn(2)−C(12)	2.126(3)	C(12)−Sn(2)−C(13)	117.75(13)		
Sn(2)−C(13)	2.119(2)	C(12)−Sn(2)−C(14)	121.40(13)		
Sn(2)−C(14)	2.120(3)	C(13)−Sn(2)−C(14)	120.84(11)		
Sn(2)−Cl(1)	2.6557(9)	Cl(1)−Sn(2)−Cl(2)	178.27(2)		
Sn(2)−Cl(2)	2.5906(9)				

[a] Esd's in parentheses. [b] Suffix A denotes symmetry operation (−*x*, 1 − *y*, 1 − *z*) in **9**. [c] Suffix A denotes symmetry operation (−*x*, 1 − *y*, 1 − *z*) in **10**. [d] Suffix A denotes symmetry operation (−*x*, −*y*, −*z*) in **18b**.

alternative improved synthesis of solvent-free **4** that involves the reaction of $C_6H_4(CH_2NMe_2)_2$-1,3 with *n*-BuLi in an alkane solvent. Although the structure of **4** in the solid state is unknown, in solution it is dimeric,[11a] with the C_{ipso} carbon atom of the aryl nucleus bridging the two lithium atoms ($^1J_{(^6Li,^{13}C)} = 20.5$ Hz)[11b] and with each lithium atom intramolecularly coordinated by two CH_2NMe_2 substituents. Furthermore, it is known from NMR spectroscopic and X-ray crystallographic studies that the analogous *p*-phenyl-substituted derivative of **4**, $[Li\{C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}C_6H_5\text{-}4\}]_2$,[11c] and the related monolithium species **7**, $[Li\{C_6H(CH_2NMe_2)_4\text{-}2,3,5,6\}]_2$,[10] are dimeric both in solution and in the solid state. Also the X-ray crystallographic analysis of the NEt_2 analog of **4**, i.e., $[Li\{C_6H_3(CH_2NEt_2)_2\text{-}2,6\}]_2$, recently reported by Schlengermann et al.,[11d] supports a dimeric solid state structure of **4**.

We are currently investigating in detail both the solution and solid-state geometries of the new organodilithium reagent $[Li_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]_\infty$ (**3**). Based on its insolubility when prepared in Et_2O, we propose that it has a highly aggregated (polymeric) structure in the solid state as illustrated schematically in Figure 5. In this form, complex **3** is insoluble in THF. However, when prepared in THF, **3** remains dissolved and in this situation it is probably present as a less aggregated dilithium species of C_2N_4 (probably monomeric or dimeric) as a result of coordination of THF to the lithium centers and involvement of lithium halide generated during the lithiation reaction.

The new organodilithium compound **3** is an interesting synthetic reagent with which we have successfully prepared 1,4-phenylene-bridged dinuclear organometallic complexes of the group 14 metals silicon and tin (this paper) and of some platinum group metals.[8b]

Unusual Geometries and Reactivity. Tetraorganosilicon and -tin compounds were long regarded as being unable to extend their coordination number due to the poor acceptor properties of the metal center in such species.[4c] However, many examples have now been reported in which the silicon or tin centers may be regarded as hypercoordinate, as a result of additional intramolecular coordination.[3−5] In this paper, we have shown that both in the solid state (X-ray crystallographic studies) and in solution (NMR spectroscopic data) the ligands NCN and C_2N_4 are able to employ the CH_2NMe_2 substituents for varying degrees of extra intramolecular N-donor coordination to the metal center. This N-donor coordination occurs even though there are no electronegative groups on the group 14 metal centers in these silanes and stannanes. The resulting silanes **5** and **9** and stannanes **6** and **10** are air-stable colorless materials that have physical properties similar to those of unsubstituted phenyl and 1,4-phenylene (bis)silanes and (bis)stannanes.

In contrast to their physical properties, the chemical properties of the new NCN and C_2N_4 organometallic complexes of Si and Sn are different from those of the corresponding "free" silanes and stannanes (e.g., $[C_6H_5\text{-}MMe_3]$ and $[(Me_3M)_2\text{-}1,4\text{-}C_6H_4]$, with M = Si, Sn). The

