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Regio- and Stereochemical Aspects of the Palladium-Catalyzed Reactions of Silanes

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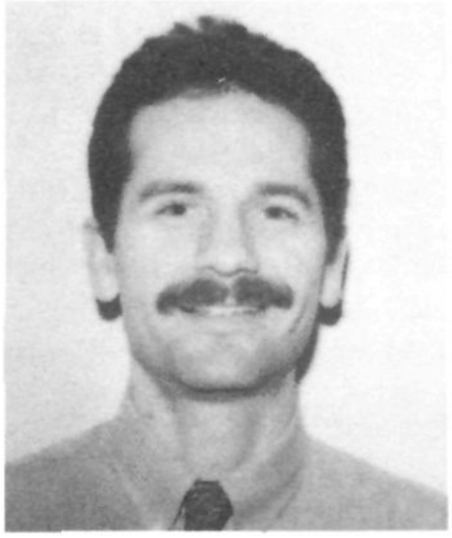

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I. Introduction

Organosilicon reagents have become major tools in organic synthesis, holding particular importance as protecting groups and regio- and stereochemical directing groups. Over the past 20 years, a wide range of scattered reports have provided evidence that unique, stereospecific chemical transformations of silanes can be carried out with homogeneous Pd(II) and Pd(0) complexes. These reagents hold definite potential to augment the synthetic applicability of a wide range of organosilicon reagents. However, until recently, investigations of the reactions of palladium complexes with both carbo- and polysilanes have generally been of a survey nature and few systematic or mechanistic investigations of the influence of the molecular structure of the palladium complexes on the silane products and their yields have been reported. In addition, investigations of the regio- and stereochemical consequences of reaction conditions and the stereoelectronic nature of the substrate have been of limited scope. Progress has been made, however, in the development of palladium

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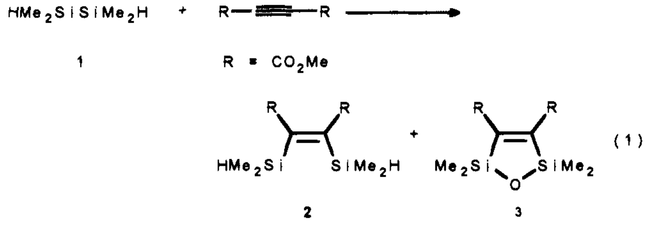
catalysts that operate effectively at room temperature producing products in high yield with well-defined regio- and stereochemistries. These catalysts now provide facile access to a wide variety of functionally activated structures for synthesis. The current review attempts to provide a comprehensive survey of the regio- and stereochemical data on these homogeneous reactions of silanes with palladium complexes. Recent advances are highlighted in such a manner as to stimulate new synthetic and mechanistic work aimed at the stereoelectronic control of these reactions. The scope of this review will involve only those reactions in which a silicon−silicon bond or carbon−silicon bond is cleaved or formed but will not cover the reactions of siloxanes with palladium catalysts or the formation of trimethylenemethane intermediates from acetoxy substituted allylsilanes, an area investigated and reviewed comprehensively by Trost.[1] The synthetic applications of the reactions of silanes with palladium catalysts have been partially reviewed elsewhere.[2]

II. Palladium-Catalyzed Addition Reactions of Disilanes

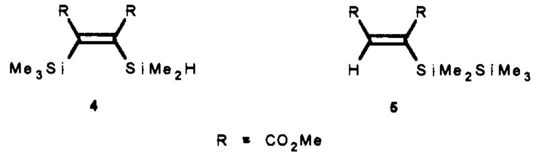
A. Addition Reactions with Acetylenes and Diacetylenes

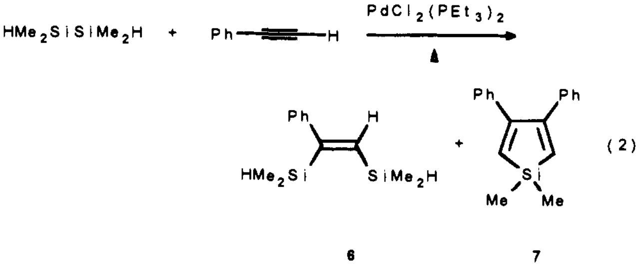
The calculated heat of reaction for the formation of disilylalkenes from substituted disilanes and acetylenes is ca. −40 kcal/mol. This suggests that high-yield double silylation reactions should be feasible even with peralkylated disilanes if appropriate catalysts and kinetically favorable reaction pathways are developed. The transformation is particularly attractive since two silicon−carbon bonds are formed simultaneously. After significant effort, this goal has been achieved, and within the last five years been demonstrated to be feasible even in room temperature reactions (*vide infra*).

The first example of the double silylation of an acetylene using a disilane and a soluble palladium catalyst was reported in 1975. On the basis of their earlier work in which acetylenes were silylated in the disproportionation reactions of disilanes catalyzed by platinum and nickel complexes, Kumada, et al. [3] explored the reaction of *sym*-tetramethyldisilane with acetylenes using soluble Pd(II) catalysts. The reaction of *sym*-tetramethyldisilane (**1**) with dimethyl acetylenedicarboxylate in benzene at reflux using $PdCl_2(PEt_3)_2$ (0.04 mol %) was found to give a 40% yield of dimethyl α,α′-bis(dimethylsilyl)maleate (**2**) as shown in eq 1.

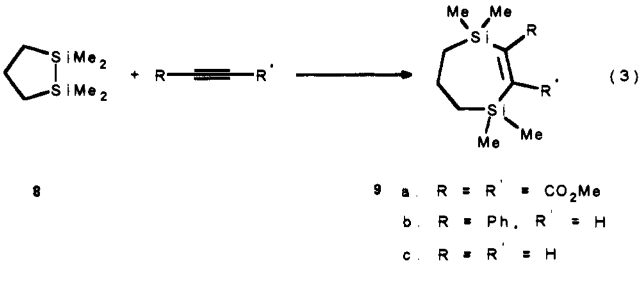


The cyclic disiloxane hydrolysis product **3** was also found in low yields and conversion of **2** to **3** with water and $PdCl_2(PEt_3)_2$ served as proof of the (*Z*) stereochemistry of the double silylation product. The reaction of pentamethyldisilane with dimethyl acetylenedicarboxylate under similar conditions gave the corresponding dimethyl α-(trimethylsilyl)-α′-(dimethylsilyl)maleate (**4**, 43%) as well as 7% of the hydrosilation product dimethyl α-(pentamethyldisilanyl)maleate (**5**). With $PdCl_2(PPh_3)_2$ the yield of **2** decreased to 20% while that of **4** increased slightly. Hexamethyldisilane failed to react under the conditions employed. However, increased temperature and/or longer reaction times can result in low yields of bis(trimethylsilyl)maleate, *vide infra*. The course of the double silylation reaction was also found to be influenced by the nature of the acetylene used. While α,β-bis(dimethylsilyl)styrene (**6**) was indeed formed in 25% yield when phenylacetylene was used, 1,1-dimethyl-3,4-diphenyl-1-silacyclopentadiene (**7**) was the major product (eq 2).

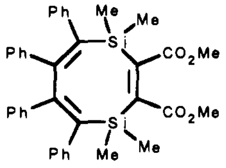




Sakurai et al.[4] also found that the addition of disilanes to acetylenes was catalyzed by Pd(II) complexes. When 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**8**) was heated in benzene for 3 h with dimethyl acetylenedicarboxylate, phenylacetylene, or acetylene, the substituted 1,1,4,4-tetramethyl-1,4-disilacyclohept-2-enes (**9a−c**) were formed in yields varying from 53 to 85%.



The reaction of hexamethyldisilane with dimethyl acetylenedicarboxylate gave only 3.4% of the double silylation product, under the same conditions, after 23 h. The rapid reaction of the cyclic disilane compared to hexamethyldisilane was attributed to the higher energy of the highest occupied molecular orbital (HOMO) of the ring-strained cyclic disilane. Once again (*Z*) stereochemistry was observed. 1,1,2,2-Tetramethyl-3,4,5,6-tetraphenyl-1,2-disilacyclo- hexadiene also reacted with dimethyl acetylenedicarboxylate to give the cyclic addition product (**10**) in good yield.



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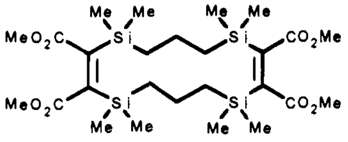
Other soluble Pd(II) complexes such as $PdCl_2(PhCN)_2$, $[(\eta^3\text{-}C_3H_5)PdCl]_2$, and $PdCl_2(PEt_2)_2$ catalyze the double silylation reactions, as does the Pd(0) complex $Pd(PPh_3)_4$. The effectiveness of the palladium(0) complex indicates that the Pd(II) catalysts may first be reduced to Pd(0) in these reactions. The formation of 1,4-dichloro-1,4-disilaoctamethylbutane from the reaction of 1 equiv of $PdCl_2(PPh_3)_2$ with octamethyl-1,2-disilacyclobutane[5] also provides circumstantial evidence that Pd(II) complexes can be reduced to a coordinatively unsaturated Pd(0) species in the presence of disilanes.

While the course of the double silylation reaction is similar with each of these palladium catalysts, often there are slight variations and different byproducts. For example, when the catalyst $PdCl_2(PhCN)_2$ is used in the reaction of 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**8**) with dimethyl acetylenedicarboxylate, the two cyclic structures **11** (benzene, reflux) and **12** (room temperature) are formed as byproducts in low yields. These products were not observed with $PdCl_2(PPh_3)_2$.



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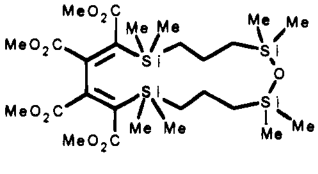

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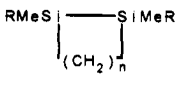
It should be noted that in some cases pentamethyldisilyacetylenes can be reacted with $Pd(PPh_3)_4$ at 100 °C, without cleavage of the silicon−silicon bond, as reported by Ishikawa et al.[6] in their investigations of the palladium-catalyzed synthesis of silyl-substituted enynes. Horn et al.[7] have also shown that silicon−silicon bond cleavage does not occur in the Heck reaction of pentamethyldisilylacetylene and heptamethyltrisilylacetylene with various aromatic halides catalyzed by $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$ and CuI.

The addition of open chain fluorodisilanes **13** and cyclic fluorodisilanes **14** to the acetylenes **15** also proceeds readily at 100 °C with either $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$ catalysts[8] and seems to be assisted by theelectron withdrawing property of the fluorine substituents.

$F_mMe_{3-m}SiSiMe_{3-n}F_n$

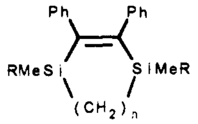
13 a. m = n = 2
b. m = n = 1
c. m = 2, n = 0
d. m = 1, n = 0



14 a. n = 3, R = Me
b. n = 4, R = F

$R-\!\!\equiv\!\!-R'$

15 a. R = R' = Ph
b. R = Ph, R' = H
c. R = R' = Et



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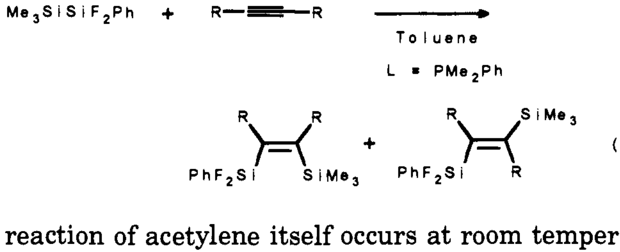
Interestingly, the reaction of the non-fluorinated tetramethyl-1,2-disilacyclopentane (**14a**) with diphenylacetylene (**15a**) was reported to proceed in 78% yield under the conditions used for the fluorinated disilanes. However, Sakurai[4] reported no reaction for the same pair at 80 °C. Not only was the double silylation reaction shown to give the (*Z*) isomers in all cases except where subsequent isomerization of the initially formed (*Z*) isomer occurred, but the reaction was also shown to be stereospecific at both silicon atoms. Thus the reactions of *cis*- and *trans*-**14b** with diphenylacetylene catalyzed by a chiral phosphine−palladium complex gave the (*Si*)-*cis*- and (*Si*)-*trans*- addition product **16** respectively. Since the (*Si*)-*trans* product was found to be optically active, it was assumed that the reaction proceeded stereospecifically with at least partial retention of configuration at both silicon atoms. The (*Si*)-*cis* product, a meso compound, was found to be optically inactive, as expected. A mechanism involving oxidative addition of the silicon−silicon bond to a low-valent palladium phosphine complex, followed by formation of a disilylpalladium(II) intermediate which subsequently adds to the acetylene, was postulated to account for the experimental observations.

Recently Ozawa and Hayashi have reported that a wide variety of acetylenes can be double silylated with Me_3SiSiF_2Ph in the presence of $[Pd(\eta^3\text{-allyl})Cl]_2$ and a basic phosphine ligand such as PMe_2Ph.[9] The highly reactive catalyst system coupled with the unsymmetrically substituted disilane typically gives yields of 95% or higher as shown in eq 4. The reaction of acetylene itself occurs at room temperature, while temperatures in the range of 40−60 °C are used for alkyl- and phenyl-substituted acetylenes. There is a high selectivity for the (*Z*) isomer (87:1 to 99:1). Internal acetylenes bearing alkyl substituents also give excellent yields.

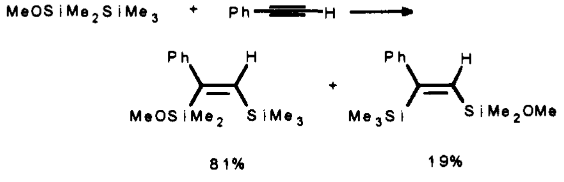


(4)

The additions of 1,1,2,2-tetrachlorodisilane and 1,2-dichlorodisilane to acetylene also proceed smoothly with $Pd(PPh_3)_4$ [1−2 mol %] in toluene or xylene at temperatures between 80 and 130 °C. Yields are in the range of 78−96%.[10] Additional substitution of chlorine for alkyl substituents increases the reactivity of the disilanes toward addition. In a direct competition between 1,2-dichlorotetramethyldisilane and 1,1,2,2-tetrachlorodimethyldisilane, the dichlorodisilane did not react until most of the tetrachlorosilane had reacted. A similar reactivity is seen in the double silylation of 1,3-butadiene, *vide infra*. The unsymmetrical chlorodisilanes such as 1,1,2-trichlorodisilane and chloropentamethyldisilane give lower yields of the 1:1 adducts due to concurrent disproportionation of the disilane to give polysilanes and dimethyldichlorodisilane. Use of $PdCl_2(PPh_3)_2$ as the catalyst resulted in lower yields of the double silylation product. These addition reactions of chlorodisilanes with acetylenes have also been explored by the Toshiba Silicone Company.[11]

A variety of methoxy-substituted disilanes such as 1,2-dimethoxytetramethyldisilane and 1,1,2,2-tetramethoxydimethyldisilane have been successfully added to phenylacetylene with either $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$,[12] further illustrating the generality of this double silylation reaction.

Once again the reaction was shown to specifically yield the (*Z*) stereochemistry products. The Pd(0) complex gave higher yields than the Pd(II) catalysts. It was also noted in this same investigation that hexamethyldisilane gives the double silylation products in low yield. When the unsymmetrical 1-methoxypentamethyldisilane and 1,1,2-trimethoxytrimethyldisilane were added to phenylacetylene, both possible regioisomers (α and *β*) were formed, although the α regioisomer predominated in both cases (eqs 5 and 6). Addition of the silyl moiety bearing the most methoxy groups to the α carbon is favored. The isomerization of the (*Z*) alkene products was catalyzed most effectively by the Pd(0) and Pd(II) complexes in the presence of the starting disilane. It was later shown that the same methoxydisilanes would form 1:1 adducts with 1-hexyne, (trimethylsilyl)acetylene, and even acetylene, in 12−76% yields. The double silylation reactions of acetylene were carried out by bubbling acetylene through a toluene or xylene solution containing 1,2-dimethoxytetramethyldisilane or 1,1,2,2-tetramethoxydimethyldisilane at 110 °C. For all of these additions, higher reaction temperatures in general gave higher yields.



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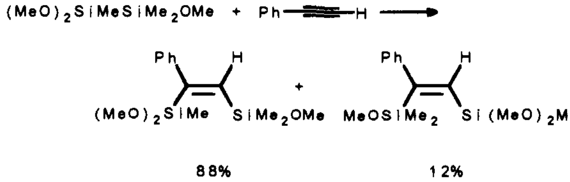
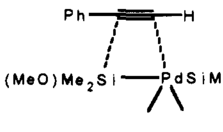


(6)

The observed regiochemistry of the addition was explained mechanistically by the addition of a disilylpalladium species (formed by the oxidative addition of the methoxydisilane to the Pd(0) complex) to the acetylene substrate in such a manner that the more electron-rich carbon forms the σ bond to the palladium metal (**17**).



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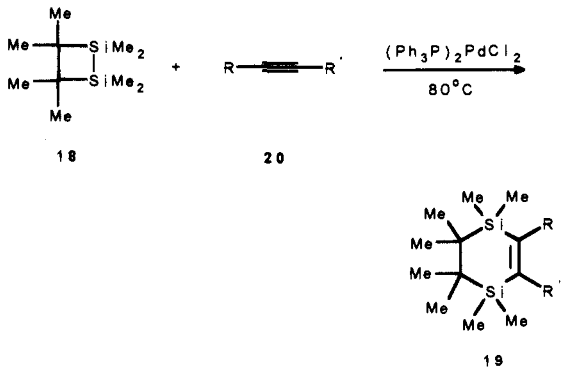
Several mechanistic details of the addition reactions of disilanes with acetylenes were clarified in an investigation of the reaction of octamethyl-1,2-disilacyclobutane with acetylenes, in the presence of Pd(II) catalysts, carried out by Seyferth et al.[5] The strained cyclodisilane **18** was found to form the 1,4-disilacyclohexenes **19** when reacted with terminal acetylenes **20** (57−100% yields).



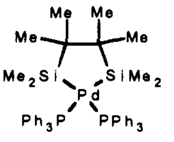
(7)

R, R'	Yield (%)	R, R'	Yield (%)
Ph, H	73	Me_3C, H	96
H, H	57	Me, H	91
H, CO_2Me	92	MeO_2C, MeO_2C	99
n-C_5H_{11}, H	83	Me, C(O)Me	100

When 1 equiv of $PdCl_2(PPh_3)_2$ was reacted with **18**, the chlorosilane **21** was formed along with the palladium species **22**. This suggests that the original Pd(II) catalyst was reduced to a coordinatively unsaturated Pd(0) species that then inserted into the silicon−silicon bond of **18**. The palladium species **22** was shown to react stoichiometrically with phenylacetylene to give the cyclic adduct **19**, the same product obtained from the catalytic reaction.

$ClSiMe_2CMe_2CMe_2SiMe_2Cl$

21



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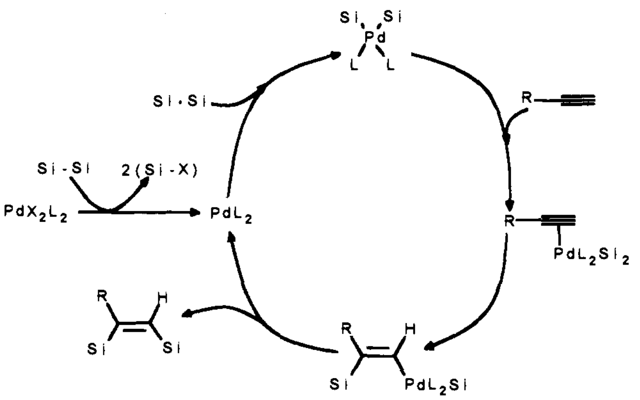
Scheme 1

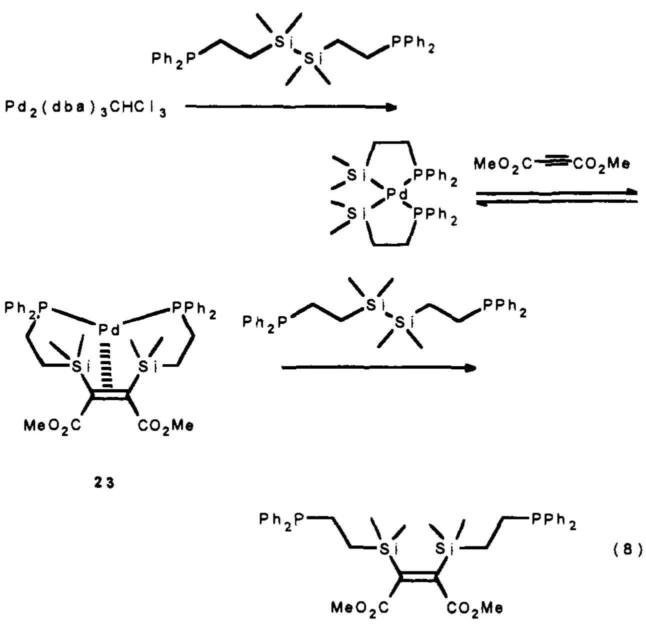


The disilylpalladium compound **22** is therefore a probable intermediate in the catalytic reaction. With this mechanistic information, Scheme 1 provides a viable unifying mechanism for the double silylation reactions of disilanes with acetylenes. The steps included are (1) formation of a Pd(0) catalyst (possibly coordinatively unsaturated), (2) oxidative addition of the disilane to this species, (3) formation of a π complex with the acetylene, (4) insertion of the acetylene into one of the palladium–silicon bonds, and (5) reductive elimination of the disilylethylene product.

