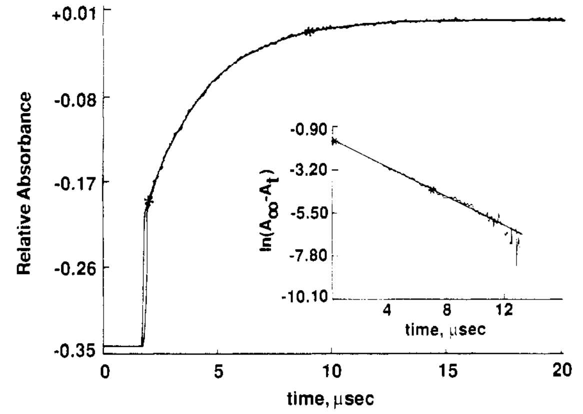


Figure 2. Plot of absorbance vs time after pulsed laser flash photolysis of W(CO)$_6$ in 4-acetylpyridine/methylcyclohexane solution (0.0110 M) at 24.5 °C. The observation wavelength is 460 nm. The inset is a plot of ln ($A_\infty - A_t$) vs time for this reaction.

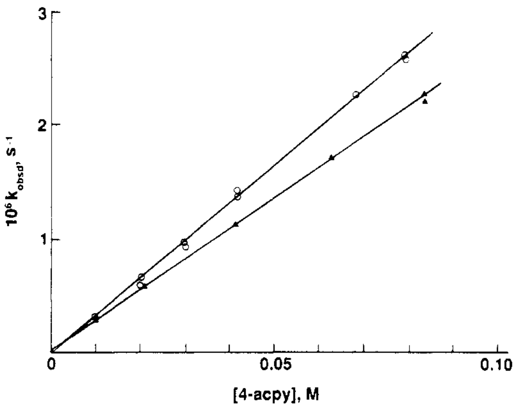


Figure 3. Plots of k_{obsd} vs [4-acetylpyridine] in (○) cyclohexane and (▲) methylcyclohexane at 24.5 °C.

solution (0.0110 M) at 24.5 °C exhibits pseudo-first-order kinetics (as do plots at other concentrations). Plots of k_{obsd} vs [4-acpy] at 24.5 °C in both MCH and CH, shown in Figure 3, exhibit similar rates, again suggestive of similar intermediates produced as predominant reactive species. In contrast to the earlier report that such plots were curved and that plots of $1/k_{obsd}$ vs 1/[4-acpy] were linear with finite intercepts (vide supra),[1] those obtained here are linear over the entire concentration range, a range similar to that employed in the earlier investigation. Values of the second-order rate constants, k ($=k_{obsd}/[\text{4-acpy}]$), at different temperatures and in CH and MCH, together with the corresponding activation parameters, are given in Table I.

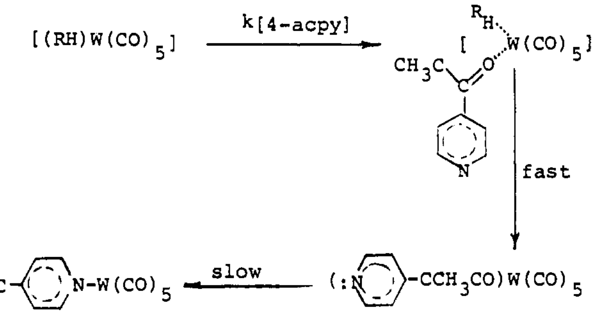
While the observed rate behavior, consistent with eq 3, could be interpreted in terms of the dissociative mechanism proposed by Lees and Adamson,[1] the activation data and other recent studies strongly support an interchange mechanism (Scheme II) in which there is appreciable 4-acpy-W bond making in the transition state. Rate constants taken over a temperature range 7.9–45.6 °C afford $\Delta H^* = 3.4$ (2) kcal/mol. This value may be contrasted to the strength of the W–H–C agostic interaction,[12,13] recently determined from photoacoustical calorimetric data to be 13.4 (28) kcal/mol in [(*n*-heptane)W(CO)$_5$].[14] The calculated entropy of activation, −13.0 (6) cal/(deg mol) (Table I), also strongly supports an interchange mechanism. Finally, other recent studies in mixed solvents have indicated such a hydrocarbon displacement pathway to be accessible in [(*n*-heptane)W(CO)$_5$] even for 1-hexene,[15] a much weaker nucleophile than 4-acetylpyridine.

