ruthenium center to allow the two resonances to be resolved.

Resolved ^{99}Ru signals can be easily detected even for asymmetrically substituted bimetallic complexes like those formed by the bridging hat ligand (Figure 2). Whereas ^{1}H or ^{13}C NMR spectroscopic methods are unable to measure the stoichiometry of the polymetallic complex due to the coexistence of a complex mixture of diastereoisomers,[18] ^{99}Ru NMR spectroscopy provides a unique method to verify that the bimetallic complex (and not the possible trimetallic) has indeed been obtained. The assignment of the different resonances to the different moieties is possible from the chemical shifts and line widths of the corresponding monometallic chelates (Table I), taking into account the deshielding effect produced by the overall 4+ charge of the bimetallic complex. This effect is even more dramatic in the case of the trimetallic $[(phen)_2Ru]_3(hat)^{6+}$ (Table I), which shows the highest chemical shift and the broadest signal of all the complexes studied. The large line width is due not only to the size of the molecule (and therefore the influence on the correlation time) but also to the presence of two diastereoisomers[18] with slightly different ^{99}Ru chemical shifts.

In conclusion, ^{99}Ru NMR spectroscopy is a powerful technique for the study of small variations around the metal core and geometrical isomerism in mono- and polynuclear ruthenium(II) polypyridyl complexes. Further work is in progress (utilizing other techniques such as temperature dependence of lifetimes combined with low-temperature emission spectra that may reveal the d-d transition energies without the use of UV-vis spectroscopy) in order to determine whether a relationship exists between the ^{99}Ru chemical shift and the ligand field strength that would allow the prediction of d-d transition energies in this class of compounds. Several other homo- and heteropolymetallic complexes are also being investigated by ^{99}Ru NMR spectroscopy as a unique way to probe their stoichiometry and isomerism.

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Adducts of 1-Vinylimidazole, 1-Benzylimidazole, and 1,2,4-Triazole with Tin(II) Chloride

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Numerous complexes involving d-block metals and imidazole derivatives are known;[2] a limited number involving group 14 metals have also been reported.[3] Some of these exhibit antimicrobial and antitumor activity,[4] an example being the complex of diethyltin dichloride with 2-(2-pyridyl)benzimidazole, which is active against renal adenocarcinoma.[5] Since divalent tin halides form complexes with a variety of donors, it was of interest to prepare and structurally characterize selected 1:2 $SnCl_2$ complexes with azoles in order to determine whether any structural features such as a cis relationship of nitrogen ligands known to be important in square-planar platinum-based antitumor agents[6] and octahedral $R_2SnX_2 \cdot 2L$ agents[7] are present in the new complexes. To our knowledge, there have been no previous structure reports of $SnCl_2 \cdot 2(N\text{-donor})$ complexes although the related germanium adduct $GeCl_2 \cdot$(benzothiazole) was structurally characterized.[8] We therefore wish to report the synthesis of three new 1:2 $SnCl_2$ complexes with azole derivatives, including X-ray structure determinations of the 1-vinyl- and 1-benzylimidazole complexes.

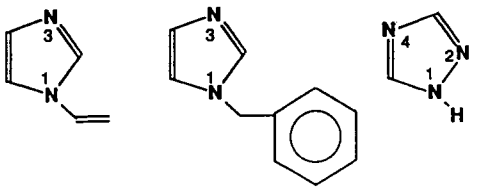

Figure 1. Azole structures and donor site numbering.

Experimental Section

Materials and Methods. Reactions and product manipulations were carried out either under flowing dry nitrogen or by using vacuum techniques.[9] ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were obtained at 300, 75.5, and 29.9 MHz, respectively. XPS (X-ray photoelectron spectroscopy) data were obtained by using a Perkin-Elmer PHI Model ESCA/SAM instrument fitted with dual anodes (Mg Kα, 1253.6 eV; Al Kα, 1486 eV). The C 1s band from residual pump oil (binding energy = 285 eV) was used to calibrate spectra.

