ELSEVIER

Journal of Organometallic Chemistry 553 (1998) 345–369

Journal of Organometallic Chemistry

Tin(IV) and organotin(IV) complexes containing mono or bidentate N-donor ligands
III. [1] 1-methylimidazole derivatives: synthesis, spectroscopic and structural characterization

C. Pettinari [a,*], M. Pellei [a], M. Miliani [a], A. Cingolani [a], A. Cassetta [b], L. Barba [b], A. Pifferi [b], E. Rivarola [c]

[a] *Dipartimento di Scienze Chimiche, Università degli Studi, via S. Agostino 1, Camerino 62032, Macerata, Italy*
[b] *Istituto di Strutturistica Chimica 'G. Giacomello', Consiglio Nazionale delle Ricerche, Padriciano 99, Trieste 30412, Italy*
[c] *Dipartimento di Chimica Inorganica, Università degli Studi di Palermo, via Archirafi 26, Palermo 90123, Italy*

Received 16 July 1997

Abstract

A series of adducts of the type $[(L^{\#})_yR_nSnX_{4-n}]\cdot zH_2O$ ($L^{\#}$ = 1-methylimidazole, $y = 1$ or 2, R = Me, Et, Bu^n or Ph, $n = 1$, 2 or 3, X = Cl, Br or I, $z = 0$, 1/2 or 1) has been characterized in the solid state and in solution by analyses, spectral (IR, ^{119}Sn Mössbauer, and ^{1}H, ^{13}C and ^{119}Sn NMR) data and conductivity measurements. The molecular weight determinations and the NMR data indicate that these organotin(IV) complexes partly dissociate in chloroform and acetone solution. The donor $L^{\#}$ interacts with $[(CH_3)_3SnNO_3]$, yielding the 2:1 ionic complex $[(L^{\#})_2(CH_3)_3Sn]NO_3$. The derivative $[(L^{\#})_2(CH_3)_2SnCl_2]$ reacts with $NaClO_4$, $AgNO_3$, $NaBPh_4$ and KSCN in ethanol and diethyl ether giving the complexes $[(L^{\#})_2(CH_3)_2Sn(ClO_4)_2]$, $[(L^{\#})(CH_3)_2Sn(NO_3)_2(H_2O)]$, $[(L^{\#})(CH_3)_2SnCl(H_2O)_2]BPh_4$ and $[(L^{\#})_2(CH_3)_2Sn(NCS)_2]$, respectively, whereas when $[(L^{\#})(CH_3)_3SnCl]$ interacts with an equimolar quantity of $NaClO_4$, $[(L^{\#})_2(CH_3)_3Sn]ClO_4\cdot 1/2H_2O$ and $(CH_3)_3Sn(ClO_4)$ in 1:1 ratio are obtained. The stability towards self-decomposition of the complexes obtained decreases with increasing number of the Sn-bonded aryl or alkyl groups. The derivative $[(L^{\#})_2(CH_3)_2SnBr_2]$ reacts with 1,10-phenanthroline (Phen), yielding immediately the complex $[(Phen)(CH_3)_2SnBr_2]$, whereas from the reaction between $[(L^{\#})_2(CH_3)_2Sn(ClO_4)_2]$ and Phen, the mixed ligand complex $[(L^{\#})(Phen)(CH_3)_2Sn](ClO_4)_2$ is obtained. A different behaviour has been shown from the diiodide complex $[(L^{\#})_2(C_2H_5)_2SnI_2]$ which reacts with Phen, yielding the compound with the 3:2 stoichiometry $[(Phen)_3\{(C_2H_5)_2SnI_2\}_2]$. Both the crystal structures of $[(L^{\#})_2(CH_3)_2SnBr_2]$ and $[(L^{\#})_2(C_2H_5)_2SnI_2]$ show the tin atom in an all-*trans* octahedral regular configuration, whereas in $[(L^{\#})(C_6H_5)_3SnCl]$ the tin atom exhibits a distorted trigonal bipyramidal geometry, with the phenyl groups in the equatorial positions. A comparison was made with structural data of other R_3SnXN-type derivatives. The molecular parameters of 1-methylimidazole in the tin(IV) complexes were used, together with other structural data in literature, to derive empirical rules concerning the imidazole donor. © 1998 Elsevier Science S.A.

Keywords: Tin(IV) complex; Organotin(IV) complex; N-donor ligand; 1-methylimidazole derivative

1. Introduction

Organotin compounds R_nSnX_{4-n} exhibit a variety of biological effects depending on the number n and on the type of organic R and X groups bound to tin. Since the first report on the antitumor activity of diorganotins appeared in 1980 [2,3], the preliminary examination was extended to a systematic study of the antitumor properties of tin compounds.

Recently our group has focused on studying tin(IV) and organotin(IV) complexes of imidazoles $[(ImH)_x\{R_nSnX_{4-n}\}_y]$. In determining the stoichiometry of the adducts obtained from this class of donors, three primary factors are involved: the nature of the organic group R, of the counter-ion X, and of the donor ligand (ImH); besides, it is interesting to note that the acceptor

* Corresponding author.
[1] Part II is Ref. [1].

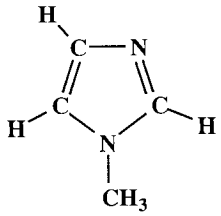


Fig. 1. Structure of the 1-methylimidazole donor.

strength of the tin derivatives R_nSnX_{4-n} decreases in the following order [4]:

$$SnX_4 > RSnX_3 > R_2SnX_2 > R_3SnX$$

$$X = NCS \sim F > Cl > Br > I$$

$$R = Ph > Me > Et > Pr > Bu > Oct$$

To investigate the influence of substituents on the imidazole ring and the role of the N–H group, which can take part in hydrogen bonding, we previously synthesized and characterized (spectral and crystal data) several new adducts between tin(IV) and organotin(IV) acceptors and 1-benzylimidazole [5] and 4-phenylimidazole [1].

As an extension of our research, we report here the synthesis, spectroscopic characterization (IR, Mössbauer, ^{1}H and ^{119}Sn NMR) and behaviour in solution (conductivity and molecular weight measurements) of new adducts between R_nSnX_{4-n} (R = Me, Et, Bu^n and Ph; n = 1, 2 or 3; X = Cl, Br, I, ClO_4, NO_3, BPh_4 and NCS) acceptors and 1-methylimidazole (Fig. 1) ($L^{\#}$). This is the most extensive study of imidazole organotin(IV) compounds to date.

We report the X-ray crystal structure determinations of three of these complexes ($[(L^{\#})(C_6H_5)_3SnCl]$, $[(L^{\#})_2(CH_3)_2SnBr_2]$ and $[(L^{\#})_2(C_2H_5)_2SnI_2]$) and investigate the influence of halide and organic substituent on the metal coordination geometry. We also made a comparison with the X-ray crystal structures of several R_3SnX(N-donor)-type compounds and also of several metal and organometal derivatives of 1-methylimidazole.

We also investigated the reactivity of $[(L^{\#})_2R_2SnX_2]$ system toward monodentate or bidentate N- and P-donors.

2. Experimental

2.1. General methods

The organotin(IV) halides were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. The ligand 1-methylimidazole ($L^{\#}$) was obtained from Aldrich and was crystallized from diethyl ether/petroleum ether (1:2). Solvent evaporations were always carried out in vacuo (water aspirator). The samples for microanalysis were dried in vacuo to constant weight (20°C, ca. 0.1 Torr). Elemental analyses (C,H,N) were performed in house with 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, ^{13}C and ^{119}Sn NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^{1}H, 75 MHz for ^{13}C and 111.9 MHz for ^{119}Sn). The chemical shifts are reported in ppm from $SiMe_4$ (^{1}H and ^{13}C, calibration by internal deuterium solvent lock) and $SnMe_4$ (^{119}Sn).

Melting points were taken on an IA 8100 Electrothermal instrument. 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. The solvent was Baker Analyzed Spectrophotometric grade chloroform. The results were reproducible to $\pm 2\%$.

^{119}Sn Mössbauer spectra were recorded at liquid nitrogen temperature by an Elscint-Laben spectrometer equipped with an Oxford cryostat model DN 700 (Oxford, UK). A $Ca^{119}SnO_3$ Mössbauer source, 10 mCi (from Radiochemical Centre, Amersham, UK) moved with constant acceleration, and a triangular waveform were used. The velocity calibration was made using a ^{57}Co Mössbauer source, 10 mCi, and an iron foil, enriched to 95% in ^{57}Fe (DuPont Pharma Italia, Firenze, Italy) was used as absorber.

2.2. Syntheses

All experiments were carried out under a dinitrogen atmosphere. Hydrocarbon solvents were dried by distillation from sodium–potassium, dichloromethane from calcium hydride and tetrahydrofuran from $LiAlH_4$. All solvents were outgassed with dry dinitrogen prior to use.

2.2.1. [Chlorotrimethyl(1-methylimidazole)tin(IV)] (1)

To a stirred refrigerated (0°C) diethyl ether solution (100 cm^3) of 1-methylimidazole $L^{\#}$ (1.00 g, 12.2 mmol), $(CH_3)_3SnCl$ (607 mg, 3.0 mmol) was added under N_2 stream. The mixture was stored at 0°C and stirred for 12 h. The solution was stored in freezer overnight. An oil was formed, which was separated from the solution. The residue was washed with diethyl ether (3×20 cm^3), dried in vacuo to constant weight (20°C, ca. 0.1 Torr) and shown to be compound **1**. Yield: 80%, m.p. 66–68°C (Found: C, 29.6; H, 5.5; N, 10.1. Calc. for $C_7H_{15}ClN_2Sn$: C, 29.9; H, 5.4; N, 10.0%). NMR ($CDCl_3$): ^{1}H, δ 7.59, 7.07, 6.93 (s, H^2, H^4 and H^5), 3.74 (s, 1-Me), 0.71 [$|^2J(^{119}Sn–H)| = 64.9$ Hz, $|^2J(^{117}Sn–H)| = 62.0$ Hz, s, SnMe]; ^{13}C, δ 34.5 (s,

1-Me), 121.1, 128.0, 137.6 (s, C^2, C^4 and C^5), 2.5 (s, Sn–Me, $[|^1J(^{119}Sn-^{13}C)| = 494.8$ Hz, $|^1J(^{117}Sn-^{13}C)| = 472.3$ Hz]. IR: 3125 w, 3092 w [ν(C–H)], 546s [ν(Sn–C)], 229s [ν(Sn–Cl)], 179s, 172s [δ(C–Sn–C) and δ(Cl–Sn–Cl)].

2.2.2. [Trimethylbis(1-methylimidazole)tin(IV)]iodide (2)

To a stirred refrigerated (0°C) THF solution (50 cm^3) of L# (130 mg, 0.46 mmol), sodium iodide (693 mg, 4.6 mmol) was added under N_2 stream. The mixture was stored at 0°C and stirred for 12 h and the solution was stored in freezer overnight. The solvent was removed with a rotary evaporator, CH_2Cl_2 (50 cm^3) was added, the suspension was filtered and the organic layer was dried on anhydrous Na_2SO_4. It was then filtered and concentrated under reduced pressure. Diethyl ether (20 cm^3) was added; the solution was left in freezer for 1 day. A yellow precipitate was formed, which was filtered off, washed with petroleum ether/diethyl ether and shown to be compound **2**. Yield: 45%, m.p. 107–110°C (Found: C, 29.1; H, 4.8; N, 12.2. Calc. for $C_{11}H_{21}N_4SnI$: C, 29.0; H, 4.6; N, 12.3%). NMR ($CDCl_3$): ^1H, δ 7.78, 6.92 (s, H^2, H^4 and H^5), 3.80 (s, 1-Me), 0.89 [$|^2J(^{119}Sn-H)| = 66.0$ Hz, $|^2J(^{117}Sn-H)| = 63.1$ Hz, s, SnMe]. IR: 3105 w, 3085 w, 3070 w [ν(C–H)], 554s, 546s [ν(Sn–C)].

2.2.3. [Trimethylbis(1-methylimidazole)tin(IV)]nitrate (3)

To a stirred refrigerated (0°C) dry ethanol solution (100 cm^3) of $(CH_3)_3SnCl$ (598 mg, 3.0 mmol), silver nitrate (1.02 g, 6.0 mmol) was added under N_2 stream. The mixture was stored at 0°C and stirred for 3 h. The solvent was removed with a rotary evaporator, CH_2Cl_2 (50 cm^3) was added, the suspension was filtered and the organic layer was dried on anhydrous Na_2SO_4. It was then filtered and concentrated under reduced pressure. The precipitate was dissolved in diethyl ether (100 cm^3) and L# (985 mg, 12.0 mmol) was added. A colorless precipitate was formed immediately, which was filtered off after 3 h, washed with diethyl ether and shown to be compound **3**. Yield: 46%, m.p. 130–134°C (Found: C, 33.5; H, 5.5; N, 17.7. Calc. for $C_{11}H_{21}N_5O_3Sn$: C, 33.9; H, 5.4; N, 18.0%). NMR ($CDCl_3$): ^1H, δ 7.67, 6.98 (s, H^2, H^4 and H^5), 3.78 (s, 1-Me), 0.67 [$|^2J(^{119}Sn-H)| = 68.3$ Hz, $|^2J(^{117}Sn-H)| = 65.8$ Hz, s, SnMe]. IR: 3112 w [ν(C–H)], 1366 m, 1348 m [$\nu(NO_3)$], 549 m [ν(Sn–C)], 180 m, 175s, 160s [δ(C–Sn–C)].

2.2.4. [Trimethylbis(1-methylimidazole)tin(IV)]perchlorate · $(H_2O)_{0.5}$ (4)

A dry ethanol solution (50 cm^3) of compound **1** (200 mg, 0.7 mmol) was introduced into a 250 cm^3 round-bottomed flask fitted with a condenser, and $NaClO_4$ (300 mg, 2.1 mmol) was added. The mixture was heated at reflux, under N_2 stream, with stirring for 2 days. The rose solution was then allowed to cool and the solvent was removed with a rotary evaporator. CH_2Cl_2 (50 cm^3) was added, the suspension was filtered and the organic layer was dried on anhydrous Na_2SO_4. It was then filtered and concentrated under reduced pressure. CH_2Cl_2 and Et_2O were added until a pale-rose precipitate was formed. This was filtered off, washed with diethyl ether and crystallized twice from CH_2Cl_2/Et_2O to yield the analytical sample **4**. Yield: 39%, m.p. 139–140°C (Found: C, 30.4; H, 5.1; N, 12.5. Calc. for $C_{11}H_{22}ClN_4O_{4.5}Sn$: C, 30.3; H, 5.1; N, 12.8%). NMR ($CDCl_3$): ^1H, δ 7.91, 7.04, 6.96 (s, H^2, H^4 and H^5), 3.85 (s, 1-Me), 3.1 (br, H_2O), 0.72 [$|^2J(^{119}Sn-H)| = 68.3$ Hz, $|^2J(^{117}Sn-H)| = 65.8$ Hz, s, SnMe]. IR: 3250br [ν(O–H)], 3123 w [ν(C–H)], 1100br, 618 m [$\nu(ClO_4)$], 547 m [ν(Sn–C)], 165s, 160s [δ(C–Sn–C)].

2.2.5. [Chlorotributyl(1-methylimidazole)tin(IV)] · (H_2O) (5)

To a stirred refrigerated (0°C) diethyl ether solution (100 cm^3) of L# (1.00 g, 12.2 mmol), $(C_4H_9)_3SnCl$ (990 mg, 3.0 mmol) was added under N_2 stream. The mixture was stored at 0°C and stirred for 12 h; the solution was stored in freezer overnight. The solvent was removed with a rotary evaporator and diethyl ether/petroleum ether 1:1 were added until an oil was formed, which was separated from the solution. The oily residue was washed with diethyl ether/petroleum ether 1:1 (3×20 cm^3), dried in vacuo to constant weight (20°C, ca. 0.1 Torr) and shown to be compound **5**. Yield: 55% (Found: C, 44.8; H, 8.1; N, 6.4. Calc. for $C_{16}H_{35}ClN_2OSn$: C, 45.1; H, 8.3; N, 6.6%). NMR ($CDCl_3$): ^1H, δ 7.6, 7.1, 6.9 (br, H^2, H^4 and H^5), 3.72 (s, 1-Me), 2.4 (br, H_2O), 1.9–1.1 (m, $SnBu^n$), 0.90 (t, $SnBu^n$). IR: 3400br [ν(O–H)], 3102 w [ν(C–H)], 602br, 508 m [ν(Sn–C)].

2.2.6. [Bromotributyl(1-methylimidazole)tin(IV)] · (H_2O) (6)

Compound **6** was prepared similarly to compound **5**. Yield: 65% (Found: C, 40.6; H, 7.4; N, 6.2. Calc. for $C_{16}H_{35}BrN_2OSn$: C, 40.9; H, 7.5; N, 6.0%). NMR ($CDCl_3$): ^1H, δ 7.49, 7.06, 6.89 (s, H^2, H^4 and H^5), 3.71 (s, 1-Me), 2.2 (br, H_2O), 1.8–1.5 (m, $SnBu^n$), 1.5–1.2 (m, $SnBu^n$), 0.90 (t, $SnBu^n$). IR: 3430br [ν(O–H)], 3104 w [ν(C–H)], 600sh, 508 m [ν(Sn–C)].

2.2.7. [Tributylbis(1-methylimidazole)tin(IV)]iodide · (H_2O) (7)

To a stirred refrigerated (0°C) diethyl ether solution (50 cm^3) of L# (500 mg, 6.1 mmol), $(C_4H_9)_3SnI$ (635 mg, 1.5 mmol) was added under N_2 stream. The mixture was stored at 0°C and stirred for 12 h; the solution was stored in freezer overnight. A colorless precipitate

was formed, which was filtered off, washed with diethyl ether and shown to be compound **7**. Yield 16%, m.p. 55–58°C (Found: C, 40.4; H, 6.9; N, 9.1. Calc. for $C_{20}H_{41}IN_4OSn$: C, 40.1; H, 6.9; N, 9.3%). NMR ($CDCl_3$): ^{1}H, δ 7.49, 7.05, 6.91 (s, H^2, H^4 and H^5), 3.71 (s, 1-Me), 3.1 (br, H_2O), 1.8–1.5 (m, $SnBu^n$), 1.5–1.2 (m, $SnBu^n$), 0.91 (t, $SnBu^n$). IR: 3400br [ν(O–H)], 3130sh, 3079sh [ν(C–H)], 600sh, 523sh, 513s [ν(Sn–C)], 161s, 154s [δ(C–Sn–C)].

2.2.8. [Chlorotriphenyl(1-methylimidazole)tin(IV)] (8)

Compound **8** was prepared similarly to compound **7**. Yield: 95%, m.p. 133–135°C (Found: C, 56.2; H, 4.6; N, 6.0. Calc. for $C_{22}H_{21}ClN_2Sn$: C, 56.5; H, 4.5; N, 6.0%). NMR ($CDCl_3$): ^{1}H, δ 7.0, 6.9 (br, H^2, H^4 and H^5), 3.69 (s, 1-Me), 7.8–7.6, 7.5–7.3 [$|^3J$(Sn–H)| = 62.5 Hz, m, SnPh]; ^{13}C, δ 34.3 (s, 1-Me) 121.0, 128.5, 137.2 (s, C^2, C^4 and C^5), 129.2 (C_{ortho}), 130.1 ($|^4J$(Sn–C)| = 14.5 Hz, C_{para}), 136.7 ($|^3J$(Sn–C)| = 47.1 Hz, C_{meta}), 141.5br (C_{ipso}); ^{119}Sn, δ −178.6. IR: 3158 w, 3132 w, 3110 w, 3063 w [ν(C–H)], 459s, 446 m [δ(Ph)], 277s [ν(Sn–C)], 226s, [ν(Sn–Cl)], 202s, 176s [δ(C–Sn–C) and δ(Cl–Sn–Cl)].

