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Platinum Complex-Catalyzed Hydrosilylation and Isomerization of Methylenecyclopropane Derivatives. Effect of Structures of the Substrate and Catalyst

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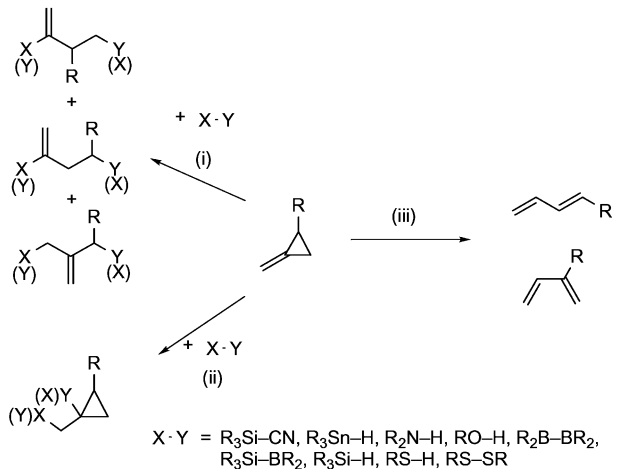
$PtI_2(PPh_3)_2$ catalyzes hydrosilylation of 2,2-diphenyl-1-methylenecyclopropane with $HSiEt_3$, $HSiPh_3$, $HSiEt_2Ph$, $HSiPhCl_2$, and $HSiCl_3$ under solvent-free conditions at 140 °C to produce the silyl compounds with a (2,2-diphenylcyclopropyl)methyl substituent in moderate to high yields without ring-opening of the substrate. $PtI_2(PPh_3)_2$ is converted by the reaction into $PtH(I)(PPh_3)_2$, which also catalyzes the hydrosilylation of the methylenecyclopropanes. The reaction of 2-phenyl-1-methylenecyclopropane, 2-methyl-2-phenyl-1-methylenecyclopropane, 2,2-diphenethyl-1-methylenecyclopropane, and alkylidenecyclopropanes with $HSiEt_3$ catalyzed by $PtI_2(PPh_3)_2$ causes addition of hydrosilane to the substrate accompanied by ring-opening. 2,2-Diphenyl-1-methylenecyclopropane undergoes ring-opening isomerization in the presence of $HSi(OEt)Me_2$ and $Pt(PEt_3)_3$ catalyst to give 1,1-diphenyl-1,3-butadiene. The pathways for the hydrosilylation and the isomerization are discussed.

Introduction

Methylenecyclopropanes, which have a highly strained structure due to a three-membered ring attached to the C═C double bond, often undergo ring-opening promoted by transition metal complexes. These reactions have been utilized in many synthetic organic reactions.[1] Scheme 1 depicts the possible reactions of organic molecules (X−Y) with substituted methylenecyclopropanes promoted by metal complexes. Addition of X−Y to the methylenecyclopropanes would cause functionalization of the substrates with and without ring-opening (Scheme 1, paths i and ii).[2−10] Simple addition of X−Y to the C═C bond catalyzed by metal complexes, giving rise to cyclopropane-containing compounds (Scheme 1, path ii),[2,3,6,9] was observed as the side reaction of the ring-opening reactions (Scheme 1, path i). Such formation of functionalized cyclopropane derivatives would be unique and important from the viewpoint of both transition metal catalysis and organic synthesis.[11]

SCHEME 1



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(1) (a) Brandi, A.; Goti, A. *Chem. Rev.* **1998**, *98*, 589−635. (b) Binger, P.; Büch, H. M. *Top. Curr. Chem.* **1987**, *135*, 77−151. (c) Ohta, T.; Takaya, H. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 5, p 1185.

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(5) (a) RO−H: Camacho, D. H.; Nakamura, I.; Saito, S.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 3365−3367. (b) Camacho, D. H.; Nakamura, I.; Saito, S.; Yamamoto, Y. *J. Org. Chem.* **2001**, *66*, 270−275.

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(9) Addition of silyl compounds to bicyclopropylidene without ring-opening has been achieved recently. See: Pohlmann, T.; de Meijere, A. *Org. Lett.* **2000**, *2*, 3877−3879.

(10) RS−H, RS−SR: Xu, B.; Chen, Y.; Shi, M. *Tetrahedron Lett.* **2002**, *43*, 2781−2784.

(11) For example; (a) de Meijere, A.; Wessjohann, L. *Synlett* **1990**, 20−32. (b) Brandi, A.; Cordero, F. M.; de Sarlo, F.; Goti, A.; Guarna, A. *Synlett* **1993**, 1−8.

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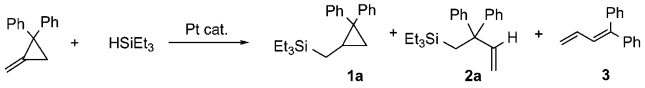
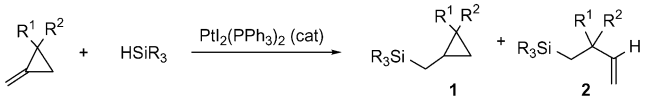
TABLE 1. Hydrosilylation of 2,2-Diphenyl-1-methylenecyclopropane with Triethylsilane[a]



			% yield[d] of product		
entry	catalyst	time/h	**1a**	**2a**	**3**
1[b]	$PtI_2(PPh_3)_2$	1	87[e]	0	0
2[b]	$Pt(H)I(PPh_3)_2$	1	87[e]	0	0
3[b]	$Pt(H)Cl(PPh_3)_2$	1	85[e]	0	0
4[b]	$PtCl_2(PPh_3)_2$	3	68[e]	0	0
5	PtI_2(cod) + PPh_3	6	67	0	9
6	PtI_2(cod) + PCy_3	6	40	47	0
7	PtI_2(cod) + P^tBu_3	6	23	39	17
8	$Pt(PPh_3)_4$	3	58	6	0
9	$H_2PtCl_6 \cdot 6H_2O$	3	trace	23	0
10[c]	$H_2PtCl_6 \cdot 6H_2O$	48	7	0	0
11	$(Bu_4N)_2PtCl_6$	1	6	62	0
12	Pt−C (10%)	48	0	40[e]	0

[a] Reactions of 2,2-diphenyl-1-methylenecyclopropane with triethylsilane (1:2) were carried out in the presence of 3 mol % of a Pt catalyst at 140 °C (cod = 1,5-cyclooctadiene). [b] No solvent was used. [c] In 2-propanol. [d] The yields were determined by ^{1}H NMR based on diphenylmethane as internal standard, unless otherwise stated. [e] Isolated yields.