Table 4. Crystallographic data for 9, 10, and 18b

compound	**9**	**10**	**18b**
Crystal Data			
formula	$C_{24}H_{50}N_4Si_2$	$C_{24}H_{50}N_4Sn_2$	$[C_{22}H_{44}N_4Sn_2][C_3H_9SnCl_2]_2$
mol wt	450.86	632.11	1071.48
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	8.4391(5)	9.7564(9)	14.8868(10)
b, Å	9.6587(6)	12.8044(12)	7.5203(10)
c, Å	9.9458(6)	12.856(2)	21.441(3)
α, deg	71.049(6)		
β, deg	83.138(5)	117.181(9)	121.317(6)
γ, deg	64.767(5)		
V, Å^3	693.42(9)	1428.7(3)	2050.7(4)
D_{calc}, g cm^{-3}	1.080	1.469	1.735
Z	1	2	2
$F(000)$	250	644	1052
μ[Mo Kα], cm^{-1}	1.5	17.6	26.9
cryst size, mm	0.25 × 0.38 × 0.50	0.25 × 0.40 × 0.40	0.2 × 0.4 × 0.6
Data Collection			
θ_{min}, θ_{max}, deg	2.2, 27.5	1.6, 27.5	1.1, 27.5
SET4 θ_{min}, θ_{max}, deg	10.27, 13.69	9.90, 14.09	11.46, 14.03
scan type	$\omega/2\theta$	ω	ω
$\Delta\omega$, deg	$0.59 + 0.35 \tan\theta$	$0.59 + 0.35 \tan\theta$	$0.71 + 0.35 \tan\theta$
Hor, vert aperture, mm	3.00, 4.00	$2.52 + 1.26 \tan\theta$, 4.00	$2.60 + 1.30 \tan\theta$, 4.00
X-ray exposure time, h	22	16	29
linear instability, %	3	2	7
ref reflctns	2 5 0, −4 −2 −2, 3 4 −2	−2 5 2, −3 2 −2, −1 3 3	0 2 −5, 2 3 −5, 1 2 −3
data set	−10:10, −12:12, −10:10	−12:12, −16:0, −16:16	−12:19, −9:9, −27:23
total no. of data	6700	7253	10316
total no. of unique data	3166 ($R_{int} = 0.0369$)	3279 ($R_{int} = 0.0485$)	4699 ($R_{int} = 0.0240$)
DIFABS cor range			0.702, 1.771
Refinement			
no. of refined params	143	211	201
final R^a	0.0327 [2779 $I > 2\sigma(I)$]	0.0225 [2741 $I > 2\sigma(I)$]	0.0214 [4224 $I > 2\sigma(I)$]
final $wR2^b$	0.0878	0.0485	0.0509
goodness of fit	1.089	1.059	1.082
$w^{-1\ c}$	$\sigma^2(F^2) + (0.0318\ P)^2 + 0.21\ P$	$\sigma^2(F^2) + (0.0196\ P)^2$	$\sigma^2(F^2) + (0.0260\ P)^2 + 0.55\ P$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.000, 0.000	0.000, 0.009	0.000, 0.001
min and max resid dens, e Å^{-3}	−0.24, 0.32	−0.45, 0.51 (near Sn)	−0.84, 0.46 (near Sn)

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

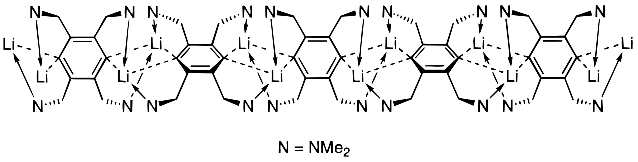

Figure 5. Schematic representation of the proposed highly aggregated (polymeric) structure of dilithiated C_2N_4, **4**, in the solid state.

intramolecularly coordinating CH_2NMe_2 groups in the silicon and tin complexes **5**, **6**, **9**, and **10** cause an increase in electron density at the metal centers and the overall metal coordination geometry and disposition of the organic groups bonded to the metal center changes significantly. In particular, as illustrated in the X-ray molecular structures of **9** and **10**, there is also a significant lengthening (i.e., probable activation) of an M−Me bond that is positioned *trans* to the N-donor atom of the coordinated CH_2NMe_2 group.

In our study, we find that the reaction of silanes **5** and **9** with $Pd(OAc)_2$ results in selective electrophilic C_{aryl}−Si bond palladation. The reason for this increased reactivity of silanes **5** and **9** can be found from the solid-state structure of bis(silane) **9**, in which each silicon(IV) center becomes pentacoordinate as a result of intramolecular N-donor coordination of one CH_2NMe_2 substituent (Figure 2). This results in higher electron density and thereby in an increased reactivity of the C_{aryl}−Si bonds of **9** (and of **5**). This reactivity can be applied in the synthesis of mononuclear and homodinuclear organometallic palladium(II) complexes of the ligands NCN and C_2N_4. Moreover, experiments involving platinum(II) substrates show that none of the C−Si bonds in **5** and **9** are susceptible to electrophilic platination. This difference between palladium(II) and platinum(II) substrates affords the opportunity to prepare heterobimetallic complexes, as we recently communicated,[8b] through selective introduction of the different metal centers in two separate steps.

Analogously, in attempted electrophilic C_{aryl}−Si bond palladation reactions, it has been found that (3-naphthyl)trimethylsilane is almost unreactive toward $Pd(OAc)_2$ or $[Li_2PdCl_4]$. However, the corresponding silane that has a CH_2NMe_2 substituent at the 2-position of the naphthyl group reacts readily with the same palladium(II) substrates to form a 3-cyclometalated product by a C−Si bond cleavage reaction (Figure 6a).[24] In addition, introduction of a trimethylsilyl group at the 1-position of 2-[(dimethylamino)methyl]naphthalene completely reverses the site selectivity from electrophilic palladation at the 3-position (C−H bond activation) to selective cyclometalation at the 1-position (C−Si bond cleavage; Figure 6b).[25]

In this paper we have shown that the new stannanes **6** and **10** have reactivity patterns that are different from

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[24] Valk, J.-M.; van Belzen, R.; Boersma, J.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Dalton Trans.* **1994**, 2293.

[25] Valk, J.-M.; Boersma, J.; van Koten, G. *J. Organomet. Chem.* **1994**, *483*, 213.

