In conclusion, neutral rhodocene and some derivatives can be obtained as stable gas-phase species (with lifetimes ~10^{-6} s) by neutralization–reionization mass spectrometry. Various cyclopentadienyl complexes of rhodium can be used for generation of these species and other rhodocene derivatives in the gas phase. In addition to the compounds studied in this work, some other rhodium complexes, (e.g. $(RC_5H_4)_2RhL_n$[24] and (cyclopentadienyl)(cyclopentadiene)rhodium derivatives[3a,c,25]), which decompose easily to $(RC_5H_4)_2Rh^+$ ions, are good sources for gas-phase substituted-rhodocenium ions. It is quite possible that rhodocenium salts,[25a] like cobaltocenium[26] derivatives, will prove to be convenient sources for the corresponding gas-phase cations and their neutral counterparts.

OM920090J

---

(24) (a) Dickson, R. S.; Falton, G. D.; Nesbit, R. J.; Pateras, H. *Organometallics* 1987, *6*, 2517. (b) Bixler, J. W.; Walton, J. K.; Williams, M. L.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* 1981, *212*, C35. (c) Mills, O. S.; Nice, J. P. *J. Organomet. Chem.* 1967, *10*, 331. (d) Herrmann, W. A.; Krüger, C.; Goddard, R.; Bernal, I. *Angew. Chem., Int. Ed. Engl.* 1977, *16*, 334. (e) Herrmann, W. A.; Krüger, C.; Goddard, R.; Bernal, I. *J. Organomet. Chem.* 1977, *140*, 73.

(25) (a) Cloke, F. G. N.; Day, J. P.; Greenway, A. M.; Seddon, K. P.; Shirman, A. A.; Swain, A. C. *J. Organomet. Chem.* 1989, *372*, 231. (b) Müller, J.; Stühler, H.-O.; Goll, W. *Chem. Ber.* 1975, *108*, 1074. (c) Müller, J. *Angew. Chem., Int. Ed. Engl.* 1972, *11*, 623.

(26) Zagorevskii, D. V.; Nekrasov, Yu. S.; Malkov, A. V.; Leonova, E. V. *J. Organomet. Chem.* 1985, *284*, 109.

Selective Formation of *cis*-$(HMe_2Si)_2Pt(PEt_3)_2$ from $HMe_2SiSiMe_2H$ and $Pt(PEt_3)_3$ and Its Reactivities Relevant to Generation of (Silylene)platinum Species Thereof

Hiroshi Yamashita, Masato Tanaka,* and Midori Goto

National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305, Japan

Received May 1, 1992

$HMe_2SiSiMe_2H$ (**1**, 3 equiv) reacted with $Pt(PEt_3)_3$ at room temperature to give *cis*-$(HMe_2Si)_2Pt(PEt_3)_2$ (**2**) and oligosilanes $H(SiMe_2)_nH$ ($1 \le n \le 7$), while **2** was selectively obtained by the reaction of **1** (1 equiv) with $Pt(PEt_3)_3$ at −30 °C. $HMe_2SiSiMe_3$ or $H_2MeSiSiMe_3$ also afforded oligomeric redistribution products when treated with $Pt(PEt_3)_3$ at room temperature, although Si–Pi species were not found. Redistribution of **1** was efficiently catalyzed by **2** at room temperature, leading to $H(SiMe_2)_nH$ with the approximate molar ratio being ≥30:10:30:5:2:1:0.3 for n = 1–7, respectively. Me_2SiH_2 was mainly formed upon thermolysis of **2** at 60 °C. Reaction of **2** with phenylacetylene (3 equiv) at 60 °C gave 4,4-dimethyl-2,6-diphenyl-1-platina-4-sila-2,5-cyclohexadiene (**4**), the structure of which was determined by X-ray crystallographic analysis: space group $P2_1/n$, a = 12.319 (1) Å, b = 20.164 (1) Å, c = 12.837 (2) Å, β = 97.03 (1)°, V = 3164.8 (7) Å^3, Z = 4. Heating **4** at 120 °C afforded 1,1-dimethyl-3,4-diphenyl-1-sila-2,4-cyclopentadiene as the sole volatile product.

Introduction

Addition of a Si–H or Si–Si bond to organic unsaturated compounds is a versatile reaction which allows us to transform various organosilanes including polymers.[1,2] Group 10 metal-catalyzed reactions of hydrodisilanes that have both Si–H and Si–Si bonds are particularly interesting since they can lead to unique products such as oligosilanes,[3a] 1,4-disila-2,5-cyclohexadiene,[3b] and 1-sila-2,4-cyclopentadiene,[3c,d] although mechanistic details have not been elucidated yet. West et al. recently reported that 1,2-dihydrosilanes reacted with (diphosphine)Pt(0) complexes to give (disilene)platinum species, and they proposed a pathway involving hydrido(disilanyl)platinum intermediates.[4] In striking contrast with this, we have found that $HMe_2SiSiMe_2H$ reacts with $Pt(PEt_3)_3$ to give a bis(hydrosilyl)platinum complex selectively.[5] Herein are reported the formation and reactivities of the bis(silyl) complex.

Results and Discussion

Reactions of $Pt(PEt_3)_3$ with Hydrodisilanes. When $HMe_2SiSiMe_2H$ (**1**, 3 equiv) was added to $Pt(PEt_3)_3$ in benzene-d_6 at room temperature, the color of the solution immediately turned from orange to pale yellow. ^1H NMR, GC, and GC–MS of the solution showed the formation of *cis*-$(HMe_2Si)_2Pt(PEt_3)_2$ (**2**, nearly quantitative yield) along with $H(SiMe_2)_nH$ ($1 \le n \le 7$).[3a,6] The approximate rel-

---

(1) For a recent review of hydrosilylation, see: Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, U.K., 1989; p 1479.

(2) For recent studies on double silylation, see: (a) Yamashita, H.; Catellani, M.; Tanaka, M. *Chem. Lett.* 1991, 241 and references cited therein. (b) Murakami, M.; Andersson, P. G.; Suginome, M.; Ito, Y. *J. Am. Chem. Soc.* 1991, *113*, 3987 and references cited therein.

(3) (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) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* 1975, *86*, C27.

(4) (a) Pham, E. K.; West, R. *J. Am. Chem. Soc.* 1989, *111*, 7667. (b) Pham, E. K.; West, R. *Organometallics* 1990, *9*, 1517.

(5) For our recent studies on the reactions of organosilanes with group 10 and/or 9 metal complexes, see: (a) Yamashita, H.; Kobayashi, T.-a.; Hayashi, T.; Tanaka, M. *Chem. Lett.* 1990, 1447. (b) Yamashita, H.; Kawamoto, A. M.; Tanaka, M.; Goto, M. *Chem. Lett.* 1990, 2107 and references cited therein.

