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Studies of biologically potent organotin(IV) and organosilicon(IV) complexes of a sulfur donor ligand derived from 1-acetylferrocene

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The coordination and organometallic chemistry of metal–nitrogen- and metal–sulfur-bonded compounds have come to occupy a prominent position in research due to their economical importance in the field of agricultural, medicinal and industrial chemistry. Although Schiff bases of ferrocene derivatives and their metal complexes with lanthanide and transition metal ions have been synthesized and some of their structures characterized, their interaction with main group metal ions and the formation of their coordination complexes are subjects of current interest. This communication deals with a description of synthetic procedure and structural characterization on the basis of analytical and spectroscopic techniques of a new class of coordination compounds of organotin(IV) and organosilicon(IV) with a sulfur-containing ligand moiety derived by the condensation of 1-acetylferrocene and thiosemicarbazide. Finally, attempts have been made to establish a correlation between a variety of biointeraction activities, including antimicrobial activity and antifertility activity, on male rats and the structures of the resulting products on the basis of different constituents and chemical phenomena. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: organotin(IV) complexes; organosilicon(IV) complexes; Schiff base; spectroscopic techniques; antimicrobial screening; antifertility test

INTRODUCTION

Ferrocene-containing metal complexes are multinuclear molecules possessing both the features of organometallics and of coordination compounds.[1] Ferrocene derivatives containing atoms with good donor abilities are of additional interest because the coordination of a metal to these heteroatoms produces heteropolynuclear organometallic compounds containing ferrocene units, in which the presence of metals in different environments may influence the interaction of these metals in a variety of processes.[2] Recently, Schiff bases of ferrocene derivatives[2–4] and their metal complexes with lanthanide[5,6] and transition metal[7,8] ions were synthesized and some of their structures characterized. Keeping in view the significance of thiosemicarbazones as chemotherapeutic agents[9] and also in biomimetic catalytic activities,[10–14] and the chemistry of ferrocenyl-containing compounds as stable intermediates and their applications in improving the medicinal properties,[14–18] an effort to join the chemistry of thiosemicarbazide and ferrocene has been made. This paper describes the synthesis of the complexes R_3ML and R_2MCl_{2-n} (L_n) (M = Sn or Si, R = Me or Ph; n = 1 or 2, L = anion of 1-acetylferrocenethiosemicarbazone) with a view to studying the effect of coordination on antimicrobial activity and to explore the possibility of their use as potential biocidal agents. The fungi and bacteria were selected in view of their economical importance. The compounds which showed good antimicrobial activity have been chosen for antifertility test in male rats.

RESULTS AND DISCUSSION

Tri- and di-organotin(IV)/silicon(IV) derivatives of 1-acetylferrocenethiosemicarbazone have been synthesized by the

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Table 1. UV–VIS spectral data of LH ligand and its metal complexes

Compound	λ_{max}/nm			
	1	**2**	**3**	**4**
LH	270	292	375	416
$Me_3Sn(L)$	261	319	365	415
$Me_2SnCl(L)$	263	312	363	416
$Me_2Sn(L)_2$	260	316	365	414
$Ph_3Sn(L)$	258	324	352	415
$Ph_2SnCl(L)$	259	318	347	413
$Ph_2Sn(L)_2$	255	226	355	417
$Me_3Si(L)$	263	316	367	416
$Me_2SiCl(L)$	266	310	364	413
$Me_2Si(L)_2$	264	314	369	416
$Ph_3Si(L)$	260	321	354	414
$Ph_2SiCl(L)$	262	316	350	417
$Ph_2Si(L)_2$	259	320	356	413

reactions of corresponding tri- and di-organotin(IV)/silicon (IV) chlorides with the sodium salt of 1-acetylferrocenethiosemicarbazone in 1:1 and 1:2 molar ratios respectively in dry methanol, as shown by the following reactions.

$$R_3MCl + \overset{\frown}{N\ S}.Na \longrightarrow R_3M(\overset{\frown}{N\ S}) + NaCl \quad (1)$$

$$R_2MCl_2 + n\overset{\frown}{N\ S}.Na \longrightarrow R_2MCl_{2-n}(\overset{\frown}{N\ S}) + nNaCl \quad (2)$$

where R = Ph or Me, M = Sn or Si, n = 1 or 2 and $\overset{\frown}{N\ S}$ is the donor set of the ligand LH.

