Synthesis, Spectroscopic, and X-ray Diffraction Structural Studies of Tin(IV) Derivatives with Tris(pyrazol-1-yl)methanes

C. Pettinari,*,† M. Pellei,† A. Cingolani,† D. Martini,† A. Drozdov,‡ S. Troyanov,‡ W. Panzeri,§ and A. Mele§

Dipartimento di Scienze Chimiche, Università degli Studi di Camerino, via S. Agostino 1, I-62032 Camerino, Macerata, Italy, Department of Chemistry, Moscow State University, Vorobjevy Gory, 119899 Moscow, Russia, and Dipartimento di Chimica del Politecnico, via Mancinelli 7, I-20131 Milano, Italy

Received June 2, 1999

The reaction of $RSnCl_3$ (R = Me, Ph, or Bu^n) and SnX_4 acceptors (X = Cl, Br, or I) with equimolar amounts of tris(pyrazol-1-yl)methane ligands L (L = $HC(pz)_3$, $HC(4\text{-}Mepz)_3$, $HC(3,5\text{-}Me_2pz)_3$, $HC(3,4,5\text{-}Me_3pz)_3$, or $HC(3\text{-}Mepz)_2(5\text{-}Mepz)$ yields ionic 1:1 $[\{LSnRCl_2\}^+][\{SnRCl_4\}^-]$ or $[\{LSnX_3\}^+][\{SnX_5\}^-]$ and 2:1 $[\{LSnRCl_2\}^+]_2[\{SnRCl_5\}^{2-}]$ or $[\{LSnX_3\}^+]_2[\{SnX_6\}^{2-}]$ complexes, depending strongly on the number and position of the Me groups on the azole ring of the neutral ligand. These complexes, stable in air, have been characterized in the solid state (IR, MS-FAB) as well as in solution (^{1}H- and ^{119}Sn-NMR, conductivity, and molecular weight determinations). The crystal and molecular structure of $[\{HC(4\text{-}Me_2pz)_3Sn^nBuCl_2\}^+]_2[\{Sn^nBuCl_5\}^{2-}]$, $[\{HC(3,5\text{-}Me_2pz)_3SnMeCl_2\}^+][\{MeSnCl_4\}^-]$, and $[\{HC(3,4,5\text{-}Me_3pz)_3SnBr_3\}^+][\{SnBr_5\}^-]$ was determined by X-ray crystallography. The structures of the cations are very similar, the Sn atom being in a strongly distorted octahedral environment with the Sn−N bonds in the range 2.22−2.33 Å, whereas in the anions the Sn atoms are five-coordinate (trigonal-bipyramidal) in $[MeSnCl_4]^-$ and $[SnBr_5]^-$ and six-coordinate (octahedral) in $[Sn^nBuCl_5]^{2-}$.

Introduction

Since poly(pyrazol-1-yl)borate ligands were discovered and used by Trofimenko in the synthesis of main group and transition metal derivatives,[1] numerous reports of poly(pyrazol-1-yl)borate−tin(IV) complexes have appeared.[2] A driving force for much of the chemistry in this area stems from its biological relevance: in the 1970s, while some research was undertaken to study the biological properties and applications of organotin compounds, it was discovered that certain organotin derivatives containing N-donor ligands exhibited antitumor activity. More recently, this preliminary examination of such complexes has been extended to a systematic study of the antitumor properties of tin compounds,[3] demonstrating[4] that the coordinated N-donor ligands favor in some way the transport of the drugs into cells; e.g., in the case of the diorganotin(IV) compounds, the antitumor activity arises from SnR_2(IV) moieties released by slow hydrolysis of the complexes. In addition organotin(IV) halides exhibit strong Lewis acidity, and their complexation chemistry has been a subject of growing interest; these species have been recently employed in the selective complexation of anionic and neutral donors by tailor-made molecular hosts.[5]

We have initiated a study on the coordination chemistry of neutral bis- and tris(pyrazol-1-yl)alkanes with several post-transition and transition metals.[6] We are interested in contrasting the chemistry of the neutral poly(pyrazol-1-yl)alkane ligands

* To whom correspondence should be addressed. Fax: 0039 0737 637345. E-mail address: Pettinar@camserv.unicam.it.

† Università degli Studi di Camerino.

‡ Moscow State University.

§ Politecnico.

(1) (a) Trofimenko, S. *J. Am. Chem. Soc.* **1966**, *88*, 1842. (b) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3165, 3170, 6288.

(2) (a) Gioia Lobbia, G.; Valle, G.; Calogero, S.; Cecchi, P.; Santini, C.; Marchetti, F. *J. Chem. Soc., Dalton Trans.* **1996**, 2475. (b) Gioia Lobbia, G.; Bonati, F.; Cecchi, P.; Cingolani A.; Lorenzotti, A. *J. Organomet. Chem.* **1989**, *378*, 139. (c) Gioia Lobbia, G.; Bonati, F.; Cecchi, P.; Lorenzotti, A.; Pettinari, C. *J. Organomet. Chem.* **1991**, *403*, 317. (d) Gioia Lobbia, G.; Cecchi, P.; Spagna, R.; Colapietro, M.; Pifferi, A.; Pettinari, C. *J. Organomet. Chem.* **1995**, *485*, 45. (e) Gioia Lobbia, G.; Cecchi, P.; Calogero, S.; Valle, G.; Chiarini, M.; Stievano, L. *J. Organomet. Chem.* **1995**, *503*, 297. (f) Calogero, S.; Valle, G.; Gioia Lobbia, G.; Santini, C.; Cecchi, P.; Stievano, L. *J. Organomet. Chem.* **1996**, *526*, 269. (g) Calogero, S.; Stievano, L.; Gioia Lobbia, G.; Cingolani, A.; Cecchi P.; Valle, G. *Polyhedron* **1995**, *14*, 1731. (h) Gioia Lobbia, G.; Calogero, S.; Bovio, B.; Cecchi, P. *J. Organomet. Chem.* **1992**, *440*, 27. (i) Nicholson, B. K. *J. Organomet. Chem.* **1984**, *265*, 153. (j) Lee, S. K.; Nicholson, B. K. *J. Organomet. Chem.* **1986**, *309*, 257. (k) Jung, O. S.; Jeong, J. H.; Sohn, Y. S. *J. Organomet. Chem.* **1990**, *399*, 235. (l) Gioia Lobbia, G.; Bonati, F.; Cecchi, P.; Leonesi, D. *J. Organomet. Chem.* **1990**, *391*, 155. (m) Gioia Lobbia, G.; Cecchi, P.; Valle, G.; Calogero, S.; Santini, C. *Main Group Met. Chem.* **1996**, *19*, 571. (n) Gioia Lobbia, G.; Cecchi, P.; Santini, C.; Calogero, S.; Valle, G.; Wagner, F. E. *J. Organomet. Chem.* **1996**, *513*, 139.

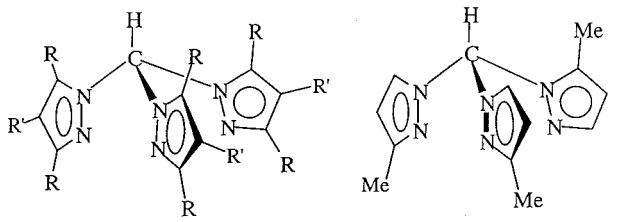
(3) (a) Cleare, M. J. *Coord. Chem. Rev.* **1974**, *12*, 349. (b) Crowe, A. J.; Smith P. J.; Atassi, G. *Chem. Ind.* **1980**, 200. (c) Crowe, A. J.; Smith P. J.; Atassi, G. *Chem. Biol. Interact.* **1980**, *32*, 171.

(4) Ruisi, G.; Silvestri, A.; Lo Giudice, M. T.; Barbieri, R.; Atassi, G.; Huber, F.; Grätz, K.; Lamartina, L. *J. Inorg. Biochem.* **1985**, *25*, 229.

(5) (a) Jurkschat, K.; Hesselbarth, F.; Dargatz, M.; Lehmann, J.; Kleinpeter, E.; Tzschach, A.; Meunier-Piret, J. *J. Organomet. Chem.* **1990**, *388*, 259. (b) Tsagatakis, J. K.; Chaniotakis, N. A.; Jurkschat, K. *Helv. Chim. Acta* **1994**, *77*, 2191. (c) Altmann, R.; Jurkschat, K.; Schürmann, M.; Dakternieks, D.; Duthie, A. *Organometallics* **1998**, *17*, 5858. (d) Dakternieks, D.; Jurkschat, K.; Zhu, H.; Tiekink, E. R. T. *Organometallics* **1995**, *14*, 2512.

(6) (a) Lorenzotti, A.; Cingolani, A.; Gioia Lobbia, G.; Leonesi, D.; Bonati, F. *Gazz. Chim. Ital.* **1987**, *117*, 191. (b) Cingolani, A., Lorenzotti, A.; Gioia Lobbia G.; Leonesi, D.; Bonati, F.; Bovio, B. *Inorg. Chim. Acta* **1987**, *132*, 167. (c) Bovio, B.; Cingolani A.; Pettinari, C.; Gioia Lobbia G.; Bonati, F. *Z. Anorg. Allg. Chem.* **1991**, *602*, 169. (d) Bonati, F.; Cingolani, A.; Gioia Lobbia, G.; Leonesi, D.; Lorenzotti, A.; Pettinari, C. *Gazz. Chim. Ital.* **1990**, *120*, 341. (e) Pettinari, C.; Lorenzotti, A.; Cingolani, A.; Leonesi, D.; Marra, M.; Marchetti, F., *Gazz. Chim. Ital.* **1993**, *123*, 481.

10.1021/ic9906252 CCC: $18.00
Published on Web 11/19/1999



HC(pz)$_3$CH: R = R' = H
HC(4-Mepz)$_3$: R = H, R' = Me
HC(3,5-Me$_2$pz)$_3$: R = Me, R' = H
HC(3,4,5-Me$_3$pz)$_3$: R = R' = Me

HC(3-Mepz)$_2$(5-Mepz)

Figure 1. Molecular structure of the tris(pyrazol-1-yl)methane ligands employed in this work.

with that previously developed for anionic poly(pyrazol-1-yl)-borates. In our previous papers, we described the interaction between several tin(IV) and organotin(IV) acceptors and the N_2-donors $H_2C(pz)_2$,[7] $H_2C(3,5\text{-}Me_2pz)_2$,[8] $Me_2C(pz)_2$,[8,9] $H_2C(4\text{-}Mepz)_2$,[10] $H_2C(3,4,5\text{-}Me_3pz)_2$,[10] $(H_2C)_2(pz)_2$,[10] and $(H_2C)_2(3,5\text{-}Me_2pz)_2$,[10] showing that different reaction patterns can take place depending on the nature of the donor and of the tin(IV) acceptor. To gain insight into the factors controlling the structure and bonding in these complexes, we have also determined the X-ray crystal structure of $[H_2C(4\text{-}Mepz)_2SnMe_2Cl_2]$.[10]

As an extension of our research, we have now decided to investigate the donor ability of neutral, tris-chelating, flexible and stable N_3-donor tris(pyrazol-1-yl)methanes toward tin(IV) and organotin(IV) acceptors. With the aim of evaluating the influence of the substituents on the structure and properties of the tin(IV) complexes, we have prepared a series of ligands containing methyl groups in the 3-, 4-, and 5-positions of the pyrazole ring: $HC(pz)_3$, $HC(4\text{-}Mepz)_3$, $HC(3,5\text{-}Me_2pz)_3$, $HC(3,4,5\text{-}Me_3pz)_3$, or $HC(3\text{-}Mepz)_2(5\text{-}Mepz)$ (Figure 1) reporting here the syntheses and properties of 27 new complexes. For the derivatives $[\{HC(3,5\text{-}Me_2pz)_3MeSnCl_2\}^+][\{MeSnCl_4\}^-]$, $[\{HC(4\text{-}Me_2pz)_3Sn^nBuCl_2\}^+]_2[\{Sn^nBuCl_5\}^{2-}]$, and $[\{HC(3,4,5\text{-}Me_3pz)_3SnBr_3\}^+][\{SnBr_5\}^-]$, the crystal and molecular structures have been determined by X-ray crystallography.

Experimental Section

General Procedures. The organotin(IV) halides were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. Solvent evaporations were always carried out under vacuum using a rotary evaporator. The samples for microanalysis were dried in vacuo to constant weight (20 °C, ca. 0.1 Torr). All syntheses were carried out under a nitrogen atmosphere. Hydrocarbon solvents were dried by refluxing with sodium, dichloromethane with calcium hydride, and tetrahydrofuran with sodium and benzophenone and then distillated. Prior to use all solvents were degassed under dry nitrogen.

