ketene ligand is bonded to the metal.

Ketene **2** can be isolated by column chromatography on silica. If adsorbed water has not been removed from the silica (by heating under vacuum) prior to use, water adds to both the coordinated and the uncoordinated ketene and both acid **4**[12] and its metal complex **5**[13] are obtained. **4** is readily cleaved from the metal by heating an acetone solution of **5** (Scheme I).

Though the hitherto unknown ketene **2** is thermally stable, it is extremely reactive toward moisture. It is a very interesting compound for organic reactions, because of the different properties of the substituents at the ketene carbon. Owing to the workup procedure (including treatment of the reaction mixture with NEt_4Cl) the isolated yield of **2** is rather low (12%). However, since we could not detect other silicon-containing products from the thermolysis of **1**, we believe that the actual yield of **2** + **3** is much higher. For instance, the isolated yield of acid **4** is 32%, if a mixture of **2** + **3** is chromatographed on (undried) silica and the resulting mixture of **4** + **5** is treated with acetone as described above. Use of ketene **2** for syntheses therefore should proceed without isolation of **2**.

The structure of **2** is shown in Figure 1.[14] The dihedral angle between the planes O, C1, C2, S, Si and C1, S, C3 is 86°. This conformation excludes conjugation between the sulfur lone pairs and the C=C bond and rather suggests hyperconjugation between the C—S and C=C bonds.[15] The latter view is also supported by the S–C1 (sp^2) distance, which is as long as S–C3 (sp^3). Similar C–S bond lengths are found in thio enol ethers, e.g., 174.8 pm in CH_2=CHSMe[16] and 176.4 (2)–177.1 (2) pm in *cis*- and *trans*-Ph(MeS)C=C(SMe)Ph.[17] Interestingly, the C1—Si distance in **2** (184.9 (6) pm) is distinctly shorter than the C(carbene)—Si distance in $(CO)_5M$=C(OEt)$SiPh_3$ (M = Cr, 200 (2)pm; M = Mo, 194 (2) pm)[6] and other silylcarbene complexes.[18]

Carbonylation of carbene ligands to yield ketenes or ketene complexes is probably an important step in catalytic reactions. Formation of these compounds has occasionally been observed in stoichiometric reactions of carbene complexes (e.g., ref. 19 and 20). For $(CO)_5M$=CPh_2 (M = Cr, W) an intramolecular carbene–CO coupling has been proven.[18] In the case of **1** attack of CO (intra- or intermolecularly) to the carbene carbon is obviously facilitated by the SEt substituent, because the corresponding ethoxy-substituted complex $(CO)_5W$=C(OEt)$SiPh_3$ only yields the corresponding ketene EtO(Ph_3Si)C=C=O at a CO pressure of about 50 atm.[3]

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Registry No. **1**, 98014-95-0; **2**, 98014-97-2; **3**, 98014-96-1; **4**, 98014-98-3; **5**, 98049-99-1.

Supplementary Material Available: Listings of final atomic parameters, bond lengths and angles, and observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

(12) **4**: mp 180 °C; ^{1}H NMR (chloroform-d_1) δ 10.73 (s, 1 H), 7.53 (m, 15 H), 3.80 (3, 1 H), 2.70 (q, 2 H), 1.2 (t, 3 H); IR (methylene chloride) ν(CO) 1691 cm^{-1}. Anal. Calcd for $C_{22}H_{22}O_2SSi$: C, 69.80; H, 5.86. Found: C, 70.00; H, 5.96.

(13) **5**: ^{1}H NMR (acetone-d_6) δ 10.8 (s, 1 H, 7.6 (m, 15 H), 4.5 (s, 1 H), 3.1 (q, 2 H), 1.0 (t, 3 H); IR (pentane) ν(CO) 2072 (m), 1982 (w), 1943 (vs), 1930 (sh), 1695 (w) cm^{-1}.

(14) Crystals obtained by cooling a pentane solution of **2**: triclinic, space group $P\bar{1}$, a = 975.7 (6) pm, b = 1015.2 (6) pm, c = 1052.3 (5) pm, α = 83.77 (4)°, β = 79.28 (4)°, γ = 76.11 (4)°; V = 992 × 10^6 pm^3; Z = 2, d(calcd) = 1.21 g cm^{-3}; Mo Kα (λ = 71.069 pm). A total of 2874 independent reflections (ω scan, 2° ≤ 2θ ≤ 49°) were reduced to structure factors by correction for Lorentz and polarization effects. Solution of the structure by MULTAN. Anisotropic refinement for all atoms by full-matrix least squares (fixed hydrogen parameters, isotropic B) resulted in R = 0.087 and R_w = 0.090 ($1/w = \sigma(F)^2$) for 2291 structure factors with $F_o \geq 4\sigma(F_o)$.

