Registry No. 1, 92670-61-6; 1·2DME, 92670-63-8; 2, 92670-66-1; 3, 92670-64-9; Yb, 7440-64-4; Ca, 7440-70-2.

Supplementary Material Available: Infrared spectra (1·2DME, 2·2DME), calculated (1·2DME) and measured (1·2DME and 2·2DME) powder patterns, least-squares plane ([8]annulene), listing of anisotropic thermal parameters, calculated hydrogen positions, C–C distances, selected angles and observed structure factors for 1·2DME (17 pages). Ordering information is given on any current masthead.

Silacyclopropenes. 3. Palladium-Catalyzed Insertion Reactions†

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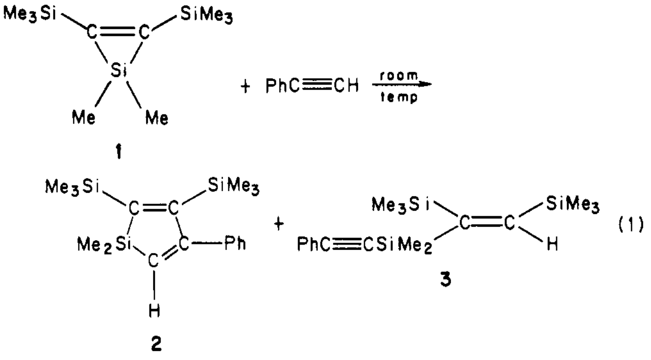
Received June 19, 1984

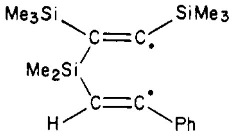
Bis(triphenylphosphine)palladium dichloride was found to catalyze two types of processes with 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene: (1) *formal* dimethylsilylene extrusion followed by trapping of this species by unsaturated organic species that are present; (2) insertion of unsaturated substrates into the silirene ring. Such catalyzed reactions with terminal acetylenes, allenes, and some terminal 1,3-dienes are described.

Introduction

In part 2[1] we reported thermal and UV-induced "two-atom" insertions of various unsaturated compounds (aldehydes, ketones, styrenes, conjugated terminal acetylenes, terminal 1,3-dienes, a conjugated imine) into the SiC$_2$ ring of 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene, 1. For instance, in the case of phenylacetylene this reaction gave the silacyclopentadiene 2 in 30% yield. In addition, an acyclic product, 3, also was produced in 70% yield (eq 1).



The available evidence suggested that a free radical process with a 1,5-diradical intermediate (4 in the case of the



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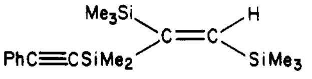
phenylacetylene reaction) was involved. When the silirene 1/phenylacetylene reaction was carried out with UV irradiation, no cyclic product was obtained. The products were the acyclic product 3 and its trans isomer 5. We have also examined reactions with silirene 1 with acetylenes and other unsaturated compounds in the presence of catalytic quantities of (Ph$_3$P)$_2$PdCl$_2$.



5

Transition-metal complex catalyzed cleavages of and insertions into Si–C and Si–Si bonds have received attention in recent years.[2] We do not intend an exhaustive review of this topic and mention only a few representative examples in eq 2–6.

In view of this fairly broad applicability of transition-metal complexes as catalysts in organosilicon reactions, we felt that a study of such catalyzed reactions of the strained, highly reactive silirene ring[1,4] might be fruitful. We report here our results of this investigation.

Results and Discussion

In view of the already demonstrated thermal and photochemical reactions of 1,1-dimethyl-2,3-bis(trimethyl-

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† Dedicated to the memory of Earl L. Muetterties, an outstanding and original scientist and an old friend from graduate school days.

(1) Part 2: Seyferth, D.; Vick, S. C.; Shannon, M. L. *Organometallics* 1984, *3*, 0000.

(2) (a) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1970**, *23*, C7. (b) Yamamoto, K.; Okinoshima, H., Kumada, M. *J. Organomet. Chem.* **1971**, *27*, C31. (c) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263. (d) Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1972**, *35*, 297. (e) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 931. (f) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *Chem. Lett.* **1975**, 887. (g) Sakurai, H.; Imai, T. *Chem. Lett.* **1975**, 891. (h) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19. (i) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* **1977**, *131*, 147. (j) Tamao, K.; Okazaki, S.; Kumada, M. *J. Organomet. Chem.* **1978**, *146*, 87. (k) Matsumoto, H.; Nagashima, S.; Kato, T.; Nagai, Y. *Angew. Chem.* **1978**, *90*, 288. (l) Matsumoto, H.; Yako, T.; Nagashima, S.; Motegi, T.; Nagai, Y. *J. Organomet. Chem.* **1978**, *148*, 97. (m) Matsumoto, H.; Motegi, T.; Hasegawa, M.; Nagai, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1913. (n) Watanabe, H.; Kobayashi, M.; Higuchi, K.; Nagai, Y. *J. Organomet. Chem.* **1980**, *186*, 51. (o) Matsumoto, H.; Matsubara, I.; Kato, T.; Shono, K.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1980**, *199*, 43. (p) Matsumoto, H.; Shono, K.; Wada, A.; Matsubara, I.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1980**, *199*, 185. (q) Watanabe, H.; Saito, M.; Sutou, N.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1981**, 617. (r) Watanabe, H.; Kobayashi, M.; Saito, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *215*, 149. (s) Watanabe, H.; Saito, M.; Sutou, N.; Kishimoto, K.; Inose, J.; Nagai, Y. *J. Organomet. Chem.* **1982**, *225*, 343.

