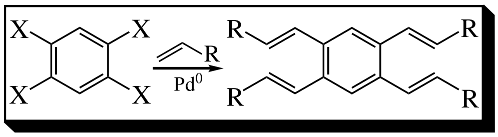

IV.2.1.2 Double and Multiple Heck Reactions

STEFAN BRÄSE and ARMIN DE MEIJERE

A. INTRODUCTION

The multiple Pd-catalyzed couplings of oligohaloarenes and -alkenes (or perfluoroalkyl- and fluorosulfonates) with alkenes (Heck reactions) offer the possibility of constructing symmetrically oligosubstituted, highly unsaturated carbon frameworks in a single synthetic operation. The Heck reaction of di- and oligoethenylarenes with di- and oligohaloarenes can be applied to produce conjugated polyvinylenearylene-type polymers that may have important applications in the future. Comparable in scope and limitations to the related multiple Stille and Suzuki couplings, the ready accessibility of starting materials and the ease of removing by-products have made multiple Heck reactions particularly attractive for various synthetic applications.

In this section, a double (or multiple) Heck reaction is defined as a coupling of two (or more) alkene molecules with di- or oligohaloarenes or -alkenes as well as a reaction of two (or more) di- or oligohaloarenes or alkenes with one alkene molecule.

B. COUPLING OF OLIGOHALOARENES WITH ALKENES

The multiple coupling of oligohaloarenes with alkenes was described early on by Heck and Nolley in one of their first papers.[1] Twofold coupling of 1,4-diiodobenzene with styrene furnished the 1,4-distyrylbenzene in 67% yield; shortly afterwards, the double Heck couplings under palladium catalysis of 4,7-diiodofluorene, *p*-diiodoterphenyl, and *p*-diiodobiphenyl with various substituted styrenes were disclosed by Japanese chemists in a patent on the synthesis of dye brighteners.[2] Since then, a large number of *ortho*-, *meta*-, and *para*-dihaloarenes and -heteroarenes have been subjected to double Heck reactions with various alkenes (**Tables 1–3**, **Scheme 1**).

However, the substitution pattern on the arene is crucial for the success of the Heck reaction. When a second Heck coupling takes place in an *ortho* position of another alkenyl unit, cyclization of the intermediately formed σ-(β-arylalkyl)palladium complex may occur, as formation of alkylideneindanes and alkylindenes, especially under classical Heck conditions with phosphines in the catalyst cocktail, was observed (**Scheme 2**, **Table 1**).

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TABLE 1. Twofold Heck Reactions on 1,2-Dihaloarenes

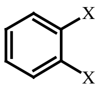
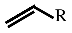
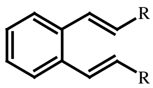
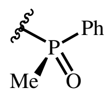
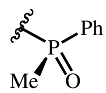
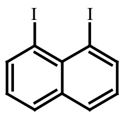
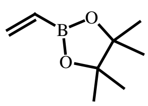
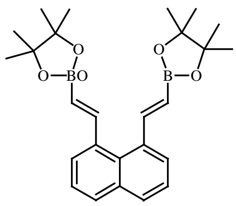
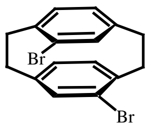
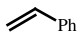
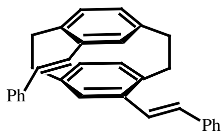
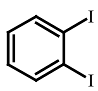
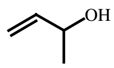
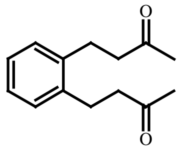
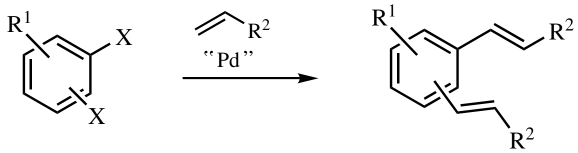
Arene 	Alkene 	Product 	Conditions	Yield (%)	Ref-erence
X = I	R = Ph	R = Ph	$Pd(OAc)_2$, Bu_3N, 100 °C, 72 h	37	[1]
X = I	R = CO_2Me	R = CO_2Me	$Pd(OAc)_2$, PPh_3, Et_3N, 100 °C, 48 h	69	[7]
X = Br	R = Ph	R = Ph	$Pd(OAc)_2$, Bu_4NBr, K_2CO_3, DMF, 100 °C, 5 d	92	[8]
X = Br	R = Ph	R = Ph	$Pd(OAc)_2$, P(*o*-Tol)$_3$, Et_3N, THF/MeCN, 55 °C, 1 d, 10 kbar	59	[9]
			$Pd(OAc)_2$, P(*o*-Tol)$_3$, Et_3N, 150 °C (microwave), 22 min	65	[10]
X = Br	R = CO_2Me	R = CO_2Me	$Pd(OAc)_2$, Bu_4NCl, LiCl, K_2CO_3, DMF, 100 °C, 12 h	86	[11]
X = Br	R = Me (5 bar)	R = Me	$Pd(OAc)_2$, Bu_4NBr, LiCl, $KHCO_3$, DMF, 100 °C, 12 h	79	[12]
X = Br	R = H (13.8 bar)	R = H	$Pd(OAc)_2$, P(*o*-Tol)$_3$, Et_3N, MeCN, 125 °C	78	[13]
X = Br	R = 	R = 	$Pd(OAc)_2$, PPh_3, Et_3N, DMF, 135 °C, 36 h	65	[14]
X = Br	R = 4-Py	R = 4-Py	$Pd(OAc)_2$, PPh_3, Et_3N, 100 °C, 3 d	80	[15]
X = Br	R = Fc	R = Fc	$Pd(OAc)_2$, (*n*-Bu)$_4$NBr, K_2CO_3, DMF, 70 °C, 3 d	74[a]	[16]
			$Pd(OAc)_2$, PPh_3, Et_3N, MeCN, reflux 16 h	77	[17]

TABLE 1. (*Continued*)

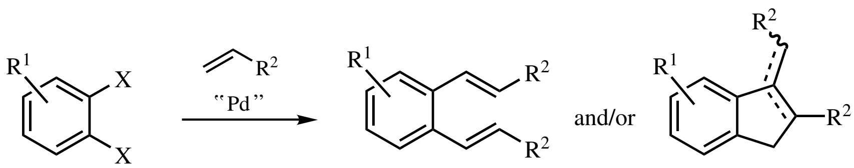
Arene	Alkene	Product	Conditions	Yield (%)	Reference
			$Pd(OAc)_2$,Bu_4NBr, K_2CO_3, LiCl, DMF, 100 °C, 3 d	35	[18]
			$Pd(OAc)_2$, P(*o*-Tol)$_3$, DMF, 100 °C, 2 d	46	[19]
			$Pd(OAc)_2$, PPh_3, *i*-Pr_2EtN, DMF, 100 °C, 3 d	56[b]	[5]

[a] Fc = ferrocenyl.
[b] The diketone was isolated.



X = Br, I; R^2 = aryl, alkyl, etc.

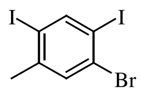
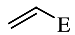
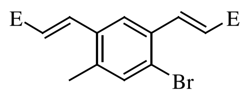
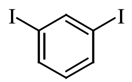
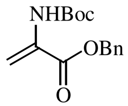
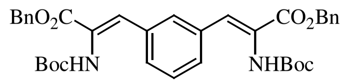
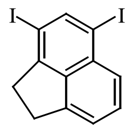
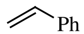
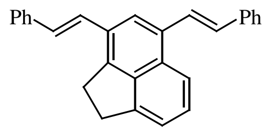
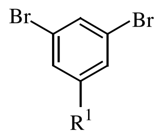
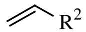
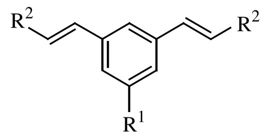
Scheme 1



Scheme 2

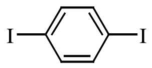
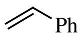
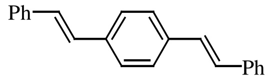
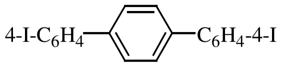
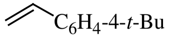
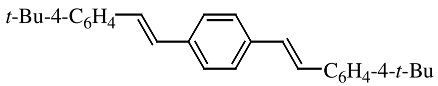
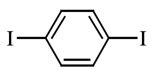
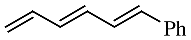
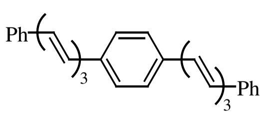
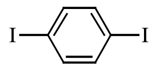
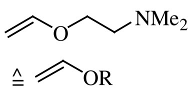
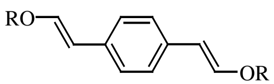
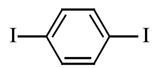
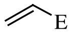
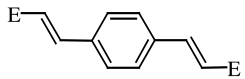
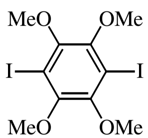
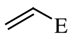
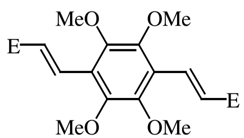
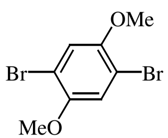
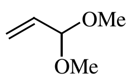
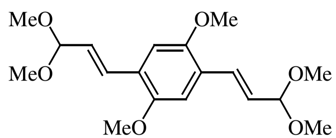
This reaction mode plays a dominant role in the sixfold Heck coupling of hexabromobenzene with styrenes yielding complex mixtures of various isomers of the sixfold coupling product. The analogous sixfold Suzuki and Stille coupling reactions with alkenylboronates and alkenylstannanes, respectively, gave the corresponding pure hexakisalkenylbenzene derivatives in high yields.[3] As shown by various experiments with *o*- and *p*-dihaloarenes, the second coupling step is generally accelerated by the first introduced alkenyl substituents in the *ortho* or *para* position, while a *meta*-alkenyl substituent does not significantly influence the rate of the second coupling.[4]