TABLE 2. Platinum-Catalyzed Hydrosilylation of Methylenecyclopropanes with Hydrosilanes[a]



	methylenecyclopropane			product			
					%		%
entry	R^1	R^2	hydrosilane	**1**	yield[c]	**2**	yield[c]
1	Ph	Ph	$HSiPh_3$	**1b**	53		
2	Ph	Ph	$HSiEt_2Ph$	**1c**	85		
3	Ph	Ph	$HSiPhCl_2$	**1d**	81		
4	Ph	Ph	$HSiCl_3$	**1e**	81		
5	Ph	Ph	$HSi(OEt)_3$		0		
6	Ph	Ph	$HSiMe_2(OEt)$		0		
7	C_6H_4F-4	C_6H_4F-4	$HSiEt_3$	**1f**	80		
8	$(CH_2)_2Ph$	$(CH_2)_2Ph$	$HSiEt_3$	**1g**	46	**2g**	40
9[b]	Ph	Me	$HSiEt_3$	**1h**	27	**2h**	40
10	Ph	H	$HSiEt_3$		0	**2i**	57
11	C_6H_4OMe-4	H	$HSiEt_3$		0	**2j**	37

[a] Reactions of disubstituted methylenecyclopropane with hydrosilane (1:2) were carried out in the presence of 3 mol % of $PtI_2(PPh_3)_2$ without solvent at 80 °C for 4 h (entry 4), for 1 h (entry 5), or at 140 °C for 1 h (other entries). [b] Two diastereomers of **1h** (1:1) and isomeric products **1h** and **2h** were not separated. [c] Isolated yields.

There have been only a few reports of hydrosilylation of methylenecyclopropanes. Rh complexes catalyzed hydrosilylation of (diphenylmethylene)cyclopropane with $HSiEt_3$ was reported to produce (4-triethylsilyl)-1,1-diphenyl-1-butene via ring-opening.[8] Use of unsymmetrically substituted methylenecyclopropanes in the hydrosilylation will render complicated hydrosilylated products, because the substrates have three different (two proximal and one distal) bonds that may be cleaved during the hydrosilylation. We recently found that the stoichiometric reaction of 2,2-disubstituted methylenecyclopropanes with a hydridorhodium complex causes the selective cleavage of the proximal C−C bond triggered by insertion of C=C double bond into the Rh−H bond.[12] It suggests a possibility of selective hydrosilylation of these sterically congested methylenecyclopropanes.

In this paper we report the reactions of triorganosilanes with methylenecyclopropanes catalyzed by platinum complexes, affording silylated cyclopropanes or 1,3-dienes selectively, depending on the kind of catalysts and organosilanes. A part of this work was reported preliminarily.[13]

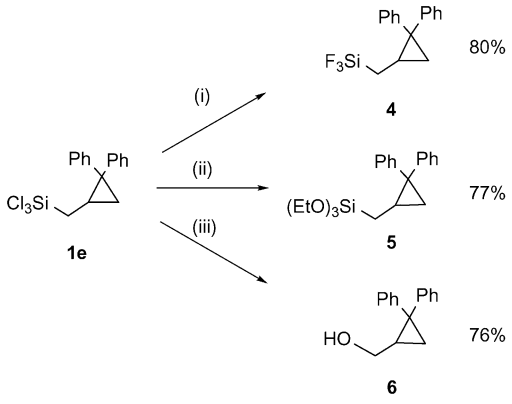
Results and Discussion

Platinum Complex-Catalyzed Hydrosilylation of Methylenecyclopropanes. Table 1 summarizes the results of the reaction of 2,2-diphenyl-1-methylenecyclopropane with $HSiEt_3$ (1:2) in the presence of various Pt complexes. Heating of the mixture and $PtI_2(PPh_3)_2$ catalyst at 140 °C without solvent produces [(2,2-diphenylcyclopropyl)methyl]triethylsilane (**1a**) in 87% isolated yield (entry 1). The reaction in toluene at 110 °C forms not only **1a** (74% by NMR) but also 1,1-diphenyl-1,3-butadiene (**3**, 10%)[14] after 3 h, while that at 110 °C without solvent **1a** is found exclusively (81% by NMR). The hydridoplatinum complexes $PtH(I)(PPh_3)_2$ and $PtH(Cl)(PPh_3)_2$ also catalyze the hydrosilylation to produce **1a** selectively (entries 2 and 3). $PtI_2(PPh_3)_2$ acts as a precursor of $PtH(I)(PPh_3)_2$, which is the actual catalyst of the reaction (vide infra). The reactions catalyzed by $PtCl_2(PPh_3)_2$ and by a mixture of PtI_2(cod) and PPh_3 form **1a** in lower yields (entries 4 and 5). PtI_2(cod) with bulky trialkylphosphine, PCy_3, or P^tBu_3, leads to a mixture of **1a** and (2,2-diphenyl-3-butenyl)triethylsilane (**2a**), the latter of which is formed via hydrosilylation accompanied by ring-opening (entries 6 and 7). Speier's catalyst ($H_2PtCl_6 \cdot 6H_2O$) and $(Bu_4N)_2PtCl_6$, which are the typical catalysts for hydrosilylation of alkenes, and heterogeneous Pt−C (10%) are not active for the hydrosilylation of 2,2-diphenyl-1-methylenecyclopropanes or form **2a** more easily than **1a** (entries 9−12). Several other transition metal complexes, such as $Pd(PPh_3)_4$, Pd−C(10%), Ni(cod)$_2$ (cod = 1,5-cyclooctadiene), and $Ni(PPh_3)_4$, do not catalyze the hydrosilylation of 2,2-diphenyl-1-methylenecyclopropane.

Table 2 summarizes the results of hydrosilylation of various methylenecyclopropanes catalyzed by $PtI_2(PPh_3)_2$. The reactions of 2,2-diphenyl-1-methylenecyclopropane with $HSiPh_3$, $HSiEt_2Ph$, $HSiPhCl_2$, and $HSiCl_3$ produce **1b**−**e** in moderate to high yields (entries 1−4) via the addition of Si−H bond to the C=C double bond without ring-opening. Alkoxysilanes such as $HSi(OEt)_3$ and $HSiMe_2(OEt)$ provide no silylated product at all under similar conditions (entries 5 and 6). The reaction of 2,2-bis(4-fluorophenyl)-1-methylenecyclopropane with $HSiEt_3$ yields the hydrosilylated product **1f** predominantly (entry 7). The reactions of 2,2-bis(2-phenylethyl)-1-methylenecyclopropane and 2-methyl-2-phenyl-1-methylenecyclopropane with $HSiEt_3$ afford mixtures of **1** and **2** in 46:40 and 27:40 ratios, respectively (entries 8 and 9). 2-Phenyl-1-

(12) Nishihara, Y.; Yoda, C.; Osakada, K. *Organometallics* **2001**, *20*, 2124−2126.
(13) Nishihara, Y.; Itazaki, M.; Osakada, K. *Tetrahedron Lett.* **2002**, *43*, 2059−2061.
(14) Drexler, J.; Lindermayer, R.; Hassan, M. A.; Sauer, J. *Tetrahedron Lett.* **1985**, *26*, 2555−2558.