(6) Heating a mixture of **1** (0.178 mmol) and *trans*-$PtCl_2(PEt_3)_2$ (1 mol %) at 90 °C for 30 min in a sealed tube provided oligosilanes which were assigned by GC and GC–MS to be $H_2Me_{2n}Si_n$ ($1 \le n \le 9$). Their approximate amounts were estimated by GC at 5, 4, 3, 4, 5, 2, 0.3, and ≤0.1 × 0.00178 mmol for n = 2–9, respectively (the amount of Me_2SiH_2 was not determined). Except for the case of the tetrasilane, one major GC peak, probably arising from $H(SiMe_2)_nH$,[3a] was observed for each oligosilane. However, the tetrasilane seemed to be a mixture of two structural isomers (3:7) as described for the reaction of $Pt(PEt_3)_3$ with **1** in the Experimental Section.

ative molar ratio of the oligomeric silanes was estimated at ≥15:14:12:3:0.4:0.1:≤0.1 for n = 1–7, respectively, the tetramer ($H_2Me_8Si_4$) of which was found by GC and GC–MS to consist of two isomers (3:7), although the structure of the second isomer has not been fully elucidated yet. On the other hand, ^{1}H NMR signals ascribable to the Pt–$SiMe_2H$ moiety of **2** were observed at 0.78 (d, $^3J_{HH} \approx 4$ Hz, $^3J_{HPt} \approx 28$ Hz, Si–CH_3) and 4.51 (sept t, $^3J_{HH} \approx 4$ Hz, $^3J_{HP} \approx 19$ Hz, $^2J_{HPt} \approx 40$ Hz, Si–H) ppm, and no signal arising from Pt–H species was found in the range −30.0 to 0.0 ppm. The ^{31}P NMR signal had cleanly shifted from 21.9 ($^1J_{PPt}$ = 4216 Hz) ppm for $Pt(PEt_3)_3$ to 18.5 ppm with a rather small coupling constant of $^1J_{PPt}$ (1621 Hz), which is consistent with the cis configuration of **2**.[7] In a separate reaction of $Pt(PEt_3)_3$ with **1** (1.05 equiv) in pentane at −30 °C, complex **2** was isolated as pale yellow plates in 90% yield (eq 1). **2** was thermally unstable and gradually decomposed in benzene-d_6 or toluene-d_8 solution even at room temperature. A very recent publication by Tilley et al. also suggested the formation of a similar complex $(H_2PhSi)_2Pt(PEt_3)_2$ from $Pt(PEt_3)_3$ and $H_2PhSiSiPhH_2$.[8]

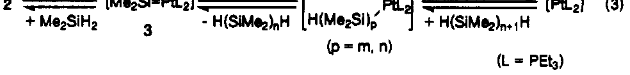
$$\underset{}{Pt(PEt_3)_3} + \underset{\mathbf{1}}{HMe_2SiSiMe_2H} \xrightarrow[-30\ ^\circ C]{pentane} \underset{\mathbf{2}}{cis\text{-}(HMe_2Si)_2Pt(PEt_3)_2} \qquad (1)$$

Even though the structure of **2** seemingly indicates that cleavage of the Si–Si bond has taken place, we believe, on the basis of MO calculations,[9] that kinetically favorable hydrido(disilanyl)platinum species are formed first and that these then somehow rearrange to the thermodynamically more stable bis(silyl) species. This reaction sequence was very recently demonstrated by Fink et al. for [1,2-bis(dicyclohexylphosphino)ethane]platinum–1,2-dihydrodisilane systems.[10] In addition, Ebsworth et al. have also reported the preferential addition of an Si–H bond in H_3SiSiH_3 to $IrCl(CO)(PEt_3)_2$.[11]

$HMe_2SiSiMe_3$[3a] also underwent redistribution at room temperature upon treatment with $Pt(PEt_3)_3$ to give oligosilanes. GC–MS suggested the formula $HMe_{2m+1}Si_m$ (1 ≤ m ≤ 7). Their approximate relative molar ratio was estimated by ^{1}H NMR and GC at ≥25:2:4:4 (three isomers, 1:5:4):3 (three isomers, 3:1:6):0.5 (two isomers, 1:9):≤0.1 (two isomers, 2:3) for m = 1–7, respectively. Similarly, $H_2MeSiSiMe_3$ gave redistribution products, which were assigned by GC–MS to be $HMe_{2p+1}Si_p$ (1 ≤ p ≤ 3), $H_2Me_{2q}Si_q$ (2 ≤ q ≤ 6), and $H_3Me_{2r-1}Si_r$ (3 ≤ r ≤ 7) with the approximate relative ratio being ≥12:≤0.1:1:14:0.2:5 (two isomers, 1:9):≤0.1:≤0.1:0.2≤0.1:0.2 (two isomers, 1:1):≤0.1:≤0.1 for p = 1–3, q = 2–6, and r = 3–7, respectively. The predominant formation of $H_2Me_8Si_4$ seems to suggest dehydrogenative coupling of two molecules of $H_2MeSiSiMe_3$ being also involved in its formation,[12] although its structure has not been fully confirmed as yet. In agreement with this, the GC–MS spectrum of $H_2Me_8Si_4$ (major isomer) obtained from $H_2MeSiSiMe_3$ was different from that of $H_2Me_8Si_4$ (major isomer) obtained from **1**. In the foregoing reactions of $HMe_2SiSiMe_3$ and $H_2MeSiSiMe_3$, possible platinum species such as bis(silyl)- and hydrido(disilanyl)platinum complexes could not be detected by ^{1}H NMR. The R_3Si–M bond lengths decrease in the order of R = Me_3Si > Me > H > F,[13] indicative of Si–M bonds being stronger in the reverse way. The lack of the observation of $(Me_3Si)(MeRHSi)Pt(PEt_3)_2$ (R = Me, H) seems to be associated with the weak Me_3Si–Pt bond in comparison with the HMe_2Si–Pt bond.

Redistribution of 1 Catalyzed by 2. Complex **2** (1 mol %) efficiently catalyzed the redistribution of **1** in toluene-d_8 as previously observed using *trans*-$PtCl_2(PEt_3)_2$ as catalyst.[3a,6,14] Monitoring by ^{1}H NMR and GC revealed that the reaction smoothly proceeded at room temperature to give an equilibrium mixture of oligosilanes $H(SiMe_2)_nH$ (1 ≤ n ≤ 7) in about 1 h, the relative molar ratio of each component being estimated at ≥30:10:30:5 (the total of the two isomers (1:4) for $H_2Me_8Si_4$):2:1:0.3 for n = 1–7, respectively (eq 2). The Me–Si proton signal of **2** was retained unchanged at 0.69 ppm (d, $^3J_{HH} \approx 4$ Hz, $^3J_{HPt} \approx 28$ Hz) throughout the reaction. In the catalytic cycle, a (silylene)platinum species (**3**),[3b,15] which is possibly generated in equilibrium with **2**, seems to interact with an α,ω-dihydrooligosilane to give a (silyl)(oligosilanyl)platinum species, and subsequent reductive elimination would form a higher homologue of the oligosilane (eq 3).

$$\mathbf{1} \xrightarrow[\substack{toluene\text{-}d_8 \\ r.\,t.}]{\mathbf{2}\ (1\ mol\%)} \underset{(n = 1\text{-}7)}{H(SiMe_2)_nH} \qquad (2)$$



$$\mathbf{2} \underset{+\,Me_2SiH_2}{\overset{-\,Me_2SiH_2}{\rightleftharpoons}} \underset{\mathbf{3}}{[Me_2Si{=}PtL_2]} \underset{-\,H(SiMe_2)_nH}{\overset{+\,H(SiMe_2)_mH}{\rightleftharpoons}} \underset{(p = m,\ n)}{\left[\begin{matrix} HMe_2Si \\ H(Me_2Si)_p \end{matrix}\right\rangle PtL_2\Big]} \underset{+\,H(SiMe_2)_{n+1}H}{\overset{-\,H(SiMe_2)_{m+1}H}{\rightleftharpoons}} [PtL_2] \qquad (3)$$

(L = PEt_3)

Thermolysis of 2. In order to obtain supportive evidence for the proposed intermediacy of a (silylene)platinum species, we examined the thermolysis of **2**. Thus, heating **2** at 60 °C for 30 min afforded Me_2SiH_2 as the main volatile product (≥30%) along with Me_3SiH (10%), hydrogen (10%), and $(HMe_2Si)_2O$ (4%).[16] (Disilene)platinum species, which might have been formed in view of the reaction of (diphosphine)Pt(0)–1,2-dihydrodisilane systems,[4] were not observed. By GC, no volatile oligosilanes were found to be formed. However, the ^{1}H NMR spectrum displayed small signals in the 0.1–0.4 ppm region arising from unknown polymeric entities, presumably formed from (silylene)platinum species **3** (eq 4).

$$\mathbf{2} \xrightarrow[60\ ^\circ C]{toluene\text{-}d_8} Me_2SiH_2 + \underset{\mathbf{3}}{[Me_2Si{=}Pt(PEt_3)_2]} \qquad (4)$$

Reactions of 2 with Silylene Trapping Agents. Thermolysis of **2** in the presence of 2,3-dimethyl-1,3-butadiene (3 equiv) or triethylsilane (2 equiv) failed to afford products with silylene incorporation. However, treatment with phenylacetylene (3 equiv) in toluene-d_8 at 60 °C for 30 min caused a color change of the solution from colorless to yellow, and gave a white precipitate of 4,4-dimethyl-2,6-diphenyl-1-platina-4-sila-2,5-cyclohexadiene (**4**, 46%

---

[7] Kobayashi, T.-a.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1988**, 1411.

