New Aspects of Synthesis and Properties of Arylated Cyclopentadienes

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Abstract: The multifold palladium-catalysed arylation is a suitable method for the synthesis of sterically crowded cyclopentadienes bearing up to five *ortho*-substituted aryl groups. A maximum of four mesitylene groups can be introduced. While penta(*para*-xylyl)cyclopentadiene and pentakis(2-chlorophenyl)-cyclopentadiene exhibit at least six rotamers in the proton NMR spectrum, only two rotamers are registered for the tetra(2-chlorophenyl)cyclopentadiene; the all-*trans* isomer is identified as the major one both by spectroscopy and by semi-empirical calculations.

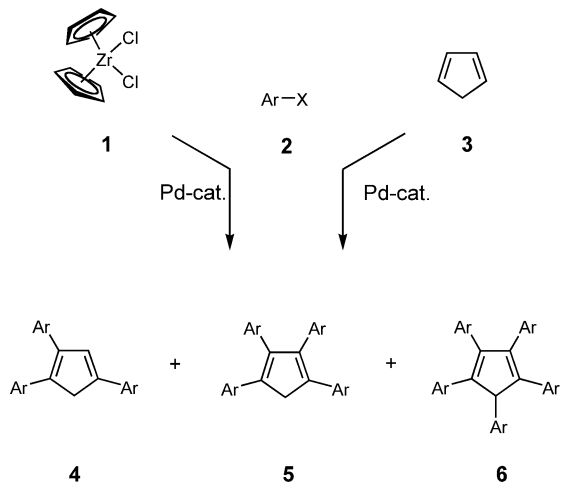
Keywords: CH activation; cyclopentadienes; palladium catalysis; rotamers

General Remarks on C–H Activation

Since the activation of C–H bonds is a fundamental task in organic synthesis, regularly facing enormous problems concerning reactivity and selectivity but simultaneously promising substantial benefits, C–H activation presumably will remain a current topic of chemistry forever. Occasionally its a matter of debate[1] which research earns the ennobling title "C–H activation": should this term be restricted to unactivated sp^3-centered C–H bonds or should aromatic C–H bonds be included? What about the role of transition metals in catalysed processes: must the C–H activation take place *via* a preceding agostic interaction or is it sufficient when an electrophilic transition metal activates the C–H bond indirectly for the deprotonation by a base? If a base is involved: does it have to be a "superbase" or isn't every deprotonation a "C–H activation"? We plead for using this term in a very general sense, simply because of its fundamental character and because there is neither a convincing definition for a borderline nor the necessity for it.

Introduction

During our studies on the arylation of electron-rich cyclopentadiene derivatives, we observed a range of different types of C–H activation, from aromatic to allylic C–H bonds, from indirect activation by transition metals to apparently simple deprotonation, although all reactions were closely related. For the palladium-catalysed arylation of azulene in the electron-rich 1-position presumably the attack of the electrophilic aryl-palladium halide is the initial step;[2] in analogy to an electrophilic aromatic substitution the C–H bond is broken by the subsequent deprotonation. The final C–C bond formation is then the result of a reductive elimination. In the case of the multifold arylation of metallocenes[3] such as zirconocene dichloride (**1**) – giving rise to arylated cyclopentadienes[4] **4**, **5** and **6** – we circumvent the first C–H activation by applying an already metallated species; for the additional arylations we assume intermediary cyclopentadienes, which are



