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**Selective access to *p*-dialkyl-*carbo*-benzenes from a [6]pericyclynedione:
the *n*-butyl nucleophile model for a metal switch study[†]**

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Abstract

The synthesis, spectroscopic properties, comparative electrochemical behavior in CHCl₃ vs CH₂Cl₂, and X-ray crystal structure of *p*-di-*n*-butyl-tetraphenyl-*carbo*-benzene are described. The selectivity of preparation of the ultimate [6]pericyclynediol precursor has been examined by comparing the reactivity of the [6]pericyclynedione substrate with four *n*-Bu-MX_n nucleophiles involving more or less halogenated metal centers MX_n (0 ≤ n ≤ 2): Li, MgBr, MgCl, CeCl₂/LiCl. The cerium reagent is found to be the most efficient, giving *ca* twice the yield given by Grignard reagents in the target diadduct (90 % vs 51-53 %). The dibutyl-*carbo*-benzene product happens to be soluble in both CHCl₃ and CH₂Cl₂, cyclic voltammograms of either solutions exhibiting almost identical peak potentials, with reduced reversibility of the redox processes in CHCl₃.

Key-words. Alkylcerium - Alkyne - Aromatics - *Carbo*-benzene - *Carbo*-mer

[†] Dedicated to Prof. Reginald H. Mitchell on the occasion of its retirement and prospect of a long remaining life in inspiring the design and study of novel aromatic compounds.

Introduction

Among π -conjugated carbon allotropes and beyond the foremost graphene type, graphynic materials, composed of both sp^2 -C and sp -C atoms, have been considered at the theoretical level,¹ but more sparingly studied experimentally. Nevertheless, several molecular fragments of γ -graphyne,² γ -graphdiyne,³ and even α -graphyne,⁴ have been described. A key issue in the synthesis and study of such carbon-rich compounds is their limiting solubility, approaching that of graphite upon increase of the size of the carbon core within a C-H bond periphery. As a recourse, peripheral decoration by lipophilic groups is currently envisaged. This can be illustrated by the recent report of a ring *carbo*-mer of naphthalene,⁵ eight *p*-pentylphenyl substituents of the C_{32} core having allowed full characterization of this first example of fused polycyclic α -graphyne fragment, in or from solutions in $CHCl_3$.⁴ The solubilizing effect of the *p*-pentylphenyl groups appeared however limited, even on the smaller *carbo*-benzene congener $C_{18}(4-n-C_5H_{11}-C_6H_4)_6$. The *carbo*-benzene C_{18} ring is actually the smallest cyclic primitive motif of α -graphyne, and most of the derivatives reported hitherto bear only H, aryl, or alkynyl substituents.⁶ Very recently, direct anchoring of alkyl chains at the sp^2 vertices of the C_{18} ring was envisaged in a series of *p*-dialkyl-tetraphenyl-*carbo*-benzenes **1a-e**, which could be obtained in two steps, by addition of alkylmagnesium bromides to the [6]pericyclynedione **2** followed by reductive aromatization of the [6]pericyclynediol products **3a-e** (Scheme 1).⁷ The Grignard approach was however found not selective: beside the di-adducts **3a-e**, the single and double reductions products **4a-e** (resulting from the mono-adduct) and **5** are also formed. The reducing power of alkyl Grignard reagents is actually known to be due to the presence of a H atom in β position of the Mg atom,⁸ but several recommended methods to overcome this effect, e. g. through the change of solvent, failed to improve the reaction outcome. The use of alternative or additive metals should thus be envisaged.

