Palladium-Catalyzed Arylation of Cyclopentadienes

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Abstract: Cyclopentadiene and metallocenes, typically zirconocene dichloride, are suitable substrates for multiple arylations with aryl bromides in palladium-catalyzed reactions. Thus, various aryl bromides bearing either an electron-donating or an electron-withdrawing substituent can react with these substrates to afford the corresponding 1,2,3,4,5-pentaaryl-1,3-cyclopentadienes in a single preparative step. Derivatives of cyclopentadiene, including di- and trisubstituted cyclopentadienes, and indene are arylated in a similar fashion.

Keywords: domino reactions · extended π-systems · palladium catalysis · rotamers

Introduction

Suitable building blocks are fundamentally important for the construction of nano-sized electronic and optoelectronic devices.[1, 2] Functionalized porphyrins, for instance, are among the most frequently incorporated elements of such devices, since they are easily accessible in one- or two-step procedures and, even more important, they offer interesting features that can be triggered by the central metal ion of the complex.[3] In this respect, we became interested in the synthesis of arylated cyclopentadienes, especially the pentaarylcyclopentadienes (**6**); they, too, are extended π-systems with remarkable optoelectronic properties, for instance, electroluminescence,[4] they can form complexes with transition metals,[5] and it has been shown that their complexes can be used for reversible switching.[6]

A multitude of potential applications arises from these fascinating properties. However, reported methods for the preparation of pentaarylcyclopentadienes (**6**) are limited to multistep procedures,[7] which are somewhat tedious and, in general, less suitable for sterically demanding aryl groups. Recently, we discovered an unprecedented palladium-catalyzed domino reaction[8] that starts with metallocenes and excess arylbromides (**2**, X = Br) to ultimately form pentaarylcyclopentadienes (**6**) in a single preparative step.[9, 10] Furthermore, cyclopentadiene and its derivatives, including di- and trisubstituted cyclopentadienes, and indene have been found to be capable of undergoing similar multiple arylations under the appropriate conditions. The details of these novel reactions are summarized herein.

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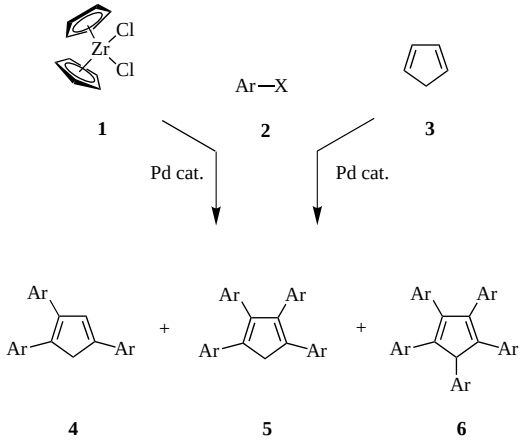
Results and Discussion

When the reaction of a number of metallocenes (Cp_2M; M = Fe, Co, Ni, $TiCl_2$, and $ZrCl_2$) (0.5 mmol) with bromobenzene (**2a**) was examined in the presence of palladium acetate (0.125 mmol), triphenylphosphine (0.5 mmol) and cesium carbonate (6 mmol) at 130 °C for 6 h, 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene (**6a**) was produced, the yield being dependent on the central metal; the best result, 70% yield of **6a**, was achieved when zirconocene dichloride (**1**) was used (Scheme 1 and Table 1, entry 1). Titanocene dichloride and



Scheme 1. Multiple palladium-catalyzed arylation of cyclopentadiene units; Ar = aryl, X = Br, Cl.

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Table 1. Arylation of zirconocene dichloride (**1**).

Entry	Compound **2**		$[Pd(OAc)_2]$	PR_3		Cs_2CO_3	solvent	*t*	*T*	Yield of products [%][a]		
	R, X	[mmol]	[mmol]	R	[mmol]	[mmol]		[h]	[°C]	**4**	**5**	**6**
1	phenyl, Br (**2a**)	6	0.125	phenyl	0.5	6	DMF	6	130	–	–	70
2	phenyl, Br (**2a**)	3	0.0125	phenyl	0.1	6	DMF	20	130	21	9	–
3	phenyl, Br (**2a**)	6	0.125	*t*Bu	0.5	6	DMF	3	130	–	–	77
4	4-methylphenyl, Br (**2b**)	6	0.125	*t*Bu	0.5	6	DMF	1	130	–	–	78
5	4-methylphenyl, Br (**2b**)	6	0.0125	*t*Bu	0.05	6	DMF	20	130	–	–	60
6	3-methylphenyl, Br (**2c**)	6	0.125	3-methylphenyl	0.5	6	DMF	6	130	–	–	70
7	3-methylphenyl, Br (**2c**)	6	0.125	*t*Bu	0.5	6	DMF	1	130	–	–	80
8	2,5-dimethylphenyl, Br (**2d**)	6	0.125	*t*Bu	0.5	6	DMF	22	130	–	–	31
9	2,5-dimethylphenyl, Br (**2d**)	6	0.125	phenyl	0.5	6	DMF	24	130	–	–	70[b]
10	3,4-dimethylphenyl, Br (**2e**)	6	0.125	3,4-dimethylphenyl	0.5	6	DMF	14	130	–	–	58
11	3,4-dimethylphenyl, Br (**2e**)	6	0.125	*t*Bu	0.5	6	DMF	3	130	–	–	85
12	3,5-dimethylphenyl, Br (**2f**)	6	0.125	*t*Bu	0.5	6	DMF	1	130	–	–	78
13	4-*t*Buphenyl, Br (**2g**)	6	0.125	*t*Bu	0.5	6	DMF	23	130	–	–	53
14	4-methoxyphenyl, Br (**2h**)	6	0.125	*t*Bu	0.5	6	DMF	1.5	130	–	–	45
15	4-*n*-butoxyphenyl, Br (**2i**)	6	0.125	*t*Bu	0.5	6	DMF	18	130	–	–	50
16	4-*n*-octyloxyphenyl, Br (**2j**)	6	0.125	*t*Bu	0.5	6	DMF	4	130	–	–	63
17	4-carboethoxyphenyl, Br (**2k**)	7	0.05	*t*Bu	0.1	6	DMF	46	140	–	15	22
18	4-fluorophenyl, Br, (**2l**)	6	0.125	4-fluorophenyl	0.5	6	DMF	24	130	–	–	38
19	4-fluorophenyl, Br, (**2l**)	6	0.125	*t*Bu	0.5	6	DMF	1	130	–	–	60
20	1-naphthyl, Br (**2n**)	6	0.125	*t*Bu	0.5	6	DMF	21	130	–	–	48

[a] Isolated yield based on the amount of cyclopentadiene moiety (1 mmol = 100 %). [b] Contaminated with $C_5H(Ph)(2,5\text{-}Me_2C_6H_3)_4$ (8 %).

nickelocene also afforded > 60 % yields of **6a**, while cobaltocene and especially ferrocene proved rather unreactive (yields of 23 % and < 1 %, respectively). Evidently, the metallocenes should fragment during the stepwise arylation; 1,2,4-triphenyl-1,3-cyclopentadiene (**4a**) (21 %) and 1,2,3,4-tetraphenyl-1,3-cyclopentadiene (**5a**) (9 %) were isolated as intermediary products (Table 1, entry 2) from the reaction of **1** with reduced amounts of **2a** (3 mmol) and palladium acetate (0.0125 mmol). It is noted that cesium carbonate proved far superior than potassium carbonate; the use of potassium carbonate led to the increased formation of biphenyl as an Ullmann-type coupling product,[11] the yield of **6a** was < 10 %, even with zirconocene dichloride.

