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REVIEW ARTICLE

C-C Forming Reactions with Palladium and Platinum: Lessons Learned in Our Group

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Abstract:

This short paper details our experiences with Pd- and Pt-catalyzed cross-coupling and cyclization reactions in investigations covering the years from 1997 until now. Pd-catalysed Suzuki-Miyaura-, Heck- and Sonogashira-type cross coupling reactions in conjunction with other transformations in one pot, especially with the Wittig reaction, are highlighted. This is followed by a description of a combination of Heck- and cyclization reactions. Finally, Pt-catalyzed diene-yne cyclization reactions are discussed.

Keywords: Suzuki-Miyaura reaction, Wittig olefination, Heck reaction, Sonogashira coupling, Diene-yne cyclization, Triene cyclization, Pd-catalysis, Pt-catalysis.

1. INTRODUCTION

Our first contact with Pd-catalyzed cross-coupling reactions came when attempting to construct functionalized estradiol derivatives as potential diagnostic agents for estrogen receptor-positive breast cancer [1 - 3]. Initially, this involved Wittig olefination reactions of formylestrane derivatives with stabilized phosphoranes [4]. In order to have a platform to diversify the molecules that could be prepared, a synthetic sequence was developed by constructing stabilized phosphoranes with a terminal haloaryl unit on a polymer backbone stemming from triphenylphosphine-polystyrene, derivatising the phosphoranes by C-C cross-coupling reaction and finally reacting the phosphoranes thus prepared with a steroidal carbaldehyde [5]. This clearly showed that stabilized phosphoranes are compatible with reaction conditions needed to carry out many of the C-C cross-coupling reactions and would lead to the development of one-pot reactions involving Pd-catalyzed cross-coupling reactions and Wittig olefinations [6 - 8].

One of our Heck-reaction cyclization sequences also came from the desire to functionalize estrane derivatives, this time at C7, by submitting a η^6-estra-1,3,5(10),6-trien-17-one 17,17-acetal tricarbonylchromium(0) [9] to a Heck reaction, which led to a surprising triarylation of the compound with concurrent cyclization. This was found to be a general reaction of η^6-dihydronaphthalene tricarbonylchromium (0) complexes [10]. In contrast, a further Heck reaction–cyclization combination, a Heck-triene-cyclization-aromatisation sequence, was a desired transformation [11]. Finally, a Pd-catalyzed arene-ene-yne cyclization was investigated [12]. Both of the latter reactions led to novel areno-annelations, and both were used to synthesize areno-annelated steroids.

Initially, $Pd(PPh_3)_4$ in a biphasic medium of aq. Na_2CO_3 and 1,2-dimethoxyethane (DME) was found to be the catalyst of choice for many of the reactions detailed here. Later on, the slightly cheaper $Pd(PPh_3)_2Cl_2$ was used as a pre-

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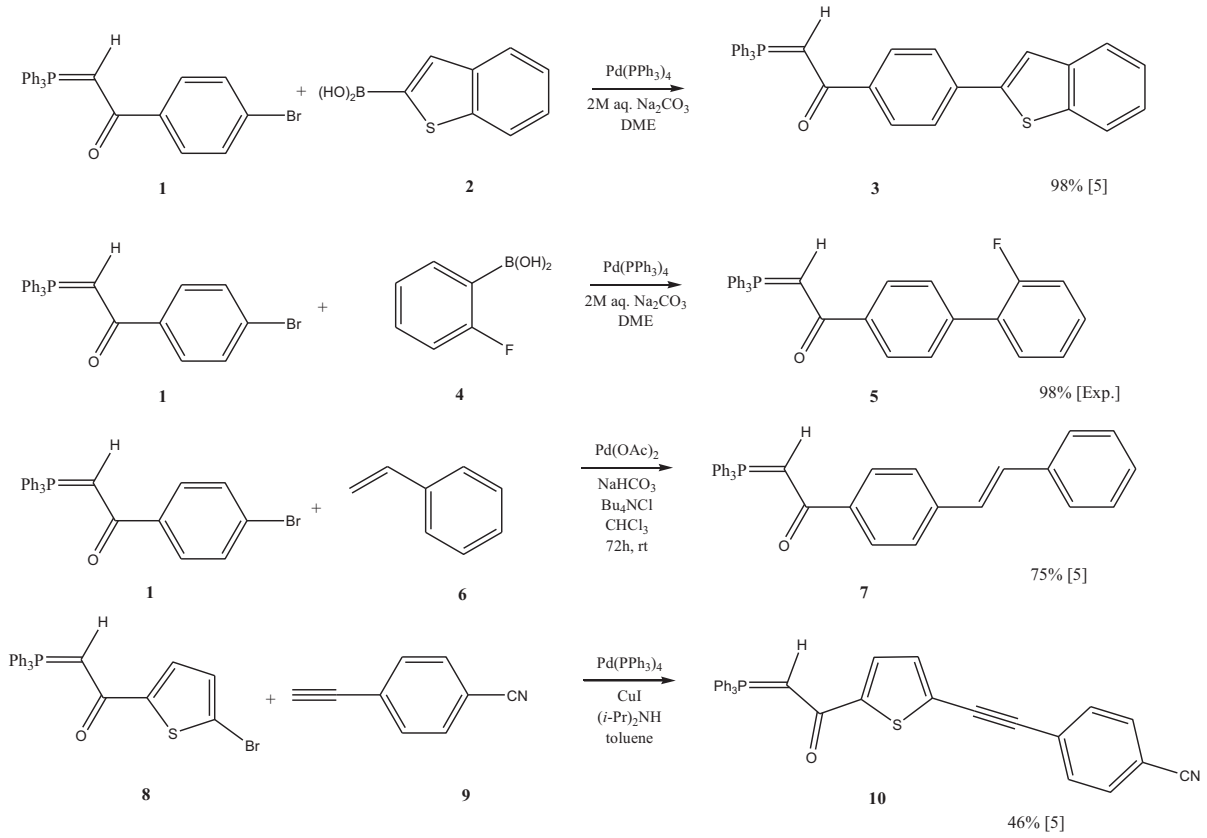
catalyst, in the presence of PPh_3 (3 equiv.). Interestingly, these were sufficiently active to catalyze Suzuki-Miyaura reactions with chloroarenes, where the chloro group was activated by a nitro substituent or as part of a quinoid system as in chloroanthraquinones [13] and 1-chloro-2,4-dinitrobenzene [14]. Nevertheless, at a later time, other reaction systems were used. Reactions were run under Jeffery conditions [15 - 17]. Also, Pd freshly deposited on carbon nanofibers was used as catalyst [18] in Suzuki and Heck reactions.

The following gives a short overview of above reactions. At the end, a number of experimental procedures can be found as representative examples.

