$$Ru_3(CO)_{12} + CH_3O^- \rightleftharpoons \underset{1}{Ru_3(CO)_{11}(CO_2CH_3)^-} \rightleftharpoons Ru_3(CO)_{10}(CO_2CH_3) + CO \quad (3)$$

investigation infrared spectral data for $Ru_3(CO)_{12}$ in pure methanol that indicate partial formation of the adduct species 1, with the principal metal containing component in solution being $Ru_3(CO)_{12}$. Whereas ν_{CO} bands attributed only to 1 prepared from an equimolar mixture of $Ru_3(CO)_{12}$/KOMe were observed in THF/MeOH at 2072 (w), 2015 (s), 1990 (s), 1965 (m), and 1603 cm^{-1}, the ν_{CO} infrared spectrum of $Ru_3(CO)_{12}$ in methanol displayed bands due to both 1 and $Ru_3(CO)_{12}$. Similarly the ^{13}C NMR spectrum of an equimolar mixture of $Ru_3(CO)_{12}$/KOMe in ^{13}CO displayed a single resonance at 206.6 ppm ($Ru_3(CO)_{12}$ in THF/MeOH has a ^{13}C signal at 199.3 ppm) at ambient temperature due to 1 that broadens below -100 °C. In the absence of KOMe the minor component (16.8%) in a MeOH/THF solution of $Ru_3(CO)_{12}$ exhibits ^{13}C NMR spectral characteristics identical with that described in the presence of KOMe, and the major species in solution is $Ru_3(CO)_{12}$ (see Figure 2).[10]

Hence both ν_{CO} infrared and ^{13}C NMR spectral data indicate that in MeOH or MeOH/THF, $Ru_3(CO)_{12}$ has acid (electrophilic) sites, presumably the carbon centers of coordinated CO ligands, for interaction with OMe^- which are moderately competitive with H^+ (eq 4). This is consistent with the high CO stretching frequencies observed for $Ru_3(CO)_{12}$.[11] In contrast, $W(CO)_6$, which possesses a considerably lower CO stretching force constant, does not show adduct formation in methanol alone nor does it display CO lability. However, $W(CO)_5CO_2Me^-$, prepared from $W(CO)_6$ and KOMe displays drastically enhanced CO lability over that of $W(CO)_6$.

$$Ru_3(CO)_{12} + MeOH \rightleftharpoons Ru_3(CO)_{11}CO_2Me^- + H^+(\text{solvated}) \quad (4)$$

Since catalysis of methyl formate synthesis via CO/MeOH occurs in the presence of equimolar quantities of $Ru_3(CO)_{12}$ and PPNOMe or KOMe in methanol, it is possible that species 1 is an intermediate in this catalytic process.[12] Consistent with the solution species described in eq 4, $Ru_3(CO)_{12}$ in the absence of added methoxide ions is a modest catalyst for methyl formate production from CO/MeOH.[12] This is an important observation in light of the fact that alkoxides alone are catalysts for this process. Protonation of 1 by MeOH leads to HCOOMe and the cocatalyst OMe^-, with subsequent rapid uptake of carbon monoxide by $[Ru_3(CO)_{11}]$ to reform the metal catalyst component $Ru_3(CO)_{12}$. It is generally assumed that the most easily protonated site in 1 is the $-OCH_3$ unit which leads to reformation of $Ru_3(CO)_{12}$ and CH_3OH. For example, it was shown by Gross and Ford[8] that the addition of excess CF_3COOH to 1 regenerated $Ru_3(CO)_{12}$, quantitatively. An analogous process has been employed in the synthesis of several monomeric metal carbonyl derivatives of manganese and rhenium from the corresponding MC(=O)OEt species provided by M^- and ClC(=O)OEt coupling reactions.[13] Nevertheless, we feel that there are other sites for protonation, most notably the metal centers, which would lead to methyl formate production via reductive elimination.[14] Indeed the reverse process, oxidative addition of methyl formate to a transition-metal center to provide an hydrido methoxycarbonyl complex has been reported in the literature.[15] We are currently investigating mechanistic aspects of protonation reactions of methoxycarbonyl adducts of low-valence transition-metal derivatives in order to gain a better understanding of these processes.

