*Inorg. Chem.* **2008**, *47*, 9804−9812


# 24- and 26-Membered Macrocyclic Diorganotin(IV) Bis-Dithiocarbamate Complexes with *N,N′*-Disubstituted 1,3- and 1,4-Bis(aminomethyl)benzene and 1,1′-Bis(aminomethyl)ferrocene as Spacer Groups

**Ericka Santacruz-Juárez, Jorge Cruz-Huerta, Irán Fernando Hernández-Ahuactzi, Reyna Reyes-Martínez, Hugo Tlahuext, Hugo Morales-Rojas, and Herbert Höpfl***

*Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, C.P. 62209 Cuernavaca, México*

Received April 14, 2008

The potassium bis-dithiocarbamate (bis-dtc) salts of 1,3-bis(benzylaminomethyl)benzene (1,3-Bn-ambdtc), 1,3-bis(*iso*-butylaminomethyl)benzene (1,3-$^{i}$Bu-ambdtc), 1,4-bis(benzylaminomethyl)benzene (1,4-Bn-ambdtc), and 1,4-bis(*iso*-butylaminomethyl)benzene (1,4-$^{i}$Bu-ambdtc) were reacted with three different diorganotin dichlorides ($R_2SnCl_2$ with R = Me, $^{n}$Bu, and Ph) in 1:1 stoichiometric ratios to give the corresponding diorganotin bis-dithiocarbamates. Additionally, the dimethyltin bis-dithiocarbamate of 1,1′-bis(benzylaminomethyl)ferrocene (1,1′-Bn-amfdtc) was prepared. The resulting complexes have been characterized as far as possible by elemental analysis, $FAB^+$ mass spectrometry, IR and NMR ($^1$H, $^{13}$C, and $^{119}$Sn) spectroscopy, and single-crystal X-ray diffraction, showing that the tin complexes are dinuclear 24- and 26-membered macrocyclic species of composition $[\{R_2Sn(bis\text{-}dtc)\}_2]$. As shown by $^{119}$Sn NMR spectroscopy, the tin centers are hexa-coordinated in all cases; however, two different coordination environments are possible, as detected by single-crystal X-ray diffraction. In the dimethyltin derivatives of 1,3-Bn-ambdtc, 1,3-$^{i}$Bu-ambdtc, 1,4-Bn-ambdtc, and 1,1′-Bn-amfdtc and the di-*n*-butyltin derivative of 1,3-$^{i}$Bu-ambdtc, the metal atoms are embedded in skewed-trapezoidal-bipyramidal coordination polyhedra with asymmetrically coordinating trans-oriented dtc groups. In contrast, in the diphenyltin derivative 1,3-$^{i}$Bu-ambdtc, the metal centers have distorted octahedral coordination with symmetrically coordinating cis-oriented dtc functions. Thus, for the complexes derived from 1,3-Bn/$^{i}$Bu-ambdtc, two different macrocyclic structures were observed. In the dimethyl- and di-*n*-butyltin derivatives, the bridging bis-dtc ligands adopt U-shaped conformations, while in the case of the diphenyltin derivative, the conformation is L-shaped. Furthermore, two different macrocyclic ring conformations can occurr, which differ in the spatial orientation of the substituents attached to the nitrogen atoms (Bn or $^{i}$Bu). The dimethyltin derivatives of 1,4-Bn-ambdtc and 1,1′-Bn-amfdtc have cavities, in which aromatic rings are accomodated in the solid state.

## 1. Introduction

The past two decades have shown that the combination of metal ions with di- or oligofunctional ligands allows the creation of a large number of metallosupramolecular architectures having either macrocyclic, cagelike or polymeric structures.[1] A series of different applications such as selective molecular and ion recognition, separation, storage, transport, and catalysis are envisioned for these systems, and one of the main targets is the generation of discrete or infinite systems having cavities, channels, or pores.[2] The evolution of this chemistry is now getting to a point, at which the cavity

* Author to whom correspondence should be addressed. Fax: (+52) 777 329 79 97. E-mail: hhopfl@ciq.uaem.mx.

(1) For recent reviews, see: (a) Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1466. (b) Ferey, C.; Mellot-Draznieks, C; Serre, C.; Millange, F. *Acc. Chem. Res.* **2005**, *38*, 217. (c) Hosseini, M. W. *Acc. Chem. Res.* **2005**, *38*, 313. (d) Nitschke, J. R. *Acc. Chem. Res.* **2007**, *40*, 103. (e) Pitt, M. A.; Johnson, D. W. *Chem. Soc. Rev.* **2007**, *36*, 1441. (f) Thomas, J. A. *Chem. Soc. Rev.* **2007**, *36*, 856. (g) Ariga, K.; Hill, J. P.; Lee, M. V.; Vinu, A.; Charvet, R.; Acharya, S. *Sci. Technol. Adv. Mater.* **2008**, *9*, 014109 (96 pp).

(2) For recent reviews, see: (a) Rowsell, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670. (b) Sanchez, C.; Julián, B.; Belleville, P.; Popall, M. *J. Mater. Chem.* **2005**, *15*, 3559. (c) Mueller, U.; Schubert, M.; Teich, F.; Puetter, H.; Schierle-Arndt, K.; Pastré, J. *J. Mater. Chem.* **2006**, *16*, 626.



10.1021/ic801464s CCC: $40.75 
Published on Web 10/01/2008

properties—size, shape, and functionality—can be tuned.[3] Possible sites for modifications in this respect are the metal centers, the metal-coordinating functions, the spacer groups between the coordinating donor atoms, and additional substituents located in the interior or at the periphery of the cavity. To reduce the synthetic effort required for this purpose to a minimum, it is important to develop metal−ligand assemblies, in which as many as possible of the above-mentioned parameters can be easily modified.

The vast majority of metallosupramolecular assemblies are constructed from ligands having nitrogen or oxygen as metal-coordinating donors.[1] Recently, the research groups of Tiekink and Beer have shown that architectures based on sulphur-containing ligands, in particular bis- and tris-dithiocarbamate ligands, are an excellent alternative choice for this purpose that merit further exploration.[4] Important differences from conventional oxygen- and nitrogen-containing ligands, such as amines, carboxylates, sulfonates, and phosphonates, arise from the formation of frequently strong, but less polar metal−sulfur bonds, which enhances the solubility of the resulting metal complexes in organic solvents and provides them with lipophilic cavities. Furthermore, using secondary amine precursors, it is possible to introduce a variety of additional substituents in dithiocarbamates.

So far, little is known about assemblies derived from organometallic building blocks, albeit they have the advantage that the organic substituents provide a further, easily accessible site for modifications of the molecular properties. The number of feasible candidates for such an application is quite reduced, first, because the building blocks should have metal−carbon bonds of reasonable stability from a kinetic and thermodynamic point of view and, second, because the organometallic entities should have a metal center large enough for combination with chelating ligand functions, since these provide stronger metal−ligand interactions.[5] Organotin moieties fullfill both requirements and are therefore ideal candidates.

Although there are several reports on macrocyclic or cagelike organotin systems with monofunctional ligands such as carboxylates, phosphates, phosphonates, and so forth,[5b,d−f] assemblies obtained from $R_{4-n}Sn(IV)$ groups and di- or oligofunctional organic ligands are rare so far and deal principally with ligands containing carboxylate functions.[6,7] With diorganotin moieties, macrocycles with sulphur-containing ligands have been explored previously mainly by the research groups of Lockhart, Gielen, and Ma.[8,9] Although the chemistry of organotin dithiocarbamate complexes has been widely explored,[10] for macrocyclic organotin bis(dithiocarbamates), there are only three reports.[9] Two date from 1986 and describe the molecular structures of $[R_2Sn(endtc)]$[9a] and $[R'_2Sn(1,3\text{-}pdtc)]$[9b] [with endtc = 1,2-ethylenebis(dithiocarbamate); 1,3-pdtc = 1,3-phenylenebis(dithiocarbamate); R = $^t$Bu, Ph, and R′ = Me, Cy, $^n$Bu]. The third dates from 2008 and describes the 26-membered macrocycles $[R_2Sn(1,6\text{-}Bn\text{-}hmdtc)]$[9c] (with 1,6-Bn-hmdtc = *N*,*N*′-dibenzyl-1,6-hexamethylenebis(dithiocarbamate); R = Me, $^n$Bu).[9c]

Herein, we report on the preparation and structural characterization of a further 13 diorganotin(IV) bis(dithiocarbamates) with 24- and 26-membered macrocyclic structures, which have been obtained from 1,3- and 1,4-bis(aminomethyl)benzene and 1,1′-bis(aminomethyl)ferrocene as spacer groups.

## 2. Experimental Section

**Instrumental.** NMR studies were carried out with Varian Gemini 200 and Varian Inova 400 instruments. Standard references were used: TMS ($\delta^1H = 0$ and $\delta^{13}C = 0$) and $SnMe_4$ ($\delta^{119}Sn = 0$). IR spectra have been recorded on a Bruker Vector 22 FT spectrophotometer. Mass spectra were obtained on a Jeol JMS 700 instrument. Elemental analyses have been carried out on Perkin Elmer Series


(3) (a) Eddahoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469. (b) Li, C.-J.; Hu, S.; Li, W.; Lam, C.-K.; Zheng, Y.-Z.; Tong, M.-L. *Eur. J. Inorg. Chem.* **2006**, 1931. (c) Sudik, A. C.; Cote, A. P.; Wong-Foy, A. G.; O′Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 2529.

(4) For reviews, see: (a) Tiekink, E. R. T. *CrystEngComm* **2003**, *5*, 101. (b) Cookson, J.; Beer, P. D. *Dalton Trans.* **2007**, 1459. (c) Tiekink, E. R. T. *Appl. Organomet. Chem.* **2008**, *22*, 533.

