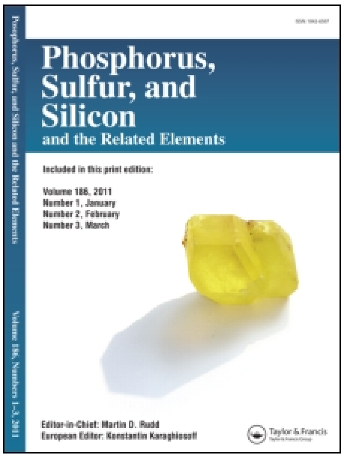

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SYNTHETIC, SPECTROSCOPIC AND APPLIED ASPECTS OF SOME OF THE ORGANOSILICON(IV) AND ORGAN0 TIN(IV) COMPLEXES

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SYNTHETIC, SPECTROSCOPIC AND APPLIED ASPECTS OF SOME OF THE ORGANOSILICON(IV) AND ORGANO TIN(IV) COMPLEXES

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Series of new trigonal bipyramidal and octahedral complexes of silicon(IV) and tin(IV) have been synthesized by the reactions of triphenylsilicon(IV) and triphenyltin(IV)chlorides with biologically potent bases derived by the condensation of heterocyclic ketones with thiosemicarbazide. Their geometries have been established on the basis of U.V., IR, ^{1}H, ^{29}Si and ^{119}Sn NMR spectral studies. The geometries of the compounds have been proposed on the basis of X-ray powder diffraction. All the bases and their metal complexes screened against several pathogenic fungal and bacterial strains. To compare the biopotency of these complexes, bases and their complexes were also tested for fungicidal properties on the brinjal plant. Key words: Silicon(IV) and tin(IV) complexes; thio-ligands; spectral studies; X-ray powder diffraction; biological screening; brinjal plant.

INTRODUCTION

There is a scope for studies on N and S/O donor systems regarding their biochemical significance. Recently, a variety of azomethine metal complexes have been synthesized[1,2]. Among the metallic compounds of p-block elements that have been studied are organosilicon and organotin compounds[3–5]. Wide use of these complexes has prompted an extensive evaluation of the general toxicology of these compounds[6,7]. The interest in organosilicon (IV) compounds is due to their versatile applicability in pharmaceutical and in chemical industries. For example use of very bulky silicon-containing ligands allows the isolation of a wide range of previ-

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ously inaccessible types of compounds and silicon substituted methyl groups are capable of making considerable adjustments, especially in the inner CSi_3 skeleton in response to the electronic demands of the adjacent element[8]. Organotin compounds are toxic to a variety of microorganisms and find widespread applications in biocidal compositions[9]. Recently, five of the dibutyltin compounds[10] were screened against six human tumour cell lines, MCF-7, EVSA-T, WiDr, IGROV, M 19 and A 498. Dibutyltin-dichloride and Sn-O bonded butyltin complexes[11] of cortexolones and erythromycine interfere with the DNA, RNA and protein synthesis and showing antitumour activity. Similarly Bu_2SnCl_2 and Ph_3SnCl inhibit selectivity in phosphorylation of lipocortin in rabbits and appeared in the recent literature dealing with the various aspects of applications[12,13]. Semicarbazones[14,15] and thiosemicarbazones[16,17] are also biologically important nitrogen and oxygen/sulphur donor ligands out of which thiosemicarbazones have been selected for the present studies.

RESULT AND DISCUSSION

Base L_1 reacts with methanolic solutions of Ph_3SiCl and Ph_3SnCl in 1:1 and 1:2 molar ratios to yield the addition products, $Ph_3MCl(L_1)$ and $Ph_3MCl(L_1)_2$.

The Ph_3SnCl and Ph_3SiCl react with the sodium salt of thiosemicarbazones L_2H and L_3H in 1:1 molar ratio in anhydrous methanol as follows (equations 1 – 4).

in case of ligand L_1

$$\mathbf{Ph_3MCl + L_1 \xrightarrow[1\,:\,1]{MeOH} Ph_3MCl(L_1)} \qquad \text{......(1)}$$

$$\mathbf{Ph_3MCl + 2L_1 \xrightarrow[1\,:\,1]{MeOH} Ph_3MCl(L_1)_2} \qquad \text{......(2)}$$

in case of ligands L_2H and L_3H

$$\mathbf{Ph_3MCl + L_2H \xrightarrow[Na]{MeOH} Ph_3M(L_2) + NaCl} \qquad \text{......(3)}$$

$$\mathbf{Ph_3MCl + L_3H \xrightarrow[Na]{MeOH} Ph_3M(L_3) + NaCl} \qquad \text{......(4)}$$

Where; M = Si or Sn

The resulting coloured solids are monomeric and possess sharp melting points. They are soluble in methanol, chloroform, DMF and DMSO.