SCHEME 2[a]

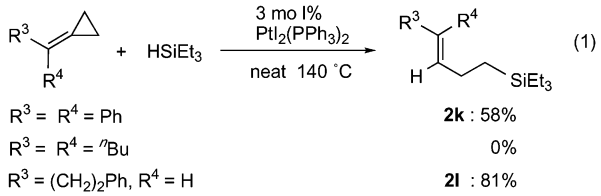


Reagents: (i) $CuF_2{\cdot}2H_2O$, Et_2O, 0 °C, 2 h. (ii) EtOH, NEt_3, rt, 16 h. (iii) H_2O_2, KF, $KHCO_3$, rt, 12 h.

[a] Reagents: (i) $CuF_2{\cdot}2H_2O$, Et_2O, 0 °C, 2 h. (ii) EtOH, NEt_3, rt, 16 h. (iii) H_2O_2, KF, $KHCO_3$, rt, 12 h.

methylenecyclopropane and 2-(4-methoxyphenyl)-1-methylenecyclopropane react with $HSiEt_3$ to give the ring-opened products **2i** and **2j** exclusively (entries 10 and 11).

The reactions of (diphenylmethylene)cyclopropane and of (3-phenylpropylidene)cyclopropane with $HSiEt_3$ afford the ring-opened products **2k**[8] (58%) and **2l** (81%) (eq 1),



similar to the findings of Beletskaya et al. in the reaction catalyzed by $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, or $Rh_2Cl_2(C_4H_6)_4$.[8] (Butylpentylidene)cyclopropane does not undergo hydrosilylation. Preferential formation of the above products suggests the selective proximal bond cleavage during the hydrosilylation.

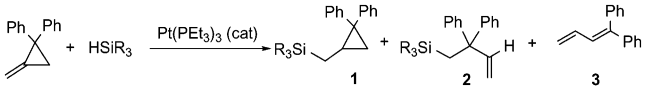
Trichlorosilylated product of the reaction, **1e**, is transformed into functionalized cyclopropane derivatives, as shown in Scheme 2. Fluorination of **1e** using $CuF_2{\cdot}2H_2O$ gives [(2,2-diphenylcyclopropyl)methyl]trifluorosilane (**4**) in 80% yield.[15] [(2,2-Diphenylcyclopropyl)methyl]triethoxysilane (**5**), which is not formed by the direct hydrosilylation of 2,2-diphenylmethylenecyclopropane with $HSi(OEt)_3$ (Table 2, entry 5), is obtained by the reaction of **1e** with EtOH in 77% yield.[15] Oxidation of **1e** with hydrogen peroxide by Tamao's method[16] gives 2,2-diphenylcyclopropylmethanol (**6**)[17] in 76% yield, in which the cyclopropane ring remains intact. These compounds **4** and **5** cannot be prepared directly by alternative methods such as cyclopropanation of the allylsilanes.[18]

(15) Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983−990.

(16) (a) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694−1696. (b) Tamao, K.; Ishida, N. *J. Organomet. Chem.* **1984**, *269*, C37−C39. (c) Tamao, K.; Nakajo, E.; Ito, Y. *J. Org. Chem.* **1987**, *52*, 4412−4414. (d) Tamao, K. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: Chichester, 1985; pp 231−242.

(17) Turnbull, M. D. *Perkin Trans. 1* **1997**, 1241−1247.

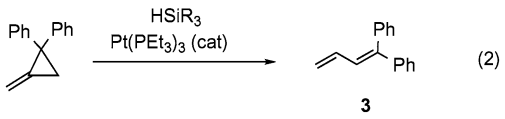
TABLE 3. $Pt(PEt_3)_3$-Catalyzed Isomerization of 2,2-Diphenyl-1-methylenecyclopropane[a]



			% yield[b] of product		
entry	hydrosilane	time/h	**1**	**2**	**3**
1[c]	$HSiEt_3$	3	31	0	49
2	$HSiEt_3$	3	26	0	70
3	$HSiEt_2Ph$	1	8	0	79
4	$HSi(OEt)Me_2$	1	0	0	92
5	$HSi(OEt)_2Me$	1	0	0	82
6[d]		3	0	0	80
7[e]		16	0	0	22
8	$HSi(OEt)_3$	16	0	7	64
9	none	16	0	0	0

[a] Reactions of methylenecyclopropanes with hydrosilanes (1:1) were carried out in the presence of 3 mol % of $Pt(PEt_3)_3$ in toluene at 110 °C. [b] The yields were determined by ^1H NMR based on diphenylmethane as an internal standard. [c] Methylenecyclopropane:hydrosilane = 1:2. [d] Methylenecyclopropane:hydrosilane = 1:0.25. [e] Methylenecyclopropane:hydrosilane = 1:0.03.

$Pt(PEt_3)_3$-Catalyzed Ring-Opening Isomerization of Methylenecyclopropanes. Use of $Pt(PEt_3)_3$ as the catalyst in the presence of $HSiR_3$ causes conversion of 2,2-diphenyl-1-methylenecyclopropane into 1,1-diphenyl-1,3-butadiene (**3**) as the main product (eq 2). The results

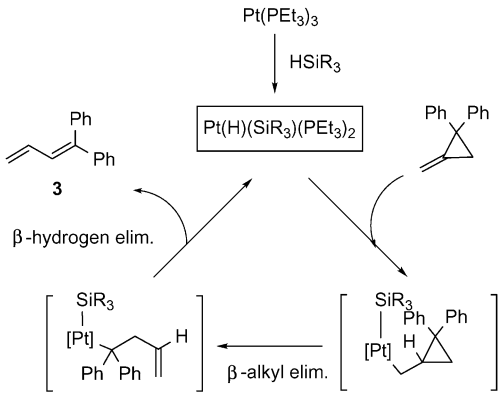


of the reactions with several organosilanes are summarized in Table 3. The reaction of 2,2-diphenyl-1-methylenecyclopropane with $HSiEt_3$ (1:2 molar ratio) gave the mixture of hydrosilylated product **1a** and **3** (entry 1), while **3** was formed in 70% yield by the same reaction using equimolar $HSiEt_3$ to 2,2-diphenyl-1-methylenecyclopropane (entry 2). Introduction of a Ph or OEt group at the Si center facilitates the ring-opening isomerization; addition of $HSiEt_2Ph$ or $HSi(OEt)Me_2$ converts 2,2-diphenyl-1-methylenecyclopropane into **3** selectively (entry 4). The reaction in the presence of $HSi(OEt)Me_2$ (100 and 25 mol %) produces **3** in 82% and 80% (entries 5 and 6), although the yield of **3** decreases to 22% in the presence of 3 mol % of $HSi(OEt)_2Me$ (entry 7). Without the organosilanes, the ring-opening isomerization does not take place at all (entry 9). These results indicate incorporation of the organosilanes in the above ring-opening isomerization.

