1000 *Inorg. Chem.* **2001,** *40,* 1000−1005

Azido Derivatives of Germanium(II) and Tin(II): Syntheses and Characterization of $[(Mes)_2DAP]GeN_3$, $[(Mes)_2DAP]SnN_3$, and the Corresponding Chloro Analogues Featuring Heterocyclic Six-π-Electron Ring Systems (where $[(Mes)_2DAP] = \{N(Mes)C(Me)\}_2CH$)

Ashley E. Ayers,[†] Thomas M. Klapötke,[‡] and H. V. Rasika Dias*,[†,§]

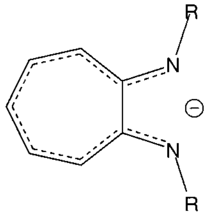
Department of Chemistry and Biochemistry, The University of Texas at Arlington,
Arlington, Texas 76019-0065, Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka, and
Department of Chemistry, Ludwig-Maximilians University of Munich, Butenandtstrasse 5-13 (Haus D),
D-81377 Munich, Germany

Received September 25, 2000

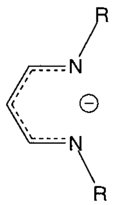
Chloro and azido germanium(II) and tin(II) 1,5-diazapentadienyl complexes have been investigated. The treatment of $GeCl_2\cdot(1,4\text{-dioxane})$ or $SnCl_2$ with $[(Mes)_2DAP]Li$ in a 1:1 molar ratio gave the corresponding germanium(II) or tin(II) chloro complexes $[(Mes)_2DAP]MCl$ (where $[(Mes)_2DAP]$ = 2,4-dimethyl-*N,N′*-bis(2,4,6-trimethylphenyl)-1,5-diazapentadienyl; M = Ge or Sn). $[(Mes)_2DAP]GeCl$ and $[(Mes)_2DAP]SnCl$ are monomeric in the solid state. The C_3N_2M rings adopt a flattened boat conformation. The metathesis reaction between $[(Mes)_2DAP]MCl$ and sodium azide affords the azido compounds $[(Mes)_2DAP]MN_3$ in excellent yield. X-ray analysis revealed that $[(Mes)_2DAP]GeN_3$ features an essentially linear azide moiety and a nearly planar heterocyclic C_3N_2Ge ring system. The azide group occupies a site above the C_3N_2Ge ring. The solid-state structure of the tin azide $[(Mes)_2DAP]SnN_3$ shows weak intermolecular Sn···N contacts. It features a linear azide moiety and a planar heterocyclic C_3N_2Sn ring system. Both azides have long (M)N−N(N) bonds and short (MN)N−N bonds. IR spectra of $[(Mes)_2DAP]GeN_3$ and $[(Mes)_2DAP]SnN_3$ display $\nu_{asym}(N_3)$ bands at 2062 and 2060 cm^{-1}, respectively. ^{14}N NMR spectroscopic data show three well-separated signals for the nitrogen atoms of the azide moieties. Structural and spectroscopic data suggest the presence of very similar azide groups in the Ge(II) and Sn(II) adducts. The dominant canonical form of the metal−azide moiety is M−N−N≡N.

Introduction

There is considerable current interest in both theoretical and practical aspects of covalent azides. Azido derivatives of carbon represent the most widely studied group of compounds among this family.[1,2] Related azides of heavier group 14 members such as those of silicon(IV) and tin(IV) are also fairly well known.[3−5] For example, the chemistry of trimethylsilyl and trimethylstannyl azides has been investigated extensively.[4,6,7] In contrast, very little is known about the azides of low-valent group 14 elements.[4,5,8] One of the difficulties in isolating such species is their tendency to decompose with the elimination of nitrogen, leading to high-valent group 14 compounds. Apart from $Pb(N_3)_2$ (a well-known primary explosive),[4,9−11] the recently reported $[HB(3,5\text{-}(CH_3)_2Pz)_3]GeN_3$,[5] $[(C_5H_5)Co\{P(O)(OEt)_2\}_3]GeN_3$,[12] and the aminotroponiminatogermanium(II) and tin(II) complexes $[(n\text{-}Pr)_2ATI]GeN_3$ and $[(n\text{-}Pr)_2ATI]SnN_3$ [8] are the only well-characterized compounds of this type in the literature to our knowledge.



Aminotroponiminato Ligand System



Diazapentadienyl Ligand System

The scarcity of information on azides of low-valent group 14 elements prompted us to explore this area in more detail. Recently, we demonstrated the successful utility of the aminotroponiminato ligand system,[13−17] which features a delocalized

---

[†] The University of Texas at Arlington.

[‡] Ludwig-Maximilians University of Munich.

[§] Institute of Fundamental Studies.

(1) *The Chemistry of the Azido Group*; Patai, S., Ed.; Interscience: New York, 1971.

(2) *Azides and Nitrenes: Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic: New York, 1984.

(3) Thayer, J. S. *Organometal. Chem. Rev.* **1966**, *1*, 157.

(4) Tornieporth-Oetting, I. C.; Klapötke, T. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 511.

(5) Filippou, A. C.; Portius, P.; Kociok-Köhn, G. *Chem. Commun.* **1998**, 2327, and references therein.

(6) Banister, A. J.; Hauptman, Z. V.; Passmore, J.; Wong, C.-M.; White, P. S. *J. Chem. Soc., Dalton Trans.* **1986**, 2371.

(7) Kricheldorf, H. R.; Schwarz, G.; Kaschig, J. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 550.

(8) Ayers, A. E.; Marynick, D. S.; Dias, H. V. R. *Inorg. Chem.* **2000**, *39*, 4147.

(9) *The Merck Index*, 11th ed.; Budavari, S., Ed.; Merck & Co., Inc.: New Jersey, 1989; p 5274, and references therein.

(10) Choi, C. S.; Prince, E.; Garrett, W. L. *Acta Crystallogr.* **1977**, *B33*, 3536.

(11) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworth-Heinemann: Woburn, MA, 1998; p 417.

(12) Filippou, A. C.; Portius, P.; Kociok-Köhn, G.; Albrecht, V. *J. Chem. Soc., Dalton Trans.* **2000**, 1759.

(13) Dias, H. V. R.; Jin, W.; Ratcliff, R. E. *Inorg. Chem.* **1995**, *34*, 6100.

(14) Dias, H. V. R.; Wang, Z.; Jin, W. *Coord. Chem. Rev.* **1998**, *176*, 67.

(15) Dias, H. V. R.; Wang, Z. *J. Am. Chem. Soc.* **1997**, *119*, 4650.

(16) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, *35*, 6546.

