1,2-Additions to Heteroatom-Substituted Olefins by Organopalladium Reagents

G. DOYLE DAVES, JR.,*,† and ANDERS HALLBERG*,‡

Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015, and Department of Organic Chemistry 1, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

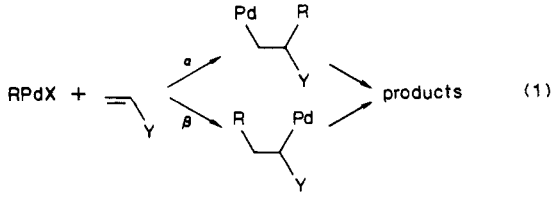
Received February 2, 1989 (Revised Manuscript Received May 8, 1989)

Contents

I. Introduction

In 1968, Heck[1] introduced a palladium-mediated reaction for arylation of vinyl and other olefinic compounds. Independently, Moritani and Fujiwara[2] discovered a closely related reaction in which arenes were coupled with olefins in the presence of palladium. In the two decades since these discoveries, there has been an explosion of activity resulting in a large number of successful palladium-mediated olefin substitution reactions.[3]

In the present article, we highlight reactions in which a new carbon–carbon bond is formed via 1,2-addition of an organopalladium species to the often strongly polarized carbon–carbon double bond of a heteroatom-substituted olefin (eq 1). During the past several years, this chemistry[4,5] has developed significantly and many synthetically useful applications have been reported.

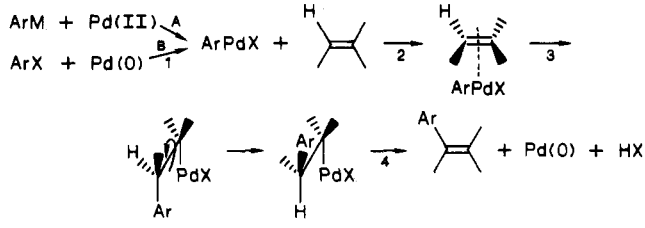


(1)

There is an inherent difficulty in discussing reactions on the basis of a unifying mechanistic concept when, often, little mechanistic information is available and, even in the best-studied cases, important detail is lacking. However, many of the key features of organometallic reactions are now generally understood, and a focus on the more important reaction mechanisms is an effective way to organize the rapidly accumulating experimental data.

† Lehigh University.
‡ University of Lund.

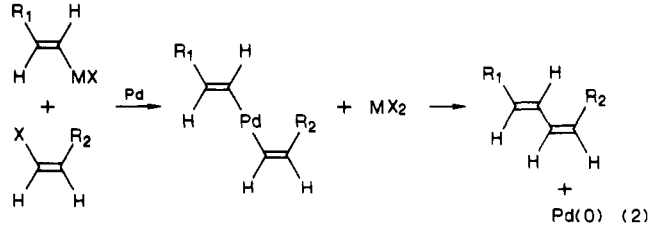
SCHEME I



The basic mechanism for olefin substitution that Heck proposed[6] has gained significant experimental support; we find it useful to view the overall process as proceeding through four discrete organometallic reactions:[4,7,8] (1) organometallic reagent formation, (2) formation of a π-complex between the organopalladium reagent and an olefin, (3) π-complex collapse by 1,2-addition of the organopalladium reagent to the olefinic carbons, and (4) decomposition of the resulting σ-adduct with elimination of palladium and product formation (Scheme I).

This general reaction mechanism provides a useful framework for discussing reactions of organopalladium reagents with enol ethers, enol carboxylates, thioenol ethers, enamides, vinylsilanes, and vinylphosphonates. These reactions and their use in synthesis are discussed in the following sections.

Omitted from this review are reactions of organopalladium reagents with metallo derivatives of olefins that do not involve 1,2-addition of the organopalladium reagent to the heteroatom-substituted olefin. These include cross-coupling reactions[9] in which palladium (or nickel) undergoes oxidative addition to a vinylic halide or trifluoromethanesulfonate[10] followed by reaction with a preformed alkenyl–metal derivative of aluminum,[11] boron,[9c] magnesium,[12] silicon,[13] tin,[14], zinc,[15] or zirconium[16] (eq 2). There are a few examples of organo-

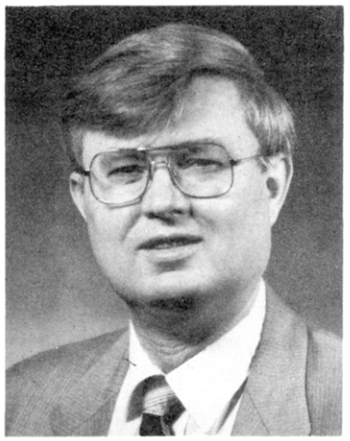


(2)

palladium reactions of vinylboranes[17] and vinylstannanes[18] that seem to occur by a 1,2-addition–elimination mechanism; however, these reactions are of limited synthetic utility and will not be discussed further.

A palladium-catalyzed reaction of trimethylsilyl enol ethers with aryl halides in the presence of tri-*n*-butyltin

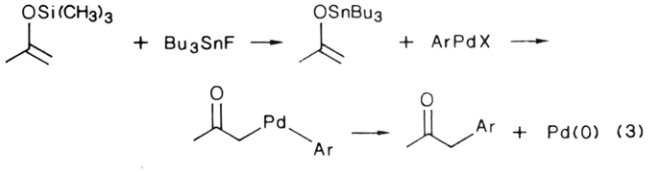
0009-2665/89/0789-1433$06.50/0



Doyle Daves, a native New Mexican, received his undergraduate education at New Mexico Highlands University and Arizona State University under the mentorship of Roland K. Robins. From 1959 to 1961 he worked with C. C. Cheng at the Midwest Research Institute in Kansas City. He then entered the Massachusetts Institute of Technology and finished work for the Ph.D. in 1964 under the direction of John. C. Sheehan. Following postdoctoral study with Karl Folkers at the Stanford Research Institute, he joined the founding faculty of the Oregon Graduate Center. In 1981, he moved to Lehigh University as Professor of Chemistry. His research interests are in the chemistry of compounds with important biological activities. For the past dozen years, a major component of his research has been in applications of palladium-mediated coupling reactions to *C*-glycoside synthesis.

Anders Hallberg received his Ph.D. from the University of Lund, Sweden, in 1980 under the direction of Professor Salo Gronowitz. He then joined Professor Arnold Martin's group at the University of Arizona and became Research Assistant Professor in the Department of Pharmaceutical Sciences in 1981. After his return to Sweden he was appointed Docent of Organic Chemistry in 1983. Since 1988, Dr. Hallberg has been Head of Organic Chemistry at AB Draco (a subsidiary of AB Astra) in Lund, Sweden. His research interests include heterocyclic chemistry and applications of organotransition-metal chemistry to organic synthesis and, increasingly, to medicinal chemistry.

fluoride[19] is best rationalized as a cross-coupling reaction (eq 3).



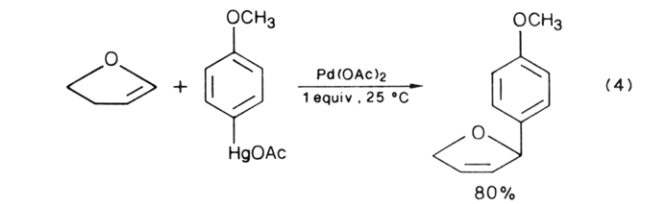
(3)

The Heck-type organopalladium coupling reactions we have selected for review differ from these cross-coupling reactions mechanistically by effecting carbon–carbon bond formation via 1,2-addition of the organopalladium reagent to the olefinic carbons (Scheme I) rather than via reductive elimination of palladium from a dialkenyl- or arylalkenyl–Pd species (eq 2 and 3).[20] A second mechanistic difference should be emphasized. Most coupling reactions involving 1,2-addition of an organopalladium reagent to a heteroatom-substituted olefin yield products in which the heteroatom–carbon bond remains intact, in contrast to cross-coupling reactions in which this bond is invariably cleaved.[9] One exception is the reaction of trimethylvinylsilane, which results in carbon–silicon bond cleavage via an addition–elimination sequence (see also Scheme III). Under certain conditions vinylsilanes undergo cross-coupling reactions;[13] although not the subject of this review, we have found it useful for clarity of presentation to discuss some of these reactions.

II. Reactions of Enol Ethers

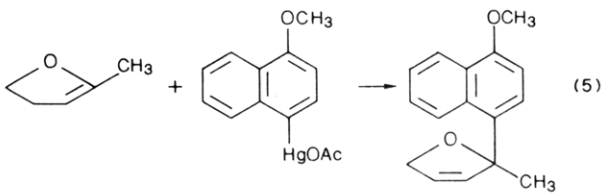
A. Cyclic Enol Ethers

Cyclic enol ethers such as 3,4-dihydropyran and 2,3-dihydrofuran readily undergo regiospecific palladium-mediated arylation with organopalladium reagents (e.g., eq 4–6).[21–24] The organopalladium reagents used in



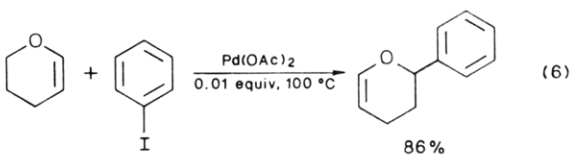
(4)

80%



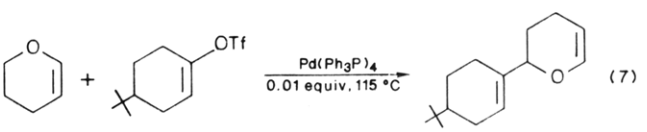
(5)

54%



(6)

86%

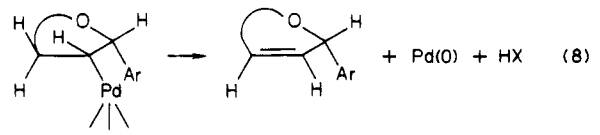


(7)

53%

these reactions are usually formed either by transmetalation from the corresponding organomercurials[21–24] or organostannanes[24] (stoichiometric palladium) or by oxidative addition of palladium(0) to aryl iodides[8,25] (catalytic palladium). A related reaction involves coupling of 3,4-dihydropyran with an organopalladium reagent formed from a vinyl triflate in the presence of Pd(0) (eq 7).[26]