SPECTRAL STUDIES

U.V. Spectra

In the electronic spectra of the bases, bands due to >C=N chromophere observed at ~365 nm, shift to the higher wave number region. Such a shift in the $n\text{-}\pi^*$ band is probably due to the donation of the lone pair of electrons by the nitrogen of the ligand to the central metal atom. Two bands at ~265 and 305 nm in the ligands attributable to $\pi\text{-}\pi^*$ transitions, remain unchanged in the complexes.

IR Spectra

IR spectra of the ligands show strong bands around 3300 and 2700 cm^{-1} due to νNH and νSH, respectively. The disappearance of both bands in case of metal complexes indicates that the S atom coordinates but not the nitrogen atom, since it is the azomethine nitrogen atom that coordinates instead. A sharp band around 1620 cm^{-1} due to νC=N of the free azomethine groups, shifts to higher frequency (*ca.* 15 cm^{-1}) in tin complexes while in case of silicon complexes there was a negative shift of same amplitude indicating coordination of the azomethine (>C=N) nitrogen atom to the metal atom.

Two sharp bands at *ca.* 3440 and 3350 cm^{-1} probably due to the asymmetric and symmetric vibrations of the NH_2 group in the ligand, remain almost unchanged in the spectra of the metal complexes, showing the non-involvement of this group in complexation. The band[19] at ~1035 cm^{-1} may be assigned to ν(C=S), which disappears in metal complexes due to covalent bond formation of the ligand with the metal through the sulphur atom.

Several new bands are observed in the spectra of complexes at ~580, ~530, ~420 and ~325 cm^{-1} due to ν(Si←N)[20], ν(Si-S)[21], ν(Sn←N)[22] and ν(Sn-S)[23] vibrations, respectively.

^{1}H NMR Spectra

The proton NMR spectra of ligands and their corresponding metal complexes were recorded in DMSO-d_6. The spectra of the ligands exhibit signals due to -CH aromatic protons, the -NH of the isatin ring and the -NH of thiosemicarbazone. The disappearance of the -NH signal of thiosemicarbazone in the organometallic derivatives indicate coordination of the azomethine nitrogen as well as covalent bond formation between metal and sulphur. Further, in the spectra of the complexes, a downfield shift in the position of the aromatic protons also indicates the coordination of the azomethine nitrogen to the metal atom.

The appearance of a signal due to the NH_2 group at about same position in the ligand and its metal complexes shows the non-involvement of this group in coordination.

^{29}Si and ^{119}Sn NMR Spectra

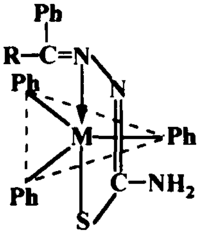
^{29}Si NMR spectra of $Ph_3SiCl(L_1)$ and $Ph_3SiCl(L_1)_2$ show signals at δ-92.04 and δ-124.08 ppm, respectively and which reveal the pentacoordinated[24] and hexacoordinated[25] environment for silicon atom. Similarly ^{119}Sn NMR spectra recorded for the triorganotin (IV) derivative $Ph_3SnCl(L_1)$ exhibits a single absorption at δ −154.0 ppm, typical of a five-coordinated central tin atom[26]. The ^{119}Sn chemical shift of the trialkyl tin(IV)complex $Ph_3SiCl(L_1)_2$ appeared at δ −238 ppm is typical of octahedral or pseudo-octahedral arrangement[27]. It has been noted[28] that the magnitude of the chemical shift (δ ^{119}Sn) of complexes having the same coordination number depends primarily on the type of substituents on the metal atom, on their electronegativity and on the geometric distortion.

