

Cooperative effects in the complexation of anions and Lewis bases by a heteronuclear bifunctional Lewis acid†

James D. Hoefelmeyer and François P. Gabbaï*

Chemistry Department, Texas A&M University, 3255 TAMU, College Station, Texas 77843, USA.

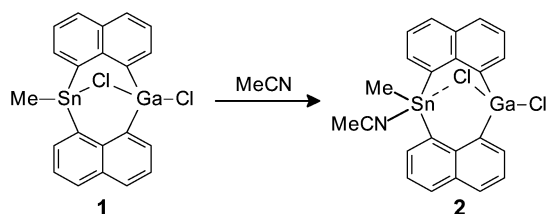
E-mail: francois@tamu.edu; Fax: +1 979 8454719; Tel: +1 979 862 2070

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As shown by the complexation of electron-rich substrates to the heteronuclear bifunctional Lewis acid bis(μ -1,8-naphthalenediyl)(μ -chloride)methyltin-chlorogallium (**1**), the primary Lewis acidic site of this molecule is the triorganotin chloride moiety whose electron deficiency is enhanced through partial abstraction of its chloride ligand by the neighbouring gallium centre.

Polyfunctional Lewis acids containing tin at the electrophilic sites have been extensively studied.^{1–6} Such compounds constitute useful receptors for anionic substrates and have been successfully incorporated into sensors.⁵ As in the case of polydentate Lewis bases, a number of molecular designs have been adopted.¹ Thus, in addition to bifunctional systems such as 1,2-distannybenzenes,² macrocyclic systems containing two, three or four Lewis acidic sites have also been investigated.^{1,3,4} While the architecture and respective location of the tin centres dictate some of the properties of these electrophilic hosts, fine-tuning of the Lewis acidity is often achieved *via* variation of the tin centre substituents. In an effort to further control the accepting properties of such systems, the incorporation of other Lewis acidic elements is now receiving attention. In particular the synthesis of complexes that combine tin and a group 13 element is attracting an increasing interest.⁷ 1-Bora-2-stannaferrocene derivatives constitute a notable recent example of such systems.⁸ As part of our contribution to this research effort, we synthesized a cyclic heteronuclear bifunctional Lewis acid containing tin and gallium linked by two naphthalenediyl ligands (**1**)^{9,10} and wish to report on the coordination chemistry of this species (Scheme 1).¹¹



Scheme 1

The reaction of equimolar quantities of 1,8-bis(trimethylstannyl)naphthalene and GaCl₃ in toluene yields **1** in a base free form.⁹ In the solid state, the ¹¹⁹Sn resonance of **1** appears at a chemical shift of δ 80 that falls in the range expected for a four-coordinate triorganotinchloride species.¹² In acetonitrile, the ¹¹⁹Sn resonance of **2** is shifted downfield to δ –102, which likely reflects the coordination of an additional ligand at tin. Upon cooling, hot solutions of **1** in acetonitrile afford colourless crystalline needles of the adduct **1**·CH₃CN (**2**) whose composition has been confirmed by elemental analysis (Scheme 1).[†] In the crystal, **2** adopts an approximate C_s-symmetry with a mirror plane containing the two metal centres and the bridging chlorine atom (Fig. 1).[‡] The two naphthalene rings are planar within

[†] Electronic supplementary information (ESI) available: synthetic and analytical results, including elemental analysis. See <http://www.rsc.org/suppdata/cc/b2/b212127a>.

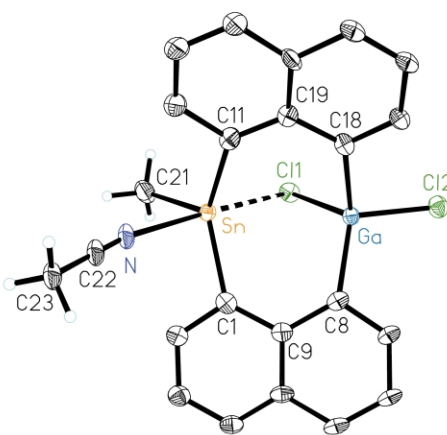
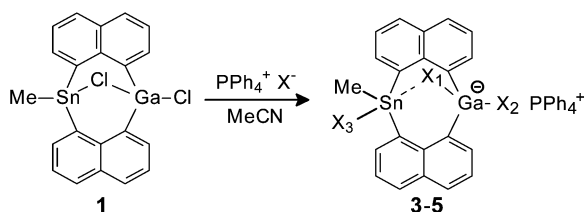