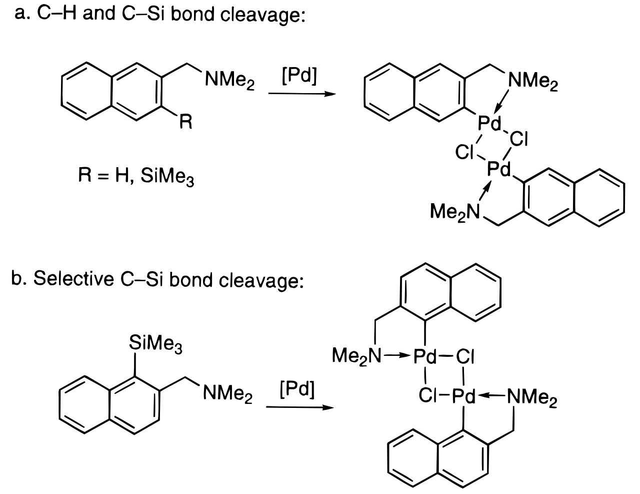

Figure 6. C−H and C−Si bond cleavage reactions (a) and the directional effect of a Me_3Si group (b) on the site of cyclopalladation of a naphthylamine.

those encountered with tetracoordinate aryltrialkyltin compounds. The C_{Me}−Sn bond elongation identified in the structure of **10** is directly translated in the reactivity of the hexacoordinate stannane **10** (and **6**) toward palladium(II) and platinum(II) substrates. Whereas interaction of these stannanes **6** and **10** with platinum(II) species [$PtCl_2$(COD)] was seen to result in selective alkyl transfer to afford methylplatinum complex [PtCl(Me)(COD)], the corresponding interaction with palladium(II) substrates results in selective aryl transfer to afford palladium(II) complexes of NCN and C_2N_4, respectively. These results with **6** and **10** contrast with those of the tetracoordinate aryltrialkyltin species $PhSnMe_3$, which reacts with [$M'Cl_2$(COD)], where M′ is either palladium or platinum, to afford in both cases via selective aryl transfer the product [M′(Ph)Cl(COD)].[2]

It has been proposed that the higher reactivity of aryltrialkylstannanes bearing intramolecularly coordinating electron donor substituents relative to that of analogs without such substituents is the result of an increase in electron density at the tin(IV) center, in combination with the elongation of C_{alkyl}−Sn bonds that are *trans* to a coordinated donor substituent.[4] For instance, Jastrzebski et al.,[4a] reported that [8-(dimethylamino)-1-naphthyl]trimethylstannane reacts with [$PtCl_2$(COD)] to afford [PtCl(Me)(COD)] through a methyl-transfer reaction and [8-(dimethylamino)-1-naphthyl]dimethyltin chloride (Figure 7b). In contrast, the group of Eaborn showed that (1-naphthyl)trimethylstannane reacts with the same substrate to afford a product that is now the result of an aryl group-transfer reaction (Figure 7a), and this type of reactivity was found to be normal for the interaction of several mixed alkyl/arylstannanes with platinum halides.[23]

Conclusion

In this investigation of the ligands $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (NCN) and $[C_6(CH_2NMe_2)_4\text{-}2,3,5,6]^{2-}$ (C_2N_4), we have found that they afford organometallic complexes of the group 14 (IVB) metals silicon and tin in which N-donor coordination of CH_2NMe_2 substituents plays an important role in the overall coordination motif. This flexible behavior of NCN and C_2N_4 results in a series of new hypercoordinate aryltrialkylsilanes and -stannanes with interesting structural and reactivity features. In particular, arylstannanes of these ligands are more reactive toward diverse platinum group metal complexes then the corresponding arylsilanes. Moreover, the silanes and stannanes derived from C_2N_4 are versatile reagents which provide synthetic pathways to new dinuclear organometallic complexes with a 1,4-phenylene bridge.

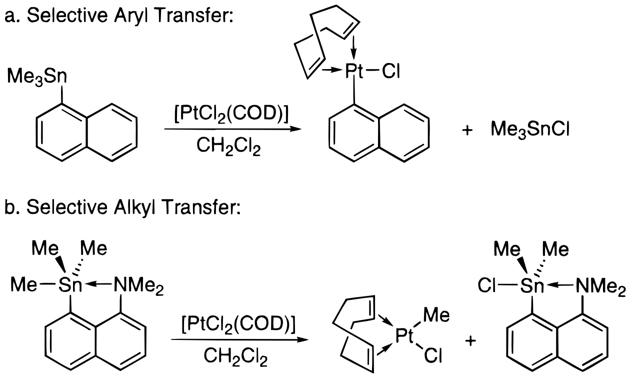

Figure 7. Selective aryl (a) vs alkyl (b) transfer to [$PtCl_2$(COD)].

Experimental Section

General Comments. All organometallic syntheses were performed in a dry dinitrogen atmosphere, using standard Schlenk techniques. The solvents were dried and freshly distilled prior to use. ^1H, ^{13}C, ^{29}Si, and ^{119}Sn NMR measurements were performed at 298 K with a Bruker AC200 or AC300 spectrometer, with chemical shifts referenced to either Me_4Si or Me_4Sn. Elemental microanalyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim, Germany. The compounds $C_6H_2(CH_2Br)_4\text{-}1,2,4,5$,[26] $[Li\{C_6H(CH_2NMe_2)_4\text{-}2,3,5,6\}]_2$ (**7**),[10] and $C_6Br_2(CH_2Br)_4\text{-}2,3,5,6$ (**1**)[27] were prepared according to previously described methods.