The monomeric nature of these coloured solids is confirmed by their molecular weights. All the complexes are soluble in most of the common organic and coordinating solvents. These were purified by repeated washing with suitable solvent and their purity was checked by thin-layer chromatography (TLC) on silica gel. The molar conductance of 10^{-3} M solutions of the compounds in anhydrous DMF lie in the range 10–23 Ω^{-1} cm^2 mol^{-1}, which shows their non-electrolytic nature.

UV spectra

The UV–VIS absorption spectral data of the ligand and its tin and silicon complexes are listed in Table 1. The spectrum of the ligand LH shows a broad band at 375 nm that can be assigned to the n–π^* transitions of the azomethine group, which undergoes a blue shift in the metal complexes due to polarization within the C═N chromophore caused by the metal–ligand interaction.[19] The K band π–π^* transitions of the ligand is observed at 292 nm, which undergoes a red shift in the complexes. This shift can be attributed to the overlap of the central metal d orbital with the p orbital of the donor atom, which causes an increase in conjugation in the ligand and thus lowers the π–π^* energy.[20,21] The B band observed at 270 nm can be attributed to the cyclopentadienyl rings that undergo a hypsochromic shift in the complexes.[22] The broad absorption band at 416 nm in the ligand is assigned to charge transfer from the iron to either the non-bonding or antibonding orbitals of the cyclopentadienyl rings. These absorption bands become weaker with no appreciable shift in the position in the spectra of their metal complexes.[21,23]

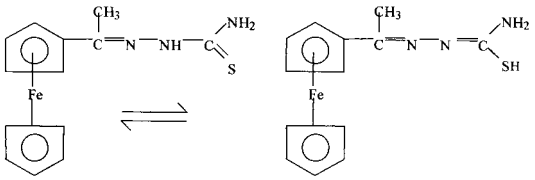
IR spectra

The most important IR adsorption frequencies, along with the relative assignments of the ligand and its metal complexes, are summarized in Table 2. The spectra of the

Table 2. IR absorption bands (cm^{-1}) of LH ligand and its metal/metalloid complexes[a]

Compound	ν(N—H)	ν(C═N)	ν(N—N)	δ(N—H)	ν(M⟶N)	ν(M—S)	ν(M—Cl)
LH	3400–3130 m	1525 vs	960 m	1610 w	–	–	–
$Me_3Sn(L)$	–	1519 vs	965 m	–	406 w	314 m	–
$Me_2SnCl(L)$	–	1515 vs	970 m	–	404 w	321 m	342 m
$Me_2Sn(L)_2$	–	1517 vs	965 m	–	409 w	316 m	–
$Ph_3Sn(L)$	–	1511 vs	976 m	–	402 w	319 m	–
$Ph_2SnCl(L)$	–	1513 vs	974 m	–	400 w	324 m	354 m
$Ph_2Sn(L)_2$	–	1510 vs	975 m	–	401 w	322 m	–
$Me_3Si(L)$	–	1522 vs	967 m	–	570 w	530 m	–
$Me_2SiCl(L)$	–	1518 vs	972 m	–	568 w	536 m	493 m
$Me_2Si(L)_2$	–	1520 vs	969 m	–	572 w	532 m	–
$Ph_3Si(L)$	–	1512 vs	979 m	–	565 w	534 m	
$Ph_2SiCl(L)$	–	1515 vs	976 m	–	562 w	539 m	504 m
$Ph_2Si(L)_2$	–	1513 vs	978 m	–	566 w	537 m	–

[a] m: medium; vs: very strong; w: weak.