(3) Atwell, W. H.; Weyenberg, D. R.; Gilman, H. *J. Org. Chem.* **1967**, *32*, 885.

(4) Seyferth, D.; Annarelli, D.; Vick, S. C. *J. Organomet. Chem.*, **1984**, *272*, 123.

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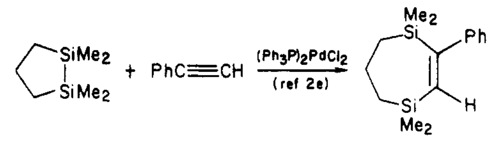
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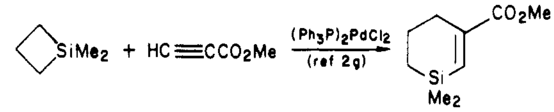
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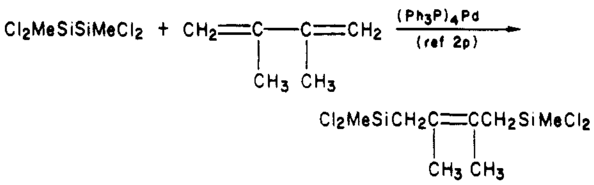
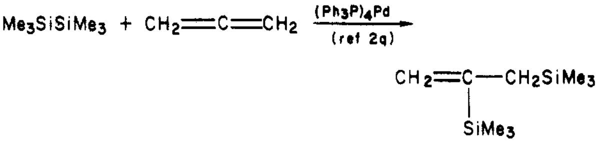
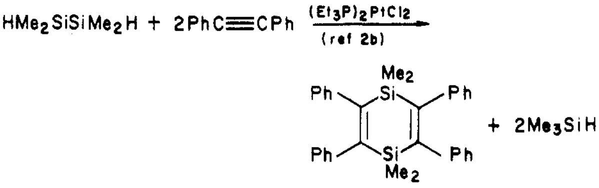
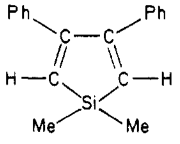

$Cl_2MeSiSiMeCl_2 + CH_2{=}C(CH_3){-}C(CH_3){=}CH_2 \xrightarrow[\text{(ref 2p)}]{(Ph_3P)_4Pd} Cl_2MeSiCH_2C(CH_3){=}C(CH_3)CH_2SiMeCl_2$ (4)

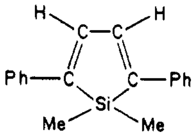

$Me_3SiSiMe_3 + CH_2{=}C{=}CH_2 \xrightarrow[\text{(ref 2q)}]{(Ph_3P)_4Pd} CH_2{=}C(SiMe_3){-}CH_2SiMe_3$ (5)


(6)

silyl)silirene with phenylacetylene mentioned in the Introduction, we investigated first the interaction of this silirene with phenylacetylene in the presence of a catalytic amount of bis(triphenylphosphine)palladium dichloride, $(Ph_3P)_2PdCl_2$. An immediate exothermic reaction occurred upon addition of silirene **1** to a benzene solution of the acetylene and the catalyst. After 1 h, GLC analysis showed that two products had been formed: $Me_3SiC{\equiv}CSiMe_3$ in 76% yield and a silacyclopentadiene, **6**, in 80% yield,


6

rather than the **2** formed in the thermal reaction. The NMR spectrum of this product revealed the presence of the phenyl, vinyl, and methyl protons in 5:1:3 ratio. The singlet attributable to the vinyl protons at δ 6.10 clearly showed that **6** was the product, not the other likely structural isomer **7**, the vinyl proton signal of which is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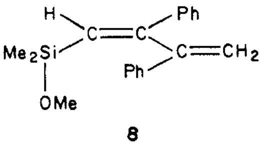
obscured by the phenyl resonance.[3] Further confirmation that the structure of the product was **6** was given by the methanolysis of the reaction mixture that produced **8**.


8

The production of **6** is extremely efficient in terms of the utilization of phenylacetylene. A reaction of equimolar quantities of silirene **1** and phenylacetylene and a catalytic amount of $(Ph_3P)_2PdCl_2$ gave a 58% yield of $Me_3SiC{\equiv}CSiMe_3$ and an 82% yield (based on $PhC{\equiv}CH$) of **6**, thus accounting for 82% of the $PhC{\equiv}CH$ and 41% of the Me_2Si moiety of **6**. After addition of methanol to the reaction mixture (exothermic reaction), a 28% yield of the methanolysis product of the silirene, **9**,[4] was obtained, as well as **8** in 80% yield, based on $PhC{\equiv}CH$.

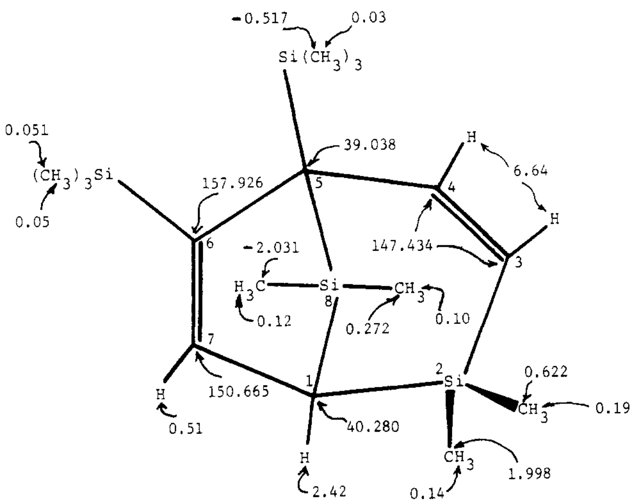
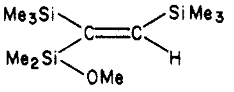
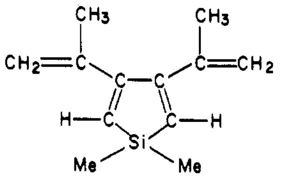


Figure 1. ^{13}C and ^1H NMR data for 2,2,8,8-tetramethyl-5,6-bis(trimethylsilyl)-2,8-disilabicyclo[3.2.1]octa-3,6-diene, **15** (NMR shifts in parts per million (δ) from $Si(CH_3)_4$ (δ 0.00).


