Organometallics **1990**, *9*, 2677–2683

Synthesis and Reactivity of 2-Lithio-1,1,3,3-tetramethyl-1,3-disilacyclobutane. Strain-Assisted Ring-Opening Processes

Dietmar Seyferth,* Jennifer L. Robison, and James Mercer

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

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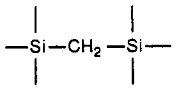
Although phenyl- and methyllithium react with 1,1,3,3-tetramethyl-1,3-disilacyclobutane (2) to open the Si_2C_2 ring, giving $RMe_2SiCH_2SiMe_2CH_2Li$, the *t*-BuLi/TMEDA reagent in hexane metalates a CH_2 group of 2, giving 2-lithio-1,1,3,3-tetramethyl-1,3-disilacyclobutane (3). In reactions of 3 with Me_3SiCl, Me_2HSiCl, Me_3SnCl, *n*-PrI, XCH_2CH_2X (X = Br, I), Me_2S_2, and I_2 the disilacyclobutane ring is retained while the methylene carbon atom is functionalized. However, ring-opened products result, very likely because of ring strain assistance, in reactions of 3 with aldehydes, benzoyl chloride, and benzonitrile.

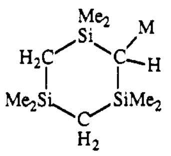
Introduction

The methylene group between two silicon atoms (A) shows enhanced reactivity with respect to proton abstraction by strong bases such as alkyllithium reagents.[1,2]

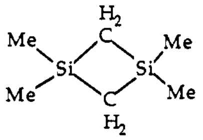


A

Thus, treatment of cyclo-$[(CH_3)_2SiCH_2]_3$ with *n*-BuLi/TMEDA[2] (TMEDA = $Me_2NCH_2CH_2NMe_2$) or *n*-BuLi/Me_3COK[3] results in monometalation to give 1. In recent work, we have found that poly(dimethylsilene), $[(CH_3)_2SiCH_2]_n$, the polymer formally derived from dimethylsilene, $(CH_3)_2Si{=}CH_2$, can be metalated by *n*-BuLi/Me_3COK to give a polycarbosilane in which, on the average, every fourth CH_2 group is metalated.[3] Among the compounds containing the A moiety 1,1,3,3-tetramethyl-1,3-disilacyclobutane (2) is a special case. This compound contains a strained ring that is opened easily by the action of electrophilic reagents such as HCl, Cl_2, Br_2, ICl, $HgCl_2$, BCl_3, $SnCl_4$, and $ZrCl_4$.[4] The action of various transition-metal complexes on 2 results in ring-opening polymerization,[5] with $H_2PtCl_6{\cdot}6H_2O$ being particularly effective.[5b–e]

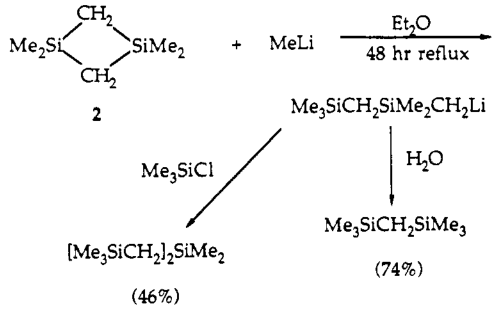


1 (M = Li, K)

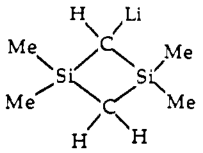


2

Scheme I



In view of the facility of the ring-opening reactions of 2, the preparation of 2-lithio-1,1,3,3-tetramethyl-1,3-disilacyclobutane (3) represented a challenge, since the strong RM bases which served well in metalation of moiety A also could be expected to attack at silicon to open the ring, giving an $R(CH_3)_2SiCH_2SiMe_2CH_2Li$ reagent instead of 3.[6]



3

In fact, Haszeldine and co-workers had reported in 1975 that the action of phenyllithium in diethyl ether results in ring opening of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, giving $PhMe_2SiCH_2SiMe_2CH_2Li$, whose subsequent hydrolysis produced $PhMe_2SiCH_2SiMe_3$.[7] We report here on the successful generation of 3 in solution and some of

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[1] Gröbel, B. T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852.

[2] Fritz, G.; Neutzner, J.; Volk, H. *Z. Anorg. Allg. Chem.* **1983**, *497*, 21.

[3] Seyferth, D., Lang, H. In *Proceedings of the Fourther International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites*; Uhlman, D. R.; Ulrich, D. R., Eds.; Wiley: New York, 1990; *Organometallics*, in press.

[4] (a) Damrauer, R. *Organomet. Chem. Rev., Sect. A* **1972**, *8*, 67. (b) Nametkin, N. S.; Vdovin, V. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 1153; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1974**, 1092.

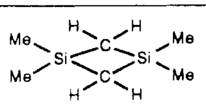
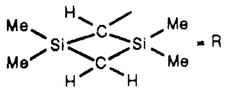
[5] (a) Nametkin, N. S.; Vdovin, V. M.; Grinberg, P. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1964**, 1123. (b) Weyenberg, D. R.; Nelson, L. E. *J. Org. Chem.* **1965**, *30*, 2618. (c) Kriner, W. A. *J. Polym. Sci., Polym. Chem. Ed.* **1966**, *4*, 444. (d) Bamford, W. R.; Lovie, J. C.; Watt, J. A. C. *J. Chem. Soc. C* **1966**, 1137. (e) Levin, G.; Carmichael, J. B. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 1. (f) Nametkin, N. S.; Ushakov, N. V.; Vdovin, V. M. *Vysokomol. Soedin.* **1971**, *A13*, 29. (g) Poletaev, V. S.; Vdovin, V. M.; Nametkin, N. S. *Dokl. Akad. Nauk SSSR* **1973**, *203*, 1324. (h) Poletaev, V. S.; Vdovin, V. M.; Nametkin, N. S. *Dokl. Akad. Nauk SSSR* **1973**, *208*, 1112.

[6] In this connection note the stoichiometric and catalytic ring opening of hexamethylcyclodisilazane by organoalkali-metal reagents and alkali-metal amides: Seyferth, D.; Schwark, J. M.; Stewart, R. A. *Organometallics* **1989**, *8*, 1980.

[7] Devine, A. M.; Griffin, P. A.; Haszeldine, R. N.; Newlands, M. J.; Tipping, A. E. *J. Chem. Soc., Dalton Trans.* **1975**, 1434.

