1826 *Organometallics* **2000,** *19,* 1826−1828

Transmetalation as a Route to a Cyclic Heteronuclear Bifunctional Lewis Acid Containing Tin and Gallium

Martin Tschinkl,† James D. Hoefelmeyer,† T. Matthew Cocker,‡
Robert E. Bachman,‡ and François P. Gabbaï*,†

*Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, and
Department of Chemistry, Georgetown University, Washington, D.C. 20057*

Received March 2, 2000

*Summary: The reaction of equimolar quantities of 1,8-bistrimethylstannylnaphthalene (**1**) and GaCl$_3$ in toluene yields a stannagallacycle, namely, bis(μ-1,8-naphthalenediyl)(μ-chloride)methyltin(IV)chlorogallium(III) (**2**). Compound **2** is insoluble in solvents of low polarity and has been characterized by EA, MSCI, and X-ray analysis. The latter revealed the existence of a folded eight-membered dimetallacycle as well as the presence of a chloride ligand bridging the two metals. When treated with pyridine, formation of a soluble bis(pyridine) adduct (**3**) occurs. Compound **3** has been characterized by EA and ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy. As shown by X-ray single-crystal analysis of **3**, the central eight-membered dimetallacycle of the molecule has remained intact on going from **2** to **3**. Compound **3** does not feature a bridging chloride, and its structure is that of a Lewis acid−Lewis base adduct in which two independent pyridine molecules coordinate the metal centers.*

Group 13 polyfunctional Lewis acids have emerged as promising compounds for the molecular recognition of anionic[1−3] and neutral guests.[4−7] Recent advances have revealed the potential of these species to activate organic substrates[8−10] and to cocatalyze olefin polymerization reactions.[11−13] In some cases, diboranes and diindanes have proved useful for the construction of supramolecular materials.[14,15] In parallel, the study of polyfunctional Lewis acids containing silicon and tin as binding sites has led to the discovery of selective halide receptors.[16−19] Interestingly, heteronuclear systems that combine a group 13 and a heavier group 14 element have received only limited attention.[20−23] This approach should, however, yield polyfunctional Lewis acids whose affinity for Lewis bases differs from that of the homonuclear systems. In this paper, we report that tin−gallium ligand exchange occurs between 1,8-bis(trimethylstannyl)naphthalene[24] (**1**) and gallium trichloride to yield a heteronuclear bifunctional Lewis acid with a central eight-membered stannagallacycle. Organotin reagents are often employed for the arylation, vinylation, and alkylation of boron halides.[22,25−27] Such reactions are not limited to boron and have been observed on a few occasions with aluminum halides.[13,28,29] To our knowledge, however, this synthetic strategy has not been previously applied to the preparation of organogallium species.[30,31]

The reaction of **1** and GaCl$_3$ in toluene at 65 °C yields after 4 h an insoluble crystalline compound (**2**) (Scheme 1) as well as Me$_2$SnCl$_2$ and Me$_3$SnCl, which could be recovered from the supernatant.[32] Compound **2** is insoluble in solvents of low polarity and readily reacts

---

* Corresponding author. E-mail: françois@tamu.edu. Fax: 979-845-4719.

† Texas A&M University.

‡ Georgetown University.

(1) Katz, H. E. *J. Org. Chem.* **1985**, *50*, 5027−5032.

(2) Tschinkl, M.; Schier, A.; Riede, J.; Gabbaï, F. P. *Inorg. Chem.* **1997**, *36*, 5706−5711.

(3) Uhl, W.; Hannemann, F. *J. Organomet. Chem.* **1999**, *579*, 18−23.

(4) Katz, H. E. *J. Org. Chem.* **1989**, *54*, 2179−2183.

(5) Nozaki, K.; Yoshida, M.; Takaya, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2043−2052.

(6) Saied, O.; Simard, M.; Wuest, J. D. *Organometallics* **1998**, *17*, 1128−1133.

(7) Gabbaï, F. P.; Schier, A.; Riede, J.; Hynes, M. J. *J. Chem. Soc., Chem. Commun.* **1998**, 897−898.

(8) Sharma, V.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1992**, *114*, 7931−7933.

(9) Hanawa, H.; Maekawara, N.; Maruoka, K. *Tetrahedron Lett.* **1999**, *40*, 8379−8382.

(10) Ooi, T.; Takahashi, M.; Maruoka, K. *J. Am. Chem. Soc.* **1996**, *118*, 11307−11308.

(11) Jia, L.; Yang, X.; Stern, C.; Marks, T. J. *Organometallics* **1994**, *13*, 3755−3767.