The phosphine ligands are also crucial for the success of the domino reaction when substituted bromobenzenes were used. Triphenylphosphine caused the contamination of phenyl groups in the products.[12] The scrambling of aryl moieties would be avoided with the use of triarylphosphines that have the same aryl groups as the starting aryl bromide. This was confirmed in reactions in which 3-methyl-, 3,4-dimethyl-, and 4-fluorobromobenzenes, (**2c**, **2e** and **2l**, respectively,) were used (Table 1, entries 6, 10, and 18, respectively), the expected products **6c**, **6e**, and **6l** were obtained. This problem was overcome in a more general manner with the use of the relatively more basic and sterically hindered tri-*tert*-butylphosphine.[13, 14] Furthermore, it was found in several examples that this phosphine can enhance the domino reaction considerably; the reaction of metallocene **1** with 4-bromotoluene (**2b**), for instance, was completed within one hour to give penta(4-methylphenyl)cyclopentadiene (**6b**) in an isolated yield of 78 % (Table 1, entry 4). Remarkably, the amount of palladium catalyst under optimized conditions can be reduced to 0.25 mol % per transferred aryl group to achieve an acceptable isolated yield (60 %), as in the case of **6b** (Table 1, entry 5). However, with a relatively bulky bromide, such as 2,5-dimethylbromobenzene (**2d**), triphenylphosphine afforded a considerably better yield of product **6d** (70 %, Table 1, entry 8) as compared with tri-*tert*-butylphosphine (31 %, Table 1, entry 7), even under consideration that an impurity of approximately 8 % of the corresponding tetra(2,5-dimethylphenyl)phenylcyclopentadiene was indicated by mass spectrometry of the crude product; the purity fortunately became 98 % (73 % recovery) after a single recrystallization from methanol/benzene. Both electron-rich aryl bromides, such as 4-bromoanisole (**2h**), and electron-poor aryl bromides, such as ethyl 4-bromobenzoate (**2k**), reacted with **1** to give the corresponding pentaarylcyclopentadienes **6h** and **6k**. Derivatives with long side chains, such as **6j**, are of possible interest as building blocks for organometallic liquid crystals.[7d]

The formation of the *ortho*-substituted and thus very sterically-crowded penta(2,5-dimethylphenyl)cyclopentadiene (**6d**) deserves special attention. Compound **6d** was found to consist of at least six rotamers at room temperature; its ^1H NMR spectrum in $CDCl_3$ showed six methine proton peaks (three major signals at $\delta = 5.10$, 5.29 and 5.46 and three minor signals at $\delta = 4.85$, 5.07 and 5.25; Figure 1a) and more than 20 methyl peaks. This spectrum resembles the spectrum

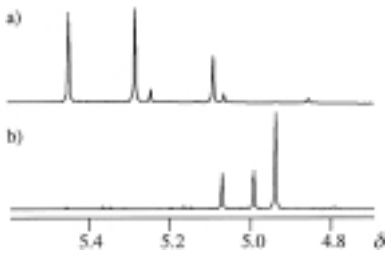

Figure 1. Methine proton peaks in ^1H NMR spectrum of compounds a) **6d** and b) **6e** in $CDCl_3$ at room temperature.

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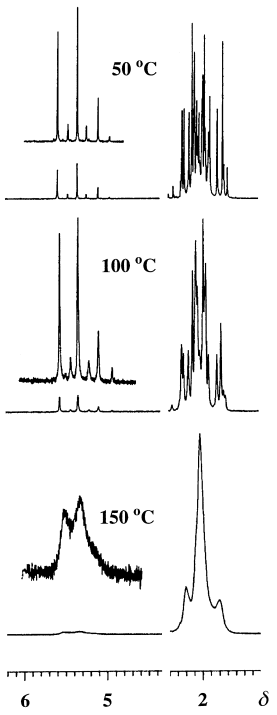

Figure 2. Temperature-dependence of ^{1}H NMR spectrum of compound **6d** in [D_6]DMSO.

previously reported for tetra(2-methylphenyl)cyclopentadienone at the low temperature of −43 °C.[14] The peaks in the ^{1}H NMR spectrum of **6d** in [D_6]DMSO were still sharp, even at 100 °C, thus reflecting its crowded nature, while at 150 °C they were completely broadened (Figure 2). It was somewhat surprising that penta(3,4-dimethylphenyl)cyclopentadiene (**6e**) also consists of several rotamers as indicated by the methine peaks (Figure 1b), whereas penta(3-methylphenyl)cyclopentadiene (**6c**) showed a single methine peak, as did its penta(4-methylphenyl) isomer **6b**. The temperature-dependent spectrum of **6e** was similar to that of **6d**. This phenomenon may arise from the restricted movement of two adjacent methyl groups which make the rotation of the phenyl rings in **6e** difficult.

It was quite interesting to find that cyclopentadiene (**3**) itself is equally suited for the multiple arylation process as metallocene **1** when the reaction is carried out in a screw-cap tube to prevent the loss of volatile substrate (Table 2). The yields achieved are similar or better than those obtained when **1** was used.

A comparison of entries 7 and 8 of Table 2 (34 h and 19 h reaction time, respectively) reveals that the arylation process is rather slow in the case of the bulky bromide **2d**; evidently the major part of the 62% yield of **6d** is formed in the last 15 h, again indicating the stepwise character of the arylation process. In the case of the relatively more hindered bromide, 2,6-dimethylbromobenzene (**2o**), the arylation is terminated at the stage of triarylcyclopentadiene **4o**. The presented arylation reactions in *o*-xylene were found to be much slower compared with those in DMF. Thus, when reduced amounts of aryl bromides **2b** and **2l** and *o*-xylene as the solvent were applied at 120 °C (Table 2, entries 5 and 13), tetra(4-methylphenyl)- and tetra(4-fluorophenyl)cyclopentadienes (**5b** and **5l**, respectively) were obtained as the major products. The coupling reaction of 2-chlorobromobenzene (**2m**) proved that aryl bromides are more reactive than aryl chlorides, as was expected (Table 2, entry 14). However, under more rigorous reaction conditions 4-chlorotoluene (**2b′**) led to an excellent result (Table 2, entry 2).

4-Bromophenol, 4-bromobenzonitrile, and 4-bromobenzaldehyde could not be used for the arylation of cyclopentadiene. This problem was solved by using an acetal as the protecting group. Thus, pentaacetal **8a** was obtained in 56% yield starting from dioxolane **7a** (Scheme 2). The synthesis of pentaketone **9b** (R = CH_3) was achieved in a one-pot procedure, including deketalization. The pentacarbonyl compounds **9** could be valuable building blocks for the construction of extended π systems by multiple condensation reactions. For instance, the fivefold condensation of **9a** with *p*-toluidine proceeds almost quantitatively to give the corresponding pentakisimine. Since its final purification by column chromatography or by crystallization proved difficult, the full characterization was performed on the reduction product **10**.

The fact that stoichiometric metalation of the cyclopentadiene unit is not a prerequisite significantly enhances the scope of the domino arylation; substituted and annulated cyclopentadienes now belong to the group of suitable starting materials. We tested the application of 1,2,4-triaryl-1,3-cyclopentadienes (**11**) to synthesize pentaarylcyclopentadienes **12** with a defined substitution pattern (Scheme 3). The arylation of di-1,4-(4-chlorophenyl)-1,3-cyclopentadiene (**13**) also led to

Table 2. Arylation of cyclopentadiene (**3**).

Entry	Compound **2**		$[Pd(OAc)_2]$	PR_3		Cs_2CO_3	solvent	*t*	*T*	Yield of products [%][a]		
	R, X	[mmol]	[mmol]	R	[mmol]	[mmol]		[h]	[°C]	**4**	**5**	**6**
1	4-methylphenyl, Br (**2b**)	6	0.025	*t*Bu	0.15	6	DMF	15	140	–	–	87[b]
2	4-methylphenyl, Cl (**2b**)	10	0.05	*t*Bu	0.12	6	DMF	72	160	–	–	87
3	4-methylphenyl, Cl (**2b**)	10	0.025	*t*Bu	0.06	6	*o*-xylene	24	140	–	46	45
4	4-methylphenyl, Cl (**2b**)	6	0.025	*t*Bu	0.06	6	*o*-xylene	24	140	–	–	60
5	4-methylphenyl, Cl (**2b**)	4	0.025	*t*Bu	0.06	4	*o*-xylene	24	120	10	32	11
6	3-methylphenyl, Br (**2c**)	6	0.05	*t*Bu	0.15	6	DMF	18	140	–	–	77
7	2,5-dimethylphenyl, Br (**2d**)	6	0.05	*t*Bu	0.12	6	DMF	34	140	–	–	62
8	2,5-dimethylphenyl, Br (**2d**)	6	0.05	*t*Bu	0.12	6	DMF	19	140	–	52	15
9	4-methoxyphenyl, Br (**2h**)	6	0.05	*t*Bu	0.12	6	DMF	6	140	–	–	61
10	4-*n*-butoxyphenyl, Br (**2i**)	6	0.05	*t*Bu	0.12	6	DMF	24	140	–	–	61
11	4-carboethoxyphenyl, Br (**2k**)	6	0.05	*t*Bu	0.1	6	DMF	41	140	–	24	30
12	4-fluorophenyl, Br (**2l**)	6	0.05	*t*Bu	0.12	6	DMF	6	140	–	–	82
13	4-fluorophenyl, Br (**2l**)	4	0.05	*t*Bu	0.12	4	*o*-xylene	6	120	–	48	9
14	2-chlorophenyl, Br (**2m**)	6	0.075	*t*Bu	0.6	6	DMF	42	140	–	18	17
15	1-naphthyl, Br (**2n**)	6	0.05	*t*Bu	0.12	6	DMF	24	140	–	–	58
16	1-naphthyl, Br (**2n**)	4	0.05	*t*Bu	0.12	4	*o*-xylene	24	140	46	–[c]	–
17	2,6-dimethylphenyl, Br (**2o**)	6	0.05	*t*Bu	0.12	6	DMF	24	140	54	–	–
18	4′-pentyl-biphenyl-1-yl, Br (**2p**)	6	0.05	*t*Bu	0.12	6	DMF	24	140	–	–	72

[a] Isolated yield based on the amount of cyclopentadiene (**3**) used. [b] Maximum yield achieved; range of yields for this reaction achieved in several laboratories in Germany and Japan was always between 70 and 87%. [c] Tetranaphthylcyclopentadiene **5n** was formed in about 15% yield, but was not fully characterized.

