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# The Chemistry and Structure of a 10-Sn-4 System:[1] Pseudo-Trigonal-Bipyramidal 4-Coordinate, 10-Electron Tin Centers

**Gerhard Bettermann and Anthony J. Arduengo, III***

*Contribution No. 4412 from the Central Research and Development Department, E.I. du Pont de Nemours & Co., Inc., Experimental Station, Wilmington, Delaware 19898.*

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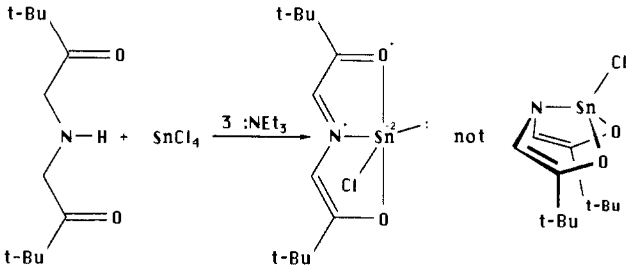
**Abstract:** A discrete pseudo-trigonal-bipyramidal tin(II) species has been prepared by the action of 5-aza-2,2,8,8-tetramethylnonane-3,7-dione (**1**) on $SnCl_4$. The unusual electronic and geometric arrangement in **2** is supported by extensive multinuclear magnetic resonance data and verified by X-ray structure analysis. The lone pair of electrons at the hypervalent tin center is chemically active as demonstrated by the oxidation of **2** with $SO_2Cl_2$ to give **4**.

In previous reports we have described the stabilization of low-coordinate hypervalent pnictogens (main group V elements: specifically P, As, and Sb) by the ligand system **1**.[2] We now report a pseudo-trigonal-bipyramidal (Ψ-TBP) geometry at a main group IV element, tin.[3] The Ψ-TBP geometry for **2** demonstrates a preference for the hypervalent 10-Sn-4 arrangement[1] over a classical 8-Sn-4 structure like **3**. The observation of structure **2** rather than **3** would not be assured by the analogous chemistry of the pnictogens since the coordination number and electronegativity both change on moving from main group V to IV.



**1** **2** **3**

## Results and Discussion

Reaction of **1** with $SnCl_4$ and 3 equiv of triethylamine affords a discrete 4-coordinate tin compound **2**. The unusual geometry of **2** is in stark contrast to the tetrahedral geometry that would be expected for structure **3**, which obeys the octet rule.

The unusual bonding arrangement in **2** is evident from the multinuclear magnetic resonance data for the system. The ring proton resonance of δ 7.79 is similar to those we observed previously in our pnictogen derived ADPnO systems.[2a] The $^{15}N$ resonance at δ −63.3 upfield of nitrate ion confirms the identity of the nitrogen center as iminium—again consistent with the ADPnO series. The $^{13}C$ NMR spectrum of **2** is likewise consistent with the trends observed with the pnictogen systems. These data suggest that the ligand backbone in **2** should be represented in a manner similar to the pnictogen systems, that is, an oxidized ligand backbone chelating a reduced metal center. This representation of the bonding system would require the tin center in **2** to correspond to a 4-coordinate tin(II) center with a lone pair of electrons at tin.

**Table I.** Selected Bond Lengths and Angles in **2**

| bond lengths | pm | bond angles | deg |
|---|---|---|---|
| Sn–Cl | 249.4 (3) | O–Sn–O | 140.7 (3) |
| Sn–O | 234.7 (6) | N–Sn–O | 70.4 (1) |
| Sn–N | 228.4 (8) | N–Sn–Cl | 85.1 (2) |
| C–O | 128.0 (10) | O–Sn–Cl | 87.0 (2) |
| C–N | 133.0 (10) | C–N–Sn | 116.5 (5) |
| $C–C_{ring}$ | 140.0 (10) | C–O–Sn | 114.5 (5) |
| $Sn–Cl_{(intermol)}$ | 331.8 (3) | C–N–C | 127.0 (9) |
| | | C–C–N | 117.5 (7) |
| | | C–C–O | 120.6 (8) |

The bond distances and angles in **2** are presented in Table I. It is instructive to compare these data with the closely related ADSbO systems.[2a,d] The Sn–O and Sn–N bonds are longer than the corresponding bonds in ADSbO systems (20 and 23 pm, respectively). These significant changes are in the opposite direction of what would be expected based on the 3 pm decrease in covalent radius on going from antimony to tin.[4] Changes in the ionic bonding components as well as the hybridization at the Sn and Sb centers may be responsible for the unusual trends in bond lengths in these systems.[5]

The identity of the tin center as formally tin(II) is supported by the $^{119}Sn$ chemical shift of δ −378.1 (ref $(CH_3)_4Sn$). The presence of a lone pair of electrons at tin is reflected in the rather small tin couplings (20.4 Hz) to the ring proton of the ligand backbone (vide infra). A lone pair of electrons at tin is consistent with the coordination geometry observed in the solid state X-ray structure of **2**.[6] The lone pair at the tin center is in an orbital

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[1] The N-X-L nomenclature system has been previously described (Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753): N valence electrons about a central atom X, with L ligands.