(12) Williams, V. C.; Dai, C.; Li, Z.; Collins, S.; Piers, W. E.; Clegg, W.; Elsegood, M. R. J.; Marder, T. B. *Angew. Chem., Int. Ed.* **1999**, *38*, 3695−3698.

(13) Eisch, J. J.; Mackenzie, K.; Windisch, H.; Krueger, C. *Eur. J. Inorg. Chem.* **1999**, 153−162.

(14) Gabbaï, F. P.; Schier, A.; Riede, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 622−624.

(15) Fontani, M.; Peters, F.; Scherer, W.; Wachter, W.; Wagner, M.; Zanello, P. *Eur. J. Inorg. Chem.* **1998**, 1453−1465.

(16) Altmann, R.; Jurkschat, K.; Schuermann, M.; Dakternieks, D.; Duthie, A. *Organometallics* **1998**, *17*, 5858−5866.

(17) Altmann, R.; Jurkschat, K.; Schuermann, M.; Dakternieks, D.; Duthie, A. *Organometallics* **1997**, *16*, 5716−5723.

(18) Horner, J. H.; Squatritto, P. J.; McGuire, N.; Riebenspies, J. P.; Newcomb, M. *Organometallics* **1991**, *10*, 1741−1750.

(19) Newcomb, M.; Horner, J. H.; Blanda, M. T.; Squattrito, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 6294−6301.

(20) Katz, H. E. *J. Am. Chem. Soc.* **1986**, *108*, 7640−7645.

(21) Wrackmeyer, B.; Dörfler, U.; Milius, W.; Herberhold, M. *Z. Naturforsch., B: Chem. Sci.* **1996**, *51*, 851−858.

(22) Eisch, J. J.; Kotowicz, B. W. *Eur. J. Inorg. Chem.* **1998**, 761−769.

(23) Jakle, F.; Lough, A. J.; Manners, I. *J. Chem. Soc., Chem. Commun.* **1999**, 453−454.

(24) Seyferth, D.; Vick, S. C. *J. Organomet. Chem.* **1977**, *141*, 173−87.

(25) Nöth, H.; Vahrenkamp, H. *J. Organomet. Chem.* **1968**, *11*, 399−405.

(26) Burch, J. E.; Gerrard, W.; Howarth, M.; Mooney, E. F. *J. Chem. Soc.* **1960**, 4916−4918.

(27) Nöth, H.; Fritz, P. *Z. Anorg. Allg. Chem.* **1963**, *322*, 297−309.

(28) Neumann, W. P.; Schick, R.; Köster, R. *Angew. Chem.* **1964**, *76*, 380.

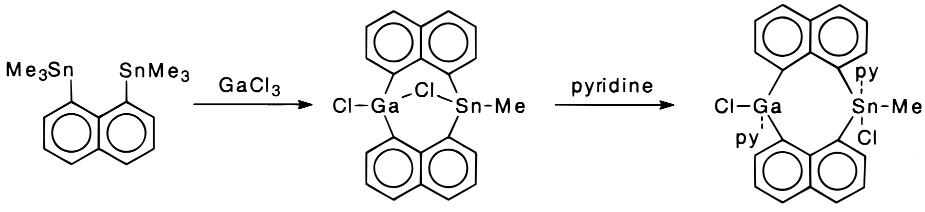
(29) Tschinkl, M.; Gabbaï, F. P.; Bachman, R. E. *J. Chem. Soc., Chem. Commun.* **1999**, 1367−1368.

(30) Ligand exchange occurs in the reaction of organosilanes with GaCl$_3$. See for example: Schmidbaur, H.; Findweiss, W. *Angew. Chem.* **1964**, *76*, 752−753.

(31) Voronkov, M. G.; Tsyrendorzhieva, I. P.; Albanov, A. I.; Shergina, N. I.; Klyba, L. V.; Dubinskaya, E. I. *Russ. J. Gen. Chem.* **1998**, *68*, 654−655.

10.1021/om0002024 CCC: $19.00

Scheme 1



1 2 3

with polar solvents such as pyridine (vide infra). While the CI mass spectrum of **2** allowed the detection of a fragment corresponding to bis(1,8-naphthalenediyl)-chlorotinchlorogallium, an X-ray analysis revealed that **2** is a stannagallacycle. While related homonuclear dimetallacycles have been isolated on several occasions,[33−36] the formation of heteronuclear systems such as **2** is a rare phenomenon and is limited to mercuraindacycles.[37] The mechanism of the reaction leading to **2** is still under investigation. The formation of tin halide species confirms, however, that ligand exchange occurs between $GaCl_3$ and **1**.

