(s, 9 H), 7.30 (br s, 2 H); MS, m/z 273 (M$^+$/2, 100%), 57 (t-Bu$^+$, 30%). Anal. Calcd for $C_{38}H_{58}O_2$: C, 83.46; H, 10.69. Found: C, 83.51; H, 10.79.

A similar coupling of 2,6-dimethylbenzoyl chloride with $(Me_3Si)_3SiLi$ at −78 °C gave no acylsilane but 25% of a yellow solid assigned the structure 2,2′,6,6′-tetramethylbenzil, mp 150–151 °C, from hexane, was isolated: IR (CCl_4) 1694 cm^{-1} (CO); ^{1}H NMR (CCl_4–CH_2Cl_2) δ 2.24 (s, 12 H), 6.9–7.3 (b m, 6 H); m/z 133 (M$^+$/2, 105 (M − CO)$^+$. Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: 80.59; H, 6.81.

Acknowledgment. This research was supported by the National Science and Engineering Research Council of Canada.

Registry No. **1c**, 81671-44-5; **1d**, 81671-45-6; **1e**, 81671-46-7; **1f**, 81671-47-8; **1g**, 81740-72-9; **1h**, 72189-49-2; **3c**, 81740-73-0; **3d**, 81740-74-1; **3e**, 81740-75-2; **3e′**, 81753-06-2; **3g**, 81753-07-3; **3h**, 72231-87-9; **4c** (R^1 = Me), 81753-08-4; **4d** (R^1 = Me), 81740-76-3; **4d** (R^1 = H), 81740-77-4; **4e** (R^1 = Me), 81740-78-5; **4f** (R^1 = Me), 81753-09-5; **5d**, 81740-79-6; (*R**,*S**)-**6**, 81740-80-9; (*R**,*R**)-**6**, 81740-81-0; **7**, 81740-82-1; **8**, 81740-83-2; **11**, 25436-32-2; **14**, 81740-84-3; **15**, 5181-43-1; **16**, 19555-07-8; (tris(trimethylsilyl)silyl)lithium, 4110-02-5; benzoyl chloride, 98-88-4; trifluoroacetyl chloride, 354-32-5; perfluorobenzoyl chloride, 2251-50-5; 2,3-dimethylbutadiene, 513-81-5; 4-(1,1-dimethylethyl)benzoyl chloride, 1710-98-1; 3,5-dimethylbenzoyl chloride, 6613-44-1; 2,4,6-tris(1,1-dimethylethyl)benzoyl chloride, 20208-55-3; 2,2′,4,4′,6,6′-hexakis(1,1-dimethylethyl)benzil, 19873-22-4; 2,6-dimethylbenzoyl chloride, 21900-37-8; 2,2′,6,6′-tetramethylbenzil, 1225-22-5.

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^{13}C and ^{29}Si Chemical Shifts and Coupling Constants Involving Tris(trimethylsilyl)silyl Systems

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^{13}C and ^{29}Si NMR data have been compiled for a variety of tris(trimethylsilyl)acylsilanes and related compounds and are compared with data for simple acylsilanes. In addition, data for the isomeric silaethylenes, obtained from the tris(trimethylsilyl)acylsilanes by photolysis, have been obtained. The chemical shifts for sp^2-hybridized silicon in these compounds lies in the range of 41–54 ppm. Several one-bond coupling constants and one two-bond coupling constant involving sp^2- and sp^3-hybridized silicon and carbon have been observed. As expected, the size of coupling constants involving sp^2-hybridized silicon are significantly larger than those involving sp^3-hybridized silicon.

In the course of investigations leading to our recently reported synthesis and isolation of a stable solid silaethylene[1] by photolysis of an isomeric acylsilane, we have synthesized a wide variety of organosilicon compounds containing the tris(trimethylsilyl)silyl [$(Me_3Si)_3Si$–] group.[2,3] During the characterization of these species by both ^{13}C and ^{29}Si NMR spectroscopy, not only was the chemical shift of sp^2-hybridized silicon observed for the first time, but also it was found possible to measure the magnitudes of several coupling constants involving both sp^2- and sp^3-hybridized silicon and carbon atoms not hitherto observed.