0276-7333/90/2309-2677$02.50/0

Table I. Reactions To Form C-Functionalized 1,3-Disilacyclobutanes

 amt, mmol	amt of t-BuLi, mmol	amt of TMEDA, mmol	electrophile (amt, mmol)	procedure	 product	% yield[a]
26.7	57.0	42.5	Me_2HSiCl (41.6)	A	Me_2HSiR (**4**)	60
23.2	30.6	34.4	Me_2HSiCl (32.6)	B	Me_2HSiR (**4**)	67
49.1	73.1	92.8	Me_3SiCl (74.1)	A	Me_3SiR (**5**)	57
6.97	9.18	10.6	Me_3SiCl (9.48)	B	Me_3SiR (**5**)	64
49.3	76.5	86.1	$CH_3CH_2CH_2I$ (88.2)	A	$CH_3CH_2CH_2R$ (**6**)	36
29.4	38.2	45.1	$CH_3CH_2CH_2I$ (38.4)	B	$CH_3CH_2CH_2R$ (**6**)	61
47.2	71.4	92.8	Me_3SnCl (70.2)	A	Me_3SnR (**7**)	41[b]
20.5	26.7	30.5	Me_3SnCl (26.7)	B	Me_3SnR (**7**)	85
94.0	129	140	I_2 (134)	B	RI (**8**)	44
48.4	62.0	72.9	ICH_2CH_2I (62.6)	A	RI (**8**)	44
6.99	9.18	15.9	ICH_2CH_2I (9.27)	B	RI (**8**)	32
48.7	62.9	72.9	$BrCH_2CH_2Br$ (64.0)	A	RBr (**9**)	59
29.6	38.8	45.7	$BrCH_2CH_2Br$ (39.4)	B	RBr (**9**)	59
25.8	37.4	39.0	MeSSMe (100)	A	MeSR (**10**)	77
19.5	25.5	30.5	MeSSMe (75.0)	B	MeSR (**10**)	53

[a] Percent yield determined by GLC. [b] Percent yield determined by distillation.

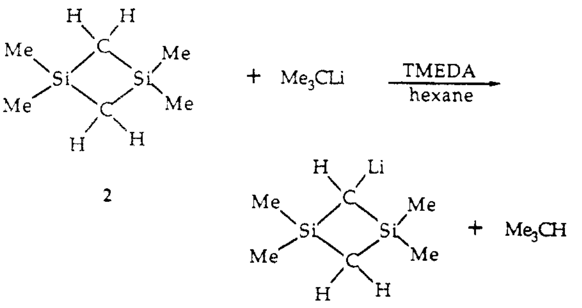
its reactions with various electrophiles.

Results and Discussion

The action of the least hindered organolithium reagent, CH_3Li, on **2** resulted in ring opening, as had been found in the case of phenyllithium[7] (Scheme I). The action of n-butyllithium on **2** in an all-hydrocarbon solvent system was less effective than that of methyllithium in diethyl ether, giving, after aqueous workup, n-$BuMe_2SiCH_2SiMe_3$ in only 18% yield.

In view of these results, the use of hindered, more proton-selective organoalkali-metal bases seemed indicated. Accordingly, we investigated the action of potassium bis(trimethylsilyl)amide, lithium tetramethylpiperidide, and t-BuLi/TMEDA (TMEDA = $Me_2NCH_2CH_2NMe_2$) on **2**. Of these, the t-BuLi/TMEDA reagent gave the best results and was used in our further studies.

The action of t-BuLi/TMEDA on **2** resulted principally in ring carbon atom lithiation (eq 1). The yields of reagent **3**, as indicated by yields of product obtained in its reactions with various electrophiles, were, in general, 60% or higher. In most cases better product yields were obtained when a hexane solution of the lithium reagent **3** was added to a solution of the electrophile in diethyl ether (procedure B) than when the electrophile, as the neat compound or in hexane solution, was added to the hexane solution of **3** (procedure A) (Tables I and II). It is likely that the high (85%) product yield obtained on treatment of such solutions of **3** with trimethyltin chloride in diethyl ether provides the best indication of the actual yield of **3** in the lithiation of **2**. The reactions of Me_3SnCl (in contrast to those of Me_3SiCl) with organolithium reagents appear to involve a nucleophilic substitution process that is not subject to much steric hindrance when bulky RLi species are used, nor do they involve electron-transfer chemistry, as occurs in RLi reactions with organic halides. For optimum results, successively 1.5–2.2 molar equiv of TMEDA in hexane and 1.3–1.6 molar equiv of t-BuLi in pentane were added to 1 molar equiv of **2** at room temperature. In all reactions of **3** with electrophiles some amount of hexane-soluble, apparently oligomeric or polymeric product was formed as well, but the constitution of this material was not examined.



2

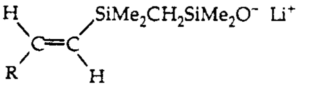
3

(1)

Reactions of the disilacyclobutyllithium reagent **3** with chlorosilanes, trimethyltin chloride, n-propyl iodide, 1,2-diiodo- and 1,2-dibromoethane, iodine, and dimethyl disulfide resulted in the formation of products containing the intact 1,3-disilacyclobutane ring (Table I). Thus, the metalation of **2** represents a useful entry to C-functionalized 1,3-disilacyclobutanes.

On the other hand, when the disilacyclobutyllithium reagent **3** was treated with various organic electrophiles in reactions followed by hydrolytic workup, products in which the 1,3-disilacyclobutane ring had been opened invariably were formed (Table II). These reactions are of some interest in that they represent known organosilicon processes—the Peterson reaction and the Brook rearrangement—which in these cases occur with particular facility, no doubt as a result of the ring strain of the 1,3-disilacyclobutane system.

Reactions of **3** with aldehydes gave acyclic products, silanols **11** and **13** in the case of hydrolytic workup and siloxanes **12** and **14** when dimethyl- or trimethylchlorosilane was added to the reaction mixture. Obviously, the anionic product present in these reaction mixtures is **17**.



17 (R = Me, Ph)

Formation of the latter may be rationalized in terms of addition of **3** to the aldehydic C=O bond followed by a modified Peterson olefination[8] process as shown in Scheme II. The stereoselectivity to form exclusively the trans isomeric products may be understood by inspection of the Newman projections of the proposed intermediate alkoxide **18** (Scheme III). The most favorable conformation is that in which the disilacyclobutane ring is directed away from

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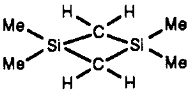
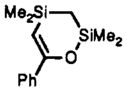
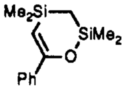
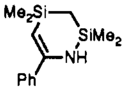
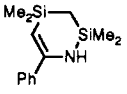
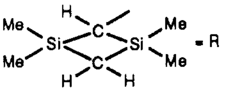
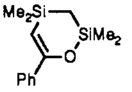
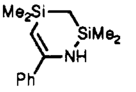
[8] Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780.

