

Organotin (IV) polypyrazolyborates

VIII. Hydridotris (4-chloro-3,5-dimethyl-1 *H*-pyrazol-1-yl) borates. Characterization, Mössbauer study and X-ray crystal structures of $[\text{SnCl}_3\{\text{HB}(4\text{-Cl-3,5-Me}_2\text{Pz})_3\}]$ and $[\text{PhSnCl}_2\{\text{HB}(4\text{-Cl-3,5-Me}_2\text{Pz})_3\}]$

Giancarlo Gioia Lobbia ^{a,*}, Patrizio Cecchi ^b, Sandro Calogero ^c, Giovanni Valle ^d,
Marco Chiarini ^a, Lorenzo Stievano ^c

^a Dipartimento di Scienze Chimiche, Università di Camerino, Via S. Agostino 1, I-62032 Camerino, Italy

^b Dipartimento di Agrobiologia ed Agrochimica, Università della Tuscia, Via S.C. De Lellis, I-01100 Viterbo, Italy

^c Dipartimento di Chimica Fisica, Università di Venezia, Calle Larga S. Marta 2137, I-30123 Venice, Italy

^d Centro di Ricerca sui Biopolimeri del CNR-Padova, I-35100 Padua, Italy

Received 22 February 1995

Abstract

Five tin(IV) and organotin(IV) hydridotris(4-chloro-3,5-dimethyl-1 *H*-pyrazol-1-yl)borates have been synthesized and characterized by ¹H, ¹³C and ¹¹⁹Sn NMR and ^{119m}Sn Mössbauer spectroscopy. The tin atom has a more or less distorted octahedral coordination both in the solid state and in solution. The X-ray crystal structures of trichlorotin(IV) and dichlorophenyltin(IV) hydridotris [4-chloro-3,5-dimethyl-1 *H*-pyrazol-1-yl)borates confirm these inferences.

Keywords: Boron; Tin; Pyrazolyborates; X-ray structure; Mössbauer; NMR spectroscopy

1. Introduction

After the investigations in organotin(IV) tris(pyrazolyl)borates made from unsubstituted-(Tp)¹, mono-(Tp^{Me}), or dimethyl-substituted pyrazole rings (Tp^{*}) [2], and more recently trimethylpyrazole rings (Tp^{*Me}) [3], the 3,5-dimethyl-4-chloropyrazole analogue (Tp^{*Cl}) is reported here. The last has received very little attention and was prepared as described in a previous paper [4].

In this work, the Tp^{*Cl}-containing complexes were investigated by ¹¹⁹Sn Mössbauer spectroscopy at 4.2 K, which provides a useful tool for obtaining bonding and structural information. Even if the Mössbauer effect is a short-range phenomenon and not particularly sensitive to the distant substitutions in Tp ligands, the tin(IV) coordination geometries can be inferred by considering the additive contributions of the ligands to the electric

quadrupole interaction. Since the detection of the Mössbauer effect is not affected by the physical state of the material investigated, Mössbauer structural information can be always obtained. If single crystals are available, X-ray diffraction and Mössbauer data can be compared. The crystal structures of SnCl₃ · Tp^{*Cl} and PhSnCl₂ · Tp^{*Cl} permit comparisons with those of related complexes and also with that of the uncomplexed borate. It was of interest to determine steric interactions arising from the bulkiness of the substituent in position 4 of the pyrazole ring, such as occur in the crystal structure of MeSnCl₂ · Tp^{*Me} [3].

2. Experimental

2.1. General laboratory equipment

Concentration of solutions was always carried out in vacuo (water aspirator). The samples were dried in vacuo to constant weight (20°C, ca. 0.1 Torr). Carbon, hydrogen and nitrogen analyses were carried out at

* Corresponding author.

¹ The ligands have been named according to Trofimenko [1].

Camerino University; molecular weight determinations were performed at Pascher Mikroanalytisches Laboratorium (Remagen, Germany). IR spectra were recorded from 4000 to 250 cm^{-1} on a Perkin-Elmer model 2000 FTIR instrument. ^1H , ^{13}C and ^{119}Sn -NMR spectra were recorded on a Varian VXR-300 spectrometer operating at room temperature (300 MHz for ^1H , 75 MHz for ^{13}C and 111.9 MHz for ^{119}Sn). Some spectra were also recorded on a Varian Gemini-200 (200 MHz for ^1H , 50 MHz for ^{13}C). The conductances of solutions were measured with a Crison CDTM 522 conductimeter at room temperature.

2.2. Syntheses

2.2.1. [Hydridotris(4-chloro-3,5-dimethyl-1H-pyrazol-1-yl)borato]trichlorotin(IV)(1)

An anhydrous solution of SnCl_4 in CH_2Cl_2 (1 M, 1 ml) was added by syringe to a cooled (ca. -10°C) solution of KTp^{Cl} (1 mmol, 0.44 g) in 30 ml of CH_2Cl_2 , previously dried over NaH. The resulting solution was purged with dry nitrogen and stirred vigorously for 3 min. Filtration and evaporation of solvent under reduced pressure in the cold afforded a residue. This was recrystallized from CH_2Cl_2 - CH_3CN (1 : 1, v/v), yielding crystals suitable for X-ray studies. Early experiments performed under less strict anhydrous conditions led to more or less hydrolysed species.

2.2.2. [Hydridotris(4-chloro-3,5-dimethyl-1H-pyrazol-1-yl)borato]dichloromethyltin(IV)(2)

A solution of MeSnCl_3 (1 mmol, 0.24 g) in 30 ml of CH_2Cl_2 was mixed with a solution of KTp^{Cl} (1 mmol, 0.44 g) in 30 ml of CH_2Cl_2 . The resulting cloudy mixture was stirred for 30 min at room temperature, filtered and the filtrate evaporated under reduced pressure. The residue was recrystallized from CH_2Cl_2 - CH_3CN (1 : 2, v/v).

2.2.3. [Hydridotris(4-chloro-3,5-dimethyl-1H-pyrazol-1-yl)borato]chlorodimethyltin(IV)(3)

Compound **3** was prepared following a procedure similar to that described for **2**.

2.2.4. [Hydridotris(4-chloro-3,5-dimethyl-1H-pyrazol-1-yl)borato]dichlorophenyltin(IV)(4)

A solution of PhSnCl_3 (1 mmol, 0.30 g) in 25 ml of CH_2Cl_2 , cooled on an ice-salt bath, was mixed with a similarly cooled solution of KTp^{Cl} (1 mmol, 0.44 g) in 30 ml of CH_2Cl_2 . The resulting mixture was stirred under nitrogen for 10 min at ca. -5°C , filtered and the filtrate was evaporated under reduced pressure. The residue was dried under reduced pressure in a desiccator. Suitable crystals for X-ray diffraction study was obtained by slow evaporation of a solution of CHCl_3 - CH_3CN (1 : 1, v/v) at ca. 4°C .