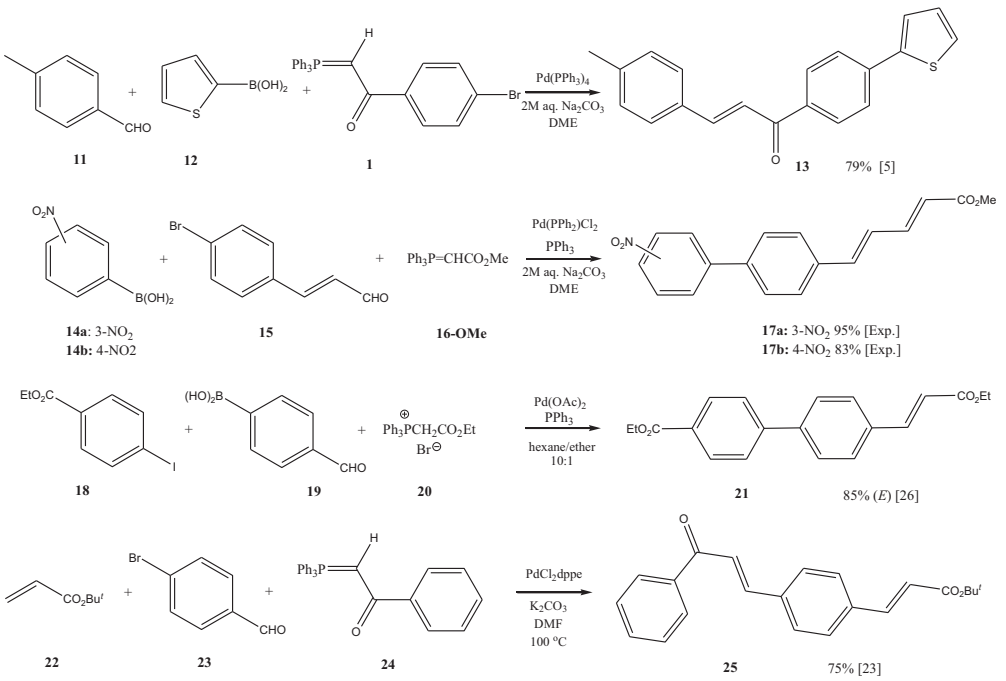
2. RESULTS AND DISCUSSION

2.1. One-Pot Cross-Coupling Reaction: Wittig Olefination Procedures

We realized that haloaroylmethylidenetriphenylphosphoranes such as **1** and **8** would be stable under conditions necessary for Suzuki- [5, 19], Sonogashira [5, 19, 20] and Heck [5, 21] reactions and hence it was possible to derivatize **1** and **8** to a plethora of phosphoranes, such as **3**, **5**, **7**, and **10** (Scheme **1**). These could be reacted subsequently with carbaldehydes in a Wittig olefination [5, 19, 21]. The reactions proceed with the corresponding phosphonium salts also [5]. Here, even Na_2CO_3 has been found to be a base strong enough to convert the phosphonium salts into the respective phosphoranes. For the most part, Suzuki-Wittig reactions were run with $Pd(PPh_3)_4$ as the catalyst in a solvent mixture of aq. Na_2CO_3 and DME [22], and Sonogashira coupling-Wittig reactions were carried out with $Pd(PPh_3)_4$/CuI as catalysts and diisopropylamine (DIPA) as base in toluene [5]. For Heck-Wittig reactions various conditions were used with $Pd(OAc)_2$ or $Pd(Cl_2)$dppe [23] as the catalyst and with Et_3N or K_2CO_3 as base in DMF at 100 °C. However, here Jeffery-type PTC conditions in aq. Na_2CO_3/$CHCl_3$ and either Bu_4NCl or $BnMe_3NCl$ as PTC catalyst were found to be favorable, where the reactions were run at room temperature (rt). Haloaroylmethylidenetriphenylphosphoranes such as **1** could also be reacted with a boronic acid, and a carbaldehyde in a one-pot Suzuki-Wittig reaction (eg. to **13** Scheme **2**) [5].



Scheme 1. Derivatisation of phosphoranes with different Pd-catalysed C-C cross coupling reactions.

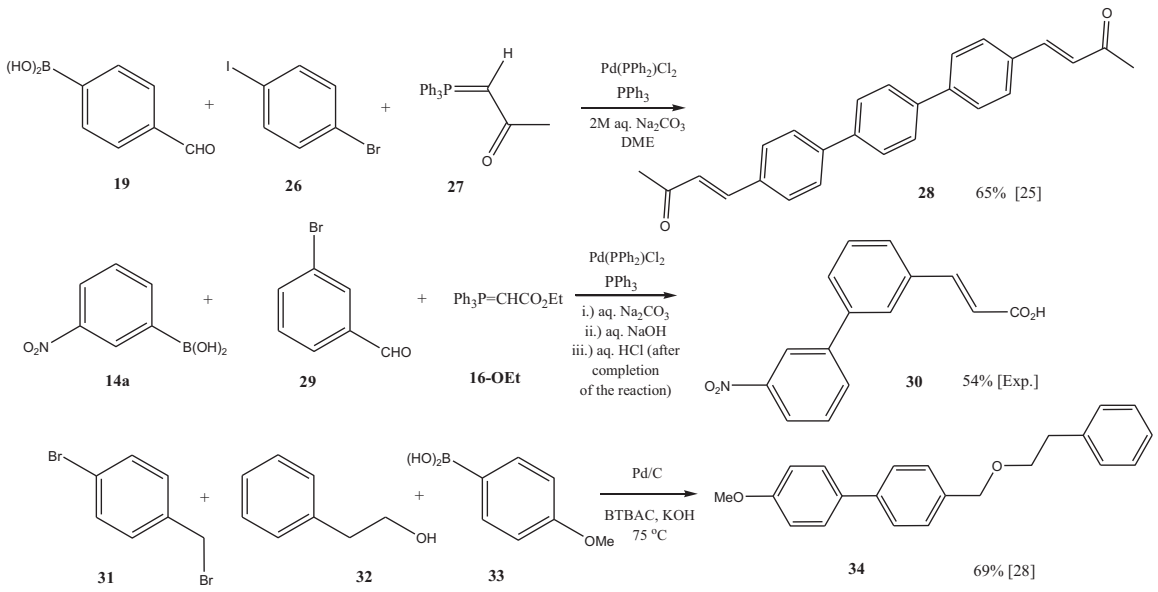


Scheme 2. Wittig olefinations with C-C cross coupling reactions in one pot, using a.) a phosphorane (**1**); b.) a haloarylaldehyde (**15**); or c.) a formylarylboronic acid as the central building block.

Alternatively, Wittig and C-C coupling reactions can be carried out with a haloaryl/hetarylcarbaldehyde (eg., with **15** and **23**) as the central building block. Recently, for instance, one pot Suzuki cross coupling–Wittig olefination procedures have been carried out with 4-bromocinnamaldehyde (**15**) and alkoxycarbonylmethylidenetriphenylphosphorane like **16-OMe** giving biphenylpentadienoates in acceptable yields (see Experimental part and Scheme **2**). In this type of reaction, there is a choice of phosphoranes, both stabilized and semi-stabilized, that can be used. In contrast to above transformations, where the Wittig olefination with the rather sparingly reactive phosphoranes **1**, **8** and **24** is more sluggish than the concomitant Suzuki reaction, reactions with semi-stabilized phosphoranes and with the stabilized alkoxycarbonylmethylideenetriphenylphosphoranes **16** are rapid [24] and the Suzuki transformation determines the completion of the process. Lastly, in the case of Suzuki-Wittig reactions in one pot, the boronic acids can act as the central building block, that is when formylarylboronic acids (*e.g.***19**) are employed [25, 26]. When dihaloarenes (*e.g.***26**) are utilized in these reactions, *p*-terphenyl derivatives **28** can be prepared easily (Scheme **3**) [25]. Instead of the phosphoranes, phosphonium salts **20** also can be used as the starting material (Scheme **2**). An easy method of separation was found for those reactions in which the Wittig-Suzuki coupling was run in a mixture of hexane/ether (10:1) aq. 2M Na_2CO_3 in the presence of either $Pd(OAc)_2$-PPh_3 (eg., Scheme **2**, to **21**) or $Pd_2(dba)_3$ as catalyst, under ultrasonication. After completion of the reaction the products are found in the organic phase, which is separated from the aq. phase and concentrated *in vacuo* to give the products in sufficient purity to be used in further transformations [26].