Elemental analyses (C, H, N, S) were performed in house using a Carlo-Erba model 1106 instrument. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin-Elmer system 2000 FT-IR instrument. ^{1}H and ^{119}Sn NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^{1}H and 111.9 MHz for ^{119}Sn). The chemical shifts (δ) are reported in parts per million (ppm) from $SiMe_4$ (^{1}H calibration by internal deuterium solvent lock) and $SnMe_4$ (^{119}Sn). Peak multiplicities are abbreviated as follows: singlet, s; doublet, d; triplet, t; multiplet, m; pseudotriplet, pt; complex multiplet, mc; broad, br. FAB mass spectra were obtained on a Finnigan-MAT TSQ70 triple-stage quadrupole instrument equipped with an Ion Tech (Teddington, U.K.) atom gun using Xe as bombarding gas. The emission current was typically set at 2 mA with an accelerating voltage of 8 keV. For all experiments the source was kept at room temperature, using CsI for mass calibration. Samples were directly dissolved in an *m*-nitrobenzyl alcohol matrix. Melting points are uncorrected and were carried out using an IA 8100 Electrothermal Instrument and on a capillary apparatus. The electrical conductance of the solutions was measured with a Crison CDTM 522 conductimeter at room temperature. The osmometric measurements were carried out at 40 °C, over a range of concentrations, with a Knauer KNA0280 vapor pressure osmometer calibrated with benzil using Baker Analyzed spectrophotometric grade chloroform as solvent, the results being reproducible to ±2%.

Preparation of the Ligands. (a) Tris(pyrazol-1-yl)methane, HC(pz)$_3$. The ligand $HC(pz)_3$ (44% yield) was obtained according to a published method:[11] mp (*n*-hexane), 104−106 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.37 (pt, 3H, 4-C*H*), 7.58 (d, 3H, 3- or 5-C*H*), 7.68 (d, 3H, 3- or 5-C*H*), 8.43 (s, 1H, C*H*). ^{1}H NMR (acetone, 300 MHz): δ 6.40 (pt, 3H, 4-C*H*), 7.63 (d, 3H, 3- or 5-C*H*), 7.86 (d, 3H, 3- or 5-C*H*), 8.74 (s, 1H, C*H*). ^{1}H NMR (CD_3OD, 300 MHz): δ 6.43 (t, 3H, 4-C*H*), 7.67 (d, 3H, 3- or 5-C*H*), 7.74 (d, 3H, 3- or 5-C*H*), 8.70 (s, 1H, C*H*). Anal. Calcd for $C_{10}H_{10}N_6$: C, 56.1; H, 4.7; N, 39.2. Found: 56.3; H, 4.8; N, 39.0. IR (cm^{-1}): 3147 w, 3123 w [ν(C−H)].

(b) Tris(3,5-dimethylpyrazol-1-yl)methane, HC(3,5-Me$_2$pz)$_3$. The ligand $HC(3,5\text{-}Me_2pz)_3$ (42% yield) was obtained according to a published method:[11] mp (*n*-hexane), 133−134 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.01 (s, 9H, 3- or 5-CH_3), 2.18 (s, 9H, 3- or 5-CH_3), 5.88 (s, 3H, 4-C*H*), 8.09 (s, 1H, C*H*). Anal. Calcd for $C_{16}H_{22}N_6$: C, 64.4; H, 7.4; N, 28.2. Found: 64.3; H, 7.5; N, 28.0. IR (cm^{-1}): 3165 w [ν(C−H)].

(c) Tris(3,4,5-trimethylpyrazol-1-yl)methane, HC(3,4,5-Me$_3$pz)$_3$. To a stirred chloroform solution (200 mL) of 3,4,5-trimethylpyrazole (9.6 g, 0.086 mol), prepared according to a published method,[12] at room temperature and under nitrogen, K_2CO_3 (60.0 g, 0.436 mol) and n-Bu_4NHSO_4 (1.5 g, 0.004 mol) were added. The reaction was carried out at 40 °C, under nitrogen and with stirring for 3 days, until the solution became orange-red. The residue was filtered off and washed with hot chloroform (2 × 80 mL). The organic layer was collected, the chloroform was removed under reduced pressure, and then diethyl ether (100 mL) was added to the residue. The colorless precipitate formed was separated by filtration, washed with diethyl ether, and recrystallized from *n*-hexane to give 3.9 g (40% yield) of $HC(3,4,5\text{-}Me_3pz)_3$: mp (*n*-hexane), 156−157 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.88 (s, 9H, 3- or 5-CH_3), 1.93 (s, 9H, 3- or 5-CH_3), 2.13 (s, 9H, 4-CH_3), 8.05 (s, 1H, C*H*). ^{1}H NMR (CD_3OD, 300 MHz): δ 1.92 (s, 18H, 3- and 5-CH_3), 2.12 (s, 9H, 4-CH_3), 8.09 (s, 1H, C*H*). Anal. Calcd for $C_{19}H_{28}N_6$: C, 67.0; H, 8.3; N, 24.7. Found: 66.6; H, 8.6; N, 24.6. IR (cm^{-1}): 3168 br [ν(C−H)].

(d) Tris(4-methylpyrazol-1-yl)methane, HC(4-Mepz)$_3$. The ligand $HC(4\text{-}Mepz)_3$ (94% yield) was prepared as $HC(3,4,5\text{-}Me_3pz)_3$ by using 4-MepzH (20.3 g, 0.247 mol), K_2CO_3 (165.8 g, 1.200 mol), and n-Bu_4NHSO_4 (4.1 g, 0.012 mol): mp (*n*-hexane), 149−151 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.06 (s, 9H, 4-CH_3), 7.30 (s, 3H, 3- or 5-C*H*), 7.46 (s, 3H, 3- or 5-C*H*), 8.17 (s, 1H, C*H*). ^{1}H NMR (CD_3OD, 300 MHz): δ 2.07 (s, 9H, 4-CH_3), 7.44 (s, 3H, 3- or 5-C*H*), 7.47 (s, 3H, 3- or 5-C*H*), 8.36 (s, 1H, C*H*). Anal. Calcd for $C_{13}H_{16}N_6$: C, 59.6; H, 6.4; N, 32.0. Found: 60.0; H, 6.7; N, 31.7. IR (cm^{-1}): 3158 w, 3128 w, 3095 w, 3074 w [ν(C−H)].

(e) Bis(3-methylpyrazol-1-yl)(5-methylpyrazol-1-yl)methane, HC(3-Mepz)$_2$(5-Mepz). To a stirred chloroform solution (240 mL) of 3-MepzH (16.0 g, 0.195 mol), at room temperature and under nitrogen, K_2CO_3 (134.7 g, 0.975 mol) and n-Bu_4NHSO_4 (3.3 g, 0.010 mol) were added. The reaction was carried out at 40 °C, under nitrogen and with stirring for 4 days, until the solution became orange-red. The residue was filtered off and washed with hot chloroform (2 × 80 mL). The organic layer was collected and the solvent removed under reduced

(7) Gioia Lobbia, G.; Cingolani, A.; Leonesi, D.; Lorenzotti, A.; Bonati, F. *Inorg. Chim. Acta* **1987**, *130*, 203.
(8) Gioia Lobbia, G.; Bonati, F.; Cingolani, A.; Leonesi D.; Lorenzotti, A. *J. Organomet. Chem.* **1989**, *359*, 21.
(9) Pettinari, C.; Cingolani, A.; Bovio, B. *Polyhedron* **1996**, *15*, 115.
(10) Pettinari, C.; Lorenzotti, A.; Sclavi, G.; Cingolani, A.; Rivarola, E.; Colapietro M.; Cassetta, A. *J. Organomet. Chem.* **1995**, *496*, 69.
(11) Trofimenko, S. *J. Am. Chem. Soc.* **1970**, *92*, 5118.
(12) Pettinari, C.; Lorenzotti, A.; Pellei, M.; Santini, C. *Polyhedron* **1997**, *16*, 3435 and references cited therein.

pressure. After the addition of diethyl ether a colorless precipitate formed. It was filtered off, washed with diethyl ether, and recrystallized from *n*-hexane to give 2.9 g (17% yield) of HC(3-Mepz)$_2$(5-Mepz): mp (*n*-hexane), 114−115 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.27 (s, 6H, 3-C*H*$_3$), 2.39 (s, 3H, 5-C*H*$_3$), 6.10 (s, 3H, 4-C*H*), 7.31 (s, 2H, 5-C*H*), 7.54 (s, 1H, 3-C*H*), 8.21 (s, 1H, C*H*). Anal. Calcd for $C_{13}H_{16}N_6$: C, 60.9; H, 6.3; N, 32.8. Found: 60.9; H, 6.6; N, 32.7. IR (cm^{-1}): 3143 br, 3120 m [ν(C−H)].

Synthesis of the Complexes. (a) [{HC(pz)$_3$SnMeCl$_2$}$^+$]$_2$[{SnMeCl$_5$}$^{2-}$, 1. To a stirred diethyl ether solution (30 mL) of HC(pz)$_3$ (0.070 g, 0.330 mmol) at room temperature and under nitrogen, $SnMeCl_3$ (0.120 g, 0.500 mmol) was added. After ca. 1 h, the colorless precipitate formed was filtered off and washed with diethyl ether to give (88% yield) the analytical sample **1**: mp (CH_2Cl_2, diethyl ether), 256 °C (dec.). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.50 (s, 6H, Sn−C*H*$_3$, ^2J(^{119}Sn−^{1}H) = 125.0 Hz, ^2J(^{117}Sn−^{1}H) = 115.3 Hz), 1.91 (s, 3H, Sn−C*H*$_3$, ^2J(^{119}Sn−^{1}H) = 119.6 Hz, ^2J(^{117}Sn−^{1}H) = 110.0 Hz), 6.40, 6.58, 6.62 (3 t, 6H, 4-C*H*), 7.62, 7.71, 8.03, 8.32, 9.25, 9.36 (6 d, 12H, 3- and 5-C*H*), 8.53, 10.44 (2 s, 2H, C*H*). ^{1}H NMR (acetone, 300 MHz): δ 1.57 (s, 6H, Sn−C*H*$_3$, ^2J(^{119}Sn−^{1}H) = 120.3 Hz, ^2J(^{117}Sn−^{1}H) = 114.7 Hz), 1.62 (s, 3H, Sn−C*H*$_3$, ^2J(^{119}Sn−^{1}H) = 120.7 Hz, ^2J(^{117}Sn−^{1}H) = 115.5 Hz), 6.40, 6.86 (2 t, 6H, 4-C*H*), 7.63, 7.86 (2 d, 6H, 3- or 5-C*H*), 8.56, 8.78 (2 s br, 6H, 3- or 5-C*H*), 8.74, 10.21 (2 s, 2H, C*H*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ −448.6. Cond. (CH_2Cl_2, concentration = 1.09 × 10^{-3} M): Λ 0.30 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 1.01 × 10^{-3} M): Λ 57.8 Ω^{-1} cm^2 mol^{-1}. MS (FAB-positive): *m*/*z* 419 ([{HC(pz)$_3$SnMeCl$_2$}]$^+$, 85%, center of isotopic cluster). MS (FAB-negative): *m*/*z* 295 ([$SnCl_5$]$^-$, 50%, center of isotopic cluster), 275 ([$SnMeCl_4$]$^-$, 25%, center of isotopic cluster). Anal. Calcd for $C_{23}H_{29}Cl_9N_{12}Sn_3$: C, 24.0; H, 2.5; N, 14.6. Found: C, 24.1; H, 2.6; N, 14.4. IR (cm^{-1}): 3152 w, 3128 w [ν(C−H)], 545 m, 525 m [ν(Sn−C)], 315 s [ν(Sn−Cl)].

(b) [{HC(pz)$_3$Sn^{n}BuCl$_2$}$^+$]$_2$[{Sn^{n}BuCl$_5$}$^{2-}$], 2. To a stirred diethyl ether solution (30 mL) of HC(pz)$_3$ (0.073 g, 0.340 mmol), at room temperature and under nitrogen, Sn^{n}BuCl$_3$ (0.147 g, 0.521 mmol) was added. After ca. 6 h, a colorless precipitate formed which was filtered off and washed with diethyl ether to give (86% yield) the analytical sample **2**: mp (CH_2Cl_2, diethyl ether), 139−141 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.98, 1.00 (2 t, 9H, Sn−^{n}*Bu*), 1.4−1.6, 1.8−2.0 (mc, 14H, Sn−^{n}*Bu*), 2.47 (t, 4H, Sn−^{n}*Bu*), 6.37, 6.56, 6.58 (3 t, 6H, 4-C*H*), 7.59, 7.69, 8.00, 8.32, 9.23, 9.34 (6 d, 12H, 3- and 5-C*H*), 8.45, 10.33 (2 s, 2H, C*H*). ^{1}H NMR (acetone, 300 MHz): δ 0.95, 0.98 (2 t, 9H, Sn−^{n}*Bu*), 1.49 (ps, 6H, Sn−^{n}*Bu*), 1.8−2.0 (mc, 6H, Sn−^{n}*Bu*), 2.1−2.4 (mc, 6H, Sn−^{n}*Bu*), 6.40, 6.85 (2 t, 6H, 4-C*H*), 7.63, 7.86, 8.54, 8.81 (4 d, 12H, 3- and 5-C*H*), 8.73, 10.19 (2 s, 2H, C*H*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ −453.3. Cond. (CH_2Cl_2, concentration = 1.21 × 10^{-3} M): Λ 0.40 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 1.04 × 10^{-3} M): Λ 31.9 Ω^{-1} cm^2 mol^{-1}. MS (FAB-positive): *m*/*z* 461 ([{HC(pz)$_3$Sn^{n}BuCl$_2$}]$^+$, 90%, center of isotopic cluster). MS (FAB-negative): *m*/*z* 317 ([Sn^{n}BuCl$_4$]$^-$, 70%, center of isotopic cluster), 295 ([$SnCl_5$]$^-$, 20%, center of isotopic cluster). Anal. Calcd for $C_{32}H_{47}Cl_9N_{12}Sn_3$: C, 30.1; H, 3.7; N, 13.2. Found: C, 30.5; H, 3.9; N, 13.3. IR (cm^{-1}): 3131 w, 3107 m [ν(C−H)], 590 m [ν(Sn−C)], 300 s [ν(Sn−Cl)].