[2] (a) Arduengo, A. J., III; Stewart, C. A.; Davidson, F.; Dixon, D. A.; Becker, J. Y.; Culley, S. A.; Mizen, M. B. *J. Am. Chem. Soc.* **1987**, *109*, 627. (b) Culley, S. A.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1984**, *106*, 116. (c) Culley, S. A.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1985**, *107*, 1089. (d) Stewart, C. A.; Harlow, R. L.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1985**, *107*, 5543.

[3] (a) Related structures for 2,2′-bipyridyl and 1,10-phenanthroline adducts of $SnCl_2$ have been reported and show geometries about Sn which are somewhat similar to **2**. However, the adducts do not have the possibility of adopting a conventional tetrahedral Sn(IV) structure analogous to **3**. The closest approach of a non-bonded Cl is also similar in **2** and these $SnCl_2$ adducts. See: Archer, S. J.; Koch, K. R.; Schmidt, S. *Inorg. Chim. Acta* **1987**, *126*, 209. (b) A tin cluster compound has been reported which also contains a Ψ-TBP Sn center: Veith, M.; Frank, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 158.

[4] (a) The radius comparison in this case should be made between parallel oxidation states at the chelated centers. Thus, Sn(II) in **2** is compared with Sb(I) in ADSbO. Alternatively, Sn(IV) in **2** could be compared with Sb(III) in ADSbO. For values of covalent radii, see: Huheey, J. E. *Inorg. Chem.* 2nd ed.; Harper and Row: New York, 1978; pp 232–233. (b) For van der Waals radii see: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

[5] We have previously discussed such factors for the ADPnO systems in ref 1, and related effects appear to be operating in the main group IV derived systems. It sould be noted that the $^{15}N$ and $^{13}C$ NMR spectra indicate charge density shifts consistent with decreased ionic character of the hypervalent Sn–O bonds relative to corresponding bonds in ADSbO systems. A detailed analysis of the bonding in **2** and related systems will be presented in subsequent publications.

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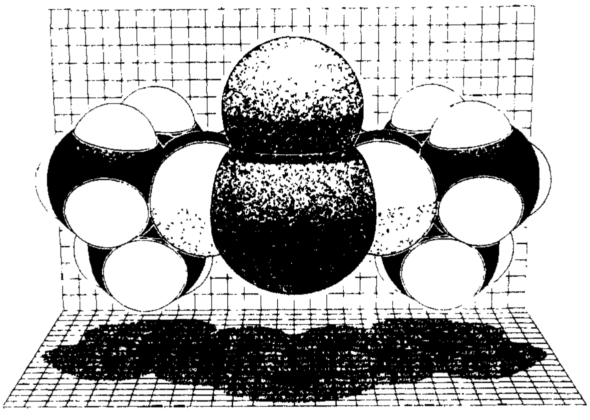
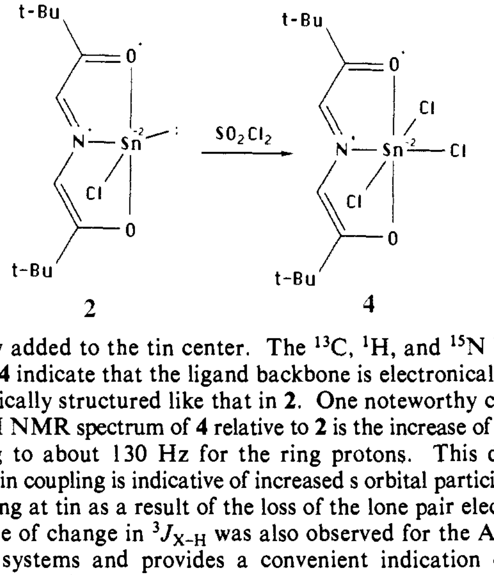


**Figure 1.** KANVAS[7] drawing of **2**.

of high s character resulting in the distorted Ψ-TBP geometry (Figure 1[7]). The extent of distortion of the Ψ-TBP geometry in tin is reflected in the Cl–Sn–N bond angle of 85° as would be expected as a consequence of the s orbital demand of the tin lone pair. It should also be noted that the solid state $^{13}C$ NMR of **2** is very similar to the solution spectra so that the solution and solid state structures must be the same.