Fig. 1 Solid-state molecular structure of **2**. Hydrogen atoms on the naphthalene have been omitted for clarity. ORTEP, 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Sn–C(1) 2.125(12), Sn–C(11) 2.122(13), Sn–C(21) 2.136(11), Sn–N 2.436(9), Sn–Cl(1) 2.629(3), Ga–C(8) 1.958(12), Ga–C(18) 1.973(11), Ga–Cl(2) 2.235(3), Ga–Cl(1) 2.359(4); C(1)–Sn–C(11) 132.5(4), C(1)–Sn–C(21) 112.9(5), C(11)–Sn–C(21) 113.5(5), N–Sn–Cl(1) 177.1(3), C(8)–Ga–C(18) 134.6(5), Cl(2)–Ga–Cl(1) 103.44(12), Ga–Cl(1)–Sn 81.89(9), C(9)–C(1)–Sn 128.9(9), C(9)–C(8)–Ga 127.8(8), C(22)–N–Sn 166.1(12).

experimental error and form a dihedral angle of 143.9°. The five-coordinate tin atom adopts a distorted trigonal bipyramidal geometry as shown by the large C(1)–Sn(1)–C(21) angle of 132.5(4)°. The axial positions are occupied by the bridging chlorine and the coordinated acetonitrile molecule, which forms an Sn–N bond of 2.436(9) Å. Due to the presence of the bridging chlorine atom Cl(1), the gallium centre is four-coordinate and features a distorted tetrahedral geometry. The largest deviation from an ideal geometry occurs in the C(8)–Ga(1)–C(18) angle (134.6(5)°). It is interesting to compare the location of the bridging chlorine in **1** with that found in **2**. While in **1**, the bridging chlorine was essentially equidistant from the gallium and tin centres (Sn–Cl 2.457 Å, Ga–Cl 2.464 Å), the coordination of the acetonitrile molecule at tin in **2** forces the μ -chloride ligand to shift toward the gallium centre resulting in Ga–Cl(1) and Sn–Cl(1) bond distances of 2.359(4) Å and 2.629(3) Å, respectively. In fact, the Ga–Cl(1) bond length approaches that observed in chlorogallate anions such as trichloro(2,6-diphenylphenyl)gallate (av. Ga–Cl 2.23 Å).¹³ In one extreme, the molecule can therefore be described as a zwitterion in which a gallate and a tin cation stabilized by an acetonitrile molecule coexist.

Treatment of **1** with one equivalent of tetraphenylphosphonium chloride, bromide and iodide in hot acetonitrile results, upon cooling, in the crystallization of the corresponding anionic adduct [2·X][–] [PPh₄]⁺ (**3**, X = Cl[–]; **4**, X = Br[–]; **5**, X = I[–]) (Scheme 2).[†] The composition and structure of **3–5** has been confirmed by elemental analysis and single crystal X-ray diffraction (Fig. 2). These salts crystallize in the P2(1)/n space group and are essentially isomorphous.[‡] The structure of their anionic component resembles that of **2** and adopts an approximate C_s-symmetry with a mirror plane containing the two



Scheme 2 Formation of **3–5**. The occupancies at each halide binding sites are given in Table 1.