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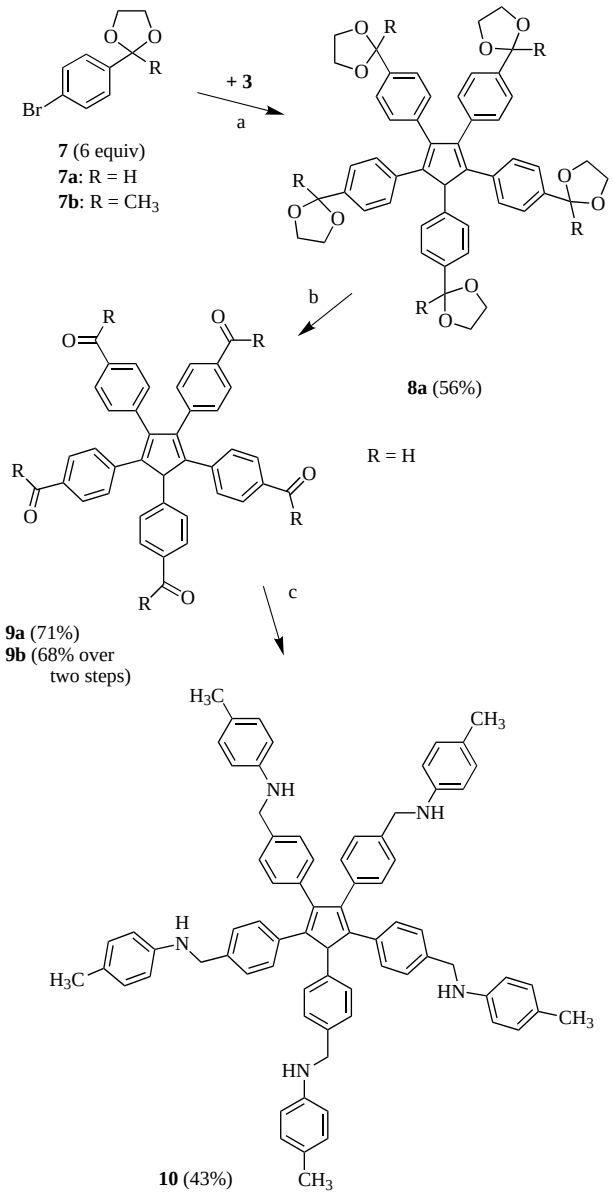
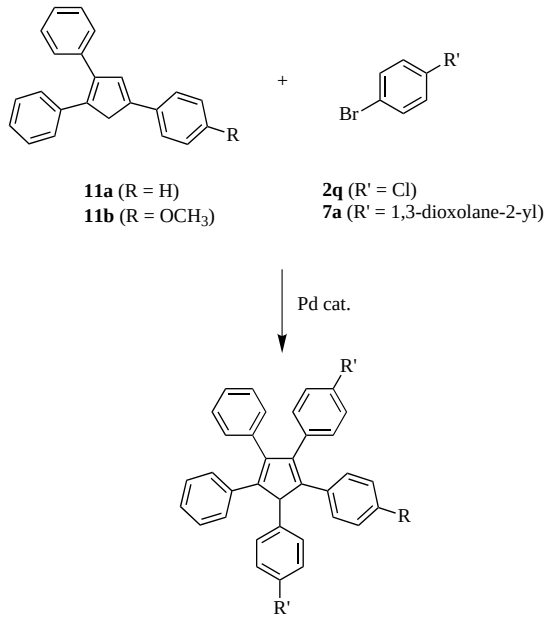
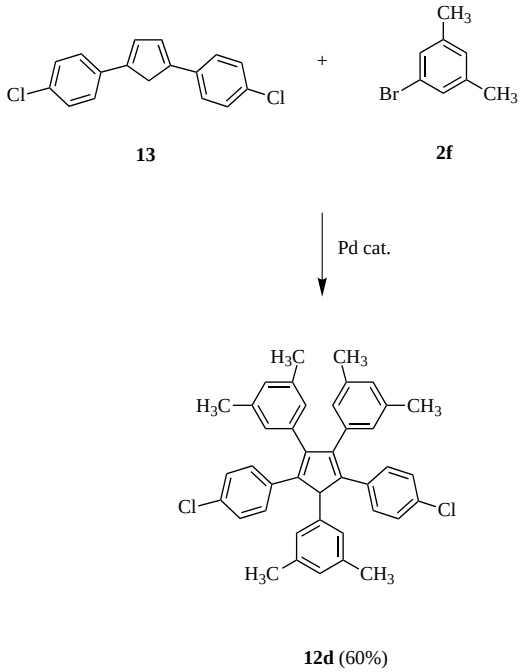


Scheme 2. Pentacarbonyl compounds and their derivatization. Reaction conditions a) 5 mol% $[Pd(OAc)_2]$, 12 mol% $P(tBu)_3$, Cs_2CO_3, DMF, 140 °C, 21 h; b) *p*-TosOH, acetone, reflux; c) 1) *p*-toluidine, benzene, *p*-TosOH, Dean-Stark trap; 2) $LiAlH_4$.



Scheme 3. Twofold arylation of triarylcyclopentadienes **11**. Reaction conditions for **12a**: 2.5 equiv aryl bromide, 2.5 mol% $[Pd(OAc)_2]$, 12 Mol% $P(tBu)_3$, Cs_2CO_3, DMF, 120 °C, 24 h; for **12b** and **12c**: 2–3 equiv aryl bromide, 2.5 mol% $[Pd(OAc)_2]$, 10 mol% $P(tBu)_3$, Cs_2CO_3, DMF, 140 °C, 20–68 h. Yields are given for the mixture of three double-bond isomers.



Scheme 4. Threefold arylation of diarylcyclopentadiene **13**. Reaction conditions: 3.6 equiv aryl bromide, 2.5 mol% $[Pd(OAc)_2]$, 12 mol% $P(tBu)_3$, Cs_2CO_3 DMF, 120 °C, 24 h; the yield is for the mixture of three double-bond isomers.

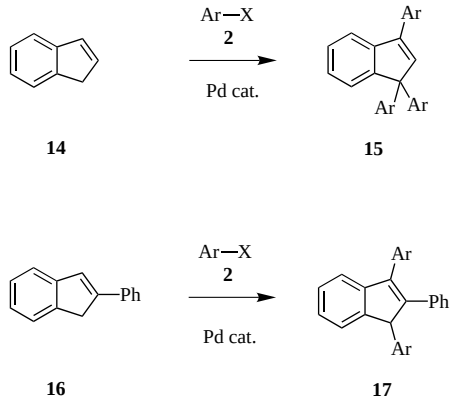
the formation of pentaarylcyclopentadiene **12d** (Scheme 4). In each case, a yield of approximately 50% or more of a mixture of double bond isomers was obtained. It is anticipated that all double bond isomers of each of the pentaarylcyclopentadienes **12** should give the same organometallic complex after metalation.

Under the applied reaction conditions, indene (**14**) was found to undergo threefold arylation exclusively at the 1- and 3-positions to give the 1:3 products **15** (Scheme 5 and Table 3, entries 1–4). This observation is important for the mechanistic interpretation of the domino reaction and implies that the successive C–C bond formation takes place by the reaction of an aryl palladium halide with indenyl anions, presumably their cesium salts, at the 1- and 3-positions, which have the highest electron density. Arylation by carbopalladation is less likely to be involved, since stoichiometric reactions of this kind in indenes are known to give arylation products at the 2-position,[16] and a catalytic Heck-type reaction under

Table 3. Arylation of indenes **15** and **17**.