Table I provides data for a series of tris(trimethylsilyl)acylsilanes, [$(Me_3Si)_3SiCOR$], and a few related compounds, all of which have sp^3-hybridized silicon adjacent to a carbonyl group. There are two chemical shifts of particular interest, that of the carbonyl carbon and that of the silicon attached thereto.

It is evident from Table I that silicon adjacent to a carbonyl group has a strong deshielding effect on the ^{13}C carbonyl–carbon chemical shift, since all the acylsilanes described absorb in the range of 230–247 ppm whereas ketones closely related in structures to the simpler acylsilanes have the carbonyl–carbon resonance in the range of 198–209 ppm. The deshielding by silicon of 30–40 ppm relative to carbon analogues (e.g., Me_3CCOPh) is virtually the same for a given carbonyl system whether the group is Me_3Si, Ph_3Si, or $(Me_3Si)_3Si$: e.g., δ(^{13}C) $Me_3SiCOPh$, 233.7, $Ph_3SiCOPh$, 230.6, $(Me_3Si)_3SiCOPh$, 233.8. In addition to the large effect caused by silicon, a smaller effect on the carbonyl–carbon chemical shift is observed which depends on whether the other group attached to the carbonyl group is alkyl or aryl. Thus alkylacylsilanes (R_3SiCOR', R′ = alkyl) are more deshielded (244–247 ppm) than their aryl counterparts R_3SiCOR' (R′ = aryl) (230–240 ppm). This latter effect is one normally also observed with simple ketones (MeCOMe, 205, MeCOPh, 197 ppm).

The observed strong deshielding of the carbonyl carbon atoms in acylsilanes, also observed previously in acylphosphines,[7] undoubtedly involves electronegativity effects, at least in part, but also may be another manifestation of the strong interaction of silicon (or the Si–C σ bond) with an attached carbonyl group (either the π system or the lone pair on oxygen), also previously observed in the abnormally low-frequency carbonyl stretching vibrations of acylsilanes (1607–1645 cm^{-1})[7] compared to structurally related ketones (1675–1712 cm^{-1}) and the long wavelength carbonyl ultraviolet absorptions of acylsilanes (380–424 nm) compared to ketones (280–329 nm). The IR and UV results have

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(5) Dexheimer, E. M.; Buell, G. R.; Le Croix, C. *Spectrosc. Lett.* **1978**, *11*, 751.

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(7) (a) For a survey of acylsilanes see: Brook, A. G. *Adv. Organomet. Chem.* **1968**, *7*, 96. (b) For a summary of interpretations of interactions in acylsilanes see: Chvalovsky, V. In "Handbook of Organosilicon Compounds-Advances Since 1961"; Marcel Dekker: New York, 1974; p 103.

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Table I. Some ^{13}C and ^{29}Si Chemical Shifts[a] and Coupling Constants[b] for Acylsilanes and Related Compounds $(Me_3Si^A)_3Si^B{-}C^B({=}O){-}R$ and $R_3Si^B{-}C^B({=}O){-}R$