Syntheses of Adducts. According to methods described previously,[10] three new $SnCl_2 \cdot 2Im$ adducts (Im = 1-vinyl- and 1-benzylimidazole and 1,2,4-triazole) were prepared and characterized. In the case of the 1-vinyl- and 1-benzylimidazole adducts, X-ray structure determinations were carried out. Anal. Calcd for $SnCl_2 \cdot 2$(1-vinylimidazole) (I, mp 98 °C dec), $C_{10}H_{12}N_4SnCl_2$: C, 31.79; H, 3.2; N, 14.83; Cl, 18.77; Sn, 31.41. Found: C, 31.81; H, 3.08; N, 14.61; Cl, 18.35; Sn, 31.44. Calcd for $SnCl_2 \cdot 2$(1-benzylimidazole) (II, mp 40 °C dec), $C_{20}H_{20}N_4SnCl_2$: C, 47.47; H, 3.98; N, 11.07; Cl, 14.01; Sn, 23.46. Found: C, 47.15; H, 3.78; N, 10.92; Cl, 13.83; Sn, 24.13. Yields of the air-sensitive, while solid products were nearly quantitative. Crystals for X-ray analysis were obtained by holding saturated THF solutions of I and II at about 0 °C.

Crystallographic Data Collection and Structure Refinement. The crystals of both I and II used for X-ray analysis were small and irregularly shaped; these were coated with an amorphous epoxy resin to reduce contact with the atmosphere. Data were collected at room temperature (~20 °C) with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corp. TEXRAY-230 modification[11] of the SDP-Plus software package.[12] Cell constants were derived from 25 centered reflections in the $14° \leq 2\vartheta \leq 26°$ range. The examination of cell constants, Laue symmetry, and systematic absences showed I to crystallize in a

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(11) TEXRAY-230 is a modification of the SDP-Plus[12] set of X-ray crystallographic programs distributed by the Molecular Structure Corp., 3304 Longmire Dr., College Station, TX 77840, for use with their automation of the CAD-4 diffractometer.
(12) SDP-Plus is the Enraf-Nonius Corp. X-ray diffraction data processing set of programs distributed by B. A. Frenz and Associates, 1140 East Harvey Rd., College Station, TX 77840.

0020-1669/90/1329-0885$02.50/0

Table I. Summary of Crystallographic Data and Processing Parameters

	$SnCl_2$(1-vinylimidazole)$_2$	$SnCl_2$(1-benzylimidazole)$_2$
space group	$P2_1/n$	$Pbcn$
a, Å	6.941 (1)	17.153 (2)
b, Å	19.123 (2)	15.111 (5)
c, Å	11.011 (2)	7.913 (4)
β, deg	11.011 (2)	7.913 (4)
β, deg	105.21 (1)	
V, Å^3	1410.35	2050.92
mol formula	$C_{10}H_{12}N_4Cl_2Sn$	$C_{20}H_{20}N_4Cl_2Sn$
mol wt	377.83	506.01
density, g/cm^3 (calcd; Z = 4)	1.779	1.639
abs coeff, cm^{-1}	μ = 21.848	μ = 15.242
rel transm coeff	0.765–0.996	0.9996–0.9694
λ, Å (Mo Kα)	0.71073	0.71073
scan range for 2ϑ, deg	$4 \le 2\vartheta \le 54$	$4 \le 2\vartheta \le 60$
scan width for each refln, deg	1.0 + 0.35 tan ϑ	0.9 + 0.35 tan ϑ
max scan time, s	150	150
total no. of data collected	3170	3132
data above $3\sigma(I)$ used in refinement	2345[a]	1342[c]
no. of variables	154	127
final $R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0282	0.0314
final $R_w = [\sum w^2(\|F_o\| - \|F_c\|)^2/\sum\|F_o^2\|]^{1/2}$	0.0297	0.0315
weights used	$w = [\sigma(F_o)]^{-2}$	$w = [\sigma(f_o)]^{-2}$

[a] The differences between this number and the previous one is due to the subtraction of reflections that were symmetry related, redundant data collected to obtain reflections suitable for absorption correction (scans), extincted reflections, or data which did not meet the criterion that $I \ge 3\sigma(I)$. [b] Not all the data available between 50 and 60° were collected. After about half of those possible were collected, it became evident that they were mostly unobserved data. Therefore, data were collected only up to the layer with I = 8. [c] The difference between this number and the previous one is due to the subtraction of reflections that were symmetry related, redundant data collected to obtain reflections suitable for absorption correction (ψ scans), extincted reflections, or data which did not meet the criterion that $\ge 3\sigma(I)$.