[8] (a) Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1917. See also: (b) Tessier, C. A.; Kennedy, V. O.; Zarate, E. A. In *Inorganic and Organometallic Oligomers and Polymers*; Harrod, J. F.; Laine, R. M., Eds.; Kluwer Academic Publishers: Dordrecht, Netherlands, 1991; p 13. (c) Reference 10.

[9] Sakaki, S. Private communication.

[10] Fink, M. J.; Recatto, C. A.; Michalczyk, M. J.; Calabrese, J. C. Presented at the 25th Silicon Symposium, Los Angeles, April 3–4, 1992.

[11] Ebsworth, E. A. V.; Fraser, T. E. *J. Chem. Soc., Dalton Trans.* **1979**, 1960.

[12] For dehydrogenative coupling of hydrodisilanes, see: Hengge, E.; Weinberger, M.; Jammegg, Ch. *J. Organomet. Chem.* **1991**, *410*, C1. See also for platinum-catalyzed dehydrocoupling of hydrosilanes: Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590. Tanaka, M.; Kobayashi, T.-a.; Hayashi, T.; Sakakura, T. *Appl. Organomet. Chem.* **1988**, *2*, 91.

[13] Aylett, B. J. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 1.

[14] For a review of redistribution of organosilanes, see: Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213.

[15] Some Si═M complexes (M = Fe, Ru, Os, Cr, W) have been isolated. For instance, see: (a) Leis, C.; Wilkinson, D. L.; Handwerker, H.; Zybill, C. *Organometallics* **1992**, *11*, 514 and references cited therein. (b) Woo, L. K.; Smith, D. A.; Young, V. G., Jr. *Organometallics* **1991**, *10*, 3977.

[16] The origin of the oxygen was ambiguous. Monitoring by ^{1}H NMR indicated that Me_3SiH was a secondary product, presumably via redistribution of Me_2SiH_2 (see Experimental Section).

Table I. Crystallographic Data for 4

formula	$PtP_2SiC_{30}H_{48}$
fw	693.824
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	12.319 (1)
b, Å	20.164 (1)
c, Å	12.837 (2)
β, deg	97.03 (2)
V, Å^3	3164.8 (7)
Z	4
calcd density, g cm^{-3}	1.456
cryst size, mm	0.6 × 0.1 × 0.12
diffractometer	Enraf-Nonius CAD4
Cu Kα radiation, λ, Å	1.5418
scan type	ω/θ scan
scan rate, deg min^{-1}	1–4 (in ω)
2θ range, deg	4–120
no. of reflens measd	5076
no. of indep reflens	4843
no. of indep reflens used ($\lvert F_o\rvert \geq 3\sigma\lvert F_o\rvert$)	4211
transm factor[a]	0.480–0.980
decay	(in glass capillary) none
μ(Cu Kα), cm^{-1}	98.57
R	0.0817
R_w[b]	0.102
differential Fourier map max/min, e Å^{-3}	3.86/−2.68 (near Pt atom)

[a] Correction: empirical Ψ scan method. [b] $w = 1/(0.0132\lvert F_o\rvert^2 - 0.826\lvert F_o\rvert + 36.01)$.

Table II. Positional and Thermal Parameters for Non-Hydrogen Atoms of 4[a]

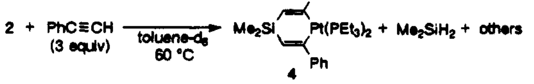
atom	x	y	z	B_{eq}, Å^2
Pt	0.31446 (4)	0.27997 (2)	0.64887 (4)	3.38 (2)
P(1)	0.4368 (3)	0.1984 (2)	0.7236 (3)	2.73 (9)
P(2)	0.2955 (3)	0.3380 (2)	0.8047 (3)	2.55 (8)
Si	0.3849 (3)	0.3707 (2)	0.4476 (3)	2.79 (9)
C(1)	0.2163 (10)	0.3531 (6)	0.5721 (10)	2.3 (3)
C(2)	0.2602 (12)	0.3932 (7)	0.5039 (10)	2.9 (3)
C(3)	0.3690 (13)	0.2791 (6)	0.4298 (12)	3.0 (4)
C(4)	0.3242 (11)	0.2429 (6)	0.5013 (10)	2.4 (3)
C(5)	0.1000 (12)	0.3599 (7)	0.5913 (10)	2.9 (3)
C(6)	0.0481 (12)	0.4232 (7)	0.5894 (11)	3.3 (4)
C(7)	−0.0617 (14)	0.4284 (8)	0.6039 (12)	3.9 (4)
C(8)	−0.1223 (14)	0.3716 (10)	0.6190 (13)	4.6 (5)
C(9)	−0.0745 (14)	0.3098 (9)	0.6200 (12)	3.9 (4)
C(10)	0.0366 (13)	0.3027 (8)	0.6055 (11)	3.5 (4)
C(11)	0.2821 (11)	0.1727 (6)	0.4706 (10)	2.4 (3)
C(12)	0.3242 (14)	0.1369 (7)	0.3908 (12)	3.7 (4)
C(13)	0.2825 (18)	0.0739 (8)	0.3625 (13)	4.7 (5)
C(14)	0.2043 (17)	0.0467 (7)	0.4136 (14)	4.6 (5)
C(15)	0.1608 (14)	0.0805 (7)	0.4931 (13)	3.9 (4)
C(16)	0.2012 (12)	0.1449 (6)	0.5205 (11)	2.9 (3)
C(17)	0.3813 (16)	0.4101 (10)	0.3138 (14)	5.1 (5)
C(18)	0.5162 (14)	0.3972 (9)	0.5215 (14)	4.5 (5)
C(19)	0.5720 (13)	0.2304 (9)	0.7839 (12)	3.8 (4)
C(20)	0.6398 (18)	0.2613 (14)	0.7088 (20)	7.3 (7)
C(21)	0.3956 (14)	0.1488 (7)	0.8316 (12)	3.7 (4)
C(22)	0.2978 (19)	0.1026 (9)	0.8007 (15)	5.6 (6)
C(23)	0.4765 (14)	0.1339 (8)	0.6316 (13)	3.9 (4)
C(24)	0.5609 (22)	0.0818 (11)	0.6806 (22)	7.7 (8)
C(25)	0.1672 (13)	0.3236 (10)	0.8587 (12)	4.4 (5)
C(26)	0.1489 (17)	0.2525 (11)	0.8935 (17)	5.4 (6)
C(27)	0.3981 (12)	0.3274 (7)	0.9189 (10)	3.0 (4)
C(28)	0.3784 (16)	0.3650 (9)	1.0177 (13)	4.8 (5)
C(29)	0.2909 (14)	0.4295 (6)	0.7912 (11)	3.5 (4)
C(30)	0.3982 (17)	0.4590 (7)	0.7670 (16)	4.9 (5)

[a] $B_{eq} = 4[a^2B_{11} + b^2B_{22} + c^2B_{33} + 2abB_{12}\cos\gamma + 2bcB_{23}\cos\alpha + 2caB_{13}\cos\beta]/3$.