Synthesis of $C_6H_4(CH_2NMe_2)_2$-1,3. To stirred formic acid (200 mL, 5.3 mol) at room temperature in a 1 L Erlenmeyer flask was added over 15 min neat α,α′-diamino-*m*-xylene (32.4 mL, 0.25 mol). Formaldehyde (200 mL of 37 wt % in water, 2.65 mol) was then added in one portion. The clear reaction mixture was heated, and the stirred solution was held at reflux temperature (~95 °C) until CO_2 evolution ceased (~4 h). The mixture was cooled to ~50 °C with an ice bath, and formic acid (50 mL, 1.3 mol) and formaldehyde (50 mL, 0.83 mol) were then added. The resulting clear reaction mixture was heated and kept at reflux temperature (~95 °C) for 16 h. The reaction mixture was cooled to room temperature with an ice bath, and concentrated aqueous HCl was then slowly added until a pH of 1−2 was reached. The mixture was washed with Et_2O (2 × 150 mL) and then neutralised with saturated aqueous NaOH until a pH of 13−14 was reached. The product was extracted from the mixture with pentane (3 × 250 mL). The combined pentane extracts were washed with saturated aqueous NaCl (200 mL), dried with K_2CO_3, and filtered. After evaporation of the volatiles *in vacuo*, the product was obtained as a pale yellow oily residue. Purification by flash distillation under reduced pressure afforded $C_6H_4(CH_2NMe_2)_2$-1,3 as a colorless oil. Yield: 38−42 g (80−90%). ^1H NMR ($CDCl_3$, 200 MHz): δ 7.23 (m, 4 H, ArH), 3.40 (s, 4 H, CH_2N), 2.22 (s, 12 H, NMe_2). ^1H NMR (C_6D_6, 200 MHz): δ 7.50 (s, 1 H, ArH), 7.21 (m, 3 H, ArH), 3.30 (s, 4 H, CH_2N), 2.10 (s, 12 H, NMe_2). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 138.7, 129.8, 128.1, 127.8 (Ar), 64.3 (CH_2N), 45.4 (NMe_2). ^{13}C NMR (C_6D_6, 50 MHz): δ 139.9, 129.7, 128.3, 127.8 (Ar), 64.6 (CH_2N), 45.5 (NMe_2).

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(26) Ried, W.; Bodem, H. *Chem. Ber.* **1956**, *89*, 2328.

(27) Hopff, H.; Doswald, P.; Manukian, B. K. *Helv. Chim. Acta* **1961**, *44*, 1231.

Synthesis of $C_6H_2(CH_2NMe_2)_4$-1,2,4,5. A modification of a literature procedure was used.[10] Solid 1,2,4,5-tetrakis(bromomethyl)benzene (31.7 g, 70.5 mmol) was added to a stirred solution of dimethylamine (63.5 g, 1.41 mol) in Et_2O (500 mL) at −10 °C, and the reaction mixture then allowed to warm slowly (1 h) to room temperature. The mixture was stirred for an additional 2 h at room temperature, and during this time a white suspension formed. Addition of an aqueous solution of NaOH (150 mL, 2 M) to the reaction mixture afforded a two-layer system. The organic layer was collected and the water layer extracted with Et_2O (2 × 250 mL). The combined organic extracts were washed with saturated aqueous NaCl (250 mL), dried with K_2CO_3, and evaporated *in vacuo* to afford the desired product as a white solid. Yield: 8.2 g (38%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.12 (s, 2 H, Ar), 3.41 (s, 8 H, CH_2N), 2.14 (s, 24 H, NMe_2). ^{1}H NMR (C_6D_6, 200 MHz): δ 7.49 (s, 2 H, Ar), 3.59 (s, 8 H, CH_2N), 2.15 (s, 24 H, NMe_2). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 136.3, 132.4 (Ar), 61.0 (CH_2N), 45.5 (NMe_2). ^{13}C NMR (C_6D_6, 50 MHz): δ 137.1, 132.7 (Ar), 61.7 (CH_2N), 45.7 (NMe_2).

Synthesis of $C_6Br_2(CH_2NMe_2)_4$-2,3,5,6 (2). Neat $HNMe_2$ (22 mL, 330 mmol) was added to a white suspension of **1** (15 g, 24.7 mmol) in THF (150 mL) at −10 °C. The reaction mixture was allowed to warm to room temperature over a period of 1 h and then heated to 55 °C for 5 min. The reaction mixture was allowed to cool to room temperature, and all volatiles were removed *in vacuo* to leave a white solid residue. This residue was suspended in aqueous NaOH (150 mL, 2 M) and with vigorous stirring of the mixture Et_2O (500 mL) was added. Stirring was stopped, and from the resulting two-layer system the organic layer was collected and the water layer extracted with Et_2O (200 mL). The combined organic layer and extracts were washed with saturated aqueous NaCl (100 mL), dried with $MgSO_4$ and evaporated *in vacuo*, to afford **2** as a white solid, which was pure enough for further synthesis. Yield: 10.7 g (93%). Analytically pure colorless crystals of **2** could be obtained by slowly cooling a Et_2O solution of **2** to −25 °C. Mp: 149−152 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.97 (s, 8H, CH_2N), 2.27 (s, 24H, NMe_2). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 139.4, 131.9 (Ar), 59.7 (CH_2N), 45.4 (NMe_2). Anal. Calcd for $C_{18}H_{32}Br_2N_4$: C, 46.56; H, 6.95; N, 12.07. Found: C, 46.63; H, 6.93; N, 12.15.

Synthesis of $[Li\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_2$ (4). *n*-BuLi (20 mL, 1.6 M in hexanes, 32 mmol) was added dropwise (5 min) to a stirred solution of $C_6H_4(CH_2NMe_2)_2$-1,3 (6.12 g, 31.8 mmol) in hexane (100 mL) at room temperature. The reaction mixture was then stirred for 18 h at room temperature. The reaction mixture was then evaporated to dryness, to afford **4** quantitatively as an off-white solid, sufficiently pure for further syntheses. Pure microcrystalline **4** could be obtained by cooling a concentrated solution of **4** in Et_2O to −25 °C. The white solid product was collected by filtration and dried *in vacuo*. Yield: 4.5−5.0 g (70−80%). Mp: 80−83 °C. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.23 (dd, 1 H, $^3J_{HH}$ = 8.0 and 6.3 Hz, ArH), 7.21 (d, 1 H, $^3J_{HH}$ = 6.3 Hz, ArH), 7.08 (d, 1 H, 3.52 (s, 4 H, CH_2N), 2.14 (s, 12 H, NMe_2), 0.38 (s, 9 H, $SiMe_3$). ^{13}C NMR (C_6D_6, 50 MHz): δ 188.4 (br m, C_{ipso}), 151.8, 124.4, 123.6 (Ar), 72.7 (CH_2N), 45.3 (NMe_2).