9

A similar $(Ph_3P)_2PdCl_2$-catalyzed reaction between silirene **1** and isopropenylacetylene was not exothermic but gave **10**, the analogue of **6**, in 42% yield. Also obtained in 10% yield was the acyclic product **11**.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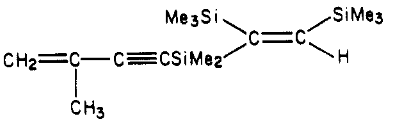
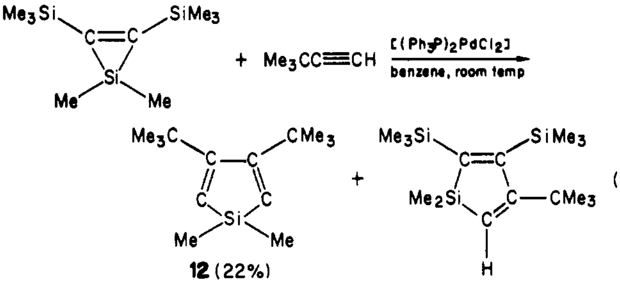

11

tert-Butylacetylene also reacted with silirene **1** in the presence of $(Ph_3P)_2PdCl_2$, giving two products in moderate yield (eq 7). Neither silacyclopentadiene was formed when a solution of silirene **1** and $Me_3CC{\equiv}CH$ was stirred at room temperature or at 75 °C for 18 h in the absence of a palladium catalyst. In contrast to the formation of **12** and **13** in the silirene **1**/$Me_3CC{\equiv}CH$ reaction, no major products were observed when similar $(Ph_3P)_2PdCl_2$-catalyzed reactions of silirene **1** were attempted with $Me_3SiC{\equiv}CH$ or 1-hexyne.

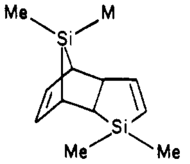
The reaction of acetylene itself with 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene in the presence of bis(triphenylphosphine)palladium dichloride was of particular interest in that the product was not the 1,1-dimethyl-1-silacyclopentadiene or its more likely Diels–Alder dimer **14**. The product, which was obtained in yields of up to



12 (22%)

13 (30%)

(7)



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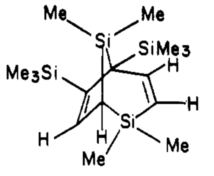
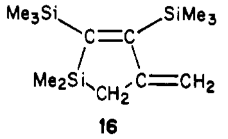


15

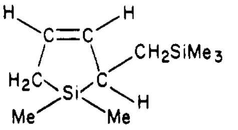
60% based on the silirene 1 charged, was identified (IR, ^1H and ^{13}C NMR, mass spectroscopy, and analysis) as **15**. The NMR spectral assignments are shown in Figure 1. Each ring Si–CH_3 appeared as a three-proton singlet. A one-proton doublet was observed at δ 2.42, somewhat upfield from the normal position for bridgehead C–*H* in bicyclic olefins[5] (δ 3.58 for norbornadiene). Since a one-proton doublet appeared in the vinyl region at δ 6.51, it can be assumed that these two protons are isolated from the vinyl protons in the 3- and 4-positions, which appeared as a singlet at δ 6.64. A proton-decoupled ^{13}C NMR spectrum of **15** showed six Si–CH_3 singlets, two singlets in the saturated carbon atom region (a singlet and a doublet upon gated decoupling), and three vinyl carbon singlets (a singlet and two doublets upon gated decoupling). The Si–CH_3 resonances were easily assigned as shown in Figure 1. The singlet at δ_C 39.038 was assigned to the bridgehead carbon atom at position 2 and that at δ_C 40.280 (a doublet upon gated decoupling) to the carbon in position 1. Of the vinyl carbon atom signals, the peaks at δ_C 150.665 and 157.926 (a doublet and singlet, respectively, upon gated decoupling) were assigned to the ring carbon atoms at positions 7 and 6, respectively. The position 3 and 4 carbon atom resonances appeared as one signal at δ_C 147.434 (doublet upon gated decoupling). The signal due to these two carbon atoms was slightly broadened, and, in the gated decoupled spectrum, each peak of the resulting doublet was seen to have a slight shoulder. The integrated area of the δ 147.434 signal was twice that of the δ 150.665 signal. Thus the assignment of structure **15** to the product of the Pd(II)-catalyzed reaction of silirene **1** with acetylene is reasonably certain.