2.2.9. [Dichlorodimethylbis(1-methylimidazole)tin(IV)] (9)

To a stirred diethyl ether solution (50 cm^3) of L# (1.00 g, 12.2 mmol), $(CH_3)_2SnCl_2$ (670 mg, 3.0 mmol) was added at room temperature. A colorless precipitate was formed immediately, which was filtered off after 3 h, washed with diethyl ether and shown to be compound **9**. Yield 95%, m.p. 200–201°C (Found: C, 31.2; H, 4.9; N, 14.5. Calc. for $C_{10}H_{18}Cl_2N_4Sn$: C, 31.3; H, 4.7; N, 14.6%). NMR ($CDCl_3$): ^{1}H, δ 8.18, 7.52, 6.94 (s, H^2, H^4 and H^5), 3.77 (s, 1-Me), 1.25 [$|^2J(^{119}Sn–H)| = 107.8$ Hz, $|^2J(^{117}Sn–H)| = 102.9$ Hz, s, SnMe]; ^{13}C, δ 34.7 (s, 1-Me), 121.1, 128.2, 138.6 (s, C^2, C^4 and C^5), 22.4 (s, Sn–Me); ^{119}Sn, δ −260.3. IR: 3156 w, 3136 w, 3125 w [ν(C–H)], 567 m [ν(Sn–C)], 236s [ν(Sn–Cl)], 178s, 150s [δ(C–Sn–C) and δ(Cl–Sn–Cl)].

2.2.10. [Dibromodimethylbis(1-methylimidazole)tin(IV)] (10)

Compound **10** was prepared similarly to compound **9**. Yield 95%, m.p. 221–223°C (Found: C, 25.8; H, 4.1; N, 11.9. Calc. for $C_{10}H_{18}Br_2N_4Sn$: C, 25.4; H, 3.8; N, 11.8%). NMR ($CDCl_3$): ^{1}H, δ 8.32, 7.55, 6.97 (s, H^2, H^4 and H^5), 3.81 (s, 1-Me), 1.49 [$|^2J(^{119}Sn–H)| = 100.3$ Hz, $|^2J(^{117}Sn–H)| = 95.7$ Hz, s, SnMe]. IR: 3131 w, 3120 w [ν(C–H)], 565s [ν(Sn–C)], 189 m [ν(Sn–Br)], 165s, 152s [δ(C–Sn–C) and δ(Br–Sn–Br)].

2.2.11. [Diiododimethylbis(1-methylimidazole)tin(IV)] (11)

A dry THF solution (100 cm^3) of compound **9** (768 mg, 2.0 mmol) was introduced into a 250 cm^3 round-bottomed flask fitted with a condenser and sodium iodide (2.40 g, 16.0 mmol) was added. The mixture was heated at reflux, under N_2 stream, with stirring for 2 days. It was then allowed to cool and the solvent was removed with a rotary evaporator. CH_2Cl_2 (50 cm^3) was added, the suspension was filtered and the organic layer was dried on anhydrous Na_2SO_4. It was then filtered and concentrated under reduced pressure. Diethyl ether was added until a brown precipitate was formed. This was filtered off, washed with diethyl ether and crystallized twice from diethyl ether to yield the analytical sample **11**. Yield 14%, m.p. 192–195°C (Found: C, 21.2; H, 3.2; N, 9.7. Calc. for $C_{10}H_{18}I_2N_4Sn$: C, 21.2; H, 3.2; N, 9.9%). NMR ($CDCl_3$): ^{1}H, δ 8.3, 7.5, 7.0 (br, H^2, H^4 and H^5), 3.83 (s, 1-Me), 1.74 [$|^2J(^{119}Sn–H)| = 91.8$ Hz, $|^2J(^{117}Sn–H)| = 87.9$ Hz, s, SnMe]. IR: 3111 w [ν(C–H)], 562 m [ν(Sn–C)].

2.2.12. [Diperchloratedimethylbis(1-methylimidazole)tin(IV)] (12)

Compound **12** was prepared similarly to compound **4**. Yield 48%, m.p. 198°C dec (Found: C, 23.9; H, 4.0; N, 10.1. Calc. for $C_{11}H_{22}Cl_2N_4O_9Sn$: C, 24.3; H, 4.1; N, 10.3%). NMR (acetone): ^{1}H, δ 8.17, 7.27, 7.17 (s, H^2, H^4 and H^5), 3.79 (s, 1-Me), 0.66 [$|^2J$(Sn–H)| = 82.6 Hz, s, SnMe]. IR: 3134 w [ν(C–H)], 1095 m, 1080sh, 618 m [$\nu(ClO_4)$], 570sh, 552 m [ν(Sn–C)], 181s, 174s [δ(C–Sn–C)].

2.2.13. [Dinitratedimethyl(aquo)(1-methylimidazole)tin(IV)] (13)

Compound **13** was prepared similarly to compound **4**. Yield 30%, m.p. 170°C dec (Found: C, 19.4; H, 3.8; N, 14.7. Calc. for $C_6H_{14}N_4O_7Sn$: C, 19.3; H, 3.8; N, 15.0%). NMR (acetone): ^{1}H, δ 8.66, 7.60, 7.50 (s, H^2, H^4 and H^5), 4.05 (s, 1-Me), 3.0 (br, H_2O), 0.87, 0.86 [$|^2J$(Sn–H)| = 90 Hz, s, SnMe]. IR: 3300br [ν(O–H)], 3147 w [ν(C–H)], 1350br, 1304br, [$\nu(NO_3)$], 585 m, 575 m, 547 m, [ν(Sn–C)].

2.2.14. [Chlorodimethylbis(aquo)(1-methylimidazole)tin(IV)]tetraphenyl borate (14)

Compound **14** was prepared similarly to compound **4**. Yield 18%, m.p. 154–156°C (Found: C, 57.8; H, 5.8; N, 4.4. Calc. for $C_{34}H_{42}BClN_4O_2Sn$: C, 58.0; H, 5.8; N, 4.5%). NMR ($CDCl_3$): ^{1}H, δ 8.0, 6.8 (br, H^2, H^4 and H^5), 7.8–6.8 (m, BPh), 3.52 (s, 1-Me), 1.6 (br, H_2O), 0.72 [$|^2J(^{119}Sn–H)| = 65$ Hz, s, SnMe]. IR: 3642 m, 3609 w, 3582 m, 3360br [ν(O–H)], 3126 w, 3108 w, 3051 w [ν(C–H)], 541s [ν(Sn–C)], 446 m, 440sh [δ(Ph)], 193s [ν(Sn–Cl)].

2.2.15. [Dimethylbis(1-methylimidazole)tin(IV)diisothiocyanate] (15)

Compound **15** was prepared similarly to compound **4**. Yield 65%, m.p. 159–160°C (Found: C, 33.4; H, 4.3;

N, 19.3. Calc. for $C_{12}H_{18}N_6S_2Sn$: C, 33.6; H, 4.2; N, 19.6%). NMR ($CDCl_3$): ^1H, δ 8.1, 7.5, 7.2 (br, H^2, H^4 and H^5), 3.83 (s, 1-Me), 0.94 [$|^2J(^{119}Sn–H)| = 110.3$ Hz, $|^2J(^{117}Sn–H)| = 105.5$ Hz, s, SnMe]. IR: 3150 w, 3132 w, 3113 w [ν(C–H)], 2046s [ν(NCS)], 581s [ν(Sn–C)], 181s [δ(C–Sn–C)].

2.2.16. [Dichlorodiethylbis(1-methylimidazole)tin(IV)] (16)

Compound **16** was prepared similarly to compound **9**. Yield 88%, m.p. 165–168°C (Found: C, 34.8; H, 5.6; N, 13.5. Calc. for $C_{12}H_{22}Cl_2N_4Sn$: C, 35.0; H, 5.4; N, 13.6%). NMR ($CDCl_3$): ^1H, δ 8.20, 7.55, 6.94 (s, H^2, H^4 and H^5), 3.77 (s, 1-Me), 1.75 [$|^2J(^{119}Sn–H)| = 97.9$ Hz, $|^2J(^{117}Sn–H)| = 93.5$ Hz, q, SnEt], 1.13 [$|^3J(^{119}Sn–H)| = 180.3$ Hz, $|^3J(^{117}Sn–H)| = 172.3$ Hz, t, SnEt]. IR: 3140 w, 3121 w, 3110 w [ν(C–H)], 534s [ν(Sn–C)], 221s [ν(Sn–Cl)], 175s [δ(C–Sn–C) and δ(Cl–Sn–Cl)].

2.2.17. [Dibromodiethylbis(1-methylimidazole)tin(IV)] (17)

Compound **17** was prepared similarly to compound **9**. Yield 81%, m.p. 174–176°C (Found: C, 28.5; H, 4.5; N, 10.9. Calc. for $C_{12}H_{22}Br_2N_4Sn$: C, 28.8; H, 4.4; N, 11.2%). NMR ($CDCl_3$): ^1H, δ 8.34, 7.64, 6.94 (s, H^2, H^4 and H^5), 3.77 (s, 1-Me), 1.94 [$|^2J(^{119}Sn–H)| = 97.4$ Hz, $|^2J(^{117}Sn–H)| = 93.1$ Hz, q, SnEt], 1.08 [$|^3J(^{119}Sn–H)| = 187.5$ Hz, $|^3J(^{117}Sn–H)| = 179.2$ Hz, t, SnEt]. IR: 3138 w, 3111 w [ν(C–H)], 525 m [ν(Sn–C)], 163s [ν(Sn–Br)], 144s [δ(C–Sn–C) and δ(Br–Sn–Br)].

2.2.18. [Diiododiethylbis(1-methylimidazole)tin(IV)] (18)

Compound **18** was prepared similarly to compound **11**. Yield 72%, m.p. 172–175°C (Found: C, 24.1; H, 3.8; N, 9.0. Calc. for $C_{12}H_{22}I_2N_4Sn$: C, 24.2; H, 3.7; N, 9.4%). NMR ($CDCl_3$): ^1H, δ 8.06, 7.41, 6.93 (s, H^2, H^4 and H^5), 3.78 (s, 1-Me), 2.02 [$|^2J(^{119}Sn–H)| = 78.1$ Hz, $|^2J(^{117}Sn–H)| = 74.5$ Hz, q, SnEt], 1.20 [$|^3J(^{119}Sn–H)| = 175.2$ Hz, $|^3J(^{117}Sn–H)| = 167.5$ Hz, t, SnEt]. IR: 3133 w, 3114 w, 3105 w [ν(C–H)], 515 m [ν(Sn–C)], 175s, 160s [δ(C–Sn–C)].

2.2.19. [Dichlorodibutylbis(1-methylimidazole)tin(IV)] · (H_2O) (19)

Compound **19** was prepared similarly to compound **9**. Yield 70%, m.p. 115–118°C (Found: C, 40.0; H, 6.7; N, 11.2. Calc. for $C_{16}H_{32}Cl_2N_4OSn$: C, 39.5; H, 6.6; N, 11.5%). NMR ($CDCl_3$): ^1H, δ 8.18, 7.50, 6.95 (s, H^2, H^4 and H^5), 3.78 (s, 1-Me), 2.94 (br, H_2O), 1.86–1.72 (m, $SnBu^n$), 1.66–1.46 (m, $SnBu^n$), 1.25 (ps, $SnBu^n$), 0.8 (t, $SnBu^n$). IR: 3400br [ν(O–H)], 3130 w, 3111 w [ν(C–H)], 552 m [ν(Sn–C)], 230s [ν(Sn–Cl)], 185s [δ(C–Sn–C) and δ(Cl–Sn–Cl)].

2.2.20. [Dibromodibutylbis(1-methylimidazole)tin(IV)] · (H_2O)$_{0.5}$ (20)

Compound **20** was prepared similarly to compound **9**. Yield 75%, m.p. 127–129°C (Found: C, 33.9; H, 5.7; N, 9.6. Calc. for $C_{16}H_{31}Br_2N_4O_{0.5}Sn$: C, 34.0; H, 5.5; N, 9.9%). NMR ($CDCl_3$): ^1H, δ 8.4, 7.7, 7.1 (br, H^2, H^4 and H^5), 3.78 (s, 1-Me), 2.44 (br, H_2O), 1.94 (t, $SnBu^n$), 1.70–1.40 (m, $SnBu^n$), 1.24 (ps, $SnBu^n$), 0.8 (t, $SnBu^n$). IR: 3400br [ν(O–H)], 3142 w, 3106 w [ν(C–H)], 611 m, 558 w [ν(Sn–C)].

2.2.21. [Diiodobutylbis(1-methylimidazole)tin(IV)] (21)

Compound **21** was prepared similarly to compound **11**. Yield 14%, m.p. 96–98°C (Found: C, 29.2; H, 4.8; N, 8.3. Calc. for $C_{16}H_{30}I_2N_4Sn$: C, 29.5; H, 4.6; N, 8.6%). NMR ($CDCl_3$): ^1H, δ 8.04, 7.34, 6.95 (s, H^2, H^4 and H^5), 3.78 (s, 1-Me), 2.03 (t, $SnBu^n$), 1.7–1.5 (m, $SnBu^n$), 1.34 (ps, $SnBu^n$), 0.88 (t, $SnBu^n$). IR: 3121 w [ν(C–H)], 548 m [ν(Sn–C)], 177s, 168s [δ(C–Sn–C)].

2.2.22. [Dichlorodiphenylbis(1-methylimidazole)tin(IV)] (22)

Compound **22** was prepared similarly to compound **9**. Yield 94%, m.p. 213–216°C (Found: C, 47.0; H, 4.5; N, 10.8. Calc. for $C_{20}H_{22}Cl_2N_4Sn$: C, 47.3; H, 4.4; N, 11.0%). NMR ($CDCl_3$): ^1H, δ 8.0–7.9, 7.5–7.1 [$|^3J(Sn–H)| = 108$ Hz, m, SnPh], 7.35, 6.95 (s, H^2, H^4 and H^5), 3.81 (s, 1-Me). IR: 3158 w, 3139 w, 3127 w, 3060 w [ν(C–H)], 463s [δ(Ph)], 286s [ν(Sn–C)], 238s, 228s [ν(Sn–Cl)], 211s, 182s, 167s [δ(C–Sn–C) and δ(Cl–Sn–Cl)].

2.2.23. [Diiododiphenylbis(1-methylimidazole)tin(IV)] (23)

Compound **23** was prepared similarly to compound **11**. Yield 69%, m.p. 190–194°C (Found: C, 35.0; H, 3.4; N, 7.8. Calc. for $C_{20}H_{22}I_2N_4Sn$: C, 34.8; H, 3.2; N, 8.1%). NMR (acetone): ^1H, δ 8.37 (s, H^2, H^4 and H^5), 8.0–7.6, 7.5–7.0 (m, SnPh), 3.95 (s, 1-Me). IR: 3151 w, 3131 w [ν(C–H)], 459s [δ(Ph)], 287s [ν(Sn–C)], 195s, 177s, 158s [ν(Sn–I)].

2.2.24. [Trichloromethylbis(1-methylimidazole)tin(IV)] (24)

Compound **24** was prepared similarly to compound **9**. Yield 96%, m.p. 340°C dec (Found: C, 27.2; H, 4.0; N, 13.7. Calc. for $C_9H_{15}Cl_3N_4Sn$: C, 26.7; H, 3.7; N, 13.9%). NMR (acetone): ^1H, δ 8.35, 7.42, 7.24 (br, H^2, H^4 and H^5), 3.88 (s, 1-Me), 1.10 [$|^2J(^{119}Sn–H)| = 101.2$ Hz, $|^2J(^{117}Sn–H)| = 96.4$ Hz, s, SnMe]. IR: 3124 w [ν(C–H)], 565 m, 526 m [ν(Sn–C)], 287s, 277s [ν(Sn–Cl)], 203s, 175s [δ(C–Sn–C) and δ(Cl–Sn–Cl)].

2.2.25. [Trichlorobutylbis(1-methylimidazole)tin(IV)] (25)

Compound **25** was prepared similarly to compound **9**. Yield 95%, m.p. 152–159°C (Found: C, 32.1; H, 4.9; N, 12.5. Calc. for $C_{12}H_{21}Cl_3N_4Sn$: C, 32.3; H, 4.7; N, 12.5%). NMR ($CDCl_3$): ^{1}H, δ 8.45, 7.6, 6.89 (s, H^2, H^4 and H^5), 3.77 (s, 1-Me), 2.0–1.8 (m, $SnBu^n$), 1.7 (br, $SnBu^n$), 1.30 (s, $SnBu^n$), 0.85 (t, $SnBu^n$). IR: 3142 w, 3123 w [ν(C–H)], 598 m [ν(Sn–C)], 266s [ν(Sn–Cl)], 194s, 180s [δ(C–Sn–C) and δ(Cl–Sn–Cl)].

2.2.26. [Trichlorophenylbis(1-methylimidazole)tin(IV)] (26)

Compound **26** was prepared similarly to compound **9**. Yield 88%, m.p. 184–185°C (Found: C, 35.9; H, 3.8; N, 12.1. Calc. for $C_{14}H_{17}Cl_3N_4Sn$: C, 36.0; H, 3.7; N, 12.0%). NMR (acetone): ^{1}H, δ, 8.50, 8.35, 7.55, 7.45 (br, H^2, H^4 and H^5), 7.84 (d, SnPh), 7.35–7.15 (m, SnPh), 3.91, 3.87 (s, 1-Me). IR: 3150 w, 3128 w [ν(C–H)], 462s, 454s [δ(Ph)], 180s, 161s [δ(C–Sn–C) and δ(Cl–Sn–Cl)].

2.2.27. [Dibromodimethyl(1,10-phenanthroline)tin(IV)] (27)

To a stirred diethyl ether solution (100 cm^3) of 1,10-phenanthroline (213 mg, 1.2 mmol), [$(L^{\#})_2(CH_3)_2SnBr_2$] (280 mg, 0.6 mmol) was added at room temperature. The colorless precipitate became immediately pale pink; it was filtered off after 1 day, washed with diethyl ether and shown to be compound **27**. Yield 95%, m.p. 258–260°C, Found: C, 34.6; H, 3.0; N, 6.0. Calc. for $C_{14}H_{14}Br_2N_2Sn$: C, 34.4; H, 2.9; N, 5.7%). NMR ($CDCl_3$): ^{1}H, δ 9.70 (br, Phen), 8.53 (d, Phen), 8.01 (s, Phen), 7.89 (m, Phen), 2.47 (br, H_2O), 1.39 [$|^2J(^{119}Sn–H)| = 111.4$ Hz, $|^2J(^{117}Sn–H)| = 106.5$ Hz, s, SnMe]. IR 3116 w, 3044 w [ν(C–H)], 570s [ν(Sn–C)].

