Structure and Lewis-base reactivity of bicyclic low-valent germanium and tin complexes bridged by bis(diisopropylphosphino)amine

Christopher J. Miller,^a Ujwal Chadha,^a Jordan R. Ulibarri-Sanchez,^a Diane A. Dickie,^a
Richard A. Kemp^{a,b*}

^a Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, NM, 87131, USA

^b Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, NM, 87106, USA

Corresponding author. E-mail: rakemp@unm.edu. Phone: (505)272-7609. Fax: (505)272-7336.

ABSTRACT

Lithium bis(diisopropylphosphino)amide $\text{LiN}[\text{P}(i\text{-Pr})_2]_2$ reacts with SnCl_2 or $\text{GeCl}_2 \cdot \text{dioxane}$ in the presence of excess $n\text{-BuLi}$ to produce the bicyclic compounds $\{\text{MN}[\text{P}(i\text{-Pr})_2]_2\}_2$ ($\text{M} = \text{Sn}, \text{Ge}$) which feature Sn_2^{2+} or Ge_2^{2+} units bridged by phosphorus. When paired with $\text{B}(\text{C}_6\text{F}_5)_3$ in THF, the Lewis-basic M_2^{2+} complexes participate in a THF ring-opening reaction. Quite surprisingly, in the absence of THF one *para*-F atom from $\text{B}(\text{C}_6\text{F}_5)_3$ is activated and displaced to B while a new M-C bond is formed. Each of these complexes, as well as $\text{Cl}_2\text{Sn}\{\text{N}[\text{P}(i\text{-Pr})_2]_2\}_2$ and $\{\text{ClSnN}[\text{P}(i\text{-Pr})_2]_2\}_2$ were characterized by a combination of multinuclear NMR spectroscopy and single-crystal X-ray diffraction.

Keywords: group 14 elements; phosphine ligands; X-ray crystallography; multinuclear NMR; small molecule activation

1. Introduction

Over approximately the last 40 years, main group chemists have created an impressive assortment of stable divalent group 14 complexes of the generic form $R_2E:$, where E is C, Si, Ge, Sn or Pb, and R is an organic ligand [1]. Early on, it was recognized that by varying the R groups, both the steric and electronic properties of these tetrylenes could be subtly altered, allowing extraordinary potential for the tuning of their unusual chemical reactivities. Recent reviews of this class of compounds cover, among other things, their coordination to transition metals [2] and the activation of small molecules [3]. It is the latter application that is of greatest significance to us, as we have had a long-standing interest in the activation and transformation of CO_2 by simple main group complexes [4]. We have previously reported several examples in which stannylenes, $R_2Sn:$, act as Lewis *acids* towards CO_2 , with the oxygen lone pairs interacting with tin's empty p-orbital via insertion into an Sn-N [5] or Sn-P [6] bond. This type of reactivity has also been seen by others [7]. This is in contrast to carbenes, $R_2C:$, which behave as Lewis *bases*, donating the carbene lone pair to the electron deficient carbon of CO_2 to form adducts [8].

In the low-valent group 14 complexes that have been shown to be useful for small molecule activation, one of two features is generally present. Either there is a bond between the two tetrels across which a substrate can be added, or the element is incorporated into a five- or six-membered ring, thus leaving the lone pair as the most accessible reactive site. Looking for molecules that combined both of these features led us to a handful of examples of bicyclic group 14 complexes with E-E bonds. First reported in 1987 by Karsch as a P,P-bridged Ge complex with the anionic ligand $[Me_3SiC(PMe_2)_2]^-$ [9], additional examples of Si [10], Ge [11], Sn [12] and Pb [13] bicyclic compounds have since been reported. Of particular interest to us were the

Ge, Pb and Sn complexes that each used an anionic bidentate phosphorus ligand to bridge the two metal centers (Fig.1). Initially these molecules were described as E^{1+} compounds, but recent reports on related compounds have used the formalism E_2^{2+} [14]. In each of these “butterfly-shaped” molecules, the stereochemically active lone pairs on the adjacent group 14 elements are accessible and are pointed in the same direction, which suggested to us that this class of molecules would be interesting Lewis bases to explore with the ultimate goal of activating CO_2 or other small molecules.

Fig. 1. Examples of bicyclic group 14 complexes with anionic P,P-bridging ligands.

2. Experimental

2.1 General Considerations

All manipulations were carried out in an argon-filled glovebox or by using standard Schlenk techniques. Anhydrous solvents were purchased from commercial sources including Aldrich or Alfa Aesar and used as received, or obtained from an LC Technology Solutions solvent purification system, after which they were stored in the glovebox over 4 Å molecular sieves. Tris(pentafluorophenyl)borane was sublimed prior to use. $HN[P(i-Pr)_2]_2$ [15] and $LiN[P(i-Pr)_2]_2$ [16] were prepared according to literature procedures. Other reagents were obtained from commercial sources such as Aldrich, Acros or Alfa Aesar and used without further purification. NMR spectra were obtained on a Bruker Avance III 300 spectrometer. $^1H\{^{31}P\}$ and

$^{13}\text{C}\{^1\text{H}\}$ spectra were referenced to residual solvent downfield of TMS. $^{31}\text{P}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$, $^{19}\text{F}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ spectra were referenced to external 85% H_3PO_4 , $\text{BF}_3\cdot\text{Et}_2\text{O}$, C_6F_6 and SnEt_4 , respectively. Elemental analyses were performed by ALS Global (Tucson, AZ) or on a Perkin Elmer 2400 Series II CHNS/O Analyzer.

2.2 Synthesis of $\text{Cl}_2\text{Sn}\{\text{N}[\text{P}(\text{i-Pr})_2]_2\}_2$ (**1**)

SnCl_4 (0.26 g, 1.0 mmol) was dissolved in ca. 15 mL toluene, then solid $\text{LiN}[\text{P}(\text{i-Pr})_2]_2$ (0.51 g, 2.0 mmol) was added over several minutes. The yellow mixture was allowed to stir at rt for 2 hr before it was filtered to remove LiCl . The toluene was removed under vacuum to give a yellow powder **1**. Yield 0.32 g (47 %), m.p. = 141-145 °C. X-ray quality single crystals were grown from concentrated toluene solution at -25 °C $^1\text{H}\{^{31}\text{P}\}$ NMR (300 MHz, C_6D_6) δ 2.83 (sept, $^3J_{\text{HH}} = 7.2$ Hz, 4H, CH), 1.36 (d, $^3J_{\text{HH}} = 7.2$ Hz, 12H, CH_3), 1.32 (d, $^3J_{\text{HH}} = 7.2$ Hz, 12H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6) δ 30.5 (vm, CH), 18.1 (s, CH_3), 17.7 (s, CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6) δ 127.1 (s) ppm. $^{119}\text{Sn}\{^1\text{H}\}$ NMR was not obtained due to poor solubility in both C_6D_6 and THF- d_8 . Anal. Calcd for $\text{C}_{24}\text{H}_{56}\text{Cl}_2\text{N}_2\text{P}_4\text{Sn}$: C, 42.01; H, 8.23; N, 4.08. Found C, 42.07; H, 8.45; N, 3.88.