compd	$\delta(Si^A)$	$\delta(Si^B)$	$\delta(C^B)$	$^1J(Si^B{-}C^B{=}O)$	$^2J(Si^A{-}C^B{=}O)$	$^1J(Si^A{-}Si^B)$	$^1J(Si^A{-}Me)$
$(Me_3Si)_3SiCOCMe_3$	−11.5	−78.1	244.6		34.3	56.7	45.9
$(Me_3Si)_3SiCOCEt_3$	−12.0	−79.4	246.7		34.3	55.8	44.9
$(Me_3Si)_3SiCO$(1-methyl-1-cyclohexyl)	−11.4	−79.2	246.3		34.8	56.1	45.4
$(Me_3Si)_3SiCO$[1-bicyclo[2.2.2]octyl]	−11.4	−78.4	245.6		33.8	56.1	45.8
$(Me_3Si)_3SiCO$(1-adamantyl)	−11.5	−78.8	245.9	63.6[c]	34.2[c]	56.2	44.9
$(Me_3Si)_3SiCOPh$	−11.3	−72.0	233.8		38.5	57.0	46.3
$(Me_3Si)_3SiCOC_6H_4$-*p*-OMe	−11.4	−72.9	230.6		37.0	56.2	45.4
$(Me_3Si)_3SiCOC_6H_4$-*o*-OMe	−11.2	−70.6	240.0		36.7	56.6	45.4
$(Me_3Si)_3SiCOCF_3$	−9.9	−70.2	225.0				
$(Me_3Si)_3SiCOC_6F_5$	−10.3	−62.9	. . .				
$(Me_3Si)_3SiCOOH$	−11.3	−78.9	196.8		37.6	55.7	45.9
$(Me_3Si)_3SiCOOSiPh_3$[d]	−10.9	−76.8	188.4		37.0	58.0	45.8
$(Me_3Si)_3SiSiMe_3$[e]	−9.8	−135.5				52.5	44.7
$Ph_3SiCOMe$		−30.4	240.1	64[f,g]			
$Me_3SiCOMe$[h]			248.7				
$Me_3SiCOPh$		−7.4	233.7	63[f]			
$Et_3SiCOPh$[h]			235.9				
$Ph_3SiCOPh$		−28.3	229.8	64.0[f,g]			
		−28.3	230.6[h]				

[a] δ in ppm relative to C_6D_6 used as solvent. [b] *J* in Hz. [c] Coupling constant observed in both ^{13}C and ^{29}Si spectra—Cr(Acac)$_3$ present. [d] $\delta(SiPh_3)$ −10.1 ppm. [e] See ref 4. [f] Seen in ^{13}C spectra. [g] Coupling constant seen in ^{29}Si spectra could be to either/both C=O or/and Ph. [h] See ref 5.

received diverse interpretations,[7b] and the NMR results warrant further study and interpretation.

The second chemical shift of interest is that of Si^B, the silicon atom attached directly to the carbonyl group. The ^{29}Si spectra of a number of $(Me_3Si^A)_3Si^B{-}X$ compounds have been reported previously,[3] and it was found that whereas $\delta(Si^A)$ varied over the narrow range of −9.7 to −15.9 ppm as X varied from Me_3Si to MeO, $\delta(Si^B)$ varied widely from +33.4 to −135.5 ppm as X changed from F to Me_3Si.[8] In our compounds, $\delta(Si^A)$ lies in the range of −10.2 to −12.0 ppm for a variety of acylsilanes, an acid, and an ester. However, $\delta(Si^B)$ was somewhat more sensitive to structural changes, alkoylsilanes lying in the range of −78.1 to −79.4 ppm while aroylsilanes absorbed between −70.7 and −72.9 ppm. Thus $\delta(Si^B)$ reflects the trends of $\delta(C^B)$. Relative to $(Me_3Si)_4Si$, where $\delta(Si^B)$ −135.5,[4,8] it is clear that an acyl group has a moderately large deshielding effect on Si^B but almost no effect on Si^A. Since simple benzoylsilanes ($R_3SiCOPh$) have δ(Si) in the range of −7.4 to −28.8 ppm[5] as R varies from methyl to phenyl whereas $(Me_3Si)_3SiCOPh$ has $\delta(Si^B)$ −71.2, it is clear that the groups attached to the silicon next to the carbonyl group also play an important role in determining $\delta(Si^B)$ and that trimethylsilyl groups are moderately shielding, as is generally observed.