primitive, monoclinic lattice belonging to the space group $P2_1/n$ (a nonstandard setting of $P2_1/c$) and II to crystallize in a primitive, orthorhombic lattice belonging to the space group $Pbcn$. Both data sets were corrected for absorption by using empirical curves derived from ψ scans.[11,12] The scattering curves were taken from Cromer and Waber's compilation.[13]

The structures of I and II were solved from their Patterson maps by using the tin atom in each as the heavy atom. The tin atom in II was found to lie on a 2-fold axis. A series of refinements of the scale factor, positional parameters, and thermal parameters followed by calculation of difference Fourier maps located the remaining non-hydrogen atoms in both cases. Idealized hydrogen atom positions were calculated for I and II by using C–H = 0.95 Å with thermal parameters of 5.0 Å^2. In both structures, non-hydrogen atoms were refined anisotropically until convergence; hydrogen positions and thermal parameters were not refined. Details of data collection and processing and refinement results are given in Table I. Bond distances and angles are given in Tables II and III.

Results and Discussion

Our previous studies of 1:2 $SnCl_2$ complexes of imidazole and methylimidazoles indicated that coordination occurs through the pyridine nitrogen (N3) of the heterocyclic ring.[10] This conclusion was based on XPS, NMR, and IR parameters; we were unable to obtain crystals of those adducts suitable for X-ray structure determination. The imidazole derivatives in the present study (Figure 1) were chosen with the goal of improving the crystallization characteristics of the adducts through the influence of the substituents and, secondarily, because of the biological activity that might be imparted to the adducts. The complexes $SnCl_2$·2(Im), where Im = 1-vinylimidazole (I), 1-benzylimidazole (II), and 1,2,4-triazole (III), were prepared by the direct combination of the constituents using a small excess of ligand[10] and identified by their composition and spectra.

Adduct Structures. The molecular structure of I (Figure 2) exhibits pseudo-five-coordination in which the substituents are arranged in a distorted trigonal-bipyramidal geometry, with the

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Table II. Positional and Thermal Parameters with Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
	A. $SnCl_2$(1-vinylimidazole)$_2$			
Sn	0.16917 (4)	0.4106 (1)	0.16161 (3)	3.213 (5)
Cl1	−0.1913 (2)	−0.03509 (6)	0.1218 (1)	4.24 (2)
Cl2	0.4274 (2)	0.14483 (6)	0.2243 (1)	4.32 (3)
N1	−0.3118 (5)	0.1803 (2)	−0.0477 (3)	3.03 (7)
N3	−0.0460 (4)	0.1272 (2)	0.0667 (3)	2.92 (7)
N1a	−0.0619 (5)	0.1021 (2)	0.4894 (3)	3.63 (8)
N3a	0.0923 (5)	0.0712 (2)	0.3478 (3)	3.32 (7)
C1	0.0108 (6)	0.1889 (2)	0.0208 (4)	3.72 (9)
C2	−0.1496 (6)	0.2212 (2)	−0.0492 (4)	3.71 (9)
C3	−0.2407 (6)	0.1239 (2)	0.0234 (3)	2.96 (8)
C4	−0.5147 (6)	0.1911 (2)	−0.1089 (4)	3.9 (1)
C5	−0.5793 (7)	0.2405 (3)	−0.1897 (5)	5.3 (1)
C1a	0.2259 (6)	0.0713 (3)	0.4636 (4)	4.5 (1)
C2a	0.1307 (7)	0.0902 (3)	0.5513 (4)	4.3 (1)
C3a	−0.0772 (6)	0.0894 (2)	0.3673 (4)	3.69 (9)
C4a	−0.2212 (7)	0.1260 (3)	0.5367 (4)	5.2 (1)
C5a	−0.2124 (8)	0.1352 (3)	0.6516 (5)	6.6 (1)
	B. $SnCl_2$(1-benzylimidazole)$_2$			
Sn	0.0000	0.05647 (3)	0.2500	3.242 (8)
Cl	0.10782 (9)	0.0830 (1)	0.4995 (2)	5.19 (3)
N1	0.1410 (2)	0.2355 (2)	−0.0658 (4)	3.07 (8)
N3	0.0659 (2)	0.1684 (2)	0.1167 (4)	3.03 (8)
C1	0.0912 (3)	0.2469 (3)	0.1856 (6)	3.2 (1)
C2	0.1374 (3)	0.2897 (3)	0.0753 (6)	3.3 (1)
C3	0.0976 (3)	0.1645 (3)	−0.0345 (6)	3.5 (1)
C4	0.1915 (3)	0.2498 (3)	−0.2143 (6)	4.2 (1)
C5	0.1667 (3)	0.3280 (3)	−0.3220 (6)	3.1 (1)
C6	0.2209 (3)	0.3911 (3)	−0.3666 (6)	3.8 (1)
C7	0.2012 (3)	0.4591 (3)	−0.4747 (7)	4.7 (1)
C8	0.1269 (3)	0.4651 (3)	−0.5355 (6)	4.6 (1)
C9	0.0707 (3)	0.4038 (3)	−0.4869 (7)	4.3 (1)
C10	0.0914 (3)	0.3347 (3)	−0.3820 (6)	3.8 (1)