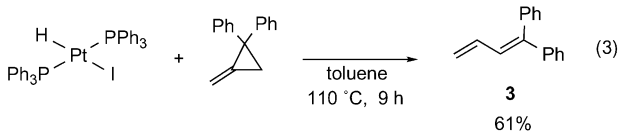
Scheme 3 depicts a plausible pathway of the reaction. The cyclopropylmethylplatinum complex is formed via insertion of 2,2-diphenyl-1-methylenecyclopropane into the Pt−H bond of an intermediate complex, $PtH(SiR_3)(PEt_3)_2$. β-Alkyl elimination[19] of the complex cleaves a proximal C−C bond of the cyclopropyl ring. Subsequent β-hydrogen elimination of the 1,1-diphenyl-3-butenylplatinum intermediate produces **3** and regenerates $PtH(SiR_3)(PEt_3)_2$.

(18) As for the synthesis of cyclopropylmethylsilanes from allylsilanes, see: Fleming, I.; Sanderson, P. E.; Terrett, N. K. *Synthesis* **1992**, 69−74.

SCHEME 3



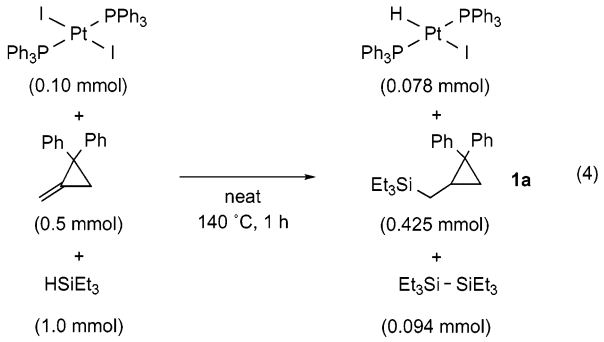
A stoichiometric reaction of 2,2-diphenyl-1-methylenecyclopropane with $Pt(H)I(PPh_3)_2$ causes the ring-opening isomerization to afford **3** in 61% yield at 110 °C (eq 3). The product **3** is formed by insertion of the C=C



(3)

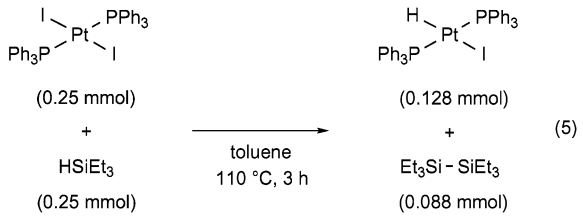
bond into a Pt−H bond, the subsequent C−C bond cleavage to form a 3-butenylplatinum complex, and β-hydrogen elimination similarly to the reaction path in Scheme 3. Analogous ring-opening isomerization of 2,2-diphenyl-1-methylenecyclopropane to **3** was found to be promoted by $RhH(CO)(PPh_3)_3$ by our group.[12] All these results suggest that the ring-opening isomerization promoted by the hydridoplatinum(II) and the hydridorhodium(I) complexes proceeds via the initial C=C bond insertion into the metal hydrido bond, while many ring-opening isomerization promoted by transition metal complexes has been accounted for an alternative pathway from direct oxidative addition of three-membered ring to transition metal.[20]

Reaction Mechanism. Several reactions were conducted in order to obtain further insights into the mechanism of the hydrosilylation of 2,2-diphenyl-1-methylenecycropropane catalyzed by $PtI_2(PPh_3)_2$. The reaction was monitored by ^1H NMR in toluene-d_8 at 110 °C, showing a short induction period (15 min) before parallel increase of **1a** and **3**. It suggests that the starting $PtI_2(PPh_3)_2$ is converted into $PtH(I)(PPh_3)_2$, the active species of the catalyst, during the induction period and that the two products are formed from independent pathways from each other. Use of $PtI_2(PPh_3)_2$ in 20 mol % in the reaction revealed conversion of the starting complex into $Pt(H)I(PPh_3)_2$[21] and formation of the silylated product **1a** (85%) and $Et_3Si-SiEt_3$ (19%) (eq 4).[22]



(4)

The equimolar reaction between $PtI_2(PPh_3)_2$ and $HSiEt_3$ led to formation of $Pt(H)I(PPh_3)_2$ (51%) and $Et_3Si-SiEt_3$ (70%) (eq 5). $PtCl_2(PPh_3)_2$ was converted into Pt(H)Cl-



(5)

$(PPh_3)_2$ during the reaction more slowly than $PtI_2(PPh_3)_2$.

The formation of $Pt(H)X(PPh_3)_2$ (X = Cl, I) is ascribed to the reaction of $HSiEt_3$ with $PtI_2(PPh_3)_2$ to generate $XSiEt_3$. Coupling of Cl and SiR_3 ligands in Ir(III) and Pt(IV) complexes was previously proposed to account for the reaction of excess hydrosilanes with chloro complexes of Ir(I) and Pt(II).[23] We recently reported the reductive elimination of $ClSiR_3$ and of $ISiR_3$ in thermal reaction of Rh(III) complexes with halogeno and SiR_3 ligands.[24]

Scheme 4 summarizes the mechanism of the hydrosilylation and isomerization in this study. Both reactions are initiated by insertion of the C=C bond of methylenecyclopropanes into the Pt−H bond to give intermediate **A**. Direct reductive elimination of **1** takes place preferentially when $PtI_2(PPh_3)_2$ and 2,2-diaryl-1-methylenecyclopropanes are used as the catalyst and substrate. Retention of the cyclopropyl group during the Pt-catalyzed hydrosilylation is explained by the Thorpe−Ingold effect, which suggests high thermodynamic stability of 3,3-disubstituted cyclopropanes.[25] Cleavage of the C−C proximal bonds i and ii of the intermediate **A** by β-alkyl elimination affords the intermediates **B** and **C**, respectively. β-Hydrogen elimination of **3** from 3-butenyl ligand

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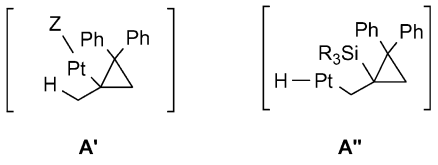
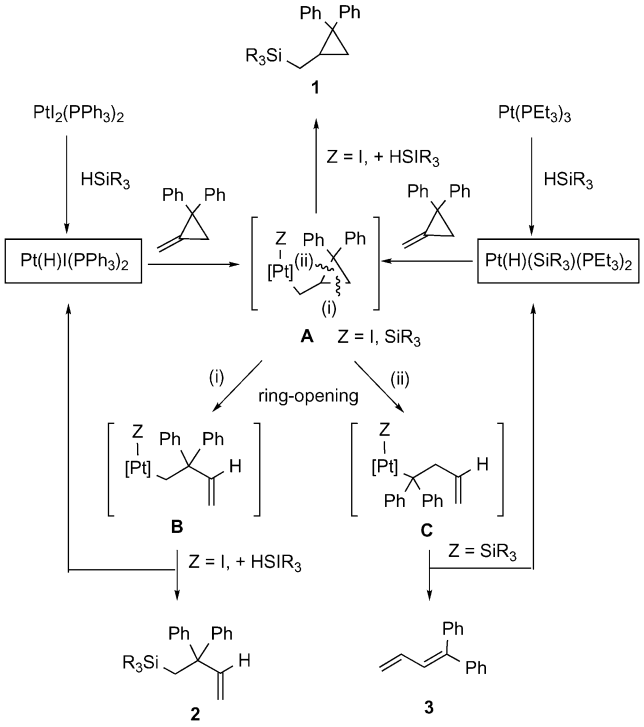


FIGURE 1.