Using high field Fourier transform spectrometers, it was possible to observe a number of coupling constants, listed in Table I, between adjacent silicon atoms or between adjacent silicon and carbon atoms in $(Me_3Si)_3SiCOR$. In the ^{13}C spectrum of polysilylacylsilanes, a coupling constant to the carbonyl carbon of about 34–38 Hz was readily observed for every compound studied. It was shown that this was not the anticipated one-bond coupling constant to Si^B but was due to two-bond coupling to the three β-silicon atoms Si^A. One-bond couplings of sp^2-hybridized carbon to adjacent silicon atoms have been previously observed to lie in the range 64–67 Hz as in $Me_3SiCH{=}CH_2$ (^1J = 64 Hz) and Me_3SiPh (^1J = 66.5 Hz).[9] There is no reason to believe that the magnitude of this coupling constant should vary markedly if the sp^2-hybridized carbon is attached to oxygen in a carbonyl group, instead of carbon in an alkene or aromatic group, and indeed, study of the ^{13}C spectra of the simple acylsilanes $Me_3SiCOPh$, $Ph_3SiCOMe$, and $Ph_3SiCOPh$ showed in each case coupling constants of 63–64 Hz to the carbonyl carbon, assigned as the one-bond coupling to silicon i.e., $^1J_{Si{-}C{=}O}$ = 63–64 Hz (in no case was a 34 Hz coupling observed). These 64-Hz couplings are very difficult to observe in the ^{13}C spectra of the polysilylacylsilanes, the 34-Hz two-bond coupling (to three β-silicon atoms) being much stronger, and neither 34- nor 64-Hz couplings are readily observed from the ^{29}Si spectrum. This is because the intensity of the coupling of Si^B with three Si^A atoms (3 × 4.7% isotopic abundance) is much stronger than the intensity of couplings of either Si^A or Si^B with carbonyl carbon (1 × 1.1% isotopic abundance). However, with use of the compound $(Me_3Si)_3SiCOR'$ (R′ = adamantyl) with Cr(Acac)$_3$ as a relaxation agent, a coupling constant of 63.6 Hz was observed in both the ^{13}C spectrum (carbonyl–carbon) and the ^{29}Si spectrum (Si^B), while a 34.2-Hz coupling was observed in the ^{13}C spectrum (carbonyl carbon) and the ^{29}Si spectrum (Si^A). This unambiguously identifies the source of these two couplings as $^1J(Si^B{-}C{=}O)$ = 63.6 Hz and $^2J(Si^A{-}C{=}O)$ = 34.2 Hz. Thus the magnitude of the ^1J-

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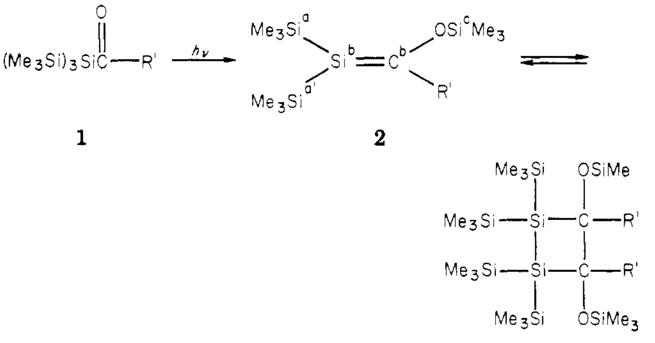
(Si–C) (sp^3–sp^2) coupling in acylsilanes is in accord with previously observed values and with a predictive equation (see below).

The ^{29}Si spectra of all the tris(trimethylsilyl)silyl compounds showed two strong couplings, one of about 56 Hz (55.8–56.6 Hz) seen with the signals of both Si^A and Si^B, thus assigned as $^1J(Si^A–Si^B) = 56$ Hz (reported for $(Me_3Si)_4Si$, 52.5 Hz),[4] and one observed for Si^A of about 45 Hz (44.9–45.9 Hz), assigned as $^1J(Si^A–CH_3) = 45$ Hz (reported for $(Me_3Si)_4Si$, 44.7 Hz).[4] Thus these couplings are perfectly normal in magnitude.