TABLE 2. Twofold Heck Reactions on 1,3-Dihaloarenes: E = CO_2Me

Arene	Alkene (Conditions)	Product	Yield (%)	Reference
	 ($Pd(OAc)_2$, PPh_3, Et_3N, 100 °C, 19 h)		46[a]	[7]
	 ($Pd(OAc)_2$, Bu_4NCl, $NaHCO_3$, DMF, 85 °C, 16 h)		52	[20]
	 (Pd/C, Bu_3N, 115–120 °C, 3 h)		21	[21]
				
	($Pd(OAc)_2$, PPh_3, Et_3N, 100 °C, 3 d)	R^1 = H, R^2 = 4-Py	77	[15]
	($Pd(OAc)_2$, PPh_3, Et_3N, DMF, 135 °C, 36 h)	R^1 = H, R^2 = P(O)MePh	92	[14]
	($Pd(OAc)_2$, P(*o*-Tol)$_3$, Et_3N, MeCN)	R^1 = HOCHPh, R^2 = CO_2Et	n.r.[b]	[22]
	($Pd(OAc)_2$, P(*o*-Tol)$_3$, Et_3N, MeCN, 90 °C, 1 h)	R^1 = CH_2OH, R = CO_2Et	94	[23]
	($Pd(OAc)_2$, P(*o*-Tol)$_3$, Et_3N, MeCN, 120 °C, 7 d)	R^1 = CO_2Et, R^2 = CN	56	[24]

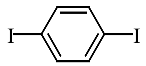
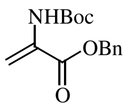
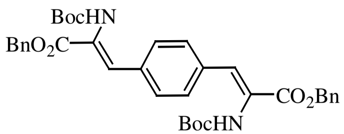
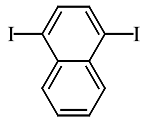
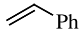
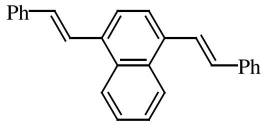
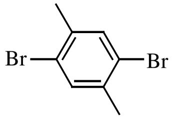
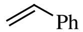
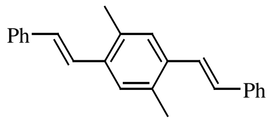
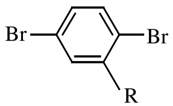
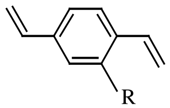
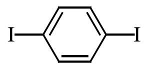
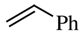
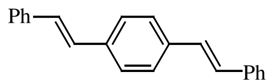
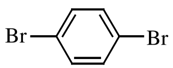
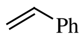
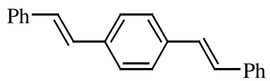
[a] The bromine substituent does not take part in the coupling under these conditions.
[b] n.r. = not reported.

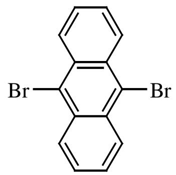
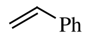
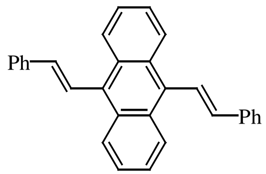
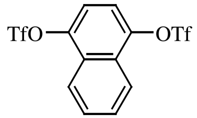
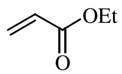
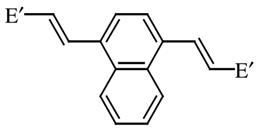
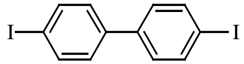
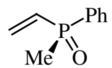
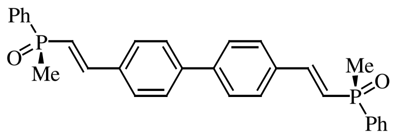
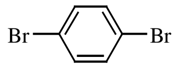
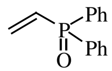
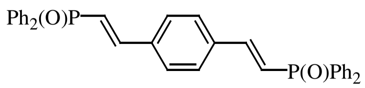
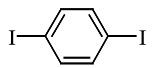
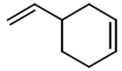
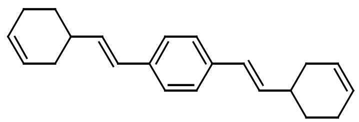
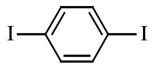
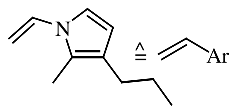
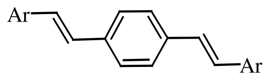
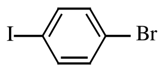
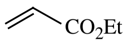
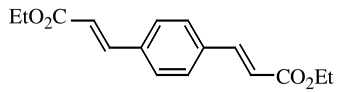
TABLE 3. Twofold Heck Reactions on 1,4- and Related *para*-Substituted Dihaloarenes: E = CO_2Me, E′ = CO_2Et

Arene	Alkene	Product	Conditions	Yield (%)	Reference
			$Pd(OAc)_2$, $(n\text{-}Bu)_3N$, 100 °C, 72 h	67	[1]
			Pd, DMF	n.r.[a]	[2]
			$Pd(OAc)_2$, $P(o\text{-}Tol)_3$, Et_3N, DMF, 100 °C, 17 h	11	[25]
			$Pd(OAc)_2$, $(n\text{-}Bu)_4NCl$, K_2CO_3, DMF, 800 °C, 16 h	76	[26]
			$Pd(OAc)_2$, PPh_3, Et_3N, 100 °C, 48 h	32	[7]
			$Pd(OAc)_2$, $P(o\text{-}Tol)_3$, Et_3N/MeCN 2:1, 70 °C, 70 h	89	[27]
			Pd(OAc)2, $P(o\text{-}Tol)_3$, Et_3N, 110 °C, 60 h	62	[28]

(*Continued*)

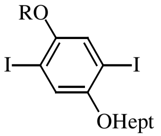
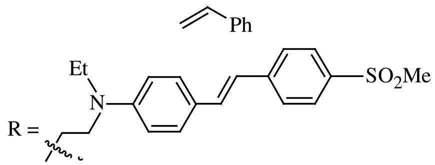
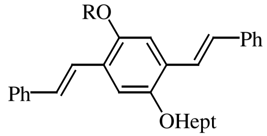
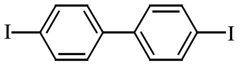
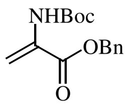
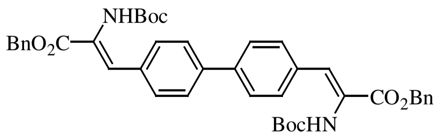
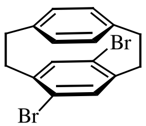
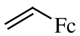
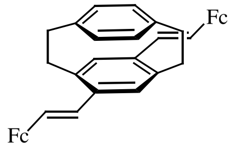
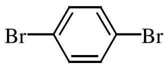
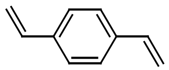
TABLE 3. (*Continued*)

Arene	Alkene	Product	Conditions	Yield (%)	Reference
			$Pd(OAc)_2$, $(n\text{-}Bu)_4NCl$, $NaHCO_3$, DMF, 85 °C, 16 h	55	[20]
			Pd/C, $(n\text{-}Bu)_3N$, 115–120 °C, 3 h	81	[21]
			$Pd(OAc)_2$, $(n\text{-}Bu)_4NBr$, LiCl, K_2CO_3, DMF, 110 °C, 5 d	61	[18]
	 R = H, CN, NO_2, $SO_2C_{10}H_{29}$		Pd(OAc)2, $P(o\text{-}Tol)_3$, Et_3N, 100–120 °C, 24 h	74–97	[29]
			$PdCl_2(PPh_3)_2$, $(n\text{-}Bu)_3N$, K_2CO_3, H_2O, 100 °C, 5 h	70	[30]
			$PdCl_2[P(o\text{-}Tol)_3]_2$ $(n\text{-}Bu)_3N$, K_2CO_3, H_2O, 100 °C, 6 h	85	[31]