Synthesis of $[Me_3Si\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (5). A solution of (trimethylsilyl)trifluoromethanesulfonate (5.7 mL, 29.3 mmol) in THF (20 mL) was added over a period of 5 min to a stirred solution of 1,3-bis[(dimethylamino)methyl]phenyllithium (**4**; 5.29 g, 13.4 mmol) in hexane (80 mL) at room temperature, and stirring was continued at this temperature for 15 min. The volatiles were then evaporated *in vacuo*, and the yellow oily residue was extracted with hexane (2 × 100 mL). The combined hexane extracts were evaporated *in vacuo*, and the resulting dark yellow oil was purified by flash distillation under reduced pressure, to afford pure **5** as a colorless oil. Yield: 5.54 g (79%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.26 (m, 3 H, ArH), 3.52 (s, 4 H, CH_2N), 2.14 (s, 12 H, NMe_2), 0.38 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 146.4, 138.6, 128.4 (Ar), 64.9 (CH_2N), 45.3 (NMe_2), 3.3 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 59.6 MHz): δ −7.7 ($SiMe_3$). Anal. Calcd for $C_{15}H_{28}N_2Si$: C, 68.12; H, 10.67; N, 10.59. Found: C, 68.25; H, 10.74; N, 10.51.

Synthesis of $[Me_3Sn\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (6). A solution of Me_3SnCl (2.10 g, 10.6 mmol) in Et_2O (10 mL) was added dropwise over a period of 5 min to a stirred solution of **4** (2.06 g, 5.2 mmol) in Et_2O (20 mL) at room temperature, and stirring of the reaction mixture was continued for 2 h. After this time, the reaction mixture was evaporated to dryness *in vacuo*, to afford a yellow oily residue. This material was diluted with hexane (50 mL) and filtered to remove LiCl. The filtrate was evaporated *in vacuo* to leave crude **6** as a yellow oil. Purification by flash distillation under reduced pressure afforded stannane **6** as a colorless oil which slowly solidified at room temperature. Yield: 3.37 g (92%). Mp: 37−39 °C. ^{1}H NMR (C_6D_6, 200 MHz, 298 K): δ 7.00 (m, 3 H, ArH), 3.34 (s, 4 H, CH_2N), 1.92 (s, 12 H, NMe_2), 0.30 (s, 9 H, $^2J_{SnH}$ = 53 Hz and 51 Hz, Me_3Sn). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.25 (m, 3 H, ArH), 3.63 (s, 4 H, CH_2N), 2.22 (s, 12 H, NMe_2), 0.37 (s, 9 H, $^2J_{SnH}$ = 53 Hz and 51 Hz, Me_3Sn). ^{13}C NMR ($CDCl_3$, 50 MHz); δ 147.4 ($^nJ_{SnC}$ = 27 Hz, Ar), 143.8 ($^1J_{SnC}$ = 555 and 530 Hz, C_{ipso}), 128.3 ($^nJ_{SnC}$ = 45 Hz, Ar), 127.8 ($^nJ_{SnC}$ = 10 Hz, Ar), 66.1 ($^3J_{SnC}$ = 21 Hz, CH_2), 44.9 (NMe_2), −3.4 ($^1J_{SnC}$ = 371 and 355 Hz, Me_3Sn). ^{119}Sn NMR (C_6D_6, 75 MHz): δ −86.9 (Me_3Sn). Anal. Calcd for $C_{15}H_{28}N_2Sn$: C, 50.74; H, 7.95; N, 7.89. Found: C, 50.72; H, 7.84; N, 7.83%.

Synthesis of $[(Me_3Si)_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]$ (9). Method A. *n*-BuLi (3.1 mL, 1.6 M solution in hexane, 5 mmol) was slowly added over 5 min to a white suspension of C_6Br_2-1,4-$(CH_2NMe_2)_4$-2,3,5,6 (**2**; 0.92 g, 2 mmol) in Et_2O (15 mL) at −78 °C. The reaction mixture was allowed to slowly warm to room temperature over a period of 1 h and then stirred for an additional 30 min at this temperature; during this latter period a white precipitate formed. The reaction mixture was centrifuged and the supernatant discarded. To the white solid residue suspended in THF (20 mL) was added neat Me_3SiOTf (1.0 g, 5 mmol) dropwise over a period of 5 min, and the resulting reaction mixture was then stirred at room temperature for 2 h. After this time, a clear yellow solution had formed, and the volatiles were then removed *in vacuo* to afford a yellow solid. This material was extracted with Et_2O (5 × 25 mL). The combined ether extracts were concentrated to ~50 mL and left at −25 °C for 16 h to afford **9** as a white microcrystalline solid. Yield: 0.84 g (93%). Mp: 194−195 °C. Analytically pure crystals of **9** that were suitable for an X-ray analysis, were obtained by slowly cooling a saturated solution of **9** in warm benzene.