2.3 Synthesis of $\{\text{ClSnN}[\text{P}(\text{i-Pr})_2]_2\}_2$ (**2**)

SnCl_2 (0.28 g, 1.49 mmol) was dissolved in ca. 10 mL THF, then solid $\text{LiN}[\text{P}(\text{i-Pr})_2]_2$ (0.38 g, 1.49 mmol) was added over several minutes to give a golden yellow solution that was allowed to stir at rt for 10 min after the $\text{LiN}[\text{P}(\text{i-Pr})_2]_2$ addition was complete. The solvent was removed under vacuum and then ca. 5 mL toluene was added. The mixture was filtered to remove LiCl and then the toluene was removed under vacuum to give **2** as a red powder. Yield = 0.57 g (98%), m.p. = 134-135 °C. X-ray quality single crystals were grown from concentrated toluene solutions at -25 °C. $^1\text{H}\{^{31}\text{P}\}$ NMR (300 MHz, C_6D_6) δ 2.40 (sept, $^3J_{\text{HH}} = 7.2$ Hz, 8H,

CH), 1.28 (d, $^3J_{\text{HH}} = 7.2$ Hz, 24H, CH₃), 1.27 (d, $^3J_{\text{HH}} = 7.2$ Hz, 24H, CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C₆D₆) δ 30.0 (vt, CH), 18.7 (s, CH₃), 17.9 (s, CH₃) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C₆D₆) δ 117.1 (s) ppm. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (112 MHz, C₆D₆) δ 124.8 (t, $^1J_{\text{SnP}} = 885$ Hz) ppm. Anal. Calcd for C₂₄H₅₆Cl₂N₂P₄Sn₂: C, 35.81; H, 7.01; N, 3.48. Found: C, 35.53; H, 7.06; N, 3.38.

2.4 Synthesis of {GeN[P(*i*-Pr)₂]₂]₂ (3)

Bis(diisopropylphosphino)amine (1.0 g, 4.0 mmol) was dissolved in ca. 15 mL THF and *n*-butyllithium (5.0 mL, 8.0 mmol, 1.6 M in hexanes) was then added via syringe. The resulting white suspension was allowed to stir at rt for 30 min, and then GeCl₂•dioxane (0.93 g, 4.0 mmol) was added as a solid. The dark yellow solution was allowed to stir at rt for 3 h before volatiles were removed under vacuum. Pentane (5 mL) was added to the residue, which was then filtered to remove LiCl. The pentane solution was concentrated and cooled to -25 °C, leading to the formation of yellow rod-like crystals of **3**. Yield = 0.081 g (6 %), m.p. = 110-112 °C. $^1\text{H}\{^{31}\text{P}\}$ NMR (300 MHz, C₆D₆) δ 2.05 (sept, $^3J_{\text{HH}} = 7.2$ Hz, 4H, CH), 2.01 (sept, $^3J_{\text{HH}} = 7.2$ Hz, 4H, CH), 1.34 (d, $^3J_{\text{HH}} = 7.2$ Hz, 12H, CH₃), 1.31 (d, $^3J_{\text{HH}} = 7.2$ Hz, 12H, CH₃), 1.30 (d, $^3J_{\text{HH}} = 7.2$ Hz, 12H, CH₃), 1.25 (d, $^3J_{\text{HH}} = 7.2$ Hz, 12H, CH₃) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C₆D₆) δ 31.6 (vt, CH), 31.3 (vt, CH), 19.7 (s, CH₃), 19.5 (s, CH₃), 19.4 (s, CH₃), 19.2 (s, CH₃) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C₆D₆) δ 103.5 (s) ppm. Anal. Calcd for C₂₄H₅₆Ge₂N₂P₄: C, 44.91; H, 8.79; N, 4.36. Found: C, 44.50; H, 8.76; N, 4.21.

2.5 Synthesis of {SnN[P(*i*-Pr)₂]₂]₂ (4)

Bis(diisopropylphosphino)amine (1.0 g, 4.0 mmol) was dissolved in ca. 15 mL THF and *n*-butyllithium (5.0 mL, 8.0 mmol, 1.6 M in hexanes) was then added via syringe. The resulting white suspension was allowed to stir at rt for 5 min, and then SnCl₂ (0.76 g, 4.0 mmol) was

added as a solid. The amber-colored solution was allowed to stir at rt overnight before volatiles were removed under vacuum. Toluene (6 mL) was added to the residue, which was then filtered to remove LiCl. The toluene was removed under vacuum and the product was dissolved in ca. 5 mL pentane. Cooling to -25 °C led to the formation of yellow rod-like crystals of **4**. Yield = 0.52 g (35%), m.p. = 145-147 °C. $^1\text{H}\{^{31}\text{P}\}$ NMR (300 MHz, C_6D_6) δ 2.05 (sept, $^3J_{\text{HH}} = 7.2$ Hz, 4H, CH), 1.92 (sept, $^3J_{\text{HH}} = 7.2$ Hz, 4H, CH), 1.28 (d, $^3J_{\text{HH}} = 7.2$ Hz, 12H, CH_3), 1.26 (d, $^3J_{\text{HH}} = 7.2$ Hz, 24H, CH_3), 1.22 (d, $^3J_{\text{HH}} = 7.2$ Hz, 12H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6) δ 31.2 (vm, CH), 30.4 (vm, CH), 19.3 (s, CH_3), 19.1 (s, CH_3), 19.0 (s, CH_3), 18.7 (s, CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6) δ 98.3 (s) ppm. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (112 MHz, C_6D_6) δ -84.5 (tt, $^1J_{\text{SnP}} = 1959$ Hz, $^2J_{\text{SnP}} = 97$ Hz) ppm. Anal. Calcd for $\text{C}_{24}\text{H}_{56}\text{N}_2\text{P}_4\text{Sn}_2$: C, 39.27; H, 7.69; N, 3.82. Found: C, 38.89; H, 7.94; N, 3.73.

2.6 Synthesis of $(\text{C}_6\text{F}_5)_3\text{BO}(\text{CH}_2)_4\{\text{SnN}[\text{P}(\text{i-Pr})_2]_2\}_2$ (**5**)

$\text{B}(\text{C}_6\text{F}_5)_3$ (0.26 g, 0.5 mmol) was dissolved in ca. 3 mL THF and then **4** (0.37 g, 0.5 mmol) was added. The golden yellow solution was allowed to stir at rt for 20 min, and then the solvent was removed under vacuum to give **5** as a yellow powder. Yield = 0.57 g (92%), m.p. = 170 °C (dec). X-ray quality single crystals were grown from a concentrated Et_2O solution at -25 °C. $^1\text{H}\{^{31}\text{P}\}$ NMR (300 MHz, THF-d_8) δ 3.23 (br, 2H, OCH_2), 2.50 (sept, $^3J_{\text{HH}} = 7.2$ Hz, 2H, CH), 2.29 (sept, $^3J_{\text{HH}} = 7.2$ Hz, 2H, CH), 1.99-2.18 (overlapping, 8H, CH and CH_2), 1.62 (br, 2H, SnCH_2), 1.45 (d, $^3J_{\text{HH}} = 7.2$ Hz, 6H, CH_3), 1.41 (d, $^3J_{\text{HH}} = 7.2$ Hz, 6H, CH_3), 1.37 (d, $^3J_{\text{HH}} = 7.2$ Hz, 6H, CH_3), 1.32 (d, $^3J_{\text{HH}} = 7.2$ Hz, 6H, CH_3), 1.19 (d, $^3J_{\text{HH}} = 7.2$ Hz, 6H, CH_3), 1.18 (d, $^3J_{\text{HH}} = 7.2$ Hz, 6H, CH_3), 1.15 (d, $^3J_{\text{HH}} = 7.2$ Hz, 6H, CH_3), 1.10 (d, $^3J_{\text{HH}} = 7.2$ Hz, 6H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, THF-d_8) δ 149.2 (d, $^1J_{\text{CF}} = 240$ Hz, CF), 139.0 (d, $^1J_{\text{CF}} = 240$ Hz, CF), 137.4 (d, $^1J_{\text{CF}} = 240$ Hz, CF), 126.5 (br, BC), 63.5 (s, OC), 38.8 s, CH_2), 32.5-33.3 (overlapping

