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Preliminary communication

Multiple arylations of aromatics via removable palladacycle scaffolds: polycyclic compounds and their way of formation

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Abstract

Palladium-promoted selective arylation of aromatic substrates can be achieved with aryl iodides or bromides in the presence of bicyclo[2.2.1]hept-2-ene. On the basis of isolation of products corresponding to multiple arylations, evidence is provided that the process occurs according to a complex sequence of steps, involving bicycloheptene insertion into arylpalladium bonds and its expulsion when steric hindrance is generated by the process.

Keywords: Arylation; C–H activation; Palladacycles; Polyaromatics

1. Introduction

Arylation of aromatics is an important topic to which palladium chemistry has contributed remarkably [1]. Some time ago [2] we observed a palladium catalyzed cyclisation leading to *cis*,*exo*-hexahydromethanotriphenylenes **7a** and **7b** (Scheme 1) which involves previous intermolecular arylation at both the aryl and alkyl sites of the alkylaromatic metallacycle **4**.

The reaction required the use of triphenylphosphine as ligand and *t*-BuOK as a base at 105°C using anisole as a solvent. The process was further studied by de Meijere and coworkers [3] using *N*,*N*-dimethylformamide (DMF) as solvent at 60–105°C in the presence of $Pd(OAc)_2$ as catalyst, K_2CO_3 as neutralizing agent and tetra-*n*-butylammonium bromide (Jeffery's protocol [4]). Under these conditions arylation generally occurs, according to path (a) of Scheme 1, at the alkyl (bicycloheptyl) site of metallacycle **4** and leads to products **7a** and **8** (Scheme 2). The latter compound results from further arylation of its precursor complex **6** (Scheme 1). Although the formation of **8** was attributed to the intermediacy of an aryne species we suspected that a process requiring insertion and deinsertion of bicycloheptene (**1**) could be involved, analogously to what was observed by ourselves on studying aromatic alkylation of type **3** complexes [5] where the presence of two alkyl substituents in *o*,*o*′ to the aryl to bicycloheptyl C–C bond causes deinsertion of **1**.

We now find that the palladium catalysed reaction of **1** with aryl iodides or bromides can be made to form significant amounts of other products which are relevant to understanding its course. While electron-releasing substituents in the *para* position of the aromatic halide essentially lead to **7a** and **8**, the electron-withdrawing substiuents also allow the formation of products deriving from the initial aryl migration to the aryl site of palladacycle **4** to give **5** according to path (b) of Scheme 1.

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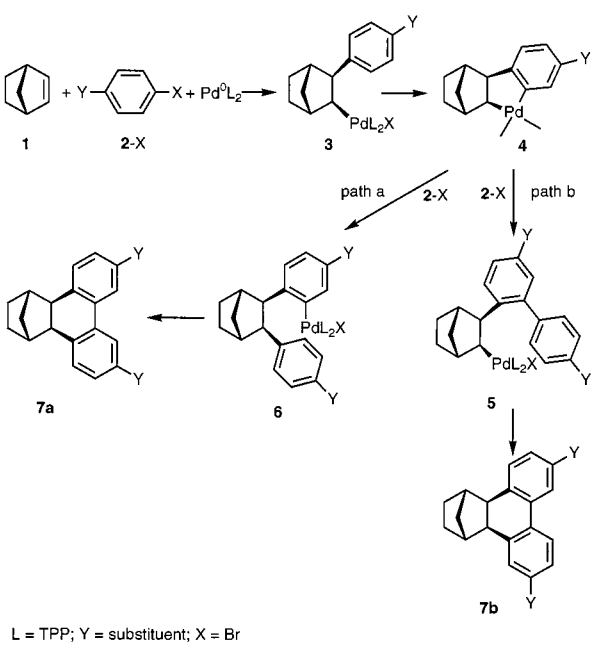
2. Results and discussion

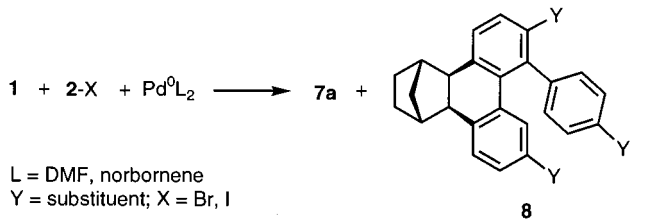
The aromatic compounds of choice for our experiments were methyl *p*-bromo- or iodobenzoate (**2**–Br,I), the *para*-substituent also being useful in following the regiochemistry of the reaction. Thus when methyl *p*-iodobenzoate (**2**–I) was allowed to react with **1** in the presence of $Pd(OAc)_2$ and K_2CO_3 in DMF at 105°C for 24 h, four main products, **7a** [3b] (30%), **8** (23%), **9** (16%) and **10** (6%), were isolated (Scheme 3).

