A Dinuclear Tin(II) Amide, a *meta*-Stannylaminocyclophane and Its Orthostannylated Derivative, a Dimeric Trinuclear Tin(II) Cluster**

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Trimethylsilylamido ligands such as $Sn(NR_2)_2$ ($R = SiMe_3$)^[1] and $Sn(NR_2)(2,6-tBu_2-4-Me-C_6H_2O)^{[2]}$ have played a pivotal role in the study and structural characterization of divalent tin compounds. In 1994 we drew attention to the ligands 1,4- $(R\bar{N})_2C_6H_4$ (X^{2-}) and trans-1,4- $(R\bar{N})_2C_6H_{10}$, which provided the first dinuclear divalent tin compounds, 1,4- $(R_2NSnNR)_2C_6H_4$ and trans-1,4- $(R_2NSnNR)_2C_6H_{10}$, respectively.^[3] The 1,2-isomer Y^{2-} of the former bisamido ligand had been employed previously as a bridging moiety in $[Mg\{1,2-(RN)_2C_6H_4\}(OEt_2)]_2$,^[4] or as a chelate in $M[1,2-(RN)_2C_6H_4]$ (M = Ge,^[5] Sn^[6]).

Herein we discuss a new bisamido ligand $(\mathbb{Z}^{2^{-}})$, the 1,3-isomer of $\mathbb{X}^{2^{-}}$ and $\mathbb{Y}^{2^{-}}$ (R = SiMe₃), which we believe will find a



 $(K = ShNe_3)$, which we believe will find a useful place in coordination chemistry, and report on 1) the synthesis of a novel, dinuclear, divalent tin(1) complex, the *meta*-bis(stannylamino)cyclophane 1, 2) the trinuclear tin(11) cluster compound 2 (a loosely bonded dimer in the crystal), formally an orthostannylated derivative of 1, and 3) structural details for 1 and 2, both in the crystalline state and in solution in benzene.

Treatment of the N,N'-dilithio derivative of the ligand \mathbb{Z}^{2^-} with an equimolar amount of $[Sn(\mu-Cl)(NR_2)]_2^{[7]}$ gave dark red crystals of 1 and $Sn(NR_2)_2$; while orange crystals of 2 were obtained from 1,3- $[R(H)N]_2C_6H_4$ (2 mol) and $Sn(NR_2)_2$ (3 mol) (Scheme 1, Table 1).



Scheme 1. Synthesis of the *meta*-bis(stannylamino)cyclophane 1 and of the Sn^n cluster 2 (R = SiMe_3).

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[**] This work was supported by the Deutsche Forschungsgemeinschaft (fellowship for H. B.), the Engineering Physical Sciences Research Council (fellowship for C. D.), and the European Union (fellowship for L. J.-M. P). Table 1. Selected analytical and spectroscopic data for 1 and 2 at 298 K in C_6D_6 (¹H) or PhMe/ C_6D_6 . ¹H NMR: 250 MHz; ¹³C(¹H) NMR: 62.86 MHz; ¹³Sn(¹H) NMR: 186.42 MHz; ²⁹Si(¹H) NMR: 99.33 MHz; ¹⁵N NMR INEPT from ¹H NMR at 500 MHz [a].

1: Dark red; 66 % yield; m. p. ca. 120 °C (decomp); δ^{119} Sn^{{1}H} NMR: $\delta = 505$; ¹H NMR: $\delta = 0.27$ (s, 18H, CH₃, SiMe₃), 5.56 (t, 1H, arom. CH. ⁴J = 2.1 Hz), 6.00 (dd, 2H, arom. CH, ⁴J = 2.2, ³J = 7.7 Hz), 6.81 (t, 1H, arom. CH, ³J = 7.7 Hz); ¹³C{¹H} NMR: $\delta = 2.49$ (CH₃), 107.29 (C3 and C5. C₆H₄), 121.67 (C1, C₆H₄), 148.55 (C2 and C6, C₆H₄), 151.78 (C4, C₆H₄); EI-MS: *m*/*z*: 738 (*M*⁺, 56%).