SCHEME 4



of **C** generates the hydridoplatinum complex, whereas the intermediate **B**, which does not undergo β-hydrogen elimination, causes coupling of the silyl and 3-butenyl ligands, leading to the open-chain silylated product **2**. The use of $Pt(PEt_3)_3$ catalyst leads preferentially to the formation of **3** via intermediate **C**. Since other possible Pt species **A′** and **A″** via addition of the H−Pt or Si−Pt bond to the C═C bond of 2,2-diphenyl-1-methylenecyclopropane give neither product **1** nor **2**, they are not related to the reactions in this study (Figure 1). The reaction of the substrate with alkyl substituents at the 2-position of the cyclopropane ring or monosubstituted methylenecyclopropanes causes the hydrosilylation with ring-opening to produce **2**.

In summary, we discovered a new methodology to prepare (cyclopropylmethyl)silanes via hydrosilylation of 2,2-disubstituted methylenecyclopropanes with various hydrosilanes. The results of this study suggest addition of other compounds to the C═C bond of substituted methylenecyclopropanes, which would produce many new cyclopropane derivatives.

Experimental Section

All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or a nitrogen atmosphere. Methylenecyclopropanes,[26] $PtI_2(PPh_3)_2$,[27] and $Pt(PEt_3)_3$[28] were prepared according to the literature methods.

Representative Procedure for Hydrosilylation of Methylenecyclopropane: Preparation of [(2,2-Diphenylcyclopropyl)methyl]triethylsilane (1a). A mixture of 2,2-diphenyl-1-methylenecyclopropane (619 mg, 3 mmol) and triethylsilane (698 mg, 6 mmol), and $PtI_2(PPh_3)_2$ (87 mg, 0.09 mmol, 3 mol %) were heated at 140 °C under argon in a pressure vial. The reaction mixture was diluted with ether and passed through a Celite pad to remove insoluble materials. Evaporation of volatiles afforded a brown oil. Column chromatography (silica gel, hexane, $R_f = 0.56$) followed by bulb-to-bulb distillation (180−190 °C/3 Torr) gave **1a** (840 mg, 87% yield) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.11$ (dd, $J = 14.7$ Hz, 11.7 Hz, 1H), 0.69 (q, $J = 8.0$ Hz, 6H), 1.05 (t, $J = 8.0$ Hz, 9H), 1.05−1.10 (overlapped, 1H), 1.24 (dd, $J = 6.0$ Hz, 5.1 Hz, 1H), 1.47 (dd, $J = 8.7$ Hz, 5.1 Hz, 1H), 1.71 (dddd, $J = 11.7$ Hz, 8.7 Hz, 6.0 Hz, 3.0 Hz, 1H), 7.20−7.48 (m, 10H). ^{13}C NMR (75.3 MHz, $CDCl_3$): $\delta = 3.50$, 7.46, 13.49, 22.74, 23.05, 35.25, 125.38, 126.12, 127.40, 128.12, 131.02, 141.79, 147.83. Anal. Calcd for $C_{22}H_{30}Si$: C, 81.92; H, 9.37. Found: C, 81.91; H, 9.12.

Synthesis of (2,2-Diphenyl-3-butenyl)triethylsilane (2a). A mixture of 2,2-diphenyl-1-methylenecyclopropane (619 mg, 3 mmol) and triethylsilane (698 mg, 6 mmol) was heated at 110 °C in 7 mL of toluene in the presence of Pt−C (10%) (176 mg, 0.09 mmol, 3 mol %). The reaction mixture was diluted with hexane and passed through a Celite pad to remove insoluble materials. Evaporation of volatiles and subsequent column chromatography (silica gel, hexane, $R_f = 0.58$) gave a colorless oil. Bulb-to-bulb distillation (180−190 °C/3 Torr) gave **2a** (381 mg, 40% yield) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.28$ (q, $J = 8.4$ Hz, 6H), 0.81 (t, $J = 8.4$ Hz, 9H), 1.73 (s, 2H), 4.59 (dd, $J = 17.4$ Hz, 1.5 Hz, 1H), 5.15 (dd, $J = 10.5$ Hz, 1.5 Hz, 1H), 6.58 (dd, $J = 17.4$ Hz, 10.5 Hz, 1H), 7.16−7.29 (m, 10H). ^{13}C NMR (75.3 MHz, $CDCl_3$): $\delta = 4.47$, 7.46, 24.59, 52.65, 114.30, 125.82, 127.68, 128.28, 146.44, 148.65. Anal. Calcd for $C_{22}H_{30}Si$: C, 81.92; H, 9.37. Found: C, 81.94; H, 9.30.

[(2,2-Diphenylcyclopropyl)methyl]triphenylsilane (1b) was isolated as a white solid (53% yield). $R_f = 0.10$ (hexane). Mp: 157−158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.77$ (dd, $J = 15.6$ Hz, 11.4 Hz, 1H), 1.14 (t, $J = 5.1$ Hz, 1H), 1.28 (dd, $J = 9.3$ Hz, 5.1 Hz, 1H), 1.85 (dd, $J = 15.6$ Hz, 3.3 Hz, 1H), 1.82−1.93 (m, 1H), 7.11−7.62 (m, 25H). ^{13}C NMR (75.3 MHz, $CDCl_3$): $\delta = 15.09$, 22.05, 23.23, 35.90, 125.48, 126.26, 127.63, 127.82, 128.07, 128.25, 129.43, 130.86, 135.02, 135.76, 141.50, 147.40. Anal. Calcd for $C_{34}H_{30}Si$: C, 87.50; H, 6.48. Found: C, 87.28; H, 6.49.

[(2,2-Diphenylcyclopropyl)methyl]diethylphenylsilane (1c) was isolated as a colorless oil (85% yield). $R_f = 0.43$ (hexane:ethyl acetate = 10:1). Bp: 210 °C/3 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.11$ (dd, $J = 15.0$ Hz, 11.4 Hz, 1H), 0.86−1.08 (m, 10H), 1.15 (dd, $J = 6.0$ Hz, 4.8 Hz, 1H), 1.27 (dd, $J = 15.0$ Hz, 3.0 Hz, 1H), 1.35 (dd, $J = 8.7$ Hz, 4.8 Hz, 1H), 1.67 (dddd, $J = 11.4$ Hz, 8.7 Hz, 6.0 Hz, 3.0 Hz, 1H), 7.13−7.57 (m, 15H). ^{13}C NMR (75.3 MHz, $CDCl_3$): $\delta = 3.67$, 3.84, 7.41, 7.46, 13.97, 22.37, 22.93, 35.33, 125.41, 126.16, 127.47, 127.67, 128.09, 128.16, 128.79, 130.93, 134.19, 137.18, 141.69, 147.63. Anal. Calcd for $C_{26}H_{30}Si$: C, 84.26; H, 8.16. Found: C, 84.19; H, 8.11.