[a] Atoms were anisotropically refined and are given in the form of the isotropic equivalent thermal treatment defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

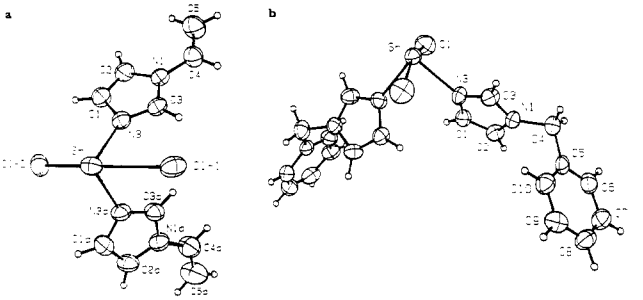

Figure 2. Molecular structures of the complexes: (a) $SnCl_2$·2(1-vinylimidazole) (I); (b) $SnCl_2$·2(1-benzylimidazole) (II).

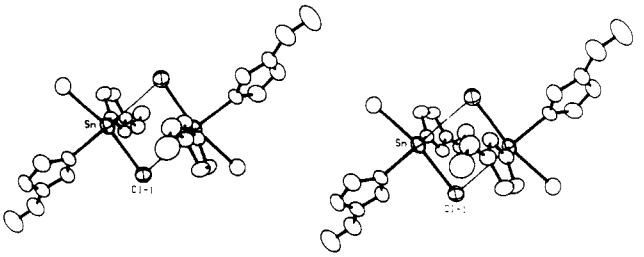

Figure 3. Views of I showing the bridging interaction.

Table III. Bond Distances (Å) and Bond Angles (deg)[a]

A. Bond Distances for $SnCl_2$(1-vinylimidazole)$_2$

Sn–Cl1	2.828 (1)	Sn–Cl_2	2.642 (1)
Sn–N3	2.284 (2)	Sn–N3a	2.323 (2)
N1–C2	1.375 (2)	N1–C3	1.347 (2)
N1–C4	1.408 (2)	N1a–C2a	1.351 (3)
N1a–C3a	1.342 (2)	N1a–C4a	1.417 (3)
N3–C1	1.382 (2)	N3–C3	1.311 (2)
N3a–C1a	1.365 (3)	N3a–C3a	1.297 (2)
C1–C2	1.329 (3)	C4–C5	1.295 (3)
C1a–C2a	1.354 (3)	C4a–C5a	1.263 (3)
Sn–Cl1[b]	3.167 (1)		

B. Bond Distances for $SnCl_2$(1-benzylimidazole)$_2$

Sn–Cl	2.734 (1)	Sn–N3	2.292 (2)
N3–C1	1.375 (3)	N3–C3	1.315 (3)
N1–C2	1.386 (3)	N1–C3	1.329 (3)
N1–C4	1.476 (3)	C1–C2	1.345 (4)
C4–C5	1.518 (4)	C5–C6	1.379 (3)
C5–C10	1.380 (3)	C6–C7	1.380 (3)
C7–C8	1.366 (1)	C8–C9	1.391 (1)
C9–C10	1.380 (1)		
Sn–Cl[c]	3.433 (1)		

