Determination of the Rate of Cis/Trans Isomerization of the Octahedral Adducts of Tin(IV) Tetrachloride with Dimethyl Sulfide by Tin-119 NMR Magnetization Transfer

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We wish to report the results of a ^{119}Sn NMR magnetization transfer experiment providing, for the first time, an unequivocal determination of the rate of cis–trans isomerization of the adducts of a tin(IV) tetrahalide with a neutral Lewis base in solution in an inert solvent. Although magnetization transfer NMR is becoming a well-established technique for quantifying chemical exchange rates,[1] it has, in general, been limited to the so-called "popular nuclei"[2] and this is a novel example of its successful application to more "exotic" systems.

The ability of tin(IV) tetrahalides to form 1:2 addition complexes with a range of neutral Lewis bases is well-known.[3] Such adducts have been characterized by X-ray diffraction analysis[4] and vibrational,[5] Mössbauer,[6] NQR,[7] and NMR[8] spectroscopy. We have shown, with infrared and Raman studies,[9] that octahedral $SnX_4 \cdot 2L$ adducts with L = dialkylchalcogens exist as either the cis or the trans isomer in the solid, although in one case both forms could be isolated. In solution in inert solvents, the presence of both isomers is not uncommon, and we have investigated the mechanism of both cis–trans isomerization and ligand exchange processes in such solutions using ^1H, ^{19}F, and ^{31}P NMR spectroscopy.[8] In the presence of excess ligand, the solution kinetics of the adducts are governed by three possible exchange processes: (a) that occurring between cis-coordinated and free ligand, (b) the equivalent reaction on the trans isomer, and (c) that of the trans to cis interconversion. These three processes may be characterized by the rate constants k_c, k_t, and k_i, respectively. In a previous article,[10] we have shown that on increasing the temperature, the ^1H NMR signal of *cis*-$SnCl_4 \cdot 2Me_2S$ and that of free Me_2S coalesce long before the effects of chemical exchange become apparent on the resonance of *trans*-$SnCl_4 \cdot 2Me_2S$. This first process was assigned, on the basis of the first-order rate law and the activation parameters, to a fast ligand exchange reaction occurring at the cis adduct via a D mechanism. In this case, the measured mean residence time of the ligand in the cis site, τ_c, is related to the chemical exchange rate constant by $1/\tau_c = k_c/2$. At higher temperatures, a coalescence is observed between the two remaining ^1H NMR signals. Here, the mean residence time of the ligand in the trans site, τ_t, can be expressed as the sum of two terms, $1/\tau_t = (1/\tau_{t\text{-}f}) + (1/\tau_{t\text{-}c})$, where $\tau_{t\text{-}f}$ is related to the rate constant for trans-coordinated/free ligand exchange by $1/\tau_{t\text{-}f} = k_t/2$ and $\tau_{t\text{-}c}$ is related to the rate constant for cis–trans isomerization by $1/\tau_{t\text{-}c} = k_i$. Under such conditions, ^1H NMR is incapable of distinguishing between cis–trans isomerization and bound ligand/free ligand exchange at the trans site. As a basis for discussion, we assumed[10] that the eventual broadening of the ^1H NMR signal of the *trans*-$SnCl_4 \cdot 2Me_2S$ adduct was solely the result of bound ligand/free ligand exchange, while noting that cis–trans isomerization could not be ruled out and indeed that the two alternatives were not mutually exclusive. In an attempt to clarify the situation, we originally undertook a ^{119}Sn NMR line-broadening study. Bound ligand/free ligand exchange does not affect the $^{119}Sn\{^1H\}$ NMR spectrum, whereas cis–trans isomerization should result in the broadening and eventual coalescence of the ^{119}Sn NMR resonances. Tin-119 NMR spectra of 0.2 m $SnCl_4 \cdot 2Me_2S$ solutions in CD_2Cl_2 are readily obtained and exhibit two sharp peaks (separated by ca. 350 Hz, with line widths of ca. 15 Hz) in the absence of exchange, corresponding to the two isomers. On increasing the temperature, both signals broaden considerably. However, this is not due to chemical exchange since the extent of broadening of both signals is unrelated to the population of the sites, but may be ascribed mainly to the effects of relaxation due to ^{119}Sn–^{35}Cl scalar coupling.[11] The effect is so pronounced as to obscure the line broadening resulting from cis–trans isomerization.