2.2.28. [Bis{diiododiethyltin(IV)}tris(1,10-phenanthroline)] (28)

To a stirred diethyl ether solution (100 cm^3) of 1,10-phenanthroline (150 mg, 0.8 mmol), [$(L^{\#})_2(C_2H_5)_2SnI_2$] (264 mg, 0.4 mmol) was added at room temperature. The yellow precipitate became black; it was filtered off after 1 day, washed with diethyl ether and shown to be compound **28**. Yield 85%, m.p. 139–142°C (Found: C, 38.0; H, 3.2; N, 6.2. Calc. for $C_{44}H_{44}I_9N_6Sn$: C, 37.7; H, 3.2; N, 6.0%). NMR ($CDCl_3$): ^{1}H, δ 9.75 (d, Phen), 8.53 (d, Phen), 8.01 (s, Phen), 7.88 (m, Phen), 1.98 [$|^2J(^{119}Sn–H)| = 93.0$ Hz, $|^2J(^{117}Sn–H)| = 88.1$ Hz, q, SnEt], 0.88 [$|^3J(^{119}Sn–H)| = 198.0$ Hz, $|^3J(^{117}Sn–H)| = 189.3$ Hz, t, SnEt]; ^{119}Sn, δ −177.7. IR: 3180 w [ν(C–H)], 520 m, 509 m [ν(Sn–C)].

2.2.29. [Dimethyl(1-methylimidazole)(1,10-phenanthroline)tin(IV)] diperchlorate (29)

To a stirred diethyl ether solution (100 cm^3) of 1,10-phenanthroline (92 mg, 0.5 mmol), [$(L^{\#})_2(CH_3)_2Sn(ClO_4)_2$] (138 mg, 0.25 mmol) was added at room temperature. The colorless precipitate became immediately pink; it was filtered off after 1 day, washed with diethyl ether and shown to be compound **29**. Yield 87%, m.p. 207–209°C (Found: C, 35.4; H, 3.6; N, 9.5. Calc. for $C_{18}H_{17}Cl_2O_8N_4Sn$: C, 35.4; H, 3.3; N, 9.2%). NMR ($CDCl_3$): δ 9.27 (m, Phen), 8.35 (d, Phen), 7.88 (s, Phen), 7.75 (m, Phen), 7.98, 7.19, 7.02 (s, H^2, H^4 and H^5), 3.85 (s, 1-Me), 1.15 (br, SnMe). IR: 3155 w [ν(C–H)], 1085s, 623s [$\nu(ClO_4)$], 570 m, 553 m [ν(Sn–C)].

2.3. Crystallography

2.3.1. [Chlorotriphenyl(1-methylimidazole)tin(IV)] (8)

A summary of the experimental conditions and solution of the structure is reported in Table 1. Atomic coordinates and isotropic equivalent thermal parameters are reported in Table 2. Colorless well-formed crystals of the adduct were obtained from the slow evaporation of an ether solution. A preliminary crystallographic study was carried out by inspection of oscillation and Weissenberg photographs, leading to the assignment of the crystal system as triclinic (space group $P\bar{1}$ after refinement). A crystal with approximate dimensions of $0.4 \times 0.4 \times 0.2$ mm was mounted on a Syntex $P2_1$ diffractometer, equipped with a sealed Mo tube (45 kV, 25 mA) and a graphite monochromator. The orientation matrix and accurate lattice parameters were obtained by least squares refinement of 15 centered reflections in the range $4.95° \leq 2\theta \leq 22.38°$; 11 255 reflections were then collected in the range $3.0° \leq 2\theta \leq 65°$. The data were then corrected for decay ($\approx 10\%$) and for Lorentz and polarization effects. A semiempirical [6] absorption correction was applied on the basis of ψ-scan of the (5–10) reflection, the transmission factor was found to vary between 0.75 and 1.0. The data were then merged together giving 10 913 reflections with an R_{int} of 0.55%.

The structure was solved by direct methods by using the SIR92 program [7]; all the non-H atoms in the asymmetric unit were located at this stage, that is two distinct organotin–imidazole adducts. The structure was then refined, using the crystallographic program package CRYSTALS [8], imposing isotropic thermal parameters for all the atoms and using only the 5705 reflections having $|F_o| \geq 3\sigma(|F_o|)$; the R factor after convergence was 0.099. A new refinement was performed treating thermal vibration anisotropically and the R factor was lowered to 0.049. At this stage, by means of a Fourier difference, we were able to locate the H atoms

Table 1
Crystal data: data collection and refinement of the structure for [(1-methylimidazole)triphenyltin(IV)]chloride (**8**), [bis(1-methylimidazole)dimethyltin(IV)dibromide] (**10**) and [bis(1-methylimidazole)diethyltin(IV)diiodide] (**18**)

Compound	**8**	**10**	**18**
Formula	$C_{22}H_{21}N_2ClSn$	$C_{10}H_{18}N_4Br_2Sn$	$C_{12}H_{22}N_4I_2Sn$
Formula weight	467.585	472.777	594.853
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a [Å]	9.561(2)	7.477(2)	8.041(2)
b [Å]	15.431(7)	7.425(1)	15.988(3)
c [Å]	15.025(6)	8.057(2)	14.702(6)
α [°]	89.36(4)	105.16(2)	–
β [°]	105.90(3)	112.32(2)	94.86(2)
γ [°]	85.02(3)	98.02(2)	–
V_c [Å^3]	2124(1)	384.9(2)	1883.4(6)
Z	4	1	4
D_c [g cm^{-3}]	1.463	2.0398	2.0980
μ(Mo Kα) [cm^{-1}]	13.409	67.962	46.32
F(000)	936	226.0	1112.0
Radiation (monochromated)	Mo K$_\alpha$ ($\lambda = 0.71069$ Å)	Mo K$_\alpha$ ($\lambda = 0.71069$ Å)	Mo K$_\alpha$ ($\lambda = 0.71069$ Å)
T of data collection [K]	293	293	293
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan width [°]	0.6° below K$_{\alpha1}$, 0.6 above K$_{\alpha2}$	0.6° below K$_{\alpha1}$, 0.6 above K$_{\alpha2}$	0.6° below K$_{\alpha1}$, 0.6 above K$_{\alpha2}$
Scan speed [° min^{-1}]	minimum = 1.502, maximum = 14.648	minimum = 1.502, maximum = 14.648	minimum = 1.502, maximum = 14.648
Background:scan ratio	0.5	0.5	0.5
Data collection range [°]	$3.0 \le 2\theta \le 65$	$5.0 \le 2\theta \le 55$	$5.0 \le 2\theta \le 60$
h; k; l range	$-12 \rightarrow 11$, $-23 \rightarrow 23$, $0 \rightarrow 21$	$-9 \rightarrow 8$, $-9 \rightarrow 9$, $0 \rightarrow 10$	$0 \rightarrow 12$, $0 \rightarrow 23$, $-21 \rightarrow 21$
Standards (measured every 97 reflections)	1 1 0, 2 2 −2, 1 3 1	2 3 0, 1 2 1, 0 4 −2	2 2 −3, 2 0 −6, 0 4 4
Number of unique reflections measured	10913	1780	6076
Number of data with $\|F_o\| \ge 3\sigma(\|F_o\|)$	5498	1715	2000
Refinement	Full − matrix least − squares on F	Full − matrix least-squares on F	Full-matrix least-squares on F
Number of parameters refined	469	79	88
R[a]	0.038	0.026	0.044
R_w[b]	0.044	0.030	0.054
S[c] (goodness of fit)	0.988	1.28	1.179

[a] $R = (\Sigma||F_o| - k|F_c||)/\Sigma|F_o|$.
[b] $R_w = [\Sigma_w(|F_o| - k|F_c|)^2/\Sigma_w|F_o|^2]^{1/2}$.
[c] $S = [\Sigma_w(|F_o| - k|F_c|)^2/(N_{obs} - N_{par})]^{1/2}$.

Table 2
Atomic fractional coordinates and isotropic equivalent thermal parameters (with e.s.d. in parentheses) for [(1-methylimidazole) triphenyltin(IV) chloride] (**8**)

Atom	*x / a*	*y / b*	*z / c*	U_{eq}^{a} (Å^2)
Sn(1a)	0.29449(4)	0.20873(2)	0.77475(3)	0.0558(2)
Cl(1a)	0.3829(2)	0.0768(1)	0.7010(1)	0.0912(7)
N(1a)	0.2248(5)	0.3409(3)	0.8423(3)	0.064 (2)
C(2a)	0.2968(8)	0.3664(4)	0.9230(4)	0.080 (3)
N(3a)	0.2413(6)	0.4430(3)	0.9434(3)	0.070 (2)
C(4a)	0.1252(7)	0.4674(4)	0.8695(5)	0.082 (3)
C(5a)	0.1174(6)	0.4058(3)	0.8077(4)	0.066 (2)
C(6a)	0.289(1)	0.4915(5)	1.0271(5)	0.112 (4)
C(7a)	0.1070(6)	0.2394(4)	0.6599(4)	0.060 (2)
C(8a)	0.1171(9)	0.2597(5)	0.5715(5)	0.088 (3)
C(9a)	−0.010(1)	0.2770(6)	0.4990(5)	0.116 (5)
C(10a)	−0.145(1)	0.2773(5)	0.5134(6)	0.105 (3)
C(11a)	−0.1547(8)	0.2587(5)	0.5992(6)	0.090 (3)
C(12a)	−0.0320(7)	0.2398(4)	0.6713(4)	0.071 (2)
C(13a)	0.2579(6)	0.1362(3)	0.8867(4)	0.057 (2)
C(14a)	0.1617(7)	0.1686(4)	0.9358(4)	0.076 (3)
C(15a)	0.1316(9)	0.1179(6)	1.0032(5)	0.094 (4)
C(16a)	0.193(1)	0.0355(7)	1.0234(5)	0.115 (5)
C(17a)	0.291(1)	0.0028(6)	0.9774(6)	0.126 (5)
C(18a)	0.3225(8)	0.0520(4)	0.9092(5)	0.085 (3)
C(19a)	0.4961(6)	0.2637(4)	0.7913(4)	0.063 (2)
C(20a)	0.6228(7)	0.2166(6)	0.8393(6)	0.098 (4)
C(21a)	0.755(1)	0.252(1)	0.8570(8)	0.140 (6)
C(22a)	0.761(1)	0.333(1)	0.828(1)	0.143 (7)
C(23a)	0.641(2)	0.3831(7)	0.7790(8)	0.136 (6)
C(24a)	0.5031(9)	0.3477(6)	0.7607(6)	0.103 (4)
Sn(1b)	0.30105(4)	0.25882(2)	0.27020(3)	0.0532(2)
Cl(1b)	0.1096(2)	0.3346(1)	0.1328(1)	0.0749(5)
N(1b)	0.4812(5)	0.1786(3)	0.3902(3)	0.058 (2)
C(2b)	0.6102(6)	0.1411(3)	0.3881(4)	0.060 (2)
N(3b)	0.6710(5)	0.0908(3)	0.4635(3)	0.067 (2)
C(4b)	0.5780(7)	0.0960(4)	0.5182(4)	0.070 (2)
C(5b)	0.4618(6)	0.1492(4)	0.4722(4)	0.067 (2)
C(6b)	0.8174(7)	0.0419(5)	0.4846(5)	0.095 (3)
C(7b)	0.4712(6)	0.2740(4)	0.2072(4)	0.059 (2)
C(8b)	0.4965(7)	0.2229(5)	0.1370(5)	0.085 (3)
C(9b)	0.610(1)	0.2367(7)	0.0977(6)	0.113 (4)
C(10b)	0.699(1)	0.3002(8)	0.1293(8)	0.126 (5)
C(11b)	0.675(1)	0.3511(7)	0.1963(8)	0.125 (5)
C(12b)	0.5634(8)	0.3389(5)	0.2357(6)	0.095 (3)
C(13b)	0.2776(7)	0.3574(4)	0.3663(4)	0.066 (2)
C(14b)	0.3881(9)	0.3691(4)	0.4468(5)	0.087 (3)
C(15b)	0.373(1)	0.4315(5)	0.5096(6)	0.109 (4)
C(16b)	0.244(2)	0.4830(5)	0.4923(7)	0.132 (6)
C(17b)	0.132(1)	0.4750(6)	0.4155(7)	0.132 (5)
C(18b)	0.1489(9)	0.4128(5)	0.3515(5)	0.097 (3)
C(19b)	0.1805(6)	0.1472(3)	0.2615(3)	0.054 (2)
C(20b)	0.0324(6)	0.1577(4)	0.2510(4)	0.070 (3)
C(21b)	−0.0463(8)	0.0877(5)	0.2472(5)	0.089 (3)
C(22b)	0.0194(9)	0.0040(5)	0.2506(5)	0.089 (3)
C(23b)	0.1663(9)	−0.0075(4)	0.2598(4)	0.078 (3)
C(24b)	0.2474(6)	0.0629(3)	0.2662(4)	0.061 (2)

[a] U_{eq} is defined as the mean of the principal axes of the thermal ellipsoid.

of the imidazoles, whereas they were introduced by model ($d = 0.96$ Å) for the phenyl rings, because no hydrogen with a reasonable geometry was found for them. The methyl groups were found to be disordered over several different conformations, the hydrogens were then modeled on the basis of the most intense peak with a reasonable geometry. The structure was refined again, by fixing the thermal (isotropic) parameters for the hydrogens at 30% greater than the value of the bonded carbons, and refining the coordinates using the riding model; the R value for the 469 parameters was 0.040. A final least squares refinement was then performed after optimizing the weighting scheme on the basis of the distribution of the mean of $w\,\Delta^2$ as function of $|F_o|$ and sin θ/λ. A robust-resistant weighting scheme (in order to properly handle possible outliers in the data set) [9,10] based on Cheybishev polynomials [11] with coefficients $a_1 = 0.381$, $a_2 = 0.320$, $a_3 = 0.181$ was used. The final R factor was 0.038.

All the refinement steps reached convergence, without showing any difficulties, or correlations between parameters greater than 0.8. The final r.m.s. shift was below 0.01; the minimum and maximum $\Delta\rho$ were −0.37 and 0.75, both near the tin atoms.

All the refinements were made taking the anomalous scattering into account, but no correction was introduced for the extinction. Scattering factors and anomalous contributions were taken from the International Tables [12]. Program PARST [13] was used for some geometrical and crystallographic calculations.

*2.3.2. [Dibromodimethylbis(1-methylimidazole)tin(IV)] (**10**)*

A summary of the experimental conditions and solution of the structure is reported in Table 1. Atomic coordinates and isotropic equivalent thermal parameters are reported in Table 3. Crystals of the compound were grown from a colorless dichloromethane/diethyl ether solution (1:1) by slow evaporation. A colorless crystal with approximate dimensions of 0.50 × 0.30 × 0.30 mm was mounted on an automatic four circle diffractometer, equipped with a sealed Mo tube (45 kV, 25 mA). The crystal system was found to be triclinic, and accurate

Table 3
Atomic coordinates and isotropic equivalent thermal parameters for dibromobis(1-methylimidazole)dimethyltin(IV) (**10**)

Atom	*x / a*	*y / b*	*z / c*	U_{eq}^{a} (Å^2)	Occupation
Sn(1)	0.000	0.0000	0.000	0.0266	1.0000
Br(1)	−0.27908(5)	0.19939(5)	−0.11291(5)	0.0433	1.0000
N(1)	−0.1613(4)	−0.2463(4)	−0.2983(4)	0.0343	1.0000
N(3)	−0.2538(4)	−0.5322(4)	−0.5163(4)	0.0356	1.0000
C(2)	−0.1584(5)	−0.4297(5)	−0.3304(5)	0.0358	1.0000
C(4)	−0.3235(6)	−0.4100(6)	−0.6089(5)	0.0447	1.0000
C(5)	−0.2663(6)	−0.2341(6)	−0.4744(6)	0.0435	1.0000
C(6)	−0.2822(7)	−0.7391(5)	−0.6032(6)	0.0496	1.0000
C(7)	0.1740(6)	0.1539(5)	−0.1002(6)	0.0399	1.0000

[a] U_{eq} is defined as the mean of the principal axes of the thermal ellipsoid.

cell parameters were obtained by least-squares refinement of 26 reflections with $11° \leq 2\theta \leq 30°$; the space group was found to be $P\bar{1}$.

A total of 1926 reflections was collected with $-9 \leq h \leq 8$, $-9 \leq k \leq 9$ and $0 \leq l \leq 10$; no decay was observed during the data collection. The ψ-scan of the reflection (−1, 6, 3) gave a minimum and a maximum transmission factor equal to 0.99993 and 1.10217, respectively; the data were then corrected for the absorption using a semi-empirical method [6].

The structure was solved by direct methods by using the SIR92 program [7], all of the 9 non-hydrogen atoms in the asymmetric unit were found at this level.

The hydrogen atoms were located by means of a Fourier difference map, performed by using the CRYSTALS package [8], and an isotropic refinement of all the atoms gave R equal to 0.0860. The structure was then anisotropically refined with the hydrogens refined as riding (U_{iso} was fixed at 30% greater than that of the bonded carbons). A final refinement was performed after an optimization of the weighting scheme [9,10], where an optimized truncated Cheybishev polynomial with coefficients $a_1 = 0.730$, $a_2 = 0.285$, $a_3 = 0.551$, $a_4 = 0.0635$, $a_5 = 0.138$ was employed [11], refining the extinction parameter as well. The R factor was 0.026 at the end of the last refinement cycle, with a maximum r.m.s. shift equal to 0.00.

2.3.3. [Diiododiethylbis(1-methylimidazole)tin(IV)] (18)

A summary of the experimental conditions and solution of the structure is reported in Table 1. Atomic coordinates and isotropic equivalent thermal parameters are reported in Table 4. Pale yellow crystals of [diiododiethylbis(1-methylimidazole)tin(IV)] were obtained by slow evaporation from an ether solution. A crystal with approximate dimensions of 0.3 × 0.4 × 0.4 mm was mounted on a Syntex P21 four-circle diffractometer and accurate lattice parameters were obtained by least-squares refinement of 40 reflections collected in the range $10° \leq 2\theta \leq 25°$. A total of 6076 unique reflections was collected in the range $5° \leq 2\theta \leq 55°$ by an $\omega/2\theta$ scan data collection; of these 2000, with I greater than $3\sigma(I)$, were used in the subsequent refinement. A continuous decay (≈ 20%) of the standard reflections intensity was observed and a correction was made; the data were also corrected for Lorentz and polarization effect. The ψ-scan of three different reflections (0 −4 4, −1 −3 6, 1 −5 7) gave a minimum and a maximum transmission factor equal to 0.81 and 1.00, respectively; the data were then corrected for the absorption using a semi-empirical method [6].

The structure was solved finding first the Sn and I atoms, by a Patterson map using the Shelxs86 program [14]. At this stage, an isotropic refinement gave an R equal to 17.74. The other non-hydrogen atoms were located by means of Fourier difference maps performed by using the CRYSTALS package [8], with the exception of the last carbon of the ethyl which was rather disordered, showing up in two different positions in the Fourier map. After a last isotropic refinement, the hydrogens were imposed by a model with $d = 1.0$ Å and U_{iso} fixed as 30% greater than the bonded carbons. The structure was then anisotropically refined with the hydrogens refined as riding. In the first cycles of the refinement, the two possible positions of the terminal carbon of the ethyl were kept fixed while their percentage of occupation was refined; then these occupations were kept fixed at the two positions refined isotropically. A final refinement was performed after an optimization of the weighting scheme [9,11] using an optimized truncated Cheybishev polynomial with coefficients $a_1 = 0.549$, $a_2 = 0.446$, $a_3 = 0.290$. The R factor was equal to 0.044 at the end of the last refinement cycle, with a maximum r.m.s. shift equal to 0.02.

