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Palladium-catalyzed cross-coupling reactions and electrocyclizations—efficient combinations for new cascade reactions

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Dedicated to Professor Jean-Pierre Genêt on the occasion of his 60th birthday

Abstract

Palladium-catalyzed cross-coupling reactions and electrocyclic transformations as well as cycloadditions can efficiently be combined in one-pot sequences to build up complex molecules from simple precursors. 1,3-Dicyclopropyl-1,2-propadiene (**1**) could be coupled to various aryl halides, and the 1,3,5-hexatrienes resulting after rearrangement were trapped with different dienophiles. Further exploration of the highly reactive building block bicyclopropylidene (**8**) demonstrates the combinatorial potential of the two reaction modes in terms of two different three-component reactions, and even a novel four-component reaction was readily developed. Additional increase of complexity was gained by combining an intramolecular Heck reaction with consecutive trapping by **8**, which can be carried out with or without 6π -electrocyclization. Finally a Stille–Heck-coupling sequence of substituted 2-bromocycloalkenyl triflates with functionally substituted alkenylstannanes and acrylic esters led to highly substituted 1,3,5-hexatrienes, which smoothly underwent 6π -electrocyclization at elevated temperatures to yield bi- and tricyclic skeletons. With this methodology at hand, a new versatile access to steroid-analogues with a diene moiety in the B ring and a functionality at C-7 was developed.

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Keywords: Palladium catalysis; Cross coupling; Cascade reactions; Combinatorial chemistry; Small rings

1. Introduction

The principle of so-called domino or cascade reactions has proved to be among the most valuable tools in modern organic synthesis [1]. By combining two or more similar or different reaction types in one single-pot operation, several new carbon–carbon or carbon–heteroatom bonds can be formed at the flip of a coin, thus leading to a significant increase in molecular complexity. Research in our group has particularly been focussed on cascades of palladium-catalyzed reactions in all their varieties [2]. While the palladium-catalyzed cross-coupling reactions are frequently employed to set up the basic carbon framework, thermal

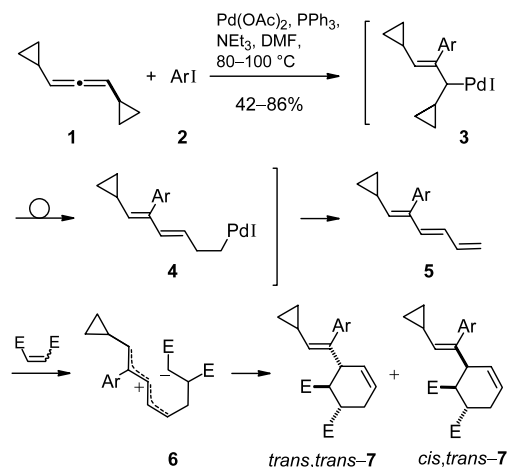
reactions (e.g. 6π -electrocyclizations and Diels–Alder reactions) are utilized to furnish the final product by rearrangement or cycloaddition to the initially generated conjugated π -bond system.

2. Results and discussion

The first C–C bond-forming step in any of the sequences discussed herein is the carbopalladation of a reactive double bond as typical for the virtually classical Heck cross-coupling reaction [3]. When this carbopalladation occurs with a suitable substrate containing cyclopropane moieties in such a way that a (cyclopropylmethyl)palladium intermediate is formed, rapid rearrangement to a homoallylpalladium species ensues, and the overall outcome of the reaction will constitute a particularly large increase of complexity of the mole-

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cule.[4] With this in mind, 1,3-dicyclopropyl-1,2-propadiene (**1**) was treated with iodobenzene in the presence of a typical Heck-catalyst system and a dienophile to yield 3-(1'-phenyl-2'-cyclopropyl)cyclohexene derivatives **7**. Thus, the initially formed phenylpalladium iodide carbopalladates **1** with the regioselectivity that is typical for allenes [5] to form a σ -allylpalladium intermediate **3**, which at the same time is a (cyclopropylmethyl)palladium species. As such, it swiftly undergoes the cyclopropylcarbonyl to homoallyl rearrangement yielding the homoallylpalladium species **4** which finally suffers β -hydride elimination. The thus formed 1-cyclopropyl-2-phenyl-1,3,5-hexatriene (**5**) is prone to undergo polymerization, but can be efficiently trapped by an appropriate dienophile present in the reaction medium. As expected, the least sterically encumbered diene moiety in the triene **5** reacts with the dienophile preferentially. The fact that the [4+2] cycloadditions with dimethyl maleate do not occur with complete diastereoselectivity, but yield both diastereomers *trans*,-*trans*-**7** and *cis*,*trans*-**7** in ratios ranging from 2.1:1 to 5.7:1, has been taken to indicate that these Diels–Alder reactions proceed stepwise via the well stabilized zwitterionic intermediate **6**. Even with diethyl fumarate, a 2.5:1 mixture of *trans*,*trans*-**7** and *cis*,*trans*-**7** was obtained (Scheme 1).