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Two-Dimensional ^{119}Sn NMR Exchange Spectroscopy as a Tool for the Elucidation of the Dynamic Stereochemistry of Tin Compounds

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Summary: The first ^{119}Sn 2D NOESY NMR spectrum allows to demonstrate unambiguously that the ditin compound $CH_2[(C_6H_5)Sn(SCH_2CH_2)_2NCH_3]_2$ isomerizes at the tin center in an uncorrelated way. The advantages of 2D NMR over traditional 1D NMR line-shape analysis are shortly emphasized.

This report describes the first two-dimensional (2D) ^{119}Sn NMR (exchange spectroscopy, EXSY) spectrum. It illustrates the power of this method in the elucidation of the dynamic stereochemistry of tin compounds. The model system examined for this purpose is a compound exhibiting two five-coordinate tin centers, $CH_2[(C_6H_5)Sn(SCH_2CH_2)_2NCH_3]_2$, hereafter compound **1**. Its synthesis, molecular structure, and solution stereochemistry were discussed recently.[2] The static stereochemistry in solution was unambiguously established from NMR data.[2] Among these the 1D ^{119}Sn NMR spectrum of **1**, at room temperature in $CDCl_3$, exhibits four signals in the approximate ratio 0.9:1:1:0.2. This was interpreted by assigning the first and the last signals to the C_{2v} isomers aa and ae, respectively, in which the two tin atoms are homotopic, while the two central, equally intense signals were

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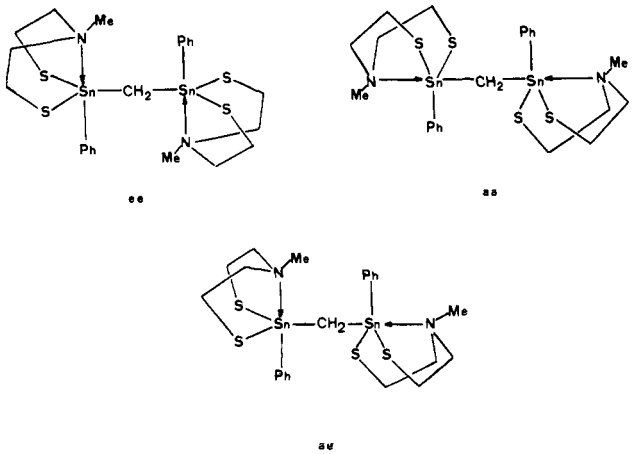

Figure 1. The three isomers of compound 1.

assigned to the C_s isomer ae.[2] These isomers are depicted in Figure 1. The letters a and e refer to whether the methylene bridge occupies the axial or equatorial position at the two tin centers. At higher temperatures these four ^{119}Sn NMR signals coalesce to a unique residual signal.[2] Two modes of isomerization are in principle[2] possible for 1: the mode M_1 in which each tin center isomerizes in an uncorrelated way, and the mode M_2 in which both tin centers isomerize in a correlated way. The presence of a unique residual signal at higher temperature can be explained in principle by the mode M_1 alone. No evidence for aggregates of 1 in solution has been found: in the solid state the species is monomeric and a cryoscopic molar weight determination in benzene showed 1 to be monomeric.

Alternative explanations are that both modes proceed at similar rates[2] or that the two residual signals under the mode M_2 are accidentally isochronous. This note shows that 2D ^{119}Sn NMR EXSY spectra[3,4] of 1 provide an unambiguous choice between these alternatives.

The 2D ^{119}Sn NMR EXSY spectra of a ca. 0.35 M solution of 1 in $CDCl_3$, presented in Figures 2 and 3 together with the 1D ^{119}Sn spectrum, were recorded at 25 °C at 186.5 MHz with a Bruker AM 500 spectrometer, working in the FT mode equipped with an Aspect 3000 computer and using the Bruker DISB 84 program.