The intermediate organopalladium σ-adducts that form regiospecifically in these reactions by syn 1,2-addition of the organopalladium reagent to the olefinic carbons[3,4,6,8] of the enol ether have the formally electropositive palladium bonded to the electron-rich β-carbon and the anionic aryl carbon bonded to the electron-poor α-carbon[4,8] (eq 8). The unstable σ-adduct

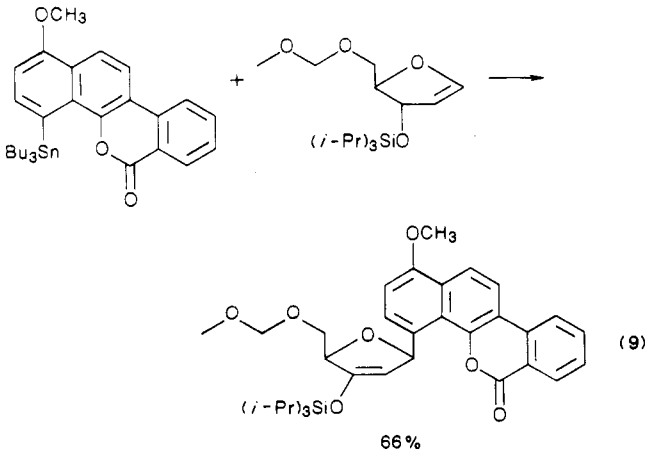


then decomposes to product by syn elimination of palladium and hydride (eq 8). Since there is no hydrogen on the arylated carbon that is cis to palladium, elimination produces a nonconjugated olefin. When reactions are carried out at room temperature, little double-bond migration occurs; however, at elevated temperatures readdition and reelimination of palladium hydride to newly formed unpolarized double bonds results in double-bond migration into conjugation with the ring oxygen π-electrons (eq 6 and 7). It is noteworthy that migration or readdition of "PdH" to the face of the olefinic cyclic ether opposite that bearing the aryl group would permit double-bond conjugation with the aryl substituent; failure to observe this product is good evidence that the "migrating PdH" remains firmly bound and that once dissociation occurs, decomposition to Pd(0) precludes readdition.[23]

Because decomposition of L_2PdHX gives rise to Pd(0), reactions in which the organopalladium reagent is formed by oxidative addition are catalytic whereas those in which reagent formation involves transmetalation by Pd(II) require stoichiometric palladium unless an oxidant to convert Pd(0) back to Pd(II) is used.[3,4,27]

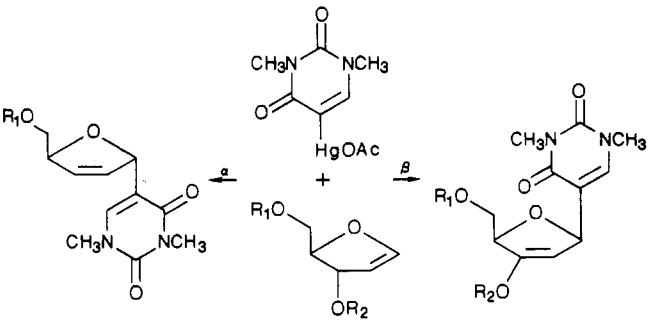
B. Glycals, Cyclic Enol Ethers Derived from Carbohydrates

Palladium-mediated reactions of cyclic enol ethers have been extended to chiral, structurally complex glycals (1,2-unsaturated carbohydrates), resulting in facile syntheses of *C*-nucleosides and *C*-glycosides.[28] In reaction of an organopalladium reagent with a glycal, two factors in addition to reaction regiochemistry become important. In this reaction, the stereochemistry of π-complex formation and the mode of σ-adduct decomposition are critical and determine the reaction course and product structure. The utility of this reaction is exemplified by the palladium-mediated coupling of an anthracycline tri-*n*-butylstannane with a furanoid glycal[29] to yield a single *C*-glycosidic product[24,30] that is structurally related to the ravidomycin–gilvocarcin antitumor antibiotic class[28] (eq 9).



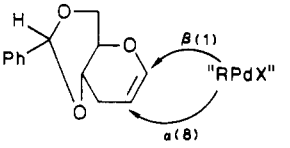
The factors that control the stereochemistry of complexation and reaction of an organopalladium reagent with a glycal were elucidated in studies like that illustrated in Scheme II. Palladium-mediated reaction of the pyrimidinylmercurial with variously substituted furanoid glycals reveals that reaction stereochemistry is controlled by steric factors affecting access of the intermediate organopalladium reagent to the two respective faces of the cyclic enol ether olefinic bond. Thus, if either O-3 or O-5 of the furanoid glycal bears a bulky substituent, reagent attack occurs from the opposite face, giving rise to a single *C*-nucleoside;[31,32] when both hydroxyls are substituted, the effect of the allylic substituent, which is closer to the reaction site, dominates and only the β *C*-glycoside is formed. Only when both hydroxyls are unsubstituted does attack occur from each side, producing both α and β *C*-nucleosides.[31] Apparently, in this case, the substituents (HO and $HOCH_2$, respectively) are too small to provide effective discrimination.

SCHEME II



R_1, R_2	% α	% β
R_1 = H, R_2 = CH_2OCH_3	0	65
R_1 = CH_2OCH_3, R_2 = H	78	0
R_1 = R_2 = CH_2OCH_3	0	71
R_1 = R_2 = H	29	45

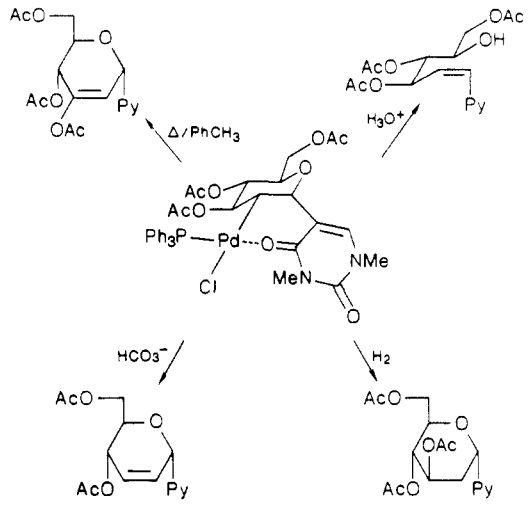
It is noteworthy that only in this case involving an underivatized furanoid glycal[31] and in one case of a pyranoid glycal unfunctionalized at the allylic carbon[33] have products resulting from organopalladium reagent attack from the two faces of the cyclic enol ether system been observed; all other palladium-mediated glycal arylation reactions studied[21,24,29-32,34-41] have been stereospecific.



In one instance, the σ-adduct resulting from reaction of an organopalladium reagent and a pyranoid glycal was sufficiently stabilized by use of a triphenylphosphine (triphenylarsine) ligand to permit isolation[34] for structural characterization[37] and detailed study of its decomposition modes.[34,39] This study reveals the richness of organopalladium adduct decomposition chemistry; thus under selected conditions, the intermediate organopalladium σ-adduct underwent four separate decomposition reactions to yield four discrete products in near-quantitative yield (Scheme III).[34]

Obviously, if reaction conditions are not controlled properly, there is potential for palladium-mediated arylation reactions of substituent-rich enol ethers to produce complex product mixtures.[39] The nature and stereochemical disposition of potential leaving groups β to palladium in the intermediate σ-adduct, the anions

SCHEME III

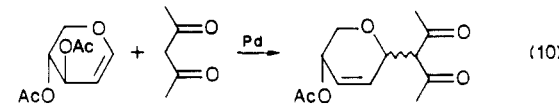


available to serve as ligands for palladium, and Lewis acids present in the reaction mixture all affect σ-adduct decomposition mode(s) and product formation.[4,34,39] By control of the ionic content of the reaction mixture,[39] manipulation of the leaving group ability of the allylic substituent of the glycal, and use of conformational constraints in the intermediate σ-adduct, it has been possible to preselect for a specific adduct decomposition mode.[38]

A number of attempts have been made to convert glycals bearing allylic leaving groups to (π-allyl)palladium complexes[42] for alkylation (Scheme IV). The high electron density of the enol ether system inhibits reactions with Pd(0)[43] under conditions typically used to prepare π-allyl complexes from allylic acetates. Thus, treatment of a glycal such as 3,4,6-tri-O-acetylglucal with $Pd(PPh_3)_4$ failed to effect π-allyl complex formation.[44,45] However, when the allylic leaving group was changed to trifluoroacetoxy,[46] the reaction proceeded and a moderate yield of the product of double inversion[42] was attained.[46] An alternative route to increased reactivity of carbohydrate-derived olefins involves conversion of glycals to the corresponding 2-hexenopyranosides followed by treatment with Pd(0) and a carbanion.[44,45,47]

A related reaction has been reported. Reaction of a glycal with a β-dicarbonyl compound in the presence of bis(benzonitrile)dichloropalladium(II) results in regiospecific alkylation of the glycal at C-1 and elimination of the C-3 (allylic) acetoxy group[48] (eq 10).

