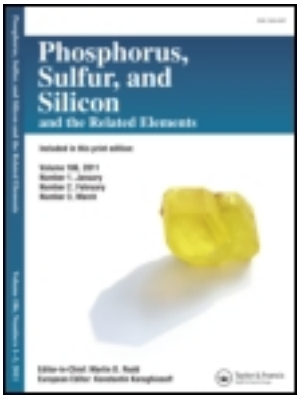

Phosphorus, Sulfur, and Silicon and the Related Elements

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Novel Bioactive Thio- and Semicarbazide Ligands and Their Organosilicon (IV) Complexes

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NOVEL BIOACTIVE THIO- AND SEMICARBAZIDE LIGANDS AND THEIR ORGANOSILICON (IV) COMPLEXES

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Ligational behavior of thiosemicarbazones and semicarbazones derived from 1-phenyl-3-arylpyrazole-4-carboxaldehydes towards triphenylchlorosilane has been investigated by elemental analysis, molar conductivity measurements, and IR, ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic studies. The ligands and their organosilicon complexes have also been evaluated for in vitro antimicrobial activity against some pathogenic bacteria and fungi.

Supplemental materials are available for this article. Go to the publisher's online edition of* Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.

Keywords Antimicrobial activity; organosilicon (IV) complexes; semicarbazones; spectral studies; thiosemicarbazones

INTRODUCTION

Thiosemicarbazones and semicarbazones are among the most widely studied nitrogen and sulfur/oxygen donor ligands.[1–5] They are capable of acting as neutral or charged ligand moieties, as they have interesting coordination properties because only the β-nitrogen coordinates to the metal atom, while the α-nitrogen atom remains uncoordinated. On the other hand, the remaining sulfur/oxygen atom has a tendency to form a strong covalent bond with metal atom. These compounds have remarkable biological activities ranging from antiprotozoa,[6] antifertility,[7] antibacterial,[8] antifungal,[9] antitumoral,[10] antiviral activities,[11] and especially anti-HIV activity,[12,13] properties which have since been shown to be related to their metal-complexing ability.[14]

The interest in organosilicon (IV) compounds is due to their versatile applicability in pharmaceutical and in chemical industries. In addition, the substituted pyrazole ring also exhibits a broad spectrum of biological activities such as antidiabetic,[15] antimicrobial,[16–19] and herbicidal.[20,21] Moreover, in many cases, by coordination to different transition metal ions that can be found in biological systems, it is possible to obtain complexes that are

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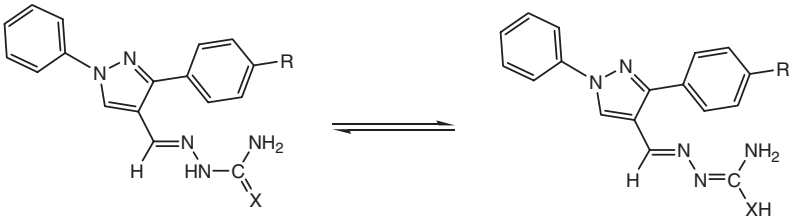


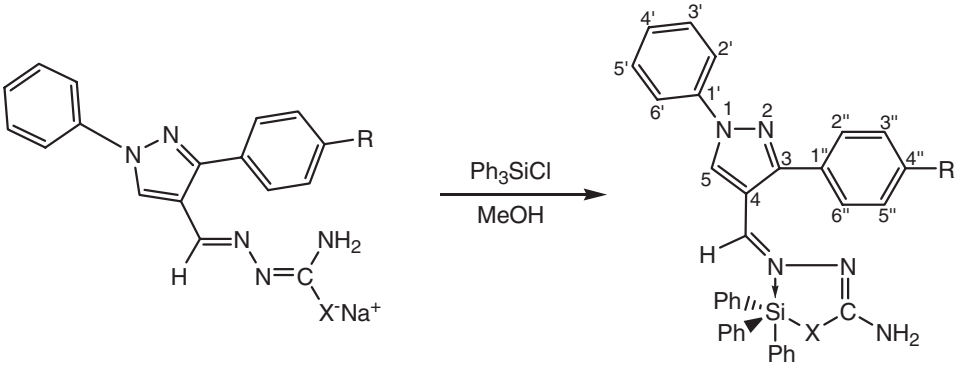
Ligand	HL_I	HL_{II}	HL_{III}	HL_{IV}	HL_V	HL_{VI}	HL_{VII}	HL_{VIII}	HL_{IX}	HL_X
R	H	CH_3	OCH_3	Br	Cl	H	CH_3	OCH_3	Br	Cl
X	S	S	S	S	S	O	O	O	O	O

Figure 1 Structure of the ligands.

more efficient drugs than the corresponding free ligands. So, the present situation prompted us to produce such work with monofunctional bidentate azomethine moieties in which the combined effect of silicon along with plus role of pyrazole ring and sulfur/oxygen is applicable. The imines used during these studies were derived from thiosemicarbazones and semicarbazones of 1-phenyl-3-arylpyrazole-4-carboxaldehyde derivatives and are shown in Figure 1.