Insert **Scheme 1** here

In general nucleophilic addition of $Nu-MX_n$ to carbonyl groups, beyond lithium ($M = Li$, $n = 0$) and magnesium ($M = Mg$, $n = 1$, $X = Br, Cl, I$) cations, cerium cations ($M = Ce$, $n = 2$, $X = Cl$) have also been reported to provide higher selectivity under smooth conditions.⁹ In the present context, targeting the [6]pericyclynediols **6a-b** from the bis-terminal tetrayne **7a-b** and dialdehyde **8**, while reactions of the $MgBr^+$ salts alone appeared almost unproductive (0-

6%),^{6a,b,h} addition of CeCl_3 was shown to improve the yield to 12-14 %, likely *via* the corresponding CeCl_2^+ salts (Scheme 2).

As part of ongoing efforts to improve access efficiency to *carbo*-benzene molecules, the study of the metal effect on the double nucleophilic addition to the diketone **2** has been undertaken for $\text{Nu} = n\text{-Bu}$, a model nucleophile of intermediate length, with the view to obtaining the hitherto unknown representative *p*-di-*n*-butyl-tetraphenyl-*carbo*-benzene **1f**. This target, bearing both aliphatic and aromatic substituents, is also devised to serve as a standard for electrochemical studies in the *carbo*-benzene series.

Insert **Scheme 2** here

Experimental

1. General

THF was dried with a PureSolv-MD-5 Innovative Technology system for the purification of solvents. All other reagents were used as commercially available. In particular, commercial solutions of *n*-BuLi were 2.5 M in hexane, solutions of HCl were 2 M in diethyl ether. All reactions were carried out under argon atmosphere using Schlenk tube and vacuum line techniques. Column chromatography was carried out on silica gel (60 Å, C.C 70-200 µm). Silica gel thin layer chromatography plates (60F254, 0.25 mm) were revealed under UV-light and/or by treatment with an ethanolic solution of phosphomolybdic acid (20%). The following analytical instruments were used: ^1H and ^{13}C NMR spectroscopy: Avance 300, Avance 400 and Avance 400 HD; mass spectrometry: Quadrupolar Nermag R10-10H; UV-visible absorption: Perkin-Elmer UV-Vis Win-Lab Lambda 950; X-ray diffraction: Apex2 Bruker, microfocus X-ray source (Mo $\text{K}\alpha$ radiation). NMR chemical shifts are given in ppm with positive values to high frequency relative to the tetramethylsilane reference. Coupling constants J are in Hertz. UV-visible absorption wavelengths λ is given in nm, and the corresponding maximum extinction molar coefficient ϵ in $\text{L mol}^{-1}\text{cm}^{-1}$.

2. Crystal structure determination

Intensity diffraction data for **1f** were collected at 100 K. The structure was solved by direct methods using SIR92, and refined by full-matrix least-square procedures on F using the programs of the PC version of CRYSTALS.¹⁰ Atomic scattering factors were taken from the

International Tables for X-ray Crystallography.¹¹ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using a riding model. Absorption corrections were introduced using the program MULTISCAN.

3. Voltammetric measurements

Voltammetric measurements were carried out with a potentiostat Autolab PGSTAT100 controlled by GPES 4.09 software. Experiments were performed at room temperature in a home-made airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of *ca* 1 cm² apparent surface. The working electrode was a Pt microdisk (0.5 mm diameter). The supporting electrolyte [*n*-Bu₄N][PF₆] was used as received (Fluka, 99 % electrochemical grade) and simply degassed under argon. The solutions used in the electrochemical study was 10⁻³ M in *carbo*-benzene and 0.1 M in supporting electrolyte. Before each measurement, the solutions are degassed by bubbling argon, and the working electrode was polished with a polishing machine (Presi P230). Typical instrumental parameters for recording square-wave voltammograms were: SW frequency *f* = 20 Hz, SW amplitude *E*_{sw} = 20 mV, scan increment *dE* = 5 mV.