Although the lone pair of electrons at the tin center in **2** is in an orbital of high s character, this electron pair is chemically active. Oxidation of **2** with $SO_2Cl_2$ gives the corresponding trichlorotin(IV) derivative **4** in which the elements of $Cl_2$ have been oxidatively added to the tin center. The $^{13}C$, $^{1}H$, and $^{15}N$ NMR data on **4** indicate that the ligand backbone is electronically and geometrically structured like that in **2**. One noteworthy change in the $^{1}H$ NMR spectrum of **4** relative to **2** is the increase of $^{3}J_{Sn-H}$ coupling to about 130 Hz for the ring protons. This drastic increase in coupling is indicative of increased s orbital participation in bonding at tin as a result of the loss of the lone pair electrons. This type of change in $^{3}J_{X-H}$ was also observed for the ADPO[2] derived systems and provides a convenient indication of the presence or absence of lone pairs of electrons at the central atom (X).



2 4

The close intermolecular approach of the chlorine of one molecule of **2** to the tin center of a second molecule in the crystal is suggestive of electrophilic reactivity of the tin center. This nonbonded distance (331.8 pm) is within the sum of the van der Waals radii (410 pm).[4b] The nonbonded chlorine is disposed above the ring system on the opposite side from the direct bonded chlorine. In this way a zig-zag chain is formed throughout the crystal as depicted in Figure 2. It can also be seen from the shadow in Figure 2 that the association of the second chlorine makes the structure very similar to the Di-*t*-BuADSbO·$Cl_2$ system we have previously reported[2a] in which the Sn–Cl unit of **2** is replaced by Sb–$Cl_2$.

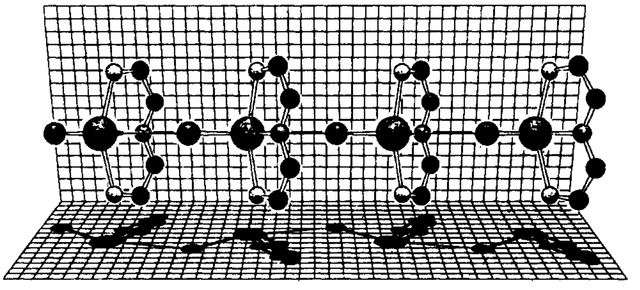
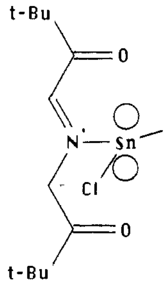


**Figure 2.** KANVAS[7] drawing of Sn–Cl chains in crystal of **2**. All but the ring atoms have been omitted for clarity.

Finally it should be emphasized that the more conventional tetrahedral 8-Sn-4 arrangement **3** is not reflected in the chemistry, spectra, or structure of **2**. Also, the stannylene structure **5** does not suggest the high degree of interaction observed between tin and oxygen centers. However, structure **5** does provide insight into the type of electronic effects that give rise to the observation of a 10-Sn-4 geometry for **2** rather than the more conventional structure **3**. It should also be mentioned that a series of compounds has been reported in which a tin(II) center is chelated by a *saturated*, *dianionic*, tridentate ligand **6**.[8] In these systems the monomers are best represented as pseudo-tetrahedral 3-coordinate tin(II) complexes with a lone pair of electrons at tin (8-Sn-3). Although some of the systems related to **6** form 4-coordinate tin centers by association of monomer units, the very different structure and chemistry observed for systems **2** and **6** demonstrates the important role played by the ligand in determining the geometry and electronics at the chelated center.



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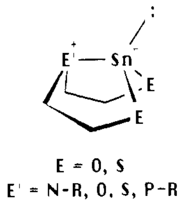

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Further work is in progress on these and the closely related lead and germanium systems to explore their chemistry and structural trends.