10.1021/ic001078j CCC: $20.00

10-π-electron ligand backbone, to stabilize germanium(II) and tin(II) azido derivatives.[8] Spectroscopic data and theoretical work indicated that Ge(II) and Sn(II) have essentially the same effect on the azide group. In this paper, we describe the use of the diazapentadienyl (also known as β-diketiniminato, β-diimine, or β-iminoamine) ligand system,[18−22] which features a delocalized six-π-electron ligand backbone, to obtain thermally stable covalent azides of Ge(II) and Sn(II).[14] Syntheses and characterization of [(Mes)$_2$DAP]MN$_3$ (where [(Mes)$_2$DAP] = 2,4-dimethyl-*N*,*N′*-bis(2,4,6-trimethylphenyl)-1,5-diazapentadienyl; M = Ge or Sn) as well as the corresponding chloro analogues [(Mes)$_2$DAP]MCl are reported.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen either using standard Schlenk techniques or in a Vacuum Atmospheres single station drybox equipped with a −25 °C refrigerator. Solvents were purchased from commercial sources and distilled from conventional drying agents prior to use. Glassware was oven-dried at 150 °C overnight. The NMR spectra were recorded at room temperature on a JEOL Eclipse 500 (^{1}H, 500.16 MHz; ^{13}C, 125.78 MHz) or JEOL Eclipse 400 spectrometer (^{119}Sn, 149.08 MHz; ^{14}N, 28.89 MHz). Proton and carbon chemical shifts are reported in parts per million vs Me$_4$Si. ^{119}Sn and ^{14}N NMR chemical shifts were referenced relative to external Me$_4$Sn and MeNO$_2$, respectively. Infrared spectra were recorded on a JASCO FT-IR 410 spectrometer. Raman spectra were recorded using the solid samples on a Perkin-Elmer 2000 NIR FT-Raman spectrometer with 100 mW laser power (1064 nm, 90°, 25 °C). Melting points were obtained on a Mel-Temp II apparatus. Elemental analyses were performed at the University of Texas at Arlington using a Perkin-Elmer Model 2400 CHN analyzer. [(Mes)$_2$DAP]H[23] and GeCl$_2$·(1,4-dioxane)[24] were synthesized as reported previously. *n*-BuLi, SnCl$_2$, and NaN$_3$ were purchased from commercial sources and used as received.

Caution: Covalent and ionic azides are very toxic, and covalent azides are potentially explosive. Appropriate safety precautions should be taken.

[(Mes)$_2$DAP]GeCl. A diethyl ether solution (25 mL) of [(Mes)$_2$DAP]H (700 mg, 2.09 mmol) was treated with *n*-BuLi (1.31 mL, 1.6 M hexane solution) at −78 °C. The colorless solution was stirred for 0.5 h, warmed to room temperature, and stirred an additional 0.5 h. This solution was then slowly added to a suspension of GeCl$_2$·(1,4-dioxane) (650 mg, 2.09 mmol) in diethyl ether (15 mL) at −78 °C. The mixture slowly turned cloudy yellow. The low temperature was kept for a further 1 h, then it was allowed to warm to room temperature and stirred overnight. After overnight stirring all volatiles were removed under vacuum. The remaining solid was extracted into toluene and filtered through Celite. The toluene was removed under vacuum to yield [(Mes)$_2$DAP]GeCl as a pale yellow solid (610 mg, 66%). It was recrystallized from toluene at room temperature. Mp: 171−174 °C. ^{1}H NMR (CDCl$_3$): δ 1.85 (s, 6H, DAP−CH$_3$), 2.12 (s, 6H, *o*-CH$_3$), 2.27 (s, 6H, *p*-CH$_3$), 2.45 (s, 6H, *o*-CH$_3$), 5.49 (s, 1H, DAP−CH), 6.90 (s, 2H, *m*-CH), 6.96 (s, 2H, *m*-CH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 19.2 (*o*-CH$_3$), 19.9 (*o*-CH$_3$), 20.8 (*p*-CH$_3$), 22.8 (DAP−CH$_3$), 100.3 (DAP−CH), 129.1 (*m*-CH), 130.1 (*m*-CH), 132.6 (*o*-*C*CH$_3$), 135.1 (*o*-*C*CH$_3$), 136.3 (*p*-*C*CH$_3$), 139.4 (C$_{\mathrm{ipso}}$), 164.5 (DAP−CN). IR (KBr, cm^{-1}): 2915 (s), 1607 (m), 1526 (s), 1475 (m), 1435 (m), 1375 (s), 1292 (m), 1246 (s), 1223 (w), 1195 (s), 1145 (s), 1017 (s), 959 (w), 866 (s), 789 (s), 723 (m), 653 (w), 635 (m), 597 (w), 566 (m), 502 (m). Anal. Calcd for C$_{23}$H$_{29}$N$_2$GeCl: C, 62.56; H, 6.62; N, 6.34. Found: C, 62.32; H, 6.58; N, 6.25.

[(Mes)$_2$DAP]SnCl. A diethyl ether solution (25 mL) of [(Mes)$_2$DAP]H (850 mg, 2.54 mmol) was treated with *n*-BuLi (1.59 mL, 1.6 M hexane solution) at −78 °C. It was stirred for 0.5 h, warmed to room temperature, and stirred an additional 0.5 h. This pale yellow solution was then slowly added to a suspension of SnCl$_2$ (482 mg, 2.54 mmol) in diethyl ether (20 mL) at −78 °C. The mixture immediately turned yellow. The low temperature was kept for a further 1 h, then it was allowed to warm to room temperature and stirred overnight. After overnight stirring all volatiles were removed under vacuum. The remaining solid was extracted into toluene and filtered through Celite. The toluene was removed under vacuum to yield a pale yellow solid (750 mg, 61%). Recrystallization from hexane−toluene (2:1) at room temperature gave X-ray quality crystals of [(Mes)$_2$DAP]SnCl. Mp: 155−160 °C. ^{1}H NMR (CDCl$_3$): δ 1.82 (s, 6H, DAP−CH$_3$), 2.13 (s, 6H, *o*-CH$_3$), 2.28 (s, 6H, *p*-CH$_3$), 2.44 (s, 6H, *o*-CH$_3$), 5.29 (s, 1H, DAP−CH), 6.90 (s, 2H, *m*-CH), 6.96 (s, 2H, *m*-CH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 19.1 (*o*-CH$_3$), 19.7 (*o*-CH$_3$), 20.8 (*p*-CH$_3$), 23.3 (DAP−CH$_3$), 99.9 (DAP−CH), 129.1 (*m*-CH), 130.1 (*m*-CH), 131.8 (*o*-*C*CH$_3$), 134.3 (*o*-*C*CH$_3$), 135.7 (*p*-*C*CH$_3$), 141.3 (C$_{\mathrm{ipso}}$), 165.3 (DAP−CN). ^{14}N NMR (CD$_2$Cl$_2$): δ −186 (N$_{\mathrm{ring}}$). ^{119}Sn NMR (CD$_2$Cl$_2$): δ −236. IR (KBr, cm^{-1}): 3466 (w), 2998 (w), 2917 (s), 1760 (w), 1734 (w), 1608 (m), 1540 (s), 1450 (s), 1371 (s), 1266 (s), 1219 (w), 1199 (s), 1145 (s), 1023 (s), 958 (w), 932 (w), 856 (s), 833 (w), 801 (m), 786 (m), 723 (w), 650 (w), 626 (w), 567 (m), 501 (m). Raman (cm^{-1}): 3112 (w), 3008 (m), 2918 (s), 2857 (m), 2739 (w), 1608 (s), 1575 (w), 1538 (m), 1475 (w), 1443 (m), 1384 (m), 1306 (s), 1280 (m), 1267 (m), 1220 (s), 1156 (m), 1028 (w), 964 (w), 934 (w), 853 (w), 787 (w), 723 (w), 654 (m), 592 (w), 576 (s), 501 (s), 409 (m), 396 (m), 384 (m), 360 (m), 326 (w), 281 (s), 249 (m), 225 (w), 203 (w), 139 (s), 112 (s). Anal. Calcd for C$_{23}$H$_{29}$N$_2$SnCl: C, 56.65; H, 5.99; N, 5.74. Found: C, 56.81; H, 5.74; N, 5.56.