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

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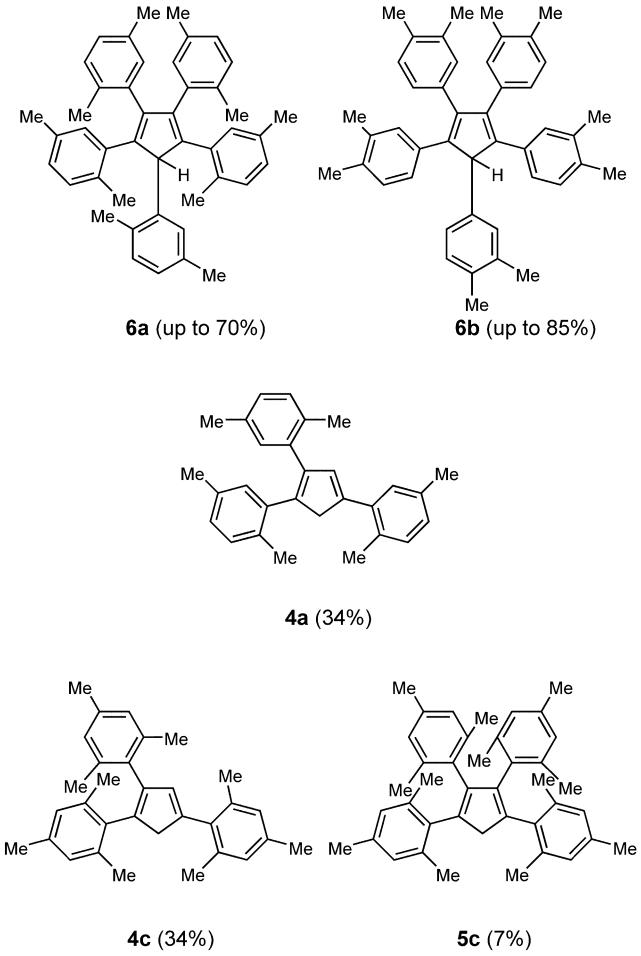
deprotonated by the present base, a process that reminds one of the arylation of other soft nucleophiles.[5] the multifold arylation is also successful when starting from cyclopentadiene (**3**), however, because of the elevated reaction temperatures and the low boiling point of **3** the reaction is preferentially performed in a sealed tube.[3b]

The product ratio of the multifold arylation, whether starting from **1** or from **3**, depends on several factors, for instance, on the polarity of the solvent and on the electronic properties and on the bulkiness of the aryl halide **2**. Generally electron-withdrawing substituents on the aryl halide **2** somewhat favour the tetraaryl-substituted product **5**. This is in accord with the mechanistic considerations outlined above: in the key step an electrophilic arylpalladium halide is interacting with a cyclopentadienyl anion; presumably the Pd catalyst is not involved in the activation of the C–H bond, which is interpreted as an apparently simple deprotonation with caesium carbonate as base.

Obviously both the deprotonation and the subsequent arylation can take place in sterically very hindered positions: rather crowded pentaarylcyclopentadienes like the pentaxylyl derivatives **6a** and **6b** are accessible in surprisingly good yield.[3b] In the following we wish to report on the influence of phosphine ligands on the arylation with sterically demanding aryl halides and on the multifold introduction of mesityl- and of 2-chlorophenyl groups on cyclopentadiene **3**.



Scheme 2. Some especially crowded cyclopentadienes.

Results and Discussion

For the arylation with *meta*- or *para*-substituted aryl halides we recommend tris(*tert*-butyl)phosphine[6] as an appropriate ligand, mainly in order to avoid ligand scrambling,[7] which is occasionally observed with triphenylphosphine, causing minor impurities of phenyl-substituted cyclopentadienes in the crude product. In the case of sterically demanding aryl halides the bulky tris(*tert*-butyl)phosphine regularly might not be the ligand of choice. For instance, with tris(*tert*-butyl)phosphine the reaction of cyclopentadiene (**3**) with 2,5-dimethylbromobenzene (**2a**) was rather sluggish, resulting in mainly tetraarylated product **5a** after 19 h (Table 1, entry 1). A yield above 60% of the pentaarylated product **6a** was obtained with prolonged reaction time (Table 1, entry 2), whereas with triphenylphosphine the process is clearly faster (Table 1, entry 3; 65% yield after column chromatography and crystallisation). The same trend – a faster reaction in the case of triphenylphosphine – was also observed in the reaction of zirconocene dichloride (**1**) with **2a**.[3b] In the case of tris(*ortho*-tolyl)phosphine[8] as sterically demanding ligand the arylation of cyclopentadiene (**3**) stopped at the stage of the triarylated product **4a** (Table 1, entry 4), in contrast to the pentaarylated cyclopentadiene **6a** with no observable rotamers according to the ^{1}H NMR at room temperature. For this rather sluggish reaction we added small amounts of iron powder, a catalyst frequently used for the retro-Diels–Alder reaction of the cyclopentadiene dimer, also with the idea to reverse a possible dimerisation of mono- or diarylated intermediates.