The one-pot Suzuki-Wittig procedure with **16** can be run with a concomitant hydrolysis step (see Experimental Part). Previously, it has been noted that Wittig reaction of aldehydes with **16** can be performed in 10w% aq. NaOH, which leads to the hydrolysis of the acrylates formed and makes a simple work-up possible. In the case of solid products, simple filtration of triphenylphosphine oxide and acidification followed by a second filtration are enough to obtain the acrylic acids [27]. In the case of combining the hydrolysis step with the Suzuki-Wittig procedure, the presence of unreacted boronic acid and the metal catalyst makes a chromatographic separation of the product **30** necessary (Scheme **3**).

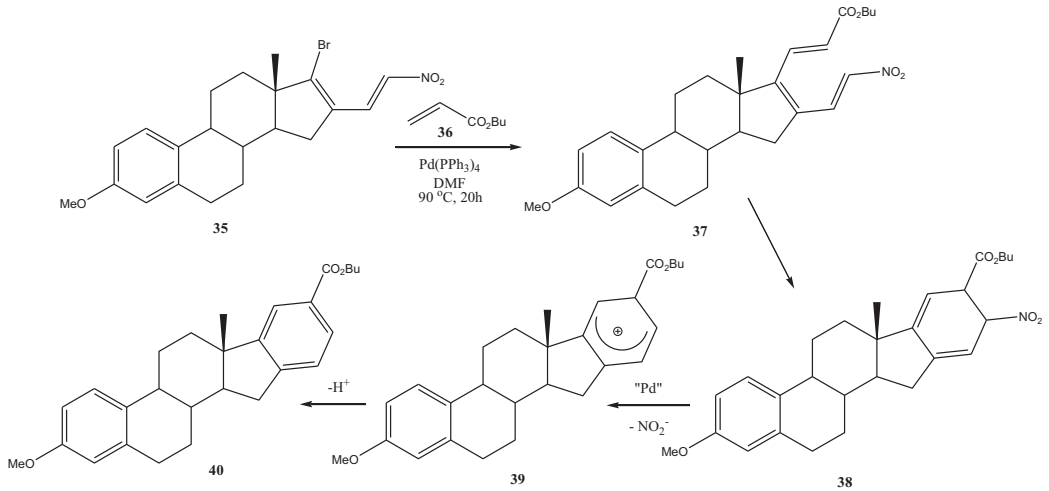
A further reaction that the authors have carried out with the Suzuki cross-coupling reaction in one pot is a Williamson-type ether synthesis, eg., to **34** (Scheme **3**). This procedure was run as a PTC reaction with solid KOH and benzyltributylammonium chloride (BTABC) as the PT catalyst and with Pd/C as the coupling catalyst (Scheme **3**) [28].



Scheme 3. Double Wittig–Suzuki reaction leading to terphenyl **28**; Wittig-Suzuki-hydrolysis reaction leading to phenylcinnamic acid **30** and Suzuki-coupling-etherfication leading to benzyl ether **34**.

2.2. Pt- and Pd-Catalyzed Cyclization Reactions

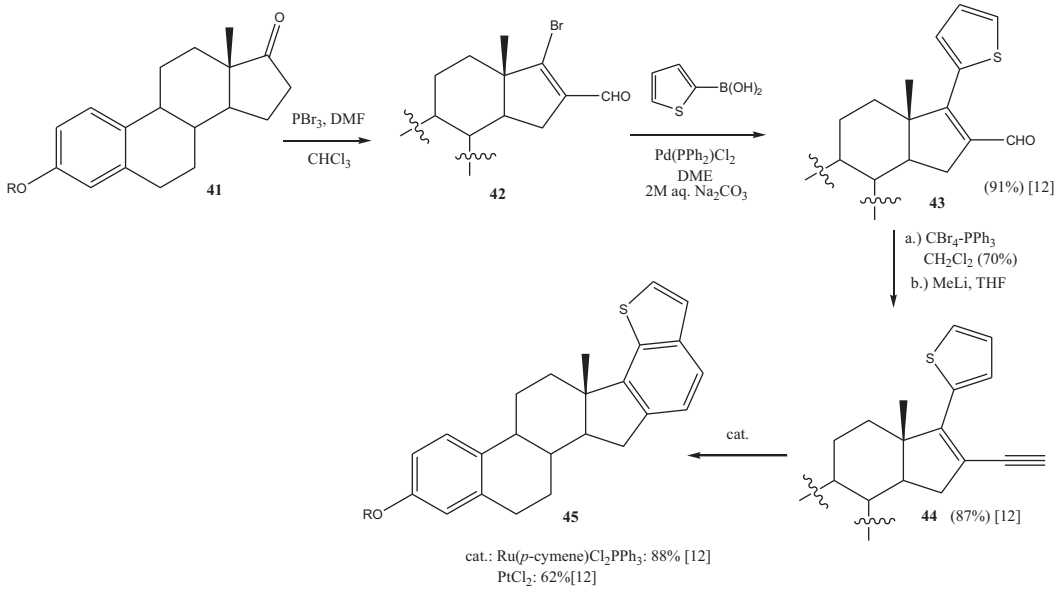
Foremost Heck-, but also Suzuki-type C-C cross-coupling reactions lead to systems that when heated undergo cyclization reactions [29, 30]. In some cases, the catalyst, such as "Pd" is essential for the reaction to proceed as in the reaction of 17-bromo-3-methoxy-16-*E*-(β-nitroethenyl)estra-1,3,5(10),16-tetraene with butyl acrylate (**26**), where the primary Heck product **37** undergoes a triene cyclization, and the cyclization product **38** subsequently aromatizes under extrusion of the nitro group (Scheme **4**) [11], giving benzoannelated estrane **40**, albeit in low yield (26-39%). This reaction has also been carried with styrene and acrylonitrile as olefin component [11]. Subsequently the benzoannelated estranes such as **40** can be dehydrogenated easily with DDQ to give benzoannelated estra-1,3,5(10),6,8,11,14,16-octatetraenes. These have one sp^3-hybridized carbon left in their framework, which at the same time remains a controlled stereocenter.



Scheme 4. Heck-reaction-triene-cyclization-aromatisation to benzo-annelated estranes.