C. Bond Angles for $SnCl_2$(1-vinylimidazole)$_2$

Sn–N3–C1	124.6 (1)	Sn–N3–C3	128.3 (1)
Sn–N3a–C1a	124.6 (1)	Sn–N3a–C3a	129.8 (1)
Cl1–Sn–Cl2	159.95 (2)	Cl1–Sn–N3	81.65 (4)
Cl1–Sn–N3a	82.29 (4)	Cl2–Sn–N3	83.99 (4)
Cl2–Sn–N3a	83.10 (4)	N3–Sn–N3a	87.18 (6)
N1–C2–C1	107.0 (2)	N1–C4–C5	124.0 (2)
N3–C1–C2	109.5 (2)	N3–C3–N1	111.0 (2)
N1a–C2a–C1a	106.7 (2)	N1a–C4a–C5a	125.2 (3)
N3a–C1a–C2a	109.1 (2)	N3a–C3a–N1a	112.1 (2)
C1–N3–C3	105.9 (2)	C2–N1–C3	106.7 (2)
C2–N1–C4	129.0 (2)	C3–N1–C4	124.3 (2)
C1a–N3a–C3a	105.6 (2)	C2a–N1a–C3a	106.4 (2)
C2a–N1a–C4a	129.3 (2)	C3a–N1a–C4a	124.2 (2)
Cl1–Sn–Cl1[b]	95.64 (1)	Cl1–Sn–Cl2[b]	94.58 (2)
Cl1–Sn–N3[b]	76.69 (4)	Cl1–Sn–N3a[b]	163.87 (4)

D. Bond Angles for $SnCl_2$(1-benzylimidazole)$_2$

Sn–N3–C1	127.5 (2)	Sn–N3–C3	126.1 (2)
Cl–Sn–Cl	163.16 (4)	Cl–Sn–N3	83.73 (6)
N3–Sn–N3	84.86 (11)	N3–C1–C2	110.1 (2)
N3–C3–N1	111.4 (3)	N1–C2–C1	105.3 (2)
N1–C4–C5	113.3 (2)	C1–N3–C3	105.6 (2)
C2–N1–C3	107.6 (2)	C2–N1–C4	125.5 (2)
C3–N1–C4	126.5 (3)	C4–C5–C6	119.5 (3)
C4–C5–C10	120.9 (2)	C5–C6–C7	120.6 (2)
C5–C10–C9	120.2 (1)	C6–C7–C8	119.8 (1)
C6–C5–C10	119.5 (2)	C7–C8–C9	120.34 (1)
C8–C9–C10	119.50 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Cl1 at $-x, -y, -z$. [c] Cl at $-x, -y, 1 - z$.

lone pair occupying an equatorial position. The vinylimidazole rings are coordinated through the pyridine nitrogen (N3), as expected from our earlier spectroscopic studies of related adducts[10] and those of others.[2,3a] The two donor molecules are structurally equivalent, but there is a significant difference in the two intramolecular Sn–Cl distances (2.642 vs 2.829 Å), indicating that the chlorides are inequivalent (Table III). We attribute the difference to dimer formation in I (Figure 3). The shortest intermolecular Sn–Cl distance (3.167 Å) is small enough to indicate a weak bridging chlorine interaction, making the tin coordination, in effect, pseudooctahedral in the dimer.

The features of the molecular structure of II (Figure 2) resemble those of I with one exception. The two intramolecular Sn–Cl distances are equal in II, and the shortest intermolecular Sn–Cl approach is considerably longer (3.433 Å) than in I. It is notable that the intramolecular Sn–Cl distance in II is close to the average of those in I. Thus, although the unit cell diagrams of the two adducts have similar appearances, dimer formation seems, on the basis of bond distances, to be minimal or absent in II. Given the close structural likeness of the two imidazoles, it is surprising to find such a difference in the solid-state behavior of their adducts. The trans-annular position of the ring substituents argues against the steric requirements of the vinyl and benzyl groups being responsible for the distinction, so electronic effects must be considered.

Table IV. XPS Data for Donors and $SnCl_2$ Adducts[a]

A. Binding Energies, eV

compd	N 1s	C 1s	Cl 2p	Sn $3d_{5/2}$
I	403.2	286.8	202.2	488.8
	401.7		200.4	
	398.5			
1-benzylimidazole	401.1	286.6		
	399.5	286.2		
		285.9		
II	402.2	287.5	201.1	487.8
	400.8	285.8	199.4	
1,2,4-triazole	402.4	288.0		
	400.8	286.4		
	399.6			
III	402.3	289.9	202.7	488.8
	401.4	288.4	200.7	
	400.3	286.2		
	399.2			

B. Coordination Shifts,[b] eV

	N 1s				
adduct	N1	N2	N3	N4	Sn $3d_{5/2}$
I					−0.8
II	−0.3		+2.7		−1.8
III	−0.1	−0.5		+1.8	−0.8

[a] 1-Vinylimidazole could not be accommodated by the XPS instrument, owing to its volatility. [b] Coordination shift = (binding energy of adduct) − (binding energy of free donor or acceptor).