Method B. *n*-BuLi (11.5 mL, 1.6 M in hexanes, 18.4 mmol) was added dropwise over 5 min to a stirred solution of $C_6H_2(CH_2NMe_2)_4$-2,3,5,6 (5.29 g, 17.3 mmol) in hexane (150 mL) at room temperature. The reaction mixture was stirred for 17 h at this temperature, and all volatiles were then removed *in vacuo* to afford a yellow oily residue. To this residue dissolved in THF (40 mL) at 0 °C was added dropwise neat Me_3SiOTf (3.6 mL, 20 mmol) over 5 min. This reaction mixture was allowed to warm to room temperature and stirred for 15 min at this temperature. The volatiles were then removed *in vacuo*, and the oily residue that was obtained was treated with a mixture of Et_2O (100 mL) and aqueous HCl (100 mL, 0.5 M) to afford a two-layer system. The water layer, containing the protonated product, was collected and washed with Et_2O (100 mL). This water layer was then neutralized with solid NaOH and the product extracted with Et_2O (3 × 50 mL). The combined organic extracts were dried with K_2CO_3 and evaporated *in vacuo* to afford a yellow oil which is mostly monosilane **8**. This crude **8** was treated with *n*-BuLi (11.5 mL, 1.6 M in hexanes, 18.4 mmol) in hexane, followed by Me_3SiOTf (3.6 mL, 20 mmol) in THF using the reaction conditions as described above. The resulting reaction mixture in THF was stirred for 15 min at room temperature. The volatiles were then removed *in vacuo*, and the oily residue, containing primarily **8** and **9**, was dissolved in a minimum amount of hexane and separated using column chromatography (neutral alumina). Elution with hexane:Et_3N = 97:3 gave a fraction containing **9**. Evaporation of this fraction *in vacuo* afforded pure **9** as a white solid. Yield: 4.6 g (59%). ^{1}H NMR (C_6D_6, 300 MHz): δ 3.74 (s, 8 H, CH_2), 2.05 (s, 24 H, NMe_2), 0.46 (s, 18 H, $SiMe_3$). ^{13}C NMR (C_6D_6, 75 MHz): δ 144.2, 143.7 (Ar), 61.9 (CH_2), 44.7 (NMe_2), 4.3 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 59.6 MHz): δ −11.2 ($SiMe_3$). Anal. Calcd for $C_{24}H_{50}N_4Si_2$: C, 63.93; H, 11.18; N, 12.43. Found: C, 63.77; H, 11.45; N, 12.33.

Further elution of the column with Et_2O:Et_3N = 97:3 gave a fraction containing **8**, i.e., $[Me_3Si\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]$. Concentration (*in vacuo*) of this fraction yielded a pale yellow oil, which solidified at room temperature. Yield: 2.4 g (36%). Mp: 38−41 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.12 (s, 1 H, ArH), 3.61 and 3.45 (s, 4 H, NCH_2), 2.16 and 2.02 (s, 12 H, NMe_2), 0.28 (s, 9 H, Me_3Si). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 144.9, 142.5, 135.5, 133.3 (Ar), 62.7, 60.4 (NCH_2), 45.4, 44.8 (NMe_2), 4.0 (Me_3Si).

Synthesis of $[(Me_3Sn)_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]$ (10). *n*-BuLi (3.3 mL, 1.5 M solution in pentane, 5 mmol) was slowly added over a period of 5 min to a stirred solution of **2** (0.92 g, 2 mmol) in THF (15 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature over a period of 30 min and stirred for an additional 30 min. Then a solution of Me_3SnCl (1.0 g, 5 mmol) in THF (10 mL) was added in one portion, and the mixture was stirred for 2 h. The resulting clear colorless solution was evaporated *in vacuo* to leave an off-white oily residue which was extracted with hot hexane (4 × 25 mL). Concentration of the combined hexane extracts *in vacuo* afforded **10** (0.67 g, 53%) as a white solid. Analytically pure colorless crystals of **10** (mp 186−189 °C), suitable for an X-ray analysis, were obtained by slowly cooling a saturated solution of **10** either in warm benzene or in hot hexane. ^{1}H NMR (C_6D_6, 200 MHz): δ 3.52 (s, 8 H, NCH_2), 1.98 (s, 24 H, NMe_2), 0.37 (s, 18 H, $^{2}J_{SnH}$ = 50 Hz, Me_3Sn). ^{13}C NMR (C_6D_6, 50 MHz): δ 147.1 ($^{1}J_{SnC}$ not observed, C_{ipso}), 142.5 ($^{2}J_{SnC}$ = 49 Hz, $^{3}J_{SnC}$ = 27 Hz, C_{ortho}), 60.6 ($^{3}J_{SnC}$ = 26 Hz, CH_2), 44.8 (NMe_2), −1.9 ($^{1}J_{SnC}$ = 371 and 355 Hz, Me_3Sn). ^{119}Sn NMR (C_6D_6, 75 MHz): δ −107.0 (s, $^{5}J_{(^{119}Sn,^{117}Sn)}$ = 75 Hz, $SnMe_3$). Anal. Calcd for $C_{24}H_{50}N_4Sn_2$: C, 45.61; H, 7.97; N, 8.86. Found: C, 45.65; H, 7.89; N, 8.81.