(5) For reviews on macrocyclic and supramolecular assemblies based on organometallic species of main group elements, see: (a) Uhl, W. *Chem. Soc. Rev.* **2000**, *29*, 259. (b) Haiduc, I.; Edelmann, F. T. *Supramolecular Organometallic Chemistry*; Wiley-VCH: Weinheim, Germany, 2000. (c) Höpfl, H. *Structure and Bonding*; Roesky, H. W., Atwood, D. A., Eds.; Springer Verlag: Berlin, 2002; Vol. *103*, pp 1−56. (d) Chandrasekhar, V.; Nagendran, S.; Baskar, V. *Coord. Chem. Rev.* **2002**, *235*, 1. (e) Chandrasekhar, V.; Gopal, K.; Thilagar, P. *Acc. Chem. Res.* **2007**, *40*, 420. (f) Höpfl, H. In *Tin Chemistry: Fundamentals, Frontiers and Applications*; Davies, A. G., Gielen, M., Panell, K. H., Tiekink, E. R. T., Eds.; Wiley: Chichester, UK, 2008; pp 117–137. (g) Chandrasekhar, V.; Singh, P.; Gopal, K. In *Tin Chemistry: Fundamentals, Frontiers and Applications*; Davies, A. G., Gielen, M., Panell, K. H., Tiekink, E. R. T., Eds.; Wiley: Chichester, UK, 2008; pp 93–116.

(6) (a) Pettinari, C.; Marchetti, F.; Pettinari, R.; Martini, D.; Drozdov, A.; Troyanov, S. *J. Chem. Soc., Dalton Trans.* **2001**, 1790. (b) Beltran, H.I.; Zamudio-Rivera, L.S.; Mancilla, T.; Santillan, R.; Farfan, N *Chem.—Eur. J.* **2003**, *9*, 2291. (c) Prabusankar, G.; Murugavel, R. *Organometallics* **2004**, *23*, 5644. (d) Baul, T. S. B.; Singh, K. S.; Lycka, A.; Holcapek, M.; Linden, A. *J. Organomet. Chem.* **2005**, *690*, 1581. (e) Baul, T. S. B.; Masharing, C.; Willem, R.; Biesemans, M.; Holcapek, M.; Jirasko, R.; Linden, A. *J. Organomet. Chem.* **2005**, *690*, 3080. (f) Baul, T. S. B.; Singh, K. S.; Holcapek, M.; Jirasko, R.; Rivarola, E.; Linden, A. *J. Organomet.Chem.* **2005**, *690*, 4232. (g) Ma, C.; Li, J.; Zhang, R.; Wang, D. *Inorg. Chim. Acta* **2005**, *358*, 4575. (h) Bowen, R. J.; Caddy, J.; Fernandes, M. A.; Layh, M.; Mamo, M. A.; Meijboom, R. *J. Organomet. Chem.* **2006**, *691*, 717. (i) Chandrasekhar, V.; Thirumoorthi, R. *Organometallics* **2007**, *26*, 5415.

(7) (a) Garcia-Zarracino, R.; Ramos-Quiñones, J.; Höpfl, H. *Inorg. Chem.* **2003**, *42*, 3835. (b) Garcia-Zarracino, R.; Höpfl, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 1507. (c) Zamudio-Rivera, L. S.; George-Tellez, R.; Lopez-Mendoza, G.; Morales-Pacheco, A.; Flores, E.; Höpfl, H.; Barba, V.; Fernandez, F. J.; Cabirol, N.; Beltran, H. I. *Inorg. Chem.* **2005**, *44*, 5370. (d) Garcia-Zarracino, R.; Höpfl, H. *J. Am. Chem. Soc.* **2005**, *127*, 3120. (e) Hernandez-Ahuactzi, I. F.; Cruz-Huerta, J.; Barba, V.; Höpfl, H.; Zamudio-Rivera, L. S.; Beltran, H. I. *Eur. J. Inorg. Chem.* **2008**, 1200.

(8) (a) Lockhart, T. P. *Organometallics* **1988**, *7*, 1438. (b) Meunier-Piret, J.; Boualam, M.; Willem, R.; Gielen, M. *Main Group Met. Chem.* **1993**, *16*, 329. (c) Ma, C.; Jiang, Q.; Zhang, R. *J. Organomet. Chem.* **2003**, *678*, 148. (d) Ma, C.; Han, Y.; Zhang, R.; Wang, D. *Dalton Trans.* **2004**, 1832. (e) Ma, C.; Jiang, Q.; Zhang, R. *Can. J. Chem.* **2004**, *82*, 608. (f) Ma, C.; Zhang, Q.; Zhang, R.; Wang, D. *Chem.—Eur. J.* **2006**, *12*, 420.

(9) (a) Jung, O.-S.; Sohn, Y. S.; Ibers, J. A. *Inorg. Chem.* **1986**, *25*, 2273. (b) Lee, W. H.; Jung, O.-S.; Sohn, Y. S.; Kim, P. *Bull. Korean Chem. Soc.* **1986**, *7*, 421. (c) Reyes-Martínez, R.; Mejia-Huicochea, R.; Guerrero-Alvarez, A. A.; Höpfl, H.; Tlahuext, H. *Arkivoc* **2008**, *V*, 19.

(10) Heard, P. J. Main Group Dithiocarbamate Complexes. In *Progress in Inorganic Chemistry*; John Wiley & Sons, New Jersey, 2005; Vol. *53*, pp 1−70.

II 2400 and Elementar Vario ELIII instruments, using samples that have been dried previously at 65 °C for 2 h in an Abderhalden instrument.

**Preparative Part.** Benzylamine, *iso*-butylamine, isophthaldehyde, terephthaldehyde, 1,1′-ferrocenedicarboxaldehyde, $Me_2SnCl_2$, $^nBu_2SnCl_2$, and $Ph_2SnCl_2$ were commercially available and have been used without further purification. The dialdehydes were reacted in one-pot syntheses with benzylamine/*iso*-butylamine and sodium borohydride to give the *N*,*N*′-disubstituted 1,3-bis(aminomethyl)benzene, 1,4-bis(aminomethyl)benzene, and 1,1′-bis(aminomethyl)ferrocene ligands in quantitative yields. For the preparation of the diorganotin compounds **1**−**13**, the same synthetic procedure has been used, which is therefore given in detail only for compound **1**.

**[{Me$_2$Sn(1,3-Bn-ambdtc)}$_2$] (1).** 1,3-Bis(benzylaminomethyl) benzene (0.100 g, 0.32 mmol), triethylamine (0.09 mL, 0.64 mmol), and carbon disulfide (0.95 mL, 15.8 mmol) were dissolved in methanol (25 mL) and stirred for 2 h, whereupon dimethyltin dichloride (0.070 g, 0.32 mmol) dissolved in 10 mL of methanol was added. The mixture was stirred for 2 h. A white powder precipitated that was filtered and recrystallized from a mixture of dichloromethane and benzene. Yield: 0.133 g (70%). Mp: 177−179 °C. IR (KBr): $\tilde{\nu}$ 3027 (w), 2917 (w), 1604 (w), 1463 $\nu$(N-CSS) (m), 1412 (m), 1352 (w), 1215 (m), 1154 (w), 1085 (w), 994 $\nu_{as}$(CSS) (w), 787 (w), 741 (w), 692 (w), 623 (w), 558 (w), 521 (w) cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 1.77 (s, 12H, $^2J_{Sn-H}$ = 79 Hz, Sn-*CH*$_3$), 5.01 (m, 16 H, $NCH_2$), 7.02 (dd, 4H, 4-H, 6-H), 7.26−7.39 (m, 24H, 2-H, 5-H, $C_6H_5$). $^{13}$C NMR (100 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 16.6 (Sn-*CH*$_3$), 55.7, 56.0 ($NCH_2$), 123.7 (C-2), 127.6 (C-p), 127.9 (C-m), 128.1 (C-4, C-6), 129.0 (C-o), 129.1 (C-5), 135.2, 136.2 (C-1, C-3, C-i), 203.1 (CSS). $^{119}$Sn NMR (74.5 MHz, $CDCl_3$, $SnMe_4$, 20 °C): $\delta$ −335.7. MS (FAB$^+$): *m*/*z* (%) 1231 ([*M* + H]$^+$, 10), 1215 ([*M* − $CH_3$]$^+$, 13). Anal. Calcd for $C_{52}H_{56}N_4S_8Sn_2 \cdot 2C_6H_6$ (1387.19): C, 55.41; H, 4.94; N, 4.04. Found: C, 55.02; H, 4.95; N, 4.31.

**[{$^n$Bu$_2$Sn(1,3-Bn-ambdtc)}$_2$] (2).** Yield: 75%. Mp: 152−154 °C. IR (KBr): $\tilde{\nu}$ 3028 (w), 2921 (m), 2859 (w), 1620 (w), 1462 $\nu$(N-CSS) (s), 1408 (m), 1352 (w), 1273 (w), 1212 (m), 1150 (m), 986 $\nu_{as}$(CSS) (m), 879 (w), 694 (m), 629 (w), 562 (w) cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 1.02 (t, 12H, $\delta$-H), 1.52−1.60 (m, 8H, $\gamma$-H), 2.05−2.09 (m, 8H, $\beta$-H), 2.22−2.28 (m, 8H, α-H), 5.08 (br, s, 16H, $NCH_2$), 7.23−7.37 (m, 28H, aromatic hydrogens). $^{119}$Sn NMR (74.5 MHz, $CDCl_3$, $SnMe_4$, 20 °C): $\delta$ −338.2. MS (FAB$^+$): *m*/*z* (%) 1399 ([*M* + H]$^+$, 18), 1341 ([*M* − $^n$Bu]$^+$, 60). Anal. calcd for $C_{64}H_{80}N_4S_8Sn_2$ (1399.29): C, 54.93; H, 5.76; N, 4.00. Found: C, 55.35; H, 5.70; N, 4.22.

