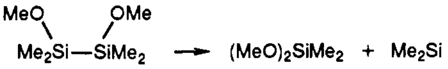
Table VI. Relative Rates of Me_2Si Insertions into $MeSiH_3$ and SiH_4

T, K	$\langle k_{18}/k_{17}\rangle^a$	no. of runs	T, K	$\langle k_{18}/k_{17}\rangle^a$	no. of runs
527.6	8.47	11	567.5	8.44	12
533.7	8.34	16	572.7	8.37	9
545.3	8.42	9	584.0	8.12	15
552.8	7.51	13			

[a] Average values of k_{18}(into methylsilane)/k_{17}(into silane) for the stated number of runs.

311G(d,p)) isodesmic calculations and with values obtained previously from the kinetics of other disilane decomposition systems with use of the same kind of kinetic analysis.[16]

Relative Insertion Rates of Me_2Si into SiH_4 and $MeSiH_3$. The relative rates of dimethylsilylene Si–H insertions into silane and methylsilane were studied at seven temperatures between 527.6 and 584 K by decomposing tetramethyl-1,2-dimethoxydisilane (TMDMODS, an excellent source of Me_2Si) in the presence of excess silane and methylsilane. Reactants were in the ratio $SiH_4/MeSiH_3$/TMDMODS = 9.63/1.00/0.435. The operative reactions (16-18) are shown in eqs 16–18. Since TMDMODS is considerably less stable[6] than any of the product disilanes, the latter did not decompose appreciably during the period of their production. Therefore, yield ratios of the product disilanes at low conversions of TMDMODS provided direct measures of the rates of the competing insertion reactions through eq II.



$$(MeO)Me_2Si{-}SiMe_2(OMe) \longrightarrow (MeO)_2SiMe_2 + Me_2Si \qquad (16)$$

$$Me_2Si + SiH_4 \longrightarrow Me_2SiHSiH_3 \qquad (17)$$

$$Me_2Si + MeSiH_3 \longrightarrow Me_2SiHSiH_2Me \qquad (18)$$

$$Y(Me_2SiHSiH_3)/Y(Me_2SiHSiH_2Me) = k_{17}[SiH_4]/k_{18}[MeSiH_3] \qquad (II)$$

The rate constant ratios so evaluated are given in Table VI. Since no temperature variation in these ratios is evident, it seems reasonable to equate k_{18}/k_{17} with the data average: $k_{18}/k_{17} = 8.22 \pm 0.31$ in the 550 ± 30 K range. Absolute rate constants determined by laser absorption techniques at 298 K ($k_{18} = (1.1 \pm 0.1) \times 10^9$ M^{-1} s^{-1}, $k_{17} = (1.2 \pm 0.2) \times 10^8$ M^{-1} s^{-1})[9] give the same value within the errors, i.e. $k_{18}/k_{17} = 9.17 \pm 2.4$. Thus, assuming Arrhenius behavior, $E_{18} = E_{17}$ and $A_{18}/A_{17} \approx 9$. This is a curious result as the 9-fold difference in the A factors of the insertion reactions at room temperature implies very different transition states for the two reactions, while the equivalancy of the decomposition reverse reaction A factors (i.e., $A_{-17} = 10^{13.18}$ s^{-1} and $A_{-18} = 10^{13.15}$ s^{-1}) implies very similar transition states. Thus, a single-transition-state, simple Arrhenius analysis produces a contradiction, and this provides further support for the Walsh argument of a consecutive-step reaction mechanism with the possibility of different transition states under different conditions.

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Registry No. 111TMDS, 18365-32-7; 112TMDS, 814-74-4; Me_2Si, 6376-86-9; SiH_4, 7803-62-5; $MeSiH_3$, 992-94-9.

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Chemical and Structural Investigations on (Ferrocenylacyl)silanes[†,1]

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(Ferrocenylacyl)silanes, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)COSiR_3$ (R_3 = Me_3, Me_2Ph, $MePh_2$, Ph_3), have been synthesized and their chemical, physical, and structural properties investigated. The compounds exhibit no photochemistry and are not subject to base-catalyzed rearrangements. Attempts to synthesize acyldisilanes, $FcCOSiR'_2SiR_3$, via hydrolysis of the corresponding ferrocenyldisilyldithianes, resulted in the formation of only $FcCOSiR_3$. In a similar manner attempts to synthesize $FcCOSiMe_2SiMe_2SiMe_3$ and $FcCOSi(SiMe_3)_3$ yielded only $FcCOSiMe_3$. Basicity measurements, via H-bonding to phenol, indicate the ferrocenyl group to be responsible for a major increase in the basicity of the acylsilanes. The structures of the four acyl complexes are reported and exhibit almost identical structural parameters about the carbonyl group, illustrating that the ferrocenyl group has a dominant steric effect upon the compounds. The steric bulk of the silyl groups is shown to be $Ph_3Si > Me_3Si > Me_2PhSi = MePh_2Si$.

Introduction

Acylsilanes have been thoroughly investigated by the comprehensive studies of Brook and co-workers and have been shown to exhibit many unusual and remarkable chemical, spectral, and photochemical properties.[2-12] Treatment of acylsilanes with an alkoxide ion, depending upon the polarity of a medium, results in formation of silyl

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[†] Dedicated to Professor A. G. Brook on the occasion of his 65th birthday.

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ethers via migration of a phenyl or methyl group from silicon to the adjacent carbon atom,[9] and in the presence of a weak base acylsilanes undergo a photochemical rearrangement to isomeric siloxycarbenes.[10] These carbenes can act as nucleophiles and insert into a polar H–X bond present in a trapping agent. In general, acylsilanes are colored due to a large bathochromic shift of the carbonyl n–π^* transition.[7,13–15] A similar shift of the ν(C=O) absorption to a lower frequency is observed in the infrared spectra.[7,16–18] Acylsilanes are useful reagents for the synthesis of a variety of α-silylcarbinols, which themselves exhibit unusual acid- and base-catalyzed chemistry.[19,20]

Reuter and Damrauer[21] in 1974 reported the only example of a (ferrocenylacyl)silane, i.e. (ferrocenylcarbonyl)trimethylsilane, $FcCOSiMe_3$. Via an H-bonding to methanol study, they concluded that the base strength was dominated by the ferrocenyl group, as was the rather low ν(C=O) stretching frequency at 1589 cm^{-1}, measured in CCl_4. Our interest in transition-metal-substituted organosilicon compounds attracted us to this class of compounds, even more since we have recently established that the ferrocenyl group has a pronounced effect upon the photochemical properties of linear polysilanes.[22] In this paper we report the synthesis (using the dithiane hydrolysis route) of a series of (ferrocenylacyl)silanes, together with studies on their chemical and photochemical, molecular structure, and basicity properties. Attempts to synthesize related (ferrocenylacyl)oligosilanes will be described.

