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Platinum complex-catalyzed hydrosilylation of 2,2-diaryl-1-methylenecyclopropane affording (silylmethyl)cyclopropane

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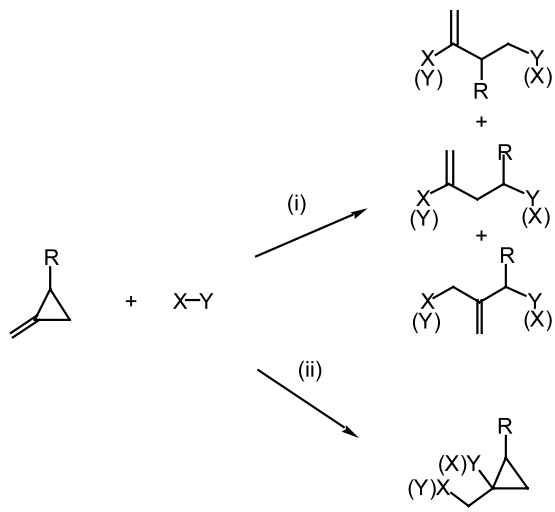
Abstract—$PtI_2(PPh_3)_2$-catalyzed hydrosilylation of 2,2-diphenyl-1-methylenecyclopropane with $HSiEt_3$ forms (2,2-diphenylcyclopropyl)methyl(triethyl)silane in 87% yield as a sole product. This highly selective addition of Si–H bond converts 2,2-diaryl-1-methylenecyclopropane into its silylated derivative without ring-opening. © 2002 Elsevier Science Ltd. All rights reserved.

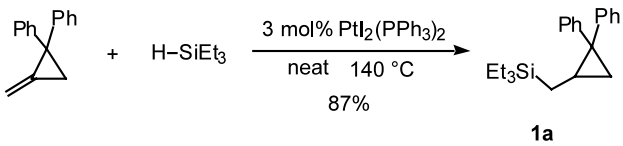
Methylenecyclopropanes[1] are reactive owing to the presence of an olefinic moiety and to the high strain energy of the molecule, and are utilized as building blocks of versatile synthetic organic reactions. Single bond addition of organic molecules (X–Y) to methylenecyclopropane promoted by transition metal complexes causes functionalization accompanied by ring-opening (Scheme 1 (i)).[2–8] Addition to the C=C double bond of methylenecyclopropanes, shown in Scheme 1 (ii), forms a functionalized cyclopropane derivative.[9] Such a reaction, however, was reported only as a minor side-reaction of the X–H addition to methylenecyclopropanes.[2,3,6] In this paper we report Pt complex-catalyzed hydrosilylation of 2,2-disubstituted-1-methylenecyclopropanes, affording the silylated cyclopropanes in high yields and selectivity.

The reaction of triethylsilane with 2,2-diphenyl-1-methylenecyclopropane in the presence of $PtI_2(PPh_3)_2$ (3 mol%) at 140°C afforded (2-triethylsilylmethyl)-1,1-diphenylcyclopropane (**1a**) in 87% yield (Scheme 2).[10]

The ^1H NMR spectrum of the reaction mixture showed no formation of other possible cyclic and acyclic organosilanes. The use of hydrido(halogeno)platinum complexes gave rise to the formation of **1a** in comparable yields, 87% ($Pt(H)I(PPh_3)_2$) and 85% ($Pt(H)Cl(PPh_3)_3$). Other platinum catalysts led to formation of **1a** in lower yields, 67% ($PtCl_2(PPh_3)_2$) and 58% ($Pt(PPh_3)_4$).[11] Table 1 summarizes the reactions of 2,2-disubstituted-1-methylenecyclopropanes with various organosilanes. The reaction catalyzed by $PtI_2(PPh_3)_2$ in toluene (0.07 M substrate) produces 1,1-diphenyl-1,3-butadiene (10%), which causes a decrease of the yield of **1a** to 74%.



Scheme 1.



Scheme 2.

Keywords: cyclopropanes; silicon and compounds; addition reactions; platinum; Thorpe–Ingold effect.