[(2,2-Diphenylcyclopropyl)methyl]dichlorophenylsilane (1d) was isolated as a pale yellow oil (81% yield). Bp: 220 °C/3 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.64$ (dd, $J = 15.0$ Hz, 10.8 Hz, 1H), 1.25 (t, $J = 5.4$ Hz, 1H), 1.39 (dd, $J = 8.7$ Hz, 5.4 Hz, 1H), 1.72 (dd, $J = 15.0$ Hz, 3.6 Hz, 1H),

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1.82 (m, 1H), 7.11−7.35 (m, 10H), 7.42−7.52 (m, 3H), 7.70−7.73 (m, 2H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 20.05, 21.98, 22.77, 35.16, 125.83, 126.61, 127.60, 128.23, 128.31, 128.44, 130.71, 131.63, 132.44, 133.44, 140.89, 146.58. Anal. Calcd for $C_{22}H_{20}Cl_2Si$: C, 68.92; H, 5.26. Found: C, 69.31; H, 5.49.

[(2,2-Diphenylcyclopropyl)methyl]trichlorosilane (1e) was isolated as a colorless oil (81% yield). Bp 150 °C/3 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.68 (dd, J = 15.3 Hz, 10.8 Hz, 1H), 1.36 (t, J = 4.8 Hz, 1H), 1.46 (dd, J = 9.0 Hz, 5.3 Hz, 1H,), 1.76 (dd, J = 15.3 Hz, 5.3 Hz, 1H), 1.78−1.92 (m, overlapped, 1H), 7.22−7.48 (m, 10H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 19.37, 21.54, 26.09, 35.20, 126.04, 126.84, 127.57, 128.32, 128.57, 130.60, 140.49, 146.08. Anal. Calcd for $C_{16}H_{15}Cl_3Si$: C, 56.23; H, 4.42; Cl, 31.12. Found: C, 56.34; H, 4.66; Cl, 30.94.

[2,2-Bis(4-fluorophenyl)cyclopropylmethyl]triethylsilane (1f) was isolated as a colorless oil (80% yield). R_f = 0.39 (hexane). Bp: 180 °C/3 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.30 (dd, J = 15.0 Hz, 11.7 Hz, 1H), 0.55 (q, J = 8.1 Hz, 6H), 0.87−0.93 (overlapped, 1H), 0.91 (t, J = 8.1 Hz, 9H), 1.04 (dd, J = 6.0 Hz, 4.5 Hz, 1H), 1.27 (dd, J = 8.7 Hz, 4.5 Hz, 1H), 1.51 (dddd, J = 11.7 Hz, 8.7 Hz, 6.0 Hz, 3.0 Hz, 1H), 6.86−6.92 (m, 2H), 6.96−7.02 (m, 2H), 7.06−7.11 (m, 2H), 7.23−7.27 (m, 2H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 3.46, 7.44, 13.41, 22.47, 22.93, 34.00, 114.85 (d, J = 21 Hz), 115.13 (d, J_{C-F} = 21 Hz), 128.90 (d, J_{C-F} = 8 Hz), 132.18 (d, J_{C-F} = 8 Hz), 137.50 (d, J_{C-F} = 3 Hz), 143.30 (d, J_{C-F} = 3 Hz), 159.56 (d, J_{C-F} = 244 Hz), 162.80 (d, J_{C-F} = 244 Hz). Anal. Calcd for $C_{22}H_{28}F_2Si$: C, 73.70; H, 7.87; F, 10.60. Found: C, 74.11; H, 7.86; F, 10.10.

[2,2-Bis(phenylethyl)cyclopropylmethyl]triethylsilane (1g) was isolated as a colorless oil (46% yield). R_f = 0.35 (hexane). Bp: 220 °C/3 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.14 (t, J = 4.4 Hz, 1H), 0.24 (dd, J = 14.7 Hz, 10.2 Hz, 1H), 0.43−0.56 (m, 2H), 0.55 (q, J = 8.0 Hz, 6H), 0.84 (dd, J = 14.7 Hz, 3.0 Hz, 1H), 0.93 (t, J = 8.0 Hz, 9H), 1.43−1.80 (m, 4H), 2.60−2.83 (m, 4H), 7.13−7.30 (m, 10H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 3.47, 7.51, 10.74, 19.85, 20.42, 23.65, 32.87, 33.08, 33.41, 40.03, 125.61, 125.63, 128.28, 128.32, 142.91, 143.20. Anal. Calcd for $C_{26}H_{38}Si$: C, 82.47; H, 10.11. Found: C, 82.57; H, 9.85.

[2,2-Bis(2-phenylethyl)-3-butenyl]triethylsilane (2g) was isolated as a colorless oil (40% yield). R_f = 0.45 (hexane). Bp: 220 °C/3 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.64 (q, J = 7.8 Hz, 6H), 0.93 (s, 2H), 0.99 (t, J = 7.8 Hz, 9H), 1.77−1.83 (m, 4H), 2.57−2.63 (m, 4H), 5.05 (dd, J = 17.7 Hz, 1.5 Hz, 1H), 5.12 (dd, J = 11.1 Hz, 1.5 Hz, 1H), 5.88 (dd, J = 17.7 Hz, 11.1 Hz, 1H), 7.20−7.36 (m, 10H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 5.07, 7.59, 22.31, 30.56, 41.13, 42.07, 111.99, 125.66, 128.29, 128.38, 143.08, 147.71. Anal. Calcd for $C_{26}H_{38}Si$: C, 82.47; H, 10.11. Found: C, 82.75; H, 10.16.