2: Orange; 75% yield; m. p. ca. 295 °C (decomp); sublimation at 5×10^{-6} Torr with bath at 190 °C; ¹¹⁹Sn{¹H} NMR: $\delta = -888$ (1Sn, ¹J(¹¹⁹Sn, ¹¹⁹N1²Sn) = 254 Hz), -501 (2Sn, ¹J(¹¹⁹Sn, ^{119/117}Sn) = 250, ¹J(¹¹⁹Sn, ¹¹⁷Sn) = 600 Hz); 1H NMR: $\delta = 0.33$ (s, 9H, CH₃, SiMe₃), 0.39 (s, 9H, CH₃, SiMe₃), 6.33 (d, 1H, arom. CH, ³J = 8.2 Hz), 6.33 (d, 1H, arom. CH, ³J = 7.5 Hz), 7.23 (t, 1H, arom. CH, ³J = 8 Hz); ¹³C{¹H} NMR: $\delta = 1.47$ (CH₃), 3.25 (CH₃), 109.75, 109.97 (C3 and C5, C₆H₃), 115.63 (C1, C₆H₃, ¹J(¹³Sn) = 100, 198 Hz), 137.76 (C4, C₆H₃), 163.85, 165.03 (C2 and C6, C₆H₃); ²⁹Si{¹H</sup> NMR: $\delta = 0.59$, 8.05; ¹⁵N{¹H</sup> NMR: $\delta = -245.5, -234.3$; EI-MS: m/z = 854 (M^+ , 70%).

[a] ¹¹⁹Sn{¹H} NMR values for Sn[N(SiMe₃)₂]₂: $\delta = +776$ at 283 K; for [Sn-(μ -Cl){N(SiMe₃)₂]₂: $\delta = +138$.

To test whether 1 was an intermediate in the formation of 2 from ZH_2 and $Sn(NR_2)_2$, two ¹¹⁹Sn{¹H} NMR spectroscopic experiments were carried out. In the first, 1 was mixed with an excess of $Sn(NR_2)_2$ in PhMe/C₆D₆ at

ambient temperature. After 24 h, three signals were recorded: a quintet centered at $\delta = 774$, due to Sn(NR₂)₂, a singlet at $\delta = 506$, due to 1, and a singlet at $\delta = 586.6$ attributed to the stannylene 3; the latter two were of comparable intensity. In the second experiment, ZH₂ was mixed with an



equimolar amount of $Sn(NR_2)_2$ under similar conditions; the same three signals were observed, although that at $\delta = 586.1$ was accompanied by a signal of roughly equal intensity at

 $\delta = 596.9$. In the two experiments, the signals at $\delta \approx 590$ had the appearance of quintets, as expected for ${}^{1}J({}^{119}\text{Sn},{}^{14}\text{N})$ coupling to two equivalent nitrogen atoms. We conclude that **3** and not **1** is an intermediate in the formation of **2** from ZH₂ and Sn(NR₂)₂, and that **3** may have the structure shown and thus may exist in two stereoisomeric forms.

Evidently, formation of 2 involves an unprecedented stannylation of the 2-position of a substituted 1,3-diaminobenzene. It is well known that lithiation of an aminobenzene is directed to the *ortho*-position, which is due in part to the increased kinetic acidity in this position as a consequence of the (-I) effect of the electronegative nitrogen atom; an *N*-stannyl substituent, such as that in 3, would further enhance the (-I) effect. A contributory, and perhaps dominant effect is the capacity of neighboring nitrogen atoms to complex the

lithium atom and hence direct it into the 2-position; divalent tin in $Sn(NR_2)_2$ has a low-lying vacant orbital and hence may act as a Lewis acid site.

The crystalline *meta*-bis(stannylamino)cyclophane 1 is a centrosymmetric molecule (Figure 1).^[8] The unit cell contains two independent molecules of essentially the same geometry; only bonds and angles for one of the two molecules are discussed. The phenylene rings, which are related by an inversion center, are necessarily parallel (their planes are separated by 3.1 Å), but

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Figure 1. Crystal structure and atom labeling scheme of 1. Selected bond lengths $[\tilde{A}]$ and angles $[\circ]$ for one of the two-independent molecules: Sn-N1 2.066(7), Sn-N2' 2.069(9), Si1-N1 1.732(9), Si2-N2 1.754(7), N1-C1 1.432(13), N2-C3 1.397(13); N1-Sn-N2' 98.3(3), Sn-N1-C1 120.4(6), Sn-N1-Si1 122.2(5), N1-C1-C2 122.1(8).

show a sideways displacement such that the angle between the N1-N2-N1'-N2' and C1-C2-C3-C4-C5-C6 planes is 74°. Each two-coordinate tin atom has a V-shaped relationship to its two nitrogen atom nearest neighbors; the Sn–N bond lengths are 2.066(7) and 2.069(9) Å, and the N-Sn-N' angle is 98.3(3)°. These values are comparable to the corresponding bond lengths and angles in Sn[N(SiMe_3)_2]_2^[1b] (2.096(1) and 2.088(6) Å and 104.7(2)°) and in 1,4-[N(R)Sn(NR_2)]_2C_6H_4 (2.066(6) and 2.082(7) Å and 101.8(3)°).^[3]