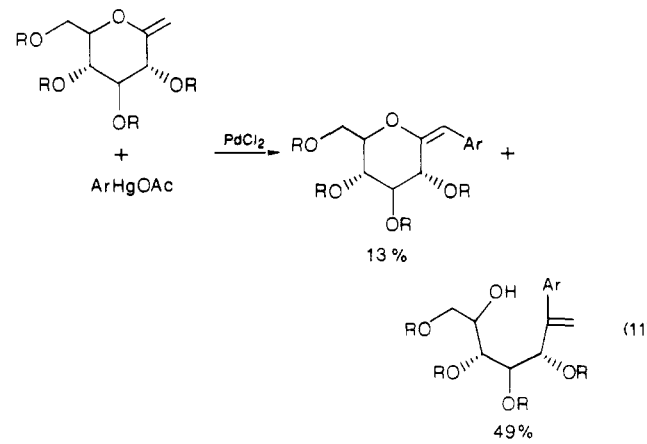
It appears likely that, in this case, Pd(II) is serving as a Lewis acid catalyzing loss of the allylic acetate



(10)

group with formation of an uncoordinated glycal-derived cation which is captured by the nucleophilic β-dicarbonyl compound since the product stereoselectivity observed is essentially the same as that obtained when the reaction is carried out with boron trifluoride as catalyst.[48]

One example of a reversal of regiochemical addition of an organopalladium reagent to a carbohydrate-derived enol ether is known[49] (eq 11). Arylation of this



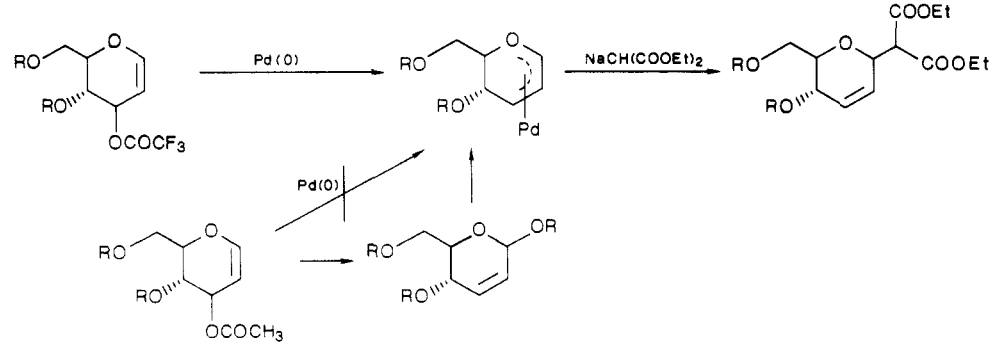
(11)

enol ether, which has an exocyclic double bond, occurs predominantly at the quite sterically hindered, disubstituted α-carbon rather than at the unsubstituted β-olefinic carbon. This result is consistent with previous experience[23] and testament to the dominance of electronic factors over steric effects in these organopalladium reactions[8,23] (see following section).

C. Acyclic Enol Ethers

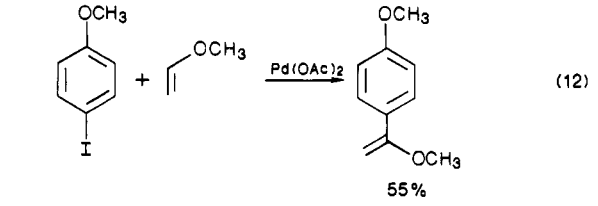
Whereas palladium-mediated reactions of cyclic enol ethers invariably involve regiospecific 1,2-addition of an organopalladium reagent to an enol ether double bond to produce a product of α-arylation, acyclic enol ethers often yield products derived from 1,2-addition of the organopalladium reagent to the enol ether double bond in both regiochemical senses.[4,5] Early studies[25,50-53] were discouraging, producing complex product mixtures involving both regioisomers and secondary products formed by further reaction of primary olefinic products with the organopalladium reagent. However, recent detailed studies have elucidated critical parameters that affect the regiochemistry of these reactions; this im-

SCHEME IV

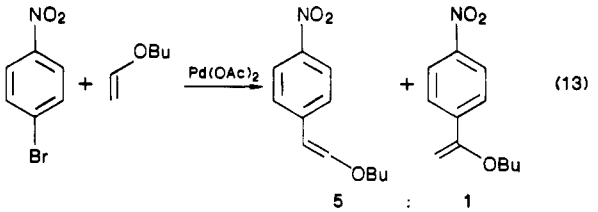


proved understanding has led to the realization of many synthetically useful regioselective acyclic enol ether arylation reactions.

These studies show that the regiochemical outcome of palladium-mediated reactions of enol ethers is determined primarily by electronic factors[8] in contrast to corresponding reactions with simple olefins where steric factors dominate.[3,6] Thus, it has been shown that the variation of electron density in the organopalladium reagent affects reaction regiochemistry;[8,54-56] aryl rings with high electron density favor arylation of the enol ether α-carbon (eq 12), whereas rings with electron-withdrawing nitro groups yield predominantly products of β-arylation (eq 13).



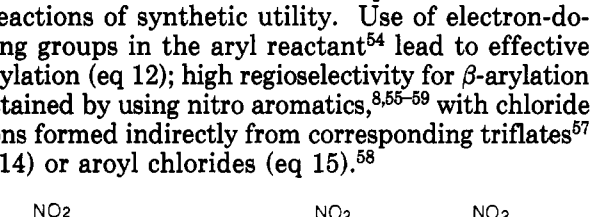
(12)



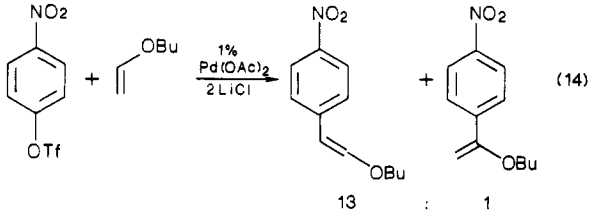
(13)

Similarly, other factors that affect electron density in the organopalladium reagent are important. Coordinating solvents (acetonitrile) or ligands (triphenylphosphine) favor α-arylation, whereas toluene as reaction solvent and the absence of added ligands favor β-arylation.[8] Also the coordinating anion (the X group in "ArPdX") affects the regiochemical outcome of enol ether arylation reactions; β-arylation is favored in the order $OAc^- > Cl^- > Br^- > I^-$, which is the inverse of the bond strength of these anions to Pd(II).[8] Surprisingly, when aryl triflates were used to form the organopalladium reagent, α-arylation was predominant; apparently, in this case, the poorly coordinating triflate anion was replaced by a better ligand.[57]

Effective control of these reaction parameters has led to reactions of synthetic utility. Use of electron-donating groups in the aryl reactant[54] lead to effective α-arylation (eq 12); high regioselectivity for β-arylation is attained by using nitro aromatics,[8,55-59] with chloride anions formed indirectly from corresponding triflates[57] (eq 14) or aroyl chlorides (eq 15).[58]



(14)



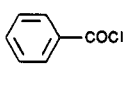
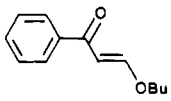
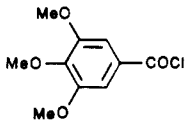
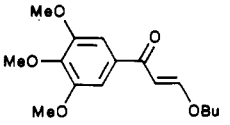
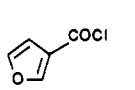
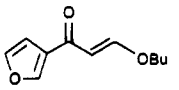
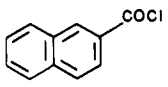
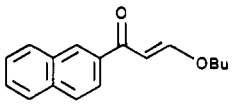
(15)

TABLE I. Palladium-Catalyzed Arylation of Butyl Vinyl Ether with Aroyl Chlorides in Refluxing Xylene[a]

aroyl chloride	product	yield, %
C_6H_5COCl	$C_6H_5CH{=}CHOBu$	53
$4\text{-}NO_2C_6H_4COCl$	$4\text{-}NO_2C_6H_4CH{=}CHOBu$	60
$4\text{-}ClC_6H_4COCl$	$4\text{-}ClC_6H_4CH{=}CHOBu$	60
$4\text{-}AcOC_6H_4COCl$	$4\text{-}AcOC_6H_4CH{=}CHOBu$	40

[a] Data taken from ref 58.

TABLE II. Palladium-Catalyzed Aroylation of Butyl Vinyl Ether with Aroyl Chlorides at 60 °C[a]

aroyl chloride	product	yield, %
		69
		57
		40
		55

[a] Data taken from ref 60 and 61.

The use of aroyl chlorides in palladium-mediated reactions of enol ethers is particularly advantageous; as noted, when the reaction is run at 130 °C decarbonylation occurs, leading to arylation[58] (eq 15, Table I). In this reaction, a nitro group on the aryl moiety is not necessary for effective β-arylation in synthetically useful yields (Table I). Alternatively, carrying out the reaction at 60 °C avoids decarbonylation and leads to regiospecific β-aroylation[60,61] (Table II). This latter process is tolerant of significant diversity in the aroylating moiety and provides a direct route to monoprotected 1-aryl-1,3-dicarbonyl systems;[60,61] it is noteworthy that even very electron rich aryls yield exclusively β-aroylation (Table II).

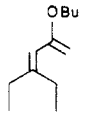
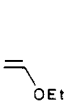
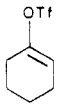
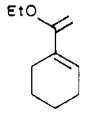
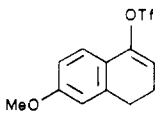
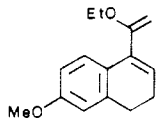
Methyl α-methoxyacrylate reacts stereoselectively with aryl iodides and vinyl triflates under phase-transfer conditions in the presence of a palladium catalyst to give enol ethers of aryl pyruvates and of β,γ-unsaturated α-keto esters respectively in moderate to good yields.[62]

An efficient synthesis of 2-alkoxy 1,3-dienes has been accomplished by reaction of acyclic or cyclic enol triflates with alkyl vinyl ethers in the presence of a palladium catalyst[63] (Table III). Using this procedure, which involves α-vinylation, transformation of ketones via their enol triflates into 2-alkoxy 1,3-dienes and to α,β-unsaturated methyl ketones by subsequent hydrolysis of the enol ether is facile. This highly selective α-vinylation, achieved by using vinyl triflates as organopalladium precursors, is notable in view of the effective use of aryl triflates[57] (eq 14) and aroyl chlorides[58,60,61] (eq 15, Tables I and II) to achieve selective β-substitution.[8]

III. Reactions of Thioenol Ethers

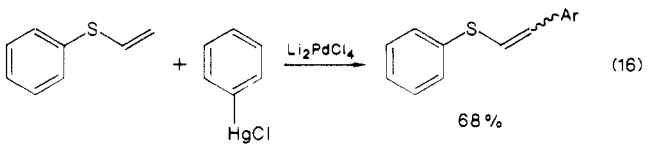
Palladium-mediated reactions of thioenol ethers, in

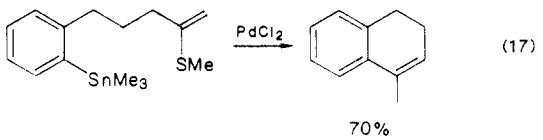
TABLE III. Palladium-Catalyzed Vinylation of Alkyl Vinyl Ether with Enol Triflates at 60 °C[a]

olefin	enol triflate	product	yield, %
			48
			72
			82
			56

[a] Data taken from ref 63.