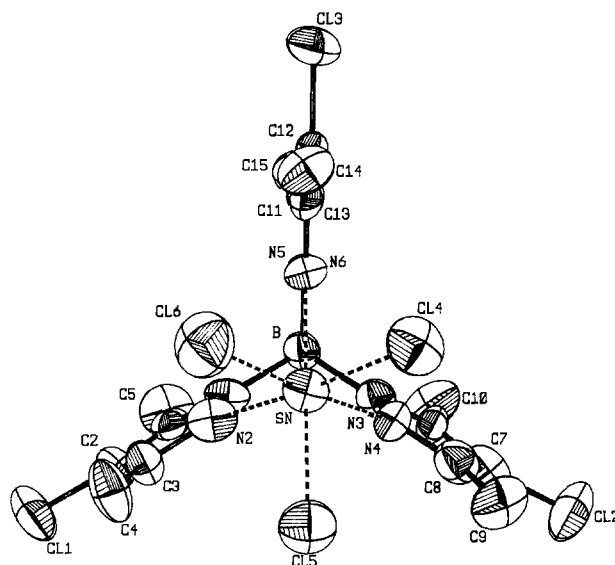


Fig. 1. Molecular structure of **1**.

2.2.5. [Hydridotris(4-chloro-3,5-dimethyl-1H-pyrazol-1-yl)borato]chlorodiphenyltin(IV)(5)

Compound **5** was prepared following a procedure similar to that for **4**.

2.3. X-ray crystal structures

Intensity data were collected at room temperature with a Philips PW 1100 diffractometer using Mo K α radiation in the range $4.2^\circ < 2\theta < 50.1^\circ$, and 2459 independent reflections were observed for **1** $\text{SnCl}_3 \cdot \text{Tp}^{\text{Cl}}$ ($4.2^\circ < 2\theta < 56.0^\circ$ and 5705 reflections for $\text{PhSnCl}_2 \cdot \text{Tp}^{\text{Cl}}$); 2129 reflections with $F > 3\sigma(F)$ for $\text{SnCl}_3 \cdot \text{Tp}^{\text{Cl}}$ and 3943 for **4** $\text{PhSnCl}_2 \cdot \text{Tp}^{\text{Cl}}$ were used in the structure analyses. The structures were resolved by SHELX 86 direct methods. Blocked full-matrix least-

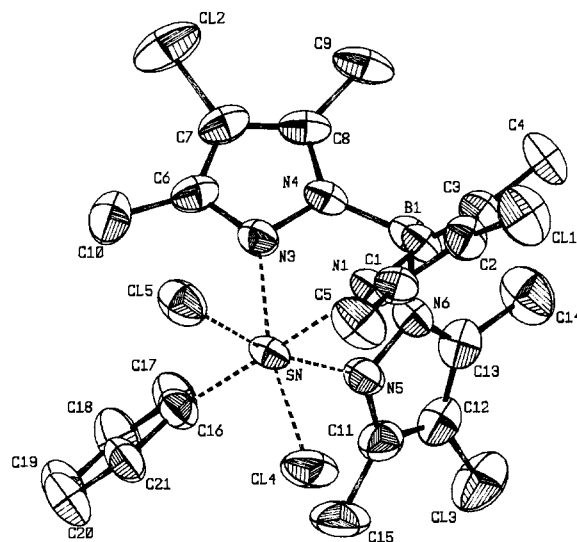


Fig. 2. Molecular structure of **4**.

squares refinement on F was computed and the function $\sum w[|F_o| - |F_c|]^2$ was minimized. The non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated but not refined.

$\text{PhSnCl}_2 \cdot \text{Tp}^{\text{Cl}}$ has a residual electronic density around the inversion centre in the final map due to the statistically disordered atoms of the acetonitrile. This residual has not been considered further as we are interested mainly in the tin(IV) coordination geometry. The final R values were 0.061 (R_w 0.061) for $\text{SnCl}_3 \cdot \text{Tp}^{\text{Cl}}$ and 0.036 (R_w 0.034) for $\text{PhSnCl}_2 \cdot \text{Tp}^{\text{Cl}}$.

The structures of $\text{SnCl}_3 \cdot \text{Tp}^{\text{Cl}}$ and $\text{PhSnCl}_2 \cdot \text{Tp}^{\text{Cl}}$ are represented in the ORTEP plots together with their numbering scheme in Figs. 1 and 2. The final atomic coordinates and selected bond distances and angles are reported in Tables 4–7. Full lists of all parameters have been deposited at the Cambridge Crystallographic Data Centre.

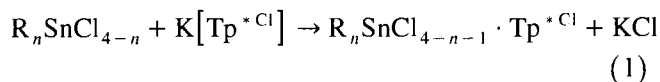
2.4. Mössbauer spectroscopy

The $\text{Ca}^{119\text{m}}\text{SnO}_3$ Mössbauer source and the absorbers were kept at 4.2 K. A sinusoidal velocity waveform and a proportional detector were used. The spectra were fitted by least squares to sets of Lorentzian lines by the MOS 90 program. The hyperfine parameters such as isomer shift (IS), average line width (LW), experimental quadrupole splitting (QS) and splittings calculated by a point-charge model are listed in Table 9. A minor component attributed to decomposition products was evident in the spectra of **2** and **5** in Table 9 (IS 0.00, LW 0.88; QS 0.60 and 0.45 mm s^{-1} , respectively).

3. Results and Discussion

3.1. Synthesis and general properties of the compounds

Compounds **1–5** reported in Table 1 are prepared by the reaction



They are colourless solids, showing good stability when stored dry but in air they are more moisture sensitive than the corresponding complexes with Tp , Tp^* or Tp^{Me} , especially **1**. In solution they are less stable and on prolonged standing transformations such as $2\text{R}_n\text{SnCl}_2 \cdot \text{Tp}^{\text{Cl}} \rightarrow \text{R}_2\text{SnCl} \cdot \text{Tp}^{\text{Cl}} + \text{SnCl}_3 \cdot \text{Tp}^{\text{Cl}}$ have been observed.

The complexes are soluble in chlorinated organic solvents, less so in aromatic hydrocarbons, not appreciably in aliphatic solvents and insoluble in water. Their solubilities vary with polarity, which increases with decreasing n , the number of tin-bonded aralkyl groups.

