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STEREOSPECIFIC PHENYLATION OF ALKENYLSILANES WITH PHENYLPALLADIUM ACETATE

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Abstract: (E)- and (Z)-RCH=CHSiMe$_3$(R=Ph, n-C$_6$H$_{13}$, CH$_3$OCH$_2$) reacted stereospecifically with Ph-Pd-OAc to give RCH=C(Ph)SiMe$_3$ and R(Ph)C=CHSiMe$_3$ with inversion of the starting geometry with respect to R and Me$_3$Si groups.

Alkenylsilanes are known to react regio- and stereospecifically with a wide range of electrophiles.[1] Palladium(II) salts reacted with (E)-1a or (E)-PhCH=CHSiF$_5^{2-}$ to give (E)-PhCH=CH-Pd-X as a key intermediate with retention of their geometry.[2,3] Unfortunately, the corresponding (Z)-isomers were not investigated in those reactions. Recently we reported non-regio- and non-stereospecific aryldesilylation of (E)- and (Z)-1a by [Ar-Pd]$^+$BF$_4^-$ generated from ArN$_2$BF$_4$ and Pd(0)(dba)$_2$ catalytically(eq. 1).[4]

$$\underset{\underline{1a}}{PhCH=CH\backsim SiMe_3} + [Ar\text{-}Pd]^+BF_4^- \longrightarrow \underset{\underline{4a}}{(E)\text{-}PhCH=CHAr} + \underset{\underline{5a}}{Ph(Ar)C=CH_2} \quad (1)$$

We now report stereospecific phenylation of alkenylsilanes((E)- and (Z)-1a-c) with Ph-Pd-OAc generated *in situ* from various sources, i.e., catalytically from the combination of PhN(NO)COCH$_3$ and Pd(0)(dba)$_2$(eq. 2),[5] or by stoichiometric reaction of Pd(II)(OAc)$_2$ with SbPh$_3$ or PPh$_3$(eq. 3).[6,7]

$$PhN(NO)COCH_3 \longrightarrow PhN_2OAc \xrightarrow[-N_2]{Pd(0)(dba)_2} Ph\text{-}Pd\text{-}OAc \quad (2)$$

$$MPh_3(M=Sb \text{ or } P) + Pd(II)(OAc)_2 \longrightarrow Ph\text{-}Pd\text{-}OAc + MPh_2(OAc) \quad (3)$$

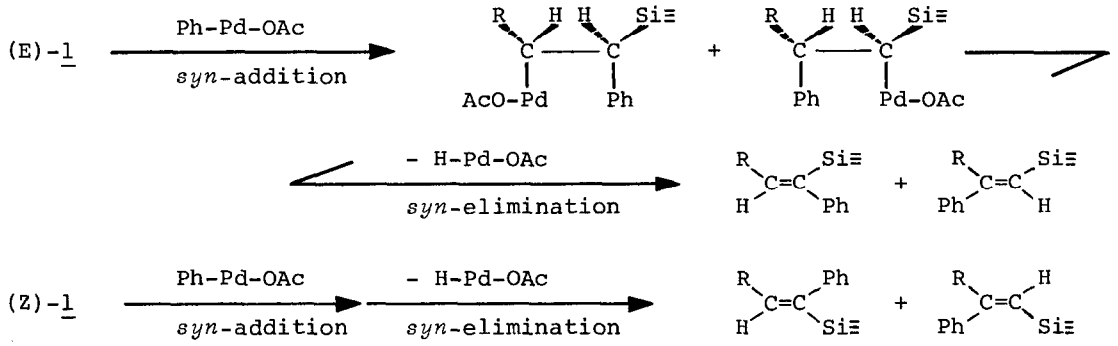
In contrast to the case with [Ph-Pd]$^+$BF$_4^-$, the reaction with Ph-Pd-OAc produced phenylated alkenylsilanes(2a-c and 3a-c) stereospecifically as main products(eq. 4 and Table I). The geometry of the starting silanes was inverted in the products with respect to R and Me$_3$Si groups. The method of

generation of Ph-Pd-OAc did not affect the feature of the phenylation. The stereochemistry can be easily explained in terms of *syn*-addition of Ph-Pd-OAc and *syn*-elimination of H-Pd-OAc as in the Heck arylation(Scheme 1, $-SiMe_3$ group is abbreviated as -Si≡ in this and the following schemes).[8]

$$\underset{\underline{1a\text{-}c}}{RCH{=}CH{\backsim}SiMe_3} + Ph\text{-}Pd\text{-}OAc \longrightarrow \underset{\underline{2a\text{-}c}}{RCH{=}C(Ph){\backsim}SiMe_3} + \underset{\underline{3a\text{-}c}}{R(Ph)C{=}CH{\backsim}SiMe_3}$$

$$(R{=}Ph(a),\ n\text{-}C_6H_{13}(b),\ CH_3OCH_2(c)) + \underset{\underline{4a\text{-}c}}{RCH{=}CH{\backsim}Ph} + \underset{\underline{5a\text{-}c}}{R(Ph)C{=}CH_2} \qquad (4)$$