(c) [{HC(pz)$_3$SnPhCl$_2$}$^+$]$_2$[{SnPhCl$_5$}$^{2-}$], 3. To a stirred diethyl ether solution (30 mL) of HC(pz)$_3$ (0.073 g, 0.340 mmol), at room temperature and under nitrogen, $SnPhCl_3$ (0.150 g, 0.496 mmol) was added. After 2 h, the colorless precipitate afforded was filtered off and washed with diethyl ether to give (88% yield) the analytical sample **3**: mp (CH_2Cl_2, diethyl ether), 204−206 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.40, 6.53, 6.59 (3 t, 6H, 4-C*H*), 7.3−7.5, 7.7−8.0 (mc, 15H, Sn*Ph*), 7.61, 7.70, 8.19, 8.40, 9.35, 9.45 (6 d, 12H, 3- and 5-C*H*), 8.55, 10.62 (2 s broad, 2H, C*H*). ^{1}H NMR (acetone, 300 MHz): δ 6.40, 6.88 (2 t, 6H, 4-C*H*), 7.38−7.60, 8.10−8.20 (mc, 15H, Sn*Ph*), 7.65, 7.90, 8.85, 8.90 (4 d, 12H, 3- and 5-C*H*), 8.62, 10.32 (2 s, 2H, C*H*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ −503.3. Cond. (CH_2Cl_2, concentration = 1.06 × 10^{-3} M): Λ 0.11 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 0.75 × 10^{-3} M): Λ 69.2 Ω^{-1} cm^2 mol^{-1}. MW ($CHCl_3$, concentration = 3.19 × 10^3 M, room temperature): 643. MS (FAB-positive): *m*/*z* 523 ([{HC(pz)$_3$SnPhCl$_2$}]$^+$, 100%, center of isotopic cluster). MS (FAB-negative): *m*/*z* 337 ([$SnPhCl_4$]$^-$, 40%, center of isotopic cluster), 295 ([$SnCl_5$]$^-$, 35%, center of isotopic cluster). Anal. Calcd for $C_{38}H_{35}Cl_9N_{12}Sn_3$: C, 34.2; H, 2.6; N, 12.6. Found: C, 34.8; H, 2.9; N, 12.3. IR (cm^{-1}): 3129 w, 3111 w [ν(C−H)], 264 s [ν(Sn−C)], 311 s [ν(Sn−Cl)], 399 m [δ(Ph)].

(d) [{HC(4-Mepz)$_3$SnMeCl$_2$}$^+$]$_2$[{SnMeCl$_5$}$^{2-}$], 4. Compound **4** (78% yield) was obtained similarly to compound **1**: mp (CH_2Cl_2, diethyl ether), 120−132 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.44 (s, 6H, Sn−C*H*$_3$, ^2J(^{119}Sn−^{1}H) = 113.9 Hz, ^2J(^{117}Sn−^{1}H) = 108.7 Hz), 1.92 (s, 3H, Sn−C*H*$_3$, ^2J(^{119}Sn−^{1}H) = 126.9 Hz, ^2J(^{117}Sn−^{1}H) = 121.1 Hz), 2.13 (s, 9H, 4-C*H*$_3$), 2.16 (s, 9H, 4-C*H*$_3$), 7.80 (s, 4H, 3- or 5-C*H*), 8.09 (s, 2H, 3- or 5-C*H*), 8.85 (s, 2H, 3- or 5-C*H*), 8.97 (s, 4H, 3- or 5-C*H*), 10.19 (s, 2H, C*H*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ −455.5. Cond. (CH_2Cl_2, concentration = 0.99 × 10^{-3} M): Λ 15.0 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 0.96 × 10^{-3} M): Λ 73.0 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{29}H_{41}Cl_9N_{12}Sn_3$: C, 28.3; H, 3.3; N, 13.6. Found: C, 28.6; H, 3.5; N, 13.3. IR (cm^{-1}): 3150 w, 3112 m [ν(C−H)], 536 m [ν(Sn−C)], 326 s, 310 sh [ν(Sn−Cl)].

(e) [{HC(4-Mepz)$_3$Sn^{n}BuCl$_2$}$^+$]$_2$[{Sn^{n}BuCl$_5$}$^{2-}$], 5. Compound **5** (85% yield) was obtained similarly to compound **2**: mp (CH_2Cl_2, diethyl ether), 97−100 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.98, 1.01 (2 t, 9H, Sn−^{n}*Bu*), 1.55 (m, 12H, Sn−^{n}*Bu*), 1.80−2.03 (mc, 4H, Sn−^{n}*Bu*), 1.91 (s, 6H, 4-C*H*$_3$), 2.12 (s, 6H, 4-C*H*$_3$), 2.15 (s, 6H, 4-C*H*$_3$), 2.48 (t, 2H, Sn−^{n}*Bu*), 7.30, 7.47, 7.77, 8.09, 8.84, 8.96 (6s, 12H, 3- or 5-C*H*), 8.16, 10.24 (2s, 2H, C*H*). Cond. (CH_2Cl_2, concentration = 1.11 × 10^{-3} M): Λ 3.2 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 0.92 × 10^{-3} M): Λ 64.4 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{38}H_{59}Cl_9N_{12}Sn_3$: C, 33.6; H, 4.4; N, 12.4. Found: C, 33.7; H, 4.6; N, 12.1. IR (cm^{-1}): 3120 w, 3104 m [ν(C−H)], 602 s [ν(Sn−C)], 312 s [ν(Sn−Cl)].

(f) [{HC(4-Mepz)$_3$SnPhCl$_2$}$^+$]$_2$[{SnPhCl$_5$}$^{2-}$], 6. Compound **6** (76% yield) was obtained similarly to compound **3**: mp (CH_2Cl_2, diethyl ether), 128−130 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.08 (s, 12H, 4-C*H*$_3$), 2.14 (s, 6H, 4-C*H*$_3$), 7.30−7.60 (mc, 12H, Sn*Ph*), 7.52 (s, 4H, 3- or 5-C*H*), 8.16 (s, 2H, C*H*), 8.32 (d, 3H, Sn*Ph*), 8.92 (s, 2H, 3- or 5-C*H*), 9.03 (s, 4H, 3- or 5-C*H*), 10.36 (s, 2H, C*H*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ −469.5. Cond. (CH_2Cl_2, concentration = 1.02 × 10^{-3} M): Λ 3.5 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 1.07 × 10^{-3} M): Λ 68.7 Ω^{-1} cm^2 mol^{-1}. MW ($CHCl_3$, concentration = 2.32 × 10^3 M, room temperature): 464. MW ($CHCl_3$, concentration = 4.90 × 10^3 M, room temperature): 560. Anal. Calcd for $C_{44}H_{47}Cl_9N_{12}Sn_3$: C, 37.2; H, 3.3; N, 11.8. Found: C, 37.6; H, 3.6; N, 11.3. IR (cm^{-1}): 3123 w, 3112 m, 3068 w, 3048 w [ν(C−H)], 292 m [ν(Sn−C)], 325 s [ν(Sn−Cl)], 460 s, 451 s [ν(Ph)].

(g) [{HC(3,5-Me$_2$pz)$_3$SnMeCl$_2$}$^+$][{SnMeCl$_4$}$^-$], 7. Compound **7** (95% yield) was obtained similarly to compound **1**: mp (CH_2Cl_2, diethyl ether), 220−223 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.62 (s, 3H, Sn−C*H*$_3$, ^2J(^{119}Sn−^{1}H) = 116.8 Hz, ^2J(^{117}Sn−^{1}H) = 115.1 Hz), 1.64 (s, 3H, Sn−C*H*$_3$, ^2J(^{119}Sn−^{1}H) = 111.6 Hz, ^2J(^{117}Sn−^{1}H) = 110.0 Hz), 2.63 (s, 6H, 3- or 5-C*H*$_3$), 2.79 (s, 3H, 3- or 5-C*H*$_3$), 2.82 (s, 9H, 3- or 5-C*H*$_3$), 6.21 (s, 1H, 4-C*H*), 6.27 (s, 2H, 4-C*H*), 8.09 (s, 1H, C*H*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ −244.0, −469.7. Cond. (CH_2Cl_2, concentration = 1.02 × 10^{-3} M): Λ 19.6 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 0.95 × 10^{-3} M): Λ 74.7 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{18}H_{28}Cl_6N_6Sn_2$: C, 27.8; H, 3.6; N, 10.8. Found: C, 28.0; H, 3.8; N, 10.7. IR (cm^{-1}): 3132 w, 3095 w [ν(C−H)], 539 m, 533 sh [ν(Sn−C)], 308 s [ν(Sn−Cl)].

(h) [{HC(3,5-Me$_2$pz)$_3$Sn^{n}BuCl$_2$}$^+$][{Sn^{n}BuCl$_4$}$^-$]·2H$_2$O, 8. Compound **8** (85% yield) was obtained similarly to compound **2**: mp (CH_2Cl_2, diethyl ether), 59−61 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.95 (t, 3H, Sn−^{n}*Bu*), 0.98 (t, 3H, Sn−^{n}*Bu*), 1.48 (ps, 4H, Sn−^{n}*Bu*), 1.7−1.9 (mc, 4H, Sn−^{n}*Bu*), 2.04 (t, 2H, Sn−^{n}*Bu*), 2.19 (t, 2H, Sn−^{n}*Bu*), 2.43, 2.61, 2.78, 2.81, 2.85 (5 s, 18H, 3- and 5-C*H*$_3$), 4.80 (br, 4H, *H*$_2$O), 6.19 (s, 1H, 4-C*H*), 6.26 (s, 2H, 4-C*H*), 8.13 (s, 1H, C*H*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ −108.5, −467.5. Cond. (CH_2Cl_2, concentration = 0.76 × 10^{-3} M): Λ 16.1 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 0.75 × 10^{-3} M): Λ 7.84 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{24}H_{44}Cl_6N_6O_2Sn_2$: C, 32.1; H, 4.9; N, 9.4. Found: C, 31.9; H, 5.1; N, 8.8. IR (cm^{-1}): 3164 w [ν(C−H)], 608 m, 594 m [ν(Sn−C)], 304 s, 278 s [ν(Sn−Cl)], 3400 br [ν(H$_2$O)].

(i) [{HC(3,5-Me$_2$pz)$_3$SnPhCl$_2$}$^+$][{SnPhCl$_4$}$^-$], 9. Compound **9** (76% yield) was obtained similarly to compound **3**: mp (CH_2Cl_2, diethyl ether), 176−179 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.95 (s, 6H, 3-

or 5-CH_3), 2.79 (s, 3H, 3- or 5-CH_3), 2.87 (s, 9H, 3- or 5-CH_3), 6.16 (s, 2H, 4-C*H*), 6.23 (s, 1H, 4-C*H*), 7.40−7.48 (mc, 8H, Sn*Ph*), 8.20 (s, 1H, C*H*), 8.25 (d, 2H, Sn*Ph*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ −320.2, −424.8. Cond. (CH_2Cl_2, concentration = 0.96×10^{-3} M): Λ 17.7 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 1.02×10^{-3} M): Λ 76.8 Ω^{-1} cm^2 mol^{-1}. MW ($CHCl_3$, concentration = 3.06×10^3 M, room temperature): 556. Anal. Calcd for $C_{28}H_{32}Cl_6N_6Sn_2$: C, 38.3; H, 3.8; N, 9.3. Found: C, 37.9; H, 3.8; N, 9.5. IR (cm^{-1}): 3138 w, 3102 w, 3054 w [ν(C−H)], 283 s [ν(Sn−C)], 320 s [ν(Sn−Cl)], 447 s [ν(Ph)].

(j) [{HC(3,4,5-Me$_3$pz)$_3$SnMeCl$_2$}$^+$][{SnMeCl$_4$}$^-$], 10. Compound **10** (82% yield) was obtained similarly to compound **1**: mp (CH_2Cl_2, diethyl ether), 128−129 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.59 (s, 6H, Sn−CH_3, $^2J(^{119}Sn-^1H)$ = 115.4 Hz, $^2J(^{117}Sn-^1H)$ = 110.3 Hz), 1.99 (s, 9H, 3- or 5-CH_3), 2.52 (s, 6H, 3- or 5-CH_3), 2.69 (s, 3H, 3- or 5-CH_3), 2.73 (s, 9H, 4-CH_3), 8.16 (s, 1H, C*H*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ −259.6, −474.6, −475.7. Cond. (CH_2Cl_2, concentration = 0.97×10^{-3} M): Λ 21.2 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 0.97×10^{-3} M): Λ 105.5 Ω^{-1} cm^2 mol^{-1}. MS (FAB-positive): *m*/*z* 545 ([{HC(3,4,5-Me$_3$pz)$_3$SnMeCl$_2$}]$^+$, 100%, center of isotopic cluster). MS (FAB-negative): *m*/*z* 275 ([SnMeCl$_4$]$^-$, 40%, center of isotopic cluster). Anal. Calcd for $C_{21}H_{34}Cl_6N_6Sn_2$: C, 30.7; H, 4.2; N, 10.2. Found: C, 31.1; H, 4.4; N, 10.4. IR (cm^{-1}): 3124 w [ν(C−H)], 544 m [ν(Sn−C)], 312 s [ν(Sn−Cl)].