In a reaction analogous to eq 7, 1,4-disilacyclohexa-2,5-dienes were formed by the palladium complex-catalyzed addition of 1,1,2,2-tetramethyl-3,4-diphenyl-1,2-disilacyclobut-3-ene or 1,1,2,2-tetramethyl-3-phenyl-4-trimethylsilyl-1,2-disilacyclobut-3-ene to diphenylacetylene or phenyl(trimethylsilyl)acetylene. The yields of the 1,4-disilacyclohexa-2,5-dienes ranged from 28 to 71% using a wide variety of palladium complexes including $PdCl_2(PPh_3)_2$, $PdCl_2(PEt_3)_2$, $PdCl_2(Ph_2PCH_2CH_2PPh_2)$, $PdCl_2(PhCN)_2$, $Pd(PPh_3)_4$, and Pd on charcoal.[13]

The mechanisms postulated for the double silylation of acetylenes propose the involvement of bis-silyl palladium complexes. Similar complexes have been suggested as intermediates in the double silylation reactions of alkenes and in hydrosilylation reactions. Several palladium complexes containing chlorinated silane ligands had been isolated[14] but were highly reactive and unstable in air. A series of palladium complexes containing simple silane ligands [(dcpe)Pd(SiHRMe)$_2$ and (dcpe)Pd(SiHRPh)$_2$] have now been isolated.[15] All are stable in air and are stable to brief heating at 120 °C. The X-ray crystal structure of (dcpe)Pd(SiHMe$_2$)$_2$ was determined. These complexes react cleanly with dimethyl acetylenedicarboxylate at 25 °C to give *cis*-bis(dimethylsilyl)maleate, thus strongly supporting the mechanism of Scheme 1. Recently a disilane containing two tethering phosphine groups was utilized to stabilize the intermediate palladium–acetylene *cis*-adduct (**23**). The phosphine tethers acted to stabilize the palladium adduct, making its isolation and characterization possible.[16]

New more highly reactive palladium catalysts have been developed which efficiently catalyze the addition of simple aryl- and alkyl-substituted disilanes to acetylenes and avoid the general necessity of utilizing disilanes bearing electron-withdrawing groups. Thus $Pd(dba)_2-2P(OCH_2)_3CEt$ is an efficient catalyst for the insertion of acetylenes into hexamethyldisilane.[17] The reaction with phenylacetylene proceeds readily at 120 °C to give (*Z*)-1,2-bis(trimethylsilyl)-1-phenylethene in 91% yield. With the conventional catalysts described earlier, the yields are typically below 10%. A unique application of this reaction is the insertion of acetylenes into the SiSi bonds of poly(disilanylene)phenylene (see eq 9), poly(disilanylene)ethylene and even poly(dimethylsilylene). It was also shown that this catalyst could be used with 1,7-octadiyne to cross-link poly(disilanylene)phenylene.



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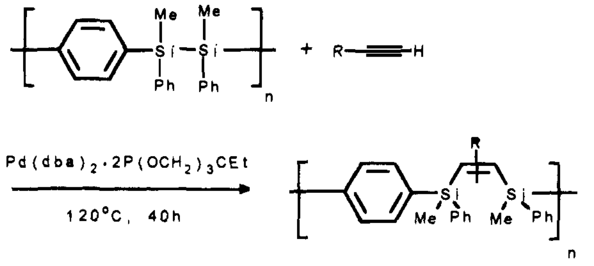
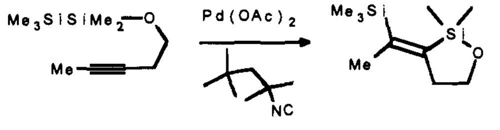
(8)



(9)

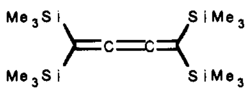
Palladium(II)acetate–*tert*-alkyl isocyanide (excess) also catalyzes the addition of simple alkyldisilanes to acetylenes.[18] Hexamethyldisilane reacts with terminal acetylenes to yield the double silylation products in yields between 80 and 98%. The addition is predominantly *cis* to give the (*Z*) product (*Z*/*E* ratio > 95:5). Aryl and alkyl terminal acetylenes react, but internal acetylenes are unreactive unless the disilane and acetylene are tethered together by a two- or three-atom tether to force an intramolecular double silylation (eq 10). Addition of 2 equiv of phenylacetylene to octamethyltrisilane was also ef-



(10)

ficient. The same catalyst system has been shown to be effective for the silastannation of 1-alkoxyalkynes to give 1-alkoxy-1-silyl-2-stannylalkenes which can be converted to acysilanes.[19]

The only known example of the double silylation of a diacetylene is the reaction of 1,4-bis(trimethylsilyl)butadiyne with chlorodisilanes to yield 1,1,4,4-tetrakis(trimethylsilyl)butatriene (**24**) and 1,1,2,4-tetrakis(trimethylsilyl)-1-buten-3-yne (**25**) (after methylation).[20] The combined yields of **24** and **25** were as high as 81%, with 1,4 addition (**24**) being favored by increased chlorine substitution on the disilane. The full report of this addition reaction showed that **24** remained the major product over a wide range of $PdCl_2(PR_3)_2$ except for R = Et and R = CH_2Ph which gave 72 and 74% yields of **25** respectively.[21] Less bulky phosphine ligands were generally more reactive. Some data indicated that the addition was *cis*. Hexamethyldisilane gave only a small amount of the 1,2-addition product **25** and hexachlorodisilane underwent only polysilane formation.



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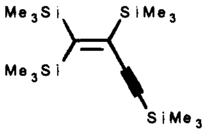
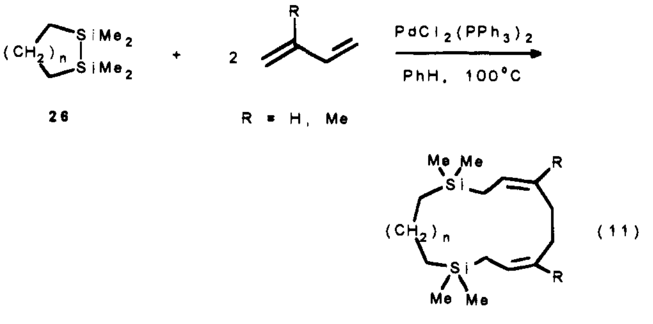


25

The best combined addition product yields were obtained with the Pd(II) catalysts $PdCl_2(PEt_3)_2$ and $PdCl_2[P(CH_2Ph)_3]_2$. The reaction forming the 1,2-addition product, **25**, was found to proceed in a *cis* fashion, as seen for the addition reactions of disilanes with simple acetylenes. The mixtures of (*E*) and (*Z*) **25** were generated by thermal isomerization during their isolation by gas chromatography.

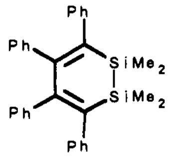
B. Addition Reactions with Dienes and Allenes

The reactions of disilanes with dienes, catalyzed by palladium complexes, result in both 1:1 and 1:2 addition products. The first report of such disilane addition reactions involved the reaction of strained cyclic disilanes **26** with excess butadiene or isoprene in benzene at 100 °C in the presence of $PdCl_2(PPh_3)_2$.[22] The 1:2 macrocyclic addition products **27** were isolated exclusively.



26 **27**

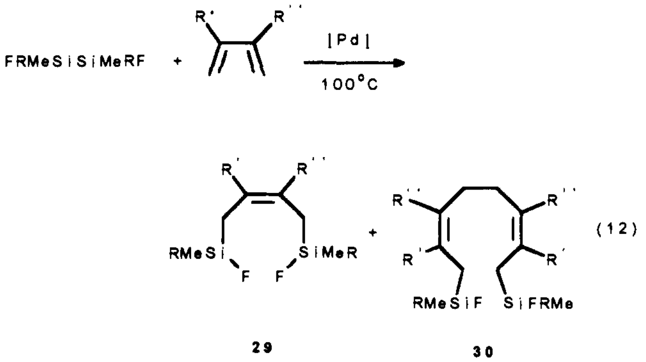
The reactions of 1,1,2,2-tetramethyl-1,2-disilacyclopentane with butadiene and isoprene were especially efficient (83 and 76% yields, respectively). Interestingly, only the head-to-head dimer structure was observed when isoprene was used. 1,1,2,2-Tetramethyl-3,4,5,6-tetraphenyl-1,2-disilacyclohexadiene (**28**) was also found to add readily to 1,3-butadiene (86%).



28

Linear disilanes such as hexamethyldisilane and 1,2-dichlorotetramethyldisilane were found to add to isoprene to give 1:2 head-to-head addition products, although in low yield (5–14%). While a variety of Pd(II) complexes were effective catalysts, Pd(0) catalysts were reported to be rather ineffective. A later report from the Toshiba Silicone Company showed that Pd(0) catalysts could also be effective for the addition to dienes when used at 130 °C in benzene.[23] When $Pd(PPh_3)_4$ was used for the addition of hexamethyldisilane to butadiene, the 1:2 adducts were formed in 76% yield. The most effective of the Pd(II) catalysts were $PdCl_2(PPh_3)_2$ and $PdCl_2(PhCN)_2$.

In contrast to the cyclic disilane reactions reported by Sakurai, the addition of difluorodisilanes to 1,3-dienes proceeded smoothly, with both $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ at 100 °C, to give predominantly (43–97%), the 1:1 adducts **29**.[24]

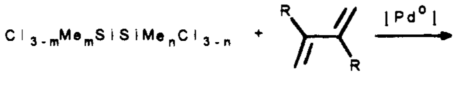


29 **30**

R = Ph or Me

No steric inhibition of the reaction was observed when a competitive reaction was run between isoprene and 2,3-dimethyl-1,3-butadiene. The 1,4 addition was found to be stereoselective with only the (*Z*) isomers of **29** being formed analogous to the addition of disilanes to acetylenes, *vide supra*. When 1:2 adducts **30** were produced, they were a mixture of *cis* and *trans* isomers, although a regioselective head-to-head coupling of the dienes was still found.

Chlorodisilanes have also been found to add to 1,3-butadienes at temperatures between 60 and 130 °C when catalyzed by both Pd(0) and Pd(II) complexes (eq 13).[25]



$$Cl_{3-m}Me_mSiCH_2CR{=}CRCH_2SiMe_nCl_{3-n} \quad (13)$$

The yields for the reactions of hexachlorodisilane, 1,1,2,2-tetrachloro-1,2-dimethyldisilane, and 1,2-dichlorotetramethyldisilane, with 1,3-butadiene ranged between 44 and 82%. In these reactions, the formation of 1:2 adducts was negligible. The 1,4 addition was observed to be stereospecific, yielding the (*Z*) isomer exclusively. In contrast to the reactions of the fluorodisilanes, the reaction was retarded by the steric hindrance of methyl groups in the 2 and 3 positions of the 1,3-butadiene substrate. Competition experiments established the relative reactivities of the chlorodisilanes to be $Cl_2MeSiSiMeCl_2$ > $Cl_2MeSiSiMe_2Cl$ > $ClMe_2SiSiMe_2Cl$. Clearly, additional chlorine substitution increases the reactivity of the disilanes toward these additions. No reaction of 1,1,2,2-tetrachloro-1,2-dimethyldisilane with 1,3-pentadiene was observed at 130 °C with $Pd(PPh_3)_4$, or with 1,3-cyclooctadiene under similar conditions. This suggests that there are significant restrictions on the synthetic utility of these reactions. Interestingly, the authors reported that under comparable conditions, phosphine complexes of platinum, nickel, rhodium, and ruthenium did not catalyze these 1,4-addition reactions though others have reported the successful use of these catalysts with *sym*-tetramethyldisilane and phenyl-substituted disilanes.[26] A mechanism for the addition was proposed which was analogous to the addition reactions of disilanes with acetylenes. The only modification was the postulate that the initial π-palladium complex collapsed to a π-allylpalladium complex rather than the σ complex formed in the reactions with acetylenes.

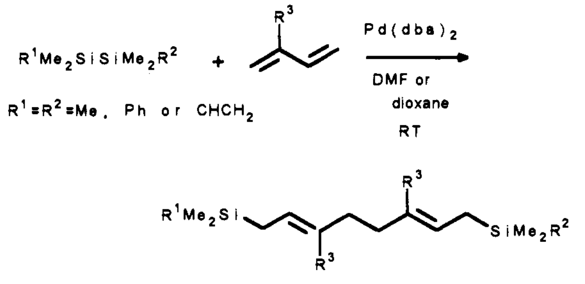
An extensive investigation of the influence of catalyst structure, solvent, and reaction temperature on the addition of hexamethyldisilane, chlorodisilanes, and methoxydisilanes to 1,3-butadienes was carried out to optimize the yields of the 1:2 adducts.[27] The 1:2 adducts were found to be formed regio- and stereoselectively as, for example, in the reaction of hexamethyldisilane with isoprene which gave all *trans*-1,8-disilyloctadiene. The yields of the 1:2 adducts were found to improve when the reaction was run without solvent. It was postulated that the coordination of solvents such as benzene, THF, and acetonitrile to the palladium catalyst retards the rate of addition to the disilanes since palladium complexes coordinate only weakly to disilanes. It has been postulated that when these addition reactions are run with neat diene as solvent, the concentration of diene is sufficiently high that the intermediate silylpalladium or palladium/diene complex (which in dilute solution reacts intramolecularly) is intercepted in an intermolecular process to produce the 1:2 adduct. A wide range of catalysts, including divalent palladium, $PdCl_2$, and $Pd(OAc)_2$ complexes were found to catalyze the addition reactions, but the reaction yield was remarkably sensitive to temperature, with each catalyst exhibiting a different optimum temperature. $PdCl_2(PhCN)_2$ and $Pd(OAc)_2$ were found to be two of the most effective catalysts for the addition of hexamethyldisilane to isoprene (70 and 87% yields at 60 and 120 °C respectively).

Substituents on the benzene ring of the $PdCl_2(PhCN)_2$ complex were found to have an effect on the yields of the reaction of hexamethyldisilane with butadiene at 90 °C. Thus with the complex $PdCl_2(p\text{-}MeOC_6H_4CN)_2$, 1,8-disilyloctadiene was formed in 80–85% yield while with $PdCl_2(PhCN)_2$ the yield was only 63% at 90 °C. At lower temperatures, the effect was not as great. In general, those complexes with the stronger donor ligands gave higher yields.

A competition reaction between 1,3-butadiene and isoprene showed that 1,3-butadiene had the highest reactivity. This may be due to a steric retardation by the additional methyl substitution when isoprene is the substrate. In this study the yield of 1,8-disilyloctadiene was eventually optimized at 85% and was used as the starting point for the synthesis of *dl*-muscone.

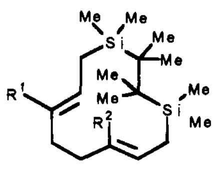
It is also interesting to note that in this investigation[27] the addition of 1,2-difluorotetramethyldisilane to isoprene was found to give the 1:2 adduct. This contrasts with the work of Kumada where the 1:1 adduct was formed. This is most likely due to the high concentration of isoprene (neat) used in this investigation.

An extremely important recent development in this area is the use of $Pd(dba)_2$ in DMF or dioxane to effect the regio- and stereoselective dimerization–double silylation of 1,3-dienes.[28] Whereas the use of $Pd(OAc)_2$ or $PdCl_2(ArCN)_2$ requires elevated temperatures (60–120 °C) and neat diene, the $Pd(dba)_2$/DMF system is effective at room temperature. In addition, vinylic and allylic substituents on the disilane are tolerated. With 1,3-butadiene, only the α,ω-disilylated (*E*)-1,4 dimer is obtained. Isoprene reacts to give the (*E*)-1,4 head-to-head dimer exclusively. Typical isolated yields are 70–90%. Platinum, ruthenium, and rhodium catalysts were ineffective. Interestingly, DMF, a strongly coordinating solvent, can either enhance the palladium catalyst's activity as with $PdCl_2(PhCN)_2$ or suppress activity as with $Pd(PPh_3)_4$. 2,3-Dimethyl-1,3-butadiene and 1,3-cyclohexadiene were inert due to steric hindrance. Interestingly, while electronegative substituents activate silanes for addition reactions with acetylenes and olefins, they were unreactive under these conditions with dienes. When equimolar mixtures of two disilanes are used, no crossover products are formed thus verifying the intramolecular double addition following the formation of the disilane complex.



(14)

Gaseous dienes were found to react with octamethyl-1,2-disilacyclobutane in refluxing toluene with $PdCl_2(PPh_3)_2$.[5] Both 1,3-butadiene and isoprene gave 1:2 cyclic adducts **31–33** in 92% yield.



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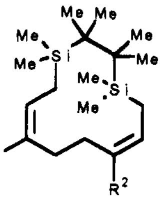

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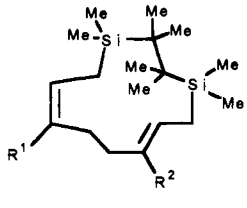


33

$R^1 = R^2 = H$, or $R^1 = R^2 = Me$

While a full characterization of the isomer distributions was not completed, a minimum of two isomers was formed in each reaction. In contrast, the reaction of 1,1,2,2-tetramethyl-1,2-disilacyclopentane was reported to give only the (*E,E*) isomer, *vide supra*.

There are only a few examples of the addition of disilanes to allenes catalyzed by Pd(II) complexes. Nagai et al.[29] reported the first double silylation of allenes using $Pd(PPh_3)_4$ to add (chloromethyl)- and methoxymethyldisilanes to allene and buta-1,2-diene, as shown in eq 15.

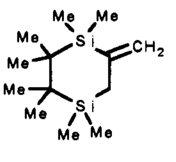
$$CH_2{=}C{=}CHR + Me_{3-n}X_nSiSiX_mMe_{3-m} \xrightarrow{Pd(PPh_3)_4}$$

$R = H, Me$ $X = Cl, OMe$

$$CH_2{=}C(SiMe_{3-n}X_n){-}CHR(SiMe_{3-m}X_m) \quad (15)$$

34

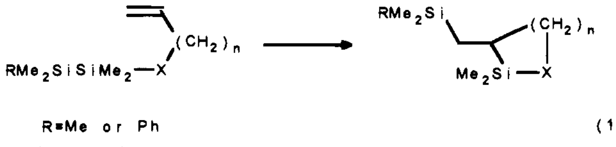
The yields of the double silylation product were increased by increasing substitution on silicon with methoxy and chloro substituents. Yields were typically in the range of 50 to 97%. Even hexamethyldisilane was found to silylate buta-1,2-diene, albeit in only 29% yield. Unsymmetrical disilanes added regiospecifically, with the silicon atom bearing the most halogen or alkoxy substituents going exclusively to the 1 position of allene and the 3 position of buta-1,2-diene. The reaction of octamethyl-1,2-disilacyclobutane with allene, at 80 °C, yielded the cyclic 1,2-addition product, **35**, in 91% yield.[5] Essentially no other information is available on the addition of disilanes to allenes.



35

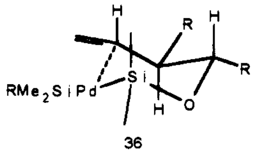
C. Addition Reactions with Alkenes

The bis-silylation of alkenes using palladium catalysts was unknown until the development of the palladium acetate–*tert*-alkyl isocyanide catalyst by Ito et al.[30] Their report encompassed the intramolecular bis-silylation of terminal alkenes leading to cyclic 1,2-oxasilolanes which could be readily converted to 1,2,4-triols. Isolated yields of the 1,2-oxasilolanes ranged from 80 to 99%. Catalytic amounts of palladium acetate were used with 0.15–0.75 equiv of the isocyanides. *Exo* ring closure occurred to give the 5-membered ring 1,2-oxasilolane products.



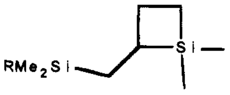
R=Me or Ph (16)
$X = CH_2$, NH or O
n= 1 or 2

When the disilane was tethered to the terminal alkene by chains of more than four atoms, the bis-silylation did not proceed. Electronegative substituents on the disilane were unnecessary. Ring closure occurred with high diastereoselectivity in those compounds having substituents α (>93:7 *trans/cis* 3,4-substituted 1,2-oxasilolanes) or *β* (>93:7 *cis/trans* 3,5-substituted 1,2-oxasilolanes) to the alkene in the tether. The selectivity was proposed to arise from a preference for a chairlike transition state (**36**) in which the substituents prefer the equatorial positions.



36

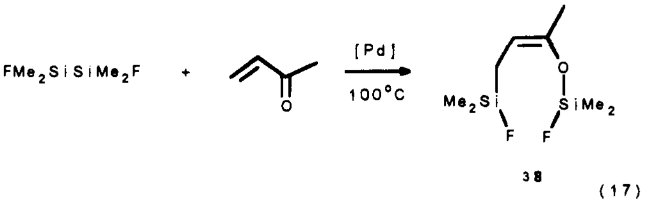
A full report providing extensive details of the yields and selectivities observed for variations in disilane structure is now available.[31] The conversion of the 1,2-oxasilolanes to 1,2,4-triols and 1,2,4,5,7- and 1,2,4,6,7-pentols is also described. The reaction can be applied to disilanes having amino groups in the tether and is also viable when the tether consists of only two carbon atoms, in which case the product is a siletane **37**.



37

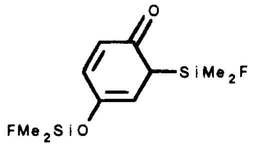
D. Addition Reactions with Enones

The highly reactive 1,2-difluorodisilanes have been reported to undergo 1,4 addition with α,*β*-unsaturated ketones in a similar fashion to their reaction with 1,3-dienes.[32] The reaction of 1,2-difluorotetramethyldisilane with neat methyl vinyl ketone at 100 °C, catalyzed by either $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$, gave an 81% yield of the addition product **38** (eq 17).



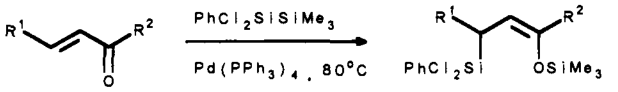
(17)

The reaction is slow (18 h) and was reported to yield the (*Z*) isomer, although complete proof of the stereochemistry was not given. When *p*-benzoquinone was reacted with 1,2-difluorotetramethyldisilane, the formal 1,6 addition product was isolated, although an initial 1,4 addition to give **39**, followed by migration from carbon to oxygen, would give the same product.



39

In 1988, Ito et al.[33] reported an efficient synthesis of β-hydroxy ketones and α-alkyl-β-hydroxy ketones in which the first step involved the 1,4 addition of 1,1-dichloro-1-phenyl-2,2,2-trimethyldisilane to enones (eq 18). Pd(PPh_3)$_4$, $PdCl_2(PPh_2)_2$, and bis(μ-chloro)bis(π-allyl)palladium (coupled with either 1,1′-bis(diphenylphosphino)ferrocene or 1,4-bis(diphenylphosphino)butane) catalyzed the addition, although other palladium complexes without phosphine ligands did not.

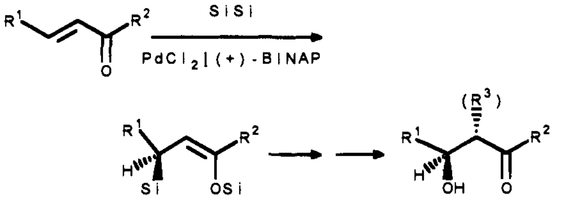


(18)

R^1 = Ph, R^2 = Me
R^1 = Me, R^2 = Ph
R^1 = R^2 = Ph
R^1 = R^2 = Me
R^1 = R^2 = (CH_2)$_3$

Generally the reactions were run at 80 °C in benzene for 1.5−6 h. Reaction yields were very good with isolated yields of the β-hydroxy ketones in the 35−80% range. Lower temperatures can be used, but the reaction times become prohibitively long as the temperature is decreased. Several rhodium, nickel, ruthenium, and platinum complexes were found to be totally inactive as catalysts. In all cases the trimethylsilyl group was found to add to the ketone oxygen and the dichlorophenylsilyl group to the β position. 1,1,1-Trichlorotrimethyldisilane could also be used, but 1,1,1-trimethoxytrimethyldisilane and 1,1-dichlorotetramethyldisilane did not add to (*E*)-4-phenyl-3-buten-2-one. Disilylation of cyclohexenone was also observed, but β,β-disubstituted enones failed to react. Once again, an oxidative addition of the disilane to the palladium complex followed by complexation with the enone in a *cisoid* conformation, and migration of the silyl groups, explains the observed product stereochemistry.