4. Experimental procedures and characterizations of new products

4.1. 1,10-dibutyl-4,7,13,16-tetraphenylcyclooctadeca-1,2,3,7,8,9,13,14,15-nonaen-5,11,17-triyn (1f)

A solution of [6]pericyclynediol **3f** (50 mg, 0.063 mmol) in DCM (30 mL) was treated with SnCl₂ (120 mg, 0.63 mmol) and HCl (1.26 mmol, 2 M in Et₂O) at -78 °C. The mixture was stirred at -78 °C for 10 min and at room temperature for 20 min. After treatment with 1 M aqueous NaOH (1.26 mL) and filtration through celite[®], the organic layer was washed with brine (3 times), dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (pentane/DCM 4:1) to give **1f** as a dark violet solid (25 mg, 0.039 mmol, 63 %).

¹H NMR (400 MHz, CDCl₃) δ 9.51 (dd, ³*J*_{HH} = 8.0, ⁴*J*_{HH} = 1.2 Hz, 8H, *o*-C₆H₅), 7.97 (dd, ³*J*_{HH} = 8.2, 7.2 Hz, 8H, *m*-C₆H₅), 7.73-7.66 (m, 4H, *p*-C₆H₅), 4.69 (t, ³*J*_{HH} = 7.5 Hz, 4H,

CH_2Pr), 3.04-2.92 (m, 4H, $\text{CH}_2\text{CH}_2\text{Me}$), 2.02 – 1.91 (m, 4H, CH_2Me), 0.91-0.82 (m, 6H, - CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 139.9 (*i*- C_6H_5), 129.8 (*o*- C_6H_5), 129.8 (*m*- C_6H_5), 129.3 (*p*- C_6H_5), 122.1, 119.4, 116.0 ($=\text{C}=\text{C}=$, $-\text{C}\equiv\text{C}-$), 106.5 (C-Bu), 103.0 (C-Ph), 40.4 (CH_2Pr), 34.0 (CH_2Et), 22.8 (CH_2Me), 14.3 ($-\text{CH}_3$).

HRMS (MALDI-TOF/DCTB): m/z : $[\text{M}]^+$ calculated for $\text{C}_{50}\text{H}_{38}$: 638.2974, found: 638.3000; $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{50}\text{H}_{38}\text{Na}$: 661.2871, found: 661.2931.

UV-visible (CHCl_3): $\lambda_{\text{max}} = 446.45 \text{ nm}$ ($\epsilon = 208\,000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$).

Melting-decomposition temperature: 188 °C.

4.2. 1-butyl-4,7,13,16-tetramethoxy-4,7,13,16-tetraphenylcyclooctadeca-2,5,8,11,14,17-hexayne-1,10-diol (**4f**). Side-product obtained during the preparation of **3f** (section 4.3.1).

^1H NMR (400 MHz, CDCl_3) δ 7.81-7.64 (m, 8H, *o*- C_6H_5), 7.45-7.31 (m, 12H, *m*-, *p*- C_6H_5), 5.43-5.24 (m, 1H, CHOH), 3.64-3.33 (m, 12H, OCH_3), 2.91-2.31 (m, 2H, OH), 2.07-1.95 (m, 2H, CH_2Pr), 1.76-1.60 (m, 2H, CH_2Et), 1.41-1.30 (m, 2H, CH_2Me), 0.93-0.82 (m, 3H, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 139.48 (*i*- C_6H_5), 129.10 (*p*- C_6H_5), 128.53 (*m*- C_6H_5), 126.46 (*o*- C_6H_5), 87.10, 84.67, 82.91 ($-\text{C}\equiv\text{C}-$), 75.96, 72.98 (C(OMe)-Ph), 63.71 (C(OH)-Bu), 53.36 - 53.31 (OCH_3), 53.26 ($>\text{CHOH}$), 42.82 (CH_2Pr), 26.66 (CH_2Et), 22.35 (CH_2Me), 11.41 (CH_2CH_3).

HRMS (MALDI-TOF/DCTB): m/z : $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{50}\text{H}_{44}\text{O}_6\text{Na}$: 763.3036, found: 763.3085.