Table II. Reactions To Form Ring-Opened or Ring-Expanded Products

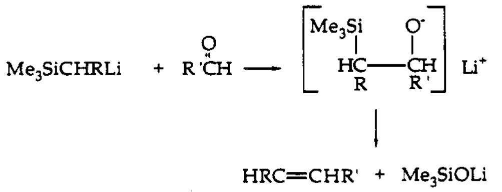
 amt, mmol	amt of t-BuLi, mmol	amt of TMEDA, mmol	electrophile (amt, mmol)	procedure	product	% yield[a]
27.6	36.6	43.1	$MeC(O)H/H_3O^+$ (41.1)	A	$MeCH{=}CHSiMe_2CH_2SiMe_2OH$ (11)	46[b]
7.90	10.2	11.9	$MeC(O)H/H_3O^+$ (11.6)	B	$MeCH{=}CHSiMe_2CH_2SiMe_2OH$ (11)	37
27.5	37.4	43.1	$MeC(O)H/Me_2HSiCl$ (41.1)	A	$MeCH{=}CHSiMe_2CH_2SiMe_2OSiMe_2H$ (12)	43
28.4	32.3	42.4	$MeC(O)H/Me_2HSiCl$ (34.0)	B	$MeCH{=}CHSiMe_2CH_2SiMe_2OSiMe_2H$ (12)	25
43.0	68.0	86.1	$PhC(O)H/H_3O^+$ (76.7)	A	$PhCH{=}CHSiMe_2CH_2SiMe_2OH$ (13)	53
6.42	8.33	9.94	$PhC(O)H/H_3O^+$ (8.36)	B	$PhCH{=}CHSiMe_2CH_2SiMe_2OH$ (13)	52
31.9	42.5	50.4	$PhC(O)H/Me_3SiCl$ (43.3)	A	$PhCH{=}CHSiMe_2CH_2SiMe_2OSiMe_3$ (14)	75
6.99	9.86	11.9	$PhC(O)H/Me_3SiCl$ (9.84)	B	$PhCH{=}CHSiMe_2CH_2SiMe_2OSiMe_3$ (14)	54
28.8	37.4	43.1	PhC(O)Cl (37.6)	A	 **15**	36
21.4	35.4	41.1	PhC(O)Cl (35.6)	B	 **15**	85
26.6	35.2	41.1	PhCN (35.3)	A	 **16**	45[b]
19.3	25.2	29.2	PhCN (26.4)	B	 **16**	51

[a] Percent yield determined by GLC. [b] Percent yield determined by distillation.

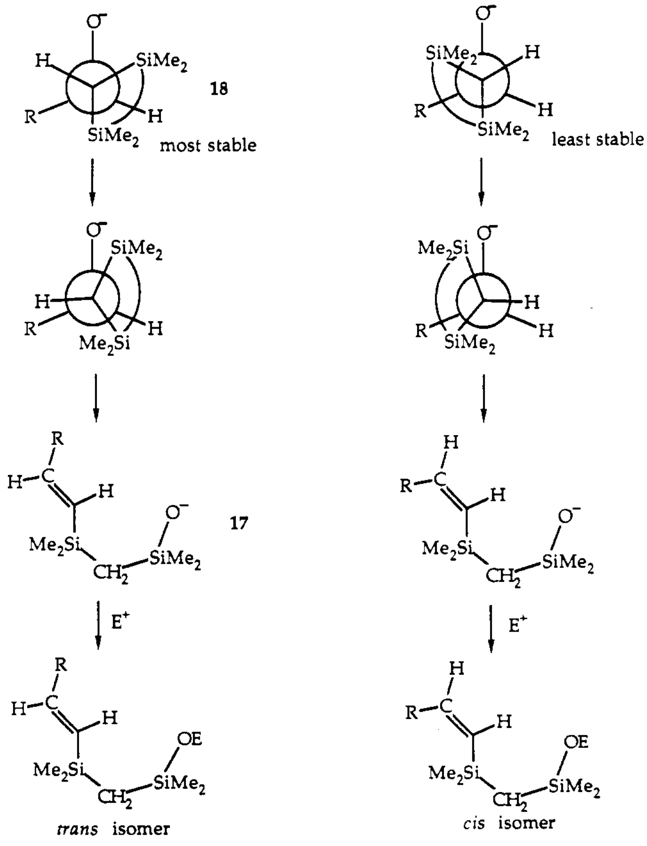
Table III. Physical Characteristics

 product	bp, °C (mmHg)	anal. % calcd/found	
		C	H
Me_2HSiR (4)	90 (40)	47.45/47.57	10.95/11.01
Me_3SiR (5)	110 (71)	49.96/50.07	11.09/11.09
$CH_3CH_2CH_2R$ (6)	84 (75)	58.03/58.25	11.81/11.92
Me_3SnR (7)	48–50 (0.1)	35.19/35.22	7.88/7.82
RI (8)	40 (0.09)	26.66/27.83	5.60/5.80
RBr (9)	90–92 (33)	32.27/32.74	6.78/6.88
MeSR (10)	30 (0.5)	44.13/44.53	9.54/9.55
$MeCH{=}CHSiMe_2CH_2$-$SiMe_2OH$ (11)	48–50 (1.5)	50.98/51.23	10.72/10.64
$MeCH{=}CHSiMe_2CH_2$-$SiMe_2OSiMe_2H$ (12)	40 (0.6)	48.70/48.83	10.65/10.60
$PhCH{=}CHSiMe_2CH_2$-$SiMe_2OH$ (13)	94 (0.07)	62.34/62.44	8.55/8.84
$MeCH{=}CHSiMe_2CH_2$-$SiMe_2OSiMe_3$ (14)	82–84 (0.07)	59.56/59.83	9.37/9.41
 **15**	70 (0.05)	62.83/62.64	8.13/8.28
 **16**	70–71 (0.05)	63.08/63.12	8.57/8.67

Scheme II



Scheme III[a]



11: R = Me; E = H
12: R = Me; E = Me_2HSi
13: R = Ph; E = H
14: R = Ph; E = Me_3Si

[a] Curved lines connecting Me_2Si groups represent CH_2 units.