## Experimental Section

**General Methods.** All solvents were freshly distilled and dried before use according to established procedures.[9] Melting points were measured on a Thomas-Hoover capillary apparatus and are uncorrected. $^{1}H$ NMR spectra were recorded on a General Electric QE-300 spectrometer. $^{13}C$, $^{15}N$, and $^{119}Sn$ NMR spectra were recorded on a Nicolet NT-300WB spectrometer. Solid state $^{13}C$ CP-MAS spectra were obtained on a GE S-100 spectrometer. All NMR spectra are reported in ppm $\delta$ (positive shifts downfield of the reference). NMR references are ($^{1}H$) $Me_4Si$, ($^{13}C$) $Me_4Si$, ($^{15}N$) $NH_4^+NO_3^-(D_2O)$, and ($^{119}Sn$) $Me_4Sn$.

Mass spectra were obtained on a VGMM 7070 double-focusing high-resolution mass spectrometer.

Manipulations of air-sensitive samples were performed in a vacuum atmospheres drybox under nitrogen. Elemental analyses were performed

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[6] The crystal data were as follows: $C_{12}H_{20}NO_2ClSn$, orthorhombic, space group *Pnma* (no. 62), $a = 1043.5$ (8) pm, $b = 2457.9$ (13) pm, $c = 612.6$ (7) pm, $Z = 4$, $D_c = 1.54$ g/cm$^3$; crystal size, 0.32 × 0.31 × 0.17 mm. With 1117 reflections of greater intensity than $3\sigma$, the structure was solved by direct methods and standard difference Fourier techniques. The final $R$ factors were $R = 0.072$ and $R_w = 0.087$. The highest peak in the final difference Fourier map, with a height of 2.52 e/Å$^3$ with an estimated error based on $\Delta F$ of 0.83, was located 92 pm from the tin.

[7] This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institut der Universität Freiburg, FRG), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE, USA) to produce the back and shadowed planes. The planes bear a 50-pm grid, and the lighting source is at infinity so that shadow size is meaningful.

[8] (a) Jurkschat, K.; Scheer, M.; Tzschach, A.; Meunier-Peret, J.; Van Meerssche, M. *J. Organomet. Chem.* **1985**, *281*, 173. (b) Baumeister, U.; Hartung, H.; Jurkschat, K.; Tzschach, A. *J. Organomet. Chem.* **1986**, *304*, 107, and references therein.

[9] *Purification of Laboratory Chemicals*, 2nd ed.; Perrin, D. D., Armarego, W. L. F., Perrin, D. R., Eds.; Pergamon: New York, 1985.

by Oneida Research Services, Whitesboro, NY, and are within 0.4% unless otherwise stated. The X-ray crystallographic structure determination on **2** was performed by Oneida Research Services.

**5-Aza-2,2,8,8-tetramethylnonane-3,7-dione (1)** was prepared by the established literature procedure.[2a]

**1-Chloro-3,7-di-*tert*-butyl-5-aza-2,8-dioxa-1-stannabicyclo[3.3.0]octa-2,4,6-triene (2).** In a typical reaction **2** is prepared under nitrogen by addition of **1** (14.6 g, 68.4 mmol) in 60 mL of $CH_2Cl_2$ via a syringe to a solution of 17 g of $SnCl_4$ (68.4 mmol) in 150 mL of $CH_2Cl_2$. After the addition of **1** is complete, triethylamine (20 g, 0.2 mol) in 40 mL of $CH_2Cl_2$ is added dropwise. The orange/brown mixture is stirred for about 16 h, and then the solvent is removed in vacuo. The solid residue of extracted with hot benzene. The benzene is removed in vacuo, and the product is recrystallized from $CH_3CN$: yield 18 g (72%); mp 240 °C; $^1H$ NMR ($CD_2Cl_2$) $\delta$ 1.27 (s, *t*-Bu, 18 H), 7.79 (s, NCH, 2 H, tin satellites, $^3J_{Sn-H}$ = 20.4 Hz (119–117 not resolved)); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 27.5 (s, $CH_3$), 40.9 (s, $CCH_3$), 120.1 (s, CN, tin satellites, $^2J_{Sn-C}$ = 17.5 Hz (119–117 not resolved)), 202.2 (s, CO); $^{119}Sn\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ −378.1; $^{15}N\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ −63.2 (s, tin satellites, $^1J_{Sn-N}$ 560 Hz (119–117 not resolved)); solid state $^{13}C$ NMR $\delta$ 29, 41, 120, 201; MS EI (70 ev), *m/z* 365.02. Anal. ($C_{12}H_{20}ClNO_2Sn$): C, H, N.