Coordinate Bonding. The p*K*a values of various methylimidazoles[14] shows an increase in basicity, compared to those of the parent heterocycle, which is greatest for 2- and 4-substitution. This trend is also reflected in the Sn $3d_{5/2}$ XPS binding energy coordination shifts[15] for $SnCl_2$·2(Im) adducts, which are more negative by roughly 1 eV for three methylimidazoles than for imidazole itself.[10] Assuming that structural differences between free and complexed $SnCl_2$ do not produce large shifts in the XPS bands, a more negative Sn $3d_{5/2}$ XPS coordination shift in a given adduct implies a greater donor–acceptor charge transfer and a stronger coordinate bond. Lacking XPS data for 1-vinylimidazole due to its volatility (Table IVA), we are unable to compare N 1s coordination shifts of I and II; however, the Sn $3d_{5/2}$ coordination shifts for I and II (Table IVB) are −0.8 and −1.8 eV, respectively. The vinyl derivative adduct shift is the same as that of $SnCl_2$·2(imidazole)[10] (−0.8 eV), while the benzyl adduct shift closely matches those of the methylimidazole adducts. We conclude that the structural difference between I and II is attributable to the greater donor influence of benzylimidazole, which, resembling the methylimidazoles, more effectively saturates the acceptor capacity of the $SnCl_2$ and thereby reduces any tendency toward increased coordination number by the tin.

Two of the nitrogens (N2 and N4) of 1,2,4-triazole can be regarded as pyridine-like, and the third (N1), pyrrole-like, so there is a question of which nitrogen is the site of coordination to tin. Of the N 1s XPS coordination shifts for III (Table IVB), that of N4 is most positive (+1.8 eV), suggesting that it is the donor site, but the coordination shift is somewhat smaller than found in other adducts (2.7–3.1 eV).[10] This relatively small N 1s coordination shift of N4 along with the small negative Sn $3d_{5/2}$ coordination shift (−0.8 eV) points to a lesser donor–acceptor

(14) Albert, A. *Heterocyclic Chemistry*; Oxford University Press: Bristol, U.K., 1959; p 345.

(15) The XPS coordination shift = (binding energy of adduct) − (binding energy of uncoordinated molecule). In the case of Sn $3d_{5/2}$, reference is to the binding energy of free $SnCl_2$, 489.6 eV.[10]

Table V

A. ^{1}H NMR Data for Donors and $SnCl_2$ Adducts (ppm)

compd	N1–H	C2–H	C4–H	C5–H	R(H)
1-vinylimidazole		7.95 (s)	7.58 (s)	7.00 (s)	4.84 (d, J = 9 Hz, C=C*H*a) 5.46 (d, J = 16 Hz, C=C*H*b) 7.13 (m, $J \sim$ 9 Hz, –(*H*)C=CH_2)
I		7.96 (s)	7.60 (s)	7.00 (s)	4.86 (d, J = 9 Hz, C=C*H*a) 5.48 (d, J = 15 Hz, C=C*H*b) 7.16 (m, J = 9 Hz, –*H*C=CH_2)
1-benzylimidazole		7.71 (s)	unresolved	6.88 (s)	7.18 (m, C_6H_5) 5.10 (s, $-CH_2C_6H_5$)
II		8.13 (s)	unresolved	7.15	7.27 (br, s, C_6H_5) 5.22 (s, $-CH_2C_6H_5$)
1,2,4-triazole	14.1 (s, br)		8.32 (s, C3 + C5)		
III	13.6 (s, br)		8.31 (s, C3 + C5)		