RESULTS AND DISCUSSION

The reactions of triphenylchlorosilane with the sodium salts of ligands in 1:1 molar ratio in dry methanol proceed smoothly with the precipitation of NaCl, and lead to the formation of triorganosilicon complexes (Scheme 1).



Scheme 1 Synthesis of triphenylsilicon (IV) complexes.

All the newly synthesized complexes have been obtained as solids and are insoluble in common organic solvents. The molar conductivities of these complexes have low values (5–15 $ohm^{-1}\,cm^2\,mol^{-1}$), indicating non-electrolytic nature. The monomeric nature of these complexes is confirmed by the molecular weight determinations. The stereochemistry of

these complexes has been determined spectroscopically using IR and NMR (^{1}H, ^{13}C, and ^{29}Si) spectral data.

IR Spectra

The infrared spectra of the complexes were compared with those of the free ligands (HL_I–HL_X) to ascertain the coordination sites on the basis of shifting in the frequency of various groups and/or from the lowering in the intensities of the absorptions. The broad and medium intensity bands attributable to ν(NH) modes in the region 3200–3100 cm^{-1} disappear in the silicon complexes, indicating the loss of a proton on the α-nitrogen due to tautomerization after complexation of the silicon atom to sulfur/oxygen atom. The bands observed at about 3446 and 3334 cm^{-1} due to the symmetric and asymmetric modes of the NH_2 group are at virtually the same frequencies in the spectra of silicon complexes, suggesting the non-involvement of this amino group in chelation.[7] In the IR spectra of the ligands, a sharp band in the region 1605 $\pm$ 15 cm^{-1} can be attributed to the C=N group.[22] This band shifts slightly toward lower frequency in the silicon complexes, indicating the coordination of the azomethine nitrogen to the silicon atom. The ν (C=S) band in thiosemicarbazones and ν (C=O) band in semicarbazones appear at 1040 and 1685 cm^{-1}, respectively. These bands disappear upon complexation, which is due to the covalent bond formation of the ligand with the silicon atom through the sulfur or oxygen atoms. The formation of the resulting complexes has also been supported by the presence of new bands due to ν(Si—O),[23] ν(Si—S), and ν(Si—N) at 740 $\pm$ 10, 540 $\pm$ 10, and 580 $\pm$ 5 cm^{-1}, respectively.[9] The appearance of medium to strong intensity bands around 1450–1400, 1130–1085, 800–685, and 690–620 cm^{-1} have been assigned to (Si—C_6H_5) modes.

^{1}H NMR Spectra

The ^{1}H NMR spectra of the ligands and their corresponding organosilicon (IV) complexes were recorded in $CDCl_3$ with a few drops of DMSO-d_6 using TMS as the internal standard and are presented in Tables I and II, respectively. In the ^{1}H NMR spectra of the free thio- and semicarbazide ligands, a broad signal due to the NH proton was observed at δ 11.14–11.33 and δ 9.98–10.13, respectively, which was absent in the spectra of complexes, showing the bonding of thiolic sulfur/enolic oxygen to silicon after the deprotonation of the functional group. The appearance of a signal due to the NH_2 group at about the same position in the ligand and its metal complexes shows the non-involvement of this group in coordination. The azomethine proton signal shifts downfield in the spectra of complexes due to the formation of a coordinate linkage between nitrogen and silicon atom. In the spectra of Ph_3SiL_I, the new complex multiplet centered at about δ 7.59–7.63 (m, 6H) was due to the *ortho-* protons, and at about δ 7.31–7.49 (m, 9H) was due to the *meta-* and *para-* protons of the triphenylsilane group.

^{13}C NMR Spectra

The ^{13}C NMR spectra of the ligands and their corresponding organosilicon (IV) complexes are presented in Tables III and IV, respectively. In the ^{13}C NMR spectra of free ligands, the thiolo, amido, and azomethine carbons showed signals at δ 177.0, 155.0, and 133.0–136.0, respectively. These peaks were slightly altered upon complexation with triphenylsilicon (IV) chloride, indicating the bonding of thiolic sulfur/enolic oxygen and

Table I ^{1}H NMR data (δ) of thiosemicarbazide ligands and their triphenylsilicon (IV) complexes