Photolysis of tris(trimethylsilyl)acylsilanes 1 yields the isomeric silaethylenes 2 by rearrangement of a trimethylsilyl group from silicon to oxygen.[2] In many cases these silaethylenes undergo head-to-head dimerization, yielding crystalline 1,2-disilacyclobutanes 3. This paper will not be concerned with this latter reaction nor with the NMR data for the dimers. In a few cases when R′ is a large bulky alkyl group such as CMe_3, CEt_3, or



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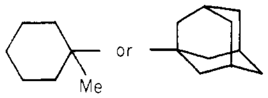
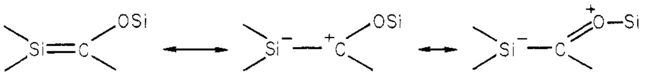


the silaethylenes have unprecedented stability and can be observed in solution at room temperature over a period of a week or more by NMR, IR, or UV spectroscopy, and in two cases, where R′ = 1-adamantyl or CEt_3, the silaethylenes have been isolated as stable but highly reactive solids. The crystal structure of the adamantyl compound, determined by X-ray techniques, unambiguously reveals the identity of the compound, indicates that Si^b is planar and hence is sp^2 hybridized and that the $Si^b{=}C^b$ bond length is 1.764 Å, much shorter than the normal carbon–silicon single bond of about 1.87–1.91 Å, and thus is consistent with a silaethylene.[1b] Table II reports the important ^{13}C and ^{29}Si NMR data of these silaethylenes.

The data for the silaethylenes has several interesting features. Si^a and $Si^{a'}$ are not magnetically equivalent, even up to 60 °C, indicating that there is no free rotation about the silicon–carbon double bond (hereafter Si=C) and hence that the bond behaves like a real double bond. The chemical shifts of Si^a and $Si^{a'}$ lie in fairly normal positions (see $\delta(Si^A)$, Table I) as does that for Si^c of the trimethylsiloxy group at about 13 ppm (reported for Me_3SiOEt, 13.5 ppm).[10] However, the chemical shifts of Si^b, in the range of 41–54 ppm, are at an extraordinarily low field for silyl-substituted silicon (e.g., see Table I) although this range is consistent with what would be expected for a change of hybridization from sp^3 to sp^2, the latter state not having been observed previously for silicon. Thus for carbon a change in hybridization from sp^3 to sp^2 causes a change in chemical shift of about 80–120 ppm to low field.[6c] The observed positions (41–54 ppm) for Si^b are about 120 ppm below Si^B in the tris(trimethylsilyl)acylsilanes (∼−78 ppm) and about 90 ppm below Si′ in $(Me_3Si)_2Si'Me_2$ (^{29}Si NMR δ −48.7[4]) and hence appear consistent with the result expected for a change in hybridization from sp^3 to sp^2.

West has recently reported[11] the chemical shift for sp^2-hybridized silicon in $(Mes)_2Si{=}Si(Mes)_2$ (Mes = mesityl) as δ 63.6, a position somewhat deshielded relative to the range 41–54 ppm observed with the silaethylenes. West's compound has two aryl groups attached to each silicon, whereas the silaethylenes have two trimethylsilyl groups, known to be strongly shielding in character. Thus, whereas Ph_2SiMe_2 has ^{29}Si NMR δ −4.5,[12] $(Me_3Si)_2SiMe_2$ has δ −48.7,[4] an upfield shift of 44 ppm on replacement of two phenyls by two trimethylsilyl groups. Hence, although mesityl and phenyl will not have identical effects on the chemical shift, it is clear that the positions of the sp^2-hybridized silicon atoms in the disilene and the silaethylene are in accord with expectations.

In the silaethylenes, the chemical shifts of the sp^2-hybridized carbon C^b at about 212 ppm are at considerably lower field than sp^2-hybridized carbons in alkenes, which normally lie in the range δ 80–150.[6c] Hence, just as $(Me_3Si)_3Si$ and R_3Si adjacent to >C=O cause deshielding (see above), so $(Me_3Si)_2Si{=}$, adjacent to =C<, apparently also causes deshielding, although it is recognized that other factors may be important, particularly the siloxy group on the carbon which, if resonance contributions of the types shown below are important, can be expected to contribute to deshielding of C^b and shielding of Si^b, consistent with the observations.