Results and Discussion

(Ferrocenylacyl)silanes were readily synthesized by hydrolysis of 2-ferrocenyl-2-silyl-1,3-dithianes in a polar medium (eq 1). The complexes are red crystalline materials that may be readily handled in air.

$$\text{Fc-C}(SCH_2CH_2CH_2S)SiR_3 \xrightarrow[H_2O/MeOH]{HgCl_2/HgO} \underset{\text{I-IV}}{FcCOSiR_3} \qquad (1)$$

R_3 = Me_3 (I), Me_2Ph (II), $MePh_2$ (III), Ph_3 (IV)

Table I. Physical and Analytical Data

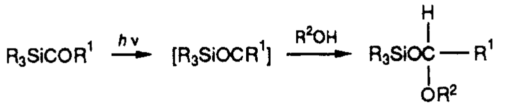
compd	anal. calcd (found), % C	H	yield, %	mp, °C
$FcCOSiMe_3$ (I)	ref 21	ref 21	72	86
$FcCOSiPhMe_2$ (II)	65.51 (65.41)	5.74 (5.97)	30	89
$FcCOSiPh_2Me$ (III)	70.24 (70.25)	5.36 (5.39)	55	92–93
$FcCOSiPh_3$ (IV)	73.72 (74.04)	5.08 (5.14)	59	95

Table II. Infrared and UV Spectral Data

compd	IR ν(C=O), cm^{-1} hexane	CH_2Cl_2	UV λ_{max}, nm (ϵ)
I[a]	1592	1578	340 (121), 369 (s),[c] 458 (44)
II[a]	1593	1578	346 (137), 379 (s), 465 (57)
III[b]	1593	1576	348 (155), 382 (s), 467 (64)
IV[b]		1575	354 (137), 386 (s), 474 (69)

[a] UV spectra in cyclohexane. [b] UV spectra in 80:20 cyclohexane–methylene chloride mixture. [c] s = shoulder.

Acylsilanes normally undergo photochemical reactions in various protic solvents via the intermediacy of isomeric siloxycarbenes, which insert into the polar H–X bond present in the solvent[10] (eq 2).



$$R_3SiCOR^1 \xrightarrow{h\nu} [R_3SiOCR^1] \xrightarrow{R^2OH} R_3SiO\overset{\displaystyle H}{\underset{\displaystyle OR^2}{C}}-R^1 \qquad (2)$$

R = Ph, naphthyl, Me; R^1 = Me, Ph; R^2 = Me, Et, *i*-Pr

In contrast, irradiation of the (ferrocenylacyl)silanes in methanol for 24 h with a 450-W medium-pressure mercury lamp did not produce a photochemical reaction; the starting material was recovered in 90% yield. Organometallic compounds derived from transition metals are known to be quenchers for triplet states of a number of molecules,[24] and ferrocene specifically is an excellent quencher for triplets of many organic molecules.[25,26] The UV data for the new complexes exhibit absorptions at λ_{max} 340–354 nm and at λ_{max} 458–475 nm, which are associated with the charge-transfer transitions of the ferrocene group.[23] This is in the region where the n → π^* excitation of the acyl group might be expected. A bathochromic shift of these CT bands is observed in (ferrocenylacyl)silanes as methyl groups on silicon are replaced by phenyl groups. Since replacement of methyl by phenyl groups does not have a significant effect upon the n → π^* transition in acylsilanes,[3] although it does have a slight bathochromic effect upon the corresponding absorbance band for ketones,[14] this shift reinforces the understanding that these bands are primarily associated with the ferrocenyl group, which mask those of the acyl group, accounting for the photoinert character of the new complexes.

Benzoyl- and acylsilanes undergo alkoxide-catalyzed rearrangements[8,9] involving the migration of phenyl or methyl groups from silicon to the adjacent carbon atom. Thus, the reaction of $PhCOSiPh_3$ in benzene–ethanol results in the formation of $Ph_2CHOSiPh_2(OEt)$ as a major product, together with $Ph_2Si(OEt)_2$ and Ph_2CHOH as minor products. Under the same conditions the (ferro-

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cenylacyl)silanes mainly undergo the displacement of the carbonyl group from silicon to yield ferrocenecarboxaldehyde and the respective silanol or siloxane (eq 3 and 4).

$$\mathrm{EtO^- + FcCOSiPh_3 \xrightarrow{C_6H_6\text{-}EtOH} HOSiPh_3 + FcCHO} \quad (3)$$

$$\mathrm{EtO^- + FcCOSiMe_3 \xrightarrow{C_6H_6\text{-}EtOH} Me_3SiOSiMe_3 + FcCHO} \quad (4)$$

In a similar manner, the (ferrocenylacyl)silanes did not undergo reduction to corresponding alcohols with lithium aluminum hydride in ethereal solvents. Infrared monitoring indicated that over a 12-h period no reaction took place.

The infrared spectra of (ferrocenylacyl)silanes (Table II) exhibit unusually low carbonyl stretching frequencies in the range 1578–1575 cm^{-1}. A number of researchers have explained the unusual spectral properties of acylsilanes with suggestions ranging from pπ–dπ bonding to strong inductive effects.[7,13-18] For FcCOSiMe$_3$, Reuter and Damrauer suggested that the lowering in carbonyl frequency was due to the steric bulk of the ferrocenyl group. Our results indicate that the position of the carbonyl stretching frequency is essentially independent of the nature of the substituent attached to the silicon atom but is clearly dependent upon the polarity of the medium. Changing solvent from methylene chloride to hexane produces a shift of 14–15 cm^{-1} to higher frequency. Similar shifts of carbonyl absorption are observed in related carbon compounds with the same change in solvent, although Brook et al.[3] have observed that the carbonyl frequencies in analogous acylsilanes are relatively insensitive to the polarity of the medium because the carbonyl group is already highly polarized. Our observation of a significant change in ν(C=O) suggests that the ferrocenyl group is the dominant feature of these acylsilanes and that solvation of the Fc group causes variation in the effect of the group upon the spectral properties of the carbonyl functionality.

(Ferrocenylacyl)silanes exhibit ^{13}C carbonyl carbon chemical shifts in the range 231–237 ppm, similar to those of acylsilanes, 230–240 ppm[27] (Table III). The analogous ketones have carbonyl carbon resonances in the range of 198–209 ppm, indicating that the silicon atom adjacent to the carbonyl carbon has a strong deshielding effect on the ^{13}C carbonyl carbon chemical shift. The ferrocenyl group does not perturb this resonance, and for example acetylferrocene, FcCOMe, exhibits a resonance at 202 ppm, well within the "normal" range for carbon ketones. A small effect on the carbonyl carbon chemical shift is observed as Me groups are replaced by Ph groups, i.e., 236.8 ppm (I) 234.7 ppm (II) 232.9 ppm (III), and 231.3 ppm (IV).

