Selective access to p-dialkyl-carbo-benzenes from a [6]pericyclynedione: the n-butyl nucleophile model for a metal switch study
Selective access to \( p \)-dialkyl-\textit{carbo-}benzenes from a [6]pericyclynedione:
the \( n \)-butyl nucleophile model for a metal switch study\(^\dagger\)

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Abstract

The synthesis, spectroscopic properties, comparative electrochemical behavior in CHCl\(_3\) vs CH\(_2\)Cl\(_2\), and X-ray crystal structure of \( p \)-di-\( n \)-butyl-tetraphenyl-\textit{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 \( \leq n \leq 2\)): Li, MgBr, MgCl, CeCl\(_2\)/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-\textit{carbo-}benzene product happens to be soluble in both CHCl\(_3\) and CH\(_2\)Cl\(_2\), cyclic voltammograms of either solutions exhibiting almost identical peak potentials, with reduced reversibility of the redox processes in CHCl\(_3\).

Key-words. Alkylcerium - Alkyne - Aromatics - \textit{Carbo-}benzene - \textit{Carbo-}mer

\(^\dagger\) 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 sp²-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 C₃₂ core having allowed full characterization of this first example of fused polycyclic α-graphyne fragment, in or from solutions in CHCl₃.⁴ The solubilizing effect of the p-pentylphenyl groups appeared however limited, even on the smaller carbo-benzene congener C₁₈(4-n-C₅H₁₁-C₆H₄)₆. The carbo-benzene C₁₈ 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 sp² vertices of the C₁₈ ring was envisaged in a series of p-dialkyl-tetraphenyld-carbo-benzenes 1a-e, which could be obtained in two steps, by addition of alkylmagnesium bromides to the [6]pericyclonediene 2 followed by reductive aromatization of the [6]pericyclonediol 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.

In general nucleophilic addition of Nu–MXₙ 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]pericyclonediols 6a-b from the bis-terminal tetrayne 7a-b and dialdehyde 8, while reactions of the MgBr⁺ salts alone appeared almost unproductive (0-
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 Nu = n-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.

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: $^1$H 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 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 $\lambda$ is given in nm, and the corresponding maximum extinction molar coefficient $\varepsilon$ in L.mol$^{-1}$.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. 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 \([n-\text{Bu}_4\text{N}]\text{PF}_6\) 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 \(\text{carbo}\)-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 \(E_{\text{sw}} = 20\) mV, scan increment \(dE = 5\) mV.

4. Experimental procedures and characterizations of new products

4.1. 1,10-dibuty1-4,7,13,16-tetraphenylecyclooctadeca1,2,3,7,8,9,13,14,15-nonaen-5,11,17-triyne (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 %).

\(^1\text{H NMR}\) (400 MHz, CDCl₃) \(\delta 9.51\) (dd, \(^3J_{\text{HH}} = 8.0, ^4J_{\text{HH}} = 1.2\) Hz, 8H, o-C₆H₅), 7.97 (dd, \(^3J_{\text{HH}} = 8.2, 7.2\) Hz, 8H, m-C₆H₅), 7.73-7.66 (m, 4H, p-C₆H₅), 4.69 (t, \(^3J_{\text{HH}} = 7.5\) Hz, 4H, m-C₆H₅).
\(CH_2Pr\), 3.04-2.92 (m, 4H, \(CH_2CH_2Me\)), 2.02 – 1.91 (m, 4H, \(CH_2Me\)), 0.91-0.82 (m, 6H, \(-CH_3\)).

\(^{13}C\{^1H\} NMR\) (101 MHz, CDCl\(_3\)) \(\delta\) 139.9 (\(i-C_3H_5\)), 129.8 (\(o-C_6H_5\)), 129.8 (\(m-C_6H_5\)), 129.3 (\(p-C_6H_5\)), 122.1, 119.4, 116.0 (\(=C=C=\), \(-C≡C-\)), 106.5 (\(C\(\text{Bu}\)), 103.0 (\(C\(\text{Ph}\)), 40.4 (\(CH_2Pr\)), 34.0 (\(CH_2Et\)), 22.8 (\(CH_2Me\)), 14.3 (\(-CH_3\)).