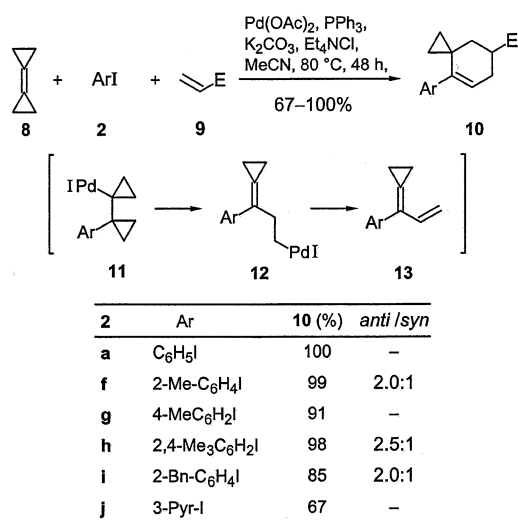
2	Ar	Dienophile ^a	7 (%)	d.r. ^b
a	C ₆ H ₅ I		86	4.0:1
a	C ₆ H ₅ I		81	2.5:1
b	2,4,6-Me ₃ C ₆ H ₂ I		68	2.1:1
c	1-Naphth-I		42	2.1:1
d	2-Pyr-I		61	4.9:1
e	2-Thioph-I		54	3.1:1

Scheme 1. Heck reaction of iodobenzene with 1,3-dicyclopropyl-1,2-propadiene, and subsequent non-stereospecific [4+2] cycloaddition. (a) E = CO₂Me; E* = CO₂tEt. (b) ratios determined by ¹H-NMR [6].

This new three-component reaction is quite versatile in terms of the applied aryl halides and dienophiles. Although best yields were achieved with simple aryl iodides, heteroaryl iodides as well as aryl bromides can also be applied [6].

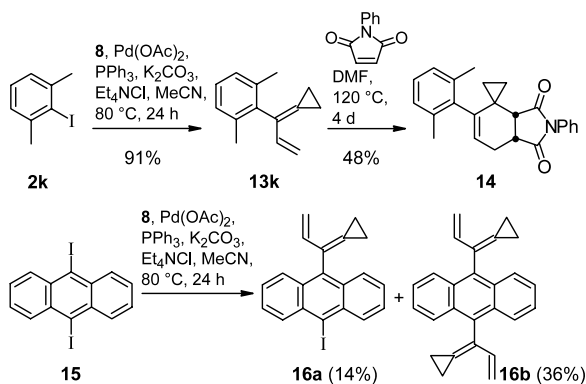
As we had previously reported, aryl halides can most efficiently be cross-coupled with bicyclopropylydene (**8**) [7]. More recently, this reaction has been widely explored and shown to have reasonably high combinatorial potential since not only can different aryl halides and different dienophiles, but even differently substituted bicyclopropylydenes, be employed [8]. Furthermore, multiple couplings with oligoiodoarenes [8b,d,9] have been performed as well as couplings with aryl iodides bound to a solid phase, employing the triazene linker methodology of Bräse and coworkers [10] (Scheme 2).

The overall reaction—after initial carbopalladation of the highly strained double bond in **8**—again involves a cyclopropylcarbonyl to homoallyl rearrangement leading to the corresponding homoallylpalladium species, which finally undergoes a β -hydride elimination to give the aryl-substituted diene **13**. This is immediately trapped by any dienophile present in the mixture of the one-pot operation. Dienes of type **13** can actually be isolated, especially when sterically shielding substituents are present in the *ortho*-positions on the aromatic core. The yields can be as high as 91% as obtained with 2,5-dimethyliodobenzene (**2k**), and the diene **13k** can be employed in [4+2] cycloadditions in spite of its sterical encumbrance, e.g. with *N*-phenylmaleimide to give **14** [8d]. An interesting case is the twofold coupling on 9,10-diiodoanthracene which produced the bisdiene **16b** (36% yield) along with the mono-coupling product **16a** (Scheme 3) [11].