Homonuclear tin–tin couplings are well visible on the 1D spectrum: the satellites of the two equally intense central ae signals are unresolved: $|^2J(^{119}Sn–^{117}Sn)| \simeq |^2J(^{119}Sn–^{119}Sn)| = 173$ Hz. The satellites of the low field aa signal are due to a pure $|^2J(^{119}Sn–^{117}Sn)|$ coupling of 192 Hz. The chemical shifts are given as previously[2] with respect to tetramethyltin as external standard. The pulse sequence used for the 2D spectra is the one proposed by Jeener, Ernst, and co-workers[3a] to observe exchange processes, preparation – 90° – evolution – 90° – mixing – 90° – detection, with experiments at two different mixing

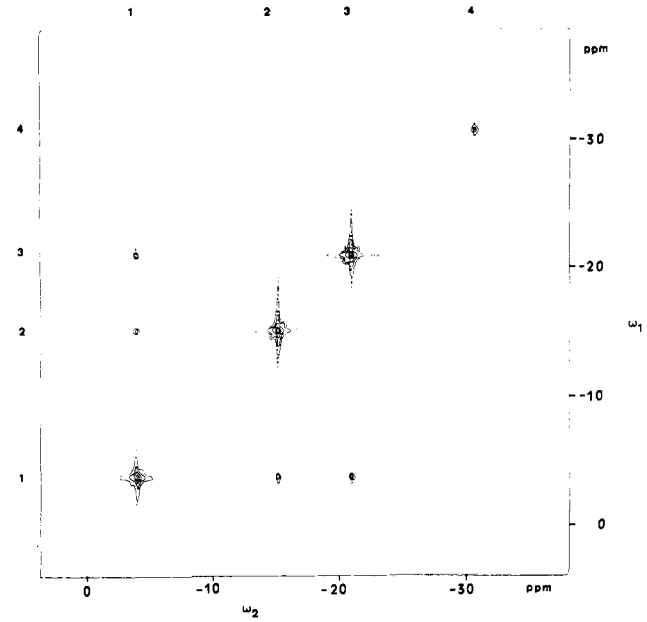

Figure 2. The 2D ^{119}Sn NMR EXSY spectrum of 1 in $CDCl_3$ at room temperature with a mixing time of $\tau_m = 5$ ms.

times[3a] (see below): $\tau_m = 5$ ms (Figure 2) and $\tau_m = 50$ ms (Figure 3). Broad-band decoupling on protons was used during the whole sequence, with, however, a lower decoupling power during the preparation period. All two-dimensional data matrices were submitted in both t_1 and t_2 dimensions to a Lorentz–Gauss transformation and zero-filled in t_1 prior to Fourier transformation.

For a system of uncoupled exchanging spins, the relevant part of the 2D spectrum, excluding the so-called axial peaks,[3a,c] is given by

$$S(\omega_1,\tau_m,\omega_2) = \sum_{k,l} \tfrac{1}{2} \frac{1/T_{2k}}{(\omega_2 - \omega_k)^2 + 1/T_{2k}^2}[\exp(\mathbf{L}\tau_m)]_{kl} \tfrac{1}{2} \frac{1/T_{2l}}{(\omega_1 - \omega_l)^2 + 1/T_{2l}^2}\mathbf{M}_{0l} \quad (1)$$

In eq 1 each term of the double sum corresponds to a peak of the 2D spectrum at the frequency coordinate ω_l,ω_k, on the frequency axes ω_1 and ω_2 associated with the evolution period t_1 and the detection period t_2, respectively. The nondiagonal elements of L_{kl} of $\mathbf{L}$ are those of the Kubo–Sack matrix[3–5] in the absence of significant dipolar relaxation[3a] and represent merely the rate constant of magnetization transfer from magnetic site l to magnetic site k. The diagonal elements of $\mathbf{L}$, which are irrelevant to the stereochemical analysis, contain terms related to both chemical exchange and longitudinal relaxation.[3a] In the type of 2D experiment described here, essentially a picture of the nondiagonal part of this matrix $\mathbf{L}$ is desired, in this case $\mathbf{L}_1$ or $\mathbf{L}_2$ (or both), since it indicates directly whether the exchange process proceeds through mode M_1 or M_2, respectively. The mixing time τ_m[3a] is the time period between the evolution and the detection periods during which the magnetization exchange due to chemical process is allowed to proceed along the z axis and M_{0l} is the equilibrium magnetization along the z axis, associated with the exchanging magnetic site l and proportional to its