In an extension of this 1,4 addition to enones, the same group[34] was able to use a chiral palladium complex, $PdCl_2$[(+)-BINAP] where BINAP stands for 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, to effect enantioselective disilylation (eq 19).

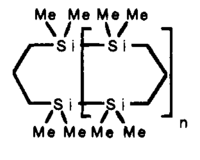


(19)

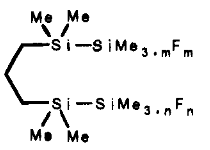
Disilylation of (*E*)-1-phenyl-2-buten-1-one with 1,1,-dichloro-1-phenyltrimethyldisilane, followed by reaction with methyllithium and hydrolysis, gave 1-phenyl- 3-(phenyldimethylsilyl)butan-1-one in 72% overall yield. The enantiomeric purity of the product, (*S*)-1-phenyl-3-hydroxybutan-1-one, derived from this disilylated intermediate was 87%. For other α,β-unsaturated ketones, the enantiomeric purity ranged from 57 to 92%. These results indicate that the chiral palladium catalyst complexes preferentially to one face of the enone π system (which is in a *cisoid* conformation) while the silyl groups are delivered to the enone oxygen and to the β position.

E. Disilane Metathesis Reactions

In a number of the disilane addition reactions discussed in the preceeding sections, small amounts of silane metathesis reaction products are formed. In 1972, Sakurai[35] reported that the thermal Si−Si/Si−Si redistribution reaction of hexaorganodisilanes proceeded only slowly at 200 °C. However, Kumada et al.[8] found that the disilane metathesis reaction of fluorinated, or strained, cyclic disilanes was catalyzed by palladium complexes bearing phosphine ligands and could be moderately efficient at 100 °C. 1,1,2,2-Tetramethyl-1,2-disilacyclopentane (**14a**, section II.A) which has a strained silicon−silicon bond and therefore a relatively high HOMO compared to the linear disilanes, was found to form the cyclic dimer **40** (n = 1) in a homometathesis reaction at 100 °C when catalyzed by $PdCl_2(PPh_3)_2$. It has now been reported that (t-BuNC)$_2$Pd catalyzes the oligomerization of **14a** through Si−Si σ-bond metathesis to give a 93% yield of cyclic oligomers without formation of high polymer.[36] The yields of the individual cyclic oligomers peaked at trimer (32%) and tetramer (34%) while the largest cyclic oligomer identified was the octamer. The metathesis reaction occurred readily at 50 °C in benzene and was found to be reversible. The crystal structure of the cyclic tetramer (**40**, n = 3) was established by X-ray crystallography. Circumstantial evidence indicated that the oligomerization occurred between **14a** and the oligomer rather than by σ-bond metathesis between two oligomers. The fluorodisilanes **13a**−**c** all react with the cyclodisilane **14a** to give selectively the cross metathesis products **41a–c** with yields ranging from 27–85%.



40



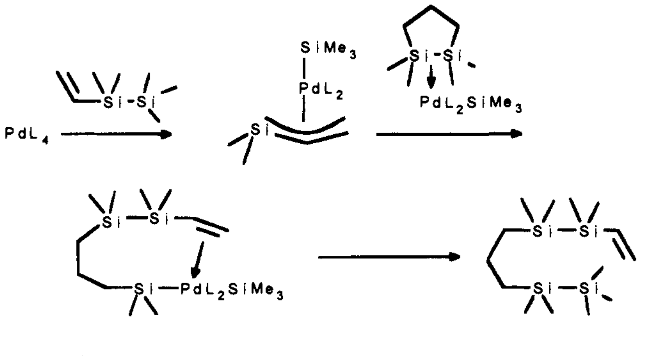
41

a. m = n = 2
b. m = n = 1
c. m = 2, n = 0

1-Fluoropentamethyldisilane, hexamethyldisilane, and 1,2-dichlorotetramethyldisilane did not react with **14a** to give the corresponding cross metathesis product. The cross metathesis reaction is reversible in at least one case since the cross metathesis product **40** gives **14a** in the presence of $PdCl_2(PPh_3)_2$. Interestingly, 1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane forms polymeric products by a consecutive metathesis reaction with these palladium complexes since the initially formed product has a reactive 1,2-disilane functionality.

The cyclic disilane **14a** also reacts readily with ethynyl and vinyl disilanes[37] to give the Si–Si/Si–Si metathesis products, in benzene, at reflux. The best palladium catalyst for the metathesis reaction of **14a** with vinylpentamethyldisilane was $Pd(PPh_3)_4$. The low product yields are only a result of the lethargy of the reaction, unreacted starting materials being recovered without byproduct formation. Once again, the palladium complexes were significantly better than any of the nickel and rhodium complexes tried. It was suggested that the addition of the silicon–silicon bond is assisted by the vinyl and ethynyl groups, as shown in Scheme 2.

Scheme 2



III. Regio- and Stereospecific Silylations of Aromatic, Allylic, and Vinylic Halides

Disilanes have been coupled with a wide variety of organic halides using homogeneous palladium complexes to give the corresponding monosilanes. Aromatic halides can be coupled with disilanes using either Pd(II) or Pd(0) complexes to give the synthetically useful arylsilanes.[38] The reaction was first reported in a patent by Atwell and Bokermann[39] and was later developed more fully by Matsumoto and Nagai.[38a,c] The reactions only proceed under rather harsh conditions in spite of the fact that the reaction is exothermic by ca. 20–30 kcal/mol. The product yields, however, are often above 80% and can be quantitative.

The initial report of Matsumoto and Nagai demonstrated that $Pd(PPh_3)_4$ could be used as an effective catalyst for the conversion of substituted bromobenzenes and hexamethyldisilane to the corresponding phenyltrimethylsilanes and trimethylbromosilane.[38a] Quantitative yields were reported for the formation of (trimethylsilyl)benzene and 4-nitro(trimethylsilyl)benzene. 1,2-Dichlorotetramethyldisilane also adds efficiently to bromobenzene to give phenylchlorodimethylsilane. When bromoanisole was used, reduction to anisole occurred as a side reaction because of subsequent protodesilylation of the initially formed 4-(trimethylsilyl)anisole. These reactions, as well as the reactions of bromo- and chlorobenzene derivatives with 1,2-dichlorotetramethyldisilane and 1,1,2,2-tetrachlorodimethyldisilane, that are catalyzed by $Pd(PPh_3)_4$, require temperatures of 140–170 °C and reaction times of 18–30 h. The silylation of chlorobenzene does not proceed at 140 °C and only gives low yields of silylated product even at temperatures up to 170 °C. Hexamethyldisilane can be particularly sluggish, and may require temperatures of 200 °C and reaction times of 40 h or more.[40]

A key application of this general silylation methodology is the synthesis of nitro(trimethylsilyl)benzenes, compounds for which few other high yield synthetic methods are available. *o*-, *m*-, *p*-Nitro and 2,4-dinitro bromo- and chlorobenzenes were converted to the trimethylsilyl compounds in yields of from 60–85% with $Pd(PPh_3)_4$.[41] The electron-withdrawing effect of the nitro group seems to facilitate reaction of the chlorobenzene derivatives. Bis(trimethylsilyl)nitrobenzenes can also be prepared from dichloro- and dibromonitrobenzenes.[42] Selective monotrimethylsilylation can be carried out with appropriate solvents. This has been illustrated by the synthesis of 2-(trimethylsilyl)-5-chloronitrobenzene from 2,5-dichloronitrobenzene and hexamethyldisilane using HMPA as the solvent. This same *ortho–para* activating effect is seen in simple monochloro derivatives such as 2- and 4-chloronitrobenzenes, which react more readily than 3-chloronitrobenzene.

Eaborn and co-workers[43] have explored the silylations of aromatic halides and have found that the bromobenzene derivatives react more readily with disilanes than the chlorobenzenes, as observed by Masumoto et al. However, in contrast to the earlier investigations, they found that moderate yields of (trimethylsilyl)benzene could be prepared from iodobenzene. Pd(II) complexes were also found to be effective catalysts with $PdBr_2(PPh_3)_2$, being somewhat better than $PdCl_2(PPh_3)_2$ and showing significantly better efficiency than $PdI_2(PPh_3)_2$. The complex $Pd(PPh_3)_2(Ph)Br$, which is formed from the oxidative addition of $Pd(PPh_3)_4$ to bromobenzene, was also an effective catalyst. Halobenzene derivatives with electron-donating substituents, which give low yields of the corresponding trimethylsilyl derivatives with $Pd(PPh_3)_4$ catalysts, gave good yields with Pd(II) complexes bearing phosphine ligands.

It has now been demonstrated that the silylation of substituted bromobenzenes can also be carried out with 1,1,2,2-*tetra*ethoxy-1,2-dimethyldisilane using $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$.[44] This development avoids the often needed conversion from an initially formed chlorosilane to the less reactive ethoxy silane. The reactions with the ethoxysilanes can be carried out in either neat bromobenzene (180 °C) or toluene (155 °C). Yields ranged from 60 to 90%. Electron-withdrawing groups activated the aromatics, facilitating the reaction at lower temperatures and allowing shorter reaction times.

Benzyl halides react more readily with disilanes at lower temperatures (130 °C, 2–3 h) in the presence of $Pd(PPh_3)_4$[45] than do the aryl halides. Once again, benzylic halides bearing electron-donating substituents give poorer yields than do (halomethyl)nitrobenzenes. Pd(0) catalysts with phosphine ligands such as PMe_2Ph and $P(C_6H_4OMe\text{-}p)_3$ were found to be more effective than the simple $Pd(PPh_3)_4$. While the yields are high even when simple alkyldisilanes are used (often in the range of 70–98%), coupling of the benzylic halides can be a problem unless 2–3 equiv of the disilane are used.[46]

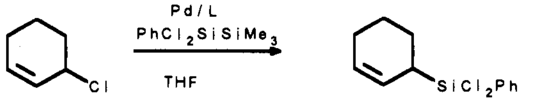
The dechlorinative silylation of benzylic chlorides proceeds efficiently with chlorinated disilanes without the complication of the coupling reaction.[45a] $Cl_2MeSiSiMeCl_2$, $Cl_2MeSiSiMe_2Cl$, and $ClMe_2SiSiMe_2Cl$ all are effective silylating agents with $Pd(PPh_3)_4$ at temperatures between 80 and 130 °C. In the reactions of unsymmetrical chlorodisilanes, the silicon bearing the greatest number of chlorines replaces the benzylic chlorine almost exclusively. Several other investigations have extended the scope of these benzylic silylation reactions.[45b]

Allylic halides[47] can be converted to allylic trimethylsilanes with high regioselectivity. This reaction was first reported in the patent of Atwell and Bokermann[39] and was more fully explored by Matsumoto et al. Allyl and methallyl chloride react readily with 1,1,2,2-tetrachlorodimethyldisilane, 1,2-dichlorotetramethyldisilane, and hexamethyldisilane to give the corresponding allylsilanes with GLC yields of ca. 90% and isolated yields of 75% or greater. Unsymmetrical chlorodisilanes gave the allyl silane bearing the greatest number of chlorines, as shown for the reaction of pentamethylchlorodisilane with allyl chloride (eq 20).

$$ClMe_2SiSiMe_3 + CH_2{=}CHCH_2Cl \xrightarrow{Pd(0)} \underset{97}{CH_2{=}CHCH_2SiMe_2Cl} + \underset{3}{CH_2{=}CHCH_2SiMe_3} \quad (20)$$

In direct competition reactions with allyl chloride as the substrate, the relative reactivities of *sym*-methylchlorodisilanes were found to be $Cl_2MeSiSiMeCl_2 > ClMe_2SiSiMe_2Cl > Me_3SiSiMe_3$. The rate of silylation of allyl bromide was found to be faster than allyl chloride. However, the allyltrimethylsilane product yield was lower with the bromide because of the facile coupling of allyltrimethylsilane and allyl bromide to give 1,5-hexadiene.

1,1-Dichloro-1-phenyl-2,2,2-trimethyldisilane has recently been found to be an effective reagent for the dichlorophenylsilylation of allylic chlorides substituted at the α or γ positions (eqs 21–23).[48] The catalyst was prepared *in situ* from bis(μ-chloro)bis(η^3-allyl)dipalladium(II) and either triphenylphosphine or 1,1′-bis(diphenylphosphino)ferrocene. The best yields were obtained with the ferrocenyl ligand. The silylation of (*E*)-1-chloro-2-butene gave a 92% yield of 3-silyl-1-butene and (*E*)-1-silyl-2-butene in an 18:82 ratio. The reaction of (*E*)-2-chloro-3-pentene gave a quantitative yield of 2-silyl-3-pentene (90:10 *E*/*Z* ratio). 1,1-Difluoro-1-phenyl-2,2,2-trimethyldisilane also was effectively used, but symmetrical disilanes were found to be less reactive and with hexamethyldisilane the silylation did not occur at all. Inversion occurred at the site of silylation. It was deduced that formation of the π-allylpalladium complex occurs with inversion of configuration followed by silylation with retention. Optically active allylsilanes were formed in high yield when (*R*)-2-[(*S*)-1,1′-bis(diphenylphosphino)ferrocenyl]ethylamine was used as a chiral ligand. Enantiomeric excesses of up to 61% were obtained.



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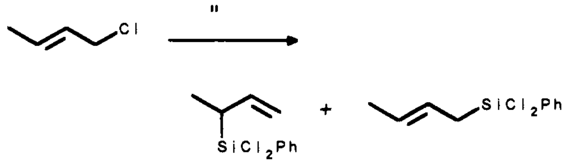

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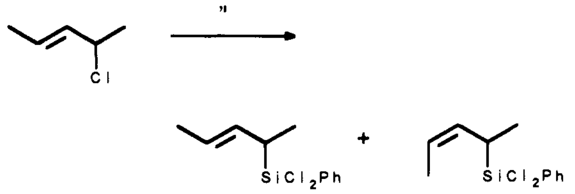


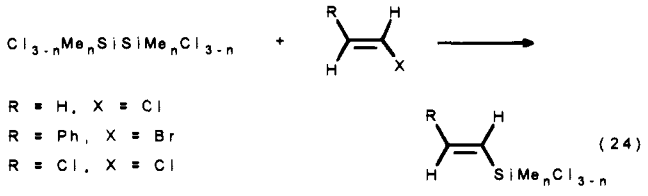
(23)

The initial step in these silylation reactions of allylic halides involves the oxidative addition of the allylic halide to the Pd(0) complex to give an intermediate Pd(II) species. This is supported by the observation that chloro(2-methylallyl)bis(triphenylphosphine)palladium(II) catalyzed the reaction of *sym*-dimethyltetrachlorodisilane and 2-methallyl chloride. Eaborn et al. have found that palladium(II) complexes can be used effectively in these reactions.[43]

The silylation of allylic acetates is analogous to the silylation of allylic halides described above. In an early report, Trost and co-workers utilized tris(trimethylsilyl)aluminum etherate in the presence of palladium and molybdenum catalysts to silylate allylic acetates.[49] Unfortunately, the regioselectivity was often low. Hexamethyldisilane has also been utilized with $Pd(PPh_3)_4$ to silylate allylic acetates, but the reaction is not applicable to substrates having a primary or secondary alkyl group at the α or γ position.[50] Often, the π-allyl palladium complex which is an intermediate in the reaction decomposes by β-hydrogen elimination. In a recent development, it has been found that $Pd(dba)_2$ with LiCl can be used to catalyze the reaction of hexamethyldisilane with allylic acetates.[51] Aliphatic and alicyclic allylic acetates were silylated in yields between 60 and 97% with good regioselectivity. Usually the *(E)* isomer predominated. LiCl or other salts were necessary for the reaction, but their concentration had little effect on the yields. The byproduct from the reaction was trimethylsilyl acetate.

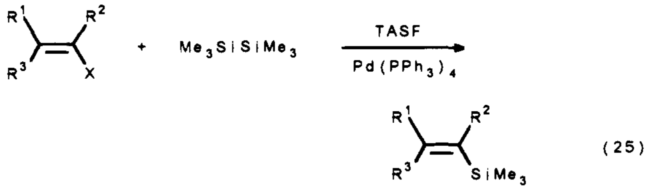
Acylsilanes[52] can be synthesized from acid chlorides and disilanes using palladium(II) complexes as catalysts. However, variations in solvent polarity and temperature can result in dramatic changes in product composition. Aromatic chlorosilanes are obtained by silylative decarbonylation of benzoyl chlorides using hexamethyldisilane and $PdCl_2(PhCN)_2$ at 145 °C.[53] At higher temperatures in nonpolar solvents (e.g. mesitylene at 165 °C) biaryls are formed from acid chlorides in a reductive coupling reaction.[54]

The dehalogenative silylation reactions described in this section all proceed more readily when the disilane is substituted with electron-withdrawing substituents such as chlorine. The electron-withdrawing character seems to facilitate the addition of the palladium complex to the silicon–silicon bond. This has been found to be true for the silylations of vinyl halides as well.[55] Nagai et al. found that vinylsilanes and vinylenebissilanes could be prepared in moderate to good yield using the appropriate vinyl chlorides and 1,2-dichlorotetramethyldisilane or 1,1,2,2-tetrachlorodimethyldisilane as shown in eq 24. However, because of their reactivity toward nucleophiles and particularly toward hydrolysis, the chlorosilanes are not always desirable synthetic reagents.



(24)

An important development in the dehalogenative silylation of vinyl halides was reported by Hiyama and Hatanaka[56] in 1987. They found that vinyl halides could be trimethylsilylated using $Pd(PPh_3)_4$, hexamethyldisilane, and tris(diethylamido)sulfonium difluoro(trimethyl)silicate (TASF) as shown in eq 25.



(25)

The reaction proceeds at room temperature in 2–10 h in HMPA/THF solution. Vinyl bromides and iodides were found to be good substrates and the reaction was relatively insensitive to the vinyl halide structure. Thus, cyclic vinyl iodides, both (*E*) and (*Z*) isomers of 2-phenyl- or 2-alkyl vinyl halides and even (*E*)-1-iodo-3-(2-phenylethyl)-1,3-butadiene were silylated under mild conditions in yields between 32 and 92%. An excess of TASF was needed in order to achieve high yields and lower yields were experienced with tetrabutylammonium fluoride. KF and CsF did not catalyze the reaction presumably because of their insolubility in HMPA. When $PdCl_2(PPh_3)_2$, $PdCl_2(MeCN)_2$, or several other Pd(II) catalysts were used, homocoupling of the vinyl halides was observed as well as silylation. Polar aprotic solvents like HMPA are necessary since the reaction is significantly retarded by even highly polar solvents like THF and acetonitrile. The reaction is completely stereospecific with (*E*)-vinylsilanes being produced exclusively from the (*E*)-vinyl halides and (*Z*)-vinylsilanes from the (*Z*)-vinyl halides. The mild reaction conditions are compatible with a wide variety of sensitive functional groups such as esters and nitriles. Aromatic halides could be silylated with the same catalyst system and TASF at room temperature, but up to 20 mol % of the catalyst and 24–48 h reaction times were needed to raise the yields to almost 100%. A similar set of reaction conditions was patented in Japan in 1989.[57]

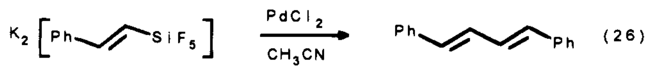
The reaction mechanism for the formation of these vinyl silanes most likely involves an initial oxidative addition of a Pd(0) complex to the vinyl halide followed by a reaction with free silyl anion or a pentacoordinated silicate formed by the reaction of TASF with hexamethyldisilane. Finally, reductive elimination produces the vinyl or aryl silanes. In the absence of the disilane, TASF, with an allylpalladium chloride dimer as catalyst, methylates aromatic halides bearing both electron-donating and electron-withdrawing substituents.[58] In this case, a transmetalation between the arylpalladium halide species and difluorotrimethylsilicate, $F_2SiMe_3^-$, generates an Ar–Pd(II)–Me species which is the active methylating agent.

IV. Stereospecific Formation of Vinylpalladium Intermediates from Vinylsilanes and Organofluorosilicates

An important advantage of organosilicon compounds for synthetic applications is the fact that they are stable under many reaction conditions, but can be readily activated by simple reagents such as fluoride ion.[59] Even hexaalkyldisilanes can be cleaved with fluoride ion from tetrabutylammonium fluoride (TBAF) to give metal-free silyl anions which add to alkyl aldehydes and 1,3-dienes.[60] The synthetic methods reviewed here involve reactions in which fluoride ion promotes formation of vinylpalladium intermediates from vinylsilanes or reactions of pentacoordinated silicates (preformed or formed *in situ* from vinyl silanes and fluoride ion) with palladium in a transmetalation reaction. The reactions may be closely related mechanistically to the coupling reactions described in section V but will be discussed separately since they involve a formal direct transmetalation induced by fluoride ion.

In two preliminary reports[61] Kumada et al. showed that organopentafluorosilicates could be coupled with allylic halides or carbonylated to stereoselectively form new carbon–carbon bonds using $Pd(OAc)_2$ or $PdCl_2$. Since the (*E*)-alkenylpentafluorosilicates can be readily prepared from alkynes in two steps (hydrosilylation followed by silicate formation), the reaction provides a reasonable methodology for the stereoselective formation of polyenes and enynes. In an extension of this early work, Kumada[62] was able to demonstrate five synthetically useful reactions of (*E*)-alkenylpentafluorosilicates that are promoted by palladium complexes and which involve the stereoselective formation of alkenylpalladium intermediates. They include (1) homocoupling of styryl- and phenylpentafluorosilicates, (2) cross coupling of alkenyl- and phenylpentafluorosilicates with activated olefins, (3) formation of (π-allyl)palladium complexes from alkenylpentafluorosilicates and activated olefins, (4) cross coupling of alkenylpentafluorosilicates and allylic halides, and (5) addition of alkenylpentafluorosilicates to carbon monoxide to give α,β-unsaturated carboxylic acid esters. Each of these reactions will be discussed separately below. It should be noted that in the investigations of these reactions only the (*E*) isomers were used as substrates; and, therefore, while the reactions are clearly stereoselective, they cannot be judged to be stereospecific.