2	Ar	10 (%)	<i>anti</i> / <i>syn</i>
a	C ₆ H ₅ I	100	–
f	2-Me-C ₆ H ₄ I	99	2.0:1
g	4-MeC ₆ H ₂ I	91	–
h	2,4-Me ₃ C ₆ H ₂ I	98	2.5:1
i	2-Bn-C ₆ H ₄ I	85	2.0:1
j	3-Pyr-I	67	–

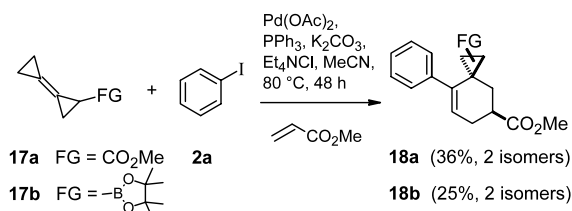
Scheme 2. The prototype domino-Heck—Diels—Alder reaction. E = CO₂Me [8c].



Scheme 3. Heck-cross coupling of bicyclopropylidene (**8**) with sterically encumbered aryl iodides [8d,11].

Spiro[2.5]octene derivatives of type **10** with substituents on the cyclopropane moiety can be prepared by employing functionally substituted bicyclopropylidenes such as the ester **17a** [8d] and the boronate **17b** [12] in the Heck–Diels–Alder three-component reaction. Although the overall yields were only 36 and 25%, respectively, the isolated products all had the functionality completely on the spirocyclopropane moiety, and NOESY-NMR experiments for the esters **18a** proved that both diastereomers have their functional groups pointing towards the phenyl substituent. In the reaction of the boronate **17b**, the unsubstituted **10a** was also isolated in 34% yield. This may actually have been formed by phenylpalladation of **17b** with the reverse regioselectivity and therefore opening of the boronate-substituted ring leading to a homoallylpalladium species that can undergo deboropalladation instead of dehydropalladation and yield the same intermediate diene **13a** as the coupling of parent bicyclopropylidene (**8**) with iodobenzene (**2a**) (Scheme 4).

The utility of bicyclopropylidene (**8**) in multicomponent reactions is greatly enhanced by the fact that an arylpalladation carried out in the presence of tris-(2-furyl)phosphine instead of triphenylphosphine does not lead to the aryl-substituted diene **13** but to a σ -allyl-/ π -allylpalladium complex **22/23** which can quite efficiently be trapped with various nucleophiles. The formal rearrangement of the homoallyl- **13** to the σ -allylpalladium intermediate **22** most probably proceeds by β -hydride elimination and immediately ensuing hydrido-palladation in the initially formed hydrido(alkene)palla-

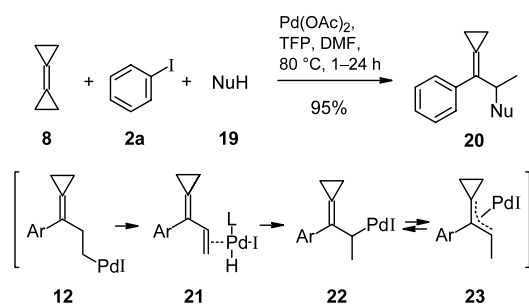


Scheme 4. Cross-coupling of iodobenzene with functionally substituted bicyclopropylidenes [8d,12].

dium iodide intermediate **21** with the reverse regioselectivity to yield **22**. Nitrogen, oxygen as well as carbon nucleophiles have successfully been employed to yield allyl substitution products of type **20**. Highest yields were obtained with amine nucleophiles (Scheme 5) [13]. The regioselectivity in these nucleophilic substitutions agrees with previous observations for such π -allylpalladium trappings [14].