vm, CH), 30.6 (vt, CH), 22.8 (s, OC), 19.9 (s, CH₃), 19.8(s, CH₃), 19.0 (s, CH₃), 18.9 (s, CH₃), 18.6 (s, CH₃), 18.5 (s, CH₃), 18.3 (s, CH₃), 17.9 (s, CH₃), 16.3 (br, SnC) ppm. ³¹P{¹H} NMR (121 MHz, THF-d₈) δ 104.3 (d, ²J_{PP} = 60 Hz), 93.4 (d, ²J_{PP} = 60 Hz) ppm. ¹¹⁹Sn{¹H} NMR (112 MHz, THF-d₈) δ 326 (tt, ¹J_{SnP} = 1140 Hz, ²J_{SnP} = 122 Hz), -803 (tt, ¹J_{SnP} = 1790 Hz, ²J_{SnP} = 175 Hz) ppm. ¹¹B{¹H} (96 MHz, THF-d₈) δ -4.5 (s) ppm. ¹⁹F{¹H} (282 MHz, THF-d₈) δ -133.5 (d, ³J_{FF} = 20Hz, *o*-C₆F₅), -165.6 (t, ³J_{FF} = 20Hz, *p*-C₆F₅), -168.5 (br, *m*-C₆F₅) ppm. Anal. Calcd for C₄₆H₆₄BF₁₅N₂OP₄Sn₂: C, 41.92; H, 4.89; N, 2.13. Found: C, 41.93; H, 5.39, N, 2.16.

2.7 Synthesis of (C₆F₅)₂BF(C₆F₄)₄{SnN[P(*i*-Pr)₂]₂}₂ (**6**)

B(C₆F₅)₃ (0.26 g, 0.5 mmol) was dissolved in ca. 3 mL toluene and then **4** (0.37 g, 0.5 mmol) was added. The mixture was allowed to stir at rt for 20 min, during which time a yellow oil formed and separated from the toluene layer. The solvent was then removed under vacuum to give a waxy pale yellow solid. Yield = 0.45 g (72%), m.p. = >200 °C. X-ray quality single crystals were grown from a saturated Et₂O solution at -25 °C. ¹H{³¹P} NMR (300 MHz, THF-d₈) δ 2.34 (sept, ³J_{HH} = 7.2 Hz, 2H, CH), 2.30 (sept, ³J_{HH} = 7.2 Hz, 2H, CH), 2.25 (sept, ³J_{HH} = 7.2 Hz, 2H, CH), 2.03 (sept, ³J_{HH} = 7.2 Hz, 2H, CH), 1.49 (d, ³J_{HH} = 7.2 Hz, 6H, CH₃), 1.47 (d, ³J_{HH} = 7.2 Hz, 6H, CH₃), 1.32 (overlapping d, ³J_{HH} = 7.2 Hz, 12H, CH₃), 1.30 (d, ³J_{HH} = 7.2 Hz, 6H, CH₃), 1.25 (d, ³J_{HH} = 7.2 Hz, 6H, CH₃), 1.11 (d, ³J_{HH} = 7.2 Hz, 6H, CH₃), 0.89 (d, ³J_{HH} = 7.2 Hz, 6H, CH₃) ppm. ¹³C{¹H} NMR (75 MHz, THF-d₈) δ 150.0 (d, ¹J_{CF} = 240 Hz, CF), 149.2 (d, ¹J_{CF} = 240 Hz, CF), 147.3 (d, ¹J_{CF} = 240 Hz, CF), 139.5 (d, ¹J_{CF} = 240 Hz, CF), 137.5 (d, ¹J_{CF} = 240 Hz, CF), 129.5 (d, ¹J_{CF} = 57 Hz, CF), 126.2 (s), 114.5 (br t), 34.0 (vt, CH), 32.3 (br, CH), 31.2 (vt, CH), 20.0 (s, CH₃), 19.1(s, CH₃), 19.0 (s, CH₃), 18.9 (s, CH₃), 18.8 (s, CH₃), 18.2 (s, CH₃), 18.0 (s, CH₃), 17.7 (s, CH₃) ppm. ³¹P{¹H} NMR (121 MHz, THF-d₈) δ 107.0 (d, ²J_{PP} = 42 Hz), 97.2 (d, ²J_{PP} = 42 Hz) ppm. ¹¹⁹Sn {¹H} NMR (112 MHz, THF-d₈) δ 274 (t, ¹J_{SnP} = 1210 Hz),

-889 (t, $^1J_{\text{SnP}} = 1745$ Hz) ppm. $^{11}\text{B}\{^1\text{H}\}$ (96 MHz, THF- d_8) δ -0.1 ppm. $^{19}\text{F}\{^1\text{H}\}$ (282 MHz, THF- d_8) δ -118.8 (br s), -128.1 (br s), -131.8 (d, $^3J_{\text{FF}} = 44$ Hz), -132.0 (d, $^3J_{\text{FF}} = 22$ Hz), -134.8 (br), -135.1 (br), -163.7 (br), -164.2 (t, $^3J_{\text{FF}} = 22$ Hz), -167.9 (br), -168.5 (br) ppm. Anal. Calcd. for $\text{C}_{42}\text{H}_{56}\text{BF}_{15}\text{N}_2\text{P}_4\text{Sn}_2$: C, 40.49; H, 4.53; N, 2.25. Found: C, 40.49; H, 4.71; N, 2.12.

2.8 Synthesis of $(\text{C}_6\text{F}_5)_3\text{BO}(\text{CH}_2)_4\{\text{GeN}[\text{P}(\text{i-Pr})_2]_2\}_2$ (**7**)

$\text{B}(\text{C}_6\text{F}_5)_3$ (0.26 g, 0.5 mmol) was dissolved in ca. 3 mL THF and then **3** (0.32 g, 0.5 mmol) was added. The orange solution was allowed to stir at rt for 20 min, and then the solvent was removed under vacuum. The residue was dissolved in ca. 1 mL Et_2O and cooled to -25°C to give **7** as a yellow powder that was shown to be impure by NMR spectroscopy. Attempts at recrystallization from Et_2O did not yield X-ray quality single crystals or analytically pure product. Yield = 0.53 g (86%). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, THF- d_8) δ 101.0 (d, $^2J_{\text{PP}} = 48$ Hz), 86.2 (d, $^2J_{\text{PP}} = 48$ Hz) ppm. $^{11}\text{B}\{^1\text{H}\}$ (96 MHz, THF- d_8) δ -0.75 (s) ppm. $^{19}\text{F}\{^1\text{H}\}$ (282 MHz, THF- d_8) δ -133.5 (br, $o\text{-C}_6\text{F}_5$), -165.3 (t, $^3J_{\text{FF}} = 21$ Hz, $p\text{-C}_6\text{F}_5$), -168.3 (br, $m\text{-C}_6\text{F}_5$) ppm.

2.8 Synthesis of $(\text{C}_6\text{F}_5)_2\text{BF}(\text{C}_6\text{F}_4)_4\{\text{GeN}[\text{P}(\text{i-Pr})_2]_2\}_2$ (**8**)

$\text{B}(\text{C}_6\text{F}_5)_3$ (0.26 g, 0.5 mmol) was dissolved in ca. 3 mL toluene and then **3** (0.32 g, 0.5 mmol) was added. The mixture was allowed to stir at rt for 20 min, during which time a yellow oil formed and separated from the toluene layer. The solvent was then removed under vacuum to give **8** as a pale yellow solid that was shown to be impure by NMR spectroscopy. Attempts at recrystallization from Et_2O did not yield X-ray quality single crystals or analytically pure product. Yield = 0.54 g (92%). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, THF- d_8) δ 103.7 (d, $^2J_{\text{PP}} = 37$ Hz), 86.4 (d, $^2J_{\text{PP}} = 37$ Hz) ppm.