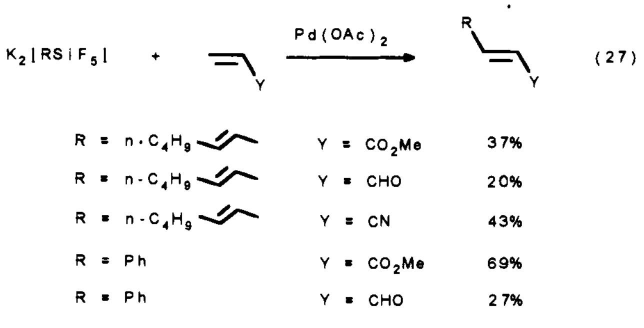
The homocoupling of styryl- and phenylpentafluorosilicates is promoted by palladium chloride in polar solvents like acetonitrile and THF. The reaction is rapid but is, unfortunately, stoichiometric in palladium since a black precipitate of palladium metal is formed. In the presence of palladium chloride (*E*)-styrylpentafluorosilicate is coupled in 54% yield to give (*E,E*)-1,4-diphenyl-1,3-butadiene as shown in eq 26.



(26)

While this reaction is stereoselective, other alkenylsilicates, such as 1-hexenylpentafluorosilicate, give only trace amounts of the coupled product. In an analogous homocoupling reaction, biphenyl is formed in moderate yield from potassium phenylpentafluorosilicate.

In the presence of palladium acetate, both alkenyl- and phenylpentafluorosilicates can be coupled with activated olefins like methyl acrylate, acrolein, and acrylonitrile. Equation 27 shows several typical substrates and product yields for these cross-coupling reactions.

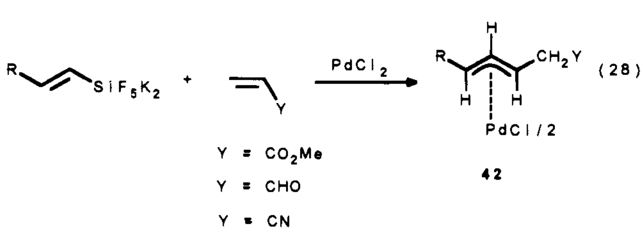


(27)

R = n-C$_4$H$_9$ Y = CO$_2$Me 37%
R = n-C$_4$H$_9$ Y = CHO 20%
R = n-C$_4$H$_9$ Y = CN 43%
R = Ph Y = CO$_2$Me 69%
R = Ph Y = CHO 27%

The reaction is once again stoichiometric in palladium. While the reaction of (*E*)-alkenylpentafluorosilicates and phenylpentafluorosilicates with these activated olefins is stereoselective with only (*E,E*) diene products being formed, the reaction yields are only poor to fair. The mechanism for the coupling reaction can be described by initial transmetalation to give the σ-bonded alkenylpalladium complex followed by *syn* addition of this complex to the olefin and *syn* β-elimination of the hydridopalladium species. This mechanism is supported by the observation of the stereoselective formation of (*E*)-3-phenylcrotonate from the reaction of phenylpentafluorosilicate with methyl crotonate.

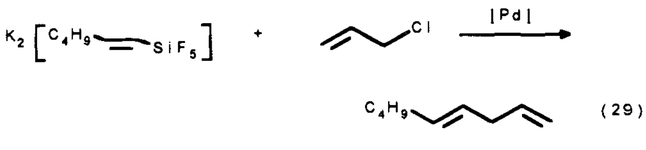
If palladium chloride is used in place of palladium acetate for the cross coupling of alkenylpentafluorosilicates with activated olefins, (π-allyl)palladium complexes (**42**) are isolated as shown in eq 28.



(28)

This provides convincing circumstantial evidence that a transmetalation of the alkenylsilane occurs as an intermediate step in the cross-coupling reaction. The formation of the alkenylpalladium intermediate occurs efficiently at −20 °C; however, yields of the (π-allyl)palladium complexes are low, indicating that the slow step in these cross-coupling reactions is the addition of the alkenylpalladium intermediate to the olefin.

The (*E*)-alkenylpentafluorosilicates were also found to couple with allylic halides to form (*E*)-1,4-dienes stereoselectively with typical yields of 30−70%. The reaction of 1-hexenylpentafluorosilicate with allyl chloride (10-fold excess in THF, room temperature, 24 h) gave (*E*)-1,4-nonadiene (**43**) in 71% yield (eq 29).



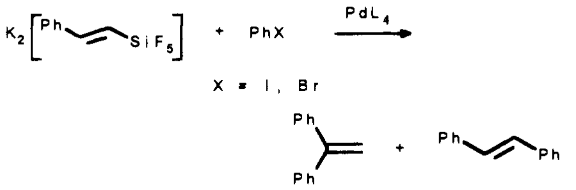
(29)

43

Palladium acetate was the most effective of the palladium catalysts used, and large excesses of the allylic halide were used to improve the yields (a 2-fold increase in coupling product was realized using a 10-fold excess of allyl chloride in the reaction of 1-hexenylpentafluorosilicate with allyl chloride). Allyl chloride was the most satisfactory allylic substrate, with significantly reduced yields being realized with allyl bromide, allyl acetate, and allyl tosylate. The reaction is also inhibited by steric hindrance in the allylic halide. Thus, the yield of cross-coupling product from methallyl chloride is lower than that from allyl chloride while crotyl chloride is almost inactive. Both internal and terminal olefinic pentafluorosilicates can be added to allyl chloride with complete regioselectivity, the allylic substrate being coupled to the carbon bearing the pentafluorosilicate group.

The mechanism of the cross coupling is analogous to that described by Heck.[63] The initially formed alkenylpalladium intermediate adds in a *syn* fashion to the allylic double bond and then eliminates palladium chloride. The palladium chloride formed is also a catalyst for the cross-coupling reaction and so the reaction is catalytic in palladium in contrast to some of the other cross-coupling reactions described above.

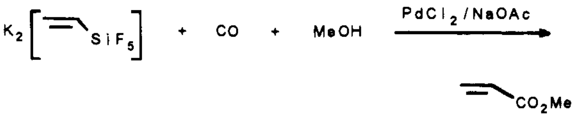
Under rather harsh conditions (135 °C) β-(*E*)-styrylpentafluorosilicate can be coupled with iodo- or bromobenzene to give (*E*)-stilbene in low to fair yields and a byproduct, 1,1-diphenylethylene (eq 30).



(30)

Both Pd(II) and Pd(0) catalysts were used, and the yields were found to be insensitive to ligand variation [PPh_3, Cl, dibenzylideneacetone (dba), OAc, $Ph_2P(CH_2)_4PPh_2$]. Only minor improvements in stilbene yields were realized with the addition of triethylamine to the palladium acetate-catalyzed reactions. The reaction of phenylpentafluorosilicate with β-(*E*)-bromostyrene gave only trace amounts of (*E*)-stilbene. These cross-coupling reactions may involve initial oxidative addition of the palladium complex to the aryl or vinyl halide followed by transfer of the alkenyl group from the pentafluorosilicate to the palladium(II) intermediate and reductive elimination of the coupled product. Little experimental evidence is available that addresses this mechanism.

(*E*)-Alkenylpentafluorosilicates also add carbon monoxide in the presence of palladium chloride or bromide, with sodium acetate as a base, to give (*E*) α,β-unsaturated carboxylic acid esters (eq 31).



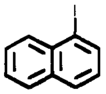
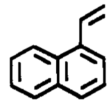
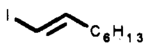
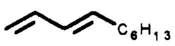
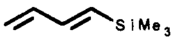
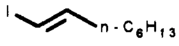
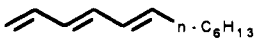
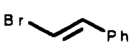
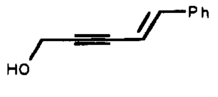
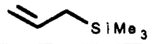
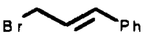
(31)

Palladium acetate and $PdCl_2(PPh_3)_2$ were not effective as catalysts. The yields are high (70–90%) but the reaction is stoichiometric in the palladium complex. The mild conditions (room temperature, 1 atm CO) and stereoselectivity could, however, make the reaction useful synthetically in some instances.

An improved method for the cross coupling of vinylsilanes with aryl, vinyl, and allyl halides was recently developed by Hiyama[64] who used tris(diethylamido)sulfonium difluoro(trimethyl)silicate (TASF) to facilitate the transmetalation reaction with palladium catalysts. It was suggested that TASF generates alkenyl pentacoordinated silicates from the vinyl silanes *in situ* which then react with the palladium complex. Other mechanistic explanations are also possible, *vide infra*. Typical reaction conditions for the coupling include 1 equiv of TASF in HMPA at 50 °C with allylpalladium dimer as the catalyst. A slight excess of TASF improves the yields. Tetrabutylammonium fluoride was inferior to TASF as a fluoride source and cesium fluoride and potassium fluoride yielded only trace amounts of the coupling product probably due to the lack of solubility of these fluorides. Table 1 shows several typical conditions and yields for the TASF-catalyzed coupling reactions of vinylsilanes and aromatic halides. The highest yields of products resulted with iodides as the substrates and HMPA solvent. The coupling of vinyl halides with vinyltrimethylsilane gave poor yields under these conditions, but could be improved by the use of triethyl phosphite in THF. Silyl alkynes can also be coupled with organic halides as illustrated by entry 3 in Table 1. The reactions are completely regioselective and stereoselective and are sufficiently mild that esters, ketones, and even aldehydes can be coupled without side reactions. However, 1-(trimethylsilyl)alkenes substituted in the 1 position failed to undergo the coupling reaction with TASF/Pd catalysis.

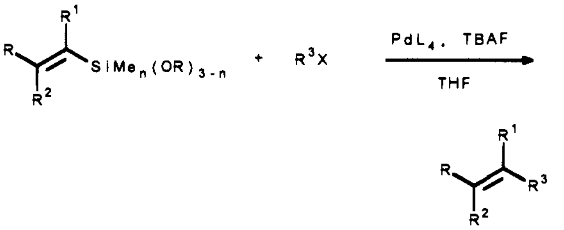
Introduction of one or two fluorines on the vinyl silane permits the cross-coupling reaction of 1-substituted 1-(trimethylsilyl)-1-alkenes.[65] Interestingly, a 1-trifluorosilyl group failed to react perhaps because it facilitates formation of a hexacoordinated

Table 1. TASF/(η^3-$C_3H_5PdCl)_2$ Cross Coupling of Silanes and Organic Halides

	Reactants		Solvent	Product	% yield
1.			HMPA		98
			P(OEt)$_3$/THF		100
2.			P(OEt)$_3$/THF		78
3.			THF		84
4.			THF		83

silicon species which is unreactive toward coupling. In cases where the use of TASF resulted in methylation of the iodoarenes used for coupling, tetrabutylammonium fluoride could be used and the methylation reaction eliminated. Retention of configuration about the starting vinylsilane and the iodoalkene was generally observed; but, when (*Z*)-1-(dimethylfluorosilyl)-1-decene was coupled with (*E*)-1-iodo-1-octene, (*Z*) to (*E*) isomerization occurred. The isomerization could be limited by using $Pd(PPh_3)_4$ as catalyst and DMF as the solvent.

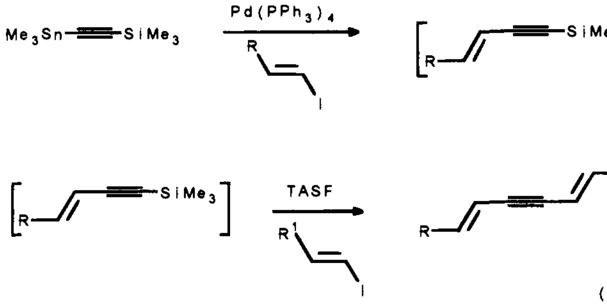
Alkenylmonoalkoxydimethylsilanes, -dialkoxymethylsilanes, and -trialkoxysilanes can also be coupled with alkenyl and aryl halides in the presence of tetrabutylammonium fluoride (eq 32).[66]



(32)

It is interesting that the trialkoxysilanes react smoothly in contrast to the trifluorosilanes which are unreactive. As for many of the other cross-coupling reactions described in this section, internal and terminal alkenylsilanes react readily, the alkenyl bromides are more sluggish and the stereochemistry of the vinyl silane is retained. Only in the case of (*Z*) silyldienes was any loss of stereochemistry observed. Allylpalladium chloride dimer and $Pd(OAc)_2$, both with and without $P(OEt)_3$ or PPh_3, as well as other palladium complexes have comparable catalytic activities.

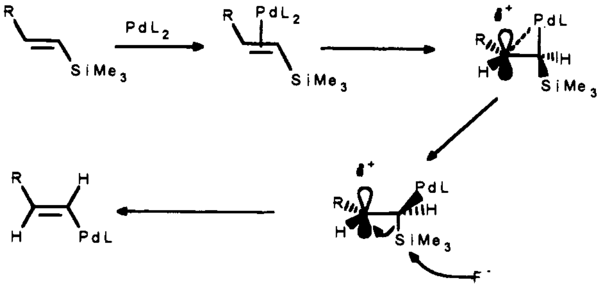
A recent report has described the use of TASF/Pd(PPh_3)$_4$ to promote the cross coupling of 1-(trimethylsilyl)butenyne intermediates with alkenyl or aryl iodides to give 1,5-dien-3-ynes. The reaction involves a one-pot sequential reaction of $Me_3SnCCSiMe_3$ with an alkenyl iodide followed by reaction with TASF and a second alkenyl iodide as shown in eq 33. The reactions are stereoselective and give high yields (50–85%) of the sensitive enynes.



(33)

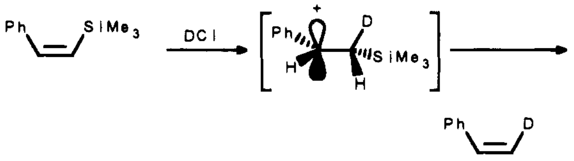
It is interesting to speculate on the mechanism of the formal transmetalation step in all of these reactions. A plausible mechanism for the formation of the reactive σ-palladium(II) intermediate from the alkenylpentafluorosilicates or the vinyltrimethylsilanes in the presence of fluoride sources is shown in Scheme 3.

Scheme 3



44

The Pd(II) salts, being moderate to strong electrophiles, initially may form a π complex with the double bond of the alkenylpentafluorosilicate or vinylsilane. This π complex then collapses toward a σ complex in which partial positive charge is developed on the carbon β to the silicon. The positive charge can be stabilized by a conformational orientation which places the carbon–silicon bond parallel to the developing vacant p orbital. Fluoride ion attack on silicon and elimination of the fluorosilane would then generate the alkenyl Pd(II) intermediate which undergoes *syn* addition to the alkenyl halide to complete the cross coupling. A least motion argument for the stabilization of the partial positive charge β to the silicon, and/or partial bridging in the palladium complex **44**, would explain the stereoselectivity of the addition–elimination. Other electrophilic reactions of vinylsilanes are also stereospecific (eqs 34 and 35) since elimination of the silane occurs from an intermediate β-silyl cation in which the carbon silicon bond is coplanar with the cation vacant p orbital.[67]



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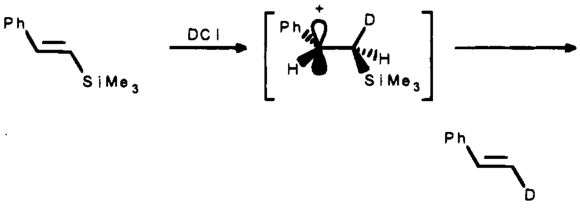
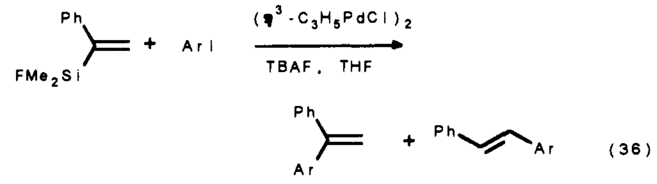


(35)

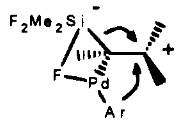
Since the (*E*) isomers were not used as substrates in these palladium-catalyzed cross-coupling reactions, it is not known whether the reactions are stereospecific. It may be that the intermediate **44** assumes the most stable conformation and eliminates the fluorosilane from that conformation rather than a least motion conformer. This mechanism clearly provides a simple and direct explanation of the stereochemistry of the reaction and is analogous to mechanisms developed for the cross-coupling reactions discussed in section V.

The cross coupling of 1-(fluorodimethylsilyl)-1-phenylethene with aryl iodides gives both *ipso* and *cine* substitution products as shown in eq 36.[68] The



Ar		
4-$CF_3C_6H_4$	93 : 7	72%
C_6H_5	75 : 25	69%
4-$C_2H_5OC_6H_4$	60 : 40	63%
1-naphthyl	100 : 0	74%

(*E*)-1-aryl-2-phenylethene product yields were found to be enhanced by electron-donating substituents on the aryl iodide. The additional steric bulk of 1-iodonaphthalene gave exclusively the *ipso* product. It was postulated that an intermediate β-cationic organosilicate–palladium complex is formed which can lead to *ipso* substitution via desilylation or to *cine* substitution via nucleophilic attack of the aryl substituent on the cationic β-carbon. This later path is the one favored by increased electron-donating substituents.

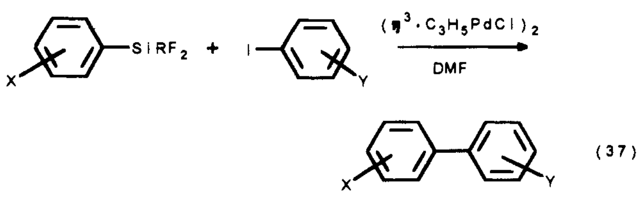


V. Regio- and Stereochemistry of the Palladium-Catalyzed Cross Coupling of Silanes with Organic Halides and Pseudohalides

A. Cross Coupling of Alkyl-, Aryl-, and Allylsilanes with Organic Halides and Pseudohalides Promoted by Fluoride Ion

A wide variety of transition metal-catalyzed cross-coupling reactions have been developed as regio- and stereoselective carbon–carbon bond forming tools for synthesis. The cross coupling of aryl-, alkenyl-, allyl-, and alkylsilanes has been developed as an alternative to the cross coupling of magnesium, boron, zinc, and tin alkyls which often show a lack of selectivity.

Arylfluorosilanes can be coupled with aryl iodides using (η^3-$C_3H_5PdCl)_2$ and potassium fluoride to give unsymmetrical biaryls[69] which can serve as useful precursors for liquid crystalline polymers. Typical reaction conditions include the use of DMF at 100 °C in the presence of 5 mol % of the palladium catalyst and 2 equiv of potassium fluoride. Tetrabutylammonium fluoride (TBAF) could also be used as the fluoride source. $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, and $Pd(dba)_2$ were ineffective. The yields range from 45 to 94%. The coupling reaction failed with $PhSiMe_3$, Ph_4Si, and $PhSiF_3$.



X = H, Me, CF_3, Cl, MeO

Y = OEt, OMe, CH_2OH, CH_2OAc, OAc, CO_2Me, CHO

In an analogous fashion, alkyltrifluorosilanes can be coupled with aryl halides using $Pd(PPh_3)_4$ and tetrabutylammonium fluoride to yield alkylated aromatics. Two equivalents of the alkylfluorosilane and 3–4 equiv of TBAF were found to be optimal.

$$ArX + F_3Si\text{-}(CH_2)_n\text{-}Y \xrightarrow[\text{TBAF, THF}]{Pd(PPh_3)_4} Ar\text{-}(CH_2)_n\text{-}Y \quad (38)$$

X = I, Br

Y = H, Ph, CO_2R, $COCH_3$, CN

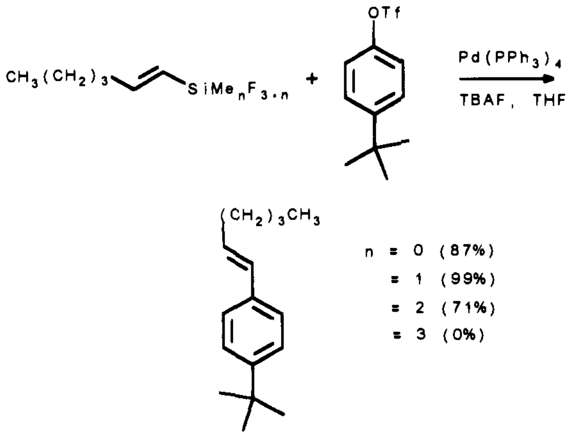
n = 2,6

While electron-withdrawing groups enhanced the reactivity of the alkylfluorosilanes, electron-withdrawing substituents on the aryl halide gave poor yields. Nitro and aldehyde functionality is compatible with the reaction conditions. Equimolar quantities of the alkylfluorosilane and fluoride ion are necessary. Dihexyldifluorosilane and triethylfluorosilane were unreactive.

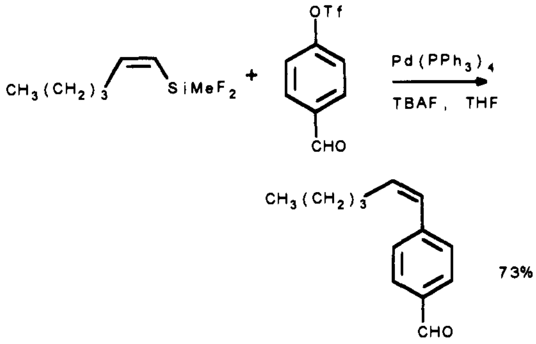
Alkyl-, alkenyl-, aryl- and alkynylsilanes can be coupled in good yields with enol and aryl triflates.[70] The triflates are more versatile substrates for the cross-coupling reactions than the halides described above since they are regioselectively prepared through standard enolate chemistry. The coupling occurs under mild conditions with TBAF in THF. TASF and KF were not effective sources of fluoride. Almost all common organosilanes can take part in the coupling reaction as shown by the illustrative examples in eqs 39–43. In contrast to the conditions utilized for the coupling of organostannanes and triflates, no LiCl is necessary for the coupling to occur efficiently. The mild conditions allow ketones and aldehydes to be coupled without using a protecting group.

The reaction was demonstrated to be stereospecific in the case of the reaction of (*E*)- and (*Z*)-1-octenyldifluoromethylsilane. Other important aspects of the reaction include the generally exclusive *ipso* substitution observed and the fact that in arylalkylfluorosilanes, only the aryl group participates in the coupling.