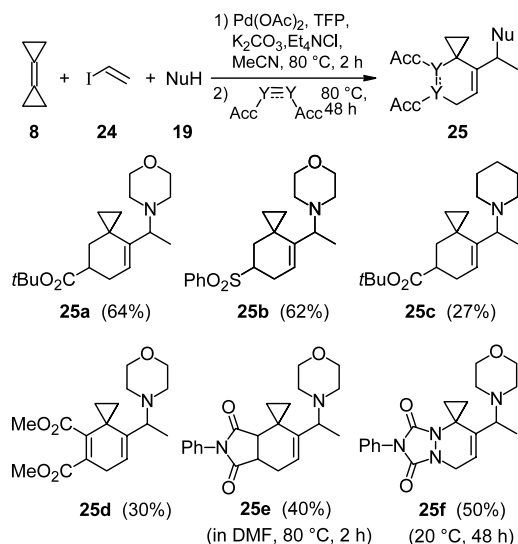
To add just another dimension in this new three-component reaction involving **8** and a nucleophile, the initial Heck coupling can be performed with an alkenyl iodide such as vinyl iodide **24**. This leads to substituted reactive dienes which can undergo [4 + 2] cycloadditions. This constitutes an overall four-component reaction in a one-pot, yet two-step operation. The Diels–Alder reactions can be performed with a wealth of dienophiles, and the initial three-component reaction allows one to introduce a vast array of different functionalities into the products **25** (Scheme 6) [12]. It is obvious that the dienophile cannot be present in the reaction mixture from the beginning, as it generally also is a Michael acceptor and as such would compete for the nucleophile.

Remarkable cascade reactions with the incorporation of one or more molecules of carbon monoxide leading to highly complex skeletons from simple precursors have been developed by Negishi and coworkers [15] and by Grigg and coworkers [16]. Such queuing cascades, as they have been termed by the latter group, can also involve the reactive alkene **8**, as has recently been demonstrated [17]. For example, *o*-iodo-*N*-tosylaniline (**26**) reacts with **8** under palladium catalysis in an atmosphere of carbon monoxide to yield the benzenelated 8-azadispiro[2.3.4.0]undeca-4,11-dione (**27**). In this cascade, two molecules of carbon monoxide are incor-



19	Nucleophile	20 (%)
a	H ₂ N <i>n</i> Bu	73
b	H ₂ N <i>t</i> Bu	95
c	(3-methylbut-1-in-3-yl)amine	41
d	piperidine	79
e	morpholine	70

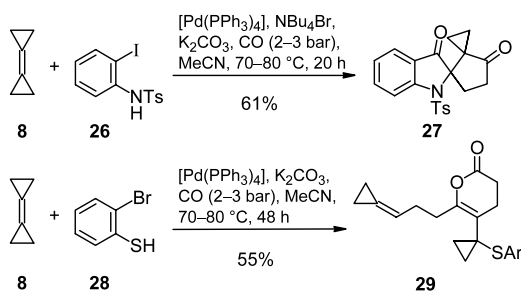
Scheme 5. A new three-component reaction involving bicyclopropylidene (**8**) and nucleophilic trapping of π -allylpalladium intermediates derived from the carbopalladium intermediate from **8**. L = TFP = tris-(2-furyl)phosphine [13].



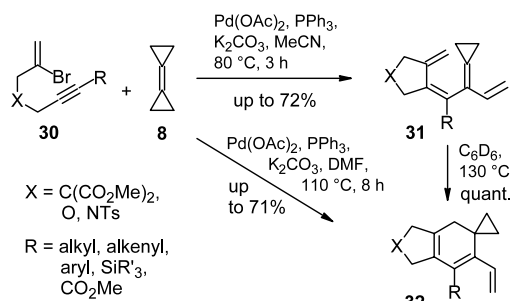
Scheme 6. A novel one-pot, yet two-step four-component reaction involving bicyclopropylidene (**8**), an alkenyl iodide, a nucleophile and a dienophile [12].

porated, and thus it constitutes a four-component reaction (Scheme 7). The analogous cascade reaction of *o*-bromothiophenol (**28**) with **8** and carbon monoxide involves two molecules each of the latter and as such is a five-component reaction leading to the completely different skeleton **29** [17].