Reaction of $[Me_3Sn\{C_6H(CH_2NMe_2)_4\text{-}2,3,5,6\}]$ with *n*-BuLi. To a stirred solution of $C_6H_2(CH_2NMe_2)_4$-2,3,5,6 (0.10 g, 0.3 mmol) in hexane (3 mL) was added *n*-BuLi (0.2 mL, 1.6 M solution in hexanes, 0.32 mmol) in one portion. The reaction mixture was stirred for 17 h at room temperature, and all volatiles were evaporated *in vacuo* to afford a yellow oily residue. This residue was dissolved in THF (4 mL), and to this solution at room temperature was added solid Me_3SnCl (60 mg, 0.3 mmol) in one portion; the resultant reaction mixture was stirred for 15 min at room temperature. After this time, the volatiles were removed *in vacuo* and the resulting oily residue was extracted with hexane (5 mL). The hexane solution obtained from this procedure, which contains mostly the monostannane $[Me_3Sn\{C_6H(CH_2NMe_2)_4\text{-}2,3,5,6\}]$, was treated with *n*-BuLi (0.2 mL, 1.6 M solution in hexanes, 0.32 mmol) as described above and the mixture stirred for 17 h at room temperature. To this solution was added H_2O (3 drops), and the reaction mixture was filtered through Celite. Evaporation of the filtrate *in vacuo* yielded a yellow oily residue, which was identified by ^{1}H NMR spectroscopy ($CDCl_3$ solution) as $C_6H_2(CH_2NMe_2)_4$-1,2,4,5.

Reactions of Silanes 5 and 9 and Stannanes 6 and 10 with $Pd(OAc)_2$ and $[M'Cl_2(COD)]$ (M′ = Pd, Pt). Reactions were performed using typically 2 mmol of silane or stannane and 2 (for **5** and **6**) or 4 mmol (for **9** and **10**) of palladium(II) or platinum(II) substrate. Products were identified based on reported NMR data: $[M'Cl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (M′ = Pd (**11**),[13] Pt (**12**)[13,17]), $[(M'Cl)_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]$ (M′ = Pd (**15**), Pt (**16**)),[8b,c] $[M'ClMe(COD)]$ (M′ = Pd[15], Pt[18]), and $[Me_2Sn\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]^+Cl^-$ (**14a**).[16]

(a) General Procedure for the Reactions of Silanes 5 and 9 and Stannanes 6 and 10 with $Pd(OAc)_2$. A solution of the silane or stannane in MeOH (~1 M) was added to a stirred solution of $Pd(OAc)_2$ (1 molar equiv for **5** and **6**, 2 molar equiv for **9** and **10**) in MeOH (~1 M) at room temperature, and the reaction mixture was stirred at this temperature until all $Pd(OAc)_2$ had been converted. A solution of excess LiCl in MeOH (~1 M) was then added at room temperature, and the reaction mixture was stirred for 15 min at this temperature. During this time a precipitate formed. The products in the MeOH solution and in the precipitate that had formed were analyzed by ^{1}H and ^{13}C NMR spectroscopy.

(b) General Procedure for the Reactions of Silanes 5 and 9 and Stannanes 6 and 10 with $[MCl_2(COD)]$ (M = Pd, Pt). A solution of the silanes or stannanes in CH_2Cl_2 (~1 M) was added to a stirred solution of $[MCl_2(COD)]$ (M = Pd, Pt; 1 molar equiv for **5** and **6**, 2 molar equiv for **9** and **10**) in CH_2Cl_2 (~1 M) at room temperature, and the reaction mixture was stirred at this temperature until all $[MCl_2(COD)]$ had been converted. If during this time a white precipitate had formed, this precipitate was filtered off, washed with CH_2Cl_2, and dried *in vacuo* prior to analysis. The products in the CH_2Cl_2 solution and in the precipitate (if formed) were analyzed by NMR spectroscopy. The reaction of **10** with $[PtCl_2(COD)]$ in CH_2Cl_2 afforded $[(Me_2Sn)_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]^{2+}(Cl^-)_2$ (**18a**) as a white solid. ^{1}H NMR (D_2O, 200 MHz): δ 3.88 (s, 8 H, NCH_2), 2.50 (s, 24 H, NMe_2), 0.81 (s, 12 H, $^{2}J_{SnH}$ = 63 Hz, Me_2Sn). ^{13}C NMR (D_2O, 50 MHz): δ 143.2 ($^{1}J_{SnC}$ not observed, C_{ipso}), 141.2 ($^{2}J_{SnC}$ = 65 Hz, $^{3}J_{SnC}$ = 40 Hz, C_{ortho}), 63.2 ($^{3}J_{SnC}$ = 35 Hz, $^{4}J_{SnC}$ = 11 Hz, NCH_2), 48.1 (NMe_2), −4.3 ($^{1}J_{SnC}$ = 453 and 434 Hz, $SnMe_2$). Evaporation of the filtrate yielded a pale yellow solid, identified as $[PtClMe(COD)]$.