Table 4
Atomic coordinates and isotropic equivalent thermal parameters (with e.s.d. in parenthesis) for diiododobis(1-methylimidazole)diethyltin(IV) (**18**)

Atom	x/a	y/b	z/c	U_{eq}^{a} (Å^2)	Occupation
I(1)	0.01229(7)	0.14348(3)	0.09482(3)	0.0741(2)	1.0000
Sn(1)	0.2500	0.2500	0.0000	0.0456(2)	0.5000
N(1)	0.2565(8)	0.3434(3)	0.1250(3)	0.057(2)	1.0000
N(3)	0.2366(7)	0.3953(3)	0.2621(3)	0.059(2)	1.0000
C(2)	0.2167(8)	0.3266(4)	0.2084(4)	0.056(2)	1.0000
C(4)	0.292(1)	0.4581(4)	0.2102(5)	0.066(2)	1.0000
C(5)	0.304(1)	0.4262(4)	0.1265(4)	0.065(2)	1.0000
C(6)	0.205(1)	0.3990(6)	0.3593(4)	0.084(3)	1.0000
C(7)	0.039(1)	0.3168(6)	−0.0629(6)	0.094(4)	1.0000
C(8)	0.002(3)	0.327(2)	−0.159(2)	0.117(7)	0.5038
C(9)	0.030(3)	0.395(2)	−0.078(2)	0.111(7)	0.4962

[a] U_{eq} is defined as the mean of the principal axes of the thermal ellipsoid.

3. Results and discussion

3.1. Synthesis, reactivity and properties of the organotin(IV) complexes

Interaction between various organotin(IV) compounds and an excess 1-methylimidazole ($L^{\#}$) in an organic solvent (diethyl ether or THF) at 0°C or at room temperature gave the compounds **1**–**2**, **5**–**10**, **16**, **17**, **19**, **20**, **22**, and **24**–**26** (Fig. 2a), in accordance with Eq. (1):

$$x(L^{\#}) + (R_nSnX_{4-n}) \cdot zH_2O \xrightarrow{\text{solvent}} \times\left[(L^{\#})_x(R_nSnX_{4-n})\right] \cdot zH_2O \quad (1)$$

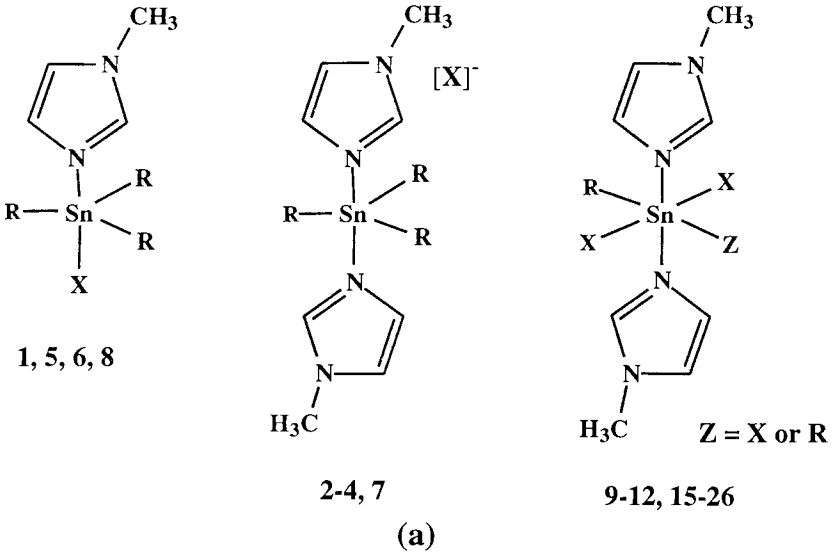
(R = Me, Et, Bu^n or Ph; X = Cl or Br, $n = 1, 2$ or 3; $x = 1$ or 2; $z = 0, 1/2$ or 1)

With the exception of the triorganotin chloride and bromide complexes **1**, **5**, **6**, and **8** (for which a ligand to metal ratio of 1 to 1 was observed) 2:1 adducts were always obtained. This fact further confirms that the possibility of obtaining 2:1 adducts with triorganotin(IV) chloride and bromide acceptors is limited to imidazole type donors able to involve the halide group in a hydrogen bonding network. On the other hand the 1-methylimidazole is able to displace the iodide from the coordination sphere of the tin center, yielding the ionic derivatives $[(L^{\#})_2R_3Sn]I \cdot zH_2O$ (**2**, **7**).

If the reaction between $L^{\#}$ and $(CH_3)_3SnCl$ was carried out in dry ethanol solution containing $AgNO_3$, the complex $[(L^{\#})_2(CH_3)_3Sn]NO_3$ (**3**) was formed.

The substitution of the Cl^- with ClO_4^- was achieved when an ethanol solution of $NaClO_4$ was added to an ethanol solution of **1**. The substitution with ClO_4^-, NO_3^-, BPh_4^- or NCS^- occurred when ethanol solutions of $NaClO_4$, $AgNO_3$, $NaBPh_4$ or KSCN were added to an ethanol solution of **9**, and the complexes **12**, **13**, **14**, and **15** were produced. They were characterized and shown to have different stoichiometries. 2:1 adducts were obtained when the counter ion was ClO_4^- or NCS^- (Fig. 2a), whereas a 1:1 ligand to metal ratio was found in the nitrato and tetraphenylborato derivatives (Fig. 2c). In the last case, the substitution of the Cl^- with BPh_4^- is only partial: one Cl^- group remains bonded to the tin(IV) center together with two molecules of water.

Substitution of Cl^- with I^- was always successful. Conversion of the chlorides into iodides produced the derivatives **2**, **11**, **18**, **21**, and **23**. The disproportionation of the tin(IV) halides previously observed in the derivatives of 4-phenylimidazole [1], in accordance with Kocheshkov's reaction [15], did not occur in this case.



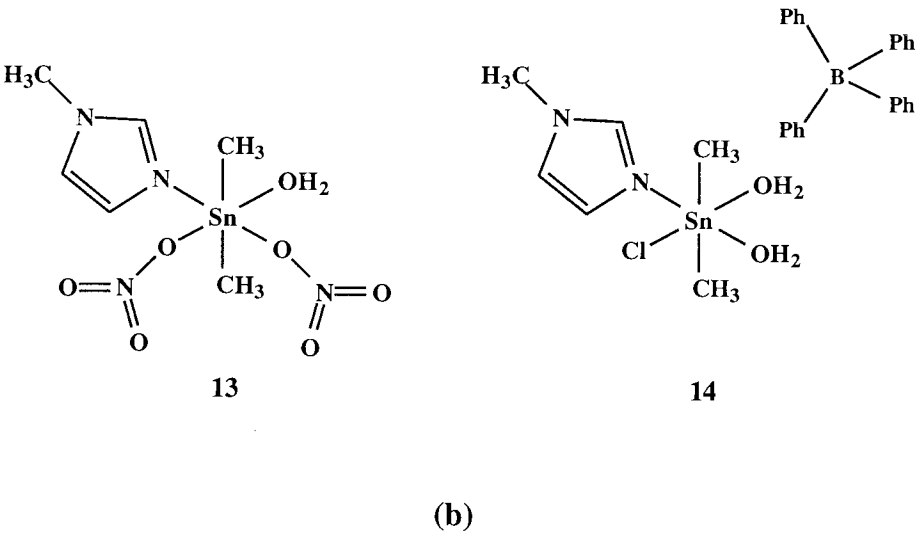


Fig. 2. Structures proposed for organotin(IV) derivatives of 1-methylimidazole.

Various degrees of hydration have been found from 0.5, as in compound **4**, to 2, as in compound **14**. In fact, tin(IV) and organotin(IV) complexes often absorb molecules of water from atmosphere and solvent and they are not easy to recrystallize. All the attempts to eliminate the presence of water from our complexes failed.

All the diorgano- and triorgano-tin(IV) derivatives are moderately soluble in chlorinated solvents, acetone and DMSO, and insoluble in diethyl ether, ethanol and water. The monoorganotin(IV) adducts are generally less soluble in all the solvents commonly used. These compounds are stable also when exposed to moisture for a long time, whereas upon prolonged standing at 120°C, or in acetone and chloroform solutions, organotin(IV) oxides and hydroxides are often recovered.

The triorganotin(IV) adducts **1–8** are often unstable also in the solid state. When **1**, **5**, and **8** are exposed to air for 4–10 h, they decompose in accordance with the following equation:

$$2(L^{\#})R_3SnCl \leftrightharpoons \left[(L^{\#})_2R_2SnCl_2\right] + R_4Sn \qquad (2)$$

Complex **10** reacts with 1,10-phenanthroline yielding the hexacoordinate 1:1 adduct $[(Phen)(CH_3)_2SnBr_2]$ **27**, resulting from the displacement of both the imidazole ligands. This kind of reactivity is due to the chelating ability of Phen, which predominates despite the greater σ-basicity of imidazole. On the other hand, if the starting tin(IV) was coordinated by a good leaving group such as ClO_4^- ($[(L^{\#})_2(CH_3)_2Sn(ClO_4)_2]$ **12**), we observed a partial substitution of imidazole and complete displacement of ClO_4^- from the coordination sphere, with formation of the mixed-ligands complex $[(L^{\#})(Phen)(CH_3)_2Sn](ClO_4)_2$ **29** (Fig. 3). A different result was obtained when Phen reacted with $[(L^{\#})_2(C_2H_5)_2SnI_2]$: in this case the donor $L^{\#}$ was displaced completely and a compound with a 3:2 stoichiometry ($[(Phen)_3\{(C_2H_5)_2SnI_2\}_2]$ **28**) afforded. Several attempts to crystallize this compound in suitable form for the X-ray analysis failed. In absence of structural data, it is very difficult to indicate with a certainty the coordination environment of the tin center; however a di- or oligo-nuclear structure with the tin(IV) atom coordinated by bridging iodide groups and monodentate Phen seems to be likely, also on the basis of literature data [16–19].

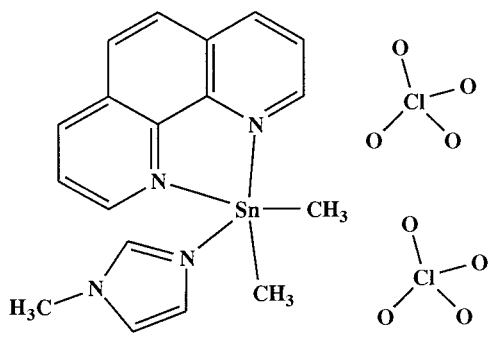


Fig. 3. Structure proposed for the ionic mixed ligand complex **29**.

3.2. IR data

By comparison with the data reported for other organotin(IV) complexes containing N-donor ligands [20,21], we suggest the following assignments for adducts **1–29**.

3.2.1. Ligand absorptions

In the 3150–2950 cm^{-1} region, the ligand exhibits weak bands typical of C–H stretching due to a pseudoaromatic ring, and in the region 1600–1500 cm^{-1} some more intense absorptions due to the ring breathing mode [22]. These bands do not shift markedly upon coordination to tin, suggesting a weak influence of the complexation on the absorptions within the donor.

3.2.2. Sn–C stretching frequencies

In the triorganotin(IV) derivatives **2** and **5–7** two strong or medium absorptions are always observed in the 600–500 cm^{-1} region. They are due to $\nu_{(asym)}$ and $\nu_{(sym)}$ Sn–C stretching vibrations and are consistent with an essentially trigonal pyramidal arrangement of organic groups with a marked deviation from planarity. The appearance of only a single Sn–C stretching bond at ca. 550 cm^{-1}, in the spectra of trimethyltin(IV) complexes **1** and **3**, is taken to imply a $C_{3\nu}$ symmetry of the C_3-skeleton [23–26].

Only a single Sn–C stretching vibration was observed in the spectra of the diorganotin(IV) derivatives **9–11** and **13–23** in accordance with a *trans*-octahedral configuration of the two alkyl groups [27,28]. In the spectrum of derivative **24**, two medium absorptions at 565 and 525 cm^{-1}, respectively, were found. In this case, the presence of two different isomers is likely.

It was noted that on changing the halide groups linked to tin(IV) little shift of the ν(Sn–C) was observed.

3.2.3. Sn-halide stretching frequencies

In the triorganotin(IV) derivative **1**, we observed the tin chloride stretching frequency as strong absorption at 229 cm^{-1}. This further supports the non-ionic nature of this compound. The absorption is markedly shifted with respect to that indicated for the starting triorganotin(IV) chloride [29].

A similar shift was observed in the case of the triphenyltin(IV) adduct **8** [30]. The tin(IV) chloride stretching frequencies in the di- and tri-halidetin(IV) derivatives fall as strong or medium broad bands at ca. 230 and 260 cm^{-1}, respectively. These bands are lowered by 90–130 cm^{-1} with respect to those found in the

starting tin(IV) reagents [29]. The tin bromide stretchings bands, where detected, are shifted with respect to tin(IV) chloride by 40–60 cm^{-1}, in accordance with trends previously observed [29].

3.2.4. Other absorptions

It is not possible to assign with certainty the δ(Cl–Sn–Cl), δ(C–Sn–C), δ(C–Sn–Cl), ρ(Sn–C_3) and ρ(Sn–Cl_3) which generally fall in the region 200–120 cm^{-1} [29], because in these complexes these bands are too close to resolve.

Several weak bands, which appeared in the spectra of all the complexes in the region 300–400 cm^{-1} and were absent in the spectra of the free donor and acceptor could be tentatively assigned to ν(Sn–N) [31,32]. Further support for this assumption derives from the observation that all the other donor absorptions, in the 3200–400 cm^{-1} region, do not markedly shift upon complexation.

The perchlorato complex **4** was found to be ionic: a single broad absorption at ca. 1100 and a sharp band at 620 cm^{-1} were observed [33], whereas derivative **12** showed a more complex pattern, analogous to that found in derivatives containing unidentate perchlorato groups. In this case, in the absence of X-ray crystal data we are unable to indicate the nature of the two ClO_4^- groups; however, we exclude a completely ionic structure with the tin(IV) tetracoordinated, such as $[(L^{\#})_2(CH_3)_2Sn]^{++}[ClO_4^-]_2$.

We use the combination band $\nu_1 + \nu_4$ of free NO_3 [34], which appears in the 1800–1700 cm^{-1} region, for structural diagnosis: in the spectrum of **13**, upon coordination, this absorption splits in two bands and the separation is of the same order of magnitude as that found in unidentate NO_3^- derivatives [35–37]. For this reason, we suggest for this compound the structure shown in Fig. 2c.

The NO_3^- group in **3** was found to be ionic. The strong absorptions at 1366 and at 1348 cm^{-1} are similar to those indicated for ionic nitrato compounds [38].

In derivative **15**, the NCS^- group could be coordinated to tin through the nitrogen or the sulfur: we propose that complex **15** is N-bonded, because it exhibits a single sharp δ(NCS) near 480 cm^{-1} and the ν(NCS) below 2050 cm^{-1}. These absorptions are comparable with those found in other isothiocyanate complexes [39–42].

3.3. Mössbauer results

The experimental Mössbauer parameters, isomer shift IS (mm s^{-1}), nuclear quadrupole splitting QS (mm s^{-1}) and full width at half-height $\Gamma\pm$ (mm s^{-1}) are listed in Table 5.

The IS value is typical of quadrivalent tin in organometallic derivatives [43]; the examined compounds are all potentially octahedral, except for derivative **1** to which a trigonal bipyramidal arrangement can be assigned. In the exa-coordinated series, the IS value increases with the covalent character of the tin-ligand bonds; however, it is lower for Me_2SnCl_2 adduct **9** than Et_2SnCl_2 derivative **16**, in keeping with the larger hyperconjugation of the methyl group bound to the tin atom. The IS values of $[(L^{\#})_2BuSnCl_3]$ **25** compares well with literature values of monoalkyltin(IV) halides [43]. The QS value of derivatives **9**, **16**–**18**, and **25** is indicative of an octahedral configuration of the tin atom; in Alk_2SnX_2 adducts a *trans* alkyl arrangement is inferred [44]. Using the Parish relationship between the QS and C–Sn–C bond angle, θ, their values, lying in the range 160–175°, were calculated [44].

Derivatives **10** and **19** show a greatly asymmetric doublet (Fig. 4). The deconvolution of the spectrum points out the presence of two Mössbauer components, the one (split line) attributed to the octahedral *trans*-R_2

Table 5
Selected Mössbauer data

Compound	Number	IS[a,b] (mm s^{-1})	QS[b] (mm s^{-1})	$\Gamma\pm$ [b] (mm s^{-1})	C–Sn–C[c] (deg)
$[(L^{\#})(CH_3)_3SnCl]$	(**1**)	1.27	3.46	0.89	
$[(L^{\#})_2(CH_3)_2SnCl_2]$	(**9**)	1.21	3.92	0.94	164
$[(L^{\#})_2(CH_3)_2SnBr_2]$	(**10**)	1.42	3.94	0.96	165
$[(L^{\#})_2(CH_3)_2SnBr_2]$ (singlet)		0.03		0.93	
$[(L^{\#})_2(C_2H_5)_2SnCl_2]$	(**16**)	1.39	4.03	0.97	175
$[(L^{\#})_2(C_2H_5)_2SnBr_2]$	(**17**)	1.48	3.86	1.00	160
$[(L^{\#})_2(C_2H_5)_2SnI_2]$	(**18**)	1.61	3.92	0.99	164
$[(L^{\#})_2(C_4H_9)_2SnCl_2]\cdot H_2O$	(**19**)	1.46	3.36	0.96	0.96
$[(L^{\#})_2(C_4H_9)_2SnCl_2]\cdot H_2O$ (singlet)		0.04		0.92	
$[(L^{\#})_2(C_4H_9)SnCl_3]$	(**25**)	0.84	1.85	1.01	

[a] With respect to an R.T. spectrum of $CaSnO_3$.
[b] $\pm$ 0.01 mm s^{-1}.
[c] Calculated by using the literature partial quadrupole splittings: [Alk] = $-$1.01 mm s^{-1}.