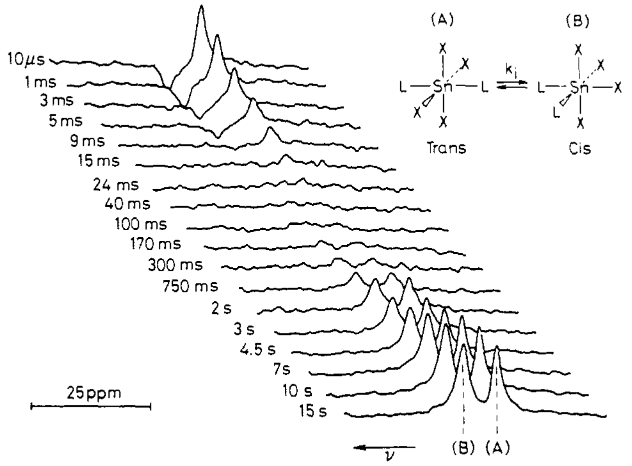

Figure 1. 74.5-MHz $^{119}Sn\{^1H\}$ NMR spectra of a 0.2 m $SnCl_4 \cdot 2Me_2S$ (cis/trans = 1.42:1.00) and 0.1 m Me_2S solution in CD_2Cl_2 at 285 K as a function of the time interval *t* between the inversion pulse train and the observation pulse. The pulse sequence employed was the following: $(-45°-D_1-90°-D_1-45°-t-90°-D_2)-$ where the delay D_1 = 0.91 ms, the 180° pulse = 40 µs, and the delay D_2 = 12 s. Each spectrum was recorded over a sweep width of 7462 Hz and required 350 pulses. 4K data points were recorded, and an exponential line broadening of 65 Hz has been applied.

Line-shape analysis is not, however, the only method of obtaining quantitative dynamic information from chemically exchanging systems. Under favorable conditions, modifications of the double-resonance techniques originally described by Hoffman and Forsén[12] may be applied to exchanging systems to yield quantitative information.[13] Magnetization transfer techniques are applicable when the exchange rate is greater or equal to the longitudinal relaxation rate, $1/T_1$. Conversely, line-shape analysis

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(1) Campbell, I. D.; Dobson, C. M.; Ratcliffe, R. G.; Williams, R. G. P. *J. Magn. Reson.* **1978**, *29*, 397–417.

(2) These are ^1H, $^{10,11}B$, $^{14,15}N$, ^{19}F, and ^{31}P as defined in: "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1977. However, a recent report on ^{113}Cd NMR saturation transfer exists by: Ellis, P. D.; Yang, P. P.; Palmer, A. R. *J. Magn. Reson.* **1983**, *52*, 254–266.

(3) Dumas, J. M.; Gomel, M. *Bull. Soc. Chim. Fr.* **1974**, 1885–1890.

(4) Beattie, I. R.; Hulme, R.; Rule, L. *J. Chem. Soc.* **1965**, 1581–1583.

(5) (a) Beattie, I. R.; McQuillan, G. P.; Rule, L.; Webster, M. *J. Chem. Soc.* **1963**, 1514–1518. (b) Beattie, I. R.; Rule, L. *Ibid.* **1964**, 3267–3273; **1965**, 2995–2996. (c) Clark, R. J. H.; Errington, W. *Inorg. Chem.* **1966**, *5*, 650–656. (d) Ohkaku, N.; Nakamoto, K. *Ibid.* **1973**, *12*, 2440–2446. (e) Ruzicka, S. J.; Merbach, A. E. *Helv. Chim. Acta* **1975**, *58*, 584–587.

(6) Barbieri, R.; Silvestri, A. *Inorg. Chim. Acta* **1981**, *47*, 201–212.

(7) (a) Kravchenko, E. A.; Maksyutin, Y. K.; Guryanova, E. N.; Semin, G. K. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1968**, *6*, 1271. (b) Maksyutin, Y. K.; Guryanova, E. N.; Kravchenko, E. A.; Semin, G. K. *J. Chem. Soc., Chem. Commun.* **1973**, 429–430. (c) Petrosyan, V. S.; Yashina, N. S.; Reutov, O. A.; Bryuchova, E. V.; Semin, G. K. *J. Organomet. Chem.* **1973**, *52*, 321–331.

(8) Ruzicka, S. J.; Merbach, A. E. *Inorg. Chim. Acta* **1977**, *22*, 191–200.

(9) Ruzicka, S. J.; Merbach, A. E. *Inorg. Chim. Acta* **1976**, *20*, 221–229.

(10) Ruzicka, S. J.; Favez, C. M. P.; Merbach, A. E. *Inorg. Chim. Acta* **1977**, *23*, 239–247.

(11) Webb, G. A. In "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1977; *Background Theory of NMR Parameters*, p 83–84.

(12) Hoffman, R. A.; Forsén, S. *J. Chem. Phys.* **1963**, *39*, 2829–2901; **1964**, *40*, 1189–1196.

