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Synthesis of 1,2,9,10-Tetrahydroxy[2.2]metacyclophanes *via* Pinacol Coupling Reaction of 1,3-Benzenedicarboxyaldehydes

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Abstract: Tetrahydroxy[2.2]metacyclophanes are formed via the aluminium mediated pinacol coupling reaction of 1,3-benzenedicarboxaldehydes. The results indicate that the presence of functional groups in the aromatic ring of the dialdehydes plays an important role in the formation of the cyclophane structure. Intramolecular coupling reactions as well as a comparison of different reductive systems are discussed in the work.

Introduction

Bridge-substituted [2.2]metacyclophanes are of special interest due to their application in the study of the reactivity of strained structures[1] as well as in the study of ring-inversion equilibria of the metacyclophane skeleton.[2] However, the methods for the synthesis of bridge-substituted [2.2]metacyclophanes, that have been described, invariably consist of numerous steps and usually give low yields.[3]

Recently, we have reported on the novel single-step synthesis of 5,13-di-*tert*-butyl-8,16-dimethyl-1,2,9,10-tetrahydroxy[2.2]metacyclophane (**2b**) *via* the aluminium-mediated pinacol coupling of 5-*tert*-butyl-2-methyl-1,3-benzenedicarboxaldehyde (**1b**).[4] Here, the synthesis of a series of bridge-hydroxylated [2.2]metacyclophanes *via* the aluminium-mediated pinacol coupling reaction is reported.

Results and Discussion

Pinacol coupling reactions of benzene-1,3-dialdehydes **1a-d** were carried out by using aluminium (powder, 150 mesh) in a 10% aqueous NaOH solution and methanol as reductive system.[5] In this way [2.2]metacyclophanes **2a-d** were obtained (Scheme 1). The best yields of [2.2]metacyclophanes were achieved in the coupling of substrates **1b** and **1c**. This result indicates that the presence of the bulky *tert*-butyl group plays an important role in the formation of the [2.2]metacyclophane structure during the reaction.

Aluminium was also found to be suitable for intramolecular reductive coupling. In this way [2.2]metacyclophanes **5**[4] and **2b** were formed from the coupling reaction of the bis-aldehydes **3** and **4**, respectively (Scheme 1).

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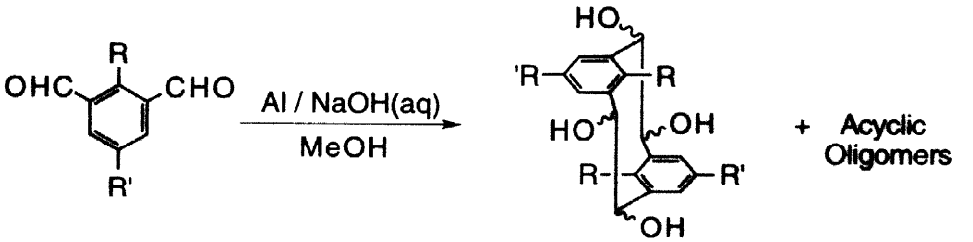
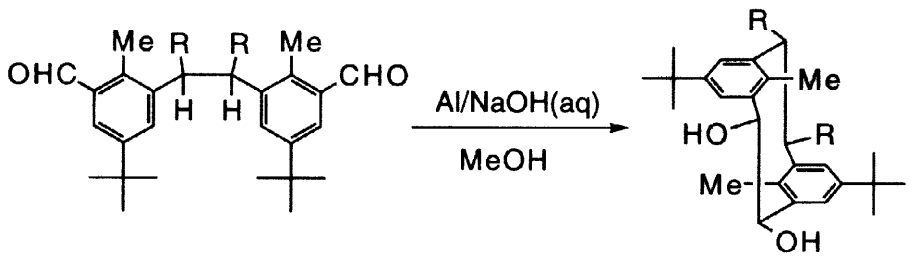


1a; R= Me, R'= H — **2a**; Y= 4% (as the tetra-methoxy derivative)