			$PdCl_2$, P(*o*-Tol)$_3$, (*n*-Bu)$_3$N, K_2CO_3, H_2O, 100 °C, 3 h	97	[30],[31]
			$PdCl_2(PPh_3)_2$, Et_3N, DMF, 130 °C, 24 h	72	[32]
			$Pd(OAc)_2$, PPh_3, Et_3N, DMF, 135 °C, 36 h	85	[14]
			$Pd(OAc)_2$, PPh_3, Et_3N, MeCN, 125 °C, 24 h	39	[33]
			$Pd(OAc)_2$, $BnEt_3NCl$, KOAc, 25 °C, 10 d	21	[34]
			$PdCl_2$, (*n*-Bu)$_3$N, DMF, 80 °C, 6 h	82	[35]
			$PdCl_2(PPh_3)_2$, Et_3N, MeCN, 80 °C, 1 h	42^b	[36]

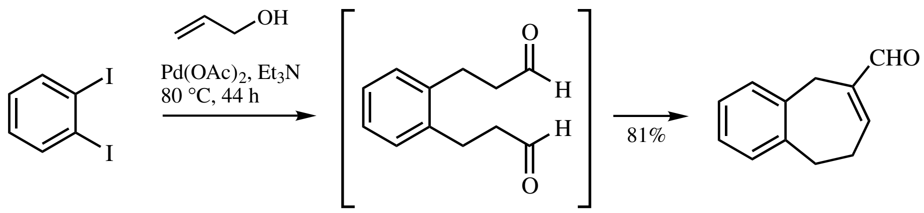
(*Continued*)

TABLE 3. (*Continued*)

Arene	Alkene	Product	Conditions	Yield (%)	Reference
			$Pd(OAc)_2$, $P(o\text{-}Tol)_3$, Et_3N, DMF, 80 °C, 5 h	90[c]	[37]
			$Pd(OAc)_2$, $(n\text{-}Bu)_4NCl$, $NaHCO_3$, DMF, 85 °C, 16 h	59	[20]
			$Pd(OAc)_2$, $(n\text{-}Bu)_4NBr$, K_2CO_3, DMF, 70 °C, 3 d	24	[38]
	 (30 bar)		$Pd(OAc)_2$, $P(o\text{-}Tol)_3$, Et_3N, DMF, 100–120 °C	74	[39]

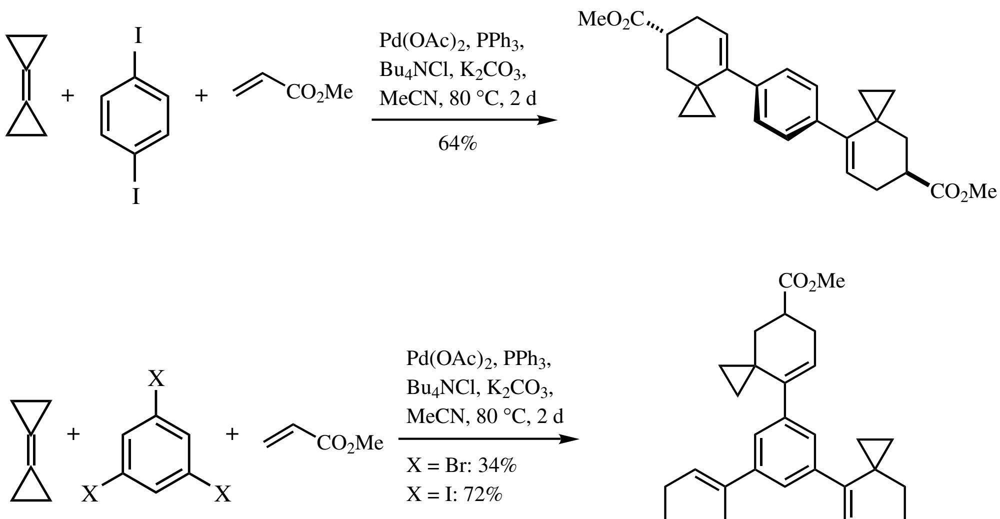
[a] n.r. = not reported.
[b] The monosubstitution product (iodine replaced) was isolated in 22% yield.
[c] Total yield of coupling products. The mono-α-substituted styrene was isolated in 12% yield.
[d] Fc = ferrocenyl.

The primary coupling product of 1,2-diiodobenzene with allyl alcohol, a dicarbaldehyde, underwent an intramolecular aldol condensation under the reaction conditions (**Scheme 3**).[5]



Scheme 3

Double and even triple Heck–Diels–Alder cascade reactions involving bicyclopropylidene and 1,4-diiodo- or 1,3,5-triiodobenzene, respectively, have been accomplished. In these sequences, the carbopalladation across the highly strained alkene is followed by a cyclopropylmethyl to homoallyl rearrangement with concomitant β-hydride elimination to yield an allylidenecyclopropane, which subsequently undergoes a smooth [4 + 2] cycloaddition to furnish the spiro[5.2]octene moiety (**Scheme 4**).[6]



Scheme 4

In later studies by Heck and co-workers,[7] extension to threefold and higher multifold couplings with the corresponding oligoiodoarenes failed, and only major fractions of reduced starting materials were observed. This drawback was completely overcome by applying the Jeffery protocol,[40] that is, with a base like potassium carbonate in the presence of a tetrabutylammonium halide.[41],[42] Under these conditions, three alkene units and more can be attached to an arene ring in excellent yields (**Tables 4** and **5**).

TABLE 4. Threefold Heck Reaction on 1,2,3-, 1,2,4-, and 1,3,5-Trihaloarenes: E = CO_2Me, Fc = Ferrocenyl

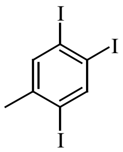
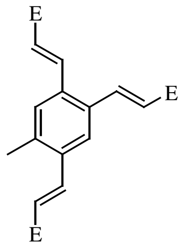
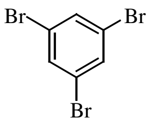
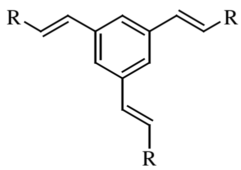
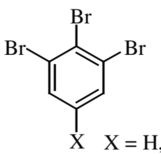
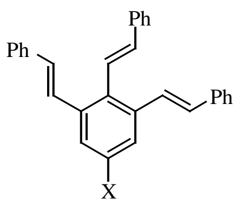
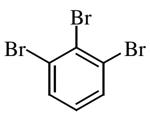
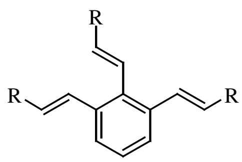
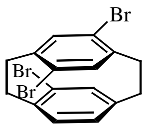
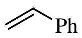
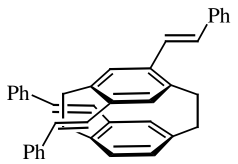
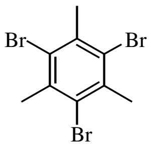
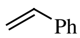
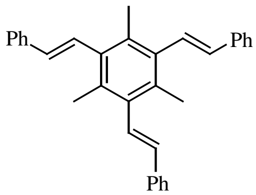
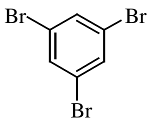
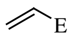
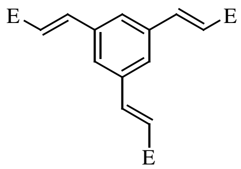
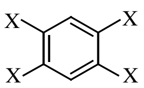
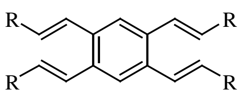
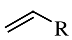
Arene Alkene	Product	Conditions	Yield (%)	Reference
 CO_2Me		$Pd(OAc)_2$, PPh_3, Et_3N, 100 °C, 12 h	52	[7]
 Fc	 R = Fc	$Pd(OAc)_2$, $(n\text{-}Bu)_4NBr$, K_2CO_3, DMF, 2 h, 60 °C	46[a]	[16]
4-Py	R = 4-Py	$Pd(OAc)_2$, PPh_3, Et_3N, 100 °C, 3 d	70 (60)	[43] ([15])
2-Py	R = 2-Py	$Pd(OAc)_2$, K_2CO_3, $(n\text{-}Bu)_4NBr$, DMF, 100 °C, 5 d	92	[44]
(8 bar)	R = H	$Pd(OAc)_2$, $P(o\text{-}Tol)_3$, Et_3N, DMF, 125 °C	71	[45]
Ph	R = Ph	$Pd(OAc)_2$, $(n\text{-}Bu)_4NCl$, K_2CO_3, LiCl, DMF, 110 °C, 30 h	82	[4]
C_6H_4-4-OMe	R = C_6H_4-4-OMe	$Pd(OAc)_2$, PPh_3, Et_3N, 100 °C, 3 d	>40	[43]
 X = H, NO_2 Ph		$Pd(OAc)_2$, $(n\text{-}Bu)_4NBr$, K_2CO_3, DMF, 100 °C, 7 d	56 X = H	[8]
		$Pd(OAc)_2$, $(n\text{-}Bu)_4NCl$, K_2CO_3, LiCl, DMF, 100 °C, 4 d	66 X = NO_2	[4]
 CO_2t-Bu	 R = CO_2t-Bu	$Pd(OAc)_2$, $(n\text{-}Bu)_4NCl$, K_2CO_3, LiCl, DMF, 3 d, 90 °C	58	[11]