Scheme 1



The marked difference between the reactions with $[Ph\text{-}Pd]^+BF_4^-$ and Ph-Pd-OAc can be accounted for by the difference in elimination pathway from the adducts formed by *syn*-addition of Ph-Pd species(Scheme 2). In the adduct 6, the cationic nature of palladium at β-carbon and the presence of BF_4^- may facilitate the elimination of Me_3Si group.[4] On the contrary, the more tight coordination of OAc^- to palladium in the adduct 7 may promote the elimination of H-Pd-OAc.

Scheme 2

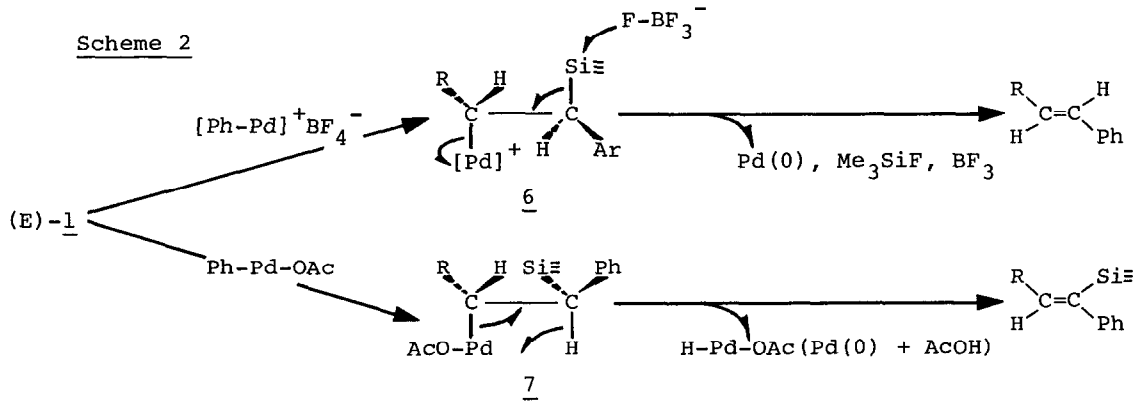


Table I. Phenylation of Alkenylsilanes with Phenylpalladium Acetate(eq. 4)

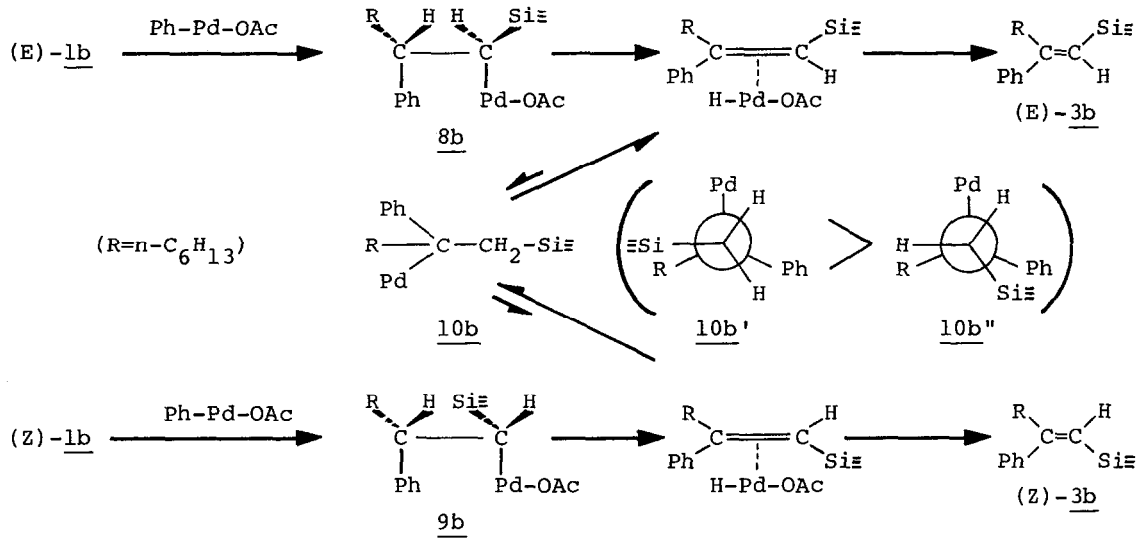
1[a]	Source of Ph-Pd-OAc[b]	Yields[c] %	Products(% ratio)[d] 2(E/Z)	3(E/Z)	4(E/Z)	5	Regioselectivity 1-Ph/2-Ph
(E)-1a	A	69	42(≈1/99)	33(-)	12(83/17)	13	54/46
(Z)-1a	A	67	66(≈99/1)	27(-)	6(≈99/1)	1	72/28
(E)-1b	A	(78)	6(0/100)	62(95/5)	0	32	6/94
"	B	73	5(0/100)	60(98/2)	0	35	5/95
"	C	46	3(0/100)	75(97/3)	0	22	3/97
(Z)-1b	A	(56)	44(86/14)	44(36/64)	2	10	46/54
"	B	65	35(94/6)	57(30/70)	0	8	35/65
"	C	34	43(86/14)	39(44/56)	0	18	43/57
(E)-1c	A	(55)	10(20/80)	88(7/93)	0	2	10/90
(Z)-1c	A	(64)	45(87/13)	52(88/12)	2	1	47/53