4.3. 1,10-dibutyl-4,7,13,16-tetramethoxy-4,7,13,16-tetraphenylcyclooctadeca-2,5,8,11,14,17-hexayne-1,10-diol (**3f**)

4.3.1. Procedure for the preparation of **3f** with *n*-BuMgBr

To a suspension of magnesium turnings (3.2 mg, 0.1324 mmol) in THF (0.5 mL) at room temperature was added dropwise *n*-BuBr (0.057 mL, 0.5296 mmol). The mixture was stirred for 2 h at room temperature. A solution of [6]pericyclinedione **2** (30 mg, 0.044 mmol) in THF (5 mL) at 0 °C was treated with the freshly prepared solution of *n*-BuMgBr. The

mixture was stirred at 0 °C for 3 h before treatment with a saturated aqueous solution of NH₄Cl. The aqueous layer was extracted with diethyl ether, and the combined organic layers were dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (pentane/EtOAc 5:1, then 3:1) to give the di-adduct **3f** (18 mg, 0.0226 mmol, 51 %), the mono-adduct **4f** (9 mg, 0.012 mmol, 28%), and the known di-reduction diol product **5** (5 mg, 0.007 mmol, 16 %),^{6h,11} as yellow oils. Characterization of **3f**: see section 4.3.4. Characterization of **4f**: see section 4.2.

4.3.2. Procedure for the preparation of **3f** with *n*-BuMgCl

A solution of [6]pericyclynedione **2** (40 mg, 0.0588 mmol) in THF (6 mL) at 0 °C was treated with commercial *n*-BuMgCl (0.176 mmol, 2 M in diethyl ether). The mixture was stirred at 0 °C for 1 h, then at room temperature for 3 h before treatment with a saturated aqueous solution of NH₄Cl. The aqueous layer was extracted with diethyl ether, and the combined organic layers were dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (pentane/EtOAc 5:1, then 3:1) to give the di-adduct **3f** as a yellow oil (25 mg, 53 %). Characterization of **3f**: see section 4.3.4.

4.3.3. Procedure for the preparation of **3f** with *n*-BuLi

A solution of [6]pericyclynedione **2** (40 mg, 0.059 mmol) in THF (6 mL) at -78 °C was treated with *n*-BuLi (0.1176 mmol, 2.5 M in hexane). The mixture was stirred while slowly warming up to -30 °C over 1.5 h before addition of an aqueous solution of NH₄Cl. The aqueous layer was extracted with diethyl ether, and the combined organic layers were dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (pentane/EtOAc 5:1) to give **3f** as a yellow oil (33 mg, 0.041 mmol, 70 %). Characterization of **3f**: see section 4.3.4.

4.3.4. Procedure for the preparation of **3f** with *n*-BuLi and CeCl₃

To a suspension of CeCl₃ (37 mg, 0.147 mmol) in THF (10 mL) at -78 °C was added *n*-BuLi (0.147 mmol, 2.5 M in hexane) and the resulting mixture was stirred for 0.5 h at this temperature. After treatment with a solution of [6]pericyclynedione **2** (50 mg, 0.0735 mmol) in THF (8 mL) at -78 °C, the mixture was slowly warmed up to -20 °C during 2 h before addition of an aqueous solution of NH₄Cl. The aqueous layer was extracted with diethyl ether, and the combined organic layers were dried over MgSO₄ and concentrated under reduced

pressure. The residue was purified by chromatography on silica gel (pentane/EtOAc 5:1) to give **3f** as a yellow oil (53 mg, 0.067 mmol, 90 %).

¹H NMR (300 MHz, CDCl₃) δ 7.81-7.64 (m, 8H, *o*-C₆H₅), 7.45-7.30 (m, 12H, *m*-, *p*-C₆H₅), 3.73-3.21 (m, 12H, OCH₃), 3.04-2.51 (m, 2H, OH), 2.10-1.89 (m, 4H, CH₂Pr), 1.78-1.51 (m, 4H, CH₂Et), 1.39-1.23 (m, 4H, CH₂Me), 1.00-0.81 (m, 6H, CH₂CH₃).