Table III. Selected Bond Lengths and Bond Angles for 4

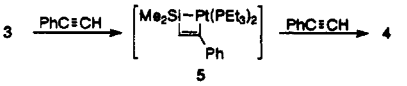
Bond Lengths (Å)			
Pt–P(1)	2.355 (4)	C(13)–C(14)	1.35 (3)
Pt–P(2)	2.354 (3)	C(14)–C(15)	1.39 (3)
Pt–C(1)	2.08 (1)	C(15)–C(16)	1.42 (2)
Pt–C(4)	2.05 (1)	C(16)–C(11)	1.37 (2)
C(1)–C(2)	1.35 (2)	Si–C(17)	1.89 (2)
C(2)–Si	1.83 (2)	Si–C(18)	1.85 (2)
Si–C(3)	1.87 (1)	P(1)–C(19)	1.86 (2)
C(3)–C(4)	1.34 (2)	C(19)–C(20)	1.49 (3)
C(1)–C(5)	1.49 (2)	P(1)–C(21)	1.83 (2)
C(5)–C(6)	1.43 (2)	C(21)–C(22)	1.54 (3)
C(6)–C(7)	1.39 (2)	P(1)–C(23)	1.86 (2)
C(7)–C(8)	1.39 (3)	C(23)–C(24)	1.56 (3)
C(8)–C(9)	1.38 (3)	P(2)–C(25)	1.83 (2)
C(9)–C(10)	1.41 (2)	C(25)–C(26)	1.53 (3)
C(10)–C(5)	1.42 (2)	P(2)–C(27)	1.83 (1)
C(4)–C(11)	1.54 (2)	C(27)–C(28)	1.52 (2)
C(11)–C(12)	1.40 (2)	P(2)–C(29)	1.85 (1)
C(12)–C(13)	1.40 (2)	C(29)–C(30)	1.52 (3)
Bond Angles (deg)			
P(1)–Pt–P(2)	97.2 (1)	C(13)–C(14)–C(15)	121.5 (14)
P(2)–Pt–C(1)	86.4 (4)	C(14)–C(15)–C(16)	118.4 (15)
P(1)–Pt–C(4)	90.9 (4)	C(15)–C(16)–C(11)	120.8 (14)
C(1)–Pt–C(4)	85.2 (5)	C(2)–Si–C(17)	109.0 (8)
Pt–C(1)–C(2)	118.4 (10)	C(2)–Si–C(18)	116.7 (7)
C(1)–C(2)–Si	121.8 (10)	C(3)–Si–C(17)	108.3 (8)
C(2)–Si–C(3)	102.3 (7)	C(3)–Si–C(18)	114.9 (7)
Si–C(3)–C(4)	119.9 (11)	C(17)–Si–C(18)	105.4 (8)
C(3)–C(4)–Pt	120.5 (9)	Pt–P(1)–C(19)	115.0 (6)
Pt–C(1)–C(5)	120.2 (9)	P(1)–C(19)–C(20)	114.8 (12)
C(1)–C(5)–C(6)	121.2 (12)	Pt–P(1)–C(21)	117.9 (5)
C(5)–C(6)–C(7)	120.4 (14)	P(1)–C(21)–C(22)	114.7 (11)
C(6)–C(7)–C(8)	120.2 (15)	Pt–P(1)–C(23)	115.7 (5)
C(7)–C(8)–C(9)	120.6 (16)	P(1)–C(23)–C(24)	115.5 (13)
C(8)–C(9)–C(10)	120.8 (16)	Pt–P(2)–C(25)	115.1 (6)
C(9)–C(10)–C(5)	119.5 (15)	P(2)–C(25)–C(26)	115.3 (13)
Pt–C(4)–C(11)	121.0 (9)	Pt–P(2)–C(27)	119.6 (5)
C(4)–C(11)–C(12)	121.1 (12)	P(2)–C(27)–C(28)	116.5 (11)
C(11)–C(12)–C(13)	120.0 (16)	Pt–P(2)–C(29)	114.9 (5)
C(12)–C(13)–C(14)	120.3 (16)	P(2)–C(29)–C(30)	113.1 (11)

yield) along with Me_2SiH_2 and other silicon-containing volatile compounds (eq 5, see Experimental Section). The



(5)

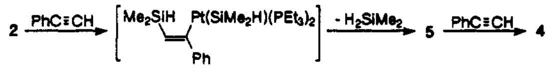
structure of 4 was unequivocally confirmed by X-ray crystallography of a pale yellow needle crystal of 4 (vide infra). As a tentative mechanism, one can envision that 4 arises from the insertion of phenylacetylene into the Si–Pt bond[17,18] of a platinasilacyclobutene intermediate (5),[19] generated by the interaction of 3 with phenylacetylene[20] (eq 6). An alternative pathway leading to 5



5

(6)

would be insertion of phenylacetylene into one of the Si–Pt bonds of 2, followed by interaction of the resulting β-SiH moiety with the platinum center (eq 7).[21] However, fur-



(7)

---

(17) Kobayashi, T.-a.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1989**, 467.

(18) As for insertion of acetylenes into C–M bonds, it seems to proceed with larger substituents lying near the metal center. For the C–Ni bond, see: Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002.

(19) Metallasilacyclobutene intermediates have been suggested in the group 10 metal-catalyzed addition of silacyclopropenes to acetylenes affording 1-sila-2,4-cyclopentadienes. (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879. (b) Ishikawa, M.; Sugisawa, H.; Harata, O.; Kumada, M. *J. Organomet. Chem.* **1981**, *217*, 43. (c) Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 57. See also: (d) Ohshita, J.; Naka, A.; Ishikawa, M. *Organometallics* **1992**, *11*, 602 and references cited therein. (e) Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem.* **1977**, *131*, 377.

(20) Addition of acetylenes to C═M bonds (M = Ir, Ti) affording metallacyclobutenes is known. (a) Calabrese, J. C.; Roe, D. C.; Thorn, D. L.; Tulip, T. H. *Organometallics* **1984**, *3*, 1223. (b) McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T. S.; Tebbe, F. N. *J. Am. Chem. Soc.* **1981**, *103*, 5584. See also: (c) Hemond, R. C.; Hughes, R. P.; Robinson, D. J.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2239.

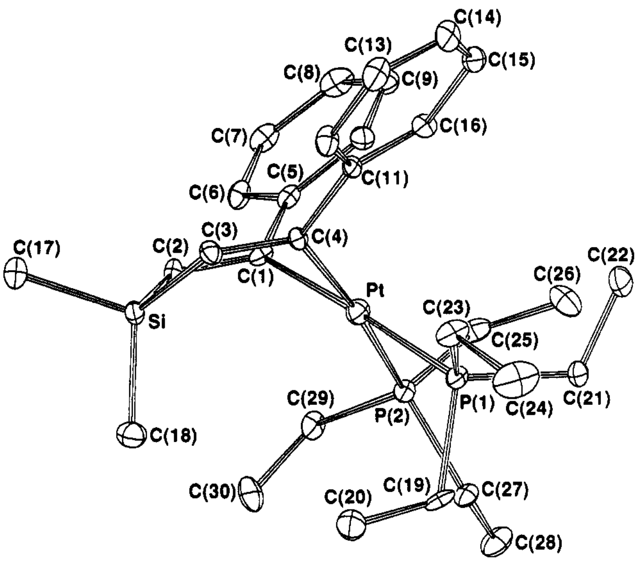


Figure 1. Perspective view of the molecular structure of 4.