TABLE 4. (*Continued*)

Arene Alkene	Product	Conditions	Yield (%)	Ref-erence
 		$Pd(OAc)_2$, $(n\text{-}Bu)_4NBr$, K_2CO_3, LiCl, DMF, 100 °C, 3 d	37	[18]
 		$Pd(OAc)_2$, $P(o\text{-}Tol)_3$, Et_3N, MeCN, 100 °C, 3 d	51	[46]
 		$Pd(OAc)_2$, $P(o\text{-}Tol)_3$, Et_3N, MeCN, 80 °C, 5 h	63 E = CO_2Me	[47]

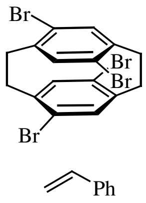
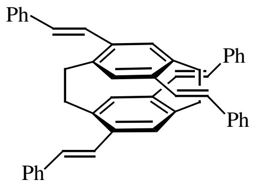
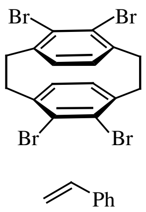
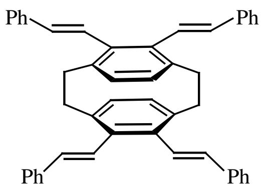
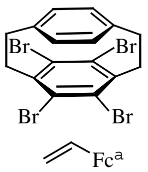
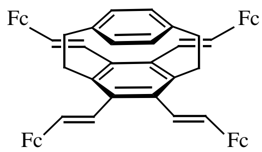
[a]Fc = ferrocenyl.

TABLE 5. Fourfold Heck Reaction on 1,2,4,5- and Related Tetrahaloarenes

Arene Alkene	Product	Conditions	Yield (%)	Reference
				
	X = I, R = CO_2Me	$Pd(OAc)_2$, PPh_3, Et_3N, 100 °C, 48 h	16	[7]
	X = Br, R = H	$Pd(OAc)_2$, $P(o\text{-}Tol)_3$, Et_3N, DMF, 125 °C, 8 d	76	[45]
	X = Br, R = Ph	$Pd(OAc)_2$, $BnEt_3NCl$, K_2CO_3, LiCl, DMF, 110 °C, 3 d	62	[8]

(*Continued*)

TABLE 5. (*Continued*)

Arene Alkene	Product	Conditions	Yield (%)	Reference
		$Pd(OAc)_2$, $(n\text{-}Bu)_4NBr$, K_2CO_3, LiCl, DMF, 100 °C, 3 d	70	[18]
		as above	45	[18]
		as above, no LiCl, 80 °C, 6 d	17	[38]

[a] Fc = ferrocenyl.

Similarly, the reaction of tetrahaloarenes with alkenes gives rise to the formation of tetraalkenylarenes.

Arenediazonium salts, which are readily available from a large stock of anilines, have proved to be valuable starting materials for Heck reactions since their reactivities exceed even those of the corresponding triflates and hence allow coupling at lower temperatures. Twofold Heck reactions of bisdiazonium salts with various substitution patterns have been investigated (**Table 6**).[48]

Even a fourfold Heck reaction utilizing the tetradiazonium salt with a tetraphenylmethane framework has been demonstrated with various alkenes to yield the corresponding fourfold coupling products.[49] Allyl alcohols did not couple with the tetradiazonium salt, but the tetrakis(*p*-iodophenyl)methane did yield the tetraaldehyde upon coupling with allyl alcohol (**Scheme 5**).[49]

The multiple Heck reaction with oligohaloheteroarenes provided a general access to highly symmetrical, often biologically active, molecules. The failure of 2,6-dihalopyridine to undergo a twofold Heck coupling was associated with the presence of a heteroatom.[50] However, 2,5-dihalothiophenes are excellent substrates for a twofold Heck coupling, even with 1,1-dimethylallene, the product of which subsequently undergoes a twofold Diels–Alder reaction (**Scheme 6**, **Table 7**).[51],[52]

TABLE 6. Twofold Heck Reaction of Arenebisdiazonium Salts[48]: E = CO_2Me

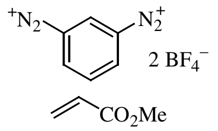
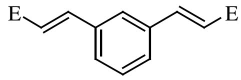
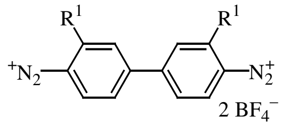
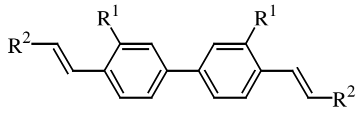
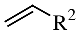
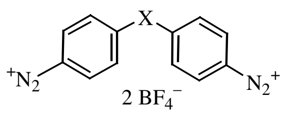
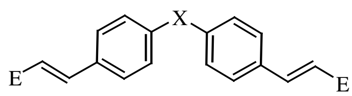
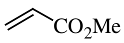
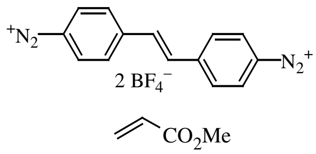
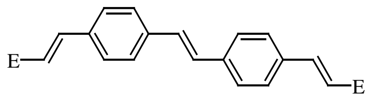
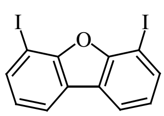
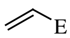
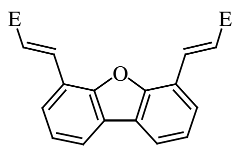
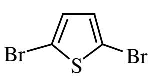
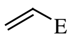
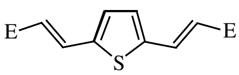
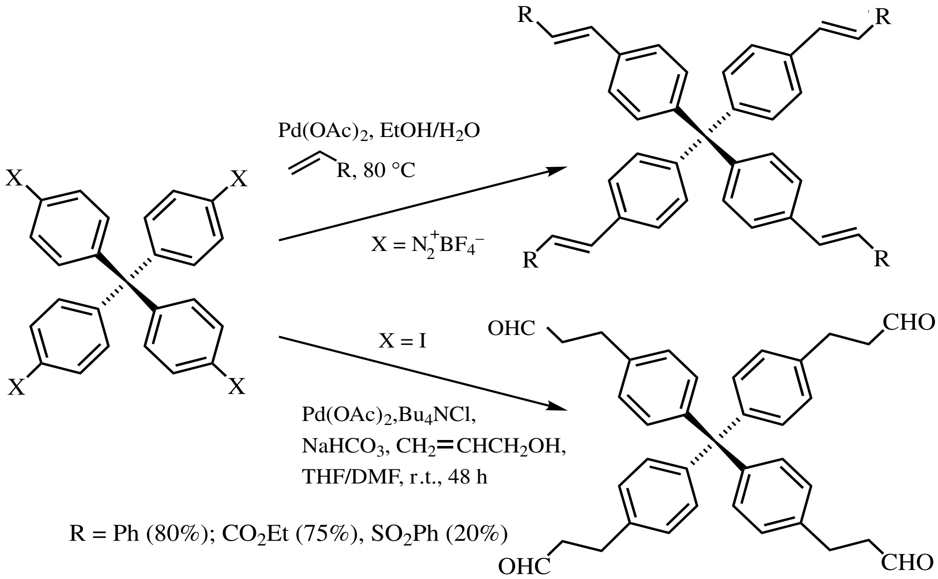
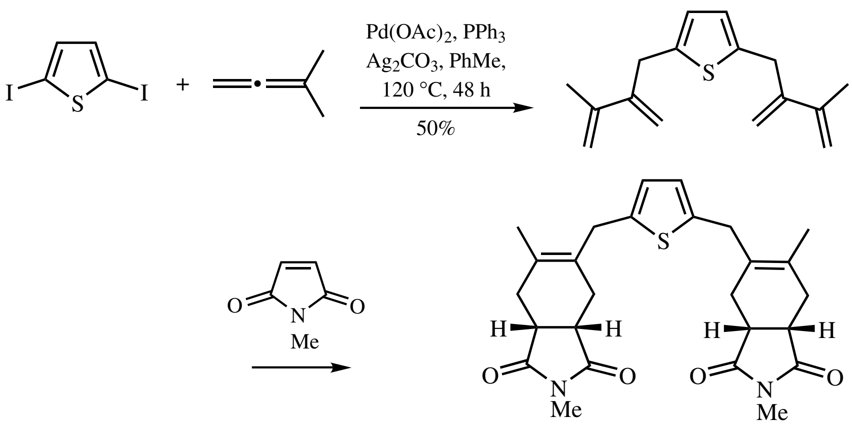
Arene Alkene	Product	Conditions	Yield (%)
		$Pd(OAc)_2$, MeOH, 65 °C, 1 h	83
		$Pd(OAc)_2$, Et OH,80 °C, 1 h	
	R^1 = H, R^2 = CO_2Me		70
	R^1 = Me, R^2 = CO_2Me		73
	R^1 = Me, R^2 = Ph		60
		$Pd(OAc)_2$, EtOH, 80 °C, 1 h	
	X = O		80
	X = SO_2		60
		$Pd(OAc)_2$, EtOH, 80 °C, 1 h	60