The coupling constants given in Table II are also of interest since each is somewhat different in magnitude from the related value found for the acylsilanes and other organosilicon compounds. Of greatest interest are the $^1J(Si{=}C)$ (sp^2–sp^2) coupling constants easily observable in the ^{13}C spectra but difficult to observe in the ^{29}Si spectra because of the presence of other more intense couplings between silicon atoms. As expected, the magnitude of these couplings, which involve sp^2-hybridized silicon interacting with sp^2-hybridized carbon, are significantly larger than the 64 Hz observed when silicon is sp^3 hybridized, and the magnitude observed is in close accord with predictions on the basis of the formula of Kovačevič and Maksič[13] $^1J(Si–C) = (5.554 \times 10^{-2})\alpha^2_{Si}\alpha^2_{C} + 18.2$ where α^2_{Si} and α^2_{C} are the percentage s character of the orbitals involved in the bonding. Calculations predict $^1J(Si{=}C) = 79.8$ Hz for $\alpha^2 = 33.3$, in reasonable agreement with the observed value of 83.5–85 Hz.

The magnitude of the coupling between Si^a (or $Si^{a'}$) and Si^b (i.e., sp^3–sp^2) of about 72 Hz also reflects the change of hybridization at silicon, since the Si^A–Si^B (sp^3–sp^3) coupling constants were about 56 Hz. Even the Si^a–Me coupling constants (48 Hz) are slightly larger than the 45 Hz observed for $^1J(Si^A–Me)$ couplings (where Si^B was sp^3 hybridized). This could be a long-range effect caused by the adjacent sp^2-hybridized silicon, but it is recognized that other effects possibly including environment and electronegativity may be involved as suggested by the unusually

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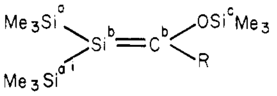
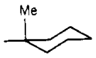
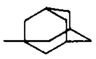
Table II. Chemical Shifts[a] and Coupling Constants[b] for Silaethylenes



R	$\delta(Si^{a,a'})$	$\delta(Si^b)$	$\delta(Si^c)$	$\delta(C^b)$	$^1J(Si=C)$	$^1J(Si^a-Si^b)$	$^1J(Si^a-Me)$
CMe_3	−12.1 −12.6	41.5	13.4	212.7	83.5	70.8	48.0
CEt_3	−12.4 −12.9	54.3	12.7	207.3	83.9	73.2	48.0
	−12.3 −12.6	43.5	13.6	212.9	85.0	72.1	47.7
	−12.8 −13.4	41.4	12.9	214.2	84.4	72.0	47.6

[a] δ in ppm relative to external Me_4Si, in C_6D_6. [b] J in Hz.

Table III. Magnitudes of One-Bond Coupling Constants Involving Silicon and Carbon[a]

hybridizatn	bond C-C	bond Me_3Si-C	bond Me_3Si-Si
sp^3-sp^3	34-35	44-50	52-64
sp^3-sp^2	38-44	64-70	71-73[b]
sp^2-sp^2	67-74	83-85[b]	unknown
sp^3-sp	55-69	84	unknown

[a] Ranges given for structurally related compounds. [b] This work.

large Si^c–Me coupling constants in the siloxy groups, observed to lie in the range of 59–61 Hz.

Both the chemical shifts and coupling constants characterize the sp^2-hybridization state of silicon as found in the silaethylenes, the data being markedly different from that found in the acylsilanes or other model compounds reported here or in the literature. Known coupling constant data involving C–C, C–Si, and Si–Si bonds are summarized in Table III, and the new data described here show trends consistent with previous observations of the way in which chemical shifts and coupling constants change as hybridization changes from sp^3 to sp^2. However, until more data on other compounds containing sp^2-hybridized silicon become available, it appears prudent not to attempt further interpretations of the causes of the observed changes.