The reaction of chiral benzylsilanes with aryl triflates using $Pd(PPh_3)_4$ and TBAF was shown to give optically active coupling products.[71] Interestingly, the optical purity and absolute configuration of the products is strongly dependent on the reaction temperature. When (*S*)-1-phenyl-1-(trifluorosilyl)-



(39)



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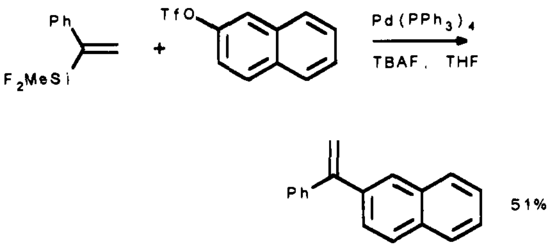

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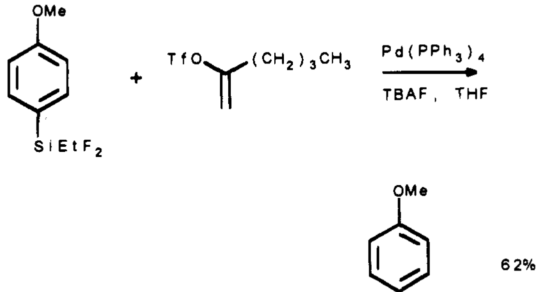
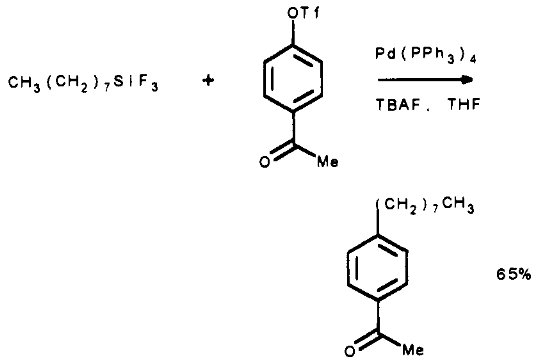
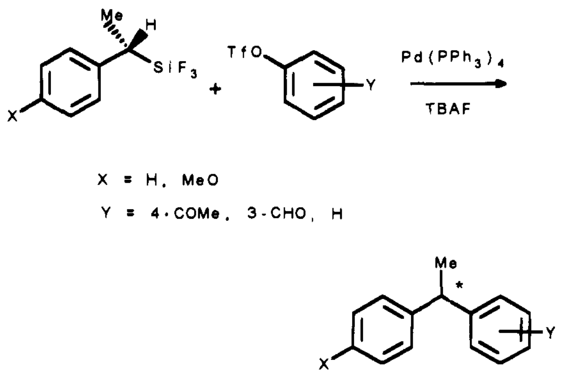


(42)



(43)

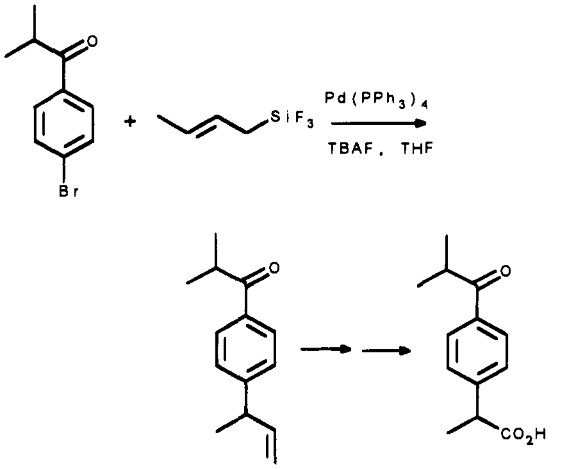
ethane (34% ee) was reacted with 4-acetylphenyl triflate at 50 °C in THF, the product, 1-phenyl-1-(4-acetylphenyl)ethane, was produced in moderate yield (31–51%) in 32–34% ee.



(44)

As the temperature was increased, the enantiomeric excess decreased until at ca. 75 °C, fully racemic product was obtained. Above 75 °C inversion occurred. When HMPA was added to the reaction medium, inversion also occurred even at low temperatures (60 °C). Since the reductive elimination of intermediate (1-phenylethyl)(aryl)palladium species is known to occur with retention of configuration of the alkyl ligand, it was deduced that the transmetalation step is the one whose stereochemical course is influenced by temperature and sovent polarity.

Hiyama et al.[72] have shown that the coupling of allyltrifluorosilanes with aromatic and enol triflates or halides takes a unique course, with coupling occurring exclusively at the γ-carbon. As in the coupling of alkylsilanes, vinylsilanes, and aromatic silanes with triflates, the $Pd(PPh_3)_4$/TBAF combination in THF was effective. $Pd(OAc)_2$/dppb with TASF was found to be particularly effective for coupling with enol triflates. In contrast, the coupling of allylmetals with vinylic, allylic, and aromatic electrophiles gives low regioselectivity. The synthetic utility of this coupling reaction was demonstrated in a short route to ibuprophen.



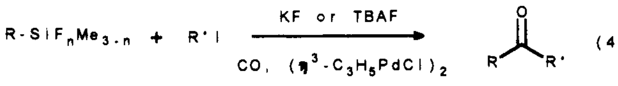
(45)

In a recent extension of these allylsilane coupling reactions, Hiyama and Hatanaka were able to utilize

$Pd(PPh_3)_4$ and TASF to couple optically active allylsilanes with aryl triflates. The stereoselectivities ranged between 58 and 99%. DMF was found to promote a high *E*/*Z* ratio of the product olefins and also to enhance the enantiomeric excess. With CsF and KF in THF the absolute configuration of the coupling products was the opposite of that formed when TASF was utilized. The addition of 18-crown-6 to the THF/CsF or KF reactions resulted in a reversal of the absolute configuration of the coupling product. The effects of DMF and the crown ether suggest that metal coordination plays an important role in defining the stereoselectivity of these S_E' reactions.

An interesting development in this area is the preparation of [η^3-1-(silyl)allyl]palladium chloride by the reaction of palladium(II) salts with allylsilanes.[73] While η^3-palladium complexes are readily formed from alkenes via deprotonation, the reaction of palladium(II) salts with allylsilane usually gives (η^3-allyl)palladium complexes via desilylation.[74] Murai and co-workers found that the addition of $PdCl_2(CH_3CN)_2$ to allyltrimethylsilane in acetonitrile without base gave 91% of the (η^3-allyl)palladium chloride as a result of desilylation, but when triethylamine was added, the [η^3-1-(trimethylsilyl)allyl]palladium chloride was formed in 41% yield. This should open up routes to cross-coupling products containing silicon as a synthetic handle for futher synthetic transformation.

Carbonylative cross coupling of aryl- and alkenylfluorosilanes with aryl iodides has been demonstrated to provide a facile route to substituted diaryl or alkenyl aryl ketones with moderate yields.[75]

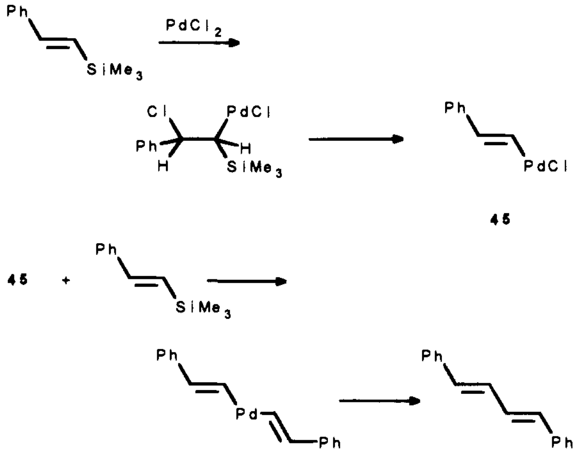


(46)

The reactions only require 1 atm of carbon monoxide in contrast to many transition metal-catalyzed carbonylative coupling reactions which require high pressures. Only fluorosilanes entered into the coupling reaction. Tetraalkyl- and arylsilanes formed biaryls instead. The optimum conditions were found to be 1 atm of CO, DMI (*N*,*N*-dimethyl-2-imidazolidinone), KF, and $(\eta^3\text{-}C_3H_5PdCl)_2$ at 100 °C. The reaction readily proceeds with either electron-withdrawing or electron-donating substituents and does not require the protection of aldehyde, nitrile, or ester groups. For the coupling of alkenylfluorosilanes with aryl and alkenyl iodides, TBAF was the fluoride ion source of choice. Some (*Z*) to (*E*) conversion was observed in the coupling of (*Z*)-alkenylfluorosilanes with aryl iodides. The loss of stereochemistry was shown to occur after the coupling.

B. Cross Coupling of Vinylsilanes with Organic Halides Promoted by Fluoride Ion

The first report of the homocoupling of a vinylsilane using a palladium complex under standard Heck reaction conditions was the coupling of (*E*)-β-(trimethylsilyl)styrene with palladium chloride to give (*E*,*E*)-1,4-diphenyl-1,3-butadiene (52%).[76] This coupling reaction set the stage for a series of investigations of the cross coupling of vinylsilanes with organic halides.[77] Weber et al. suggested that the homocoupling reaction proceeded according to the mechanism shown in eq 47.

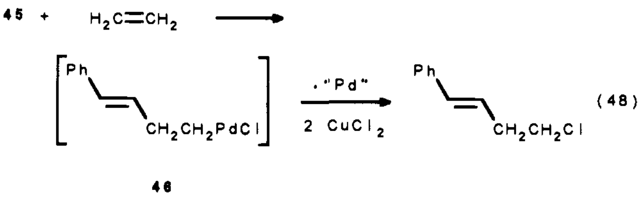


(47)

Initial addition of $PdCl_2$ to the double bond of the vinyl silane, elimination of trimethylsilyl chloride to give the β-styrylpalladium chloride (**45**) and addition of this Pd(II) intermediate to a second equivalent of (*E*)-β-(trimethylsilyl)styrene produces a bis(β-styryl)palladium intermediate. Reductive elimination of Pd(0) then oxidatively couples the two styryl groups. The postulated mechanism was based on the precedent of the addition of palladium chloride to olefins,[78] and the solvolytic fragmentation of (β-chloroethyl)trimethylsilane to give chlorotrimethylsilane and ethylene[79] as well as the known decomposition of diaryl palladium species to produce biphenyls and Pd(0).

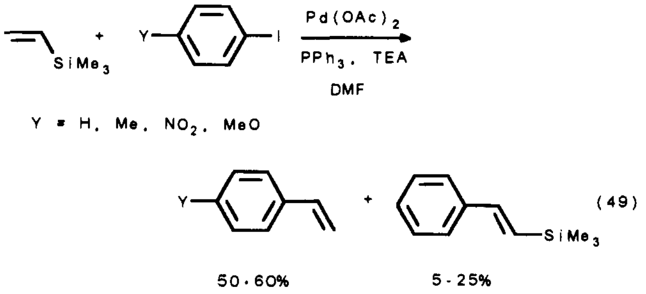
In a similar reaction, (*E*)-β-(trimethylsilyl)styrene was coupled with methyl acrylate using $PdCl_2$ to give methyl cinnamate in good yield. The initial step in the coupling reaction is formation of the intermediate Pd(II) species **45** which adds in a 1,2 fashion to the methyl acrylate. The final step in the formation of methyl cinnamate is then presumably the *syn* elimination of HPdCl. In this reaction and the homocoupling reaction of (*E*)-β-(trimethylsilyl)styrene, $CuCl_2$ was used to reoxidize the Pd(0) to $PdCl_2$. Two of the key features of the mechanism for this cross-coupling reaction, the *syn* addition of the Pd(II) complex to methyl acrylate with the Pd attached to the most sterically hindered carbon of the double bond and the *syn* elimination of a hydrido palladium species to generate the new double bond, are also characteristic of many of the cross-coupling reactions of vinylsilanes with organic halides, *vide infra*.

Weber et al. also demonstrated that the Pd(II) species **45** would add to ethylene to give 1-chloro-4-phenyl-3-butene in 30% yield (95:5 *E*/*Z*). In this coupling reaction, the addition product **46** is apparently oxidized to regenerate the $PdCl_2$ before HPdCl can be eliminated (eq 48).



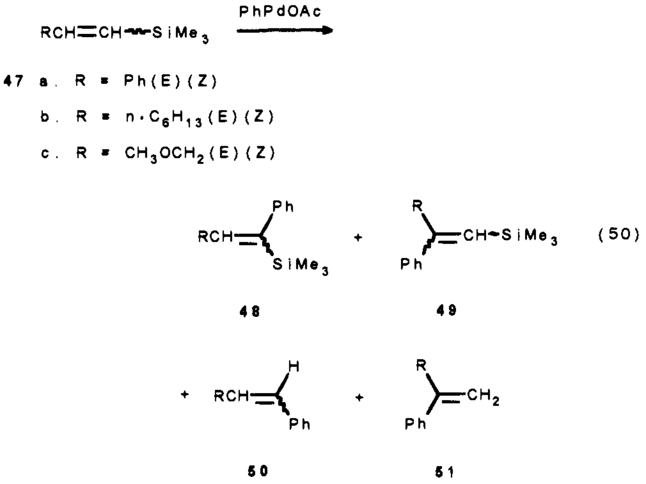
Both acetonitrile and methanol were used as solvents for these coupling reactions. When methanol was used, 1 equiv of a tertiary amine was used to remove the acid formed by methanolysis of the chlorotrimethylsilane.

In 1982 Hallberg and Westerlund[80] reported the efficient synthesis of styrene derivatives by a Heck-type coupling of substituted aromatic iodides with vinyltrimethylsilane (eq 49). The reactions were run at temperatures between 70 and 125 °C with $Pd(OAc)_2/PPh_3$ in DMF. The yields were consistently between 50 and 60%, independent of the 4-position substituent (MeO, NO_2, Me, H).



It was found that the yields dropped if triphenylphosphine was not used or if the catalyst was changed to Pd/C. Only small amounts of the product in which the trimethylsilyl group was retained were observed. Later investigations have suggested that the formation of these desilylated products results from an elimination of a hydrido palladium species which adds, again, to the initially formed arylated vinylsilane followed by elimination of the trimethylsilyl group and the palladium salt. A variety of other aromatic halides, such as 1-iodo- or bromonaphthalene, 9-iodo-*m*-carborane, and α-iodo- or bromopyridine were also shown to couple with vinyltrimethylsilane.[81]

Unfortunately, in these initial investigations of the palladium-catalyzed coupling reactions of vinylsilanes with organic halides, either no stereochemical markers were available or only the (*E*) isomer of the silane was investigated. The first investigation of the stereochemistry of the reactions of alkenyl silanes under Heck-type reaction conditions was reported by Kikukawa and co-workers in 1984.[82] They generated Ph−Pd−OAc *in situ* from several sources and used it to phenylate a series of (*E*)- and (*Z*)-alkenylsilanes (**47a−c**) (eq 50).



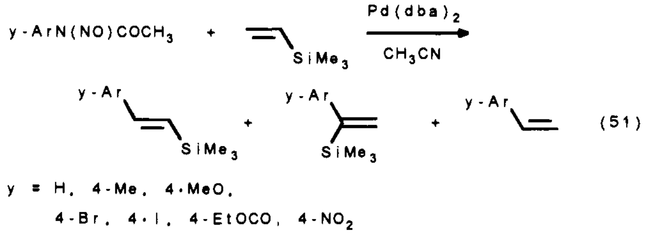
In contrast to the reactions studied by Weber et al., the products retaining the trimethylsilyl group predominated (**48** and **49** > **50** and **51**). Slight variations in the reaction conditions and the catalyst can affect the product distribution. The regiochemistry of the arylation was found to depend on both the specific substituents and the stereochemistry of the vinylsilane. In general, the phenyl group was added to the carbon bearing the least bulky substituents but in all cases mixtures of phenylation at the 1 and the 2 positions were obtained. Phenylation occurred in the 2 position in the order **47b** > **47c** > **47a**. The phenylations were predominantly stereospecific, with the geometry of the starting silanes being inverted in the products. Thus (*E*)-β-(trimethylsilyl)styrene (**47a**) gave 42% of **48a** (*E*/*Z* 1/99) and 33% of **49a** while the (*Z*) isomer gave 66% of **48a** (*E*/*Z* 99/1) and 27% of **49a**. Similar results were found for **47b,c**. Little isomerization of the products was observed even with long reaction times and thus the product stereochemistries reported represent the stereochemistry of the coupling reaction itself.

The stereochemistry of these reactions is fundamentally explained by a *syn* addition of Ph−Pd−OAc and a *syn* elimination of HPdOAc, as shown in Scheme 4.

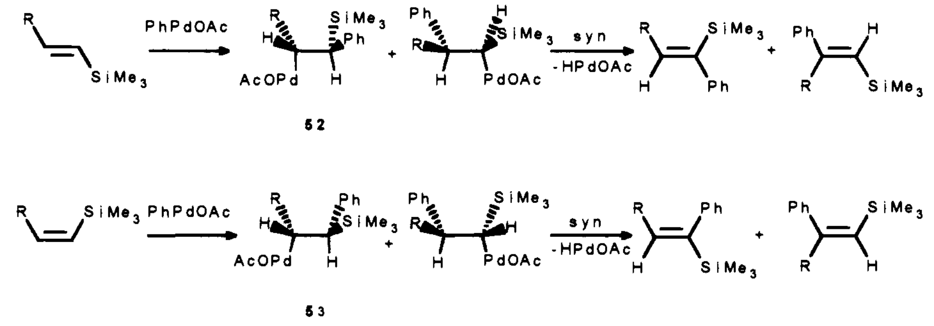
This mechanism is corroborated by the results obtained from the reaction of (*E*)- and (*Z*)-*n*-C_6H_{13}-$CH=CDSiMe_3$ with Ph−Pd−OAc, as shown in Scheme 5.

The retention of the deuterium in **54** and the loss of deuterium in **55** are consequences of the *syn*-elimination mechanism shown in Scheme 4. The desilylated products were not formed via a protodesilylation reaction. It was postulated that desilylation occurred through the intermediates **52** and **53**.

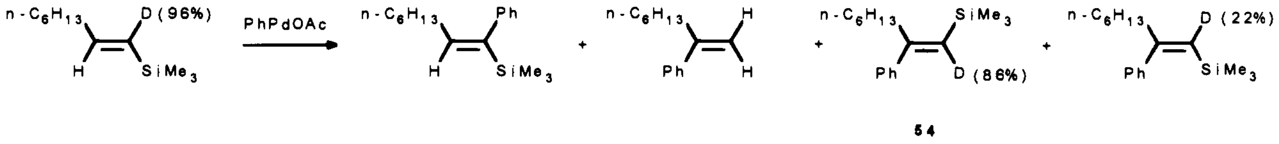
Vinyltrimethylsilane is also readily phenylated to give the corresponding styryl silanes using similar conditions, as shown in eq 51.[83]



Scheme 4



Scheme 5

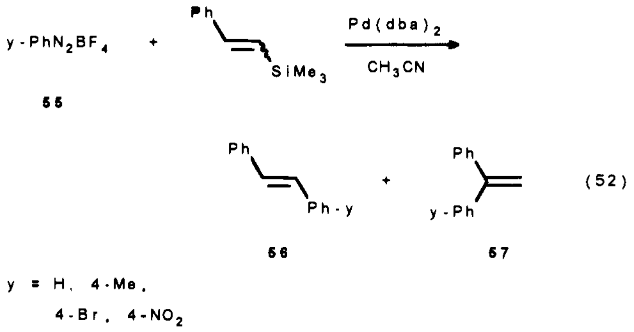


The yields are generally fair to good (34–78%) with electron-withdrawing groups facilitating the reaction. This reaction (under conditions of $Pd(OAc)_2/PPh_3$ in refluxing triethylamine) has been used recently in the preparation of electron-rich, sterically hindered styrenes as intermediates for the synthesis of colchicine.[84]

An interesting development in this area is the report that (*E*)-trialkyl-(2-arylethenyl)silanes can be prepared in high yield (91–96%) by the arylation of trialkylvinylsilanes using aryl iodides and palladium acetate under phase transfer conditions.[85] The unique aspect of this reaction is that the phase transfer conditions completely suppress the cleavage of the carbon–silicon bond, a reaction which is often predominant under the normal Heck-type reaction conditions. The reaction is carried out at 50 °C using DMF with $NaHCO_3$ and a phase transfer catalyst consisting of either $Bu_4N^+HSO_4^-$ or 18-crown-6. The mechanism is once again postulated to involve initial addition of an $ArPdIL_2$ intermediate to the double bond followed by *syn* elimination of $HPdIL_2$. The HCO_3^- is thought to react with the $HPdIL_2$ to generate carbonic acid, which decomposes to CO_2 and H_2O, and thereby prevents isomerization by HI and/or $HPdIL_2$ readdition and elimination. The thermodynamically more stable (*E*) isomer is produced in all cases.

C. Cross Coupling of Vinylsilanes with Arenediazonium Tetrafluoroborates

A number of reports have described the reactions of alkenylsilanes with arylpalladium tetrafluoroborates generated from arenediazonium tetrafluoroborates and Pd(0) complexes. The reactions of substituted arenediazonium tetrafluoroborates **55** with (*E*)- or (*Z*)-β-(trimethylsilyl)styrene catalyzed by bis(benzylideneacetone)palladium(0) proceed rapidly at 25 °C, with gas evolution, to give (*E*)-**56** and a minor product, **57**, in very high combined yields (84–100%).[86]

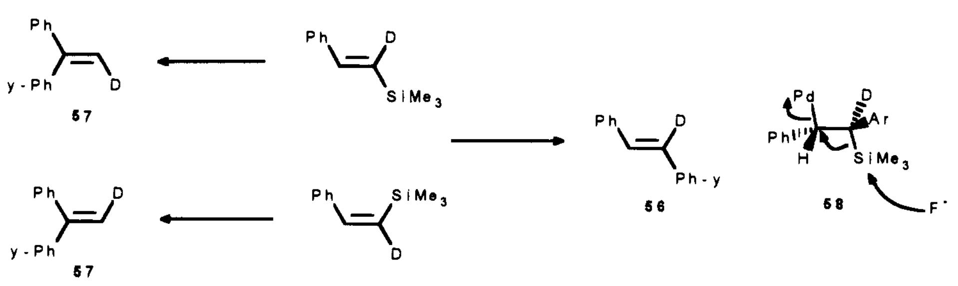


The addition product **56** always predominates and the (*E*) isomer is produced independently of the stereochemistry of the starting vinylsilane. (*E*)- and (*Z*)-β-*d*-4-nitrostyrene were used to demonstrate that the reaction to form (*E*)-**56** was stereoselective, but not stereospecific, while formation of the minor isomer **57** is stereospecific (Scheme 6). It was speculated that fluoride ion assists the elimination of fluorotrimethylsilane and the palladium salt from the most stable conformer of the initial 1,2-addition product, as illustrated for the case of the (*E*) silane addition intermediate product **58** in Scheme 6.