^{29}Si NMR spectral data for the (ferrocenylacyl)silanes (Table III) show chemical shifts ranging from −9.5 ppm for I to −30.9 ppm for IV. Simple benzoylsilanes (R$_3$SiCOPh) have δ(Si) in the range of −7.4 to −28.8 ppm as R$_3$Si varies from Me$_3$Si to Ph$_3$Si.[14,27] The effect of exchanging methyl groups for phenyl groups is the same in both systems and is almost identical with that observed for the ^{29}Si NMR data of the methylphenylsilanes (CH$_3$)$_{4-n}$Si(C$_6$H$_5$)$_n$.[28]

Basicity Measurements. Relative base strengths of the (ferrocenylacyl)silanes, and some related ketones, were determined by measuring the effect of these compounds on the O–H stretching frequency of phenol, the hydrogen bond donor, in dilute carbon tetrachloride solutions (0.05 M for the ketone, 0.01 M in phenol). The shift between the free OH and the H-bonded OH, $\Delta\nu$, was taken as a

Table III. NMR Data for New Compounds[a,b]

	FcCOSiMe$_3$ (I)
^{1}H	0.31 (9 H, s, SiMe$_3$); 4.15 (5 H, s, C$_5$H$_5$); 4.49 (2 H, t, C$_5$H$_4$); 4.75 (2 H, t, C$_5$H$_4$)
^{13}C	−1.07 (SiMe$_3$); 69.09, 69.82, 72.43, 85.50 (C$_5$H$_5$); 236.78 (C=O)
^{29}Si	−9.5
	FcCOSiMe$_2$Ph (II)
^{1}H	0.57 (6 H, s, SiMe$_2$); 3.91 (5 H, s, C$_5$H$_5$); 4.40 (2 H, t, C$_5$H$_4$); 4.61 (2 H, t, C$_5$H$_4$); 7.38 (2 H, m, Ph); 7.63 (3 H, m, Ph)
^{13}C	−2.61 (SiMe$_2$); 69.54, 69.70, 72.24, 85.73 (C$_5$H$_5$); 136.34, 134.70, 130.40, 128.71 (Ph); 234.72 (C=O)
^{29}Si	−16.5
	FcCOSiMePh$_2$ (III)
^{1}H	0.83 (3 H, s, SiMe); 3.89 (5 H, C$_5$H$_5$); 4.40 (2 H, t, C$_5$H$_4$); 4.58 (2 H, t, C$_5$H$_4$); 7.36–7.38 (5 H, m, Ph); 7.62–7.65 (5 H, m, Ph)
^{13}C	−3.06 (SiMe); 69.70, 69.95, 72.59, 86.47 (C$_5$H$_5$); 135.68, 134.53, 130.35, 128.47 (Ph); 232.86 (C=O)
^{29}Si	−21.9
	FcCOSiPh$_3$ (IV)
^{1}H	3.94 (5 H, s, C$_5$H$_5$); 4.39 (2 H, t, C$_5$H$_4$); 4.51 (2 H, t, C$_5$H$_4$); 7.43 (5 H, m, Ph); 7.68–7.72 (10 H, m, Ph)
^{13}C	69.58, 72.22, 86.91 (C$_5$H$_5$); 136.42, 132.68, 130.01, 128.03 (Ph); 231.29 (C=O)
^{29}Si[c]	−30.9
	Fc(dithiane)SiMe$_3$
^{1}H	0.4 (9 H, s, Me$_3$Si); 2.06 (2 H, m, CH$_2$); 3.06 (4 H, m, CH$_2$S); 4.11–4.23 (9 H, m, s, Fc)
	Fc(dithiane)SiMe$_2$Ph
^{1}H	0.32 (6 H, s, Me$_2$Si); 2.04 (2 H, m, CH$_2$); 2.86 (4 H, m, SCH$_2$); 4.12–4.32 (9 H, m, s, Fc); 7.32–7.46 (m, 6 H, Ph)
	Fc(dithiane)SiMePh$_2$
^{1}H	0.40 (3 H, s, MeSi); 1.95 (2 H, m, CH$_2$); 2.75 (4 H, m, SCH$_2$); 4.12–4.56 (9 H, m, s, Fc); 7.16–7.43 (10 H, m, Ph$_2$)
	Fc(dithiane)SiPh$_3$
^{1}H	2.01 (2 H, m, CH$_2$); 3.46 (4 H, m, SCH$_2$); 4.02–4.15 (9 H, m, s, Fc); 7.12–7.76 (15 H, m, Ph)
	Fc(dithiane)SiMe$_2$SiPh$_3$
^{1}H	0.25 (6 H, s, SiMe$_2$); 1.82 (2 H, m, CH$_2$); 2.68–3.02 (4 H, m, SCH$_2$); 4.19–4.25 (9 H, m, s, Fc); 7.22–7.64 (15 H, m, Ph)
	Fc(dithiane)SiMe$_2$SiMePh$_2$
^{1}H	0.03 (6 H, s, SiMe$_2$); 0.67 (3 H, s, SiMe); 1.96 (2 H, m, CH$_2$); 2.69 (2 H, m, SCH$_2$); 3.32 (2 H, m, SCH$_2$); 4.15–4.36 (9 H, m, s, Fc); 7.24–7.56 (10 H, m, Ph)
	Fc(dithiane)SiMe$_2$SiMe$_2$Ph
^{1}H	−0.04 (6 H, s, SiMe$_2$); 0.35 (6 H, s, SiMe$_2$Ph); 1.96 (2 H, m, CH$_2$); 2.67 (2 H, m, SCH$_2$); 3.35 (2 H, m, SCH$_2$); 4.12–4.26 (9 H, m, s, Fc); 7.23–7.45 (5 H, m, Ph)
	Fc(dithiane)SiMe$_2$SiMe$_3$
^{1}H	0.13 (6 H, s, SiMe$_2$); 0.27 (9 H, s, SiMe$_3$); 2.18 (2 H, m, CH$_2$); 3.36 (4 H, m, SCH$_2$); 4.00–4.35 (9 H, m, s, Fc)
^{29}Si	−1.96 (SiMe$_2$); −18.05 (SiMe$_3$)
	Fc(dithiane)SiMe$_2$SiMe$_2$SiMe$_3$
^{1}H	−0.02 (9 H, s, SiMe$_3$); 0.16 (6 H, s, SiMe$_2$); 0.26 (6 H, s, SiMe$_2$); 2.1 (2 H, m, CH$_2$); 2.75 (2 H, m, SCH$_2$); 3.72 (2 H, m, SCH$_2$); 4.24–4.48 (9 H, m, s, Fc)
^{29}Si	0.76 (CSiMe$_2$); −15.27 (SiMe$_2$); −45.95 (SiMe$_3$)
	Fc(dithiane)Si(SiMe$_3$)$_3$
^{1}H	−0.02 (27 H, s, SiMe$_3$); 1.72 (2 H, m, CH$_2$); 3.39–3.42 (4 H, SCH$_2$); 4.04–4.29 (9 H, m, s, Fc)
^{29}Si	8.84 (SiMe$_3$); −85.74 (Si)

[a] In ppm relative to TMS; s = singlet, d = doublet, t = triplet. [b] NMR spectra run in CDCl$_3$. [c] 4–5 mg of Cr(acac)$_3$ present.