Table IV. NMR Data

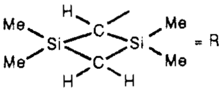
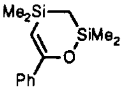
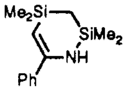
 product	^1H NMR (250 MHz, $CDCl_3$), δ_H	^{13}C NMR (75.4 MHz, $CDCl_3$), δ_C	^{29}Si NMR (59.59 MHz, $CDCl_3$), δ_{Si}
Me_2HSiR (4)	–0.33 (s, 1 H, CH), 0.02 (d, J = 3.8 Hz, 6 H, $Si\mathit{Me}_2H$), 0.04 (s, 2 H, CH_2), 0.23 (s, 6 H, 2 SiMe), 0.26 (s, 6 H, 2 SiMe), 3.99 (m, 1 H, SiH)[a]	–0.56 (q, ^1J = 129.9 Hz, $SiMe_2$), 1.56 (q, J = 120.2 Hz, $Si\mathit{Me}_2H$), 3.90 (d, J = 129.6 Hz, CH), 5.89 (d of d, ^1J = 81.8 Hz, ^2J = 28.1 Hz, CH_2)	–19.56 (d, J = 181.7 Hz, $SiMe_2H$), 2.63 (s, $SiMe_2$)
Me_3SiR (5)	–0.36 (s, 1 H, CH), 0.09 (s, 9 H, $SiMe_3$), 0.12 (s, 2 H, CH_2), 0.23 (s, 6 H, 2SiMe), 0.29 (s, 6 H, 2 SiMe)	2.21 (q, J = 117.2 Hz, $SiMe_2$), 2.38 (q, J = 117.2 Hz, $SiMe_2$), 4.16 (q, J = 118.9 Hz, $SiMe_3$), 4.36 (t, J = 123.6 Hz, CH_2), 9.88 (d, J = 107.4 Hz, CH)	–2.73 (s, 1 Si, $SiMe_3$), 2.72 (s, 2 Si, 2 $SiMe_2$)
$CH_3CH_2CH_2R$ (6)	–0.15 (AB, J = 12.2 Hz, 2 H, CH_2), 0.15 (s, 6 H, 2 SiMe), 0.20 (s, 6 H, 2 SiMe), 0.41 (m, 1 H, CH), 0.82 (t, J = 7.2 Hz, 3 H, CH_3), 1.18 (sextet, J = 7.4 Hz, 2 H, $CH_2C\mathit{H}_2CH_3$), 1.39 (m, J = 8.2 Hz, 2 H, $C\mathit{H}_2CH_2CH_3$)	–1.79 (q, J = 121.2 Hz, 2 SiMe), 1.38 (t, J = 123.7 Hz, $SiCH_2Si$), 3.03 (q, J = 120.0 Hz, 2 SiMe), 13.96 (q, J = 124.2 Hz, CH_3), 20.22 (d, J = 114.6 Hz, CH), 26.92 (t, J = 118.0 Hz, CH_2), 28.02 (t, J = 126.7 Hz, CH_2)	4.51 (s)
Me_3SnR (7)	–0.28 (d, J = 2.4 Hz, 1 H, CH), 0.05 (d, J = 2.4 Hz, 2 H, CH_2), 0.06 (s, 9 H, $SnMe_3$), 0.20 (s, 6 H, 2 SiMe), 0.22 (s, 6 H, 2 SiMe)	–6.67 (q, J = 127.8 Hz, $J_{Sn,inner}$ = 158.6 Hz, $J_{Sn,outer}$ = 165.9 Hz, $SnMe_3$), 0.38 (d, J = 120.0 Hz, $J_{Sn,inner}$ = 102.0 Hz, $J_{Sn,outer}$ = 108.4 Hz, CH), 3.91 (q, J = 119.1 Hz, 2 SiMe), 4.01 (q, J = 119.1 Hz, 2 SiMe), 5.14 (t, J = 124.2 Hz, CH_2)	5.39 (s)
RI (8)	0.18 (d, J = 2.6 Hz, 2 H, CH_2), 0.30 (s, 6 H, 2 SiMe), 0.39 (s, 6 H, 2 SiMe), 1.92 (d, J = 1.6 Hz, CH)	–13.01 (d, J = 137.2 Hz, CH), 1.34 (q, J = 119.5, Hz, 2 SiMe), 2.52 (t, J = 125.3 Hz, CH_2), 2.74 (q, J = 121.7 Hz, 2 SiMe)	9.27 (s)
RBr (9)	0.09 (d or d, ^1J = 15.5 Hz, ^2J = 2.6 Hz, 2 H, CH_2), 0.32 (s, 6 H, 2 SiMe), 0.39 (s, 6 H, 2 SiMe), 2.44 (s, 1 H, CH)	–0.32 (q, J = 120.3 Hz, 2 SiMe), 1.25 (q, J = 120.0 Hz, 2 SiMe), 2.18 (t, J = 126.7 Hz, CH_2), 19.96 (d or d, ^1J = 139.0 Hz, ^2J = 7.4 Hz, CH)	8.94 (s)
MeSR (10)	–0.01, 0.14 (AB, J = 15.6 Hz, 2 H, CH_2), 0.28 (s, 6 H, 2 SiMe), 0.31 (s, 6 H, 2 SiMe), 1.62 (d, ^2J = 1.2 Hz, 1 H, CH)8 2.01 (s, 3 H, SMe)	–1.32 (q, J = 120.6 Hz, 2 SiMe), 1.76 (t, J = 122.2 Hz, CH_2), 2.79 (q, J = 120.8 Hz, 2 SiMe), 20.60 (q, J = 136.6 Hz, SMe), 21.22 (d, J = 126.9 Hz, CH)[b]	5.19 (s)[b]
$MeCH{=}CHSiMe_2CH_2$-$SiMe_2OH$ (11)	–0.09 (s, 2 H, CH_2), 0.08 (s, 6 H, $SiMe_2$) 0.11 (s, 6 H, $SiMe_2$), 1.49 (s, 1 H, OH), 1.80 (d of d, ^1J = 6.1 Hz, ^2J = 1.1 Hz, 3 H, CH_3), 5.68 (d of d, ^1J = 18.3 Hz, ^2J = 1.2 Hz, $MeHC{=}CSi\mathit{H}$), 6.06 (d of q, ^1J = 18.3 Hz, ^2J = 6.1 Hz, 1 H, $SiHC{=}CMe\mathit{H}$)	–0.38 (q, J = 118.5 Hz, $SiMe_2$), 2.56 (q, J = 118.1 Hz, $SiMe_2$), 5.27 (t, J = 109.0 Hz, CH_2), 22.41 (q of t, ^1J = 124.8 Hz, ^2J = 6.0 Hz, CH_3), 132.15 (d, J = 131.4 Hz, $MeHC{=}\mathit{C}SiH$), 141.80 (d of t, ^1J = 148.1 Hz, ^2J = 6.0 Hz, $MeH\mathit{C}{=}CSiH$)[b]	–9.45 (s, 1 Si, $HOSiMe_2CH_2$), 15.28 (s, 1 Si, $HCSiMe_2CH_2$)[b]
$MeCH{=}CHSiMe_2CH_2$-$SiMe_2OSiMe_2H$ (12)	–0.16 (s, 2 H, CH_2), 0.05 (s, 6 H, $SiMe_2$), 0.07 (s, 6 H, $SiMe_2$), 0.14 (d, J = 2.5 Hz, 6 H, $Si\mathit{Me}_2H$), 1.78 (d of d, ^1J = 6.1 Hz, ^2J = 1.3 Hz, 3 H, CH_3), 4.65 (m, J = 2.8 Hz, 1 H, SiH), 5.64 (d of d, ^1J = 18.3 Hz, ^2J = 1.8 Hz, 1 H, $HMeC{=}C\mathit{H}Si$), 6.00 (d of q, ^1J = 18.4 Hz, ^2J = 6.1 Hz, $\mathit{H}MeC{=}CHSi$)	–0.23 (q, J = 121.1 Hz, $SiMe_2$), 0.95 (q of d, ^1J = 118.6 Hz, ^2J = 11.1 Hz, $SiMe_2H$), 2.99 (q, J = 120.7 Hz, $OSiMe_2$), 5.55 (t, J = 109.0 Hz, CH_2), 22.55 (q of q, ^1J = 125.1 Hz, ^2J = 5.3 Hz, CH_3), 132.40 (d, J = 125.4 Hz, $Si\mathit{C}H{=}CHMe$), 141.48 (d of q, ^1J = 152.6 Hz, ^2J = 5.4 Hz, $SiCH{=}\mathit{C}HMe$)	–9.01 (s, 1 Si, $OSiMe_2CH_2$), –7.44 (d, J = 199.9 Hz, 1 Si, $OSiMe_2H$), 8.94 (s, 1 Si, $HCSiMe_2CH_2$)
$PhCH{=}CHSiMe_2CH_2$-$SiMe_2OH$ (13)	0.02 (s, 2 H, CH_2), 0.16 (s, 6 H, $SiMe_2$), 0.20 (s, 6 H, $SiMe_2$), 1.47 (s, 1 H, OH), 6.43, 6.87 (AB, J = 19.2 Hz, 2 H, $HC{=}CH$), 7.26–7.43 (m, 5 H, C_6H_5)	–0.34 (q, J = 119.0 Hz, $SiMe_2$), 2.60 (q, J = 119.1 Hz, $SiMe_2$), 5.27 (t, J = 109.5 Hz, CH_2), 126.29 (d, J = 156.3 Hz, ortho C), 127.81 (d, J = 159.3 Hz, para C), 128.37 (d of d, ^1J = 159.5 Hz, ^2J = 7.0 Hz, meta C), 129.93 (d, J = 130.6 Hz, $HC{=}\mathit{C}HSiMe_2$), 138.32 (s, ipso C), 143.59 (d, J = 149.8 Hz, $C_6H_5\mathit{C}H{=}CH$)	–7.47 (s, 1 Si, $HOSiMe_2CH_2$), 15.25 (s, 1 Si, $HCSiMe_2CH_2$)