(k) [{HC(3,4,5-Me$_3$pz)$_3$Sn^{n}BuCl$_2$}$^+$][{Sn^{n}BuCl$_4$}$^-$], 11. Compound **11** (79% yield) was obtained similarly to compound **1**: mp (CH_2Cl_2, diethyl ether), 138−139 °C. ^{1}H NMR (CD_3OD, 300 MHz): δ 0.94 (t, 6H, Sn−^{n}*Bu*), 1.3−1.6 (mc, 8H, Sn−^{n}*Bu*), 1.73 (t, 4H, Sn−^{n}*Bu*), 1.92 (s, 9H, 3- or 5-CH_3), 2.03 (s, 6H, 3- or 5-CH_3), 2.11 (s, 3H, 3- or 5-CH_3), 2.35 (s, 9H, 4-CH_3), 8.09 (s, 1H, C*H*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ −271.0, −472.7. Cond. (CH_2Cl_2, concentration = 0.97×10^{-3} M): Λ 18.9 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 1.02×10^{-3} M): Λ 79.0 Ω^{-1} cm^2 mol^{-1}. MS (FAB-positive): *m*/*z* 587 ([{HC(3,4,5-Me$_3$pz)$_3$Sn^{n}BuCl$_2$}]$^+$, 100%, center of isotopic cluster). MS (FAB-negative): *m*/*z* 317 ([Sn^{n}BuCl$_4$]$^-$, 60%, center of isotopic cluster). Anal. Calcd for $C_{27}H_{46}Cl_6N_6Sn_2$: C, 35.8; H, 5.1; N, 9.3. Found: C, 36.1; H, 5.4; N, 9.5. IR (cm^{-1}): 3132 w [ν(C−H)], 608 w [ν(Sn−C)], 318 s [ν(Sn−Cl)].

(l) [{HC(3,4,5-Me$_3$pz)$_3$SnPhCl$_2$}$^+$][{SnPhCl$_4$}$^-$]·H$_2$O, 12. Compound **12** (58% yield) was obtained similarly to compound **3**: mp (CH_2Cl_2, diethyl ether), 213-214 °C. ^{1}H NMR (CD_3OD, 300 MHz): δ 1.87, 1.93, 2.01, 2.67, 2.69, 2.79 (6 s, 27H, 3-, 4-, and 5-CH_3), 2.36 (br, 2H, H_2O), 7.30−7.60 (mc, 8H, Sn*Ph*), 7.80−7.95 (mc, 2H, Sn*Ph*), 8.28 (s, 1H, C*H*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ −529.7. Cond. (CH_2Cl_2, concentration = 1.08×10^{-3} M): Λ 11.79 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 1.08×10^{-3} M): Λ 58.9 Ω^{-1} cm^2 mol^{-1}. MS (FAB-positive): *m*/*z* 607 ([{HC(3,4,5-Me$_3$pz)$_3$SnPhCl$_2$}]$^+$, 100%, center of isotopic cluster). MS (FAB-negative): *m*/*z* 337 ([SnPhCl$_4$]$^-$, 20%, center of isotopic cluster). Anal. Calcd for $C_{31}H_{40}Cl_6N_6Sn_2O$: C, 38.7; H, 4.2; N, 8.7. Found: C, 39.0; H, 4.5; N, 8.6. IR (cm^{-1}): 3124 w [ν(C−H)], 290 sh [ν(Sn−C)], 310 br [ν(Sn−Cl)], 454 m [ν(Ph)].

(m) [{HC(3-Mepz)$_2$(5-Mepz)SnMeCl$_2$}$^+$][{SnMeCl$_4$}$^-$], 13. Compound **13** (53% yield) was obtained similarly to compound **1**: mp (CH_2Cl_2, diethyl ether), 208 °C (dec.). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.67 (s, 3H, Sn−CH_3, $^2J(^{119}Sn-^1H)$ = 117.7 Hz, $^2J(^{117}Sn-^1H)$ = 112.5 Hz), 1.78 (s, 3H, Sn−CH_3, $^2J(^{119}Sn-^1H)$ = 121.2 Hz, $^2J(^{117}Sn-^1H)$ = 115.7 Hz), 2.63, 2.82, 2.91, 2.95 (4 s, 9H, 3- and 5-CH_3), 6.39 (s, 3H, 4-C*H*), 8.33 (s, 1H, 3- or 5-C*H*), 8.99 (s, 2H, 3- or 5-C*H*), 10.00 (s, 1H, C*H*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ −422.9, −463.8. Cond. (CH_2Cl_2, concentration = 1.03×10^{-3} M): Λ 0.83 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 0.98×10^{-3} M): Λ 34.1 Ω^{-1} cm^2 mol^{-1}. MS (FAB-positive): *m*/*z* 461 ([{HC(3-Mepz)$_2$-(5-Mepz)SnMeCl$_2$}]$^+$, 20%, center of isotopic cluster). MS (FAB-negative): *m*/*z* 295 ([SnCl$_5$]$^-$, 20%, center of isotopic cluster), 225 ([SnCl$_3$]$^-$, 20%, center of isotopic cluster). Anal. Calcd for $C_{15}H_{22}Cl_6N_6Sn_2$: C, 24.5; H, 3.0; N, 11.4. Found: C, 25.0; H, 3.2; N, 11.4. IR (cm^{-1}): 3133 br, 3119 m [ν(C−H)], 533 w [ν(Sn−C)], 316 s [ν(Sn−Cl)].

(n) [{HC(3-Mepz)$_2$(5-Mepz)SnPhCl$_2$}$^+$]$_2$[{SnPhCl$_5$}$^{2-}$]·H$_2$O, 14. Compound **14** (70% yield) was obtained similarly to compound **3**: mp (CH_2Cl_2, diethyl ether), 203 °C (dec.). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.62 (br, 2H, H_2O), 1.98, 2.17, 224, 2.27 (4s, 12H, 3- or 5-CH_3), 2.88, 2.95, 3.03 (3s, 6H, 3- or 5-CH_3), 6.12, 6.27, 6.39, 6.40 (4s, 6H, 4-C*H*), 7.20−7.50 (mc, 12H, Sn*Ph*), 8.21 (d, 3H, Sn*Ph*), 8.39, 9.23 (2 d, 6H, 3- or 5-C*H*), 10.50, 10.60 (2 s, 2H, C*H*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ −516.7, −518.8. Cond. (CH_2Cl_2, concentration = 1.02×10^{-3} M): Λ 1.51 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 0.85×10^{-3} M): Λ 103.3 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{44}H_{47}Cl_9N_{12}Sn_3$: C, 37.2; H, 3.3; N, 11.8. Found: C, 37.3; H, 3.6; N, 11.9. IR (cm^{-1}): 3125 br [ν(C−H)], 292 sh [ν(Sn−C)], 309 s [ν(Sn−Cl)], 456 m [ν(Ph)].

(o) [{HC(pz)$_3$SnCl$_3$}$^+$]$_2$[{SnCl$_6$}$^{2-}$]·H$_2$O, 15. To a stirred dichloromethane solution (10 mL) of HC(pz)$_3$ (0.073 g, 0.340 mmol), at −40 °C and under nitrogen, a 1.0 M solution of $SnCl_4$ in the same solvent (1.0 mL) was added. After ca. 3 h, the colorless precipitate obtained was filtered off and washed with diethyl ether to give (97% yield) the analytical sample **15**: mp (CH_2Cl_2, diethyl ether), 286 °C (dec.). ^{1}H NMR (CD_3OD, 300 MHz): δ 1.86 (br, 2H, H_2O), 6.43 (pt, 6H, 4-C*H*), 7.67, 7.73 (2 d, 12H, 3- and 5-C*H*), 8.69 (s, 2H, C*H*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ −611.8. Cond. (acetone, concentration = 1.04×10^{-3} M): Λ 58.9 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{20}H_{22}Cl_{12}N_{12}OSn_3$: C, 19.8; H, 1.7; N, 13.9. Found: C, 19.5; H, 1.8; N, 13.4. IR (cm^{-1}): 3110 w [ν(C−H)], 349 s [ν(Sn−Cl)], 3429 br [ν(H$_2$O)].

(p) [{HC(pz)$_3$SnBr$_3$}$^+$]$_2$[{SnBr$_6$}$^{2-}$], 16. To a stirred dichloromethane solution (10 mL) of HC(pz)$_3$ (0.070 g, 0.330 mmol), at −40 °C and under nitrogen, a 1.0 M solution of $SnBr_4$ in the same solvent (1.0 mL) was added. After 4 h, the yellow precipitate formed was filtered off and washed with diethyl ether to give (97% yield) the analytical sample **16**: mp (CH_2Cl_2, diethyl ether), 281 °C (dec.). ^{1}H NMR (CD_3OD, 300 MHz): δ 6.44 (pt, 6H, 4-C*H*), 7.68, 7.74 (d, 12H, 3- and 5-C*H*), 8.69 (s, 2H, C*H*). Cond. (acetone, concentration = 0.99×10^{-3} M): Λ 85.1 Ω^{-1} cm^2 mol^{-1}. MS (FAB-positive): *m*/*z* 573 ([{HC(pz)$_3$SnBr$_3$}]$^+$, 15%, center of isotopic cluster). MS (FAB-negative): *m*/*z* 518 ([SnBr$_5$]$^-$, 35%, center of isotopic cluster), 359 ([SnBr$_3$]$^-$, 100%, center of isotopic cluster). Anal. Calcd for $C_{20}H_{20}Br_{12}N_{12}Sn_3$: C, 13.8; H, 1.2; N, 9.7. Found: C, 14.1; H, 1.3; N, 9.4. IR (cm^{-1}): 3107 w [ν(C−H)], 249 s [ν(Sn−Br)].

(q) [{HC(pz)$_3$SnI$_3$}$^+$]$_2$[{SnI$_6$}$^{2-}$]·H$_2$O, 17. To a stirred dichloromethane solution (10 mL) of HC(pz)$_3$ (0.068 g, 0.320 mmol), at room temperature and under nitrogen, SnI_4 (0.310 g, 0.495 mmol) was added. After 10 h, the brown precipitate formed was filtered off and washed with diethyl ether to give (91% yield) the analytical sample **17**: mp (CH_2Cl_2, diethyl ether), 168−169 °C. ^{1}H NMR (CD_3OD, 300 MHz): δ 1.30 (s, 2H, H_2O), 6.44 (s br, 6H, 4-C*H*), 7.68, 7.75 (s br, 12H, 3- and 5-C*H*), 8.70 (d, 2H, C*H*). Cond. (CH_2Cl_2, concentration = 0.86×10^{-3} M): Λ 0.76 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 0.84×10^{-3} M): Λ 235.0 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{20}H_{22}I_{12}N_{12}OSn_3$: C, 10.3; H, 1.0; N, 7.2. Found: C, 10.7; H, 1.0; N, 6.8. IR (cm^{-1}): 3124 w [ν(C−H)], 151 s [ν(Sn−I)], 3429 br [ν(H$_2$O)].

(r) [{HC(4-Mepz)$_3$SnCl$_3$}$^+$]$_2$[{SnCl$_6$}$^{2-}$]·H$_2$O, 18. Compound **18** (66% yield) was obtained similarly to compound **15**: mp (CH_2Cl_2, diethyl ether), 239 °C (dec.). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.21 (s, 18H, 4-CH_3), 2.30 (br, 2H, H_2O), 8.05 (s, 6H, 3-C*H*, $^3J(Sn-^1H)$ = 10.4 Hz), 9.05 (s, 6H, 5-C*H*), 10.08 (s, 2H, C*H*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ −615.4. Cond. (CH_2Cl_2, concentration = 0.90×10^{-3} M): Λ 0.16 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 0.98×10^{-3} M): Λ 37.9 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{26}H_{34}Cl_{12}N_{12}OSn_3$: C, 23.8; H, 2.6; N, 12.8. Found: C, 23.4; H, 2.5; N, 12.3. IR (cm^{-1}): 3097 w [ν(C−H)], 351 s [ν(Sn−Cl)], 3453 br [ν(H$_2$O)].