[(2-Methyl-2-phenylcyclopropyl)methyl]triethylsilane (1h) and (2-Methyl-2-phenyl-3-butenyl)triethylsilane (2h) were obtained in 67% yield as a mixture in 41 (two diastereomers 1:1):59 (determined by ^{1}H NMR) molar ratio, respectively. R_f = 0.71 (hexane). Bp: 145 °C/3 Torr. Although all of signals in ^{1}H NMR were not assigned, the characteristic signals indicate the formation of **1h** and **2h**. ^{1}H NMR (300 MHz, $CDCl_3$) for **1h** (for two diastereomers): δ = −0.39 (dd, J = 14.7 Hz, 10.8 Hz, 1H), 0.43−0.47 (m, 1H), 0.54 (q, J = 8.1 Hz, 6H), 0.63 (q, J = 8.1 Hz, 6H), 0.65−0.72 (m, 1H), 0.82−0.91 (m, 1H), 0.91−1.04 (m, 1H), 0.93 (t, J = 8.1 Hz, 9H), 1.00 (t, J = 8.1 Hz, 9H), 1.01−1.05 (m, 1H), 1.18−1.30 (m, 4H), 1.39 (s, 3H), 1.49 (s, 3H), 7.15−7.38 (m, 10H). ^{1}H NMR (300 MHz, $CDCl_3$) for **2h**: δ = 0.28−0.34 (m, 1H), 0.42 (dq, J = 7.8 Hz, 3.5 Hz, 6H), 0.88 (t, J = 7.8 Hz, 9H), 1.14−1.18 (m, 1H), 1.42 (s, 3H), 5.05 (dd, J = 10.5 Hz, 1.2 Hz, 1H), 5.08 (dd, J = 17.1 Hz, 1.2 Hz, 1H), 6.12 (dd, J = 17.1 Hz, 10.5 Hz, 1H), 7.15−7.28 (m, 5H). ^{13}C NMR (75.3 MHz, $CDCl_3$) for **1h** (for two diastereomers): δ = 3.41, 3.44, 7.45, 7.49, 11.13, 12.91, 21.43, 22.47, 23.76, 25.70 (overlapped with two carbons), 26.16, 27.80, 28.47, 125.62, 125.67, 126.43, 127.91, 128.14, 129.55, 148.99, 149.31. ^{13}C NMR (75.3 MHz, $CDCl_3$) for **2h**: δ = 4.60, 7.40, 19.95, 22.81, 43.28, 110.24, 125.09, 126.28, 127.97, 144.13, 149.26. Anal. Calcd for $C_{17}H_{28}Si$: C, 78.38; H, 10.61. Found: C, 78.23; H, 10.61.

(2-Phenyl-3-butenyl)triethylsilane (2i) was isolated as a colorless oil (57% yield). R_f = 0.68 (hexane). Bp: 140 °C/3 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.43−0.52 (dq, J = 8.1 Hz, 4.2 Hz, 6H), 0.93 (t, J = 8.1 Hz, 9H), 1.12 (d, J = 7.8 Hz, 2H), 3.46 (dt, J = 7.8 Hz, 7.8 Hz, 1H), 4.98 (ddd, J = 9.9 Hz, 1.5 Hz, 0.9 Hz, 1H), 5.06 (dt, J = 17.1 Hz, 1.5 Hz, 1H), 6.04 (ddd, J = 17.1 Hz, 9.9 Hz, 7.8 Hz, 1H), 7.20−7.36 (m, 5H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 3.63, 7.34, 18.44, 45.76, 112.30, 126.06, 127.31, 128.35, 145.00, 146.56. Anal. Calcd for $C_{16}H_{22}Si$: C, 77.97; H, 10.63. Found: C, 77.80; H, 10.37.

(2-*p*-Methoxyphenyl-3-butenyl)triethylsilane (2j) was isolated as a colorless oil (37% yield). R_f = 0.60 (hexane:ethyl acetate = 10:1). Bp: 120 °C/3 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.39−0.48 (dq, J = 8.1 Hz, 4.5 Hz, 6H), 0.89 (t, J = 8.1 Hz, 9H), 1.05 (d, J = 7.5 Hz, 2H), 3.38 (dt, J = 7.5 Hz, 1H), 3.80 (s, 3 H), 4.91 (ddd, J = 9.9 Hz, 1.5 Hz, 1H), 4.98 (ddd, J = 17.1 Hz, 1.5 Hz, 1H), 5.97 (m, J = 17.1 Hz, 9.9 Hz, 1H), 6.84 (d, J = 9.0 Hz, 2H), 7.14 (d, J = 9.0 Hz, 2H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 3.65, 7.35, 18.44, 44.84, 55.24, 111.88, 113.74, 128.19, 138.64, 145.39, 157.93. Anal. Calcd for $C_{17}H_{28}Si$: C, 73.85; H, 10.21. Found: C, 73.44; H, 10.07.

(4,4-Diphenyl-3-butenyl)triethylsilane (2k) was isolated as a colorless oil (58% yield). R_f = 0.45 (hexane). Bp: 185 °C/3 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.49 (q, J = 8.0 Hz, 6H), 0.71 (m, 2H), 0.91 (t, J = 8.0 Hz, 9H), 2.13 (m, 2 H), 6.16 (t, J = 7.7 Hz, 1H), 7.19−7.42 (m, 10H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 3.24, 7.36, 11.97, 24.04, 126.64, 126.80, 127.15, 128.04, 128.07, 129.89, 133.01, 139.95, 140.18, 142.88. Anal. Calcd for $C_{22}H_{30}Si$: C, 81.92; H, 9.37. Found: C, 81.54; H, 9.40.

Triethyl(6-phenyl-3-hexenyl)silane (2l) was isolated in 81% yield as a colorless oil. R_f = 0.74 (hexane). Bp: 155 °C/3 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.56 (q, J = 8.1 Hz, 6H), 0.63 (m, 2H), 0.98 (t, J = 8.1 Hz, 9H), 2.04 (m, 2H), 2.34 (m, 2H), 2.72 (dd, J = 10.2, 8.1 Hz, 2H), 5.48 (dt, J = 15.3 Hz, 6.3 Hz, 1H), 5.56 (dt, J = 15.3 Hz, 6.3 Hz, 1H), 7.20−7.35 (m, 5H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 3.35, 7.43, 11.32, 26.78, 34.39, 36.16, 125.67, 127.70, 128.22, 128.44, 134.05, 142.24. Anal. Calcd for $C_{18}H_{30}Si$: C, 78.75; H, 11.01. Found: C, 78.63; H, 10.80.

Fluorination of 1e: Synthesis of [(2,2-Diphenylcyclopropyl)methyl]trifluorosilane (4). To a suspension of CuF_2·$2H_2O$ (2.06 g, 15 mmol) in diethyl ether (20 mL) in a 50 mL of Schlenk tube was added slowly **1e** (1.71 g, 5.00 mmol) at 0 °C, and the mixture was stirred at ambient temperature for 2 h under Ar atmosphere. The reaction mixture was diluted with diethyl ether and passed through a Celite pad to remove insoluble materials. Evaporation of volatiles afforded a brown oil, which was subjected to bulb-to-bulb distillation (130−140 °C/3 Torr), giving **4** (1.17 g, 80% yield) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.50 (ddq, J = 15.9 Hz, 10.2 Hz, J_{H-F} = 3.0 Hz, 1H), 1.24−1.33 (m, overlapped, 1H), 1.32 (t, J = 5.1 Hz, 1H), 1.48 (dd, J = 8.7 Hz, 5.1 Hz, 1H), 1.84 (m, 1H), 7.18−7.43 (m, 10H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 9.11 (q, J_{C-F} = 18 Hz), 17.66, 21.11, 36.03, 126.09, 126.86, 127.67, 128.34, 128.60, 130.59, 140.25, 146.07. ^{19}F NMR (282.3 MHz, $CDCl_3$): δ = −137.14 (satellite, J_{Si-F} = 286 Hz). IR (KBr): 3085, 3061, 3027, 2934, 2897, 1599, 1497, 1447, 1219 cm^{-1}. Anal. Calcd for $C_{16}H_{15}F_3Si$: C, 65.73; H, 5.17. Found: C, 66.10; H, 5.23.