Table I. Bimolecular Rate Constants for Reactions Taking Place after Flash Photolysis of W(CO)$_6$ in 4-Acetylpyridine Solutions (Solvent = Methylcyclohexane, Cyclohexene) at Various Temperatures[a]

T, °C	solvent	$10^{-7}k$, M^{-1} s^{-1}
7.9	cyclohexane	2.28 (3)
14.8		2.73 (3)
24.5		3.17 (18)
24.9		3.37 (9)
35.7		4.32 (2)
45.6		5.30 (8)
24.5	methylcyclohexane	2.78 (4)

[a] Activation parameters: $\Delta H^* = 3.4$ (2) kcal/mol; $\Delta S^* = -13.0$ (6) cal/(deg mol).

Scheme II



Acknowledgment. Support of this research by the National Science Foundation under Grant CHE-8800127 and the Robert A. Welch Foundation (Grant B-434) is gratefully acknowledged. The experiments and analyses of the data produced were performed at the Center for Fast Kinetics Research (CFKR), University of Texas at Austin. The CFKR is supported jointly by the Biomedical Research Technology Program of the Division of Research Resources of NIH (Grant RR000886) and by the University of Texas at Austin. The advice and technical assistance of the staff at the CFKR are much appreciated. We also thank Shulin Zhang for experimental assistance and Prof. Theodore J. Burkey for permission to cite his work in advance of publication.

Registry No. W(CO)$_5$, 30395-19-8; 4-acpy, 1122-54-9.

Supplementary Material Available: Supplementary Table I, giving pseudo-first-order rate constants for reactions taking place after pulsed laser flash photolysis of W(CO)$_6$ in 4-acetylpyridine/alkane solutions (alkane = cyclohexane, methylcyclohexane) at various temperatures (3 pages). Ordering information is given on any current masthead page.

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(12) It is probable that interaction between CH and MCH with the W(CO)$_5$ moiety is via a linear "agostic" R–C–H interaction, see: (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

(13) For a dissociative (D) mechanism leading to formation of a [W(CO)$_5$] intermediate, the enthalpy of activation should be equal to or greater than the solvent–W bond strength.

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Contribution from the Department of Chemistry,
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^{99}Ru NMR Spectroscopy of Ruthenium(II) Polypyridyl Complexes

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The ground- and excited-state properties of ruthenium(II) polypyridyls have been the subject of enormous attention in recent

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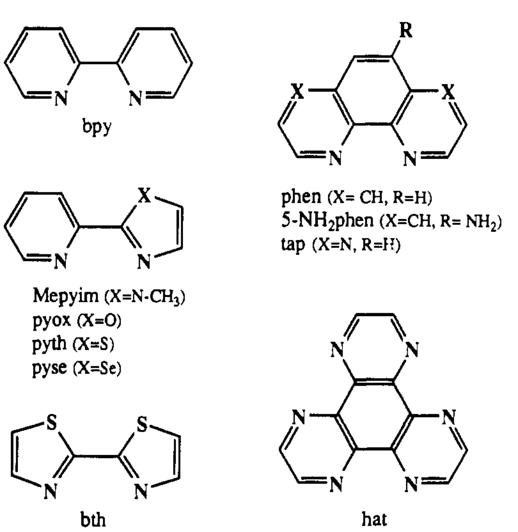

Figure 1. Structures and abbreviations of the heterocyclic chelating ligands.

years.[1] This class of compounds has provided a benchmark for the application of new experimental techniques to the study of inorganic and organometallic materials, such as time-resolved resonance Raman spectroscopy,[2a] magnetic circular dichroism,[2b] laser or FAB mass spectrometry,[2c] picosecond laser photolysis in single crystals at very low temperatures,[2b] and triplet–triplet absorption spectroscopy.[2d] Moreover, $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) and related complexes have become a paradigm in the study of photoinduced electron-transfer reactions.[3]

The last 10 years have also been a very exciting time for transition-metal NMR studies, mainly due to the widespread introduction of Fourier-transform superconducting magnet spectrometers with broad-band capabilities. Traditionally, the cobalt-59 nucleus has occupied the central role for understanding the different factors that determine the chemical shifts of transition-metal nuclei.[4] Ruthenium NMR spectroscopy was introduced recently,[5,6] but subsequent reports in the literature have been scarce.[7-11] Two of the ruthenium isotopes are magnetically active: ^{99}Ru and ^{101}Ru (both possess $I = {}^5/_2$ but are in natural abundances of 12.72 and 17.07%, respectively). The former is the preferred nucleus for observation mainly because of its lower quadrupolar moment (0.076×10^{-28} m^2 vs 0.44×10^{-28} m^2),[5] which makes the resonances relatively narrow. However, the lack of research in ^{99}Ru NMR spectroscopy is somewhat surprising in light of the not too unfavorable magnetic features of this nucleus: moderate quadrupolar moment (comparable to ^{51}V or ^{53}Cr) and receptivity similar to that of ^{13}C.[4a] The major drawback is its very low resonance frequency (Ξ = 4.605 MHz for $Ru(CN)_6^{4-}$ in D_2O),[6] which requires the use of relatively high sample concentrations in order to overcome the acoustic waves generated in the spectrometer probe at these frequencies (*acoustic ringing*).[12] Nevertheless, the huge ^{99}Ru chemical shift range (over 9000 ppm),[7,13] makes this nucleus a very attractive probe for the detection of very subtle changes in the coordination sphere of the metal.