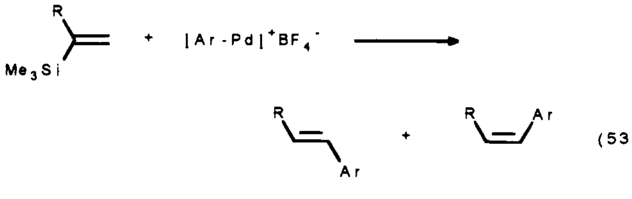
Formation of the minor product **57** requires an initial addition of the phenyl group to the 2 position carbon followed by the loss of $HPdL_2$, readdition of the $HPdL_2$ in a *syn* addition with the Pd species bonded to the 2 position, and then, fluoride ion assisted elimination of fluorotrimethylsilane and the palladium salt (perhaps by a *syn* elimination mechanism?). Protodesilylation was determined not to be a primary mode of formation of the minor desilylated product in these reactions. The stereochemistry of these reactions and the alternative plausible mechanisms considered for product stereochemistry are discussed in a summary paper by Kikukawa.[87]

The α-substituted vinylsilanes react very rapidly with $[Ar\text{-}Pd]^+BF_4^-$ formed from $Pd(dba)_2$ and arene-

Scheme 6



diazonium tetrafluoroborates (eq 53). The (*E*)-stilbene derivatives **59** are formed almost exclusively with no detectable amounts of 1,1-diphenylethylene derivatives. The reactions are complete in 10 min at 25 °C and the yields are good to excellent.[88]



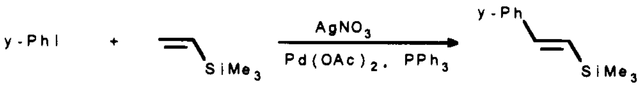
(53)

59

Vinyltrimethylsilane (excess) was also found to react with arenediazonium tetrafluoroborates to give predominantly (*E*)-ArCH=CHSiMe$_3$ using Pd(dba)$_2$ in acetonitrile.[89] Vinyltrimethoxysilane also reacted but gave only low yields of styrenes.

D. The Influence of Silver Salts on the Cross-Coupling Reactions of Vinylsilanes

Prevention of the loss of the trimethylsilyl group from the vinylsilane in all of these cross-coupling reactions is desirable since the vinylsilane products are more versatile synthetic building blocks than the simple substituted alkenes which result from desilylation. The desilylation reaction was found to be completely suppressed in the cross-coupling of aromatic halides with vinylsilanes by the addition of silver nitrate in acetonitrile (compare eqs 49 and 54).[90]



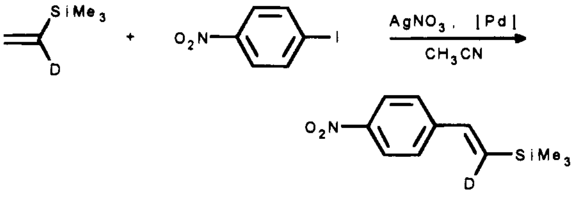
a.	y = H	32%
b.	y = 4-Me	67%
c.	y = 4-MeO	68%
d.	y = 4-NO$_2$	70%
e.	y = 3-NO$_2$	68%
f.	y = 2-CO$_2$Me	85%

(54)

Silver tetrafluoroborate was also effective, even at 100 °C when DMSO was used as solvent instead of acetonitrile. In addition to the suppression of the loss of the trimethylsilyl group, the rate of cross coupling is also increased by the addition of silver salts.

The reaction is highly regioselective. The (*E*)-trimethyl(2-phenylethenyl)silanes were formed in essentially all cases with less than 5% of the addition yielding product in which the aryl group is added to the 1-position carbon. The mild reaction conditions (50 °C, 5–20 h) allow most functional groups to be used and both aromatic and heteroaromatic iodides are appropriate substrates.[91] Triethoxyvinylsilane requires higher temperatures and gives lower yields of the coupling product.

It was postulated that the silver ion complexes with the iodide ion in the Ar–Pd–I complex assisting its addition to the double bond of the vinylsilane. When (1-deuteriovinyl)trimethylsilane was arylated with 4-nitroiodobenzene, no deuterium scrambling or loss was observed (eq 55).

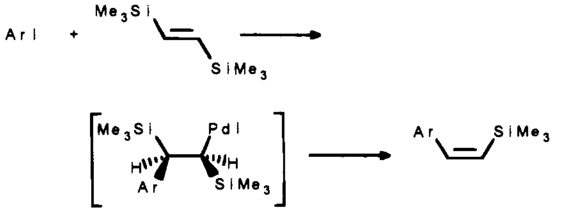


(55)

60

Thus, the final elimination of the PdH species is irreversible in the presence of the added silver ion. PdH does not add to the product **60**, and subsequently eliminate PdD or the trimethylsilyl group and the Pd salt.

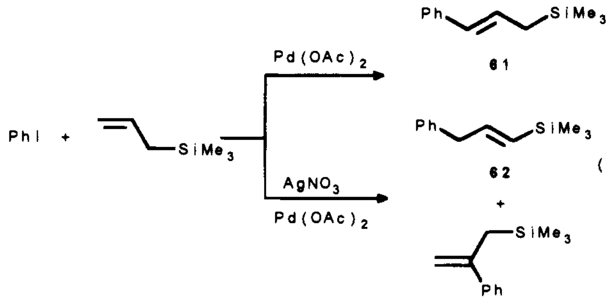
The use of (*E*)-1,2-bis(trimethylsilyl)ethylene with aryl iodides and Pd(OAc)$_2$ provides a route to the (*Z*)-trimethyl(2-arylethenyl)silanes which are not available by the cross coupling of aromatic halides with vinylsilanes.[92] The two reactions are therefore complimentary. The reaction apparently proceeds with a *syn* elimination of trimethylsilyl/PdI from the initial oxidative addition complex as shown in eq 56.



(56)

This is in direct contrast to the *anti* elimination observed in the reactions of aryl palladium tetrafluoroborates with vinylsilanes. It was suggested that the reaction could be used to prepare other (*Z*)-1,2-disubstituted olefins by using (*E*)-2-substituted vinylsilanes though this was not demonstrated.

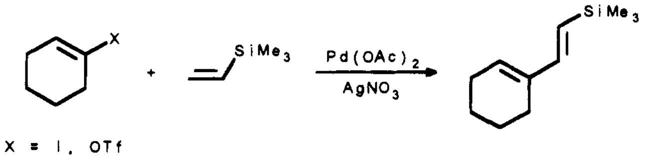
Palladium acetate also catalyzes the reaction of aromatic halides with allyltrimethylsilane as shown in eq 57.[93]



(57)

At 120 °C, without added silver salt, arylation occurred predominantly at the terminal position giving (*E*)-1-phenyl-3-(trimethylsilyl)-1-propene (**61**) as the major silylated product. Addition of silver nitrate fully suppressed the desilylation, increased the rate of reaction and gave (*E*)-3-phenyl-1-(trimethylsilyl)-1-propene (**62**) as the major product.

In analogous fashion to the coupling of aromatic halides with vinylsilanes, vinyl iodides, and vinyl triflates can be added to vinylsilanes to prepare 1-(trimethylsilyl)-1,3-dienes, valuable Diels–Alder substrates.[94] The reaction is illustrated for cyclohexenyl iodide (triflate) in eq 58.

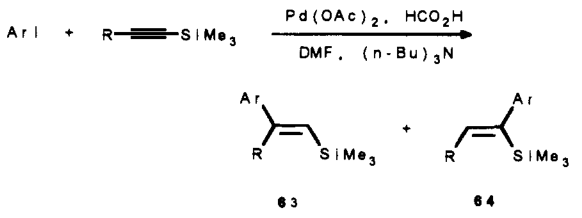


(58)

Once again silver salts are needed to prevent elimination of the trimethylsilyl group. Even in the presence of silver nitrate the product from cyclopentenyl iodide and vinyltrimethylsilane still undergoes desilylation. Electron withdrawing groups activate the vinyl iodides and triflates and substituents on the carbon bearing the iodide assure addition of the vinyl group to the terminal carbon of the vinylsilane double bond.

E. The Cross Coupling of Ethynylsilanes with Organic Halides

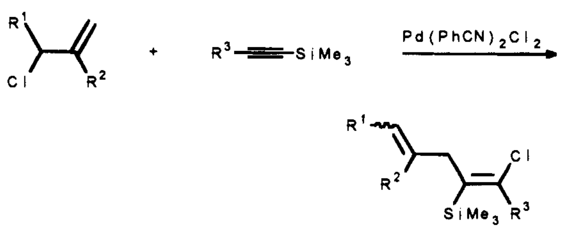
The palladium-catalyzed addition of aryl iodides to ethynylsilanes has been found to provide a regio- and stereoselective route to functionalized 2,2-disubstituted vinylsilanes (eq 59).[95]



(59)

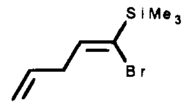
Palladium acetate with tertiary amines and formic acid in DMF were used to catalyze the addition. The 2,2-disubstituted vinylsilanes **63** are the major product (generally 40–70%) with less than 20% of the 1,2-substituted vinylsilanes **64** being formed. The corresponding desilylated alkenes are also formed in variable yields. The bulky trimethylsilyl group on the acetylene controls the carbo-palladation step, causing arylation to occur at the carbon bearing the alkyl or aryl group. Strongly electron-withdrawing substituents on the arylacetylene cause some arylation to occur at the carbon bearing the trimethylsilyl group. A 4-hydroxy group can also affect the regiochemistry of the carbo-palladation step, perhaps by complexing to the approaching palladium atom, thereby causing arylation on the carbon bearing the trimethylsilyl group, and formation of the carbon palladium σ bond at the 2 position.

Allylic halides can also be added to alkynylsilanes using soluble palladium complexes to create 1,4-dienes.[96] When allylic chlorides are coupled to *n*-butynyl-, *n*-pentynyl, and *n*-hexynyltrimethylsilane using $PdCl_2(PhCN)_2$, the 5-chloro-4-trimethylsilyl substituted 1,4-diene is formed as a result of the 1,2-addition with the allylation occurring at the carbon bearing the trimethylsilyl group (eq 60).



(60)

The yields range between 75 and 92% and the stereochemistry of the addition is exclusively *syn* (>95%). These chlorinated 1,4-dienes can be converted to the corresponding 1,4-enyne using tetrabutylammonium fluoride in THF. Interestingly, when allyl bromide is coupled with (trimethylsilyl)acetylene, using $PdBr_2(PhCN)_2$, 1-bromo-1-(trimethylsilyl)-1-(*Z*)-4-pentadiene (**65**) is formed.[97] The reason for the opposite regiochemistry of the addition is not known.



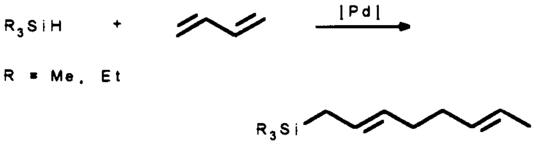
65

VI. Regiochemistry of Palladium-Catalyzed Hydrosilylation Reactions

A. Hydrosilylation of Olefins and Dienes

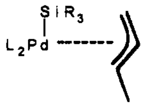
The hydrosilylation of olefins is catalyzed by transition metal complexes, with platinum complexes being the most common. These reactions have been thoroughly investigated and reviewed.[98] However, no compilation of palladium-catalyzed hydrosilylation reactions and their stereochemical outcomes has been provided. Palladium catalysts have been generally regarded as inactive for hydrosilylation reactions because they are often reduced to the metallic state.[99] As the reactions reviewed in this section demonstrate, however, there are a variety of hydrosilylation reactions that proceed nicely with palladium catalysts and which in several instances give product regiochemistries and stereochemistries not available using other catalysts.

The hydrosilylation of butadiene was one of the earliest successful hydrosilylation reactions catalyzed by palladium complexes. Takahashi et al.[100] reported in 1969 that the reaction of either trimethylsilane or triethylsilane with butadiene and bis(triphenylphosphine)(maleic anhydride)palladium or bis(triphenylphosphine)(*p*-benzoquinone)palladium, at 85 °C, gave 1-(trimethylsilyl)octa-2,6-diene or 1-(triethylsilyl)octa-2,6-diene (1:2 adducts) respectively (eq 61).



(61)

$Pd(PPh_3)_4$ was found to be a less effective catalyst. In contrast, trichlorosilane and dimethylphenylsilane reacted to give the normal 1:1 hydrosilylation products [e.g. 1-(trichlorosilyl)-2-butene].[101] It was suggested that the palladium catalyst reacts with the silanes to form a palladium hydride that inserts butadiene to form a π-allyl complex **66** which either adds another molecule of butadiene to form the 1:2 adduct or collapses to the 1-silyl-2-butene, the 1:1 adduct.



66

An investigation of the mechanism of the reaction of $(\eta^3\text{-}C_3H_5PdCl)_2$ with trimethylsilane was recently reported.[102]

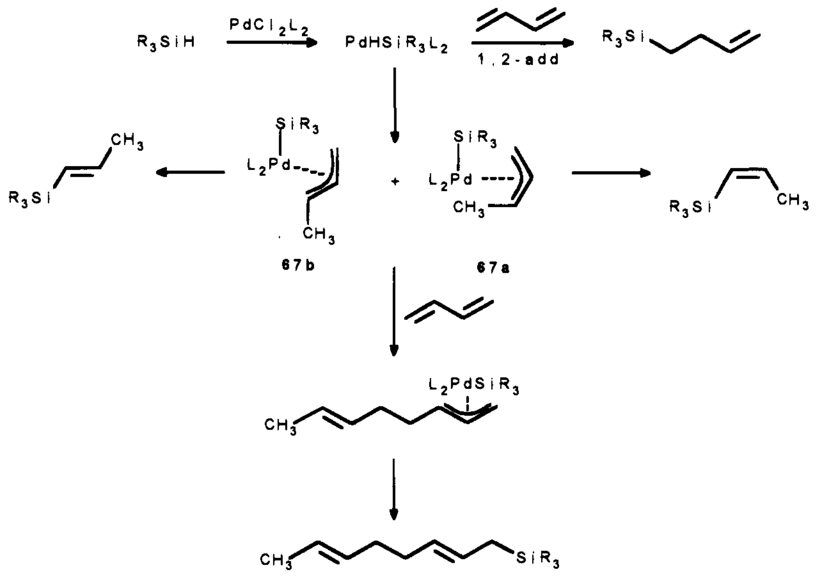
Palladium metal will also catalyze the hydrosilylation of butadiene if triphenylphosphine is added.[103] Once again the course of the reaction is dependent on the nature of the silane used. Trichlorosilane gives the 1:1 adduct, and trimethylsilane yields the 1:2 adduct while a mixture of the 1:1 adduct (83%) and 1:2 adduct (5%) result when dichloromethylsilane is used.

An extensive set of experiments designed to delineate the key reaction parameters controlling the hydrosilylation of butadiene by palladium complexes was carried out by the group of Hetflejs.[104] A series of Pd(II) catalysts including $PdCl_2(C_6H_5CN)_2$, $[PdCl(\pi\text{-}C_3H_5)]_2$, $PdCl_2[P(C_6H_5)_3]_2$, $PdCl_2(C_6H_{11}NC)_2$, and $PdCl_2[C_6H_{11}NC]P(C_6H_5)_3$ were used and similar results to those obtained by Takahashi with Pd(0) catalysts were found. In general the reactions proceeded readily in the absence of solvent. Addition of benzene favored the 1:2 adduct over the 1:1 adduct, although the total product yield was decreased. Increasing the temperature increased the amount of 1:1 adduct formed at the expense of the 1:2 adduct and if a sufficient excess of 1,3-butadiene was added, the formation of 1:1 adducts could be suppressed.

The reaction is also influenced by the nature of the silane used. The reaction of trichlorosilane with butadiene proceeded rapidly at room temperature to give selectively 1-trichloro-(*Z*)-2-butene while the less reactive triethoxysilane gave 1-(triethoxysilyl)-2,6-octadiene. At elevated temperatures, triethoxysilane gave both 1-(triethoxysilyl)-(*Z*)- and (*E*)-2-butene. It was demonstrated that the (*E*) isomer was not formed by isomerization of the (*Z*) isomer. Diethoxypropyl- and ethoxydipropylsilane unexpectedly produced 4-silyl-substituted 3-butenes and 1-silyl-substituted 1,3-butadienes. Trimethylsilane, on the other hand, gave 1-(trimethylsilyl)-1-butene and 1-(trimethylsilyl)-2,6-octadiene. The experimental data are consistent with the reaction mechanism suggested in Scheme 7, which is a modification of that given initially by Takahashi.[97]

The formation of the 1-silyl-substituted 2-butenes is readily explained by the π-allyl palladium intermediate with the (*E*) and (*Z*) isomers originating from the *syn* and *anti* conformers **67a** and **67b**. The 4-silyl-substituted 1-butene may derive from a direct 1,2-addition reaction. The reaction of trimethylsilane-d_1 with 1,3-butadiene gave 4-(trimethylsilyl)-1-butene-3-d_1, 1-(trimethylsilyl)-1,3-butadiene-d_0, and 1-(trimethylsilyl)-2,6-octadiene-8-d_1. These products are all consistent with the mechanism given in Scheme 7. The mechanism for formation of 1,4-bis(trimethylsilyl)-2-butene was not clearly defined;

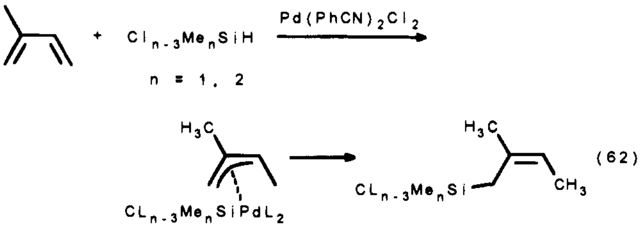
Scheme 7



however, it apparently arises from initially formed 1-(trimethylsilyl)-1,3-butadiene.

Hetflejs et al. also developed a series of palladium catalysts bound to inorganic supports that could be used for the hydrosilylation of 1,3-butadiene.[105] The two catalysts, alumina$\cdot\cdot$$OSi(CH_2)_2P(C_6H_5)_2\cdot\cdot PL_x$ and alumina$\cdot\cdot$$OSi(CH_3)(CH_2)_3CN\cdot\cdot PdL_x$ gave essentially quantitative yields of 1-(trichlorosilyl)-(*Z*)-2-butene and thus were more selective and slightly more effective than the soluble palladium complexes. The catalysts could not be reused due to abstraction of the palladium from the support.

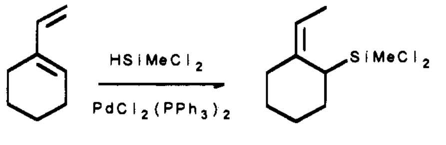
The hydrosilylation of isoprene, 1,3-pentadiene, and 1,3,7-octatriene gives only the 1:1 adducts.[106] Hydrosilylation of 1,3-pentadiene with trichlorosilane gave 2-(trichlorosilyl)-3-pentene and, since conjugated dienes are more reactive toward hydrosilylation than terminal olefins, 1,3,7-octatriene gave 4-(trichlorosilyl)-2,7-octadiene exclusively. The hydrosilylation of isoprene is interesting in that it is both regioselective and stereoselective[107] producing only (*Z*)-2-methylbuten-2-ylsilanes as shown in eq 62.



(62)

Only the chlorosilanes were reactive. Other silanes such as triethoxysilane, triethylsilane, and phenyldimethylsilane did not react. The hydrosilylations of myrcene and ocimene also proceed regio- and stereoselectively to give the 1,4-addition product. Only in the case of the hydrosilylation of ocimene with trichlorosilane is 1,2 addition found. The decrease in reactivity of the silanes in diene hydrosilylations parallels the decreasing electronegativity of the substituents attached to silicon.[108]

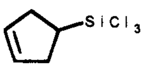
The hydrosilylation of 1-vinylcycloalkenes with methyldichlorosilane using $PdCl_2(PPh_3)_2$ has been reported to proceed with high regioselectivity and stereoselectivity to give the (*Z*)-1-ethylidene-2-silylcycloalkanes.[109] The reaction is illustrated below for 1-vinylcyclohexene. The isolated yields range from 38 to 84% with typical (*E*)/(*Z*) ratios in the range of 5/95. This reaction provides a regio- and stereoselective route to cyclic allylsilanes.



(63)

The addition of trichlorosilane to cyclopentadiene using Pd(II) catalysts gives predominantly 3-(trichlorosilyl)cyclopentene (**68**) (60–86%) and minor amounts of mono(trichlorosilyl)-4,7-methylene-4,7,8,9-tetrahydroindans (**69**).[110]

This contrasts with the same reaction catalyzed by nickel complexes which gives predominantly the indans **69**. The reaction proceeds at temperatures as low as 80 °C, but less dicyclopentadiene is obtained at higher temperatures. The formation of the indans is a result of hydrosilylation of dicyclopentadiene. 3-(Trimethylsilyl)cyclopentene prepared by this route has been used to prepare other cyclopentene derivatives.[111]



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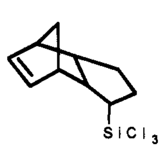

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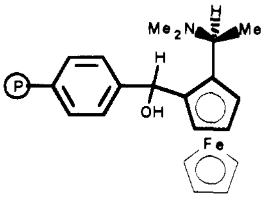
A variety of complexes of palladium have been found to be active hydrosilylation catalysts for simple alkenes. The early investigations were carried out by Tsuji et al.[103,106] The yields can be very good, with 1-octene being hydrosilylated by trichlorosilane, using $Pd(PPh_3)_4$, in 90% yield at 100 °C to give exclusively 1-(trimethylsilyl)octane after methylation. In general the hydrosilyation of terminal olefins by trichlorosilane gives yields greater than 85%. Formation of the terminal silyl-substituted product is the normal course for these palladium-catalyzed hydrosilylations, in contrast to the hydrosilylations catalyzed by platinum and nickel complexes[98]. Even palladium metal can be used if triphenylphosphine is incorporated in the solution. Pd(II) catalysts such as $PdCl_2$ and palladium acetylacetonate are also effective and several new catalysts have been patented.[112]

Inner olefins are not hydrosilylated by these same palladium catalysts. This is especially important because unlike chloroplatinic acid, palladium does not isomerize the inner olefins to the terminal position. Thus 1,4-hexadiene can be hydrosilylated to give 1-(trichlorosilyl)-4-hexene and only the vinyl group of vinylcyclohexene is hydrosilylated. The following order was observed for the reactivity of various silanes $HSiCl_3 > HSiCl_2Me > HSiClMe_2 > HSiCl_2(OMe) > HSiMe_3 > HSi(C_2H_5)_3 > HSi(OMe)_3$. (Trichlorosilyl)propionitrile was obtained from acrylonitrile and trichlorosilane. In this case, as in the case of styrene, the α-silylated product predominates over the β-silyl adduct which would result from the normal regiochemistry of addition.