2.8 X-ray crystallography

Crystallographic data (Table 1) were collected on a Bruker Kappa APEXII CCD X-ray diffractometer using monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The single crystals **1-6** were coated in oil (Paratone-NTM) and mounted on MiTiGen MicroloopsTM. Bruker APEX2 software was used to collect and process the data [17]. The structures were solved by direct methods and were refined by full matrix least-squares method on F² with SHELX software [18]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed at calculated geometric positions with $U_{iso} = 1.2U_{equiv}$ of the parent atom ($U_{iso} = 1.5U_{equiv}$ for methyls). All crystallographic figures were prepared using DIAMOND 3.2k software [19]. Disordered Et₂O solvent in **6** was accounted for using SQUEEZE [20].

Table 1. Crystallographic data for compounds **1-6**, including both polymorphs of **4**.

	1	2	3	4	4	5	6
Empirical Formula	C ₂₄ H ₅₆ Cl ₂ N ₂ P ₄ Sn	C ₂₄ H ₅₆ Cl ₂ N ₂ P ₄ Sn ₂	C ₂₄ H ₅₆ Ge ₂ N ₂ P ₄	C ₂₄ H ₅₆ N ₂ P ₄ Sn ₂	C ₂₄ H ₅₆ N ₂ P ₄ Sn ₂	C ₄₆ H ₆₄ BF ₁₅ N ₂ OP ₄ Sn ₂	C ₄₆ H ₆₆ BF ₁₅ N ₂ OP ₄ Sn ₂
Formula weight	686.17	804.86	641.76	733.96	733.96	1318.06	1320.07
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Color	yellow	red	yellow	yellow	yellow	yellow	yellow
Crystal habit	block	block	rod	rod	rod	block	block
Crystal size (mm)	0.230 x 0.264 x 0.335	0.204 x 0.335 x 0.421	0.216 x 0.314 x 0.397	0.316 x 0.370 x 0.508	0.148 x 0.162 x 0.381	0.322 x 0.346 x 0.540	0.279 x 0.436 x 0.547
Crystal System	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic	triclinic	triclinic
Space Group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> -1
Unit cell dimensions							
<i>a</i> (Å)	12.1022(3)	10.4783(5)	18.7188(6)	8.3865(2)	11.5568(3)	12.6698(7)	12.5012(8)
<i>b</i> (Å)	15.0049(4)	16.0615(9)	8.2605(3)	11.5769	36.2084(8)	13.6229(7)	14.0587(9)
<i>c</i> (Å)	17.9158(4)	21.5280(12)	20.7072(7)	18.8336(5)	8.3873(2)	15.8321(8)	20.0207(12)
α (°)				74.3810(10)		84.325(2)	91.931(2)
β (°)		104.057(2)	91.2170(10)	86.2910(10)	110.1120(10)	82.592(2)	104.936(2)
γ (°)				70.0470(10)		89.589(2)	115.397(2)
<i>V</i> (Å ³)	3253.37(14)	3514.6(3)	3201.16(1)	1654.57(7)	3295.68(1)	2696.5(2)	3029.0(3)

	)		9)		4)		
Z	4	4	4	2	4	2	2
D_{calc} (g/cm ³)	1.401	1.521	1.332	1.473	1.479	1.623	1.447
μ (mm ⁻¹)	1.163	1.772	2.093	1.718	1.725	1.133	1.009
Measured reflections	30366	50742	49038	53893	38028	54522	62091
Independent reflections (R_{int})	8580 (0.0306)	10754 (0.0255)	11662 (0.0271)	9278 (0.0207)	9251 (0.0306)	15145 (0.0249)	12392 (0.0589)
Absorption correction ($T_{\text{max}}/T_{\text{min}}$)	Multi-scan (0.7760/0.6970)	Multi-scan (0.7140/0.5230)	Multi-scan (0.6610/0.4900)	Multi-scan (0.6130/0.4760)	Multi-scan (0.7840/0.5590)	Multi-scan (0.7120/0.5800)	Multi-scan (0.7660/0.6080)
R_1^a , wR_2^b (all data)	0.0248, 0.0448	0.0246, 0.0406	0.0353, 0.0562	0.0161, 0.0331	0.0300, 0.0455	0.0346, 0.0700	0.0772, 0.1471
R_1^a , wR_2^b [$I > 2\sigma(I)$]	0.0214, 0.0435	0.0191, 0.0389	0.0241, 0.0532	0.0143, 0.0325	0.0240, 0.0440	0.0269, 0.0663	0.0503, 0.1298

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; ^b R(\omega F^2) = \{ \sum [\omega(F_o^2 - F_c^2)^2] / \sum [\omega(F_o^2)^2] \}^{1/2}$$

3. Results and discussion

In his synthesis of the Pb_2^{2+} compound shown in Fig. 1, Ellermann reported oxidative scrambling of the $[\text{N}(\text{PPh}_2)_2]^-$ ligand [13]. We observed similar issues in our synthesis of the Sn_2^{2+} analog [21], as well as during CO_2 reactivity studies with other main group complexes utilizing that ligand [22]. In contrast, the closely related alkylated ligand $\{\text{N}[\text{P}(i\text{-Pr})_2]_2\}^-$ remained intact throughout the syntheses of the P,P-chelated complexes $\text{M}\{\text{N}[\text{P}(i\text{-Pr})_2]_2\}_2$ ($\text{M} = \text{Sn}$ [6], Zn [22b], InCl [16]) and the subsequent CO_2 activation of each, and so it became our ligand of choice for this study. The known Pb and Sn bicyclic complexes were prepared from the reaction of four equivalents of $\text{LiN}(\text{PPh}_2)_2$ with two equivalents of either PbCl_2 or SnCl_2 . We

Fig. 2. Structure of $\text{Cl}_2\text{Sn}\{\text{N}[\text{P}(\text{i-Pr})_2]_2\}_2$ **1**. Thermal ellipsoids are shown at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sn1-Cl1 2.5476(5), Sn1-Cl2 2.5505(6), Sn1-P1 2.6725(6), Sn1-P2 2.6812(7), Sn1-P3 2.6588(6), Sn1-P4 2.6902(7), N1-P1 1.617(2), N1-P2 1.625(2), N2-P3 1.619(2), N2-P4 1.620(2), P1-N1-P2 113.23(12), P3-N2-P4 114.54(12).

The yellow crystals **1** were found to be $\text{Cl}_2\text{Sn}\{\text{N}[\text{P}(\text{i-Pr})_2]_2\}_2$ (Fig. 2). This structure, while not desired, was not entirely unexpected as Karsch had reported isolating the related, formally oxidized complex $\text{Cl}_2\text{Ge}[\text{Me}_3\text{SiC}(\text{PMe}_2)_2]_2$ during his initial preparation of the formally reduced $\{\text{Ge}[\text{Me}_3\text{SiC}(\text{PMe}_2)_2]_2\}_2$ [9]. Compound **1** was subsequently independently prepared from the reaction of SnCl_4 with isolated $\text{LiN}[\text{P}(\text{i-Pr})_2]_2$ rather than the in situ generated reagent. That method allowed preparation of sufficient quantities of **1** for complete spectroscopic characterization. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a singlet at 127.1 ppm with doublet ^{117}Sn and ^{119}Sn satellites ($^1J_{\text{SnP}} = 425$ and 445 Hz). This matched the downfield signal that had been observed in the reactions that led to the mixtures of **1** and **2**. The regular ^1H NMR spectrum contained broad signals with chemical shifts in the regions associated with isopropyl groups, but it was not possible to resolve any coupling. A much clearer spectrum was obtained instead by

running a $^1\text{H}\{^{31}\text{P}\}$ NMR experiment instead. That spectrum consisted of a septet at 2.83 ppm and a pair of doublets at 1.36 and 1.32 ppm, consistent with the single isopropyl environment in the X-ray crystal structure.