The crystalline trinuclear cluster 2 has a nearly equilateral triangular Sn_3 skeleton (Figure 2), which is closely associated with a neighboring Sn_3 unit (Figure 3).^[8] The $Sn \cdots Sn$ contacts may be compared with 1) the Sn-Sn bond length in tetrahedral tin (2.810 Å), 2) the $Sn \cdots Sn$ contacts in polyhedral tin clusters such as penta[1.1.1.]propellane $Sn_5(2,6-iPr_2C_6H_3)_6$ (A) (mean $Sn_{br}-Sn_{bh}$ 2.858, $Sn_{bh}-Sn_{bh}$ 3.367 Å (br = bridging, bh = bridgehead)),^[9] and 3) the $Sn \cdots Sn$ contacts in iminostannylene



Figure 2. Crystal structure and atom labeling scheme of **2**. Selected bond lengths [Å] and angles [°]: sn1-N2 2.160(13), sn1-N4 2.212(13), sn2-N4 2.483(12), sn1-C1 2.45(2), sn2-C1 2.31(2), sn3-C13 2.42(2), C6-C1 1.39(2), C1-C2 1.41(2), C3-C4 1.37(2); N2-Sn1-N4 104.0(5), N2-Sn1-C1 60.6(5), C1-Sn2-C13 98.7(5), N4-Sn1-C1 90.7(5), sn2-C1-Sn1 87.9(5), N2-C2-C1 114.4(13), C1-C6-N1 114.6(13), N2-C2-C3 125.9(14).



Figure 3. The Sn \cdots Sn distances and atom labeling scheme of the Sn₆ skeleton (2)₂.

 $[Sn(NtBu)]_4$ (B) (3.321-3.348 Å);^[10] in A and B and related compounds the longer contacts are regarded as implying little or no bonding interaction.^[9-11] The central tin atom Sn2 forms bonds to the 2-phenylene carbon atoms C1 and C13 (mean Sn-C 2.31(2) Å), comparable in length to those in Sn[2,4,6tBu₃C₆H₂]₂^[12] (mean Sn-C 2.261(4) Å); the other two tin atoms (Sn1 and Sn3) of the Sn₃ unit form somewhat longer contacts to C1 and C13 (mean 2.44(2) Å), respectively. The Sn1-N2 and Sn3-N3 bonds have mean lengths of 2.15(1) Å, while those for Sn1-N4 and Sn3-N1 have mean lengths of 2.22(1) Å; Sn2 also has close contacts to N1 and N4 (2.426(14) and 2.483(12) Å, respectively).

Whereas a solution of 1 in PhMe/C₆D₆ is highly symmetrical, the ²⁹Si{¹H} and ¹⁵N{¹H} NMR spectra (Table 1) reveal that the two trimethylsilylamido groups in **2** are magnetically inequivalent. Furthermore, the ¹H and ¹³C{¹H} NMR spectra (Table 1) show that the symmetry is not retained within the aromatic ring.

The reactions of the ligand 1,3-($R\bar{N}$)₂C₆H₄ to give the highly novel complexes **1** and **2**, are being extended to other divalent elements and to heterometallic analogues. The metalation of arenes has previously been reported for lithium, mercury(II), boron (BCl₃/AlCl₃), thallium(III), lead(Iv), antimony(v) [(SbF₅)₂], tellurium(IV) (e.g. TeCl₄ + PhOMe), and some noble metals^[13] such as gold(III). For metals of variable oxidation state, these reactions proceed through a higher oxidation state complex; therefore, the present stannylation by a tin(II) amide to give **2** is especially noteworthy and is likely to have further implications.

Experimental Section

1: *n*BuLi (8 mL of a 1.6 M solution in *n*-hexane, 12.69 mmol) was added to a stirred solution of 1,3-[H(SiMe₃)N]₂C₆H₄ [14] (1.6 g. 6.35 mmol) in *n*-hexane (100 mL). The solution was gently heated to reflux for 1 h, then cooled to room temperature. $[Sn(\mu-Cl){N(SiMe_3)_2}]_2$ [7] (4.0 g. 6.35 mmol) was added, and the mixture was stirred for 12 h at 25 °C and then at about 60 °C for 1 h. The precipitate was filtered off, and the filtrate was concentrated to about 40 mL in vacuo and cooled to -30 °C to afford dark red crystals of 1 (1.50 g. 66%); correct elemental analysis.

2: 1,3-[H(SiMe₃)N]₂C₆H₄ [14] (2.0 g. 7.75 mmol) in *n*-hexane (70 mL) was added dropwise to a solution of Sn[N(SiMe₃)₂]₂ [1] (5.1 g. 11.6 mmol) in *n*-hexane (40 mL) at about 25 °C. The reaction mixture was stirred overnight. Volatiles were removed in vacuo to yield an orange solid, which was extracted with toluene (40 mL). Filtration to remove a slight cloudiness, followed by concentration of the filtrate in vacuo, and cooling at -5 °C, yielded orange crystals of 2 (2.6 g. 75%); correct elemental analysis.