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE 83-08281) is greatly appreciated.

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[10] ^{13}C NMR spectra were determined in THF/MeOH (2:1, v/v) because of the limited solubility of $Ru_3(CO)_{12}$ in methanol. Spectra were measured on a Varian XL-200 spectrometer.

[11] Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1970**, *9*, 1691.

[12] A 0.30-mol sample of $Ru_3(CO)_{12}$ and KOMe was dissolved in 15 mL of degassed methanol (distilled under nitrogen over magnesium turning and iodine), and the internal standard (hexane) was added. This reaction mixture was transferred to a stirred (magnetically activated, packless impeller system) 300-mL Parr reactor in a drybox. The reactor was then sealed and pressurized to 250 psi (at 25 °C) with pure CO and heated to 125 °C (reaching a final total pressure of 500 psi). After 24 h, the reactor was cooled and the pressure released. The reactor was then returned to the drybox and opened, and the reaction solution was transferred to a septum-capped vial. This solution was analyzed by GC (Perkin-Elmer Model Sigma 2, column used was 10% Carbowax 20M over Chromosorb) which showed 23 mmol of HCO_2Me was produced. This represents a turnover number (mol of HCO_2Me/mol of catalyst) of 80. Independent experiments were performed in a completely analogous manner employing $Ru_3(CO)_{12}$ or KOMe alone as catalysts, with turnover numbers of 21 and 115 being determined. Hence, although $Ru_3(CO)_{11}CO_2Me^-$ is the principal species present in solutions of $Ru_3(CO)_{12}$ and OMe^-, catalysis could be proceeding (at least in part) by way of uncomplexed methoxide.[4]

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[14] It is important to note here that we are quite certain that methyl formate is not produced via hydrogenation of the methoxycarbonyl ligand by H_2 afforded from water-gas shift chemistry. Ford and co-workers have reported that such a process does occur.[5] In our catalytic conversion of CO/MeOH to HCO_2Me little water-gas shift chemistry occurs simultaneously. In addition the other product of the WGS reaction CO_2 has been shown to effectively inhibit catalysis by reacting with the cocatalyst OMe^- to provide carbonates.

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Silicon-Carbon Unsaturated Compounds. 18. Nickel-Catalyzed Reactions of (Phenylethynyl)polysilanes with Phenyl(trimethylsilyl)acetylene and Molecular Structure of 3-Phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris(trimethylsilyl)-1-silacyclobut-2-ene

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Summary: The reactions of (phenylethynyl)polysilanes with phenyl(trimethylsilyl)acetylene (**2**) in the presence of a catalytic amount of $NiCl_2(PEt_3)_2$ gave products arising from isomerization of the (phenylethynyl)polysilanes, followed by addition to **2**. Similar reaction of (phenylethynyl)pentamethyldisilane in the absence of **2** afforded