**[{Ph$_2$Sn(1,3-Bn-ambdtc)}$_2$] (3).** Yield: 70%. Mp: 107−109 °C. IR (KBr): $\tilde{\nu}$ 3028 (w), 2915 (w), 1711 (w), 1605 (w), 1493 (w), 1469 $\nu$(N−CSS) (m), 1451 (m), 1411 (m), 1355 (m), 1215 (s), 1150 (m), 1078 (w), 977 $\nu_{as}$(CSS) (m), 789 (m), 734 (w), 699 (m), 626 (w), 555 (w), 516 (w) cm$^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 4.96 (s, 16H, $NCH_2$), 6.92−7.26 (m, 40H, aromatic hydrogens), 7.90 (d, 8H, o-H). $^{13}$C NMR (50 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 56.9, 57.5 ($NCH_2$), 127.5, 127.9, 128.2, 128.4, 129.0, 129.1 (C-2, C-4, C-5, C-6, C-o, C-m, C-p, $C_{Sn}$-m, $C_{Sn}$-p), 134.4, 134.6, 135.6 (C-1, C-3, C-i, $C_{Sn}$-o), 150.9 ($C_{Sn}$-i), 202.3 (CSS). $^{119}$Sn NMR (74.5 MHz, $CDCl_3$, $SnMe_4$, 20 °C): $\delta$ −491.0. MS (FAB$^+$): *m*/*z* (%) 1402 ([*M* − Ph]$^+$, 1), 1047 (21), 663 ([*M* − 2Ph]$^{2+}$, 72). Anal. calcd for $C_{72}H_{64}N_4S_8Sn_2$ (1479.25): C, 58.46; H, 4.36; N, 3.79. Found: C, 58.72; H, 4.71; N, 4.04.

**[{Me$_2$Sn(1,3-$^i$Bu-ambdtc)}$_2$] (4).** Yield: 83%. Mp: 232−234 °C. IR (KBr): $\tilde{\nu}$ 2959 (m), 2926 (m), 2870 (w), 1611 (w), 1470 $\nu$(N-CSS) (s), 1416 (m), 1350 (w), 1280 (w), 1228 (m), 1179 (m), 1116 (m), 993 $\nu_{as}$(CSS) (m), 879 (w), 790 (m), 700 (w), 608 (w), 556 (w) cm$^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 0.94 (d, 24H, CH-*CH*$_3$), 1.63 (s, 12H, $^2J_{Sn-H}$ = 84 Hz, Sn-*CH*$_3$), 2.35 (m, 4H, *CH*-$CH_3$), 3.59 (br, s, 8H, *CH*$_2$$^i$Pr), 5.10 (br, s, 8H, N*CH*$_2$$C_6H_4$), 7.08 (m, 6H, 2-H, 4-H, 6-H), 7.33 (t, 2H, 5-H). $^{13}$C NMR (50 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 16.1 (Sn-*CH*$_3$), 20.6 (CH-*CH*$_3$), 27.4 (*CH*-$CH_3$), 57.7 (*CH*$_2$$^i$Pr), 60.3 (N*CH*$_2$$C_6H_4$), 123.5 (C-2), 127.2 (C-4, C-6), 129.0 (C-5), 136.4 (C-1, C-3), 202.4 (CSS). $^{119}$Sn NMR (149 MHz, $CDCl_3$, $SnMe_4$, 20 °C): $\delta$ −339.3. MS (FAB$^+$): *m*/*z* (%) 1095 ([*M* + H]$^+$, 5), 1079 ([*M* − $CH_3$]$^+$, 6). Anal. calcd for $C_{40}H_{62}N_4S_8Sn_2$ (1094.90): C, 43.88; H, 5.89; N, 5.12. Found: C, 43.63; H, 5.78; N, 5.15.

**[{$^n$Bu$_2$Sn(1,3-$^i$Bu-ambdtc)}$_2$] (5).** Yield: 78%. Mp: 157−159 °C. IR (KBr): $\tilde{\nu}$ 2958 (m), 2921 (m), 2865 (w), 1609 (w), 1467 $\nu$(N-CSS) (s), 1416 (m), 1347 (w), 1281 (w), 1230 (m), 1179 (m), 1117 (m), 994 $\nu_{as}$(CSS) (w), 875 (w), 693 (w), 608 (w) ppm. $^1$H NMR (200 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 0.93 (m, 36H, CH-*CH*$_3$, $\delta$-H), 1.45 (m, 8H, $\gamma$-H), 1.96 (m, 8H, $\beta$-H), 2.12 (m, 8H, α-H), 2.34 (m, 4H, *CH*-$CH_3$), 3.63 (d, 8H, *CH*$_2$$^i$Pr), 5.20 (s, 8H, N*CH*$_2$$C_6H_4$), 7.07−7.20 (m, 6H, 2-H, 4-H, 6-H), 7.32 (t, 2H, 5-H). $^{13}$C NMR (50 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 14.2 (C-$\delta$), 20.4 (CH-*CH*$_3$), 26.6, 26.7 (*CH*-$CH_3$, C-$\gamma$), 29.0 (C-$\beta$), 34.7 (C-α), 57.6 (*CH*$_2$$^i$Pr), 60.5 (N*CH*$_2$$C_6H_4$), 123.2 (C-2), 126.5, 127.2 (C-4, C-6), 129.3 (C-5), 136.1, 136.5 (C-1, C-3), 203.1 (CSS). $^{119}$Sn NMR (74.5 MHz, $CDCl_3$, $SnMe_4$, 20 °C): $\delta$ −340.6. MS (FAB$^+$): *m*/*z* (%) 1263 ([*M* + H]$^+$, 1), 1205 ([*M* − $^n$Bu]$^+$, 2). Anal. calcd for $C_{52}H_{88}N_2S_8Sn_2$ (1263.22): C, 49.44; H, 7.02; N, 4.44. Found: C, 49.32; H, 7.58; N, 4.29.

**[{Ph$_2$Sn(1,3-$^i$Bu-ambdtc)}$_2$] (6).** Yield: 82%. Mp: 144−147 °C. IR (KBr): $\tilde{\nu}$ 3051 (w), 2957 (m), 2611 (w), 2494 (w), 1623 (w), 1479 $\nu$(N-CSS) (s), 1422 (m), 1348 (w), 1233 (m), 1176 (m), 1114 (m), 983 $\nu_{as}$(CSS) (m), 730 (m), 693 (m), 611 (w), 451 (w) cm$^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 0.92 (d, 24H, CH-*CH*$_3$), 2.25 (m, 4H, *CH*-$CH_3$), 3.50 (d, 8H, *CH*$_2$$^i$Pr), 5.01 (s, 8H, N*CH*$_2$$C_6H_4$), 7.10−7.35 (m, 20H, 2-H, 4-H, 5-H, 6-H, m-H, p-H), 7.88 (m, 8H, $^3J_{Sn-H}$ = 77 Hz, o-H). $^{13}$C NMR (50 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 20.4 (CH-*CH*$_3$), 27.3 (*CH*-$CH_3$), 58.7 (*CH*$_2$$^i$Pr), 61.8 (N*CH*$_2$$C_6H_4$), 121.8 (C-2), 125.9 (C4, C-6), 126.9 (C-p), 128.2 (C-m), 129.5 (C-5), 134.2 (C-o), 135.5 (C-1, C-3), 151.6 (C-i), 201.9 (CSS). $^{119}$Sn NMR (74.5 MHz, $CDCl_3$, $SnMe_4$, 20 °C): $\delta$ −499.6. MS (FAB$^+$): *m*/*z* (%) 1343 ([*M* + H]$^+$, 1), 1265 ([*M* − Ph]$^+$, 2). Anal. calcd for $C_{60}H_{72}N_2S_8Sn_2$ (1343.18): C, 53.65; H, 5.40; N, 4.17. Found: C, 53.69; H, 5.73; N, 4.41.

**[{Me$_2$Sn(1,4-Bn-ambdtc)}$_2$] (7).** Yield: 75%. Mp: 128−130 °C (dec.). IR (KBr): $\tilde{\nu}$ 3028 (w), 2917 (w), 1606 (w), 1512 (w), 1494 (w), 1470 $\nu$(N-CSS) (s), 1452 (m), 1408 (s), 1354 (m), 1270 (w), 1217 (s), 1151 (m), 1078 (w), 976 $\nu_{as}$(CSS) (m), 937 (w), 790 (m), 733 (w), 698 (m), 606 (w), 554 (w) cm$^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta$ 1.60 (s, 12H, $^2J_{Sn-H}$ = 81 Hz, Sn-*CH*$_3$), 5.00 (br, s, 16H, $NCH_2$), 7.19−7.35 (m, 28H, aromatic hydrogens). $^{119}$Sn NMR (74.5 MHz, $CDCl_3$, $SnMe_4$, 20 °C): $\delta$ −338.4. MS (FAB$^+$): *m*/*z* (%) 1231 ([*M* + H]$^+$, 5), 1215 ([*M* − $CH_3$]$^+$, 6). Anal. calcd for $C_{52}H_{56}N_4S_8Sn_2$ (1230.97): C, 50.74; H, 4.59; N, 4.55. Found: C, 50.57; H, 5.10; N, 4.96.

**[{$^n$Bu$_2$Sn(1,4-Bn-ambdtc)}$_2$] (8).** Yield: 75%. Mp: 158−159 °C. IR (KBr): $\tilde{\nu}$ 3029 (w), 2955 (m), 2922 (m), 2854 (w), 1638 (w), 1512 (w), 1494 (w), 1468 $\nu$(N-CSS) (s), 1408 (s), 1353 (m), 1216 (s), 1150 (m), 1078 (w), 976 $\nu_{as}$(N-CSS) (m), 876 (w), 732 (m), 697 (s), 605 (m) 554 (m) cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 0.94 (t, 12H, $\delta$-H), 1.47 (m, 8H, $\gamma$-H), 1.99 (m, 8H, $\beta$-H), 2.15 (m, 8H, α-H), 5.01 (s, 16H, $NCH_2$), 7.20−7.26 (m, 28H, aromatic hydrogens). $^{13}$C NMR (50 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 14.2 (C-$\delta$), 26.7 (C-$\gamma$), 29.0 (C-$\beta$), 35.0 (C-α), 55.6, 56.0 ($NCH_2$),

127.8 (C-p), 128.0, 128.2, 128.9 (C-2, C-3, C-5, C-6, C-o, C-m), 135.2, 135.3 (C-1, C-4, C-i), 203.6 (SCS). $^{119}$Sn NMR (74.5 MHz, $CDCl_3$, $SnMe_4$, 20 °C): $\delta$ −339.0. MS (FAB$^+$): *m/z* (%) 1399 ([*M* + H]$^+$, 2), 1341 ([*M* − $^n$Bu]$^+$, 5). Anal. calcd for $C_{64}H_{80}N_4S_8Sn_2$ (1399.29): C, 54.93; H, 5.76; N, 4.00. Found: C, 54.37; H, 5.93; N, 4.31.