Entry	Indeneq	Compound **2** R, X	[mmol]	$[Pd(OAc)_2]$ [mmol]	PR_3 R	[mmol]	Cs_2CO_3 [mmol]	Solvent	*t* [h]	*T* [°C]	Product	Yield [%][a]
1	**14**	phenyl, Br (**2a**)	3.6	0.025	*t*Bu	0.06	3.6	DMF	3	140	**15a**	81
2	**14**	4-methylphenyl, Br (**2b**)	3.6	0.025	*t*Bu	0.06	3.6	DMF	6	140	**15b**	80
3	**14**	4-methoxyphenyl, Br (**2f**)	3.6	0.025	*t*Bu	0.06	3.6	DMF	1	140	**15f**	45
4	**14**	3,5-dimethylphenyl, Br (**2n**)	3.6	0.025	*t*Bu	0.06	3.6	DMF	5	140	**15n**	72
5	**16**	4-methylphenyl, Br (**2b**)	2.5	0.025	*t*Bu	0.06	2.5	DMF	6	140	**17b**	58

[a] Isolated yield based on the amount of indene.



Scheme 5. Double palladium-catalyzed arylation of indenes **14** and **16;** Ar = aryl, X = Br, Ph = phenyl.

somewhat different conditions was reported to start with the arylation at the 2-position.[17] For the multiple arylation of cyclopentadiene (**3**) there is a possibility that a Heck-type mechanism partially contributes to the reaction sequence. However, since intermolecular Heck arylation of tri- and tetrasubstituted alkenes is generally slow, the third to fifth arylations of cyclopentadiene (**3**) would preferably occur by coupling with the corresponding cyclopentadienyl anions. Note that the pKa value of cyclopentadiene in dimethylsulfoxide at 25 °C (18.0) is known to be smaller than that of indene (20.1),[18] hence, it should be relatively more susceptible toward reaction with the base. Therefore, even the first arylation could occur on the cyclopentadienyl anion. It may be reasonable to consider that the first arylation involves transmetalation when metallocenes are used.[19] The inefficiency of ferrocene may be attributed to the fact that it is an 18-electron complex with substantial stability. In turn, the formal 16- and 20-electron complexes, zirconocene dichloride and nickelocene, are considered to be reactive, as was experimentally observed. In the reaction of 2-phenylindene (**16**) with **2b**, we observed a twofold arylation, again at the 1- and 3-positions (Scheme 5 and Table 3, entry 5); due to steric hindrance, the third arylation is inhibited. This agrees with the lack of hexaarylated products in the reaction of zirconocene dichloride (**1**) and cyclopentadiene (**3**).

In summary, we have shown that various cyclopentadienes as well as metallocenes can be multiply arylated by a single reaction with aryl halides in a palladium catalyzed reaction. This novel synthetic method represents an efficient and straightforward alternative to classical methods, thus opening up opportunities for the construction of even extremely sterically crowded pentaarylcyclopentadienes. While the method which uses cyclopentadiene itself without the use of a stoichiometric amount of a metal is more economical than that with metallocenes, the latter has some advantages, however; metallocenes are commercially available, so that predistillation of dicyclopentadiene is not required, and the reaction can be carried out using a standard flask. We will further investigate synthetic applications of multiple-arylated cyclopentadienes, such as the electropolymerization of chlorosubstituted derivatives of **12** and the polymerization by McMurry reaction of the dicarboxaldehyde derived from **12c**, in order to develop a route to a new type of conducting polymer.

Experimental Section

General: Melting points are uncorrected. ^{1}H NMR spectra (300 or 500 MHz) were recorded in $CDCl_3$ with TMS as the internal standard unless otherwise noted. ^{13}C NMR spectra (75 or 125 MHz) were measured with $CDCl_3$ as the solvent and as the internal standard ($\delta = 77.05$). MS data were obtained by EI; all samples were measured at 70 eV and 295 °C unless otherwise stated. Substituted cyclopentadienes **11a**,[20] **11b**,[21] and **13**[22] were prepared according to or in analogy to published procedures.

General procedure for palladium-catalyzed cross-coupling reactions of aryl halides (2) with zirconocene dichloride (1) or with cyclopentadiene (3): A mixture of zirconocene dichloride (**1**, 146 mg,500 μmol) or of cyclopentadiene (**3**, 66 mg, 1.0 mmol) and aryl halide (**2**, 6.00 mmol), cesium carbonate (1.96 g, 6.00 mmol), palladium acetate (12.5 – 125 μmol), dimethyl formamide, (10 mL) and an appropriate phosphine ligand (50 – 150 μmol) was heated under argon in a screw-cap tube for 1 – 72 h at 120 – 160 °C (see below and also Tables 1 and 2; further remarks: 1. sensitive phosphine ligands such as tri-*tert*-butylphosphine are added after the solvent; 2. the oil bath is preheated to the reaction temperature before the tube is inserted; 3. for the reaction with **1**, a two-necked flask with a balloon that is filled with nitrogen may also be used, which gives essentially the same results as when a sealed tube is used). After cooling to room temperature, CH_2Cl_2 (50 mL) and *p*-toluene sulfonic acid (12 mmol) were added while stirring. After 10 min the mixture was filtered through silica gel (5 g) with CH_2Cl_2 (25 mL) as eluent. The solvent was removed in vacuo at 50 °C and 15 mbar, the residue dried in vacuo at 50 °C and 0.5 mbar and separated by flash chromatography on silica gel.

1,2,3,4-Tetrakis-(4-carboethoxyphenyl)-cyclopentadiene (5k) and 1,2,3,4,5-pentakis-(4-carboethoxyphenyl)-cyclopentadiene (6k) from cyclopentadiene (3): 4-Bromobenzoic acid ethyl ester (**2k**) (1.37 g, 6.00 mmol) was coupled with cyclopentadiene (**3**) according to the general procedure; for detailed reaction conditions see Table 2, entry 11 (for comparison: data of the corresponding synthesis from zirconocene dichloride is given in Table 1, entry 15). Thin-layer chromatography of the crude product: $R_f = 0.49$ (biphenyl-4,4′-dicarboxylic acid diethyl ester), 0.29 (**5k**), 0.22 (**6k**) (petroleum ether/ethyl acetate 3:1, silica gel). Separation of the products by flash chromatography (petroleum ether/ethyl acetate 3:1, silica gel) yielded three fractions.

0947-6539/00/0618-3430 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 18

First fraction: Biphenyl-4,4′-dicarboxylic acid diethyl ester (159 mg, 18%) as colorless crystals with m.p. 220 °C; its NMR spectroscopic data matched published data.[23]

Second fraction: Tetraarylcyclopentadiene **5k** (152 mg, 24%) as a yellow solid: m.p. 203–208 °C; IR (film): $\tilde{\nu}$ = 2981 (m), 2935 (w), 2905 (w), 1718 (s), 1604 (s), 1563 (w), 1511 (w), 1463 (w), 1445 (w), 1405 (m), 1367 (s), 1309 (s, sh), 1273 (s), 1206 (m), 1180 (s), 1109 (s), 1020 (s), 890 (w), 865 (m), 850 (m), 771 (s), 747 (m), 704 cm^{-1} (m); UV/Vis (acetonitrile): λ_{max} (lg ε) = 370 (4.35), 284 (4.42), 254 (4.44, sh), 230 nm (4.50); ^{1}H NMR: δ = 1.36 (t, J = 7.2 Hz, 6H), 1.38 (t, J = 7.2 Hz, 6H), 4.12 (s, 1H, C_5H), 4.35 ("quintet", "J" = 7.5 Hz, 8H), 7.03 (d, J = 8.6 Hz, 4H), 7.21 (d, J = 8.7 Hz, 4H), 7.86 ("d", "J" = 8.6 Hz, 8H); ^{13}C NMR: δ = 14.31 (q), 14.32 (q), 45.90 (t, C_5H), 60.94, 61.05 (all t), 127.68 (d), 128.74, 129.41 (all s), 129.62, 129.70 (all d), 139.86, 140.40, 141.11, 145.08 (all s), 166.26, 166.31 (all s, *C*O), one d is superimposed; MS: m/z (%): 659 (45) $[M+1]^+$, 658 (100) $[M]^+$, 57 (10), 44 (55), 41 (10); elemental analysis calcd (%) for $C_{41}H_{38}O_8$ (658.7): C 74.76, H 5.81; found C 74.62, H 5.79.