Compounds **8**, **9** and **10** (all with $Y = CO_2Me$) were not reported by de Meijere, who obtained **7a** as the only reaction product [3b]. Compounds **9** and **10** were not observed previously. Using methyl *p*-bromobenzoate (**2**–Br) led to the formation of the same products with 32, 39, 8 and 12% yield, respectively. The use of *p*-bromotrifluoromethylbenzene under similar conditions gave compounds **7a** (62%) and **10** (16%) exclusively thus indicating that even slight changes in the nature of substituents in the aromatic ring can influence the migration of the aryl group (to the aryl or the bicycloheptyl site of palladacycle **4**) and the subsequent step (aryl–aryl coupling or bicycloheptene insertion, as we shall see later). The structure of compound **10** ($Y = CF_3$), a 5-aryl-substituted *exo*-hexahydromethanotriphenylene derivative, was determined by X-ray analysis and the data are shown in Fig. 1 and Table 1.

Compounds **8** and **9** and **10** ($Y = CO_2Me$) were fully characterized by NMR, IR and mass spectrometry. NMR assignments are based on COSY, NOESY, decoupling and C–H correlations experiments. The structure of compound **9** (*exo*, $Y = CO_2Me$) was unambiguously assigned on the basis of the many dipolar interactions observed in the NOESY spectrum. Particularly informative is the presence of a strong NOE effect between the two aliphatic protons H4a and H4 and the two aromatic protons H2′, H6′ of a *p*-methoxycarbonylphenyl ring clearly indicating that the latter is placed on carbon 5 of the hexahydromethanetriphenylene skeleton as shown in the drawing. Similar dipolar interactions were observed in the NOESY spectra of compound **10** ($Y = CO_2Me$, CF_3). Moreover, ^{1}H-NMR spectra of both compounds **8** ($Y = CO_2Me$) and **9** ($Y = CO_2Me$), recorded at 20°C, show four very broad doublets for the *p*-substituted aryl ring bonded to carbon 8 of the hexahydromethanotriphenylene derivative. These data together with the four signals observed in the ^{13}C-NMR spectrum indicate that rotation is hindered.



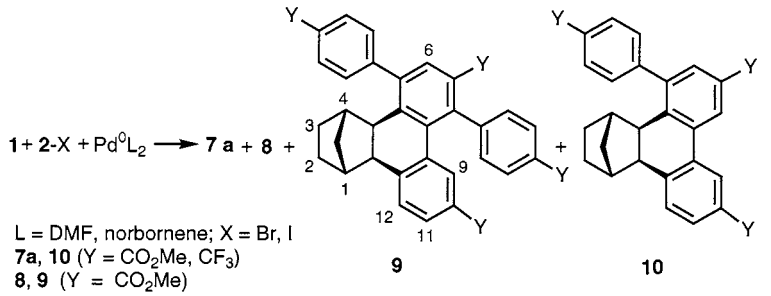
Scheme 1.



Scheme 2.

Although a systematic study is needed to obtain detailed information on substituent effects, the results reported above, combined with our knowledge of the organic species and organometallic intermediates involved in aromatic alkylation via palladacycles [5] enable us to fully explain the course of aromatic arylation (Schemes 2 and 3) on the basis of palladacycle formation by insertion of **1** into the arylpalladium bond, followed by arylation and dismantling of the palladacycle, **1** acting as a provisional scaffold. Scheme 4 shows the proposed way of formation of compounds **8**–**10**.

In the presence of the weak DMF ligand complex **6** coordinates and inserts **1** instead of undergoing ring closure to **7a** as in Scheme 1. This leads to the new palladacycle **11** (the intermediacy of which was proved by us in the case of similar compounds [10] by isolating the benzocyclobutene product deriving from reductive elimination), followed by a new arylation at the aromatic site to give **12**. The intermediate may be a palladium(IV) metallacycle (not shown) formed by oxidative addition analogously to the correspondent alkylpalladium(IV) metallacycle compounds already isolated by us [11,12]. A concerted attack by the halide and aryl groups of the aryl halide on the palladium–bicycloheptyl bond, which would circumvent the formation of a palladium(IV) intermediate [13], is a possible alternative, but no evidence has been gained so far on the nature of the intermediate involved. Whatever the latter might be, the result is aryl migration to the aryl carbon atom of a palladium–bicycloheptyl bond to afford **12**.



Scheme 3.