TABLE 7. Twofold Heck Reaction on Dihaloheteroarenes: E = CO_2Et

Arene	Alkene	Conditions	Product	Yield (%)	Ref-erence
		$Pd(OAc)_2$, PPh_3, Et_3N, DMF,		86	[53]
		$Pd(OAc)_2$, PPh_3, Et_3N, MeCN, 100 °C, 12–20 h		83–85	[51]



Scheme 5

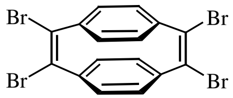
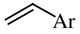
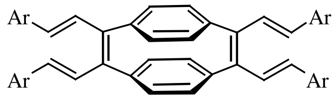
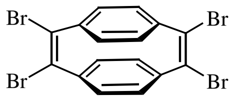
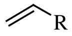
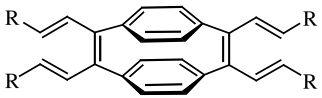
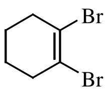
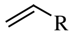
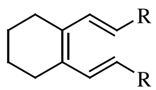
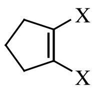
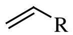
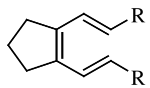


Scheme 6

C. MULTIPLE HECK COUPLINGS OF 1,2-DIBROMOCYCLOALKENES AND RELATED COMPOUNDS

Double Heck reactions of vicinal *cis*-1,2-dihaloalkenes provide an easy access to (*E,Z,E*)-1,3,5-hexatrienes, which are valuable building blocks for organic synthesis.[11],[40],[54] The first example of a twofold double, that is, essentially a fourfold, Heck reaction with a bis(dibromo)cycloalkene has been conducted on the strained 1,2,9,10-tetrabromo[2.2] paracyclophane-1,9-diene, which is available in multigram quantities. The Heck reaction proceeded cleanly under phase transfer conditions, as developed by Jeffery,[41],[42] to give the tetraalkenylated products in moderate to good yields (**Table 8**). The resulting bishexatrienes

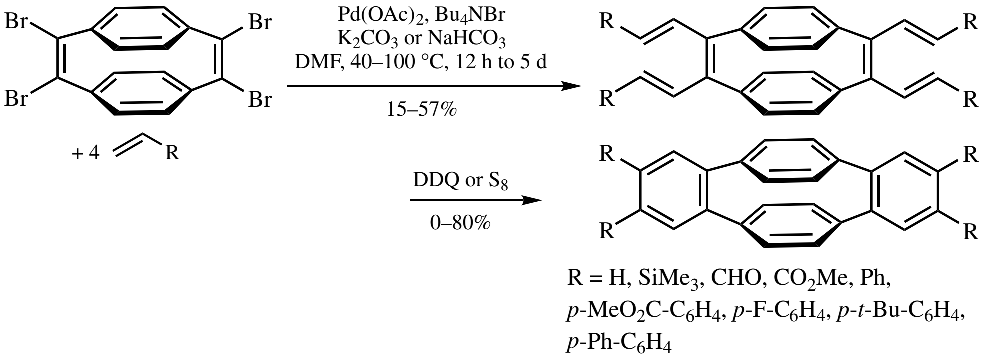
TABLE 8. Multiple Heck Reaction on 1,2-Dibromocycloalkenes and Related Compounds

Oligobromocycloalkenes	Alkene	Oligobromocycloalkenes		Conditions	Yield (%)	Reference
				$Pd(OAc)_2$, Bu_4NBr, K_2CO_3, DMF, 100 °C, 3 d		
			Ar = Ph		50 (50)[a]	[40]
			Ar = C_6H_4-4-CO_2Me	As above, 70 °C, 36 h	58 (80)[a]	[54]
			Ar = C_6H_4-4-F	As above, 70 °C, 2 d	(20)[b]	[40],[54]
			R = CHO	$Pd(OAc)_2$, Bu_4NBr, K_2CO_3, DMF, 40 °C, 2 d	38 (0)[a]	[54]
			R = CO_2Me	$Pd(OAc)_2$, PPh_3, Et_3N, DMF, 100 °C, 72 h	55	[11],[56]
			R = Ph	As above, 90 °C, 4 d	69	[56]
			R = CO_2t-Bu	As above, 90 °C, 20 h	57 (41)[b]	[11]
 X = Br			R = CO_2Me	$Pd(OAc)_2$, PPh_3, Et_3N, DMF, 100 °C, 40 h	81	[9],[56]
X = Br			R = Ph	$Pd(OAc)_2$, $P(o\text{-Tol})_3$, Et_3N, THF/MeCN, 55 °C, 1 d, 10 kbar	82	[9]
X = I			R = $SiMe_3$	$Pd(OAc)_2$, $AgNO_3$, Et_3N, DMSO, 20 °C, 2 d, 5 bar Ar	90	[56]

[a] Isolated yield of 1,2-dicoupling product after aromatization.
[b] Isolated yield of the reduced monocoupling product.

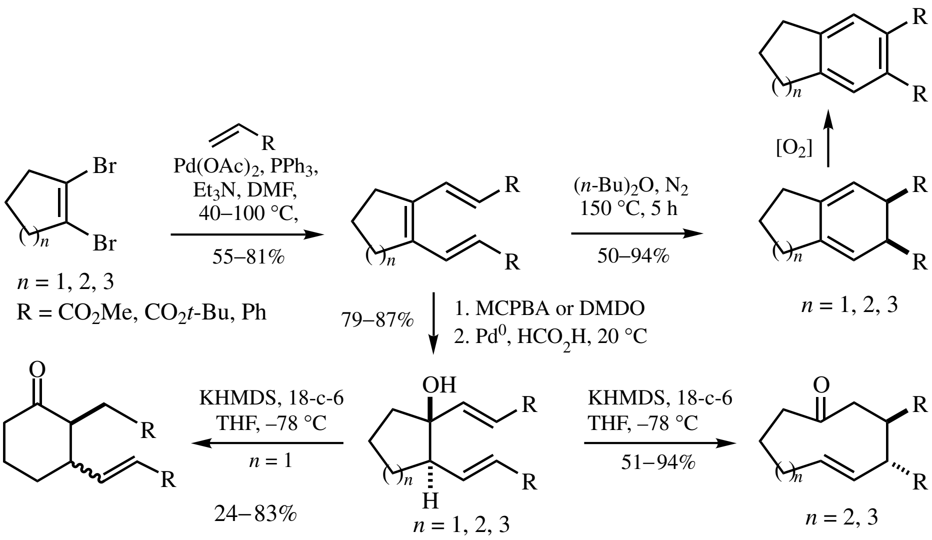
upon heating underwent a clean twofold 6π-electrocyclization to yield, after subsequent dehydrogenation, the bisbenzoannelated [2.2]paracyclophanediene derivatives (**Scheme 7**).

