Identification of new N–Sb topologies: understanding the sequential dehydrochloride coupling of primary amines and trichloropnictines

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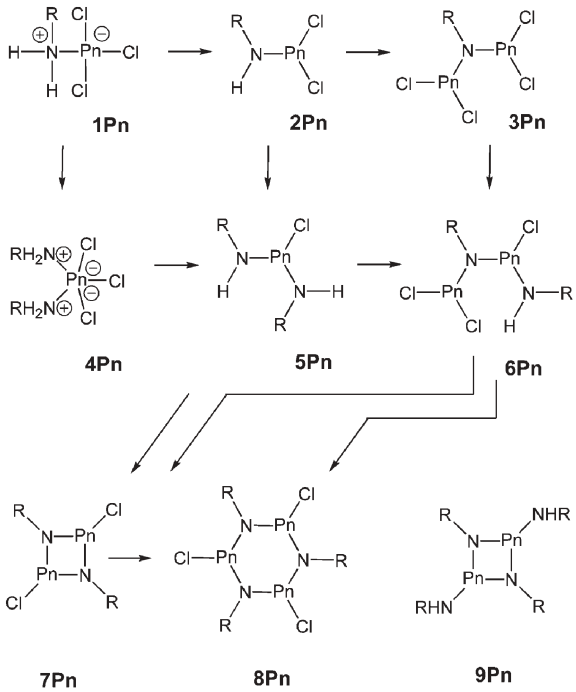
Subtle steric strain imposed by 2,6-dimethylphenyl substituents on N–Sb frameworks has enabled identification of the first acyclic dipnictadiazane and the first six-membered cyclotristibatriazane providing insight into the dehydrohalide coupling reaction of amines with halopnictines.

Polymers with inorganic backbones exhibit new and diverse properties,[1] however examples are limited and development of preparative procedures represents a prominent research focus. The versatility of ring opening polymerization prompts the search for appropriate heterocyclic frameworks to provide new polymer backbone compositions. We are targeting nitrogen–pnictogen (Pn = P, As, Sb, Bi) systems as precursors to the, as yet unknown, polypnictazanes. Dehydrochloride coupling reactions of chlorophosphines and primary amines are well established to give cyclo-2,4-diphospha-1,3-diazanes **7P** and **9P**[2–4] (Scheme 1).



Scheme 1 Potential outcomes for dehydrochloride coupling of RNH_2 and $PnCl_3$ (Pn = P, As, Sb, Bi; R = Dmp for Pn = Sb).

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The mechanism of these reactions is not known, but likely begins with the formation of an N–P adduct **1P** followed by deprotonation at nitrogen and subsequent elimination of chloride. While specific examples of the consequential aminodichlorophosphines **2P**,[5,6] diphosphinoamines **3P**[6,7] and diaminophosphines **5P**[5] have been isolated, the intramolecular dehydrochloride cyclization to **7P** is highly favored and acyclic diphosphadiazanes, such as **6P** have not been observed. Dehydrochloride coupling reactions have been reported for $AsCl_3$[8] and $SbCl_3$,[9] but not for $BiCl_3$, although reactions of alkali metal amides with $PnCl_3$ have been generally applied to prepare 2,4-substituted cyclo-2,4-dipnicta-1,3-diazanes (Pn = As,[10–14] Pn = Sb,[9,14–22] Pn = Bi[14,22,23]).

Cyclotripnictatriazanes **8Pn** are rare,[24–26] but recently we have realized that the presence of the medium sized substituents 2,6-dimethylphenyl- (Dmp) or 2,6-diisopropylphenyl- (Dipp) at nitrogen facilitates transformation of the dimer **7** to the trimer **8** for Pn = P[27] or As.[28] Imposition of this subtle substituent steric strain on the stibazane system has now allowed for the identification of the amine–stibine adduct **1Sb**, the bisamine–stibine adduct **4Sb**, the first acyclic dipnictadiazane **6Sb** and the first six-membered cyclotristibatriazane **8Sb**.