Ligand/ complex	−NH	$-NH_2$	H−C=N	Aromatic	Si−Ph	R
HL_I	11.28	3.15	8.13	8.72 (s, 1H, C_5-H), 7.83–7.85 (m, 2H, C'_2-H & C'_6-H), 7.67–7.70 (m, 2H, C''_2-H & C''_6-H), 7.31–7.54 (m, 6H, C''_3-H, C''_4-H, C''_5-H, C'_3-H, C'_4-H & C'_5-H)	—	—
Ph_3SiL_I	—	3.34	8.25	8.57 (s, 1H, C_5-H), 7.82 (d, 2H, C'_2-H & C'_6-H), 7.71 (d, 2H, C''_2-H & C''_6-H), 7.31–7.49 (m, 6H, C''_3-H, C''_4-H, C''_5-H, C'_3-H, C'_4-H & C'_5-H)	7.59–7.63 (m, 6H), 7.31–7.49 (m, 9H)	—
HL_{II}	11.14	2.80	8.20	8.50 (s, 1H, C_5-H), 7.78–7.80 (m, 2H, C'_2-H & C'_6-H), 7.57 (d, 2H, C''_2-H & C''_6-H), 7.45–7.49 (m, 2H, C'_3-H & C'_5-H), 7.30–7.33 (m, 1H, C'_4-H), 7.25 (d, 2H, C''_3-H & C''_5-H)	—	2.40 (s, 3H, C''_4-CH_3)
Ph_3SiL_{II}	—	2.90	8.33	8.40 (s, 1H, C_5-H), 7.79 (d, 2H, C'_2-H & C'_6-H), 7.65 (d, 2H, C''_2-H & C''_6-H), 7.29–7.48 (m, 5H, C''_3-H, C''_5-H, C'_3-H, C'_4-H & C'_5-H)	7.55–7.61 (m, 6H), 7.29–7.48 (m, 9H)	2.39 (s, 3H, C'_4-CH_3)
HL_{III}	11.31	3.33	8.23	9.14 (s, 1H, C_5-H), 7.88 (d, 2H, C'_2-H & C'_6-H), 7.53–7.62 (m, 4H, C''_2-H, C''_6-H, C'_3-H & C'_5-H), 7.34–7.38 (m, 1H, C'_4-H), 7.06 (d, 2H, C''_3-H & C''_5-H)	—	3.82 (s, 3H, C''_4-OCH_3)
Ph_3SiL_{III}	—	3.30	8.35	9.00 (s, 1H, C_5-H), 7.86 (d, 2H, C'_2-H & C'_6-H), 7.35–7.73 (m, 7H, C''_2-H, C''_3-H, C''_5-H, C''_6-H, C'_3-H, C'_4-H & C'_5-H)	7.35–7.73 (m, 15H)	3.80 (s, 3H, C''_4-OCH_3)
HL_{IV}	11.18	3.30	8.21	9.15 (s, 1H, C_5-H), 7.90–7.93 (m, 2H, C'_2-H & C'_6-H), 7.62–7.72 (m, 4H, C''_2-H, C''_6-H, C'_3-H & C'_5-H), 7.54–7.60 (m, 2H, C''_3-H & C''_5-H), 7.40–7.55 (m, 1H, C'_4-H)	—	—
Ph_3SiL_{IV}	—	3.35	8.39	8.80 (s, 1H, C_5-H), 7.90 (d, 2H, C'_2-H & C'_6-H), 7.32–7.70 (m, 7H, C''_2-H, C''_3-H, C''_5-H, C''_6-H, C'_3-H, C'_4-H & C'_5-H)	7.32–7.70 (m, 15H)	—
HL_V	11.33	3.37	8.28	9.19 (s, 1H, C_5-H), 8.21–8.27 (m, 2H, C'_2-H & C'_6-H), 7.89–7.91 (d, 2H, C''_3-H & C''_5-H), 7.54–7.73 (m, 4H, C''_2-H, C''_6-H, C'_3-H & C'_5-H), 7.37–7.41 (m, 1H, C'_4-H)	—	—
Ph_3SiL_V	—	3.33	8.40	9.00 (s, 1H, C_5-H), 8.11–8.20 (m, 2H, C'_2-H & C'_6-H), 7.84–7.89 (m, 2H, C''_3-H & C''_5-H), 7.32–7.76 (m, 5H, C''_2-H, C''_6-H, C'_3-H, C'_4-H & C'_5-H)	7.32–7.76 (m, 15H)	—

Table II ^{1}H NMR data (δ) of semicarbazide ligands and their triphenylsilicon (IV) complexes