¹³C{¹H} NMR (75 MHz, CDCl₃) δ 139.6-139.3 (*i*-C₆H₅), 129.1-129.0 (*p*-C₆H₅), 128.5-128.4 (*m*-C₆H₅), 126.5-126.4 (*o*-C₆H₅), 87.4-87.0, 84.5-84.3, 81.2-80.1 (-C $\equiv$ C-), 71.9-71.8 (C(OMe)-Ph), 63.7 (C(OH)-Bu), 53.4-53.3 (OCH₃), 43.0-42.8 (CH₂Pr), 26.8-26.5 (CH₂Et), 22.4-22.3 (CH₂Me), 14.2-13.9 (CH₂CH₃).

HRMS (MALDI-TOF/DCTB): *m/z*: [M+H]⁺ calculated for C₅₄H₅₃O₆: 797.3842, found: 797.3771.

Results and discussion

p-Di-*n*-butyl-tetraphenyl-carbo-benzene **1f** was targeted through the classical route, i.e. by reductive aromatization of the corresponding [6]pericyclynediol **3f**, itself envisaged from the [6]pericyclynedione **2** and various *n*-Bu-MX_n reagents, MX_n = MgBr, MgCl, Li, CeCl₂ (Scheme 3).¹²

Following previous experiences (Scheme 1), addition of two equivalents of *n*-butylmagnesium bromide to **2** gave **3f** in 51 % yield, along with the reduced mono-adduct **4f** and the known bis-secondary [6]pericyclynediol **5**,^{6h,13} isolated in 28 % and 16 % yield, respectively.

Replacing *n*-BuMgBr by *n*-BuMgCl led to the diadduct **3f** with a similar 53 % yield, but without reduction side-product, as indicated by the absence of any CHOH ¹H NMR signal in the range 5-6 ppm. This change in nucleophilic vs redox selectivity can be attributed to the electronegativity-driven higher nucleophilic reactivity of the chlorinated magnesium salt as compared to the brominated congener. Traces of the non-reduced mono-ketone mono-adduct were detected by ¹H NMR spectroscopy, but could not be separated from other unidentified products, likely polymeric in nature.

Addition of two equivalents of *n*-butyllithium to **2** followed by aqueous quenching at -30°C was found to proceed selectively, allowing the diadduct **3f** to be isolated in 70 % yield. This result contrasts with the poor efficiency of the addition of aryllithium reagents to the same diketone **2**, the intermediate lithium alkoxide evolving by retro-additive opening of the

macrocycle towards stabilized arylketones such as **9** (Scheme 3).¹⁴ Such a ring opening was not observed with *n*-BuLi, provided that the reaction mixture was quenched at $-30\text{ }^{\circ}\text{C}$.

Finally, addition of two equivalents of *n*-butylcerium dichloride, assumed to be formed *in situ* from *n*-BuLi and dry CeCl_3 , to **2** was found to proceed very selectively, affording the [6]pericyclynediol **3f** with a 90 % isolated yield. This result is in line with the ones disclosed above ($\text{M} = \text{Li} > \text{Mg}$, $\text{X} = \text{Cl} > \text{Br}$), and with previous reports on the general use of cerium reagents.^{6a-b,9}

Insert here the **Scheme 3**

The target di-*n*-butyl-tetraphenyl-*carbo*-benzene **1f** was finally obtained by classical reductive treatment of the [6]pericyclynediol **3f** with SnCl_2 and HCl in dichloromethane (DCM).⁶ It was isolated with 63 % yield as a stable dark red solid, soluble in chlorinated organic solvents (chloroform and DCM).