Bicycloheptene expulsion (also proved by us for *o*,*o*′-dialkylarylbicycloheptylpalladium iodide [5]) to form **13** and cyclization to **8** complete the process.

A minor and more complex pathway starting from complex **5** (from arylation of **4** at the aryl site, Scheme 1), gives rise to compounds **14** and **15**. The latter either forms **10** by cyclisation or undergoes a series of steps (from **16** to **18**) perfectly analogous to those involved in the formation of **8** eventually leading to **9**.

An interesting feature emerges from inspection of Scheme 4. As can be inferred from the much higher yields of **7a** + **8** compared with that of **9** and **10**, the initial attack of the aromatic iodide or bromide on the first metallacycle formed (**4**) mainly leads to complex **6**, resulting from aryl migration to the bicycloheptyl site. However, when a second metallacycle **11** (as well as **16**) is formed by further insertion of **1**, arylation becomes regioselective, occurring exclusively at the aryl site, as observed for **12**, which gives **13** by deinsertion of **1** and cyclizes to **8** and palladium(0). Apparently the *p*-methoxycarbonylphenylbicycloheptyl group *ortho* to the metallacycle C–C bond as in **11,** directs arylation towards the aryl site owing to steric hindrance, leading to preferential weakening of the palladium–aryl bond of the intermediate metallacycle. Similar considerations also hold for complex **16**.

Further evidence for our interpretation involving bicycloheptene insertion–deinsertion was gained by reacting complex **3** (Y = CO_2Me, prepared as a dimer according to the procedure described in the literature for the unsubstituted parent complex [14]), with methyl *p*-iodobenzoate (in excess to obtain a good conversion) and treating the final product with sodium borohydride (Scheme 5).

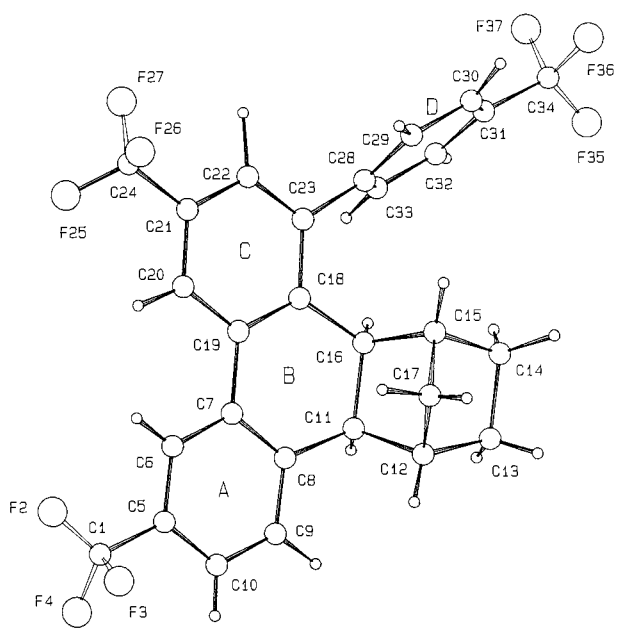
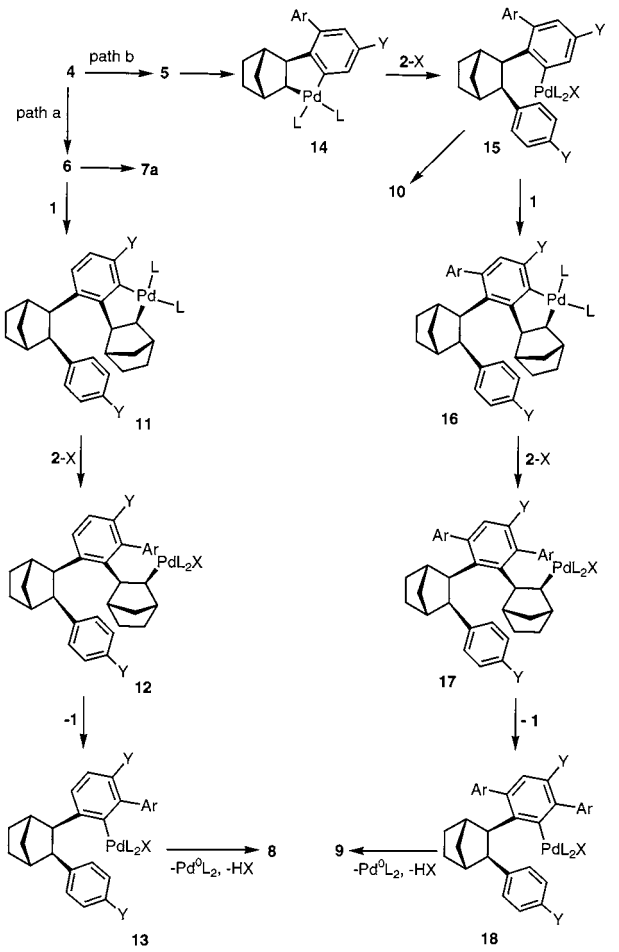


Fig. 1. Projection of **10** (Y = CF_3) with arbitrary numbering scheme.