Ligand/ complex	−NH	$-NH_2$	H−C=N	Aromatic	Si−Ph	R
HL_{VI}	10.04	3.07	7.96	8.47 (s, 1H, C_5-H), 7.80 (d, 2H, C'_2-H & C'_6-H), 7.67–7.69 (m, 2H, C''_2-H & C''_6-H), 7.30–7.52 (m, 6H, C''_3-H, C''_4-H, C''_5-H, C'_3-H, C'_4-H & C'_5-H)	—	—
Ph_3SiL_{VI}	—	3.15	8.26	8.27 (s, 1H, C_5-H), 7.82 (d, 2H, C'_2-H & C'_6-H), 7.63–7.66 (m, 2H, C''_2-H & C''_6-H), 7.30–7.50 (m, 6H, C''_3-H, C''_4-H, C''_5-H, C'_3-H, C'_4-H & C'_5-H)	7.55–7.60 (m, 6H), 7.30–7.50 (m, 9H)	—
HL_{VII}	9.98	2.91	7.94	8.42 (s, 1H, C_5-H), 7.78 (d, 2H, C'_2-H & C'_6-H), 7.57 (d, 2H, C''_2-H & C''_6-H), 7.45–7.49 (m, 2H, C'_3-H & C'_5-H), 7.29–7.33 (m, 1H, C'_4-H), 7.25 (d, 2H, C''_3-H & C''_5-H)	—	2.39 (s, 3H, C''_4-CH_3)
Ph_3SiL_{VII}	—	3.10	8.15	8.32 (s, 1H, C_5-H), 7.80 (d, 2H, C'_2-H & C'_6-H), 7.55 (d, 2H, C''_2-H & C''_6-H), 7.30–7.48 (m, 5H, C''_3-H, C''_5-H, C'_3-H, C'_4-H & C'_5-H)	7.59–7.64 (m, 6H), 7.30–7.48 (m, 9H)	2.40 (s, 3H, C''_4-CH_3)
HL_{VIII}	10.09	3.35	7.95	9.04 (s, 1H, C_5-H), 7.90 (d, 2H, C'_2-H & C'_6-H), 7.52–7.61 (m, 4H, C''_2-H, C''_6-H, C'_3-H & C'_5-H), 7.34–7.38 (m, 1H, C'_4-H), 7.06 (d, 2H, C''_3-H & C''_5-H)	—	3.81 (s, 3H, C''_4-OCH_3)
Ph_3SiL_{VIII}	—	3.25	8.20	8.82 (s, 1H, C_5-H), 7.92 (d, 2H, C'_2-H & C'_6-H), 7.36–7.74 (m, 7H, C''_2-H, C''_3-H, C''_5-H, C''_6-H, C'_3-H, C'_4-H & C'_5-H)	7.36–7.74 (m, 15H)	3.79 (s, 3H, C''_4-OCH_3)
HL_{IX}	10.13	3.38	7.98	9.11(s, 1H, C_5-H), 7.91–7.94 (m, 2H, C'_2-H & C'_6-H), 7.63–7.73 (m, 4H, C''_2-H, C''_6-H, C'_3-H & C'_5-H), 7.53–7.59 (m, 2H, C''_3-H & C''_5-H), 7.36–7.53 (m, 1H, C'_4-H)	—	—
Ph_3SiL_{IX}	—	3.45	8.22	8.85 (s, 1H, C_5-H), 7.89–7.93 (m, 2H, C'_2-H & C'_6-H), 7.30–7.70 (m, 7H, C''_2-H, C''_3-H, C''_5-H, C''_6-H, C'_3-H, C'_4-H & C'_5-H)	7.30–7.70 (m, 15H)	—
HL_X	10.12	3.38	8.00	9.12 (s, 1H, C_5-H), 7.91–7.96 (m, 2H, C'_2-H & C'_6-H), 7.70–7.76 (m, 2H, C''_3-H & C''_5-H), 7.53–7.63 (m, 4H, C''_2-H, C''_6-H, C'_3-H & C'_5-H), 7.35–7.40 (m, 1H, C'_4-H)	—	—
Ph_3SiL_X	—	3.48	8.17	8.99 (s, 1H, C_5-H), 7.88–7.92 (m, 2H, C'_2-H & C'_6-H), 7.71–7.75 (m, 2H, C''_3-H & C''_5-H), 7.35–7.73 (m, 5H, C''_2-H, C''_6-H, C'_3-H, C'_4-H & C'_5-H)	7.35–7.73 (m, 15H)	—

Table III ^{13}C NMR data (δ) of thiosemicarbazide ligands and their triphenylsilicon (IV) complexes