(s) [{HC(4-Mepz)$_3$SnBr$_3$}$^+$]$_2$[{SnBr$_6$}$^{2-}$], 19. Compound **19** (61% yield) was obtained similarly to compound **16**: mp (CH_2Cl_2, diethyl ether), 263 °C (dec.). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.23 (s, 18H, 4-CH_3), 8.08 (s, 6H, 3-C*H*), 9.26 (s, 6H, 5-C*H*, $^3J(Sn-^1H)$ = 12.2 Hz), 10.12 (s, 2H, C*H*). Cond. (CH_2Cl_2, concentration = 1.01×10^{-3} M): Λ 0.18 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 1.01×10^{-3} M): Λ 79.4 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{26}H_{32}Br_{12}N_{12}Sn_3$: C, 17.1; H, 1.8; N, 9.2. Found: C, 16.8; H, 1.7; N, 8.9. IR (cm^{-1}): 3065 w [ν(C−H)], 247 sh [ν(Sn−Br)].

(t) [{HC(4-Mepz)$_3$SnI$_3$}$^+$]$_2$[{SnI$_6$}$^{2-}$], 20. Compound **20** (25% yield) was obtained similarly to compound **17**: mp (CH_2Cl_2, diethyl ether), 209 °C (dec.). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.24 (s, 18H,

Table 1. Crystallographic Data and Details of Structure Refinements for Compounds **5**, **7**, and **25**

	5	**7**	**25**
formula	$C_{38}H_{59}Cl_9N_{12}Sn_3$	$C_{18}H_{28}Cl_6N_6Sn_2 \cdot 0.69CH_2Cl_2$	$C_{19}H_{28}Br_8N_6Sn_2 \cdot 0.86CH_2Cl_2$
fw	1053.51	873.05	1290.17
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
λ, Å	0.710 73	0.710 73	0.710 73
a/Å	12.476(4)	18.917(5)	9.456(1)
b/Å	23.363(6)	9.888(3)	26.452(5)
c/Å	23.540(6)	17.858(4)	14.758(2)
β/deg	90	110.75(3)	92.17(2)
V/Å^3	6861(3)	3123.7(14)	3688.8(9)
Z	4	4	4
d_{calc}/(g·cm^{-3})	1.489	1.780	2.324
μ/cm^{-1}	15.88	22.50	101.66
cryst dimens/mm	0.3 × 0.3 × 0.3	0.4 × 0.2 × 0.2	0.64 × 0.24 × 0.08
type of diffractometer	STADI-4(Stoe)	IPDS-4(Stoe)	IPDS-4(Stoe)
T/K	293	190	190
θ_{max}/deg	22.2	23.3	26.2
reflns collected	8433	17398	29032
reflns unique	7634	4349	7219
reflns with $I > 2\sigma(I)$	4230	3869	4632
data/params	5544/589	4349/328	6188/353
wR2 (F^2)[a]	0.1704	0.1112	0.0815
R1[b]	0.0818	0.0452	0.0387
largest peak and hole in ΔF/(e·Å^{-3})	0.62/−0.48	0.95/−0.92	1.19/−1.08

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

4-C*H*$_3$), 8.09 (s, 6H, 3-C*H*, ^3J(Sn−^{1}H) = 12.8 Hz), 8.68 (s, 6H, 5-C*H*), 10.36 (s, 2H, C*H*). Cond. (CH_2Cl_2, concentration = 1.00 × 10^{-3} M): Λ 2.34 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 0.85 × 10^{-3} M): Λ 247.0 Ω^{-1} cm^2 mol^{-1}. (FAB-negative): *m*/*z* 1270 ([I_{10}]$^-$, 20%, center of isotopic cluster), 888 ([I_7]$^-$, 55%, center of isotopic cluster), 507 ([I_4]$^-$, 100%, center of isotopic cluster), 381 ([I_3]$^-$, 50%, center of isotopic cluster). Anal. Calcd for $C_{26}H_{32}I_{12}N_{12}Sn_3$: C, 13.1; H, 1.4; N, 7.0. Found: C, 13.6; H, 1.5; N, 6.9. IR (cm^{-1}): 3166 w [ν(C−H)], 132 s [ν(Sn−I)].

(u) [{HC(3,5-Me$_2$pz)$_3$SnCl$_3$}$^+$]$_2$[{SnCl$_6$}$^{2-}$]·H$_2$O, 21. Compound **21** (26% yield) was obtained similarly to compound **15**: mp (CH_2Cl_2, diethyl ether), 248 °C (dec.). ^{1}H NMR (CD_3OD, 300 MHz): δ 2.17 (br, 2H, H_2O), 2.75 (s, 18H, 3- and 5-C*H*$_3$), 2.77 (s, 18H, 3- and 5-C*H*$_3$), 6.47 (s, 6H, 4-C*H*), 8.21 (s, 2H, C*H*). ^{119}Sn NMR (CD_3OD, 111.9 MHz): δ −577.1, −583.2. Cond. (CH_2Cl_2, concentration = 0.92 × 10^{-3} M): Λ 7.87 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 0.74 × 10^{-3} M): Λ 58.1 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{32}H_{46}Cl_{12}N_{12}OSn_3$: C, 27.5; H, 3.3; N, 12.0. Found: C, 27.7; H, 3.4; N, 11.9. IR (cm^{-1}): 3122 w [ν(C−H)], 344 s, 280 sh [ν(Sn−Cl)], 3483 br [ν(H_2O)].

(v) [{HC(3,5-Me$_2$pz)$_3$SnBr$_3$}$^+$]$_2$[{SnBr$_6$}$^{2-}$], 22. Compound **22** (98% yield) was obtained similarly to compound **16**: mp (CH_2Cl_2, diethyl ether), 242 °C (dec.). ^{1}H NMR (CD_3OD, 300 MHz): δ 2.75 (s, 18H, 3- or 5-C*H*$_3$), 2.86 (s, 18H, 3- or 5-C*H*$_3$), 6.44 (s, 6H, 4-C*H*), 8.20 (s, 2H, C*H*). Cond. (acetone, concentration = 0.98 × 10^{-3} M): Λ 90.9 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{32}H_{44}Br_{12}N_{12}Sn_3$: C, 20.1; H, 2.3; N, 8.8. Found: C, 19.7; H, 2.4; N, 8.3. IR (cm^{-1}): 3086 w [ν(C−H)], 237 s [ν(Sn−Br)].

(w) [{HC(3,5-Me$_2$pz)$_3$SnI$_3$}$^+$]$_2$[{SnI$_6$}$^{2-}$]·H$_2$O, 23. Compound **23** (57% yield) was obtained similarly to compound **17**: mp (CH_2Cl_2, diethyl ether), 166−167 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.05 (s, 18H, 3- or 5-C*H*$_3$), 2.18 (s, 18H, 3- or 5-C*H*$_3$), 2.42 (br, 2H, H_2O), 7.26 (s, 6H, 4-C*H*), 8.09 (s, 2H, C*H*). Cond. (CH_2Cl_2, concentration = 0.80 × 10^{-3} M): Λ 48.6 Ω^{-1} cm^2 mol^{-1}. MS (FAB-negative): *m*/*z* 1270 ([I_{10}]$^-$, 30%, center of isotopic cluster), 888 ([I_7]$^-$, 60%, center of isotopic cluster), 507 ([I_4]$^-$, 100%, center of isotopic cluster). Anal. Calcd for $C_{32}H_{46}I_{12}N_{12}OSn_3$: C, 15.4; H, 1.9; N, 6.7. Found: C, 15.6; H, 1.8; N, 6.5. IR (cm^{-1}): 3078 w [ν(C−H)], 159 m [ν(Sn−I)], 3565 br [ν(H_2O)].

(x) [{HC(3,4,5-Me$_3$pz)$_3$SnCl$_3$}$^+$]$_2$[{SnCl$_6$}$^{2-}$]·2H$_2$O, 24. Compound **24** (78% yield) was obtained similarly to compound **15**: mp (CH_2Cl_2, diethyl ether), 227−228 °C. ^{1}H NMR (CD_3OD, 300 MHz): δ 2.03 (s, 18H, 3-, 4-, or 5-C*H*$_3$), 2.36 (br, 4H, H_2O), 2.67 (s, 18H, 3-, 4-, or 5-C*H*$_3$), 2.69 (s, 18H, 3-, 4-, or 5-C*H*$_3$), 8.26 (s, 2H, C*H*). Cond. (CH_2Cl_2, concentration = 1.07 × 10^{-3} M): Λ 5.31 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 0.96 × 10^{-3} M): Λ 117.2 Ω^{-1} cm^2 mol^{-1}. MS (FAB-positive): *m*/*z* 565 ([{HC(3,4,5-Me$_3$pz)$_3$SnCl$_3$}]$^+$, 100%, center of isotopic cluster). MS (FAB-negative): *m*/*z* 295 ([$SnCl_5$]$^-$, 100%, center of isotopic cluster). Anal. Calcd for $C_{38}H_{60}Cl_{12}N_{12}O_2Sn_3$: C, 30.5; H, 4.0; N, 11.2. Found: C, 30.7; H, 4.2; N, 10.9. IR (cm^{-1}): 3036 w [ν(C−H)], 341 s [ν(Sn−Cl)], 3574 s [ν(H_2O)].

(y) [{HC(3,4,5-Me$_3$pz)$_3$SnBr$_3$}$^+$][{SnBr$_5$}$^-$], 25. Compound **25** (97% yield) was obtained similarly to compound **16**: mp (CH_2Cl_2, diethyl ether), 227 °C (dec.). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.02, 2.45, 2.79, 2.82 (4 s, 27H, 3-, 4-, and 5-C*H*$_3$), 8.24 (s, 1H, C*H*). Cond. (CH_2Cl_2, concentration = 1.20 × 10^{-3} M): Λ 16.13 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 0.97 × 10^{-3} M): Λ 80.9 Ω^{-1} cm^2 mol^{-1}. MS (FAB-positive): *m*/*z* 699 ([{HC(3,4,5-Me$_3$pz)$_3$SnBr$_3$}]$^+$, 100%, center of isotopic cluster). MS (FAB-negative): *m*/*z* 519 ([$SnBr_5$]$^-$, 100%, center of isotopic cluster), 438 ([$SnBr_4$]$^-$, 60%, center of isotopic cluster), 359 ([$SnBr_3$]$^-$, 100%, center of isotopic cluster). Anal. Calcd for $C_{19}H_{28}Br_8N_6Sn_2$: C, 18.5; H, 2.4; N, 6.8. Found: C, 18.4; H, 2.4; N, 6.5. IR (cm^{-1}): 3089 w [ν(C−H)], 246 br [ν(Sn−Br)].

(z) [{HC(3-Mepz)$_2$(5-Mepz)SnCl$_3$}$^+$]$_2$[{SnCl$_6$}$^{2-}$]·2H$_2$O, 26. Compound **26** (47% yield) was obtained similarly to **15**: mp (CH_2Cl_2, diethyl ether), 248 °C (dec.). ^{1}H NMR (CD_3OD, 300 MHz): δ 2.20 (br, 4H, H_2O), 2.46, 2.80, 3.10 (3 s, 18H, 3- and 5-C*H*$_3$), 6.46, 6.50 (2 s br, 6H, 4-C*H*), 7.27 8.24, 9.35, 9.52 (4 s, 6H, 3- and 5-C*H*), 11.3 (br, 2H, C*H*). ^{119}Sn NMR ($CDCl_3$, 111.9 MHz): δ −629.1. Cond. (CH_2Cl_2, concentration = 0.99 × 10^{-3} M): Λ 0.37 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 1.00 × 10^{-3} M): Λ 113.7 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{26}H_{36}Cl_{12}N_{12}O_2Sn_3$: C, 23.5; H, 2.7; N, 12.6. Found: C, 23.0; H, 2.7; N, 12.2. IR (cm^{-1}): 3103 br [ν(C−H)], 341 s [ν(Sn−Cl)], 3454 br [ν(H_2O)].

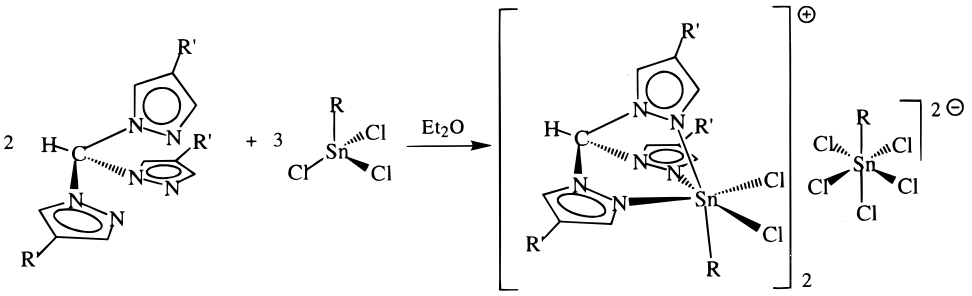
(aa) [{HC(3-Mepz)$_2$(5-Mepz)SnBr$_3$}$^+$]$_2$[{SnBr$_6$}$^{2-}$], 27. Compound **27** (35% yield) was obtained similarly to **16**: mp (CH_2Cl_2, diethyl ether), 141−142 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.47, 2.51, 2.89, 3.10 (4 s, 18H, 3- and 5-C*H*$_3$), 6.45 (br, 6H, 4-C*H*), 8.33, 9.31 (2 s br, 6H, 3- and 5-C*H*), 9.89 (s, 2H, C*H*). Cond. (CH_2Cl_2, concentration = 0.46 × 10^{-3} M): Λ 2.46 Ω^{-1} cm^2 mol^{-1}. Cond. (acetone, concentration = 0.48 × 10^{-3} M): Λ 76.5 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{26}H_{32}Br_{12}N_{12}Sn_3$: C, 17.1; H, 1.8; N, 9.2. Found: C, 16.7; H, 1.8; N, 8.9. IR (cm^{-1}): 3104 m [ν(C−H)], 237 s [ν(Sn−Br)].