Synthesis of $[Me_2Sn\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]^+([Me_3SnCl_2]^-)$ (14b). A stirred solution of Me_3SnCl (270 mg, 1.35 mmol) and **6** (228 mg, 0.64 mmol) in CH_2Cl_2 (5 mL) was heated at reflux temperature for 72 h. Then the reaction mixture was evaporated *in vacuo* to ~1 mL, and hexane (4 mL) was added, which resulted in the precipitation of a white solid. This precipitate was filtered off, washed with hexane (3 × 5 mL), and dried *in vacuo*. Yield: 350 mg (95%) of a white solid, identified as **14b**. Colorless crystals (mp 154−157 °C) were obtained by layering a solution of **14b** in MeOH with Et_2O. ^{1}H NMR (D_2O, 200 MHz): δ 7.41 (t, 1 H, $^{3}J_{HH}$ = 7.5 Hz, ArH), 7.23 (d, 2 H, $^{3}J_{HH}$ = 7.5 Hz, ArH), 3.82 (s, 4 H, NCH_2), 2.44 (s, 12 H, NMe_2), 0.82 (s, 6 H, $^{2}J_{SnH}$ = 64 Hz, Me_2Sn), 0.53 (s, 9 H, $^{2}J_{SnH}$ = 68 Hz, Me_3Sn). ^{13}C NMR (D_2O, 50 MHz): δ 145.3 ($^{3}J_{SnC}$ = 36 Hz, Ar), 138.4 ($^{1}J_{SnC}$ not observed, C_{ipso}), 133.8 ($^{4}J_{SnC}$ = 11 Hz, Ar), 128.5 ($^{2}J_{SnC}$ = 57 Hz, Ar), 66.3 ($^{3}J_{SnC}$ = 34 Hz, CH_2), 47.8 (NMe_2), 1.5 ($^{1}J_{SnC}$ = 499 and 478 Hz, Me_3Sn), −3.7 ($^{1}J_{SnC}$ = 454 and 434 Hz, Me_2Sn). ^{119}Sn NMR (CD_3OD, 74.85 MHz): δ 72.0 (br s, cation), 34.1 (s, anion). Anal. Calcd for **14b** corrected for 15 mol % loss of Me_3SnCl: C, 36.48; H, 6.05; N, 5.14. Found: C, 36.50; H, 6.20; N, 5.09.

Synthesis of $[(Me_2Sn)_2\text{-}1,4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]^{2+}([Me_3SnCl_2]^-)_2$ (18b). A stirred solution of Me_3SnCl (250 mg, 1.26 mmol) and **10** (196 mg, 0.31 mmol) in CH_2Cl_2 (10 mL) was heated at reflux temperature (~40 °C) for 72 h, and this resulted in the formation of a white precipitate. This precipitate was filtered off, washed with CH_2Cl_2 (3 × 5 mL), and dried *in vacuo*. Yield: 195 mg (59%) of **18b** as a white solid, mp >200 °C. Analytically pure colorless crystals, suitable for an X-ray analysis, were obtained by slow evaporation in air of a solution of **18b** in a 1:1 mixture of MeOH and dibutyl ether. ^{1}H NMR (D_2O, 200 MHz): δ 3.62 (s, 8 H, NCH_2), 2.45 (s, 24 H, NMe_2), 0.76 (s, 12 H, $^{2}J_{SnH}$ = 62 and 65 Hz, Me_2Sn), 0.52 (s, 12 H, $^{2}J_{SnH}$ = 66 and 69 Hz, Me_3Sn). ^{13}C NMR (D_2O, 50 MHz): δ 143.2 ($^{1}J_{SnC}$ not observed, C_{ipso}), 141.2 ($^{2}J_{SnC}$ = 65 Hz, $^{3}J_{SnC}$ = 40 Hz, Ar), 63.2 ($^{3}J_{SnC}$ = 35 Hz, $^{4}J_{SnC}$ = 11 Hz, CH_2), 48.1 (NMe_2), 1.5 ($^{1}J_{SnC}$ = 501 and 479 Hz, Me_3Sn), −4.2 ($^{1}J_{SnC}$ = 453 and 433 Hz, Me_2Sn). ^{119}Sn NMR (CD_3OD, 75 MHz): δ 53.6 (br s, $^{5}J_{(^{119}Sn,^{117}Sn)}$ = 75 Hz, $^{1}J_{SnC(Me)}$ = 453 Hz, $^{1}J_{SnC(Ar)}$ = 730 Hz, dication), 35.2 (s, $^{1}J_{SnC(Me)}$ = 489 Hz, anion). Anal. Calcd for $C_{28}H_{62}Cl_4N_4Sn_4$: C, 31.39; H, 5.83; N, 5.23. Found: C, 31.44; H, 5.78; N, 5.21%.

X-ray Structure Determination of Complexes 9, 10, and 18b. Crystals suitable for X-ray diffraction were mounted on the tip of a glass fiber and were placed in the cold nitrogen stream on an Enraf-Nonius CAD4-T diffractometer on rotating anode (T = 150 K, Mo Kα radiation, graphite monochromator, λ = 0.710 73). Accurate unit cell parameters and an orientation matrix were determined by least-squares fitting of the setting angles of 25 well-centered reflections (SET4).[28] The unit cell parameters were checked for the presence of higher lattice symmetry.[29] Crystal data and details on data collection and refinement are collected in Table 4. Data were corrected for *Lp* effects and for the observed linear instability of the reference reflections. An empirical absorption correction was applied for complex **18b** (DIFABS,[30] as implemented in PLATON[31]); no absorption correction was applied for complexes **9** and **10**.

The structure of **9** was solved by automated direct methods (SHELXS86).[32] The structures of complexes **10** and **18b** were solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92).[33] The structures were refined on F^2, using full-matrix least-squares techniques (SHELXL-93[34] for complex **9** and SHELXL-96[35] for complexes **10** and **18b**); no observance criterion was applied during refinement.

For complex **10** hydrogen atom coordinates were refined; the starting positions were obtained from a difference Fourier synthesis. Hydrogen atoms of complexes **9** and **18b** were included in the refinement on calculated positions, riding on their carrier atoms. The methyl hydrogen atoms were refined in a rigid group, allowing for rotation around the N−C, Si−C, or Sn−C bonds; the methyl group containing C(12) of complex **9** was refined using an idealized disordered geometry.

The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms by a constant factor.

Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 36. Geometrical calculations and illustrations were performed with PLATON;[31] all calculations were performed on a DECstation 5000 cluster.

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Supporting Information Available: Further details of the structure determinations, including tables of atomic coordinates, bond lengths and angles, and thermal parameters for **9**, **10**, and **18b** (12 pages). Ordering information is given on any current masthead page.

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