2,4,6-Trimethylbromobenzene (**2c**) is certainly the bulkiest aryl halide we have hitherto applied in the multifold arylation: with tris(*ortho*-tolyl)phosphine no arylation of cyclopentadiene takes place, but when using triphenylphosphine as ligand the main product is the triarylated cyclopentadiene **4c** accompanied by a substantial amount of the tetraarylated product **5c**, whereas the pentaarylated product could not be detected. Because of the symmetry of **5c** of course no rotamers are observed (in contrast to **5d**, see below).

The arylation of cyclopentadiene (**3**) with 2-chlorobromobenzene (**2d**, X = Br) using tris(*tert*-butyl)phosphine as ligand leads to the tetra- **5d** and the pentaarylated product **6d**, both isolated with 17–18% yield. With the less reactive *ortho*-dichlorobenzene (**2d**, X = Cl) the process stops on the stage of the triarylated species **4d**, which then can be further arylated with 2-chlorobromobenzene (**2d**, X = Br).

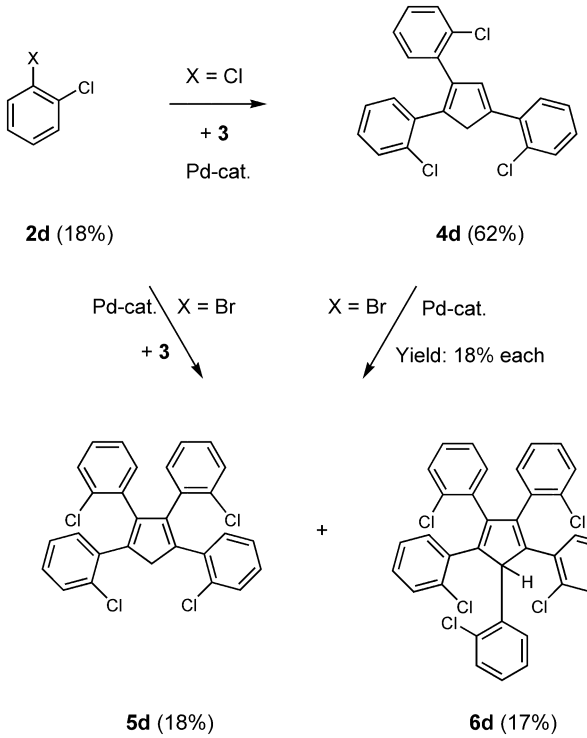
Table 1. Arylation of cyclopentadiene (**3**) with sterically demanding aryl halides **2**.

Entry	**2:** R; X; [mmol]	$Pd(OAc)_2$ [mmol]	PR_3 R; [mmol]	t [h]	T [°C]	Products: [% yield][a]	**4**	**5**	**6**
1	**2a**: 2,5-$Me_2C_6H_3$; Br; 6	0.05	*t*-Bu; 0.12	19	140		–	52	15[3b]
2	**2a**: 2,5-$Me_2C_6H_3$; Br; 6	0.05	*t*-Bu; 0.12	34	140		–	–	62[3b]
3	**2a**: 2,5-$Me_2C_6H_3$; Br; 6	0.05	Ph; 0.20	23	140		–	–	65
4	**2a**: 2,5-$Me_2C_6H_3$; Br; 6	0.05	2-MeC_6H_4; 0.10	42	140		34	–	–
5	**2c**: 2,4,6-$Me_3C_6H_2$; Br; 6	0.05	Ph; 0.10	64	140		34	7	–
6	**2d**: 2-ClC_6H_4; Br; 6	0.75	*t*-Bu; 0.60	42	140		–	18	17[3b]
7	**2d**: 2-ClC_6H_4; Cl; 30	1.50[b]	*t*-Bu; 0.60	65	160		62	–	–