Ligand/ complex	C=S	C=N	Aromatic	Si−Ph	R
HL_I	177.44	135.91	151.64 (C_3), 138.86 (C'_1), 131.97 (C''_1), 128.98 (C'_3 & C'_5), 128.02 (C''_3 & C''_5), 127.97 (C''_2 & C''_6), 127.90 (C_5), 126.61(C''_4), 126.46 (C'_4), 118.40 (C'_2 & C'_6), 116.55 (C_4)	—	—
Ph_3SiL_I	168.34	127.43	152.58 (C_3), 138.80 (C'_1), 132.28 (C''_1), 128.48 (C'_3 & C'_5), 128.51 (C''_3 & C''_5), 127.26 (C''_2 & C''_6), 128.90 (C_5), 126.36 (C''_4), 126.08 (C'_4), 118.44 (C'_2 & C'_6), 116.15 (C_4)	136.13, 134.48, 128.99, 127.43	—
HL_{II}	177.36	136.63	152.04 (C_3), 138.89 (C'_1), 137.92 (C''_4), 129.02 (C''_1), 129.01 (C''_3 & C''_5), 128.75 (C'_3 & C'_5), 127.94 (C''_2 & C''_6), 126.52 (C_5), 126.37 (C'_4), 118.57 (C'_2 & C'_6), 116.15 (C_4)	—	20.86 (C'_4−CH_3)
Ph_3SiL_{II}	169.21	129.23	152.83 (C_3), 138.82 (C'_1), 137.63 (C''_4), 129.32 (C''_1), 128.97 (C''_3 & C''_5), 127.95 (C'_3 & C'_5), 128.25 (C''_2 & C''_6), 127.57 (C_5), 126.05 (C'_4), 118.62 (C'_2 & C'_6), 116.00 (C_4)	136.25, 135.03, 129.12, 127.12	20.65 (C'_4−CH_3)
HL_{III}	177.53	135.14	159.56 (C''_4), 151.21(C_3), 139.05 (C'_1), 129.61 (C'_3 & C'_5), 129.41 (C''_2 & C''_6), 127.52 (C_5), 126.80 (C'_4), 124.49 (C''_1), 118.38 (C'_2 & C'_6), 116.93 (C_4), 114.15 (C''_3 & C''_5)	—	55.24 (C''_4−OCH_3)
Ph_3SiL_{III}	168.31	129.24	159.37 (C''_4), 152.09 (C_3), 139.00 (C'_1), 129.69 (C'_3 & C'_5), 129.27 (C''_2 & C''_6), 128.21 (C_5), 126.51 (C'_4), 124.29 (C''_1), 116.99 (C'_2 & C'_6), 116.62 (C_4), 114.06 (C''_3 & C''_5)	136.15, 134.78, 128.96, 127.36	55.02 (C''_4−OCH_3)
HL_{IV}	177.38	134.60	150.97 (C_3), 139.00 (C'_1), 131.59 (C''_3 & C''_5), 130.09 (C''_2 & C''_6), 129.70 (C'_3 & C'_5), 129.63 (C''_1), 127.50 (C_5), 127.03 (C'_4), 122.05 (C''_4), 118.53 (C'_2 & C'_6), 117.26 (C_4)	—	—
Ph_3SiL_{IV}	169.00	128.55	151.98 (C_3), 139.05 (C'_1), 131. 67 (C''_3 & C''_5), 131.67 (C''_3 & C''_5), 130.13 (C''_2 & C''_6), 129.67 (C'_3 & C'_5), 129.60 (C''_1), 129.00 (C_5), 126.94 (C'_4), 121.85 (C''_4), 118.48 (C'_2 & C'_6), 117.31 (C_4)	136.26, 134.63, 129.00, 127.48	—
HL_V	177.59	134.69	150.10 (C_3), 138.95 (C'_1), 133.39 (C''_4), 130.98 (C''_1), 129.83 (C'_3 & C'_5), 129.71 (C''_3 & C''_5), 128.81 (C''_2 & C''_6), 127.93 (C_5), 127.12 (C'_4), 118.56 (C'_2 & C'_6), 117.34 (C_4)	—	—
Ph_3SiL_V	168.50	129.00	151.21 (C_3), 139.01 (C'_1), 133.03 (C''_4), 131.23 (C''_1), 128.73 (C'_3 & C'_5), 129.75 (C''_3 & C''_5), 128.84 (C''_2 & C''_6), 128.59 (C_5), 126.82 (C'_4), 118.62 (C'_2 & C'_6), 117.04 (C_4)	135.92, 134.50, 128.96, 126.94	—

Table IV ^{13}C NMR data (δ) of semicarbazide ligands and their triphenylsilicon (IV) complexes

Ligand/ complex	C=O	C=N	Aromatic	Si−Ph	R
HL_{VI}	157.20	133.44	151.32 (C_3), 138.97 (C'_1), 132.17 (C''_1), 129.01 (C'_3 & C'_5), 128.08 (C''_3 & C''_5), 128.05 (C''_2 & C''_6), 127.95 (C_5), 126.43 (C''_4), 125.95 (C'_4), 118.51 (C'_2 & C'_6), 116.87 (C_4)	—	—
Ph_3SiL_{VI}	149.80	129.16	152.00 (C_3), 138.94 (C'_1), 132.36 (C''_1), 129.03 (C'_3 & C'_5), 127.49 (C''_3 & C''_5), 128.10 (C''_2 & C''_6), 129.01 (C_5), 126.16 (C''_4), 125.63 (C'_4), 118.61 (C'_2 & C'_6), 116.26 (C_4)	136.05, 134.28, 128.85, 127.06	—
HL_{VII}	157.15	133.63	151.40 (C_3), 138.95 (C'_1), 137.70 (C''_4), 129.17 (C''_1), 128.94 (C''_3 & C''_5), 128.69 (C'_3 & C'_5), 127.89 (C''_2 & C''_6), 126.32 (C_5), 125.72 (C'_4), 118.46 (C'_2 & C'_6), 116.66 (C_4)	—	20.79 (C'_4−CH_3)
Ph_3SiL_{VII}	150.00	128.11	152.31 (C_3), 138.90 (C'_1), 137.25 (C''_4), 129.46 (C''_1), 128.24 (C''_3 & C''_5), 128.25 (C'_3 & C'_5), 127.93 (C''_2 & C''_6), 128.01 (C_5), 125.33 (C'_4), 118.52 (C'_2 & C'_6), 116.17 (C_4)	136.43, 134.36, 128.94, 127.33	20.57 (C'_4−CH_3)
HL_{VIII}	159.46	131.18	156.71(C''_4), 150.57 (C_3), 139.17 (C'_1), 129.59 (C'_3 & C'_5), 129.44 (C''_2 & C''_6), 126.98 (C''_1), 126.62 (C_5), 124.78 (C'_4), 118.30 (C'_2 & C'_6), 117.50 (C_4), 114.12 (C''_3 & C''_5)	—	55.24 (C''_4−OCH_3)
Ph_3SiL_{VIII}	151.24	127.45	156.56 (C''_4), 151.42 (C_3), 138.96 (C'_1), 129.13 (C'_3 & C'_5), 129.48 (C''_2 & C''_6), 127.28 (C''_1), 127.98 (C_5), 124.37 (C'_4), 117.55 (C'_2 & C'_6), 117.14 (C_4), 114.12 (C''_3 & C''_5)	135.88, 134.08, 129.06, 127.13	55.23 (C''_4−OCH_3)
HL_{IX}	156.70	131.62	149.46 (C_3), 139.05 (C'_1), 131.67 (C''_3 & C''_5), 130.13 (C''_2 & C''_6), 129.67 (C'_3 & C'_5), 129.60 (C''_1), 127.48 (C_5), 126.94 (C'_4), 121.85 (C''_4), 118.48 (C'_2 & C'_6), 117.87 (C_4)	—	—
Ph_3SiL_{IX}	148.78	128.23	151.73 (C_3), 138.55 (C'_1), 131.73 (C''_3 & C''_5), 130.19 (C''_2 & C''_6), 129.12 (C'_3 & C'_5), 129.85 (C''_1), 128.72 (C_5), 126.94 (C'_4), 121.42 (C''_4), 118.57 (C'_2 & C'_6), 117.06 (C_4)	136.02, 134.17, 128.83, 127.31	—
HL_X	156.70	131.46	149.42 (C_3), 139.05 (C'_1), 133.22 (C''_4), 131.27 (C''_1), 129.86 (C''_3 & C''_5), 129.67 (C'_3 & C'_5), 128.76 (C''_2 & C''_6), 127.45 (C_5), 126.93 (C'_4), 118.48 (C'_2 & C'_6), 117.87 (C_4)	—	—
Ph_3SiL_X	149.23	128.50	152.27 (C_3), 138.70 (C'_1), 132.93 (C''_4), 131.53 (C''_1), 129.23 (C'_3 & C'_5), 129.11 (C''_3 & C''_5), 128.80 (C''_2 & C''_6), 128.27 (C_5), 126.62 (C'_4), 118.53 (C'_2 & C'_6), 117.20 (C_4)	136.10, 134.23, 128.75, 127.22	—