In contrast, the twofold alkenylations of *cis*-1,2-dibromoethene, 1,2-dibromocyclopentene, and 1,2-dibromocyclohexene proceed in better yields under the classical Heck conditions (**Table 8**).[11] The (*E,Z,E*)-1,3,5-hexatrienes resulting from 1,2-dibromocycloalkenes undergo 6π-electrocyclizations reasonably cleanly upon heating (130–150 °C) in an inert



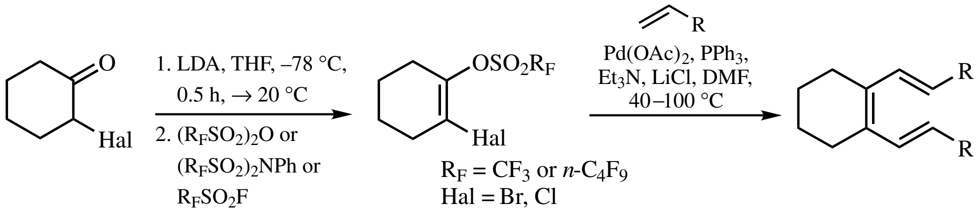
Scheme 7

solvent such as di-*n*-butyl ether or xylene in the absence of oxygen to give the ring-annelated *cis*-5,6-disubstituted 1,3-cyclohexadienes. In the presence of oxygen these products are easily dehydrogenated to the corresponding ring-annelated benzene derivatives (**Scheme 8**). Another use of these hexatrienes was demonstrated by the epoxidation of the tetrasubstituted double bond to give dialkenylepoxides, which in turn were selectively ring-opened by Pd-catalyzed reduction. The alcohols resulting from the six- and seven-membered ring epoxides, upon deprotonation at −78 °C, undergo an oxyanion-accelerated Cope rearrangement to give the corresponding *trans*-cycloalkenones.[55],[56]



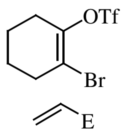
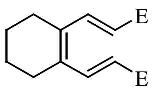
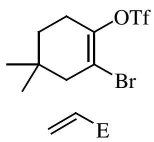
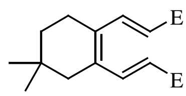
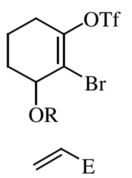
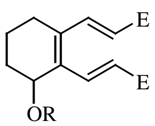
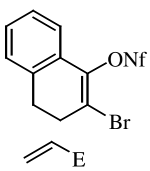
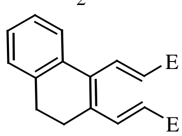
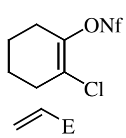
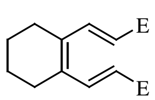
Scheme 8

As alternatives to the 1,2-dihalocycloalkenes, 1-halo-2-perfluoroalkanesulfonyloxycycloalkenes may serve as starting materials for twofold Heck reactions. Since they can easily be prepared from the corresponding ketones via the α-haloketones and subsequent sulfonylation of the enolates, this sequence provides a straightforward access to various substituted 1,3,5-hexatrienes (**Scheme 9**, **Table 9**).[57]



Scheme 9

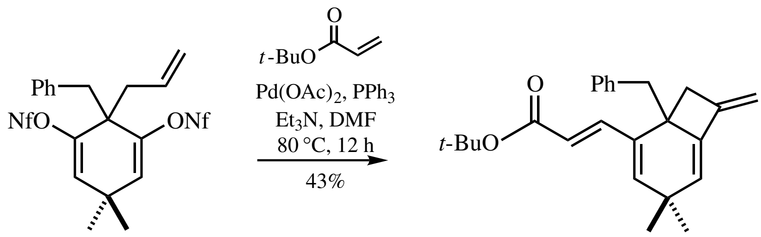
TABLE 9. Twofold Heck Reaction on 1-Halo-2-perfluoroalkanesulfonyloxycyclo-alkenes[56],[57]

1-Halo-2-perfluoroalkane-sulfonyloxycycloalkane Alkene	Product	Conditions	Yield (%)
	 E = CO_2t-Bu	$Pd(OAc)_2$, PPh_3, Et_3N, LiCl, DMF, 90 °C, 96 h	73
	 R = CO_2t-Bu	$Pd(OAc)_2$, PPh_3, Et_3N, LiCl, DMF, 90 °C, 40 h	86
	 R = $SiMe_2t$-Bu E = CO_2t-Bu	$Pd(OAc)_2$, PPh_3, Et_3N, DMF, 80 °C, 20 h	64
	 E = CO_2Me	$Pd(OAc)_2$, PPh_3, Et_3N, LiCl, DMF, 90 °C, 40 h	71
	 E = CO_2Me	$Pd(OAc)_2$, PPh_3, Et_3N, DMF, 75 °C, 8 d	23 (64)[a]

[a] Yield of the monocoupling product in parentheses.

D. INTRA–INTERMOLECULAR TWOFOLD HECK COUPLING OF 1,3-BIS(NONAFLUOROBUTANESULFONYLOXY)CYCLOHEXADIENE

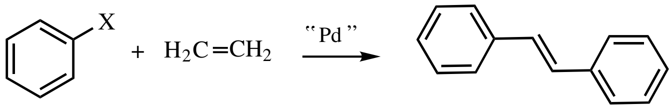
The intra–intermolecular Heck reaction of dienediol bisnonaflates containing an ω-alkenyl substituent with an external alkene such as an acrylate gives rise to the formation of a bicyclic tetraene by an intramolecular coupling followed by an intermolecular Heck reaction (**Scheme 10**).[58]



Scheme 10

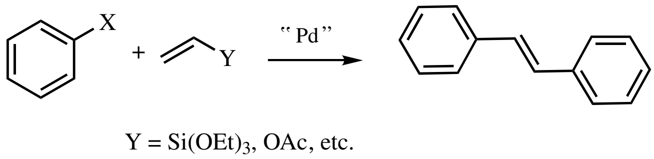
E. MULTIPLE HECK 1,1- AND 1,2-BISARYLATIONS OF ETHYLENE AND RELATED COMPOUNDS

The twofold Heck arylation of ethylene[13],[59] and ethylene equivalents provides an easy access to stilbene derivatives (**Scheme 11**, **Table 10**). In the case of ethylene, the pressure has to be carefully controlled, otherwise styrene derivatives, which are the primary products in this process, will be found as major products. In general, slightly pressurized (1 – 5 bar) reaction conditions are suitable for the twofold coupling and lead to stilbenes in up to 91% yield and with turnover numbers up to 18,200. The linear dependency on ethylene pressure in the arylation of ethylene with aroyl chlorides to give stilbenes (low pressure of ethenyl) or styrenes (high pressure) has been shown previously.[60]



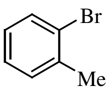
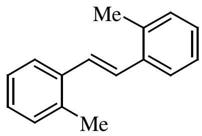
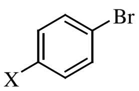
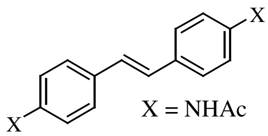
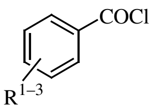
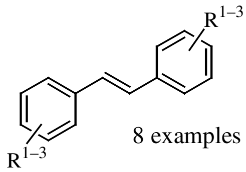
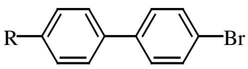
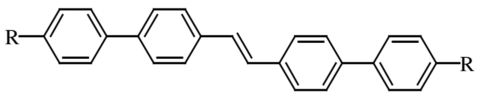
Scheme 11

Besides ethylene, ethenylsilanes and ethenyl acetate, which are easy to handle, can yield stilbenes by 1,2-arylation with elimination of the functionality, in good yields (**Scheme 12**, **Table 11**).



Scheme 12

TABLE 10. Double Heck 1,2-Arylations of Ethylene

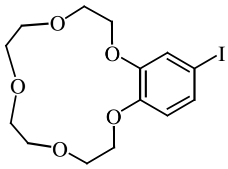
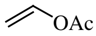
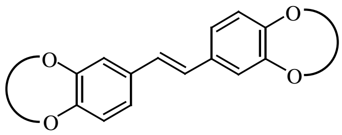
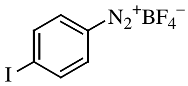
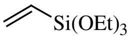
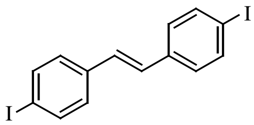
Halorene	Ethylene (Pressure)	Product (Conditions)	Yield (%) (Reference)
	20 psi	 ($Pd(OAc)_2$, P(o-Tol)$_3$, MeCN, 125 °C, 20 h)	34 (54)[a] ([13])
	120 psi	 X = NHAc ($Pd(OAc)_2$, P(o-Tol)$_3$, DMF, 125 °C, 2 h)	48 ([13])
		X = CHO (as above, 8 h, 1 bar ethylene)	75 ([61])
 8 examples	1 bar	 8 examples ($Pd(OAc)_2$, P(o-Tol)$_3$, $BnMe_2N$ or N-ethylmorpholine, p-xylene, 120 °C, 4.5–7.5 h)	45 ([60])
 R = H or SO_3H	1.5 bar	 R = H or SO_3H ($Pd(OAc)_2$, P(o-Tol)$_3$, Et_3N, MeCN or NMP, 125 °C)	66–72 ([59])

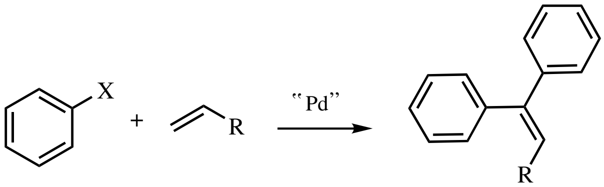
[a] Yield of the styrene formed is given in parentheses.

In general, the Heck coupling of aryl halides with terminal alkenes yields styrene derivatives. However, under certain conditions such as with an excess of the aryl halide,[64] at elevated temperatures, under high pressure,[65] and with electron-deficient alkenes, a terminal twofold coupling to yield 1,1-diarylalkene derivatives may take place (**Scheme 13**, **Table 12**).