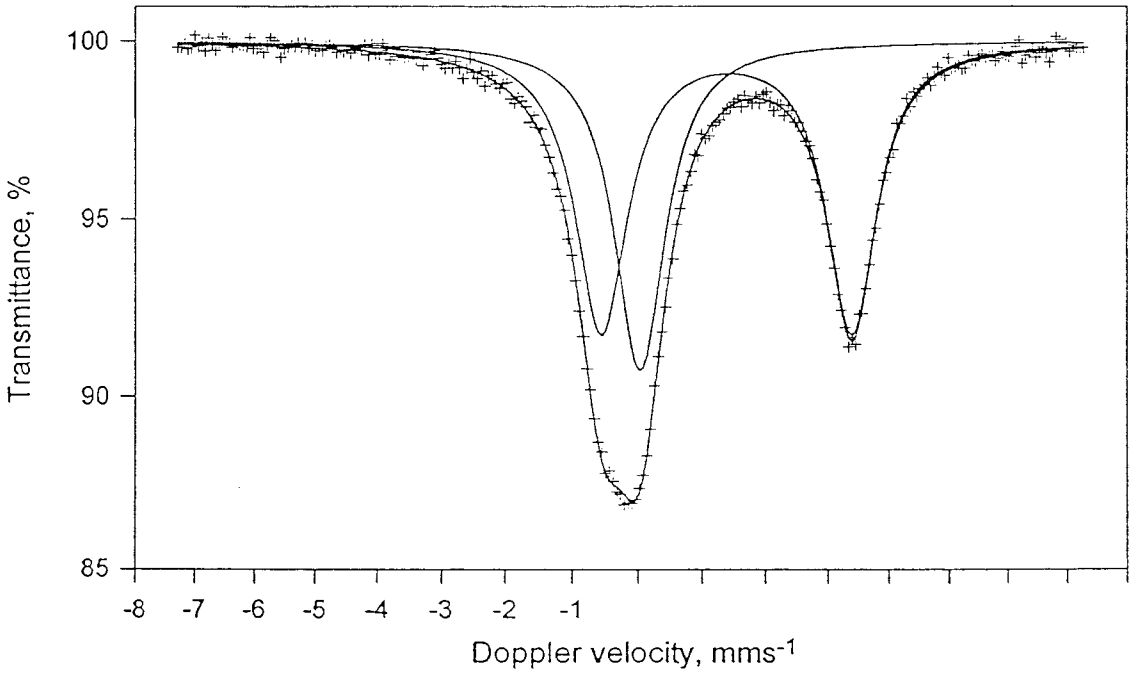


Fig. 4. Mössbauer spectrum of $[(L^{\#})_2(CH_3)_2SnBr_2]$ (**10**). Experimental points shown by crosses, continuous lines show the fitted curve and the deconvoluted components.

tin atom, the other (unsplit line) to SnO_2, obtained probably because of the presence of moisture.

The QS value of adduct **1** is in consonance with a trigonal bipyramidal structure with axial chlorine and nitrogen atoms [45].

3.4. Behaviour in solution

The conductivity measurements (Table 6) were carried out in acetone solution for all the soluble compounds and in CH_2Cl_2 and DMSO only for selected derivatives, whereas the molecular weight determinations were performed in chloroform solution only on sufficiently soluble and stable adducts. The data show that triorganotin(IV) halide adducts **1**–**3** and **5**–**8**, and the mono- and di-organotin(IV) choride and bromide complexes are not electrolytes in acetone and CH_2Cl_2, even if they dissociate in $CHCl_3$ solution (r = ratio between the vaporimetric molecular weight and formula weight lying in the range 0.30–0.58), in accordance with the Eq. (3), which indicates ligand loss in solution.

$$(L^{\#})_xR_nSnX_{4-n} \leftrightharpoons [(L^{\#})_{x-1}R_nSnX_{4-n}] + L^{\#} \leftrightharpoons R_nSnX_{4-n} + xL^{\#} \quad (3)$$

Several trends emerged: for example we noted that dissociation (Eq. (3)) is dependent on the nature of the halide and organic substituent: r has the greatest value when X = Cl, and the smallest when X = I. The dissociation is complete in the triorganotin(IV) adducts, whereas it is only partial in the di- and mono-organotin(IV) derivatives. We also found that in this kind of compounds the dissociation is not very dependent on the concentration of the solution: for example r for compound **1** is 0.53 at concentration 0.84 mg g^{-1} and 0.58 at 2.35 mg g^{-1} of $CHCl_3$.

The diorganotin(IV)diiodide adducts **18**, **21**, and **23** exhibit a value of conductivity in acetone typical of a 1:1 electrolyte, whereas the dimethyltin(IV)diiodide **11** shows a value in the same solvent typical of a 2:1 electrolyte: this compound is also strongly dissociated in $CHCl_3$ solution. On the basis of this evidence, we hypothesized an ionic nature in solution of complex **11** in accordance with Eq. (4):

$$[(L^{\#})_2(CH_3)_2SnI_2] + n(\text{solvent}) \leftrightharpoons [(L^{\#})_2(CH_3)_2Sn \times (\text{solvent})_n]^{++} + 2[I]^{-} \quad (4)$$

Compounds **13** and **15** are partly ionized: similar behaviour has been previously observed for analogous organotin(IV) complexes containing imidazole-type donors [1,5].

3.5. NMR data

The ^1H NMR spectra of the donor $L^{\#}$ and of the organotin(IV) complexes **1**–**29** were recorded in $CDCl_3$, and for some derivatives in acetone due to poor solubility in the former solvent.

The spectra of the triorganotin(IV) complexes **1**–**7** indicate a nearly complete dissociation into the starting

Table 6
Selected conductivity and molecular weight measurements of organotin(IV) derivatives of $L^{\#}$

Compound		Conductivity[a]			Molecular weight[b]			
		Solvent	Concentration	Λ	Formula weight	Molecular weight	r	Concentration
$[(L^{\#})(CH_3)_3SnCl]$	(**1**)	Acetone	0.79	4.5	281.3	148	0.53	0.84
		CH_2Cl_2	0.53	0.8		164	0.58	2.35
		DMSO	1.28	4.4				
$[(L^{\#})_2(CH_3)_3Sn]I$	(**2**)	Acetone	0.57	30.0				
		CH_2Cl_2	0.48	4.0				
		DMSO	0.28	30.2				
$[(L^{\#})_2(CH_3)_3Sn](NO_3)$	(**3**)	Acetone	0.73	19.9				
		CH_2Cl_2	1.02	3.9				
		DMSO	0.96	32.8				
$[(L^{\#})_2(CH_3)_3Sn](ClO_4) \cdot 1/2H_2O$	(**4**)	Acetone	0.82	145.7				
		CH_2Cl_2	0.79	43.4				
$[(L^{\#})(C_4H_9)_3SnCl] \cdot H_2O$	(**5**)	Acetone	1.10	1.2				
$[(L^{\#})(C_4H_9)_3SnBr] \cdot H_2O$	(**6**)	Acetone	0.52	8.4				
$[(L^{\#})_2(C_4H_9)_3Sn]I \cdot H_2O$	(**7**)	Acetone	0.35	10.3				
$[(L^{\#})(C_6H_5)_3SnCl]$	(**8**)	Acetone	1.02	3.3				
$[(L^{\#})_2(CH_3)_2SnCl_2]$	(**9**)	Acetone	0.73	18.9	383.9	169	0.44	0.78
		CH_2Cl_2	0.95	1.0		178	0.46	1.93
						208	0.54	4.10
$[(L^{\#})_2(CH_3)_2SnBr_2]$	(**10**)	Acetone	0.69	34.0	472.8	166	0.35	0.77
		CH_2Cl_2	0.51	1.4		206	0.44	1.79
						215	0.45	2.49
$[(L^{\#})_2(CH_3)_2SnI_2]$	(**11**)	Acetone	0.36	186.9	566.8	182	0.32	0.49
		CH_2Cl_2	0.07	10.6		175	0.31	0.92
						216	0.38	1.98
$[(L^{\#})_2(CH_3)_2Sn(ClO_4)_2]$	(**12**)	Acetone	0.82	197.6				
		CH_2Cl_2	0.90	10.0				
		DMSO	0.52	37.7				
$[(L^{\#})(CH_3)_2Sn(NO_3)_2(H_2O)]$	(**13**)	Acetone	0.15	93.9				
$[(L^{\#})(CH_3)_2SnCl(H_2O)_2](BPh_4)$	(**14**)	Acetone	0.97	65.0				
		CH_2Cl_2	Insoluble					
$[(L^{\#})_2(CH_3)_2Sn(NCS)_2]$	(**15**)	Acetone	1.09	60.0				
		CH_2Cl_2	0.99	1.7				
$[(L^{\#})_2(C_2H_5)_2SnCl_2]$	(**16**)	Acetone	0.75	13.9				
$[(L^{\#})_2(C_2H_5)_2SnBr_2]$	(**17**)	Acetone	0.80	26.7				
$[(L^{\#})_2(C_2H_5)_2SnI_2]$	(**18**)	Acetone	1.48	97.1				
$[(L^{\#})_2(C_4H_9)_2SnCl_2] \cdot H_2O$	(**19**)	Acetone	0.47	16.7	486.0	151	0.31	0.60
						146	0.30	1.00
						182	0.37	2.11
$[(L^{\#})_2(C_4H_9)_2SnBr_2] \cdot 1/2H_2O$	(**20**)	Acetone	0.78	29.2				
$[(L^{\#})_2(C_4H_9)_2SnI_2]$	(**21**)	Acetone	0.58	134.1				
$[(L^{\#})_2(C_6H_5)_2SnCl_2]$	(**22**)	Acetone	0.98	25.0				
		CH_2Cl_2	1.00	0.4				
$[(L^{\#})_2(C_6H_5)_2SnI_2]$	(**23**)	Acetone	0.98	134.1				
		CH_2Cl_2	1.00	4.3				
$[(L^{\#})_2CH_3SnCl_3]$	(**24**)	Acetone	0.85	27.3	404.3	175	0.43	0.40
		CH_2Cl_2	0.78	0.9		168	0.42	0.45
		DMSO	0.51	27.9				
$[(L^{\#})_2(C_4H_9)SnCl_3]$	(**25**)	Acetone	0.89	18.4				
$[(L^{\#})_2(C_6H_5)SnCl_3]$	(**26**)	Acetone	1.01	18.3				
$[(Phen)(CH_3)_2SnBr_2]$	(**27**)	Acetone	0.78	3.4				
		CH_2Cl_2	0.99	0.3				
$[(Phen)_3\{(C_2H_5)_2SnI_2\}_2]$	(**28**)	Acetone	0.71	23.6				
		CH_2Cl_2	0.91	25.8				
$[(L^{\#})(Phen)(CH_3)_2Sn](ClO_4)_2$	(**29**)	Acetone	1.01	171.0				
		CH_2Cl_2	1.01	12.9				

[a] In Ω^{-1} cm^2 mol^{-1} at room temperature; concentration is molar concentration ($\times 10^3$).
[b] Temperature = 40°C, in $CHCl_3$; r = molecular weight/formula weight; concentration is mg of compound/g of $CHCl_3$.

reagents. In fact, the Δ value (difference in chemical shift for the same type of proton in the free base and in its organotin(IV) complexes) is in the range 0.01–0.54 ppm and the tin-proton coupling constants are of the same order of magnitude as those reported for the starting triorganotin(IV) acceptors [46]. However, the Δ observed in these derivatives, which is evidence of the existence of the complexes in solution, is bigger with respect to those observed in other derivatives containing imidazole-type donors and triorganotin(IV) acceptors [1,5].

Instead, in the spectrum of the triphenyltin(IV) complex **8**, the signals of the ligand are displaced upfield and the Δ value is in the range -0.37–-0.09 ppm. This peculiarity can be explained by considering the shielding effect exerted on H2, H4 and H5 protons by aromatic protons of the phenyl rings linked to tin(IV); the tin-proton coupling constants are greater than that reported for the starting triorganotin(IV) acceptor, in accordance with a partial dissociation of the complex in $CDCl_3$ solution. Compound **8** shows the ^{119}Sn NMR absorption at -178.6 ppm; this value is upfield shifted with respect to that observed for Ph_3SnCl in the same solvent [47].

In the ^{13}C NMR spectra of triorganotin(IV) compounds **1** and **8** the $^nJ(^{119}Sn-^{13}C)$ ($n = 1$, 2, 3 or 4) are of the same order of magnitude of those observed in pentacoordinate organotin(IV) compounds and greater than those in the starting organotin(IV) derivatives [47].

In the spectra of the diorganotin(IV) complexes **9**–**23**, the signals of the ligand $L^{\#}$ are generally displaced to lower field. The deshielding observed is attenuated at a position remote from the metal (methyl protons). The Δ observed is likely due to a σ-charge donation from the N-donor to tin(IV) acceptor and is evidence of the existence of the complexes in solution. However, the magnitude of the tin(IV)-proton coupling constants for all these diorganotin(IV) complexes, even if it is different from that reported in literature for the starting tetracoordinate diorganotin(IV) halides [48], is smaller with respect to that indicated for hexacoordinate undissociated organotin(IV) complexes containing N-donor ligands [49,50]: this suggests a partial dissociation of our complexes in chlorinate solution in accordance with the data derived from molecular weight measurements (Table 6). The ^{119}Sn NMR spectrum of **9** confirms the partial dissociation observed: the $\delta(^{119}Sn)$ is upfield shifted with respect to that found in other completely

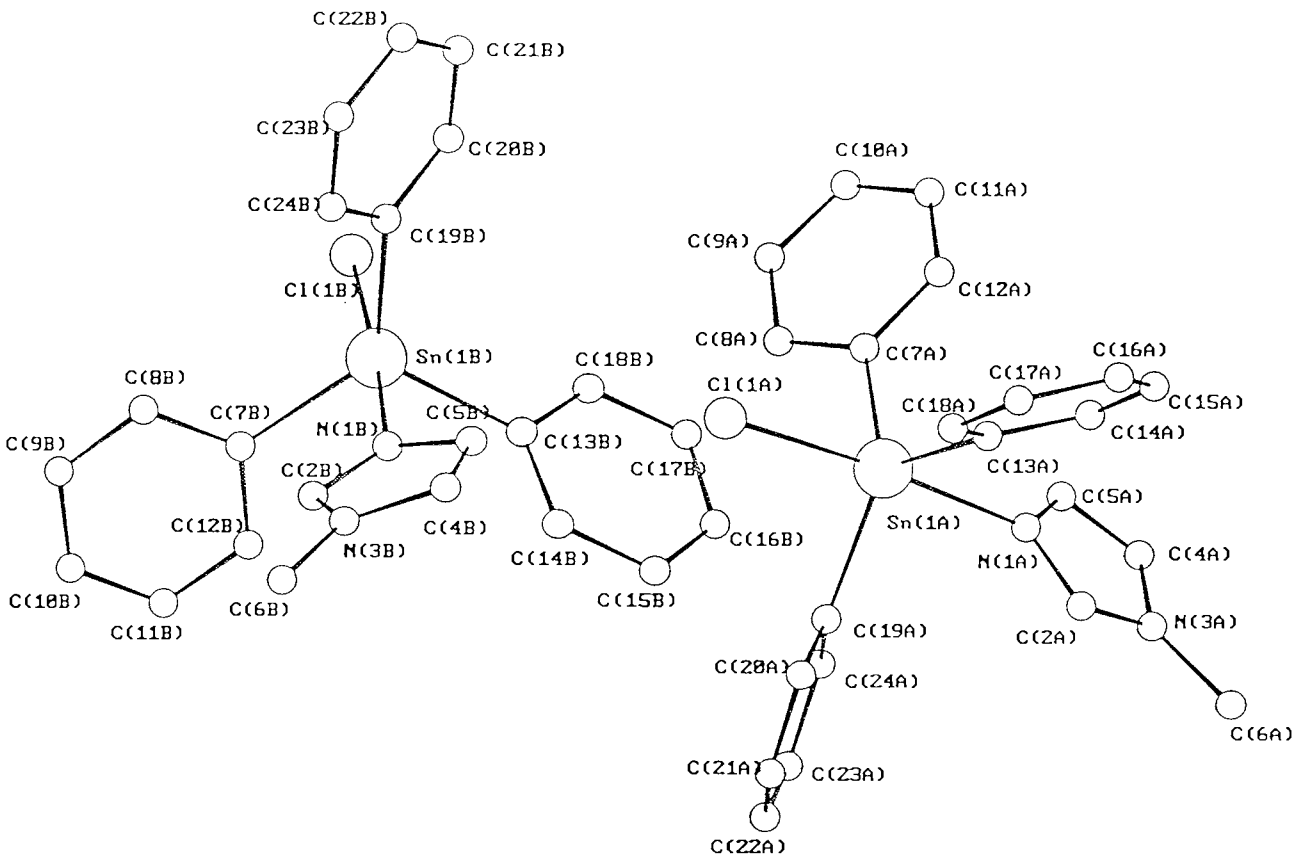


Fig. 5. The molecular structure of $[(L^{\#})Ph_3SnCl]$ (**8**) with atom numbering, as used in the crystallographic work.

dissociated azole complexes (C. Pettinari and M. Pellei, unpublished results).

In the ^{1}H NMR spectrum of **14**, the deshielding observed in the resonance due to H2, H4, and H5 protons of the ligands is the smallest of the diorganotin(IV) derivatives investigated; besides the signal of the CH_3 of the imidazole moiety is observed upfield shifted with respect to the same resonance in the free donor ($\Delta = +0.12$). This trend could be explained by considering the shielding effect exerted on CH_3, H2, and H4 or H5 by the aromatic protons of BPh_4^- counterion.

The diiodide 3:2 complex **28** shows a value of $\delta(^{119}Sn)$ typical of pentacoordinate tin(IV) derivatives, in accordance with a ionic dissociation in solution hypothesized also on the basis of conductivity data. On the other hand in the solid state, if the phenanthroline were coordinated in the bidentate fashion, the tin(IV) atom should be hepta- or even octa-coordinate; however, in view of the rarity of these coordination numbers for $R_2Sn(IV)$ adducts and on the basis of literature data [16–18] we suggest for compound **28** a hexacoordinate dinuclear configuration with bridging iodide groups and at least two monodentate Phen molecules.

3.6. Crystal structures

3.6.1. Diffraction study of [(L#)Ph$_3$SnCl] (8)

The molecular structure of [(L#)Ph_3SnCl] **8** is shown in Fig. 5, together with the numbering scheme. Selected bond distances and angles are reported in Table 7.