Scheme 1.

free ligand LH display absorption bands at 3130–3420 cm^{-1}, 1525 cm^{-1}, 1610 cm^{-1}, 1046 cm^{-1} and 960 cm^{-1} and are assigned to ν(N—H), ν(C=N), δ(N—H), ν(C=S) and ν(N—N) respectively.[7] The characteristic bands of the ferrocenyl group[24] appear at 3080 cm^{-1}, 1449 cm^{-1}, 1110 cm^{-1} and 827 cm^{-1} arising from ν(C—H), ν(C=C), δ(C—H) and π(C—H) respectively.

Several significant changes with respect to the ligand are observed in the corresponding metal complexes. The ν(N—H), δ(N—H) and ν(C=S) absorption bands are absent in complexes, indicating ligand enolization[25] followed by deprotonation during complexation to the metalloid and metal (Scheme 1). A sharp band at 1525 cm^{-1} due to ν(=C=N) is shifted to a lower frequency (*ca* 15 cm^{-1}) in the complexes. Several new bands observed in the far IR region of the tin complxes[26,27] at ~325 cm^{-1}, 415 cm^{-1} and 360 cm^{-1} are assigned to ν(Sn—S), ν(Sn ⟶ N) and ν(Sn—Cl) modes respectively, and bands in silicon complexes at ~540 cm^{-1}, 580 cm^{-1} and 510 cm^{-1} are assigned to ν(Si—S),[28] ν(Si ⟶ N)[29] and ν(Si—Cl)[30] modes respectively. Some strong- to medium-intensity bands appear in the spectra of complexes in the regions 1260–1250 cm^{-1}, 1230–1180 cm^{-1} and 1125–1100 cm^{-1} and can be assigned to the (Si—CH_3), (Sn—CH_3) and (Si—Ph) stretching vibrations respectively.

The presence of only one ν(Si ⟶ N) band in the silicon complexes suggests that 1:2 complexes exist in the trans form. Similarly, the presence of only one (Sn—C) stretching frequency at 556 cm^{-1} suggests that the 1:2 complexes of tin exist in the trans form. For the trimethyltin and trimethylsilicon complexes one band is observed at ~560 cm^{-1} and 730 cm^{-1} respectively, due to Sn—C and Si—C stretching frequencies, suggesting planar arrangements of the M—Me moiety; i.e. the two donor atoms from the Schiff base occupy cis-axial-equatorial positions, which has been confirmed based on Mössbauer spectroscopy and X-ray crystallography.[31,32] The proposed structure is also supported by the comparatively low δ(^{119}Sn) and δ(^{29}Si) values of the triphenyltin and triphenylsilicon complexes.

^{1}H NMR Spectra

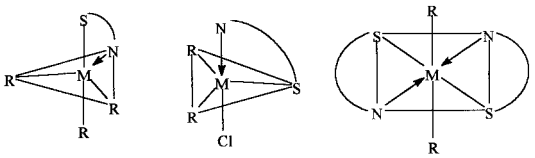
The proton magnetic resonance spectral data of the ligand LH and its corresponding metal/metalloid complexes were recorded in DMSO-d_6. The chemical shift values relative to the tetramethylsilane (TMS) peak are listed in Table 3. The broad signal due to the —NH proton in the ligand disappears in the case of metal/metalloid complexes, showing the bonding of thiolic sulfur to the metal/metalloid after the deprotonation of the functional group. The signals observed at δ 2.11 and 2.24 ppm in the ligand LH are due to methyl protons of the (H_3C—C=N) group. The downfield shift of these positions in the spectra of the complexes substantiates the coordination of azomethine nitrogen to the metal atom. The protons on the substituted cyclopentadienyl ring undergo a downfield shift relative to that of the ligand.

