The further simplifications hold if $^3t'^* \rightarrow {}^3p^*$ and $^3c'^* \rightarrow {}^3p^*$ relaxations are faster than back energy transfer, i.e., $k_3^{t,c} > k_{-2}^{t,c}$. Failure of appropriate acceptors to quench stilbene triplets to ^1c suggests that this relationship is valid at least for the cis isomer. In any case, since fast processes are involved, the $k_{-2}^{t,c}/k_3^{t,c}$ ratios are expected to be temperature insensitive. Assuming no exothermicity in the initial donor–acceptor encounters, $\Delta H_1^{t,c} = 0$,[14] the $K_1^{t,c}$ reflect the entropy change (cratic) for bringing two solutes together.[15]

The lines in Figure 2 give log A values of 9.66 ± 0.30 and 8.80 ± 0.13 and E values of 6.03 ± 0.30 and 4.74 ± 0.20 kcal/mol for ^1t and ^1c, respectively. Both A factors are smaller than 10^{12} s^{-1}, the value expected for a strictly vertical excitation transfer, eq 1.[16] Converting E values to activation enthalpies gives $\Delta H_2^{t} = 5.4 \pm 0.3$ kcal/mol and $\Delta H_2^{c} = 4.1 \pm 0.2$ kcal/mol, invalidating the postulation[6] that the 0-0 band in the $T_1 \leftarrow S_0$ transition requires no more than 42.7 kcal/mol for ^1c. Finite activation enthalpies also invalidate Bylina's mechanism[5] which ascribes all inefficiency in the excitation transfer process to the magnitude of F–C overlap factors. The ΔH_2 values, E_T for anthracene, and the 2.3-kcal/mol enthalpy difference[17] between ^1t and ^1c give 48.1 and 49.1 kcal/mol as the energies of $^3t'^*$ and $^3c'^*$, respectively.[14,18] The energy of $^3t'^*$ is very near that of the F–C allowed spectroscopic $^3t^*$–^1t transition, ~49 kcal/mol.[4,19] In contrast, the energy of $^3c'^*$ is substantially lower than that of $^3c^*$, ~59 kcal/mol,[4] but very close to that expected for $^3p^*$,[11] suggesting sufficient distortion in the excitation transfer process to achieve nearly all possible energy stabilization.[20] The low A_t value, compared with the 10^{12} s^{-1} predicted by eq 1,[16] appears to contradict the conclusion that excitation transfer is vertical for ^1t. Since A_t is approximately equal to k_{dif} at room temperature, a transition from vertical to nonvertical energy transfer would not be reflected in deviation from eq 2. Alternatively, if distortion of $^3t^*$ offers no enthalpy advantage, vertical excitation transfer may be followed by an entropy-driven twisting to $^3p^*$ which diminishes back energy transfer.[21]

Experiments with other donors and acceptors are in progress.