Table 1
Crystallographic data and experimental information for compound **10** (Y = CF_3)

Empirical formula	$C_{28}H_{19}F_9$
Formula weight (g mol^{-1})	526.4
Temperature (K)	r.t.
Wavelength CuKα (Å)	1.5418
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	11.692(2)
b (Å)	16.281(3)
c (Å)	13.146(2)
β (°)	109.96(2)
V (Å^3)	2352.12
Z	4
$D_{calc.}$ (g cm^{-3})	1.49
$\mu_{calc.}$	11.73
Crystal size (mm)	$0.11 \times 0.22 \times 0.27$
Crystal shape	Prism
Theta range for data collection (°)	3–70
Index ranges: *h*, *k*, *l*	0/14, −14/19, −16/14
Reflections collected	2937 [$R_{int} = 0.056$]
Reflections observed [$I > 2\sigma(I)$]	2912
Independent reflections	2919
Parameters	471
Final *R* indices [$I > 2\sigma(I)$]	$R = 0.062$, [a] $R_w = 0.186$
$\Delta\rho_{min./max.}$	−0.64/0.55
Computer programs	
Solution	SIR 97 [6]
Refinement	SHELX 93 [7]
Figures	PLUTO [8]
Geometry	PARST [9]

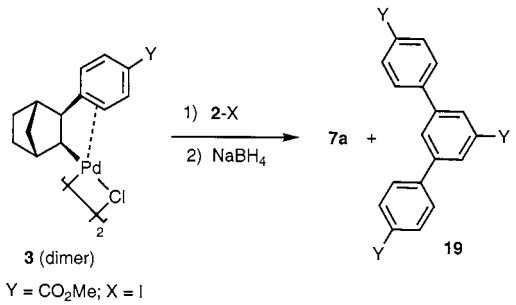
[a] Weighting scheme calc. $w = 1/[(\sigma^2 F_o + 0.0160P)^2 + 1.92P]$.



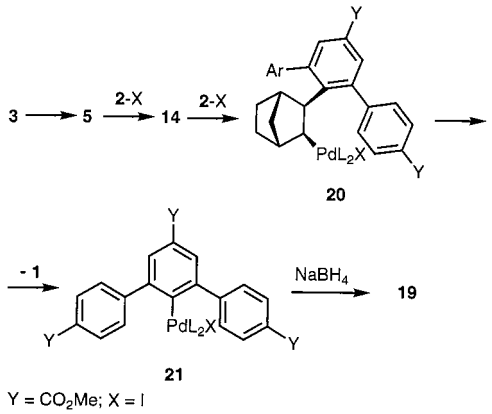
Scheme 4. Proposed mechanism for the formation of compounds **7a**, **10** (Y = CO_2Me, CF_3) and **8**, **9** (Y = CO_2Me); L = DMF, bicycloheptene; X = Br, I.

While compounds **8** and **9** were not formed because, in agreement with the above mechanism, **1** would be required, compounds **7a** (Y = CO_2Me, 48%) and **19** (15%) were found with 80% conversion at 20°C in DMF for 6 h. As shown in Scheme 6 formation of compound **19** implies the intermediacy of **5** which undergoes ring closure to afford palladacycle **14**.

The methoxycarbonylphenyl group, generated from the reaction of **14** with methyl *p*-iodobenzoate, then



Scheme 5.



Scheme 6.

migrates towards the aromatic site of the metallacycle giving **20**. At this point the presence of two substituents in the *o*,*o*′-position causes steric strain and bicycloheptene expulsion (which is also favoured by the absence of bicycloheptene). Hydrogenolysis of the complex obtained (**21**) affords **19**. It still remains to be clarified why the addition of **1** (Scheme 4) to the same complex **14** directs the *p*-methoxycarbonylphenyl group towards the bicycloheptyl moiety to form **15**. This might be due to stabilisation of complex **15** with respect to complex **20** (Scheme 6) by bicycloheptene.

The reason why insertion of **1** competes with ring closure at various stages of the process (to form **11** instead of **7a** from **6** or **16** instead of **10** from **15**) seems to be ascribed to the different degrees of stabilisation of **6** and **15** by the bicycloheptene ligand, which can compete with a weaker ligand such as DMF and with the anionic ligands I^- and Br^- to different extents.