[a] Isomeric purity of the starting alkenylsilanes was 99.9% or more except for (Z)-1a(96.0%) and (E)-1c(99.5%). [b] Ph-Pd-OAc was prepared *in situ* from the following sources, A: $PhN(NO)COCH_3$(1.0 mmol), $Pd(0)(dba)_2$(0.2 mmol) and an alkenylsilane(1.5 mmol) in CH_3CN(5 ml) at 40 °C for 2 h, B: Ph_3Sb(0.5 mmol), $Pd(OAc)_2$(0.5 mmol) and an alkenylsilane(1.0 mmol) in CH_3CN(4 ml) at 25 °C for 2 h, and C: Ph_3P(0.4 mmol), $Pd(OAc)_2$(0.5 mmol) and an alkenylsilane(1.0 mmol) in CH_3CN(4 ml) at 40 °C for 2 h. [c] GLC yields based on $PhN(NO)COCH_3$(method A) or on $Pd(OAc)_2$(methods B and C). Values in the parenthesis are isolated yields. [d] Determined by GLC.

The poor stereospecificity of 3b from (Z)-1b might be explained in terms of the isomerization of 9b through the elimination and re-addition of H-Pd-OAc (Scheme 3). The stability of the two conformers of the adduct 10b may be determined by the relative bulkiness of $n\text{-}C_6H_{13}$ and $Ph(Ph > n\text{-}C_6H_{13})$. The more stable conformer, 10b', produces (E)-3b by H-Pd-OAc elimination. Thus, the reaction of (Z)-1b gives (E)-3b along with (Z)-3b, whereas the product from (E)-1b is little contaminated by (Z)-3b. Since the product compositions listed in Table I proved to be little effected by the reaction time under the present reaction conditions except for the very slow desilylation of 3 to 5, isomerization of the products once formed did not explain the behavior of (Z)-1b.

The regiochemistry of the arylation depends on the substituents and the geometry of 1. The electronic and steric factors of substituents on olefins affect the orientation of the addition of Ar-Pd-X. The aryl group of Ar-Pd-X usually binds to the carbon atom possessing less bulky and more electron-donating group.[8] The order of electron donating effect of 2-substituents on 1($n\text{-}C_6H_{13} > CH_3OCH_2 > Ph$) and the bulkiness($Ph > n\text{-}C_6H_{13} \simeq CH_3OCH_2$) easily accounts

Scheme 3



for the order of regioselectivity for 2-phenylation in the substrates of same geometry, i.e., 1b ≳ 1c > 1a. At present, there is no clear-cut explanation for the remarkable difference in the regioselectivity between the (E)- and (Z)-substrates. The steric factor of the substituents on 1 seems to be a principal reason for the difference. Usually the steric effect works more effectively in (E)-isomers than (Z)-isomers in the coordination of olefins to palladium(II).[9] Since Me_3Si group is the most bulky substituent in 1, its steric effect giving 2-phenylated products may play effectively in (E)-1a-c than (Z)-1a-c.

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