Third fraction: Pentaarylcyclopentadiene **6k** (233 mg, 30%) as a yellow solid with m.p. 160 °C (Lit.: m.p. 160 °C)[7d]; IR (film): $\tilde{\nu}$ = 2981 (w), 2938 (w), 2904 (w), 2873 (w), 1719 (s), 1606 (m), 1463 (w), 1445 (w), 1404 (w), 1367 (m), 1308 (w), 1278 (s), 1178 (m), 1107 (s), 1021 (m), 860 (w), 775 (w), 749 (w), 735 (w), 706 cm^{-1} (w); UV/Vis (acetonitrile): λ_{max} (lg ε) = 361 (4.34), 275 (4.54), 239 nm (4.77); ^{1}H NMR: δ = 1.30 (m, 6H), 1.34 (m, 3H), 1.35 (t, J = 7.0 Hz, 6H), 4.30 (m, 4H), 4.33 (m, 2H), 4.35 (q, J = 7.0 Hz, 4H), 5.25 (s, 1H, C_5H), 6.99 (d, J = 8.7 Hz, 4H), 7.09 (d, J = 8.6 Hz, 4H), 7.26 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.7 Hz, 4H), 7.85 (d, J = 8.5 Hz, 4H), 7.88 (d, J = 8.4 Hz, 2H); ^{13}C NMR: δ = 14.24 (q), 14.27 (q), 60.86 (t), 60.97 (t), 61.04 (t), 62.63 (d, C_5H), 128.24, 128.72, 129.28 (all d), 129.53, 129.83, 130.26, 128.93, 129.51, 139.03, 139.55, 141.89, 144.65, 147.21, 166.08, 166.18 (all s), three q and one t are superimposed; MS: m/z (%): 807 (55.1) $[M+1]^+$, 806 (100) $[M]^+$, 660 (10), 351 (12), 323 (12), 177 (11), 44 (36); elemental analysis calcd (%) for $C_{50}H_{46}O_{10}$ (806.9): C 74.43, H 5.78; found C 74.32, H 5.75.

1,2,4-Tri(4-methylphenyl)-1,3-cyclopentadiene (4b): M.p. 151–154 °C; ^{1}H NMR: δ = 2.31 (s, 3H), 2.35 (s, 3H), 2.36 (s, 3H), 3.88 (s, 2H), 6.32 (s, 1H), 6.96 (s, 1H), 7.03 (d, J = 8.1 Hz, 2H), 7.12–7.30 (m, 8H), 7.46 (d, J = 8.1 Hz, 2H); ^{13}C NMR: δ = 21.32, 21.36, 21.42, 45.03, 124.63, 127.41, 128.09, 128.79, 128.98, 129.18, 131.01, 132.98, 134.04, 134.21, 135.86, 136.37, 136.50, 138.15, 141.14, 144.34; MS: m/z (%): 336 $[M]^+$; elemental analysis calcd (%) for $C_{26}H_{24}$ (336.47): C 92.81, H 7.19; found C 92.58, H 7.19.

1,2,3,4-Tetra(4-methylphenyl)-1,3-cyclopentadiene (5b): M.p. 179–180 °C; ^{1}H NMR: δ = 2.27 (s, 6H), 2.28 (s, 6H), 3.94 (s, 2H), 6.85 (d, J = 8.1 Hz, 4H), 6.95 (d, J = 7.8 Hz, 4H), 6.97 (d, J = 8.1 Hz, 4H), 7.08 (d, J = 8.1 Hz, 4H); ^{13}C NMR: δ = 21.27, 21.43, 45.87, 127.49, 128.56, 128.64, 129.56, 133.65, 133.77, 135.63, 135.78, 138.89, 143.77; MS: m/z (%): 426 $[M]^+$; elemental analysis calcd (%) for $C_{33}H_{30}$ (426.60): C 92.91, H 7.09; found C 92.74, H 6.98.

1,2,3,4,5-Penta(4-methylphenyl)-1,3-cyclopentadiene (6b): M.p. 250 °C; ^{1}H NMR: δ = 2.17 (s, 6H), 2.20 (s, 3H), 2.26 (s, 6H), 4.97 (s, 1H), 6.81–6.95 (m, 18H), 7.07 (d, J = 7.8 Hz, 2H); ^{13}C NMR: δ = 21.26, 21.42, 61.97, 128.10, 128.20, 128.36, 128.63, 129.02, 129.81, 133.05, 133.35, 135.25, 135.34, 135.38, 135.69, 143.24, 145.70; MS: m/z (%): 516 $[M]^+$; elemental analysis calcd (%) for $C_{40}H_{36}$ (516.72): C 92.98, H 7.02; found C 92.56, H 7.04.

1,2,3,4,5-Penta(3-methylphenyl)-1,3-cyclopentadiene (6c): M.p. 163–164 °C; ^{1}H NMR: δ = 2.08 (s, 6H), 2.15 (s, 6H), 2.23 (s, 3H), 5.02 (s, 1H), 6.77–6.93 (m, 15H), 6.99–7.04 (m, 5H); ^{13}C NMR: δ = 21.29, 21.37, 21.48, 62.19, 125.43, 126.10, 126.87, 127.14, 127.17, 127.19, 127.38, 127.52, 128.20, 129.27, 129.73, 130.80, 135.79, 136.32, 136.75, 137.00, 137.70, 138.32, 144.09, 146.08; MS: m/z (%): 516 $[M]^+$; elemental analysis calcd (%) for $C_{40}H_{36}$ (516.72): C 92.98, H 7.02; found C 92.94, H 7.10.

1,2,3,4-Tetra(2,5-dimethylphenyl)-1,3-cyclopentadiene (5d, mixture of rotamers): M.p. 73–74 °C; ^{1}H NMR: δ = 1.77–2.20 (m, 24H), 3.63–4.03 (m, 2H), 6.61–6.97 (m, 12H); MS: m/z (%): 482 $[M]^+$; elemental analysis calcd (%) for $C_{37}H_{38}$ (482.71): C 92.07, H 7.93; found C 91.77, H 7.85.

1,2,3,4,5-Penta(2,5-dimethylphenyl)-1,3-cyclopentadiene (6d, mixture of rotamers): M.p. 194–196 °C; ^{1}H NMR: δ = 1.72–2.46 (m, 30H), 4.86–5.45 (m, 1H), 6.46–7.10 (m, 15H); MS: m/z (%): 586 $[M]^+$; elemental analysis calcd (%) for $C_{45}H_{46}$ (586.86): C 92.10, H 7.90; found C 91.92, H 7.97.

1,2,3,4,5-Penta(3,4-dimethylphenyl)-1,3-cyclopentadiene (6e, mixture of rotamers): M.p. 168–170 °C; ^{1}H NMR: δ = 1.97–2.22 (m, 30H), 4.97–5.10 (m, 1H), 6.62–7.24 (m, 15H); MS: m/z (%): 586 $[M]^+$; elemental analysis calcd (%) for $C_{45}H_{46}$ (586.86): C 92.10, H 7.90; found C 91.98, H 8.01.

1,2,3,4,5-Penta(3,5-dimethylphenyl)-1,3-cyclopentadiene (6f): M.p. 213–214 °C; ^{1}H NMR: δ = 2.05 (s, 12H), 2.12 (s, 12H), 2.18 (s, 6H), 4.98 (s, 1H), 6.61–6.82 (m, 15H); ^{13}C NMR: δ = 21.17, 21.26, 21.36, 61.54, 126.33, 126.86, 127.61, 127.87, 127.92, 135.72, 136.39, 136.51, 136.61, 137.26, 138.62, 144.28, 145.57; MS: m/z (%): 586 $[M]^+$; elemental analysis calcd (%) for $C_{45}H_{46}$ (586.86): C 92.10, H 7.90; found C 92.20, H 7.86.

1,2,3,4,5-Penta(4-*t*-butylphenyl)-1,3-cyclopentadiene (6g): M.p. 243–245 °C; ^{1}H NMR: δ = 1.19 (s, 18H), 1.23 (s, 9H), 1.25 (s, 18H), 5.05 (s, 1H), 6.89–7.18 (m, 20H); ^{13}C NMR: δ = 31.33, 31.46, 34.42, 34.50, 61.31, 124.27, 124.32, 125.16, 127.79, 128.07, 129.45, 132.84, 133.73, 135.73, 143.89, 144.84, 148.33, 148.50, 148.87; MS: m/z (%): 726 $[M]^+$; elemental analysis calcd (%) for $C_{55}H_{66}$ (727.12): C 90.85, H 9.15; found C 90.58, H 9.12.

1,2,3,4,5-Penta(4-methoxyphenyl)-1,3-cyclopentadiene (6h): M.p. 193–194 °C; ^{1}H NMR: δ = 3.68 (s, 6H), 3.71 (s, 3H), 3.75 (s, 6H), 4.89 (s, 1H), 6.56–6.58 (m, 4H), 6.67–6.71 (m, 6H), 6.88–6.92 (m, 8H), 7.08–7.10 (m, 2H); ^{13}C NMR: δ = 55.00, 55.04, 55.06, 61.68, 113.00, 113.19, 113.80, 128.71, 128.76, 129.18, 129.88, 130.56, 131.14, 142.06, 144.87, 157.50, 157.67, 157.84; MS: m/z (%): 596 $[M]^+$; elemental analysis calcd (%) for $C_{40}H_{36}O_5$ (596.72): C 80.51, H 6.08; found C 80.28, H 6.07.