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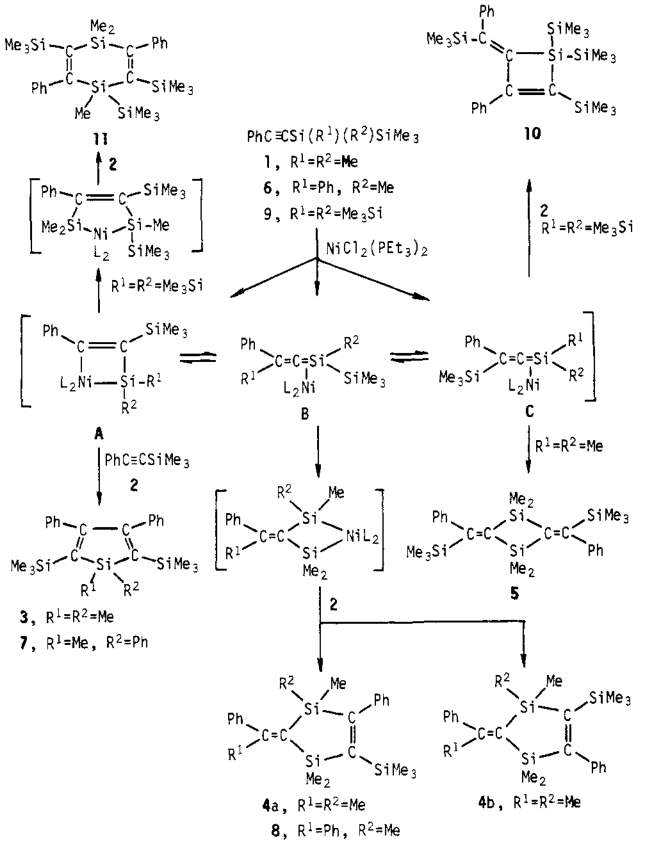
1,1,3,3-tetramethyl-2,4-bis[phenyl(trimethylsilyl)methylene]-1,3-disilacyclobutane. Preliminary results of an X-ray diffraction study of 3-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris(trimethylsilyl)-1-silacyclobut-2-ene are described.

There has been a considerable interest recently concerning the transition-metal complex catalyzed reaction of disilanes with unsaturated compounds.[2-10] In this paper we report the first examples of the nickel-catalyzed reaction of (phenylethynyl)polysilanes with phenyl(trimethylsilyl)acetylene, which afford products arising from the isomerization of the (phenylethynyl)polysilanes, followed by addition to a triple bond of phenyl(trimethylsilyl)acetylene.

When a mixture of (phenylethynyl)pentamethyldisilane (**1**, 1.72 mmol) and phenyl(trimethylsilyl)acetylene (**2**, 2.38 mmol) in the presence of $NiCl_2(PEt_3)_2$ (2.8×10^{-2} mmol) was heated in a sealed glass tube at 200 °C for 20 h, four products 1,1-dimethyl-3,4-diphenyl-2,5-bis(trimethylsilyl)silole (**3**), two isomers of 1,1,4,4-tetramethyl-5-(methylphenylmethylene)-3-phenyl-2-(trimethylsilyl)-1,4-disilacyclopent-2-ene (**4a** and **4b**), and 1,1,3,3-tetramethyl-2,4-bis[phenyl(trimethylsilyl)methylene]-1,3-disilacyclobutane (**5**) were obtained in 32, 23, 23, and 15% yields. Products **3**, **5**, and a mixture of **4a** and **4b** could readily be separated by medium-pressure liquid chromatography. Unfortunately, **4a** could not be separated from **4b** in a pure form by either GC or HPLC.[11] All spectral data obtained for **3** were identical with those of an authentic sample.[12] The structures of **4a** and **4b** were confirmed by mass and ^1H NMR spectroscopic methods[13] and by a chemical reaction. The fact that cleavage of the mixture of **4a** and **4b** by hydrogen chloride in benzene, followed by methylation of the resulting products with methyllithium, gave α-methylstyrene and phenyltris(trimethylsilyl)ethylene[14] in 36 and 56% yields was wholly consistent with the proposed structure.

Heating **1** with $NiCl_2(PEt_3)_2$ in the absence of **2** under the same conditions afforded no product. The starting **1** was recovered unchanged. Surprisingly, when **1** was heated with a catalytic amount of $NiCl_2(PEt_3)_2$–PhC≡CPh at 180 °C for 20 h, compound **5** was obtained in 74% yield, as the sole product.[15,16] In this reaction, no isomers were detected by either spectroscopic or GC analysis, indicating that dimerization proceeded with high stereoselectivity.