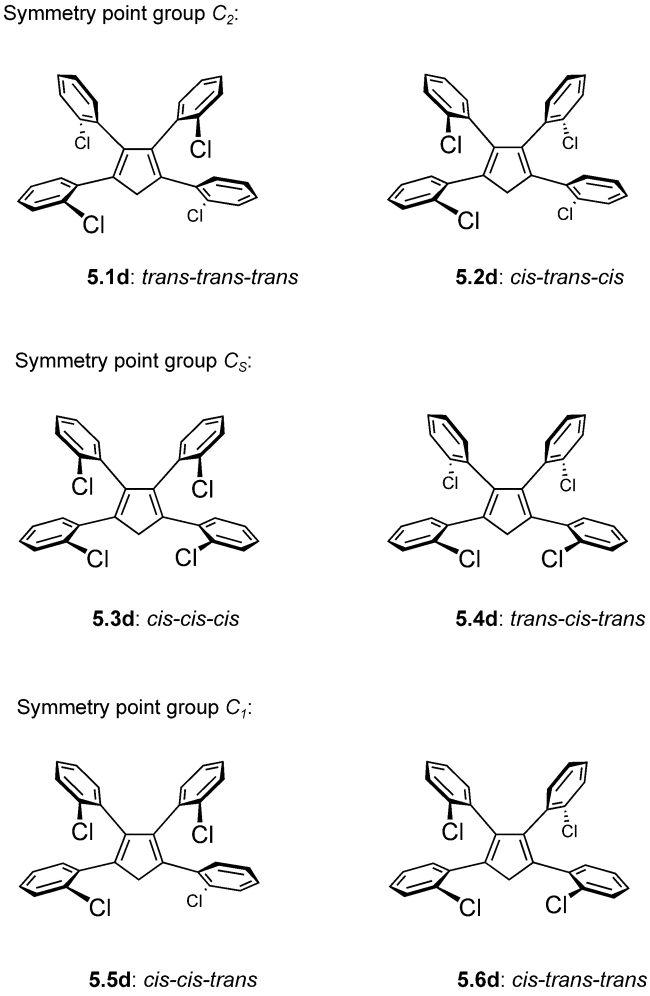
[a] Isolated yield based on the amount of cyclopentadiene used (in general 1 mmol).
[b] This reaction was performed on a 3 mmol scale.

Surprisingly, the ^1H and the ^{13}C NMR spectra of **5d** clearly show the presence of two isomers: the proton decoupled carbon NMR shows two sets of 15 chemically different carbon atoms, revealing that both isomers with 29 carbon atoms each must have a high degree of symmetry. In the proton NMR two methylene groups are registered by their diagnostic signals, a singlet at 4.21 ppm and an AB signal with $\delta_A = 4.11$ ppm, $\delta_B =$ 4.43 ppm and a geminal coupling constant of 24.3 Hz. The data is best interpreted by the assumption of two rotamers[9] in the ratio 100:85, the major rotamer with the methylene protons in symmetrical positions.

In order to identify the observed rotamers we have calculated the relative energies of the whole set of six possible rotamers (ordered in Scheme 4 according to symmetry point groups C_2, C_S and C_1; of course ten rotamers if enantiomers are taken into account) and some selected rotation barriers by semi-empirical methods (both AM1 and PM3). Clearly the all-*cis*-rotamer **5.3d** is thermodynamically disfavoured compared to the C_2-symmetric all-*trans*-rotamer **5.1d** ($\delta\Delta H$ ~1.7 kcal/mol). The latter represents the thermodynamic minimum, about 0.8 kcal/mol favoured compared to the also



Scheme 3. 2-Chlorophenyl-substituted cyclopentadienes.



Scheme 4. Rotamers of tetrakis(2-chlorophenyl)-cyclopentadiene **5d**.

C_2-symmetric *cis-trans-cis*-rotamer **5.2d**. Since the C_2-symmetry is in accord with the singlet of the methylene protons in the ^{1}H NMR spectrum, the all-*trans*-rotamer **5.1d** is identified as the major one. Also in the case of the tetrakis(2-methylphenyl)cyclopentadienone the all-*trans*-rotamer was reported[10] to be the major one, profiting from the complete absence of αβ*cis*- and ββ*cis*-interaction of the *ortho*-substituents.

The *cis-cis-trans*-rotamer **5.5d** and the *cis-trans-trans*-rotamer **5.6d** are both unsymmetric and therefore ruled out by the ^{13}C NMR. The C_S-symmetric *trans-cis-trans*-rotamer **5.4d** is the only remaining candidate for the second observed isomer: the calculated energy difference of +0.6 kcal/mol compared to **5.1d** is somewhat higher than anticipated by the observed ratio of **5.1d** and **5.4d**; however, the calculation predicts, that the transformation between **5.1d** and **5.4d** should be slow on the NMR time scale (one barrier > 18 kcal/mol), while the equilibrium of **5.1d** with **5.2d** and **5.6d** is a relatively fast process (calculated barrier ~4 kcal/mol), since the chloro atoms of the 2-chlorophenylgroups in the 1- and 4-position can rather easily pass the methylene group.