X-ray diffraction Spectra

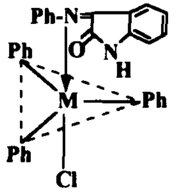
Further, to see the crystal lattice of the resulting compounds the X-ray powder diffraction studies of the products, $Ph_3Si(L_3)$ and $Ph_3Sn(L_3)$ have been carried out. The results show that both the compounds belong to the "orthorhombic" crystal system. Values of cell dimentions in case of $Ph_3Si(L_3)$ and $Ph_3Sn(L_3)$ are:

$Ph_3Si(L_3) \rightarrow$ a = 8.5528 A°, b=17.5255 A°, c=22.1243 A°
and V= 3316.2580 $(A°)^3$

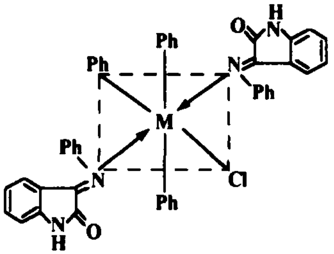
$Ph_3Sn(L_3) \rightarrow$ a = 8.1464 A°, b=23.9514 A°, c=23.7554 A°
and V= 4576.564 $(A°)^3$



(1:1 complex with Base L_2H or L_3H)

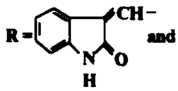


(1:1 complex with Base L_1)



(1:2 complex with Base L_1)

Where M = Si or Sn and



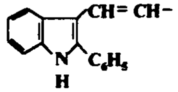


TABLE I ^{1}H NMR spectral data of bases and corresponding metal complexes

Compound	*NH (b) (ring)*	*NH (bs) free*	*NH_2 (bs)*	*Aromatic (m)*	*>C-N (s)*
L_1	11.16	–	–	6.95 – 6.32	7.72
$Ph_3SiCl(L_1)_2$	11.84	–	–	7.24–6.96	8.16
$Ph_3SnCl(L_1)_2$	11.24	–	–	7.08 – 6.56	8.08
L_2H	12.80	10.32	3.46	7.94 – 7.54	8.64
$Ph_3Si(L_2)$	12.96	–	3.72	8.64 – 7.16	9.12
$Ph_3Sn(L_2)$	12.64	–	3.52	8.24 – 7.72	9.08
L_3H	10.04	9.72	2.04	8.16–6.96	8.24
$Ph_3Si(L_3)$	10.72	–	3.12	8.40 – 7.12	8.56
$Ph_3Sn(L_3)$	10.08	–	2.08	8.48 – 6.96	8.80

Where, bs = broad singlet, s = singlet, m = multiplet.

The inter planer spacing values (d in A°), hkl values and 2θ angles are reported in Tables II and III.

TABLE II X-Ray diffraction data of compound $Ph_3Si(L_3)$

S. No.	*h*	*k*	*l*	*d*	*2Q*
1	o	1	3	6.8044	13.0
2	1	1	2	6.2759	14.10
3	1	2	1	5.9013	15.0
4	0	1	4	5.2729	16.8
5	0	3	3	4.5485	19.5
6	2	0	1	4.2070	21.10
7	0	5	0	3.4902	25.5
8	0	5	1	3.4902	25.5
9	3	3	4	2.3248	38.7
10	2	6	8	2.3248	38.7
11	3	6	1	2.0300	44.0

Refine, a = 8.5440 A°, b= 17.5570 A° and c = 22.1290 A°

TABLE III X-Ray diffraction data of compound $Ph_3Sn(L_3)$

S. No.	*h*	*k*	*l*	*d*	*2Q*
1.	0	2	3	6.6022	13.40
2.	1	2	2	5.9013	15.00
3.	0	4	2	5.3360	16.00
4.	1	4	0	4.8970	18.10
5.	0	3	3	4.5717	19.40
6.	0	2	5	4.4140	21.10
7.	1	5	0	4.1874	21.20
8.	1	1	5	4.0551	21.90
9.	2	0	0	4.0551	21.90
10.	2	2	3	4.4635	25.70
11.	2	3	2	3.4635	25.70
12.	0	0	7	3.3905	26.20
13.	1	4	5	3.3985	26.60
14.	1	5	4	3.3985	26.20
15.	0	5	5	3.3985	26.20
16.	2	3	3	3.2996	26.20
17.	1	0	7	3.1401	27.00
18.	0	8	1	2.9957	29.80
19.	2	2	5	2.9957	29.80
20.	0	8	3	2.8203	29.80