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Table IV. K_F for Phenol/Acylsilane Complexes and $\Delta\nu$ for Phenol ν(OH)

compd	K_F	$\Delta\nu$, cm^{-1}	compd	K_F	$\Delta\nu$, cm^{-1}
$PhCOCH_3$	6.6	232	$FcCOSiMe_3$	32.0	261
$PhCOCMe_3$		162[17]	$FcCOSiMe_2Ph$	30.8	258
$PhCOSiMe_3$	4.5	173 (180[17])	$FcCOSiMePh_2$	26.2	252
$FcCOCH_3$	30.7	269	$FcCOSiPh_3$	17.2	248

measure of the base strength of the ketone. The order of base strength as shown in Table IV is

$$FcCOMe > FcCOSiMe_3 > FcCOSiMe_2Ph > FcCOSiMePh_2 > FcCOSiPh_3 \gg PhCOSiMe_3$$

This order indicates that (ferrocenylacyl)silanes are more basic than, for example, $PhCOSiMe_3$. The basicity-enhancing effect of the Fc group confirms the result of Reuter and Damrauer[21] and the general understanding that ferrocene can promote stabilization of electron-deficient centers directly bonded to the cyclopentadienyl ring. Yates and Agolini[16] have shown that benzoylsilanes are more basic than their carbon analogues; however, FcCOMe was found to be more basic than the (ferrocenylacyl)silanes. Substituents on the silyl group have a moderate effect on basicity in the expected order; introduction of phenyl groups decreases the base strength of the acylsilane.

Attempted Synthesis of (Ferrocenylacyl)oligosilanes. All attempts to synthesize (ferrocenylacyl)disilanes by hydrolysis of the appropriate disilyldithiane were unsuccessful and resulted in the formation of acylmonosilanes (eq 5).

$$Fc\text{-}C(SCH_2CH_2CH_2S)SiMe_2SiR_3 \xrightarrow{\text{hydrolysis}} FcCOSiR_3 \quad (5)$$

$$SiR_3 = SiMe_3,\ SiPhMe_2,\ SiPh_2Me,\ SiPh_3$$

Along with the isolation of acylmonosilanes we obtained unidentified material containing Si-O-Si linkages, as determined by IR and ^{29}Si NMR spectroscopy. We always obtained the acylsilane that resulted from the migration of the terminal silyl ($-SiR_3$) group; no alkyl/aryl scrambling or migration was observed. Brook et al.[15] have reported that attempts to synthesize acetyl- and benzoylpentamethyldisilanes resulted in the formation of impure materials; i.e., they obtained the required compounds together with other materials and suggested that the silicon-silicon bond was cleaved by mercuric chloride used in the hydrolysis of 1,3-dithiane system. Kumada et al.[29] have shown that alkyldisilanes are moderately sensitive to attack by electrophilic reagents.

The hydrolysis of 2-ferrocenyl-2-oligosilyl-1,3-dithianes, i.e. 2-ferrocenyl-2-(tris(trimethylsilyl)silyl)-1,3-dithiane and 2-ferrocenyl-2-(heptamethyltrisilyl)-1,3-dithiane, resulted in the formation of $FcCOSiMe_3$ and unidentified siloxane materials.

Structural Analysis of (Ferrocenylacyl)silanes. Since there is no relationship between the infrared stretching frequencies of the acylsilanes and their base strength with respect to H-bonding to phenol, we attempted to gain a further insight into these compounds via X-ray analysis of their structures. There is only one report of the structure of a simple acylsilane, $Ph_3SiCOCH_3$,[30] although several examples of transition-metal-substituted acylsilanes have been recently prepared and structurally analyzed.[31] Pertinent bond lengths and angles of the (ferrocenylacyl)silanes are presented in Table VI.

The C=O bond lengths in the four (ferrocenylacyl)silanes are, within experimental error, equivalent at 1.230 (3) Å. Clearly the variation of the substituents on the silicon atom have no effect upon the C=O bond length, paralleling the infrared stretching frequencies. The C=O bond lengths are somewhat longer than that reported for acetylferrocene,[32] 1.220 (3) Å, and significantly longer than that reported for acetyltriphenylsilane,[30] 1.211 Å. This latter comparison does directly reflect the exceptionally low stretching frequencies of the (ferrocenylacyl)silanes compared to those of the regular acylsilanes.

The $Si-C_{carbonyl}$ bond lengths are also equivalent at 1.935 (5) Å and are considerably elongated in comparison with the normal range of Si-C bond lengths, both $Si-C_{aryl}$ and $Si-C_{alkyl}$, which are generally in the range 1.85-1.90 Å. The elongation of the $Si-C_{carbonyl}$ bond also was observed in the structural analysis of $Ph_3SiCOMe$ and attributed to the contribution of a resonance structure in which there is no formal bond between the silicon and carbonyl carbon atom.[30]

As noted in Table VI, the bond angles Si-C-O for I-IV are comparable to (I, II) or smaller than (III, IV) that reported for $Ph_3SiCOMe$. It is apparent that of the three angles about the ketone group, i.e. Fc-C-Si, Fc-C-O, and Si-C-O, it is the last that is most susceptible to compression, the least susceptible being the Fc-C-O angle. This type of structural data supports the contention of Reuter and Damrauer[21] that the steric requirement of the ferrocenyl group was the dominant feature of I. The compression of the Si-C-O angle is not uniform, being greatest for those silyl groups containing at least two phenyl groups. Related to this observation are the dihedral angles between the cyclopentadienyl ring plane and the various Si—C=O planes. For the four complexes these values are 8.4° (I), 5.7° (II), 6.8° (III), and 10.2° (IV). The corresponding out-of-plane distances for the four silicon atoms are 0.22 Å (I), 0.09 Å (II), 0.04 Å (III), and 0.24° Å (IV). These combined data indicate that the steric requirements of the four silyl groups do not have a simple relationship with respect to the number of Me and Ph substituents. The trimethylsilyl and triphenylsilyl groups appear to be more restrictive than the other two groups. The phenyl groups of II, III, and IV are not oriented in a propeller fashion with respect to the Si atom. This is in direct constrast to the arrangement noted in the structures of both $Ph_3SiCOMe$ and $Ph_3GeCOMe$. For example, whereas the three angles between the planes of the phenyl groups and that of $C_{aryl}-Si-C_{acyl}$ in $Ph_3Si-CO-Me$ are 58, 55, and 55°, the corresponding values in complex IV are 60, 67, and 9.6°, a very clear deviation from the generality of propeller staggering of Ph_3E groups.