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References and Notes

(1) K. Sandros, *Acta Chem Scand.*, **18**, 2355 (1964).
(2) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **85**, 2516 (1963).
(3) W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).
(4) For a review see J. Saltiel et al., *Org. Photochem.*, **3**, 1 (1973).
(5) A. Bylina, *Chem. Phys. Lett.*, **1**, 509 (1968).
(6) S. Yamauchi and T. Azumi, *J. Am. Chem. Soc.*, **95**, 2709 (1973).
(7) A. A. Lamola, *Tech. Org. Chem.*, **14**, 17 (1969).
(8) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice Hall, Englewood Cliffs, N.J., 1969, p 160.
(9) Anthracene triplet decay was measured at 430 nm using a Northern-Precision kinetic flash spectrometer. A 1,4-diphenyl-1,3-butadiene–methanol solution was circulated through the triple jacketed cell to provide temperature control and prevent excitation of the sample below 330 nm. Emission measurements were simultaneously made to correct for delayed fluorescence effects. Absorption decay was analyzed for first- and second-order decay components using GENLSS.[10]
(10) D. F. DeTar, *Comput. Programs Chem.*, **4**, 71 (1972).
(11) J. Saltiel, D. W. L. Chang, E. D. Megarity, A. D. Rousseau, P. T. Shannon, B. Thomas, and A. K. Uriarte, *Pure Appl. Chem.*, **41**, 559 (1975).
(12) J. Saltiel and B. Thomas, *J. Am. Chem. Soc.*, **96**, 5660 (1974); *Chem. Phys. Lett.*, **37**, 147 (1976).
(13) M. Sumitani, K. Yoshihara, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **51**, 2503 (1978). We thank Professor K. Yoshihara for a preprint of this paper.
(14) In cases involving triplet exciplex formation $\Delta H_1 < 0$ and $E = \Delta H_1 + E_2$ is expected. The large activation energies observed support the notion that $\Delta H_1 \sim 0$ in our systems.
(15) For a net change of one solute the cratic part of the entropy is $-R$ ln [M] where [M] is the molarity of the solvent; thus, $K_1^{t,c} = 1/[M]$. For toluene at 20 °C [M] $\simeq$ 9.4. See R. W. Gurney, "Ionic Processes in Solution", McGraw-Hill, New York, 1953.
(16) Activation parameters for exothermic triplet excitation transfer from indeno[2,1-*a*]indene to azulene in toluene give log $A_\eta = 12.0$ and $E_\eta = 2.70$ kcal/mol.[11]
(17) G. Fischer, K. A. Muszkat, and E. Fischer, *J. Chem. Soc. B*, 1156 (1968).
(18) Enthalpy change is used to estimate electronic energy assuming $P\Delta V \simeq 0$.
(19) Phosphorescence from $^3t^*$ has been observed: J. Saltiel, G.-E. Khalil, and K. Schanze, unpublished results.
(20) For a related intramolecular study, see D. G. Whitten, P. D. Wildes, and C. A. DeRosier, *J. Am. Chem. Soc.*, **94**, 7811 (1972).
(21) The latter interpretation is suggested by the treatment of the temperature dependence of azulene quenching of stilbene triplets.[11] However, this treatment is in doubt since it omitted an explicit step for excitation transfer.
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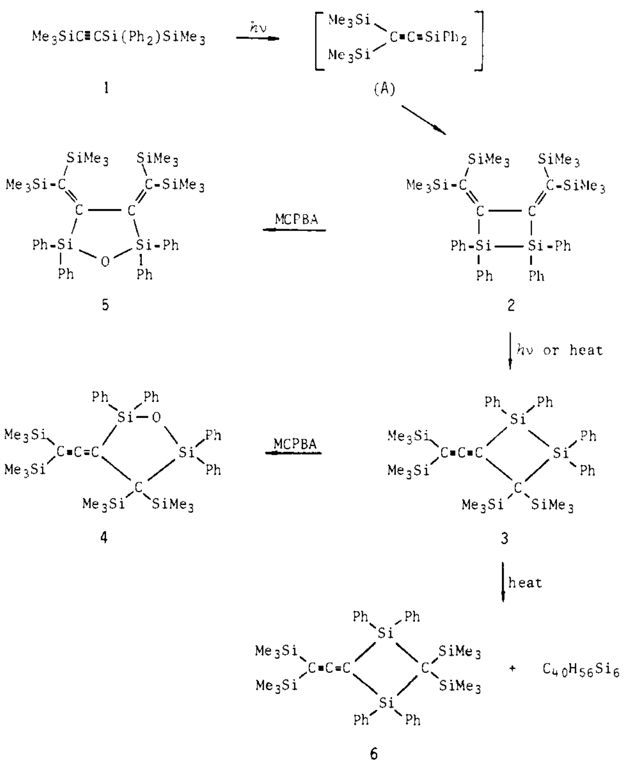
Photochemically Generated Silicon–Carbon Double-Bonded Intermediates. 9. Synthesis, Reactions, and Molecular Structure of a 1,2-Disilacyclobutane

Sir:

Small-ring systems involving a silicon–silicon bond in the ring are interesting because of their high strain energy. Only a few examples for the formation of 1,2-disilacyclobutanes have been reported to date[1-4] with limited information about their chemical behavior. We report here the formation and reactions of a novel 1,2-disilacyclobutane and preliminary results of X-ray diffraction study of this compound.