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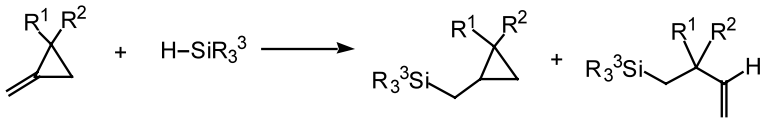
Table 1. Platinum-catalyzed hydrosilylation of methylenecyclopropanes with hydrosilanes[a]



1 **2**

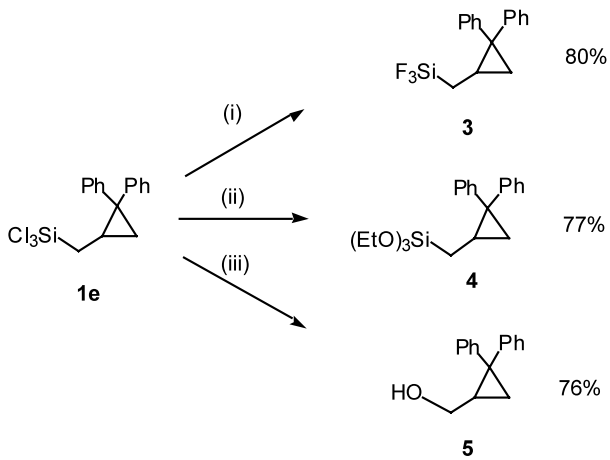
Entry	Methylenecyclopropane		Hydrosilane	Product			
	R^1	R^2		**1**	Yield (%)[b]	**2**	Yield (%)[b]
1	Ph	Ph	$HSiEt_3$	**1a**	87		
2	Ph	Ph	$HSiPh_3$	**1b**	53		
3	Ph	Ph	$HSiEt_2Ph$	**1c**	85		
4	Ph	Ph	$HSiPhCl_2$	**1d**	81		
5	Ph	Ph	$HSiCl_3$	**1e**	81		
6	Ph	Ph	$HSi(OEt)_3$		0		
7	Ph	Ph	$HSiMe_2(OEt)$		0		
8	C_6H_4F-4	C_6H_4F-4	$HSiEt_3$	**1f**	80		
9	$(CH_2)_2Ph$	$(CH_2)_2Ph$	$HSiEt_3$	**1g**	46	**2g**	40
10[c]	Ph	Me	$HSiEt_3$	**1h**	27	**2h**	40
11	Ph	H	$HSiEt_3$		0	**2i**	57

[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] Isolated yields, unless otherwise specified.
[c] Two diastereomers of **1h** (1:1) and isomeric products **1h** and **2h** were not separated.

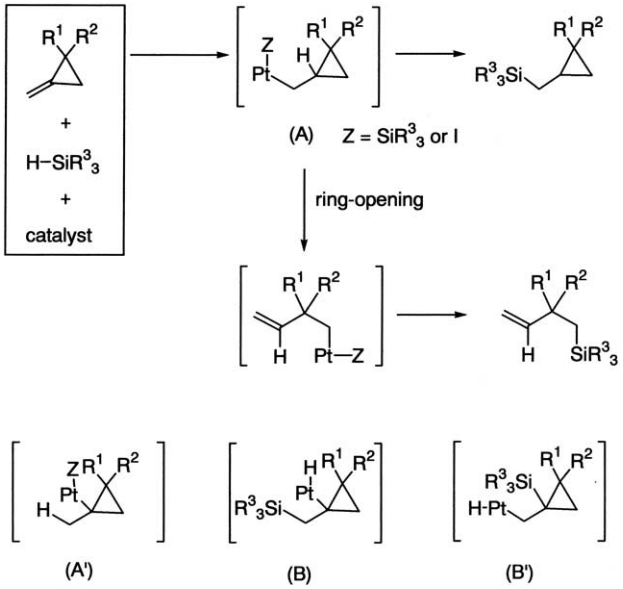
The reaction of triorganosilanes with 2,2-diaryl-1-methylenecyclopropane produces the (silylmethyl)-cyclopropanes as a sole product in 53–87% yields (entries 1–3 and 8). Chlorosilanes, such as $HSiPhCl_2$ and $HSiCl_3$, yielded analogous hydrosilylation products **1d** and **1e** in 81 and 81% yields, respectively (entries 4 and 5). Alkoxysilanes $HSi(OEt)_3$ and $HSiMe_2(OEt)$ did not cause the hydrosilylation. The methylenecyclopropanes bearing a 2-phenethyl or methyl substituent at 2-position afforded mixtures of (silylmethyl)-cyclopropane **1** and 3-butenyl(triethyl)silane **2** (entries 9 and 10). The latter product is formed via hydrosilylation accompanied by ring opening. 2-Phenyl-1-methylenecyclopropane reacts with $HSiEt_3$ to give the ring-opened product **2i** exclusively (entry 11).