[(Mes)$_2$DAP]GeN$_3$. [(Mes)$_2$DAP]GeCl (200 mg, 0.45 mmol) and NaN$_3$ (29 mg, 0.45 mmol) were mixed in THF (10 mL) at room temperature. After the solution was stirred for 3 h, the THF was removed under vacuum. The remaining solid was extracted into toluene and filtered through Celite. Removal of toluene under vacuum gave a pale yellow solid (170 mg, 83%). X-ray quality crystals of [(Mes)$_2$DAP]GeN$_3$ were grown from hexane−toluene (2:1) at room temperature. Mp: 164−166 °C. ^{1}H NMR (CDCl$_3$): δ 1.83 (s, 6H, DAP−CH$_3$), 2.11 (s, 6H, *o*-CH$_3$), 2.29 (s, 6H, *p*-CH$_3$), 2.43 (s, 6H, *o*-CH$_3$), 5.36 (s, 1H, DAP−CH), 6.91 (s, 2H, *m*-CH), 6.99 (s, 2H, *m*-CH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 18.2 (*o*-CH$_3$), 19.0 (*o*-CH$_3$), 20.8 (*p*-CH$_3$), 22.7 (DAP−CH$_3$), 99.7 (DAP−CH), 129.2 (*m*-CH), 130.0 (*m*-CH), 132.7 (*o*-*C*CH$_3$), 134.9 (*o*-*C*CH$_3$), 136.5 (*p*-*C*CH$_3$), 139.6 (C$_{\mathrm{ipso}}$), 164.9 (DAP−CN). ^{14}N NMR (CD$_2$Cl$_2$): δ −291 (N2), −136 (N3), −215 (N4), −196 (N$_{\mathrm{ring}}$). IR (KBr, cm^{-1}): 3308 (m), 2919 (s), 2732 (w), 2576 (w), 2062 (s, asym N$_3$), 1609 (m), 1531 (s), 1477 (m), 1442 (m), 1361 (s), 1271 (m), 1251 (m), 1223 (w), 1197 (s), 1146 (s), 1020(s), 901 (w), 888 (w), 860 (s), 783 (s), 722 (w), 647 (m), 604 (w), 568 (m), 499 (m). Raman (cm^{-1}): 3091 (w), 3018 (m), 2989 (m), 2923 (s), 2857 (w), 2732 (w), 2059 (w, asym N$_3$), 1610 (s), 1569 (w), 1532 (m), 1480 (w), 1448 (w), 1384 (m), 1307 (s), 1272 (w), 1254 (m), 1225 (s), 1160 (m), 1020 (w), 969 (w), 939 (w), 838 (w), 784 (w), 651 (w), 597 (w), 578 (s), 501 (s), 410 (s), 371 (m), 354 (w), 328 (w), 292 (m), 210 (m), 114 (s). Anal. Calcd for C$_{23}$H$_{29}$N$_5$Ge: C, 61.65; H, 6.52; N, 15.63. Found: C, 61.28; H, 6.73; N, 15.49.

[(Mes)$_2$DAP]SnN$_3$. [(Mes)$_2$DAP]SnCl (200 mg, 0.41 mmol) and NaN$_3$ (27 mg, 0.41 mmol) were mixed in THF (10 mL) at room temperature. After the solution was stirred for 3 h, the THF was removed under vacuum. The remaining solid was extracted into toluene and filtered through Celite. Removal of toluene under vacuum gave [(Mes)$_2$DAP]SnN$_3$ as a white solid (180 mg, 89%). It was recrystallized from hexane−toluene (2:1) at room temperature. Mp: 146−148 °C. ^{1}H NMR (CDCl$_3$): δ 1.82 (s, 6H, DAP−CH$_3$), 2.11 (s, 6H, *o*-CH$_3$), 2.29 (s, 6H, *p*-CH$_3$), 2.44 (s, 6H, *o*-CH$_3$), 5.21 (s, 1H, DAP−CH), 6.91 (s, 2H, *m*-CH), 6.99 (s, 2H, *m*-CH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 18.3 (*o*-CH$_3$), 18.9 (*o*-CH$_3$), 20.8 (*p*-CH$_3$), 23.2 (DAP−CH$_3$), 99.8 (DAP−

---

(17) Dias, H. V. R.; Jin, W. *J. Am. Chem. Soc.* **1996**, *118*, 9123.

(18) Clegg, W.; Cope, E. K.; Edwards, A. J.; Mair, F. S. *Inorg. Chem.* **1998**, *37*, 2317.

(19) Clegg, W.; Coles, S. J.; Cope, E. K.; Mair, F. S. *Angew. Chem., Int. Ed.* **1998**, *37*, 796.

(20) Parks, J. E.; Holm, R. H. *Inorg. Chem.* **1968**, *7*, 1408.

(21) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 1699.

(22) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384, and references therein.

(23) Budzelaar, P. H. M.; Oort, A. B. v.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485.

(24) Fjeldberg, T.; Haaland, A.; Schilling, B. E.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551.