The additional signals in the region δ 0.63–1.17 ppm, δ 7.52–8.34 ppm, δ 0.5–0.8 ppm and δ 6.20–6.34 ppm are due to (CH_3Sn), (C_6H_5Sn), (CH_3Si) and (C_6H_5Si) groups respectively.

Table 3. ^{1}H NMR spectral data of the ligand and its complexes (δ/ppm)[a]

Compound	C_5H_5	C_5H_4		CH_3	NH_2	M—CH_3/C_6H_5	NH	^{119}Sn/^{29}Si
		2,5-H	3, 4-H					
LH	4.28 (s, 5H)	4.74 H (s, 2H)	4.56 (s, 2H)	2.24 (s, 3H)	2.63 (br, 2H)	–	8.82 (br, 1H)	–
Me_3Sn(L)	4.23 (s, 5H)	4.83 (s, 2H)	4.53 (s, 2H)	2.29 (s, 3H)	2.46 (br, 2H)	0.66	–	−172.36
Me_2SnCl(L)	4.24 (s, 10H)	4.81 (s, 2H)	4.54 (s, 4H)	2.34 (s, 3H)	6.24 (br, 2H)	1.12	–	−155.12
$Me_2Sn(L)_2$	4.23 (s, 5H)	4.79 (s, 4H)	4.52 (s, 2H)	2.31 (s, 6H)	2.43 (br, 4H)	1.03	–	−362.28
Ph_3Sn(L)	4.22 (s, 10H)	4.80 (s, 2H)	4.54 (s, 4H)	2.27 (s, 3H)	2.50 (br, 2H)	8.08	–	−153.53
Ph_2SnCl(L)	4.23 (s, 5H)	4.77 (s, 2H)	4.52 (s, 2H)	2.31 (s, 3H)	2.61 (br, 2H)	7.86	–	−120.64
$Ph_2Sn(L)_2$	4.25 (s, 5H)	4.76 (s, 4H)	4.53 (s, 2H)	2.29 (s, 6H)	2.56 (br, 4H)	8.26	–	−335.41
Me_3Si(L)	4.18 (s, 10H)	4.79 (s, 2H)	4.37 (s, 4H)	2.28 (s, 3H)	2.23 (br, 2H)	0.62	–	−99.35
Me_2SiCl(L)	4.19 (s, 5H)	4.73 (s, 2H)	4.38 (s, 2H)	2.30 (s, 3H)	2.92 (br, 2H)	0.78	–	−88.66
$Me_2Si(L)_2$	4.18 (s, 10H)	4.70 (s, 4H)	4.39 (s, 4H)	2.24 (s, 6H)	2.81 (br, 4H)	0.71	–	−116.53
Ph_3Si(L)	4.19 (s, 5H)	4.78 (s, 2H)	4.38 (s, 2H)	2.25 (s, 3H)	2.72 (br, 2H)	6.30	–	−90.45
Ph_2SiCl(L)	4.20 (s, 5H)	4.76 (s, 2H)	4.37 (s, 2H)	2.26 (s, 3H)	2.80 (br, 2H)	6.22	–	−79.38
$Ph_2Si(L)_2$	4.21 (s, 10H)	4.67 (s, 4H)	4.40 (s, 4h)	2.29 (s, 6H)	2.73 (br, 4H)	6.34	–	−108.07

[a] s: singlet; br: broad.



Scheme 2.

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

Quantitatively, $\delta(^{119}Sn)$ values depend on the coordination number,[33] on the nature of the ligand, and on the ligand bite.[34] In any series of organotin compounds, factors leading to increase in electron density (shielding) of the tin atom would shift the $\delta(^{119}Sn)$ to higher field. Structurally, a more informative property of the ^{119}Sn chemical shifts is the growing upfield shift of $\delta(^{119}Sn)$ with increasing coordination number of the tin atom from 4 to 5, 6 or 7. Sharp signals at $\sim\delta$ −120.64 to −172.36 ppm and δ −335.41 to −362.28 ppm in the ^{119}Sn NMR spectra strongly support penta- and hexa-coordination around the tin atom. Similarly, in the case of silicon complexes, sharp signals at $\sim\delta$ −79.38 to −99.35 ppm and δ −108.07 to −116.53 ppm clearly indicate the penta- and hexa-coordination environments respectively around the silicon atom.