Under high pressure (10 kbar), the β-hydride elimination is retarded and the metastable σ-alkylpalladium halide may insert into the double bond of a second acrylate

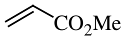
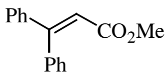
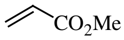
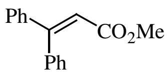
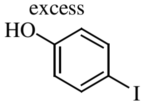
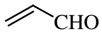
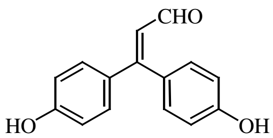
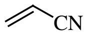
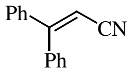
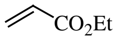
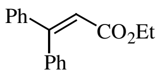
TABLE 11. Double Heck 1,2-Diarylation of Ethylene Equivalents

Haloarene	Ethylene Equivalent	Product (Conditions)	Yield (%) (Reference)
		 (polymer supported Pd, Bu_3N, MeCN, 130 °C, 16 h)	50 ([62])
		 $(Pd(OAc)_2$, PPh_3, MeOH, 25 °C, 30 min)	62 ([63])

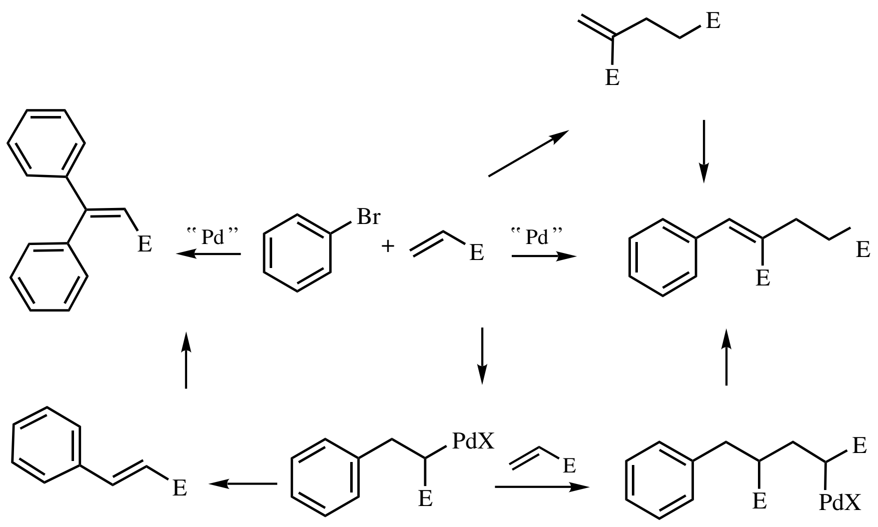


Scheme 13

TABLE 12. Double Heck 1,1-Arylation of Acrylates and Related Compounds

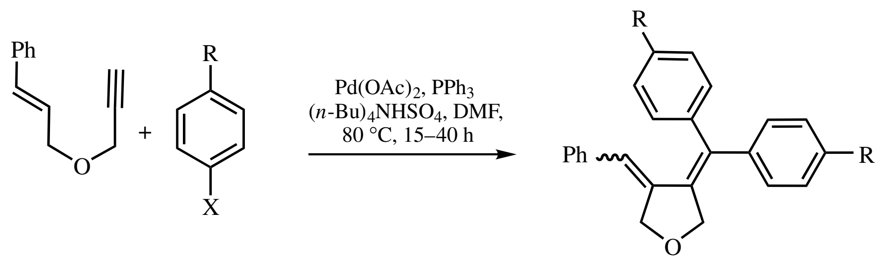
Haloarene Alkene	Product	Conditions	Yield (%) (Reference)
PhBr  excess		$Pd(OAc)_2$, $P(o\text{-}Tol)_3$, Et_3N, 100 °C, 34 h	78 ([64])
PhI  excess		$Pd(OAc)_2$, $P(o\text{-}Tol)_3$, Et_3N, MeCN, 100 °C, 43 h	52 ([66])
 		$Pd(OAc)_2(PPh_3)_2$, Et_3N, MeCN, 80 °C, 10 h	73 ([67])
PhI 		$PdCl_2$ on modified montmorillonite, Bu_3N, 100 °C, 4 h	90 ([68])
PhI 		$Pd(OAc)_2(PPh_3)_2$,Et_3N, DMF, 140 °C, 4 h, 10 kbar	76 ([65])

to eventually—after double shift—yield a diethyl(arylmethylene)glutarate.[65] Alternatively, the acrylate may dimerize first,[69] and the diethyl-2-methyleneglutarate may subsequently undergo a Heck arylation (**Scheme 14**).



Scheme 14

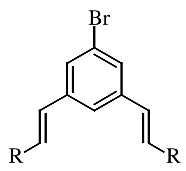
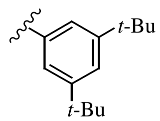
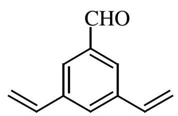
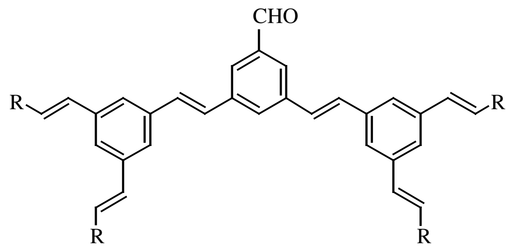
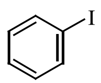
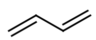
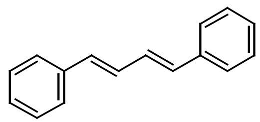
Alkynes may undergo a threefold coupling if suitably substituted. For example, 3-phenylallyl propargyl ether yields an *E/Z* mixture of 3-diarylmethylene-4-benzylidenetetrahydrofuran, when treated with an aryl halide under Jeffery conditions (**Scheme 15**).[70] This domino reaction starts with an intermolecular coupling, followed by intramolecular coupling of the intermediate σ-ethenylpalladium complex and finally a second intermolecular Heck coupling.



X	R	%
I	H	46
Br	OMe	53
Br	NO_2	36

Scheme 15

TABLE 13. Heck Reaction of Haloarenes and Haloalkenes with Diethenylarenes, Conjugated Dienes, and Trienes

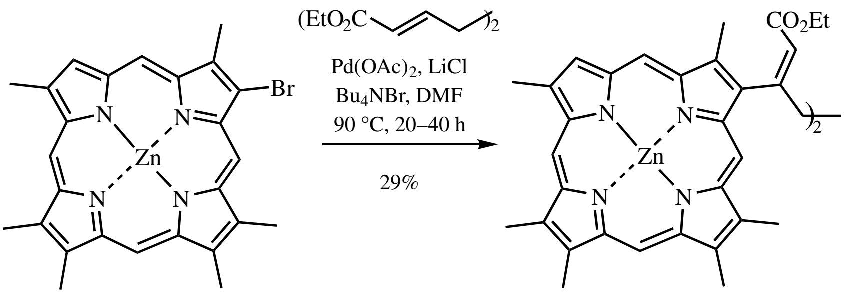
Haloarene	Oligo(ethenyl)arene Conditions	Product	Yield (%) (Reference)
 R = 	 $Pd(OAc)_2$, Bu_4NBr, K_2CO_3, 90 °C, 2 d		56 ([71])
	 $Pd(OAc)_2$, Et_3N, P(*o*-Tol)$_3$, 100 °C, 17 h		43 ([25])

F. REACTION OF HALOARENES AND HALOALKENES WITH DIETHENYLARENES, CONJUGATED DIENES, AND TRIENES

The multiple arylation of oligoenes was investigated in the early 1980's by Heck and colleagues. While conjugated dienes such as 1,3-butadiene in the presence of secondary amines with haloarenes yield monoarylated allylamines by nucleophilic substitution on the intermediately formed π-allylpalladium complexes, 1,ω-diaryldienes are formed by twofold coupling. Even 1,3,5-hexatriene can serve as a substrate to give 1,6-diarylsubstituted 1,3,5-hexatrienes (**Table 13**). In general, electron-withdrawing substituted haloarenes give higher yields (up to 89%) than donor-substituted ones. Similarly, bromoalkenes such as β-bromostyrenes can be used. In this case, the reaction with 1,3,5-hexatriene gave a decapentaene derivative, though in low yield. However, this coupling provides an easy access to conjugated oligoene hydrocarbon skeletons.

As by-products, Diels–Alder adducts from the newly formed oligoene reacting as the dienophile and the starting material were observed.

Even the successful twofold coupling of brominated zincatoporphyrins with diethyl octa-2,6-dienoate to give all-carbon tethered bisporphyrins has been reported (**Scheme 16**).[72] Although the yields were low to moderate, the example demonstrates the feasibility of this coupling methodology for the preparation of highly functionalized molecules.