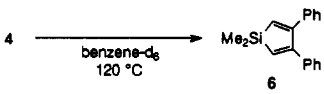
ther studies are required to reveal the provenance of 4 more definitely, since the reactivity of bis(hydrosilyl)platinum species is extremely dependent on the nature of the phosphine ligand and/or the substituent bound to the silicon. For instance, it is interesting to note the formation of a 1-platina-2,5-disila-3-cyclopentene, $PhR\overline{SiCH{=}CR'(PhRSi)Pt}(PMe_2Ph)_2$, from *cis*-$(HPhRSi)_2Pt(PMe_2Ph)_2$ and $R'C{\equiv}CH$ (R = Ph, R′ = H, Ph, *p*-BrC_6H_4, *p*-FC_6H_4; R = Me, R′ = Ph).[19e]

Structure of 4. Details of the data collection, positional and thermal parameters for non-hydrogen atoms, and selected bond lengths and angles are summarized in Tables I–III, respectively. A perspective view of the molecule with labeling scheme is shown in Figure 1.

Complex 4 has slightly distorted square-planar geometry, with a dihedral angle between P(1)–Pt–P(2) and C(1)–Pt–C(4) being 5.2°. The platinasilacyclohexadiene ring exists in the boat conformation with a nearly planar mean plane (A) consisting of four carbons C(1)–C(2)–C(3)–C(4); dihedral angles between C(1)–Pt–C(4) and A and A and C(2)–Si–C(3) are 129.7 and 149.1°, respectively. Because of this conformation, the two methyl groups attached to the silicon are not equivalent to each other. This is consistent with the appearance of the two Si–Me proton signals (0.21 and 0.48 ppm in $CDCl_3$).

The Pt–P bond lengths (2.355 and 2.354 Å) are slightly longer than those of $RR'PtP_2$ complexes reported before (2.25–2.33 Å).[22] On the other hand, the Pt–C lengths (2.05 and 2.08 Å) are a little bit shorter than those reported (2.06–2.22 Å). The other bond lengths are unexceptional.

Thermolysis of 4. The 1,2-dihydrodisilane 1 is known to react with acetylenes in the presence of Ni[3c] or Pd[3d] complex catalysts to give 1-sila-2,4-cyclopentadienes. The formation of 4 indicates a possible intermediate of the type 4 complex involved in the catalysis. Indeed, heating 4 at 120 °C for 40 min in benzene-d_6 afforded 1,1-dimethyl-3,4-diphenyl-1-sila-2,4-cyclopentadiene (6) in 30% yield as the sole volatile product (eq 8). Exactly the same compound with the same locations of phenyl groups was previously obtained in the Pd-catalyzed reaction of 1 with phenylacetylene.[3d]



(8)

Experimental Section

^1H and ^{31}P NMR spectra were measured on Bruker AC-200 and JEOL FX-90 instruments, respectively (200 MHz for ^1H NMR and 36.2 MHz for ^{31}P NMR). Chemical shifts are referred to C_6D_5H (7.16 ppm), $C_6D_4HCD_3$ (6.98 ppm), or $CHCl_3$ (7.25 ppm) for ^1H NMR and H_3PO_4 (0 ppm) for ^{31}P NMR. Infrared spectra were recorded on a JASCO A-302 spectrometer. Mass spectra were measured on a Shimadzu QP-1000 spectrometer (EI, 70 eV). GC and GC–MS analyses were carried out using columns of OV-101 (1 m, 3 m), OV-17 (1 m), and/or OV-1701 (25 m). Gas analyses were performed on a Gasukuro Kogyo Model 373FG fuel gas analyzer.

All manipulations were carried out under nitrogen. Solvents were dried by usual methods and distilled under nitrogen. 2,3-Dimethyl-1,3-butadiene, triethylsilane, and phenylacetylene were dried with molecular sieve 4A and distilled under nitrogen or a reduced pressure. $Pt(PEt_3)_3$[23a] was prepared by heating $Pt(PEt_3)_4$[23b] at around 60 °C for about 5 min in vacuo. *trans*-$PtCl_2(PEt_3)_2$ was obtained by the method reported for *trans*-$PtCl_2(PBu_3)_2$.[24] $HMe_2SiSiMe_2H$,[25] $HMe_2SiSiMe_3$,[25] and an authentic sample of Me_2SiH_2[26] were synthesized according to the literature reactions. $H_2MeSiSiMe_3$ was prepared by the reduction of $Cl_2MeSiSiMe_3$[27] with $LiAlH_4$ in a way similar to that of $HMe_2SiSiMe_2H$.[25]

Reaction of $Pt(PEt_3)_3$ with $HMe_2SiSiMe_2H$ (1). To a benzene-d_6 (0.30 mL) solution of $Pt(PEt_3)_3$ (0.05 mmol) in an NMR tube was added 1 (0.15 mmol) at room temperature, and the tube was sealed under nitrogen. ^1H NMR spectra after about 15 min indicated the formation of *cis*-$(HMe_2Si)_2Pt(PEt_3)_2$ (2) in nearly quantitative yield at 0.78 (d, $^3J_{HH} \approx 4$ Hz, $^3J_{HPt} \approx 28$ Hz, Si–CH_3) and 4.51 (sept t, $^3J_{HH} \approx 4$ Hz, $^3J_{HP} \approx 19$ Hz, $^2J_{HPt} \approx 40$ Hz, Si–H) ppm. In addition, the proton signals of Me_2SiH_2 and other Si–Me species emerged at −0.02 (t, $^3J_{HH} = 4.1$ Hz, Si–CH_3) ppm and at 0.0–0.3 ppm, respectively, with Si–H protons being observed at 3.8–4.2 ppm. No signal arising from Pt–H species was found in the range −30.0 to 0.0 ppm. In ^{31}P NMR, the signal at 21.9 ($^1J_{PPt} = 4216$ Hz) ppm for $Pt(PEt_3)_3$ disappeared with appearance of new signals at 18.5 ($^1J_{PPt} = 1621$ Hz) and −15.3 (broad) ppm arising from 2 and the liberated triethylphosphine, respectively. On the other hand, GC and GC–MS of the solution showed the formation of $H_2Me_{2n}Si_n$ ($1 \le n \le 7$) with other unidentified products. For $H_2Me_8Si_4$, two structural isomers seemed to be formed as judged from GC (OV-1701) and GC–MS. However, for other oligosilanes, almost one major GC peak was observed for each oligosilane. By the comparison of their GC retention times and GC–MS fragmentation patterns with those of the oligosilanes obtained by the redistribution of 1 catalyzed by *trans*-$PtCl_2(PEt_3)_2$,[3a,6] they were assigned to be $H(SiMe_2)_nH$ ($1 \le n \le 7$) with an exception of the second isomer of the tetramer. From the ^1H NMR and GC measurement after about 2 h, their approximate amounts were estimated at ≥15, 14, 12, 3 (the total of the two isomers (3:7) for $H_2Me_8Si_4$), 0.4, 0.1, and ≤0.1 × 0.0015 mmol for *n* = 1–7, respectively. The GC–MS spectral data (*m/z* (relative intensity)) for $H(SiMe_2)_nH$ ($3 \le n \le 9$) obtained in the above reaction and/or the reported reaction[3a,6] were as follows. $H(SiMe_2)_3H$: 176 (M^+, 5), 161 (13), 117 (76), 116 (97), 101 (24), 73 (100), 59 (30), 45 (21), 43 (33). $H_2Me_8Si_4$ minor isomer: 234 (M^+, 7), 219 (17), 175 (33), 174 (51), 173 (20), 161 (25), 160 (100), 159 (41), 145 (31), 131 (15), 129 (19), 117 (22), 116 (23), 115 (29),

---

[21] We cannot completely exclude intervention of another route involving generation of PtL_2 species (L = PEt_3) from 3, addition of Me_2SiH_2 giving $(Me_2HSi)HPtL_2$, insertion of phenylacetylene into the Si–Pt bond, intramolecular Si–H addition to the Pt center, and reductive elimination of hydrogen to result in 5.