3. Conclusion

In conclusion, the unusual selective arylations of arene substrates can be obtained by means of appropriate alkylaromatic palladacycles. While further study is required to elucidate subtle substituent, anion and solvent effects the insertion–deinsertion mechanism of arylation via a palladacycle explains all the facts observed so far, including reactions of the type shown in Scheme 2 for which an aryne mechanism of arylation had been proposed [3b].

4. Experimental

4.1. General procedure for the reaction of bicycloheptene with aryl bromides or iodides

$Pd(OAc)_2$ (27 mg, 0.12 mmol) and K_2CO_3 (167 mg, 1.2 mmol) were placed in a Schlenk-type flask contain-

ing a magnetic stirring bar. Bicycloheptene (169 mg, 1.8 mmol) and the desired aryl halide (1.2 mmol) dissolved in DMF (4 ml) were added under nitrogen. The resulting mixture was stirred at 105°C for 24 h. After conventional workup the products were separated by flash chromatography on a SiO_2 column with hexane–ethyl acetate as eluent. Small amounts of other unidentified compounds were also obtained. In the spectroscopic data following, "*" indicates interchangeable assignments. Satisfactory elemental analyses were obtained for all compounds: C ± 0.28, H ± 0.30.

4.1.1. ***8*** *(Y = CO_2Me), dimethyl exo-1,2,3,4,4a,12b-hexahydro-8-(p-methoxycarbonylphenyl)-1,4-methanotriphenylene-7,10-dicarboxylate*

M.p. (MeOH) 202°C. ^{1}H-NMR ($CDCl_3$): δ 8.14 (1H, brdd, $J = 8.0$, 1.6 Hz, H *ortho* to CO_2Me), 8.02 (1H, brdd, $J = 8.0$, 1.7 Hz, H *ortho* to CO_2Me), 7.65 (1H, dd, $J = 8.0$, 1.7 Hz, H11), 7.53 (1H, d, $J = 8.0$ Hz, H6), 7.41 (1H, brdd partly overlapping with H9, H *meta* to CO_2Me), 7.39 (1H, d, $J = 1.7$ Hz, H9), 7.33 (1H, dd, $J = 8.0$, 0.8 Hz, H5), 7.28 (1H, brdd, $J = 8.0$, 1.7 Hz, H *meta* to CO_2Me), 7.20 (1H, d, $J = 8.0$ Hz, H12), 3.94 (3H, s, CO_2Me), 3.56 (3H, s, CO_2Me), 3.52 (3H, s, CO_2Me), 3.36 (1H, d, $J = 9.7$ Hz, H4a), 3.19 (1H, d, $J = 9.7$ Hz, H12b), 2.44 (1H, brs, H1), 2.29 (1H, brs, H4), 1.79–1.70 (2H, m, H2 *exo*, H3 *exo*), 1.70–1.61 (2H, m, H2 *endo*, H3 *endo*), 1.41 (1H, d quintets, $J = 10.2$, 1.5 Hz, H13 *syn*), 1.09 (1H, d quintets, $J = 10.2$, 1.3 Hz, H13 *anti*). ^{13}C-NMR ($CDCl_3$): δ 169.5, 167.0, 166.5, 146.8, 144.6, 143.7, 137.1, 132.6 (quaternary carbons), 130.9 (C9), 130.8 (q), 130.1 (C3′*, C12), 130.0 (C5′*), 129.7 (C2′**), 129.4 (C5), 129.2 (C6′**), 128.9 (q), 128.1 (C11), 127.8 (C6), 126.8 (q), 52.1 (CO_2Me), 52.0 (CO_2Me), 51.3 (CO_2Me), 50.0 (C4), 49.2 (C1), 47.2 (C4a), 46.6 (C12b), 33.3 (C13), 30.7 (C2***), 29.7 (C3***). IR (cm^{-1}): 1720.7. MS (EI): 496 (M^+, 100), 464 (16), 404 (21), 397 (41), 337 (20), 336 (18), 278 (16), 250 (16).