Scheme 3 depicts the transformation of **1e** into cyclopropane derivatives with other functional groups. Fluorination and alkoxylation lead to the fluorosilane **3** and alkoxysilane **4**, respectively.[12] Tamao oxidation[13] of **1e** using H_2O_2, KF and $KHCO_3$ gave (2-hydroxymethyl)-1,1-diphenylcyclopropane (**5**) in 76% yield.

The hydrosilylation product presented in this study is accounted for by the reaction mechanism shown in Scheme 4. Simple Chalk–Harrod type hydrosilylation of methylenecyclopropane via intermediate (A) (Scheme 4)[14] forms the (cyclopropylmethyl)silanes that are the products of the reactions in Table 1 (entries 1–5 and 8). Although the addition of a H–Si bond in the modified Chalk–Harrod manner via intermediate (B) would also give the same product, it is much less favorable due to steric congestion of the intermediate. Other possible Pt species (A′) and (B′) via addition of H–Pt or Si–Pt bonds do not give the products in Table 1; they are not related to the reactions in this study. The reaction of the substrate with alkyl substituents at the cyclopropyl group initially forms the intermediate (A), which undergoes silylation of the intermediate accompanied by C–C bond cleavage of the three-membered ring via β-alkyl elimination.[15] β-Alkyl elimination of the cyclopropylmethyl complex was proposed to be involved in the ring-opening of 2,2-diaryl-1-methylenecyclopropanes, giving 1,1-diaryl-1,3-butadienes, promoted by a hydridorhodium complex.[16] The above kinetic reason for retaining the cyclopropyl group in the Pt-catalyzed hydrosilylation seems to be as important as the thermodynamic stability of disubstituted cyclopropanes, explained by the Thorpe–Ingold effect.[17]



Scheme 3. *Reagents and conditions*: (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.



Scheme 4.

In summary, we discovered a new methodology to prepare (cyclopropylmethyl)silanes via hydrosilylation of 2,2-disubstituted methylenecyclopropanes catalyzed by the Pt complex. It is in sharp contrast to Rh-catalyzed hydrosilylation of methylenecyclopropanes, which mainly provides the open-chain products.[8]

Acknowledgements

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10. Representative procedure for hydrosilylation of methylenecyclopropane: Synthesis of **1a**. The 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%) was heated to 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, $R_f = 0.56$) gave colorless oil. Bulb to bulb distillation (180–190°C/3 Torr) gave **1a** (840 mg, 87% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ –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{^{1}H} NMR ($CDCl_3$, 75.3 MHz): δ 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; IR (KBr): 3083, 3060, 3025, 2998, 2953, 2874, 1599, 1495, 1456, 1445, 1416, 1238 cm^{-1}. Anal. calcd for $C_{22}H_{30}Si$: C, 81.92; H, 9.37. found: C, 81.91; H, 9.12.
11. Several other catalysts were found to be ineffective for the formation of **1a**: H_2PtCl_6 (7%), Pd–C (0%), $Pd(PPh_3)_4$ (0%), $Ni(cod)_2$ (cod = 1,5-cyclooctadiene) (trace), and $Ni(PPh_3)_4$ (0%).
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