Allene, which did not appear to react with silirene **1** thermally in the absence of a catalyst, inserted into the silacyclopropene ring of **1** in the presence of $(Ph_3P)_2PdCl_2$ to give a methylenesilacyclopentene, **16**, in 23% yield. In



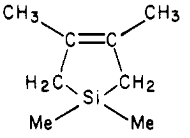
16

a Pd(II)-catalyzed reaction of silirene **1** with (*E*)-2,4-pentadienyltrimethylsilane at room temperature only the Me_2Si adduct **17** was obtained in 40% yield. None of the two-atom insertion product or of the acyclic product that

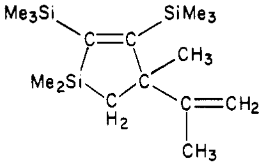


17

had been formed in the thermal, uncatalyzed reaction[1] appeared to have been formed. In contrast, 2,3-dimethyl-1,3-butadiene did not react with silirene **1** at room temperature in the presence of $(Ph_3P)_2PdCl_2$. However, when the reaction mixture was heated at 75 °C for 18 h, two products were obtained, the Me_2Si adduct **18** (21%) and the two-atom insertion product **19** (26%). The latter



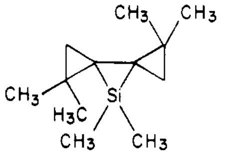
18



19

is produced in the thermal, uncatalyzed reaction, along with an isomeric acyclic compound,[1] but **18** is not produced in the thermal reaction. Thus the formation of the "1,4" Me_2Si adduct appears to be a characteristic of the palladium-catalyzed reactions of 1,3-dienes with silirene **1**.

The possible mechanism of the palladium catalysis of these reactions of 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene is of interest. The first point one must consider is the oxidation state of the active catalyst. It appears to be a characteristic chemical property of silicon-containing strained ring compounds to be able to reduce a Pd(II) compound to a Pd(0) species. Thus silirene **20** had been



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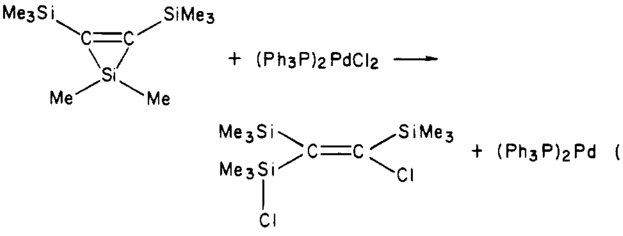
found to reduce $(PhCN)_2PdCl_2$ to metallic palladium.[6] Also, it has been shown recently that octamethyl-1,2-disilacyclobutane will reduce $(Ph_3P)_2PdCl_2$ to form $ClMe_2SiCMe_2CMe_2SiMe_2Cl$ and $(Ph_3P)_2Pd^0$, which then inserts into the Si–Si bond of the disilacyclobutane.[7] In view of such observed chemistry, we assume that the active catalyst in the $(Ph_3P)_2PdCl_2$/silirene reactions is $(Ph_3P)_2Pd^0$, formed as shown in eq 8. This low-valent,



(8)

reactive, coordinatively unsaturated species, we suggest, then inserts into the silacyclopropene ring to give **21**. There is more than one possibility for pathways from **21** to the observed product. One of these involves the collapse of **21** to form $Me_3SiC{\equiv}CSiMe_3$ and a palladium–silylene

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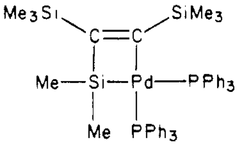
[5] Silverstein, R. M.; Bassler, G. C.; Merrill, T. C. "Spectrometric Identification of Organic Compounds", 3rd ed.; Wiley: New York, 1974.

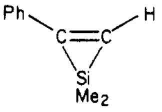
[6] Haas, C. K. Ph.D. Thesis, Massachusetts Institute of Technology, 1974, p 219.

[7] Seyferth, D.; Goldman, E. W.; Escudie, J. *J. Organomet. Chem.* **1984**, *271*, 337.



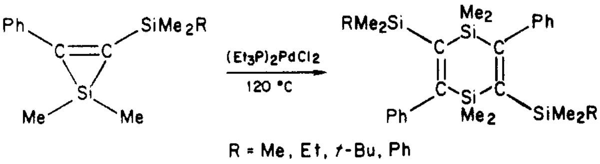
21

complex, $(Ph_3P)_2Pd{-}SiMe_2$. Reaction of the latter with PhC≡CH then would give a new silacyclopropene, **22**, whose further reaction with PhC≡CH would produce **6**. On the other hand, it might be **21** that reacts with the acetylene, forming **6** in several steps as shown in Scheme I. The intervention of an intermediate such as **23** could serve to explain the formation of **15** in the reaction of acetylene with silirene **1** in the presence of $(Ph_3P)_2PdCl_2$. However, attempts to isolate Pd-containing intermediates in stoichiometric reactions were not successful, so the chemistry in Scheme I is only a suggestion, as is the alternate proposal of an intermediate palladium–silylene complex. It might be expected that in the case of more kinetically stable silacyclopropenes the transition-metal intermediates are capable of isolation.

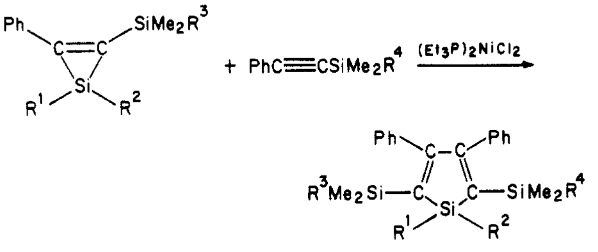


22

Ishikawa et al.[8] have examined the $(Et_3P)_2PdCl_2$-catalyzed decomposition of various silacyclopropenes (eq 9), but no mechanism was suggested for this formal silacyclopropene dimerization. On the other hand, for the $(Et_3P)_2NiCl_2$-catalyzed reactions of the same silacyclopropenes with acetylenes (eq 10), the same authors[9] suggested a mechanism involving intermediate **24**. However, no experimental support for such an intermediate was obtained.



(9)



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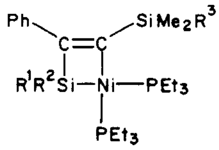

24

A more systematic investigation of this interesting silacyclopropene chemistry would be of interest, but this is beyond the scope of our present interests.