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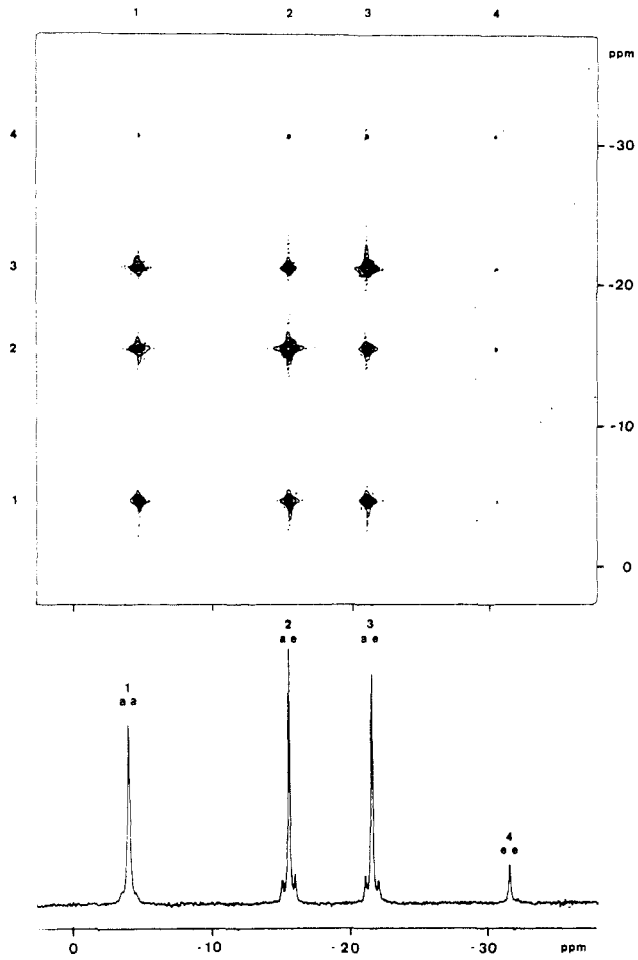

Figure 3. The 2D ^{119}Sn NMR EXSY spectrum, with τ_m = 50 ms, and the corresponding 1D spectrum of 1 in $CDCl_3$ at room temperature.

population. The matrices $\mathbf{L}_1$ and $\mathbf{L}_2$ associated with the modes M_1 and M_2 are

$$\mathbf{L}_1 = \begin{array}{c|cccc} & 1 & 2 & 3 & 4 \\ \hline 4 & 0 & k_1 & k_1 & l_1^4 \\ 3 & k_1'' & 0 & l_1^3 & k_1' \\ 2 & k_1'' & l_1^2 & 0 & k_1' \\ 1 & l_1^1 & k_1''' & k_1''' & 0 \end{array} \qquad (2)$$

$$\mathbf{L}_2 = \begin{array}{c|cccc} & 1 & 2 & 3 & 4 \\ \hline 4 & k_2 & 0 & 0 & l_2^4 \\ 3 & 0 & k_2' & l_2^3 & 0 \\ 2 & 0 & l_2^2 & k_2' & 0 \\ 1 & l_2^1 & 0 & 0 & k_2'' \end{array} \qquad (3)$$

The matrix entry indices 1, 2, 3, and 4 refer to the ^{119}Sn magnetic sites of isomer aa, to both sites of ae, and to the one of ee, respectively. As in the experimental spectra, the main diagonals of $\mathbf{L}_1$ and $\mathbf{L}_2$ are read from the bottom left to the top right.

Equation 1 shows that the 2D spectrum can exhibit only a cross peak at the frequency coordinates ω_k,ω_l if the matrix element $\exp(\mathbf{L}\tau_m)_{kl}$ is nonzero. Series expansion of the operator $\exp(\mathbf{L}\tau_m)$ of eq 1 gives

$$\mathbf{K} = \exp(\mathbf{L}\tau_m) = \mathbf{I} + \mathbf{L}\tau_m + \mathbf{L}^2\frac{\tau_m^2}{2!} + \mathbf{L}^3\frac{\tau_m^3}{3!} + \ldots \qquad (4)$$

Hence, the choice of the length of τ_m becomes of prime importance. Indeed if τ_m is very short, the operator $\mathbf{K}$ reduces to the identity and no cross peak at all will appear in the 2D spectrum. For a suitably choosen value of τ_m, the operator $\mathbf{K}$ is approximated by $\mathbf{I} + \mathbf{L}\tau_m$ and the cross peaks of the 2D spectrum are in one-to-one correspondence to the desired nondiagonal elements of $\mathbf{L}$ that establish the nature of chemical exchange. When the mixing time is too long, higher order terms of $\mathbf{L}$ appear, and the 2D spectrum can exhibit cross peaks at entries where $\mathbf{L}$ itself exhibits zero nondiagonal elements, so that the 2D spectrum can no longer be the desired picture of $\mathbf{L}$. The 2D spectrum of Figures 2 and 3 illustrate this. The spectrum 2, with the shorter τ_m, 5 ms, shows that mode M_1 alone proceeds. Indeed, all cross peaks are zero, except those at the entries 12, 13, 21, and 31. These correspond to nonzero nondiagonal elements in $\mathbf{L}_1$ but zero elements in $\mathbf{L}_2$. That cross peaks associated with row and column 4 are absent at this short τ_m is attributed to the low intensity of signal 4 and a slight overenhancement.[6]