S. No.	h	k	l	d	2Q
21.	2	1	6	2.8203	29.80
22.	1	8	3	2.6574	31.70
23.	3	5	1	2.3481	38.30
24.	4	0	0	2.0343	44.50
25.	3	6	5	2.0343	44.50
26.	1	7	9	2.0343	44.50
27.	4	1	2	1.9960	44.50
28.	1	11	4	1.9960	44.40
29.	3	1	8	1.9960	44.40
30.	4	6	2	1.7925	50.90
31.	3	6	8	1.7925	50.90
32.	0	13	7	1.6300	56.40
33.	2	6	12	1.6300	56.40

Refine, a = 8.1300 A°, b = 24.1500 A° and c = 23.8000

BIOCIDAL SCREENING

The bases and their metal complexes have been screened against antibacterial and antifungal activities *in vitro* as well as *in vivo.*

Antifungal Activity (Hanging drop method)

This method is also known as spore germination method[29]. This includes depositions of chemicals on a slide, evaporation to dryness and addition of a drop of water containing spores of the test fungus.

Place a drop of spore suspension on a clear slide. Determine the number of spores in the drop under low power magnification and adjust the suspension to obtain nearly ten spore per microscopic field. These slides were incubated for 12 hours at 25 °C in petridishes working as moisture chambers. Slides were put in such a position that spore drops keep hanging. After incubation spore germination was counted. The each treatment was replicated thrice. In this technique total number of spores, number of germinated spores and number of ungerminated spores were counted. Lethal Dose (LD_{50}) values have been calculated to compare the activity of ligands with their chelates by plotting graphs between the concentration of ligands/complexes with the number of germinated spores.

The organisms selected for this method are; *Alternaria alternata* and *Helminthosporium gramineum.*

Comparison of LD_{50} values of bases with their complexes obtained from antifungal activity by Hanging Drop Method

Compound	*LD_{50} value in Alternaria alternata*	*LD_{50} values in Helminthosporium gramineum*
L_2H	150	90
$Ph_3Si(L_2)$	125	75
$Ph_3Sn(L_2)$	110	65
L_3H	130	80
$Ph_3Si(L_3)$	120	70
$Ph_3Sn(L_3)$	100	60

Antibacterial Activity (Paper disc method)

In this technique sterilized hot nutrient agar and 5 mm diameter paper disc of Whatman No. 1 were used. The agar medium was poured in the petri-plates. After solidifications the plates were stored in inverted position so that there was condensation of water in upper lid. Now bacterial suspension uniformly spreads on solidified nutrient agar. The solutions of test compounds in methanol, 500 and 1000 ppm concentrations were prepared in which discs were dipped in solution of the test sample placed on seeded plates. The petriplates having these discs on the seeded agar should be placed at low temperature for two or four hours to allow for the diffusion of chemical before being incubated at suitable optimum temperature 28 ± 2 °C for 24–30 hours and the inhibition zone around each disc was measured.

Antibacterial activity of bases and their corresponding metal complexes (after 96 h)

Compound	*Diameter of Inhibition Zone (mm)*			
	Pseudomonas cepacicola(-)		*Staphylococcus aureus(+)*	
	500	*1000*	*500*	*1000*
L_2H	10	11	8	9
$Ph_3Si(L_2)$	13	15	11	12
$Ph_3Sn(L_2)$	14	17	12	14
L_3H	12	14	10	11
$Ph_3Si(L_3)$	14	16	12	13
$Ph_3Sn(L_3)$	15	18	14	16

Percent Disease Incidence[30] (in vivo test)

The chemicals, found most effective against fungal and bacterial strains which were tested *in vitro*, were also tested in field for controlling the leaf spot of brinjal plant caused by *Alternaria alternata*.

Field experiments were laid out in randomized block design with three replications. The crops were raised in each plot. Compounds with a standard fungicide, Bavistin [2-(methoxycarbamyl)benzimidazole] were tried.