Since alkenylpalladium halides, which have proved to rapidly carbopalladate the double bond in bicyclopropylidene (**8**), cannot only be generated intermolecularly by oxidative addition of an alkenyl halide to a palladium(0) species, but also intramolecularly by carbopalladation of an alkyne [18], one may extrapolate the all-intermolecular cascades involving **8** to intra-intermolecular variants. Indeed, 2-bromo-1,6-enynes of type **30**, under palladium catalysis react with bicyclopropylidene (**8**) to yield cross-conjugated tetraenes **31** or their electrocyclization products **32**, depending on the reaction temperature (Scheme 8). Apparently, the cascade reaction starts with an intramolecular Heck-type reaction leading to a 'living' alkenylpalladium halide intermediate which intermolecularly carbopalladates **8**. The resulting intermediate is of the same type as **11** (Scheme



Scheme 7. Novel multicomponent queuing cascades involving bicyclopropylidene (**8**) and carbon monoxide [17].



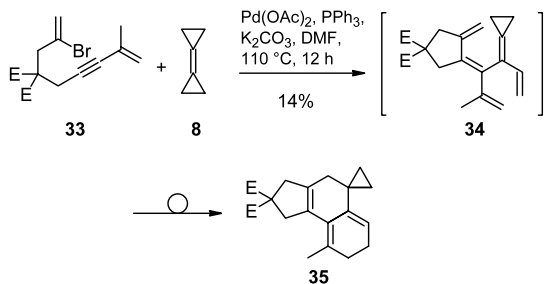
30	X	R	31 (%)	32 (%)
a	C(CO ₂ Me) ₂	<i>t</i> Bu	66	56
b	C(CO ₂ Me) ₂	SiMe ₂ <i>t</i> Bu	72	65
c	C(CO ₂ Me) ₂	Ph	38	49
d	O	SiMe ₂ <i>t</i> Bu	34	41
e	O	Ph	54	71
f	NTs	Ph	–	44

Scheme 8. Intra-intermolecular Heck-reaction cascades [19].

2) and undergoes the same sequence of rearrangement and β -hydride elimination. When the reaction is performed in acetonitrile at 80 °C, the tetraenes **31** can be isolated and were found to be remarkably stable. Molecular mechanics calculations with the MM2 program as well as NMR findings corroborate that these molecules are strongly forced to adopt an almost 90° dihedral angle between the two diene moieties [19].

Upon heating in [*D*₆]-benzene solution at 130 °C, the tetraenes **31** cleanly and quantitatively rearrange to compounds **32** by 6 π -electrocyclization (as monitored by ¹H-NMR spectroscopy). By performing the palladium-catalyzed reaction of bromoenynes **30** with **8** at elevated temperature (e.g. 110 °C in DMF) the spiro[cyclopropane-1,4']-bicyclo[4.3.0]nona-1(6),2-dienes **32** can be isolated in up to 71% yield. The yields positively correlate with the stability of the intermediate tetraenes, they in general were higher with bulky substituents on the former triple bond terminus in **30**, which are assumed to stabilize the 'orthogonal' conformation of the tetraenes **31** and thereby inhibit their polymerization. Within the examined temperature range (110–140 °C), the higher temperatures cause only little effect on the 6 π -electrocyclization, but decrease the overall yield, probably by damaging the catalyst system.

To enhance the scope of this reaction even further, an alkenyl substituent was introduced in **30** in conjugation with the terminal triple bond. This additional double bond remains untouched in the course of the palladium-catalyzed reaction cascade, but can be involved in a second 6 π -electrocyclization succeeding the first one in the cross-conjugated pentaene product **34**. Thus, the 2-bromo-1,8-diene-6-yne **33** can be converted to the spirocyclopropanated tricycle **34** via **33** which, in contrast to the tetraenes, cannot be isolated, but undergoes



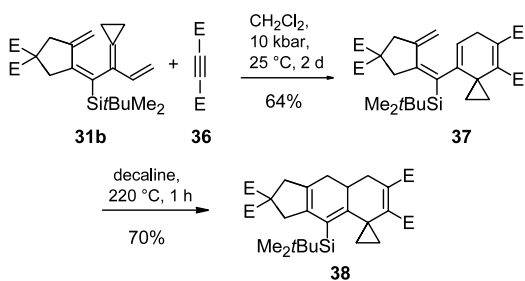
Scheme 9. Three rings in one step by a transmissive 6π -electrocyclization. E = CO₂Me [19b].

a transmissive 6π -electrocyclization [20] to give **35**, albeit in low yield (Scheme 9).