1,2,3,4,5-Penta(4-butoxyphenyl)-1,3-cyclopentadiene (6i): M.p. 83–84 °C; ^{1}H NMR: δ = 0.91–0.98 (m, 15H), 1.37–1.52 (m, 10H), 1.64–1.77 (m, 10H), 3.80–3.90 (m, 10H), 4.86 (s, 1H), 6.54–7.07 (m, 20H); ^{13}C NMR: δ = 14.01, 14.08, 19.40, 19.44, 31.50, 31.56, 61.64, 67.40, 67.51, 96.06, 96.37, 96.70, 113.50, 113.74, 114.34, 128.60, 128.70, 129.17, 129.87, 130.48, 131.14, 142.04, 144.82, 157.09, 157.25, 157.41; MS: m/z (%): 806 $[M]^+$; elemental analysis calcd (%) for $C_{55}H_{66}O_5$ (807.12): C 81.85, H 8.24; found C 81.48, H 8.26.

1,2,3,4,5-Penta(4-octyloxyphenyl)-1,3-cyclopentadiene (6j): viscous oil; ^{1}H NMR: δ = 0.85–0.90 (m, 15H), 1.23–1.43 (m, 50H), 1.65–1.78 (m, 10H), 3.79–3.89 (m, 10H), 4.86 (s, 1H), 6.53–7.07 (m, 20H); MS: m/z (%): 1086 $[M]^+$; elemental analysis calcd (%) for $C_{75}H_{106}O_5$ (1087.66): C 82.82, H 9.82; found C 82.39, H 9.86.

1,2,3,4-Tetra(4-fluorophenyl)-1,3-cyclopentadiene (5l): M.p. 208–209 °C; ^{1}H NMR: δ = 3.94 (s, 2H), 6.85–6.91 (m, 10H), 7.11–7.14 (m, 4H); ^{13}C NMR: δ = 46.06, 115.10 (d, J = 24.2 Hz), 115.23 (d, J = 21.2 Hz), 129.19 (d, J = 7.8 Hz), 131.24 (d, J = 7.8 Hz), 131.84, 132.04, 138.79, 142.67, 161.30 (d, J = 246.7 Hz), 162.57 (d, J = 245.7 Hz); MS: m/z (%): 442 $[M]^+$; elemental analysis calcd (%) for $C_{29}H_{16}F_4$ (440.43): C 78.72, H 4.10; found C 78.72, H 4.16.

1,2,3,4,5-Penta(4-fluorophenyl)-1,3-cyclopentadiene (6l): M.p. 186–187 °C; ^{1}H NMR: δ = 4.90 (s, 1H), 6.73–6.77 (m, 4H), 6.84–6.95 (m, 14H), 7.07–7.10 (m, 2H); ^{13}C NMR: δ = 62.12, 114.97 (d, J = 22.4 Hz), 115.22 (d, J = 22.1 Hz), 115.77 (d, J = 21.5 Hz), 129.73 (d, J = 7.4 Hz), 130.50 (d, J = 8.3 Hz), 131.32, 131.35, 131.63 (d, J = 8.3 Hz), 132.96, 142.55, 145.62, 161.56 (d, J = 247.3 Hz), 161.63 (d, J = 244.3 Hz), 161.84 (d, J = 247.3 Hz); MS: m/z (%): 536 $[M]^+$; elemental analysis calcd (%) for $C_{35}H_{21}F_5$ (536.54): C 78.35, H 3.94; found C 78.13, H 3.95.

1,2,4-Tri(1-naphthyl)-1,3-cyclopentadiene (4n): M.p. 213–214 °C; ^{1}H NMR: δ = 4.27 (s, 2H), 7.13–7.91 (m, 19H), 7.98 (d, J = 8.5 Hz, 1H), 8.24–8.26 (m, 1H), 8.54–8.56 (m, 1H); MS: m/z (%): 444 $[M]^+$; elemental analysis calcd (%) for $C_{35}H_{24}$ (444.57): C 94.56, H 5.44; found C 94.04, H 5.48.

1,2,3,4,5-Penta(1-naphthyl)-1,3-cyclopentadiene (6n, mixture of rotamers): M.p. 248–250 °C; ^{1}H NMR: δ = 4.25–4.63 (m, 1H), 6.78–8.23 (m, 35H); MS: m/z (%): 696 $[M]^+$; elemental analysis calcd (%) for $C_{55}H_{36}$ (696.89): C 94.69, H 5.21; found C 94.18, H 5.26.

1,2,4-Tri(2,6-dimethylphenyl)-1,3-cyclopentadiene (4o): M.p. 182–183 °C; ^{1}H NMR: δ = 2.15 (s, 6H), 2.16 (s, 6H), 2.30 (s, 6H), 3.58 (s, 2H), 6.32 (s, 1H), 6.94–7.15 (m, 9H); ^{13}C NMR: δ = 20.89, 21.08, 21.29, 48.35, 126.56, 126.60, 126.77, 127.04, 127.54, 134.93, 136.16, 136.31, 136.33, 136.53, 137.62, 141.01, 141.63, 144.51; MS: m/z (%): 378 $[M]^+$; elemental analysis calcd (%) for $C_{29}H_{30}$ (378.56): C 92.01, H 7.99; found C 91.98, H 7.84.

1,2,3,4,5-Penta(4′-*n*-pentyl-1-biphenyl-4-yl)-1,3-cyclopentadiene (6p): M.p. 133–135 °C; ^{1}H NMR: δ = 0.86–0.89 (m, 15H), 1.31–1.32 (m, 20H), 1.61–1.62 (m, 10H), 2.62 (m, 10H), 5.20 (s, 1H), 7.10–7.51 (m, 40H); MS: m/z (%): 1176 $[M]^+$; elemental analysis calcd (%) for $C_{90}H_{96}$ (1176.74): C 91.78, H 8.22; found C 91.72, H 8.13.

1,2,3,4,5-Penta(4-(1,3-dioxolan-2-yl)phenyl)-1,3-cyclopentadiene (8a): Dioxolane **7a** (1.38 g, 6.00 mmol, 6 equiv) was coupled with cyclopentadiene (**3**) according to the general procedure; for detailed reaction conditions see Scheme 2. Thin-layer chromatography of the crude product: $R_f = 0.69$, 0.54, 0.27 (**8a**), 0.01 (petroleum ether/ethyl acetate 1:2, silica gel). Separation of the products by flash chromatography (petroleum ether/ethyl acetate 1:2, silica gel) gave 450 mg (56%) of **8a** as yellow solid with m.p. 248–250 °C; IR (film): $\tilde{\nu} = 3036$ (w), 2952 (w), 2883 (s), 1611 (w), 1512 (w), 1471 (w), 1418 (m), 1387 (s), 1307 (w), 1283 (w), 1220 (m), 1185 (w), 1083 (s), 1020 (s), 980 (s), 943 (s), 831 (s), 760 (w), 717 (w), 667 (w), 584 cm^{-1} (w); UV/Vis (acetonitrile): λ_{max} (lg ε) = 341 (4.17), 269 (4.35, sh), 246 nm (4.43); ^{1}H NMR: $\delta = 3.93-4.11$(m, 20H), 5.06 (s, 1H, C_5H), 5.63 (s, 2H), 5.68 (s, 1H), 5.70 (s, 2H), 6.92 ("d", "J" = 8.4 Hz, 4H), 6.99 ("d", "J" = 8.4 Hz, 4H), 7.12 ("d", "J" = 8.3 Hz, 4H), 7.17 ("d", "J" = 8.3 Hz, 2H), 7.23 ("d", "J" = 8.1 Hz, 4H), 7.26 ("d", "J" = 8.1 Hz, 2H); ^{13}C NMR: $\delta = 62.46$(d, C_5H), 65.16, 65.22, 65.24 (all t), 103.53, 103.57, 103.68 (all d), 126.00, 126.28, 126.83, 128.42, 128.98, 130.06 (all d), 135.69, 136.12, 136.36, 136.62, 138.55, 143.81, 146.66 (all s), one s is superimposed; MS (70 eV, 305 °C): m/z (%): 808 (18) $[M+2]^+$, 807 (57) $[M+1]^+$, 806 (100) $[M]^+$, 762 (18), 734 (12); elemental analysis calcd (%) for $C_{50}H_{46}O_{10}$ (806.9): C 74.43, H 5.75; found C 74.54, H 5.78.