When a solution of 1.51 g (2.95 mmol) of trimethylsilyl(1,1-diphenyltrimethyldisilanyl)acetylene (**1**)[5] in 80 mL of dry benzene was photolyzed by irradiation with a low-pressure mercury lamp bearing a Vycor filter for 5 h, yellow crystals of 1,1,2,2-tetraphenyl-3,4-bis[bis(trimethylsilyl)-methylene]-1,2-disilacyclobutane (**2**) were formed which could be readily isolated by evaporation of the solvent from the resulting mixture (18% yield after recrystallization from hexane, mp 199 °C dec, UV λ_{max} 420 nm). The formation of **2** can be explained



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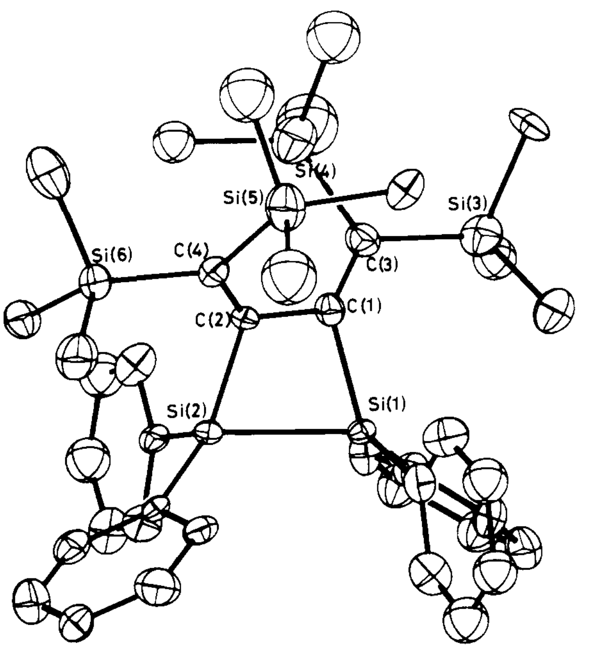

Figure 1. Molecular structure of 1,1,2,2-tetraphenyl-3,4,-bis[bis(trimethylsilyl)methylene]-1,2-disilacyclobutane.

in terms of head to head dimerization of transiently formed silapropadiene (A). The head to head dimerization of a silaethene-type intermediate has recently been reported by Brook and Harris.[4]

The ^{1}H and ^{13}C NMR spectra of **2** prove its structure: ^{1}H NMR (in CCl_4) δ (ppm) −0.16 (Me_3Si, s, 18 H), 0.30 (Me_3Si, s, 18 H), 6.9–7.8 (Ph, m, 20 H); proton-decoupled and off-resonance ^{13}C NMR (in $CDCl_3$) δ (ppm down field from Me_4Si) 2.58 (q, CH_3Si), 5.70 (q, CH_3Si), 127.16 (d, Ph), 127.75 (d, Ph), 129.15 (d, Ph), 132.59 (s, Ph), 134.31 (s, Ph), 136.95 (d, Ph), 137.21 (d, Ph), 163.39 (s, $=C(SiMe_3)_2$), 187.57 (s, $=C(SiPh_2)(C)$). The single-crystal X-ray diffraction study is also consistent with the proposed structure. The crystals of **2** are monoclinic and belong to space group $P2_1/n$ with cell dimensions a = 21.460 (3), b = 19.304 (6), c = 10.482 (2) Å; β = 99.09 (2)°; V = 4287.6 (15) Å^3; D_x = 1.093 (Z = 4), D_m = 1.06 g cm^{-3}. A total of 4009 independent reflections was collected[6] and the crystal structure was solved by direct methods.[7] Only the 1517 reflections with $I > 3\sigma(I)$ were used in the least-squares refinement (R = 0.099). All silicon atoms and 29 carbon atoms were refined with anisotropic thermal parameters and 11 carbon atoms with isotropic parameters. The molecular structure and atom labeling scheme is shown in Figure 1. The molecule has approximately the twofold symmetry, within 0.4 Å except for two methyl groups on Si(4) and two methyl groups on Si(5), along the direction through two midpoints of Si(1)–Si(2) and C(1)–C(2) bonds. The four-membered ring consisting of Si(1), Si(2), C(2), and C(1) has a puckered structure in which a maximum deviation from the best plane is 0.25 Å: Si(1) (−0.11), Si(2) (0.08), C(2) (−0.21), and C(1) (0.25 Å). The bond angles of C(1)–Si(1)–Si(2), Si(1)–Si(2)–C(2), Si(1)–C(1)–C(2), and C(1)–C(2)–Si(2) are 75.6 (7), 74.5 (6), 99.7 (13), and 101.0 (13)°, respectively. The bond lengths of Si(1)–Si(2) (2.344 (9)), Si(1)–C(1) (1.93 (2)), Si(2)–C(2) (1.94 (2)), and C(1)–C(2) (1.46 (3) Å) in the ring are consistent with those of single bonds, and C(1)–C(3) (1.34 (3)) and C(2)–C(4) (1.38 (3) Å) with the double bond length. The C(1), C(2), C(4), Si(5), and Si(6) atoms and also C(2), C(1), C(3), Si(3), and Si(4) atoms make planes within 0.08 and 0.10 Å, respectively. The dihedral angle formed by these two planes is 81.8°.