Mixtures of $DmpNH_2$ with $SbCl_3$ in toluene give a co-crystalline mixture of **1Sb** and **4Sb** that has been crystallographically characterized.† One signal corresponding to the methyl groups of the Dmp substituents is observed in the ^1H NMR spectrum. Structural parameters for **1Sb** and **4Sb** compare with those for **1Sb** (R = Ph),[29] the only previously reported example of a primary amine–stibine adduct. Antimony adopts a predictable disphenoidal environment in **1Sb** and a square pyramidal environment in **4Sb**. The N–Sb distances in **4Sb** [2.614(2); 2.799(2) Å] are longer than that in **1Sb** [2.596(2) Å] due to crowding imposed by the higher coordination number at antimony. A variety of products are apparent in the ^1H NMR spectrum when NEt_3 is present in mixtures of $DmpNH_2$ and $SbCl_3$. Two types of crystal have been isolated in small quantities and have been identified as **6Sb** (Fig. 1) and **8Sb** (Fig. 2) by X-ray crystallography.

The alternating N–Sb backbone of **6Sb** is terminated by two Sb–Cl bonds and an N–H bond, but a close intra-molecular interaction occurs between these sites (N1 to Sb2) imposing a conformation that is reminiscent of a cyclodistibadiazane (**7Sb** and **9Sb**).[20] The N1–Sb distances are significantly longer than N2–Sb, and N1–Sb2 is comparable to those in **1Sb**, **1Sb** (R = Ph)[29] and **4Sb**. Samples of **6Sb** decay slowly in solution, precluding attempts to purify bulk samples.

The solid state structure of **8Sb** is disordered as a 55 : 45 mixture of an envelope conformer (Fig. 2) and a boat conformer. The chlorine substituents adopt a *syn,anti* configuration consistent with

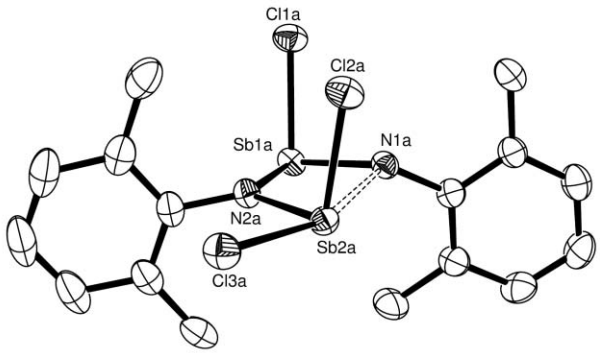

Fig. 1 Solid state molecular structure of **6Sb**. Ellipsoids drawn at 50% probability and hydrogen atoms omitted for clarity. Selected bond lengths (Å): N1–Sb1 2.108(2), N1–Sb2 2.521(2), N2–Sb1 2.023(2), N2–Sb2 2.039(2), Sb1–Cl1 2.409(1), Sb2–Cl2 2.425(1), Sb2–Cl3 2.450(1).

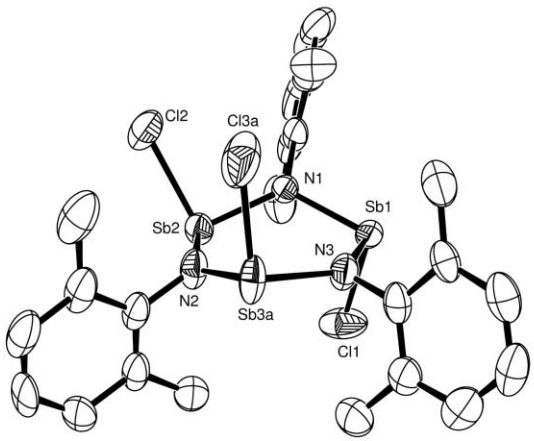

Fig. 2 Solid state molecular structure of one conformer of **8Sb**. Ellipsoids drawn at 50% probability and hydrogen atoms omitted for clarity. Selected bond lengths (Å): Sb–N 2.012(8)–2.071(8), Sb–Cl 2.364(7)–2.403(3).

observations for both the phosphorus **8P**[27] and arsenic **8As** analogues.[28] Restricted rotation of the Dmp substituents of **8Sb** at room temperature is responsible for a 1 : 2 : 1 : 2 ^{1}H NMR signal pattern observed for the *ortho*-methyl groups.