Table 1 Occupancies (%) at each of the halide binding sites in **3–5**

	X	X ₁	X ₂	X ₃
3	Cl	Cl (100)	Cl (100)	Cl (100)
4	Br	Cl (73), Br (27)	Cl (78), Br (22)	Cl (49), Br (51)
5	I	Cl (80), I (20)	Cl (84), I (16)	Cl (36), I (64)

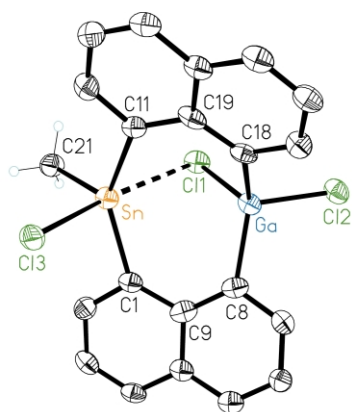


Fig. 2 Solid-state molecular structure of the anionic component of **3**. Hydrogen atoms on the naphthalene have been omitted for clarity. ORTEP, 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Sn–C(21) 2.117(6), Sn–C(11) 2.147(6), Sn–C(1) 2.156(6), Sn–Cl(3) 2.4694(15), Sn–Cl(1) 2.9088(15), Ga–C(18) 1.986(6), Ga–C(8) 1.987(6), Ga–Cl(2) 2.2305(17), Ga–Cl(1) 2.3201(16); C(21)–Sn–C(11) 109.3(2), C(21)–Sn–C(1) 108.6(2), C(11)–Sn–C(1) 140.6(2), Cl(3)–Sn–Cl(1) 172.04(5), C(18)–Ga–C(8) 126.5(2), Cl(2)–Ga–Cl(1) 103.25(6), Ga–Cl(1)–Sn 78.76(4), C(9)–C(1)–Sn 130.1(4), C(9)–C(8)–Ga 125.7(5).

metal centers and the bridging halide atom. The two naphthalene rings of **3–5** are planar within experimental error and form a dihedral angle (147.6, 147.6 and 146.4°, respectively) that only slightly exceed that encountered in **2**. The five-coordinate tin atom adopts a distorted trigonal bipyramidal geometry. The strongest angular deviation from a trigonal bipyramidal geometry occurs in the equatorial plane, as shown by the large C(1)–Sn(1)–C(11) angle (140.6(2), 140.9(2) and 140.6(2)° for **3–5**, respectively).

In **3**, inspection of the Sn–Cl(1) and Ga–Cl(1) bond lengths indicates that the shift of the bridging chloride ligand (Cl(1)) toward the gallium center is more acute than in **2**. While the Ga–Cl(1) bond (2.358(4) Å in **2**/2.320(2) Å in **3**) slightly shortens on going from **2** to **3**, the Sn–Cl(1) bond (2.629(3) Å in **2**/2.909(2) Å in **3**) undergoes noticeable elongation. With a bond length approaching 3 Å, the coordination of Cl(1) to the tin centre can only be weak. Hence, it appears appropriate to describe the anionic component of **3** as a diorganodichlorogallate anion with a weak intramolecular Sn–Cl coordination. In accordance with this view, we note that while the bridging and terminal Ga–Cl

bond distances are close (Ga–Cl(1) 2.320(2) Å/Ga–Cl(2) 2.231(2) Å), the Sn–Cl(3) bond (2.469(2) Å) formed by the terminal Cl(3) atom is much shorter than the bond formed between tin and the bridging Cl(1) atom (Sn(1)–Cl(1) 2.909(2) Å). In **4** and **5**, the two chloride ligands and the heavier halide (Br in **4**, I in **5**) are disordered over the three halide binding sites present in the molecule. At each of these sites, the disorder was modelled by refining the respective occupancy of the chloride and the heavy halide anions in split positions (Scheme 2, Table 1). It is interesting to note that the heavy halide atom shows a clear preference for the terminal halide-binding site at tin. This preference can be accounted for on the basis of the hard soft acid base principle, which would predict preferential binding of the larger halide at the soft tin centre.¹⁴ Despite the disorder, which impairs an accurate determination of the bond lengths, the anionic components of **4** and **5** are best described as gallate anions.

The results presented herein indicate that the two Lewis acidic centres of **1** cooperate in the binding of neutral and anionic electron rich substrates. This synergy arises from the presence of a bridging chloride atom by which the gallium centre transfers its Lewis acidity to the four coordinate tin centre.

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Notes and references

‡ CCDC 199217 199218 199219 and 199220. See <http://www.rsc.org/suppdata/cc/b2/b212127a/> for crystallographic data in CIF or other electronic format.

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