Table 1. Crystal Data and Summary of Data Collection and Refinement

	[(Mes)$_2$DAP]GeCl	[(Mes)$_2$DAP]SnCl	[(Mes)$_2$DAP]GeN$_3$	[(Mes)$_2$DAP]SnN$_3$
formula	$C_{23}H_{29}ClN_2Ge$	$C_{23}H_{29}ClN_2Sn$	$C_{23}H_{29}N_5Ge$	$C_{23}H_{29}N_5Sn$
fw	441.52	487.62	448.10	494.20
space group	$C2/c$	$Pnma$	$P2_1/n$	$P2_1/c$
a, Å	26.967(4)	6.881(1)	7.469(2)	10.821(1)
b, Å	12.369(4)	25.530(5)	23.637(5)	15.254(2)
c, Å	14.555(1)	12.770(3)	12.788(4)	14.923(1)
α, deg	90	90	90	90
β, deg	114.144(6)	90	91.13(3)	108.285(9)
γ, deg	90	90	90	90
vol, Å^3	4430.2(17)	2243.5(8)	2257.4(10)	2338.8(5)
Z	8	4	4	4
T, K	203(2)	203(2)	203(2)	228(2)
λ (Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73
density (calc), g/cm^3	1.324	1.444	1.319	1.404
abs coeff, mm^{-1}	1.513	1.268	1.375	1.110
GOOF	1.069	1.032	1.039	1.058
R1, wR2^a [$I > 2\sigma(I)$]	0.0306, 0.0794	0.0294, 0.0737	0.0473, 0.1130	0.0442, 0.1077
R1, wR2 [all data]	0.0342, 0.0818	0.0373, 0.0778	0.0678, 0.1242	0.0464, 0.1098

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

CH), 129.2 (m-CH), 130.0 (m-CH), 131.8 (o-CCH$_3$), 134.0 (o-CCH$_3$), 135.9 (p-CCH$_3$), 141.2 (C$_{ipso}$), 165.8 (DAP−CN). ^{14}N NMR (CD$_2$Cl$_2$): δ −292 (N2), −136 (N3), −223 (N4), −186 (N$_{ring}$). ^{119}Sn NMR (CD$_2$Cl$_2$): δ −276; IR (KBr, cm^{-1}): 3347 (w), 2916 (s) 2060 (s, asym N$_3$), 1608 (m), 1531 (s), 1475 (m), 1450 (m), 1373 (s), 1310 (s), 1262 (s), 1220 (w), 1197 (s), 1146 (s), 1020 (s), 959 (w), 932 (w), 893 (w), 860 (s), 829 (w), 803 (m), 632 (w), 594 (w), 566 (m), 495 (m). Raman (cm^{-1}): 3102 (w), 3013 (m), 2919 (s), 2857 (m), 2731 (w), 2070 (w), 2058 (w, asym N$_3$), 1609 (s), 1554 (m), 1478 (m), 1440 (m), 1382 (s), 1305 (s), 1279 (m), 1264 (m), 1222 (s), 1157 (m), 1024 (w), 963 (w), 934 (w), 827 (w), 722 (w), 652 (w), 595 (w), 577 (s), 496 (s), 403 (m), 359 (m), 330 (s), 279 (w), 258 (s), 235 (w), 174 (w), 133 (w), 109 (s). Anal. Calcd for $C_{23}H_{29}N_5Sn$: C, 55.90; H, 5.91; N, 14.17. Found: C, 55.63; H, 5.77; N, 13.94.

X-ray Structure Determination. A suitable crystal covered with a layer of hydrocarbon oil was selected and attached to a glass fiber and immediately placed in the low-temperature nitrogen stream. Data collections were carried out at low temperature on a Siemens P4 diffractometer equipped with a LT-2A device for low-temperature work and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The unit cell parameters of [(Mes)$_2$DAP]GeCl, [(Mes)$_2$DAP]SnCl, [(Mes)$_2$DAP]GeN$_3$, and [(Mes)$_2$DAP]SnN$_3$ were determined by least-squares refinement of 38, 56, 39, and 41 reflections, respectively. Three standard reflections were measured at every 97 data points to check for crystal deterioration and/or misalignment. No significant deterioration in intensity was observed. Structures were solved by direct methods followed by successive cycles of full-matrix least-squares refinement on F^2 and difference Fourier analysis. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at calculated positions. Software programs and the sources of scattering factors are contained in the Bruker SHELXTL 5.1 software package provided by Bruker Analytical X-ray Instruments, Inc. Some details of data collection and refinement are given in Table 1. Selected bond distances and angles are given in Tables 2−5.

Results and Discussion

Table 2. Selected Bond Lengths [Å] and Angles [deg] for [(Mes)$_2$DAP]GeCl

Ge−N(1)	1.958(2)	C(2)−C(6)	1.505(4)
Ge−N(5)	1.980(2)	C(3)−C(4)	1.399(4)
Ge−Cl	2.328(1)	C(4)−N(5)	1.330(4)
N(1)−C(2)	1.348(4)	C(4)−C(7)	1.501(4)
N(1)−C(8)	1.444(4)	N(5)−C(17)	1.443(4)
C(2)−C(3)	1.382(4)		
N(1)−Ge−N(5)	90.44(9)	N(5)−C(4)−C(3)	122.4(3)
N(1)−Ge−Cl	96.19(7)	N(5)−C(4)−C(7)	119.2(3)
N(5)−Ge−Cl	93.39(7)	C(3)−C(4)−C(7)	118.4(2)
C(2)−N(1)−C(8)	120.0(2)	C(4)−N(5)−C(17)	121.5(2)
C(2)−N(1)−Ge	123.3(1)	C(4)−N(5)−Ge	125.3(2)
C(8)−N(1)−Ge	116.7(1)	C(17)−N(5)−Ge	113.3(2)
N(1)−C(2)−C(3)	123.1(3)	C(13)−C(8)−N(1)	120.6(2)
N(1)−C(2)−C(6)	118.8(3)	C(9)−C(8)−N(1)	118.7(2)
C(3)−C(2)−C(6)	118.1(3)	C(22)−C(17)−N(5)	120.4(3)
C(2)−C(3)−C(4)	126.3(3)	C(18)−C(17)−N(5)	118.4(3)

Table 3. Selected Bond Lengths [Å] and Angles [deg] for [(Mes)$_2$DAP]SnCl

Sn−N(0A)	2.162(3)	N−C(5)	1.437(5)
Sn−N	2.162(3)	C(2)−C(3)	1.392(4)
Sn−Cl	2.468(1)	C(2)−C(4)	1.506(5)
N−C(2)	1.330(5)	C(3)−C(2A)	1.392(4)
N(0A)−Sn−N	87.38(17)	N−C(2)−C(3)	124.9(4)
N(0A)−Sn−Cl	90.52(9)	N−C(2)−C(4)	119.2(3)
N−Sn−Cl	90.52(9)	C(3)−C(2)−C(4)	115.7(4)
C(2)−N−C(5)	119.6(3)	C(2A)−C(3)−C(2)	129.3(5)
C(2)−N−Sn	122.1(2)	C(10)−C(5)−N	119.2(3)
C(5)−N−Sn	118.3(2)	C(6)−C(5)−N	120.5(4)

The synthesis of the chloro adduct [(Mes)$_2$DAP]GeCl was achieved by the treatment of GeCl$_2$·(1,4-dioxane) with [(Mes)$_2$DAP]Li in a 1:1 molar ratio in Et$_2$O. It was isolated as a pale yellow solid in 66% yield (Scheme 1). The ^{1}H NMR spectrum of [(Mes)$_2$DAP]GeCl taken in CDCl$_3$ shows a singlet at δ 5.49, which can be assigned to the diazapentadienyl ring proton. The corresponding signal for the free ligand appears at a significantly upfield position (δ 4.29).[23] In contrast to the free ligand, the ortho methyl groups of [(Mes)$_2$DAP]GeCl appear as two broad, well-separated singlets in the ^{1}H NMR spectrum. A similar pattern was observed for the signals due to protons at the meta-position. Overall, the ^{1}H NMR and ^{13}C NMR spectra of [(Mes)$_2$DAP]GeCl are consistent with a C_s-symmetric structure and restricted rotation around the N−Mes bonds.