1,2,3,4,5-Penta(4-formylphenyl)-1,3-cyclopentadiene (9a): Compound **8a** (485 mg, 0.60 mmol) and *p*-toluene sulfonic acid monohydrate (43.0 mg, 0.23 mmol) were dissolved in wet acetone (75 mL), and the mixture was refluxed for 20 h. The solvent was partially removed in vacuo to a final mixture volume of approximately 20 mL (50 °C and 400 mbar). Thin-layer chromatography: $R_f = 0.43$ (**9a**), 0.29, 0.00(petroleum ether/ethyl acetate 1:2, silica gel). Compound **9a** was isolated by flash chromatography (petroleum ether/ethyl acetate 1:2, silica gel) as a yellow foam (320 mg, 91%) with m.p. 115 °C after drying in vacuo at 75 °C at 0.2 mbar; IR (film): $\tilde{\nu} = 3047$ (w), 2971 (w), 2829 (w), 2735 (w), 1701 (s), 1601 (s), 1565 (m), 1509 (w), 1413 (w), 1388 (w), 1361 (w), 1306 (m), 1285 (w), 1210 (s), 1170 (s), 1127 (w), 1104 (w), 1079 (w), 1015 (w), 846 (s), 752 (w), 736 (w), 710 (w), 513 cm^{-1} (w); UV/Vis (acetonitrile): λ_{max} (lg ε) = 374 (4.22), 291 (4.38, sh), 256 (4.66), 198 nm (4.93); ^{1}H NMR: $\delta = 5.35$ (s, 1H, C_5H), 7.11 ("d", "J" = 8.3 Hz, 4H), 7.21 ("d", "J" = 8.1 Hz, 4H), 7.39 ("d", "J" = 8.1 Hz, 2H), 7.60 ("d", "J" = 8.3 Hz, 4H), 7.73 ("d", "J" = 8.3 Hz, 4H), 7.76 ("d", "J" = 8.2 Hz, 2H), 9.85 (s, 2H), 9.90 (s, 1H), 9.95 (s, 2H); ^{13}C NMR: $\delta = 62.85$(d, C_5H), 128.86, 129.34, 129.60, 129.80, 130.46, 130.61 (all d), 135.05, 135.54, 135.72, 140.17, 140.71, 143.14, 145.06, 147.63 (all s), 191.34 (s), 191.50 (s), one d is superimposed; MS (70 eV, 325 °C): m/z (%) = 588 (11) $[M+2]^+$, 587 (44) $[M+1]^+$, 586 (100) $[M]^+$, 762 (18), 734 (12); HRMS: calcd for $C_{40}H_{26}O_5$ 586.17803; found: 586.17980.

1,2,3,4,5-Penta(4-acetylphenyl)-1,3-cyclopentadiene (9b): Dioxolane **7b** (1.46 g, 6.00 mmol) was coupled with cyclopentadiene (**3**) according to the general procedure; for detailed reaction conditions see Scheme 2. After acidic workup the reaction directly led to the unprotected pentaarylketone **9b**. Thin-layer chromatography of the crude product: $R_f = 0.83$, 0.67, 0.36 (**9b**), 0.17, 0.06 (petroleum ether/ethyl acetate 1:2, silica gel). The products were separated by flash chromatography (petroleum ether/ethyl acetate 1:2, silica gel). Biphenyl and unreacted dioxolane **7b** were found only in marginal amounts as these compounds were removed during the drying of the product mixture in vacuo. The fraction with $R_f = 0.36$ was isolated by flash chromatography to yield pentaarylcyclopentadiene **9b** as a yellow solid (449 mg, 68%) after drying in vacuo at 100 °C at 0.5 mbar, its NMR spectroscopic data matched published data.[7d] ^{1}H NMR: $\delta = 2.47$ (s, 6H), 2.51 (s, 3H) 2.55 (s, 6H), 5.31 (s, 1H, C_5H), 7.04 ("d", "J" = 8.6 Hz, 4H), 7.14 ("d", "J" = 8.6 Hz, 4H), 7.31 ("d", "J" = 8.5 Hz, 2H), 7.65 ("d", "J" = 8.6 Hz, 4H), 7.79 ("d", "J" = 8.5 Hz, 4H), 7.81 ("d", "J" = 8.5 Hz, 2H); ^{13}C NMR: $\delta = 26.38$(q), 26.40 (q), 26.48 (q), 62.42 (d, C_5H), 128.11, 128.33, 128.38, 128.86, 129.09, 129.99 (all d), 135.47, 136.02, 136.14, 139.11, 139.71, 142.08, 144.74, 147.27 (all s), 197.31 (s), 197.49 (s), one s is superimposed.

1,2,3,4,5-Penta(4-(*N*-4-methylphenyl)aminomethylphenyl)-1,3-cyclopentadiene (10): A mixture of pentaaldehyde **9a** (58 mg, 0.10 mmol), *p*-toluidine (161 mg, 1.50 mmol) and *p*-TosOH monohydrate (5.0 mg, 30 µmol) in dry benzene (20 mL) was refluxed for 15 h with a Dean-Stark trap. After filtration through celite (2 g) with dry dichloromethane (30 mL) as eluent the solvent was removed in vacuo. The residue was treated at 100 °C and 0.3 mbar to remove excess *p*-toluidine by sublimation. The remaining crude product, an orange-red solid (110 mg), was identified by NMR spectroscopy as slightly impure pentakisimine; ^{1}H NMR: $\delta = 2.33$ (s, 6H), 2.34 (s, 3H), 2.36 (s, 6H), 7.20–6.95 (m, 28H), 7.35 ("d", "J" = 8.2 Hz, 2H), 7.59 ("d", "J" = 8.55, 4H), 7.76–7.72 (m, 6H), 8.30 (s, 2H), 8.35 (s, 1H,), 8.40 (s, 2H); ^{13}C NMR: $\delta = 21.01$ (q), 21.04 (q), 62.65 (d), 120.79, 120.84, 128.43, 128.68, 128.86, 129.33, 129.39, 129.74, 129.78, 130.47 (all d), 134.85, 135.29, 135.33, 135.76, 135.80, 135.89, 137.96, 138.45, 140.80, 144.75, 147.23, 149.38, 149.42, 149.47 (all s), 158.88, 159.09, 159.13 (all d), one q and two d are superimposed.

Since the final purification of the pentakisimine by column chromatography or by crystallization proved difficult, the full characterization was performed on the reduction product **10**. Therefore, a solution of crude pentakisimine in dry THF (5 mL) was added dropwise at room temperature to a solution of $LiAlH_4$ (228 mg, 6.00 mmol)in dry THF(5 mL). After stirring for 2 h the reaction mixture was hydrolyzed with a saturated aqueous solution of ammonium chloride(50 mL) and washed with brine (50 mL). The combined water layers were extracted three times with ethyl acetate(30 mL), the combined organic extracts were then filtered through celite (2 g), and the solvent was removed in vacuo. Thin-layer chromatography: $R_f = 0.46$, 0.40 (**10**), 0.30, 0.13, 0.00 (hexanes/ethyl acetate 2:1, silica gel). The fraction with $R_f = 0.40$ was isolated by flash chromatography to yield pentakisamine **10** (45 mg, 43%) as a yellow solid. M.p. 93–96 °C; IR (film): $\tilde{\nu} = 3413$ (s, br, -NH), 3018 (s), 2917 (s), 2862 (s), 1616 (s), 1522 (s), 1466 (m), 1406 (m), 1321 (s), 1301 (m), 1249 (m), 1182 (w), 1126 (w), 1019 (w), 807 cm^{-1} (m); UV/Vis (acetonitrile): λ_{max} (lg ε) = 346 (4.18), 306 (4.33, sh), 251 nm (4.94); ^{1}H NMR: $\delta = 2.21$ and 2.22 (both s, overall 15H), 3.76 (s, br, 5H), 4.11 (s, 4H), 4.14 (s, 2H), 4.21 (s, 4H), 5.04 (s, 1H), 6.50 ("dd", "J" = 15.3, 8.5 Hz, 10H), 7.00–6.91 (m, 22H), 7.11 ("d", "J" = 8.3 Hz, 4H), 7.14 ("d", "J" = 2.7 Hz, 4H); ^{13}C NMR: $\delta = 20.41$ (q), 20.43 (q), 48.37, 48.50, 48.55 (all t), 61.99 (d), 112.93, 113.00, 113.11 (all d), 126.70 (s), 126.76 (s), 127.00, 127.15, 127.99, 128.58, 129.07, 129.70, 129.72, 130.27 (all d), 134.62, 135.06, 137.12, 137.54, 137.67, 138.01, 143.86, 145.97, 146.00, 146.03, 146.10 (all s), one q, one d and one s are superimposed; MS (70 eV, 350 °C): m/z (%): 1041(1.9) $[M]^+$, 936 (2.7), 827 (11), 723 (25), 618 (21), 515 (10), 361 (16), 106 (100); elemental analysis calcd (%) for $C_{75}H_{71}N_5$ (1042.4): C 86.42, H 6.87, N 6.72; found C 86.37, H 6.85, N 6.63.