Since the yellow crystals **1** were analogous to the oxidized Ge product reported by Karsch, we expected that the red crystals **2** would be the formally reduced Sn_2^{2+} species, particularly since the upfield $^{31}\text{P}\{^1\text{H}\}$ NMR signal in the spectra of the mixtures was a singlet with tin satellites at 117.1 ppm. Surprisingly, single crystal X-ray diffraction (Fig. 3) revealed a very different solid-state structure. Two different tin atoms were found in the asymmetric unit, each of which retained one chloride atom. Two bis(diisopropylphosphino)amido ligands were also present, one of which acts as a symmetrical P,P-bridge between the two tin atoms. The other ligand chelates through phosphorus to a single tin atom, leaving an open coordination site on the remaining tin. Examination of the packing diagram showed that each tin complex is associated with a neighboring dimer, thus forming a four-tin chain. The Sn1-Sn2 bond of 2.84672(16) Å is shorter than the mean Sn-Sn single bond length of 2.994 Å reported in the CSD [23] while the intermolecular $\text{Sn2}\cdots\text{Sn2}'$ of 3.429(5) Å is in the range of what is seen in tin clusters.

Fig. 3. Structure of **2** showing intermolecular $\text{Sn}\cdots\text{Sn}$ interaction. Thermal ellipsoids are shown at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and

1
2
3
4 angles (°): Sn1-Sn2 2.84672(16), Sn2...Sn2' 3.429(5), Sn1-Cl1 2.6184(4), Sn2-Cl2 2.4935(4),
5
6 Sn1-P1 2.6081(4), Sn1-P3 2.5905(4), Sn1-P4 2.8366(4), Sn2-P2 2.6668(4), N1-P1 1.5984(12),
7
8 N1-P2 1.6176(12), N2-P3 1.6136(12), N2-P4 1.6486(12), P1-N1-P2 132.85(8), P2-N3-P4
9
10 113.12(7).
11
12
13

14 In order to more fully explore the differences suggested by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum
15
16 between the apparent solution and solid-state structures of **2**, we developed a synthetic route
17
18 targeted to produce **2** in order to obtain enough analytically pure material for further
19
20 characterization. As with **1**, we found that **2** can be prepared cleanly in high yield by a slight
21
22 alteration of the original reaction conditions described above. If $\text{LiN}[\text{P}(i\text{-Pr})_2]_2$ is isolated rather
23
24 than being prepared in situ, and is then added slowly as a solid to a THF solution of SnCl_2 , only
25
26 **2** is formed. Multinuclear NMR studies confirmed that the unusual dimeric solid-state structure
27
28 of **2** is not retained in solution. The ^1H spectrum showed broad, featureless peaks but in the
29
30 $^1\text{H}\{^{31}\text{P}\}$ spectrum, the signals were readily resolved into a septet at 2.40 ppm and two doublets at
31
32 1.28 and 1.27 ppm. These were assigned, respectively, to the CH and CH_3 fragments of the
33
34 isopropyl groups. The corresponding signals in the $^{13}\text{C}\{^1\text{H}\}$ spectrum were at 30.0, 18.7 and 17.9
35
36 ppm, with the downfield CH signal appearing as a virtual triplet due to coupling with
37
38 phosphorus. Finally, the $^{31}\text{P}\{^1\text{H}\}$ spectrum displayed the above-mentioned single peak with tin
39
40 satellites at 117.1 ppm, while in the $^{119}\text{Sn}\{^1\text{H}\}$ spectrum a broad triplet at 124.8 with a $^{119}\text{Sn}\text{-}^{31}\text{P}$
41
42 coupling constant of 885 Hz was observed. This coupling pattern indicates that each tin is
43
44 coordinated to two phosphorus atoms. No substantial differences were noted between spectra
45
46 obtained in polar (THF) or non-polar (toluene or C_6D_6) solvents.
47
48
49
50
51
52
53
54

55 Based on the NMR evidence, several possibilities were considered for the solution-state
56
57 structure of **2**, three of which are shown in Scheme 2. Option **2a** is a monomeric Sn complex
58
59
60
61
62
63
64
65

with a chelating bis(diisopropylphosphino)amide ligand, while **2b** is a dimer of **2a** bridged through the chlorides. Finally, **2c** is a symmetric Sn₂ complex with bridging {N[P(*i*-Pr)₂]₂}⁻ ligands. The chelation in both **2a** and **2b** resembles what has been previously reported for Sn{N[P(*i*-Pr)₂]₂}₂ [6] and for **1**. Those molecules also showed one CH and two CH₃ signals in their ¹H and ¹³C{¹H} spectra, comparable to the solution spectrum of **2**. Before drawing firm conclusions, however, we decided that it would be helpful to have molecules resembling **2c** for comparison, namely the chloride-free complex analogous to the Fig. 1 compounds.

Scheme 2. Solid state and possible solution state structures of **2**.

Karsch [9] found that his Ge₂²⁺ compound could be obtained in high yields when excess Mg⁰ was added to the reaction mixture containing his lithiated ligand and GeCl₂•dioxane. In our hands, combining Mg⁰ with LiN[P(*i*-Pr)₂]₂ and either GeCl₂•dioxane or SnCl₂ did not lead to clean reactions. Instead, using a second equivalent of *n*-BuLi allowed complete removal of the chloride ligands and formation of {MN[P(*i*-Pr)₂]₂}₂ (M = Ge **3**; M = Sn **4**), albeit in lower than desired isolated yields (Scheme 3).

Scheme 3. Syntheses of M₂²⁺ complexes **3** (M = Ge) and **4** (M = Sn).

As with both **1** and **2**, the standard ^1H NMR spectra of **3** and **4** showed rather broad peaks that only became well-resolved upon decoupling of the ^{31}P nuclei. Each spectrum revealed two different isopropyl environments, as indicated by two septets and four doublets for the CH and CH_3 groups, respectively. This is in stark contrast to **2**, in which all eight isopropyl groups were equivalent, and suggests that the proposed structure **2c** is not present in solution. The $^{31}\text{P}\{^1\text{H}\}$ spectrum of the Ge_2^{2+} compound **3** displayed a singlet at 103.5 ppm. For the Sn_2^{2+} compound **4**, the signal was found at 98.3 ppm with ^{119}Sn and ^{117}Sn satellites. Both **3** and **4** were highly soluble in a variety of polar and non-polar solvents, allowing the preparation of a highly concentrated sample of **4** for $^{119}\text{Sn}\{^1\text{H}\}$ NMR. The spectrum (Fig. 4) is a triplet of triplets at -84.5 ppm, with ^{119}Sn - ^{31}P coupling constants of 1959 and 97 Hz. This coupling pattern is the same as that reported by Ellermann [13] for his Pb_2^{2+} compound (Fig. 1). This, along with the significant upfield shifts of the ^{31}P and ^{119}Sn signals relative to **2** are consistent with the loss of chloride and formation of the desired bicyclic structures.

Fig. 4. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **4**.