[22] Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; p 532.

[23] (a) Yoshida, T.; Matsuda, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 107. (b) Yoshida, T.; Matsuda, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 110.

[24] Kauffmann, B.; Teter, L. A. *Inorg. Synth.* **1963**, *7*, 245.

[25] Urenovitch, J. V.; West, R. *J. Organomet. Chem.* **1965**, *3*, 138.

[26] Bond, A. C.; Brockway, L. O. *J. Am. Chem. Soc.* **1954**, *76*, 3312.

[27] Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 139.

101 (24), 99 (14), 73 (89), 59 (31), 45 (27), 43 (23). $H_2Me_8Si_4$ major isomer: 234 (M^+, 14), 219 (16), 175 (68), 174 (48), 173 (25), 160 (29), 159 (27), 145 (19), 131 (19), 129 (14), 117 (47), 116 (82), 115 (22), 101 (35), 99 (13), 73 (100), 59 (35), 45 (27), 43 (29). Some fragment peaks of these two isomers might involve a considerable error because of the insufficient GC peak separation. $H(SiMe_2)_5H$: 292 (M^+, 6), 233 (100), 203 (14), 175 (27), 174 (14), 173 (21), 159 (39), 157 (12), 116 (22), 101 (13), 73 (56), 59 (14). $H(SiMe_2)_6H$: 350 (M^+, 6), 291 (27), 261 (12), 233 (100), 217 (35), 215 (10), 175 (19), 174 (10), 173 (18), 159 (48), 157 (13), 116 (11), 73 (42). $H(SiMe_2)_7H$: 408 (M^+, 5), 291 (50), 233 (82), 217 (100), 175 (20), 173 (21), 159 (62), 157 (23), 73 (69). $H(SiMe_2)_8H$: 466 (M^+, 2), 291 (42), 275 (12), 233 (55), 217 (100), 201 (17), 199 (13), 173 (14), 159 (38), 157 (21), 73 (67). $H(SiMe_2)_9H$: 524 (M^+, 2), 291 (38), 275 (18), 233 (46), 217 (100), 201 (21), 199 (16), 159 (27), 157 (20), 73 (67).

In a separate experiment, to a pentane (2 mL) solution of $Pt(PEt_3)_3$ (0.47 mmol) in a Schlenk tube cooled at −30 °C was added 1 (0.49 mmol) and the resulting mixture was stirred at −30 °C for 5 min. The volatiles were removed in vacuo at −30 to −20 °C, and pentane (1 mL) was added to the residue. When the pentane solution was cooled to −80 °C, pale yellow plate crystals of 2 were obtained (0.42 mmol, 90% yield): mp 63–65 °C (under N_2). ^1H NMR ($CDCl_3$, 0 °C): δ 0.28 (d, $^3J_{HH} = 4.0$ Hz, $^3J_{HPt} = 27.5$ Hz, 12 H, $SiCH_3$), 0.99 (td, $2\,^3J_{HH} \approx {}^3J_{HP} \approx 15.0$ Hz, 18 H, $PCCH_3$), 1.90 (qd, $^3J_{HH} \approx {}^2J_{HP} \approx 7.5$ Hz, 12 H, PCH_2), 3.89 (sept t, $^3J_{HH} \approx 4.0$ Hz, $^3J_{HP} \approx 18.5$ Hz, $^2J_{HPt} \approx 39.4$ Hz, 2 H, SiH). ^{31}P NMR ($C_6D_5CD_3$, 0 °C): δ 23.8 ($^1J_{PPt} = 1626$ Hz). IR (Nujol): 2020 (s), 1234 (m), 1032 (m), 922 (s), 832 (s), 770 (s), 736 (m), 710 (m), 680 (m), 626 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{44}P_2PtSi_2$: C, 34.96; H, 8.07. Found: C, 35.04; H, 7.94.

Reaction of $Pt(PEt_3)_3$ with $HMe_2SiSiMe_3$. To a benzene-d_6 (0.30 mL) solution of $Pt(PEt_3)_3$ (0.05 mmol) in an NMR tube was added $HMe_2SiSiMe_3$ (0.15 mmol) at room temperature, and the tube was sealed under nitrogen. ^1H NMR of the resulting mixture after about 2 h indicated the formation of Me_3SiH at 0.02 (d, $^3J_{HH} = 3.6$ Hz, Si–CH_3) ppm (~0.03 mmol) along with other Si–Me species at 0.0–0.8 ppm. The Si–H protons of Me_3SiH and other species appeared at 3.8–4.7 ppm. However, Pt–Si–CH_3 signals with satellite bands arising from ^1H–^{195}Pt coupling were not found. On the other hand, GC and GC–MS analyses of the solution indicated the formation of oligosilanes with other unidentified products. The oligosilanes were assigned by GC–MS to be $HMe_{2m+1}Si_m$ ($1 \le m \le 7$). From ^1H NMR and GC (OV-1701, FID, tetradecane as an internal standard), the approximate amounts of the oligosilanes were estimated at ≥25, 2, 4, 4 (three isomers, 1:5:4), 3 (three isomers, 3:1:6), 0.5 (two isomers, 1:9), and ≤0.1 (two isomers, 2:3) × 0.0015 mmol for m = 1–7, respectively (the figures in the parentheses represent the approximate ratios of the structural isomers distinguished by GC). The GC–MS spectral data (m/z (relative intensity)) for $HMe_{2m+1}Si_m$ ($3 \le m \le 7$) were as follows. HMe_7Si_3: 190 (M^+, 5), 175 (10), 131 (27), 116 (56), 102 (15), 101 (14), 73 (100), 59 (17), 45 (30), 43 (21). HMe_9Si_4: 248 (M^+, 5), 174 (40), 159 (23), 131 (25), 116 (34), 73 (100), 59 (21), 45 (30), 43 (18). $HMe_{11}Si_5$: 306 (M^+, 6), 233 (36), 217 (13), 173 (28), 159 (25), 131 (17), 116 (25), 73 (100), 59 (19), 45 (24), 43 (13). $HMe_{13}Si_6$: 364 (M^+, 7), 305 (17), 290 (11), 233 (17), 231 (15), 217 (24), 215 (12), 173 (15), 171 (11), 159 (15), 157 (14), 131 (11), 73 (100), 59 (16), 45 (20). $HMe_{15}Si_7$ minor isomer (20 eV): 422 (M^+, 13), 349 (32), 291 (16), 275 (85), 259 (17), 232 (47), 217 (100), 201 (23), 173 (30), 159 (15). $HMe_{15}Si_7$ major isomer (20 eV): 422 (M^+, 2), 349 (44), 291 (31), 275 (38), 232 (22), 217 (100), 189 (12).