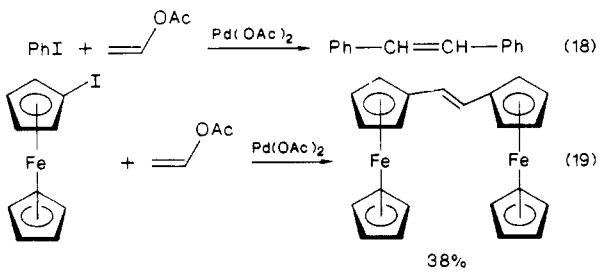
contrast to enol ethers, have been little studied. Palladium-mediated arylation of phenyl vinyl sulfide was shown to occur exclusively at the β-carbon[64] (eq 16). In an interesting intramolecular example of this reaction (eq 17), the opposite regiochemistry was observed owing to steric constraints.[64]



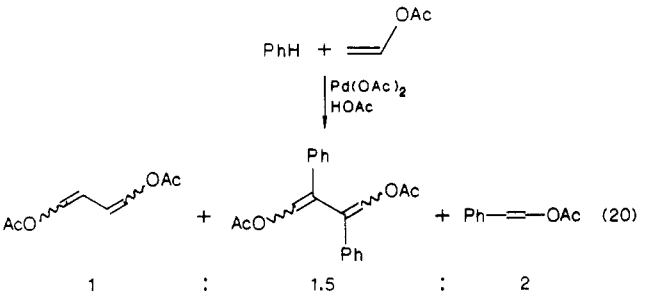


IV. Reactions of Enol Carboxylates

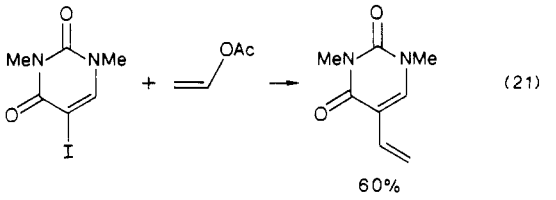
The double bond in vinyl acetates is significantly less polarized than in alkyl vinyl ethers. For this reason and because carboxylates are effective leaving groups, palladium-mediated reactions of enol carboxylates are complex, and few useful synthetic reactions have been reported. Most common are reactions in which vinyl acetate serves as an ethylene equivalent undergoing two sequential arylations to form stilbenes[25,50,52,65] (eq 18). In a particularly interesting example of this reaction, iodoferrocene underwent reaction with vinyl acetate in the presence of palladium acetate to form an ethylene-linked diferrocene system[65] (eq 19).

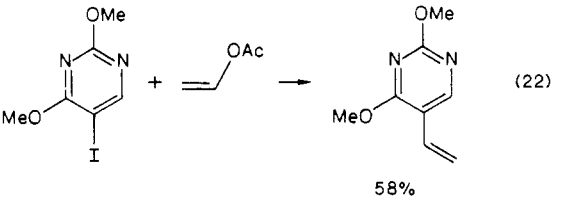


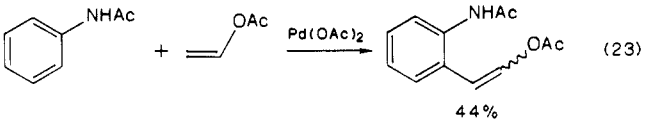
A different result was obtained when vinyl acetate and benzene were heated in acetic acid in the presence of palladium acetate.[52] Under these conditions, the reaction mixture contained significant amounts of 1,3-dienes (eq 20).



Use of vinyl acetate proved effective for preparation of 5-vinylpyrimidines[66] (eq 21 and 22). This reaction involves organopalladium reagent attack at the α-carbon followed by loss of palladium and acetate. In contrast, palladium-mediated ortho vinylation of acetanilide involved aryl attack at the β-carbon of vinyl acetate[67] (eq 23).

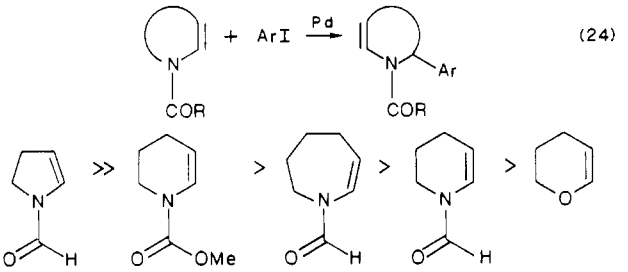






V. Reactions of Enamides and Enamines

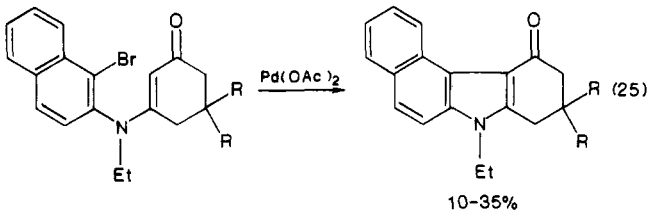
Cyclic enamides undergo facile palladium-catalyzed arylation with aryl iodides[68] (eq 24). Arylation occurs

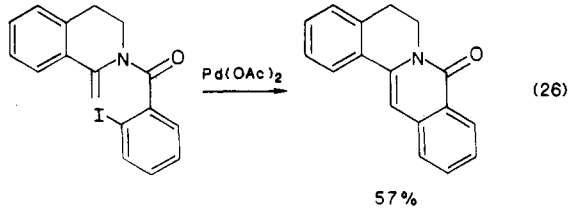


regiospecifically at the olefinic α-carbon and is accompanied by migration of the double bond around the ring to reconjugate with the ring nitrogen π-electrons in a reaction analogous to that previously observed for cyclic enol ethers (eq 6 and 7). A comparison of arylation reaction rates produced the order shown, indicating that enamides are more reactive than enol ethers.[68]

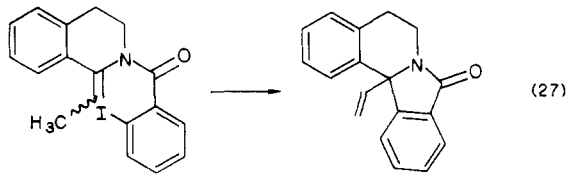
A number of heterocyclic syntheses have utilized intramolecular arylation reactions of enamides and enamines[69-71] (e.g., eq 25 and 26).

Grigg et al.[71] report a particularly fascinating study of reactions of this type with results that have important mechanistic implications. Thus, when the reaction

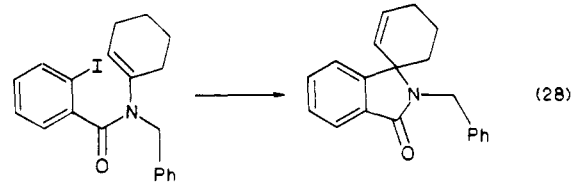




substrate shown in eq 26 was modified such that the exocyclic enamide double bond bore a methyl substituent, the arylation reaction occurred at the α-carbon (eq 27) instead of the β-carbon (eq 26). This result was



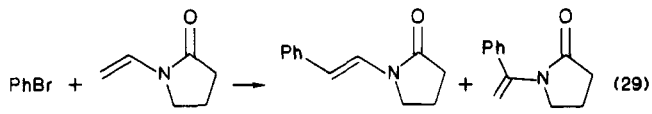
rationalized by assuming that successful reaction requires that the intermediate σ-adduct have a syn β-hydrogen for elimination. For the first reaction (eq 26) such a hydrogen is available only if ring closure occurs by β-arylation; addition of a methyl group on the double bond provides a β-hydrogen for both α- and β-arylation reactions and permits the inherent electronic bias for α-arylation to prevail. This work was extended by realization of a number of ring closures in which quaternary carbon centers were constructed (eq 28). When alkyl groups were placed in the olefin-bearing ring such that decomposition of the σ-adduct resulting from α-arylation was blocked, no reaction of the enamide system was observed.[71]

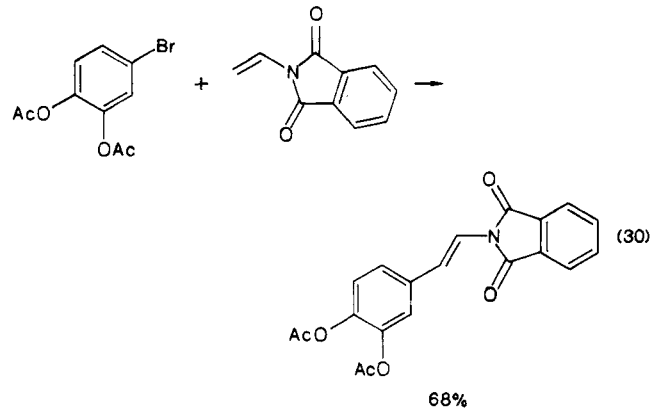


The rationalization of Grigg et al.[71] has interesting and important implications. It requires that formation of the σ-organopalladium adduct, which involves formation of a carbon–carbon σ-bond, is reversible or that, in some way, the absence of a facile decomposition mode precludes σ-adduct formation. This is difficult to reconcile with reactions that involve σ-adduct accumulation owing to the absence of a facile decomposition mode.[36,72]

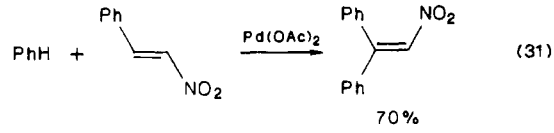
In intermolecular arylations, acyclic enamides, like enol ethers and enol carboxylates (see prior sections), yield regioisomeric mixtures (eq 29); however, depletion of the electron density at nitrogen favors regioselective β-arylation (eq 30).[73]

Alkylation of *N*-vinylacetamide with carbanions at low temperature following coordination of the enamide with Pd(II) occurs only at the α-carbon.[74,75] Palladium-catalyzed β-arylation[76] or β-heteroarylation[77] of α-acetamidoacrylic acid or methyl α-acetamidoacrylate



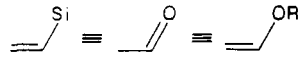


provides α-amino acid precursors. Palladium-mediated arylation of nitrostyrenes exhibits high β-selectivity[78] (eq 31).



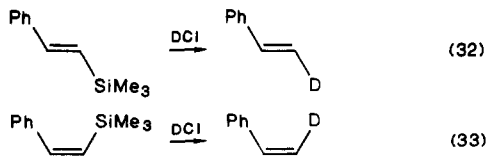
VI. Reactions of Vinylsilanes

Vinylsilanes are important intermediates in synthesis[79] and can be transformed into alkyl vinyl ethers,[80] silyl vinyl ethers,[81] enamines,[82] diols,[83] or carbonyl compounds.[84] Vinylsilanes, like enol ethers, can be regarded as acetaldehyde equivalents.