On the basis of the results discussed so far, including the analytical and spectral data, a pentacoordinated trigonal bipyramidal geometry is suggested for 1:1 tri- and diorganometal derivatives and hexacoordinated octahedral geometry for 1:2 diorganometal derivatives (Scheme 2).

Biocidal screening

The fungicidal and bactericidal data reported in Tables 4 and 5 indicate that the activity of the ligand was

Table 4. Average percentage inhibition after 96 h

Compound	*F. oxysporum*			*A. niger*			*M. phaseolina*		
	50 ppm	100 ppm	200 ppm	50 ppm	100 ppm	200 ppm	50 ppm	100 ppm	200 ppm
LH	74	80	86	83	88	92	85	88	92
$Me_3Sn(L)$	88	97	98	95	96	96	96	97	98
$Me_2SnCl(L)$	80	88	91	88	92	95	88	92	94
$Ph_3Sn(L)$	92	98	98	94	99	100	95	100	100
$Ph_2SnCl(L)$	86	97	98	92	95	96	94	96	98
$Ph_2Sn(L)_2$	98	100	100	96	100	100	98	100	100
$Me_3Si(L)$	84	89	89	88	91	96	91	95	95
$Me_2SiCl(L)$	74	79	83	79	84	86	81	87	91
$Ph_3Si(L)$	88	91	92	91	92	95	94	96	96
$Ph_2SiCl(L)$	81	85	91	83	86	94	84	90	90
$Ph_2Si(L)_2$	90	92	95	93	92	95	94	96	96
Standard (Bavstin®)	91	100	100	86	98	100	82	96	100

Table 5. Diameter of inhibition zone (mm) after 24 h

Compounds	*E. coli* (−)		*K. aerogenous* (−)		*P. cepaciocola* (−)		*S. aureus* (+)	
	500 ppm	1000 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm
LH	7	10	7	10	8	12	12	16
$Me_3Sn(L)$	10	13	12	15	11	14	17	19
$Me_2SnCl(L)$	8	11	9	12	9	12	14	18
$Ph_3Sn(L)$	12	16	13	16	14	17	17	20
$Ph_2SnCl(L)$	11	13	12	14	12	15	15	14
$Ph_2Sn(L)_2$	14	16	13	17	16	18	17	21
$Me_3Si(L)$	8	11	8	10	9	12	14	19
$Me_2SiCl(L)$	7	10	7	8	8	11	12	16
$Ph_3Si(L)$	11	14	13	14	13	16	15	18
$Ph_2SiCl(L)$	9	12	8	12	10	12	12	16
$Ph_2Si(L)_2$	12	15	14	14	13	16	16	19
Standard (streptomycin)	1	2	3	5	2	3	15	17

Table 6. Effects of various compounds on sperm dynamics and fertility of male rats (values are expressed as mean plus/minus SE)

Compound	Sperm motility (Cauda epididymis) (%)	Sperm density		Fertility test
		Testes	Cauda epididymis	
Vehicle alone (olive oil)	78.5 ± 4.8	4.3 ± 0.42	61.1 ± 4.8	100% positive
LH	42.5 ± 3.5^b	2.4 ± 0.10^b	49.5 ± 3.5^b	80% negative
$Ph_2Sn(L)_2$	34.0 ± 4.8^a	1.2 ± 0.12^c	30.0 ± 3.2^c	95% negative
$Ph_3Si(L)$	40.0 ± 5.5^c	1.9 ± 0.15^c	35.5 ± 4.7^c	88% negative
$Ph_2Sn(L)Cl$	38.0 ± 3.6^b	1.6 ± 0.14^c	33.6 ± 5.5^b	91% negative
$Ph_3Sn(L)$	35.0 ± 4.2^c	1.3 ± 0.18^b	31.4 ± 6.1^c	92% negative