The crystallographic study of [(L#)Ph_3SnCl] clearly shows that two independent molecules (**A** and **B** hereafter) are present in the asymmetric units. The coordination geometry at Sn can be described as a distorted trigonal bipyramid with nitrogen and halogen in axial positions and three phenyl groups in equatorial positions. The distortion from the ideal trigonal bipyramidal geometry in both the molecules is evident from the magnitude of the Cl–Sn–N (175.5(1)° and 175.3(1)°) and Cl–Sn–C bond angles (which range from 91.5(2)° to 95.0(2)°). Moreover, an almost planar Sn–C_3 unit ($\sum$C–Sn–C 359.1° and 359.3° in **A** and **B**, respectively) is present in the structure, with the tin atom residing slightly below that plane on the side of the axial chlorine atom, onto the side opposite the attacking nitrogen atom. This geometry corresponds to an intermediate stage of the S_N2 reaction pathway of a nucleophilic attacked triorganotin(IV) halide, during its passage from

Table 7
Selected interatomic distance (Å) and bond angles (deg) with e.s.d. in parentheses, for [(1-methylimidazole) triphenyltin(IV)] chloride (**8**)

Molecule A		Molecule B	
Bond lengths			
Sn(1A)–Cl(1A)	2.520(2)	Sn(1B)–Cl(1B)	2.546(2)
Sn(1A)–N(1A)	2.412(4)	Sn(1B)–N(1B)	2.372(4)
Sn(1A)–C(7A)	2.134(6)	Sn(1B)–C(7B)	2.122(5)
Sn(1A)–C(13A)	2.134(6)	Sn(1B)–C(13B)	2.148(6)
Sn(1A)–C(19A)	2.126(6)	Sn(1B)–C(19B)	2.140(5)
N(1A)–C(2A)	1.304(7)	N(1B)–C(2B)	1.324(7)
N(1A)–C(5A)	1.359(7)	N(1B)–C(5B)	1.374(7)
N(3A)–C(2A)	1.328(7)	N(3B)–C(2B)	1.328(7)
N(3A)–C(4A)	1.360(8)	N(3B)–C(4B)	1.364(8)
N(3A)–C(6A)	1.455(8)	N(3B)–C(6B)	1.483(7)
C(4a)–C(5A)	1.329(8)	C(4B)–C(5B)	1.339(8)
Bond angles			
Cl(1A)–Sn(1A)–N(1A)	175.5(1)	Cl(1B)–Sn(1B)–N(1B)	175.3(1)
Cl(1A)–Sn(1A)–C(7A)	93.5(2)	Cl(1B)–Sn(1B)–C(7B)	92.1(1)
N(1A)–Sn(1A)–C(7A)	87.6(2)	N(1B)–Sn(1B)–C(7B)	86.3(2)
Cl(1A)–Sn(1A)–C(13A)	94.5(2)	Cl(1B)–Sn(1B)–C(13B)	95.0(2)
N(1A)–Sn(1A)–C(13A)	89.0(2)	N(1B)–Sn(1B)–C(13B)	89.7(2)
C(7A)–Sn(1A)–C(13A)	115.4(2)	C(7B)–Sn(1B)–C(13B)	114.4(2)
Cl(1A)–Sn(1A)–C(19A)	91.5(2)	Cl(1B)–Sn(1B)–C(19B)	91.6(1)
N(1A)–Sn(1A)–C(19A)	84.2(2)	N(1B)–Sn(1B)–C(19B)	85.8(2)
C(7A)–Sn(1A)–C(19A)	123.7(2)	C(7B)–Sn(1B)–C(19B)	125.6(2)
C(13A)–Sn(1A)–C(19A)	120.0(2)	C(13B)–Sn(1B)–C(19B)	119.3(2)
Sn(1A)–N(1A)–C(2A)	123.5(4)	Sn(1B)–N(1B)–C(2B)	128.6(4)
Sn(1A)–N(1A)–C(5A)	131.0(4)	Sn(1B)–N(1B)–C(5B)	125.7(4)
C(2A)–N(1A)–C(5A)	105.4(5)	C(2B)–N(1B)–C(5B)	105.0(4)
C(2A)–N(3A)–C(4A)	105.4(5)	C(2B)–N(3B)–C(4B)	107.8(5)
C(2A)–N(3A)–C(6A)	128.5(6)	C(2B)–N(3B)–C(6B)	125.0(6)
C(4A)–N(3A)–C(6A)	126.1(6)	C(4B)–N(3B)–C(6B)	127.1(5)
N(1A)–C(2A)–N(3A)	112.4(5)	N(1B)–C(2B)–N(3B)	111.1(5)
N(3A)–C(4A)–C(5A)	107.7(5)	N(3B)–C(4B)–C(5B)	106.0(5)
N(1A)–C(5A)–C(4A)	109.1(6)	N(1B)–C(5B)–C(4B)	110.1(5)

a monocapped tetrahedron to an ideal trigonal bipyramid as deduced by Britton and Dunitz [51].

The Sn–N distances are 2.412(4) Å (**A**) and 2.372(4) Å (**B**). They are longer than the sum of the covalent radii of tin and nitrogen (2.15 Å) and significantly shorter than the sum of their van der Waals radii (3.75 Å) thus indicating a substantial bonding interaction [52]. The Sn–N bond distances found here are longer with respect to those observed in diorganotin(IV)bis(imidazole) complexes [53–55] in accordance with stronger Lewis acidity of R_2SnX_2 with respect to R_3SnX acceptors. However, the Sn–N distances in **8** are longer also with respect to those in [bis(4-phenylimidazole)trimethyltin(IV)]chloride [1], in which both the azoles occupy the apical positions. The Sn–Cl bond distances (2.520(2) Å in **A** and 2.546(2) Å in **B**) are as long as those found in another tbp chlorotriphenyltin(IV) complexes [56,57]. The values observed are at the top of the ranges observed for this kind of fragment (2.475–2.535 Å, twelve entries in the Cambridge Crystallographic Data Files) [58]. There is also a correlation along the Cl–Sn–N axis in **A** and **B**: as the Sn–N distance becomes shorter, the Sn–Cl one tends to become longer, in accordance with the Dunitz curve [51] for SnC_3XY ensembles. The Sn–C bond distances (2.122(5)–2.148(6) Å) fall within the range expected for triphenyltin(IV) structures [56–58].

The two molecules **A** and **B** are significantly different: for example in **A** the Sn(1A)–N(1A)–C(2A) angle was greater than Sn(1A)–N(1A)–C(5A), whereas the opposite trend was observed in **B**; in addition in **B** the tin atom was displaced by 0.307(2) Å out of the imida-

Table 8
Comparison of selected bond distances and angles in R_3SnNX-type compounds

Compound[a]	Sn–N	Sn–X	Sn–C	X–Sn–N	Ref.
[(L#)Ph_3SnCl]	2.412(4)	2.520(2)	2.134(6), 2.134(6), 2.126(6)	175.5(1)	this work
	2.372(4)	2.546(2)	2.122(5), 2.148(6), 2.140(5)	175.3(1)	
[$(Ph_3SnCl)_2(\mu$-NC)$_2Fe(CN)_2(dmso)_2$]	2.340(7)	2.535(3)	2.140(4), 2.149(4), 2.144(6)	175.5(2)	[57]
C,N-{$Me_2NCH_2C_6H_4$}$SnPh_2Br$	2.511(12)	2.630(2)	2.115(10), 2.124(9), 2.150(12)	171.0(1)	[60]
2-(Me_2NCHBu^t)$C_6H_4SnMePhBr$	2.552(5)	2.6725(9)	2.143(5), 2.142(5), 2.137(6)	167.2(1)	[61]
	2.482(5)	2.6702(7)	2.139(5), 2.122(6), 2.128(6)	169.4(1)	
1-Aza-5-stanna-5-Cl–tricycloundecane	2.372(29)	2.613(7)	2.169(8)	180.0(0)	[62]
[8-(NMe_2)-1-naphthyl]SnMePhBr	2.496(6)	2.667(1)	2.131(6), 2.151(6), 2.144(9)	171.5(1)	[63]
{2-[1-(S)-(Me_2N)Et]Ph}SnMePhBr	2.476(7)	2.683(1)	2.158(9), 2.160(10), 2.127(8)	168.9(2)	[64]
$N(CH_2CH_2CH_2)_3SnFd \cdot H_2O$	2.426(6)	2.121(5)	2.146(7), 2.132(9), 2.145(9)	172.7(2)	[65]
	2.393(5)	2.115(6)	2.145(8), 2.135(8), 2.126(7)	174.0(2)	
$N(CH_2CH_2CH_2)_3SnCl$ (hex)	2.37(2)	2.52(1)	2.14(1)	180.0(0)	[65]
$N(CH_2CH_2CH_2)_3SnCl$ (mon)	2.384(4)	2.554(1)	2.157(5)	179.7(1)	[65]
$N(CH_2CH_2CH_2)_3SnBr$	2.28(2)	2.693(2)	2.20(1)	180	[65]
$N(CH_2CH_2CH_2)_3SnI$	2.375(6)	2.896(1)	2.152(8)	179.6(1)	[65]
[$Me_2ClSn(CH_2)Sn(NC_5H_5)ClMe_2$]	2.439(9)	2.638(2)	2.089(12), 2.099(8), 2.148(11)	175.4(2)	[66]
[$Me_2Cl(N_2C_3H_3)Sn(CH_2)Sn(N_2C_3H_3)ClMe_2$]	2.459(15)	2.578(4)	2.114(14), 2.154(16), 2.162(20)	174.6(4)	[66]
	2.453(14)	2.603(5)	2.142(14), 2.106(18), 2.132(17)	174.6(4)	
[$Me_2ClSn(CH_2)(N_2C_4H_4)SnClMe_2$]	2.651(6)	2.473(2)	2.115(7), 2.128(8), 2.30(8)	177.6(2)	[66]
	2.715(6)	2.456(2)	2.129(7), 2.129(8), 2.125(8)	177.7(1)	
[$Me_2ClSn(CH_2)SnClMe_2]_2(N_2C_4H_4)$	2.622(14)	2.524(6)	2.120(15), 2.128(18), 2.184(20)	176.2(5)	[66]
[$Ph_3SnCl(\mu$-CN)Ag(CN)]$^-$	2.436(5)	2.518(2)	2.155(5), 2.138(4), 2.151(6)	175.5(1)	[67]
[8-(Me_2N)-1-naphthyl]-(−)-menthyl-MeSnBr	2.55(1)	2.630(2)	2.19(1), 2.11(2), 2.13(1)	168.1(2)	[68]
	2.55(1)	2.641(2)	2.16(1), 2.13(1), 2.18(1)	168.1(3)	
[2-(4,4-Me_2-2-oxazoline)-5-MePh]MePhSnBr	2.414(5)	2.6788(8)	2.148(6), 2.128(7), 2.125(6)	171.3(1)	[69]
[Sn(2-C_6H_4N=NPh)Ph_2Cl]	2.560(4)	2.445(2)	2.130(4), 2.141(4), 2.129(4)	167.0(1)	[70]
[2-(4,4-Me_2-2-oxazolinyl)-3-thienyl]Ph_2SnCl	2.580(8)	2.451(3)	2.12(1), 2.13(1), 2.13(3)	168.4(2)	[71]
	2.525(7)	2.469(3)	2.10(1), 2.12(1), 2.128(9)	169.9(2)	
[$BrPh_2SnCH_2$-1,2,4-triazole]$_2$	2.463(7)	2.693(1)	2.168(10), 2.131(11), 2.135(10)	170.5(2)	[72]
	2.474(7)	2.653(1)	2.182(10), 2.131(10), 2.138(10)	171.8(2)	
[IPh_2SnCH_2-1,2,4-triazole]$_2$	2.45(2)	2.856(3)	2.18(3), 2.10(2), 2.13(3)	174.1(5)	[72]
	2.36(2)	2.944(3)	2.19(3), 2.09(3), 2.15(3)	171.8(5)	
[{2-(Me_2N)Ph}(Me_3Si)Me-*C,N*]MePhSnBr	2.492(3)	2.663(1)	2.144(3), 2.134(5), 2.121(4)	171.3(1)	[73]
[8-(Me_2N)-1-naphthyl]$_2$-MeSnI	2.53(1)	2.950(2)	2.13(1), 2.16(1), 2.21(1)	171.5(2)	[74]
(C_5H_5N)Me_3SnCl		2.42(4)			[75]
[$C_{10}H_5$(OMe-5)(CH_2NMe_2-8)]MePhSnBr	2.401(4)	2.7391(7)	2.147(4), 2.134(6), 2.141(4)	174.32(8)	[76]
[(CN)Me_3SnCl)]	2.654(17)	2.73(2)	2.128(12), 2.128(14), 2.129(15)	177.3(4)	[77]

[a] When there are two independent molecules, two lines of data are found.

zole plane, whereas in **B** the tin was almost coplanar with the plane of the imidazole donor. The donor $L^{\#}$ also shows different conformations in adducts **A** and **B**. This is most evident when considering the dihedral angles C(7)–Sn(1)–N(1)–C(2) and C(7)–Sn(1)–N(1)–C(5) which have values of 178.7(5)° and −6.4(6)° for molecule **A** and −19.2(5)° and 172.4(5)° for molecule **B**. In molecule **A** C(2) adopts a *trans* conformation with respect to C(7), whereas the *cis* is preferred in molecule **B**. This different orientation of the ligand may explain the small but not negligible difference between the geometry of the two molecules. In particular, the angles Sn(1)–N(1)–C(2) and Sn(1)–N(1)–C(5) which change from 128.6(4) and 125.7(4)° in **B** to 123.5(4)° and 131.0(4)° in **A**, with a tilting of the plane around its normal position of more than 5°. The rotation of almost all of the imidazole passing from **A** to **B** seems to affect even the bond lengths. The N(1)–C(2) bond, which has a value of 1.304(7) Å in **A** becomes 1.324(7) Å in **B**, and the same is true for N(1)–C(5) (1.359(7) Å in **A** and 1.374(7) Å in **B**). It is also interesting to note that the shorter bond lengths around N(1A) are more similar to the non-perturbed (or weakly perturbed) 1-methylimidazole [59] (G.W. Rabe et al., not published, 1996), and that is consistent with the longer Sn(1A)–N(1A) bond length observed.

The other major difference between molecules **A** and **B** is in the N–CH_3 fragment. The N–C bond length is remarkably shorter in adduct **A** (1.455(8) Å) with respect to adduct **B** (1.483(7) Å; the bond angles for C(2)–N(3)–C(6) and C(4)–N(3)–C(6) are, respectively, 128.5(6)° and 126.1(6)° for **A**, whereas they are 125.0(6)° and 127.1(5)° for **B**. A probable explanation in this case is the different environment around C(6). In **A**, the methyl group seems to have more, and relatively stronger, repulsive interaction with the surrounding atoms than in **B**. In fact C(6A) (according to the model adopted for the hydrogens) has 5 interactions below 3.6 Å with atoms not belonging to the same imidazole group (3.348 Å with C(23A) and 3.580 Å with C(22A), for example), whereas in **B** there are no intermolecular contacts below 3.8 Å.

The phenyl rings seem to adopt substantially the same conformation in adducts **A** and **B**. In fact, for the same adduct, the dihedral angles between phenyl planes, do not differ by more than 20°, and in many cases not more than 5°.

In Table 8, selected bond distance and angles of $[(L^{\#})Ph_3SnCl]$ **8** are compared with the values reported for other R_3SnXN compounds [57,60–77]. Several general patterns emerge: all the complexes have a distorted trigonal bipyramidal configuration with the organic groups in the equatorial position and the more electronegative nitrogen and halide in the axial positions. The most interesting feature is that the minimum Sn–N distance, and hence the strong donor interaction, is found in the derivatives showing the maximum Sn–X distance. The relevant geometrical data match perfectly well with the curves deduced by Britton and Dunitz [51]; the axial arrangement of N and X can be seen as a 'snapshot' of the S_N2 pathway for substitution with inversion at tetrahedral Sn, where the N-lone pair acts as the incoming nucleophile and X as the leaving group.

3.6.2. Diffraction study of $[(L^{\#})_2Me_2SnBr_2]$ (10)

The molecular structure of $[(L^{\#})_2Me_2SnBr_2]$ **10** is shown in Fig. 6, together with the numbering scheme. The bond distances and angles are reported in Table 9.

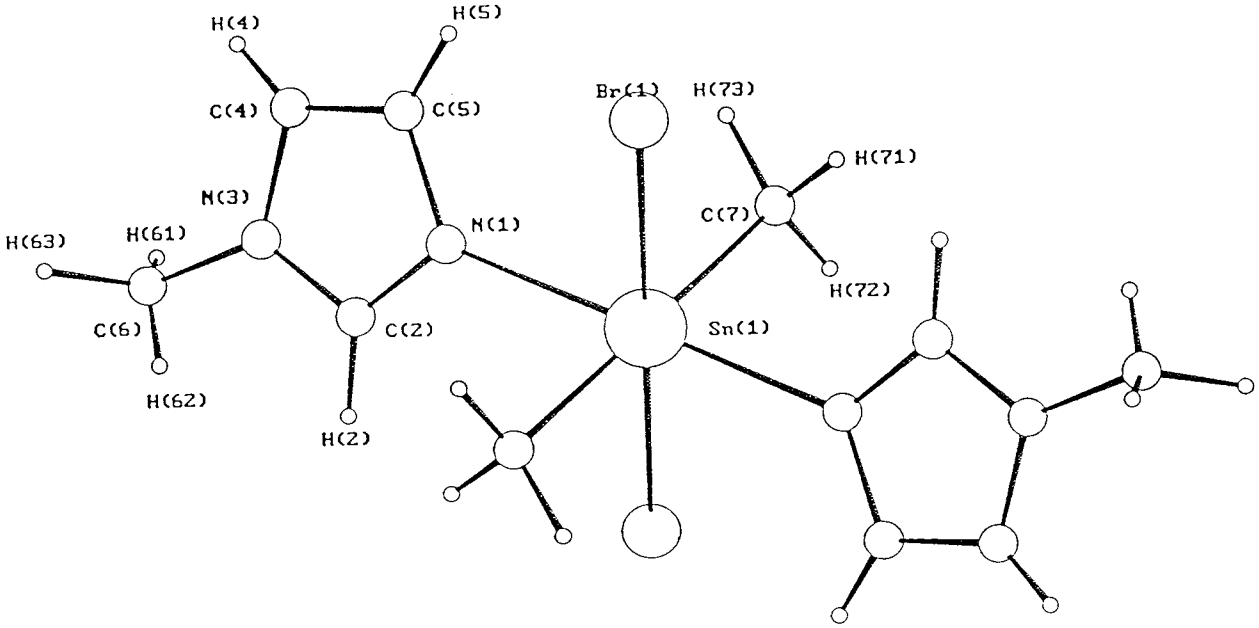


Fig. 6. The molecular structure of $[(L^{\#})_2(CH_3)_2SnBr_2]$ (**10**) with atom numbering, as used in the crystallographic work.