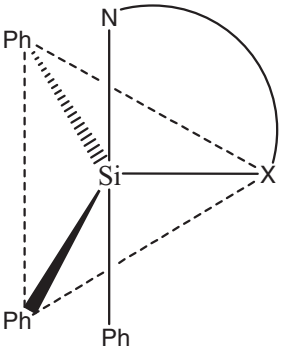


Figure 2 Suggested structure for the complexes, X = S or O, and N X donor sites for the ligand molecules.

azomethine nitrogen to the silicon atom. The signals due to ring carbons of phenyl group attached to silicon appeared at δ 124.5, 128.2, 134.1, and 140.2.

^{29}Si NMR Spectra

The ^{29}Si NMR of complexes gives sharp signals at δ −80 to −110, which clearly indicates the pentacoordinated environment around the silicon atom and is well in agreement with the reported values.[24] Thus on the basis of the foregoing spectral features, the pentacoordinated structure of the complexes shown in Figure 2 has been proposed.

ANTIMICROBIAL ACTIVITY

The ligands and their silicon complexes were evaluated for *in vitro* antibacterial activity against Gram-positive bacteria *Bacillus subtilis* and *Staphylococcus aureus* and Gram-negative bacteria *Escherichia coli*, and *in vitro* antifungal activity against *Candida albicans* and *Aspergillus niger* fungi. Minimum inhibitory concentrations (MICs) were determined by means of twofold serial dilution technique[25,26] and are presented in Table S1 (available online in the Supplementary Materials).

CONCLUSION

Isolated organosilicon (IV) complexes of thiosemicarbazones and semicarbazones derived from 1-phenyl-3-arylpyrazole-4-carboxaldehydes were tested against pathogenic bacteria and fungi. The activity of the ligands were due to the presence of toxophorically important −CON= or −CSN= groups. Upon complexation, the activity was further enhanced against the most of the microorganisms under identical experimental conditions.

EXPERIMENTAL

All the operations were carried out under nitrogen atmosphere using vacuum line. All the solvents used were dried by conventional methods. Triphenylchlorosilane was obtained through Aldrich and was used as such without any further purification. IR spectra were obtained as KBr pellets using a Perkin Elmer Spectrum RX1 instrument. ^{1}H, ^{13}C NMR, and ^{29}Si spectra were determined on a Bruker Avance II 400 MHz NMR Spectrometer in $CDCl_3$

and two drops of DMSO-d_6 using TMS as an internal standard. Elemental analyses were carried out on Perkin Elmer 2400. Molecular weights of the complexes were determined by cryoscopic method in dry nitrobenzene. Molar conductance measurements were carried out using a Model-306 Systronics conductivity bridge in DMSO solvent. Silicon was determined gravimetrically as SiO_2.