[a] $P < 0.001$.
[b] $P < 0.01$.
[c] $P < 0.02$.

appreciably enhanced on complexation with organotin/silicon halides. This may be explained by chelation theory,[35] according to which chelation reduces the polarity of the central metal atom because of partial sharing of its positive charge with the donor groups and possible π-electron delocalization within the whole chelate ring. This chelation increases the lipophilic nature of the central atom, which favours the permeation of the complexes through the lipid layer of the cell membrane. Compounds inhibit the growth of fungi and bacteria to a greater extent as concentration is increased. Also, the complexes of organotin chlorides were found to be more potent than organosilicon complexes and free ligand. In addition, the complexes of triorganotin halide were found to possess higher activity than their diorganotin counterparts, which is in agreement with earlier reports.[16]

From the bactericidal activity, it is apparent that the complexes were more toxic towards Gram(+) strains than Gram(−) strains. The reason is the difference in the structures of the cell walls. The walls of Gram(−) cells are more complex than those of Gram(+) cells. Lipopolysaccharides form an outer lipid membrane and contribute to the complex antigenic specificity of Gram(−) cells.

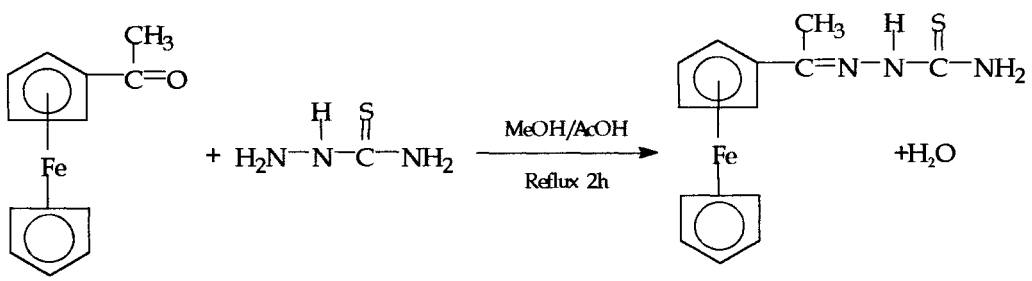
Experiments were conducted *in vivo* in male rats to check antifertility activity. Compounds that showed good antifungal and antibacterial activity were chosen for antifertility tests on male rats. The results reported in Table 6 reveal that there is a significant decrease ($P < 0.01$) in the motility, from 78.5 ± 4.8 to 42.5 ± 3.5, in the animals treated with ligand; the sperm density also decreased ($P < 0.001$) from 4.3 ± 0.42 to 2.4 ± 0.10 in testes, and from 61.1 ± 0.8 to 49.5 ± 3.5 in Cauda epididymis. A highly significant ($P < 0.001$) decline in the motility of sperm was observed in the case of tin complexes compared with silicon complexes. These results may also be correlated with the well-known fact that sulfur-containing compounds produce infertility in male rats.[36] Thus, it can be postulated that chelation through sulfur atoms induces the sterilizing activity in the biological systems.

EXPERIMENTAL

All the chemicals and solvents used were dried and purified by standard methods. The thiosemicarbazone ligand of 1-acetylferrocene was prepared by the method below, and was purified by recrystallizing in the same solvent and drying the crystals under reduced pressure. The purity was checked by TLC.

Preparation of 1-acetylferrocenethiosemicarbazone ligand (LH)

The ligand (LH) was prepared by the condensation of 1-acetylferrocene (1.0 g, 4.4 mmol) dissolved in MeOH (25 cm^3) with thiosemicarbazide (0.4 g, 4.4 mmol) in the presence of a few drops of AcOH. The contents were



Scheme 3.