Yet another reaction mode has been realized for the cross-conjugated tetraene **31**. When first subjected to a [4+2] cycloaddition, e.g. with dimethyl acetylenedicarboxylate (**36**) under high pressure (10 kbar), the resulting product **37** still contains a 1,3,5-hexatriene moiety, which can undergo a 6π -electrocyclization upon heating at 220 °C furnishing a spirocyclopropanated linearly annelated tricyclic system with one five- and two six-membered rings (Scheme 10) [19].

Our previously published twofold Heck coupling of 1,2-dibromocycloalkenes with subsequent 6π -electrocyclizations of the resulting 1,3,5-hexatrienes [21] has one serious limitation in that it cannot be applied for the preparation of unsymmetrically 1,6-disubstituted 1,3,5-hexatrienes and their cyclization products, because the second coupling step proceeds about 50 times faster than the first one [22]. This problem could, however, more recently be overcome by the discovery that a 2-bromocycloalkenyl triflate undergoes Stille couplings with alkenylstannanes with virtually complete chemoselectivity for the triflate leaving group and subsequent Heck coupling at the remaining cycloalkenyl bromide moiety [23]. Following this protocol, which in several cases can be carried out as a one-pot operation, various terminally differentiated 1,3,5-hexatrienes can be assembled and subsequently cyclized by simple heating in solution (Scheme 11) [23].

The applicable alkenylstannanes can be functionally substituted including cyclic ones. For example, this sequential coupling with (1-methoxyethenyl)tributyl-



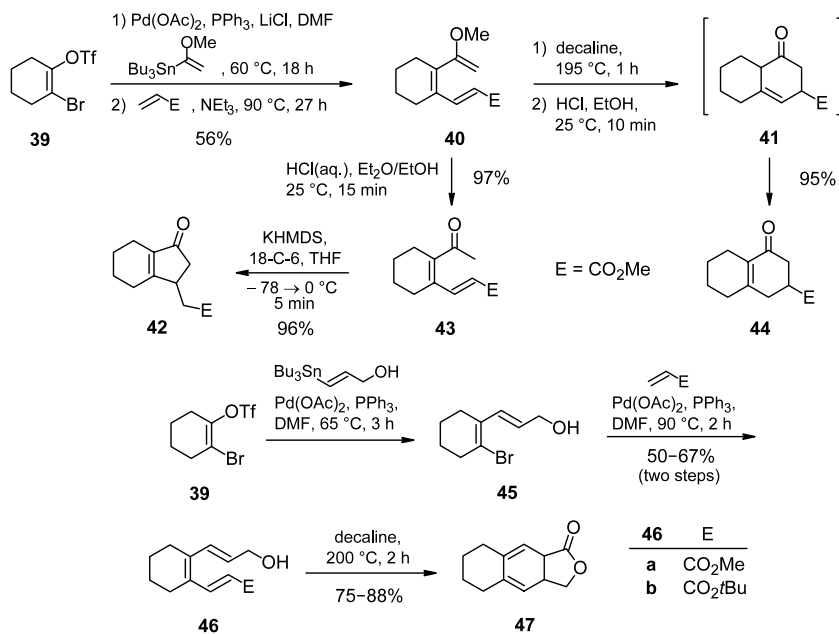
Scheme 10. Diels–Alder reaction of the tetraene **31b** with subsequent 6π -electrocyclization. E = CO₂Me [19b].

stannane and methyl acrylate leads to the triene **40** with an enol ether and an acrylate moiety which, upon heating in decaline at 195 °C and acidic work-up yields the cyclohexene-annellated oxocyclohexenecarboxylate **44** by 6π -electrocyclization, hydrolysis of the enol ether moiety and double bond migration in the primary product **41** (Scheme 11). The overall outcome of this sequence is essentially a cyclohexenone annelation onto a cyclohexanone, from which **39** is prepared. This methodology may complement the well-known Robinson annelation which yields analogous products, yet with a different substitution pattern. The intermediate triene **40** can also first be hydrolyzed to the dienyl methyl ketone **43** which, upon treatment with potassium hexamethyldisilazide, furnishes the cyclopentenone-annelation product **42** in high yield (93% over two steps). The same coupling sequence carried out with 3-(tributylstannyl)allyl alcohol and an alkyl (methyl or *t*-butyl) acrylate leads to the trienes **46** which, upon heating at 200 °C, not only undergo 6π -electrocyclization, but also subsequent intramolecular transesterification leading to tricyclic lactones **47**.