1b; R= Me, R'= t-Bu — **2b**; Y= 33%

1c; R= OMe, R'= t-Bu — **2c**; Y= 23 %

1d; R= R'= OMe — **2d**; Y= 5%

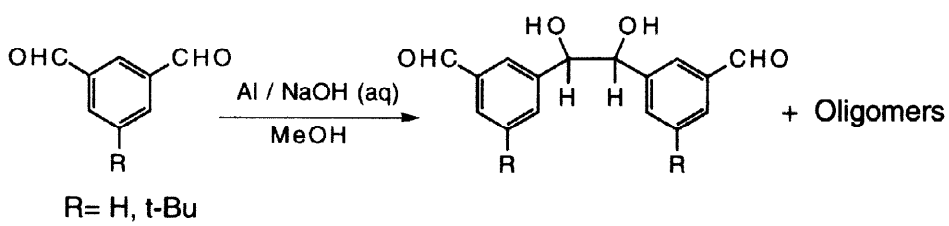


3; R= H — **5**; Y= 18% (R= H)

4; R= OH (*dl* Isomer) — **2b**; Y= 17% (R= OH)

Scheme 1

Interestingly, we noted that in the coupling of compound **4** only the *dl*-isomer afforded the [2.2]metacyclophane and no formation of a [2.2]metacyclophane structure could be observed in the coupling of compound *meso*-**4**. On the other hand, we have observed that, when 1,3-benzenedicarboxaldehydes carrying a proton at C-2 are used as substrate, there is no formation of [2.2]metacyclophanes (Scheme 2).[6]



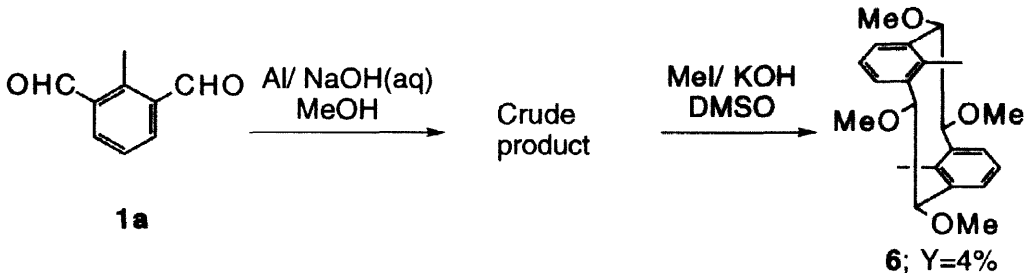
R= H, t-Bu

Scheme 2

Therefore, the presence of functional groups, such as the methyl- or methoxy-functionality, could provide the driving force required for the formation of the strained [2.2]metacyclophane structure in the aluminium-mediated coupling reaction. Although the precise mechanism of the coupling is not clear, a contribution to the formation of the [2.2]metacyclophane structure due to a CH-π interaction[7] in the case of the methyl substituent and in the case of the methoxy substituent due to an intermediate formation of an oxygen-aluminium complex[8]

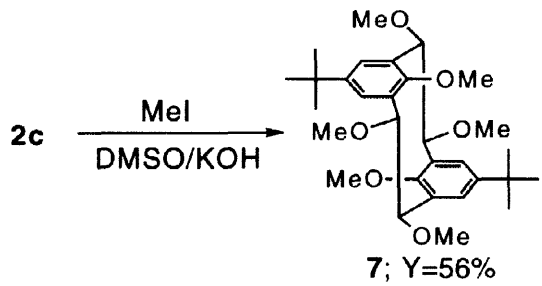
with participation of the methoxy group itself should be taken into account.

The coupling of dialdehydes **1a**, **1b**, **3** and **4** proceeds with high stereoselectivity; thus, metacyclophanes **2a**, **2b** and **5** were obtained as a single isomer. All the hydroxy groups of **2b** are in an equatorial position as is shown by X-ray crystallography.[4] Metacyclophane **2a** shows poor solubility in most solvents; therefore, after the coupling reaction, the crude product was methylated[9] in order to obtain a more soluble product. In this way, **2a** was isolated as the tetramethoxy derivative **6** (Scheme 3). From a comparison of the ^{1}H-NMR spectra, **5** and **6** were deduced to have their hydroxy groups in an equatorial position.



Scheme 3

The coupling of compounds **1c** and **1d**, which possess a methoxy group in the 2-position, also afforded stereoselectively the [2.2]metacyclophanes **2c** and **2d** with all hydroxy groups in equatorial positions as the major compounds, but a very small amount of another isomer could be detected in their ^{1}H-NMR spectra. In order to confirm the stereochemistry of **2c**, it was methylated to afford the tetramethoxy derivative **7** in good yield (Scheme 4). Compound **7** was analyzed by X-ray crystallography which showed the bridge methoxy groups of the [2.2]metacyclophane to occupy the equatorial positions (Fig 1).