4.1.2. ***9*** *(Y = CO_2Me), dimethyl 5,8-di-(p-methoxycarbonylphenyl)exo-1,2,3,4,4a,12b-hexahydro-1,4-methanotriphenylene-7,10-dicarboxylate*

M.p. (MeOH) 203°C. ^{1}H-NMR ($CDCl_3$): δ 8.17 (1H, vbrd, H *ortho* to CO_2Me of the aryl group at C8), 8.13 (2H, part AA′ of an AA′BB′ system, Hs *ortho* to CO_2Me of the aryl group at C5), 8.01 (1H, vbrd, H *ortho* to CO_2Me of the aryl group at C8) 7.67 (1H, dd, $J = 8.0$, 1.7 Hz, H11), 7.49 (3H, m, H *meta* to CO_2Me of the aryl group at C8 + 2H *meta* to CO_2Me of the aryl group at C5), 7.46 (1H, d, $J = 1.7$ Hz, H9), 7.44 (1H, s, H6), 7.30 (1H, vbrd, H *meta* to CO_2Me of the aryl group at C8), 7.19 (1H, d, $J = 8.0$, H12), 3.96 (3H, s, CO_2Me), 3.94 (3H, s, CO_2Me), 3.59 (3H, s, CO_2Me), 3.55 (3H, s, CO_2Me), 3.53 (1H, brd, $J = 9.8$ Hz, H4a), 3.15 (1H, brd, $J = 9.8$ Hz, H12b), 2.40 (1H, m, H1), 1.87 (1H, m, H4), 1.54–1.51 (1H, m, H2 *exo*), 1.50–1.36 (2H, m, H2 *endo*, H13 *syn* centred at 1.40), 1.35–1.24 (1H, m, H3 *exo*), 0.99 (1H, brd, $J = 10.2$ Hz, H13 *anti*), 0.90–0.76 (1H, m, H3 *endo*). ^{13}C-NMR ($CDCl_3$): δ 169.2, 166.9, 166.8, 166.5, 146.4, 145.7, 144.4, 141.8, 141.2, 136.6, 132.5, 132.2 (quaternary carbons), 131.7 (C9), 131.4 (q), 130.2 (C3′′*), 130.0 (C5′′*), 129.8 (C2′′**, C12), 129.7 (C3′, C5′), 129.6 (C6), 129.5 (C2′, C6′), 129.3 (C6′′**), 129.2 (q), 129.0 (q), 128.3 (C11), 126.9 (q), 52.3 (CO_2Me), 52.2 (CO_2Me), 52.1 (CO_2Me), 51.4 (CO_2Me), 48.7 (C1), 48.6 (C4), 47.3 (C12b), 44.5 (C4a), 32.9 (C13), 30.1 (C2), 29.7 (C3). IR (cm^{-1}): 1720.7. MS (CI): 631 ($M^+ + 1$, 100).

4.1.3. ***10*** *(Y = CO_2Me), dimethyl exo-1,2,3,4,4a,12b-hexahydro-5-(p-methoxycarbonylphenyl)-1,4-methanotriphenylene-7,10-dicarboxylate*

M.p. (hexane) 231–232°C. ^{1}H-NMR ($CDCl_3$): δ 8.66 (2H, pst, $J = 1.9$, H8, H9), 8.13 (2H, part AA′ of an AA′BB′system, H3′, H5′), 7.90 (1H, dd, $J = 8.0$, 1.6 Hz, H11), 7.76 (1H, d, $J = 1.6$ Hz, H6), 7.44 (2H, part BB′ of an AA′BB′ system, H2′, H6′), 7.31 (1H, d further split, $J = 8.0$ Hz, H12), 3.97 (3H, s, CO_2Me), 3.96 (3H, s, CO_2Me), 3.95 (3H, s, CO_2Me), 3.42 (1H, brd, $J = 9.7$ Hz, H4a), 3.25 (1H, brd, $J = 9.7$ Hz, H12b), 2.33 (1H, m, H1), 1.94 (1H, m, H4), 1.58 (1H, tt, $J = 12.4$, 4.3 Hz, H2 *exo*), 1.43 (1H, m, H2 *endo*), 1.26–1.16 (2H, m, H13 *syn*, H3 *exo*), 0.90 (1H, d further split, $J = 10.3$ Hz, H13 *anti*), 0.73 (1H, m, H3 *endo*). IR (cm^{-1}): 1719.8. MS (CI): 497 ($M^+ + 1$, 100).