In comparison, for pentakis(2-chlorophenyl)cyclopentadiene (**6d**) the additional aryl substituent generally reduces symmetry and increases the number of principally possible rotamers by the factor 4. In the proton NMR of **6d** at least six preferred rotamers are registered by the singlets of their methine protons, the same pattern was found before for the pentakis(2,5-dimethylphenyl)-substituted cyclopentadiene **6a** (three major and three minor rotamers).[2b] Surprisingly, the pentakis(3,4-dimethylphenyl)-substituted derivative **6b** although lacking substituents in the 2′-positions also exhibits three major rotamers in the ^{1}H NMR; obviously two adjacent methyl groups slow down the rotation, since for the pentakis(3-methylphenyl)cyclopentadiene with only one methyl group on each benzene ring only a single isomer is registered.

Initial tests for the synthesis of bowl-shaped molecules from **6d** by flash vacuum pyrolysis failed: according to mass spectra of the crude product the cyclising dehydrochlorination takes place three times before the fifth aryl group is eliminated, a reaction pathway which obviously profits from the stability of an intermediary tetraarylcyclopentadienyl radical.

We are currently investigating the synthesis of various extended π-systems by multifold palladium-catalysed arylation, such as overcrowded dihydropentalenes and pentaarylcyclopentadienyl-substituted porphyrins.

Experimental Section

General Remarks

M.p. (uncorrected): Reichert Thermovar. IR: Perkin Elmer 841. NMR: Bruker DRX 500, Bruker DRX 400; ^{1}H NMR spectra (500 MHz or 400 MHz) were recorded in $CDCl_3$ or with TMS as the internal standard. ^{13}C NMR spectra (125.8 MHz or 100.6 MHz) were measured by using $CDCl_3$ as the solvent and the internal standard. MS: MAT 700 ITD (70 eV) and Varian MAT 311 A. For analytical TLC precoated plastic sheets "POLYGRAM SIL G/UV254" from "Macherey-Nagel" were used.

General Procedure for the Palladium-Catalysed Arylation of Cyclopentadiene (3)

A mixture of 66 mg (1.0 mmol) of cyclopentadiene (**3**), aryl halide (**2**, generally 6.00 mmol), caesium carbonate (1.96 g, 6.00 mmol), palladium acetate (50 μmol), phosphine ligand (2 equiv. based on the Pd catalyst) and 10 mL of DMF was heated under argon in a screw-capped tube for 2 – 3 d. After cooling to room temperature CH_2Cl_2 (50 mL) and *p*-toluenesulfonic 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 under vacuum at 50 °C and 15 mbar, the residue dried under vacuum at 50 °C and 0.5 mbar and separated by flash chromatography on silica gel.

1,2,4-Tris(2,5-dimethylphenyl)-cyclopenta-1.3-diene (4a)

1.11 g (6.00 mmol) of l-bromo-2,5-dimethylbenzene (**2a**, X = Br) were coupled with cyclopentadiene (**3**) according to the general procedure: 11.2 mg (50.0 μmol) $Pd(OAc)_2$ and 30.4 mg (100 μmol) tris(2-methylphenyl)phosphine as catalyst system, 42 h at 140 °C. The colour of the reaction mixture was dark purple after 2 min and changed to blue at the end of the reaction. Isolation of the product was achieved by flash chromatography (silica, 50:1, PE/EtOAc, R_f = 0.29) and subsequent drying under vacuum (125 °C/0.3 mbar) afforded triarylated product **4a** as a yellow sticky oil; yield: 129 mg (34%). IR (KBr): $\tilde{\nu}$ = 3016 (s, sh), 3948 (s, sh), 2921 (s), 2864 (m, sh), 2731 (w), 1888 (w, br), 1754 (w, br), 1609 (m), 1571 (w), 1499 (s), 1452 (s), 1373 (m), 1221 (w), 1133 (w), 1036 (m), 949 (w), 898 (w), 854 (w), 808 (s), 726 cm^{-1} (w); UV/VIS (acetonitrile): λ_{max} (log ε) = 215 nm (4.08, br, sh), 241 nm (4.20, sh). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.94 (s, 3H), 2.14 (s, 3H), 2.18 (s, 3H), 2.27 (s, 3H), 2.33 (s, 3H), 2.47 (s, 3H), 3.87 (s, 2H, 5-H), 6.75 (s, 1H, 3-H), 7.03 – 6.87 (m, 7H), 7.12 ("d", "*J*" = 7.8 Hz, 1H), 7.25 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 19.95, 19.96, 20.90, 20.97, 21.05, 22.13 (all q), 49.13 (t, C-5), 127.28, 127.48, 127.77, 128.88, 130.14, 130.15, 130.43, 131.24 (all d), 132.25, 132.51, 132.77, 134.52, 134.74, 135.26 (all s), 135.27 (d), 135.77, 137.02, 137.21, 141.10, 142.94, 144.48 (all s); MS (70 eV,125 °C): *m/z* (%) = 379 (32), 378 (100) [M$^+$], 363 (18); elemental analysis: calcd. for $C_{29}H_{30}$ (378.56 g/mol): C 92.01, H 7.99; found: C 91.94, H 7.97.