Palladium-catalyzed cross-coupling reactions of aryl halides (2) with substituted or annelated cyclopentadienes; typical example: 1-(4-anisyl)-2,5-di(4-chlorophenyl)-3,4-diphenylcyclopentadiene (12b): A mixture of 1-(4-anisyl)-3,4-diphenylcyclopentadiene (**11b**, synthesized by an analogous procedure to that in ref. [21], 649 mg, 2.00 mmol), 4-chlorobromobenzene (**2q**) (575 mg,3.00 mmol), Cs_2CO_3 (2.61 g, 8.00 mmol), $[Pd(OAc)_2]$ (11 mg, 50 µmol), and tri-*tert*-butylphosphine(39.1 mg, 200 µmol) in DMF (10 mL) was heated under argon in a screw-cap tube for 68 h at 140 °C. After cooling to room temperature CH_2Cl_2 (30 mL) was added and the mixture was filtered through silica gel (5 g) with CH_2Cl_2 (50 mL) as eluent. The solvent was evaporated at 50 °C and 15 mbar, the residue was subsequently dried in vacuo at 50 °C and 0.5 mbar and finally separated by flash chromatography on silica gel. Thin-layer chromatography: $R_f =$ 0.51 (4,4′-dichlorobiphenyl), 0.31–0.29 (silica, petroleum ether/ethyl acetate 25:1). The fraction with $R_f = 0.31-0.29$ was isolated to give **12b** (533 mg, 49%, mixture of three double bond isomers) as a yellow solid. M.p. 90–95 °C; IR (KBr): $\tilde{\nu} = 3060$ (w), 2952 (w), 1606 (w), 1508 (s), 1487 (s), 1289 (w), 1249 (s), 1177 (m), 1091 (m), 1032 (w), 1014 (w), 830 (m), 698 cm^{-1} (s); UV/Vis (acetonitrile): λ_{max} (lg ε) = 344 (4.08), 277 (4.24, sh), 250 (4.37, sh), 226 nm (4.47, sh); ^{1}H NMR: $\delta = 3.69$, 3.72 and 3.76 (s, 3H, OCH_3), 4.94, 4.98 and 5.00 (s, 1H, C_5H), 6.60–6.70 (m, 2H), 6.84–7.16 (m, 20H); MS (70 eV; 250 °C); m/z (%): 548 (19) $[M+4]^+$, 547 (33) $[M+3]^+$, 546 (78) $[M+2]^+$, 545 (51) $[M+1]^+$, 544 (100) $[M]^+$; elemental analysis calcd (%) for $C_{36}H_{26}Cl_2O$ (545.5): C 79.26, H 4.80; found C 79.18, H 4.75.

2,5-Di(4-chlorophenyl)-1,3,4-triphenyl-1,3-cyclopentadiene (12a, mixture of double bond isomers): M.p. 104–108 °C; ^{1}H NMR: $\delta = 4.99-5.04$ (m, 1H), 6.86–7.19 (m, 23H); MS: m/z (%): 514, 516 $[M]^+$; elemental analysis calcd (%) for $C_{35}H_{24}Cl_2$ (515.48): C 81.55, H 4.69; found C 81.35, H 4.76.

1-(4-Anisyl)-2,5-di(4-(1,3-dioxolan-2-yl)phenyl)-3,4-diphenylcyclopentadiene (12c, mixture of double bond isomers): M.p. 80–83 °C; ^{1}H NMR: $\delta = 3.66$, 3.70 and 3.73 (s, 3H, OCH_3), 3.95–4.11 (m, 8H, O-CH_2CH_2-O), 5.02, 5.05 and 5.08 (s, 1H, C_5H), 5.62, 5.66 and 5.70 (s, 1H, O-C*H*-O), 6.56–6.65 (m, 2H, *o*-Ansiyl-*H*), 7.29–6.85 (m, 20H); MS: m/z (%): 622 (11), 621 (46) $[M+1]^+$, 620 (100) $[M]^+$; elemental analysis calcd (%) for $C_{42}H_{36}O_5$ (620.74): C 81.27, H 5.85; found C 81.19 H 5.92.

0947-6539/00/0618-3432 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 18

1,4-Di(4-chlorophenyl)-2,3,5-tri(3,5-dimethylphenyl)-1,3-cyclopentadiene (12d, mixture of double bond isomers): M.p. 172–175 °C; ^{1}H NMR: δ = 1.90–2.24 (m, 18H), 4.99–5.02 (m, 1H), 6.50–7.27 (m, 17H); MS: *m*/*z* (%): 589, 600 $[M]^+$; elemental analysis calcd (%) for $C_{41}H_{36}Cl_2$ (599.64): C 82.12, H 6.05; found C 82.00, H 6.47.

1,1,3-Triphenylindene (15a): M.p. 134–135 °C (Lit.: 132–134 °C[24]); ^{1}H NMR: δ = 6.82 (s, 1H), 7.20–7.32 (m, 13H), 7.35–7.46 (m, 3H), 7.56 (d, J = 7.3 Hz, 1H), 7.64 (d, J = 7.1 Hz, 2H); ^{13}C NMR: δ = 65.62, 121.22, 125.57, 125.71, 126.55, 126.82, 127.61, 127.72, 128.17, 128.42, 135.12, 141.47, 142.28, 143.54, 150.94; MS: *m*/*z* (%): 344 $[M]^+$.

1,1,3-Tri(4-methylphenyl)indene (15b): M.p. 63–64 °C; ^{1}H NMR: δ = 2.30 (s, 6H), 2.40 (s, 3H), 6.75 (s, 1H), 7.04 (d, J = 8.1 Hz, 4H), 7.17 (d, J = 8.1 Hz, 4H), 7.20–7.29 (m, 4H), 7.37 (d, J = 7.3 Hz, 1H), 7.52–7.54 (m, 3H); ^{13}C NMR: δ = 21.13, 21.43, 64.88, 121.13, 125.37, 125.55, 126.62, 127.48, 127.59, 128.81, 129.05, 132.33, 135.98, 137.40, 140.72, 141.23, 141.78, 142.39, 151.33; MS: *m*/*z* (%): 386 $[M]^+$; elemental analysis calcd (%) for $C_{30}H_{26}$ (386.53): C 93.22, H 6.78; found C 92.83, H 6.81.

1,1,3-Tri(4-methoxyphenyl)indene (15f): M.p. 70 °C; ^{1}H NMR: δ = 3.75 (s, 6H), 3.85 (s, 3H), 6.71 (s, 1H), 6.75–6.79 (m, 4H), 6.95–6.99 (m, 2H), 7.18–7.37 (m, 8H), 7.52–7.59 (m, 3H); ^{13}C NMR: δ = 55.22, 55.35, 64.07, 113.64, 113.99, 121.23, 125.44, 125.68, 126.77, 127.92, 128.84, 128.91, 136.01, 141.06, 141.31, 142.56, 151.87, 158.33, 159.36; MS: *m*/*z* (%): 434 $[M]^+$; elemental analysis calcd (%) for $C_{30}H_{26}O_3$ (434.53): C82.92, H 6.03; found C 82.82, H 6.01.

1,1,3-Tri(3,5-dimethylphenyl)indene (15n): M.p. 145–146 °C; ^{1}H NMR: δ = 2.22 (s, 12H), 2.37 (s, 6H), 6.76 (s, 1H), 6.85–6.87 (m, 5H), 7.01 (s, 1H), 7.20–7.31 (m, 4H), 7.39 (d, J = 7.3 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H); ^{13}C NMR: δ = 21.51, 21.60, 65.37, 121.15, 125.39, 125.50, 125.56, 126.52, 128.18, 129.29, 135.19, 137.38, 137.87, 141.70, 141.83, 142.41, 143.65, 151.11; MS: *m*/*z* (%): 428 $[M]^+$; elemental analysis calcd (%) for $C_{33}H_{32}$ (428.61): C 92.47, H 7.53, found C 92.22, H 7.53.

1,3-Di(4-methylphenyl)-2-phenylindene (17b): M.p. 146–147 °C; ^{1}H NMR: δ = 2.23 (s, 3H), 2.40 (s, 3H), 5.06 (s, 1H), 6.97–7.08 (m, 7H), 7.11–7.16 (m, 3H), 7.20–7.31 (m, 7H); ^{13}C NMR: δ = 21.23, 21.53, 57.64, 120.34, 123.67, 125.44, 126.38, 126.60, 127.63, 127.85, 129.15, 129.21, 129.24, 132.39, 135.57, 135.83, 136.54, 136.86, 140.42, 144.88, 145.12, 148.18; MS: *m*/*z* (%): 372 $[M]^+$; elemental analysis calcd (%) for $C_{29}H_{24}$ (372.50): C 93.51, H 6.49; found C 93.43, H 6.39.

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