Examination of eq 3 shows that the matrix $\mathbf{L}$ is in fact block diagonal, which implies that the higher powers of $\mathbf{L}_2$ will never exhibit cross peaks at entries where $\mathbf{L}_2$ itself exhibits zero nondiagonal elements. The spectrum of Figure 3 with the longer τ_m, 50 ms, displays crosspeaks where spectrum 2 with the shorter τ_m, 5 ms, does not. Hence, mode M_2 can proceed neither alone nor with a rate that is significant with respect to that of mode M_1.

This excludes clearly the second alternative explanation that the residual signal at high temperature could be due to two accidentally isochronous residual signals arising from mode M_2 alone. Therefore the isomerization can be considered as essentially uncorrelated. These straightforward 2D NMR arguments show the power of this technique in elucidating stereochemical problems which could not be solved by traditional 1D NMR, especially in the present case in which line-shape analysis would have required the tedious determination of the strong temperature dependence of signal intensities, chemical shifts, and line widths.

On the other hand, however, spectrum 3 illustrates the importance of finding the correct mixing time. This spectrum, obtained with the longer τ_m, 50 ms, does exhibit cross peaks at all entries. Either this reflects the higher powers of $\mathbf{L}_1$ in the series expansion 4 becoming significant, i.e., two-step isomerizations of M_1 become observable or M_2 one-step isomerizations become just observable at mixing times for which M_1 one-step isomerizations can be considered as rapid. Hence such 2D EXSY spectra should always be recorded with different mixing times.

When the optimal τ_m has been found, the stereochemical information provided is much more straightforward than that available from 1D NMR spectra. Furthermore, the data were obtained for several spectra in only a few hours. We are currently developing the application of 2D EXSY ^{119}Sn NMR to other stereochemically nonrigid tin compounds.

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knowledge Prof. Dr. M. Pereyre and Mr. M. Pêtraud of the University of Bordeaux for the opportunity offered to R.W. in 1983 to discuss deeply the specific experimental and theoretical facets of ^{119}Sn NMR.

A Model for Thiophene Chemisorption: A Stabilized, η^1,S-Thiophene Complex and Its Relationship to η^5-Coordination

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Summary: The unstable species $[(C_5H_5)Ru(PPh_3)_2(\eta^1,S\text{-}C_4H_4S)]^+$ has been observed in solution and shown to convert to $[Ru(C_5H_5)(\eta^5\text{-}C_4H_4S)]^+$. An η^1,S-thiophene complex has been stabilized in the form $[(C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2]X$ (**2**). An X-ray structural study of **2** (X = BPh_4) confirms the structure and shows that the sulfur is pyramidal. Displacement reactions of **2** have been studied.

Although $\pi(\eta^5)$-complexation of thiophenes has been recognized for many years,[1] it is only recently that η^1,S-coordination has been demonstrated for a dibenzothiophene derivative.[2] This report describes the characterization of a simple η^1,S-thiophene complex, its stabilization by chelation, and evidence that this type of complex is a precursor to η^5-thiophene coordination. We suggest that the dynamics of thiophene coordination are relevant to the chemisorption of thiophene on metal surfaces.[3,4]

Treatment of CD_2Cl_2 solutions of $(C_5H_5)Ru(PPh_3)_2Cl$ with $AgBF_4$ in the presence of thiophene gives a yellow, thermally unstable compound assigned as $[(C_5H_5)Ru(PPh_3)_2(C_4H_4S)]BF_4$ (**1**). The ^1H and ^{31}P NMR spectra show that **1** is a cyclopentadienyl complex (δ_{Cp} 4.52) which contains equivalent phosphine ligands (δ_P 38.7). Compound **1** could not be obtained in pure form, and the microanalytical data were generally low in carbon and high in sulfur. Both compound **1** and the recently reported $[(C_5H_5)Fe(CO)_2(C_4H_4S)]BF_4$ are proposed to contain S-bound thiophene ligands.[5] Upon standing in solution **1** steadily decomposed to give a new complex whose ^1H NMR spectrum was characterized by a Cp singlet (δ 5.40) and a pair of multipets (6.32, 6.16 ppm) in a 5:4 ratio (Figure 1). This new complex has been identified as $[(C_5H_5)Ru(\eta^5\text{-}C_4H_4S)]BF_4$ (eq 1).[6]