Table I. ^{99}Ru NMR Chemical Shifts of Ruthenium(II) Polypyridyl Complexes[a]

complex	X^-	*C*, M	δ, ppm[b]	$W_{1/2}$, Hz
$Ru(bpy)_2(hat)^{2+}$	PF_6^-	0.08	4548	220
$Ru(tap)_2(bpy)^{2+}$	PF_6^-	0.08	4574	180
$Ru(bpy)_3^{2+}$	PF_6^-	0.15	4575	65
	PF_6^-	0.10[c]	4540	170
	Cl^-	0.18[d]	4534	140
$Ru(tap)_2(hat)^{2+}$	PF_6^-	0.10	4594	180
$Ru(tap)_3^{2+}$	PF_6^-	0.10	4606	180
	Cl^-	0.10[d]	4576	200
$Ru(5\text{-}NH_2phen)_3^{2+}$	PF_6^-	0.10	4618 (*mer* + *fac*)	170
$Ru(phen)_3^{2+}$	ClO_4^-	0.20	4683	120
	Cl^-	0.18[d]	4642	250
$Ru(Mepyim)_3^{2+}$	PF_6^-	0.10	4726 (*fac*, 25%)[e]	90
			4732 (*mer*, 75%)[e]	150
$Ru(pyse)_3^{2+}$	PF_6^-	0.09	4839 (*fac*, 25%)	90
			4855 (*mer*, 75%)	130
$Ru(pyth)_3^{2+}$	PF_6^-	0.06	4868 (*fac*, 23%)[e]	170
			4882 (*mer*, 77%)[e]	260
$Ru(pyox)_3^{2+}$	PF_6^-	0.08	4876 (*fac*, 41%)	120
			4904 (*mer*, 59%)	160
$Ru(bth)_3^{2+}$	PF_6^-	0.10	5040	140
$[(tap)_2Ru(hat)Ru(bpy)_2]^{4+}$	PF_6^-	0.09	4674 (Ru-bpy)	450
			4788 (Ru-tap)	350
$[(phen)_2Ru]_3(hat)^{6+}$	PF_6^-	0.10	5086	800

[a] At 22 ± 3 °C in acetonitrile-d_3, unless otherwise specified. [b] From $Ru(CN)_6^{4-}$ in D_2O (0.5 M) at 11.519 MHz. Estimated error ±5 ppm. [c] In DMSO-d_6. [d] In D_2O. [e] Relative percentages from ^1H NMR data.

Herein we report a detailed investigation on ^{99}Ru NMR spectroscopy of ruthenium(II) polypyridyls in order to gain further insight into the various factors that determine the ^{99}Ru chemical shifts, as well as to demonstrate the enormous potential of the technique to sort out geometrical features of this class of compounds. Different types of chelating ligands (Figure 1) have been selected for systematically studying monometallic as well as polymetallic complexes.

Experimental Section

The preparation of the chelating ligands containing five-membered heterocyclic moieties, 1-methyl-2-(2-pyridyl)imidazole (Mepyim), 2-(2-pyridyl)oxazole (pyox), 2-(2-pyridyl)thiazole (pyth), 2-(2-pyridyl)selenazole (pyse), and 2,2′-bithiazole (bth), as well as the corresponding homoleptic complexes, has been reported previously.[14] The six-membered polyaza heterocycles 1,4,5,8-tetraazaphenanthrene (tap)[15] and 1,4,5,8,9,12-hexaazatriphenylene (hat),[16] and the complexes $Ru(tap)_3^{2+}$,[17]