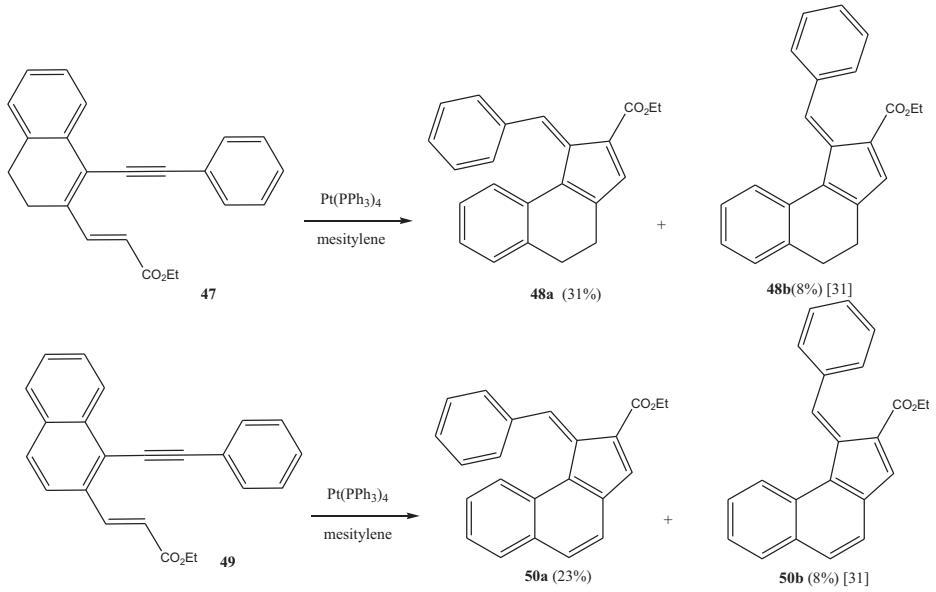
A Pt-mediated process is the cyclization of 16-ethynyl-17-hetarylestra-l,3,5(10),16-tetraen-3-ols to hetarenoestranes. The 16-ethynyl-17-hetarylestra-l,3,5(10),16-tetraen-3-ols can easily be prepared from the 17-ketosteroids by consecutively performed Vilsmeier-Arnold formylation, Suzuki-cross coupling, and Corey-Fuchs reaction. Initially, the 16-ethynyl-17-hetarylestra-l,3,5(10),16-tetraen-3-ols were cyclized to heteroestranes with Ru(*p*-cymene)Cl_2PPh_3 as the

catalyst (Scheme **5**). In slightly lower yields, the cyclization proceeds with $PtCl_2$ as well [12]. Pt-, Pt-Ru nanoparticles, and $PtCl_2$ immobilized on carbon black gave the cyclization products in much lower yield under otherwise identical reaction conditions [12]. For both the platinum and the ruthenium-mediated reactions a metal carbine was postulated as the intermediate in the cyclization.



Scheme 5. Thienyl-ene-yne cyclization to benzothieno[b]estrane derivative **45**.

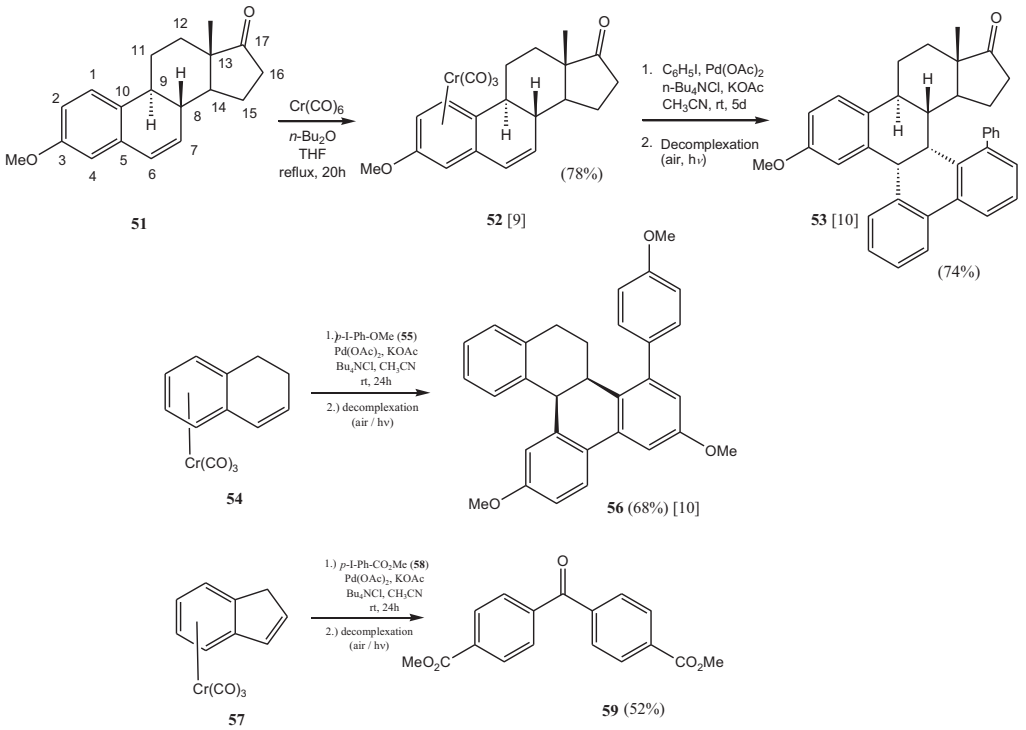
In the case where the terminal alkene moiety is substituted with an electron withdrawing substituent such as an ester group instead of being part of a heterocyclic system, the cyclization takes a different pathway leading to fulvenes. The reactions are run with $Pt(PPh_3)_4$ as catalyst in mesitylene at elevated temperatures [31]. Here it is irrelevant whether the central alkene moiety is part of an aromatic system as in **49,** or not, as in **47**. The reactions produce two well-separable, relatively polar, reddish products, ***E*/*Z*-48** and ***E*/*Z*-50**, respectively (Scheme **6**). The phenyl group of the phenylethynyl can carry substituents such as a cyano or methyl group.



Scheme 6. Diene-yne cyclization with $Pt(PPh_3)_4$ as catalyst leading to fulvenes **48** and **50**.

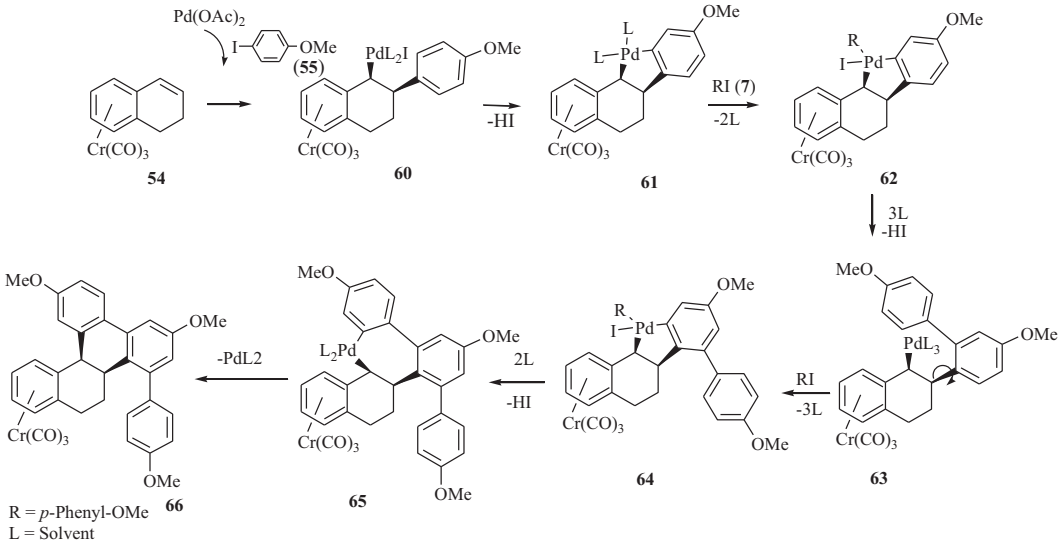
In our final mediated Pd-catalyzed reaction, η^6-dihydronaphthalene tricarbonylchromium(0) complexes were reacted with haloarenes. As mentioned above, the idea was to introduce an aryl substituent selectively at C7 of an