Confirmation of the structures of **3** and **4** was obtained by single crystal X-ray diffraction (Figs. 5 and 6, respectively). We note that two polymorphs of **4** were obtained – one that crystallized as monoclinic $\text{P}2_1/\text{c}$ and one that crystallized as triclinic $\text{P}-1$. For completeness, both

are included in the tables and supporting information, but only the monoclinic polymorph will be discussed as their bonding is very similar in both structures. In contrast to **2**, both **3** and **4** appear to retain their solid-state structure in solution. The tin-phosphorus coupling of 1959 Hz in **4** is assigned to the two directly bound P atoms, while the smaller 97 Hz coupling is due to interactions with the more distant phosphorus centers. For Sn1, these would be P1/P4 and P2/P3, respectively, with the opposite assignments for Sn2. The stereochemically-active lone pairs present on the Ge and Sn atoms fold the ligands back in butterfly-like fashion to the opposite face of the molecules, as illustrated by the P-M-P angles of 105.771(11) and 106.131(11)° for **3** and 101.005(15) and 103.110(15)° for **4**. These angles are wider than those reported for the related compounds (Fig. 1) by Karsch [96.1(1) and 96.9(1)°] [9], Ellermann [84.32(12) and 88.30(12)°] [13] or Kemp [91.77(4)°] [12], reflecting the greater steric hindrance of the isopropyl substituents relative to methyl or phenyl groups. This bent geometry is consistent with the two different isopropyl environments seen in the solution NMR spectra. Four isopropyl groups are on the same side of the molecule as the metal lone pairs, while the other four are opposite it. Since this difference was not seen in **2**, and since the splitting pattern and coupling constants in the $^{119}\text{Sn}\{^1\text{H}\}$ NMR are very different between **2** and **4**, this suggests that the proposed structure **2c** is not present in solution.

Fig. 5. Structure of **3**. Thermal ellipsoids are shown at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1-Ge2 2.54929(17), Ge1-P1 2.4379(3), Ge1-P4 2.4083(3), Ge2-P2 2.4002(3), Ge2-P3 2.4487(3), N1-P1 1.6236(9), N1-P2 1.6229(10), N2-P3 1.6250(9), N2-P4 1.6151(10), P1-N1-P2 121.80(6), P3-N2-P4 122.46(6), P1-Ge1-P4 105.771(11), P2-Ge2-P3 106.131(11).

Fig. 6. Structure of **4**. Thermal ellipsoids are shown at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sn1-Sn2 2.89536(18), Sn1-P1 2.6457(5), Sn1-P4 2.6214(5), Sn2-P2 2.6431(5), Sn2-P3 2.6607(5), N1-P1 1.6174(16), N1-P2 1.6241(16), N2-P3 1.6206(16), N2-P4 1.6210(15), P1-N1-P2 124.91(10), P3-N2-P4 125.26(10), P1-Sn1-P4 101.005(15), P2-Sn2-P3 103.110(15).

Given the prominent lone pairs on **3** and **4**, we were eager to explore their chemistry as Lewis bases. Previously, we have shown that the Sn atom in the P,P-chelated complex $\text{Sn}\{\text{N}[\text{P}(i\text{-Pr})_2]_2\}_2$ behaves as a Lewis *acid* in the reaction with CO_2 [6]. The driving force in that reaction and in the related Zn [22b] and In [16] complexes is likely due at least in part to the release of strain energy in the four-membered MP_2N rings upon insertion of CO_2 into the metal-phosphorus bonds to give more stable six-membered rings. Since no such strain is present in the five-membered $\text{M}_2\text{P}_2\text{N}$ rings of **3** and **4**, reactivity at the Ge-P or Sn-P bonds seemed unlikely, and we hoped to obtain coordination between the Sn lone pair and the electrophilic CO_2 carbon.

Solutions of **4** in both polar and non-polar solvents were prepared, and exposed to CO₂ at atmospheric pressure for up to 1 hour. There were no changes in color or solubility, and no absorbances in regions of the IR spectrum associated with CO₂-related products were observed. As well, the ³¹P{¹H} NMR spectra indicated only starting material present after reaction. While carbenes have been shown to form unsupported adducts with CO₂ (vide supra), other Lewis bases such as phosphines typically do not, so the lack of reactivity of **4** was not entirely unexpected. Phosphines are able to capture CO₂ when paired with a Lewis acid as part of a frustrated Lewis pair (FLP) [24].

One of the most popular Lewis acids in FLP chemistry is tris(pentafluorophenyl)borane B(C₆F₅)₃ and we have previously used this acid to activate CO₂ in combination with HN[(*i*-Pr)₂P]₂ [4b], so it became our choice for this study as well. As it was unclear whether one, both or neither Sn lone pair would interact with the borane, we performed the initial screening reactions with both 1:1 and 1:2 ratios of **4** to B(C₆F₅)₃. In each case, when combined in THF an immediate color change was observed, suggesting that the pair were reactive and there was some sort of acid-base adduct forming between the B and the Sn atoms. Later analyses (vide infra) showed that only one borane was participating, so a 1:1 ratio was used in all subsequent preparations (Scheme 4).

Scheme 4. THF ring-opening and C-F bond activation by **3** and **4**.

After a 20 minute reaction time, the solvent was removed under vacuum to give **5** as a bright yellow powder. At first glance, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** appeared to consist of two doublets at 104.3 and 93.4 ppm, with coupling constant of 60 Hz. Upon closer examination, it was apparent that the spectrum was instead a complex AA'BB' pattern. The $^{119}\text{Sn}\{^1\text{H}\}$ spectrum revealed two distinct triplet of triplets at 326 (tt, $^1J_{\text{SnP}} = 1140$ Hz, $^2J_{\text{SnP}} = 122$ Hz) and -803 (tt, $^1J_{\text{SnP}} = 1790$ Hz, $^2J_{\text{SnP}} = 175$ Hz) ppm. Taken together, these two spectra indicated that the bicyclic core was still intact and suggested one of the two tin atoms had formed an adduct with the borane. The sharp $^{11}\text{B}\{^1\text{H}\}$ signal indicative of four-coordinate boron at -4.5 ppm seemed to confirm this assumption, but when the $^1\text{H}\{^{31}\text{P}\}$ and $^{13}\text{C}\{^1\text{H}\}$ spectra were examined, it became clear that something else had happened.

In addition to four methine septets and eight methyl doublets (twice as many as were present in **4** and consistent with the reduced symmetry noted in the $^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ spectra), there were four additional peaks between 3.23 and 1.62 ppm integrating to two H atoms each. Because these unidentified peaks were too broad to resolve any coupling that might be present to help with their assignment, we turned to X-ray crystallography to determine the true identity of **5**.

Fig. 7. Structure of **5**. Thermal ellipsoids are shown at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sn1-Sn2 2.8166(2), Sn1-P1 2.5769(5), Sn1-P4 2.5883(5), Sn2-P2 2.6811(5), Sn2-P3 2.6604(5), N1-P1 1.5976(17), N1-P2 1.6206(17), N2-P3 1.6161(17), N2-P4 1.5976(16), B1-O1 1.459(2), C46-Sn1 2.1605(18), P1-N1-P2 131.24(11), P3-N2-P4 130.24(11), P1-Sn1-P4 117.317(16), P2-Sn2-P3 107.655(16).

Single crystals of **5** were grown from a concentrated diethyl ether solution (Fig. 7). The structure revealed that rather than there being a direct Sn-B interaction as we had presumed, there was instead a ring-opened THF molecule between the borane and the Sn₂²⁺ complex. The oxygen is bound to the B while a CH₂ is attached to Sn1. Since **4** was prepared in THF, and THF is known to form adducts with B(C₆F₅)₃ and other boranes, it was clear that the presence of both components is necessary for the ring-opening to occur to form **5**. Recent examples of Lewis bases that have been paired with THF-adducts of B(C₆F₅)₃ and related boron compounds include imides [25], pyridines [26], phosphines [27], phosphoniums [28] and carbenes [29].