**[{$Ph_2Sn$(1,4-Bn-ambdtc)}$_2$] (9).** Yield: 76%. Mp: 196−198 °C. IR (KBr): $\tilde{\nu}$ 3059 (w), 2960 (m), 2928 (w), 2870 (w), 1637 (w), 1478 $\nu$(N-CSS) (m), 1428 (w), 1414 (w), 1388 (w), 1353 (w), 1271 (w), 1230 (w), 1174 (w), 1115 (w), 1065 (w), 1019 (w), 981 $\nu_{as}$(CSS) (w), 729 (w), 694 (w) 608 (w), 450 (w) cm$^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 4.79, 4.85 (s, 16H, $NCH_2$), 6.95−7.34 (m, 40H, aromatic hydrogens), 7.98 (m, 8H, o-H). $^{119}$Sn NMR (74.5 MHz, $CDCl_3$, $SnMe_4$, 20 °C): $\delta$ −495.8. MS (FAB$^+$): *m/z* (%) 1265 (5). Anal. calcd for $C_{72}H_{64}N_4S_8Sn_2$ (1479.25): C, 58.46; H, 4.36; N, 3.79. Found: C, 58.76; H, 4.71; N, 4.51.

**[{$Me_2$Sn(1,4-$^i$Bu-ambdtc)}$_2$] (10).** Yield: 70%. Mp: 114−116 °C. IR (KBr): $\tilde{\nu}$ 2959 (w), 1628 (w), 1471 $\nu$(N-CSS) (s), 1414 (m), 1350 (w), 1277 (w), 1231 (m), 1176 (m), 1116 (w), 985 $\nu_{as}$(CSS) (m), 790 (m), 611 (w), 553 (w) cm$^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 0.95 (d, 24H, CH-$CH_3$), 1.58 (br, s, 12H, $^2J_{Sn-H}$ = 82 Hz, Sn-$CH_3$), 2.34 (m, 4H, $CH$-$CH_3$), 3.59 (d, 8H, $J$ = 7.0 Hz, $CH_2$$^i$Pr), 5.18 (s, 8H, $NCH_2C_6H_4$) 7.24 (s, 8H, 2-H, 3-H, 5-H, 6-H). $^{13}$C NMR (50 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 16.4 (Sn-$CH_3$), 20.5 (CH-$CH_3$), 27.4 ($CH$-$CH_3$), 57.5 ($CH_2$$^i$Pr), 60.6 ($NCH_2C_6H_4$), 127.9 (C-2, C-3, C-5, C-6), 134.9 (C-1, C-4), 202.3 (CSS). $^{119}$Sn NMR (74.5 MHz, $CDCl_3$, $SnMe_4$, 20 °C): $\delta$ −339.3. MS (FAB$^+$): *m/z* (%) 1095 ([*M* + H]$^+$, 12), 1079 ([*M* − $CH_3$]$^+$, 18). High resolution MS (FAB$^+$) for $C_{40}H_{63}N_4S_8Sn_2$ ([*M*+H]$^+$): *m/z* (%) 1095.0681 (20). Error: −16.6 ppm. Anal. calcd for $C_{40}H_{62}N_4S_8Sn_2$ (1094.90): C, 43.88; H, 5.89; N, 5.12. Found: C, 43.63; H, 5.78; N, 5.15.

**[{$^n$$Bu_2$Sn(1,4-$^i$Bu-ambdtc)}$_2$] (11).** Yield: 75%. Mp: 214−216 °C. IR (KBr): $\tilde{\nu}$ 2957 (m), 2921 (m), 2866 (w), 1628 (w), 1468 $\nu$(N-CSS) (s), 1412 (m), 1348 (w), 1277 (w), 1229 (m), 1176 (m), 1114 (m), 984 $\nu_{as}$(CSS) (w), 876 (w), 687 (w), 609 (w) cm$^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 0.96 (d, 24H, CH-$CH_3$, $\delta$-H), 1.47 (m, 8H, $\gamma$-H), 1.95 (br, m, 8H, $\beta$-H), 2.09 (br, m, 8H, α-H), 2.34 (m, 4H, $CH$-$CH_3$), 3.62 (d, 8H, $CH_2$$^i$Pr), 5.21 (s, 8H, $NCH_2C_6H_4$), 7.23 (s, 8H, 2-H, 3-H, 5-H, 6-H). $^{13}$C NMR (50 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 14.2 (C-$\delta$), 20.4 (CH-$CH_3$), 26.6 (C-$\gamma$), 27.3 ($CH$-$CH_3$), 28.8 (C-$\beta$), 34.7 (C-α), 57.3 ($CH_2$$^i$Pr), 60.4 ($NCH_2C_6H_4$), 127.8 (C-2, C-3, C-5, C-6), 135.0 (C-1, C-4), 203.1 (CSS). $^{119}$Sn NMR (74.5 MHz, $CDCl_3$, $SnMe_4$, 20 °C): $\delta$ −340.1. MS (FAB$^+$): *m/z* (%) 1263 ([*M* + H]$^+$, 2), 1205 ([*M* − $^n$Bu]$^+$, 5). Anal. calcd for $C_{52}H_{88}N_2S_8Sn_2$ (1263.22): C, 49.44; H, 7.02; N, 4.44. Found: C, 49.34; H, 7.32; N, 4.29.

**[{$Ph_2$Sn(1,4-$^i$Bu-ambdtc)}$_2$] (12).** Yield: 83%. Mp: 215−217 °C. IR (KBr): $\tilde{\nu}$ 3055 (m), 2960 (m), 2923 (m), 2867 (m), 1572 (w), 1480 $\nu$(N-CSS) (s), 1418 (s), 1346 (m), 1274 (w), 1230 (s), 1174 (s), 1113 (s), 1061 (m), 1019 (w), 976 $\nu_{as}$(CSS) (w), 949 (m), 808 (w), 755 (m), 728 (s), 692 (m), 608 (m), 544 (w), 446 (m) cm$^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 0.92 (d, 24H, CH-$CH_3$), 2.28 (m, 4H, $CH$-$CH_3$), 3.51 (d, 8H, $CH_2$$^i$Pr), 5.05 (br, s, 8H, $NCH_2C_6H_4$), 7.06−7.34 (m, 20H, 2-H, 3-H, 5-H, 6-H, m-H, p-H), 7.91 (d, 8H, $^3J_{Sn-H}$ = 84 Hz, o-H). $^{13}$C NMR (200 MHz, $CDCl_3$): $\delta$ 20.4 (CH-$CH_3$), 27.4 ($CH$-$CH_3$), 58.6 ($CH_2$$^i$Pr), 61.6 ($NCH_2C_6H_4$), 127.9 (C-2, C-3, C-5, C-6, C-p), 128.3 (C-m), 134.2 (C-o), 151.4 (C-i), 201.7 (CSS). $^{119}$Sn NMR (74.5 MHz, $CDCl_3$, $SnMe_4$, 20 °C): $\delta$ −494.6. MS (FAB$^+$): *m/z* (%) 1265 ([*M* − Ph]$^+$, 1). Anal. calcd for $C_{60}H_{72}N_2S_8Sn_2$ (1343.18): C, 53.65; H, 5.40; N, 4.17. Found: C, 53.46; H, 5.88; N, 4.43.

**[{$Me_2$Sn(1,1′-Bn-amfdtc)}$_2$] (13).** Yield: 64%. Mp: 180−182 °C (dec.). IR (KBr): $\tilde{\nu}$ 3085 (w), 3028 (w), 2916 (w), 1630 (w), 1471 $\nu$(N-CSS) (s), 1418 (m), 1352 (m), 1267 (m), 1234 (m), 1198 (s), 1136 (m), 1076 (w), 1032 (m), 989 $\nu_{as}$(CSS) (w), 923 (w), 875 (w), 790 (m), 732 (m), 691 (m), 628 (w), 579 (w), 519 (w), 487 (m) cm$^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$, TMS, 20 °C): $\delta$ 1.57 (s, 12H, $^2J_{Sn-H}$ = 84 Hz, Sn-$CH_3$), 4.06 (dd, 8H, 3-H, H-4), 4.49 (dd, 8H, 2-H, 5-H), 4.66 (s, 8H, $NCH_2Cp$), 5.11 (s, 8H, $NCH_2Ph$), 7.26−7.39 (m, 20H, $C_6H_5$). $^{119}$Sn NMR (74.5 MHz, $CDCl_3$, $SnMe_4$, 20 °C): $\delta$ −350.0. MS (FAB$^+$): *m/z* (%) 1447 ([*M*]$^+$, 0.5), 1038 ([$C_{34}H_{38}FeN_3S_8Sn_2$]$^+$, 100). Anal. calcd for $C_{60}H_{64}Fe_2N_4S_8Sn_2$ (1446.81): C, 49.81; H, 4.46; N, 3.87. Found: C, 50.69; H, 4.48; N, 3.95.

**X-Ray Crystallography.** X-ray diffraction studies were performed on a Bruker-APEX diffractometer with a CCD area detector ($\lambda_{MoK\alpha}$ = 0.71073 Å; monochromator, graphite). Frames were collected at $T$ = 293 K (compounds **1**, **6**, and **7**), $T$ = 200 K (compound **13**), and $T$ = 100 K (compounds **4** and **5**) via $\omega/\phi$ rotation at 10 s per frame (SMART).[11a] The measured intensities were reduced to $F^2$ and corrected for absorption with SADABS (SAINT-NT).[11b] Corrections were made for Lorentz and polarization effects. Structure solution, refinement, and data output were carried out with the SHELXTL-NT program package.[11c,d] Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions using a riding model.