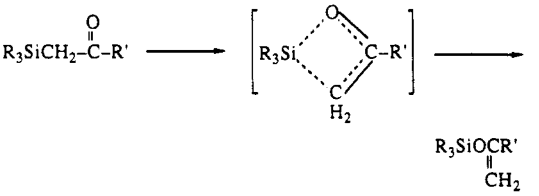
Table IV (Continued)

	^{1}H NMR (250 MHz, $CDCl_3$), δ_H	^{13}C NMR (75.4 MHz, $CDCl_3$), δ_C	^{29}Si NMR (59.59 MHz, $CDCl_3$), δ_{Si}
$PhCH{=}CHSiMe_2CH_2SiMe_2OSiMe_3$ (14)	−0.06 (s, 2 H, CH_2), 0.06 (s, 9 H, $SiMe_3$), 0.08 (s, 6 H, $SiMe_2$), 0.17 (s, 6 H, $SiMe_2$), 6.48, 6.83 (AB, J = 19.1 Hz, 2 H, HC=CH), 7.22–7.42 (m, 5 H, C_6H_5)	−0.29 (q, J = 120.2 Hz, $HCCHSiMe_2CH_2$), 2.09 (q, J = 116.8 Hz, CH_2SiMe_2O), 3.41 (q, J = 117.0 Hz, $SiMe_3$), 5.60 (t, J = 98.5 Hz, CH_2), 126.36 (d, J = 160.0 Hz, ortho C), 127.84 (d of t, ^1J = 160.7 Hz, ^2J = 8.0 Hz, para C), 128.50 (d of d, ^1J = 158.9 Hz, ^2J = 7.0 Hz, meta C), 130.47 (d, J = 136.4 Hz, $Me_2SiCH{=}CH$), 138.52 (s, ipso C), 143.23 (d of d, ^1J = 151.4 Hz, ^2J = 7.0 Hz, $C_6H_5CH{=}CH$)	−7.25 (s, 1 Si, $OSiMe_3$), 6.51 (s, 1 Si, $SiMe_2$), 6.84 (s, 1 Si, $SiMe_2$)
 **15**	0.09 (s, 2 H, CH_2), 0.19 (s, 6 H, $SiMe_2$), 0.31 (s, 6 H, $SiMe_2$), 5.22 (s, 1 H, CH), 7.34 (m, 3 H, meta and para), 7.68 (d of d, ^1J = 7.7 Hz, ^2J = 1.8 Hz, 2 H, ortho)	−0.17 (t, J = 116.4 Hz, CH_2), 0.34 (q, J = 118.1, $SiMe_2$), 0.95 (q, J = 120.1, $SiMe_2$), 96.86 (d, J = 139.3 Hz, PhC=CH), 125.23 (d of t, ^1J = 159.7 Hz, ^2J = 8.3 Hz, ortho C), 127.78 (d of d, ^1J = 160.0 Hz, ^2J = 7.4 Hz, meta C), 128.10 (d of t, ^1J = 160.3 Hz, ^2J = 8.4 Hz, para C), 138.29 (t, J = 5.4 Hz, ipso C), 161.86 (s, PhC=CH)	−13.73 (s, 1 Si, $OSiMe_2CH_2$), 17.72 (s, 1 Si, $HCSiMe_2CH_2$)
 **16**	−0.02 (s, 2 H, CH_2), 0.14 (s, 6 H, $SiMe_2$), 0.22 (s, 6 H, $SiMe_2$), 3.29 (broad, 1 H, NH), 4.36 (s, 1 H, PhC=C*H*), 7.29 (m, 3 H, meta and para), 7.45 (d of d, ^1J = 7.6 Hz, ^2J = 1.7 Hz, 2 H, ortho)	−0.71 (t, J = 116.4 Hz, CH_2), 0.85 (q, J = 119.0 Hz, $SiMe_2$), 1.63 (q, J = 119.0 Hz, $SiMe_2$), 94.01 (d, J = 139.2 Hz, PhC=CH), 125.72 (m), 127.80 (m), 127.95 (m), 128.23 (m), 144.20 (d, ^2J =6.8 Hz, ipso C), 157.10 (s, PhC=CHN)	−14.04 (s, 1 Si, $HNSiMe_2CH_2$), 2.42 (s, 1 Si, $HCSiMe_2CH_2$)

[a] 300 MHz. [b] In C_6D_6.