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

**UV-visible** (CHCl\(_3\)): \(\lambda_{\text{max}}\) = 446.45 nm (\(\varepsilon = 208\ 000\ \text{L·mol}^{-1}\cdot\text{cm}^{-1}\)).

**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\(_3\)) \(\delta\) 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, \(OC_3H_3\)), 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, \(CH_3\)).

\(^{13}C\{^1H\} NMR\) (101 MHz, CDCl\(_3\)) \(\delta\) 139.48 (\(i-C_3H_5\)), 129.10 (\(p-C_6H_5\)), 128.53 (\(m-C_6H_5\)), 126.46 (\(o-C_6H_5\)), 87.10, 84.67, 82.91 (\(-C≡C-\)), 75.96, 72.98 (\((OMe)\text{-Ph})\)), 63.71 (\((OH)\text{-Bu})\)), 53.36 - 53.31 (\(OCH_3\)), 53.26 (>\(CHOH\)), 42.82 (\(CH_2Pr\)), 26.66 (\(CH_2Et\)), 22.35 (\(CH_2Me\)), 11.41 (\(CH_2CH_3\)).

**HRMS** (MALDI-TOF/DCTB): \(m/z\): [\(M+Na\)]\(^+\) calculated for \(C_{44}H_{44}O_6Na\): 763.3036, found: 763.3085.

4.3. 1,10-dibuty1-4,7,13,16-tetramethoxy-4,7,13,16-tetraphenylcyclooctadeca-2,5,8,11,14,17-hexayne-1,10-di0l (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]pericycycledione 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 %),⁶,¹¹ 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.
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 %).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.81-7.64 (m, 8H, o-C\(_6\)H\(_5\)), 7.45-7.30 (m, 12H, m-, p-C\(_6\)H\(_5\)), 3.73-3.21 (m, 12H, OMePh), 3.04-2.51 (m, 2H, OH), 2.10-1.89 (m, 4H, CH\(_2\)Pr), 1.78-1.51 (m, 4H, CH\(_2\)Et), 1.39-1.23 (m, 4H, CH\(_2\)Me), 1.00-0.81 (m, 6H, CH\(_2\)CH\(_3\)).

\(^{13}\)C\(^{1\)H\}) NMR (75 MHz, CDCl\(_3\)) \(\delta\) 139.6-139.3 (i-C\(_6\)H\(_5\)), 129.1-129.0 (p-C\(_6\)H\(_5\)), 128.5-128.4 (m-C\(_6\)H\(_5\)), 126.5-126.4 (o-C\(_6\)H\(_5\)), 87.4-87.0, 84.5-84.3, 81.2-80.1 (C≡C-), 71.9-71.8 (C(OMe)-Ph), 63.7 (C(OH)-Bu), 53.4-53.3 (OCH\(_3\)), 43.0-42.8 (CH\(_2\)Pr), 26.8-26.5 (CH\(_2\)Et), 22.4-22.3 (CH\(_2\)Me), 14.2-13.9 (CH\(_2\)CH\(_3\)).

HRMS (MALDI-TOF/DCTB): m/z: [M+H]\(^+\) calculated for C\(_{54}\)H\(_{53}\)O\(_6\): 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]pericyclediols 3f, itself envisaged from the [6]pericyclediones 2 and various \(n\)-Bu-MX\(_n\) reagents, MX\(_n\) = MgBr, MgCl, Li, CeCl\(_2\) (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]pericyclediol 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 \(^1\)H 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 \(^1\)H 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). Such a ring opening was not observed with n-BuLi, provided that the reaction mixture was quenched at −30 °C.

Finally, addition of two equivalents of n-butylerium dichloride, assumed to be formed in situ from n-BuLi and dry CeCl₃, 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 (M = Li > Mg, X = Cl > 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 SnCl₂ 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 C₁₈ macrocycle of 1f is quasi-planar with a quasi-regular hexagonal shape, the maximal deviation from planarity being of 0.028 Å. The measured bond lengths in the C₁₈ ring are classical for a carbo-benzene (spC-spC ≈ 1.22-1.23 Å, sp²C-spC ≈ 1.37-1.38 Å). The n-butyl chains exhibit a zig-zag arrangement almost perfectly coplanar with the C₁₈ ring, as previously observed for some dialkyl-carbo-benzenes.⁷ᵃ Two of the phenyl substituents are also quasi-coplanar with the C₁₈ ring, while the two others adopt a torsion angle of ca 25°. The distance between two successive C₁₈ mean planes is 3.445 Å, which is longer than the shortest corresponding distance of 3.206 Å measured for the bis-tetradecyl-carbo-benzene: no direct π−π stacking between C₁₈ 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 ¹³C NMR in CDCl₃ 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.\textsuperscript{7a} This effect reveals the strength of the diatropic C\textsubscript{18} ring current, which also affects the \textsuperscript{1}H signals of the \textit{n}-butyl chain, progressively vs the distance of the CH\textsubscript{2} groups to the C\textsubscript{18} ring border, as previously analyzed for other \textit{n}-alkyl-\textit{carbo}-benzenes (Figure S1 in the S.I.).\textsuperscript{7a}