The geometrical parameters related to the two cyclopentadienyl rings are also recorded in Table VI. The rings are slightly staggered with respect to each other, 2.0° (I), 3.3° (II), 5.3° (III), and 4.9° (IV). The $Fe-(\eta^5-C_5H_n)$ ring

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(30) (a) Chieh, P. C.; Trotter, J. *J. Chem. Soc. A* **1969**, 1778. (b) Harrison, R. W.; Trotter, J. *J.Chem. Soc. A* **1968**, 258.

(31) (a) Schubert, U.; Hörnig, H. *J. Organomet. Chem.* **1984**, *273*, C11. (b) Anglin, J. R.; Calhoun, H. P.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 2281. (c) Arnold, J.; Tilley, T. D.; Rhiengold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 5355. (d) Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049.

(32) Liu, Q.; Hu, Y.; Li, F.; Huang, J. *Wuli Huaxue Xuabao* **1986**, *2*, 68.

centroid distances also vary, but no clear trend is apparent.

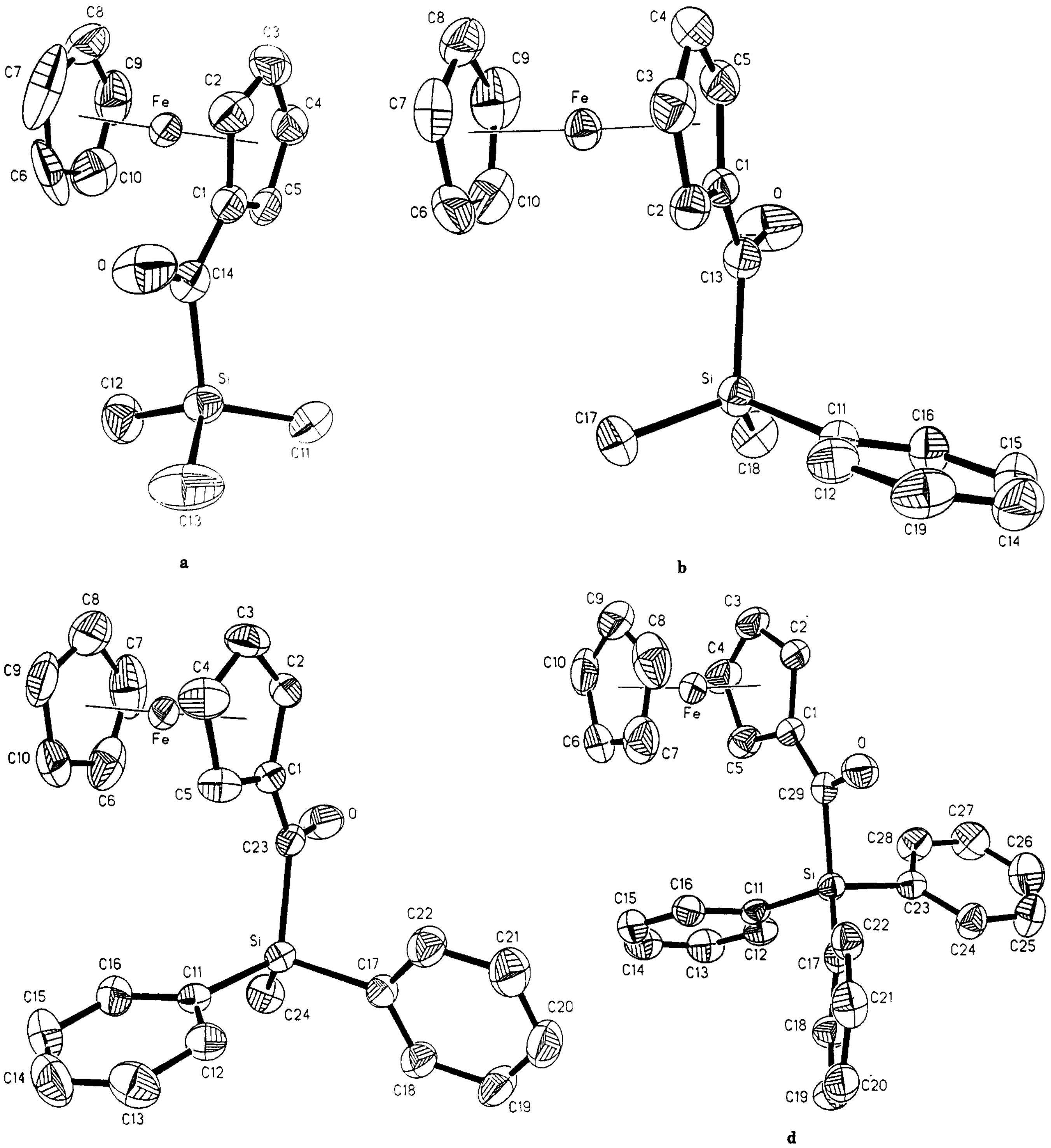


Figure 1. Structures of (ferrocenylacyl)silanes: (a) $FcCOSiMe_3$ (I); (b) $FcCOSiMe_2Ph$ (II); (c) $FcCOSiMePh_2$ (III); (d) $FcCOSiPH_3$ (IV).

Experimental Section

All reactions were performed under a nitrogen atmosphere. Solvents used were dry and oxygen free; Me_3SiCl, $PhMe_2SiCl$, $Ph_2MeSiCl$, and Ph_3SiCl were obtained from Petrarch Systems Inc., Bristol, PA. Ferrocenecarboxaldehyde, 1,3-propanedithiol, and *n*-BuLi (1.6 M in hexane) were purchased from Aldrich Chemical Co., Milwaukee, WI. Silica gel (grade 950, 60–200 mesh) was purchased from MCB Reagents, Gibbstown, NJ.

Infrared spectra were recorded on a Perkin-Elmer 580B spectrophotometer, UV spectra on a Perkin-Elmer Lambda 4C UV/vis spectrophotometer, and NMR spectra on an IBM NR/200 FT NMR spectrometer. All analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

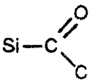
2-Ferrocenyl-1,3-dithiane was prepared from ferrocenecarboxaldehyde by the reported methods.[4,5,21] Typical reactions are described below, and all the analytical and spectral data are provided in Tables I–III.