For compound **4**, the asymmetric unit contains two independent molecule halves. Solvent molecules were present in the crystal lattices of compounds **1** (benzene), **7** (dichloromethane), and **13** (benzene and dichloromethane), of which the dichloromethane molecules in the crystal lattice of compound **7** were disordered over three positions. For compounds **5** and **6**, the crystals were of lower quality ($R_{int}$ = 0.084 and 0.105, respectively); however, the data were of sufficient quality to determine the molecular and crystal structures. In compound **6**, one of the four *iso*-butyl groups is disordered over two positions. In the final electron density map of compound **6**, there are two peaks with residual electron densities of $\Delta\rho$ = 2.27 and 2.18, which, however, are located in the proximity of one of the tin atoms. There was no further peak with a residual electron density larger than $\Delta\rho$ = 0.76.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications, nos. CCDC-682738-682740 and 697178-697180. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

## 3. Results and Discussion

**3.1. Preparation and Spectroscopic Characterization.** Since it is well-known that dithiocarbamates obtained from secondary amines give more stable metal complexes,[10] the

(11) (a) *SMART*, versions 5.057, 5.618; Bruker Analytical X-ray Systems: Madison, WI, 1997, 2000. (b) *SAINT + NT*, versions 6.01, 6.04; Bruker Analytical X-ray Systems: Madison, WI, 1999, 2001. (c) Sheldrick, G. M. *SHELX-86*; University of Göttingen: Göttingen, Germany, 1986. (d) *SHELXTL-NT*, versions 5.10, 6.10; Bruker Analytical X-ray Systems: Madison, WI, 1999, 2000.

(12) Isophthaldehyde, terephthaldehyde, and 1,1′-ferrocenedicarboxaldehyde were reacted in one-pot syntheses with benzylamine/*iso*-butylamine and sodium borohydride to give 1,3-bis(benzylaminomethyl)benzene (1,3-Bn-amb), 1,3-bis(*iso*-butylaminomethyl)benzene (1,3-$^i$Bu-amb), 1,4-bis(benzylaminomethyl)benzene (1,4-Bn-amb), 1,4-bis(*iso*-butylaminomethyl)benzene (1,4-$^i$Bu-amb), and 1,1′-bis(benzylaminomethyl)ferrocene (1,1′-Bn-amf) in quantitative yields. The spectroscopic data of these ligands will be reported in a forthcoming article.

**Scheme 1.** Reaction Sequence for the Preparation of Compounds **1**−**13**

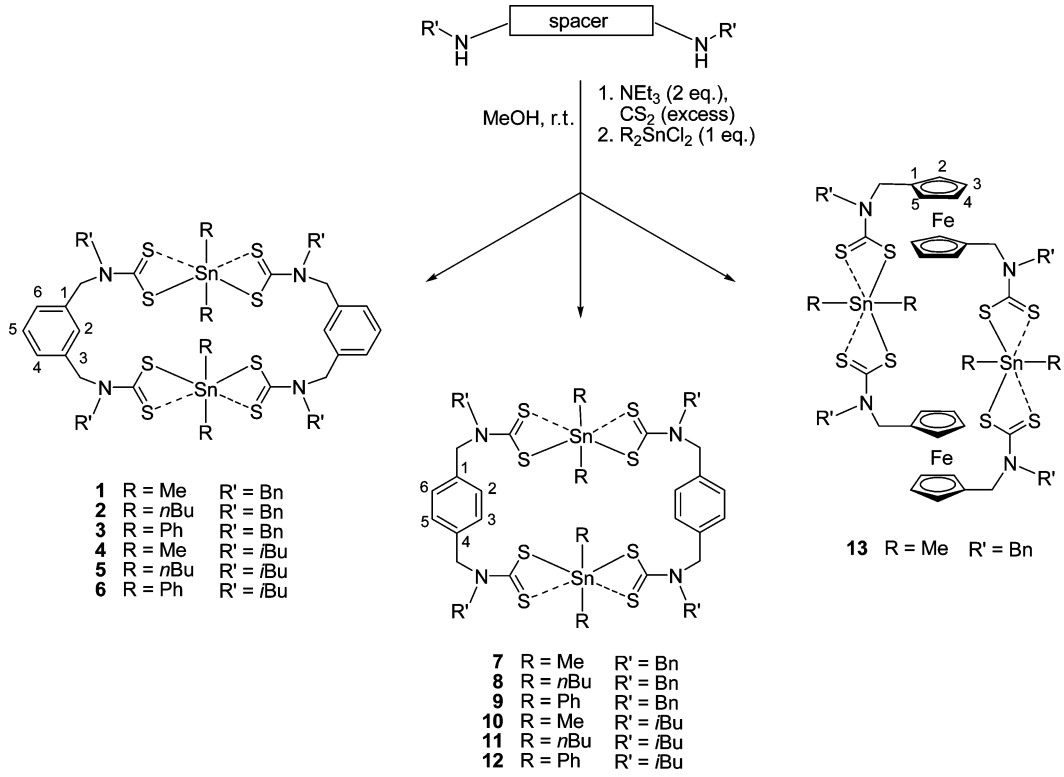



**Table 1.** Selected NMR Spectroscopic Data for Compounds **1**−**13** (in $CDCl_3$, ppm)

| compound | $\delta^1$H N−$CH_2$−spacer | $\delta^1$H N−$CH_2$−R′ | $\delta^1$H Sn−C*H*, ($^2J_{Sn-H}$) | $\delta^{13}$C N−$CH_2$−spacer | $\delta^{13}$C N−$CH_2$−R′ | $\delta^{13}$C Sn−C | $\delta^{13}$C CSS | $\delta^{119}$Sn |
|---|---|---|---|---|---|---|---|---|
| 1,3-Bn-amb | 3.77 | 3.77 | | 53.1[a] | 53.3[a] | | | |
| **1** | 5.01 | 5.01 | 1.77 (79) | 55.7[a] | 56.0[a] | 16.6 | 203.1 | −335.7 |
| **2** | 5.08 | 5.08 | 2.26 | *b* | *b* | *b* | *b* | −338.2 |
| **3** | 4.96 | 4.96 | 7.90 | 56.9[a] | 57.5[a] | 150.9 | 202.3 | −491.0 |
| 1,3-*i*Bu-amb | 3.72 | 2.40 | | 57.1 | 53.7 | | | |
| **4** | 5.10 | 3.59 | 1.63 (84) | 60.3 | 57.7 | 16.1 | 202.4 | −339.3 |
| **5** | 5.20 | 3.63 | 2.12 | 60.5 | 57.6 | 34.7 | 203.1 | −340.6 |
| **6** | 5.01 | 3.50 | 7.88 (77) | 61.8 | 58.7 | 151.6 | 201.9 | −499.6 |
| 1,4-Bn-amb | 3.88[a] | 3.91[a] | | 52.8[a] | 53.0[a] | | | |
| **7** | 5.00 | 5.00 | 1.60 (81) | *b* | *b* | *b* | *b* | −338.4 |
| **8** | 5.01 | 5.01 | 2.15 | 55.6[a] | 56.0[a] | 35.0 | 203.6 | −339.0 |
| **9** | 4.85 | 4.85 | 7.98 | *b* | *b* | *b* | *b* | −495.8 |
| 1,4-*i*Bu-amb | 3.74 | 2.41 | | 57.5 | 53.9 | | | |
| **10** | 5.18 | 3.59 | 1.58 (82) | 60.6 | 57.5 | 16.4 | 202.3 | −339.3 |
| **11** | 5.21 | 3.62 | 2.09 | 60.4 | 57.3 | 34.7 | 203.1 | −340.1 |
| **12** | 5.05 | 3.51 | 7.91 (84) | 61.6 | 58.6 | 151.4 | 201.7 | −494.6 |
| 1,1′-Bn-amf | 3.42 | 3.76 | | 48.1 | 53.4 | | | |
| **13** | 4.66 | 5.11 | 1.57 (84) | *b* | *b* | *b* | *b* | −350.0 |

[a] Signals might be interchanged. [b] Low solubility.

*N*,*N*′-dibenzyl and *N*,*N*′-di-*iso*-butyl derivatives of 1,3-bis(aminomethyl)benzene and 1,4-bis(aminomethyl)benzene were prepared[12] and then combined in methanol with carbon disulfide, triethylamine, and the corresponding diorganotin dichloride $R_2SnCl_2$ (R = Me, *n*Bu, and Ph) to give compounds **1**−**12** in yields varying from 70 to 83%. Additionally, using the same methodology, the dimethyltin bis-dithiocarbamate of 1,1′-bis(aminomethyl)ferrocene was synthesized in 64% yield (Scheme 1). All products have been characterized as far as possible by elemental analysis, $FAB^+$ mass spectrometry, IR and NMR ($^1$H, $^{13}$C, $^{119}$Sn) spectroscopy, and single-crystal X-ray diffraction (compounds **1**, **4**, **5**, **6**, **7**, and **13**).

The formation of dithiocarbamate complexes could be evidenced by the IR spectra, which showed strong bands in the region of 1462−1480 and 976−994 $cm^{-1}$, resulting from the $\nu$(N-CSS) and $\nu_{as}$(CSS) vibrations of metal-coordinated dithiocarbamate functions.[13]

A comparison of the $^1$H NMR spectra between the starting *N*,*N*′-disubstituted diamines and the resulting products (Table 1) showed significant shift displacements to lower fields for the N-$CH_2$ methylene hydrogen atoms ($\Delta\delta$ = 0.97−1.48 for the N-$CH_2$-spacer methylene group and $\Delta\delta$ = 0.97−1.35

(13) (a) Durgaprasad, G.; Sathyanarayana, D. N.; Patel, C. C. *Can. J. Chem.* **1969**, *47*, 631. (b) Brown, D. A.; Glass, W. K.; Burke, M. A. *Spectrochim. Acta* **1976**, *32A*, 137. (c) Chandra, S.; Magee, R. J.; James, B. D. *Main Group Met. Chem.* **1988**, *11*, 57.