estra-1,3,5(10),6-tetraene derivative by means of a Pd-catalyzed Heck reaction. The reaction with the non-complexed estra-1,3,5(10),6-tetraen-3-ol-17-one led to a mixture of C6- and C-7 arylated estra-1,3,5(10),6-tetraenes in poor yield. 3-*O*-Methylestra-1,3,5(10),16-tetraen-17-one (**51**) could be converted to the respective chromiumtricarbonyl complex **52** easily by reaction with chromium hexacarbonyl [$Cr(CO)_6$] in a mixture of dibutyl ether–THF. The complexation proceeds stereoselectively to give the β-facial complex **52** exclusively. The stereochemistry was established by single crystal X-ray crystallography of the complex [9]. The stereochemistry can be explained by the directing effect of the alkene-moiety at C6/C7 [9]. When the steroidal chromium complex **52** is reacted with iodobenzene under $Pd(OAc)_2$ catalysis under PTC conditions, a triarylation happens with a concomitant ring-closure reaction and **53** is obtained after decomplexation (Scheme **7**) [10]. The transformation also works with other η^6-dihydronaphthalene tricarbonyl-chromium(0) complexes, *e.g.* with **54** (Scheme **7**). The reason for this reaction pathway over the common Heck-type arylation of the alkene moiety can be envisaged to be the difficulty in cyclic alkenes for a single bond rotation to occur after the *syn*-addition of the arylpalladium halide species to the double bond.This rotation is needed in most cases for a subsequent *syn*-hydridopalladium elimination to occur, a pathway that can easily be followed by non-cyclic alkenes. Interestingly, this has been found to lead to cascade reactions also in selected other, non-complexed cyclic alkenes, as was shown by de Meijere [32, 33], Catellani [34 - 36] and Carretero [37].



Scheme 7. Reaction cascades with η^6-dihydronaphthalene tricarbonylchromium(0) complexes.

We believe that a possible mechanism in our case starts with a standard *syn*-addition of the arylpalladium iodide to the double bond of the η^6-dihydronaphthalene tricarbonylchromium(0). As there is no possibility for a *syn*-hydridopalladium elimination, the Pd inserts into the neighboring aryl C-H bond leading to a palladacycle, *e.g.* to **61** (Scheme **8**). Then, follows an oxidative addition to the Pd of the palladacyle, followed by the first aryl-aryl coupling. This step is repeated after a C-C single bond rotation linking the aryl unit to the tetrahydronaphthalene system. A reductive elimination on the Pd leads to the final ring closure. The exact intermediates and the oxidation states of Pd in these intermediates still need to be ascertained. The chromium complexes, *e.g.***66**, can be purified by column chromatography under inert atmosphere. In the solid state, they are fairly stable over a short period of time. They can be decomplexed by exposing the substances in solution to air and light, eg., to UV irradiation. The regiochemistry of the arylations was determined by single crystal X-ray crystallography of the chromium complexes of type **66** [10].

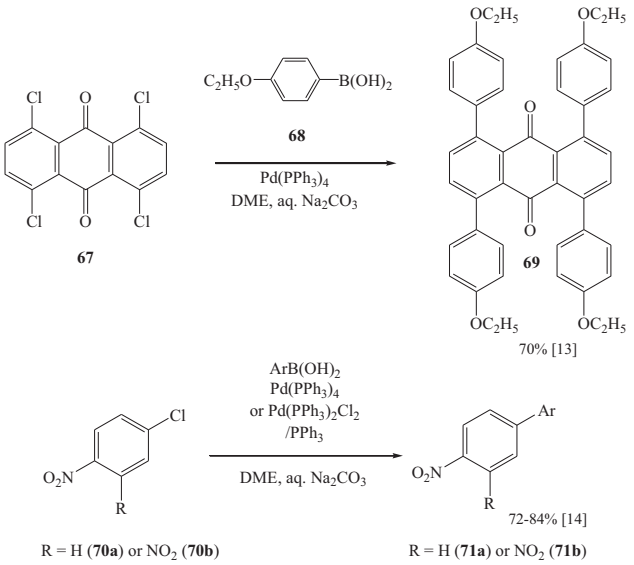


Scheme 8. Tentative mechanism of the triarylation of η^6-dihydronaphthalene tricarbonylchromium(0).

η^6-Indene tricarbonylchromium(0) (**57**) behaves differently under the reaction conditions, where the tricarbonyl chromium moiety offers a carbon monoxide ligand for a carbonylation of the haloarene, leading to benzophenones such as **59** after complete decomplexation, exposing the reaction mixtures in solution to air and light after completion of the carbonylation. Enquist *et al*. had noted a direct carbonylation of aryl iodides to benzophenones when they were reacted with dicobalt octacarbonyl [$Co_2(CO)_8$] under microwave irradiation [38].

2.3. A short Word on Pd-Catalysts

Many Pd- and Pt-catalysts have been developed [39 - 41] for C-C cross-coupling reactions. Recyclability of the catalyst, low catalyst loading and high turnover frequencies are some important characteristics of the catalyst. Equally important, however, are versatility, cost, and ease of preparation. Many of the reactions above were run with commercially available $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$ and $Pt(PPh_3)_4$ or with $Pd(OAc)_2$ under Jeffery [15 - 17] conditions. It must be noted that the commonly used reaction system with the commercially available $Pd(PPh_3)_4$ in DME/aq. Na_2CO_3 satisfactorily facilitates the Suzuki cross-coupling of chloroarenes with differently substituted arylboronic acids, when the chloro-substituent is activated as in 1-chloro-2,4-dinitrobenzene (**70b**) [14] and chloroanthraquinones [13] such as in **67** (Scheme **9**). It must be noted that 1-chloro-2,4-dinitrobenzene (**70b**) is often used as a substrate to test the activity of new Pd-catalysts in Suzuki reactions and thus it must be realized that **70b** undergoes cross-coupling reactions with ease and other substrates would put the new catalyst to a more rigorous test.



Scheme 9. Facile arylations of tetrachloroanthraquinone (**67**) and chloronitrobenzenes (**70**).

Lastly, we studied the catalytic activity of Pd immobilized as nanoparticles on carbon nanofibers (CNFs) [42]. These vapor-grown carbons over different catalysts [eg., with reactant gases CO/H_2 (4:1) or ethylene/H_2 (4:1) over [reduced] Co-Mo (9:1) cat., prepared from $(NH_4)_6Mo_7O_{24}$ and $Co(NO_3)_2 \cdot 6H_2O$, carbon nanofibers grown in a flow reactor at 480–600 °C are made of graphene layers, formed into stacked cones, cups or plates. The positioning of the stacks in relation to each other then leads to platelet-type and herring (fish-bone)-type CNFs. In addition, there are the tubular-type CNFs (Fig. **1**).