Scheme I



The reaction of 1-phenyl-1-(phenylethynyl)tetramethyldisilane (**6**) with **2** in the presence of $NiCl_2(PEt_3)_2$ at 200 °C for 20 h gave a product determined to be 1,1,4,4-tetramethyl-3-phenyl-5-(diphenylmethylene)-2-(trimethylsilyl)-1,4-disilacyclopent-2-ene[17] (**8**) by ^1H and ^{13}C NMR spectroscopic analyses, in 52% yield, in addition to a 10% yield of a known compound, 1-methyl-1,3,4-triphenyl-2,5-bis(trimethylsilyl)silole[12] (**7**). As expected, cleavage of **8** with hydrogen chloride in benzene afforded 1,1-diphenylethylene and phenyltris(trimethylsilyl)ethylene[14] in 25 and 40% yields, respectively.

A reasonable, although unproven, pathway for the formation of the products obtained is shown in Scheme I. We suggest that nickelasilacyclobutene intermediate A is involved in the formation of siloles **3** and **7** while a 1-silapropadiene intermediate, presumably its nickel complex C, is involved for compound **5**. The intervention of intermediate B could serve to explain the production of compounds **4** and **8**. The formation of the metalasilacyclobutene such as A has been proposed for the synthesis of siloles in the reaction of 1-silacyclopropenes with an acetylene in the presence of the transition-metal complex.[12,18,19] The reaction of (phenylethynyl)tris(trimethylsilyl)silane (**9**) with **2** in the presence of the nickel

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(12) Ishikawa, M.; Sugisawa, H.; Harata, O.; Kumada, M. *J. Organomet. Chem.* **1981**, *217*, 43.

(13) Compound **4a**: ^1H NMR δ –0.35 (6 H, s, Me_2Si), –0.18 (9 H, s, Me_3Si), 0.43 (6 H, s, Me_2Si), 2.30 (3 H, s, MeC), 6.65–7.35 (10 H, m, ring protons). Compound **4b**: ^1H NMR δ –0.25 (9 H, s, Me_3Si), –0.11 (6 H, s, Me_2Si), 0.20 (6 H, s, Me_2Si), 2.26 (3 H, s, MeC), 6.65–7.35 (10 H, m, ring protons); MS, *m/e* 406. Anal. Calcd for $C_{24}H_{34}Si_3$: C, 70.86; H, 8.42. Found: C, 70.57; H, 8.33.

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(15) Heating **1** with a catalytic amount of $NiCl_2(PEt_3)_2$–$Me_3SiSiMe_2H$ at 180 °C for 20 h gave **5** in 78% yield, while **1** with $NiCl_2(PEt_3)_2$–PhC≡CSiMe$_3$ at 200 °C for 20 h afforded **5** in 28% yield, together with **3** (3%), **4a**, and **4b** (5%).

(16) Compound **5**: mp 204–205 °C; ^1H NMR δ –0.04 (6 H, s, Me_2Si), –0.02 (9 H, s, Me_3Si), 6.84–7.41 (5 H, m, ring protons); ^{13}C NMR δ 0.3, 1.8, 125.4, 126.5, 127.6, 149.9, 170.4, 176.2; MS, *m/e* 464. Anal. Calcd for $C_{26}H_{40}Si_4$: C, 67.16; H, 8.67. Found: C, 67.07; H, 8.81.

(17) Compound **8**: mp 157–157.5 °C; ^1H NMR δ –0.23 (15 H, s, Me_2Si and Me_3Si), 0.01 (6 H, s, Me_2Si), 6.72–7.31 (15 H, m, ring protons); ^{13}C NMR δ –0.7, 1.5, 1.6, 125.3, 126.3, 126.8, 126.8, 127.4, 127.5, 127.8, 127.8, 142.6, 146.2, 146.5, 146.9, 163.5, 166.9, 181.2. Anal. Calcd for $C_{29}H_{36}Si_3$: C, 74.49; H, 7.74. Found: C, 74.49; H, 7.83.