Interestingly, compound **2** undergoes a novel isomerization photochemically or thermally, producing another type of 1,2-disilacyclobutane. Thus, irradiation of a benzene solution of **2** with a high-pressure mercury lamp with a Pyrex filter for 10 h gave colorless crystals in 90% yield, mp 184–185 °C, UV λ_{max} 250 nm. The product was determined to be 1,1,2,2-tetraphenyl-3-[bis(trimethylsilyl)ethenylidene]-4,4-bis(trimethylsilyl)-1,2-disilacyclobutane (**3**) by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic analysis: ^{1}H NMR δ (ppm) 0.03 (Me_3Si, s, 18 H), 0.09 (Me_3Si, s, 18 H), 7.0–7.8 (Ph, m, 20 H); ^{13}C NMR δ (ppm) 1.82 (q, CH_3Si), 4.64 (q, CH_3Si), 29.28 (s, $C(SiMe_3)_2(SiPh_2)(C)$), 76.71 (s, $=C(SiPh_2)(C)$),[8] 127.43 (d, Ph), 127.85 (d, Ph), 128.98 (d, Ph), 129.50 (d, Ph), 136.39 (s, Ph), 136.52 (d, Ph), 136.84 (d, Ph), 137.94 (s, Ph), 203.49 (s, $=C=$); ^{29}Si NMR (in $CDCl_3$) δ (ppm down field from Me_4Si) 8.21 ($SiMe_3$), 5.00 ($SiMe_3$), 2.41 ($SiPh_2$), −0.61 ($SiPh_2$). A strong band at 1860 cm^{-1} in the IR spectrum of **3** clearly indicates that it must have an allenic structure. The mass spectrum of this compound showed the presence of the parent ion at 704, corresponding to the calculated molecular weight for **3**. Compound **3** was also obtained in 99% yield, when 152 mg (0.215 mmol) of **2** was heated at 250 °C for 10 min in a sealed glass tube. The presence of a silicon–silicon bond in the ring was confirmed by its oxidation. Treatment of **3** with 1 equiv of *m*-chloroperoxybenzoic acid (MCPBA) in methylene chloride at 0 °C afforded the corresponding 1-oxa-2,5-disilacyclopentane (**4**)[9] in 91% yield, mp 225 °C after recrystallization from ethanol. Similar treatment of **2** with MCPBA produced yellow crystals of compound **5**[10] having a 1-oxa-2,5-disilacyclopentane ring, 92% yield, mp 240 °C, UV λ_{max} 370 nm.