Experimental Section

General Comments. The general comments of parts 1[4] and 2[1] are applicable. Note, in particular, the absolute necessity of excluding atmospheric oxygen and moisture during all operations involving the synthesis, handling, and reactions of silacyclopropene and the need to use rigorously dried glassware and scrupulously dry and degassed solvents.

1,1-Dimethyl-2,3-bis(trimethylsilyl)silirene was prepared as described in part 1.[4]

Reaction of Silirene 1 with Phenylacetylene in the Presence of $(Ph_3P)_2PdCl_2$. A flame-dried 25-mL one-necked round-bottomed flask equipped with a magnetic stir bar, a no-air rubber septum, and a syringe needle for maintaining an argon atmosphere was charged with 0.75 mL (7.0 mmol) of phenylacetylene, 0.005 g (1 mol %, based on the silirene) of $(Ph_3P)_2PdCl_2$, and 3.0 mol of dry benzene, and then 0.127 g (0.56 mmol) of silirene 1 was added by syringe. An immediate exothermic reaction was observed. After 1 h, GLC analysis showed the presence of two products: bis(trimethylsilyl)acetylene, identified by comparison of its IR and ^1H NMR spectra with those of authentic material, in 76% yield, and 1,1-dimethyl-3,4-diphenyl-1-silacyclopenta-2,4-diene, **6**, in 80% yield. A sample of the latter was collected by GLC as a solid: mp 98–99 °C; NMR (CCl_4/CH_2Cl_2) δ 0.37 (s, 6 H, Me_2Si), 6.1 (s, 2 H, =CH), 6.72 (br s, 10 H, Ph). Anal. Calcd for $C_{18}H_{18}Si$: C, 82.38; H, 6.91. Found: C, 81.85; H, 7.12.

In another experiment 1.6 mmol of silirene 1 was added to 160 mmol of phenylacetylene and 1 mol % of $(Ph_3P)_2PdCl_2$ in 3 mL of benzene. After the reaction was completed, GLC standards (decane, dodecane, hexadecane) were added, and the product yields were determined by GLC: $Me_3SiC{\equiv}CSiMe_3$ (58%) and **6** (82%). Subsequently, an excess (400 μL) of methanol was added to the reaction mixture to give a mildly exothermic reaction. After 18 h at room temperature, examination of the mixture by GLC revealed the presence of two new products: methoxysilane **9**,[1] in 28% yield, identified by its IR and NMR spectra, and the diene **8** in 80% yield (based on **6**). A sample of the latter, $n^{25}{}_D$ 1.5470, was collected by GLC: NMR (CCl_4/CH_2Cl_2) δ 0.15 (s, 6 H, Me_2Si), 3.35 (s, 3 H, OMe), 5.29 (d, J = 2 Hz, 1 H, =CH), 5.77 (d, J = 2 Hz, 1 H, =CH), 6.19 (s, 1 H, SiC(H)=), 6.90–7.47 (m, 10 H, Ph). Anal. Calcd for $C_{19}H_{22}OSi$: C, 77.49; H, 7.53. Found: C, 77.04; H, 7.65.

Reaction of Silirene 1 with Isopropenylacetylene in the Presence of $(Ph_3P)_2PdCl_2$. Using the procedure described above, a solution of 1.9 mL (19.6 mmol) of isopropenylacetylene (Farchan) and 0.01 g of $(Ph_3P)_2PdCl_2$ in 5 mL of benzene was prepared and 2.1 mmol of silirene 1 was added. An exotherm was not observed. After the reaction mixture had been stirred at room temperature for 14 h, GLC showed the presence of one major and one minor product (in addition to bis(trimethylsilyl)acetylene): **1,1-Dimethyl-3,4-diisopropenyl-1-silacyclopenta-2,4-diene, 10**, $n^{25}{}_D$ 1.5334, in 42% yield: NMR ($CCl_4/CHCl_3$) δ 0.27 (s, 6 H, Me_2Si), 1.89 (s, 6 H, CCH_3), 4.87 (br s, 2 H, =C*H*H), 5.02 (br s, 2 H, =CH*H*), 5.89 (s, 2 H, =CH). Anal. Calcd for $C_{12}H_{18}Si$: C, 75.71; H, 9.53. Found: C, 75.64; H, 9.55. **Compound 11**, 10% yield, whose ^1H NMR and IR spectra were identical with those of this compound as obtained in the uncatalyzed reaction of silirene 1 with isopropenylacetylene.[1]

Reaction of Silirene 1 with *tert*-Butylacetylene in the Presence of $(Ph_3P)_2PdCl_2$. No exotherm was observed when 2.3 mmol of silirene 1 was added to a solution of 1 mL (8.2 mmol) of *tert*-butylacetylene and 0.01 g of $(Ph_3P)_2PdCl_2$ in 5 mL of benzene. After the reaction mixture had been stirred for 18 h at room temperature, GLC showed the presence of two products (in addition to bis(trimethylsilyl)acetylene): **1,1-Dimethyl-3,4-di-*tert*-butyl-1-silacyclopenta-2,4-diene, 12**, $n^{25}{}_D$ 1.4822, in 22% yield: NMR (CCl_4/CH_2Cl_2) δ 0.07 (s, 6 H, Me_2Si), 1.29 (s, 18 H, Me_3C), 5.92 (s, 2 H, =CH). Anal. Calcd for $C_{14}H_{26}Si$: C, 75.59; H, 11.78. Found: C, 75.19; H, 11.72. **2,3-Bis(trimethylsilyl)-4-*tert*-butyl-1-silacyclopenta-2,4-diene, 13**, mp 42.0–42.5 °C, in 30% yield: NMR (CCl_4/CH_2Cl_2) δ 0.24 (s, 6 H, Me_2Si), 0.27 (s, 9 H, Me_3Si), 0.37 (s, 9 H, Me_3Si), 1.22 (s, 9 H, Me_3C), 5.77 (s, 1 H, =CH). Anal. Calcd for $C_{16}H_{34}Si_3$: C, 61.84; H, 11.03. Found: C, 61.96; H, 10.91.