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$Ru(bpy)_2(hat)^{2+}$,[18] and $Ru(tap)_2(bpy)^{2+}$,[19a] have also been described. The synthesis of $Ru(tap)_2(hat)^{2+}$, $[(tap)_2Ru(hat)Ru(bpy)_2]^{4+}$, and $[(phen)_2Ru]_3(hat)^{6+}$ (phen = 1,10-phenanthroline) will be published elsewhere.[19b] $Ru(5\text{-}NH_2phen)_3^{2+}$ was synthesized by a published procedure.[20] $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ (as chloride salts) were purchased from Aldrich. Their counteranions have been replaced as needed. The reference compound $Na_4Ru(CN)_6$ was prepared according to Pascal.[21]

Ruthenium-99 NMR spectra have been recorded at 22 ± 3 °C with an IBM-Bruker AF-250 spectrometer tuned at 11.541 MHz and equipped with a broad-band probe. A 0.06–0.2 M solution of the complex salt in acetonitrile-d_3 (+99% atom D), DMSO-d_6 (+99% atom D), or D_2O (+99.8% atom D) (Aldrich) was placed in a 5-mm tube. Typically the spectra were acquired in a 3000–6000-Hz window with 20-μs pulses, and the individual free induction decays (FID, 40 000–1 000 000) were collected for 0.085 s after a 900-μs preacquisition delay. A trapezoidal apodization function or initial zero filling was applied to the resulting averaged FID before Fourier transform analysis.[12] Positive chemical shifts indicate downfield shifts from $Ru(CN)_6^{4-}$ (0.5 M in D_2O), which has been used as reference (in our spectrometer this compound resonates at 11.519 MHz, in agreement with the value reported by Dykstra and Harrison[6,8]).

Results and Discussion

^{99}Ru NMR chemical shifts of the different ruthenium(II) polypyridyl complexes are collected in Table I, along with the observed line width at half-height ($W_{1/2}$) of the corresponding signals. The latter have been routinely obtained without strict control of the temperature and should be taken only as upper values for comparison purposes. The chemical shift of $Ru(bpy)_3^{2+}$ is the only value previously reported,[7] and our measurement for this complex is in excellent agreement. (It should be pointed out that although the ^{99}Ru chemical shifts in ref 7 are reported with respect to $Ru(CN)_6^{4-}$, they have probably been calculated from the resonance frequency of RuO_4, which leads to slightly different ppm values. This would explain the "disturbing" discrepancy[4d] between the values reported in refs 7 and 8 for the two reference compounds.) The ^{99}Ru resonances of the studied polypyridyl complexes span a range of more than 500 ppm, showing the high sensitivity to the environment around the metal center. A solvent effect is also evident from the values displayed in Table I: upfield shifted and relatively wider signals are observed in changing from acetonitrile to water. Whereas the shielding effect is still unclear, the larger line width in D_2O should be related to the higher viscosity of this solvent due to the dependence of the relaxation rate of an electric quadrupole mechanism on the correlation time.[4d] Similar line width broadening has been described[8] for *fac*-$Ru(CO)_3I_3$, although in this case the resonance in water is deshielded with respect to that in acetonitrile. However, the carbonyl–iodide complex might form a new species (with a different chemical shift) in an aqueous medium due to solvolysis of a halide ligand, as evidenced by the chloride analogue.[7]

From the data displayed in Table I it is evident that the complexes containing six-membered ligands resonate at higher field than those containing five-membered heterocycles. No correlation with other ground- or excited-state parameters (d–π^* or π–π^* absorption energies, π^*–d emission energy, redox potentials, or triplet lifetimes)[18,22] has been found. As a case in point, the absorption maxima of the bpy and Mepyim tris chelates (452 and 445 nm, respectively) or the oxidation potentials of the bpy and pyox complexes (1.26 and 1.27 V/SHE, respectively) are very similar but their ^{99}Ru chemical shifts lie far apart.

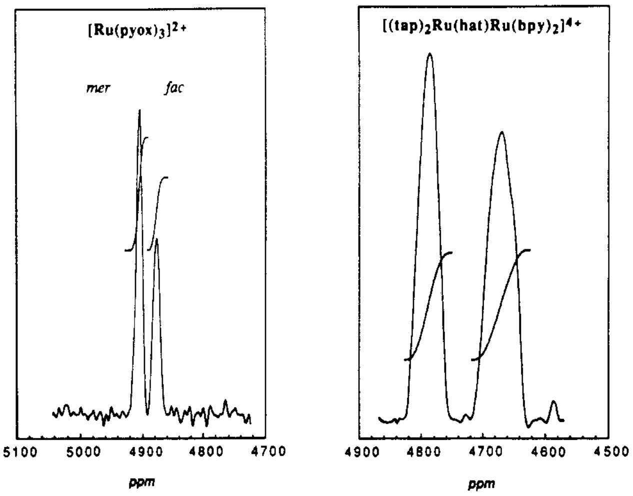

Figure 2. ^{99}Ru NMR spectra (at 11.519 MHz) in CD_3CN of $[Ru(pyox)_3]^{2+}$ and $[(tap)_2Ru(hat)Ru(bpy)_2]^{4+}$ (chemical shift from $Ru(CN)_6^{4-}$).