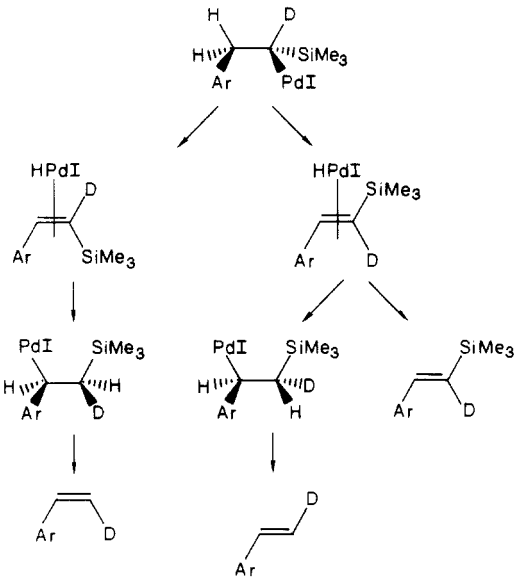


The polarization of the carbon–silicon bond due to the relatively high electronegativity of carbon compared with silicon[85] results in hyperconjugative stabilization of a carbonium ion center β to silicon. The stabilization, due to overlap of the σ-orbital of the carbon–silicon bond with the vacant p-orbital of the carbocation center, is often referred to as the "β-effect".[86] Like heteroatom substituents more electronegative than carbon, a silicon substituent influences the regiochemical outcome of reactions at an attached carbon–carbon double bond, though in the opposite sense. Thus, vinylsilane reactions complement reactions of alkyl vinyl ethers.

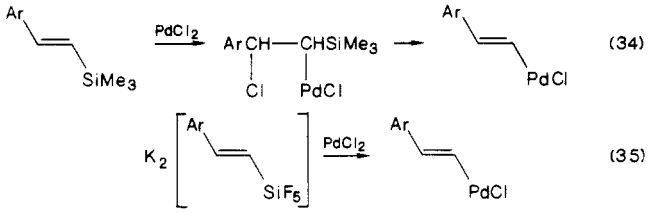
Vinylsilanes, although considerably less reactive than allylsilanes,[87,88] are attacked by electrophiles at the α-carbon, affording, after cleavage of the silicon–carbon bond, products of replacement.[89] Electrophilic reactions of vinylsilanes are stereospecific, exhibiting retention of configuration[90] (eq 32 and 33) owing to the facile cleavage of the silicon–carbon bond in a maximally stabilized β-silyl cation intermediate in which the carbon–silicon σ-bond is coplanar with the adjacent vacant p-orbital.



SCHEME V



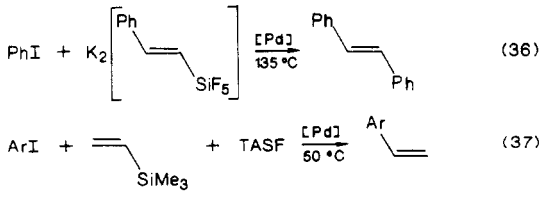
Reactions of palladium and platinum complexes with vinylsilanes promote cleavage of the carbon–silicon bond.[91] In the presence of palladium chloride, both (*E*)-β-(trimethylsilyl)styrene[92] and (*E*)-styrylpentafluorosilicate[93] yield products derived from ArCH=C-HPdCl, although different mechanisms for cleavage of the silicon–carbon bond have been proposed (eq 34 and 35).



(34)

(35)

(*E*)-Styrylpentafluorosilicate undergoes a cross-coupling reaction with iodo- or bromobenzene in the presence of catalytic palladium at 135 °C, yielding (*E*)-stilbene[93] (eq 36). Recently, a modification was reported[13] in which palladium-mediated cross-coupling of trimethylvinylsilane with iodo aromatics occurred in yields of 84–98% when tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF) was provided as a fluoride ion source to activate the carbon–silicon bond for cleavage (eq 37). Both these reactions (eq 36 and

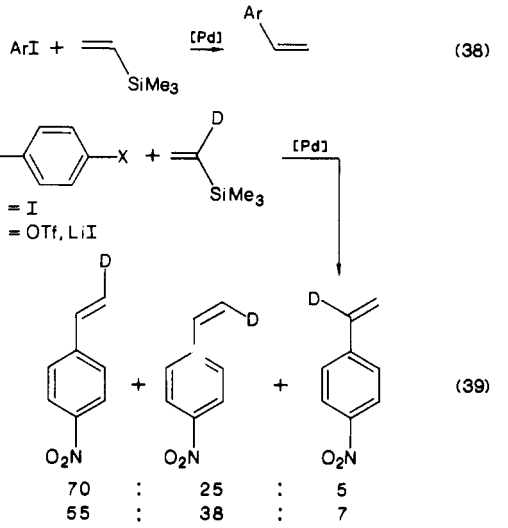


(36)

(37)

37) probably involve transmetalation and reductive elimination of palladium rather than 1,2-addition of organopalladium to the vinylsilane double bond. However, the transmetalation mechanism in the reaction of vinylsilanes (and vinyl IVA element compounds) with organopalladium reagents may be closely related to the 1,2-addition–elimination mechanism; both mechanisms involve π-complex formation in the initial stages.

Palladium-catalyzed arylation of trimethylvinylsilane with aryl iodides under ordinary Heck arylation conditions yields mostly styrene with small amounts of trimethyl(2-phenylethenyl)silane (eq 38).[94] Styrene formation, under these conditions, appears to proceed by 1,2-addition of "ArPdI" to the double bond of the vinylsilane followed by HPdI elimination–readdition and eventual silicon–carbon bond cleavage[95] since (a) under the same conditions, arylation of 1-(trimethylsilyl)-1-propene furnished 2-phenylpropene and (b) arylation of trimethyl(1-deuterioethenyl)silane with 1-iodo-4-nitrobenzene (or the corresponding triflate and iodide ion[96]) produce predominantly β-deuterated styrenes (eq 39).



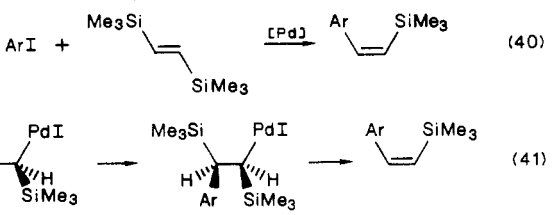
(38)

(39)

A proposed mechanism to account for the formation of these products and the minor product trimethyl(2-arylethenyl-*1-d*)silane also formed is depicted in Scheme V; the α-deuterio product probably results from α-arylation. If the products are formed by a cross-coupling reaction, α-deuteriostyrene should be the major product. It is also unlikely that arylation occurs predominantly at the α-carbon. Involvement of a protiodesilylation process (see eq 32 and 33) by triethylammonium hydriodide formed during reaction is ruled out since no styrene is detected when trimethyl(2-phenylethenyl)silane is treated with 1 equiv of triethylammonium hydriodide or triethylammonium hydrochloride at 120 °C for 16 h. Furthermore, the ratio of desilylated to silylated products is independent of reaction time.[95]

The desilylation is suppressed when ortho substituents are present in the aryl iodide,[97] e.g., with 1-iodo-2,4,6-trimethylbenzene;[98] presumably such suppression is the result of a steric influence on readdition of HPdI.[98]

Arylation of (*E*)-1,2-bis(trimethylsilyl)ethylene provides (*Z*)-trimethyl(2-arylethenyl)silanes[96] (eq 40 and Table IV). The *Z*/*E* isomer ratio is greater than 13.

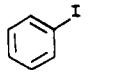
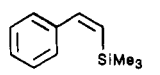
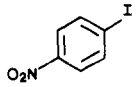
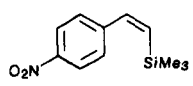
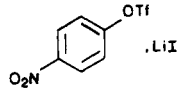
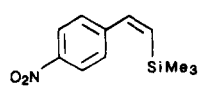
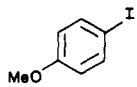
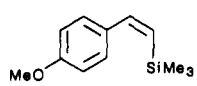
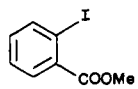
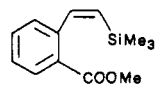


(40)

(41)

The main side reaction is formation of biaryls, which, unfortunately, limits the yields of the desired products considerably. Results are comparable when 4-nitro-

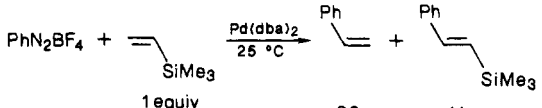
TABLE IV. Palladium-Catalyzed Arylation of (*E*)-1,2-Bis(trimethylsilyl)ethene at 110 °C[a]

arylating agent	product	yield, %
		43
		23
		25
		57
		49

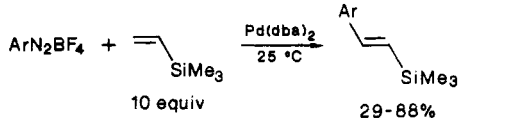
[a] Data taken from ref 96.

phenyl triflate in combination with a lithium halide[14c] is used rather than 1-iodo-4-nitrobenzene.[99] The formation of *Z* products suggests that syn elimination of (trimethylsilyl)palladium halide occurs (eq 41). It is notable that while (*E*)-1,2-bis(trimethylsilyl)ethylene furnishes the *Z* product, the related tin compound (*E*)-1-(trimethylsilyl)-2-(tri-*n*-butylstannyl)ethylene provides (*E*)-1-aryl-2-(trimethylsilyl)ethylene after arylation as a result of cross-coupling.[14c]

Arylation of vinylsilanes using aryldiazonium salts as arylpalladium precursors has been studied.[100-104] Styrene is the major product produced in reaction of phenyldiazonium tetrafluoroborate with 1–3 equiv of trimethylvinylsilane[100] (eq 42). With an excess of the vinylsilane, the major product formed is trimethyl(2-phenylethenyl)silane (eq 42). An electron-withdrawing group in the aryl moiety disfavors desilylation. A number of trimethyl(2-arylethenyl)silanes have been prepared in variable yields (eq 43).