Preparation of Ligands

The 1-phenyl-3-arylpyrazole-4-carboxaldehydes were prepared in two steps. The first one was the reaction between acetophenone derivatives (20.0 mmol) and phenylhydrazine (2.16 g, 20.0 mmol) in ethanol (50 mL). The hydrazone derivatives (4.00 mmol) were treated with the Vilsmeier–Haack reagent, i.e., a cold solution of dimethylformamide (10 mL) and phosphorus oxychloride (0.5 mL, 6 mmol), leading to the corresponding 4-carboxaldehyde functionalized pyrazole heterocyclic ring in mild operating conditions. Three equivalents of this reagent, instead of two as described by Kira et al.,[27] were necessary to obtain the aldehydes in good yields. The condensation of 1-phenyl-3-arylpyrazole-4-carboxaldehydes (10.0 mmol) with thiosemicarbazide (0.91 g, 10.0 mmol) and semicarbazide hydrochloride (1.11 g, 10.0 mmol) in the presence of sodium acetate (0.86 g, 10.5 mmol) in ethanol (30 mL) resulted in the formation of thiosemicarbazone and semicarbazone derivatives, respectively. These were characterized by elemental analyses, IR and NMR spectra studies.

Preparation of Complexes

To a weighed quantity of triphenylchlorosilane (1.18 g, 4.0 mmol) in dry methanol (20 mL), sodium salt of the ligands (4.0 mmol) was added. Sodium salt of the ligands was prepared by adding sodium (0.10 g, 4.50 mmol) to the ligands (4.0 mmol) in dry methanol (10 mL). The mixture was refluxed for 12–16 h. After the completion of the reaction, the precipitated sodium chloride was filtered off, and the excess solvent was removed under vacuum. The residues were dried under vacuum for 3–4 h. The compound was washed with n-hexane or a mixture of methanol and n-hexane (50:50 v/v) to ensure the purity of the product and finally dried over a vacuum pump. The elemental analyses and physical properties of these silicon complexes are given in Table V.

Biological Assays: Antimicrobial Activity

The *in vitro* antibacterial and antifungal activity of ligands and their organosilicon (IV) complexes were carried out against the bacteria *Bacillus subtilis*, *Staphylococcus aureus*, and *Escherichia coli* and fungi *Candida albicans* and *Aspergillus niger* using serial dilution technique in double strength nutrient broth-I.P. and Sabouraud dextrose broth-I.P. as a medium. The conventional bactericides tetracycline, chloramphenicol, kanamycin, cefazoline sodium, and cefotaxime and fungicides cycloheximide, carbendazim, and fluconazole were used as standards for comparing the activity of compounds. Experimental details for the antibacterial and antifungal assays are presented in the Supplemental Materials.

Table V Analysis and percent yield of ligands and their triphenylsilicon (IV) complexes

Ligand/complexes	Molecular formula	Yield (%)	Analysis (%) Found (Calcd.)				
			C	H	N	S	Si
HL_{I}	$C_{17}H_{15}N_5S$	80	63.35 (63.53)	4.32 (4.70)	21.80 (21.79)	9.89 (9.98)	—
HL_{II}	$C_{18}H_{17}N_5S$	74	64.32 (64.45)	5.09 (5.11)	20.90 (20.88)	9.51 (9.56)	—
HL_{III}	$C_{18}H_{17}N_5OS$	85	61.34 (61.52)	4.84 (4.88)	19.95 (19.93)	9.11 (9.12)	—
HL_{IV}	$C_{17}H_{15}BrN_5S$	83	51.06 (51.01)	3.50 (3.53)	17.47 (17.50)	8.04 (8.01)	—
HL_{V}	$C_{17}H_{15}ClN_5S$	82	57.34 (57.38)	3.99 (3.97)	19.62 (19.68)	9.04 (9.01)	—
HL_{VI}	$C_{17}H_{15}N_5O$	67	66.89 (66.87)	4.99 (4.95)	22.91 (22.94)	—	—
HL_{VII}	$C_{18}H_{17}N_5O$	73	67.71 (67.70)	5.31 (5.37)	21.90 (21.93)	—	—
HL_{VIII}	$C_{18}H_{17}N_5O_2$	90	64.44 (64.47)	5.09 (5.11)	20.83 (20.88)	—	—
HL_{IX}	$C_{17}H_{15}BrN_5O$	84	53.16 (53.14)	3.63 (3.67)	18.25 (18.23)	—	—
HL_{X}	$C_{17}H_{15}ClN_5O$	78	60.11 (60.09)	4.13 (4.15)	20.65 (20.61)	—	—
Ph_3SiL_{I}	$C_{35}H_{29}N_5SSi$	64	72.49 (72.50)	5.02 (5.04)	12.04 (12.08)	5.50 (5.53)	4.82 (4.84)
Ph_3SiL_{II}	$C_{36}H_{31}N_5SSi$	69	72.85 (72.81)	5.23 (5.26)	11.70 (11.79)	5.38 (5.40)	4.70 (4.73)
Ph_3SiL_{III}	$C_{36}H_{31}N_5OSSi$	71	70.88 (70.90)	5.10 (5.12)	11.45 (11.48)	5.23 (5.26)	4.60 (4.61)
Ph_3SiL_{IV}	$C_{35}H_{28}BrN_5SSi$	78	63.80 (63.82)	4.23 (4.28)	10.60 (10.63)	4.85 (4.87)	4.22 (4.26)
Ph_3SiL_{V}	$C_{35}H_{28}ClN_5SSi$	72	68.40 (68.44)	4.55 (4.59)	11.38 (11.40)	5.20 (5.22)	4.55 (4.57)
Ph_3SiL_{VI}	$C_{35}H_{29}N_5OSi$	63	74.50 (74.57)	5.20 (5.19)	12.40 (12.42)	—	4.99 (4.98)
Ph_3SiL_{VII}	$C_{36}H_{31}N_5OSi$	61	74.84 (74.87)	5.45 (5.41)	12.15 (12.12)	—	4.90 (4.86)
Ph_3SiL_{VIII}	$C_{36}H_{31}N_5O_2Si$	69	72.86 (72.82)	5.29 (5.26)	11.78 (11.80)	—	4.70 (4.73)
Ph_3SiL_{IX}	$C_{35}H_{28}BrN_5OSi$	73	65.40 (65.42)	4.36 (4.39)	10.88 (10.90)	—	4.39 (4.37)
Ph_3SiL_{X}	$C_{35}H_{28}ClN_5OSi$	65	70.25 (70.28)	4.70 (4.72)	11.74 (11.71)	—	4.68 (4.70)