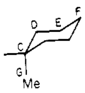
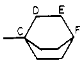
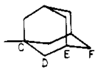
For completeness, Table IV reports full ^{13}C chemical shift data available for acylsilanes and silaethylenes.

Experimental Section

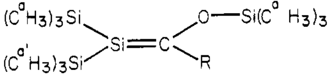
The syntheses of most of the compounds employed have been reported[2] or are about to be published.[1b,14]

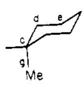
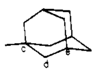
Table IV. ^{13}C Chemical Shifts of Tris(trimethylsilyl)acylsilanes and Related Compounds—Data for R Groups[a]

(a) $((C^AH_3)_3Si)_3SiCOR$

R	$\delta(C^A)$	$\delta(C^C)$	$\delta(C^D)$	$\delta(C^E)$	$\delta(C^F)$	$\delta(C^G)$	$\delta(C^{other})$
C^C-$(C^DH_3)_3$	2.1	49.3	25.1				
C^C-$(C^DH_2C^EH_3)_3$	2.1	59.4	24.4	8.5			
	2.0	53.0	33.7	23.0	22.7	26.2	
	2.3	50.4	26.8	26.0	25.5		
	2.1	51.7	37.2	37.0	38.4		
Ph	1.6						144.5, 132.5, 128.4, 128.0
C_6H_4-*p*-OMe	1.9						55.1 (MeO), 163.5, 138.1, 130.3, 113.7
C_6H_4-*o*-OMe	1.6						54.9 (MeO), 155.5, 140.7, 130.3, 124.8, 120.8, 111.3
CF_3	1.1	115.6[b]					

(b)



R	$\delta(C^{a,a',a''})$	$\delta(C^c)$	$\delta(C^d)$	$\delta(C^e)$	$\delta(C^f)$	$\delta(C^g)$
C^c-$(C^dH_3)_3$	1.8, 2.7, 3.5	43.1	31.2			
C^c-$(C^dH_2C^eH_3)_3$	1.9, 2.8, 3.5	52.6	27.0	8.5		
	1.8, 2.7, 3.1	46.2	38.6	23.1	22.4	26.6
	2.0, 2.7, 3.6	45.2	42.7	37.3	29.4	

[a] δ in ppm, relative to C_6D_6 used as solvent. [b] $^1J(CF)$ = 296 Hz; $^2J(CF)$ = 36 Hz.

The spectra were usually acquired from concentrated solutions in pure C_6D_6. Where photolyses to silaethylenes were involved, NMR tubes were sealed under an argon atmosphere. ^{13}C spectra were acquired on a Varian CFT 20, a Bruker WM-250 instrument, or more usually on the Bruker WH-400 spectrometer operating in the FT mode at a frequency of 100.62 MHz, operated by the Southwestern Ontario NMR Centre located at the University of Guelph, Guelph, Ontario. The spectra were run with level decoupling with the decoupler set at low power between acquisitions in order to obtain proton–^{13}C NOE. Moderately long delays (~30 s) were allowed between pulses, especially when the carbonyl-carbon was being studied. C_6D_6 was used as internal lock and internal chemical shift callibration for ^{13}C.

^{29}Si spectra were obtained on the same Bruker WH-400 spectrometer operating at a frequency of 79.495 MHz in the FT mode. The chemical shifts are reported relative to the silicon resonance of Me_4Si, used as an external reference. All of the spectra were obtained by using a gated decoupling sequence in which the protons were broad-band decoupled only during acquisition of the silicon free induction decay. This results in the complete suppression of the nuclear Overhauser enhancement. In the cases where no relaxation agent was added, spectra were accumulated by using approximately a 30° pulse width and approximately a 1-min relaxation delay between pulses. In some of the spectra Gaussian multiplication was employed to provide resolution enhancement.