Compounds **1Sb** and **4Sb** represent kinetically stable adducts of the primary amine with $SbCl_3$. The introduction of NEt_3, as a stronger Brønsted base than $DmpNH_2$, effects deprotonation of the adduct securing the N–Sb bond in **2Sb**. Repetition of this process may effect sequential association of a second amine and a second unit of $SbCl_3$ (*via* **3Sb** or **5Sb**) to give **6Sb**. Alternatively, dehydrochloride coupling of two molecules of **2Sb** provides access to **6Sb**. Irrespective of these possible mechanisms, the isolation of **6Sb** implies a unique kinetic stabilization with respect to the cyclodipnictadiazane framework **7Sb** in the context of the acyclic phosphazanes that have only been devised using skeletal stabilization to topologically restrict cyclization.[30] The impeded cyclisation of **6Sb** may allow for additional dehydrochloride coupling steps with a third molecule of **2Sb**, or through further sequential association of an amine and $SbCl_3$ to give **8Sb**.

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Notes and references

† Experimental

Isolation of **1Sb/4Sb**: $DmpNH_2$ (2.40 mL, 19.5 mmol) added to $SbCl_3$ (1.78 g, 7.81 mmol) in toluene, filtered and removal of solvent under reduced pressure gave a precipitate that was dissolved in minimal CH_2Cl_2 and vapour diffusion of pentane over 2 days gave crystals (1.23 g) of empirical formula $(DmpNH_2)_3Sb_2Cl_6{\cdot}0.5CH_2Cl_2$: mp 81–82 °C; Anal. Calcd. for $C_{24}H_{33}N_3Cl_6Sb_2$ (Found): C 35.16 (33.01), H 4.06 (4.04), N 5.13 (5.97); IR (order of intensities): 280(1), 326(5), 436(9), 494(14), 543(11), 670(13), 770(2), 769(3), 928(11), 1027(15), 1098(12), 1139(19), 1154(20), 1211(6), 1262(7), 1577(10), 1598(8), 3295(17), 3357(16), 3374(18); NMR: ^{1}H ($CDCl_3$): 2.18 (s), 3.86 (s), 6.69 (t), 6.94 (d); Crystal Data: $C_{24.5}H_{34}Cl_7N_3Sb_2$, M = 862.20 g mol^{-1}, triclinic, P-1, a = 9.9556(7) Å, b = 10.4211(7) Å, c = 16.9114(12) Å, α = 85.8918(10)°, β = 84.9494(10)°, γ = 73.7057(9)°, V = 1675.5(2) Å^3, T = 193(2) K, Z = 2, μ(MoKα) 0.71073 (Å), Reflections; 6811 unique, 6180 observed, R (for 6180 reflections with ($I > 2\sigma(I)$)) = 0.0220; wR(all) = 0.0600.