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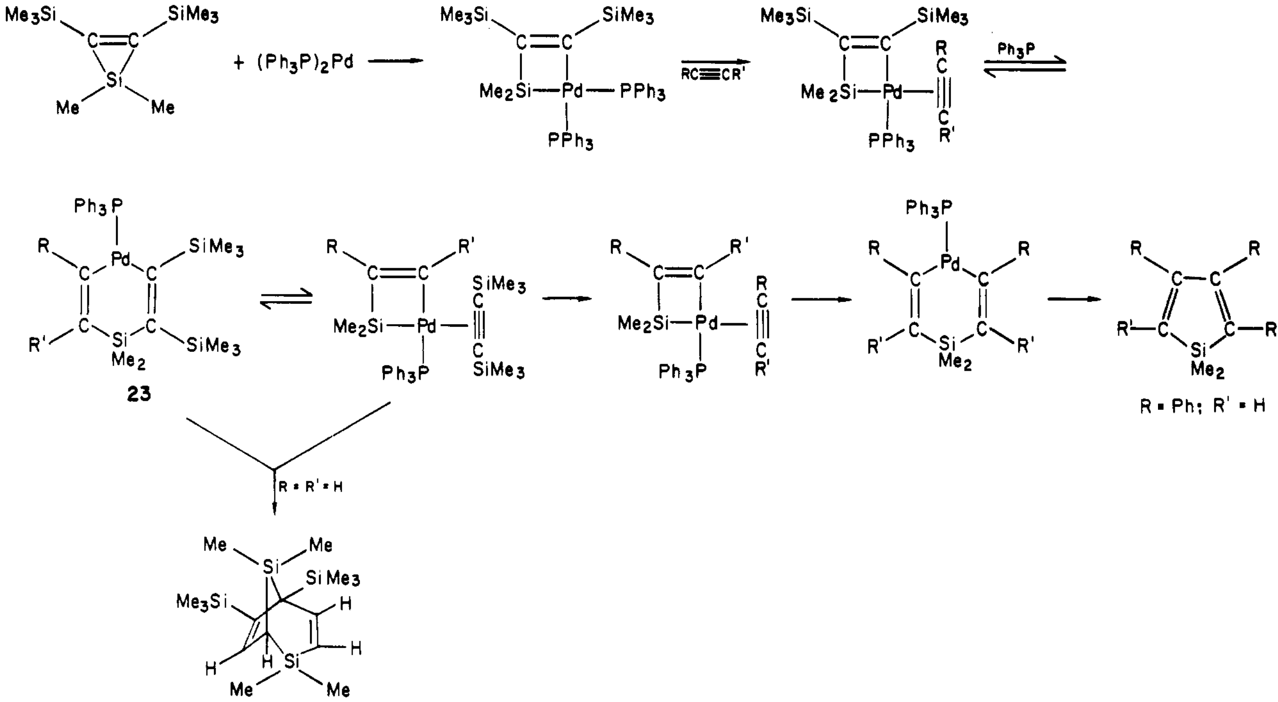
Scheme I



Reaction of Silirene 1 with Acetylene in the Presence of $(Ph_3P)_2PdCl_2$. The usual reaction flask was charged with 0.5 g of $(Ph_3P)_2PdCl_2$ and 5.0 mL of dry toluene, and this solution was cooled to −78 °C. Gaseous acetylene (purified by passage through concentrated H_2SO_4 and soda lime towers) was introduced to saturation through a needle extending into the solution, and then 0.8134 g (3.56 mmol) of silirene 1 was added by syringe while a slow acetylene flow was continued. After 4 h, the acetylene flow was stopped and the solution was stirred for another 10 min at −78 °C. Subsequently, the reaction mixture was allowed to warm to room temperature while being stirred overnight. While being warmed, the solution turned a clear red color.

Trap-to-trap distillation (room temperature, 0.01 mmHg) into a receiver at −78 °C gave a distillate containing (by GLC) toluene and bis(trimethylsilyl)acetylene. Diethyl ether was added to the orange distillation residue, and the resulting dark yellow suspension was filtered through a pad of silicic acid to give a clear, colorless filtrate. Examination of the latter by GLC (10% SE30, 90–200 °C program) showed the presence of one major product, 2,2,8,8-tetramethyl-5,6-bis(trimethylsilyl)-2,8-disilabicyclo[3.2.1]octa-3,6-diene, **15**, $n^{25}{}_D$ 1.4931, in 60% yield (0.362 g, 1.08 mmol): mass spectrum (70 eV), *m/z* (relative intensity) 339 (M^+ + 1, 0.66), 338 (M^+, 1.67), 265 ($M^+ - Me_3Si$, 4.18), 250 (8.48), 235 (8.83), 191 (4.50), 177 (11.54), 162 (3.33), 141 (3.24), 129 (1.54), 125 (2.54), 99 (2.13), 83 (8.95), 73 (Me_3Si^+, 100), 58 (Me_2Si^+, 2.73); ^1H NMR (CCl_4/CH_2Cl_2) δ 0.03 (s, 9 H, Me_3Si), 0.05 (s, 9 H, Me_3Si), 0.10 (s, 3 H, bridge $SiCH_3$), 0.12 (s, 3 H, bridge $SiCH_3$), 0.14 (s, 3 H, ring $SiCH_3$), 0.19 (s, 3 H, ring $SiCH_3$), 2.42 (d, J = 1 Hz, bridgehead CH), 6.51 (d, J = 1 Hz, 1 H, =CH), 6.64 (s, 2 H, =CH). ^{13}C NMR (C_6D_6, proton coupled) δ_C −2.0310, −0.5168, 0.0508, 0.2719, 0.6217, 1.9983 (individual coupling not discernible due to overlap of signals; all Si–CH_3), 39.0383 (s, quaternary bridgehead carbon), 140.2804 (d, tertiary bridgehead carbon), 147.4336 (d, seen as two overlapping doublets in the gated decoupled spectrum, vinyl carbon atoms), 156.6652 (d, vinyl carbon), 157.9263 (s, vinyl carbon). (For assignments see Results and Discussion.) Anal. Calcd for $C_{16}H_{34}Si_4$: C, 56.71; H, 10.11. Found: C, 56.77; H, 10.21.