The compounds are non-electrolyte in acetone (Table 1) and the molecular weight determinations in CH_2Cl_2 indicate that discrete monomeric units are present in solution, as expected in neutral complexes.

The IR spectra exhibit the typical bands of the pyrazole rings. Strong ring “breathing” vibrations appear at 1532–1557 cm^{-1} and medium-intensity $\nu(\text{B-H})$ peaks at around 2550–2555 cm^{-1} . This frequency increases slightly with increasing number of tin-bonded chlorine atoms. Moreover, others bands are visible in the low-frequency region because of $\nu(\text{Sn-C})$ vibra-

Table 1
Yields, analyses and physical properties of the compounds

No.	Compound ^a	Yield (%)	Elemental analysis (found/calcd.) (%)			M.W.	M.p. (°C)	Λ^b
			C	H	N			
–	KTp^{Cl}	72	41.13 41.09	4.25 4.37	19.20 19.18			
1	$\text{SnCl}_3 \cdot \text{Tp}^{\text{Cl}}$	49	29.09 28.80	3.30 3.06	13.13 13.43		– ^c 5.4 (0, 9)	
2	$\text{MeSnCl}_2 \cdot \text{Tp}^{\text{Cl}}$	65	32.03 31.76	3.92 3.66	13.48 13.89	589 ^d	275–277 ^e 7.5 (1.1)	
3	$\text{Me}_2\text{SnCl} \cdot \text{Tp}^{\text{Cl}}$	70	34.54 34.92	4.26 4.31	14.68 14.37		160–163 ^e 9.1. (1.0)	
4	$\text{PhSnCl}_2 \cdot \text{Tp}^{\text{Cl}}$	58	37.48 37.80	3.87 3.63	12.47 12.60	639 ^d	246–248 5.8 (1.0)	
5	$\text{Ph}_2\text{SnCl} \cdot \text{Tp}^{\text{Cl}}$	62	46.03 45.75	4.05 4.12	12.06 11.86		180–182 ^e 5.4 (0, 9)	

^a Tp^{Cl} is hydridotris(4-chloro-3,5-dimethyl-1-*H*-pyrazol-1-yl)borate, $\text{C}_{15}\text{H}_{10}\text{BCl}_3\text{N}_6$.

^b Specific conductivity ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) in acetone solution at room temperature; the molar concentration $\times 10^{-3}$ is given in parentheses.

^c Chars without melting.

^d Monomer, judged by molecular weight determination by osmometry in dichloromethane.

^e Melted with decomposition.

Table 2
¹H NMR data

No.	Compound	5- or 3-Me δ ^{a,b}		R-Sn, ^a J (¹¹⁹ Sn, H)/Hz
–	KTp ^{*Cl}	2.16	2.03	
1	SnCl ₃ ·Tp ^{*Cl}	2.41	2.72	
2	MeSnCl ₂ ·Tp ^{*Cl}	2.40	2.57	Me: 1.50; 119.1
		2.26	2.80	
3	Me ₂ SnClTp ^{*Cl}	2.35	2.60	Me: 0.95; 68.2
		2.25	2.41	
4	PhSnCl ₂ ·Tp ^{*Cl}	1.85	2.46	Ph: 7.13–7.28
		2.45	2.87	
5	Ph ₂ SnClTp ^{*Cl}	1.80	2.42	Ph: 7.25–7.40
		1.25	2.53	

^a CDCl₃ solution, in ppm from Me₄Si, calibration from internal deuterium solvent lock.

^b The signal in the upper line has twice the intensity of that in the lower line.

tions at 560–500 cm⁻¹ (R = Me), 460–450 cm⁻¹ and 250 cm⁻¹ (R = Ph) and ν(Sn–Cl) vibrations at 280–320 cm⁻¹.

The NMR spectra (¹H, ¹³C and ¹¹⁹Sn) for the compounds support the proposed formulae and are comparable to those found in the corresponding compounds containing other tris(pyrazolyl)borato ligands (Tables 2 and 3).

3.2. Description of molecular structures

Crystal data are as follows: SnCl₃·Tp^{*Cl} [hydridotris(4-chloro-3,5-dimethyl-1*H*-pyrazol-1-yl)borato] trichlorotin(IV) (1), formula SnN₆C₁₅BH₁₉Cl₆, formula weight *M* = 625.6, orthorhombic, space group *P*₂₁₂₁ (No 19)₂ with *a* = 19.418(2) Å, *b* = 15.690(2) Å, *c* = 9.081(2) Å, *V* = 2766.7(8) Å³, *Z* = 4, *D*_c = 1.50 g cm⁻³, *F*(000) = 1232.0; PhSnCl₂·Tp^{*Cl}(CH₃CN)-[hydridotris(4-chloro-3,5-dimethyl-1*H*-pyrazol-1-yl)borato]dichlorophenyltin(IV)], formula SnN₇C₂₃BH₂₇Cl₅,

Table 4
Fractional coordinates for SnCl₃·Tp^{*Cl} (1) (with e.s.d.s in parentheses)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Sn	0.00484(6)	0.60324(8)	0.04266(9)
Cl(1)	-0.1252(4)	0.3107(4)	-0.2666(7)
Cl(2)	0.2733(2)	0.6055(6)	-0.2775(6)
Cl(3)	-0.1262(3)	0.8942(4)	-0.2744(6)
Cl(4)	0.0589(4)	0.7165(4)	0.1696(6)
Cl(5)	0.0582(4)	0.4922(5)	0.1730(6)
Cl(6)	-0.0975(4)	0.6022(8)	0.1749(7)
B	0.0043(9)	0.601(1)	-0.322(1)
N(1)	-0.0325(7)	0.5250(8)	-0.265(1)
N(2)	-0.0395(7)	0.5106(9)	-0.118(1)
N(3)	0.0768(6)	0.603(1)	-0.265(1)
N(4)	0.0909(6)	0.604(1)	-0.119(1)
N(5)	-0.0322(6)	0.6827(8)	-0.263(1)
N(6)	-0.0400(7)	0.6939(9)	-0.115(1)
C(1)	-0.060(1)	0.459(1)	-0.340(2)
C(2)	-0.0844(9)	0.401(2)	-0.231(2)
C(3)	-0.071(1)	0.435(1)	-0.097(2)
C(4)	-0.088(1)	0.400(2)	0.044(2)
C(5)	-0.062(1)	0.453(1)	-0.498(2)
C(6)	0.1373(7)	0.601(1)	-0.340(1)
C(7)	0.1892(8)	0.603(1)	-0.239(2)
C(8)	0.1601(9)	0.608(1)	-0.103(2)
C(9)	0.1945(9)	0.608(2)	0.040(2)
C(10)	0.1403(8)	0.601(2)	-0.504(1)
C(11)	-0.0597(9)	0.746(1)	-0.336(2)
C(12)	-0.084(1)	0.802(1)	-0.237(2)
C(13)	-0.0711(9)	0.767(1)	-0.100(2)
C(14)	-0.096(1)	0.807(1)	0.037(2)
C(15)	-0.063(1)	0.749(1)	-0.502(2)

formula weight *M* = 708.3, monoclinic, space group *P*₂₁/*n* (No. 14), *a* = 12.782(2) Å, *b* = 15.464(2) Å, *c* = 15.845(2) Å, β = 104.9(2), *V* = 3026(3) Å³, *Z* = 4, *D*_c = 1.55 g cm⁻³, *F*(000) = 1416.0.