**Table 2.** Crystallographic Data for Compounds **1**, **4**, **5**, **6**, **7**, and **13**

| crystal data[a] | **1** | **4** | **5** | **6** | **7** | **13** |
|---|---|---|---|---|---|---|
| formula | $C_{52}H_{56}N_4S_8Sn_2 \cdot 2C_6H_6$ | $C_{40}H_{64}N_4S_8Sn_2$ | $C_{52}H_{88}N_4S_8Sn_2$ | $C_{60}H_{72}N_4S_8Sn_2$ | $C_{52}H_{56}N_4S_8Sn_2 \cdot 2CH_2Cl_2$ | $C_{60}H_{64}Fe_2N_4S_8Sn_2 \cdot 2CH_2Cl_2 \cdot 4C_6H_6$ |
| MW (g mol$^{-1}$) | 1387.08 | 1094.81 | 1263.12 | 1343.08 | 1400.72 | 1929.00 |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ | $Pca2_1$ | $P\bar{1}$ | $P2_1/c$ |
| temp (K) | 293 | 100 | 100 | 293 | 293 | 200 |
| $a$ (Å) | 8.8321(7) | 10.2879(8) | 12.3452(12) | 24.8002(16) | 10.674(6) | 10.7077(6) |
| $b$ (Å) | 12.5154(10) | 13.5669(12) | 13.4135(14) | 14.7940(9) | 10.774(6) | 23.1803(14) |
| $c$ (Å) | 15.5870(13) | 19.2408(16) | 18.2726(18) | 17.2450(11) | 14.854(8) | 17.9389(11) |
| $\alpha$ (deg) | 70.199(1) | 104.915(1) | 90 | 90 | 101.994(9) | 90 |
| $\beta$ deg) | 82.954(1) | 103.964(2) | 98.842(2) | 90 | 109.034(8) | 95.917(1) |
| $\gamma$ (deg) | 81.590(1) | 96.073(2) | 90 | 90 | 90.062(9) | 90 |
| $V$ (Å$^3$) | 1598.7(2) | 2477.7(4) | 2989.8(5) | 6327.1(7) | 1575.1(14) | 4428.9(5) |
| $Z$ | 1 | 2 | 2 | 4 | 1 | 2 |
| $\mu$ (mm$^{-1}$) | 1.084 | 1.377 | 1.151 | 1.093 | 1.265 | 1.233 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.441 | 1.467 | 1.403 | 1.410 | 1.477 | 1.447 |
| $R^{b,c}$ | 0.045 | 0.056 | 0.078 | 0.081 | 0.048 | 0.058 |
| $R_w{}^{d,e}$ | 0.121 | 0.119 | 0.146 | 0.171 | 0.139 | 0.125 |

[a] $\lambda_{MoK\alpha} = 0.71073$ Å. [b] $I > 2\sigma(I)$. [c] $R = \sum(F_o^2 - F_c^2)/\sum F_o^2$. [d] All data. [e] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

**Table 3.** Selected Bond Lengths [Å], Bond Angles [deg], Intramolecular Distances [Å], and Cavity Dimensions [Å$^2$] for Compounds **1**, **4**, **5**, **6**, **7**, and **13**

| | | **4**[d] | | | | | |
|---|---|---|---|---|---|---|---|
| | **1** | molecule 1 | molecule 2 | **5** | **6**[e] | **7** | **13** |
| | | | | Bond Lengths | | | |
| Sn−C | 2.112(5) | 2.109(6) | 2.124(5) | 2.131(7) | 2.155(13)/2.154(10) | 2.117(6) | 2.116(5) |
| | 2.116(5) | 2.121(6) | 2.126(6) | 2.132(5) | 2.168(10)/2.163(12) | 2.123(5) | 2.129(5) |
| Sn−$S_{cov}$ | 2.5086(13) | 2.5319(16) | 2.5306(17) | 2.5230(19) | 2.571(3)/2.571(3) | 2.5320(17) | 2.5147(15) |
| | 2.5217(12) | 2.5356(17) | 2.5401(17) | 2.524(2) | 2.580(3)/2.575(3) | 2.5364(17) | 2.5205(13) |
| Sn···$S_{coord}$ | 2.8791(15) | 2.8855(17) | 2.949(2) | 2.895(2) | 2.701(3)/2.662(3) | 2.9078(19) | 2.9667(14) |
| | 3.1519(14) | 2.966(2) | 2.963(2) | 2.994(2) | 2.713(3)/2.708(3) | 3.0496(19) | 2.9977(15) |
| C−S | 1.741(4) | 1.750(6) | 1.739(7) | 1.750(7) | 1.707(11)/1.700(12) | 1.747(5) | 1.750(5) |
| | 1.697(5) | 1.694(7) | 1.699(7) | 1.683(8) | 1.721(12)/1.702(12) | 1.701(6) | 1.697(5) |
| | 1.744(5) | 1.752(6) | 1.762(6) | 1.757(8) | 1.723(12)/1.704(12) | 1.754(5) | 1.755(5) |
| | 1.681(5) | 1.695(7) | 1.675(7) | 1.703(8) | 1.736(11)/1.707(12) | 1.697(5) | 1.697(5) |
| C−$N_{dtc}$ | 1.323(6) | 1.320(8) | 1.340(7) | 1.314(9) | 1.353(12)/1.339(14) | 1.335(6) | 1.331(6) |
| | 1.331(6) | 1.329(7) | 1.340(8) | 1.336(10) | 1.318(12)/1.373(14) | 1.338(7) | 1.335(6) |
| | | | | Bond Angles | | | |
| C−Sn−C | 131.9(2) | 139.9(2) | 142.6(3) | 141.9(3) | 102.2(4)/102.3(4) | 139.1(3) | 137.9(2) |
| $S_{cov}$−Sn−$S_{cov}$ | 81.60(4) | 84.24(5) | 83.07(5) | 82.87(6) | 150.17(10)/148.25(11) | 84.19(5) | 81.05(4) |
| S−Sn−S (chelate) | 62.12(4) | 64.60(5) | 64.87(5) | 64.48(6) | 67.58(9)/67.19(10) | 63.91(5) | 64.49(4) |
| | 65.89(4) | 65.80(5) | 65.01(5) | 65.82(6) | 67.79(9)/68.43(9) | 65.67(5) | 64.76(4) |
| $S_{coord}$···Sn···$S_{coord}$ | 150.40(4) | 145.31(5) | 147.55(5) | 147.04(6) | 82.17(9)/81.83(10) | 146.26(4) | 149.85(4) |
| S−C−S | 118.0(3) | 118.1(4) | 119.3(4) | 117.6(4) | 118.2(6)/116.8(6) | 118.9(3) | 118.5(3) |
| | 120.7(3) | 118.6(4) | 119.7(4) | 119.8(5) | 119.5(6)/118.3(7) | 119.9(3) | 118.7(3) |
| | | | | Others | | | |
| Sn···$Sn_{transannular}$ | 5.72 | 5.63 | 5.74 | 5.86 | 11.02 | 9.70 | 11.53 |
| N···$N_{spacer}$[a] | 5.40 | 5.07 | 5.01 | 5.18 | 6.34 | 7.56 | 8.71 |
| centroid···centroid[b] | 13.67 | 12.97 | 12.46 | 12.76 | 9.09 | 9.09 | 10.00[f] |
| cavity dimensions[c] | | | | | | 3.09 × 4.56 | 3.44 × 3.65 |

[a] N···N distance within the spacer. [b] Distances between the phenylene centroids. [c] Effective cavity size. [d] Two molecule halves in the asymmetric unit. [e] Molecule with two independent tin atoms (molecule without crystallographic symmetry element). [f] Transannular Fe···Fe interaction.

for the N-*CH*$_2$-R′ methylene group). The dimethyltin moieties gave signals at $\delta = 1.77$, 1.63, 1.60, 1.58, and 1.57 with $^2J_{Sn-H}$ coupling constants of 79, 84, 81, 82, and 84 Hz for **1**, **4**, **7**, **10**, and **13**, respectively, thus giving, according to Lockhard's equation,[14] calculated C−Sn−C bond angles of 129.6, 136.1, 131.9, 133.4, and 136.1°. Because of the low solubility of compounds **1**−**13**, $^{13}$C NMR spectra could only be measured for the more soluble compounds, **1**, **3**−**6**, **8**, and **10**−**12**. As in the case of the $^1$H NMR data, the signals for the N*CH*$_2$ carbon atoms are low-field-shifted when compared to the starting diamine ($\Delta\delta = 2.6-4.7$ for the N-*CH*$_2$-spacer methylene group and $\Delta\delta = 3.4-5.0$ for the N-*CH*$_2$-R′ methylene group). The $NCS_2$ groups gave signals varying from $\delta = 201.7$ to 203.6 that are in the region typically observed for diorganotin dithiocarbamates.[15] Interestingly, in the $^1$H NMR spectra, the signals for the *N*-methylene hydrogen atoms are broadened, indicating that the complexes are involved in at least one dynamic process. Both intra- and intermolecular ligand exchange reactions and configurational or conformational equilibria are possible.[7,16] The $^{119}$Sn NMR chemical shifts for the dimethyltin derivatives **1**, **4**, **7**, **10**, and **13** vary from $\delta = -335.7$ to −350.0;

(14) Lockhart, T. P.; Manders, W. F. *Inorg. Chem.* **1986**, *25*, 892.

(15) (a) Smith, P. J.; Tupciauskas, A. P. *Ann. Rep. NMR Spectrosc.* **1978**, *8*, 291. (b) Wrackmeyer, B. *Ann. Rep. NMR Spectrosc.* **1985**, *16*, 73. (c) Lockhart, T. P.; Manders, W. F.; Schlemper, E. O. *J. Am. Chem. Soc.* **1985**, *107*, 7451. (d) Dakternieks, D.; Zhu, H.; Masi, D.; Mealli, C. *Inorg. Chem.* **1992**, *31*, 3601. (e) Seth, N.; Gupta, V. D.; Nöth, H.; Thomann, M. *Chem. Ber.* **1992**, *125*, 1523. (f) Sharma, J.; Singh, Y.; Bohra, R.; Rai, A. K. *Polyhedron* **1996**, *15*, 1097.