4.2. ***7a*** *(Y = CF_3), 7,10-ditrifluoromethyl-exo-1,2,3,4,4a,12b-hexahydro-1,4-methanotriphenylene*

M.p. (hexane) 156–157°C. ^{1}H-NMR ($CDCl_3$): δ 8.04 (2H, s, H8, H9), 7.48 (2H, brd, $J = 8.1$ Hz, H6, H11), 7.36 (2H, d, $J = 8.1$ Hz, H5, H12), 3.27 (2H, s, H4a, H12b), 2.40 (2H, m, H1, H4), 1.80–1.60 (4H, m, H2 *exo*, H3 *exo*, H2 *endo*, H3 *endo*), 1.32 (1H, d quintets, $J = 10.2$, 1.7 Hz, H13 *syn*), 1.09 (1H, d quintets, $J = 10.2$, 1.5 Hz, H13 *anti*). ^{13}C-NMR ($CDCl_3$): δ 141.57 (q, $J_{C/F} = 1.3$ Hz), 130.87 (C5, C12), 130.77 (q), 128.91 (q, $J_{C/F} = 32.3$ Hz, C7, C10), 124.82 (q, $J_{C/F} = 3.5$ Hz, C6, C11), 124.22 (q, $J_{C/F} = 272.0$ Hz, CF_3), 119.10 (q, $J_{C/F} = 3.7$ Hz, C8, C9), 49.68 (C1, C4), 45.77 (C4a, C12b), 33.25 (C13), 30.17 (C2, C3). MS (EI): 382 (M^+, 11), 314 (80), 207 (29), 67 (100), 48 (95).

4.2.1. ***10*** *(Y = CF_3), 7,10-ditrifluoromethyl-exo-1,2,3,4,4a,12b-hexahydro-5-(p-trifluoromethylphenyl)-1,4-methanotriphenylene*

M.p. (hexane) 197–198°C. ^{1}H-NMR ($CDCl_3$): δ 8.12 (1H, brs, H8), 8.10 (1H, brs, H9), 7.74 (2H, part AA′ of an AA′BB′ system, H3′, H5′), 7.54–7.48 (3H, m, H11,

H2′, H6′), 7.37 (1H, d, $J = 7.4$ Hz, H12), 7.35 (1H, s, H6), 3.38 (1H, d, $J = 9.9$ Hz, H4a), 3.28 (1H, d, $J = 9.9$ Hz, H12b), 2.35 (1H, m, H1), 1.94 (1H, m, H4), 1.62 (1H, tt, $J = 12.5$, 4.3 Hz, H2 *exo*), 1.52–1.40 (1H, m, H2 *endo*), 1.30–1.28 (2H, m, H13 *syn*, H3 *exo*), 0.95 (1H, d quintets, $J = 10.3$, 1.4 Hz, H13 *anti*), 0.75 (1H, m, H3 *endo*). ^{13}C-NMR ($CDCl_3$): δ 144.56, 142.65, 141.43, 139.24, 131.63, 131.25 (quaternary C), 130.47 (C12), 129.88 (quartet, $J_{C/F} = 32.6$ Hz, C4′), 129.57 (C2′, C6′), 129.06 (quartet, $J_{C/F} = 32.4$ Hz, C7*), 128.95 (quartet, $J_{C/F} = 32.5$ Hz, C10*), 126.70 (quartet, $J_{C/F} = 3.5$ Hz, C6), 125.49 (quartet, $J_{C/F} = 3.5$ Hz, C3′, C5′), 125.17 (quartet, $J_{C/F} = 3.5$ Hz, C11), 124.18 (quartet, $J_{C/F} = 272.1$ Hz, CF_3), 124.06 (quartet, $J_{C/F} = 272.1$ Hz, CF_3), 124.02 (quartet, $J_{C/F} = 272.2$ Hz, CF_3), 119.59 (quartet, $J_{C/F} = 3.6$ Hz, C9), 119.20 (quartet, $J_{C/F} = 3.6$ Hz, C8), 48.90 (C1), 48.46 (C4), 46.21 (C12b), 42.66 (C4a), 33.01 (C13), 30.41 (C3), 29.70 (C2). ^{19}F NMR ($CDCl_3$, external $CFCl_3$): δ −63.68, −63.72, −63.78. MS (EI): 526 (M^+, 57), 507 (15), 458 (100), 389 (42), 369 (31), 320 (56), 67 (77).

4.3. Reaction of complex **3** (dimer, $Y = CO_2Me$) with methyl p-iodobenzoate

Dimeric complex **3** ($Y = CO_2Me$) [14] (37 mg, 0.05 mmol) and K_2CO_3 (42 mg, 0.3 mmol) were dissolved in DMF (3 ml) in a Schlenk-type flask under nitrogen. Methyl *p*-iodobenzoate (131 mg, 0.5 mmol) in DMF (2 ml) was then added and the resulting mixture was stirred at room temperature for 6 h. After treatment with $NaBH_4$ in excess followed by conventional work-up, 80% conversion of **3** ($Y = CO_2Me$) was achieved as determined by GC quantitative analysis of methyl *exo*-2-bicyclo[2.2.1]heptylbenzoate resulting from the decomposition of the starting complex. Products **7** ($Y = CO_2Me$, 18 mg, 49%) and **19** ($Y = CO_2Me$, 6 mg, 15%) were separated by flash chromatography on a SiO_2 column with hexane–ethyl acetate 8:2 as eluent. Small amounts of other unidentified compounds were also obtained.