1,2,4-Tris(2,4,6-trimethylphenyl)-cyclopenta-1.3-diene (4c) and 1,2,3,4-Tetrakis(2,4,6-trimethylphenyl)-cyclopenta-1.3-diene (5c)

1.20 g (6.00 mmol) of l-bromo-2,4,6-trimethylbenzene (**2c**, X = Br) were coupled with cyclopentadiene (**3**) according to

the general procedure: 11.2 mg (50.0 μmol) $Pd(OAc)_2$ and 26.2 mg (100 μmol) PPh_3 as catalyst system, 64 h at 140 °C. The colour of the reaction mixture was dark purple. Isolation of the products was achieved by flash chromatography (silica, 25:1, PE/EtOAc) giving a mixture of **4c** and **5c** with $R_f = 0.32 - 0.29$, which was further separated by Kugelrohr distillation at 235 °C /0.3 mbar, affording the more volatile triarylated product **4c** as a yellow solid with mp 68 – 71 °C; yield: 116 mg (34%). The residue was crystallised from ethyl acetate to give the tetraarylated product **5c** as a slightly coloured solid with mp 317 °C; yield: 39 mg (7%).

Spectroscopic data of **4c**: IR (KBr): $\tilde{\nu} = 2950$ (s, br), 2917 (s, sh), 2856 (m), 1725 (w), 1609 (s), 1563 (s), 1476 (s, br), 1437 (s, br), 1371 (s), 1300 (w, sh), 1265 (w, sh), 1238 (m), 1211 (m, sh), 1195 (s), 1159 (m), 1103 (w), 1031 (s), 1014 (s, sh), 961 (w), 935 (w), 891 (s), 849 (s), 732 (s), 705 (w, sh), 687 (w), 641 cm^{-1} (s); UV/VIS (acetonitrile): λ_{max} (log ε) = 278 (3.98, br, sh), 245 nm (4.18, sh); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.12 (2 s, overall 12H), 2.21 (2 s, overall 6H), 2.26 (s, 6H), 2.30 (s, 3H), 3.52 (d, $J = 1.1$ Hz, 2H, 5-H), 6.27 (t, $J = 1.1$ Hz, 1H, 3-H), 6.77 (s, 4H), 6.93 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 20.67, 20.86, 20.92, 20.94, 21.02, 21.07 (all q), 48.57 (t, C-5), 128.03 (d), 128.57 (d), 133.65, 134.00, 135.02 (all s), 135.52 (d), 136.12, 136.13, 136.22, 136.39, 136.49, 136.51, 141.10, 141.79, 144.46 (all s); MS (70 eV,115 °C): *m/z* (%) = 421 (34), 420 (100) [M^+], 405 (12); elemental analysis: calcd. for $C_{32}H_{36}$ (420.64 g/mol): C 91.39, H 8.61; found: C 91.28, H 8.55.