Reaction of Silirene 1 with Allene in the Presence of $(Ph_3P)_2PdCl_2$. A solution of 1.80 mmol of silirene 1 and 0.01 g of $(Ph_3P)_2PdCl_2$ in 5.0 mL of toluene was cooled to −78 °C, and gaseous allene (Matheson, ca. 2 mL of the condensed liquid) was condensed into the reaction flask. The reaction mixture was stirred at −78 °C for 4 h. The solution then was allowed to warm slowly to about −34 °C, at which temperature the excess allene boiled off. The solution that remained was stirred and allowed to warm slowly to room temperature.

Trap-to-trap distillation (room temperature, 0.05 mmHg) into a cold receiver gave a colorless distillate. GLC examination (10% SE-30, 140 °C) of the latter showed the presence of a single product, 1,1-dimethyl-2,3-bis(trimethylsilyl)-5-methylene-1-silacyclopent-2-ene, **16**, $n^{25}{}_D$ 1.4931, in 23% yield: NMR ($CCl_4/CHCl_3$) δ 0.15, 0.18 (2s, 24 H, all $SiCH_3$), 3.34 (t, J = 2 Hz, 2 H, ring CH_2), 5.40 (m, J = 2 Hz, =C*H*H), 5.67 (m, J = 2 Hz, =CH*H*). Anal. Calcd for $C_{13}H_{28}Si_3$: C, 58.12; H, 10.50. Found: C, 58.20; H, 10.55.

Reaction of Silirene 1 with (*E*)-2,4-Pentadienyltrimethylsilane in the Presence of $(Ph_3P)_2PdCl_2$. A solution of 1.77 mmol of silirene 1, 0.887 g (6.33 mmol) of the diene,[10] and 0.01 g of $(Ph_3P)_2PdCl_2$ in 5.0 mL of benzene was stirred at room temperature for 18 h. Subsequent trap-to-trap distillation (room temperature, 0.07 mmHg) gave a clear yellow distillate. GLC examination (10% SE-30, 140 °C) showed the presence of a single product, 1,1-dimethyl-2-((trimethylsilyl)methyl)-1-silacyclopent-3-ene, **17**, $n^{25}{}_D$ 1.4611, in 40% yield: NMR ($CCl_4/CHCl_3$) δ 0.05 (s, 9 H, Me_3Si), 0.10 (s, 3 H, ring $SiCH_3$), 0.19 (s, 3 H, ring $SiCH_3$), 0.58 (dd, 2 H, J = 7 Hz, J = 4 Hz, 2 H, Me_3SiCH_2), 1.27 (br s, 2 H, ring CH_2), 1.38–1.85 (m, 1 H, methine CH), 5.68 (br, 2 H, HC=CH). Anal. Calcd for $C_{10}H_{22}Si_2$: C, 60.51; H, 11.17. Found: C, 60.59; H, 11.20.

Reaction of Silirene 1 with 2,3-Dimethyl-1,3-butadiene in the Presence of $(Ph_3P)_2PdCl_2$. A solution of 3.2 mmol of silirene 1, 1.5 mL (13.3 mmol) of the diene, and 0.01 g of $(Ph_3P)_2PdCl_2$ in 4 mL of benzene was stirred at room temperature for 24 h. Subsequent GLC analysis showed that no new products had been formed and so the reaction mixture was stirred and heated at 75 °C for 18 h. GLC analysis showed the presence of two products: 1,1,3,4-tetramethyl-1-silacyclopent-3-ene, **18** (21% yield), and 2,3-bis(trimethylsilyl)-4-methyl-4-isopropenyl-1-silacyclopent-2-ene, **19** (26% yield). Identification of **18** and **19** was effected by comparison of their IR and NMR spectra with those of authentic samples.[1]

Acknowledgment. We are grateful to the U.S. Air Force Office of Scientific Research (NC)-AFSC for generous support of this research. D.S. acknowledges, with thanks, an Alexander von Humboldt Prize, awarded by the Alexander von Humboldt Foundation, Bad Godesberg,

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during the tenure of which this paper was written.