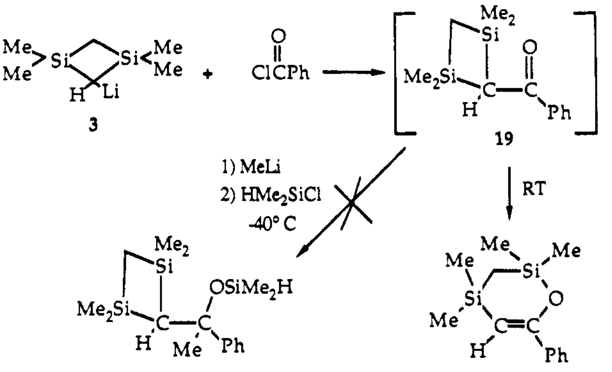
the organic group, R, of the aldehyde (Scheme III). Such selectivity to form only trans products has been observed previously when sterically hindered aldehydes were employed in olefin rearrangements.[9] Reactions of **3** with alkyl ketones resulted in enolization, regenerating **2**, rather than in addition across C=O.

The reaction of the disilacyclobutyllithium reagent **3** with benzoyl chloride gave the novel cyclic silyl enol ether **15**. A possible mechanism for the formation of this product involves initial benzoylation of **3** to give the β-ketosilane **19**. This then can isomerize via a Brook rearrangement to give **15** as shown in Scheme IV. Studies of the Brook rearrangement[10,11] have suggested a mechanism that proceeds by a four-center intramolecular attack by the carbonyl oxygen atom at silicon with simultaneous cleavage of the Si–C bond to form the olefin (eq 2). This is consistent with the mechanism proposed in Scheme IV. While the rearrangement of β-ketosilanes normally is a thermal process, occurring on heating the compound in question for several hours at temperatures ranging from 80 to 200 °C, **15** is formed readily at room temperature as evidenced by ^{1}H NMR examination of a **3** + PhC(O)Cl reaction mixture after solvent removal in vacuo at room temperature. In an attempt to trap β-ketosilane **19**, MeLi was added to a **3** + PhC(O)Cl reaction mixture (reaction and MeLi quench carried out at −40 °C). If **19** had been present, the subsequent addition of Me_2HSiCl to this reaction mixture should have given **20** (Scheme IV). However, in this case, **15** again was the observed product, providing another example of the chemical consequences of the high ring strain of the 1,3-disilacyclobutane ring.

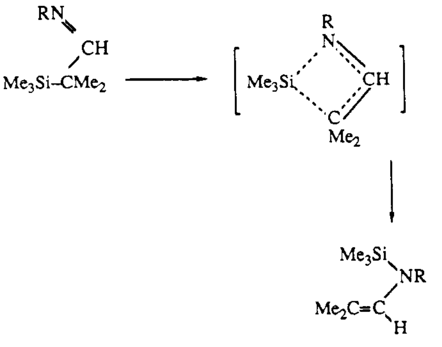


(2)

Scheme IV



β-Iminosilanes are similar to β-ketosilanes in that they are known to undergo slow 1,3-rearrangement in the presence of catalytic amounts of trimethylbromosilane (eq 3).[12] Thus, when disilacyclobutyllithium reagent **3** reacted



(3)

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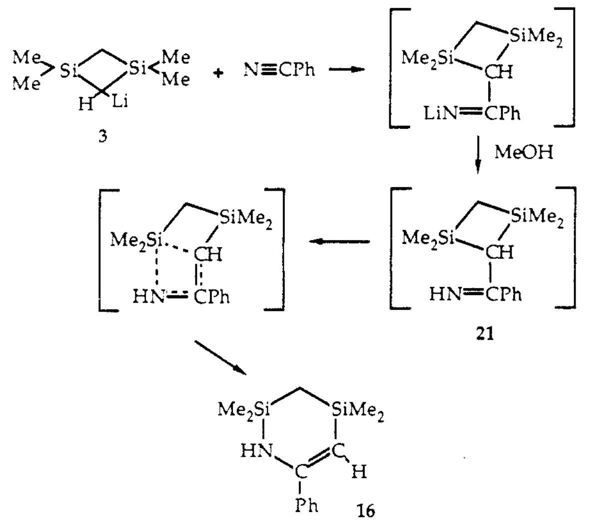
Scheme V



with benzonitrile and the reaction mixture was treated with methanol, the product that was isolated was **16** rather than the expected β-iminosilane **21**. Scheme V shows the proposed reaction course. In this case also, the ring opening occurs as a result of the strain in the Si_2C_2 ring.

The current study has developed a useful preparation of 2-lithio-1,1,3,3-tetramethyl-1,3-disilacyclobutane (**3**). A study of its reactivity has uncovered interesting examples of ring-strain-assisted organosilicon rearrangement processes. Our studies in this area are continuing.

Experimental Section

General Comments. All reactions were performed under an argon atmosphere with use of standard Schlenk techniques. All solvents were distilled under nitrogen from the appropriate drying agents. Chlorosilanes were purchased from Petrarch Systems, Inc., or Silar, and distilled from magnesium chips before use. *tert*-Butyllithium was purchased from Aldrich and titrated for RLi content by the Gilman double-titration method. Tetramethylethylenediamine (TMEDA) was purchased from Aldrich and distilled from calcium hydride before use. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane (**2**) was prepared according to the method of Kriner.[13]

Gas chromatographic (GLC) analyses were performed on a Hewlett-Packard 5890A gas chromatograph equipped with a 6-ft, 0.25-in. column packed with 10% SE-30 silicone rubber gum on Chromosorb P. The internal standard (C_{14}) method was used in yield determinations, when applicable, with a temperature program of 10 °C/min from 40 to 275 °C. Preparative GLC (Gow Mac 550 thermal conductivity detector gas chromatograph, 6-ft, 0.25-in. 10% SE-30 on Chromosorb P column) was used to collect some samples for analysis and spectroscopy.