After sowing of forty five days, the plants were inoculated artificially by spraying the conidial suspension. The suspension was prepared by crushing the infected leaves in water. The first spray of the respective fungicide was given, when lesions were first seen and were repeated after ten days. Disease intensity was analysed statistically[31]and (%) disease control was worked out.

Present disease incidence (PDI), is given by,

$$\text{PDI} = \frac{\begin{array}{c}\text{Number of plant}\\ \text{units infected}\end{array} \times 100}{\begin{array}{c}\text{Total number}\\ \text{of plants observed}\end{array} \times \begin{array}{c}\text{Maximum}\\ \text{rating of score (10)}\end{array}}$$

The effectiveness of the compounds was calculated using equation –

$$\%\ \text{Disease control} = \frac{\begin{array}{c}\text{PDI in}\\ \text{treated plants}\end{array} - \begin{array}{c}\text{PDI in}\\ \text{untreated plants}\end{array}}{\begin{array}{c}\text{PDI in}\\ \text{untreated plants}\end{array}} \times 100$$

Two concentrations, i.e. 100 and 200 ppm were used in different plots and observations were recorded below in table.

The efficacy of compounds against leaf spot of Brinjal has been evaluated using percent disease incidence technique (PDI)

Treatment	*PDI in Treated Plants*	*% Disease Control*
L_2H	12	57
$Ph_3Si(L_2)$	9	68
$Ph_3Sn(L_2)$	8	71
L_3H	11	60
$Ph_3Si(L_3)$	7	75
$Ph_3Sn(L_3)$	6	78

PDI in Untreated Plants = 28

TABLE IV Physical properties and analytical data of complexes

Complex	*Colour*	*M.P. (°C)*	*Elemental Analysis (%)*				
			C Found (Calcd.)	*H Found (Calcd.)*	*N Found (Calcd.)*	*S Found (Calcd.)*	*Sn/Si Found (Calcd.)*
$Ph_3SiCl(L_1)$	Reddish yellow	240d	76.12	4.38	5.10	–	5.05
			(74.32)	(4.87)	(5.25)		(5.15)
$Ph_3SiCl(L_1)_2$	Mustard yellow	180	74.20	4.32	8.96	–	9.12
			(74.72)	(4.77)	(9.02)		(9.20)
$Ph_3Si(L_2)$	Reddish brown	137	72.17	4.98	7.40	4.50	4.32
			(72.38)	(5.03)	(7.50)	(4.40)	(4.28)
$Ph_3Si(L_3)$	Dark brown	110	77.00	5.13	9.81	6.05	4.50
			(77.08)	(5.38)	(10.03)	(5.85)	(4.80)
$Ph_3SnCl(L_1)$	Light yellow	138	63.04	4.01	4.40	–	19.39
			(63.24)	(4.14)	(4.60)		(19.50)
$Ph_3SnCl(L_1)_2$	Yellow	165	66.15	4.08	3.18	–	28.50
			(66.57)	(4.25)	(3.38)		(28.50)
$Ph_3Sn(L_2)$	Orangish yellow	210	62.02	4.18	7.02	4.48	10.29
			(62.61)	(4.35)	(7.51)	(4.30)	(10.56)
$Ph_3Sn(L_3)$	Greenish black	Sticky	67.15	4.50	8.06	4.93	17.11
			(67.66)	(4.73)	(8.15)	(4.70)	(17.60)

CONCLUSION

Knowledge of the mechenism of the action of compound is important from a purely scientific point of view. Here we have distinguished three different methods by which complexes can exert their action.

(1) The effect of resonating structures[32], such as benzene rings (in present case) may serve as powerhouse to activate potentially reactive groupings. If toxicity is dependent on one or more chemical reactions, then any molecule which would increase the rate of chemical reactions must, perforce, enhance toxicity.

(2) The introduction of a lipophilic substituent, either aryl or alkyl, often conferred toxicity as did the substitution of polar groups[33].

(3) Complexes having amido groups or reactive halogen atoms tend to hydrolyse to form compounds, which have modified activity spectrum. The halogen replaced by hydroxyl ion and as a result of slight alkaline pH the increase in activity was observed.