Crystals of [(Mes)$_2$DAP]GeCl were studied by X-ray diffraction, and the thermal ellipsoid plot is shown in Figure 1. [(Mes)$_2$DAP]GeCl has a monomeric structure. The heterocyclic C$_3$N$_2$Ge ring is not planar. The germanium atom is displaced from the diazapentadienyl ring plane by about 0.58 Å. The Ge−Cl distance is slightly shorter than the corresponding distance of [(i-Pr)$_2$ATI]GeCl (2.368(2) Å),[15] whereas the Ge−N distances are essentially identical between the two systems.

The tin analogue [(Mes)$_2$DAP]SnCl was synthesized from SnCl$_2$ and [(Mes)$_2$DAP]Li. The ^{1}H NMR and ^{13}C NMR spectra are essentially identical to those of [(Mes)$_2$DAP]GeCl, suggesting very similar solution structures. The ^{14}N NMR spectrum displays a broad peak at δ −186. It can be assigned to the

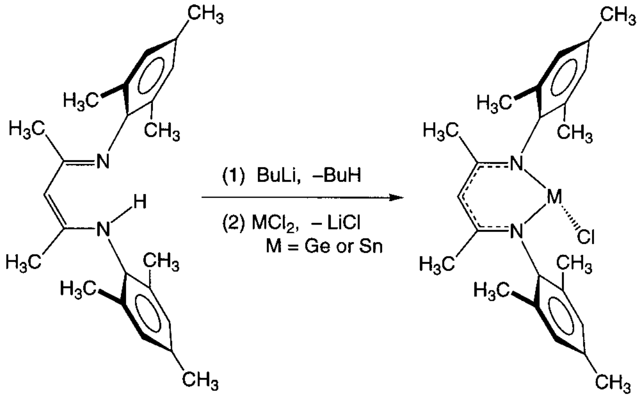
Table 4. Selected Bond Lengths [Å] and Angles [deg] for $[(Mes)_2DAP]GeN_3$

Ge−N(1)	1.972(4)	N(5)−C(4)	1.323(6)
Ge−N(5)	1.975(4)	N(5)−C(17)	1.449(6)
Ge−N(2)	1.979(5)	C(2)−C(3)	1.396(7)
N(2)−N(3)	1.199(7)	C(2)−C(6)	1.503(7)
N(3)−N(4)	1.152(8)	C(3)−C(4)	1.388(7)
N(1)−C(2)	1.322(6)	C(4)−C(7)	1.493(7)
N(1)−C(8)	1.451(6)		
N(1)−Ge−N(5)	90.13(17)	N(1)−C(2)−C(3)	122.9(5)
N(1)−Ge−N(2)	96.08(19)	N(1)−C(2)−C(6)	119.2(4)
N(5)−Ge−N(2)	96.45(19)	C(3)−C(2)−C(6)	117.9(5)
N(3)−N(2)−Ge	121.1(4)	C(4)−C(3)−C(2)	127.3(5)
N(4)−N(3)−N(2)	176.3(6)	N(5)−C(4)−C(3)	122.5(5)
C(2)−N(1)−C(8)	121.2(4)	N(5)−C(4)−C(7)	118.9(4)
C(2)−N(1)−Ge	127.4(3)	C(3)−C(4)−C(7)	118.5(5)
C(8)−N(1)−Ge	111.3(3)	C(13)−C(8)−N(1)	120.7(4)
C(4)−N(5)−C(17)	121.0(4)	C(9)−C(8)−N(1)	117.8(4)
C(4)−N(5)−Ge	127.7(3)	C(18)−C(17)−N(5)	118.2(4)
C(17)−N(5)-Ge	111.2(3)	C(22)−C(17)-N(5)	120.5(4)

Table 5. Selected Bond Lengths [Å] and Angles [deg] for $[(Mes)_2DAP]SnN_3$

Sn−N(1)	2.177(4)	C(2)−C(6)	1.514(8)
Sn−N(2)	2.198(5)	N(3)−N(4)	1.109(8)
Sn−N(5)	2.210(4)	C(3)−C(4)	1.397(8)
N(1)−C(2)	1.332(7)	C(4)−N(5)	1.318(7)
N(1)−C(8)	1.443(7)	C(4)−C(7)	1.503(8)
N(2)−N(3)	1.208(8)	N(5)−C(17)	1.442(7)
C(2)−C(3)	1.382(8)		
N(1)−Sn−N(2)	94.49(19)	C(2)−C(3)−C(4)	129.7(5)
N(1)−Sn−N(5)	85.17(17)	N(5)−C(4)−C(3)	123.8(5)
N(2)−Sn−N(5)	88.69(18)	N(5)−C(4)−C(7)	119.2(5)
C(2)−N(1)−C(8)	119.5(5)	C(3)−C(4)−C(7)	116.9(5)
C(2)−N(1)−Sn	126.7(4)	C(4)−N(5)−C(17)	121.6(5)
C(8)−N(1)−Sn	113.3(3)	C(4)−N(5)−Sn	127.7(4)
N(3)−N(2)−Sn	124.1(4)	C(17)−N(5)−Sn	110.5(3)
N(1)−C(2)−C(3)	125.6(5)	C(13)−C(8)−N(1)	121.5(5)
N(1)−C(2)−C(6)	118.4(5)	C(9)−C(8)−N(1)	117.9(5)
C(3)−C(2)−C(6)	115.8(5)	C(18)−C(17)−N(5)	118.5(5)
N(4)−N(3)−N(2)	176.0(7)	C(22)−C(17)−N(5)	120.6(5)

Scheme 1



[(Mes)₂DAP]H **[(Mes)₂DAP]MCl**

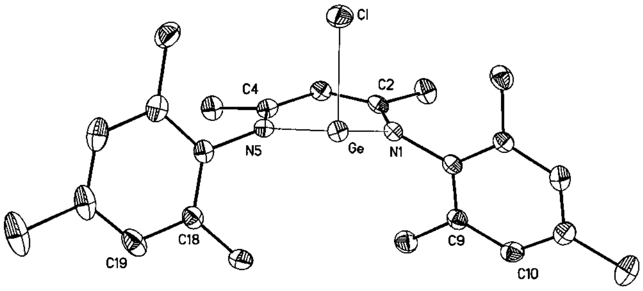


Figure 1. Molecular structure of $[(Mes)_2DAP]GeCl$. Hydrogen atoms have been omitted for clarity.