It has been demonstrated[4c,d] that the shielding of transition-metal nuclei in complexes with singlet ground states is usually dominated by the residual paramagnetism contribution. For octahedral complexes, and assuming a crystal-field approach, this term is inversely proportional to the energy separation of the $^1T_{1g}$ state from the $^1A_{1g}$ ground state (ΔE). Therefore, the higher the ligand field strength, the lower the chemical shift of the central metal nucleus.[4d,13,23] It has even been suggested that transition-metal NMR spectroscopy might be more sensitive than optical spectroscopy for placing ligands in the spectrochemical series.[24] Unfortunately, the metal-centered transitions in the absorption spectra of ruthenium(II) polypyridyls are obscured by the strong ligand-centered and metal-to-ligand charge-transfer transitions, rendering a correlation with the ^{99}Ru chemical shifts impossible. Nevertheless, the weaker σ-donation and π-back-bonding of the five-membered heterocycles[25] and their larger bite angle should yield a lower ligand field strength and therefore a higher ^{99}Ru chemical shift. The first two effects would account again for the shielding differences between the ligands containing a single azole ring (Table I), whereas the second one would make the phen complex resonate at a lower field than the bpy complex, as observed also for the Co(III) chelate.[4d] The less favorable bite angle of the tap and hat ligands might be balanced by their high π-acceptor properties,[17-19,22b] yielding a larger effective ligand field strength.

The chemical shift differences between the mixed-ligand complexes are more difficult to rationalize. It should be noted that if the replacement of a reference ligand by another causes a significant variation in ΔE, the change in chemical shift, which depends on ΔE^{-1}, will not be constant.[4d]

Our results show also that ^{99}Ru NMR spectroscopy is a sensitive tool to differentiate geometrical isomers. For example, Figure 2 depicts the ^{99}Ru NMR spectrum of a *mer*/*fac* mixture (60:40, as determined by ^{1}H and ^{13}C NMR spectroscopy) of $Ru(pyox)_3^{2+}$. The signals may be easily assigned by their line width since the electric field gradient (which determines the electric quadrupole relaxation of spin $>^1/_2$ nuclei) should be smaller for the more symmetric *fac* isomer.[4d,9,10] Similar results have been obtained for other unsymmetrical ligands (Table I). The relative amount of the isomers may be determined by integration, provided the ^{99}Ru signals are separated by more than ca. 20 ppm. Introduction of one amino group in the 5-position of the phen ligand also yields a mixture of *mer* and *fac* isomers; however, this minor modification does not produce sufficient differences in the proximity of the

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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 $[(\mathrm{phen})_2\mathrm{Ru}]_3(\mathrm{hat})^{6+}$ (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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and I. Bernal[1b]

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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 $\mathrm{SnCl_2}$ 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 $\mathrm{R_2SnX_2{\cdot}2L}$ agents[7] are present in the new complexes. To our knowledge, there have been no previous structure reports of $\mathrm{SnCl_2{\cdot}2}$(*N*-donor) complexes although the related germanium adduct $\mathrm{GeCl_2}$·(benzothiazole) was structurally characterized.[8] We therefore wish to report the synthesis of three new 1:2 $\mathrm{SnCl_2}$ complexes with azole derivatives, including X-ray structure determinations of the 1-vinyl- and 1-benzylimidazole complexes.

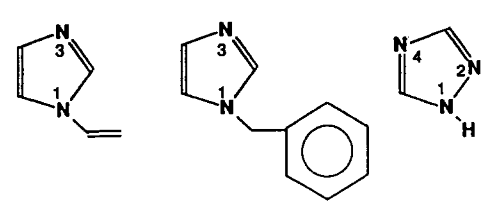

Figure 1. Azole structures and donor site numbering.

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 $\mathrm{SnCl_2{\cdot}2Im}$ 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 $\mathrm{SnCl_2{\cdot}2}$(1-vinylimidazole) (I, mp 98 °C dec), $\mathrm{C_{10}H_{12}N_4SnCl_2}$: 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 $\mathrm{SnCl_2{\cdot}2}$(1-benzylimidazole) (II, mp 40 °C dec), $\mathrm{C_{20}H_{20}N_4SnCl_2}$: 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 $14^\circ \leq 2\vartheta \leq 26^\circ$ 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.