Synthesis of 2-Ferrocenyl-2-(triphenylsilyl)-1,3-dithiane. Into a 100-mL Schlenk flask equipped with a magnetic stirring bar and septum was placed 5.0 g (16.4 mmol) of 2-ferrocenyl-1,3-dithiane dissolved in 25 mL of THF (freshly distilled from $LiAlH_4$). The solution was maintained at −25 °C as 6.8 mL (17.0 mmol) of a 1.6 M *n*-butyllithium solution was added slowly via a syringe. The color of the reaction mixture immediately changed to dark red, and the solution was stirred at −25 °C for 15 min. To this solution was added dropwise 15 mL of a THF solution of triphenylchlorosilane (5.06 g, 17.2 mmol). An orange compound

Table V

	I	II	III	IV
empirical formula	$C_{14}H_{18}OSiFe$	$C_{19}H_{20}OSiFe$	$C_{24}H_{22}OSiFe$	$C_{29}H_{24}OSiFe$
fw	286.2	348.3	410.4	472.4
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a, Å	13.891 (6)	15.276 (3)	8.847 (3)	8.848 (3)
b, Å	16.231 (4)	6.3625 (15)	9.249 (2)	14.294 (6)
c, Å	6.1817 (15)	18.301 (6)	14.441 (4)	18.719 (7)
α, deg			75.64	
β, deg	95.18 (3)	109.54 (2)	74.33	95.50 (3)
γ, deg			62.93	
V, Å^3	1388.0 (3)	1676.2 (7)	1002.2 (5)	2356.6 (16)
Z	4	4	2	4
D_{calc}, Mg m^{-3}	1.370	1.380	1.360	1.332
μ(Mo K$\bar{\alpha}$), mm^{-1}	1.152	0.967	0.819	0.706
F(000)	600	728	428	984
approx cryst size, mm	0.1 × 0.2 × 0.5	0.08 × 0.26 × 0.4	0.26 × 0.26 × 0.36	0.26 × 0.20 × 0.40
cryst color	red	red	red	red
scan speed, deg min^{-1}	3.0–15.0	3.0–15.0	3.0–15.0	3.0–15.0
index ranges	$3 \le h \le 14, -2 \le k \le 17, -6 < l \le 6$	$0 \le h \le 16, 0 \le k \le 6, -19 \le l \le 18$	$-3 \le h \le 9, -8 \le k \le 9, -14 \le l \le 15$	$-4 \le h \le 9, -3 \le k \le 15, -20 \le l \le 20$
no. of rflns collected	2022	2551	2932	3629
no. of indep rflns	1810	2181	2613	3083
R_{int}	0.012	0.053	0.082	0.009
no. of obs data ($F > X\sigma(F)$)	1807 (X = 4.0)	1749 (X = 3.0)	2450 (X = 3.0)	3082 (X = 6.0)
struct soln	heavy-atom meth	heavy-atom meth	heavy-atom meth	heavy-atom meth
weighting g	0.0083	0.0002	0.0003	0.0038
R_{obs}	0.0579	0.0479	0.0289	0.0415
R_w	0.0811	0.0430	0.0404	0.0620
R_{tot}	0.0581	0.0629	0.0310	0.0417
goodness of fit	0.70	1.34	1.75	0.81
largest and mean Δ/σ	0.974, 0.019	0.107, −0.002	0.444, 0.003	0.247, 0.016
data to param ratio	11.7:1	8.8:1	10.0:1	10.6:1
largest diff peak, e Å^{-3}	0.33	0.38	0.00	0.22
largest diff hole, e Å^{-3}	−0.37	−0.30	0.00	−0.22

Table VI. Bond Lengths and Angles about the Ketone Group, Fe–(η^5-C_5H_n) Centroid Bond Lengths, and η^5-C_5H_n Stagger Angles[a]



bond/angle	I	II	III	IV
Si–C[b]	1.940 (5)	1.929 (5)	1.930 (3)	1.935 (3)
C–O	1.231 (6)	1.233 (6)	1.227 (3)	1.231 (3)
C–C	1.475 (7)	1.472 (7)	1.464 (4)	1.467 (4)
Si–C–C	123.6 (4)	124.7 (3)	125.2 (1)	123.5 (2)
Si–C–O	117.2 (4)	117.2 (4)	114.5 (2)	115.7 (2)
O–C–C	119.2 (5)	118.0 (4)	120.0 (2)	120.2 (3)
Fe–(η^5-C_5H_5)	1.664	1.648	1.646	1.657
Fe–(η^5-C_5H_4)	1.643	1.641	1.639	1.645
ring stagger	2	3.3	5.3	4.9

[a] Bond lengths in Å and angles in degrees. [b] The average Si–C_{methyl} bond length is 1.857 (6) Å; the average Si–C_{phenyl} bond length is 1.873 (3) Å.

started precipitating after 5 min.

The reaction mixture was stirred at −25 °C for 1 h and further stirred for 2 h at room temperature. At this time the solid compound was filtered through a sintered glass crucible and washed with cold THF. Recrystallization from hexane yielded 7.2 g (78%); mp 177–178 °C.

2-Ferrocenyl-2-silyl-1,3-dithianes were characterized by ^1H NMR spectroscopy, and 2-ferrocenyl-2-disilyl-, 2-ferrocenyl-2-trisilyl-, and 2-ferrocenyl-2-(tris(trimethylsilyl)silyl)-1,3-dithianes were characterized by ^1H NMR and ^{29}Si NMR spectroscopy. The crude materials were used for hydrolysis reactions. The data are reported in Table III.

Hydrolysis of 2-Ferrocenyl-2-silyl-1,3-dithianes. This reaction was carried out under two different literature reaction conditions:[5,21] (i) with 2 equiv of $HgCl_2/CdCO_3/H_2O$ in a 2:1 acetone–THF mixture or (ii) with 2.2 equiv of $HgCl_2$ and 1.5 equiv of HgO in aqueous methanol. Method ii gave better yields. A typical example of this procedure is outlined below in detail.

Hydrolysis of 2-Ferrocenyl-2-(triphenylsilyl)-1,3-dithiane. A 250-mL two-necked flask equipped with a magnetic stirring bar and a reflux condenser was charged with 4.0 g (7.1 mmol) of crude 2-ferrocenyl-2-(triphenylsilyl)-1,3-dithiane, 4.25 g (15.6 mmol) of $HgCl_2$, and 2.27 g (10.5 mmol) of HgO. Aqueous methanol (98 mL of methanol + 2 mL of water) was then added, and the mixture was stirred vigorously and heated at reflux for 2 h. The color of the solution changed to dark red. The red solution was filtered through a sintered-glass crucible, and the residue was washed with 15 mL of methanol. The filtrate was poured into three times its volume of water, and the organic layer was extracted three times with 150 mL of methylene chloride. This solution was washed once with concentrated ammonium acetate solution and twice with water and dried over sodium sulfate. The solvent was removed on a rotary evaporator to give the crude product as a red solid. Recrystallization of this crude material from an 80:20 hexane–methylene chloride mixture yielded $FcCOSiPh_3$: 1.97 g (59%); mp 95 °C. Full spectral and analytical data are recorded in Tables I–III.