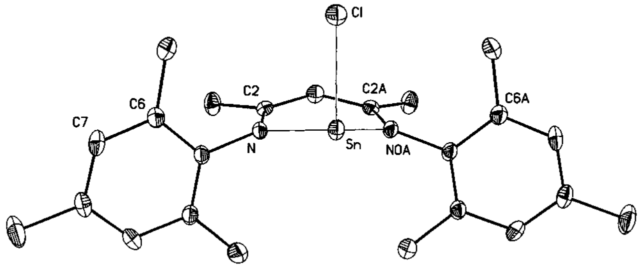


Figure 2. Molecular structure of $[(Mes)_2DAP]SnCl$. Hydrogen atoms have been omitted for clarity.

nitrogens of the C_3N_2Sn ring. This may be compared to the chemical shift of δ −199 for the nitrogen atoms of the aminotroponiminato derivative $[(n\text{-}Pr)_2ATI]SnCl$. This compound features a heterobicyclic C_7N_2Sn ring system. The ^{119}Sn NMR spectrum of $[(Mes)_2DAP]SnCl$ shows a signal at δ −236. This resonance appears at the region expected for three-coordinate tin atoms, e.g., $[(i\text{-}Pr)_2ATI]SnCl$, δ −68;[17] $[(n\text{-}Pr)_2ATI]SnCl$, δ −84; $[H_2B(Pz)_2]SnCl$, δ −307.[25] Two-coordinate tin(II) adducts show ^{119}Sn signals at significantly higher chemical shift values (e.g., $\{[(i\text{-}Pr)_2ATI]Sn\}^+$, δ 734;[17] $[(Me_3Si)_2N]_2Sn$, δ 759),[26] whereas four-coordinate chloro tin(II) complexes show ^{119}Sn signals at relatively upfield regions (e.g., $[HB(Pz)_3]SnCl$, δ −569; $[HB(3,5\text{-}Me_2Pz)_3]SnCl$, δ −567).[25]

The X-ray crystal structure of $[(Mes)_2DAP]SnCl$ and the atom-numbering scheme is shown in Figure 2. The $[(Mes)_2DAP]SnCl$ molecule has C_s symmetry with a crystallographically imposed mirror plane containing Cl, Sn, and C3. The heterocyclic C_3N_2Sn ring is not planar. The tin atom is displaced from the diazapentadienyl ring plane by 0.70 Å. The Sn−Cl and Sn−N distances are 2.468(1) and 2.162(3) Å, respectively. The Sn−Cl distance is shorter than the corresponding distances of $[(i\text{-}Pr)_2ATI]SnCl$ (2.542(2) Å)[17] and $[HB(3,5\text{-}Me_2Pz)_3]SnCl$ (2.629(1) Å).[27,28] There are no intermolecular interactions between the Sn atoms (closest Sn···Sn separation is about 5.63 Å) or Sn and Cl atoms (closest intermolecular Sn···Cl contact is about 5.54 Å) of neighboring $[(Mes)_2DAP]SnCl$ molecules.

The treatment of $[(Mes)_2DAP]GeCl$ or $[(Mes)_2DAP]SnCl$ with NaN_3 in THF led to the corresponding azide $[(Mes)_2DAP]GeN_3$ or $[(Mes)_2DAP]SnN_3$ in excellent yield (Scheme 2). These Ge(II) and Sn(II) azides are stable in the absence of moisture and air. They possess considerable thermal stability, with melting points above 145 °C. Both $[(Mes)_2DAP]GeN_3$ and $[(Mes)_2DAP]SnN_3$ are very soluble in solvents such as toluene, CH_2Cl_2, and THF.

$[(Mes)_2DAP]GeN_3$ and $[(Mes)_2DAP]SnN_3$ were characterized by NMR and IR spectroscopy. ^1H and ^{13}C NMR spectra are very similar to the corresponding spectra of the chloro adduct, indicating the presence of a C_s-symmetric species in solution. The ^{119}Sn NMR spectrum of $[(Mes)_2DAP]SnN_3$ exhibits a resonance at δ −276. This shows an upfield shift relative to the chloro analogue $[(Mes)_2DAP]SnCl$ (δ −236), perhaps as a result of the lower effective electronegativity of the azido moiety

---

(25) Reger, D. L.; Knox, S. J.; Huff, M. F.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1991**, *30*, 1754.

(26) Wrackmeyer, B.; Schiller, J. *Z. Naturforsch.* **1992**, *47B*, 662.

(27) Cowley, A. H.; Geerts, R. L.; Nunn, C. M.; Carrano, C. J. *J. Organomet. Chem.* **1988**, *341*, C27.

(28) See also for a related Sn(II) chloride: Hitchcock, P. B.; Hu, J.; Lappert, M. F.; Layh, M.; Liu, D.-S.; Severn, J. R.; Shun, T. *Ann. Quim. Int. Ed.* **1996**, *92*, 186.

Scheme 2

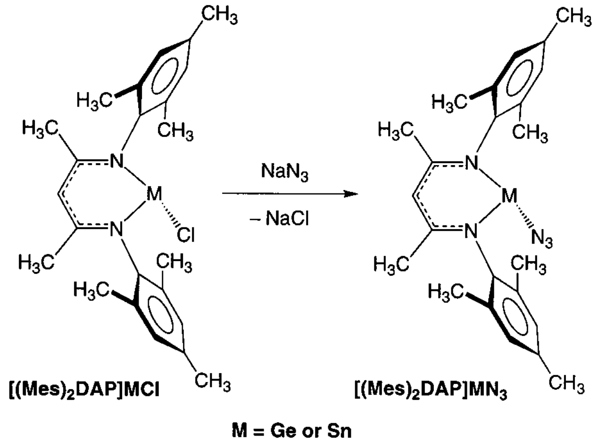


Table 6. ^{14}N NMR Data (CD_2Cl_2, 25 °C, Relative to $\delta(CH_3NO_2) = 0.00$), ^{119}Sn NMR Data (CD_2Cl_2, 25 °C, Relative to $\delta(Me_4Sn) = 0.00$), and Selected Infrared Spectroscopic Data (KBr Pellet, cm^{-1}) of [(Mes)$_2$DAP]MX and [(n-Pr)$_2$ATI]MX Adducts (where M = Ge or Sn, X = Cl or N_3)[a]

compound	nitrogen-14	tin-119	$\nu_{asym}(N_3)$
[(Mes)$_2$DAP]GeN$_3$	−291 (N2); −136 (N3); −215 (N4); −196 (N$_{ring}$)		2062
[(Mes)$_2$DAP]SnN$_3$	−292 (N2); −136 (N3); −223 (N4); −186 (N$_{ring}$)	−276.2	2060
[(Mes)$_2$DAP]SnCl	−186 (N$_{ring}$)	−236.0	
[(n-Pr)$_2$ATI]GeN$_3$	−250 (N2); −135 (N3); −213, −230 (N4, N$_{ring}$)		2048
[(n-Pr)$_2$ATI]SnN$_3$	−256 (N2); −136 (N3); −202, −217 (N4, N$_{ring}$)	−122.4	2039
[(n-Pr)$_2$ATI]SnCl	−199 (N$_{ring}$)	−83.7	

[a] Connectivity: (N$_{ring}$)$_2$M−N(2)−N(3)−N(4).