Alkoxylation of 1e: Synthesis of [(2,2-Diphenylcyclopropyl)methyl]triethoxysilane (5). To the mixture of 1 mL of EtOH, 2 mL of Et_3N, and 150 mL of pentane was added **1e** (1.02 g, 3.00 mmol) at ambient temperature with vigorous stirring. The resulting white suspension was stirred for 16 h and then filtered through a Celite pad. Evaporation of volatiles afforded a pale yellow oil. Bulb-to-bulb distillation (180−190 °C/3 Torr) gave **5** (0.86 g, 77% yield) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.04 (dd, J = 15.3 Hz, 10.2 Hz, 1H),

0.93 (dd, J = 15.3 Hz, 3.9 Hz, 1H), 1.19 (t, J = 7.2 Hz, 9H), 1.14−1.20 (overlapped, 1H), 1.32 (dd, J = 9.0 Hz, 4.8 Hz, 1H), 1.68 (dddd, J = 10.2 Hz, 9.0 Hz, 6.0 Hz, 3.9 Hz, 1H), 3.78 (q, J = 7.2 Hz, 6H), 7.05−7.31 (m, 10H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 12.51, 18.28, 20.83, 22.50, 35.52, 58.36, 125.46, 126.19, 127.57, 128.07, 128.15, 130.95, 141.43, 147.49. Anal. Calcd for $C_{22}H_{30}O_3Si$: C, 71.31; H, 8.16. Found: C, 71.56; H, 8.44.

Preparation of 2,2-Diphenylcyclopropylmethanol (6). To a suspension of KF (1.73 g, 30.0 mmol) and $KHCO_3$ (6.00 g, 60.0 mmol) in 240 mL of THF/MeOH (1:1) was added **1e** (1.71 g, 5.00 mmol) at room temperature and the mixture was stirred for 1 h. To the resulting white suspension was added 4.98 mL of 30% H_2O_2 at room temperature. Then the reaction mixture was vigorously stirred for 12 h. To this reaction mixture was added 6 g of $Na_2S_2O_3{\cdot}5H_2O$ and then the entire mixture was stirred for 1 h. The mixture was filtered through a Celite plug, and the filter cake was rinsed with 50 mL of diethyl ether. The filtrate was concentrated under vacuum and the resulting residue was dissolved in 50 mL of CH_2Cl_2. After drying over $MgSO_4$, the volatiles were removed in vacuo to afford a a colorless liquid. Bulb-to-bulb distillation (190−200 °C/4 Torr) gave **6** (0.856 g, 76% yield) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = −1.25 (dd, J = 9.0 Hz, 5.1 Hz, 1H), 1.35 (t, J = 5.1 Hz, 1H), 1.64 (br s, 1H, OH), 1.96 (m, 1H), 3.34 (dd, J = 11.4 Hz, 7.8 Hz, 1H), 3.42 (dd, J = 11.4 Hz, 6.3 Hz, 1H), 7.09−7.39 (m, 10H). ^{13}C NMR (75.3 MHz, $CDCl_3$): δ = 17.89, 27.65, 35.55, 63.69, 125.91, 126.62, 127.77, 128.23, 128.48, 130.06, 141.03, 146.23. Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.65; H, 7.21.

Reaction of 2,2-Diphenyl-1-methylenecyclopropane with Triethylsilane on NMR Tube Scale. To a toluene-d_8 (0.6 mL) solution of $PtI_2(PPh_3)_2$ (2.9 mg, 3×10^{-3} mmol, 3 mol %) in an NMR tube were added 2,2-diphenyl-1-methylenecyclopropane (206.3 mg, 0.1 mmol) and triethylsilane (23.3 mg, 0.2 mmol). The NMR sample tube was sealed and heated at 110 °C. The NMR spectra were recorded at 110 °C over 200 min. After 200 min, **1a** and **3** were formed in 64% and 22% yield, respectively.

Reaction of 2,2-Diphenyl-1-methylenecyclopropane with an Equimolar Amount of $PtH(I)(PPh_3)_2$ (eq 3). To a toluene-d_8 (0.6 mL) solution of $PtH(I)(PPh_3)_2$ (21 mg, 0.025 mmol) was added 2,2-diphenyl-1-methylenecyclopropane (5.1 μL, 0.025 mmol). The mixture was heated at 110 °C for 9 h to give 1,1-diphenyl-1,3-butadiene (**3**) in 61% yield. Data of **3**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.11 (ddd, J = 10.2 Hz, 1.8 Hz, 0.9 Hz, 1H), 5.38 (ddd, J = 16.8 Hz, 1.8 Hz, 0.9 Hz, 1H), 6.43 (ddd, J = 16.8 Hz, 11.1 Hz, 10.2 Hz, 1H), 6.70 (d, J = 11.1 Hz, 1H), 7.19−7.40 (m, 10H).

Reaction of 2,2-Diphenyl-1-methylenecyclopropane with $HSiEt_3$ in the Presence of 20 mol % of $PtI_2(PPh_3)_2$ (eq 4). To $PtI_2(PPh_3)_2$ (97 mg, 0.10 mmol) in a 20 mL of Schlenk tube were added 2,2-diphenyl-1-methylenecyclopropane (50 μL, 0.5 mmol) and triethylsilane (160 μL, 1.0 mmol). The reaction mixture was heated at 140 °C. After 1 h, the reaction mixture were washed with hexane (10 mL × 3 times) and dried in vacuo to give $Pt(H)I(PPh_3)_2$ (66 mg, 0.078 mmol, 78% based on Pt complex). The combined hexane solutions were concentrated under vacuum to give a brown oil. After addition of diphenylmethane (42 mg, 0.25 mmol) as an internal standard, ^{1}H NMR measurement revealed that [(2,2-diphenylcyclopropyl)methyl]triethylsilane (**1a**; 0.425 mmol, 85% based on methylenecyclopropane) and hexaethyldisilane (0.094 mmol, 19% based on hydrosilane) were formed.

Reaction of $HSiEt_3$ with $PtI_2(PPh_3)_2$ (eq 5). To a toluene (5 mL) solution of $PtI_2(PPh_3)_2$ (244 mg, 0.25 mmol) was added $HSiEt_3$ (29 mg, 0.25 mmol). The reaction mixture was heated at 110 °C for 3 h. The volatiles were evaporated in vacuo to give the dark brown oily substances, and the addition of hexane gave a pale brown precipitate, which was washed with hexane (5 mL × 3) and dried under vacuum to yield a mixture of the unreacted $PtI_2(PPh_3)_2$ and $PtH(I)(PPh_3)_2$ (0.13 mmol, 51% NMR yield based on Pt complex). From the hexane extracts hexaethyldisilane was isolated (20 mg, 0.088 mmol, 70% isolated yield based on hydrosilane) as a colorless oil.

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