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Highly Selective Allylic Alkylation with a Carbon Nucleophile at the More Substituted Allylic Terminus Catalyzed by an Iridium Complex: An Efficient Method for Constructing Quaternary Carbon Centers**

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Iridium complexes have been studied as models for intermediates in catalytic reactions. For example, the oxidative addition reaction of $[IrCl(CO)(PPh_3)_3]$ is well known.^[1] Since Crabtree reported that a cationic iridium complex is a highly active catalyst for hydrogenation of alkenes,^[2] iridium complexes have received much attention as potential hydrogenation catalysts. Recently an iridium complex catalyzed asymmetric hydrogenation was reported.^[3] In contrast, the development of carbon– carbon bond forming reactions catalyzed by iridium complexes lags far behind.^[4] Synthetically useful stereo- and regiocontrolled carbon-carbon bond forming reactions are unexplored. We report here on highly selective allylic alkylations with carbon nucleophiles that are catalyzed by an iridium complex [Eq. (a)].



a: $R^1 = nPr$, $R^2 = R^3 = R^4 = H$; **b**: $R^1 = Ph$, $R^2 = R^3 = R^4 = H$ **c**: $R^1 = Me$, $R^2 = R^3 = R^4 = H$; **d**: $R^1 = R^2 = Me$, $R^3 = R^4 = H$ **e**: $R^1 = R^2 = H$, $R^3 = R^4 = Me$; **f**: $R^1 = R^2 = H$, $R^3 = Me$, $R^4 = nBu$ **g**: $R^1 = R^2 = H$, $R^3 = Me$, $R^4 = CH_2CH_2CH=CMe_2$

Transition metal complex catalyzed allylic alkylation with carbon nucleophiles is an essential method for constructing complex organic molecules. Palladium,^[5] nickel,^[6] molybde-num,^[7] iron,^[8] tungsten,^[9] and ruthenium^[10] complexes can serve as catalysts. Oxidative addition of the allylic substrate to a low-valent transition metal complex produces a π -allyl complex, which is then attacked by the nucleophile to give the final product. The control of regioselectivity in this reaction is important. One of the most extensively studied transition metals in allylic alkylation is palladium. Generally palladium complexes direct attack at the less substituted allylic terminus. In contrast, molybdenum, tungsten, and ruthenium complexes tend to lead to preferential attack at the more substituted allylic terminus. Complete regiocontrol of the nucleophilic attack at the more substituted allylic terminus is a challenging problem.

The reaction of (E)-2-hexenyl acetate (1a, X = Ac) with diethyl malonate anion in the presence of $[Ir(cod)Cl]_2$ gave a mixture of 2a and 3a. Product 2a arose from alkylation at the more substituted allylic terminus and 3a from alkylation at the less substituted allylic terminus. The addition of phosphorus ligands had a significant effect on the selectivity and yield of products. The results are summarized in Table 1. P(OPh)₃ was found to be

Table 1. Effect of the phosphorus ligand on the iridium complex catalyzed allylic alkylation of 1a, X = Ac, with the anion of diethyl malonate [a].

Entry	Ligand	Conditions	Yield[%][b]	2a:3a[c]
1	P(OPh),	room temperature, 3 h	89	96:4
2	P(OEt) ₃	THF, reflux, 3 h	81	59:41
3	$P(O_i Pr)_i$	THF, reflux, 9 h	44	53:47
4	PPh,	THF, reflux, 16 h	6	24:76
5	PnBu ₃	THF, reflux, 16 h	0	to the

[a] A mixture of 1a. X = Ac (2 mmol), NaCH(CO₂Et)₂ (4 mmol), [Ir(cod)Cl]₂ (0.04 mmol), the phosphorus ligand (0.16 mmol), and THF (10 mL) was stirred under Ar. [b] Yield of isolated product. [c] Determined by gas chromatography.

the most effective ligand. The reaction was complete in three hours at room temperature to give an excellent yield of products. Compound **2a** was obtained in 96% selectivity (entry 1); the alkylation was highly selective at the more substituted allylic terminus. The reaction using $P(OEt)_3$ as a ligand gave a comparable yield of products with much less selectivity (entry 2). When a more electron-donating phosphorus ligand such as PPh₃ and $P(nBu)_3$ was used, products were obtained in poor yields (entries 4 and 5).

We examined the reaction of a series of allylic compounds. The results summarized in Table 2 indicate that alkylation at the

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