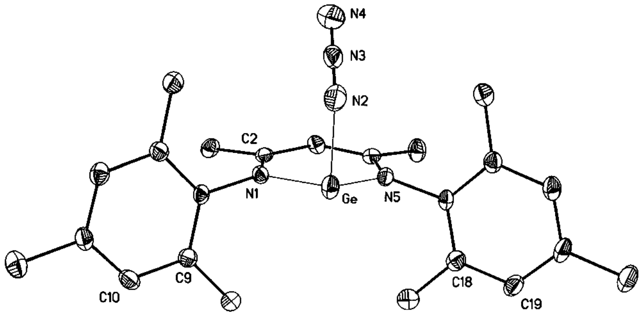


Figure 3. Molecular structure of [(Mes)$_2$DAP]GeN$_3$. Hydrogen atoms have been omitted for clarity.

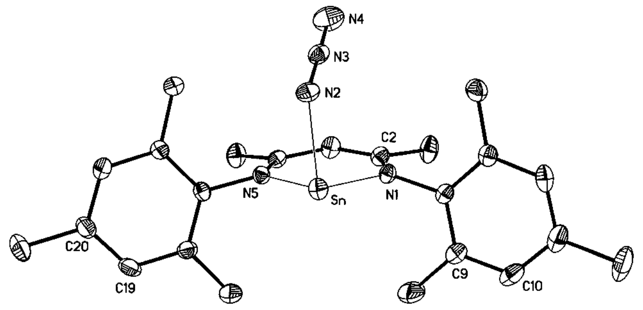


Figure 4. Molecular structure of [(Mes)$_2$DAP]SnN$_3$. Hydrogen atoms have been omitted for clarity.

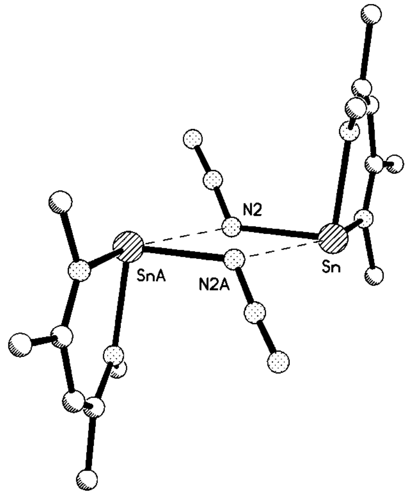


Figure 5. View of [(Mes)$_2$DAP]SnN$_3$ showing intermolecular Sn···N contacts. Only selected atoms have been included.

compared to the chloride.[29−31] A similar trend has been observed in other tin compounds, e.g., [(n-Pr)$_2$ATI]SnCl (δ −84), [(n-Pr)$_2$ATI]SnN$_3$ (δ −122), [Fe(CO)$_2$(Cp)]$_2$SnCl$_2$ (δ 550.5), and [Fe(CO)$_2$(Cp)]$_2$Sn(N$_3$)$_2$ (δ 520.9).[30]

IR spectra of [(Mes)$_2$DAP]GeN$_3$ and [(Mes)$_2$DAP]SnN$_3$ in KBr display strong absorption bands at 2062 and 2060 cm^{-1}, respectively. These bands can be assigned to the N_3 asymmetric stretching vibrations.[1,3] It is also possible to observe these bands as very weak signals in the Raman spectra (2059 and 2058 cm^{-1}, respectively). The IR spectra of [(n-Pr)$_2$ATI]GeN$_3$ and [(n-Pr)$_2$ATI]SnN$_3$ also show $\nu_{asym}(N_3)$ bands in the same region. Neither infrared nor Raman spectra were useful for clearly identifying the $\nu_{sym}(N_3)$ band. This vibration is expected in the 1350−1250 cm^{-1} region.[12,30] Raman spectra of the chloro and the azido tin adducts [(Mes)$_2$DAP]SnCl and [(Mes)$_2$DAP]SnN$_3$ show essentially identical peaks in this region.

We have also studied [(Mes)$_2$DAP]GeN$_3$ and [(Mes)$_2$DAP]SnN$_3$ using ^{14}N NMR spectroscopy. The ^{14}N chemical shift values are summarized in Table 6. The assignment of individual resonances to different nitrogen atoms (connectivity (N$_{ring}$)$_2$M−N2−N3−N4) was based on previous work on covalent azides.[32] These spectra show three well-resolved signals for the azide moiety. This suggests that the interaction between the azide group and Ge(II) or Sn(II) is predominantly covalent in nature. Furthermore, chemical shift values are nearly identical between the germanium and tin adducts. This, combined with the IR data, indicates that the Ge(II) and Sn(II) ions have similar effects on the azide moiety. We have also examined the aminotroponiminato adducts [(n-Pr)$_2$ATI]GeN$_3$ and [(n-Pr)$_2$ATI]SnN$_3$ using ^{14}N NMR spectroscopy (Table 6). Again, the three azide nitrogens resonate at different chemical shift values. Due to peak broadness and closeness, we could not assign chemical shift values unambiguously to the N(ring) and N(4) atoms. However, ^{14}N NMR spectroscopic data of [(n-Pr)$_2$ATI]MN$_3$ are in good agreement with those of [(Mes)$_2$DAP]MN$_3$ adducts.

[(Mes)$_2$DAP]GeN$_3$ and [(Mes)$_2$DAP]SnN$_3$ were also characterized by X-ray crystallography, and the molecular structures are illustrated in Figures 3 and 4, respectively. [(Mes)$_2$DAP]GeN$_3$ has a monomeric structure. The six-membered C_3N_2Ge ring is significantly more planar compared to that of the chloro analogue. The germanium atom is displaced from the diazapentadienyl ring plane by about 0.29 Å. The Ge−N(azide) and

---

(29) Li, Y.; Xiao, H. *Huaxue Xuebao* **1993**, *51*, 313.
(30) Hampden-Smith, M. J.; Lei, D.; Duesler, E. N. *J. Chem. Soc., Dalton Trans.* **1990**, 2953.
(31) Schulz, A.; Tornieporth-Oetting, I. C.; Klapötke, T. M. *Inorg. Chem.* **1995**, *34*, 4343.
(32) Geissler, P.; Klapotke, T. M.; Kroth, H.-J. *Spectrochim. Acta* **1995**, *51A*, 1075.