(13) (a) Anet, F. A. L.; Bourn, A. J. R. *J. Am. Chem. Soc.* **1967**, *89*, 760–768. (b) Sherrod, S. A.; Boekelheide, V. *Ibid.* **1972**, *94*, 5513–5515. (c) Bleich, H. E.; Glasel, J. A. *Ibid.* **1975**, *97*, 6585–6586. (d) Waelder, S.; Lee, L.; Redfield, A. G. *Ibid.* **1975**, *97*, 2927–2928. (e) Dahlquist, F. W.; Longmuir, K. J.; Du Vernet, R. B. *J. Magn. Reson.* **1975**, *17*, 406–410. (f) Alger, J. R.; Prestegard, J. H. *Ibid.* **1977**, *27*, 137–141. (g) Campbell, I. D.; Dobson, C. M.; Ratcliffe, R. G. *Ibid.* **1977**, *27*, 455–463. (h) Morris, G. A.; Freeman, R. *Ibid.* **1978**, *29*, 433–462. (i) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650–2659. (j) Hennig, J.; Limbach, H. H. *J. Magn. Reson.* **1982**, *49*, 322–328. (k) Lambert, J. B. In "The Multinuclear approach to NMR Spectroscopy"; Lambert, J. B., Riddell, F. G., Eds.; Reidel: Dordrecht, 1983; NATO ASI Series, *Dynamic NMR Processes*, p 91–110.

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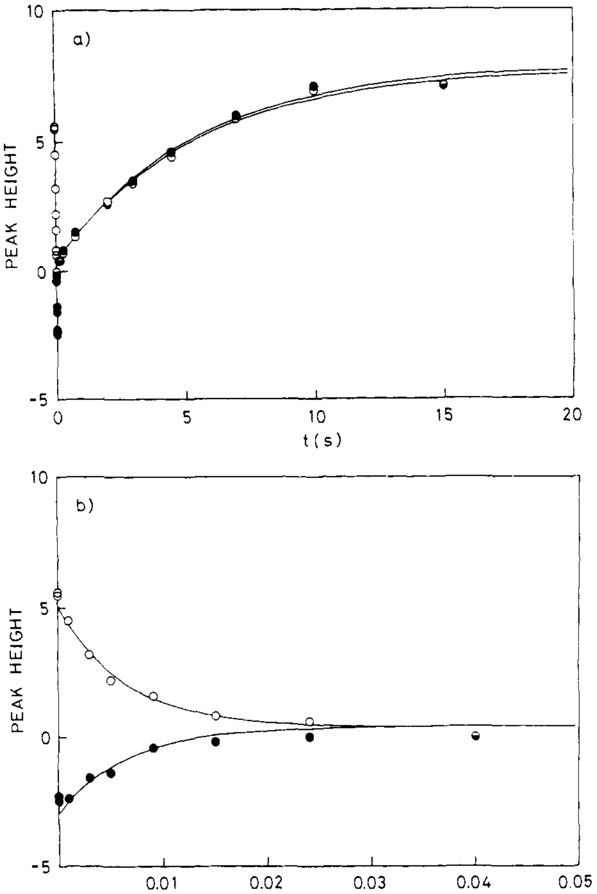

Figure 2. Plot of peak heights (arbitrary units) against time for the peaks illustrated in Figure 1 ((○) trans, (●) cis). The peak heights were obtained directly from the spectra. Plot b is an x-axis expansion of plot a. The solid lines are generated by the equations given in ref 16 and are fitted to the experimental data by an interative routine. Numerical analysis yields values of k_i = 94.0 ± 8.3 s^{-1} and an exchange averaged value of $1/T_1(^{119}Sn) = 0.19 \pm 0.02\ s^{-1}$.

is most accurate around the coalescence point, becoming less sensitive to the rate of exchange as the line shape approaches either the slow or fast exchange limits.[14] Values of the tin-119 longitudinal relaxation rate, $1/T_1(^{119}Sn)$, measured on the *cis*- and *trans*-$SnCl_4{\cdot}Me_2S$ adducts were determined at 285 K to be 0.24 ± 0.02 and 0.22 ± 0.02 s^{-1}, respectively, using an inversion recovery pulse sequence ($T_1 \neq T_2$ for these compounds because of the scalar coupling contribution to T_2). Since these values are considerably less than the exchange rate at the trans site, as measured by ^1H NMR line-shape analysis, we felt that this system was an ideal candidate for a magnetization transfer experiment.