In the crystal, **2** adopts an approximate C_s-symmetry with a mirror plane containing the two metal centers and the bridging chlorine atom (Figure 1).[38] The two naphthalene rings are planar within experimental error and form a dihedral angle of 130.2°. Consequently, the central eight-membered dimetallacycle is folded so that the structure of **2** is reminiscent of a roof, with the gallium, tin, and chlorine atoms sitting on the ridge. The four-coordinate tin atom adopts a distorted tetrahedral geometry with an especially large C(1)−Sn(1)−C(21) angle (125.50(9)°). A similar deviation has been observed in the structure of the known distannacycle 7,7,14,14-tetramethyldinaphtho[1,8-*bc*:1′,8′-*fg*][1,5]-distannocine (av 127.0°).[34] The *peri*-carbon tin distances Sn(1)−C(1) (2.129(2) Å) and Sn(1)−C(21) (2.122(2) Å) are slightly shorter than those observed in 1,8-bis-(trimethylstanny)naphthalene (av 2.16 Å).[39] Due to the presence of the bridging chlorine atom Cl(1), the gallium center is four-coordinate and features a distorted tetrahedral geometry. The largest deviation from an ideal geometry occurs in the C(8)−Ga(1)−C(28) angle (129.57-(9)°). The tight geometrical constraints present in the structure of **2** induce distortions of the naphthalenediyl fragments. Especially noteworthy are the C(9)−C(1)−Sn(1) (127.25(16)°), C(9)−C(8)−Ga(1) (127.45(16)°), C(29)−C(21)−Sn(1) (126.63(16)°), and C(29)−C(28)−Ga-(1) (127.54(16)°) angles, which are larger than the ideal value of 120°. Similar distortions are encountered in the structure of sterically hindered *peri*-substituted naphthalene systems[37] such as 1,8-disilylnaphthalene[40] or 1,8-bis(trimethylstannyl)naphthalene.[39]

To assess the ability of **2** to behave as a bifunctional Lewis acid, **2** was treated with excess pyridine, which resulted in the formation of a soluble adduct (**3**) (Scheme 1).[32] The spectroscopic features of **3** suggested that the eight-membered stannagallacycle had remained intact on going from **2** to **3**. The ^1H and ^{13}C NMR spectra of **3** revealed the existence of an unsymmetrically substituted 1,8-naphthalenediyl moiety. The presence of a tin atom was confirmed by the detection of a ^{119}Sn NMR signal at −156 ppm as well as a ^1H NMR signal (1.16 ppm) flanked by pairs of $^{117}Sn/^{119}Sn$ satellites. Crystals of **3** suitable for X-ray analysis were obtained by cooling a pyridine solution to −30 °C for a period of two weeks.[38] Compound **3** does not feature a bridging chloride (Figure 2). Its structure is that of a Lewis adduct in which two independent pyridine molecules coordinate the metal centers. Its structure differs from that of **2** in several features. The eight-membered dimetallcycle is twisted, and the dihedral angle formed by the two naphthalene rings (158.6°) is much larger than in **2**. The tin center is pentacoordinate and approaches a trigonal bipyramidal geometry. The equatorial sites are occupied by the methyl group and the *peri*-carbon atoms. The coordination sphere is completed by axial ligation of the

---

(32) Synthesis of **2** and **3**. A solution of gallium trichloride (97 mg, 0.55 mmol) in toluene (1.5 mL) was added to a solution of 1,8-bis-(trimethyltin)naphthalene (250 mg, 0.55 mmol) in toluene (3 mL). The resulting solution was kept at 65 °C for 6 h, during which time the product crystallized. Yield: 55% (80 mg); mp 252−255 °C (decomp). Anal. Calcd for $C_{21}H_{15}Cl_2GaSn$: C 47.9, H 2.9. Found: C 47.3, H 2.9. Compound **2** is quantitatively converted into **3** by addition of pyridine. **3** crystallizes with 1.5 solvate pyridine molecules from a pyridine solution after 3 weeks at −30 °C, mp 55−60 °C (decomp). Upon standing at room temperature, the solvate pyridine component is lost. Anal. Calcd for $C_{31}H_{25}N_2Cl_2GaSn$: C 54.36, H 3.68. Found: C 54.66, H 3.89. ^1H NMR (pyridine-d_5): $\delta = 1.16$ (br s, $J^2{}_{H-117/119Sn} = 30/32$ Hz, 3H), 7.59 (m, 4H), 8.02 (t, 4H), 8.31/8.39 (br, 2H), 8.92 (d, 2H). ^{13}C NMR ([D_5]pyridine): $\delta = 6.7$ (s), 125.0 (s, C-3,6), 125.6 (s, C-3,6), 130.15 (s, C-4,5), 131.2 (s, C-4,5), 134.5 (s, C-2,7), 136.9 (s, C−*ipso*-Sn), 139.7 (s, C−*ipso*-Ga), 142.8 (s, C-2,7). ^{119}Sn NMR (pyridine-d_5): $\delta = -156.0$.