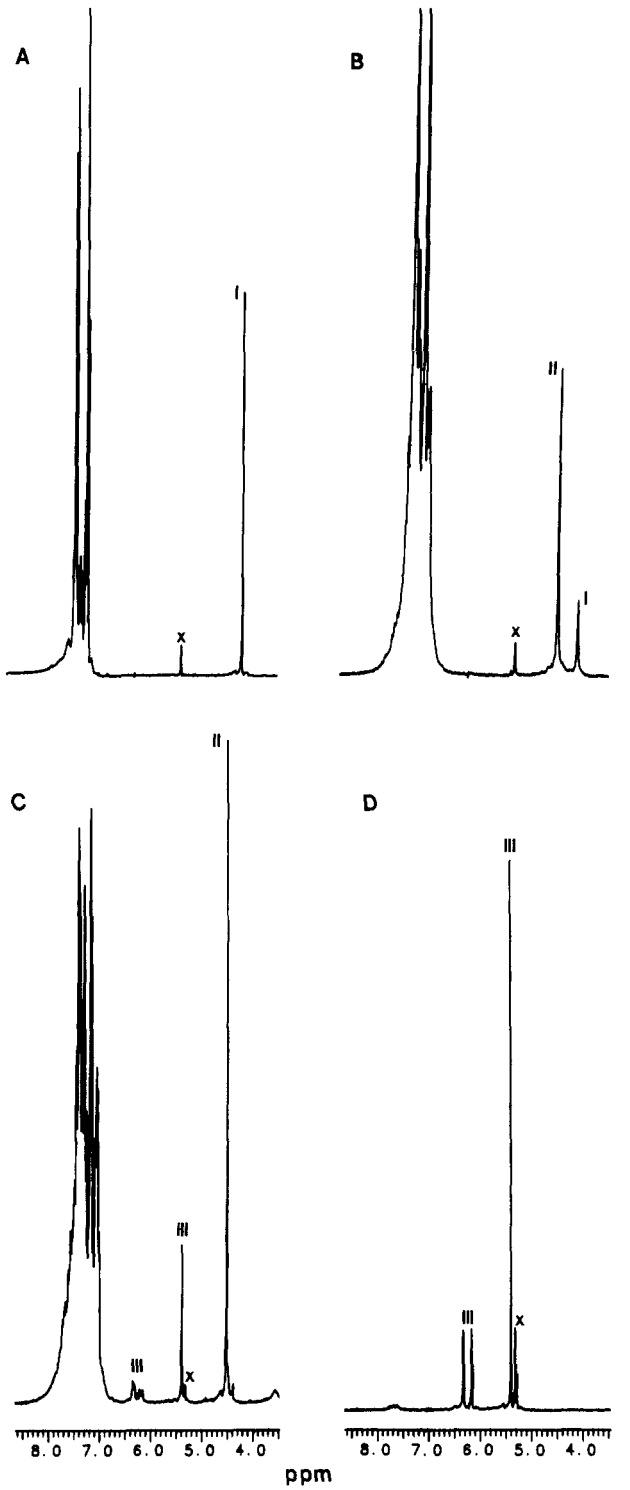
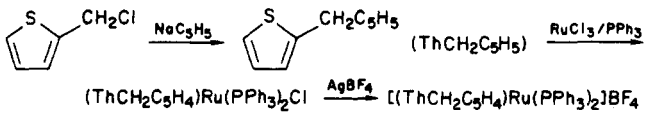


Figure 1. 200-MHz ^1H NMR spectra of $(C_5H_5)Ru(PPh_3)_2Cl$ and thiophene (10 equiv) (spectrum A), the same solution 4 min after addition of 1 equiv of $AgBF_4$ (spectrum B), the same solution 30 min later (spectrum C), and purified $[(C_5H_5)Ru(C_4H_4S)]BF_4$ in CD_2Cl_2. Signals are labeled I for $(C_5H_5)Ru(PPh_3)_2Cl$, II for $[(C_5H_5)Ru(PPh_3)_2(C_4H_4S)]^+$, III for $[(C_5H_5)Ru(C_4H_4S)]^+$, and x for CH_2Cl_2.

Scheme I



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