**1,1,1-Trichloro-3,7-di-*tert*-butyl-5-aza-2,8-dioxa-1-stannabicyclo[3.3.0]octa-2,4,6-triene (4).** In a typical reaction **4** is prepared under nitrogen by addition of a solution of 0.45 g (3.4 mmol) of $SO_2Cl_2$ to the suspension of 1.0 g (2.8 mmol) of **2** in toluene at 0 °C. The color of the solution changes from reddish/brown to yellow, and slowly all of **2** dissolves. The product begins to precipitate shortly after the addition of the $SO_2Cl_2$ is started. The product is collected by filtration, and the mother liquor is cooled to give a second crop. The crude product is recrystallized from toluene to yield 980 mg (73%) of pure **4** as a toluene solvate. A sample gave the following data: mp 251.5–252 °C (dec); $^1H$ NMR ($CD_2Cl_2$) $\delta$ 1.37 (s, *t*-Bu, 18 H), 7.66 (s, NCH, 2 H, tin satellites, $^3J_{Sn-H}$ 129.0/135.0 Hz ($^{117}Sn/^{119}Sn$); $^{13}C\{^1H\}$ NMR $\delta$ ($CD_2Cl_2$) 27.0 (s, $CH_3$), 41.8 (s, $CCH_3$), 114.6 (s, CN, tin satellites, $^1J_{Sn-C}$ = 90 Hz (119–117 not resolved)), 202.8 (s, CO); $^{119}Sn\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ −511.0; $^{15}N\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ −79.6. Anal. Calcd for ($C_{12}H_{20}NO_2Cl_3Sn\cdot{}^1/_2(C_6H_5CH_3)$): C, 38.12; H, 4.92; N, 2.84. Found: C, 38.67; H, 5.03; N, 2.91.

Acknowledgement is made to H. A. Craig for his excellent technical assistance.

**Registry No. 1**, 88686-46-8; **4**, 112070-04-9.

**Supplementary Material Available:** A complete description of the X-ray crystallographic structure determination of **2**, including experimental procedures, tables of data, and an ORTEP drawing (11 pages). Ordering information is given on any current masthead page.

# Molecular Recognition during 1,2-Addition of Chiral Vinyl Organometallics to Chiral β,γ-Unsaturated Ketones. Case Studies of Three 7,7-Disubstituted 2-Norbornenones[1]

**Leo A. Paquette,* Keith S. Learn, Jeffrey L. Romine, and Ho-Shen Lin**

*Contribution from Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210.*

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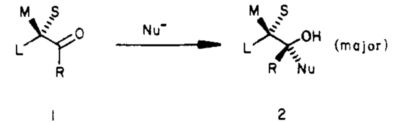
**Abstract:** The level of double diastereoselection attainable upon 1,2-addition of several chiral vinylorganocerium reagents to 7,7-disubstituted 5-norbornen-2-ones has been assessed. The effect of functional group variation at C-7 and bulk solvent influences have also been studied. The extent of diastereoselection has been found to vary with the degree and stereochemistry of pendant alkyl substitution or annulation of the cyclopentenyl nucleophiles at positions 4 and 5. When the purified alcohols so produced are subjected to anionic oxy-Cope rearrangement, polycyclic compounds are produced that carry a multitude of stereogenic centers installed in a predictable way. The methodology therefore constitutes a short and enormously powerful synthetic tool. Mechanistic considerations of these reactions are discussed in light of existing theory and available experimental facts.

Because of the central role played by carbon–carbon bond-forming reactions in organic synthesis, considerable attention has been focused over the years on the stereochemical course of nucleophilic addition to a carbonyl group. The particular diastereoselectivity encountered in those examples where the carbonyl functionality is specifically positioned adjacent to a chiral center has been rationalized in the context of Cram's rule.[2,3] That the pathway followed usually takes place in the sense **1** → **2** has attracted many others, most notably Cornforth,[4] Karabatsos,[5] Felkin,[6] Anh,[7] Houk,[8] and Fraser,[9] to offer comment on whether the reaction course is indeed governed by steric factors or whether electronic control is responsible.



1 2

3 4

Immense effort has also been expended on assessing the stereoselectivity of alkylation reactions involving chiral metal enolates,[10] the diastereoselectivity of aldol reactions involving enolates and aldehydes or ketones with prochiral faces in both components,[11] and the level of stereocontrol attainable with flanking

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(1) Part 5. Part 4: Paquette, L. A.; Learn, K. S.; Romine, J. L. *Tetrahedron*, in press. Part 3: Paquette, L. A.; Learn, K. S.; Romine, J. L. *Synth. Commun.*, in press.

(2) Cram, D. J.; Abd Elhafez, F. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828.

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