Table 7. Synthetic and analytical data of metal complexes

Compound	Reactant (g [mmol])			M.p. (°C)	Yield (%)	Elemental analysis (%)[a]					MW[a]
	M	LH	Na			C	H	Sn/Si	N	S	
$Me_3Sn(L)$	1.14 [5.72]	1.72 [5.71]	0.14 [6.09]	178	74	42.41 (42.52)	4.98 (5.12)	26.23 (26.26)	9.21 (9.30)	6.94 (7.09)	429 (451.96)
$Me_2SnCl(L)$	1.36 [6.19]	1.86 [6.18]	0.15 [6.49]	203	73	37.02 (37.19)	4.09 (4.16)	24.48 (24.50)	8.44 (8.67)	6.49 (6.62)	470 (484.39)
$Me_2Sn(L)_2$	1.21 [5.51]	3.32 [11.02]	0.29 [11.74]	162	70	44.65 (44.89)	4.72 (4.84)	15.80 (15.84)	11.09 (11.22)	8.45 (8.56)	732 (749.12)
$Ph_3Sn(L)$	1.78 [4.62]	1.39 [4.62]	0.12 [5.22]	134	77	57.09 (57.27)	4.38 (4.50)	18.22 (18.25)	6.31 (6.46)	4.79 (4.93)	631 (650.18)
$Ph_2SnCl(L)$	1.56 [4.54]	1.36 [4.52]	0.10 [4.35]	240	82	49.23 (49.34)	3.79 (3.98)	19.44 (19.50)	6.82 (6.91)	5.14 (5.27)	592 (608.53)
$Ph_2Sn(L)_2$	1.45 [4.22]	2.54 [8.43]	0.19 [8.26]	254	70	52.19 (52.27)	4.26 (4.39)	13.53 (13.59)	9.44 (9.62)	7.21 (7.34)	858 (873.26)
$Me_3Si(L)$	1.55 [14.27]	4.30 [14.28]	0.34 [14.95]	232	72	53.01 (53.18)	6.28 (6.42)	7.72 (7.77)	11.50 (11.63)	8.64 (8.87)	342 (361.36)
$Me_2SiCl(L)$	1.74 [13.48]	4.06 [13.48]	0.32 [14.13]	108	79	45.43 (45.75)	5.04 (5.12)	7.06 (7.13)	10.48 (10.67)	8.06 (8.14)	377 (393.79)
$Me_3Si(L)_2$	1.19 [9.22]	5.55 [18.43]	0.44 [19.14]	170	72	50.91 (51.07)	5.16 (5.20)	4.19 (4.26)	12.59 (12.76)	9.62 (9.74)	635 (658.52)
$Ph_3Si(L)$	1.82 [6.17]	1.86 [6.17]	0.15 [6.47]	146	70	66.37 (66.47)	5.08 (5.22)	4.97 (5.02)	7.36 (7.51)	5.52 (5.73)	540 (552.50)
$Ph_2SiCl(L)$	1.63 [6.44]	1.94 [6.44]	0.16 [6.75]	>300	82	57.84 (57.98)	4.48 (4.67)	5.36 (5.42)	8.06 (8.11)	6.08 (6.19)	502 (517.93)
$Ph_2Si(L)_2$	1.23 [4.86]	2.93 [9.73]	0.23 [10.20]	270	76	58.21 (58.32)	4.73 (4.86)	3.55 (3.59)	10.57 (10.74)	8.06 (8.19)	756 (782.66)

[a] Calculated values are given in parentheses.

refluxed for 2 h in a flask fitted with a nitrogen gas inlet and condenser. The solution was then concentrated under reduced pressure, which on cooling gave an orange–yellow crystalline solid (m.p. 143 °C). This was recrystallized twice with petroleum ether (b.p. 30–40 °C) and dried under vacuum (Scheme 3).