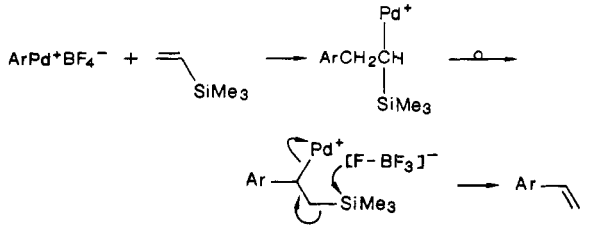


(42)



(43)

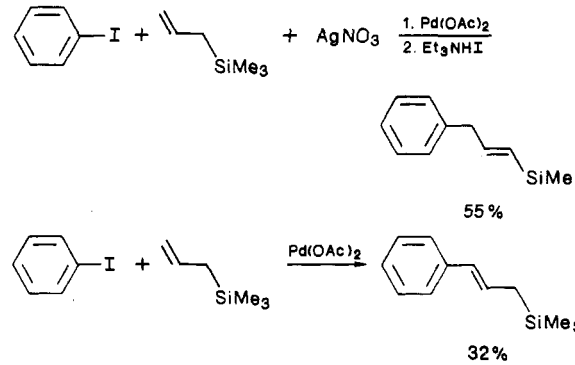
Styrene formation in these reactions is rationalized as resulting from attack on silicon by an external fluoride ion inducing cleavage of the silicon–carbon bond[100] (eq 44). Palladium-catalyzed aryldesilylation



(44)

of (*E*)- and (*Z*)-PhCH=CHSiMe$_3$ with arenediazonium salts proceeds with loss of regio- and stereospecificity.[101] However, Ph(R$_3$Si)C=CH$_2$ reacts readily with arenediazonium tetrafluoroborates at 25 °C to give (*E*)-PhCH=CHAr under palladium catalysis.[102]

The use of silver ion as a halide ion abstractor[105] during palladium-catalyzed arylation of allyltrimethylsilane has a dramatic effect: (a) increasing the reaction rate, (b) completely suppressing desilylation, and (c) altering the direction of palladium hydride elimination[106] (compare eq 45 and 46). However, the presence of silver ion does not affect the regiochemistry of the reaction as expected if a cationic center β to the silyl group had developed during the course of the reaction (β-effect).



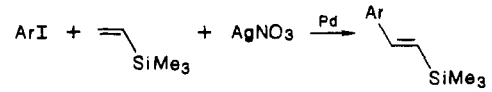
(45)

55%

(46)

32%

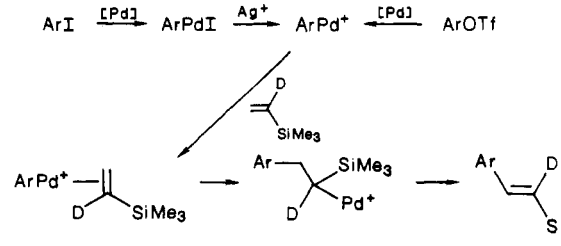
Arylation of trimethylvinylsilane in the presence of silver ion furnishes good isolated yields of (*E*)-trimethyl(2-arylethenyl)silanes[95] (eq 47). Desilylation is fully suppressed and the reaction rate is enhanced.



(47)

Preparative results of this study are summarized in Table V. A variety of functional groups are tolerated and the reaction proceeds smoothly with both aryl and heterocyclic iodides. The presence of ortho substituents in the organopalladium reagent precursor slows the reaction rate. Arylation of triethoxyvinylsilane requires higher reaction temperature and results in diminished yields. The reaction exhibits high regioselectivity for β-substitution, forming <5% of products derived from α-substitution, with all iodides except 4-iodo-1-methylpyrazole. Use of 4-nitrophenyl triflate in the absence of silver ion yields results similar to those obtained with aryl halides and silver ions. An activating nitro group is necessary for effective conversion of the triflates.

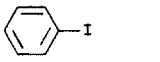
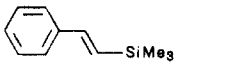
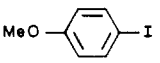
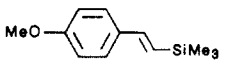
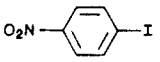
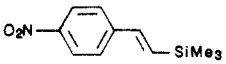
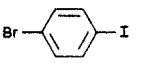
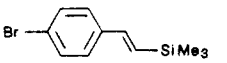
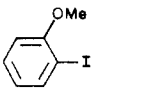
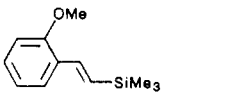
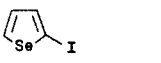
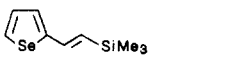
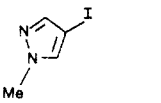
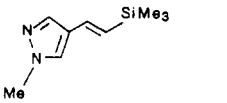
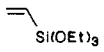
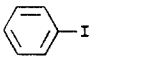
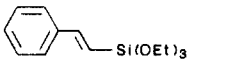
A mechanistic rationale for formation of an arylvinylsilane is exemplified for the case of trimethyl(1-deuterioethenyl)silane in reaction with 1-iodo-4-nitrobenzene as the arylpalladium precursor (eq 48). It



(48)

appears that silver ion not only acts as an iodide abstractor[105] but also facilitates the oxidative addition of Pd(0) by attachment to the iodo substituent and/or by

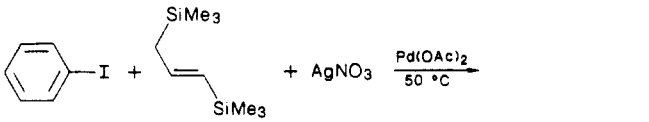
TABLE V. Palladium-Catalyzed Arylation of Trimethylvinylsilane and Triethoxyvinylsilane in the Presence of Silver Nitrate[a]

olefin	aryl iodide	product	yield, %
			74
			68
			70
			84
			79
			79
			68
			47

[a] Data taken from ref 95.

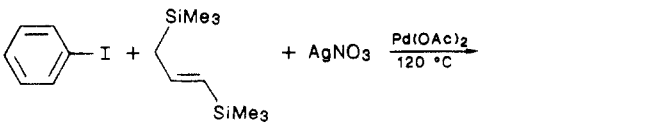
formation of an electron donor–acceptor complex with the aromatic ring. The aryl group is transferred to the olefinic β-carbon from the intermediate π-complex to give an adduct that is not prone to desilylate.

Arylation of (*E*)-1,3-bis(trimethylsilyl)propene at 50 °C occurs regio- and stereospecifically[106] (eq 49). When the reaction temperature is increased to 120 °C, desilylation occurs probably as a result of protiodesilylation by ammonium salt formed in the reaction[106] (eq 50). Arylation of (*E*)-1,2-bis(trimethylsilyl)ethylene in the presence of silver ion occurs stereospecifically[96] (eq 51). Throughout these studies, silver nitrate has been the



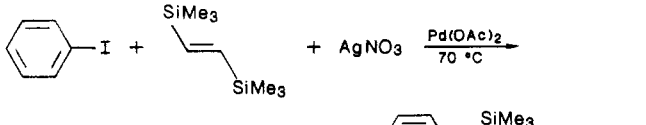
(49)

52%



(50)

53%

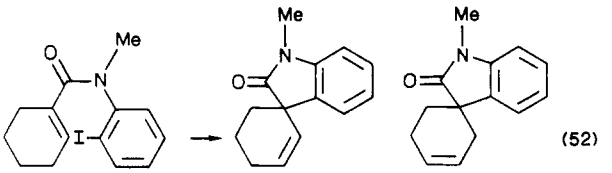


(51)

40%

source of silver ions. Silver tetrafluoroborate, silver acetate, silver triflate, and silver carbonate are also effective; in view of earlier results,[100] it is notable that the tetrafluoroborate anion does not effect product desilylation under the stated conditions.

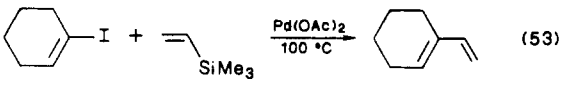
Recently, other examples of the successful use of the palladium/silver ion combination have been reported.[107,108] An intramolecular ring closure[107a] (eq 52) illustrates the impressive effect silver ion can have on palladium-mediated reactions.



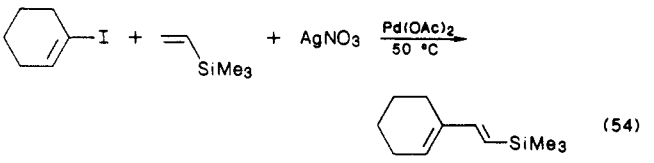
(52)

[Pd], 82 °C	1	:	1
[Pd], $AgNO_3$, 25 °C	26	:	1

Multifunctional 1-(trimethylsilyl) 1,3-dienes are potentially useful intermediates in synthesis, since exposure to Diels–Alder reaction conditions furnishes allylsilane adducts that are susceptible to a series of further transformations.[109] Reaction of 1-cyclohexenyl iodide with trimethylvinylsilane under Heck conditions provides the desilylated diene as the major product in 57% yield[110] (eq 53); the desilylation probably occurs analogously to the mechanism proposed in Scheme V. Again, addition of silver nitrate suppresses desilylation and enhances the reaction rate, yielding the 1-trimethylsilyl diene[110] with β/α regioselectivity >20 (eq 54).