Pd(II) complexes of the polymer-supported ferrocenes, **70–72**, have been shown to be effective catalysts for the hydrosilylation of simple alkenes.[113]



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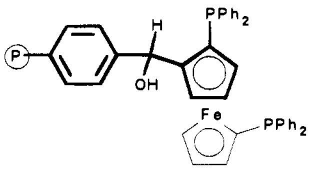

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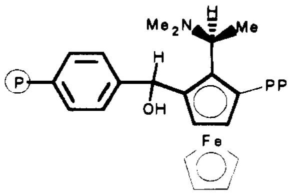


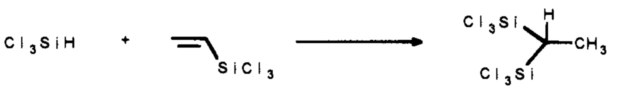
72

The hydrosilylation of styrene with trichlorosilane, using these catalysts at 70–90 °C, gives predominantly the (1-phenylethyl)trichlorosilane. The yields can be quantitative, the α/β selectivity is >95/5 and the catalysts can be used at least 5 times with essentially no decrease in catalytic activity. Even the unactivated olefin 1-hexene is hydrosilylated, albeit in low yield. In this case only 1-(trichlorosilyl)hexane is obtained.

Recently dinuclear palladium complexes containing bis(diphenylphosphino)methane (dpm) such as $Pd_2(dpm)_3$ and $Pd_2Cl_2(dpm)_2$ have been shown to catalyze the addition of trichlorosilane to vinyltrichlorosilane, hexene and styrene.[114] β-Addition is observed exclusively in the case of hexene, α-addition with vinyltrichlorosilane and mixtures for styrene. The yields are moderate to high.

trans-Dichlorobis(4-benzyl-1-menthyl-2,2,3,3-tetramethylphosphetane)palladium(II) has been shown to be a less effective catalyst for the hydrosilylation of cyclopentadiene and styrene than a 1:1 complex prepared from the phosphetane ligand and $Cl_2Pd(PhCN)_2$, the latter giving quantitative yields.[115] This phenomenon seems to be general with phosphetane ligands and was suggested to be consistent with the postulate initially made by Hayashi that the hydrosilylation proceeds through an active square planar palladium intermediate.

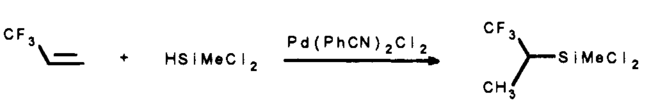
There have been several reports of the hydrosilylation of vinyltrichlorosilane with trichlorosilane catalyzed by palladium complexes.[116] In the presence of $Pd(PPh_3)_4$, the α-silylated product, 1,1-bis(trichlorosilyl)ethane, is formed in high yield (eq 64).



(64)

At 60 °C the total yield is 76% and the α/β ratio is 35:3, while at reflux (neat trichlorosilane) the total yield is 98% and the α/β ratio is 48:1. The reaction has an induction period of 2–5 h depending on whether oxygen is present. The α-silylated product formation is specific to palladium complexes while β-silylated products are formed with complexes of other metals. When dichloromethylvinylsilane, chlorodimethylvinylsilane, and trimethylvinylsilane are hydrosilylated with trichlorosilane, using $Pd(PPh_3)_4$, the β-silylated product is formed. The β-silylated product is also formed when dichloromethylsilane is used with any of these vinylsilane substrates. Palladium metal and $PdCl_2$ do not catalyze the reaction. Oligomeric $Pd(PPh_3)_2$ species and palladium-silyl complexes have both been postulated to be the palladium species to which the silane adds oxidatively to generate the $L_2Pd(II)(R_3Si)H$ reactive intermediate. When $PdCl_2(PPh_3)_2$ is treated with trichlorosilane at 120 °C, complex mixtures were formed which were active catalysts at 45 °C.

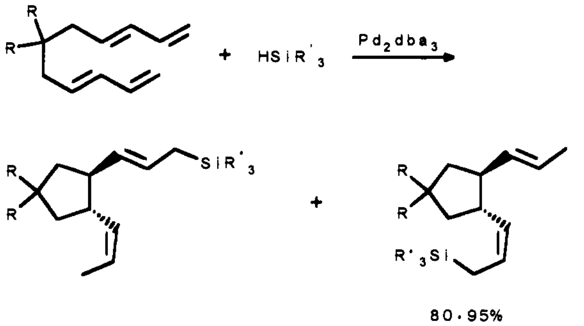
Trifluoropropene and pentafluorostyrene were inert to hydrosilylation by trialkylsilanes, phenyldialkylsilane, and chlorodimethylsilane in the presence of $PdCl_2(PhCN)_2/PPh_3$. However, trifluoropropene reacted smoothly with dichloromethylsilane to give [α-(trifluoromethyl)ethyl]dichloromethylsilane in 88% yield at 100 °C (eq 65).



(65)

The α-silylated product was also formed when 3,3,4,4,4-pentafluorobutene was hydrosilylated with dichloromethylsilane. These products provided new monomers for fluorosilicones. There has been some commercial interest in the hydrosilylation of fluorinated olefins.[117]

Several other miscellaneous hydrosilylation reactions catalyzed by palladium have been described. Allene reacts with trichlorosilane at 120 °C to give 1-(trichlorosilyl)-2-propene in 70% yield and, upon prolonged reaction, 1,3-bis(trichlorosilyl)propane.[106] Pyridine is also hydrosilylated yielding 1-(trimethylsilyl)aza-2,5-cyclohexadiene.[118] 2- and 4-vinylquinoline have also been hydrosilylated with palladium catalysts.[119] Recently a novel palladium-mediated tetraene tandem carbocyclization/hydrosilylation has been reported[120] (eq 66). The reaction produces six

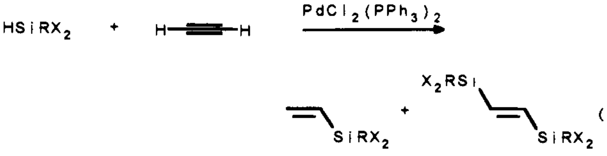


(66)

contiguous stereochemical centers, and yet the two diastereomeric products differ only by which terminus the silane is attached to. A recent mechanistic study[121] indicates that the cyclization does not occur by a carbocylization–hydrosilylation mechanism but instead involves a palladacycle such as those postulated in the telomerization of butadiene.

B. Hydrosilylation of Acetylenes

Acetylene can be hydrosilylated by various silanes with either $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ to give the vinylsilane and 1,2-bis-silylated ethane, as shown in eq 67, however, many other metal complexes were more effective.[122,98] With the palladium catalysts, the combined yields of the two products in all cases were less than 70%.



(67)

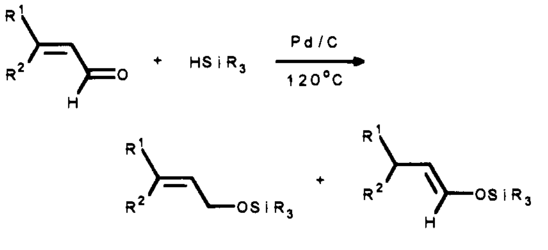
a. R = Me, X = Cl	30%	40%
b. R= Me, X = OEt	24%	23%
c. R = n-C_6H_{13}, X = Cl	55%	5%
d. R = X = OEt	0%	0%

A series of new cationic (triphenylphosphine)-palladium complexes containing polyhedral borane anions $B_{10}Cl_{10}^{2-}$ and $B_{12}Cl_{12}^{2-}$ have been shown to be promising catalysts for the hydrosilylation of alkyl and aryl acetylenes.[123] For example, 1-hexyne is hydrosilylated in 90% yield by triethylsilane and $[(Ph_3P)_4Pd_2Cl_2]B_{10}Cl_{10}$. (*E*)-1-(Triethylsilyl)-1-hexene predominates. When phenylacetylene is the substrate, the product yields are generally below 30% and the α-adduct predominates.[124] Trichloro- and triethoxysilane were considerably less reactive. Other soluble palladium complexes such as $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ only catalyzed the polymerization of phenylacetylene and 1-hexyne.

Hiyama has reported the hydrosilylation of 1,4-bis(trimethylsilyl)butadiyne with triethylsilane using $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$.[125] The yields of 1,4-bis(trimethylsilyl)-3-(triethylsilyl)buta-3-ene-1-yne were 18 and 8% respectively. This is the only reported instance of the hydrosilylation of a diacetylene using a palladium catalyst.

C. Hydrosilylation of α,β-Unsaturated Aldehydes

While the hydrosilylation of ketones and aldehydes have been extensively investigated[126] there are very few instances of palladium-catalyzed silylations. However, Pd/C (10%) has been found to hydrosilylate α,β-unsaturated aldehydes in excellent yields (eq 68).[127]



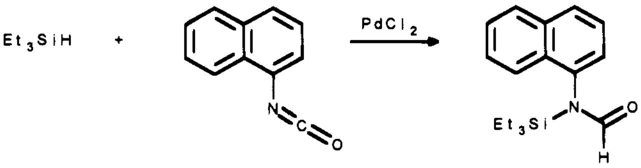
73

(68)

The major product in all cases is the 1,4-addition product **73** although yields of the 1,2-addition product, as high as 37%, were found for those aldehydes substituted with phenyl groups. Thus, the reaction of acrolein with triethylsilane gave an 86% total yield of hydrosilylated product (83% of the 1,4-addition product and 3% of the 1,2-addition product). The *trans/cis* selectivity is also high (92:8). Similar product yields and stereoselectivities are found for crotonaldehyde, methacrolein, hexen-2-al, and ethyl-2-hexen-2-al. Cinnamaldehyde only gave a 49% total product yield (18% 1,2- and 22% 1,4-addition product, 9% saturated). The *trans/cis* selectivity is also reduced (80:20).

D. Hydrosilylation of Isocyanates, Imines, and Carbodiimides

Isocyanates are hydrosilylated by triethylsilane with $PdCl_2$ or Pd/C.[128] The regiochemistry of the silylation is substrate dependent. α-Naphthyl isocyanate gave a quantitative yield of *N*-α-naphthylformamide from N-silylation (eq 69) while phenyl- and *n*-butylisocyanate gave carbamoyl silanes from C-silylation (eq 70).



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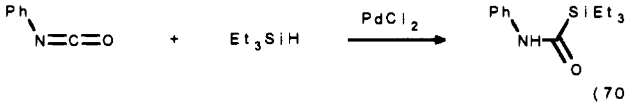
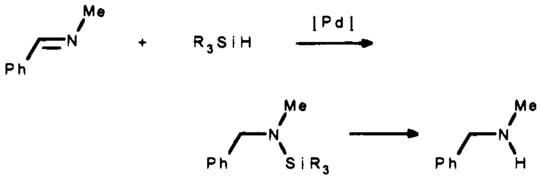


(70)

The reduction of Schiff bases can be accomplished in a two-step process that involves an initial hydrosilylation (eq 71).[129] While palladium catalysts were the most effective when monohydrosilanes were used, rhodium complexes were better with dihydrosilanes. Benzylidenemethylamine was hydrosilylated with triethylsilane in 90% yield using $PdCl_2$ at 55 °C.



(71)

The hydrosilylation of carbodiimides is also catalyzed by $PdCl_2$.[130] The reaction proceeds with N-silylation to yield *N*-silylformamidines (eq 72).

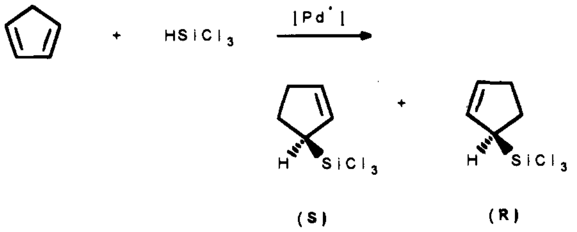
(72)

Only alkylcarbodiimides were hydrosilylated. The primary drawback to this reaction is that temperatures between 140 and 200 °C are required.

VII. Asymmetric Hydrosilylation by Chiral Palladium Complexes

A number of asymmetric homogeneous hydrosilylations have been carried out with chiral palladium complexes. Preliminary experiments with (*R*)-benzylmethylphenylphosphine complexes of palladium showed very little asymmetric induction in the hydrosilylation of olefins. However, the addition of trichlorosilane to styrene, using $PdCl_2(PhCN)_2$ in the presence of menthyldiphenylphosphine (MDPP) at room temperature, gave α-phenylethyltrichlorosilane in 87% yield. While the initial paper reported a minimum of 5.1% enantiomeric excess on the basis of the rotations of a series of (*S*)-1-phenylethyl derivatives,[131] a stereospecific synthesis of 1-phenylethyl alcohol showed that the enantiomeric excess was 34%.[132] When neomenthyldiphenylphosphine (NMDPP) was used, the opposite enantiomer was formed (22% ee).

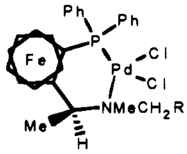
The hydrosilylation of conjugated dienes with trichlorosilane required high temperatures (ca. 120 °C) using Pd(II) MDPP and NMDPP catalysts. Both enantiomeric ligands resulted in the formation of an excess of the same enantiomer. In the case of cyclopentadiene, 2-cyclopentenyltrichlorosilane is formed in 81% yield (eq 73).



(73)

Each of the epimeric phosphine ligands gave only (*S*)-2-cyclopentenyltrimethylsilane (after methylation of the trichlorosilane adduct). The enantiomeric excess was not determined. $PdCl_2[(R)-(PhCH_2)-MePhP]_2$ was also found to be an effective catalyst for the asymmetric hydrosilylation of cyclopentadiene. 1,3-Cyclohexadiene gave optically active isomeric cyclohexenyltrichlorosilanes with these same catalysts. It was suggested that the initially formed silylhydridopalladium intermediates in these reactions add to the dienes to form π-allylpalladium intermediates. The cyclic π-allylpalladium complexes have a local symmetry plane, and so, the induction of asymmetry probably involves diastereomeric transition states for delivery of the trichlorosilyl group. No direct experimental evidence has been provided on this specific system, however, the structures of two related asymmetric hydrosilylation catalysts ($PdCl_2[(Me_2neomenthyl)P]_2$ and $PdCl_2[(Me_2menthyl)P]_2$) have since been determined by X-ray diffraction.[133]

Cyclopentadiene has been converted to (*R*)-2-cyclopentenyltrimethylsilane with high ee by several new palladium catalysts bearing chiral ferrocenylmonophosphine ligands **74**.[134] The perfluoroalky substituents on the amino group of the complex were necessary to maintain solubility of the catalyst in the cyclopentadiene/trichlorosilane reaction mixture. The highest ee (60%) was obtained with the $CH_2C_3F_7$ side chain at a product yield of 73%. 1-Alkylbutadienes were also hydrosilylated via these complexes to give (*Z*)-2-butenylsilanes regio- and stereoselectively. The enantiomeric purities of the allylic alcohols produced from these silanes were over 50%.



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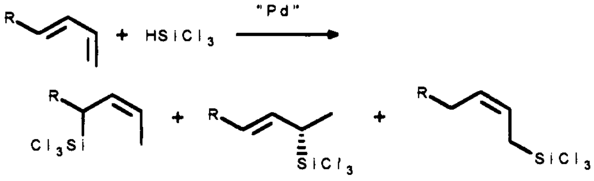
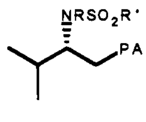


(74)

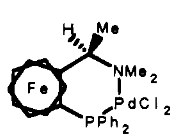
The asymmetric hydrosilylation of cyclopentadiene is also catalyzed by $PdCl_2(CH_3CN)_2$ in the presence of *N*-sulfonyl-substituted aminophosphines **75** prepared from (*S*)-valinols.[135]



75

Product yields are typically between 85 and 95% with enantiomeric excesses of 50−70%. The complexes were active even at 0 °C and in one case even at −20 °C. When the NH group of the sulfonamides was methylated, the selectivity decreased dramatically. These same ligands were effective in inducing chirality during the hydrosilylation of styrene with trichlorosilane. Good yields and ee of 50−65% were achieved with β-position regioselectivity.

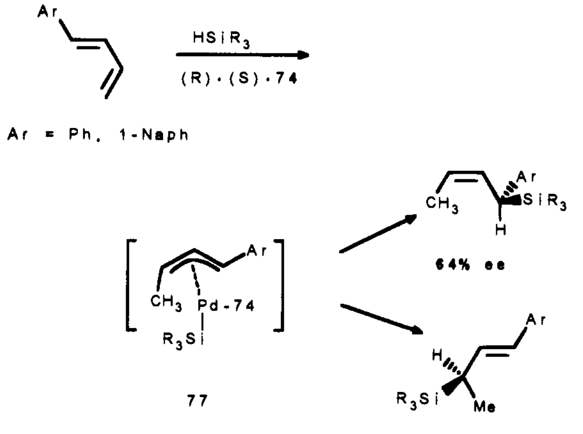
Optically active allylic silanes have also been prepared by the hydrosilylation of dienes using (*R*)-(*S*)-**76**.



76

((R)-(S)-PPFA-Pd)

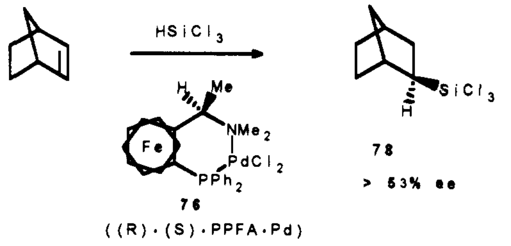
When cyclopentadiene was reacted with dichloromethylsilane in the presence of 0.01 mol % **76**, 3-(dichloromethylsily)cyclopentene was obtained in 87% yield with an enantiomeric excess of ca. 25%.[136] The enantiomeric excess produced in the hydrosilylation of 1,3-cyclohexadiene with dichloromethylsilane under similar conditions, however, was only on the order of 1%. Hydrosilylation of 1-phenylbutadiene and 1-napthylbutadiene with trichlorosilane (catalyst (*R*)-(*S*)-**76**) gave significantly higher asymmetric induction.[137] As shown for 1-phenylbutadiene in eq 75, both regioisomeric addition products are formed. The product stereochemistries can be rationalized from the π-allylpalladium complex **77** which results from complexation with the *si* face (designated on the basis of position 1).



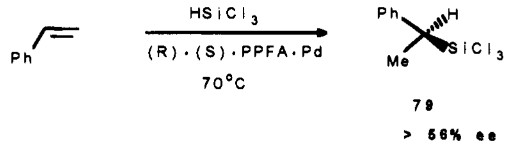
(75)

Syn−anti isomerization in the complex must be slower than transfer of the silyl group from palladium to either C-1 or C-4. The enantiomeric excesses in these allylic silanes and various methylated derivatives were generally in the range of 30−60%.

The chiral (ferrocenylphosphine)palladium complex **76** has been used for the asymmetric hydrosilylation of norbornene and styrene (eqs 76 and 77).[138]



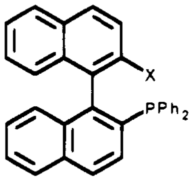
(76)



(77)

These prochiral olefins were converted to the trichlorosilanes **78** and **79** in good yields (53 and 95%, respectively) with about 50% ee. The product trichlorosilanes were converted to norbornyl and phenylethyl alcohols and bromides through the corresponding pentafluorosilicates. The polymer-bound, chiral ferrocene palladium complex prepared from polymer **70** (*R*,*S* configuration) was also found to produce an enantiomeric excess (15.2%) of the (*R*)-(α-phenylethyl)trichlorosilane.[113] This enantiomer is the same as that obtained from the homogeneous catalyst system though the enantiomeric excess is not as significant. When the catalyst is recycled the stereoselectivity decreases.

Over the past three years Hayashi et al. have developed the chiral monodentate phosphine ligands (MOP, **80**) for the palladium-catalyzed asymmetric hydrosilylation of olefins.[139] The yields are excellent

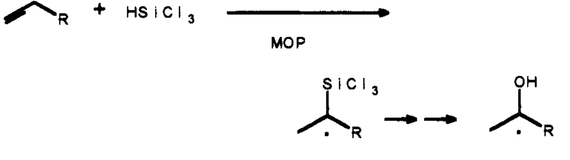


80

MOP: X=OMe, OPr-*i*, OCH$_2$Ph, Et

(80−100%) with high regioselectivity for the 2-position. The lowest regioselectivity was observed for the sterically hindered vinylcyclohexane (66:34). The enantiomeric purities observed are astounding, in no case being less than 86% and in most cases being ca. 95%.

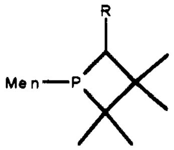
The reaction has been extended to the hydrosilylation of styrenes bearing β-substituents with trichlorosilane. The 1-aryl-1-silylalkane products are ob-



(78)

tained as single regioisomers with 80−85% ee.[140] Asymmetric hydrosilylation of dihydrofurans using the palladium−MOP catalyst system proceeded in analogous fashion with enantiomeric excesses of up to 95%.[141] Ring opening of the hydrosilylation product of 7-oxabicyclo[2.2.1]heptene yielded highly functionalized cyclohexanes in optically active form.

The asymmetric hydrosilylation of cyclopentadiene and styrene has also been carried out using palladium complexes bearing chiral phosphetane ligands.[142] With trichlorosilane, quantitative product yields are observed for styrene, while dicyclopentadiene formation results in lower yields for cyclopentadiene. The enantiomeric excesses observed ranged between 18 and 44%. The most active catalyst system resulted from a 1:1 mixture of $PdCl_2(PhCN)_2$ and the phosphetane.



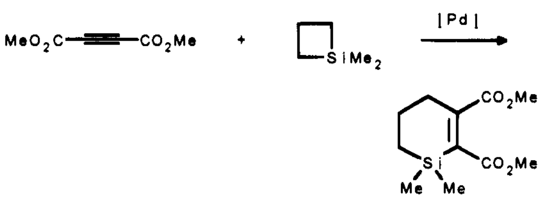
81

Men = L-menthyl

VIII. Palladium-Catalyzed Reactions of Carbocyclic Silanes with Alkenes and Acetylenes

Other than the disilanes discussed in section 1, only two carbocyclic ring systems, silacyclobutanes and silacyclopropenes (silarenes), have been reacted with alkenes and acetylenes in the presence of palladium complexes.

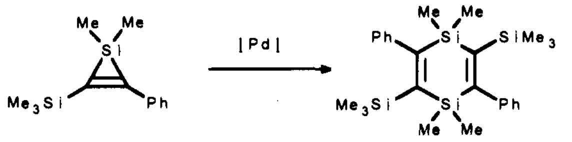
On the basis of their earlier work on the addition of cyclic disilanes to acetylenes in the presence of palladium catalysts, Sakurai et al.[143] investigated the reaction of silacyclobutanes with dimethyl acetylenedicarboxylate. It was found that 1,1-dimethyl-1-silacyclobutane reacted smoothly with dimethyl acetylenedicarboxylate in the presence of $PdCl_2(PPh_3)_2$, in benzene at reflux, to give 1,1-dimethyl-2,3-bis(methoxycarbonyl)-1-silacyclohex-2-ene in quantitative yield (eq 79).