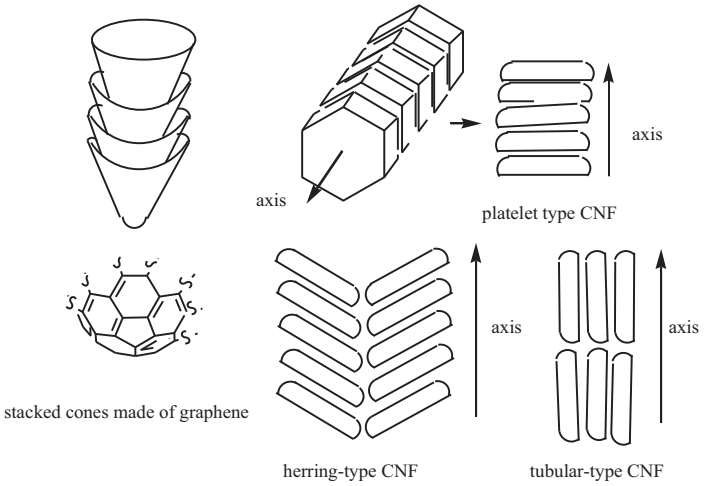
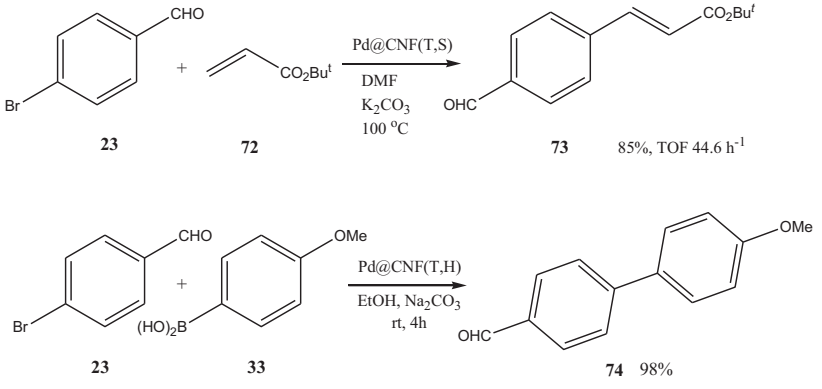


Fig. (1). Schematic representation of different types of carbon nanofibers (CNFs).

With these CNFs in hand, Pd was immobilized on them by reduction, starting out from either $PdCl_2$ [microwave irradiation, 650 W, 2 min. (free-running temperature), CNF, in ethylene glycol with or without the surfactant polyvinylpyrrolidone K-30 (PVP)], from H_2PdCl_4 prepared from $PdCl_2$ and 1.5 N aq. HCl solution [immobilization of Pd on CNF using sodium formate, hydrazine or $NaBH_4$ as reductant in H_2O with and without the surfactant PVP] or from $Pd_2(dba)_3 \cdot CHCl_3$ [reduction: CNF, H_2 [1 atm], toluene]. Good results in the Heck reaction of 4-bromobenzaldehyde and *tert*-butyl acrylate were obtained with Pd on tubular CNF, which had been prepared by the permeation technique described above, starting out from $PdCl_2$ in aq. HCl, reducing the Pd(II) with hydrazine in H_2O in the presence of surfactant PVP. This Pd-doped tubular CNF was found to carry 4.6-5.6wt% Pd with a Pd-particle size of 10-15 nm. For the Heck reaction, this catalyst gave a turnover frequency of 44.6 h^{-1} in DMF at 100 °C, where solid K_2CO_3 was used as the base. This compared well with pre-catalysts $PdCl_2$ (TOF 1.9 h^{-1}), $Pd(OAc)_2$ (TOF >10.8 h^{-1}), and $Pd(PPh_3)_2Cl_2$ (TOF 29.0 h^{-1}) [18, 43]. Also, Pd immobilized on tubular CNF served as a satisfactory catalyst for the Suzuki reaction of 4-methoxyphenylboronic acid and 4-bromobenzaldehyde (Scheme **10**), providing 4-methoxy-4'-formylbiphenyl in more than 98% yield, when the reaction was run with a catalyst loading of 0.02 mol% in Pd at rt for 4h, utilizing ethanol as solvent and Na_2CO_3 as base. The Pd@CNF catalysts could be recycled.



(T,S) = tubular, Pd doped CNF by permeation in presence of PVP as surfactant
(T,H) = tubular, Pd doped CNF by reduction of $Pd_2(dba)_3$ with hydrogen

Scheme 10. Heck and Suzuki reactions with Pd-doped carbon nanofibers.

3. EXPERIMENTAL

3.1. General

Melting points were measured on a Stuart SMP 10 melting point apparatus or on a Yanaco microscopic hotstage and are uncorrected. Infrared spectra were measured with a Thermo/Nicolet Nexus 470 FT-IR ESP or a JASCO IR-700 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with a Varian 400 NMR spectrometer (^{1}H at 395.7 MHz, ^{13}C at 100.5 MHz) or a JEOL EX-270 spectrometer (^{1}H at 270 MHz, ^{13}C at 67.8 MHz). The assignments of the carbon signals were aided by DEPT 90 and DEPT 135 experiments (DEPT = Distortionless Enhancement by Polarisation Transfer). The chemical shifts are relative to tetramethylsilane (TMS) (solvent $CDCl_3$, unless otherwise noted). Mass spectra were measured with a JMS-01-SG-2 or with an Agilent QTOF 6540 UHD. Column chromatography, when necessary, was performed on silica gel (S, 0.063 mm - 0.1 mm, Riedel de Haen and Merck grade 9385 or on Wakogel 300).

3.2. Representative Procedures

3.2.1. 4-(2'-Fluorophenyl)benzoylmethylidenetriphenylphosphorane (5):

A mixture of **1** (153 mg, 0.33 mmol), 2-fluorophenylboronic acid (**4**, 100 mg, 0.70 mmol) and $Pd(PPh_3)_4$ (20 mg, 1.7 X 10^{-2} mmol) in aq. Na_2CO_3 (2M, 2.3 mL) and DME (4.5 mL) was heated at 70 ºC for 14 h. Then, water (15 mL) was added to the cooled solution, and the mixture was extracted with chloroform (3 X 10 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (ether) to give **5** (155 mg, 98%) as colorless needles; mp. 244–245 ºC (ether); IR (KBr/cm^{-1}) ν = 3048, 1581, 1518, 1481, 1436, 1408, 1385, 1103, 881, 756, 747, 692; ^{1}H NMR (270 MHz, $CDCl_3$) 4.48 (1H, d, $^{2}J_{P\text{-}H}$ 23.7 Hz), 7.10 – 7.77 (21H, m), 8.04 (2H, d, ^{3}J 8.2 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 51.08 (+, CH, $^{1}J_{C=P}$ 110.8 Hz), 116.03 (+, CH, $^{3}J_{C\text{-}F}$ 23.1 Hz), 124.25 (+, CH, *J* 3.6 Hz), 126.78 (Cquat, $^{1}J_{C\text{-}P}$ 97.7 Hz), 127.03 (+, CH), 128.44 (+, CH, *J* 2.5 Hz), 128.87 (+, CH, $J_{C\text{-}P}$ 12.2 Hz), 130.74 (+, CH, *J* 3.6 Hz), 132.07 (+, CH, *J* 2.4 Hz), 133.15 (+, CH, $J_{C\text{-}P}$ 9.8 Hz), 133.44 (C_{quat}), 136.69 (C_{quat}), 140.41 (C_{quat}, *J* 14.7 Hz), 159.79 (C_{quat}, $^{1}J_{C\text{-}F}$ 248 Hz), 184.32 (C_{quat}, *J* 3.7 Hz, C=O). MS (70 eV) *m/z* (%) 474 (M^+, 40), 445 (11), 303 (65), 183 (100). HRMS Found: 474.1550. Calcd. for $C_{32}H_{24}OFP$: 474.1549. Found: C, 81.13; H, 5.18%. Calcd. for $C_{32}H_{24}OFP$: C, 81.00; H, 5.10%.