X-ray Diffraction Studies. The details of crystal data collection and refinement for complexes **5**, **7**, and **25**, collected at low temperatures on an IPDS (Stoe) diffractometer, are given in Table 1. Graphite-

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **5**, **7**, and **25**

5		**7**		**25**	
Sn(1)−C(14)	2.17(2)	Sn(1)−C(1)	2.214(5)	Sn(1)−Br(1)	2.4823(8)
Sn(1)−N(1)	2.30(2)	Sn(1)−N(1)	2.259(6)	Sn(1)−Br(2)	2.5598(9)
Sn(1)−N(3)	2.27(2)	Sn(1)−N(3)	2.310(5)	Sn(1)−Br(3)	2.5616(9)
Sn(1)−N(5)	2.33(2)	Sn(1)−N(5)	2.282(5)	Sn(1)−Br(4)	2.505(1)
Sn(1)−Cl(1)	2.379(8)	Sn(1)−Cl(1)	2.387(2)	Sn(1)−Br(5)	2.5108(8)
Sn(1)−Cl(2)	2.406(7)	Sn(1)−Cl(2)	2.372(2)		
Sn(2)−C(31)	2.26(2)	Sn(2)−C(18)	2.167(6)	Sn(2)−N(1)	2.234(5)
Sn(2)−N(7)	2.22(2)	Sn(2)−Cl(3)	2.486(2)	Sn(2)−N(1)	2.225(5)
Sn(2)−N(9)	2.32(2)	Sn(2)−Cl(4)	2.455(2)	Sn(2)−N(5)	2.242(4)
Sn(2)−N(11)	2.23(2)	Sn(2)−Cl(5)	2.349(2)	Sn(2)−Br(6)	2.5057(9)
Sn(2)−Cl(3)	2.393(9)	Sn(2)−Cl(6)	2.319(2)	Sn(2)−Br(7)	2.5128(9)
Sn(2)−Cl(4)	2.35(1)			Sn(2)−Br(8)	2.5185(10)
Sn(3)−C(35)	2.21(2)				
Sn(3)−Cl(5)	2.466(6)				
Sn(3)−Cl(6)	2.483(6)				
Sn(3)−Cl(7)	2.510(6)				
Sn(3)−Cl(8)	2.503(6)				
Sn(3)−Cl(9)	2.499(6)				
C(14)−Sn(1)−N(3)	166.7(9)	N(1)−Sn(1)−N(3)	77.7(2)	N(1)−Sn(2)−N(3)	80.6(2)
N(3)−Sn(1)−N(5)	75.8(7)	N(1)−Sn(1)−Cl(2)	87.7(2)	N(1)−Sn(2)−N(5)	79.4(2)
N(3)−Sn(1)−Cl(2)	85.4(5)	C(1)−Sn(1)−N(5)	92.3(2)	N(3)−Sn(2)−N(5)	79.9(2)
Cl(1)−Sn(1)−Cl(2)	98.6(3)	C(1)−Sn(1)−Cl(2)	100.3(2)	N(1)−Sn(2)−Br(7)	90.61(12)
Cl(14)−Sn(1)−Cl(1)	103.1(7)	Cl(1)−Sn(1)−Cl(2)	99.51(8)	Br(6)−Sn(2)−Br(7)	97.40(3)
Cl(6)−Sn(3)−Cl(8)	171.6(3)	Cl(5)−Sn(2)−Cl(6)	118.09(7)	Br(2)−Sn(1)−Br(3)	174.84(3)

Scheme 1



1: R = Me, R' = H
2: R = ^{n}Bu, R' = H
3: R = Ph, R' = H
4: R = Me, R' = Me
5: R = ^{n}Bu, R' = Me
6: R = Ph, R' = Me

monochromated Mo *K*α radiation was used for the measurements. The lattice parameters of compound **5** were optimized from a least-squares calculation on 24 carefully centered reflections at 16−18° (*θ*). The lattice parameters of both **7** and **25** were calculated from positions of 5000 scanned reflections in the range 3−24° (*θ*). No absorption correction was applied for **5** and **7**. A numerical absorption correction was applied for **25** after crystal shape optimization using X-SHAPE (Stoe).

Structure solutions and refinements were carried out by using SHELXS-97[13] and SHELXL-93[14] programs. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques based on F^2. Hydrogen atoms were placed at the calculated positions and were included in the final refinements in a riding mode. Occupancies of the solvated CH_2Cl_2 molecules in the structures of **7** and **25** were refined to 0.689(9) and 0.860(9), respectively. Selected bond lengths and angles for **5**, **7**, and **25** are listed in Table 2.

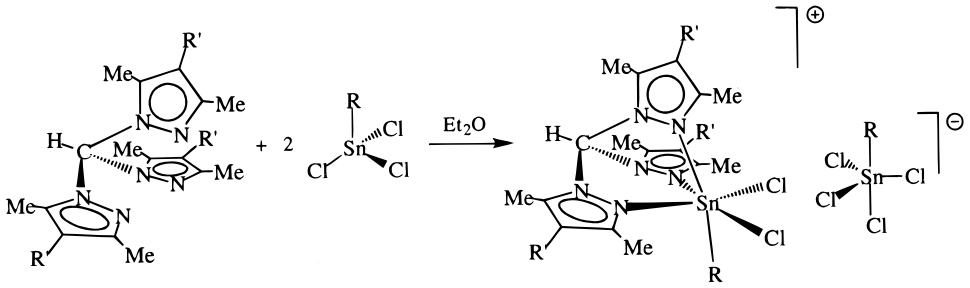
Results and Discussion

Syntheses and Properties. From the interaction of the tris(pyrazol-1-yl)methane donors $HC(pz)_3$, $HC(4\text{-}Mepz)_3$, $HC(3,5\text{-}Me_2pz)_3$, and $HC(3,4,5\text{-}Me_3pz)_3$ with R_2SnCl_2 acceptors (R = Me, ^{n}Bu, or Ph) in diethyl ether or CH_2Cl_2 solution, no products were obtained, even if the reaction was carried out under forcing conditions (i.e. strong excess of the donor and refluxing solvent). When this reaction was carried out in *n*-hexane (suspension), an oil was obtained which seemed to be a mixture of the starting reagents, without evidence of any bonding interaction. In fact, the IR and NMR spectra of the oil obtained are almost identical to those found for the free ligand and the organotin(IV) acceptor.

On the other hand the interaction between monoorganotin(IV) acceptors $RSnCl_3$ (R = Me, ^{n}Bu, or Ph) and $HC(pz)_3$, $HC(4\text{-}Mepz)_3$, $HC(3,5\text{-}Me_2pz)_3$, $HC(3,4,5\text{-}Me_3pz)_3$, or $HC(3\text{-}Mepz)_2(5\text{-}Mepz)$ in diethyl ether resulted in compounds **1**−**14** (Schemes 1−3) independently of the reaction conditions and acceptor:ligand ratio employed. The analytical and spectral data of complexes **1**−**14** are listed in the Experimental Section. The stoichiometries of compounds **1**−**14** differ from those reported in the literature for other poly(pyrazol-1-yl)alkane−organotin(IV) derivatives:[7−10] the tris(pyrazol-1-yl)methane ligands are potentially tridentate and usually tend to bind a metal as tridentates, the presence of only two free coordination sites on the $RSnCl_3$ acceptor in this case inducing a charge separation,

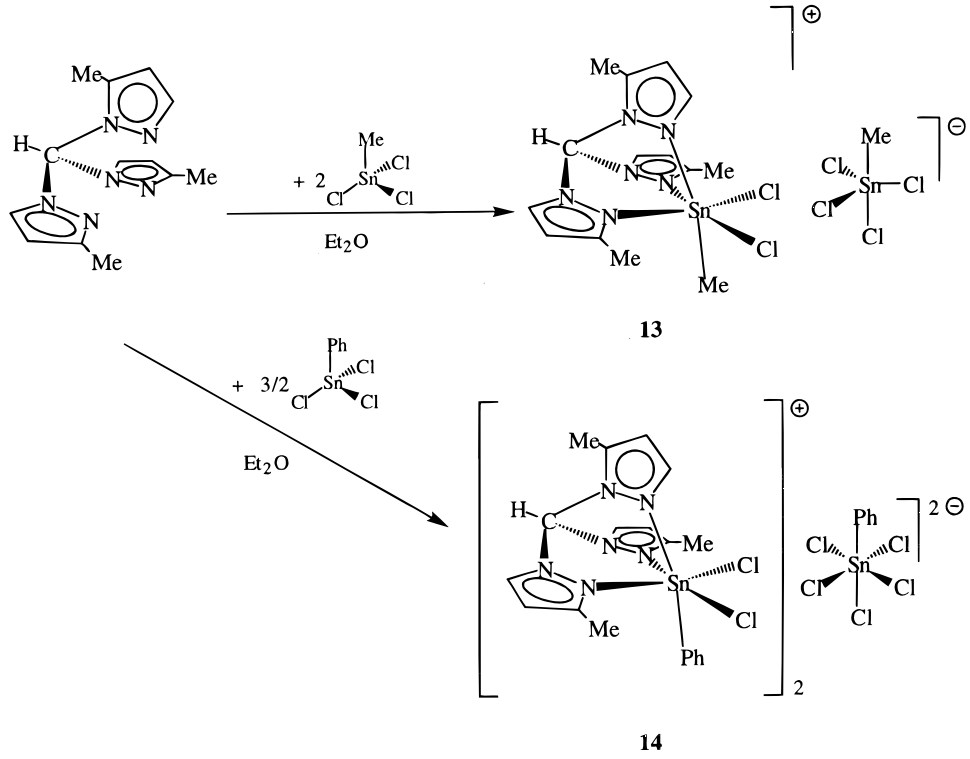
(13) Sheldrick, G. M. *SHELXL-93. Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1993.
(14) Sheldrick, G. M. *SHELXS-97. Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997.

Scheme 2



7: R = Me, R' = H
8: R = ^{n}Bu, R' = H
9: R = Ph, R' = H
10: R = Me, R' = Me
11: R = ^{n}Bu, R' = Me
12: R = Ph, R' = Me

Scheme 3



13

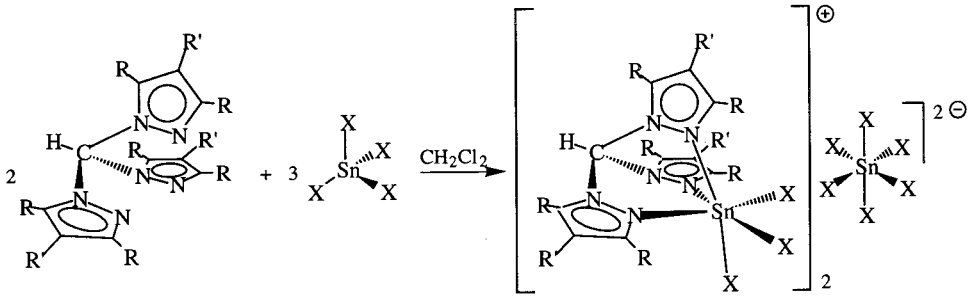
14

with formation of 1:1 or 2:1 ionic complexes in the solid state. The presence of methyl groups in the 3,5-positions of the azole rings influences the stoichiometry of products **1**−**14**, the ligands $HC(pz)_3$ and $HC(4\text{-}Mepz)_3$, without any substituent in the 3- and 5-positions, yielding, independently of the nature of the acceptor and of the reaction conditions, the 2:1 ionic derivatives **1**−**6** with general formula $[\{LSnRCl_2\}^+]_2[\{SnRCl_5\}^{2-}]$ as shown in Scheme 1, whereas the interaction of the ligands $HC(3,5\text{-}Me_2pz)_3$ and $HC(3,4,5\text{-}Me_3pz)_3$ with $RSnX_3$ acceptors gave ionic compounds **7**−**12** $[\{LSnRCl_2\}^+][\{SnRCl_4\}^-]$ with 1:1 stoichiometry (Scheme 2).