Spectroscopic data of **5c**: IR (KBr): $\tilde{\nu} = 2981$ (s, sh), 2957 (s, sh), 2919 (s), 2859 (m, sh), 1610 (m), 1480 (s), 1441 (s), 1370 (s), 1265 (w), 1202 (m), 1161 (w), 1100 (w), 1030 (m), 882 (w), 853 (s), 735 cm^{-1} (m); UV/VIS (acetonitrile): λ_{max} (log ε) = 299 (3.86, br, sh), 246 nm (4.44); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.26 (s, 12H), 2.30 (s, 18H), 2.21 (s, 6H), 3.72 (s, 2H), 6.52 (s, 4H), 6.76 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 20.90 20.91, 21.34, 21.35 (all q), 49.12 (t, C-5). 128.37 (d), 128.62 (d), 132.84, 134.35, 135.54, 136.05, 136.44, 136.84,142.53, 145.31 (all s); MS (70 eV, 205 °C): *m/z* (%) = 539 (45), 538 (100) [M^+]; elemental analysis: calcd. for $C_{41}H_{46}$ (538.82 g/mol): C 91.37, H 8.63; found: C 91.29, H 8.58.

1,2,3,4-Tetrakis(2-chlorophenyl)-cyclopenta-1.3-diene (5d) and 1,2,3,4-Pentakis(2-chlorophenyl)-cyclopenta-1.3-diene (6d)

1.15 g (6.00 mmol) of l-bromo-2-chlorobenzene (**2d**, X = Br) were coupled with cyclopentadiene (**3**) according to the general procedure: 16.8 mg (75.0 μmol) $Pd(OAc)_2$ and 121 mg (600 μmol) P*tert*Bu_3 as catalyst system, 42 h at 140 °C. The colour of the reaction mixture was black. Isolation of the products was achieved by flash chromatography (silica, 25:1, PE/EtOAc) and crystallised from dichloromethane/hexanes; 1st fraction with $R_f = 0.28$: the tetraarylated product **5d** as slightly yellow crystals with mp 154 – 156 °C; yield: 90 mg (18%). 2nd fraction with $R_f = 0.25$: the pentaarylated product **6d** as a colourless powder with mp 299 – 300 °C; yield: 105 mg (17%).

Spectroscopic data of **5d**: IR (KBr): $\tilde{\nu} = 3058$ (w), 1591 (w), 1561 (w), 1476 (m, sh), 1464 (m), 1432 (m), 1369 (w), 1257 (w), 1199 (w), 1125 (w), 1072 (w), 1054 (w), 1038 (s), 944 (w), 750 (s), 737 (m, sh), 710 cm^{-1} (m); UV/VIS (acetonitrile): λ_{max} (log ε) = 309 nm (3.86, sh), 239 (4.27), 213 nm (4.63, sh); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.10 (d, $J = 24.3$ Hz, 1H, rotamer A), 4.21 (s, 2H, rotamer B), 4.42 (d, $J = 24.3$ Hz, 1H, rotamer A), 6.96 – 7.32 (m, 16H, Aryl-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 47.54 (t, C-5, rotamer A), 47.68 (t, C-5, rotamer B), 125.84, 125.94, 126.28, 126.31, 128.32, 128.34, 128.36, 128.46, 128.74, 129.40, 129.57, 129.75, 131.42, 131.56, 131.60, 132.34 (all d), 133.22, 133.39, 133.48, 134.15, 134.54, 134.75, 135.93, 136.10, 142.09, 142.36, 142.75, 143.34 (all s); MS (70 eV,160 °C): *m/z* (%) = 514(1), 513 (4), 512 (13), 511 (14), 510 (53), 509 (30), 508 (100), 507 (23), 506 (75), 438 (13), 436 (18), 401 (14), 399 (10), 365 (12), 364 (14), 363 (20), 361 (12), 359 (13), 325 (13), 289 (29), 183 (14), 182 (24), 181 (29), 180(17); elemental analysis: calcd. for $C_{29}H_{18}Cl_4$ (508.31 g/mol): C 68.53, H 3.57; found: C 68.61, H 3.55.