3.2.2. Methyl (E,E)-5-(3'-nitrobiphenyl)penta-2,4-dienoate (17a):

A reaction mixture of 3-nitrophenylboronic acid (**14a**, 270 mg, 1.62 mmol), 4-bromocinnamaldehyde (**15**, 260 mg, 1.23 mmol), methoxycarbonylmethylidenetriphenylphosphorane (**16-OMe**, 600 mg, 1.80 mmol), $Pd(PPh_3)_2Cl_2$ (25 mg, 3.6 X 10^{-5} mol), and triphenylphosphine (PPh_3, 25 mg, 9.5 X 10^{-5} mol) in the biphasic solvent system aq. Na_2CO_3 (7 mL, 2.32 g Na_2CO_3 in 10 mL H_2O) and 1,2-dimethoxyethane (DME, 10 mL) was stirred at 70 ºC for 24 h. Thereafter, the cooled mixture was extracted with chloroform (3 X 20 mL) and water (50 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel to give **17a** (362 mg, 95%) as a bright-yellow solid; IR (KBr/cm^{-1}) ν = 1685, 1618, 1529, 1354, 1242, 1144, 997; ^{1}H NMR (400 MHz, $CDCl_3$) 3.78 (3H, s, OCH_3), 6.08 (1H, d, ^{3}J = 15.6 Hz), 6.93 – 6.95 (2H, m), 7.45 – 7.59 (1H, m), 7.58 (2H, d, ^{3}J = 8.4 Hz), 7.62 (dd, ^{3}J = 8.0 Hz, ^{3}J = 8.0 Hz), 7.63 (2H, d, ^{3}J = 8.4 Hz), 7.92 (1H, d, ^{3}J = 8.0 Hz), 8.20 (1H, d, ^{3}J = 8.0 Hz), 8.45 (1H, s); ^{13}C NMR (68.7 MHz, $CDCl_3$) 51.7 (OCH_3), 121.4, 121.7, 122.3, 127.0, 127.5 (2C), 127.9 (2C), 129.9, 132.8, 136.3, 138.9, 139.4, 141.9, 144.5, 148.7, 167.4 (C_{quat}, CO); UV (CH_2Cl_2) λ_{max} = 330 nm (ε = 36690 M^{-1}cm^{-1}).

3.2.3. Methyl (E,E)-5-(4'-nitrobiphenyl)penta-2,4-dienoate (17b):

A reaction mixture of 4-nitrophenylboronic acid (**14b**, 375 mg, 2.25 mmol), 4-bromocinnamaldehyde (**15**, 360 mg, 1.70 mmol), methoxycarbonylmethylidenetriphenylphosphorane (**16-OMe**, 830 mg, 2.49 mmol), $Pd(PPh_3)_2Cl_2$ (25 mg, 3.6 X 10^{-5} mol), and triphenylphosphine (PPh_3, 25 mg, 9.5 X 10^{-5} mol) in the biphasic solvent system aq. Na_2CO_3 (2.32 g Na_2CO_3 in 10 mL H_2O) and 1,2-dimethoxyethane (DME, 10 mL) was stirred at 70 ºC for 24 h. Thereafter, the cooled mixture was extracted with chloroform (3 X 20 mL) and water (50 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel to give **17b** (431 mg, 83%) as a bright-yellow solid; IR (KBr/cm^{-1}) ν = 1707, 1618, 1591, 1514, 1341, 1239, 1134, 1010, 844, 757, 731; ^{1}H NMR (400 MHz, $CDCl_3$) 3.79 (3H, s, OCH_3), 6.05 (1H, d, ^{3}J = 15.2 Hz), 6.95 (2H, m), 7.44 – 7.51 (1H,

m), 7.61 (2H, d, ^3J = 8.4 Hz), 7.63 (2H, d, ^3J = 8.4 Hz), 7.74 – 7.77 (2H, m), 8.29 – 8.32 (2H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$) 51.7 (OCH_3), 121.6, 124.2 (2C), 127.2, 127.2(5), 127.6 (2C), 127.8, 136.6, 139.0, 139.3, 144.4, 146.7, 147.2, 167.4 (C_{quat}, CO); UV (CH_2Cl_2) λ_{max} = 345 nm (ε = 45980 $M^{-1}cm^{-1}$).

3.2.4. 3-(3"-Nitrobiphen-3'-yl)acrylic acid (21):

To a mixture of 3-bromobenzaldehyde (**29**, 858 mg, 4.64 mmol), ethoxycarbonylmethylidenetriphenylphosphorane (**16-OEt**, 2.0 g, 5.74 mmol), 3-nitrophenylboronic acid (771 mg, 4.64 mmol), bistriphenylphosphinopalladium dichloride (38 mg, 0.05 mmol) and triphenylphosphine (35 mg, 0.13 mmol) aq. Na_2CO_3 (2.52 g Na_2CO_3 on 10 mL H_2O) was added, and the resulting mixture was stirred for 24 h at 75 ºC. Thereafter, aq. NaOH (2.05 g NaOH on 10 mL H_2O) was added and the mixture was stirred a further 24 h at 95ºC. The mixture was cooled, and water was added (20 ml). Thereafter, the ensuing precipitate was filtered off. The aqueous filtrate was acidified with half conc. HCl, and the aqueous layer was extracted with EtOAc (2 X 75 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, evaporated *in vacuo* and the residue was subjected to column chromatography on silica gel (EtOAc/hexane: 1/3) to give **21** (670 mg, 54%) as a colorless solid (mp. > 230 °C); IR (KBr/cm^{-1}) ν = 3500 – 2550 (bs, OH), 3019, 1690 (s, C=O), 1631, 1532, 1221, 790, 682; ^{1}H-NMR (400 MHz, DMSO-d^6) 6.70 (1H, d, ^3J = 16.0 Hz), 7.54 – 7.84 (7H, m), 8.12 (1H, m), 8.21 (1H, m); ^{13} C-NMR (100.5 MHz, $CDCl_3$): 120.7, 121.8, 122.9, 127.3, 128.7, 129.1, 130.2, 130.9, 133.9, 135.7, 138.9, 141.5, 143.9, 148.9, 168.1.

3.2.5. 3-Methoxy-2'-butoxycarbonyl- [[17, 16]benzoestra-1,3,5(10),16-tetraene (40):

A deaerated solution of **35** (126 mg, 0.3 mmol), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol), butyl acrylate (615 mg, 4.8 mmol) and Et_3N (215 mg, 2.1 mmol) in DMF (0.7 mL) was heated at 90 °C for 20 h. Thereafter, the cooled solution was poured into water (60 mL) and extracted with ether (3 X 80 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (hexane/ether 5:1) to give **40** as a yellowish solid (33 mg, 26%), mp. 195–197 °C; ^{1}H-NMR (270 MHz, $CDCl_3$) 0.96 (3H, s, CH_3), 0.93 – 3.02 (20H, m), 3.79 (3H, s, OCH_3), 4.32 (2H, t, OCH_2, ^3J = 6.5 Hz), 6.66 (1H, d, ^4J = 2.6 Hz), 6.74 (1H, d, ^3J = 8.4 Hz, ^4J = 2.6 Hz), 7.21 (1H, d, ^3J = 8.4 Hz), 7.30 (1H, d, ^3J = 7.6 Hz), 7.79 (1H, s), 7.85 (1H, d, ^3J = 7.6 Hz); ^{13} C-NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135): 13.8 (+, CH_3), 19.3 (+, CH_3), 26.4 (-), 27.8m (-), 29.7 (-), 30.8 (-), 32.2 (-), 35.0 (-), 37.7 (+, CH), 44.3 (+, CH), 45.5 (C_{quat}), 55.2 (+, CH), 56.5 (+, OCH_3), 64.7 (-, OCH_2), 111.5 (+, CH), 113.9 +, CH), 121.9 (+, CH), 124.9 (+, CH), 126.1 (+, CH), 127.8 (+, CH), 128.7 (C_{quat}), 132.6 (C_{quat}), 137.8 (Cq_{uat}), 148.4 (C_{quat}), 154.8 (C_{quat}), 157.5 (C_{quat}), 167.2 (C_{quat}); MS (70 eV) *m/z* (%) 418 (M^+, 100). HRMS Found: 418.2510. Calcd. for $C_{28}H_{34}O_3$: 418.2508.