Because **4** and B(C₆F₅)₃ did not react directly with one another, but instead with THF solvent, we next tested whether they would coordinate or exhibit the desired “frustrated” behavior in a non-polar solvent such as toluene (Scheme 4). As in the THF reaction that led to **5**, there was a rapid color change in the toluene reaction. In this case, there was also a phase separation, with the product forming an oily layer below the toluene solvent. After work-up **6** was isolated as a pale yellow powder. Qualitatively, little was different in the ³¹P{¹H}, ¹¹⁹Sn{¹H}, and ¹¹B{¹H} spectra of **6** compared to **5**, other than slight difference in the chemical shifts and the fact that the ¹¹⁹Sn{¹H} signals were too broad to resolve the smaller Sn-P coupling. The ¹H{³¹P} spectrum of **6** lacked the signals that had been assigned to the ring-opened THF in **5** but was otherwise also quite similar. It was the ¹³C{¹H} spectrum that again revealed a more

1
2
3
4 complicated reaction than simple adduct formation had occurred. Two sets of signals were
5
6 observed in the aromatic region, indicating that one perfluoroaryl ring was different from the
7
8 other two.
9

10
11 As with **5**, single crystal X-ray diffraction was used to determine the exact nature of **6**.
12
13 Suitable crystals were grown from diethyl ether and showed that one of the C₆F₅ rings had
14
15 undergone a *para*-substitution reaction with one of the Sn atoms with the displaced F atom
16
17 ending up on the B. Similar aromatic substitution reactions have been previously been reported
18
19 by Stephan [27b, 30] and others [8a, 29c, 31] primarily in the context of frustrated Lewis pairs,
20
21 and it has been shown that the more sterically-hindered the pair, the more rapid the attack at the
22
23 *para*-F. As our reaction is complete in less than 20 minutes at room temperature, this suggests
24
25 that B(C₆F₅)₃ and **4** do constitute a frustrated Lewis pair.
26
27
28
29
30

31
32
33
34
35
36
37
38
39
40
41
42
43
44
45 Fig. 8. Structure of **5**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms and co-
46
47 crystallized Et₂O solvent are omitted for clarity. Selected bond lengths (Å) and angles (°): Sn1-
48
49 Sn2 2.7956(5), Sn1-P1 2.5616(14), Sn1-P4 2.5761(13), Sn2-P2 2.6609(13), Sn2-P3 2.6347(14),
50
51 N1-P1 1.597(4), N1-P2 1.627(4), N2-P3 1.620(4), N2-P4 1.587(5), B1-F13 1.458(6), C40-Sn1
52
53 2.144(4), P1-N1-P2 129.9(3), P3-N2-P4 132.3(3), P1-Sn1-P4 116.32(4), P2-Sn2-P3 102.10(4).
54
55
56
57

58 Finally, the analogous B(C₆F₅)₃ reactions were performed with the germanium complex **3**
59
60 (Scheme 4). The ³¹P NMR spectra of the products **7** and **8** each consisted of a complex AA'BB'
61
62
63
64
65

1
2
3
4 pattern that grossly resembled a pair of doublets. This is essentially identical to the patterns
5
6 obtained for the Sn-containing products **5** and **6**, suggesting that the same THF-ring opening
7
8 (**5/7**) and F-atom abstraction (**6/8**) occurred. Unfortunately, neither reaction produced
9
10 analytically pure material, and we were unable to obtain X-ray quality single crystals for
11
12 structural conformation.
13
14

15 16 **4. Summary**

17
18 We have found that upon deprotonation, bis(diisopropylphosphino)amine is able to bind
19
20 low-valent germanium and tin to produce several novel compounds with E-E bonds that show
21
22 promising reactivity as Lewis bases. Specifically, the bicyclic P, P-bridged M_2^{2+} compounds
23
24 $\{GeN[P(i-Pr)_2]_2\}_2$ **3** and $\{SnN[P(i-Pr)_2]_2\}_2$ **4** participate in THF-ring opening and aromatic
25
26 substitution reactions when paired with tris(pentafluorophenyl)borane $B(C_6F_5)_3$. The bicyclic
27
28 core structure was maintained throughout, with only one metal atom participating in the ring-
29
30 opening and substitution reactions. We hope to exploit the lone pair of the second metal atom in
31
32 future reactions.
33
34
35
36
37

38 39 **Appendix A. Supplementary Material**

40
41 CCDC 1427440-1427446 contain the supplementary crystallographic data for complexes
42
43 **1-6**. These data can be obtained free of charge via
44
45 <http://www.ccdc.cam.ac.uk/conts/retrieving/html>, or from the Cambridge Crystallographic Data
46
47 Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail:
48
49 deposit@ccdc.cam.ac.uk.
50
51
52

53 54 **Acknowledgements**

55
56 This work was financially supported by the National Science Foundation (Grant CHE12-
57
58 13529). The Bruker X-ray diffractometer was purchased via a National Science Foundation
59
60
61
62
63
64
65

CRIF:MU award to the University of New Mexico (CHE04-43580), and the NMR spectrometers were upgraded via grants from the NSF (CHE08-40523 and CHE09-46690). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000. Prof. Roger Cramer (University of Hawaii) provided helpful discussions about the polymorphs of **4**. Mr. Jeremiah Sears (Sandia National Laboratories) performed the elemental analyses of compounds **1** and **6**.

References

- [1] Y. Mizuhata, T. Sasamori, N. Tokitoh, *Chem. Rev.*, 109 (2009) 3479-3511.
- [2] J. Baumgartner, C. Marschner, *Rev. Inorg. Chem.*, 34 (2014) 119-152.
- [3] (a) S. Yao, Y. Xiong, M. Driess, *Organometallics*, 30 (2011) 1748-1767; (b) P.P. Power, *Chemical Record*, 12 (2012) 238-255; (c) Z.D. Brown, P.P. Power, *Inorg. Chem.*, 52 (2013) 6248-6259.
- [4] (a) G.I. McGrew, P.A. Khatri, W.E. Geiger, R.A. Kemp, R. Waterman, *Chem. Commun.*, 51 (2015) 15804-15807; (b) B.M. Barry, D.A. Dickie, L.J. Murphy, J. Clyburne, R.A. Kemp, *Inorg. Chem.*, 52 (2013) 8312-8314; (c) L.J. Murphy, K.N. Robertson, R.A. Kemp, H.M. Tuononen, J.A.C. Clyburne, *Chem. Commun.*, 51 (2015) 3942-3956; (d) C.A. Stewart, D.A. Dickie, R.A. Kemp, *Inorg. Chim. Acta*, 392 (2012) 268-276; (e) L.A.M. Steele, T.J. Boyle, R.A. Kemp, C. Moore, *Polyhedron*, 42 (2012) 258-264; (f) A.M. Felix, B.J. Boro, D.A. Dickie, Y. Tang, J.A. Saria, B. Moasser, C.A. Stewart, B.J. Frost, R.A. Kemp, *Main Group Chem.*, 11 (2012) 13-29; (g) C.A. Stewart, D.A. Dickie, B. Moasser, R.A. Kemp, *Polyhedron*, 32 (2012) 14-23; (h) D.A. Dickie, K.B. Gislason, R.A. Kemp, *Inorg. Chem.*, 51 (2012) 1162-1169; (i) Y. Tang, A.M. Felix, V.W. Manner, L.N. Zakharov, A.L. Rheingold, B. Moasser, R.A. Kemp, *ACS Symp. Ser.*, 917 (2006) 410-421; (j) Y. Tang, W.S. Kassel, L.N. Zakharov, A.L. Rheingold, R.A. Kemp, *Inorg. Chem.*, 44 (2005) 359-364; (k) Y. Tang, A.M. Felix, B.J. Boro, L.N. Zakharov, A.L. Rheingold, R.A. Kemp, *Polyhedron*, 24 (2005) 1093-1100; (l) Y. Tang, L.N. Zakharov, A.L. Rheingold, R.A. Kemp, *Organometallics*, 23 (2004) 4788-4791.
- [5] (a) C.A. Stewart, D.A. Dickie, Y. Tang, R.A. Kemp, *Inorg. Chim. Acta*, 376 (2011) 73-79; (b) C.A. Stewart, D.A. Dickie, M.V. Parkes, J.A. Saria, R.A. Kemp, *Inorg. Chem.*, 49 (2010) 11133-11141.
- [6] D.A. Dickie, E.N. Coker, R.A. Kemp, *Inorg. Chem.*, 50 (2011) 11288-11290.
- [7] (a) L.R. Sita, J.R. Babcock, R. Xi, *J. Am. Chem. Soc.*, 118 (1996) 10912-10913; (b) L.A.-M. Harris, M.P. Coles, J.R. Fulton, *Inorg. Chim. Acta*, 369 (2011) 97-102.
- [8] (a) E. Theuergarten, T. Bannenberg, M.D. Walter, D. Holschumacher, M. Freytag, C.G. Daniliuc, P.G. Jones, M. Tamm, *Dalton Trans.*, 43 (2014) 1651-1662; (b) A. Winkler, M. Freytag, P.G. Jones, M. Tamm, *J. Organomet. Chem.*, 775 (2015) 164-168; (c) N. Kuhn, M. Steimann, G. Weyers, *Z. Naturforsch., B: Chem. Sci.*, 54b (1999) 427-433; (d) Z.