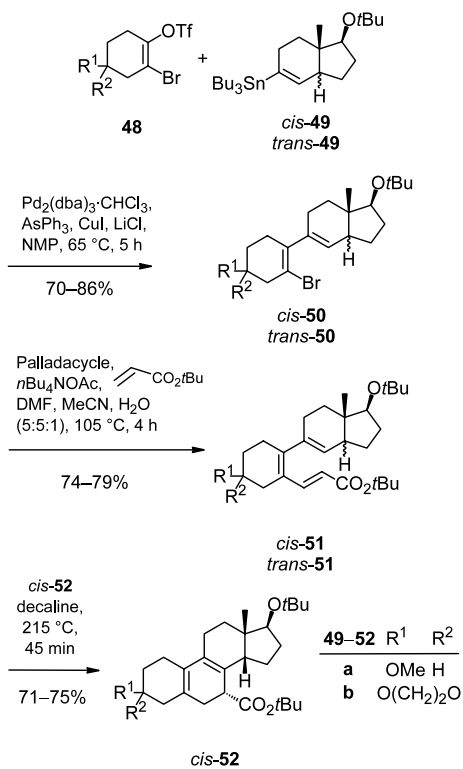
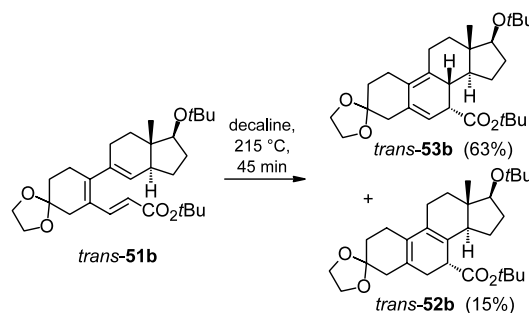
With monocyclic alkenylstannanes, tricyclic skeletons can be assembled easily [23], and an extrapolation to a new approach towards the steroid skeleton is obvious. Starting with an appropriately 4-substituted 2-bromocyclohexenyl triflate **48** to become the A-ring fragment, the sequential coupling with the novel bicyclo[4.3.0]nonenylstannanes *cis*-**49** as well as *trans*-**49** (representing the later CD fragment) and *t*-butyl acrylate in two steps occurred with very good chemoselectivities and yields, when the catalyst system was optimized individually for each of the two steps. Thus, the first step was best achieved with the catalyst cocktail containing triphenylarsine and copper(I) salt, first introduced by Farina et al. [24] (Scheme 12).

The Heck couplings of the intermediate *cis*-**50** and *trans*-**50** required rather high temperatures and thus gave best yields with the thermally relatively stable palladacycle (from tris-(*o*-tolyl)phosphine and palladium acetate), first introduced by Herrmann et al. [25], in the presence of tetrabutylammonium acetate as a base. Under these conditions, *t*-butyl acrylate could be coupled smoothly to give the tricyclic hexatrienes *cis*-**51** and *trans*-**51**, while methyl acrylate required addition of a second portion of the catalyst system, due to precipitation of palladium black during the course of the reaction (Scheme 13).

Thermal 6π -electrocyclizations of *cis*-**51a,b** upon heating at 215 °C in decaline gave single stereoisomers of the tetracyclic products *cis*-**52a,b** arising from a subsequent 1,5-*H* shift in the initially formed dienes. Under the same conditions, *trans*-**51b** yields a separable mixture of the initial 6π -electrocyclization product formed with the same virtually quantitative outward disrotational selectivity, and diene product *trans*-**53b**

Scheme 11. A chemoselective Stille–Heck coupling sequence with subsequent 6 π -electrocyclization and further transformation [22].

resulting from a subsequent 1,5-*H* shift [26]. These steroid-like products have the particularly favorable—with respect to potential biologically active derivatives—feature of a *tert*-butoxycarbonyl functionality on C-7.

Scheme 12. Stille–Heck coupling sequences of 2-bromocyclohexenyl triflates **48** with *cis*-**49** as well as *trans*-bicyclo[4.3.0]nonenylstannane *trans*-**49** and *tert*-butyl acrylate [26]. Palladacycle prepared from tris(*o*-tolyl)phosphine and palladium acetate [25].Scheme 13. Completion of the steroid skeleton by thermal 6 π -electrocyclization [26].

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