All of the 1,2-disilacyclobutanes reported to date are quite air sensitive. The present compounds **2** and **3**, however, are never affected by molecular oxygen at room temperature. Photochemical and thermal transformation of **2** into **3** can best be explained in terms of a 1,3-silyl shift[11–13] in the disilacyclobutane ring.

The thermal behavior of **3** is of considerable interest, because the 1,2-disilacyclobutane ring changes readily to a 1,3-disilacyclobutane system. Thus, heating of **3** at 250 °C for 3 h in a sealed glass tube gave 1,3-disilacyclobutane derivative (**6**) in 47% yield, in addition to an unidentified crystalline compound, 48% yield, M$^+$ 704. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra and IR and mass spectra of compound **6** are wholly consistent with the proposed structure: ^{1}H NMR δ (ppm) −0.13 (Me_3Si, s, 18 H), 0.28 (Me_3Si, s, 18 H), 7.2–8.0 (Ph, m, 20 H); ^{13}C NMR δ (ppm) 2.08 (q, CH_3Si), 6.49 (q, CH_3Si), 12.60 (s, $C(SiMe_3)_2(SiPh_2)_2$), 59.28 (s, $=C(SiMe_3)_2$), 60.71 (s, $=C(SiPh_2)(SiPh_2)$), 127.33 (d, Ph), 129.40 (d, Ph), 136.10 (d, Ph), 138.69 (s, Ph), 196.93 (s, $=C=$); ^{29}Si NMR δ 0.87 ($SiMe_3$), −1.19 ($SiMe_3$), −10.93 ($SiPh_2$); IR (cm^{-1}) 1880, 1430, 1270, 1255, 1100; mass M$^+$ 704.

The chemical behavior of 1,2-disilacyclobutanes is currently being examined and will be reported elsewhere.

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References and Notes

(1) W. H. Atwell and J. G. Uhlmann, *J. Organomet. Chem.*, **52**, C21 (1973).
(2) T. J. Barton and J. A. Kilgour, *J. Am. Chem. Soc.*, **98**, 7746 (1976).
(3) D. Seyferth and S. C. Vick, *J. Organomet. Chem.*, **125**, C11 (1977).
(4) A. G. Brook and J. W. Harris, *J. Am. Chem. Soc.*, **98**, 3381 (1976).
(5) Compound 1: bp 150 °C (3 Torr); n^{20}_D 1.5476; ^{1}H NMR δ (ppm) 0.20 (Me_3Si, s, 9 H), 0.27 (Me_3Si, s, 9 H), 7.3–7.8 (Ph, m, 10 H); IR (cm^{-1}) 1430; mass M$^+$ 352. Photolysis of 1 in the presence of methanol affords methoxysilanes arising from both silapropadiene A and 1,1-diphenyl-2,3-bis(trimethylsilyl)-1-silacyclopropene (B): M. Ishikawa, T. Fuchikami, and M. Kumada, *J. Am. Chem. Soc.*, **99**, 245 (1977). However, prolonged irradiation of B results in formation of nonvolatile polymeric substances.
(6) The intensities of 4009 independent reflections (3° $< 2\theta <$ 40°) using Mo