The cell of SnCl₃·Tp^{*Cl} (1) contains discrete molecular units whose packing in the crystal is determined by normal van der Waals contacts. The geometry

Table 3
¹³C and ¹¹⁹Sn NMR data

No.	Compound	C-3 δ ^{a,b}	C-5 δ ^{a,b}	C-4 δ ^{a,b}	3- or 5-Me δ ^{a,b}	R-Sn δ ^a	¹¹⁹ Sn - δ ^c
–	KTp ^{*Cl}	144.7	141.4	107.5	12.2	11.1	
1	SnCl ₃ ·T·p ^{*Cl}	149.7	141.5	111.5	11.4	10.2	653.7
2	MeSnCl ₂ ·Tp ^{*Cl}	147.3	141.6	110.9	11.8	10.6	501.1
		149.1	141.5	111.6	13.3	11.0	
3	Me ₂ SnCl·Tp ^{*Cl}	146.6	141.1	110.3	12.3	10.3	337.8
		145.1	140.3	108.2	11.4	10.8	
4	PhSnCl ₂ ·Tp ^{*Cl}	149.2	142.4	111.4	12.0	11.2	548.2
		149.7	142.1	112.2	13.7	11.5	
5	Ph ₂ SnCl·Tp ^{*Cl}	148.1	140.5	110.3	11.4	10.9	468.1
		147.8	141.8	110.0			

^a In ppm from Me₄Si, calibration from internal deuterium solvent lock; when coupling constants are detected they are indicated by a footnote.

^b The signals in the upper line are more intense than those in the lower line.

^c In ppm from external Me₄Sn.

^d |¹J(¹¹⁹Sn, ¹³C)| = 648 Hz.

^e |J(¹¹⁹Sn, ¹³C)| = 84.98 Hz.

around the tin atom (see Fig. 1) is that of a distorted octahedron with average bond angles N–Sn–N and Cl–Sn–Cl of 81.8° and 96.9°, respectively, and average bond lengths Sn–Cl and Sn–N of 2.344 and 2.210 Å, respectively.

Atomic coordinates and selected bond lengths and angles for **1** are reported in Tables 4 and 5.

PhSnCl₂·Tp*^{Cl} (**4**) (Fig. 2) consists of discrete molecules with a distorted octahedral coordination geometry. Average values of bond angles N–Sn–N and Cl–Sn–Cl are 81.7 and 95.5°, respectively, and Sn–Cl and Sn–N bond lengths are 2.421 and 2.249 Å, respectively.

Atomic coordinates and bond distances and angles for PhSnCl₂·Tp*^{Cl} (**4**) and acetonitrile, the crystallization solvent, are reported in Tables 6 and 7. No close contact between the atoms of acetonitrile and those of PhSnCl₂·Tp*^{Cl} was observed. The pyrazolato and phenyl rings are almost planar. The largest isotropic thermal parameters are exhibited by the chloride atoms bonded to tin and the carbon atoms furthest from the tin coordination site.

A comparison of structural data among them the angular values shown in the relevant figure are reported

in Table 8. The angles γ show some correlation with electronic effects but not with the steric effects. The same holds for β , although attenuated, while the α values do not seem to be correlated.

The exchange of a chlorine atom for a hydrogen in the pyrazole rings of Tp* lowers its ability to donate electron density to a metal, but may slightly increase its steric bulk so that the Cl may hinder the bending of 3-Me away from the metal. This has been observed comparing the crystal structures of ionic KTp*^{Me} and molecular MeCl₂SnTp*^{Me} [3], but the size of chlorine in the present case is not so effective as when the H-4 is substituted by a Me group.

A comparison of structure (bond distances and angles) for compound **1** with the corresponding data for compounds containing Tp* or Tp illustrates the trends shown in Fig. 3. There is some parallelism with the expected electron-donating power of the ligands, and this can also be checked with the ¹¹⁹Sn NMR data plotted in Fig. 4. The latter values for the present ligand are intermediate between those of Tp* and Tp. Considering related crystal structures, the N–Sn–N and Cl–Sn–Cl angles and Sn–N bond distances are all similar whereas the value of Sn–Cl formed here is the lowest.

Table 5
Selected bond distances (Å) and angles (°) for SnCl₃·Tp*^{Cl} (**1**)