Single crystals of **1f** deposited from a DCM solution were analyzed by X-ray diffraction, confirming the anticipated structure (Figure 1). The C_{18} macrocycle of **1f** is quasi-planar with a quasi-regular hexagonal shape, the maximal deviation from planarity being of $0.028\text{ }\text{\AA}$. The measured bond lengths in the C_{18} ring are classical for a *carbo*-benzene ($\text{spC-spC} \approx 1.22\text{-}1.23\text{ }\text{\AA}$, $\text{sp}^2\text{C-spC} \approx 1.37\text{-}1.38\text{ }\text{\AA}$). The *n*-butyl chains exhibit a zig-zag arrangement almost perfectly coplanar with the C_{18} ring, as previously observed for some dialkyl-*carbo*-benzenes.^{7a} Two of the phenyl substituents are also quasi-coplanar with the C_{18} ring, while the two others adopt a torsion angle of *ca* 25° . The distance between two successive C_{18} mean planes is $3.445\text{ }\text{\AA}$, which is longer than the shortest corresponding distance of $3.206\text{ }\text{\AA}$ measured for the bis-tetradecyl-*carbo*-benzene: no direct π - π stacking between C_{18} rings of **1f** is observed in the crystal, where co-crystallized DCM molecules prevent van der Waals contact between nearest macrocycles.^{7a}

Insert here the **Figure 1**

The dibutyl-*carbo*-benzene **1f** was also characterized by ^1H and ^{13}C NMR in CDCl_3 solution. The ^1H NMR spectral profile is similar to those reported for other dialkyl-*carbo*-benzenes, with a strong deshielding at 9.51 ppm of the *o*-CH nuclei of the four equivalents

phenyl substituents.^{7a} This effect reveals the strength of the diatropic C₁₈ ring current, which also affects the ¹H signals of the *n*-butyl chain, progressively vs the distance of the CH₂ groups to the C₁₈ ring border, as previously analyzed for other *n*-alkyl-*carbo*-benzenes (Figure S1 in the S.I.).^{7a}

The UV-vis absorption pattern of **1f** in chloroform solution is classical for dialkyl-tetraphenyl-*carbo*-benzenes ($\lambda_{\text{max}} = 446 \pm 0.5$ nm), with one main band at 446 nm, accompanied by three smaller bands at higher wavelength (Figure S2 in the S.I.).^{7a} The chromophoric intensity of **1f** is also classical in this series, with a maximum extinction coefficient of 208 000 L.mol⁻¹.cm⁻¹.

The title target **1f** has been selected as a model for an analysis of the solvent effect on the electrochemical behavior of *carbo*-benzene derivatives, that might be not soluble enough in DCM to allow the study of redox properties in this solvent, requiring the use of chloroform instead.¹⁵ For the sake of comparison, solutions of **1f** in both chloroform and DCM were thus investigated by square-wave (SW) and cyclic (CV) voltammetry (Table 1).

In the reference DCM solvent, **1f** lends itself to three successive reduction processes, two of them being reversible at $E_{1/2}^{\text{red}} = -0.82$ V and -1.26 V, those values being comparable to those previously reported for other *carbo*-benzene derivatives.^{6f,6i,15} The aromaticity of the C₁₈ ring indeed attenuates its sensitivity to substituents.^{6f} In chloroform, the two first reductions occur at similar potentials (albeit turning less reversible at -0.82 V, -1.32 V), while the third reduction peak occurring at $E_p^{\text{red}} = -1.98$ V in DCM cannot be detected because of the narrower electrochemical observation window of CHCl₃, which is reduced at this potential. These results also show that replacement of two aryl substituents by alkyl counterparts has a weak but electronically consistent effect on the reduction potential values (-0.72 V, -1.15 V for hexaphenyl-*carbo*-benzene).¹⁵

In both solvents, three oxidation processes are also observed at comparable potentials, with a loss of reversibility of the second wave observed in DCM ($E_{1/2}^{\text{ox2}} = +1.63$ V) by passing to chloroform ($E_p^{\text{ox2}} = +1.69$ V).