4.3.1. **19** ($Y = CO_2Me$), trimethyl 4,5′,4″-m-terphenyltricarboxylate

M.p. (MeOH) 112–113°C. ^{1}H-NMR ($CDCl_3$): δ 8.32 (2H, d, $J = 1.7$ Hz, H4′, H6′), 8.15 (4H, part AA′ of two equivalent AA′BB′ systems, H3, H5, H3″, H5″), 8.03 (1H, t, $J = 1.7$ Hz, H2′), 7.75 (4H, part BB′ of two equivalent AA′BB′ systems, H2, H6, H2″, H6″), 3.99 (3H, s, CO_2Me), 3.96 (6H, s, 2 CO_2Me). IR (cm^{-1}): 1722.6. MS (CI): 405 ($M^+ + 1$, 100).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 114320 for compound **10**. Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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References

[1] (a) D.E. Ames, D. Bull, Tetrahedron 38 (1982) 383. (b) D.E. Ames, A. Opalko, Tetrahedron 40 (1984) 1919. (c) A. Suzuki, Pure Appl. Chem. 66 (1994) 213. (d) A. Suzuki, Pure Appl. Chem. 57 (1985) 1749. (e) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457. (f) M. Beller, H. Fischer, W.A. Herrmann, K. Öfele, C. Brossmer, Angew. Chem. Int. Ed. Engl. 34 (1995) 1848. (g) G. Dyker, Chem. Ber./Recueil 130 (1997) 1567.
[2] M. Catellani, G.P. Chiusoli, J. Organomet. Chem. 286 (1985) C13.
[3] (a) O. Reiser, M. Weber, A. de Meijere, Angew. Chem. Int. Ed. Engl. 28 (1989) 1037. (b) K. Albrecht, O. Reiser, M. Weber, B. Knieriem, A. de Meijere, Tetrahedron 50 (1994) 383.
[4] (a) T. Jeffery, Tetrahedron Lett. 35 (1994) 3051. (b) T. Jeffery, J.-C. Galland, Tetrahedron Lett. 35 (1994) 4103.
[5] (a) M. Catellani, M.C. Fagnola, Angew. Chem. Int. Ed. Engl. 106 (1994) 2559. (b) M. Catellani, F. Frignani, A. Rangoni, Angew. Chem. Int. Ed. Engl. 36 (1997) 119.
[6] A. Altomare, G. Cascarano, C. Giacovazzo, A, Guagliardi, A.G.G. Moliterni, M.C. Burla, G. Polidori, M. Camalli, R. Spagna, private communication, 1997.
[7] G.M. Sheldrick, SHELX 93: Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993.
[8] W.D.S. Motherwell, W. Clegg, PLUTO: A program for plotting molecular and crystal structures, University of Cambridge, England, 1978.
[9] M. Nardelli, Comput. Chem. 7 (3) (1983) 95.
[10] (a) M. Catellani, G.P. Chiusoli, C. Castagnoli, J. Organomet. Chem. 407 (1991) C30. (b) M. Catellani, L. Ferioli, Synthesis (1996) 769.
[11] (a) M. Catellani, G.P. Chiusoli, J. Organomet. Chem. 346 (1988) C27. (b) M. Catellani, B.E. Mann, J. Organomet. Chem. 390 (1990) 251. (c) G. Bocelli, M. Catellani, S. Ghelli, J. Organomet. Chem. 458 (1993) C12.
[12] (a) A.J. Canty, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 9, Pergamon, Oxford, 1995, p. 272. (b) W. de Graaf, J. Boersma, W.J.J. Smeets, A.L. Spek, G. van Koten, Organometallics 8 (1989) 2907. (c) R. van Asselt, E. Rijnberg, C. Elsevier, Organometallics 13 (1994) 706. (d) M. Catellani, in: S.G. Davies, S.-I. Murahashi (Eds.), Transition Metal Catalysed Reactions, Blackwell Science, Oxford, in press.
[13] (a) G. Dyker, Angew. Chem. Int. Ed. Engl. 31 (1992) 1023. (b) G. Dyker, Angew. Chem. Int. Ed. Engl. 33 (1994) 103. (c) D.J. Cárdenas, C. Mateo, A.M. Echavarren, Angew. Chem. Int. Ed. Eng. 33 (1994) 2445.
[14] H. Horino, M. Arai, M. Inoue, Tetrahedron Lett. (1974) 647.