(33) Schmidbaur, H.; Öller, H. J.; Wilkinson, D. L.; Huber, B.; Mueller, G. *Chem. Ber.* **1989**, *122*, 31−36.

(34) Meinwald, J.; Knapp, S.; Tatsuoka, T.; Finer, J.; Clardy, J. *Tetrahedron Lett.* **1977**, 2247−2250.

(35) Tinga, M. A. G. M.; Buisman, G. J. H.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1994**, *484*, 137−145.

(36) Fujihara, H.; Yabe, M.; Chiu, J. J.; Furukawa, N. *Tetrahedron Lett.* **1991**, *32*, 4345−4348.

(37) Gabbaï, F. P.; Schier, A.; Riede, J.; Sladek, A.; Görlitzer, H. W. *Inorg. Chem.* **1997**, *36*, 5694−5698.

(38) Crystal and structure determination data for **2**: $C_{21}H_{15}Cl_2GaSn$, $M = 526.64$, monoclinic, space group $P2_1/n$, $a = 8.6968(4)$ Å, $b = 15.8714(7)$ Å, $c = 13.9556(6)$ Å, $\beta = 104.680(1)°$, $V = 1863.4(1)$ Å^3, $Z = 4$, $D_c = 1.877$ g cm^{-3}, $F(000) = 1024$, Siemens SMART-CCD area detector diffractometer, Mo Kα radiation ($\lambda = 0.71069$ Å), $T = -100$ °C. Crystal size 0.26 × 0.20 × 0.12 mm, ω-scan mode, measurement range $1.98° \le \theta \le 28.31°$, 4574 unique reflections, 3602 reflections with $I > 2\sigma(I)$, $\mu = 3.073$ mm^{-1}. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 using the SHELXTL/PC (ver. 5.10) package, 286 parameters, R1 = 0.0399, wR2 = 0.0453 (all data), max/min residual electron density 0.365/−0.510 e/Å^3. Crystal and structure determination data for **3**: $C_{38.5}H_{32.5}Cl_2Ga\,N_{3.5}Sn$, $M = 803.49$, triclinic, space group $P\bar{1}$, $a = 9.7751(6)$ Å, $b = 9.9648(6)$ Å, $c = 17.3582(11)$ Å, $\alpha = 83.7350(10)°$, $\beta = 89.6830(10)°$, $\gamma = 89.1000(10)°$, $V = 1680.49(18)$ Å^3, $Z = 2$, $D_c = 1.588$ g cm^{-3}, $F(000) = 806$, Siemens SMART-CCD area detector diffractometer, Mo Kα radiation ($\lambda = 0.71069$ Å), $T = -163$ °C. Crystal size 0.32 × 0.22 × 0.05 mm, ω-scan mode, measurement range $2.06° \le \theta \le 28.81°$, 7610 unique reflections, 6223 reflections with $I > 2\sigma(I)$, $\mu = 1.737$ mm^{-1}. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 using the SHELXTL/PC (ver. 5.10) package, 416 parameters, R1 = 0.0460, wR2 = 0.0960 (all data), max/min residual electron density 2.24/−1.114 e/Å^3.

(39) Blount, J. F.; Cozzi, F.; Damewood, J. R., Jr.; Iroff, L. D.; Sjostrand, U.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 99−103.

(40) Schröck, R.; Angermaier, K.; Sladek, A.; Schmidbaur, H. *Organometallics* **1994**, *13*, 3399−3401.