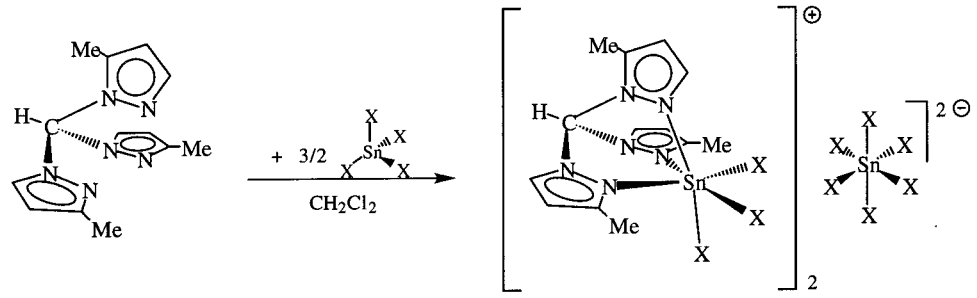
To demonstrate that the steric effects of Me groups in a position near the coordination site influence the stoichiometry of the final product, we synthesized a new tridentate ligand, $HC(3\text{-}Mepz)_2(5\text{-}Mepz)$, according to literature procedures.[11] From the interaction of $HC(3\text{-}Mepz)_2(5\text{-}Mepz)$ with $RSnCl_3$ (R = Me or Ph), the adducts $[\{LSnMeCl_2\}^+][\{SnMeCl_4\}^-]$ (**13**) and $[\{LSnPhCl_2\}^+]_2[\{SnPhCl_5\}^{2-}]$ (**14**) were isolated, independently of the acceptor:ligand ratio used (Scheme 3); no adduct was obtained under the same conditions when ^{n}BuSnCl$_3$ as acceptor was employed.

From the interaction of $HC(pz)_3$, $HC(4\text{-}Mepz)_3$, $HC(3,5\text{-}Me_2pz)_3$, $HC(3,4,5\text{-}Me_3pz)_3$, or $HC(3\text{-}Mepz)_2(5\text{-}Mepz)$ with the tetrahalidetin(IV) acceptors SnX_4 (X = Cl, Br, or I), in CH_2Cl_2 solution, in nitrogen atmosphere, at −40 °C, adducts **15**−**27** were obtained (Schemes 4 and 5). Independently of the nature of the acceptor and from these reaction conditions the 2:1 ionic adducts $[\{LSnX_3\}^+]_2[\{SnX_6\}^{2-}]$ were isolated for $HC(pz)_3$, $HC(3,5\text{-}Me_2pz)_3$, $HC(4\text{-}Mepz)_3$, or $HC(3\text{-}Mepz)_2(5\text{-}Mepz)$ ligands (Scheme 4). The only exception is represented by the ligand $HC(3,4,5\text{-}Me_3pz)_3$, which gives the 2:1 adduct $[\{LSnCl_3\}^+]_2[\{SnCl_6\}^{2-}]$ (**24**) for X = Cl and the 1:1 adduct $[\{LSnBr_3\}^+][\{SnBr_5\}^-]$ (**25**) for X = Br (Scheme 5). It is interesting to note that no derivative was afforded from the interaction of HC-

Scheme 4

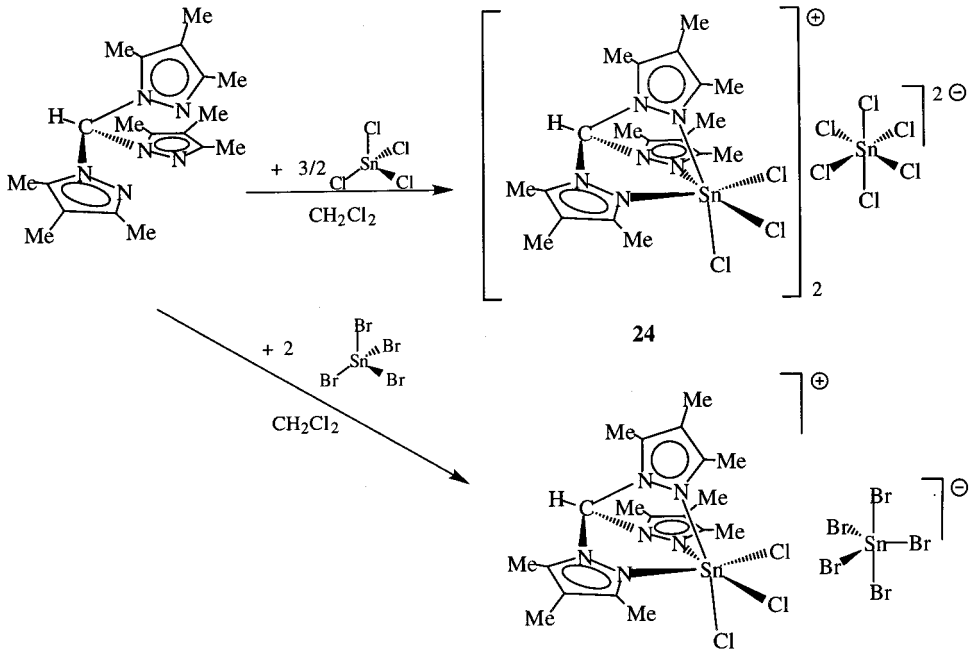


15: R = R' = H, X = Cl
16: R = R' = H, X = Br
17: R = R' = H, X = I
18: R = H, R' = Me, X = Cl
19: R = H, R' = Me, X = Br
20: R = H, R' = Me, X = I
21: R = Me, R' = H, X = Cl
22: R = Me, R' = H, X = Br
23: R = Me, R' = H, X = I



26: X = Cl
27: X = Br

Scheme 5



24

25

$(3,4,5\text{-}Me_3pz)_3$ and $HC(3\text{-}Mepz)_2(5\text{-}Mepz)$ with SnI_4 under the conditions indicated in the Experimental Section.

All of these tin(IV) and organotin(IV) complexes at room temperature are colorless solids, very soluble in chlorinated

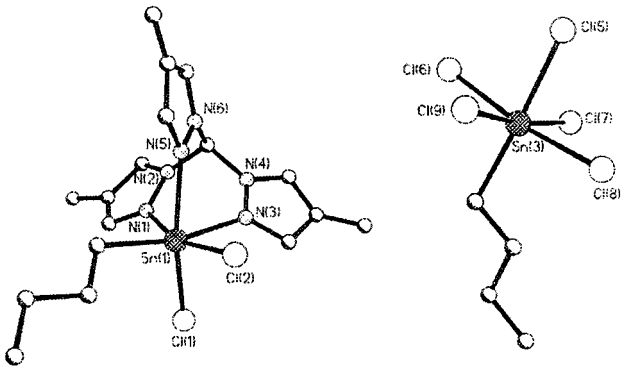


Figure 2. PLUTO representation of the molecular structure of complex **5**.

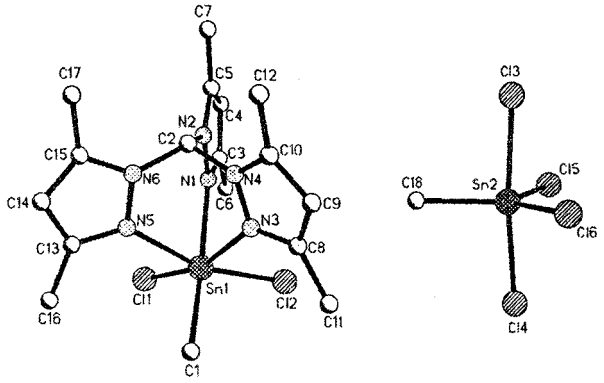


Figure 3. PLUTO representation of the molecular structure of complex **7**.

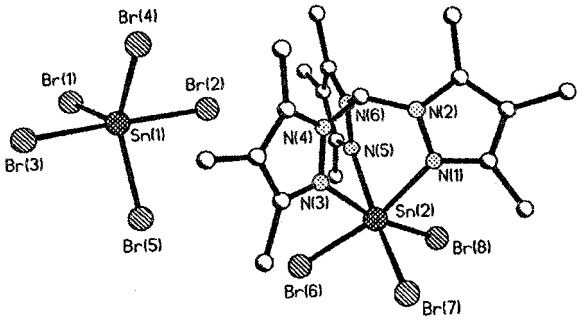


Figure 4. PLUTO representation of the molecular structure of complex **25**.

solvents and acetone. They can be handled in air for a short time without any significant decomposition. However, prolonged storage in air at room temperature or in solutions leads to slow decomposition.

The conductivity measurements (see Experimental Section) indicated that among the $HC(pz)_3$ and $HC(4\text{-}Mepz)_3$ derivatives, only $[\{HC(pz)_3SnI_3\}^+]_2[\{SnI_6\}^{2-}]\cdot H_2O$ and $[\{HC(4\text{-}Mepz)_3SnI_3\}^+]_2[\{SnI_6\}^{2-}]$ are electrolytes in CH_2Cl_2 and acetone. A similar behavior has been previously observed for analogous organotin(IV) complexes containing N-donor ligands: generally, the chloro and bromo derivatives are not electrolytes in CH_2Cl_2 and acetone, whereas the corresponding iodo derivatives exhibit in the same solutions a conductivity typical of a strong electrolyte.[10,15] The derivatives of $HC(3,5\text{-}Me_2pz)_3CH$ are partly ionized in CH_2Cl_2 and acetone solutions. The complexes of $HC(3,4,5\text{-}Me_3pz)_3CH$, the most basic and the most sterically hindered ligand, exhibit a value of conductivity in CH_2Cl_2 and acetone typical of a 1:1 electrolyte. Finally, the derivatives of $HC(3\text{-}Mepz)_2(5\text{-}Mepz)$ are nonelectrolytes in CH_2Cl_2, whereas they are partly ionized in acetone. The vaporimetric molecular weight determinations, carried out only for sufficiently soluble and stable compounds, gave values always greater than those expected for the ionic 1:1 and 2:1 formulas, in accordance with formation of ion-pairing compounds, as resulted from the conductivity data.

The tin(IV) derivatives **1**−**3** and **15**−**17** are generally less soluble and more dissociated in chloroform solution with respect to all the other derivatives containing a methyl-substituted ligand. The total or partial lack of conductivity observed in **1**−**9**, **11**−**16**, **18**−**19**, **21**, **25**, and **27** can be attributed to ion-pair couple formation or else to dissociation of the Sn−N bond and re-formation of the starting reagents, as is clear from NMR data.

Solid State Structures of $[\{HC(4\text{-}Me_2pz)_3Sn^nBuCl_2\}^+]_2[\{Sn^nBuCl_5\}^{2-}]$ (5), $[\{HC(3,5\text{-}Me_2pz)_3SnMeCl_2\}^+][\{SnMeCl_4\}^-]$ (7), and $[\{HC(3,4,5\text{-}Me_3pz)_3SnBr_3\}^+][\{SnBr_5\}^-]$ (25). Diagrams of the cations and anions in **5**, **7**, and **25** are provided in Figures 2−4. All three compounds are ionic: in the cation, the tin atom is always situated in a pseudooctahedral environment coordinated by a tridentate tris(pyrazol-1-yl)methane, an alkyl and two chloride groups (**5** and **7**), or a tridentate tris(pyrazol-1-yl)methane and three bromine atoms (**25**). The Sn−N distances, lying in the range 2.22−2.33 Å, are not greatly influenced by the nature of the other ligands in the coordination environment of the tin. Nevertheless, as previously observed also in poly(pyrazol-1-yl)borate−monoorganotin(IV) derivatives,[2] those Sn−N bonds trans to carbon atoms are slightly shorter than those trans to halides. In derivative **25**, with three bromine atoms in trans positions, there is practically no difference in Sn−N and, as a consequence of the small tripod ligand "bite", all N−Sn−N angles are appreciably less than 90°. Similar Sn−N bond distances have been found in complexes containing an anionic tris(pyrazolyl)borate ligand $[Sn\{HB(3,4,5\text{-}Me_3pz)_3\}MeCl_2]$ (Sn−N = 2.24−2.25 Å).[2d] By contrast, the Sn−C, Sn−N, and Sn−Cl distances are all markedly different from those found in the cation of $[\{(2,2',2''\text{-terpyridyl})SnMe_2Cl\}^+][\{SnMe_2Cl_3\}^-]$,[16] presumably due to the lower Lewis acidity of the $[SnR_2Cl]^+$ moiety with respect to that of the $[SnRCl_2]^+$ acceptor. In the crystal structures of $[H_2C(4\text{-}Mepz)_2Me_2SnCl_2]$ [10] and $[H_2C(3,5\text{-}Me_2pz)_2Ph_2SnCl_2]$ [17] the Sn−N bond distances are substantially longer (in the range of 2.40−2.50 Å) because of the electroneutrality of this type of compound.

In the anionic components of these complexes, the tin is five-coordinate (trigonal-bipyramidal) in **7** and **25** and six-coordinate (octahedral) in derivative **5**. In **7**, the axial distances Sn−Cl (2.46, 2.49 Å) are longer than equatorial ones (2.32−2.35 Å). These values can be compared to those found in $[\{AsPh_4\}^+][\{SnMeCl_4\}^-]$: Sn−Cl (axial), 2.49 Å; Sn−Cl (equatorial), 2.27 Å.[18] The Sn−C bond distances are also similar: 2.15 Å in **7** and 2.17 Å in $[\{AsPh_4\}^+][\{SnMeCl_4\}^-]$.[18] As observed in other examples of trigonal-bipyramidal structures with two different ligand types coordinated to a tin(IV) center, the more elec-

(15) (a) Pettinari, C.; Marchetti, F.; Cingolani, A.; Bartolini, S. *Polyhedron*, **1996**, *8*, 1263. (b) Pettinari, C.; Marchetti, F.; Pellei, M.; Cingolani, A.; Barba, L.; Cassetta, A. *J. Organomet. Chem.* **1996**, *515*, 119. (c) Pettinari, C.; Pellei, M.; Miliani, M.; Cingolani, A.; Cassetta, A.; Barba, L.; Pifferi, A.; Rivarola, E. *J. Organomet. Chem.* **1998**, *553*, 345. (d) Holecek, J.; Licka, A. *Inorg. Chim. Acta* **1986**, *118*, L15. (e) Lockhart, T. P.; Manders, W. F. *J. Am. Chem. Soc.* **1987**, *109*, 7015. (f) Lockhart, T. P.; Manders, W. F. *J. Am. Chem. Soc.* **1986**, *108*, 892.