Table 9
Selected interatomic distance (Å) and bond angles (deg) with e.s.d. in parentheses, for [bis(1-methylimidazole)dimethyltin(IV) dibromide] (**10**)

Bond lengths	
Sn(1)–Br(1)	2.7384(3)
Sn(1)–N(1)	2.336(3)
Sn(1)–C(7)	2.125(3)
N(1)–C(2)	1.323(4)
N(1)–C(5)	1.370(5)
N(3)–C(2)	1.331(4)
N(3)–C(4)	1.358(5)
N(3)–C(6)	1.459(4)
C(4)–C(5)	1.347(5)
Bond angles	
Br(1)–Sn(1)–Br(1)	180.00
N(1)–Sn(1)–N(1)	180.00
C(7)–Sn(1)–C(7)	180.00
C(7)–Sn(1)–Br(1)	88.3(1)
C(7)–Sn(1)–N(1)	89.5(1)
Br(1)–Sn(1)–N(1)	88.99(7)
Sn(1)–N(1)–C(2)	125.2(2)
Sn(1)–N(1)–C(5)	129.1(2)
N(1)–C(2)–N(3)	111.0(3)
C(2)–N(3)–C(6)	126.0(3)
C(2)–N(3)–C(4)	107.5(3)
C(4)–N(3)–C(6)	126.5(3)
N(3)–C(4)–C(5)	106.7(3)
C(4)–C(5)–N(1)	109.2(3)
C(5)–N(1)–C(2)	105.6(3)

Table 10
Selected interatomic distance (Å) and bond angles (deg) with e.s.d. in parentheses, for [bis(1-methylimidazole)diethyltin(IV) diiodide] (**18**)

Bond lengths	
Sn(1)–I(1)	2.9904(4)
Sn(1)–N(1)	2.366(5)
Sn(1)–C(7)	2.148(9)
N(1)–C(2)	1.321(7)
N(1)–C(5)	1.377(8)
N(3)–C(2)	1.354(8)
N(3)–C(4)	1.358(8)
N(3)–C(6)	1.473(8)
C(4)–C(5)	1.345(9)
C(7)–C(8)	1.42(3)
C(7)–C(9)	1.27(3)
Bond angles	
I(1)–Sn(1)–I(1)	180.00
N(1)–Sn(1)–N(1)	180.00
C(7)–Sn(1)–C(7)	179.99
C(7)–Sn(1)–I(1)	88.3(3)
C(7)–Sn(1)–N(1)	89.2(3)
I(1)–Sn(1)–N(1)	88.3(1)
Sn(1)–N(1)–C(2)	127.0(4)
Sn(1)–N(1)–C(5)	127.4(4)
N(1)–C(2)–N(3)	110.5(5)
C(2)–N(3)–C(6)	125.2(6)
C(2)–N(3)–C(4)	107.5(5)
C(4)–N(3)–C(6)	127.2(6)
N(3)–C(4)–C(5)	106.6(6)
C(4)–C(5)–N(1)	109.8(6)
C(5)–N(1)–C(2)	105.6(5)
Sn(1)–C(7)–C(8)	124.8(12)
Sn(1)–C(7)–C(9)	126.6(14)

The tin atom exhibits a slightly distorted octahedral coordination geometry with two Br atoms, two methyl C atoms and the N atoms of two 1-methylimidazole ligands in all-*trans* configuration. The Sn–C, Sn–N, Sn–Br and ligand bond distances are identical in pairs. The bond angles around the six-coordinated tin do not deviate more than 1.7° from ideality and they are similar to those found in $[(L^{\#})_2Me_2SnCl_2]$[55]. The 1-

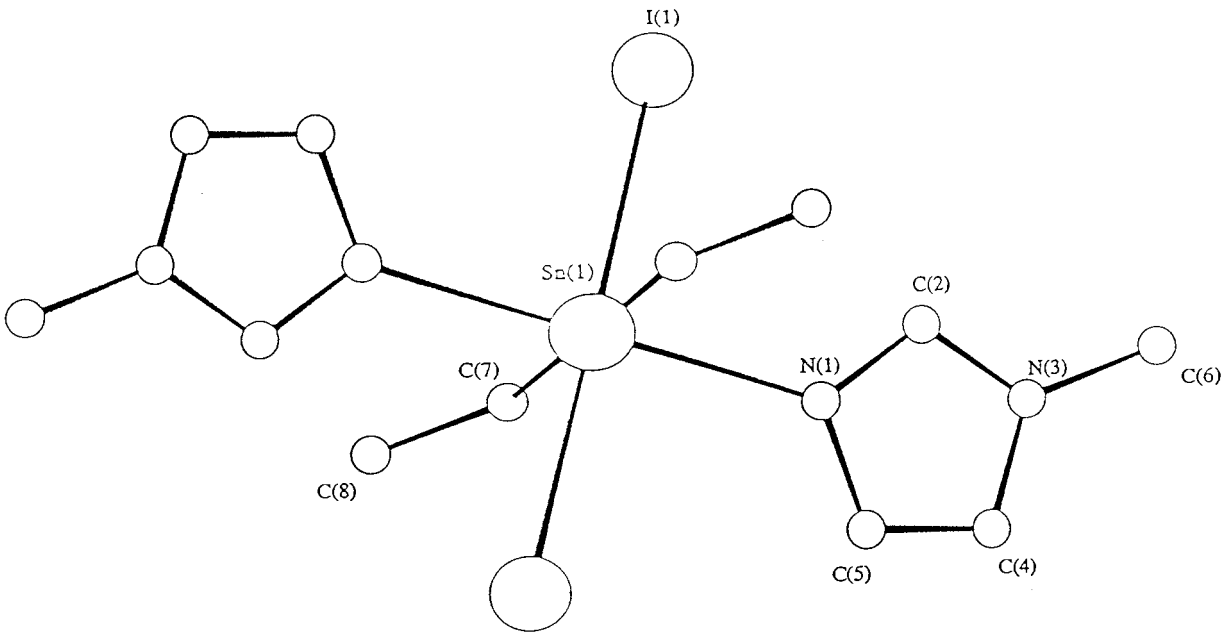


Fig. 7. The molecular structure of $[(L^{\#})_2(C_2H_5)_2SnI_2]$ (**18**) with atom numbering, as used in the crystallographic work.

Table 11
Values of the angles (°) and bond lengths (Å) concerning 1-methylimidazole derivatives[a]

Compound	N1–C2–N3	C2–N3–C4	N3–C4–C5	C4–C5–N1	C5–N1–C2	N1–C2	C2–N3	N3–C4	C4–C5	C5–N1	Ref.
$[(L^{\#})_2Me_2SnBr_2]$	111.0(3)	107.5(3)	106.7(3)	109.2(3)	105.6(3)	1.323(4)	1.331(4)	1.358(5)	1.347(5)	1.370(5)	this work
$[(L^{\#})_2Et_2SnI_2]$	110.5(5)	107.5(5)	106.6(6)	109.8(6)	105.6(5)	1.321(7)	1.354(8)	1.358(8)	1.345(9)	1.377(8)	this work
$[(L^{\#})Ph_3SnCl]$	112.4(5)	105.4(5)	107.7(5)	109.1(6)	105.4(5)	1.304(7)	1.328(7)	1.360(8)	1.329(8)	1.359(7)	this work
	111.1(5)	107.8(5)	106.0(5)	110.1(5)	105.0(5)	1.324(7)	1.328(7)	1.364(8)	1.339(8)	1.374(7)	
$[(L^{\#})_2Me_2SnCl_2]$	111.0(2)	107.2(2)	106.8(2)	109.1(2)	105.9(2)	1.322(3)	1.338(2)	1.362(3)	1.349(3)	1.371(2)	[55]
$L^{\#}$	112.2(3)	106.6(3)	106.2(3)	110.1(3)	104.9(3)	1.288(3)	1.338(3)	1.347(3)	1.335(3)	1.363(3)	[59]
trans-$[Fe(bpc)(L^{\#})_2]ClO_4$[b]	111.8(4)	106.8(4)	106.8(4)	109.7(4)	104.8(4)	1.323(6)	1.331(6)	1.364(6)	1.341(7)	1.373(5)	[81]
	111.5(4)	107.2(4)	106.9(4)	108.7(4)	105.7(4)	1.318(6)	1.338(6)	1.370(6)	1.350(7)	1.390(5)	
trans-$Cl_2(L^{\#})_2Cu$	110.6(4)	107.6(4)	106.6(4)	108.8(4)	106.4(4)	1.325(6)	1.351(7)	1.382(6)	1.356(8)	1.395(6)	[82]
	109.7(4)	108.4(5)	107.0(6)	107.9(5)	107.1(5)	1.333(6)	1.345(7)	1.371(7)	1.363(9)	1.392(8)	
cis-$(CO)_2Cl(L^{\#})Rh$	112.1(5)	107.5(5)	105.9(6)	111.1(6)	103.5(5)	1.327(7)	1.338(7)	1.357(8)	1.343(9)	1.381(9)	[83]
$(L^{\#})$-Porph-Zn[d]	–	–	–	–	–	1.307(6)	1.345(6)	1.372(7)	1.336(8)	1.377(6)	[84]
cis-$Cl_2(L^{\#})_2Pt$	110.5(7)	107.0(7)	106.7(7)	108.9(7)	107.0(6)	1.301(10)	1.345(10)	1.370(10)	1.338(11)	1.369(10)	[85]
$(L^{\#})$-Porph*-Co[e]	111.5(4)	106.5(4)	106.5(4)	110.0(4)	105.6(3)	1.316(6)	1.365(6)	1.371(6)	1.355(7)	1.377(5)	[86]
$(L^{\#})$-Porph*-Mn[e]	111.8(3)	107.1(2)	107.0(2)	109.7(3)	104.4(2)	1.295(4)	1.348(4)	1.326(4)	1.338(5)	1.378(4)	[87]
$(L^{\#})_6Fe(BPh_4)_2(CH_2Cl_2)$	–	–	–	–	–	1.270(23)	–	–		1.382(25)	[88]
	–	–	–	–	–	1.320(24)	–	–	–	1.426(24)	
	–	–	–	–	–	1.325(26)	–	–	–	1.325(24)	
	–	–	–	–	–	1.309(23)	–	–	–	1.367(26)	
	–	–	–	–	–	1.347(26)	–	–	–	1.397(23)	
	–	–	–	–	–	1.308(30)	–	–	–	1.407(28)	
$(L^{\#})_6Cd(NO_3)_2$	111.3(4)	107.8(4)	105.2(4)	110.5(4)	105.2(4)	1.312(5)	1.327(6)	1.347(7)	1.355(7)	1.343(6)	[89]
	111.1(4)	107.1(5)	106.6(6)	109.1(5)	106.1(4)	1.337(7)	1.329(7)	1.379(8)	1.359(9)	1.363(7)	
	110.5(4)	108.2(4)	105.6(5)	110.1(5)	105.6(5)	1.306(7)	1.345(7)	1.345(8)	1.346(8)	1.365(7)	
$(L^{\#})_4Cu\{ONC(CN)_2\}_2$	–	–	–	–	–	1.314(3)	–	–	–	1.375(2)	[90]
	–	–	–	–	–	1.314(2)	–	–	–	1.367(2)	
$[(L^{\#})Co(Q)]$[c]	112.0(9)	105.4(9)	108.2(9)	109.2(9)	105.3(8)	1.30(1)	1.35(2)	1.34(1)	–	1.36(1)	[91]
	110.0(1)	110.0(1)	104.0(1)	111.0(1)	104.4(9)	1.34(1)	1.31(2)	1.36(1)	–	1.38(1)	
$[(L^{\#})_6Ni]S_8$					103.8(5)	1.327(8)	1.324(9)	1.354(9)	1.362(9)	1.365(9)	[92]
					105.3(5)	1.324(8)	1.343(8)	1.363(9)	1.345(9)	1.364(8)	
					105.2(5)	1.329(8)	1.360(9)	1.363(9)	1.34(1)	1.383(8)	

Compound	N1–C2–N3	C2–N3–C4	N3–C4–C5	C4–C5–N1	C5–N1–C2	N1–C2	C2–N3	N3–C4	C4–C5	C5–N1	Ref.
$[(L^{\#})_4F_2Fe]BF_4$	110.8(4)	107.5(4)	106.9(4)	108.6(4)	106.2(3)	1.319(6)	1.348(6)	1.370(6)	1.351(7)	1.394(6)	[93]
	110.9(4)	107.1(4)	107.6(4)	107.8(4)	106.5(4)	1.316(6)	1.336(6)	1.360(7)	1.349(7)	1.383(6)	
$[(L^{\#})_4Co(NCS)_2]$	111.7(3)	106.7(2)	106.6(3)	109.4(3)	105.5(2)	1.318(4)	1.349(4)	1.370(4)	1.358(4)	1.378(4)	[94]
	111.1(3)	108.1(3)	106.1(3)	109.4(3)	105.3(3)	1.321(4)	1.333(4)	1.337(4)	1.366(4)	1.359(4)	
$[(L^{\#})_2Re(PPh_3)Cl_3]$	111.5(7)	107.8(7)	106.1(7)	108.9(7)	105.6(7)	1.328(10)	1.335(10)	1.377(13)	1.368(12)	1.391(10)	[95]
	110.6(7)	108.3(7)	105.7(7)	109.4(8)	106.0(7)	1.331(11)	1.336(10)	1.351(12)	1.375(13)	1.355(11)	
$[(L^{\#})_4ReO_2]^+$	109.9(7)	108.1(7)	105.8(7)	109.4(7)	106.8(7)	1.330(9)	1.344(12)	1.370(11)	1.366(13)	1.359(11)	[96]
	108.5(9)	108.3(13)	112.7(14)	104.4(10)	105.7(8)	1.329(12)	1.369(13)	1.381(21)	1.378(16)	1.367(12)	
	112.7(8)	107.3(9)	105.1(11)	111.2(11)	103.7(8)	1.289(11)	1.326(12)	1.313(16)	1.352(17)	1.333(14)	
	110.1(5)	108.4(5)	106.0(6)	109.4(0)	106.0(6)	1.329(8)	1.342(7)	1.345(9)	1.368(10)	1.357(9)	
$[(L^{\#})_4ReO(OCH_3)](PF_6)_2$	111.7(4)	106.9(4)	107.3(4)	109.4(4)	104.7(4)	1.319(5)	1.326(5)	1.359(6)	1.325(7)	1.381(5)	[97]
$[(L^{\#})_4ReO\{OP(O)(OCH_3)\}]^{2+}$	110.5(5)	107.3(5)	108.2(5)	107.7(5)	106.4(5)	1.333(7)	1.326(6)	1.364(7)	1.339(7)	1.385(6)	[97]
	110.2(5)	107.4(5)	107.3(5)	108.4(5)	106.7(4)	1.320(6)	1.330(6)	1.373(7)	1.331(7)	1.378(6)	
	109.9(6)	108.9(5)	106.9(6)	108.0(6)	106.3(5)	1.326(7)	1.324(7)	1.351(8)	1.349(8)	1.386(7)	
	109.6(5)	108.4(5)	107.3(5)	107.9(5)	106.9(4)	1.336(7)	1.326(6)	1.370(8)	1.343(8)	1.387(6)	
$[(L^{\#})_4ReO(OBF_3)](I_3)$	111.1(10)	106.9(10)	107.7(10)	107.3(11)	107.0(9)	1.300(12)	1.347(12)	1.33(2)	1.37(2)	1.364(12)	[97]
	111.1(10)	107.3(9)	107.2(11)	109.1(10)	105.3(9)	1.307(12)	1.324(12)	1.349(14)	1.322(13)	1.375(12)	
	109.0(9)	107.9(8)	107.1(10)	108.6(11)	107.4(8)	1.315(12)	1.338(11)	1.350(14)	1.331(14)	1.357(12)	
	109.9(9)	107.3(8)	108.5(9)	109.6(10)	104.6(8)	1.333(11)	1.333(11)	1.325(13)	1.301(12)	1.366(12)	
Minimum	108.5	105.4	104.0	104.4	103.5	1.270	1.31	1.313	1.301	1.325	
Maximum	112.7	110.0	112.7	111.2	107.4	1.347	1.369	1.382	1.378	1.426	
Average	110.9	107.5	106.8	109.1	105.6	1.32	1.34	1.36	1.35	1.38	
Number of entries	38	38	38	38	40	50	42	42	40	50	

[a] When there are two independent molecules or two or more different imidazoles, two or more lines of data are found.
[b] H_2bpc = 4,5-dichloro-1,2-bis(2-pyridinecarboxamido)benzene).
[c] H_2Q = *N*,*N*′-bis(5-mercapto-3-methyl-1-phenylpyrazol-4-ylmethylene)-*ortho*-phenylenediamine.
[d] Porph = 2,3,7,8,12,13,17,18-octaethylporphinato.
[e] Porph* = $\alpha,\beta,\delta,\lambda$-tetraphenyl-porphinato.

methylimidazole ligands are bonded to the metal through their pyridine-like nitrogen atom.

The Sn–N distance compares well with those of similar all-*trans* complexes, having an sp^2 nitrogen containing ligands, which span between 2.311 Å and 2.393 Å with a mean value of 2.359 Å (16 entries on CCDC data base) [78]. The Sn–N distance in our determination is slightly longer with respect to $Me_2SnCl_2(L^{\#})_2$, the same kind of behaviour being found for $Me_2SnX_2(pyrazole)_2$ (X = Cl, Br) [79,80]. The azole rings are planar, with no atom deviating from the least-squares plane through the five atoms by more than 0.004 Å. The N–CH_3 bond is also very close to the ring plane. On the other hand, the tin atom deviates by 0.1239(8) Å out of the imidazole plane. It is interesting to note that in our study the N–CH_3 bond is shorter than in $[(L^{\#})_2Me_2SnCl_2]$ [55] by 0.024 Å. The angle between the imidazole ring and the Sn–Br–N plane is 30.0°(1) greater than the values found for the chloro analogue (26°) and in the range of values found for 16 independent all-*trans* $SnR_2X_2N_2$ adducts (5–46°).

The bond distances and bond angles of $L^{\#}$ found in this complex are very similar to those observed in other 1-methylimidazole complexes [55,59,81–97]. The Sn–Br bond length is similar to that in other Me_2SnBr_2(N-donor)$_2$ [80,98,99] and longer than that observed in the Me_2SnBr_2(2,2′-azopyridine) [100], in which the N-donor is a chelating ligand. The Sn–N distance is similar to those in $[(L^{\#})_2Me_2SnCl_2]$[55], but slightly shorter than that in $[(L^{\#})Ph_3SnCl]$ **8**. The Sn(1)–N(1)–C(5) angle is greater than the Sn(1)–N(1)–C(2) one. These angles are of the same order of magnitude as those in $[(L^{\#})_2Me_2SnCl_2]$[55] and in molecule **A** of $[(L^{\#})Ph_3SnCl]$ **8**, whereas they have an opposite trend with respect to those observed in molecule **B**.

*3.6.3. Diffraction study of $[(L^{\#})_2Et_2SnI_2]$ (**18**)*

The molecular structure of $[(L^{\#})_2Et_2SnI_2]$ **18** is shown in Fig. 7, together with the numbering scheme. The bond distances and angles are reported in Table 10.

The tin atom is octahedrally coordinated to two I atoms, two ethyl groups and the N atoms of two 1-methylimidazole ligands in an all-*trans* configuration. The adduct shows a C_i internal symmetry, with the Sn on a crystallographic center of symmetry, bond angles and distances are then equal in pairs. The ethyl groups in this structure seem to have the CH_3 group disordered over two different sites with almost equal occupation (occupation 0.504 and 0.496). This occurrence is not new in compounds of this kind [101] and is probably due to a large thermal motion (the crystal seems to decay for a ≈20% during data collection) and to the peripheric position of the disordered carbon. It is therefore impossible to make any precise statement on the geometry of the ethyl group. The C–C distance is in fact alternatively too long or too short (1.61(4) Å and 1.27(3) Å) compared with the expected values for this kind of bond.

The 1-methylimidazole ligands are bonded to the metal through their pyridine-like nitrogen atom. The azole rings are planar, with no atom deviating from the least-squares plane through the five atoms by more than 0.001 Å. The N–CH_3 bond is also very close to the ring plane. Unlike $[(L^{\#})_2Me_2SnCl_2]$[55] and $[(L^{\#})_2Me_2SnBr_2]$ **10** (where the Sn atom deviates out of the imidazole plane by 0.1473(3) Å and 0.1239(8) Å, respectively) the tin atom in $[(L^{\#})_2Et_2SnI_2]$ is almost coplanar with the imidazole plane. The Sn–I bond distance (2.9904(4) Å) compares well with the value (2.950(2) Å) found in the bis[8-(dimethylamino)-1-naphthyl]methyltin(IV)iodide, for which a hexacoordinate octahedral configuration has been attributed by the authors [74], and also with the few other cases of *trans* diiodo six-coordinate tin (values of 3.016 Å, and 2.965 Å, and 3.009 Å are reported by Tursina et al. [102] and Jastrzebski et al. [103] respectively, for similar *trans* SnI_2Y_4 compounds). As already pointed out [104] for dichloro diorganotin adducts, considerable evidence exists for the Sn-halogen bond length differences between the *trans* and *cis* arrangements, the latter having shorter distances with typical values for SnI_2Y_4 in the 2.7–2.8 Å range [105–108]. The Sn–N bond (2.366 Å) is slightly longer than that found in $[(L^{\#})_2Me_2SnCl_2]$[55] and $[(L^{\#})_2Me_2SnBr_2]$ **10**, in agreement with the lower Lewis acidity of diiodo with respect to dichloro and dibromo diorganotin compounds, but shorter than both in the two molecules of $[(L^{\#})Ph_3SnCl]$ **8**, in agreement with the lower Lewis acidity of triorgano compared to diorganotin(IV) derivatives.