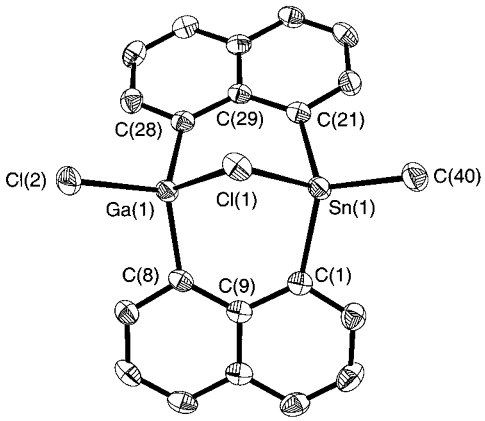


Figure 1. Structure of **2** in the crystal. Selected bond lengths (Å) and angles (deg): Sn(1)−C(40) 2.117(3), Sn(1)−C(1) 2.129(2), Sn(1)−C(21) 2.122(2), Sn(1)−Cl(1) 2.4571(6), Ga(1)−C(8) 1.966(2), Ga(1)−C(28) 1.968(2), Ga(1)−Cl(2) 2.2059(6), Ga(1)−Cl(1) 2.4645(7); C(1)−Sn(1)−C(21) 125.50(9), Cl(1)−Sn(1)−C(40) 106.01(10), C(8)−Ga(1)−C(28) 129.57(9), Cl(1)−Ga(1)−Cl(2) 98.03(2).

pyridine molecule and the chloride ligand. The strongest deviation from a trigonal bipyramidal geometry occurs in the equatorial plane, as shown by the large C(1)−Sn(1)−C(21) (144.26(12)°). The gallium center is four-coordinate and departs drastically from a tetrahedral geometry. The large C(8)−Ga(1)−C(28) angle (136.87(12)°) and the acute N(2)−Ga(1)−Cl(2) angle (94.53(8)°) are especially noteworthy. As in **2**, the naphthalendiyl fragments suffer noticeable distortions (C(9)−C(1)−Sn(1) = 130.8(2)°, C(9)−C(8)−Ga(1) = 127.5(2°), C(29)−C(21)−Sn(1) = 130.0(2)°, and C(29)−C(28)−Ga(1) = 127.7(2)°).

It is noteworthy that gallium has rarely been incorporated in polyfunctional Lewis acids.[41] The cyclization reaction leading to the formation of **2** is unexpected. Interestingly, however, Jurkschat et al. have observed that, when treated with dimethyldichlorostannane, **1** undergoes ring-closure to yield a distannacycle.[16] The stannagallacycle **2** herein reported combines a gallium and a tin center separated by approximately 3.2 Å. As demonstrated by the isolation of **3**, the complexation of a base at each Lewis acidic center occurs readily. Heteronuclear bifunctional Lewis acids containing boron and silicon as the binding sites have already shown unusual properties.[20] Current studies are centered on the use of **2** as a receptor for the cooperative binding of polyatomic anions.

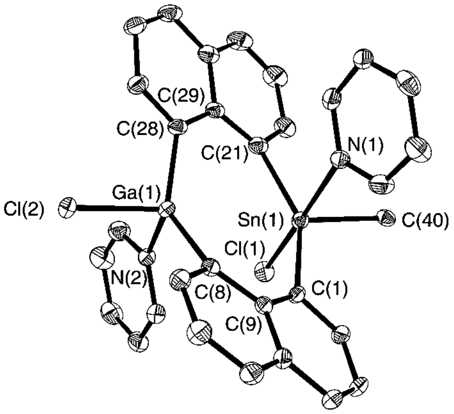


Figure 2. Structure of **3** in the crystal. Selected bond lengths (Å) and angles (deg): Sn(1)−C(40) 2.164(3), Sn(1)−C(1) 2.144(3), Sn(1)−C(21) 2.137(3), Sn(1)−Cl(1) 2.45198(8), Ga(1)−C(8) 1.984(3), Ga(1)−C(28) 1.987(3), Ga(1)−Cl(2) 2.2498(9); C(21)−Sn(1)−C(1) 144.26(12), C(21)−Sn(1)−C(40) 108.50(13), C(1)−Sn(1)−C(40) 105.78(12), N(1)−Sn(1)−Cl(1) 177.81(6), C(8)−Ga(1)−C(28) 136.87(12), N(2)−Ga(1)−Cl(2) 94.53(8).

Acknowledgment. We thank the Robert A. Welch Foundation (Grant A-1423) for generous financial support. The purchase of the CCD X-ray diffractometers was made possible by two grants from the National Science Foundation (CHE-9115394 (Georgetown University) and CHE-98 07975 (Texas A&M)).

Supporting Information Available: Tables of structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for complexes **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0002024

---

[41] Dam, M. A.; Nijbacker, T.; de Kanter, F. J. J.; Akkerman, O. S.; Bickelhaupt, F.; Spek, A. L. *Organometallics* **1999**, *18*, 1706−1709.