3.2.6. 2,12-Dimethoxy-8-(4'-methoxyphenyl)-8b,9,10,14b-tetrahydrobenzo[b]chrysene (56):

A mixture of η^6-1,2-dihydronaphthalene chromiumtricarbonyl complex (**54**, 70 mg, 0.26 mmol), palladium acetate ($Pd(OAc)_2$, 4.5 mg, 0.02 mmol), *p*-iodo-anisole (**55**, 190 mg, 0.80 mmol), *n*-tetra-butyl ammonium chloride (195 mg, 0.70 mmol), and potassium acetate (50 mg, 0.50 mmol) in acetonitrile (1 mL) was stirred for 24 h at rt. After evaporation of the solvent *in vacuo*, a yellow solid was obtained. The solid was decomplexed by exposing it to air and light. The decomplexed mixture was purified by column chromatography (SiO_2, hexane/Et_2O) and compound **56** (80 mg, 0.18 mmol, 68%) was obtained as a colorless solid, mp. 167 °C; IR (KBr/cm^{-1}) ν = 3437, 2953, 2925, 2855, 2359, 1727, 1599, 1511, 1462, 1428, 1340, 1289, 1247, 1203, 1173, 1100, 1049, 835; ^{1}H-NMR (270 MHz, $CDCl_3$) 1.67 (2H, m), 2.64 (2H, m), 3.12 (1H, m), 3.68 (3H, s, OCH_3), 3.83 (3H, s, OCH_3), 3.88 (3H, s OCH_3), 4.11 (1H, d, ^3J = 4.3 Hz), 6.34 (1H, d, *J* = 2.6 Hz), 6.72 (1H, d, *J* = 2.6 Hz), 6.78 (2H, dd, ^3J = 5.9 Hz, *J* = 2.6 Hz), 6.93 (d, 1H, ^3J = 8.57 Hz), 7.10 (1H, s), 7.14 (2H, d, ^3J = 6.9 Hz), 7.19 (1H, d, *J* = 4.0 Hz), 7.29 (2H, d, ^3J = 3.6 Hz), 7.70 (2H, dd, ^3J = 6.2 Hz, *J* = 3.6 Hz); ^{13} C-NMR (67.8 MHz, $CDCl_3$): 23.7, 28.5, 35.1, 43.2, 55.0, 55.3, 55.4, 108.6, 110.9, 113.5, 114.3, 115.0, 125.5, 125.1, 125.5, 126.7, 128.8, 129.7, 130.0, 130.7, 130.9, 131.4, 132.4, 133.8, 134.8, 136.4, 141.1, 157.9, 159.5. EI-MS: *m/z* (%) = 448 [M^{+1}](100), 405, (M^+-CH_3CO, 4), 358 (M^+-CH_3CO,C_2H_6O +1, 53), 342 (23), 327 (5), 295 (5), 230 (15), 215 (6), 189 (9), 149 (44), 141 (20), 111 (15), 83 (26), 71 (22). HRMS Found: 448.2037. Calcd. for $C_{31}H_{28}O_3$: 448.2034. Found: C, 65.55; H, 3.48%. Calcd. For $C_{31}H_{28}O_3$: C, 66.14; H, 3.48%.

3.2.7. Dimethyl benzophenone-4,4'-dicarboxylate (59):

A deaerated mixture of η^6- indenetricarbonylchromium(0) complex (**57**, 100 mg, 0.40 mmol), palladium acetate

($Pd(OAc)_2$, 4.5 mg, 0.02 mmol), methyl 4-iodobenzoate (**58**, 205 mg, 0.8 mmol), *n*-tetra-butyl ammonium chloride (195 mg, 0.70 mmol), and potassium acetate (50 mg, 0.50 mol) in acetonitrile (1 mL) was stirred at rt for 24 h. After evaporation of the solvent *in vacuo*, a yellow solid was obtained, which was decomplexed by exposing it to light and air. Column chromatography on silica gel (hexane/ether) gave **59** (60 mg, 0.2 mmol, 52%) as a colorless solid (mp. 221 °C [Lit. 228 °C [44]]); IR (neat): ν_{max} = 2958 (w), 1720 (s), 1610 (w), 1559 (w), 1433 (m), 1397 (w), 1285 (s), 1180 (m), 1112 (s), 1017 (w), 954 (m), 849 (m), 757 (m); ^{1}H-NMR ($CDCl_3$, 270 MHz) δ = 3.97 (6H, s, CO_2CH_3), 7.85 (dd, 4H, ^3J = 6.6 Hz, ^4J = 2.0 Hz), 8.15 (dd, 4H, ^3J = 6.6 Hz, J = 2.0 Hz). ^{13} C-NMR ($CDCl_3$, 67.8 MHz) δ = 52.2, 127.3, 129.8, 130.2, 144.4, 166.8, 196.0; MS (EI, 70 eV) *m/z* (%) = 298 [M^+] (22), 267 (M^+- OCH_3, 15), 239 (M^+- OCH_3, -CO, 10), 208 (M^+- OCH_3, -CO, -OCH_3, 3), 180 (M^+- OCH_3,-CO, -OCH_3, -CO,11), 163 (C_6H_4-CO_2CH_3, 100), 152 (15), 135 (23), 120 (17), 104 (46), 76 (69), 59 (5). HRMS Found: 298.0846. Calcd. for $C_{17}H_{14}O_5$: 298.0841.

CONCLUSION

This was a short tour-de-force of some of the work on Pd- and Pt-catalysis that we have carried out over the years. The focus has been to develop strategies of combining various reactions with Pd- or Pt-catalyzed C-C cross coupling reactions in one pot. Furthermore, diene-yne cyclizations were studied under Pt-catalysis that led either to arenes or fulvenes. A triarylation of η^6-dihydronaphthalene tricarbonylchromium complexes with concomitant ring closure was more of a serendipitous discovery.

The authors believe that studies of metal-catalyzed directed cascade reactions will continue to open up new synthetic strategies to complex molecules of value. The recycling and reuse of Pd- and Pt-catalysts will remain to be of great importance for their use in industrial processes. Equally important may be continued investigations on the mechanisms of cross-coupling reactions with heterogeneous Pt- and Pd-catalysts as well as a better understanding of leaching phenomena of these catalysts and their mitigation. This should lead to more facile work-up procedures and to even lower levels of metal contamination of the products.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest, financial or otherwise.

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