REFERENCES

1. M. J. Campbell, *Coord. Chem. Rev.*, **15,** 279 (1975).
2. S. Padhye and G. B. Kauffman, *Coord. Chem. Rev.*, **63,** 127 (1985).
3. D. X. West, A. Liberta, S. B. Padhye, R. C. Chikate, P. B. Sonawane, A. S. Kumbhar, and R. G. Yerande, *Coord. Chem. Rev.*, **123,** 49 (1993).
4. D. X. West, S. B. Padhye, and P. B. Sonawane, *Structure and Bonding*, Vol. 76 (Springer-Verlag, New York, 1991), pp. 1–49.
5. J. S. Casas, M. S. Garcia-Tasende, and J. Sordo, *Coord. Chem. Rev.*, **209,** 197 (2000).
6. H. Cerecetto and M. Gonzalez, *Curr. Topics Med. Chem.*, **2,** 1187 (2002).
7. R. V. Singh, S. C. Joshi, A. Gajraj, and P. Nagpal, *Appl. Organomet. Chem.*, **16,** 713 (2002).
8. T. Rosu, A. Gulea, A. Nicolae, and R. Georgescu, *Molecules*, **12,** 782 (2007).
9. S. Belwal, N. Fahmi, and R. V. Singh, *Appl. Organomet. Chem.*, **22,** 615 (2008).
10. D. K. Sau, R. J. Butcher, S. Chaudhuri, and N. Saha, *Mol. Cell Biochem.*, **253,** 21 (2003).
11. T. Vardinova, D. K. Demertzi, M. Rupelieva, M. Demertzis, and P. Genova, *Acta Virol*., **45,** 87 (2001).
12. V. Mishra, S. N. Pandeya, C. Pannecouque, M. Witvrouw, and E. D. Clercq, *Arch Pharm*., **335,** 183 (2002).
13. T. R. Bal, B. Anand, P. Yogeeswari, and D. Sriram, *Bioorg. Med. Chem. Lett.*, **15,** 4451 (2005).
14. H. Beraldo and D. Gambinob, *Mini Rev. Med. Chem.*, **4,** 31 (2004).
15. K. L. Kees, J. J. Fitzgerald Jr., K. E. Steiner, J. F. Mattes, B. Mihan, T. Tosi, D. Mondero, and M. L. McCaled, *J. Med. Chem.*, **39,** 3920 (1996).
16. R. Aggarwal, V. Kumar, P. Tyagi, and S. P. Singh, *Bioorg. Med. Chem.*, **14,** 1785 (2006).
17. V. Kumar, R. Aggarwal, P. Tyagi, and S. P. Singh, *Eur. J. Med. Chem.*, **40,** 922 (2005).
18. O. Prakash, R. Kumar, and V. Parkash, *Eur. J. Med. Chem.*, **43,** 435 (2008).
19. O. Prakash, R. Kumar, and R. Sehrawat, *Eur. J. Med. Chem.*, **44,** 1763 (2009).
20. G. Meazz, F. Bettarini, P. La Porta, and P. Piccardi, *Pest Manag. Sci.*, **60,** 1178 (2004).
21. J. C. Jung, E. B. Walkins, and M. A. Avery, *Tetrahedron*, **58,** 3639 (2002).
22. R. Malhotra, J. Mehta, and J. K. Puri, *Cent. Eur. J. Chem.*, **5,** 858 (2007).
23. S. P. Narula, N. Kapur, C. R. Rana, and R. Malhotra, *Inorg. Chim. Acta*, **159,** 87 (1989).
24. J. Wagler, U. Bohme, E. Brendler, B. Thomas, S. Goutal, H. Mayr, B. Kempf, G. Y. Remennikov, and G. Roewer, *Inorg. Chim. Acta*, **358,** 4270 (2005).
25. R. Malhotra, J. Mehta, K. Bala, and A. K. Sharma, *Indian J. Chem.*, **47A,** 58 (2008).
26. B. G. Tweedy, *Phytopathology*, **55,** 910 (1964).
27. M. A. Kira, M. O. Abdel-Raeman, and K. Z. Gadalla, *Tetrahedron Lett.*, **2,** 109 (1969).