Kα radiation were measured by the θ–2θ scan technique.
(7) G. Germain and M. M. Woolson, *Acta Crystallogr., Sect. B*, **24**, 91 (1968).
(8) The ^{13}C NMR spectrum of **3** in C_6D_6 showed resonances at 73.62 and 79.66 ppm, due to the carbon atoms of $=C(SiMe_3)_2$ and $=C(SiPh_2)(C)$, respectively.
(9) Compound **4:** ^1H NMR δ (ppm) 0.02 (Me_3Si, s, 36 H), 7.0–7.9 (Ph, m, 20 H); ^{13}C NMR δ (ppm) 1.95 (q, CH_3Si), 4.80 (q, CH_3Si), 20.13 (s, $C(SiMe_3)_2$), 73.11 (s, $=C(SiMe_3)_2$), 73.70 (s, $=C(SiPh_2)[C(SiMe_3)_2]$), 127.39 (d, Ph), 127.65 (d, Ph), 129.60 (d, Ph), 130.25 (d, Ph), 135.83 (d, Ph), 136.35 (s, Ph), 137.55 (s, Ph), 205.44 (s, $=C=$); ^{29}Si NMR δ (ppm) 4.13 ($SiMe_3$), 2.83 ($SiMe_3$), −0.31 ($SiPh_2$), −4.08 ($SiPh_2$); IR (cm^{-1}) 1870, 1830, 1430, 1255, 1110, 945; mass M^+ 720.
(10) Compound **5**: ^1H NMR δ (ppm) 0.03 (Me_3Si, s, 18 H), 0.06 (Me_3Si, s, 18 H), 7.1–8.0 (Ph, m, 20 H); ^{13}C NMR δ (ppm) 3.98 (q, CH_3Si), 6.06 (q, CH_3Si), 127.56 (d, Ph), 127.66 (d, Ph), 130.22 (d, Ph), 134.11 (s, Ph), 136.26 (d, Ph), 136.31 (d, Ph), 137.06 (s, Ph), 169.92 (s, $=C(SiMe_3)_2$), 183.69 (s, $=C(SiPh_2)(C)$); ^{29}Si NMR δ (ppm) −5.92 ($SiMe_3$), −6.85 ($SiMe_3$), −20.72 ($SiPh_2$); IR (cm^{-1}) 1430, 1270, 1255, 1110, 950; mass M^+ 720.
(11) M. Ishikawa, T. Fuchikami, and M. Kumada, *J. Organomet. Chem.*, **149,** 37 (1978).
(12) M. Ishikawa, K. Nakagawa, M. Ishiguro, F. Ohi, and M. Kumada, *J. Organomet. Chem.*, **152,** 155 (1978).
(13) H. Kwart and J. Slutsky, *J. Am. Chem. Soc.*, **94,** 2515 (1972).

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Lanthanum-139 Nuclear Magnetic Resonance Chemical Shifts

Sir:

Lanthanum-139 with spin, $I = 7/2$ is an abundant nucleus (99.9% natural abundance) with a relatively high NMR sensitivity (300 times that of ^{13}C). However, since it has a quadrupole moment, when ^{139}La is not located in a symmetric electronic environment, rapid quadrupolar relaxation causes extensive line broadening. Several reports have appeared in the literature which utilize relaxation data of ^{139}La to study chemical exchange and coordination of lanthanum(III) in aqueous solution;[1-3] however, no mention was made of ^{139}La chemical shifts.

This communication is the first report of measurements demonstrating that ^{139}La chemical shifts provide a sensitive probe to lanthanide ion complexation. In this initial study the inner (i.e., direct contact) and outer (i.e., solvent separated) sphere complexation of La(III) with acetate and the chloroacetates is examined. Preliminary results on the La/Cl and La/SCN systems are also reported. Introduction of a ligand in the outer sphere should have little effect on the ^{139}La resonance, while inner sphere complexation could be expected to cause a significant change in chemical shift and in line width (due to the resultant asymmetric charge distribution around the metal). The thermodynamic parameters of complexation have been interpreted[4] as reflecting 100% inner sphere formation for $LaAc^{+2}{}_{(aq)}$, 100% outer sphere complex for $La(Cl_3Ac)^{+2}$, and mixtures for $La(ClAc)^{+2}{}_{(aq)}$ and $La(Cl_2Ac)^{+2}{}_{(aq)}$. Consequently, for equal amounts of 1:1 complex formed, acetate is expected to induce the largest change in chemical shift (and line width) and trichloroacetate is expected to induce little or no change.

In a totally outer sphere complex such as $La(ClO_4)_3$, ^{139}La line widths are ~120–150 Hz. Relaxation times ($T_1 = T_2$) are thus always short enough so that several thousand scans (necessary for the dilute solutions studied) can be obtained in 1–10 min, the data acquisition rate being the limiting factor.