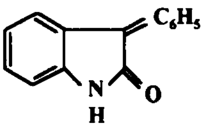
EXPERIMENTAL

Adequate precautions were taken to exclude moisture while carring out the reactions. The reactions were carried out in glass apparatus fitted with interchangeable joints. The reagents methanol (BDH), toluene (BDH) and ethanol (BDH) were dried and distilled before use. Ph_3SiCl (Aldrich), Ph_3SnCl (Merck-Schuchardt), thiosemicarbazide (Sisco-Chem), aniline (BDH) and derivatives of indol (Fluka) were used as such. Reactions were carried out in a distillation assembly, fitted with condenser and protected by guard tubes.

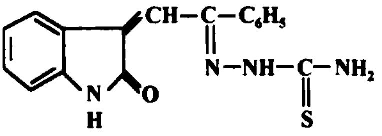
Preparation of Bases

The following bases were prepared and used in present investigations:

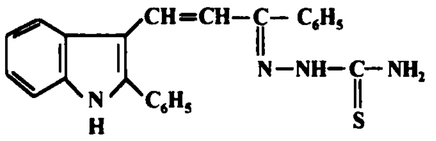
Base (L_1) was prepared by the reaction of aniline (0.043 mol, 4.0 g) with 2,3-indolenedione (0.04 mol, 6.3 g) in dry toluene. The reaction mixture was refluxed for 5–6 hours under anhydrous conditions. The resulting product, 3-phenylimino-2H-indol-2-one was isolated and recrystallized in 100 cm^3 ethanol.



(L_1)



(L_2H)



(L_3H)

Base L_2H was prepared by the refluxing of 1,3-dihydro-3-[2-(phenyl)-2-oxoethylidene]-2H-indol-2-one (0.028 mol, 7 g) with thiosemicarbazide (0.27 mol, 2.55 g) in the presence of absolute alcohol (60 cm^3). The product (Ligand L_2H) was isolated by recrystallization from ethanol (50 cm^3).

Base L_3H was synthesized by the reaction of 2-phenyl-3-(3-phenyl-3-oxoprop-1-enyl)-indole (0.026 mol, 8.5 g) with thiosemicarbazide (0.026 mol, 2.39 g) in absolute alcohol (100 cm^3) for half an hour. The product L_3H was isolated after removing the solvent and recrystallised from 100 cm^3 ethanol.

Preparation of complexes

To Ph_3SiCl (0.01 mol, 2.94 g) and Ph_3SnCl (0.01 mol, 3.85 g) the methanolic solution of L_1 (0.01 mol, 2.22 g) was added in 1:1 and 1:2 molar ratios. For bases L_2H and L_3H a weighed amount (as above) of Ph_3SiCl and Ph_3SnCl was added in sodium salt of bases L_2H (0.01 mol, 3.22 g) and L_3H (0.01 mol, 3.96 g) in 1:1 molar ratio and mixtures were mixed in dry methanol (60 cm^3). Resulting solution was refluxed for 5–6 hours, filtered to remove sodium chloride (in case of Bases 2 and 3). The compounds were purfied by crystallization. Their purity was checked by TLC.

The U.V. spectra were recorded on a Perkin Elmer Ultraviolet/Visible spectrophotometer in the range of 200–500 nm. IR spectra were recorded as KBr pellets on a FTIR spectrophotometer, model Megna IR-550. ^1H NMR spectra were recorded on Jeol FX 90Q spectrometer in DMSO-d_6

using TMS as internal standard. ^{29}Si and ^{119}Sn NMR spectra were also recorded in same spectrometer. Carbon and hydrogen analyses were performed at the microanalytical laboratory of the Department. Nitrogen and sulphur were determined by Kjeldahl's and Messenger's methods, respectively. Tin was estimated as tin oxide and silicon was estimated as SiO_2. The X-ray powder diffraction of the complexes were obtained on a Philips PW 1130/00 automatic diffractometer using Cu-Kα target with nickel filter at the Department of Zoology, University of Delhi, Delhi.

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References

[1] A. Arquero, M. A. Mendiola, P. Souza and M. T. Sevilla, Polyhedron, 15, 1657 (1996).

[2] Y. P. Tian, C. Y. Duan, Z. L. Lu, X. Z. You, H. K. Fun and S. Kandasamy, Polyhedron, 15, 2263 (1996).