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Registry No. $(Me_3Si)_3SiCOCMe_3$, 69397-47-3; $(Me_3Si)_3SiCOCEt_3$, 72214-49-4; $(Me_3Si)_3SiCO$(1-methyl-1-cyclohexyl), 81671-42-3; $(Me_3Si)_3SiCO$(1-bicyclo[2.2.2]octyl), 81671-43-4; $(Me_3Si)_3SiCO$(1-adamantyl), 72189-53-8; $(Me_3Si)_3SiCOPh$, 60154-95-2; $(Me_3Si)_3SiCOC_6H_4$-*p*-OMe, 81671-44-5; $(Me_3Si)_3SiCOC_6H_4$-*o*-OMe, 81671-45-6; $(Me_3Si)_3SiCOCF_3$, 81671-46-7; $(Me_3Si)_3SiCOC_6F_5$, 81671-47-8; $(Me_3Si)_3SiCOOH$, 70096-33-2; $(Me_3Si)_3SiCOOSiPh_3$, 81671-48-9; $(Me_3Si)_3SiSiMe_3$, 4098-98-0; $Ph_3SiCOMe$, 4916-42-1; $Me_3SiCOMe$, 13411-48-8; $Me_3SiCOPh$, 5908-41-8; $Et_3SiCOPh$, 63935-93-3; $Ph_3SiCOPh$, 1171-49-9; $(Me_3Si)_2Si{=}C(OSiMe_3)(CMe_3)$, 81671-49-0; $(Me_3Si)_2Si{=}C(OSiMe_3)(CEt_3)$, 81671-50-3; $(Me_3Si)_2Si{=}C(OSiMe_3)$(1-methyl-1-cyclohexyl), 81671-51-4; $(Me_3Si)_2Si{=}C(OSiMe_3)$(1-adamantyl), 72189-54-9.

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Crystal and Molecular Structure of Cyclopentadienylerbium Dichloride Tris(tetrahydrofuranate), $(C_5H_5)ErCl_2(THF)_3$

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The nature of the $(C_5H_5)LnCl_2(THF)_3$ compounds has been investigated by an X-ray structural determination of the Ln = Er complex. The compound crystallizes in the monoclinic space group $P2_1/n$ with four molecules in a unit cell of dimensions a = 7.822 (2) Å, b = 17.096 (4) Å, c = 15.162 (3) Å, and β = 95.80 (2)°. Least-squares refinement of the 208 variables led to a value for the conventional R index (on F) of 0.029 for 4207 independent reflections having $2\theta_{MoK\bar{\alpha}} < 58.7°$ and $I > 3\sigma(I)$. Although this complex is formally eight coordinate, octahedral is a simple and accurate description of the erbium(III) coordination sphere with the C_5H_5–Er interaction formally considered to occupy a single polyhedral vertex; the THF ligands have a meridional disposition and the chloride ligands occupy trans sites on this octahedron. The Er–C and Er–Cl bond distances average 2.667 (3) and 2.617 (2) Å, respectively. Two different Er–O bond distances were observed, averaging 2.358 (3) Å cis to the cyclopentadienyl ligand and 2.452 (4) Å trans to the cyclopentadienyl ligand. The major distortion observed in the structure involves a 0.54 Å displacement of the erbium atom out of the equatorial plane toward the cyclopentadienyl ligand. A number of comparisons are made to $(\eta^5\text{-}CH_3C_5H_4)UCl_3(THF)_2$ and other related structures.

While organolanthanide complexes containing cyclooctatetraene, cyclopentadienyl, π-allylic and σ-allyl ligands, among others, have been well established stoichiometrically,[3] structural progress has naturally lagged somewhat behind.[4] For the specific class of trivalent organolanthanides containing the cyclopentadienyl ligand as the only anionic carbon-bound ligand, structures have been reported for $(C_5H_5)_3Sm$,[5] $(C_9H_7)_3Sm$[6] (C_9H_7 = indenyl), $[(CH_3C_5H_4)_3Nd]_4$,[7] $(C_5H_5)_3Pr(CNC_6H_{11})$,[8] $(C_5H_5)_3Gd(THF)$,[9] $[(C_5H_5)_3Yb]_2(C_4H_4N_2)$[10] ($C_4H_4N_2$ = pyrazine), and

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