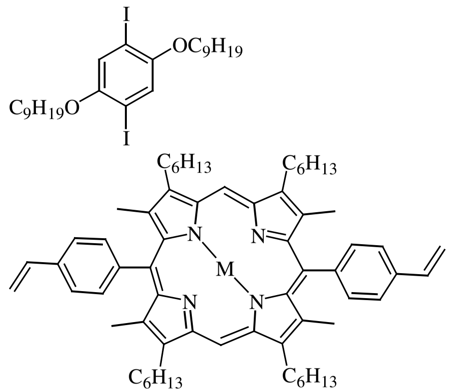
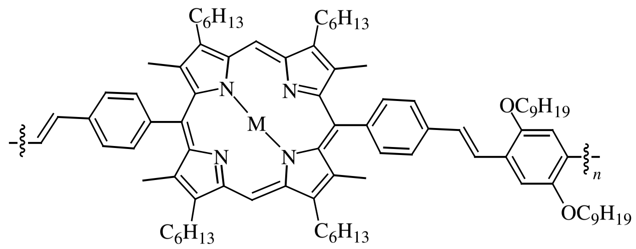
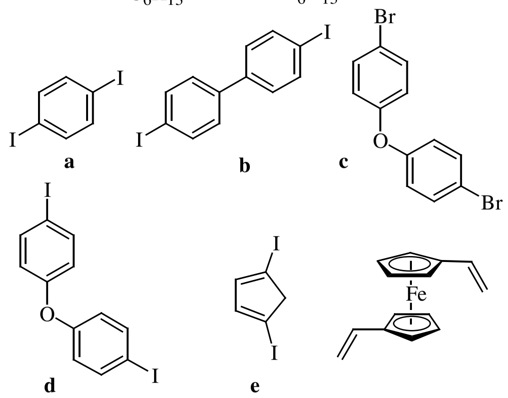
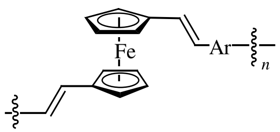


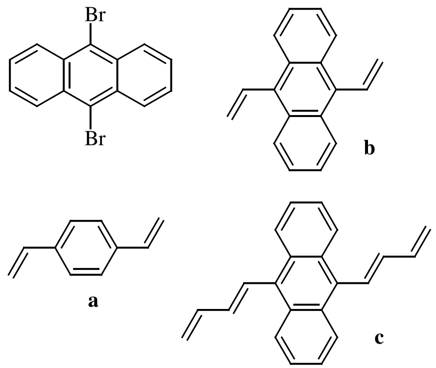
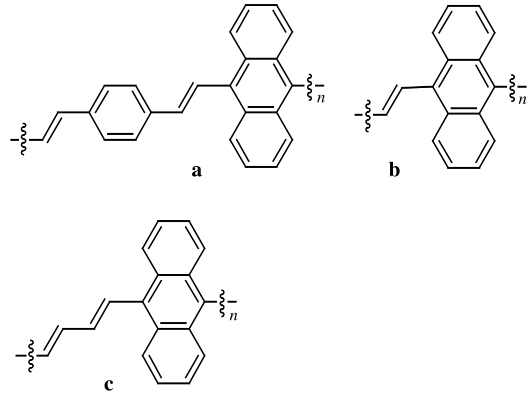
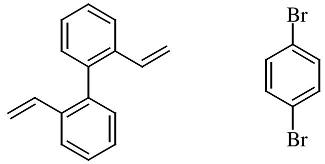
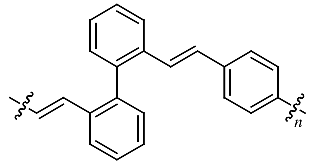
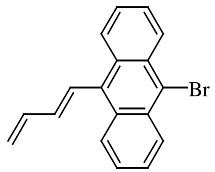
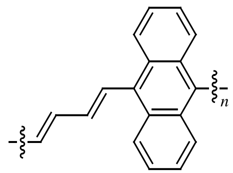
Scheme 16

G. FORMATION OF POLYMERS BY THE REACTION OF DIHALOARENES WITH DIETHENYLARENES

The Heck reaction has been applied to couple quite a variety of dihaloarenes with different diethenylarenes to give various polyvinylenearylene polymers. In some cases, analogous polymers have been obtained by Heck coupling of α-ethenyl-ω-haloarenes (**Table 14**)

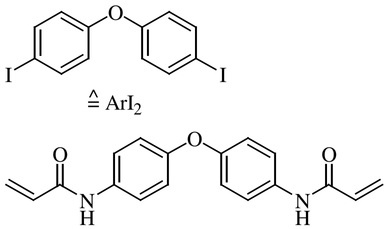
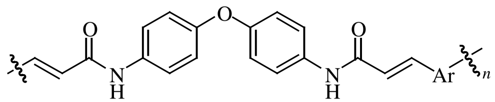
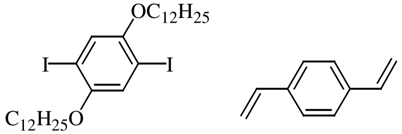
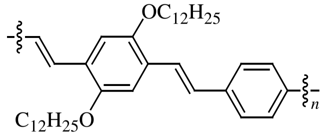
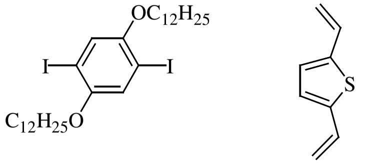
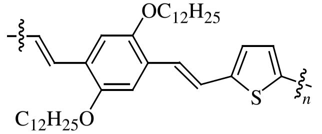
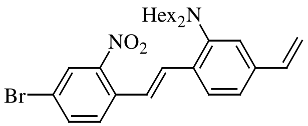
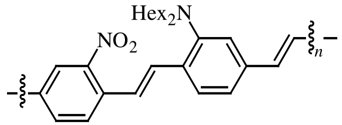
TABLE 14. Heck Reactions of Oligohaloarenes with Oligoethenylarenes to Give Polymers

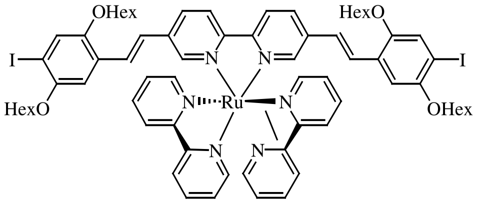
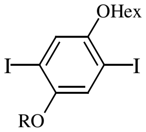
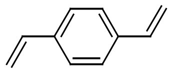
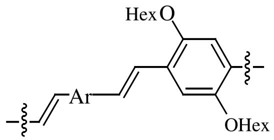
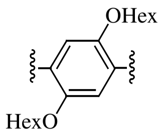
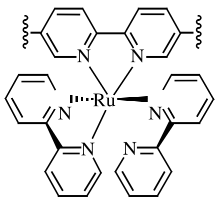
Oligohaloarene, Oligoethenylarenes	Product	Conditions	Yield (%) (MW)	Reference
		$Pd(OAc)_2$, $P(o\text{-}Tol)_3$, Bu_3N, DMF, 100 °C, 3–4 h	$M = H_2$: 3 h: 73 (4.6×10^4) 3 h: 73 (5.3×10^3) M = Zn: 4 h: 75 (8.3×10^3) 4 h: 78 (1.3×10^4)	[73]
 **a–e** ≙ ArX_2		$Pd(OAc)_2$, PPh_3, Et_3N, DMA, 100 °C, 3–4 h	n.r.[a] DP[b] = 2.1–6.4	[74]

		$Pd(OAc)_2$, $P(o\text{-}Tol)_3$, Et_3N, DMF, 90 °C, 1 d	~100	[75] [76]
		$Pd(OAc)_2$, $P(o\text{-}Tol)_3$, Et_3N, DMF, 90 °C, 1 d	15 repeat units per chain	[75]
		$Pd(OAc)_2$, $P(o\text{-}Tol)_3$, Et_3N, DMF, 90 °C, 1 d	DP = 12	[75] [76]

(*Continued*)

TABLE 14. (*Continued*)

Oligohaloarene, Oligoethenylarenes	Product	Conditions	Yield (%) (MW)	Reference
		Pd-graphite, Bu_3N, DMF, 100 °C, 40 h	95 0.95 dL g^{-1}	[78]
		$PdCl_2(PPh_3)_2$, Et_3N, DMF, 100 °C, 12 h	62	[79]
		$PdCl_2(PPh_3)_2$, Et_3N, DMF	n.r.	[79]
		$Pd(OAc)_2$, $P(o\text{-}Tol)_3$, Bu_3N, DMF	>95 (35,000)	[77]

  R = 	 with Ar =  and  at random	$Pd(OAc)_2$, P(*o*-Tol)$_3$, Bu_3N, DMF	—[c]	[37]

[a] n.r. = not reported.
[b] Degree of polymerization.
[c] Various ratios of starting materials lead to different degrees of polymerization/properties, but all polymers were obtained in excellent yields.

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