A significant difference between $[(L^{\#})_2Et_2SnI_2]$ **18** and the other structurally characterized diorganotin(IV) derivatives, containing 1-methylimidazole ligands, is in the relative magnitudes of the Sn(1)–N(1)–C(5) and Sn(1)–N(1)–C(2) angles which are similar only in **18** (127.0(4)° and 127.4(4)°, respectively). Bond distance and angles for 1-methylimidazole are substantially similar to the values found in $[(L^{\#})_2Me_2SnBr_2]$ except for the N–CH_3 bond distance, which is longer in **18** than in **10** and closer to the value reported for $[(L^{\#})_2Me_2SnCl_2]$. The angle between the imidazole ring and the Sn–I–N

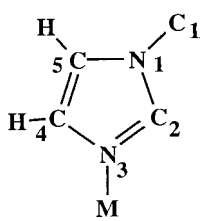


Fig. 8. Atom numbering scheme of the imidazole ring used throughout this paper.

plane is 23.5°, remarkably lower than in $[(L^{\#})_2Me_2SnBr_2]$ and more similar to $[(L^{\#})_2Me_2SnCl_2]$.

Examination of the imidazole moiety (Fig. 8) in the molecular structures of $[(L^{\#})_2Me_2SnCl_2]$, $[(L^{\#})_2Me_2SnBr_2]$, $[(L^{\#})_2Et_2SnI_2]$ and $[(L^{\#})Ph_3SnCl]$ allows some empirical rules to be made. Some of them are probably valid for all the 1-methylimidazole derivatives [55,59,91–94], some only for organotin(IV) complexes. Several general patterns emerge which had not been noted previously; this may be due to the fact that the first structural data reported for imidazole (those concerning non-coordinated imidazoles [109–113] and some of their zinc(II) derivatives [114,115]), and discussed in literature, were peculiar and that often structures were not published but only selected data; sometimes, no data, not even atomic coordinates are available.

In all the 1-methylimidazole derivatives listed in Table 11 it is found that:

1. N(1)–C(2)–N(3) is never the smallest internal angle; rather, it is often the widest.
2. C(4)–N(3)–C(2) is always the smallest internal angle.
3. C(5)–C(4)–N(3) is always larger than N(1)–C(5)–C(4) and C(2)–N(1)–C(5).
4. C(2)–N(1)–C(5) is not significantly different from N(1)–C(5)–C(4).
5. N(3)–C(2) is often the shortest bond length.
6. N(3)–C(4) is the longest bond length.
7. N(1)–C(5) is generally longer than C(2)–N(1) and C(4)–C(5).
8. C(4)–C(5) and C(2)–N(1) are not significantly different.

No pattern is evident for the external bond angle M–N(3)–C(2), M–N(3)–C(4), C(1)–N(1)–C(2) and C(1)–N(1)–C(5).

Although the eight generalizations seem to be supported by abundant evidence, we do not state that structural parameters which do not fit into the patterns defined above are impossible. They will probably be found for imidazole derivatives characterized by some singular or remarkable property. To date, we have observed only few exceptions which are or associated with either steric hindrance or strong metal–azole interactions [116–120].

4. Supplementary material available

Tables of atomic coordinates, isotropic equivalent thermal parameters, tables of structures factors, full list of bond lengths and angles, tables of isotropic displacement parameters, and dihedral angles between least-square planes are available from one of the authors.

Acknowledgements

We thank the MURST, CNR-Rome and the Universities of Camerino and Palermo for financial help.

References

[1] C. Pettinari, F. Marchetti, M. Pellei, A. Cingolani, L. Barba, A. Cassetta, J. Organomet. Chem. 515 (1996) 119.
[2] A.J. Crowe, P.J. Smith, Chem. Ind. (London) (1980) 200.
[3] A.J. Crowe, P.J. Smith, G. Atassi, Chem. Biol. Interact. 32 (1980) 171.
[4] A.G. Davies, P.J. Smith, Comprehensive Organometallic Chemistry, G. Wilkinson (Ed.), Pergamon, Oxford, 1982, pp. 519–627.
[5] C. Pettinari, F. Marchetti, A. Cingolani, S. Bartolini, Polyhedron 15 (1996) 1263.
[6] A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr. A24 (1968) 351.
[7] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Cryst. 26 (1993) 343.
[8] D.J. Watkin, J.R. Carruthers, P.W. Bettridge, CRYSTALS User Guide, Chemical Crystallography Laboratory, University of Oxford, Oxford.
[9] D.J. Watkin, Acta Crystallogr. A50 (1994) 411.
[10] E. Prince, P.T. Boggs, International Tables for Crystallography, A.J.C. Wilson (Ed.), Vol. C, Kluwer Academic Publishers, Dordrecht, 1992.
[11] J.R. Carruthers, D.J. Watkin, Acta Crystallogr. A35 (1979) 698.
[12] A.J.C. Wilson (Ed.), International Tables for Crystallography, Vol. C, Kluwer Academic Publishers, Dordrecht, 1992.
[13] M. Nardelli, Comput. Chem. 7 (1983) 95.
[14] G.M. Sheldrick, Acta Crystallogr. A46 (1990) 467.
[15] K.A. Kocheshkov, Chem. Ber. 62 (1926) 996.
[16] R.J. Watts, J.S. Harrington, J. Van Houten, J. Am. Chem. Soc. 99 (1977) 2179.
[17] G.W. Bushnell, K.R. Dixon, M.A. Khan, Can. J. Chem. 52 (1974) 1367.
[18] K.R. Dixon, Inorg. Chem. 16 (1977) 2618.
[19] N.W. Alcock, J.F. Sawyer, J. Chem. Soc. Dalton Trans. (1977) 1090.
[20] N. Ohkaku, K. Nakamoto, Inorg. Chem. 12 (1993) 2440.
[21] I.R. Beattie, G.P. McQuillan, J. Chem. Soc. (1963) 1519.
[22] G. Nieuwpoort, J.G. Vos, W.L. Groeneveld, Inorg. Chim. Acta 29 (1978) 117.
[23] R.C. Poller, The Chemistry of Organotin Compounds, Logos, London, 1970.
[24] W.P. Newman, The Organic Chemistry of Tin, Wiley, New York, 1970.
[25] B.W.K. Ho, J.J. Zuckerman, Inorg. Chem. 12 (1973) 1552.
[26] F. Huber, M. Vornefeld, G. Ruisi, R. Barbieri, Appl. Organomet. Chem. 7 (1993) 243.
[27] W.F. Edgell, C.H. Ward, J. Mol. Spectrosc. 8 (1962) 343.
[28] J.K. Sandhu, G. Kaur, J. Holecek, A. Licka, J. Organomet. Chem. 345 (1988) 51.
[29] R.J.H. Clark, A.G. Davies, R.J. Puddephatt, J. Chem. Soc. A (1968) 1828.
[30] A.L. Smith, Spectrochim. Acta 24A (1968) 695.
[31] J.R. Durig, R. Layton, D.W. Sink, B.R. Mitchell, Spectrochim. Acta 21 (1965) 1367.
[32] R.J. Inskeep, J. Inorg. Nucl. Chem. 24 (1962) 763.
[33] L.E. Moore, R.B. Gayhart, W.E. Bull, J. Inorg. Nucl. Chem. 26 (1964) 896.

[34] A.B.P. Lever, E. Mantovani, B.S. Ramaswamy, Can. J. Chem. 49 (1971) 1957.
[35] F.A. Cotton, D.M.L. Goodgame, J. Chem. Soc. (1960) 5267.
[36] R.J. Restivo, A. Costin, G. Ferguson, A.J. Carty, Can. J. Chem. 53 (1975) 1949.
[37] W.A. Anderson, A.J. Carty, G.J. Palenik, G. Schreiber, Can. J. Chem. 49 (1971) 761.
[38] I. Nakagawa, J.L. Walter, J. Chem. Phys. 51 (1969) 1389.
[39] P.C.H. Mitchell, R.J.P. Williams, J. Chem. Soc. (1960) 1912.
[40] A. Turco, C. Pecile, Nature 191 (1961) 66.
[41] J. Lewis, R.S. Nyholm, P.W. Smith, J. Chem. Soc. (1961) 4590.
[42] A. Sabatini, I. Bertini, Inorg. Chem. 4 (1965) 959.
[43] P.A. Flinn, in: K.G. Shenoy, F.E. Wagner (Eds.), Mössbauer Isomer Shift, Chap. 9a, North-Holland, Amsterdam, 1978, p. 593.
[44] R.V. Parish, in: G.J. Long (Ed.), Mössbauer Spectroscopy Applied to Inorganic Chemistry, Vol. 1, Plenum, New York, 1984, pp. 528 and 544.
[45] G.M. Bancroft, R.M. Platt, Adv. Inorg. Chem. Radiochem. 15 (1972) 59.
[46] B. Wrackmeyer, Ann. Rep. NMR Spectrosc. 16 (1985) 73.
[47] R.K. Harris, A. Sebald, D. Furlani, G. Tagliarini, Organometallics 7 (1988) 388.
[48] P.G. Harrison, Investigating tin using spectroscopy, in: P.G. Harrison (Ed.), Chemistry of Tin, Chap. 3, Chapman & Hall, London, 1989, pp. 61–115.
[49] W.D. Honnick, M.C. Hughes, C.D. Schaeffer Jr., J.J. Zuckerman, Inorg. Chem. 15 (1976) 1391, and references cited therein.
[50] T.P. Lockart, W.F. Manders, Inorg. Chem. 25 (1986) 892.
[51] D. Britton, J.D. Dunitz, J. Am. Chem. Soc. 103 (1981) 2971.
[52] J.E. Huheey, Inorganic Chemistry Principles of Structure and Reactivity, 2nd edn, Chap. 6, Harper & Row, New York, 1978.
[53] E. Garcìa Martìnes, A. Sànchez Gonzàles, A. Macìas, M.V. Castano, J.S. Casas, J. Sordo, J. Organomet. Chem. 385 (1990) 329.
[54] U. Casellato, R. Graziani, A. Sànchez Gonzàles, Acta Crystallogr. C48 (1992) 2125.
[55] R. Bardi, A. Piazzesi, R. Ettorre, G. Plazzogna, J. Organomet. Chem. 270 (1984) 171.
[56] C. Pelizzi, G. Pelizzi, J. Chem. Soc., Dalton Trans. (1983) 847.
[57] C. Carini, C. Pelizzi, G. Pelizzi, G. Predieri, P. Tarasconi, F. Vitali, J. Chem. Soc., Chem. Commun. (1990) 613.
[58] P.G. Harrison, K. Molloy, R.C. Phillips, P.J. Smith, A.J. Crowe, J. Organomet. Chem. 160 (1978) 421.
[59] A. Wang, B.M. Craven, J. Pharm. Sci. 68 (1979) 361.
[60] G. van Koten, J.G. Noltes, A.L. Spek, J. Organomet. Chem. 118 (1976) 183.
[61] J.T.B.H. Jastrzebski, J. Boersma, G. van Koten, J. Organomet. Chem. 413 (1991) 43.
[62] K. Jurkschat, A. Tzschach, J. Meunier-Piret, M. van Meerssche, J. Organomet. Chem. 290 (1985) 285.
[63] J.T.B.H. Jastrzebski, J. Boersma, P.M. Esch, G. van Koten, Organometallics 10 (1991) 930.
[64] G. van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, W.M.G.F. Pontenagel, J. Kroon, A.L. Spek, J. Am. Chem. Soc. (1978) 5021.
[65] U. Kolb, M. Dräger, M. Dargatz, K. Jurkschat, Organometallics 14 (1995) 2827.
[66] M. Austin, K. Gebreyes, H.G. Kuivila, K. Swami, J.A. Zubieta, Organometallics 6 (1987) 834.
[67] M. Carcelli, C. Ferrari, C. Pelizzi, G. Pelizzi, G. Predieri, C. Solinas, J. Chem. Soc., Dalton Trans. (1992) 2127.
[68] H. Schumann, B.C. Wassermann, G. Pickardt, Organometallics 12 (1993) 3051.
[69] J.T.B.H. Jastrzebski, E. Wehman, J. Boersma, G. van Koten, K. Goubitz, D. Heijdenrijk, J. Organomet. Chem. 409 (1991) 157.
[70] J. Vicente, M.T. Chicote, M.C. Ramirez-de-Arellano, P.G. Jones, J. Organomet. Chem. 394 (1990) 77.
[71] K.M. Lo, S. Selvaratnan, S.W. Ng, C. Wei, V.G. Kumar Das, J. Organomet. Chem. 430 (1992) 149.
[72] P.J. Cox, S.M.S.V. Doidge-Harrison, R.A. Howie, J.L. Wardell, J. Chem. Research (S) (1994) 163.
[73] J.T.B.H. Jastrzebski, G. van Koten, C.T. Knaap, A.M.M. Schreurs, J. Kroon, A.L. Spek, Organometallics 5 (1986) 1551.
[74] J.T.B.H. Jastrzebski, P.A. van der Schaaf, J. Boersma, G. van Koten, D.J.A. de Ridder, D. Heijdenrijk, Organometallics 11 (1992) 1521.
[75] R. Hulme, J. Chem. Soc. (1963) 1524.
[76] G. van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, G.J. Verhoeckx, A.L. Spek, J. Kroon, J. Chem. Soc., Dalton Trans. (1980) 1352.
[77] S.E. Johnson, C.B. Knobler, Organometallics 11 (1992) 3684.
[78] F. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans. 2 (1987) S1.
[79] G. Valle, R. Ettorre, V. Peruzzo, G. Plazzogna, J. Organomet. Chem. 326 (1987) 169.
[80] B. Alberte, A. Sànchez Gonzàles, E. Garcìa, J.S. Casas, J. Sordo, J. Organomet. Chem. 338 (1988) 187.
[81] C.M. Che, W.H. Leung, C.K. Li, H.Y. Cheng, S.M. Peng, Inorg. Chim. Acta 196 (1992) 43.
[82] J.A.C. van Ooijen, J. Reedijk, A.L. Spek, J. Chem. Soc., Dalton Trans. (1979) 1183.
[83] F. Bonati, L.A. Oro, M.T. Pinillos, C. Tejel, M.C. Apreda, C. Foces-Foces, F.H. Cano, J. Organomet. Chem. 369 (1989) 253.
[84] T.D. Brennan, W.R. Scheidt, Acta Crystallogr. C44 (1988) 478.
[85] B.J. Graves, D.J. Hodgson, C.G. van Kralingen, J. Reedijk, Inorg. Chem. 17 (1978) 3007.
[86] W.R. Scheidt, J. Am. Chem. Soc. (1974) 90.
[87] J.F. Kirner, C.A. Reed, W.R. Scheidt, J. Am. Chem. Soc. (1977) 2557.
[88] L.L. Miller, R.A. Jacobson, Y.S. Chen, D.M. Kurtz Jr, Acta Crystallogr. C45 (1989) 527.
[89] P.F. Rodesiler, N.G. Charles, E.A.H. Griffith, K. Lewinski, E.L. Amma, Acta Crystallogr. C42 (1986) 396.
[90] M. Hvastijovà, J. Kozìsek, J. Kohout, J. Mrozinski, L. Jäger, I. Svoboda, Polyhedron 16 (1997) 463.
[91] A.L. Nivorozhkin, H. Toftlund, M. Nielsen, J. Chem. Soc., Dalton Trans. (1994) 361.
[92] S. Dev, E. Ramli, T.B. Rauchfuss, S.R. Wilson, Inorg. Chem. 30 (1991) 2514.
[93] S. Christie, S. Subramanian, L. Wang, M.J. Zaworotko, Inorg. Chem. 32 (1993) 5415.
[94] A. Maslejova, S. Uhrinova, J. Mrozinski, B. Zurowska, M.C. Munoz, M. Julve, Inorg. Chim. Acta 255 (1997) 343.
[95] C. Pearson, A.L. Beauchamp, Can. J. Chem. 75 (1997) 220.
[96] S. Bélanger, A.L. Beauchamp, Inorg. Chem. 35 (1996) 7836.
[97] S. Bélanger, A.L. Beauchamp, Inorg. Chem. (1996) submitted.
[98] L.A. Aslanov, V.M. Ionov, V.M. Attiya, A.B. Permin, V.S. Petrosyan, Zh. Strukt. Khim. 19 (1978) 185.
[99] E. Rivarola, M. Camalli, F. Caruso, Inorg. Chim. Acta 126 (1987) 1.
[100] M. Camalli, F. Caruso, G. Mattogno, E. Rivarola, Inorg. Chim. Acta 170 (1990) 225.
[101] V. Peruzzo, G. Plazzogna, G. Valle, J. Organomet. Chem. 375 (1989) 167.
[102] A.I. Tursina, L.A. Aslanov, V.V. Chernyshev, S.V. Medvedev, A.V. Yatsenko, Koord. Khim. 11 (1985) 696.
[103] J.T.B.H. Jastrzebski, P.A. Van der Schaaf, J. Boersma, G. van Koten, M. de Wit, Y. Wang, D. Heijdenrijk, C.H. Stam, J. Organomet. Chem. 407 (1991) 301.

[104] R. Graziani, U. Casellato, R. Ettorre, G. Plazzogna, J. Chem. Soc., Dalton Trans. (1982) 805.
[105] K.C. Molloy, M.B. Hossain, D. van der Helm, F.P. Mullins, Inorg. Chem. 20 (1981) 2172.
[106] R.W. Gable, C.L. Raston, G.L. Rowbottom, A.H. White, G. Winter, J. Chem. Soc., Dalton Trans. (1981) 1392.
[107] R.O. Day, R.R. Holmes, A. Scmidpeter, K. Stoll, L. Howe, Chem. Ber. (1991) 2443.
[108] S.M.S.V. Doidge-Harrison, R.A. Howie, J.T.S. Irvine, J.L. Wardell, Polyhedron 11 (1992) 2223.
[109] P.J. Wheatley, Acta Crystallogr. 6 (1953) 369.
[110] S. Martinez-Carrera, Acta Crystallogr. 20 (1966) 783.
[111] H. Fujiwara, A.K. Bose, M.S. Manhas, J.M. van der Veen, J. Chem. Soc., Perkin Trans. 2 (1979) 1327.
[112] M.R. Grimmett, Adv. Heterocycl. Chem. 27 (1980) 151.
[113] K. Schofield, M.R. Grimmett, B.R.T. Keene, Heteroaromatic Nitrogen Compounds: The Azoles, Cambridge Univ. Press, Cambridge, 1976, pp. 346–392.
[114] B.K.S. Lundberg, Acta Crystallogr. 21 (1966) 901.
[115] C. Sandmark, C.-I. Brändén, Acta Chem. Scand. 21 (1967) 993.
[116] G.B. Jameson, G.A. Rodley, W.T. Robinson, R.R. Gagne, C.A. Reed, J.P. Collman, Inorg. Chem. 17 (1978) 850.
[117] R.G. Little, K.R. Dymock, J.A. Ibers, J. Am. Chem. Soc. 97 (1975) 4532.
[118] M. Momenteau, W.R. Scheidt, C.W. Eigenbrot, C.A. Reed, J. Am. Chem. Soc. 110 (1988) 1207.
[119] F. Bonati, A. Burini, B.R. Pietroni, B. Bovio, J. Organomet. Chem. 375 (1989) 147.
[120] C.R. Johnson, C.M. Jones, S.A. Asher, J.E. Abola, Inorg. Chem. 30 (1991) 2120.