(16) (a) Wengrovius, J. H.; Garbauskas, M. F. *Organometallics* **1992**, *11*, 1334. (b) Beckmann, J.; Jurkschat, K. *Coord. Chem. Rev.* **2001**, *215*, 267.

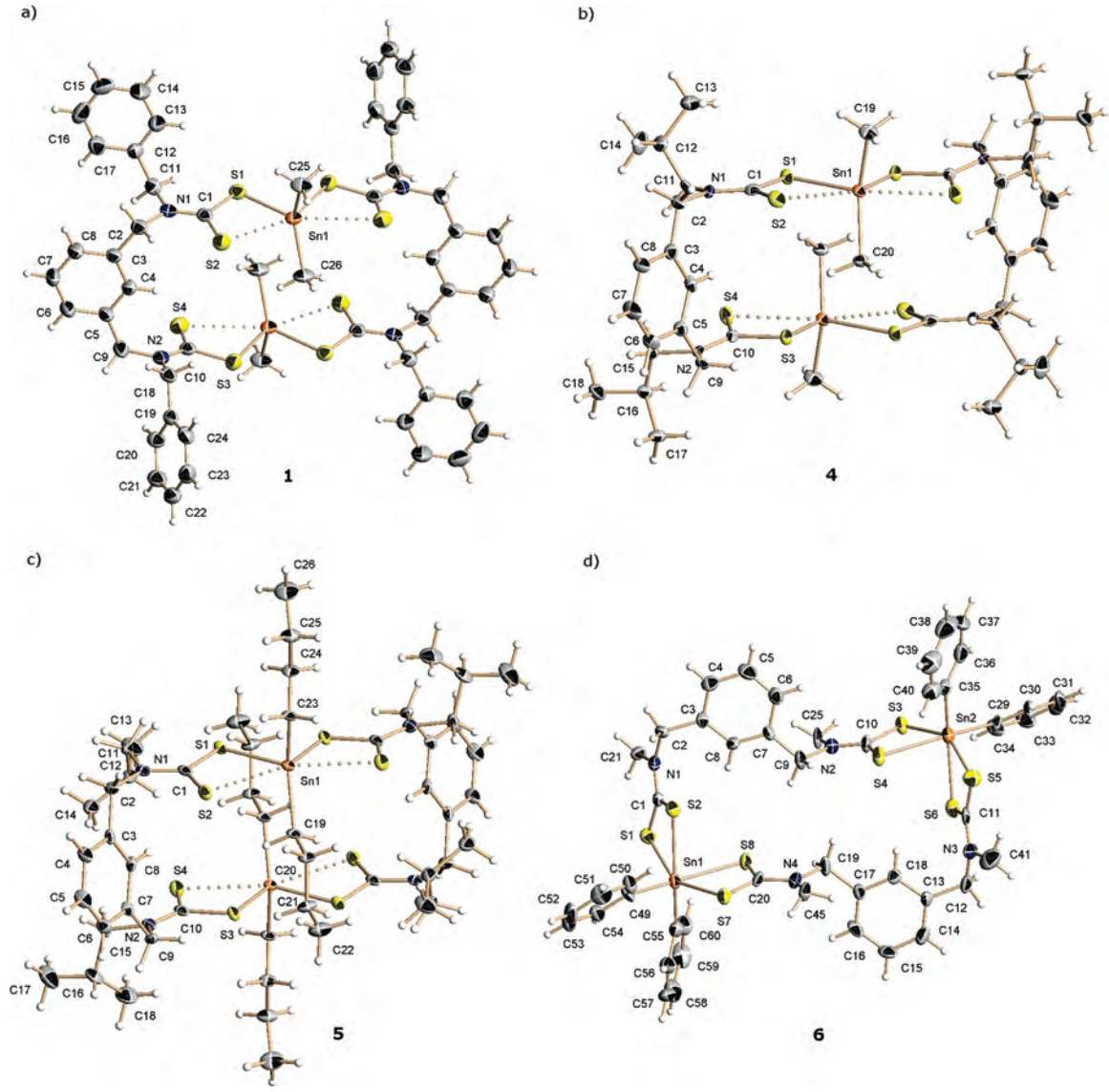



**Figure 1.** Perspective views of the molecular structures of (a) compound **1**, (b) compound **4**, (c) compound **5**, and (d) compound **6**. Ellipsoids are shown at the 30 % (**1** and **6**) and 50 % (**4** and **5**) probability levels. For clarity, in compound **6**, the *iso*-butyl groups are only represented by the corresponding α-$CH_2$ groups.

those for the di-*n*-butyltin derivatives **2**, **5**, **8**, and **11** from $\delta = -338.2$ to $-340.6$; and those for the diphenyltin derivatives **3**, **6**, **9**, and **12** from $\delta = -491.0$ to $-499.6$ (Table 1). These are typical ranges for diorganotin dithiocarbamates.[15]

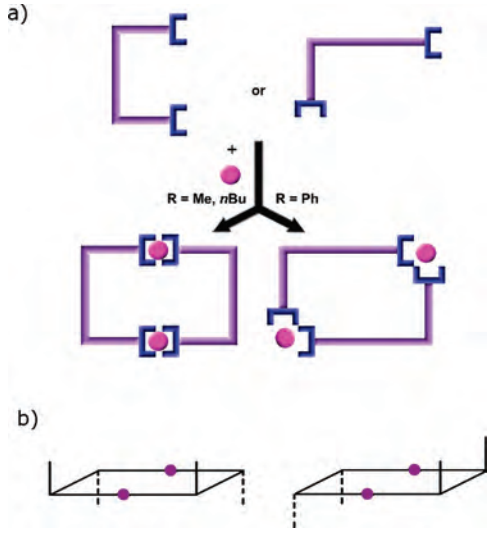
For compounds **1**, **4**, **5**, **6**, **7**, and **13**, crystals suitable for X-ray diffraction analysis could be grown, which revealed dinuclear macrocyclic structures in all six cases. The molecular structures are shown in Figures 1−3. The most relevant crystallographic data and selected geometric parameters are summarized in Tables 2 and 3.

As shown in Figure 1, the diorganotin complexes of the ligands derived from 1,3-bis(aminomethyl)benzene are 24-membered dinuclear $\{C_{14}N_4S_4Sn_2\}$ macrocyclic ring structures, however, with different tin−atom configurations as well as ligand and ring conformations. In the molecular structures of the dimethyl- and di-*n*-butyltin derivatives **1**, **4**, and **5** (Figures 1a−c), the tin atoms have skewed-trapezoidal-bipyramidal coordination geometries, in which both the organic and the dtc functions are trans-oriented. In contrast, in diphenyltin compound **6** (Figure 1d), the coordination polyhedra of the tin atoms are distorted octahedral with cis-oriented dtc functions. This coordination geometry has been already observed for other diphenyltin dithiocarbamates[17] but is unknown for dialkyltin derivatives.[4c]

For dimethyltin derivatives **1** and **4**, the calculated and experimental Me−Sn−Me bond angles agree very well (129.6 versus 131.9(2) ° for **1**, 136.1 versus 139.9(2) and 142.6(3)° for **4**), thus indicating that the structures in solution and the solid state are similar. The trapezoidal planes are formed by the sulfur atoms of the chelating ligands, which are coordinated in an anisobidentate manner (Sn−S = 2.5086(13)−2.5401(17) Å, Sn···S = 2.8791(14)−3.1519(14)

(17) (a) Alcock, N. W.; Culver, J. *J. Chem. Soc., Dalton Trans* **1992**, 1477. (b) Hook, J. M.; Linahan, B. M.; Taylor, R. L.; Tiekink, E. R. T.; van Gorkom, L.; Webster, L. K. *Main Group Met. Chem.* **1994**, *17*, 293. (c) Farina, Y.; Othman, A. H.; Razak, I. A.; Fun, H.-K.; Ng, S. W.; Baba, I. *Acta Crystallogr.* **2001**, *E57*, m46. (d) Menezes, D. C.; de Lima, G. M.; Porto, A. O.; Donnici, C. L.; Ardisson, J. D.; Doriguetto, A. C.; Ellena, J. *Polyhedron* **2004**, *23*, 2104.

**Scheme 2.** Graphical Illustration of (a) the Differences in the Tin−Atom Configurations and Ligand Conformations and (b) the Conformational Ring Isomerism Found in Compounds **1**, **4**, **5**, and **6**




Å for **1** and **4**), as it is generally observed for diorganotin dithiocarbamates.[4c] The bonding asymmetry of the ligands is reflected in the C−S bonds, which are significantly different from each other (1.681(5)−1.703(8) Å versus 1.739(7)−1.762(6) Å). Within the dithiocarbamate function, the C−$N_{dtc}$ bond lengths of 1.320(8)−1.340(8) Å indicate a substantial delocalization of $\pi$-electron density in this bond.[18] The coordination geometry in the di-*n*-butyltin complex **5** is very similar (Table 3).