Table I. Molar Concentrations, Chemical Shifts, and Line Widths of ^{139}La in Acetate Solutions[a]

$[X]_T$	$[X^-]$	$[LaX^{+2}]$	$[LaX_2^+]$	$[La^{+3}]$	^{139}La shift[b]	$\Delta\nu_{1/2}$[c]
0.008	0.0023	0.0046	0.00009	0.055	6.2	204
0.016	0.0047	0.0087	0.0003	0.051	12.0	326
0.024	0.0073	0.012	0.0007	0.047	20	562
0.04	0.013	0.018	0.0019	0.040	30	600
0.06	0.020	0.024	0.0040	0.032	41	670
0.08	0.028	0.027	0.0064	0.026	46	800
0.12	0.047	0.030	0.012	0.018	51	980
0.15	0.063	0.031	0.016	0.013	55	910
0.20	0.091	0.029	0.022	0.009	60	1000
0.30	0.152	0.025	0.031	0.004	74	1100
0.40	0.218	0.020	0.037	0.003	83	1200
0.80	0.495	0.012	0.048	0.0006	108	1300

[a] pH 5.0, $pK_a = 4.6$, $\beta_1 = 36.3$, $\beta_2 = 8.3$, $I = 2.0$ M ($NaClO_4$); other data sets were obtained for the chloroacetates. [b] Chemical shifts downfield from external 0.5 M ($La(ClO_4)_3$). [c] In hertz.

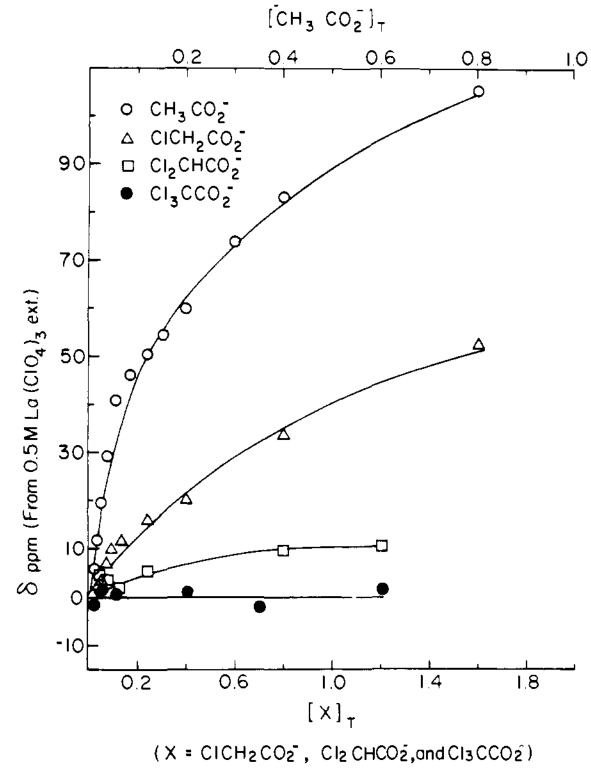

Figure 1. Variation of chemical shift with total added ligand ($Cl_nCH_{3-n}CO_2^-$, n = 0-3.

Observed shifts and line widths for the acetate solutions, relative to an external standard of 0.5 M $La(ClO_4)_3$ solution, are presented in Table I.[5,6] The variation in shift for the different ligand systems is shown in Figure 1, with the largest slope for acetate and essentially zero slope for trichloroacetate. Monochloroacetate and dichloroacetate are intermediate in their ability to shift and to broaden ^{139}La resonances. Using reported stability constants,[4] it is possible to calculate a limiting shift for the LaX^{+2} species. These shifts are, respectively, 100, 50, 22, and 0 ppm for acetate, chloroacetate, dichloroacetate, and trichloroacetate, relative to $La^{+3}{}_{(aq)}$. Using the crude approximation that the differences in observed limiting shifts are due solely to the amounts of inner sphere complex formed (i.e., the shifts for all 1:1 inner sphere complexes are the same), an estimate of inner/outer sphere complexation can be obtained. Assuming acetate interacts solely by inner sphere complexation, it is predicted that the portion of inner sphere complexation is ~50% for chloroacetate, 22% for dichloroacetate, and

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