SnCl(4)	2.365(7)	Sn–Cl(5)	2.347(7)	N(4)–Sn–N(6)	82.3(5)	N(2)–Sn–N(6)	81.1(5)
Sn–Cl(6)	2.322(7)	Sn–N(2)	2.23(1)	N(2)–Sn–N(4)	82.1(5)	Cl(6)–Sn–N(6)	90.1(4)
Sn–N(4)	2.22(1)	Sn–N(6)	2.19(1)	Cl(6)–Sn–N(4)	169.9(3)	Cl(6)–Sn–N(2)	90.1(4)
Cl(1)–C(2)	1.66(2)	Cl(2)–C(7)	1.67(2)	Cl(5)–Sn–N(6)	169.7(4)	Cl(5)–Sn–N(4)	90.3(4)
Cl(3)–C(12)	1.70(2)	B–N(1)	1.49(2)	Cl(5)–Sn–N(2)	90.9(4)	Cl(5)–Sn–Cl(6)	96.4(3)
B–N(3)	1.50(2)	B–N(5)	1.56(2)	Cl(4)–Sn–N(6)	90.3(4)	Cl(4)–Sn–N(4)	89.1(4)
N(1)–N(2)	1.36(2)	N(1)–C(1)	1.36(2)	Cl(4)–Sn–N(2)	168.4(4)	Cl(4)–Sn–Cl(6)	97.7(3)
N(2)–C(3)	1.35(2)	N(3)–N(4)	1.35(1)	Cl(4)–Sn–Cl(5)	96.7(2)	N(3)–B–N(5)	107(1)
N(3)–C(6)	1.36(2)	N(4)–C(8)	1.35(2)	N(1)–B–N(5)	109(1)	N(1)–B–N(3)	110(1)
N(5)–N(6)	1.37(2)	N(5)–C(11)	1.31(2)	B–N(1)–C(1)	129(1)	B–N(1)–N(2)	122(1)
N(6)–C(13)	1.30(2)	C(1)–C(2)	1.41(3)	N(2)–N(1)–C(1)	109(1)	Sn–N(2)–N(1)	120(1)
C(1)–C(5)	1.44(3)	C(2)–C(3)	1.35(3)	N(1)–N(2)–C(3)	109(1)	Sn–N(2)–C(3)	131(1)
C(3)–C(4)	1.43(3)	C(6)–C(7)	1.36(2)	B–N(3)–C(6)	129(1)	B–N(3)–N(4)	122(1)
C(6)–C(10)	1.49(2)	C(7)–C(8)	1.36(2)	N(4)–N(3)–C(6)	108(1)	Sn–N(4)–N(3)	119.6(9)
C(8)–C(9)	1.46(2)	C(11)–C(12)	1.34(2)	N(3)–N(4)–C(8)	108(1)	Sn–N(4)–C(8)	132(1)
C(11)–C(15)	1.51(2)	C(12)–C(13)	1.39(3)	B–N(5)–C(11)	129(1)	B–N(5)–N(6)	120(1)
C(13)–C(14)	1.47(3)			N(6)–N(5)–C(11)	111(1)	Sn–N(6)–N(5)	121(1)
				N(5)–N(6)–C(13)	106(1)	Sn–N(6)–C(13)	133(1)
				N(1)–C(1)–C(5)	124(1)	N(1)–C(1)–C(2)	106(1)
				C(2)–C(1)–C(5)	130(1)	Cl(1)–C(2)–C(1)	125(1)
				C(1)–C(2)–C(3)	108(1)	Cl(1)–C(2)–C(3)	127(1)
				N(2)–C(3)–C(2)	108(1)	C(2)–C(3)–C(4)	128(2)
				N(2)–C(3)–C(4)	125(1)	N(3)–C(6)–C(10)	122(1)
				N(3)–C(6)–C(7)	107(1)	C(7)–C(6)–C(10)	130(1)
				Cl(2)–C(7)–C(6)	126(1)	C(6)–C(7)–C(8)	108(1)
				Cl(2)–C(7)–C(8)	126(1)	N(4)–C(8)–C(7)	108(1)
				C(7)–C(8)–C(9)	128(1)	N(4)–C(8)–C(9)	124(1)
				N(5)–C(11)–C(15)	123(1)	N(5)–C(11)–C(12)	108(1)
				C(12)–C(11)–C(15)	129(1)	Cl(3)–C(12)–C(11)	126(1)
				C(11)–C(12)–C(13)	106(1)	Cl(3)–C(12)–C(13)	127(1)
				N(6)–C(13)–C(12)	110(1)	C(12)–C(13)–C(14)	122(1)
				N(6)–C(13)–C(14)	128(1)		

Table 6
Fractional coordinates for $\text{SnCl}_2\text{Ph}\cdot\text{Tp}^*\text{Cl}$ (**4**) (with e.s.d.s in parentheses)

Atom	x	y	z
Sn	0.85460(3)	0.35746(2)	0.17782(2)
Cl(1)	0.7517(1)	0.0462(1)	-0.0582(1)
Cl(2)	0.8609(1)	0.1834(1)	0.5206(1)
Cl(3)	1.3381(1)	0.3744(1)	0.2213(1)
Cl(4)	0.8393(1)	0.42256(9)	0.03585(9)
Cl(5)	0.6615(1)	0.35511(8)	0.1620(1)
N(1)	0.8409(3)	0.2282(2)	0.1125(2)
N(2)	0.9142(3)	0.1641(2)	0.1485(2)
N(3)	0.8858(3)	0.2752(2)	0.2994(2)
N(4)	0.9465(3)	0.2004(2)	0.3051(3)
N(5)	1.0325(3)	0.3317(2)	0.1955(3)
N(6)	1.0751(3)	0.2520(2)	0.2219(2)
B	1.0019(4)	0.1769(3)	0.2335(4)
C(1)	0.7756(4)	0.1971(3)	0.0386(3)
C(2)	0.8085(4)	0.1133(3)	0.0278(3)
C(3)	0.8936(4)	0.0937(3)	0.0968(3)
C(4)	0.9574(4)	0.0115(3)	0.1167(4)
C(5)	0.6820(4)	0.2435(4)	-0.0201(4)
C(6)	0.8482(4)	0.2797(3)	0.3711(3)
C(7)	0.8857(4)	0.2071(4)	0.4214(3)
C(8)	0.9461(4)	0.1588(3)	0.3797(3)
C(9)	1.0020(5)	0.0742(3)	0.4075(4)
C(10)	0.7767(5)	0.3517(4)	0.3885(4)
C(11)	1.1152(4)	0.3836(3)	0.1908(3)
C(12)	1.2094(4)	0.3367(4)	0.2148(3)
C(13)	1.1832(4)	0.2533(4)	0.2328(3)
C(14)	1.2552(5)	0.1750(4)	0.2575(5)
C(15)	1.1042(5)	0.4764(4)	0.1639(4)
C(16)	0.8871(4)	0.4744(3)	0.2522(3)
C(17)	0.9689(4)	0.4789(3)	0.3285(4)
C(18)	0.9917(5)	0.5561(4)	0.3749(4)
C(19)	0.9300(5)	0.6288(4)	0.3446(5)
C(20)	0.8473(5)	0.6237(3)	0.2698(4)
C(21)	0.8238(4)	0.5474(3)	0.2233(4)
C(1)N	0.5549(8)	0.1740(7)	0.4407(7)
C(2)N	0.5672(7)	0.2569(6)	0.4877(6)
N(1)N	0.5922(6)	0.3178(4)	0.5297(5)

Besides the values of α , β and γ , no other structural data in Table 8 show any straightforward relation to steric bulk.