According to the cis orientation of the organic substituents and the dtc groups in compound **6**, the C−Sn−C bond angles are 102.2(4) and 102.3(4)°, while the three types of S−Sn−S bond angles range from 67.19(10) to 68.43(9), 81.83(10) to 89.80(10), and 148.25(11) to 150.17(10)°. The coordination of the dtc ligands approximates an isobidentate mode, since the differences between the Sn−S bond lengths are smaller than 0.2 Å (2.571(3)−2.713(3) Å). As a consequence, the

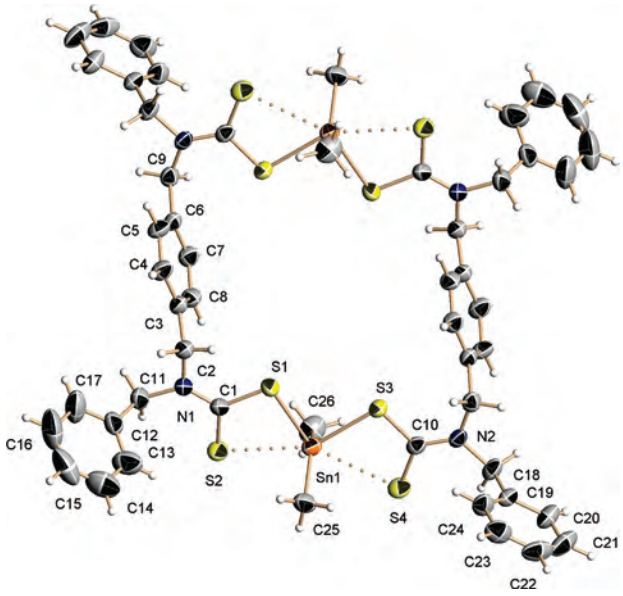



**Figure 2.** Perspective view of the molecular structure of compound **7**. Ellipsoids are shown at the 30% probability level.

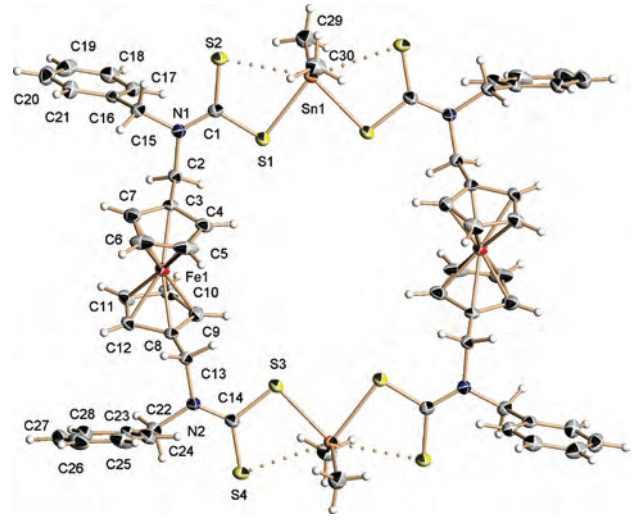



**Figure 3.** Perspective view of the molecular structure of compound **13**. Ellipsoids are shown at the 30% probability level.

$\pi$-electron density within the $CS_2$ groups is delocalized, as can be seen from the relatively small differences between the C−S bond lengths that range from 1.700(12) to 1.736(11) Å. The C−$N_{dtc}$ bonds vary from 1.318(12) to 1.373(14) Å and are comparable to those found for the above-discussed complexes.

Due to the variation in the metal coordination environment, the ligand conformation changes from syn−syn (compounds **1**, **4**, and **5**) to syn−anti (compound **6**), thus giving different spatial distributions of the dtc functions. The $C_{SS}$−N−N′−$C_{SS}$′ torsion angles for compounds **1**, **4**, **5**, and **6** are 56.4, 48.5/46.3, 50.6, and −67.6/31.1°, respectively. The conformational flexibility of the bis-dithiocarbamates can be attributed to the rotational degree of freedom of the $C_6H_4$-$CH_2$-N methylene groups and is intermediate, when compared to connectors that contain only rigid $\pi$-conjugated or extended aliphatic spacer groups, which makes these ligands ideal candidates for the self-assembly of metal−organic macrocyclic structures. The impact of the flexibility provided by the cis/trans tin coordination environment and the ligand conformation on the macrocycle structure is illustrated in Scheme 2a.

There are further variables in the conformation of the macrocyclic rings. The first is in regard to the orientation of the Bn and $^i$Bu substituents attached to the nitrogen atoms, as can be seen from a comparison of the molecular structures of dimethyltin derivatives **1** and **4** (Figure 1a and b). In compound **1**, the substituents of each ligand are trans-oriented, while they are cis-oriented in compound **4**. As shown in Scheme 2b, the conformational isomers of **1** and **4** can be distinguished by the sequence of the substituent orientations with respect to the macrocyclic ring plane. Since both molecules possess crystallographic inversion centers, this results in different orientations of the pseudo-$C_2$ symmetry axes; however, it should be noticed that both molecules are 1,3-alternated conformers when applying the nomenclature used for the conformational isomerism of calixarenes.[19]

(18) Wheeler, K. A.; Harrington, B.; Zapp, M.; Casey, E. *CrystEngComm* **2003**, *5*, 337.

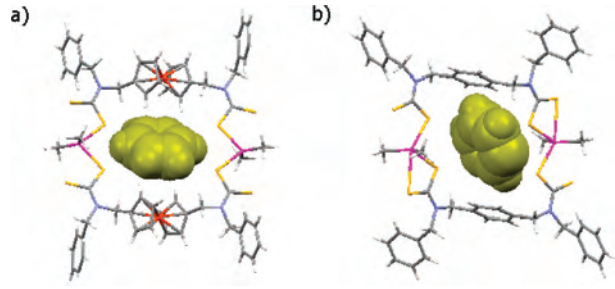



**Figure 4.** Fragments of the crystal lattices of compounds **13** (a) and **7** (b), showing the inclusion of aromatic rings within the macrocycle voids. For clarity, the aromatic guest molecules are uniformly colored (dark yellow).

The conformations of di-*n*-butyl and diphenyltin complexes **5** and **6** are analogous to that of compound **4**. Secondly, there are differences in the orientation of the aromatic rings forming part of the macrocycles. This can be evidenced by the angles formed between the mean planes of the macrocycle and the phenylene groups. While the mutual orientation of the macrocycle (mean planes calculated from the four nitrogen atoms) and the phenylene rings is close to parallel in compound **1** (21.1°), it approximates a perpendicular disposition in compounds **4**, **5**, and **6** (35.5/55.0° for **4**, 43.9° for **5**, and 41.9/44.8° for **6**).

Compounds **7** and **13** have 26- and 24-membered $\{C_{16}N_4S_4Sn_2\}$ and $\{C_{12}Fe_2N_4S_4Sn_2\}$ macrocyclic structures. In both cases, the tin atoms have skewed-trapezoidal-bipyramidal coordination geometries, whose geometric parameters are very similar to that found for dimethyltin complex **1** (Table 3). Also in this case, the calculated and experimental Me−Sn−Me bond angles agree reasonably well (131.9 versus 139.1(3)° for **7**, 136.1 versus 137.9(2)° for **13**). Albeit the macrocycle of compound **13** contains a smaller number of ring members than that of **7**, the transannular Sn···Sn distances are significantly larger (9.70 Å for **7** versus 11.53 Å for **13**). This can be attributed to the larger separation of the N-CSS functions in the 1,1′-bis(aminomethyl)ferrocene groups of compound **13** when compared to the 1,4-bis(aminomethyl)benzene spacer of compound **7** (8.71 Å versus 7.56 Å for the N···N distance within the spacer). However, since in compound **7** the orientation of the phenylene rings is almost perpendicular to the macrocyclic ring plane, the effective cavity sizes of **7** and **13** are comparable: 3.09 × 4.56 Å$^2$ for **7** and 3.44 × 3.65 Å$^2$ for **13**. The Fe···Fe distance in compound **13** is 10.00 Å.

Beer et al. have prepared related macrocycles using transition metal ions such as Zn(II), Cu(II), Cu(III), Ni(II), Pd(II), Pt(II), and Au(III) ions as metal nodes for the macrocycle assembly process.[4b,20] Their binding studies have shown that dinuclear assemblies can selectively bind diamines and dicarboxylates within the macrocyclic cavities, taking advantage of the Lewis-acidic metal sites. Related experiments with organotin macrocycles have been carried out by Jurkschat et al.[21]

As shown in Figure 4a, the macrocyclic voids of compound **13** allow for the inclusion of two benzene molecules, which in the solid-state structure are accomodated above and below the molecule center. Similarly, in the crystal lattice of compound **7**, phenyl groups of neighboring molecules are located within the cavity (Figure 4b). UV−vis and NMR titrations were carried out to test the possibility of inclusion of small aromatic molecules in solution. Thus, nitrobenzene was added to chloroform solutions of **7** or **13** (15 mM for $^1$H NMR), covering a concentration range from 2 mM up to 30 mM; however, no significant changes in the signals corresponding to the aromatic regions were observed under these conditions.

## 4. Conclusions

This report has shown that diorganotin moieties and bis-dithiocarbamates can be easily assembled to dinuclear macrocyclic rings, when the coordinating functional groups are separated by an adequate spacer. The bis(aminomethyl) benzene and -ferrocene connectors used herein are ligands with intermediate flexibility when compared to other $\pi$-delocalized and aliphatic connectors, thus giving rise to conformational isomers of the macrocyles. The macrocyclic structures described herein can be modified at the organic substituents attached to the tin and nitrogen atoms for further studies.

**Acknowledgment.** The authors thank CONACyT for financial support (Project number: 47347-Q).

IC801464S

(19) Vögtle, F. *Supramolekulare Chemie*; Teubner Verlag: Stuttgart, Germany, 1992.

(20) (a) Lai, S. W.; Drew, M. G. B.; Beer, P. D. *J. Organomet. Chem.* **2001**, *637−639*, 89. (b) Beer, P. D.; Berry, N.; Drew, M. G. B.; Fox, O. D.; Padilla-Tosta, M. E.; Patell, S. *Chem. Commun.* **2001**, 199. (c) Wong, W. W. H.; Curiel, D.; Cowley, A. R.; Beer, P. D. *Dalton Trans.* **2005**, 359. (d) Wong, W. W. H.; Cookson, J.; Evans, E. A. L.; McInnes, E. J. L.; Wolowska, J.; Maher, J. P.; Bishop, P.; Beer, P. D. *Chem. Commun.* **2005**, 2214.

(21) (a) Jurkschat, K.; Uhlig, W.; Mügge, C.; Tzschach, A. Z. *Anorg. Allg. Chem.* **1988**, *556*, 161. (b) Altmann, R.; Gausset, O.; Horn, D.; Jurkschat, K.; Schürmann, M. *Organometallics* **2000**, *19*, 430.