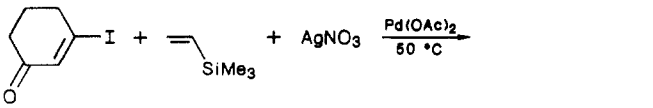
(53)



(54)

64%

The vinylation reaction is very sensitive to the reaction medium and to the substituent pattern of the vinyl iodides (Table VI). A substituent on the iodo-bearing carbon is necessary for regiocontrol of the reaction; similar observations were reported[111] for vinylations of 1-hexene. A carbonyl substituent on the β-carbon does not affect the reaction regiochemistry (eq 55) in sharp contrast to reaction of alkyl vinyl ether in the absence of silver ion.[63]

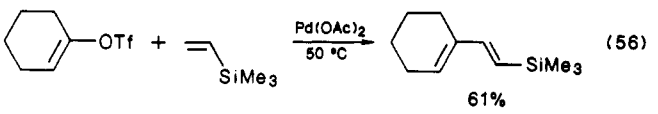


(55)

77%

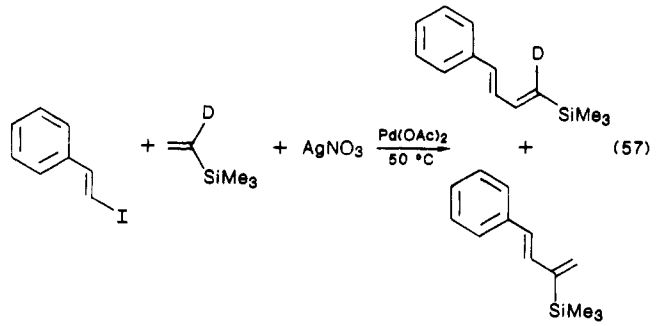
Vinyl triflates as vinylpalladium reagent precursors[26,62,112] give similar product distributions and exhibit reactivity similar to that attained with vinyl iodides and silver ion[110] (eq 56, Table VI).

To gain some mechanistic insight, an experiment was performed in which trimethyl(1-deuterioethenyl)silane



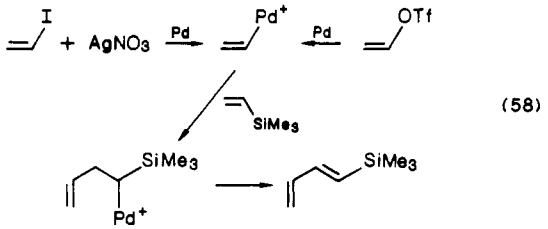
61% (56)

and (*E*)-β-iodostyrene were treated with a palladium catalyst in the presence of silver ion; no scrambling of deuterium in the product was observed (eq 57).



(57)

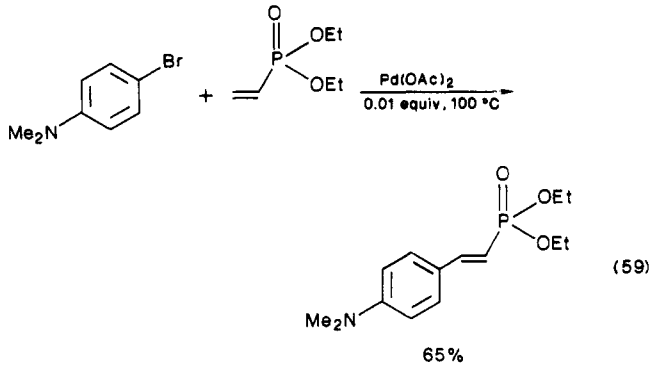
It is reasonable to assume that the palladium-catalyzed vinylation of trimethylvinylsilane using either vinyl triflates or vinyl iodides and silver ion as halide abstractor[113] proceeds via a common intermediate (eq 58).



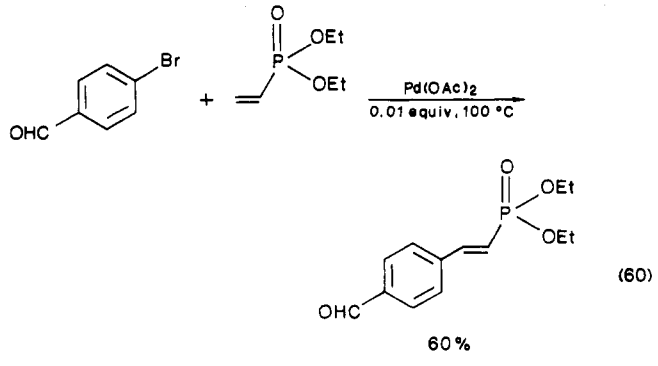
(58)

VII. Reactions of Vinylphosphonates

Diethyl vinylphosphonate undergoes regiospecific β-arylation with aryl bromides in the presence of palladium acetate.[114] This reaction, which appears to give exclusively (*E*)-2-arylethenylphosphonates, is quite tolerant of functional groups (eq 59 and 60).

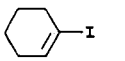
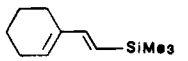
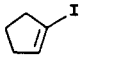
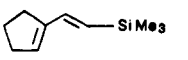
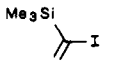
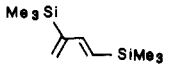
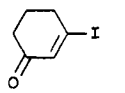
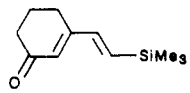
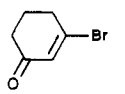
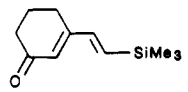
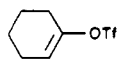
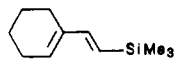
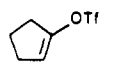
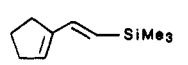
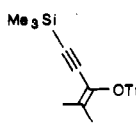
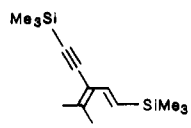


65% (59)



60% (60)

TABLE VI. Palladium-Catalyzed Vinylation of Trimethylvinylsilanes in the Presence of Silver Nitrate[a]

vinyl compd	product	yield, %
		64
		36
		66
		77
		70
		61
		38
		72

[a] Data taken from ref 110.

VIII. Conclusions

Carbon–carbon bond-forming reactions of heteroatom-substituted olefins that involve 1,2-addition of an organopalladium reagent to the double bond afford versatile and efficient synthetic routes to a wide variety of compounds. Increased understanding of the pathways by which these reactions occur, delineation of the factors that determine reaction regio- and stereochemistry, and control of competing modes of σ-organopalladium adduct decomposition to products make possible the utilization of these reactions in synthesis of complex structures. The selectivity of these reactions and their toleration of diverse functional groups are especially advantageous. The complementary nature of enol ethers and olefinic silanes in which the attached heteroatoms direct the reaction regiochemistry in opposite senses provides useful synthetic versatility. The facile nature of these organopalladium reactions and the direct entry they afford to an impressive array of important structure types foretell their increased application in synthesis.

Acknowledgments. We are grateful to the National Institutes of Health, the American Cancer Society, and the Swedish National Research Council for financial support. We express appreciation to our co-workers, whose names are included in the references, for their critical contributions to the work described.

References

(1) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5518, 5526, 5531, 5535, 5538, 5542, 5546.
(2) Moritani, I.; Fujiwara, Y. *Tetrahedron Lett.* **1967**, 1119.
(3) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.
(4) Daves, G. D., Jr. In *Advances in Metal-Organic Chemistry*, Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, Vol. 2, in press.