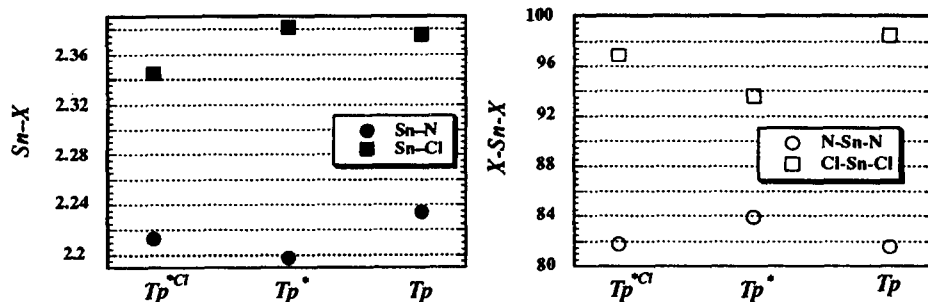


Fig. 3. Comparison of structural data for differently substituted ligands attached to the same tin fragment (SnCl_3^+): (left) average Sn–N and Sn–Cl bond lengths and (right) average N–Sn–N and Cl–Sn–Cl angles.

3.3. Mössbauer spectra

The line widths in Table 9 are close to the minimum observable width [8] of 0.67 mm s^{-1} , indicating one tin site in the specimens, consistent with the crystallographic data for **1** and **4**.

The agreement between observed and calculated electric quadrupole splitting (QS) in Table 9 suggests an octahedral Sn^{IV} site.

Compound **1** exhibits the singlet absorption expected for a regular octahedral geometry. The deviations from ideal octahedral geometry in the bond angles around the tin site in the crystallographic data for $\text{SnCl}_3\cdot\text{Tp}^*\text{Cl}$ would not be expected to show a significant QS .

In the geometry for **2**, **4** and **5**, the facial *N*-tridentate pyrazolylborate ligand does not contribute to the principal components of the e.f.g. The values of these components for $\text{R}_2\text{SnCl}_2\cdot\text{Tp}^*\text{Cl}$ and $\text{R}_2\text{SnCl}\cdot\text{Tp}^*\text{Cl}$ are equivalent but opposite in sign. The sign of V_{zz} can be estimated considering the relative electronic donor powers of the various ligands. In the octahedral compounds **2** and **4** more electronic charge is concentrated along the R–Sn–N axis and in **5** less charge along the Cl–Sn–N axis, giving a negative and a positive V_{zz} , respectively. Because of the $^{119\text{m}}\text{Sn}$ nuclear quadrupole moment, the QS and V_{zz} values are of opposite sign.

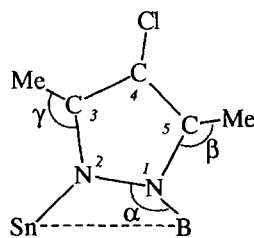
3.4. NMR spectra and concluding remarks

The NMR spectra show two sets of signals for the pyrazole protons (ratio 2:1) or carbon atoms (one set more intense than the other), except for $n=0$. This cannot be due to the presence of isomers because only one signal (*Sn*-Me) or set of signals (*Sn*-Ph) is present for tin-bonded organic groups, and only one sharp signal is seen in the ^{119}Sn spectra. In the more or less distorted octahedral geometry around tin, two different pyrazole groups are discernable with the obvious exception of **1**. This indicates that the compounds are not fluxional in solution.

Table 7
Selected bond distances (Å) and angles (°) for SnCl₂Ph · Tp*Cl (4)

Sn–Cl(4)	2.426(2)	Sn–Cl(5)	2.416(2)	N(5)–Sn–C(16)	92.0(2)	N(3)–Sn–C(16)	92.3(2)
Sn–N(1)	2.237(3)	Sn–N(3)	2.257(4)	N(3)–Sn–N(5)	81.0(2)	N(1)–Sn–C(16)	172.2(2)
Sn–N(5)	2.254(4)	Sn–C(16)	2.140(5)	N(1)–Sn–N(5)	81.7(2)	N(1)–Sn–N(3)	82.3(1)
Cl(1)–C(2)	1.719(5)	Cl(2)–C(7)	1.721(6)	Cl(5)–Sn–C(16)	96.8(2)	Cl(5)–Sn–N(5)	168.9(1)
Cl(3)–C(12)	1.724(6)	N(1)–N(2)	1.381(5)	Cl(5)–Sn–N(3)	91.8(2)	Cl(5)–Sn–N(1)	89.0(3)
N(1)–C(1)	1.341(6)	N(2)–B(1)	1.529(7)	Cl(4)–Sn–C(16)	96.8(1)	Cl(4)–Sn–N(5)	91.5(2)
N(2)–C(3)	1.347(6)	N(3)–N(4)	1.383(5)	Cl(4)–Sn–N(3)	168.5(1)	Cl(4)–Sn–N(1)	87.9(1)
N(3)–C(6)	1.344(7)	N(4)–B(1)	1.527(8)	Cl(4)–Sn–Cl(5)	94.2(2)	Sn–N(1)–C(1)	133.0(3)
N(4)–C(8)	1.347(6)	N(5)–N(6)	1.368(5)	Sn–N(1)–N(2)	119.1(3)	N(2)–N(1)–C(1)	107.8(4)
N(5)–C(11)	1.344(7)	N(6)–B(1)	1.531(7)	N(1)–N(2)–C(3)	108.9(4)	N(1)–N(2)–B(1)	122.4(3)
N(6)–C(13)	1.347(6)	C(1)–C(2)	1.386(7)	B(1)–N(2)–C(3)	128.7(4)	Sn–N(3)–C(6)	132.0(4)
C(1)–C(5)	1.497(7)	C(2)–C(3)	1.363(7)	Sn–N(3)–N(4)	120.0(3)	N(4)–N(3)–C(6)	107.7(4)
C(3)–C(4)	1.499(7)	C(6)–C(7)	1.388(7)	N(3)–N(4)–C(8)	109.1(4)	N(3)–N(4)–B(1)	120.7(4)
C(6)–C(10)	1.510(8)	C(7)–C(8)	1.361(8)	B(1)–N(4)–C(8)	130.2(4)	Sn–N(5)–C(11)	132.1(3)
C(8)–C(9)	1.501(7)	C(11)–C(12)	1.372(7)	Sn–N(5)–N(6)	120.4(4)	N(6)–N(5)–C(11)	107.3(5)
C(11)–C(15)	1.494(8)	C(12)–C(13)	1.381(8)	N(5)–N(6)–C(13)	109.9(4)	N(5)–N(6)–B(1)	120.8(5)
C(13)–C(14)	1.511(8)	C(16)–C(17)	1.382(8)	B(1)–N(6)–C(13)	129.3(4)	N(4)–B(1)–N(6)	108.9(4)
C(16)–C(21)	1.396(7)	C(17)–C(18)	1.393(8)	N(2)–B(1)–N(6)	108.9(4)	N(2)–B(1)–N(4)	108.1(6)
C(18)–C(19)	1.386(8)	C(19)–C(20)	1.373(9)	N(1)–C(1)–C(5)	126.1(4)	N(1)–C(1)–C(2)	107.6(5)
C(20)–C(21)	1.382(8)	C(1)N–C(2)N	1.47(1)	C(2)–C(1)–C(5)	126.2(5)	Cl(1)–C(2)–C(1)	125.6(5)
C(2)N–N(1)N	1.15(1)			C(1)–C(2)–C(3)	108.3(4)	Cl(1)–C(2)–C(3)	126.1(4)
				N(2)–C(3)–C(2)	107.3(4)	C(2)–C(3)–C(4)	129.5(5)
				N(2)–C(3)–C(4)	123.1(5)	N(3)–C(6)–C(10)	123.8(5)
				N(3)–C(6)–C(7)	107.3(5)	C(7)–C(6)–C(10)	128.9(5)
				Cl(2)–C(7)–C(6)	125.3(5)	C(6)–C(7)–C(8)	108.7(5)
				Cl(2)–C(7)–C(8)	125.9(4)	N(4)–C(8)–C(7)	107.1(5)
				C(7)–C(8)–C(9)	128.6(5)	N(4)–C(8)–C(9)	124.3(5)
				N(5)–C(11)–C(15)	124.9(7)	N(5)–C(11)–C(12)	108.4(5)
				C(12)–C(11)–C(15)	126.7(7)	Cl(3)–C(12)–C(11)	126.4(5)
				C(11)–C(12)–C(13)	108.0(7)	Cl(3)–C(12)–C(13)	125.6(6)
				N(6)–C(13)–C(12)	106.4(6)	C(12)–C(13)–C(14)	129.7(7)
				N(6)–C(13)–C(14)	123.9(6)	Sn–C(16)–C(21)	119.3(4)
				Sn–C(16)–C(17)	121.4(4)	C(17)–C(16)–C(21)	119.3(5)
				C(16)–C(17)–C(18)	120.9(6)	C(17)–C(18)–C(19)	119.3(6)
				C(18)–C(19)–C(20)	119.6(5)	C(19)–C(20)–C(21)	121.5(6)
				C(16)–C(21)–C(20)	119.2(6)	C(1)N–C(2)N–N(1)N	170(1)