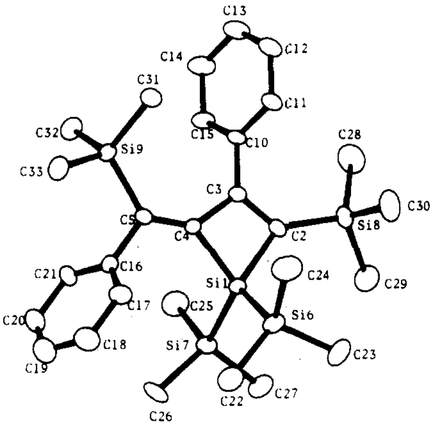

Figure 1. Molecular structure of 3-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris(trimethylsilyl)-1-silacyclobut-2-ene (**10**).

catalyst at 200 °C for 20 h produced two products identified as 3-phenyl-4-[phenyl(trimethylsilyl)methylene]-1,1,2-tris(trimethylsilyl)-1-silacyclobut-2-ene (**10**) and 1,4,4-trimethyl-3,6-diphenyl-1,2,5-tris(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (**11**) in 19 and 58% yields, respectively. Again, no products were observed in the absence of the catalyst under the same conditions. The starting compound **9** was recovered unchanged. Compounds **10** and **11** could readily be isolated by medium-pressure liquid chromatography. All spectral data obtained for **10** and **11** were consistent with the proposed structures.[20,21]

The structure of **10** was also determined by an X-ray diffraction study, which is the first example for the silacyclobutene system. The crystals of **10** are monoclinic and belong to space group $P2_1/n$ with cell dimensions a = 18.336 (3) Å, b = 16.002 (3) Å, c = 11.759 (1) Å, β = 95.34 (1)°, and Z = 4. Refinement by block-diagonal least-squares methods on F, with the use of 2280 diffractometer data, converged to an R value of 0.074. The molecular structure and the atom labeling scheme are shown in Figure 1. The central four-membered ring is almost planar, a maximum deviation from the best plane being 0.01 (1) Å. Endocyclic bond angles ∠C2–Si1–C4, ∠Si1–C2–C3, ∠C2–C3–C4, and ∠C3–C4–Si1 are 74.0 (4), 91.9 (5), 106.6 (7), and 87.5 (5)°, respectively. Bond lengths (Å) of Si1–C2 (1.906 (8)), Si1–C4 (1.915 (8)), and C3–C4 (1.500 (11)) in the ring are consistent with those of single bonds, while C2–C3 (1.367 (11) Å) is rather longer than that of the carbon–carbon double bond. The exocyclic C4–C5 bond (1.334 (12) Å) is in accord with the normal bond length of the double bond. The dihedral angles between the plane of the four-membered ring and the best plane through each of the C10 phenyl and C16 phenyl rings are 65.1 (9) and 26.4 (8)°, respectively. The structure of **11** was also verified by an X-ray diffraction study that will be reported elsewhere.

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Supplementary Material Available: A listing of observed and calculated structure factors and tables of positional and anisotropic thermal parameters and bond lengths and angles (10 pages). Ordering information is given on any current masthead page.

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(20) Compound **10**: mp 70 °C; ^{1}H NMR δ –0.42 (9 H, s, Me$_3$Si), –0.19 (9 H, s, Me$_3$Si), 0.02 (18 H, s, Me$_3$Si), 6.8–7.4 (10 H, m, ring protons); MS, *m/e* 522. Anal. Calcd for $C_{28}H_{46}Si_5$: C, 64.29; H, 8.86. Found: C, 64.23; H, 9.10.

(21) Compound **11**: mp 80 °C; ^{1}H NMR δ –0.20 (9 H, s, Me$_3$Si), 0.03 (9 H, s, Me$_2$Si and MeSi), 0.32 (18 H, s, Me$_3$Si), 6.4–7.3 (10 H, m, ring protons); MS, *m/e* 522. Anal. Calcd for $C_{28}H_{46}Si_5$: C, 64.29; H, 8.86. Found: C, 64.20; H, 9.11.

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