Proton NMR spectra were obtained with either a Bruker WM-250 or Varian XL-300 NMR spectrometer using $CDCl_3/CHCl_3$ or C_6D_6/C_6H_6 as a reference at 7.24 or 7.15 ppm downfield from tetramethylsilane, respectively. ^{13}C NMR spectra, both proton coupled and decoupled, were obtained with a Varian XL-300 NMR spectrometer operating at 75.4 MHz in $CDCl_3$ or C_6D_6. ^{29}Si NMR spectra were obtained with a Varian XL-300 NMR spectrometer operating at 59.59 MHz in $CDCl_3$ or C_6D_6 using tetramethylsilane (0.00 ppm) as the external standard.

Elemental analysis were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Preparation of 2-Lithio-1,1,3,3-tetramethyl-1,3-disilacyclobutane (3). A 100-mL three-necked round-bottomed flask equipped with a rubber septum, a gas inlet/outlet tube connected to an oil bubbler on a Schlenk line, a glass stopper, and a magnetic stirbar was evacuated and back-filled with argon and then was charged with 1,1,3,3-tetramethyl-1,3-disilacyclobutane (**2**) and hexane. The flask was placed in a room-temperature water bath, and then 1.5–2.2 molar equiv (based on **2**) of TMEDA was added. Dropwise addition of 1.3–1.6 molar equiv of *tert*-butyllithium (1.5–1.7 M solution in pentane) over a period of 3–5 min followed. The resulting mixture was stirred at room temperature under argon for 25–35 min.

Two different procedures were used in carrying out reactions of the solution of **3** thus prepared.

Procedure A. To the solution of **3** in hexane was added, dropwise with stirring, the electrophile, either as the neat compound or as a solution in hexane. The reaction mixture was stirred at room temperature for about 50 min, and then a saturated aqueous solution of ammonium chloride was added until a clear organic layer resulted. The latter was separated and dried over anhydrous $MgSO_4$. After filtration, the organic layer was trap-to-trap distilled at room temperature (60 mmHg) into a cold trap to remove solvent. The residue was analyzed by GLC and then distilled at reduced pressure to obtain the product.

Procedure B. A 250-mL round-bottomed three-necked flask equipped with a pressure-equalizing addition funnel, a rubber septum, a gas inlet/outlet tube (connected to an oil bubbler on a Schlenk line), and a magnetic stirbar was charged with the electrophile and diethyl ether and cooled at −78 °C. A solution of lithium reagent **3**, prepared as described above, was transferred to the addition funnel (under argon) and then was added dropwise with stirring to the solution of the electrophile. Upon completion of the addition, the mixture was warmed to room temperature and stirred under argon for up to 18 h. Hydrolytic workup as described for procedure A followed, and the product was isolated by distillation at reduced pressure. In two experiments (Table II) the reaction mixture was treated with Me_2HSiCl or Me_3SiCl instead of aqueous NH_4Cl. Methanol, rather than aqueous NH_4Cl, was added to the **3**/PhCN reaction mixture.

Reaction of 2 with Methyllithium. A 50-mL three-necked, round-bottom flask equipped with a pressure-equalizing addition funnel, a gas inlet/outlet tube connected to an oil bubbler on a Schlenk line, a rubber septum, and a magnetic stirbar was charged with 15.6 mL of 2.06 M MeLi in diethyl ether (0.0321 mol) under an atmosphere of dry nitrogen. To this solution was added with stirring 3.09 g (0.0214 mol) of **2**. The reaction mixture was stirred and heated at reflux for 48 h. Subsequently, it was cooled to 0 °C and 10 mL of water was added very slowly. The organic layer was evaporated, washed once with water, and dried over anhydrous $MgSO_4$. After removal of solvent, GLC analysis showed the presence of $Me_3SiCH_2SiMe_3$ in 74% yield. The refractive index ($n^{25}{}_D$ 1.4149), the infrared spectrum, and the proton NMR spectrum were in good agreement with literature data (IR, NMR, $n^{25}{}_D$ 1.4155[14]).

A similar reaction of 0.0216 mol of **2** and 0.0324 mol of MeLi was quenched with trimethylchlorosilane (0.056 mol). The product in this case (46% yield, by GLC) was $[Me_3SiCH_2]_2SiMe_2$, $n^{25}{}_D$ 1.4402 (lit.[15] $n^{25}{}_D$ 1.4391).

The reaction of **2** (0.0218 mol) with *n*-butyllithium (2.31 M in 11.4 mL of hexane) was carried out in a similar fashion with 11.4 mL of *n*-heptane diluent. The reaction mixture was heated and concentrated to remove 12.5 mL of solvent and then was stirred and heated at reflux for 24 h. An aqueous workup was followed by removal of solvent from the organic layer and GLC analysis of the residue. The expected product, $n\text{-}C_4H_9Me_2SiCH_2SiMe_3$, $n^{25}{}_D$ 1.4317 (lit.[14] $n^{25}{}_D$ 1.4325), was present in 18% yield. Its IR and proton NMR spectra agreed with literature data.[14] Anal. Calcd for $C_{10}H_{27}Si_2$: C, 59.32; H, 12.94. Found: C, 59.46; H, 12.95.

The following reactions are typical for those listed in Tables I and II.

Reaction of 3 with Trimethyltin Chloride (Example of Procedure B). A solution of **3** was prepared by reaction of 2.965 g (0.0205 mol) of **2** in 16 mL of hexane with 4.6 mL (0.0305 mol) of TMEDA and 15.7 mL of 1.7 M *t*-BuLi in pentane (0.0267 mol). With use of procedure B (above) the solution of **3** thus prepared was added to a solution of 5.32 g (0.0267 mol) of Me_3SnCl in 32 mL of diethyl ether at −78 °C. The resulting reaction mixture

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was warmed to room temperature and then was stirred for 2 h 45 min. Then a saturated aqueous solution of NH_4Cl was added until a clear organic layer resulted. Subsequent drying ($MgSO_4$) and removal of solvent at reduced pressure was followed by GLC analysis of the residue and then fractional distillation of the product, **7**, bp 48–50 °C (0.1 mmHg).