Reaction of (Ferrocenylcarbonyl)triphenylsilane with Sodium Ethoxide. To a solution of 0.2 g (0.42 mmol) of (ferrocenylcarbonyl)triphenylsilane in 10 mL of benzene was added 0.8 mL of a solution containing 0.12 mmol of sodium ethoxide in ethanol, and the resulting solution was stirred for 15 h at room temperature. The reaction was quenched with 50 mL of 0.1 N HCl, and the aqueous layer was extracted twice with diethyl ether. The combined benzene and ether layers were dried over magnesium sulfate and concentrated. The red viscous compound was extracted with 5 mL of hexane and placed upon a 2 × 18 cm silica gel column. Elution with a 50:50 hexane–methylene chloride solvent mixture yielded 0.04 g (20%) of (ferrocenylcarbonyl)triphenylsilane. Further elution with a 30:70 hexane–methylene chloride mixture gave 0.05 g (55%) of ferrocenecarboxaldehyde, and final elution with pure methylene chloride yielded 0.025 g (18%) of triphenylsilanol.

Reaction of (Ferrocenylcarbonyl)triphenylsilane with Lithium Aluminum Hydride. To a slurry of 0.06 g (1.6 mmol) of lithium aluminum hydride in 10 mL of THF at 0 °C was added 0.78 g (1.6 mmol) of (ferrocenylcarbonyl)triphenylsilane in 30 mL of THF. The reaction mixture was stirred for 12 h at room

Table VII. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\times 10^3$ Å^2)

	x	y	z	U(eq)[a]		x	y	z	U(eq)[a]
(a) Compound I									
Fe	4805 (1)	2137 (1)	2266 (1)	42 (1)	C(12)	2255 (5)	3947 (4)	2348 (10)	71 (2)
Si	3155 (1)	4465 (1)	775 (2)	45 (1)	C(8)	4764 (6)	889 (4)	2695 (17)	89 (4)
O	3720 (4)	3422 (3)	−2338 (6)	82 (2)	C(3)	6163 (4)	2476 (4)	1569 (11)	63 (2)
C(14)	3642 (4)	3627 (3)	−442 (8)	45 (2)	C(13)	2584 (6)	5025 (5)	−1639 (10)	92 (3)
C(5)	5096 (4)	3327 (3)	3019 (8)	46 (2)	C(9)	4574 (6)	1257 (5)	4492 (12)	77 (3)
C(4)	5934 (4)	2854 (3)	3491 (10)	56 (2)	C(10)	3801 (7)	1728 (5)	4195 (18)	96 (4)
C(1)	4797 (4)	3249 (3)	755 (8)	43 (2)	C(7)	4092 (11)	1121 (6)	1084 (14)	123 (5)
C(2)	5469 (5)	2712 (3)	−116 (9)	55 (2)	C(6)	3471 (5)	1672 (6)	1980 (23)	128 (5)
C(11)	3893 (5)	5191 (4)	2557 (11)	71 (2)					
(b) Compound II									
Fe	3374 (1)	1203 (1)	1027 (1)	36 (1)	C(4)	4061 (3)	283 (9)	294 (3)	51 (2)
Si	5317 (1)	−92 (2)	3360 (1)	38 (1)	C(2)	4752 (3)	1824 (7)	1481 (3)	40 (2)
C(12)	6803 (4)	2515 (8)	3224 (3)	49 (2)	C(18)	5297 (4)	−2082 (8)	4099 (3)	57 (2)
C(13)	4779 (3)	−1420 (8)	2362 (3)	43 (2)	C(14)	8381 (4)	1384 (11)	3533 (3)	64 (3)
O	4648 (3)	−3333 (5)	2356 (2)	82 (2)	C(10)	2513 (4)	1227 (13)	1664 (3)	69 (3)
C(11)	6544 (3)	562 (7)	3448 (3)	37 (2)	C(17)	4644 (3)	2250 (8)	3461 (3)	53 (2)
C(7)	2392 (4)	3507 (10)	682 (4)	63 (3)	C(15)	8149 (4)	−538 (10)	3760 (3)	66 (3)
C(3)	4437 (3)	2166 (9)	669 (3)	48 (2)	C(1)	4581 (3)	−343 (7)	1612 (3)	38 (2)
C(8)	2022 (3)	1589 (11)	357 (3)	61 (2)	C(19)	7708 (4)	2902 (10)	3262 (3)	60 (3)
C(16)	7245 (3)	−940 (8)	3716 (3)	49 (2)	C(9)	2086 (4)	167 (11)	962 (4)	72 (3)
C(5)	4138 (3)	−1243 (9)	864 (3)	51 (2)	C(6)	2703 (4)	3281 (11)	1495 (4)	67 (3)
(c) Compound III									
Fe	3239 (1)	3753 (1)	3313 (1)	39 (1)	C(12)	4080 (3)	−924 (3)	1339 (2)	48 (1)
Si	1034 (1)	731 (1)	2681 (1)	38 (1)	C(13)	5757 (4)	−2059 (3)	1089 (2)	64 (1)
O	−835 (2)	3413 (2)	3559 (2)	72 (1)	C(14)	6751 (4)	−2915 (4)	1787 (2)	73 (2)
C(1)	1579 (3)	3768 (3)	2579 (2)	40 (1)	C(15)	6100 (4)	−2641 (4)	2733 (2)	70 (2)
C(2)	1118 (3)	5390 (3)	2748 (2)	47 (1)	C(16)	4435 (3)	−1516 (3)	2984 (2)	53 (1)
C(3)	2511 (4)	5806 (3)	2305 (2)	55 (1)	C(17)	−184 (3)	1321 (3)	1669 (2)	40 (1)
C(4)	3863 (4)	4466 (3)	1854 (2)	59 (1)	C(18)	−1120 (3)	483 (3)	1624 (2)	51 (1)
C(5)	3285 (3)	3215 (3)	2021 (2)	48 (1)	C(19)	−2054 (4)	943 (4)	888 (2)	62 (2)
C(6)	3309 (5)	2144 (5)	4556 (2)	81 (2)	C(20)	−2067 (4)	2241 (4)	184 (2)	65 (2)
C(7)	2667 (5)	3743 (6)	4766 (2)	92 (2)	C(21)	−1144 (4)	3084 (4)	199 (2)	67 (2)
C(8)	3941 (6)	4315 (5)	4356 (3)	93 (2)	C(22)	−213 (3)	2630 (3)	934 (2)	56 (1)
C(9)	5344 (5)	3087 (5)	3903 (3)	87 (2)	C(23)	543 (3)	2821 (3)	3007 (2)	43 (1)
C(10)	4961 (4)	1740 (4)	4015 (2)	75 (2)	C(24)	122 (4)	−383 (3)	3766 (2)	58 (1)
C(11)	3371 (3)	−627 (3)	2292 (2)	39 (1)					
Compound IV									
Fe	1644 (1)	2788 (1)	8074 (1)	49 (1)	C(14)	350 (4)	1749 (3)	5111 (2)	68 (1)
Si	4995 (1)	2340 (1)	6447 (1)	38 (1)	C(15)	789 (3)	1275 (2)	5731 (2)	63 (1)
O	5752 (2)	2579 (2)	7871 (1)	61 (1)	C(16)	2177 (3)	1458 (2)	6109 (2)	50 (1)
C(29)	4696 (3)	2742 (2)	7410 (2)	42 (1)	C(11)	3162 (3)	2139 (2)	5881 (1)	40 (1)
C(2)	3293 (3)	3769 (2)	8262 (2)	56 (1)	C(18)	6170 (3)	766 (2)	5796 (2)	50 (1)
C(3)	1859 (4)	4192 (2)	8238 (2)	72 (1)	C(19)	6911 (3)	−78 (2)	5747 (2)	59 (1)
C(4)	1068 (4)	4024 (2)	7557 (2)	69 (1)	C(20)	7583 (3)	−495 (2)	6361 (2)	57 (1)
C(5)	2007 (3)	3485 (2)	7152 (2)	54 (1)	C(21)	7525 (3)	−70 (2)	7007 (2)	56 (1)
C(1)	3412 (3)	3321 (2)	7584 (1)	45 (1)	C(22)	6781 (3)	781 (2)	7062 (2)	48 (1)
C(6)	465 (4)	1577 (2)	7832 (2)	73 (1)	C(17)	6078 (3)	1214 (2)	6454 (1)	39 (1)
C(7)	1842 (5)	1371 (3)	8198 (2)	77 (2)	C(24)	7641 (3)	3215 (2)	5997 (2)	55 (1)
C(8)	1902 (6)	1810 (3)	8872 (2)	95 (2)	C(25)	8506 (4)	3966 (3)	5792 (2)	71 (1)
C(9)	540 (6)	2310 (3)	8895 (3)	100 (2)	C(26)	7857 (5)	4839 (3)	5710 (2)	81 (2)
C(10)	−348 (4)	2165 (3)	8253 (3)	87 (2)	C(27)	6364 (5)	4963 (2)	5824 (2)	75 (1)
C(12)	2709 (4)	2603 (2)	5241 (2)	51 (1)	C(28)	5504 (4)	4224 (2)	6029 (2)	60 (1)
C(13)	1304 (4)	2405 (3)	4865 (2)	63 (1)	C(23)	6117 (3)	3326 (2)	6113 (1)	43 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