Figure 1 illustrates the effect of selectively inverting the ^{119}Sn NMR resonance of the cis isomer in a 0.2 m $SnCl_4{\cdot}2Me_2S$ solution in CD_2Cl_2 at 285 K by using a modification of the so-called "1-2-1" pulse train.[15] From the decrease in intensity of the trans isomer signal, it is clear that magnetization is being transferred between the two sites, providing unambiguous evidence of a cis-trans isomerization process.

Figure 2 shows the plot of peak height against time for both signals. In the absence of cross relaxation, the return to equilibrium of the magnetization may be described by the equations given by Led and Gesmar.[16] The experimental data were fitted to these equations by an iterative, nonlinear least-squares routine to yield a value of k_i of 94 ± 8 s^{-1}. Proton NMR line-shape analysis[10] provides a value of $1/\tau_t = k_i + (k_t/2)$ of 101 ± 4 s^{-1} at the same temperature. It is clear from the comparison of the results of magnetization transfer and line-broadening experiments that the cis-trans isomerization rate is much greater than that of bound ligand/free ligand exchange at the trans site. This is contrary to the working hypothesis assumed previously.[10]

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Registry No. *cis*-$SnCl_4{\cdot}2Me_2S$, 63038-92-6; *trans*-$SnCl_4{\cdot}2Me_2S$, 62182-06-3; Me_2S, 75-18-3; ^{19}Sn, 14314-35-3.

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[14] Mann, B. E. *J. Magn. Reson.* **1976**, *21*, 17-23.

[15] Sklenar, V.; Starcuk, Z. *J. Magn. Reson.* **1982**, *50*, 495-501.

[16] Led, J. J.; Gesmar, H. *J. Magn. Reson.* **1982**, *49*, 444-463.

Effective, Thermal Three-Carbon + Two-Carbon Cycloaddition for Cyclopentenone Formation: Formal 1,3-Dipolar Cycloaddition of Cyclopropenone Ketals

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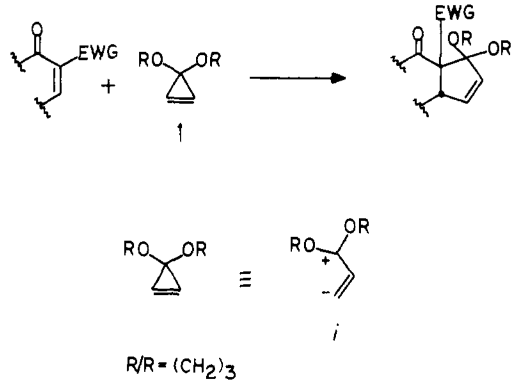
Increasing efforts have been expended to develop general 3-carbon + 2-carbon cycloadditions for functionalized cyclopentane formation with the expectation that such a process could prove to be an effective complement to the [4 + 2] Diels-Alder reaction used for the regio- and stereocontrolled preparation of functionalized six-membered rings. A number of approaches have been explored and a summary of the work to date has been compiled.[2] Although a number of multistep procedures are available for the introduction of cyclopentane systems, their direct formation by a single cycloaddition is rare.[3,4] Transition-metal-promoted reactions have emerged as the single most explored approach to the effective mediation of such 3-carbon + 2-carbon addition reactions.[2,4]

Herein, we describe a preliminary study of the *thermal* reaction of cyclopropenone ketals **1**[5] with electron-deficient olefins,[6] eq 1,



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[1] (a) Searle Scholar Recipient, 1981-1984. Recipient of a National Institutes of Health career development award, 1983-1988 (CA 00898). (b) National Institutes of Health predoctoral fellow (GM 07775).

[2] Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2315, 2326.

[3] For recent work, see: (a) Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1981**, *103*, 1604. (b) Mayr, H.; Seitz, B.; Halberstadt-Kausch, I. K. *J. Org. Chem.* **1981**, *46*, 1041. (c) Little, R. D.; Muller, G. W.; Venegas, M. G.; Carroll, G. L.; Bukhari, A.; Patton, L.; Stone, K. *Tetrahedron* **1981**, *37*, 4371 and references cited therein.

[4] (a) Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61 and references cited therein. (b) Fierz, G.; Chidgey, R.; Hoffmann, M. H. R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 410. (c) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495. Abram, T. S.; Baker, R.; Exon, C. M.; Rao, V. B. *J. Chem. Soc., Perkin Trans. 1* **1982**, *285*, 301. (d) Binger, P. *Synthesis* **1973**, 427. Binger, P.; Germer, A. *Chem. Ber.* **1981**, *114*, 3325. Binger, P.; Schuchardt, U. *Ibid.* **1981**, *114*, 3313. Noyori, R.; Yamakawa, M.; Takaya, H. *Tetrahedron Lett.* **1978**, 4823 and references cited therein.

0002-7863/84/1506-0805$01.50/0