[3] M. Kumada, J. Organometal, Chem., 500, 195 (1995).

[4] T. Hamasaki, T. Sato, H. Nagase and H. Kito, Appl. Organometal. Chem., 9, 693 (1995).

[5] H.-S. Dang and A. G. Davies, J. Organomet. Chem., 430, 287 (1992).

[6] D. W. Allen, D. J. Derbyshire, J. S. Brooks and P. J. Smith, J. Organomet. Chem., 251, 45 (1983).

[7] M. Gielen, Main Group Met. Chem., 1, 17 (1994).

[8] C. Eaborn, K. Izod and J. D. Smith, J. Organometal. Chem., 500, 89 (1995).

[9] M. Gielen, P. Lelieveld, D. de Vos and R. Williem, Metal – based Antitumor Drugs, 2, 29 (1992).

[10] M. Gielen, A. Bouhdid, F. Kayser, M. Biesemans, D. de Vos, B. Mahieu and R. Willem, Appl. Organometal. Chem., 9, 251 (1995).

[11] A. H. Penninks, M. Bol-Schoenmakers, M. Gielen and W. Seinen, Main Group Met. Chem., 12, 1(1989).

[12] Y. Arakawa, Main Group Met. Chem., 12, 31 (1989).

[13] L. Pellerito, F. Maggio, M. Consiglio, A. Pellerito, G.C. Stocco and S. Grimaudo, Appl. Organomet. Chem., 9, 227 (1995).

[14] A. Saxena and J.P. Tandon, Polyhedron, 3, 681 (1984).

[15] T. N. Srivastava and M. A. Siddiqui, J. Indian Chem., Soc., 64, 500 (1987).

[16] M. A. Ali, K. K. Dey, M. Nazimuddin, F. E. Smith, R. J. Butcher, J. P. Jasinski and J. M. Jasinski, Polyhedron, 15, 3331 (1996).

[17] L. Labib, T.E. Khalil and M. F. Iskander, 15, 349 (1996).

[18] S. V. Singh and R. V. Singh, Synth. React. Inorg. Met. – Org. Chem., 17, 947 (1987).

[19] M. N. Mookerjee, R. V. Singh and J. P. Tandon, Synth. React. Inorg. Met. – Org. Chem., 12, 621 (1982).

[20] E. A. V. Ebsworth and M. J. Mays, J. Chem. Soc., 3450 (1964).

[21] R. Dashora, R. V. Singh and J. P. Tandon, Synth. React. Inorg. Met.-Org. Chem., 13, 209 (1983).

[22] A. Saxena, J. P. Tandon, K. C. Molloy and J. J. Zukerman, Inorg. Chim. Acta, 63, 71 (1982).

[23] G. Domazetis, R. J. Magee and B. D. James, J. Inorg. Nucl. Chem., 43, 1351 (1981).

[24] I. Kalikhman, S. Krivonos, A. Ellern and D. Kost, Organometallics, 15, 5073 (1996).
[25] B. Stadelmann, P. Lassacher, H. Stiiger and E. Hengge, J. Organometal. Chem., 482, 201 (1994).
[26] M.F. Mahon, K.C. Molloy, B. A. Omotowa and M. A. Mesubi, J. Organometal. Chem., 511, 227 (1996).
[27] C. Pettinari, F. Marchetti, A. Cingolani and S. Bartolini, Polyhedron, 15, 1263 (1996).
[28] P. G. Harrison (Ed.), Investigating Tin Compounds Using Spectroscopy in Chemistry of Tin, Ch. 3, 71 (1989).
[29] Y. L. Nane and P. N. Thapliyal, "Fungicides in Plant Disease Control", II ed. Oxford and IBH Publishing Co., 105 (1979).
[30] D.P. Thakur, S.B. Mathur and J. Khandhari, Seed and Farms, 8 (4), 25 (1982).
[31] W. C. James, Can Plant Dis. Surv., June issue, 51 (2) (1971).
[32] J. D. Froyd, C. J. Paget, L. R. Guse, B. A. Dreikorn and J. P. L. Pafford: Tricyclazole: "A New Systemic Fungicide for Control"; (1976).
[33] M. C. Tokousbalides and H. D. Sisler, Pestic. Biochem. Physiol., 8, 26 (1978).