Reaction of $Pt(PEt_3)_3$ with $H_2MeSiSiMe_3$. In a way similar to that of $HMe_2SiSiMe_3$, $H_2MeSiSiMe_3$ (0.15 mmol) was treated with $Pt(PEt_3)_3$ (0.05 mmol) in benzene-d_6 (0.30 mL). ^1H NMR after about 2 h indicated the formation of Me_3SiH (~0.02 mmol) at 0.02 (d, $^3J_{HH} \approx 3.6$ Hz, Si–CH_3) ppm and other Si–Me species at 0.0–0.7 ppm, with their Si–H protons being observed at 3.5–4.5 ppm. However, no proton signal for Pt–Si–CH_3 species was found. On the other hand, GC measurement of the solution showed the existence of the volatile compounds, some of which were assigned by GC–MS to be $HMe_{2p+1}Si_p$ ($1 \le p \le 3$), $H_2Me_{2q}Si_q$ ($2 \le q \le 6$), and $H_3Me_{2r-1}Si_r$ ($3 \le r \le 7$). From ^1H NMR and GC (OV-1701, FID, decane as an internal standard), the approximate amounts were estimated at ≥12, ≤0.1, 1, 14, 0.2, 5 (two isomers, 1:9), ≤0.1, ≤0.1, 0.2, ≤0.1, 0.2 (two isomers, 1:1), ≤0.1, and ≤0.1 × 0.0015 mmol for p = 1–3, q = 2–6, and r = 3–7, respectively. The GC–MS spectral data (m/z (relative intensity)) of the oligosilanes (3 ≤ p, q, or r ≤ 7) were as follows. For $HMe_{2p+1}Si_p$ ($p = 3$): HMe_7Si_3 190 (M^+, 17), 175 (16), 131 (10), 116 (42), 102 (36), 101 (21), 73 (100), 59 (14), 45 (27), 43 (17). For $H_2Me_{2q}Si_q$ ($3 \le q \le 6$): $H_2Me_6Si_3$ 176 (M^+, 5), 161 (14), 116 (16), 102 (88), 73 (100), 59 (23), 45 (27), 43 (30); $H_2Me_8Si_4$ minor isomer 234 (M^+, 5), 219 (11), 160 (100), 145 (29), 131 (14), 129 (13), 115 (26), 73 (81), 59 (19), 45 (31), 43 (19); $H_2Me_8Si_4$ major isomer 234 (M^+, 6), 219 (12), 160 (100), 145 (34), 129 (13), 115 (27), 73 (60), 59 (17), 45 (23), 43 (16); $H_2Me_{10}Si_5$ (20 eV) 292 (M^+, 5), 232 (9), 218 (100), 203 (12), 160 (22), 144 (38); $H_2Me_{12}Si_6$ (20 eV) 350 (M^+, 4), 276 (43), 261 (10), 202 (100), 187 (11), 157 (11). For $H_3Me_{2r-1}Si_r$ ($3 \le r \le 7$): $H_3Me_5Si_3$ 162 (M^+, 12), 147 (12), 116 (17), 101 (15), 88 (50), 73 (100), 62 (14), 59 (21), 45 (28), 43 (30); $H_3Me_7Si_4$ (20 eV) 220 (M^+, 3), 205 (8), 160 (16), 146 (100), 115 (12), 73 (11); $H_3Me_9Si_5$ (20 eV) 278 (M^+, 2), 204 (100), 189 (12), 144 (44), 130 (22); $H_3Me_{11}Si_6$ (20 eV) 336 (M^+, 4), 262 (54), 247 (12), 218 (12), 202 (42), 188 (100), 157 (16), 144 (15); $H_3Me_{13}Si_7$ (20 eV) 394 (M^+, 3), 320 (54), 260 (16), 246 (100), 231 (15), 202 (33), 187 (13), 172 (61).

Redistribution of 1 Catalyzed by 2. To a toluene-d_8 (0.25 mL) solution of 2 (0.002 mmol) in an NMR tube cooled at about 0 °C was added 1 (0.20 mmol), and the tube was sealed under nitrogen. Monitoring the reaction by ^1H NMR indicated the redistribution proceeded with 2 being apparently unchanged. The ^1H NMR signals of 2 were observed at 0.69 (d, $^3J_{HH} \approx 4$ Hz, $^3J_{HPt} \approx 28$ Hz, Si–CH_3), 0.87 (td, $2\,^3J_{HH} \approx {}^3J_{HP} \approx 14.4$ Hz, $PCCH_3$), and 1.75 (qd, $^3J_{HH} \approx {}^2J_{HP} \approx 7.2$ Hz, 12 H, PCH_2) ppm, while the Si–H proton was not clearly distinguished because of the existence of Si–H protons of $H(SiMe_2)_nH$ at 3.2–5.0 ppm. After about 1 h, an equilibrium state was attained, and no more ^1H NMR change was observed in the Si–Me region. By ^1H NMR at −30 °C, the amount of the formed Me_2SiH_2 in solution was estimated at 30 × 0.002 mmol. GC and GC–MS revealed the formation of $H(SiMe_2)_nH$ ($n \ge 2$) along with small amounts of several unidentified products (the total of their GC areas (OV-101, TCD) was almost the same as that of $H(SiMe_2)_5H$). The amounts of $H(SiMe_2)_nH$ ($n \ge 2$) were estimated by GC (OV-101, TCD) using an internal standard (tetradecane) at 10, 30, 5 (the total of the two isomers (1:4) for $H_2Me_8Si_4$), 2, 1, and 0.3 × 0.002 mmol for n = 2–7, respectively.

Thermolysis of 2. A toluene-d_8 (0.25 mL) solution of 2 (0.020 mmol) in a sealed NMR tube was left for about 15 min at room temperature. ^1H NMR measurement showed the formation of Me_2SiH_2 (~5%) without other Si–Me products. When the NMR tube was heated at 60 °C for 30 min, the color of the solution turned from colorless to light brown. ^1H NMR of the resulting solution at −30 °C showed the formation of Me_2SiH_2 at −0.04 (t, $^3J_{HH} = 4.1$ Hz, Si–CH_3) ppm (22%), Me_3SiH at 0.02 (d, $^3J_{HH} = 3.6$ Hz, Si–CH_3) ppm (10%), and $(HMe_2Si)_2O$ at 0.14 (d, $^3J_{HH} = 2.8$ Hz, Si–CH_3) ppm (4%). These products were additionally confirmed by GC and GC–MS. In GC (OV–101, 240 °C), no other volatile products were detected. However, several small proton signals were observed in the 0.1–0.4 ppm region, presumably arising from some polymeric Si–Me species.

In a separate experiment, a toluene (0.29 mL) solution of 2 (0.021 mmol) was heated at 60 °C for 30 min in a closed Schlenk tube (43 mL) under nitrogen. Gas analysis of the vapor phase showed the formation of Me_2SiH_2 (30%) and H_2 (10%).

Reaction of 2 with 2,3-Dimethyl-1,3-butadiene or Triethylsilane. To a toluene-d_8 (0.25 mL) solution of 2 (0.023 mmol) in an NMR tube cooled at about −30 °C was added 2,3-dimethyl-1,3-butadiene (0.069 mmol) or triethylsilane (0.046 mmol), and the tube was sealed under nitrogen. Heating the NMR tube at 60 °C for 30 min gave essentially the same products as those in the thermolysis of 2. The product with silylene incorporation such as 1,1,3,4-tetramethyl-1-sila-3-cyclopentene or 1,1,1-triethyl-2,2-dimethyldisilane was not found by ^1H NMR and/or GC–MS.

Reaction of 2 with Phenylacetylene. To a toluene-d_8 (0.25 mL) solution of 2 (0.023 mmol) in an NMR tube cooled at about −30 °C was added phenylacetylene (0.069 mmol), and the tube was sealed under nitrogen. When the solution was heated at 60 °C for 30 min, a white precipitate of 4 was formed. The NMR tube was opened, and the precipitate was separated. Washing the precipitate with pentane and drying in vacuo gave a white solid of 4 (0.011 mmol, 46% yield). Pure 4 of pale yellow needle crystals for microanalysis and X-ray diffraction study was obtained by recrystallization from benzene–pentane (v/v = 1/1) down to −10 °C. 4: mp 159–161 °C (under N_2). ^1H NMR ($CDCl_3$): δ 0.21 (s, 3 H, $SiCH_3$), 0.48 (s, 3 H, $SiCH_3$), 0.96 (td, $2{}^3J_{HH} \approx {}^3J_{HP} \approx 14.8$ Hz, 18 H, $PCCH_3$), 1.18–1.68 (m, 12 H, PCH_2), 6.83 (d, $^4J_{HP(trans)} \approx 14.6$ Hz, $^3J_{HPt} \approx 122.9$ Hz, 2 H, CH═), 6.99–7.37 and 7.61–7.83 (each m, 10 H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ −2.7 ($^1J_{PPt} = 1741$ Hz). IR (Nujol): 1510 (m), 1232 (m), 1038 (m), 868 (m), 836 (m), 760 (s), 716 (m), 698 (m), 570 (m) cm^{-1}. Anal. Calcd for $C_{30}H_{48}P_2PtSi$: C, 51.93; H, 6.97. Found: C, 52.33; H, 7.01.