(79)

Reactions with methyl propiolate and phenylacetylene gave the corresponding silacyclohexenes although in low yields (<35%). With unsymmetrical acetylenes regioselective product formation was observed, with the aryl or alkyl group of the acetylene being found exclusively in the 3 position of the product silacyclohexene. A variety of other palladium catalysts such as Pd/C, $PdCl_2(PhCN)_2$, and $Pd(PPh_3)_4$ were also effective but Co, Ni, Rh, Ir, and Pt complexes were ineffective.

In 1977 two reports of the reactions of silacyclopropenes catalyzed by palladium complexes were reported. Ishikawa and Kumada[144] reported that the silacyclopropene **82** (formed from the photolysis of phenylpentamethyldisilane) dimerized in the presence of $PdCl_2(PEt_3)_2$ to give 1,4-disilacyclohexa-2,5-diene (**83**) in 67% yield.

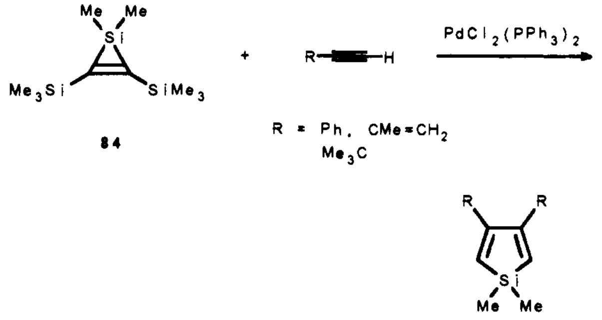


(80)

82 83

It was clearly shown that the silacyclohexadiene product was not formed by a thermal dimerization of the silacyclopropene. It was later shown that the dimerization reaction is stereoselective when the silacyclopropene is substituted in the 1-position with two different substituents. The *trans* analog of **83** is produced exclusively.[145] Bulky groups on the silicon atom of the silacyclopropene retarded the dimerization.

Seyferth et al.[146] found that the reaction of silacyclopropene **84** with terminal acetylenes gave silacyclopentadienes **85** in an exothermic reaction with $PdCl_2(PPh_3)_2$ (eq 81).

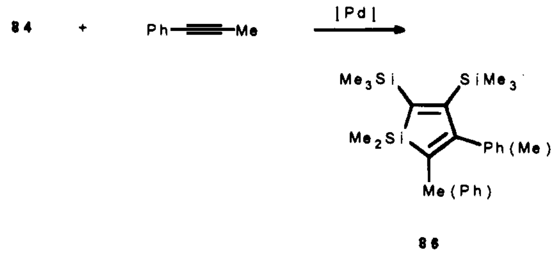


84

(81)

85

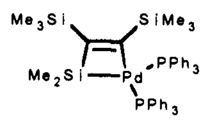
With disubstituted acetylenes, the silacyclopentadienes **86** were formed instead (mixture of regiochemical isomers).



(82)

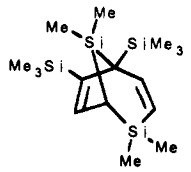
86

The key intermediate in the formation of each of these products is presumably the insertion product **87**. The formation of **86** simply requires the insertion of the acetylene into the Pd–Si or Pd–C bond of the intermediate **87**. The formation of **85**, on the other hand, requires extrusion of bis(trimethylsilyl)acetylene from **87**, formation of a dimethylsilylene–palladium complex, and reaction of this complex with the acetylene. In support of the proposed mechanism, bis(trimethylsilyl)acetylene was isolated in approximately equal yield to that of **85**.



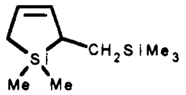
87

The reaction of **84** with acetylene takes a different course, however, with formation of only small amounts of the 1-silacyclopentadiene. The primary isolated product had the bicyclic structure **88** (up to 60% yield).



88

The addition of dienes to the silirene **84** took two different regiochemical courses depending on the structure of the diene.[147] (*E*)-2,4-Pentadienyltrimethylsilane gave only the dimethylsilylene addition product **89**; while in contrast, 2,3-dimethyl-1,3-butadiene gave the dimethylsilylene addition product **90** and the silirene-to-diene 1:1 addition product **91**. The reaction with allene gave the adduct **92** in 23% yield.



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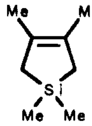
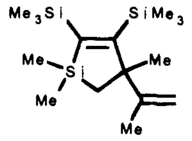


90



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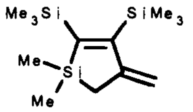
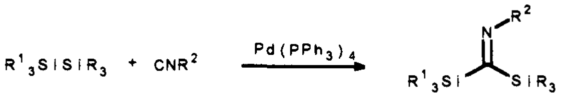


92

All of these products can be rationalized by a mechanism that involves the initial reduction of the Pd(II) complex to a coordinatively unsaturated Pd(0) species and formation of an intermediate analogous to **87**. Partitioning of this intermediate between two reaction pathways, insertion of the acetylene and loss of a dimethylsilylene–palladium complex provides a formal mechanistic path to each of the isolated products.

IX. Palladium-Catalyzed Reactions of Polysilanes with Isocyanides

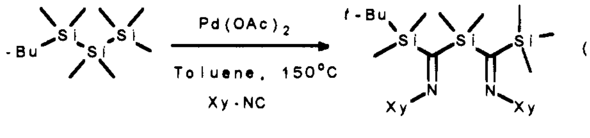
The group of Ito et al. have shown that bis(silyl) imines can be prepared by the reaction of alkyl and aryl isocyanides with disilanes (eq 83).[148]



(83)

In the initial work, the reaction was catalyzed by $Pd(PPh_3)_4$. If the disilane bears electron-withdrawing groups such as in 1,1-difluorotetramethyldisilane or 1,2-difluorotetramethyldisilane, the reaction is exothermic and proceeds rapidly at room temperature. With electron-donating groups such as methoxy or even simple alkyl, the reaction proceeds at a reasonable rate only in toluene at reflux. Even the ring-strained 1,1,2,2-tetramethyl-1,2-disilacyclopentane does not react with *o*-tolyl isocyanide, except at reflux. The yields of bis(silyl) imine vary between ca. 25 and 80% depending on the substrate. The bis(silyl) imines can be hydrolyzed to the interesting bis(silyl) ketones or reduced with sodium borohydride or $LiAlH_4$ to the corresponding bis(silyl)methylamines.

The insertion of isocyanides into higher polysilanes has been found to be catalyzed by $Pd(OAc)_2$.[149] The interesting regiochemical feature of this reaction is that the isocyanide is inserted regularly into each silicon–silicon bond of the polysilane. Thus the reaction of 2,6-xylyl isocyanide with octamethyltrisilane yields 1,1,1,3,3,5,5,5-octamethyl-2,4-bis(2,6-xylylimino)-1,3,5-trisilapentane. Decamethyltetrasilane and permethylhexasilane react similarly. Recent reports by the same group have detailed the stereoelectronic factors affecting these isocyanide insertion reactions in the linear oligosilanes up to hexasilane.[150] The use of 2,6-disubstituted aryl isocyanides yielded oligo(silylimine) derivatives that were more stable than those from aliphatic and *o*-tolyl isocyanides. An excess of isocyanide in either toluene or DMF was utilized to assure insertion into each silicon–silicon bond of the higher oligosilanes. Equation 84 shows the particularly efficient reaction of 1-*tert*-butylheptamethyltrisilane with 2,6-xylyl isocyanide to give the double insertion product **93** (82% yield).



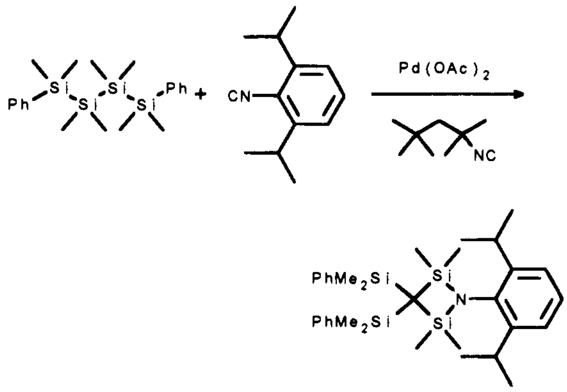
(84)

93

Xy-NC = 2,6-xylylisocyanide

When a limiting amount of isocyanide was used, the insertion was found to occur predominantly in the terminal silicon–silicon bonds. The same effect was observed when the oligosilane was substituted with phenyl groups on the interior silicon atoms. In fact, in those cases, partial insertion occurred even when excess isocyanide was used. The effect seems to be directly associated with steric hindrance to the insertion. On the basis of a series of examples in which partial insertion occurred, the efficiency of insertion for methyl-substituted oligosilanes was estimated to be 80% per insertion reaction. Evidence was provided that the insertion is reversible.

When the insertion of aryl isocyanides with tetrasilanes was catalyzed by $Pd(OAc)_2$ in the presence of 1,1,3,3-tetramethylbutyl isocyanide, an unusual skeletal rearrangement occurred, yielding a 3,3-disilyl-2,4-disila-1-azacyclobutane **94**.[151] Depending on the substitution patterns of the tetrasilanes and the aryl isocyanides the rearrangement yields ranged between 28 and 62%. A palladium–silylene complex was postulated as an intermediate, however, no supporting data was available.



(85)

94

X. Reactions of Trimethylsilyl Cyanide Catalyzed by Palladium

Trimethylsilyl cyanide has been widely used synthetically as a reagent for cyanation. While few of the primary reactions have involved palladium catalysis, soluble palladium complexes have been used for the cyanation of aromatic iodides with trimethylsilyl cyanide and for the addition of trimethylsilyl cyanide to carbon–carbon multiple bonds.

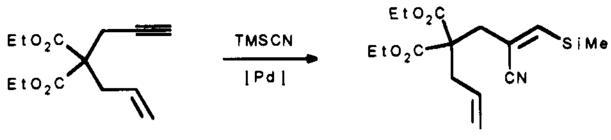
The reaction of substituted iodobenzenes with trimethylsilyl cyanide, in the presence of $Pd(PPh_3)_4$, provides good yields of the corresponding benzonitriles.[152] Iodobenzene itself gives 88% of benzonitrile but satisfactory yields are obtained only in refluxing triethylamine. Bromo- and chlorobenzene are unreactive and, thus, 1-chloro-4-iodobenzene gives 4-chlorobenzonitrile as the only product with trimethylsilyl cyanide. Both electron-withdrawing and electron-donating substituents are tolerated. The initial step in the cyanation probably involves an insertion of the Pd(0) into the aromatic carbon iodine bond in a manner similar to that observed for cross coupling. However, palladium complexes have been found to react with trimethylsilyl cyanide to produce palladium species that are catalytic, *vide infra*.

Palladium-catalyzed addition reactions of trimethylsilyl cyanide to various acetylenes have also been reported. As shown in eq 86, the combination of $PdCl_2$ and pyridine promotes the addition of trimethylsilyl cyanide to arylacetylenes.[153]

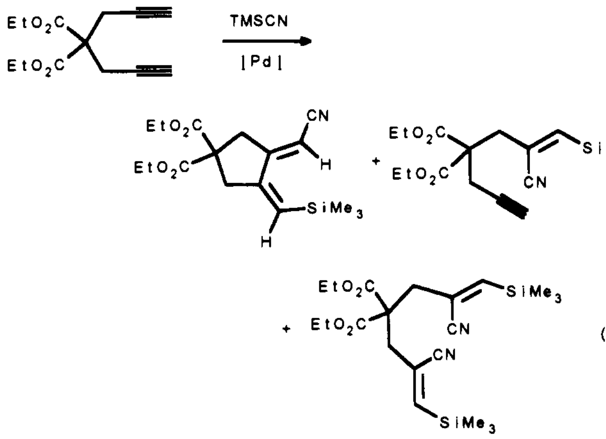
(86)

This was the first reported reaction of trimethylsilyl cyanide with a carbon–carbon multiple bond, catalyzed by a transition metal complex. The regiochemistry of the addition results in bonding of the trimethylsilyl group to the terminal, unsubstituted carbon. In the initial investigations, the addition was established to be predominantly a *syn* addition with (*Z*)/(*E*) product ratios being in the range of 95:5. A wide variety of terminal acetylenes were explored in later work, confirming this general regio- and stereochemistry.[154] The yields are generally good even with heterocyclic acetylenes such as 2-ethynylthiophene and ferrocenylacetylene. One exception is the reaction of 4-(bromophenyl)acetylene. In that case ring cyanation at the 4-position is a competing reaction. A number of Pd(II) catalysts [$Pd(OAc)_2$, $PdBr_2$, $PdCl_2(PhCN)_2$] are effective, but Pd/C and $PdCl_2$/DIBAL were ineffective. Phosphine ligands tend to retard the addition and many Co, Fe, Pt, Ni, and Ru complexes are not catalysts for the reaction.

Terminal aliphatic acetylenes in general gave good yields of the 1,2-addition product with the notable exceptions of propargyl acetate, propargyl bromide, and propargyl phenoxide which gave no addition product. The reaction of 1,6-enynes with trimethylsilyl cyanide gave the simple addition product with no cyclization product as shown in eq 87, whereas diethyl propargylmalonate gave a cyclization product (eq 88). Internal acetylenes react more slowly than terminal acetylenes.

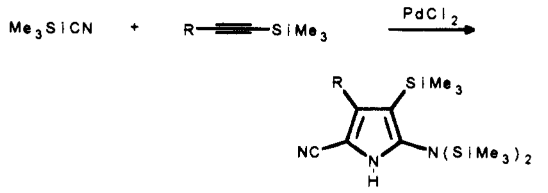


(87)



(88)

(Trimethylsilyl)acetylenes react with trimethylsilyl cyanide and $PdCl_2$ at 120–160 °C to give 3-substituted 5-[*N*,*N*-bis(trimethylsilyl)amino]-2-cyano-4-silylpyrroles (**95**).[155] The least bulky substituents from the acetylene always reside at C-4 of the pyrrole product. The yields range from about 49 to 84% except for the case of bis(trimethylsilyl)acetylene which gives no pyrrole product.

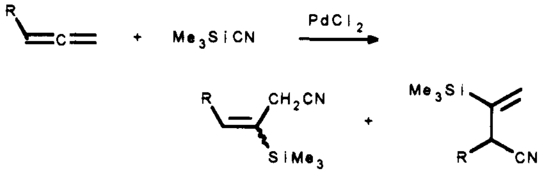


(89)

95

While a wide variety of palladium complexes and even Pd black and Pd/C catalyze the reaction, phosphine ligands tend to retard the reaction. It was reported that when $PdCl_2$ was heated in the presence of trimethylsilyl cyanide at 120 °C, a colorless solid (not palladium cyanide) was formed which could catalyze the formation of the pyrroles.

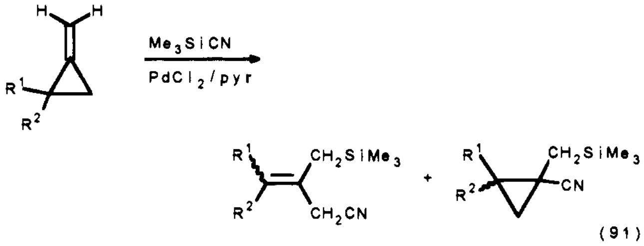
$PdCl_2$ also catalyzes the addition of trimethylsilyl cyanide to allenes.[156] The addition occurs regioselectively with the formation of the vinylsilane **96** as the predominant product. In all addition products, the nitrile group is located at the terminal carbon and the trimethylsilyl group at the interior position. The yields are greater than 60% and the (*E*) isomer always predominates. For example, in the reaction of phenylallene catalyzed by $PdBr_2$ and pyridine, 75% of **96** (R = Ph) is formed and the (*E*)/(*Z*) ratio is 89:11. While three mechanisms for the reaction regio- and stereochemistry were suggested, no experimental evidence to distinguish among them was presented.



(90)

96 **97**

Several reactions of trimethylsilyl cyanide with methylenecyclopropanes can be catalyzed by $PdCl_2$/pyridine in toluene at reflux.[157] As shown in eq 91, two primary products are formed.



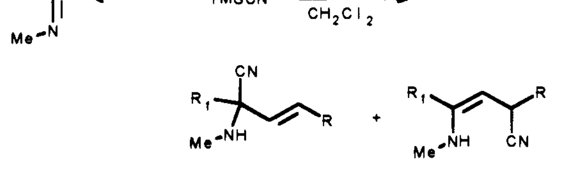
(91)

98 **99**

	98	**99**
$R^1 = R^2 = R^3 = R^4 = H$	41%	9%
$R^2 = Ph, R^1 = R^3 = R^4 = H$	71% (E)/(Z) 49:51	8%
$R^1 = R^2 = Ph, R^3 = R^4 = H$	56%	28%

The major product in all cases is the [*β*-(cyanomethyl)allyl]silane **98** which results from cleavage of the 2,3-*σ* bond of the cyclopropane ring and migration of the double bond. The minor product is the cyclopropanecarbonitrile **99**, a 1,2 adduct. The (*Z*) isomer of **98** predominates in most instances. If the exocyclic double bond is disubstituted, the reaction does not occur.

Trimethylsilyl cyanide has also been found to add to 2-perfluoroalkyl-1-aza-1,3-dienes in the presence of either $Pd(OAc)_2$ or $PdCl_2$ as shown in eq 92.[158]



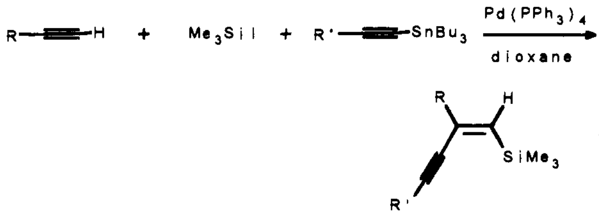
(92)

The reaction requires up to 20 mol % of the palladium catalyst and results in both 1,2- and 1,4-addition products. The Pd(0) complex $Pd(PPh_3)_4$ is ineffective as a catalyst for this reaction. If the substituent at the 4 position of the diene is either aromatic or vinylic then the 1,2 adduct is formed regioselectively.

XI. Reactions of Trimethylsilyl Iodide with Acetylenes and Stannylacetylenes

The oxidative addition of halosilanes to palladium was not known prior to 1991 in spite of ample precedent with platinum(0) and iridium(I) complexes.[159] However, Tanaka and co-workers have now shown that Me_3SiI reacts with styrenes in the presence of $PdCl_2(PEt_3)_2$ and triethylamine to give β-styrylsilanes.[160] An oxidative addition of Me_3SiI to the palladium complex was suggested as the key initiating step in the catalytic reaction.

The second apparent example of an oxidative addition of trimethylsilyl iodide to palladium is found in a report on the reaction of acetylenes with trimethylsilyl iodide and stannylacetylenes.[161]

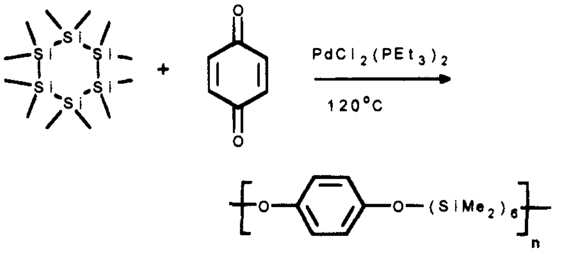


(93)

The yields of the silylenynes are moderate (70–80%) with typically very high regio- and stereoselectivity. Both aromatic and aliphatic terminal acetylenes can be utilized. Trimethylsilyl bromide and triflate were inactive, but $Me_3SiSiMe_2I$ reacted without silicon–silicon bond cleavage. these two examples suggest that new synthetic methodologies are feasible on the basis of the oxidative addition reactions of halosilanes with palladium complexes.

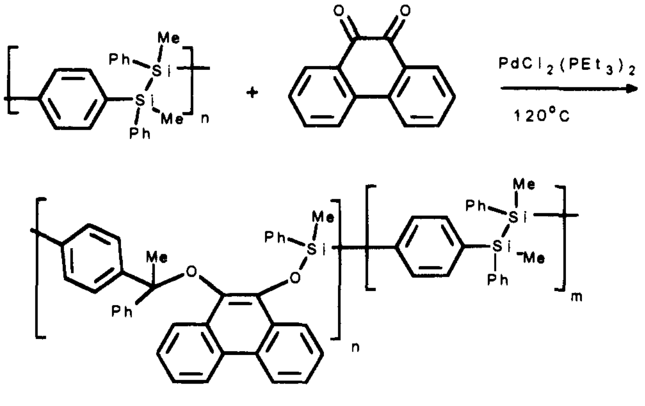
XII. Palladium-Catalyzed Insertion of Quinones into Silicon–Silicon Bonds

Examples of the ring opening polymerization of cyclic polysilanes and carbosilanes are rare; however, recently $PdCl_2(PEt_3)_2$ and $Pd(dba)_2P(OCH_2)_3CEt$ have been shown to catalyze the copolymerization of 1,4-naphthoquinone (or *p*-benzoquinone) and dodecamethylcyclohexasilane and 1,1,2,2-tetramethyl-1,2-disilacyclohexane.[162] These ring-opening polymerizations result in regular polymers of alternating 1,4-naphthylenedioxy (or *p*-phenylenedioxy) and dimethylsilylene groups. Molecular weights ranging from 4000 to 82000 were observed. Polydispersities varied from 2.1 to 11.



(94)

Similarly, benzoquinones and phenanthraquinone can be inserted into the silicon–silicon bonds of poly[(1,2-dimethyl-1,2-diphenyldisilanylene)(*p*-phenylene)] in benzene at 120 °C.[163] The isolated yield with 1.05 equiv of phenanthraquinone was 90% (*n*:*m* = 100:~0). The resulting polymer (**100**) was soluble in aromatic solvents and was very thermally stable (TGA 5% weight loss at 480 °C). $PdCl_2(PEt_3)_2$ was even found to be effective for the insertion of *p*-benzoquinone into poly(dimethylsilylene).



100

(95)

XIII. Conclusion

While in many ways the investigations of the reactions of carbo- and polysilanes catalyzed by palladium complexes are still in their initial stages, sufficient work has been completed to show that these reactions are potentially powerful tools for access to organosilanes of well-defined regio- and stereochemistries. The initial investigations reviewed in this report provide significant latitude for further mechanistic work as well as for the exploration of new reactions between palladium and silanes. Future work should open a wide door for the development of stereochemically controlled, synthetic methodologies based on these palladium-catalyzed reactions.

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