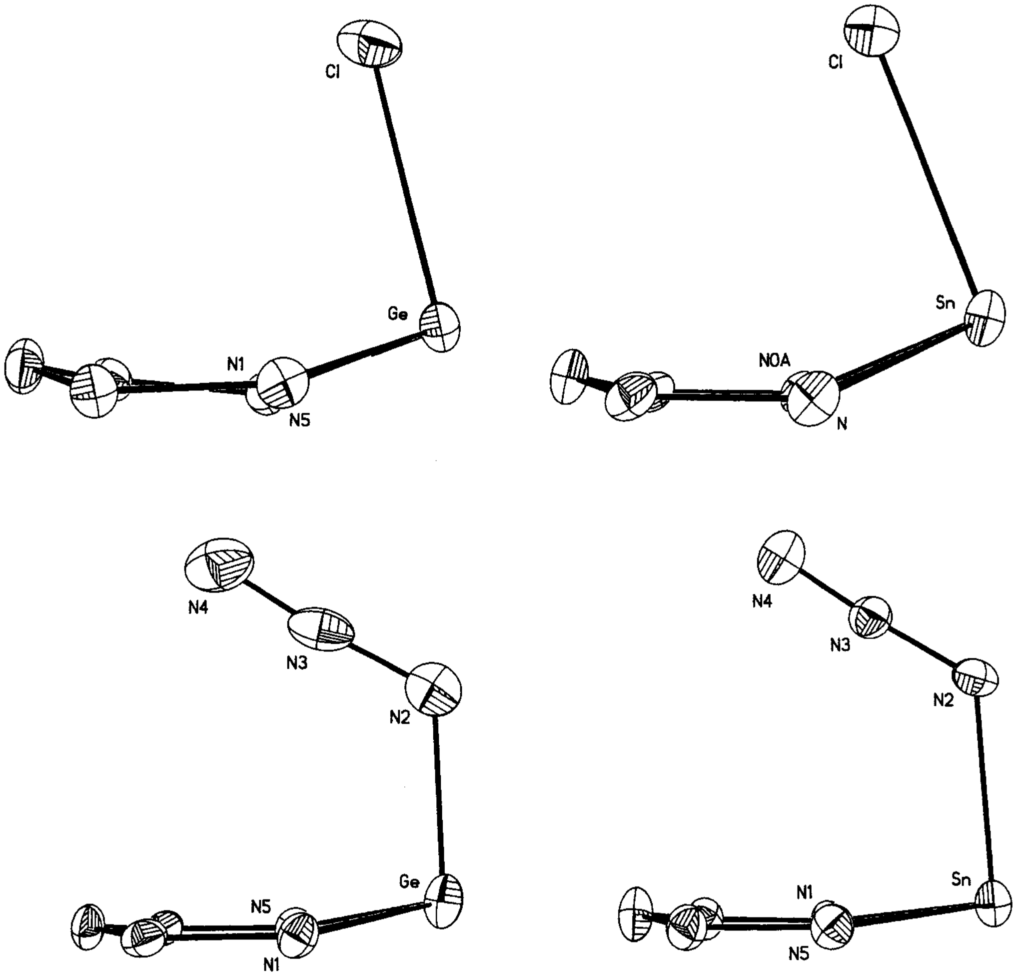


Figure 6. Side view of [$(Mes)_2$DAP]GeCl (top left), [$(Mes)_2$DAP]SnCl (top right), [$(Mes)_2$DAP]GeN_3 (bottom left), and [$(Mes)_2$DAP]SnN_3 (bottom right) showing C_3N_2M ring and geometry at Ge and Sn. Only selected atoms have been included.

Ge−N(ring) bond distances are very similar. They are 1.972(4) Å and 1.975(4), 1.979(5) Å, respectively. The Ge−N(azide) bond distance is shorter than those found in the three-coordinate germanium adduct [$(n\text{-}Pr)_2$ATI]GeN_3 (2.047(2) Å)[8] or four-coordinate complexes [HB(3,5-$(CH_3)_2Pz)_3$]GeN_3 (2.262(2) Å)[5] and [(C_5H_5)Co{P(O)$(OEt)_2$}$_3$]GeN_3 (2.094(7) Å).[12] The azide group of [$(Mes)_2$DAP]GeN_3 is almost linear, as evident from the N−N−N bond angles of 176.3(6)°. The N−N bond distances of [$(Mes)_2$DAP]GeN_3 are 1.199(7) and 1.152(8) Å. The corresponding N−N bond distances of [$(n\text{-}Pr)_2$ATI]GeN_3 are 1.197(3) and 1.144(4) Å.[8]

In contrast to the germanium adduct, the tin analogue [$(Mes)_2$DAP]SnN_3 shows weak intermolecular Sn···N2 contacts (2.91 Å) in the solid state (Figure 5). This Sn···N contact between neighboring molecules is significantly longer than the Sn−N2 bond distance (2.198(5) Å). The Sn−N(azide) bond length is comparable to that observed for [$(n\text{-}Pr)_2$ATI]SnN_3 (2.241(4) Å). The six-membered C_3N_2Sn ring is planar. The azide moiety is essentially linear (N−N−N 176.0(7)°). The two N−N bond distances are 1.208(8) and 1.109(8) Å.

Figure 6 shows a side view of the four adducts described above. The germanium and tin centers adopt a pyramidal geometry, as evident from the sum of the bond angles at germanium (281°) and tin (268°). The azido tin adduct has the most planar C_3N_2M ring, whereas the corresponding chloride shows the greatest deviation from planarity. The azide groups occupy a site above the C_3N_2M ring system (cis). DFT calculations on [$(Me)_2$ATI]MN_3 indicate that the trans arrangements are only very slightly less stable.[8] Overall, the structural data of [$(Mes)_2$DAP]GeN_3 and [$(Mes)_2$DAP]SnN_3 suggest that the dominant canonical form of the M-azide moiety is M−N−N≡N. This is consistent with the results from theoretical calculations.[8]

In summary, this work shows that germanium(II) and tin(II) azide derivatives can be isolated as thermally stable solids using the [$(Mes)_2$DAP]$^-$ ligand system. [$(Mes)_2$DAP]GeN_3 and [$(Mes)_2$DAP]SnN_3 represent a rare group of covalent azides that feature low-valent group 14 elements. Both germanium(II) and tin(II) ions have similar effects on the azide moiety. This is in good agreement with the theoretical work.

Acknowledgment. We thank The Robert A. Welch Foundation for support of this work. We also thank the National Science Foundation (CHE-9601771) for providing funds to purchase the 500 MHz NMR spectrometer. We are deeply grateful to Dr. Konstantin Karaghiosoff and Dr. Burkhard Krumm for recording tin-119 NMR, nitrogen-14 NMR, and Raman spectra. We are also thankful to Dr. Hongming Zhang (SMU) for collecting X-ray data of [$(Mes)_2$DAP]SnN_3.

Supporting Information Available: X-ray crystallographic files for [$(Mes)_2$DAP]GeCl, [$(Mes)_2$DAP]SnCl, [$(Mes)_2$DAP]GeN_3, and [$(Mes)_2$DAP]SnN_3 in CIF format are available free of charge via the Internet at http:// pubs.acs.org.

IC001078J