Registry No. **1**, 61059-04-9; **6**, 55227-55-9; **8**, 92671-61-9; **9**, 60890-82-6; **10**, 64588-24-5; **11**, 92014-16-9; **12**, 64588-25-6; **13**, 64588-26-7; **15**, 92671-62-0; **16**, 92671-63-1; **17**, 88296-48-4; **18**, 16109-39-0; **19**, 64588-17-6; $Me_3SiC{\equiv}CSiMe_3$, 14630-40-1; $(Ph_3P)_2PdCl_2$, 13965-03-2; phenylacetylene, 536-74-3; isopropenylacetylene, 78-80-8; *tert*-butylacetylene, 917-92-0; acetylene, 74-86-2; allene, 463-49-0; (*E*)-2,4-pentadienyltrimethylsilane, 72952-73-9; 2,3-dimethyl-1,3-butadiene, 513-81-5.

Anions of the Type $(RMOH_2)_3W_{18}P_2O_{68}{}^{9-}$ and $[H_2OCo]_3W_{18}P_2O_{68}{}^{12-}$. A Reinvestigation of "B,β-$W_9PO_{34}{}^{9-}$"†,‡

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Received July 3, 1984

$Na_8HW_9PO_{34}$ reacts with $RMCl_3$ (RM = PhSn, $CpFe(CO)_2Sn$, CpTi) to form the corresponding $(RMOH_2)_3W_{18}P_2O_{68}{}^{9-}$ anions and with cobalt(II) to form $(H_2OCo)_3W_{18}P_2O_{68}{}^{12-}$. Thermolysis of $Na_8HW_9PO_{34}$ at 140–150 °C causes a solid-state isomerization; reactions of the resulting isomer with $RMCl_3$ and with cobalt(II) follow a different course than those involving unthermolyzed $Na_8HW_9PO_{34}$. The ^{31}P chemical shift anisotropy establishes that unthermolyzed $Na_8HW_4PO_{34}$ has an A-type structure and that thermolysis produces a B-type isomer.

Introduction

The preparations of the monosubstituted Keggin anions $RMW_{11}PO_{39}{}^{4-}$ (RM = PhSn, $CpFe(CO)_2Sn$, CpTi) and the disubstituted Keggin anions $(RM)_2W_{10}PO_{38}{}^{5-}$ (RM = PhSn, $CpFe(CO)_2Sn$) have been reported previously.[1-5] Continuing with this theme, we have attempted to prepare Keggin anions that are trisubstituted with organometallic groups by starting with the reported[6] trivacant lacunary anion $W_9PO_{34}{}^{9-}$. The preparations of two distinctly different classes of trisubstituted Keggin anions from $W_9PO_{34}{}^{9-}$ have already been described. Trisubstituted anions with a normal Keggin structure have been prepared from W_9P and early transition metals by Massart ($Mo_3W_9PO_{40}{}^{3-}$)[6] and by Domaille ($V_3W_9PO_{40}{}^{6-}$),[7] while Finke[8] and Tourne[9] have reported that $W_9PO_{34}{}^{9-}$ reacts with divalent group 8 metals and with zinc(II) to form species that have structures[10] based on two fused trisubstituted Keggin anions, such as $(H_2O)_2Co_4W_{18}P_2O_{68}{}^{10-}$.

Results and Discussion

$(RMOH_2)_3W_{18}P_2O_{68}{}^{9-}$ Anions. Reactions of $Na_8HW_9PO_{34}$, prepared as described in the literature[6] and *vacuum dried at room temperature*, with $RMCl_3$ (RM = PhSn, $CpFe(CO)_2Sn$, CpTi) do not give substituted Keggin anions. Instead, a series of anions with a general formula $(RMOH_2)_3W_{18}P_2O_{68}{}^{9-}$ is formed. The infrared spectra (Figure 1) of potassium salts of these anions are similar in the 1200–600 cm^{-1} region, suggesting that they are grossly isostructural. The ^{31}P NMR spectra in water contain one major line. Although $^2J_{Sn-P}$ coupling satellites are easily seen in the ^{31}P NMR spectra of $PhSnW_{11}PO_{39}{}^{4-}$ and $(PhSn)_2W_{10}PO_{38}{}^{5-}$,[2] no such coupling is observed in the spectrum of $(PhSnOH_2)_3W_{18}P_2O_{68}{}^{9-}$. The ^{183}W NMR spectra of $(PhSnOH_2)_3W_{18}P_2O_{68}{}^{9-}$ (lithium salt in water) and the corresponding $CpFe(CO)_2Sn$ derivative (tetrahexylammonium salt in slightly aqueous acetone) have been measured and consist of two lines in a 1:2 ratio. Both lines (−138.6, −190.0 ppm) in the spectrum of the phenyltin derivative exhibit tungsten–tungsten coupling satellites of 16 Hz, implying that the two sets of tungsten-centered octahedra are corner coupled, as in an A-type W_9P structure.[11,12] The more intense ^{183}W line (−190.0 ppm) has additional satellites (J = 40 Hz) assigned to overlapped $^2J_{^{117}Sn-W}$ and $^2J_{^{119}Sn-W}$ coupling. Line widths in the ^{183}W NMR spectrum of the $CpFe(CO)_2Sn$ derivative are too great to observe similar couplings.

All of our data are consistent with a structure in which two A-type W_9P units are connected through a belt of three RM units as in Figure 2. We have no evidence as to whether the W_9P units are α, as shown in Figure 2, or β. Weakley has determined[13] the structure of $W_{21}P_2O_{73}H_6{}^{4-}$, which is a useful precedent for our proposed structure for two reasons. First, it contains two A,α-W_9P units connected through a belt of three tungsten-centered polyhedra; secondly, two of the tungsten atoms in the belt are connected to terminal oxygen atoms that are *inside* the cavity and that may be protonated. This strongly suggests

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† This paper is dedicated to the memory of Earl Muetterties in recognition of his many contributions to inorganic and organometallic chemistry.

‡ Contribution No. 3522.

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