Isolation of **6Sb** and **8Sb**: $DmpNH_2$ (4.94 mL, 39.3 mmol) added to NEt_3 (5.71 mL, 39.6 mmol) and $SbCl_3$ (6.23 g, 27.3 mmol) in toluene (110 mL) at 0 °C, stirred for 1.5 h at RT. Filtered and the solvent was removed *in vacuo* to 5 mL, addition of pentane (5 mL) gave a yellow precipitate after 4 days at −24 °C, which was dissolved in minimal CH_2Cl_2 and vapour diffusion of pentane gave a mixture of crystals (0.13 g) with two distinct morphologies and colours, manually separated. Pale yellow (< 0.02 g) **6Sb**; Crystal Data: $C_{16}H_{19}Cl_3N_2Sb_2$, M = 589.18 g mol^{-1}, Monoclinic, $P2_1/c$, a = 13.0005(9) Å, b = 20.8528(14) Å, c = 15.5863(10) Å, β = 108.9580(10)°, V = 3996.2(5) Å^3, T = 193(2) K, Z = 8, μ(MoKα) 0.71073 (Å), Reflections; 8121 unique, 7448 observed, R (for 7448 reflections with ($I > 2\sigma(I)$)) = 0.0211; wR(all) = 0.0555. Colourless (~0.10 g) **8Sb**, mp 269–271 °C; Anal. Calcd. for $C_{24}H_{27}N_3Cl_3Sb_3$ (Found): C 34.77 (31.52), H 3.28 (3.45), N 5.07 (5.25); IR: 229(5), 325(9), 373(11), 486(15), 522(8), 690(10), 707(7), 790(3), 811(2), 839(4), 901(16), 984(12), 1023(13), 1097(6), 1164(1), 1252(14), 1586(17), 1799(19), 1867(20), 1934(18); NMR: ^{1}H ($CDCl_3$): 2.60 (s, 3H), 2.66 (s, 6H), 2.69 (s, 3H), 2.74 (s, 6H), 7.02–7.17 (m, 9H); Crystal Data: $C_{24}H_{27}Cl_3N_3Sb_3$, M = 829.09 g mol^{-1}, Monoclinic, $P2_1/c$, a = 16.376(3) Å, b = 8.9041(14) Å, c = 19.122(3) Å, β = 96.817(3)°, V = 2768.6(7) Å^3, T = 193(2) K, Z = 4, μ(MoKα) 0.71073 (Å), Reflections; 5572 unique, 4468 observed, R (for 4468 reflections with ($I > 2\sigma(I)$)) = 0.0687; wR(all) = 0.1960. CCDC 271559–271561. See http://dx.doi.org/10.1039/b509481j for crystallographic data in CIF or other electronic format.

1 I. Manners, *Angew. Chem., Int. Ed.*, 1996, **35**, 1602–1621.
2 R. Keat, *Top. Curr. Chem.*, 1982, **102**, 89–116.
3 H.-J. Chen, R. C. Haltiwanger, T. G. Hill, M. L. Thompson, D. E. Coons and A. D. Norman, *Inorg. Chem.*, 1985, **24**, 4725–4730.
4 L. Stahl, *Coord. Chem. Rev.*, 2000, **210**, 203–250.
5 R. A. Shaw, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1978, **4**, 101–121.
6 N. Burford, T. S. Cameron, K. D. Conroy, B. Ellis, C. L. B. Macdonald, R. Ovans, A. D. Phillips, P. J. Ragogna and D. Walsh, *Can. J. Chem.*, 2002, **80**, 1404–1409.
7 M. S. Balakrishna, V. S. Reddy, S. S. Krishnamurthy, J. F. Nixon and J. C. T. R. Burckett St.Laurent, *Coord. Chem. Rev.*, 1994, **129**, 1–90.
8 G. A. Olah and A. A. Oswald, *Can. J. Chem.*, 1960, **38**, 1428–1430.
9 D. C. Haagenson, L. Stahl and R. J. Staples, *Inorg. Chem.*, 2001, **40**, 4491–4493.
10 R. Bohra, H. W. Roesky, M. Noltemeyer and G. M. Sheldrick, *Acta Crystallogr., Sect. C*, 1984, **40**, 1150–1152.
11 J.-T. Ahlemann, H. W. Roesky, R. Murugavel, E. Parisini, M. Noltemeyer, H.-G. Schmidt, O. Müller, R. Herbst-Irmer, L. N. Markovskii and Y. G. Shermolovich, *Chem. Ber.*, 1997, **130**, 1113–1121.
12 E. V. Avtomonov, K. Megges, X. Li, J. Lorberth, S. Wocadlo, W. Massa, K. Harms, A. V. Churakov and J. A. K. Howard, *J. Organomet. Chem.*, 1997, **544**, 79–89.
13 C. L. Raston, B. W. Skelton, V.-A. Tolhurst and A. H. White, *Dalton Trans.*, 2000, 1279–1285.
14 N. Burford, T. S. Cameron, K.-C. Lam, D. J. LeBlanc, C. L. B. Macdonald, A. D. Phillips, A. L. Rheingold, L. Stark and D. Walsh, *Can. J. Chem.*, 2001, **79**, 342–348.
15 B. Ross, J. Belz and M. Nieger, *Chem. Ber.*, 1990, **123**, 975–978.
16 R. Garbe, J. Pebler, K. Dehnicke, D. Fenske, H. Goesmann and G. Baum, *Z. Anorg. Allg. Chem.*, 1994, **620**, 592–598.