(16) Einstein, F. W. B.; Penfold, B. R. *J. Chem. Soc. A* **1969**, 3019.

(17) Cox, J. M.; Rainone, S.; Siasios, G.; Tiekink, E. R. T.; Webster, L. K. *Main Group Met. Chem.* **1995**, *18*, 93.

(18) Webster, M.; Mudd, K. R.; Taylor, D. J. *Inorg. Chim. Acta* **1976**, *20*, 231.

tronegative ligands (Cl in our case) are linked preferentially in the axial positions.[19] In **25**, the distribution of the axial and equatorial bonds is also similar: Sn−Br (axial) 2.56 Å, Sn−Br (equatorial) 2.48−2.51 Å. As expected, the Sn−Br distances in $[\{SnBr_5\}^-]$ are shorter than in octahedral $[\{SnBr_6\}^{2-}]$ compounds such as, for example, in $[\{Me_2NH_2\}^+]_2[\{SnBr_6\}^{2-}]$ (2.60 Å).[20] In the anion of **5** $[\{Sn^nBuCl_5\}^{2-}]$, the tin is octahedrally coordinated with the shorter Sn−Cl distance (2.43 Å) situated trans to the Sn−C bond (2.21 Å). The other four Sn−Cl distances are in the range 2.48−2.51 Å. It is worth noting that, due to the increase of tin coordination number, the Sn−Cl equatorial distances in $[\{Sn^nBuCl_5\}^{2-}]$ are very close to the equatorial Sn−Br distances in $[\{SnBr_5\}^-]$. Similar relationships between the Sn−Cl and Sn−C distances in octahedral anions $[\{SnRCl_5\}^{2-}]$ can be found in $[\{SnPhCl_5\}^{2-}]$ [21] and in $[\{SnEtCl_5\}^{2-}]$.[22]

Another interesting feature is that, in the cations of compounds **5**, **7**, and **25**, there is very little torsion of the pyrazolyl rings with respect to the C_{3v} axis of the molecule; the Sn−N−N−C torsion angles of the pyrazolyl rings average 2.2°, 4.8°, and 3.4° for **5**, **7**, and **25**, respectively. The lack of twist contrasts with recent results on Tl[23] and Cd[24] complexes but is in good agreement with the data on Ag[25] and Cu[26] complexes. Apparently in these tris(pyrazol-1-yl)methane−tin(IV) complexes, no distortion of the ligand is required, the size of tin(IV) matching the bite of the ligand.

Spectroscopy. The most important IR data of the free donors and their corresponding tin(IV) complexes are listed in the Experimental Section. The ligand absorptions are not markedly shifted upon coordination to tin(IV), suggesting a weak influence of the complexation on the absorptions within the donor. The Sn−C[27] and Sn−Cl[28] stretching vibrations agree well with the trends previously observed in similar complexes containing N-donor chelating ligands.[10,29] In compounds **15**, **18**, **21**, **24**, and **26**, the Sn−Cl stretching frequencies are shifted to higher fields with respect to those reported in tri- and tetrachlorotin(IV) derivatives; an increase of the stretching frequencies suggests a strengthening of the Sn−Cl bond and then a weakening of the Sn−N bond.

The ^{1}H NMR spectra of derivatives **1**−**6** contain signals not only due to the complex but also attributed to the uncoordinated ligand; the dissociation is minimal in chloroform and greater in acetone solutions. Near the signals of the free ligand, it is always possible to detect at least two different absorptions for each pyrazole proton, and one absorption for the bridged CH group. This excludes the existence of different isomers in solution, indicative of inequivalence of the three pyrazole rings, in accordance with the solid-state data. The tin−proton coupling constants are different from those observed for the starting organotin(IV) derivatives,[30] being of the same order of magnitude as those observed in six-coordinated tin(IV) complexes.[15] The ^{1}H NMR spectra of **1**−**6** exhibit also two different sets of signals for the alkyl and the aryl groups linked to the tin, in accordance with the presence of two different organotin(IV) centers. In the ^{119}Sn NMR spectra of **1**−**6** a signal typical of six-coordinated organotin(IV) derivatives only was found.

The spectra of **7**−**12** exhibit at least two different groups of signals for each heterocyclic proton and one signal for the bridged C−H group, suggesting an inequivalence of the three pyrazole rings in accordance with the solid-state structure, the downfield shifts clearly indicating the existence of complexes **7**−**12** in solution. The tin−proton coupling constants are different from those observed for the starting organotin(IV) derivatives and of the same order of magnitude as those observed in six- or five-coordinated tin(IV) complexes.[10,15,30] The ^{119}Sn NMR spectra of **7**−**12** are in accordance with the solid-state structure: in $CDCl_3$ solution, two signals, typical of a five- and six-coordinate tin(IV) site, respectively, were generally found.

In the spectra of the SnX_4 derivatives **15**−**27**, the Δ values (Δ = difference in chemical shift for the same type of proton in the free base and in its tin(IV) complex) are strongly dependent on the nature of the N_3-donor, on the halide, and on the structure of the complex.

The derivatives **15**−**17** are partially dissociated in solution. In the spectra of complexes **24** and **25** the Δ values of the methyls of the pyrazole ring are indeterminate, due to uncertainty in the assignment of the signals, whereas Δ for the bridging C−H proton is in the range 0.19−0.21 ppm.

The Δ values for the derivatives **18**−**20** prove the existence of the complexes in solution, these Δ values being larger than those observed in all the other derivatives, in accordance with a stronger Sn−N bonding interaction and perhaps with a greater stability in solution. Moreover, the derivatives **18**−**20** are more soluble than the other complexes, so that it has been possible to detect the H-3 satellite peaks due to the tin−proton coupling constants that are typical of undissociated six-coordinate organotin(IV) complexes in solution.[28,30]

The structures of complexes containing tris(pyrazol-1-yl)borates[2] and tris(pyrazol-1-yl)methanes are presumably similar, the tripodal arrangement of the pyrazole rings being the dominant controlling factor. The difference in the charge between the two types of ligands produces only small effects on the structure of related complexes, not only in the solid state but also in solution, as demonstrated by the very close values of the ^{119}Sn chemical shift: the $\delta(^{119}Sn)$ of **1** and **4** (−448 and

(19) Muetterties, E. L.; Mahler, W.; Packer, K. J.; Schmultzer, R. *Inorg. Chem.* **1964**, *3*, 1298.
(20) Dilton, K. B.; Halfpenny, J.; Marshall, A. *J. Chem. Soc., Dalton Trans.* **1983**, 1091.
(21) Storck, P.; Weiss, A. *Acta Crystallogr. C* **1990**, *46*, 767.
(22) Paseshnitchenko, K. A.; Aslanov, L. A.; Jatsenko, A. V.; Medvedev, S. V. *J. Organomet. Chem.* **1985**, *267*, 187.
(23) Reger, D. L.; Collins, J. E.; Layland, R.; Adams, R. D. *Inorg. Chem.* **1996**, *35*, 1372.
(24) Reger, D. L.; Collins, J. E.; Myers, S. M.; Liable-Sands, L. M.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 4904.
(25) Rasika Dias, H. V.; Wang, Z.; Jin, W. *Inorg. Chem.* **1997**, *36*, 6205.
(26) Reger, D. L.; Collins, J. E.; Rheingold, A. L.; Liable-Sands, L. M. *Organometallics* **1996**, *15*, 2029.
(27) (a) Clark, J. P.; Wilkins, C. J. *J. Chem. Soc. A* **1966**, 871. (b) Clark, R. J. H.; Davies A. G.; Puddephatt, R. J. *J. Chem. Soc. A* **1968**, 1828. (c) Edgell, W. F.; Ward, W. H. *J. Mol. Spectrosc.* **1962**, *8*, 343. (d) Sandhu, J. K.; Kaur, G.; May, J. R.; McWhinnie, W. R.; Poller, R. C. *Spectrochim. Acta A* **1971**, *27*, 969. (e) Smith, A. L. *Spectrochim. Acta A* **1968**, *24*, 695. (f) Dance, M. S.; McWhinnie, W. R.; Poller, R. C. *J. Chem. Soc., Dalton Trans.* **1976**, 2349. Poller, R. C. *The Chemistry of Organotin Compounds*; Logos: London, 1970. (g) Newman, W. P. *The Organic Chemistry of Tin*; Wiley: New York, 1970. (h) Ho, B. W. K.; Zuckerman, J. J. *Inorg. Chem.*, **1973**, *12*, 1552.
(28) (a) Alleston, D. L.; Davies, A. G. *J. Chem. Soc.* **1961**, 2050. (b) Ohkaku, N.; Nakamoto, K. *Inorg. Chem.* **1973**, *12*, 2440. (c) de Sousa, G. F.; Filgueiras, C. A. L.; Darensbourg, M. Y.; Reibenspies, J. H. *Inorg. Chem.* **1992**, *31*, 3044. (d) Caruso, F.; Giomini, M.; Giuliani A. M.; Rivarola, E. *J. Organomet. Chem.* **1996**, *506*, 67.
(29) (a) Harrison, P. G.; King, T. J.; Richards, J. A. *J. Chem. Soc., Dalton Trans.* **1974**, 1723. (b) Lopez, C.; Sanchez Gonzales, A.; Garcia, M. E.; Casas, J. S.; Sordo J.; Graziani, R.; Casellato, U. *J. Organomet. Chem.* **1992**, *434*, 261.
(30) (a) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73. (b) Harris, R. K.; Sebald, A.; Furlani, D.; Tagliarini, G. *Organometallics* **1988**, *7*, 388. (c) Kennedy, J. D.; McFarlane, W. Silicon, Germanium, Tin and Lead. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; pp 305−333.

−455 ppm, respectively) and those of the isoelectronic $[MeSnCl_2\{HB(pz)_3\}]$ [2b] and $[MeSnCl_2\{HB(4\text{-}Mepz)_3\}]$ [2a] (−478 and −486 ppm, respectively) clearly indicate that the bonding is dominated by the σ-donating ability of the ligand.

Positive and negative fast atom bombardment (FAB) mass spectrometric data for the tin and organotin(IV) complexes **1**−**3**, **10**−**13**, **16**, **20**, and **23**−**25** are reported in the Experimental Section. The fragment ions containing tin(IV) and halide atoms are identified by the presence of the characteristic clusters of isotopic peaks, corresponding to the relative abundance of tin and halide isotopes. In the FAB-MS analysis of our tin(IV) complexes, the intact cation and anion are often the major fragment ions, and with the exception of the protonated ligand molecule the other diagnostic fragments are generally very poor. In some cases in the high-mass region of the ligands and their complexes there are also a few characteristic peaks due to interaction with the *m*-nitrobenzyl alcohol matrix.

The initial fragmentation pathway of the tin(IV) halide anions $[\{SnX_5\}^-]$ and $[\{RSnX_4\}^-]$ generally consists of sequential loss of the radicals X and R. In the negative-FAB spectra of $[\{LSnRCl_2\}^+]_2[\{SnRCl_5\}^{2-}]$ and $[\{LSnX_3\}^+]_2[\{SnX_6\}^{2-}]$ complexes, no peak attributable to the intact dianions $[\{SnRCl_5\}^{2-}]$ or $[\{SnX_6\}^{2-}]$ is present: the most important fragment ions are those obtained by the subtraction of one halide or one R radical from these ionic species.

In conclusion both 1:1 and 2:1 ionic tin(IV) and organotin(IV) compounds can be synthesized by modifying the steric properties of the tris(pyrazol-1-yl)methane ligands: for example, the donors having a Me in a position near the coordination site allow the preparation of 2:1 $[\{LSnRCl_2\}^+]_2[\{SnRCl_5\}^{2-}]$ or $[\{LSnX_3\}^+]_2[\{SnX_6\}^{2-}]$, whereas those without Me in the 3 position allow the 1:1 $[\{LSnRCl_2\}^+][\{SnRCl_4\}^-]$ or $[\{LSnX_3\}^+][\{SnX_5\}^-]$ species to be obtained. To date it has not proven possible to prepare new tin(IV) complexes containing a tridentate tris(pyrazol-1-yl)methane and two organic groups linked to a tin center. Studies are in progress to evaluate the coordinating ability of tris(pyrazol-1-yl)methane ligands toward tin(IV) and organotin(IV) centers containing different counterions.

Acknowledgment. We are grateful to the "CARIMA Foundation", the University of Camerino, and the Consiglio Nazionale delle Ricerche (CNR—Rome) for financial support.

Supporting Information Available: Three X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC9906252