Table 8
Comparison of structural data for related organotin(IV) compounds R_nSnX_{4-n-1} · Tp*



Tp [#]	R	n	Sn–N (Å)	Sn–C (Å)	Sn–Cl (Å)	N–Sn–N (°)	C–Sn–C (°)	Cl–Sn–Cl (°)	α (°)	β (°)	γ (°)	Ref.
Tp*Cl	–	0	2.213	–	2.345	81.8	–	96.9	121.3	123.1	125.4	This work
Tp*Cl	Ph	1	2.249	2.140	2.422	81.7	–	95.5	121.3	123.8	124.9	This work
Tp*Me	Me	1	2.242	2.244	2.438	82.0	–	94.5	120.4	122.7	123.1	[3]
Tp*	–	0	2.198	–	2.382	83.9	–	93.6	120.4	122.5	123.7	[5]
Tp*	Ph	2	2.296	2.164	2.456	80.1	107.2	–	120.2	121.8	123.3	[2d]
Tp ^{Me}	Ph	1	2.249	2.228	2.429	81.6	–	93.8	120.1	–	125.1	[2c]
Tp	–	0	2.234	–	2.376	81.6	–	98.5	119.5	–	–	[2d]
Tp	Ph	2	2.285	2.168	2.445	78.0	103.9	–	120.4	–	–	[2d]
Tp	R ^a	1	2.218	2.140	2.428	80.3	–	94.3	121.7	–	–	[6]
Tp	Me	3	2.388	2.165	–	74.8	105.2	–	120.4	–	–	[7]

^a R = MeOOC–CH₂CH₂–.

Table 9
 ^{119}Sn Mössbauer parameters at 4.2 K

No.	Compound	$IS^{a,b}$	QS^b	QS (calc.) ^{b,c}	$LW-1^{b,d}$	$LW-2^{b,d}$
1	$\text{SnCl}_3 \cdot \text{Tp}^{\text{Cl}}$	0.32(1)	0.14(3)	0	0.83(2)	0.89(3)
2	$\text{MeSnCl}_2 \cdot \text{Tp}^{\text{Cl}}$	0.73(1)	1.63(1)	+2.06	0.98(2)	0.91(2)
3	$\text{Me}_2\text{SnCl} \cdot \text{Tp}^{\text{Cl}}$	0.88(1)	2.20(1)	-2.06	0.96(2)	0.90(2)
4	$\text{PhSnCl}_2 \cdot \text{Tp}^{\text{Cl}}$	0.70(1)	1.61(1)	+1.90	0.89(1)	0.87(1)
5	$\text{Ph}_2\text{SnCl} \cdot \text{Tp}^{\text{Cl}}$	0.86(1)	2.11(1)	-1.90	0.90(1)	0.88(2)

^a The shifts are relative to SnO_2 .

^b In mm^{-1}s .

^c Calculated assuming a regular octahedral geometry and the literature [8] partial quadrupole splittings, $Cl = 0.00$, $Me = -1.03$, $Ph = -0.95$, together with the working approximations of $-0.04 \text{ mm}^{-1}\text{s}$ (i.e. the value of $\frac{1}{2}\text{phen}$ as bridging ligand (for $\frac{1}{3} \text{Tp}^{\text{Cl}}$). The calculated e.f.g. components are: $V_{XX} = V_{YY} = V_{ZZ} = 0$ for 1; $V_{XX} = V_{YY} = -R + Cl$, $V_{ZZ} = 2R - 2Cl$ for 2; $V_{XX} = V_{YY} = R - Cl$, $V_{ZZ} = -2R + 2Cl$ for 4 and 5.

^d $LW-1$ referred to the line at less positive shift, $LW-2$ to the line at more positive shift.

The ^{13}C NMR data show that the C-3 and C-4 resonances of the pyrazole rings (which are closer to the coordination site than C-5 or pz-Me groups) always shift to lower fields upon complexation, reflecting the flow of charge from the anionic ligand to the positive metal ion. Within the complexes, the resonance positions for C-3 are responsive to the Lewis acidity of the tin fragment to which it is bonded, and they are shifted to lower fields with decreasing n . This is a general trend among organotin(IV) tris(pyrazolyl)borates. It can be highlighted, choosing (when $n \neq 0$) for evenness the pyrazole opposed (in an idealised octahedral geometry) to a chlorine atom, by plotting the chemical shift of C-3

against n . Almost parallel linear plots are obtained, as illustrated in Fig. 4a for $\text{Tp}^{\#} = \text{Tp}^{\text{Me}}$, Tp^* and Tp^{Cl} . The line for Tp , which lies well below the others, is not included for reasons of clarity.