Spectroscopic data of **6d**: IR (KBr): $\tilde{\nu} = 3182$ (w), 2945 (w), 2863 (w), 1473 (m), 1464 (m, sh), 1433 (m), 1122 (w), 1060 (w), 1051 (w, sh), 1034 (w), 946 (w), 770 (w), 746 (s), 709 cm^{-1} (w). UV/VIS (acetonitrile): λ_{max} (log ε) = 301 (3.76, sh), 240 (4.20, sh), 213 nm (4.66, sh); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.29, 6.06, 6.10, 6.12, 6.44, 6.45 (all s, C5-H, overall 1H), 6.84 – 7.56 (m, 20H, aryl-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 59.31, 59.63, 59.78, 63.20 (all d, C5), 125.50, 25.59, 125.69, 125.84, 125.91, 126.26, 126.71, 127.03, 127.99, 128.17, 128.32, 128.34, 128.42, 128.48, 128.50, 128.56, 128.61, 128.76, 128.85, 129.05, 129.05, 129.09, 129.12, 129.16, 129.37, 129.43, 129.51, 129.55, 129.87, 131.26, 131.29, 131.50, 131.56, 131.69, 131.84, 131.90, 132.01, 132.34, 132.37, 132.52 (all d), 133.09, 133.38, 133.43, 133.49, 133.51, 133.72, 133.78, 133.82, 133.89, 133.98, 134.04, 134.05, 134,26, 134.44, 134.61, 134.86, 135.46, 135.76, 142.90, 143.13, 143.34, 143.38, 144.02, 144.04, 144.18, 144.32, 146.38, 146.51, 146.73, 147.31 (all s); MS (70 eV, 160 °C): *m/z* (%) = 625 (2), 624 (5), 623 (8), 622 (23), 621 (24), 620 (68), 619 (37), 618 (100), 617 (23), 616 (59), 582 (2), 546 (8), 511 (7), 471 (5), 437 (7), 399 (11), 363 (13); elemental analysis: calcd. for $C_{35}H_{21}Cl_5$ (618.82 g/mol): C 67.93, H 3.42; found: C 67.74, H 3.37.

1,2,4-Tris(2-chlorphenyl)-cyclopenta-1.3-diene (4d)

4.41 g (30.0 mmol) of l,2-dichlorobenzene (**2d**, X = Cl) were coupled with 198 mg (3.00 mmol) cyclopentadiene (**3**) according to the general procedure: 5.87 g (18.0 mmol) Cs_2CO_3, 33.7 mg (150 μmol) $Pd(OAc)_2$, 121 mg (600 μmol) P(*t*-Bu)$_3$ as catalyst system in 20 mL of DMF, 65 h at 160 °C. Isolation of the product was achieved by flash chromatography (silica, 25:1, PE/EtOAc, $R_f = 0.31$) to furnish triarylated product **4d** as a brownish solid; slightly coloured powder with mp. 130 °C after crystallisation from dichloromethane/hexanes; yield: 740 mg (62%). IR (KBr): $\tilde{\nu} = 3065$ (w), 1590 (w), 1559 (w), 1468 (m), 1429 (m), 1364 (w), 1215 (w), 1198 (w), 1159 (w), 1125 (w), 1056 (m), 1035 (w), 1001 (w), 897 (w), 758 (s), 732 (w, sh), 712 cm^{-1} (w). UV/VIS (acetonitrile): λ_{max} (log ε) = 315 (4.14), 257 (4.11, sh), 241 nm (4.22); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.13 (d, $J = 1.2$ Hz, 2H, 5-H), 7.09 – 7.06 (m, 4H), 7.18 – 7.12 (m, 3H), 7.25 ("td", "J" = 7.7, 1.4 Hz, 1H), 7.39 – 7.34 (m, 3H), 7.42 ("dd", "J" = 8.0, 1.3 Hz, 1H), 7.53 ("dd", "J" = 7.9, 1.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 47.52 (t, C-5), 126.50, 126.53, 126.85, 127.78, 128.39, 128.63, 129.70, 129.77, 129.80, 130.91, 131.29, 131.58 (all d), 132.03, 133.19, 133.32, 134.54, 135.43 (all s), 135.90 (d), 135.94, 141.58, 142.40, 142.42 (all s); MS (70 eV, 135 °C): *m/z* (%) = 401 (33), 400 (24), 399 (97), 398 (17), 397 (24), 396 (100), 328 (15), 327 (17), 326 (44), 325 (18), 291 (21),

290 (10), 289 (20), 288 (37), 287 (12); elemental analysis: calcd. for $C_{23}H_{15}Cl_3$ (397.73 g/mol): C 69.46, H 3.80; found: C 69.54, H 3.88.

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