temperature. Infrared monitoring of the reaction did not show any change in the carbonyl stretching frequency. After 12 h the reaction was quenched with 10 mL of ethyl acetate and the resulting mixture was added to 50 mL of 0.1 N hydrochloric acid. The aqueous layer was extracted twice with ether and dried over sodium sulfate. After the ether layer was filtered and the solvent removed, the red viscous material was extracted with hexane and placed on a 2 × 20 cm silica gel column. Elution with 50:50 hexane–methylene chloride produced a red band, which was collected. Removal of the solvent yielded 0.42 g (54%) of the starting material.

Structure Determination and Refinement. All data were collected at room temperature on a Nicolet R3m/V four-circle diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Unit cell parameters and standard deviations were obtained by a least-squares fit to 25 reflections randomly distributed in reciprocal space and lying in the 2θ range 15–30°. Details of the structure determination are presented in Table V. The data were corrected for Lorentz and polarization effects. An absorption correction was not applied, and considering the shape and size of crystals II and III, this may account for the rather large merging R values for these cases. However, the final refinement was not significantly affected in either case. The structures were solved and refined with use of the SHELTL-PLUS software on a Microvax-II computer. The hydrogen atoms were placed at calculated positions (C–H = 0.96 Å, $U_H = 0.08$ Å^2) during refinement. Full-matrix least-squares refinement, minimizing $\sum w(F_o - F_c)^2$, was carried out with anisotropic thermal parameters for non-hydrogen atoms. Selected bond angles and bond lengths are presented in Table VI. Atomic coordinates are presented in Table VII.

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Supplementary Material Available: Tables of crystal data, data collection, and refinement, complete bond lengths and bond angles, anisotropic thermal parameters, and H atom positional parameters (28 pages); listings of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

Scope and Regiochemistry of Ligand C–H Activation Reactions of $Cp_2Zr(CH_3)(THF)^+$

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The cationic complex $Cp_2Zr(CH_3)(THF)^+$ (1) reacts with a series of N-heterocycles derived from pyridine via ligand substitution followed by ligand C–H activation (σ-bond metathesis). Complex 1 reacts with 2,5-dimethylpyrazine, 2-phenylpyridine, phenanthridine, and 7,8-benzoquinoline to yield cyclometalated products **5–8**, which contain three-membered Zr–N–C rings. The reaction of **1** with quinoline yields primarily the α-C–H activation product **9**, but a minor product **10**, resulting from activation of H-8, is also observed. Complex 1 also reacts with more remote C–H bonds of acridine, phenazine, and 2,6-dimethylpyridine (which lack α-hydrogens) to yield the four-membered-ring products **11**, **12**, and **14**. The general trend for ortho C–H activation and formation of three-membered-ring products exhibited by $Cp_2Zr(CH_3)^+$ contrasts with the preference for activation of more remote C–H bonds and formation of four- or five-membered-ring products exhibited by late-metal systems. No ligand C–H activation is observed for $Cp_2Zr(CH_3)(N\text{-methylimidazole})^+$ (**16**), $Cp_2Zr(CH_3)(N\text{-methylimidazole})_2{}^+$ (**17**), or $Cp_2Zr(CH_3)(4,4'\text{-}Me_2bpy)^+$ (**18**). The lack of reactivity in the latter two cases is ascribed to the lack of a low-lying Zr-based LUMO. Substrates that do not displace the THF ligand of 1, such as 2-phenylquinoline and 2-methylthiophene, do not undergo C–H activation.

Introduction

Several facile C–H activations involving counterion or ligand C–H bonds have been observed recently for cationic d^0 complexes $Cp^*{}_2ZrR^+$ and $Cp_2Zr(R)(L)^+$.[1,2] These reactions are believed to proceed by σ-bond metathesis mechanisms involving four-center transition states that are accessed by initial interaction/coordination of the C–H bond with/to the electrophilic metal center.[3-5] We are exploring the possibility of developing productive σ-bond metathesis reaction schemes by combining these reactions with insertion, β-H elimination, Zr–R bond hydrogenolysis, and ligand-exchange reactions.[6,7] We reported previously that $Cp_2Zr(Me)(THF)^+$ (1)[8] reacts with pyridine and 2-

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[8] The counterion is $BPh_4{}^-$ in all cases.

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