B. ^{13}NMR Data for Donors and $SnCl_2$ Adducts (ppm)

compd	C2	C4	C5	R
1-vinylimidazole	136.6	129.6	129.9	116.1 (–*C*H=CH_2) 100.8 (–CH=*C*H_2)
I	136.8	129.7	129.8	116.3 (–*C*H=CH_2) 102.0 (–CH=*C*H_2)
1-benzylimidazole	137.4	127.7	128.8	137.7 (aromatic, C1) 128.6 (aromatic, ortho) 127.4 (aromatic, meta) 119.5 (aromatic, para) 49.5 (–*C*H_2Ph)
II	137.0	129.0 (4, 5)		137.8 (aromatic, C1) 128.7 (aromatic, ortho) 127.7 (aromatic, meta) 120.0 (aromatic, para) 50.1 (–*C*H_2Ph)
1,2,4-triazole	147.1 (C3 + C5)			
III	148.4 (3 or 5)		145.6 (5 or 3)	

C. ^{119}Sn NMR Data for $SnCl_2$ Adducts (ppm)

adduct	$\delta(^{119}Sn)$	adduct	$\delta(^{119}Sn)$
I	–368.5 (s)	III	–374.8 (s)
II	–340.9 (s), –271.1 (s)[a]		

[a] Unidentified impurity.

charge transfer in the triazole adduct, comparable to the case of the weakest imidazole adducts.

NMR Spectra. The ^{1}H NMR data for the heterocycles and the three adducts appear in Table VA along with assignments of the resonances. Except for C4–H in benzylimidazole, which was not resolved, all magnetically distinct hydrogens were identified. The C3 and C5 hydrogens of 1,2,4-triazole and III were found to be equivalent either by coincidence or due to tautomerism between N1 and N2 in dimethyl sulfoxide solution. The corresponding resonance in the heterocycle appeared as a broad singlet near δ 14, which shifted upfield about 0.5 ppm in III. The ^{1}H coordination shifts of the 1-vinylimidazole and 1,2,4-triazole adducts were quite small, consistent with the indication from XPS coordination shifts that the donor–acceptor interactions in I and III are relatively weak. The considerably larger coordination shifts of the 1-benzylimidazole adduct appear to support the indication from XPS shifts that II is a stronger adduct than the others.

The ^{13}C NMR data (Table VB) are generally consistent with the conclusions drawn from ^{1}H NMR results. Separate resonances were resolved for each structurally distinct carbon except in 1,2,4-triazole, where C3 and C5 were not resolved. The N1–N2 tautomerism suggested above would account for the ^{13}C equivalences in the heterocycle, but it should be noted that the C3 and C5 resonances *were* resolved in III. Assuming a static N–Sn bond at N4, the presence of a fast N1–N2 tautomerism would cause C3 and C5 to appear equivalent, in contrast to what was seen. If tautomerism is absent in III, it is probably also absent in the heterocycle, so we conclude that the magnetic environments of the 3- and 5-positions are coincidentally equivalent.

The ^{119}Sn NMR spectra of the adducts consisted of single lines with chemical shifts (Table VC) in the same range as those of imidazole– and methylimidazole–$SnCl_2$ adducts.[10] The report of a rough correlation between ^{119}Sn NMR shifts and coordination number in tin(IV) adducts[16] allows a comparison with the tin(II) azole adducts, the shifts of which correspond to those reported for five- and six-coordinate tin(IV) adducts, perhaps indicating that one or more molecules of solvent are coordinated to tin in solutions of these adducts.

The fact that the azole ligands occupy equatorial positions around tin and so are cis to one another in the solid-state structures of I and II shows a similarity to the structures of *cis*-diamine complexes of platinum[6] and tin(IV) dialkyl dihalides[7] known to exhibit antitumor activity. Whether the cis configuration of the N-donors in I and II, believed to be important to the antitumor function, persists in solution is unclear at present. The indication from the ^{119}Sn NMR shifts of the complexes that at least one solvent molecule enters the coordination sphere of tin in solution opens the possibility that the cis relationship is not retained. Studies of the biological activity of these complexes are planned.

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Supplementary Material Available: Tables of positonal parameters for hydrogen atoms, torsional angles, general temperature factor expressions, and refined temperature factor expressions for I and packing diagrams of I and II (3 pages); a listing of observed and calculated structure factors for I (13 pages). Ordering information is given on any current masthead page.

(16) Carini, C.; Pelizzi, G.; Tarasconi, P.; Pelizzi, C.; Molloy, K. C.; Waterfield, P. C. *J. Chem. Soc., Dalton Trans.* **1989**, 289.