(5) Andersson, C.-M. Ph.D. Dissertation, University of Lund, 1988.
(6) Heck, R. F. *J. Am. Chem. Soc.* **1969**, *91*, 6707.
(7) Kalinoski, H. T.; Hacksell, U.; Barofsky, D. F.; Barofsky, E.; Daves, G. D., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 6476.
(8) Andersson, C.-M.; Hallberg, A.; Daves, G. D., Jr. *J. Org. Chem.* **1987**, *52*, 3529.
(9) (a) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669. (b) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340. (c) Suzuki, A. *Pure Appl. Chem.* **1985**, *57*, 1749. (d) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771. (e) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.
(10) Scott, W. J.; McMurry, J. E. *Acc. Chem. Res.* **1988**, *21*, 47.
(11) Baba, S.; Negishi, E. *J. Am. Chem. Soc.* **1976**, *98*, 6729.
(12) Dang, H. P.; Linstrumelle, G. *Tetrahedron Lett.* **1978**, *19*, 191.
(13) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918.
(14) (a) Stille, J. K.; Groh, B. L. *J. Am. Chem. Soc.* **1987**, *109*, 813. (b) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033. (c) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.
(15) Jabri, N.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1981**, *22*, 959. Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254.
(16) Okukado, N.; Van Horn, D. E.; Klima, W. L.; Negishi, E. *Tetrahedron Lett.* **1978**, *19*, 1027.
(17) Miyaura, N.; Suzuki, A. *J. Organomet. Chem.* **1981**, *213*, C53. Nilsson, K.; Hallberg, A. *Acta Chem. Scand. Ser. B* **1987**, *B41*, 569.
(18) Kikukawa, K.; Umekawa, H.; Matsuda, T. *J. Organomet. Chem.* **1986**, *311*, C44.
(19) Kuwajima, I.; Urabe, H. *J. Am. Chem. Soc.* **1982**, *104*, 6831.
(20) Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393.
(21) Arai, I.; Daves, G. D., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 287.
(22) Arai, I.; Daves, G. D., Jr. *J. Org. Chem.* **1978**, *43*, 4110.
(23) Lee, T. D.; Daves, G. D., Jr. *J. Org. Chem.* **1983**, *48*, 399.
(24) Outten, R. A.; Daves, G. D., Jr. *J. Org. Chem.* **1989**, *54*, 29.
(25) Arai, I.; Daves, G. D., Jr. *J. Org. Chem.* **1979**, *44*, 21.
(26) Scott, W. J.; Pena, M. R.; Swärd, K.; Stoessel, S. J.; Stille, J. K. *J. Org. Chem.* **1985**, *50*, 2302.
(27) Bäckvall, J. E.; Nordberg, R. E.; Wilhelm, D. *J. Am. Chem. Soc.* **1985**, *107*, 6892.
(28) Hacksell, U.; Daves, G. D., Jr. *Prog. Med. Chem.* **1985**, *22*, 1.
(29) Cheng, J. C.-Y.; Hacksell, U.; Daves, G. D., Jr. *J. Org. Chem.* **1985**, *50*, 2778.
(30) Outten, R. A.; Daves, G. D., Jr. *J. Org. Chem.* **1987**, *52*, 5064.
(31) Cheng, J. C.-Y.; Hacksell, U.; Daves, G. D., Jr. *J. Org. Chem.* **1986**, *51*, 3093.
(32) Hacksell, U.; Daves, G. D., Jr. *J. Org. Chem.* **1983**, *48*, 2870.
(33) Kwok, D.-I.; Daves, G. D., Jr., unpublished results.
(34) Arai, I.; Daves, G. D., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 7683.
(35) Arai, I.; Lee, T. D.; Hanna, R.; Daves, G. D., Jr. *Organometallics* **1982**, *1*, 742.
(36) Hacksell, U.; Daves, G. D., Jr. *Organometallics* **1983**, *2*, 772.
(37) Hacksell, U.; Kalinoski, H. T.; Barofsky, D. F.; Daves, G. D., Jr. *Acta Chem. Scand., Ser. B* **1985**, *B39*, 469.
(38) Cheng, J. C.-Y.; Daves, G. D., Jr. *Organometallics* **1986**, *5*, 1753.
(39) Cheng, J. C.-Y.; Daves, G. D., Jr. *J. Org. Chem.* **1987**, *52*, 3083.
(40) Czernecki, S.; Dechavanne, V. *Can. J. Chem.* **1983**, *61*, 533.
(41) Czernecki, S.; Gruy, F. *Tetrahedron Lett.* **1981**, *22*, 437.
(42) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385.
(43) Trost, B. M.; Gowland, F. W. *J. Org. Chem.* **1979**, *44*, 3448.
(44) Dunkerton, L. V.; Euske, J. M.; Serino, A. J. *Carbohydr. Res.* **1987**, *171*, 89.
(45) Brakta, M.; Lhoste, P.; Sinou, D. *J. Org. Chem.* **1989**, *54*, 1890.
(46) RajanBabu, T. V. *J. Org. Chem.* **1985**, *50*, 3642.
(47) Brakta, M.; Le Borgne, F.; Sinou, D. *J. Carbohydr. Chem.* **1987**, *6*, 307.
(48) Yougai, S.; Miwa, T. *J. Chem. Soc., Chem. Commun.* **1983**, 68.
(49) RajanBabu, T. V.; Reddy, G. S. *J. Org. Chem.* **1986**, *51*, 5458.
(50) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5535.
(51) Asano, R.; Moritani, I.; Sonoda, A.; Fujiwara, Y.; Teranishi, S. *J. Chem. Soc. C* **1971**, 3691.
(52) Danno, S.; Moritani, I.; Fujiwara, Y. *Tetrahedron* **1969**, *25*, 4819.
(53) Kikukawa, K.; Matsuda, T. *Chem. Lett.* **1977**, 159.
(54) Hallberg, A.; Westfelt, L.; Holm, B. *J. Org. Chem.* **1981**, *46*, 5414.
(55) Hallberg, A.; Westfelt, L. *J. Chem. Soc., Perkin Trans. 1* **1984**, 933.
(56) Hallberg, A.; Westfelt, L.; Andersson, C.-M. *Synth. Commun.* **1985**, *15*, 1131.
(57) Andersson, C.-M.; Hallberg, A. *J. Org. Chem.* **1988**, *53*, 2112.
(58) Andersson, C.-M.; Hallberg, A. *J. Org. Chem.* **1988**, *53*, 235.
(59) Kasahara, A.; Izumu, T.; Xiao-ping, L. *Chem. Ind. (London)* **1988**, 50.
(60) Andersson, C.-M.; Hallberg, A. *J. Org. Chem.* **1988**, *53*, 4257.
(61) Andersson, C.-M.; Hallberg, A. *Tetrahedron Lett.* **1987**, *28*, 4215.
(62) Cacchi, S.; Ciattini, P. G.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1987**, *28*, 3039.
(63) Andersson, C.-M.; Hallberg, A. *J. Org. Chem.* **1989**, *54*, 1502.
(64) Trost, B. M.; Tanigawa, Y. *J. Am. Chem. Soc.* **1979**, *101*, 4743.
(65) Kasahara, A.; Izumi, T.; Maemura, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1021.
(66) Arai, I.; Daves, G. D., Jr. *J. Heterocycl. Chem.* **1978**, *15*, 351.
(67) Horino, H.; Inoue, N. *J. Org. Chem.* **1981**, *46*, 4416.
(68) Nilsson, K.; Hallberg, A., unpublished results.
(69) Iida, H.; Yuasa, Y.; Kibayashi, C. *J. Org. Chem.* **1980**, *45*, 2938.
(70) Kasahara, A.; Izumi, T.; Kikuchi, T.; Xiao-ping, L. *J. Heterocycl. Chem.* **1987**, *24*, 1555.
(71) Grigg, R.; Sridharan, V.; Stevenson, P.; Worakun, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1697.
(72) Kurosawa, H.; Emoto, M.; Urabe, A.; Miki, K.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 8253.
(73) Ziegler, C. B.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2949.
(74) Hegedus, L. S.; Williams, R. E.; McGuire, M. A.; Hayashi, T. *J. Am. Chem. Soc.* **1980**, *102*, 4973.
(75) Hegedus, L. S.; Darlington, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 4980.
(76) Cutolo, M.; Fiandanese, V.; Naso, F.; Sciacovelli, O. *Tetrahedron Lett.* **1983**, *24*, 4603.
(77) Harrington, P. J.; Hegedus, L. S. *J. Org. Chem.* **1984**, *49*, 2657. Harrington, P. J.; Hegedus, L. S.; McDaniel, K. F. *J. Am. Chem. Soc.* **1987**, *109*, 4335.
(78) Yamamura, K.; Watarai, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3757.
(79) (a) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (b) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (c) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983.
(80) Hudrlik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1993.
(81) Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 4260.
(82) Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *Tetrahedron Lett.* **1985**, *26*, 139.
(83) Tamao, K.; Nakajo, E.; Ito, Y. *J. Org. Chem.* **1987**, *52*, 4412.
(84) (a) Stork, G.; Colvin, E. *J. Am. Chem. Soc.* **1971**, *93*, 2080. (b) Tamao, K.; Kumada, M.; Maeda, K. *Tetrahedron Lett.* **1984**, *25*, 321. (c) Tamao, K.; Maeda, K. *Tetrahedron Lett.* **1986**, *27*, 65.
(85) Simons, G.; Zandler, M. E.; Talaty, E. R. *J. Am. Chem. Soc.* **1976**, *98*, 7869.
(86) (a) Hanstein, W.; Bervin, H. J.; Traylor, T. G. *J. Am. Chem. Soc.* **1970**, *92*, 829, 7476. (b) Jarvie, A. W. P. *Organomet. Chem. Rev., Sect A* **1970**, *6*, 153. (c) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496, and references cited therein.
(87) Paquette, L. A. *Science* **1981**, *217*, 793.
(88) Daniels, R. G.; Paquette, L. A. *J. Org. Chem.* **1981**, *46*, 2901, and references 2–8 cited therein.
(89) Fleming, I. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 3, p 539.
(90) Koenig, K. E.; Weber, W. P. *J. Am. Chem. Soc.* **1973**, *95*, 3416.
(91) Akhrem, I. S.; Chistovalova, N. M.; Volpin, M. E. *Russ. Chem. Rev. (Engl. Transl.)* **1983**, *52*, 542.
(92) Weber, W. P.; Felix, R. A.; Willard, A. K.; Koenig, K. E. *Tetrahedron Lett.* **1971**, 4701.
(93) Yoshida, J.; Tamao, K.; Yamamoto, H.; Kakui, T.; Uchida, T.; Kumada, M. *Organometallics* **1982**, *1*, 542.
(94) (a) Hallberg, A.; Westerlund, C. *Chem. Lett.* **1982**, 1993. (b) For a related report see: Chistovalova, N. M.; Akhrem, I. S.; Reshetova, E. V.; Volpin, M. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 2342.
(95) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1986**, *51*, 5286.
(96) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1989**, *54*, 1773.
(97) Garst, M. E.; McBride, B. J. *J. Org. Chem.* **1989**, *54*, 249.
(98) Nilsson, K.; Karabelas, K.; Hallberg, A., unpublished results.
(99) No conversion was observed after lithium fluoride addition.
(100) Kikukawa, K.; Ikenaga, K.; Kono, K.; Toritani, K.; Wada, F.; Matsuda, T. *J. Organomet. Chem.* **1984**, *270*, 277.
(101) (a) Kikukawa, K.; Ikenaga, K.; Wada, F.; Matsuda, T. *Chem. Lett.* **1983**, 1337. (b) Ikenaga, K.; Kikukawa, K.; Matsuda, T. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1959.
(102) Ikenaga, K.; Matsumoto, S.; Kikukawa, K.; Matsuda, T. *Chem. Lett.* **1988**, 873.
(103) Kikukawa, K.; Ikenaga, K.; Wada, F.; Matsuda, T. *Tetrahedron Lett.* **1984**, *25*, 5789.

(104) Ikenaga, K.; Kikukawa, K.; Matsuda, T. *J. Org. Chem.* **1987**, *52*, 1276.
(105) (a) Rimml, H.; Venanzi, L. M. *J. Organomet. Chem.* **1984**, *260*, C52–C54. (b) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609.
(106) Karabelas, K.; Westerlund, C.; Hallberg, A. *J. Org. Chem.* **1985**, *50*, 3896.
(107) (a) Abelman, M. M.; Oh, T.; Overman, L. E. *J. Org. Chem.* **1987**, *52*, 4130. (b) Abelman, M. M.; Overman, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 2328.
(108) Larock, R. C.; Song, H.; Baker, B. E.; Gong, W. H. *Tetrahedron Lett.* **1988**, *28*, 2919.
(109) (a) Carter, M. J.; Fleming, I.; Percival, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2415. (b) Jung, M. E.; Gaede, B. *Tetrahedron* **1979**, *35*, 621. (c) Koreeda, M.; Ciufolini, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 2308. (d) Oppolzer, W.; Burford, S. C.; Marazza, F. *Helv. Chim. Acta* **1980**, *63*, 555. (e) Burke, S. D.; Smith-Strickland, S. M.; Powner, T. H. *J. Org. Chem.* **1983**, *48*, 454.
(110) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1988**, *53*, 4909.
(111) Patel, B. A.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 3898.
(112) (a) Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1984**, *25*, 2271. (b) Harnisch, W.; Morera, E.; Ortar, G. *J. Org. Chem.* **1985**, *50*, 1990. (c) Hirota, K.; Kitade, Y.; Isobe, Y.; Maki, Y. *Heterocycles* **1987**, *26*, 355. (d) Pena, M. R.; Stille, J. K. *Tetrahedron Lett.* **1987**, *28*, 6573.
(113) Moritani, I.; Fujiwara, Y.; Danno, S. *J. Organomet. Chem.* **1971**, *27*, 279.
(114) Xu, Y.; Jin, X.; Huang, G.; Huang, Y. *Synthesis* **1983**, 556.