^1H NMR measurement before opening the NMR tube indicated the presence of Me_2SiH_2 in solution (−0.02 (t, $^3J_{HH} = 4.1$ Hz, Si–CH_3) ppm, ~5%). In addition, GC analysis (OV-1701) of the solution showed at least 20 peaks arising from unreacted phenylacetylene (A, ~0.007 mmol), styrene (B, ~0.004 mmol), and other volatile products. The structures of the products except for Me_2SiH_2 and styrene were not fully confirmed yet because of the difficulty of their separation. However, some of them were tentatively assigned by GC–MS to be 1:1 adducts of Me_2SiH_2 with phenylacetylene (C1, C2) and five- and six-membered silacycles such as 1,1-dimethyl-2,4-, 1,1-dimethyl-2,5-, or 1,1-dimethyl-3,4-diphenyl-1-sila-2,4-cyclopentadiene (D), 1,1-dimethyl-2,4-, 1,1-dimethyl-2,5-, 1,1-dimethyl-3,4-, or 1,1-dimethyl-3,5-diphenyl-1-sila-2-cyclopentene (E), 1,1,4,4-tetramethyl-2,5- or 1,1,4,4-tetramethyl-2,6-diphenyl-1,4-disila-2,5-cyclohexadiene (F), 1,1,4,4-tetramethyl-2,5- or 1,1,4,4-tetramethyl-2,6-diphenyl-1,4-disila-2-cyclohexene (G), and 1,1,4,4-tetramethyl-2,5- or 1,1,4,4-tetramethyl-2,6-diphenyl-1,4-disialcyclohexene (H). The approximate GC area ratio of A:B:C1:C2:D:E:F:G:H was estimated at ~20:~10:0.5:0.5:5:3:8:14:1 (OV-1701, FID). The GC–MS spectral data (*m/z* (relative intensity)) of the products (C–H) are as follows. C1: 162 (M^+, 26), 147 (100), 145 (29), 121 (38), 59 (21), 58 (22), 43 (22). C2: 162 (M^+, 28), 147 (100), 145 (45), 121 (20), 59 (12), 58 (25), 43 (24). D: 262 (M^+, 100), 247 (60), 145 (15), 105 (15), 43 (22). E: 264 (M^+, 86), 249 (52), 205 (36), 204 (27), 173 (34), 161 (68), 145 (100), 135 (57), 121 (39), 59 (71), 43 (28). F: 320 (M^+, 85), 305 (100), 203 (24), 173 (20), 145 (38), 73 (41), 43 (31). G: 322 (M^+, 80), 263 (29), 218 (46), 161 (36), 135 (40), 73 (40), 43 (18). H: 324 (M^+), fragment peaks could not be confirmed to have come from H because of the partial overlapping of the GC peak with G.

Thermolysis of 4. A benzene-d_6 (0.30 mL) solution of 4 (0.0014 mmol) in a sealed NMR tube was heated at 120 °C for 40 min. The ^1H NMR signals for 4 disappeared, and new Si–CH_3 proton signals emerged at 0.24, 0.41, 0.45, and 0.55 ppm with an integral ratio of 2.9:3.1:1:3.5. GC and GC–MS analyses of the solution revealed the formation of 6 as the sole volatile product. 6 was separated by short-path silica gel chromatography using hexane as eluent. The ^1H NMR spectrum of 6 in $CDCl_3$ was in good agreement with the reported one[28] (in benzene-d_6, 0.40 (Si–CH_3) and 6.24 (═CH) ppm). The yield of 6 was estimated at 30% by means of the ^1H NMR of the reaction mixture. The GC–MS fragmentation pattern of 6 was the same as that of the compound D formed in the reaction of 2 with phenylacetylene.

X-ray Crystallographic Analysis for 4. A crystal was sealed in a glass capillary tube and an empirical absorption correction (ψ scan) was applied to the data. Cell constants were obtained from 25 higher angle (30 < 2θ < 40°) reflections. The structure was solved by MULTAN 78,[29] and the program system UNICS III[30] was used for calculations. A total of 4211 reflections ($|F_o| \geq 3\sigma|F_o|$) was used. Six hydrogen atoms were taken from a difference Fourier map; the remainder were located with calculated positions. Refinement was by full matrix least squares, $R = 0.0817$ ($R_w = 0.102$); the position and temperature factors of hydrogen atoms were not refined. Scattering factors for atoms were taken from ref 31.

Acknowledgment. We are indebted to Dr. Andrew J. Wynd who participated in the preliminary experiments.

Supplementary Material Available: Tables of the coordinates of hydrogen atoms, thermal parameters, complete bond lengths and angles, least-squares planes with atomic deviations, and angles between the planes for 4 (19 pages). Ordering information is given on any current masthead page.

OM920239R

---

(28) Henry, G. K.; Shinimoto, R.; Zhou, Q.; Weber, W. P. *J. Organomet. Chem.* **1988**, *350*, 3.

(29) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. MULTAN78. A system of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. University of York, England, and Louvain, Belgium, 1978.

(30) Sakurai, T.; Kobayashi, K. *Rep. Inst. Phys. Chem. Res.* **1979**, *55*, 69.

(31) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

Synthesis, Structure, and Reactivity of Allene Complexes of the Chiral Rhenium Fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$

Jiaqi Pu, Tang-Sheng Peng, Atta M. Arif, and J. A. Gladysz*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received May 11, 1992

Reactions of the chlorobenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ and excess (a) allene, (b) methylallene, and (c) 1,1-dimethylallene give the π adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}C{=}CRR')]^+BF_4^-$ (**1a–c**) in 90–91% yields. The crystal structure of **1a** (monoclinic, $P2_1/n$, $a = 10.327$ (1) Å, $b = 10.401$ (1) Å, $c = 23.919$ (2) Å, $\beta = 99.233$ (2)°, $Z = 4$) shows the coordinated ═CH_2 group to be syn to the PPh_3 ligand, with a 23.7° angle between the Re—P bond and the $\overline{\mathrm{Re{-}C{=}C}}$ plane. NMR data show that the methyl groups in **1b,c** occupy the less hindered positions on the free C═C linkages. Analogous reactions of chiral 1,3-dialkylallenes give mixtures of diastereomeric adducts with modest selectivities. Reaction of **1a** and $t\text{-}BuO^-K^+$ in THF (−80 to +25 °C) gives the methylacetylide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CCH_3)$ (**3**, 92%). A similar reaction of **1a** and CH_3Li gives the allenyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}C{=}CH_2)$ (**4**, 70%), which upon treatment with $HBF_4{\cdot}OEt_2$ gives mainly the propyne complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HC{\equiv}CCH_3)]^+BF_4^-$ (**5**). Reaction of $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ and $HC{\equiv}CCH_2OTs$ gives the propargyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C{\equiv}CH)$, which isomerizes to **4** at 67–80 °C. Thus, the conversion of **1a** to **3** is proposed to involve **4** and **5** as intermediates.

The physical and chemical properties of transition-metal allene complexes have been the subject of numerous investigations.[1–4] Depending upon the C═C═C substitution pattern, a diverse array of linkage isomers and ste-

0276-7333/92/2311-3232$03.00/0 © 1992 American Chemical Society