Preparation of the complexes

To a weighed quantity of the organotin/silicon chloride in dry methanol, a calculated amount of the sodium salt of the 1-acetylferrocenethiosemicarbazone (prepared by adding the corresponding weight of sodium to the 1-acetylferrocenethiosemicarbazone in dry methanol) was added in 1:1 molar ratio for triorganotin/silicon complexes and in 1:1 and 1:2 stoichiometric proportions for diorganotin/silicon complexes. The reaction mixture was refluxed for about 8–10 h. The sodium chloride so obtained was filtered off; on removing the solvent under vacuum, the compound was washed with a suitable solvent to ensure the purity of the product and finally dried over a vacuum pump. The details and important physical characteristics are recorded in Table 7.

Analytical methods and physical measurements

The various analytical methods adopted for the proper characterization of the compounds are as follows.

Carbon and hydrogen analyses were performed at the RSIC Chennai. Nitrogen and sulfur were estimated by Kjeldahl's and Messenger's methods respectively. Tin and silicon were determined gravimetrically as SnO_2 and SiO_2 respectively, and molecular weights were determined by the Rast Camphor method. IR spectra were recorded as KBr discs on a Perkin–Elmer 577 grating spectrophotometer in the range 4000–200 cm^{-1}. ^1H, ^{119}Sn and ^{29}Si NMR spectra were recorded on a Bruker AM 270 spectrometer. All chemical shifts are reported in parts per million (ppm) relative to TMS as an internal standard in DMSO-d_6.

Antimicrobial screening

The synthesized ligand and its organotin/silicon complexes were evaluated for *in vitro* growth inhibitory activity against the phytopathogenic fungi *Fusarium oxysporium, Aspergillus niger* and *Macrophomina phaseolina*, and against the bacteria *Escherchia coli, Klebsiella aerogenous, Pseudomonas cepacicola* and *Staphylococcus aureus*. Adequate temperature, requisite nutrient, and growth media free from other microorganisms were employed for the growth of cultures of both the fungi and the bacteria.[37] The incubation periods for the fungi and bacteria were 96 h at 37 °C and 24 h at 28 °C respectively. The conventional fungicide 2-(methoxylcarbenyl)benzimidazol (Bavistin®) and the bactericide streptomycin were used as standards for comparing the activities of the compounds.

Antifungal activity (radial growth method)

For the evaluation of the antifungal activity of the ligand and its metal complexes, these were dissolved at 50, 100 and 200 ppm concentrations in DMF and were then incorporated in potato-dextrose agar (PDA) medium against different types of fungus. The growth inhibition percentage was calculated on the basis of the average diameter of the fungal colony according to[38]

$$\text{Inhibition}(\%) = \frac{100(C - T)}{C} \quad (3)$$

where C and T are the average diameters of the fungal colonies in the control plate and the test plate respectively.

Antibacterial activity (paper-disc plate method)

For the evaluation of antibacterial activity, a nutrient media containing 0.5% peptone, 0.15% yeast, 0.15% beef extract, 0.35% sodium chloride and 0.13% KH_2PO_4 in distilled water (1000 cm^3) was autoclaved for 20 min at 15 psi before inoculation. The compounds were dissolved in DMF at 500 and 1000 ppm concentrations. The 5 mm diameter Whatman No. 1 paper discs were soaked in different solutions of the compounds, dried and then placed in Petri plates previously seeded with the test organism. The plates were incubated for 24 h at 28 °C and the inhibition zone around each disc was measured.

Antifertility activity

The antifertility activity in male rats was carried out by using the following method. Thirty adult male rats (body weight 40–50 g) were divided into six groups of five animals each. The animals were maintained and fed with balanced pellet diet and tap water was provided *ad libitum*. One group was used as a control, and each animal of this group received 0.2 cm^3 olive oil per day orally. The thiosemicarbazone and its complexes were suspended in olive oil separately and given to animals orally at a dose level of 20 mg day^{-1} per kilogram body weight for 60 days. At 24 h after the last administration of the compound, the animals were autopsied and the reproductive tract was dissected out and the motility and the sperm count were measured.

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