- Kelemen, B. Péter-Szabó, E. Székely, O. Hollóczki, D.S. Firaha, B. Kirchner, J. Nagy, L. Nyulászi, *Chem. Eur. J.*, 20 (2014) 13002-13008.
- [9] H.H. Karsch, B. Deubelly, J. Riede, G. Müller, *Angew. Chem. Int. Ed.*, 26 (1987) 673-674.
- [10] H. Kobayashi, T. Iwamoto, M. Kira, *J. Am. Chem. Soc.*, 127 (2005) 15376-15377.
- [11] J. Hlina, J. Baumgartner, C. Marschner, L. Albers, T. Müller, V.V. Jouikov, *Chem. Eur. J.*, 20 (2014) 9357-9366.
- [12] R.A. Kemp, D.A. Dickie, A.M. Felix, CCDC 661038: Private communication to the Cambridge Structural Database (2007), DOI: 10.5517/ccq5vtj.
- [13] A. Winkler, W. Bauer, F.W. Heinemann, V. Garcia-Montalvo, M. Moll, J. Ellermann, *Eur. J. Inorg. Chem.*, (1998) 437-444.
- [14] K.M. Marzec, B. Gawel, K.K. Zborowski, W. Lasocha, L.M. Proniewicz, K. Malek, *Inorg. Chim. Acta*, 376 (2011) 581-589.
- [15] J.S. Ritch, T. Chivers, K. Ahmad, M. Afzaal, P. O'Brien, *Inorg. Chem.*, 49 (2010) 1198-1205.
- [16] D.A. Dickie, M.T. Barker, M.A. Land, K.E. Hughes, J.A.C. Clyburne, R.A. Kemp, *Inorg. Chem.*, 54 (2015) 11121-11126.
- [17] Bruker AXS, Inc., Madison, Wisconsin, USA (2012).
- [18] G.M. Sheldrick, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 71 (2015) 3-8.
- [19] Crystal Impact GbR, Bonn, Germany (1999).
- [20] A.L. Spek, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 71 (2015) 9-18.
- [21] A.M. Felix, Ph.D. Dissertation, Department of Chemistry and Chemical Biology, University of New Mexico (2007).
- [22] (a) D.A. Dickie, M.V. Parkes, R.A. Kemp, *Angew. Chem. Int. Ed.*, 47 (2008) 9955-9957; (b) D.A. Dickie, R.A. Kemp, *Organometallics*, 33 (2014) 6511-6518; (c) D.A. Dickie, R.A. Kemp, *Acta Crystallogr. Sect. E: Struct. Rep. Online*, E64 (2008) o1449.
- [23] C.R. Groom, F.H. Allen, *Angew. Chem. Int. Ed.*, 53 (2014) 662-671.
- [24] D.W. Stephan, G. Erker, *Angew. Chem. Int. Ed.*, 54 (2015) 6400-6441.
- [25] T. Chivers, G. Schatte, *Eur. J. Inorg. Chem.*, 2003 (2003) 3314-3317.
- [26] S.J. Geier, D.W. Stephan, *J. Am. Chem. Soc.*, 131 (2009) 3476-3477.
- [27] (a) M.J. Sgro, J. Dömer, D.W. Stephan, *Chem. Commun.*, 48 (2012) 7253-7255; (b) G.C. Welch, R. Prieto, M.A. Dureen, A.J. Lough, O.A. Labeodan, T. Höltrichter-Rossmann, D.W. Stephan, *Dalton Trans.*, (2009) 1559-1570; (c) G.C. Welch, J.D. Masuda, D.W. Stephan, *Inorg. Chem.*, 45 (2006) 478-480; (d) B. Birkmann, T. Voss, S.J. Geier, M. Ullrich, G. Kehr, G. Erker, D.W. Stephan, *Organometallics*, 29 (2010) 5310-5319.
- [28] X. Zhao, A.J. Lough, D.W. Stephan, *Chem. Eur. J.*, 17 (2011) 6731-6743.
- [29] (a) D. Holschumacher, T. Bannenberg, C.G. Hrib, P.G. Jones, M. Tamm, *Angew. Chem. Int. Ed.*, 47 (2008) 7428-7432; (b) D. Holschumacher, C. Taouss, T. Bannenberg, C.G. Hrib, C.G. Daniliuc, P.G. Jones, M. Tamm, *Dalton Trans.*, (2009) 6927-6929; (c) M. Alcarazo, C. Gomez, S. Holle, R. Goddard, *Angew. Chem. Int. Ed.*, 49 (2010) 5788-5791.
- [30] (a) S.J. Geier, M.A. Dureen, E.Y. Ouyang, D.W. Stephan, *Chem. Eur. J.*, 16 (2010) 988-993; (b) G.C. Welch, L. Cabrera, P.A. Chase, E. Hollink, J.D. Masuda, P. Wei, D.W. Stephan, *Dalton Trans.*, (2007) 3407-3414; (c) G.C. Welch, T. Höltrichter-Rößmann, D.W. Stephan, *Inorg. Chem.*, 47 (2008) 1904-1906; (d) S.L. Granville, G.C. Welch, D.W. Stephan, *Inorg. Chem.*, 51 (2012) 4711-4721.

1
2
3
4 [31] (a) P. Cui, C.C. Comanescu, V.M. Iluc, Chem. Commun., 51 (2015) 6206-6209; (b) A.J.
5 Marwitz, J.L. Dutton, L.G. Mercier, W.E. Piers, J. Am. Chem. Soc., 133 (2011) 10026-
6 10029; (c) S. Döring, G. Erker, R. Fröhlich, O. Meyer, K. Bergander, Organometallics,
7 17 (1998) 2183-2187.
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

For Graphical Entry Use Only

Synopsis:

The bicyclic compounds $\{MN[P(i\text{-Pr})_2]_2\}_2$ ($M = \text{Sn, Ge}$) contain Sn_2^{2+} or Ge_2^{2+} units bridged by phosphorus. With $\text{B}(\text{C}_6\text{F}_5)_3$, the Lewis basic Sn_2^{2+} complex participates in THF ring-opening or *para*-F atom activation. These complexes, as well as $\text{Cl}_2\text{Sn}\{N[P(i\text{-Pr})_2]_2\}_2$ and $\{\text{ClSnN}[P(i\text{-Pr})_2]_2\}_2$ were characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction.