

The complex $\nu(\text{CO})$ IR band patterns for $\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$ and $\text{HFeW}(\text{CO})_9^-$ are practically identical. All band positions of $\text{HFeW}(\text{CO})_9^-$ are displaced to higher frequencies by $\sim 20 \text{ cm}^{-1}$ from those of $\text{Et}_4\text{N}^+\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$ (in THF, 2043 m, 1967 ms, 1917 s, 1895 sh, 1849 m). The lower field ^{13}C resonances of the carbonyl carbons of $\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$ compared to $\text{HFeW}(\text{CO})_9^-$ are, like the comparative $\nu(\text{CO})$ IR data, consistent with greater negative charge on the carbonyl groups of the gold derivative.^{7b,12}

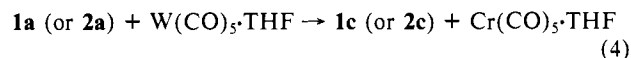
X-ray Crystal Structure.¹³ Two views of $\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$ (**2c**) shown in Figure 1, were selected to easily relate to those presented earlier for $\text{HFeW}(\text{CO})_9^-$. The Fe, W, and CO arrangements and distances are practically identical for the two structures. Tungsten is in a regular octahedral array in both. In **2c**, the iron center is six-coordinate and may be described as a highly distorted octahedron or as a bicapped tetrahedron. Carbonyls **7** and **8**, bound to Fe and mutually cis to both Au and W, are bent ($\angle\text{Fe-C-O}$ av 171.6 (26)^o). The Au-C7 and Au-C8 distances (2.776 (23) and 2.688 (28) Å, respectively) but not the W-C7 and W-C8 distances (3.201 (28) and 3.129 (29) Å, respectively) are within van der Waals radii. All other intermetal-ligand distances are >3.3 Å.

The gross coordination environment about Fe is reminiscent of structures of $\text{Fe}(\text{CO})_4^{2-}$ which show hard cations penetrating the tetrahedral anion: $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5$ dioxane,¹⁴ [(dipy)- $\text{CdFe}(\text{CO})_4$]₃,¹⁵ and [$\text{CdFe}(\text{CO})_4$]₄·2 acetone.¹⁶ In the case of $\text{Na}_2\text{Fe}(\text{CO})_4$, the similar bent Fe-C-O and close $\text{Na}^+ \cdots \text{C}$ interaction distance (2.86 Å) are accepted as a way of gaining electrostatic interaction between Na^+ and Fe^{2-} via the electrons delocalized into C_{π^*} .¹⁴ The arrangement in $\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$ suggests a similar *inverse* direct donation¹⁷ of $\text{Fe}_{d\pi}$ electrons to Ph_3PAu^+ via C_{π^*} .

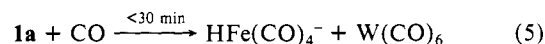
The W-Au distance of 4.12 Å rules out any bonding between these atoms. In contrast, the distance between Cr and Au in $(\text{OC})_5\text{Cr-H-AuPPh}_3$ is 2.770 Å,¹⁰ between W and Au in $(\text{OC})_2\text{W}(\mu\text{-CHR})\text{AuPPh}_3$ is 2.729 Å, and between Au atoms in $\text{Fe}(\text{CO})_4(\text{AuPPh}_3)_2$ is 3.028 (1) Å.⁸ The Fe-Au distance of 2.520 (3) Å is identical with that of the one known compound which has a terminal Fe-Au bond, $(\eta^3\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_3\text{AuPPh}_3$.¹⁸

In summary, the structure of **2c** is viewed as the interaction of $\text{Fe}(\text{CO})_4^{2-}$ with two metalloelectrophiles: one, 16-electron $\text{W}(\text{CO})_5$ forms a metal-metal donor-acceptor bond with the iron nucleophile; the second, the more demanding 12-electron Ph_3PAu^+ accepts electrons both directly from the iron and indirectly from the electron-rich iron carbonyl carbons. The extreme similarity of the metal carbonyl frameworks suggests the hydrogen in **1c**, like the Ph_3PAu in **2c**, to be a terminal ligand.

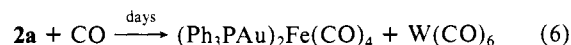
Despite identical Fe-W and nearly identical M-C bond distances in $\text{HFeW}(\text{CO})_9^-$ and $\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$, the latter is substantially more robust. The anions are reactive to both electrophiles and nucleophiles. For example, $\text{HFeCr}(\text{CO})_9^-$ reacts with $\text{THF} \cdot \text{W}(\text{CO})_5$ within time of mixing to generate **1c**. The analogous reaction of $\text{Ph}_3\text{PAuFeCr}(\text{CO})_9^-$ (**2a**) requires 2 h (eq 4). Carbon monoxide disrupts **1c** within minutes according to



eq 5. Complete reaction of **2a** with CO requires several days



and the iron-containing product is the neutral bis((triphenylphosphine)gold) complex (eq 6). Phosphines also cleave the



dimers, much more slowly than CO, with similar results. That is, the very stable $\text{HFe}(\text{CO})_4^-$ ligand is readily displaced from $\text{W}(\text{CO})_5^0$ whereas the $\text{Ph}_3\text{PAuFe}(\text{CO})_4^-$ "ligand" is unknown as an isolated species.^{19,20} Whether this fact bears on the reactivity, and indeed the mechanism of these cleavage reactions, warrants future study.

Acknowledgment. We appreciate helpful discussions with Professors M. B. Hall and D. J. Darensbourg and acknowledge support from the National Science Foundation (CHE 83-04162, to M.Y.D.) and (CHE 84-08414, to J.P.F.).

Supplementary Material Available: Detailed synthesis, characterization, X-ray structural analysis, atomic positional and thermal parameters, all bond lengths and angles, anisotropic thermal parameters, and observed and calculated structure factors for $\text{Et}_4\text{N}^+\mathbf{2c}$ (27 pages). Ordering information is given on any current masthead page.

(19) Several attempts to prepare $\text{Ph}_3\text{PAuFe}(\text{CO})_4^-$ via reaction of Ph_3PAuCl with $\text{Fe}(\text{CO})_4^{2-}$, all resulted in formation of $(\text{Ph}_3\text{PAu})_2\text{Fe}(\text{CO})_4$. In contrast, we have good evidence for the anion *cis*- $\text{Ph}_3\text{PAuW}(\text{CO})_4\text{PMe}_2^-$ prepared via a similar route.²⁰

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Direct Observation of the Initial Insertion of an Unsaturated Hydrocarbon into the Titanium-Carbon Bond of the Soluble Ziegler Polymerization Catalyst, $\text{Cp}_2\text{TiCl}_2\text{-MeAlCl}_2^1$

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Received May 7, 1985

Despite more than 25 years of intensive study, the precise nature of the active center formed from the soluble, two-component ethylene polymerization catalyst $\text{Cp}_2\text{TiCl}_2\text{-R}_n\text{AlCl}_{3-n}$ has remained uncertain.²⁻⁵ We therefore are pleased to report that by using a highly substituted surrogate for ethylene, namely, trimethyl-(phenylethynyl)silane (**1**), we have been able, for the first time, to intercept, isolate, and determine the crystal structure of the initial insertion product formed in such a so-called Ziegler catalyst

* State University of New York at Binghamton.

† The National Research Council of Canada

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(13) Single crystals of $\text{Et}_4\text{N}^+\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$ were grown from THF/hexane. Data collection was carried out at 22 °C, using a Nicolet P3F automated diffractometer, Mo $K\alpha$ radiation. The space group is $P\bar{1}$ with $a = 13.008$ (5) Å, $b = 13.974$ (6) Å, $c = 14.110$ (7) Å, $\alpha = 99.14$ (4)^o, $\beta = 116.63$ (3)^o, $\gamma = 101.01$ (3)^o. Intensity data were collected for 5989 reflections of which 2766 were unique and measured $F_o^2 > 3\sigma F_o^2$ and were used for structure solution and refinement using SHELXTL. The last cycle of least-squares refinement gave residuals of $R = 0.0569$, $R_w = 0.068$, and a goodness of fit indicator of 1.786 for a fit of 419 variables to 2766 observations. Complete details of the refinement along with tables are available as supplementary material.

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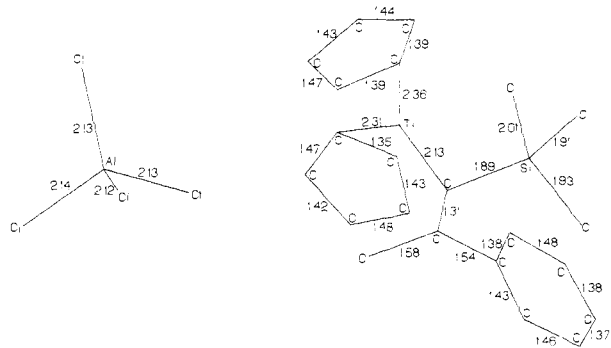


Figure 1. Interatomic separations (Å) in dicyclopentadienyl[(E)-2-methyl-2-phenyl-1-(trimethylsilyl)ethenyl]titanium(IV) tetrachloroaluminate, $C_6H_5(CH_3)C=C(TiCp_2)Si(CH_3)_3^+ AlCl_4^-$ (**4**). The lines do not, in every instance, represent chemical bonds. The lines between Ti and cyclopentadienyl rings, for example, are merely the distances of closest approach. The separations of 2.31 and 2.36 Å represent the nearest approach between carbon atoms in the C_5H_5 rings and the titanium center. Important bond angles (deg): Ti-C₁-Si, 88.9; Ti-C₁-C₂, 144.9; Si-C₁-C₂, 125.6; C₁-C₂-CH₃, 123.5°; C₁-C₂-Ph, 122°; C₃-C₂-Ph, 114.3°; Cl-Al-Cl, approximately tetrahedral, from 108.0° to 111.8°. If a plane is passed through the Ti, Si, vinylic carbon and the methyl and C₁-phenyl atoms, the respective atoms project out of the plane by at most 0.01–0.05 Å.

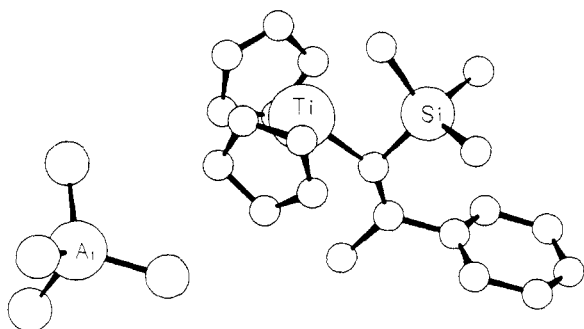
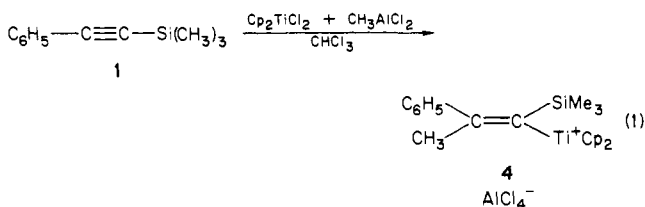


Figure 2. Stereoscopic view of dicyclopentadienyl[(E)-2-methyl-2-phenyl-1-(trimethylsilyl)ethenyl]titanium(IV) tetrachloroaluminate (**4**), showing the orientation of the titanium-carbon and carbon-silicon bonds to C₁. Note that the vacant site on titanium and the carbon-silicon σ bond lie in the same plane (cf. ref 8).

system.⁶ The interaction of equimolar amounts of titanocene dichloride (**2**) and methylaluminum dichloride (**3**) in $CHCl_3$ with **1** at $-20^\circ C$ led to the deposition of dicyclopentadienyl[(E)-2-methyl-2-phenyl-1-(trimethylsilyl)ethenyl]titanium(IV) tetrachloroaluminate (**4**) (eq 1), whose structure and molecular pa-

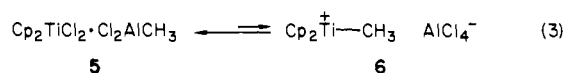
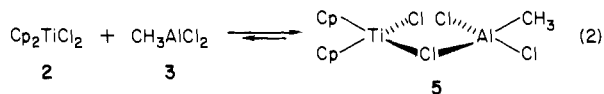


rameters are given in Figure 1 and a stereoscopic view of which is offered in Figure 2.⁷ The unusually small Ti-C-Si angle of 88.9° is noteworthy, since the steric repulsion of the Cp_2Ti and

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(7) The diffraction intensities of moderate quality were collected from a crystal of **4** at 115 K with graphite monochromatized $Cu K\alpha$ radiation using the $\theta/2\theta$ scan technique with profile analysis to $2\theta_{max} = 100^\circ$. A total of 2602 unique reflections were measured of which 1452 reflections were considered significant with $I_{net} = 2.5\sigma(I_{net})$. The crystal is monoclinic and belongs to the space group $P2_1/n$. The crystal is monoclinic and belongs to the space group $P2_1/n$. Real cell lattice constants are $a = 9.8240$ (7) Å, $b = 16.899$ (8) Å, $c = 15.591$ (3) Å, and $\beta = 102.83$ (1)°. The structure was solved by a direct method and refined anisotropically for the heavy atoms and isotropically for the light atoms. The agreement indices were $R_F = 0.121$, $R_W = 0.093$.

Me_3Si groups might have been expected to widen the angle to $>120^\circ$.⁸ By means of 1H , ^{13}C , and ^{27}Al NMR spectroscopy the formation of **4** from **1–3** could be monitored in solution and the conclusion reached that **4** is the first and only insertion product formed from this catalyst system. The structure of **4** clearly proves that the surrogate hydrocarbon **1** undergoes insertion into the carbon-titanium bond in a regiospecific and syn-stereospecific manner. This finding permits the conclusion that the active component formed from **2** and **3** is dicyclopentadienylmethyl-titanium(IV) tetrachloroaluminate (**6**, eq 3). However, the amount



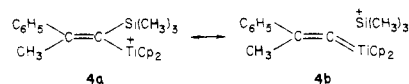
of **6** in equilibrium with **2** and **3** is spectroscopically undetectable, as our present NMR and other previous UV studies⁹ have shown. In fact, admixture of **2** and **3** leads to the formation of the red, chloride-bridged complex **5** (eq 2), which we have likewise been able to isolate and whose crystal structure we have also determined.¹⁰

In view of these structural insights, we conclude that the crucial step in the activation of this ethylene polymerization catalyst is the isomerization of **5** into **6**. The possibility that **5** itself might be the active catalyst is ruled out by the prior work of Long⁹ and the elegant kinetic studies of Fink,¹¹ who found that the rate of ethylene polymerization could be only satisfactorily explained if two equilibria were involved in converting the $Cp_2TiCl_2-R_nAlCl_{3-n}$ system into the active catalyst. The foregoing equilibria (eq 2 and 3) would accommodate Fink's kinetic analysis.

Furthermore, the ion-pair nature of the active catalyst (**6**) is consistent with the following observations: (1) the conductivity and electroanalysis studies of Dyachkovskii pointing to a cationic titanocene ion in CH_2Cl_2 ;¹² (2) the accelerated polymerization of ethylene¹³ and the rapidity of the carbotitanation of unsaturated hydrocarbons¹⁴ by **2** and **3** in CH_2Cl_2 , compared with the rate in aromatics; (3) the complete inhibition of such carbotitanation by Lewis bases;¹⁴ (4) the polymerization of styrene by **2** and **3** to give a polystyrene whose molecular weight distribution is that characteristic of cationic processes.¹⁵

Finally, for initiating the carbotitanation the methyltitanocene cation in **6** has a vacant coordination site available, into which ethylene or its surrogate, **1**, can enter. The steric constraints for such coordination are manifested in the failure of trimethyl-(3,3-dimethyl-1-butynyl)silane, $(CH_3)_3CC \equiv CSi(CH_3)_3$, to undergo carbotitanation with **2** and **3**.¹⁴ The regiochemistry of the ensuing syn carbotitanation of **1** reflects the electrophilic attack of **6** at C₁, so that the incipient carbenium ionic character at C₂ (**7a**) can be stabilized by conjugation with the Si-C σ bond (**7b**, eq 4).¹⁶

(8) The small Ti-C-Si angle suggests hyperconjugation of the C-Si σ bond electrons with the vacant 4p orbital of the titanium cation (Figure 2):



Such an interaction would tend to narrow the Ti-C-Si angle, since C₁ would thereby assume more sp character (cf. the analogous M-C α -C β angles in early-transition-metal alkylidene complexes: Churchill, M. R.; Hollander, F. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 647).

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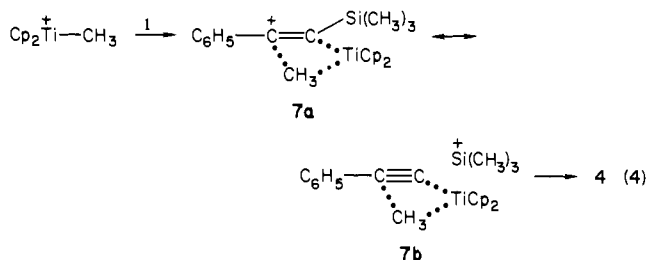
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(15) We thank Dr. S. Bywater of the National Research Council, Ottawa, for this interpretation of the results that we obtained in the polymerization of styrene by **2** and **3**.



Acknowledgment. We gratefully acknowledge the support of this research by Grant CHE-8308251 from the National Science Foundation.

Supplementary Material Available: Listings of atomic coordinates, standard deviations, and temperature factors for structures **4** and **5** (53 pages). Ordering information is given on any current masterhead page.

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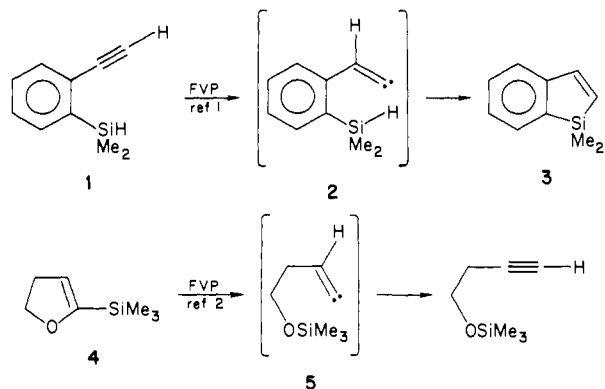
Thermal Extrusion of Dimethylsilanone from (Hydridosilyl)ketenes. A Retro-Wolff Rearrangement?

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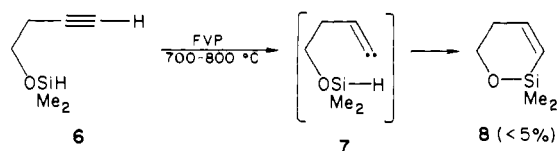
Received July 15, 1985

Recently we reported that the Si-H bond serves as an efficient intramolecular trap for a vinylidene **2**, produced by thermal isomerization of arylacetylene **1**, to afford in high yield silaindene **3**.¹ As we have also discovered that vinylidenes can be produced by reductive elimination in the flash vacuum pyrolysis (FVP) of α -silyl cyclic enol ethers (e.g., **4** \rightarrow **5**),² we thought to couple these



two reactions to provide a novel and convenient route to dihydrosilapyrans which were needed for another study.

The reductive elimination approach to the desired vinylidene for dihydrosilapyran synthesis was prompted by the failure of acetylene **6** to serve as a dihydrosilapyran precursor. It was hoped that **6** would thermally isomerize to vinylidene **7** and cyclize to dihydropyran **8**. However, FVP of **6**³ at 700 °C produced only



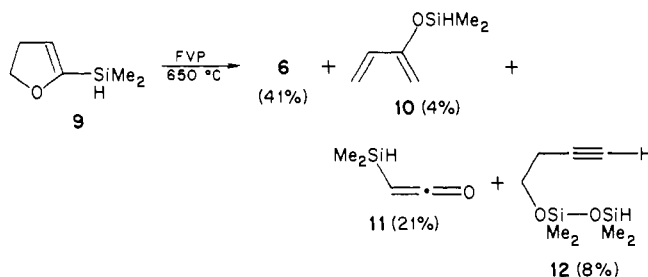
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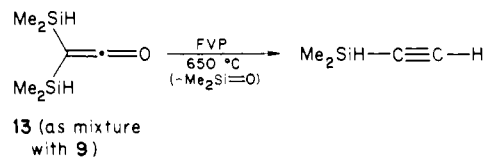
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a trace (ca. 5%) of **8**⁴ with very little decomposition of **6**. Although major decomposition occurred at 800 °C, there was no improvement in the yield of **8**, and numerous products were formed in very low yields.

Thus, we turned to the reductive elimination route to vinylidene **7** using α -(dimethylsilyl)dihydrofuran (**9**)⁵ as its precursor. FVP of **9** at 650 °C produced no evidence of silapyran **8** although the intermediacy of vinylidene **7** was clearly established through the formation of acetylene **6** (41%). Formation of 2-siloxy-1,3-butadiene (**10**, 4%)⁴ and (dimethylsilyl)ketene (**11**, 21%)⁴ was preceded from the pyrolysis of **4**.² The only surprising product was disiloxane **12**⁴ whose presence strongly suggested the intermediacy of dimethylsilanone, $\text{Me}_2\text{Si}=\text{O}$. The well-precedented⁶ insertion of $\text{Me}_2\text{Si}=\text{O}$ into the Si-O bond of **6** is the most likely origin of disiloxane **12**.



As the pyrolysis of **6** was already established as not being the source of **12**, the only candidate appeared to be silylketene **11**. Although **11** would appear to be a most unlikely precursor to $\text{Me}_2\text{Si}=\text{O}$, this possibility was experimentally explored. Silylketene **11** proved to be too unstable and/or reactive for convenient isolation or handling. Thus, an inseparable mixture of **9** and bis(dimethylsilyl)ketene (**13**)^{4,7} (73:27) was copolyzed and found to produce (dimethylsilyl)acetylene, the expected product from



extrusion of $\text{Me}_2\text{Si}=\text{O}$ from **13**. This acetylene is not formed in the FVP of **9** alone.

Finally, to unambiguously demonstrate that (hydridosilyl)ketenes do indeed thermally decompose by loss of $\text{Me}_2\text{Si}=\text{O}$ and that only a single hydridosilyl group is required, (trimethylsilyl)(dimethylsilyl)ketene (**14**)⁴ was synthesized⁸ and pyrolyzed.

(4) Compounds **9**, **12**, and **14** were completely characterized by ¹H NMR, ¹³C NMR, MS, and combustion analysis. Compounds **10**, **11**, and **13** were characterized only by spectral means due to insufficient sample, instability, and separation difficulty, respectively. Compound **8** was identified by GC-MS and ¹H NMR comparison with an authentic sample.

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(7) The surprising formation of ketene **13** during the synthesis of **9** is the subject of a separate paper currently submitted for publication.

(8) Synthesis of **14** was serendipitously accomplished by the method of Pirrung and Hwu⁹ through dehydrohalogenation of 1-bromo-2-(trimethylsilyloxy)ethene with LDA. Quenching of the resulting anion with Me_2SiHCl and workup involving distillation (maximum temperature 125 °C), heating with MeI to remove $i\text{-Pr}_2\text{SiMe}_2$ (sealed tube, 70 °C, 14 h), and preparative GC provided **14** (11%) instead of the expected⁹ $\text{Me}_2\text{HSiC}(\text{OSiMe}_3)=\text{C}(\text{OSiMe}_3)$. Spectral distinction is from the observation of the expected¹⁰⁻¹² ketene bond at 2077 cm^{-1} , absence of the acetylenic stretch in the region of 2250 cm^{-1} ,¹¹ and the unique silylketene ¹³C NMR spectrum [δ 166.58 (SiC=), 0.97 (MeSi), -1.34 (MeSi), -1.53 (=C=O)]. For comparison, the unsaturated carbons of $\text{Me}_2\text{SiHC}=\text{C}=\text{O}$ and $(\text{Me}_2\text{Si})_2\text{C}=\text{C}=\text{O}$ absorb at δ 179, -0.1 and δ 166.8, 1.7.¹³ We are actively studying this problem and will report our findings at a later date.

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