The influence of the solvent on the redox potentials is thus limited, but affects the reversibility of the processes, possibly because of the higher viscosity and lower dielectric constant of chloroform ($\eta(\text{CHCl}_3) = 0.537$ mPa.s $>$ $\eta(\text{DCM}) = 0.413$ mPa.s, $\epsilon(\text{CHCl}_3) = 4.81$ $<$ $\epsilon(\text{DCM}) = 8.93$). A high dielectric constant indeed favors charge dissociation thus enhancing the conductivity of the electrolytic solution.

solvent / redox event no	reductions			oxidations		
	$E_{1/2}^a$ (ΔE_P) ^b	RI_P^c	$E_P^{\text{red d}}$	$E_{1/2}^a$ (ΔE_P) ^b	RI_P^c	$E_P^{\text{ox d}}$
DCM 1st 2nd 3rd	− 0.82 (68)	0.97		1.15 (78)	1.04	
	−1.26 (63)	0.97		1.63 (107)	1.15	
			−1.98			2.06
CHCl ₃ 1st 2nd 3rd	−0.82 ^e (59)	1.01		1.18 ^e (53)	0.68	
			−1.32 _f			1.69
						2.05

Table 1. Voltammetric data for 1f in DCM and chloroform solutions. Supporting electrolyte: solvent + 0.1 M [TBA][PF₆]; scan rate: 0.2 V/s. ^a Half-wave potential $E_{1/2} = (E_P^{\text{red}} + E_P^{\text{ox}})/2$, in V/SCE. ^b Separation between the two peak potentials: $\Delta E_P = |E_P^{\text{red}} - E_P^{\text{ox}}|$, in V. ^c Peak current ratio $RI_P = |I_P^{\text{ox}}/I_P^{\text{red}}|$. ^d E_P values measured from CV in V/SCE. ^e Reversibility observed at high scan rates only. ^f The third reduction cannot be observed in CHCl₃ because the solvent is reduced at this potential.

Conclusion

The metal switch study of the reaction of a model alkyl nucleophile with the [6]pericyclynedione **2** brings out the dichlorocerium(III) reagent as the most selective for the production of **3f**. The improvement is particularly eloquent by comparison to the bromomagnesium reagent affording also the double reduction product **5** and the single addition/reduction product **4f** (that could however be profitably used for a *carbo*-benzene library purpose).^{7a} The synthesis results provide a global increase of the yield of preparation of *p*-di-*n*-butyl-tetraphenyl-*carbo*-benzene **1f**, from 32 % to 57 % over the two last steps. The cerium method can thus henceforth be envisaged for the synthesis of other alkyl-*carbo*-benzenes.

The disclosed voltammetry results, the first ones in the alkyl-*carbo*-benzene series, indicate that the electrochemical behavior of *carbo*-benzenes is little sensitive to solvent (DCM vs chloroform) and substituent (alkyl vs aryl) effects. More generally, the "hybrid" member of the *carbo*-benzene family **1f**, with two standard alkyl chain and four phenyl ring substituents, could now serve as a soluble standard for other comparative studies.

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Supporting Information: ^1H NMR and UV-vis. absorption spectra of **1f**.

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Scheme 1. Last two steps of previous syntheses of *p*-dialkyl-*carbo*-benzenes. The intermediates **2-5** were used as mixtures of stereoisomers.

Scheme 2. Improvement of a [11+7] macrocyclization from a C₁₁ tetrayne and a C₇ dialdehyde through the use of a cerium(III) reagent.

Scheme 3. En route and access to *p*-di-*n*-butyl-tetraphenyl-carbo-benzene.

Figure 1. Molecular view of the X-ray crystal structure of **1f**. Thermal ellipsoids at the 50 % probability level. For clarity, hydrogen atoms are omitted.

GRAPHICAL ABSTRACT

Increasing yield from 32 % to 57 %: **MgBr < MgCl < Li < CeCl₂**

Draft