17 A. J. Edwards, N. E. Leadbeater, M. A. Paver, P. R. Raithby, C. A. Russell and D. S. Wright, *Dalton Trans.*, 1994, 1479–1482.
18 A. J. Edwards, M. A. Paver, M.-A. Rennie, P. R. Raithby, C. A. Russell and D. S. Wright, *Dalton Trans.*, 1994, 2963–2966.
19 M. A. Beswick, C. N. Harmer, A. D. Hopkins, M. A. Paver, P. R. Raithby and D. S. Wright, *Polyhedron*, 1998, **17**, 745–748.
20 R. Bryant, S. C. James, J. C. Jeffrey, N. C. Norman, A. G. Orpen and U. Weckenmann, *Dalton Trans.*, 2000, 4007–4009.
21 M. A. Beswick, B. R. Elvidge, N. Feeder, S. J. Kidd and D. S. Wright, *Chem. Commun.*, 2001, 379–380.
22 G. G. Briand, T. Chivers and M. Parvez, *Can. J. Chem.*, 2003, **81**, 169–174.
23 U. Wirringa, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Inorg. Chem.*, 1994, **33**, 4607–4608.
24 W. Zeiss and K. Barlos, *Z. Naturforsch., B*, 1979, **34**, 423–426.
25 D. A. Harvey, R. Keat and D. S. Rycroft, *Dalton Trans.*, 1983, 425–431.
26 J. Weiss and W. Eisenhuth, *Z. Naturforsch., B*, 1967, **22**, 454–455.
27 N. Burford, K. D. Conroy, J. C. Landry, P. J. Ragogna, M. Ferguson and R. McDonald, *Inorg. Chem.*, 2004, **43**, 8245–8251.
28 N. Burford, J. C. Landry, M. Ferguson and R. McDonald, *Inorg. Chem.*, 2005, **44**, 5897–5902.
29 R. Hulme and J. C. Scruton, *J. Chem. Soc. A*, 1968, 2448–2452.
30 J. M. Barendt, R. C. Haltiwanger, C. A. Squier and A. D. Norman, *Inorg. Chem.*, 1991, **30**, 2342–2349; J. M. Barendt, E. G. Bent, R. C. Haltiwanger and A. D. Norman, *Inorg. Chem.*, 1989, **28**, 2334–2339; E. G. Bent, R. Schaeffer, R. C. Haltiwanger and A. D. Norman, *Inorg. Chem.*, 1990, **29**, 2608–2613; S. A. Katz, V. S. Allured and A. D. Norman, *Inorg. Chem.*, 1994, **33**, 1762–1769; M. L. Helm, S. A. Katz, T. W. Imiolczyk, R. M. Hands and A. D. Norman, *Inorg. Chem.*, 1999, **38**, 3167–3172.