Reaction of 3 with Benzaldehyde/Me_3SiCl (Example of Procedure A). A solution of **3** in 40 mL of hexane was prepared by reaction of 4.610 g (0.0319 mol) of **2**, 7.6 mL (0.0504 mol) of TMEDA, and 25 mL of 1.7 M *t*-BuLi (0.0425 mol) in pentane. With use of procedure A (above), 4.4 mL (0.0433 mol) of benzaldehyde was added by syringe over a period of 5 min. After the mixture had been stirred for 15 min at room temperature, 5.8 mL (0.046 mol) of Me_3SiCl was added dropwise by syringe. After 20 min the mixture was filtered through Celite. Removal of solvents from the filtrate at reduced pressure (room temperature, 60 mmHg) was followed by GLC analysis of the residue and then fractional distillation of the product, **14**, at 82.5–84 °C (0.07 mmHg).

Reaction of 3 with Benzoyl Chloride (Procedure B). A solution of **3** in 20 mL of hexane was prepared by the reaction of 3.929 g (0.0214 mol) of **2**, 6.2 mL (0.0411 mol) of TMEDA, and 20.8 mL of 1.7 M *t*-BuLi (0.0354 mol) in pentane. It then was added to a solution of 5.00 g (0.0356 mol) of benzoyl chloride in 30 mL of Et_2O at −40 °C over a period of 10 min. After the mixture had been stirred at −40 °C for 45 min, it was warmed to room temperature and stirred for 14 h. Standard workup with saturated aqueous NH_4Cl followed. Subsequent drying ($MgSO_4$) and removal of solvent at reduced pressure was followed by GLC analysis of the residue and then fractional distillation of the product, **15**, bp 70 °C (0.05 mmHg).

Reaction of 3 with Benzonitrile (Procedure B). The same general procedure as described in the experiment above was used in the reaction of **3** (from 0.0266 mol of **2**) and 0.0353 mol of benzonitrile at −78 °C and then at room temperature. Subsequently, 1.1 mL of MeOH was added dropwise. Filtration through Celite was followed by solvent removal at reduced pressure and then fractional distillation of the product, **16**, at 70–71 °C (0.05 mmHg).

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Registry No. **2**, 1627-98-1; **3**, 129152-58-5; **4**, 129152-59-6; **5**, 129152-60-9; **6**, 129152-61-0; **7**, 129152-62-1; **8**, 129152-63-2; **9**, 129152-64-3; **10**, 129152-65-4; **11**, 129152-66-5; **12**, 129152-67-6; **13**, 129152-68-7; **14**, 129152-69-8; **15**, 129152-70-1; **16**, 129152-71-2; Me_3SiCl, 75-77-4; Me_2HSiCl, 1066-35-9; $CH_3CH_2CH_2I$, 107-08-4; Me_3SnCl, 1066-45-1; ICH_2CH_2I, 624-73-7; $BrCH_2CH_2Br$, 106-93-4; MeSSMe, 624-92-0; MeC(O)H, 75-07-0; PhC(O)H, 100-52-7; PhC(O)Cl, 98-88-4; PhCN, 100-47-0.

Facile Conversion of Organometallic Halide Complexes to Halomethyl Derivatives: Synthesis, Structure, and Reactivity of the $(\eta^5\text{-}C_5R_5)Cr(NO)_2CH_2X$ Series ($R = H, CH_3$; $X = Cl, Br, I, OCH_3, OCH_2CH_3, PPh_3, CN, SO_3C_6H_4CH_3$)

John L. Hubbard*,[1a] and William K. McVicar[1b]

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300,
and Department of Chemistry, University of Vermont, Burlington, Vermont 05405

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Treatment of $(\eta^5\text{-}C_5R_5)Cr(NO)_2X$ with ethereal diazomethane in the presence of Cu powder provides access to the new $(\eta^5\text{-}C_5R_5)Cr(NO)_2CH_2X$ derivatives in 88–93% yield ($R = H, CH_3$; $X = Cl, Br$). In contrast to the chemistry of the isoelectronic/isostructural $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2X$ systems, the CH_2 of the halomethyl ligand in the $(\eta^5\text{-}C_5H_5)Cr(NO)_2CH_2Cl$ complex undergoes a remarkably facile migration into a C–H bond of the coordinated $\eta^5\text{-}C_5H_5$ ring upon abstraction of the α-halide, giving the $(\eta^5\text{-}C_5H_4Me)Cr(NO)_2^+$ cation in >80% yield. Deuterium labeling shows the process to be *intramolecular*. Methylene migration is attributed to the extremely electrophilic nature of the Cr–alkylidene species generated upon halide abstraction. Intermolecular CH_2 transfer is only observed when $\eta^5\text{-}C_5Me_5$ derivatives are treated with Ag^+ in the presence of excess cyclohexene. The stable iodomethyl derivatives are obtained in high yield by simple NaI/THF metathesis from the chloromethyl complexes. The $(\eta^5\text{-}C_5Me_5)Cr(NO)_2CH_2I$ complex has been characterized by single-crystal X-ray diffraction methods: monoclinic space group $P2_1/a$, $a = 10.366$ (3) Å, $b = 10.974$ (2) Å, $c = 12.818$ (3) Å, $\beta = 90.81$ (2)°, $Z = 4$, final $R/R_w = 7.47\%/6.86\%$. The iodomethyl carbon–Cr distance of 2.093 (11) Å can be considered short for a Cr^0–C single bond. The halomethyl halide is irreversibly displaced by Y^- (Y^- = cyanide, tosylate, and alkoxides) to give stable $(\eta^5\text{-}C_5R_5)Cr(NO)_2CH_2Y$ derivatives. Reaction of $(\eta^5\text{-}C_5H_5)Cr(NO)_2CH_2I$ with PPh_3 followed by $NaBPh_4$ gives the cationic ylide $(\eta^5\text{-}C_5H_5)Cr(NO)_2CH_2PPh_3^+BPh_4^-$, which has been characterized by X-ray crystallography: monoclinic space group $P2_1/c$, $a = 10.038$ (2) Å, $b = 23.587$ (4) Å, $c = 17.150$ (3) Å, $\beta = 102.35$ (1)°, $Z = 4$, final $R/R_w = 4.81\%/5.42\%$. A C–P bond distance of 1.748 (3) Å indicates considerable ylide character for the CH_2PPh_3 ligand; the IR and NMR data show the CH_2PPh_3 ligand to be a stronger donor than the CH_2I ligand. The Cr–C distance for the CH_2PPh_3 ligand is 2.115 (3) Å in this case.

Introduction

α-substituted alkyl ligands (CH_2X) coordinated to transition metals continue to attract attention with regard to fundamental metal–carbon interactions. Hydroxymethyl and alkoxymethyl complexes are closely tied to the chemistry of vitamin B_{12},[2] the reduction of carbon monoxide in catalytic schemes such as the Fischer–Tropsch process,[3] and hydroformylation reactions.[4] Halomethyl

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[1] (a) Utah State University. (b) University of Vermont.

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