For complexes containing Ph groups instead of Me, similar trends are observed, although the linearity is worse and the slopes are smaller. A smaller slope is because Ph is more electronegative than Me, so that the difference from Cl is smaller. The poorer linearity may reflect the greater steric requirements of Ph than Me. The same trend (but weaker, since the slopes are smaller) is observed for the corresponding C-4, while C-5 does not correlate in this manner. As previously observed, the ^{119}Sn chemical shifts for $\text{R}_n\text{SnCl}_{4-n-1} \cdot \text{Tp}^{\#}$ follow approximately straight lines, which are almost parallel [1,2]. In the present case the slope is slightly greater than those found for other ligands. Fig. 4b shows a comparison together with the fitted equations and correlation coefficients. The line for Tp^{Cl} falls between those for Tp^{Me} and Tp . If the hypothesis that empirically correlates a greater electron-donating power of the ligand with a greater negative value of $\delta(^{119}\text{Sn})$ of the relevant complex holds true, then the present ligand appears less electron-donating than Tp^{Me} and Tp^* (see the equations in Fig. 4b) but more donating than the unsubstituted Tp . This is also consistent with the structural comparisons illustrated in Fig. 3.

Acknowledgements

MURST and the Consiglio Nazionale delle Ricerche (CNR) are gratefully acknowledged.

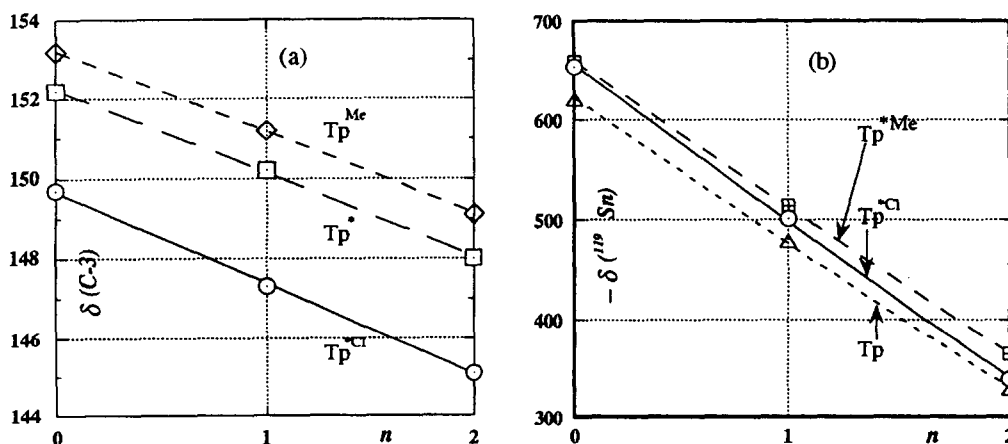


Fig. 4. (a) Correlation between the chemical shift of the pyrazole C-3 opposing a tin-bonded Cl and the number (n) of tin-bonded alkyl groups (R) in $\text{R}_n\text{SnCl}_{4-n-1} \cdot \text{Tp}^{\#}$, for $\text{Tp}^{\#} = \text{Tp}^{\text{Cl}}$ (\odot), Tp^* (\square) and Tp^{Me} (\diamond). The relevant fitted equations are $\delta_{\text{Tp}^{\text{Cl}}}(n) = -2.3n + 149.67$ ($r = 0.99969$); $\delta_{\text{Tp}^*}(n) = -2.1n + 152.23$ ($r = 0.99962$); $\delta_{\text{Tp}^{\text{Me}}}(n) = -2.05n + 153.22$ ($r = 0.99990$). The values for Tp also follow a straight line lying well below the others; if been reported in the same plot they would have unacceptably compressed the other lines. (b) Correlation between the ^{119}Sn chemical shift and the number (n) of tin-bonded alkyl groups (R) in $\text{R}_n\text{SnCl}_{4-n-1} \cdot \text{Tp}^{\#}$, for $\text{Tp}^{\#} = \text{Tp}^{\text{Cl}}$ (\odot), Tp^{Me} (\square) and Tp (\triangle). The relevant fitted equations are $\delta_{\text{Tp}^{\text{Cl}}}(n) = -157.35n + 655.28$ ($r = 0.99985$); $\delta_{\text{Tp}^{\text{Me}}}(n) = -147.00n + 659.67$ ($r = 0.99997$); $\delta_{\text{Tp}}(n) = -145.85n + 621.75$ ($r = 0.99989$).

References

- [1] S. Trofimenko, *Chem Rev.*, 93 (1993) 943.
- [2] G. Gioia Lobbia, F. Bonati, P. Cecchi, A. Cingolani and A. Lorenzotti, *J. Organomet. Chem.*, 378 (1989) 139; (b) G. Gioia Lobbia, F. Bonati, P. Cecchi, A. Lorenzotti and C. Pettinari, *J. Organomet. Chem.*, 403 (1991) 317; (c) G. Gioia Lobbia, S. Calogero, B. Bovio and P. Cecchi, *J. Organomet. Chem.*, 440 (1992) 27; (d) S. Calogero, L. Stievano, G. Gioia Lobbia, A. Cingolani, P. Cecchi and G. Valle, *Polyhedron*, in press (1995).
- [3] G. Gioia Lobbia, P. Cecchi, R. Spagna, M. Colapietro, A. Pifferi and C. Pettinari, *J. Organomet. Chem.*, 485 (1995) 45.
- [4] S. Calogero, G. Gioia Lobbia, P. Cecchi, G. Valle and J. Friedl, *Polyhedron*, 13 (1994), 87–97.
- [5] D. Collison, D.R. Eardley, F.E. Mabbs, K. Rigby, M.A. Bruk, J.H. Enemark, P.A. Wexler, *J. Chem. Soc., Dalton Trans.*, (1994) 1003.
- [6] O.S. Jung, J.H. Jeong and Y.S. Sohn, *J. Organomet. Chem.*, 399 (1990) 235.
- [7] B.K. Nicholson, *J. Organomet. Chem.*, 265 (1984) 153.
- [8] R.W. Parish, in G.J. Long (ed.), *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, Vol. 1, Plenum, New York, 1984.