The UV-vis absorption pattern of \textit{1f} in chloroform solution is classical for dialkyl-tetraphenyl-\textit{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.).\textsuperscript{7a} The chromophoric intensity of \textit{1f} is also classical in this series, with a maximum extinction coefficient of 208 000 L.mol\textsuperscript{-1}.cm\textsuperscript{-1}.

The title target \textit{1f} has been selected as a model for an analysis of the solvent effect on the electrochemical behavior of \textit{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.\textsuperscript{15} For the sake of comparison, solutions of \textit{1f} in both chloroform and DCM were thus investigated by square-wave (SW) and cyclic (CV) voltammetry (Table 1).

In the reference DCM solvent, \textit{1f} lends itself to three successive reduction processes, two of them being reversible at $E_{1/2}^{\text{red}} = \text{–0.82 V}$ and \text{–1.26 V}, those values being comparable to those previously reported for other \textit{carbo}-benzene derivatives.\textsuperscript{6f,6i,15} The aromaticity of the C\textsubscript{18} ring indeed attenuates its sensitivity to substituents.\textsuperscript{6f} In chloroform, the two first reductions occur at similar potentials (albeit turning less reversible at \text{–0.82 V}, \text{–1.32 V}), while the third reduction peak occurring at $E_p^{\text{red}} = \text{–1.98 V}$ in DCM cannot be detected because of the narrower electrochemical observation window of CHCl\textsubscript{3}, 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 (\text{–0.72 V}, \text{–1.15 V} for hexaphenyl-\textit{carbo}-benzene).\textsuperscript{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 ($\eta$(CHCl\textsubscript{3}) = 0.537 mPa.s > $\eta$(DCM) = 0.413 mPa.s, $\varepsilon$(CHCl\textsubscript{3}) = 4.81 < $\varepsilon$(DCM) = 8.93). A high dielectric constant indeed favors charge dissociation thus enhancing the conductivity of the electrolytic solution.
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 $R_{I_p} = |I_{P_{\text{ox}}}^\text{ox}/I_{P_{\text{red}}}^\text{red}|$. 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.

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<td>$E_{1/2}$</td>
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<td>2nd</td>
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<tr>
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<td>CHCl₃</td>
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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.
Acknowledgements

C. Z. thanks the China Scholarship Council for his Ph.D. scholarship. The ANR program (ANR-11-BS07-016-01) is acknowledged for funding. R. C. thanks the Centre National de la Recherche Scientifique (CNRS) for half a teaching sabbatical in 2015-2016.

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

References


(14) Zhu, C.; Maraval, V.; Chauvin, R. unpublished results.

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

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<th>4a-e, 20-28%</th>
<th>5, 6-20%</th>
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**Scheme 2.** Improvement of a [11+7] macrocyclization from a C11 tetrayne and a C7 dialdehyde through the use of a cerium(III) reagent.

<table>
<thead>
<tr>
<th></th>
<th>6a: R = THP</th>
<th>6b: R = Me</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a: R = THP</td>
<td>6 %</td>
<td>14 %</td>
</tr>
<tr>
<td>7b: R = Me</td>
<td>0 %</td>
<td>12 %</td>
</tr>
</tbody>
</table>

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1) RMgBr
2) H<sup>+</sup>
3) SnCl<sub>2</sub>/HCl
4) DCM - 78 °C

**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-tetraphenyldi-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

\[ E_{1/2}^{\text{red}} = -0.82 \text{ V (in CH}_2\text{Cl}_2 \text{ or CHCl}_3) \]