Scheme 4

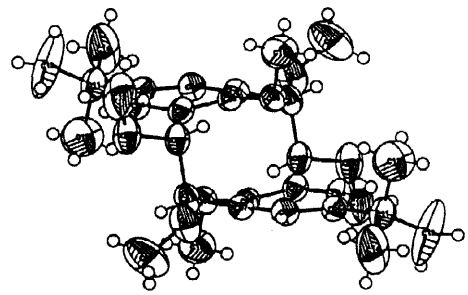


Fig 1. ORTEP View of Compound **7**

The coupling reaction of **1b** was carried out by using different systems such as SmI_2[10], $TiCl_4/Zn$[11] and Cp_2TiCl_2/Zn.[12] As shown in Table 1, only Al/NaOH(aq) and SmI_2 yielded **2b**.

In conclusion, the aluminium-mediated pinacol coupling reaction presents a convenient method for the preparation of bridge-substituted [2.2]metacyclophanes in a single step. The reductive system affords better yields of [2.2]metacyclophanes than others the authors have tried. Also, it only requires very simple operations and inexpensive reagents.

Table 1. Pinacol Coupling of **1b** by Using Different Reductive Systems.

Entry	Reagent	Yield of **2b**(%)[a]
1	Al / NaOH(aq)	33
2	$TiCl_4$ / Zn	-
3	Cp_2TiCl_2 / Zn	-
4	SmI_2	28

[a] Isolated yields.

Experimental

General. Melting points were determined on a YANAKO MP-500D Micro Melting Point apparatus and are uncorrected. IR spectra were recorded on a JASCO IR 700 Infrared Spectrometer in KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a JEOL JMN-EX 270 (270 MHz) Spectrometer using $SiMe_4$ as internal standard; *J* values are given in Hertz. Mass spectra were recorded on a JEOL JMS-70 Spectrometer. 3-Nitrobenzyl alcohol was used as a matrix for MS (FAB). Elemental analyses were determined on a YANAKO MT-S CHN Corder apparatus. Column chromatography was done on Wako gel C-300 (200-300 mesh). Commercially available aluminium powder (mesh 150, Kishida Chemical Co.) was used as received. Dialdehyde **1a** was prepared as described in the literature.[13]

2-Methyl-5-*tert*-butyl-1,3-benzenedicarboxaldehyde (1b). A solution of 2,6-bis(chloromethyl)-4-*tert*-butyl- toluene[14] (6.14 g, 25.04 mmol) in pyridine (150 ml) was heated under gentle reflux and under vigorous stirring for 2 h. The reaction mixture was cooled and the formed precipitate was filtered, washed several times with benzene, and dried to afford a quantitative yield of bis-pyridinium salt. To a stirred solution of this bis-pyridinium salt (9.84 g) and *N,N*-dimethyl-4-nitrosoaniline (7.33 g, 49 mmol) in ethanol (70 ml), was added 10% aqueous sodium hydroxide solution (35 ml) at rt. After 90 min, 5N hydrochloric acid (40 ml) was added at rt. The mixture was stirred for 30 min, then water (50 ml) was added to it. The yellowish crystals obtained in this way were filtered and washed with water affording the crude product, which was purified by chromatography (hexane / ethyl acetate, 9 / 1) to give **1b** (3.99 g, 19.53 mmol, 78%) as colorless prisms (hexane): mp 90-95°C; IR 2958, 2872, 1682; ^{1}HNMR ($CDCl_3$) 1.38 (s, 9H), 2.96 (s, 3H), 8.08 (s, 2H), 10.44 (s, 2H);^{13}CNMR ($CDCl_3$) 12.90, 31.01, 34.71,,133.22,,135.29, 139.99, 149.91, 191.87; MS *m/z* 204 (M^+), 189 (M^+-CH3); Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.28; H, 8.18.

2-Methoxy-5-*tert*-butyl-1,3-benzenedicarboxaldehyde (1c). A solution of 2,6-bis(chloromethyl)-4-*tert*-butyl-anisole[14] (1.30 g, 5 mmol) in pyridine (20 ml) was heated under gentle reflux and under vigorous stirring for 10 min. The reaction mixture was cooled and the precipitates formed were filtered, washed several times with benzene, and dried to afford a quantitative yield of bis-pyridinium salt. To a stirred solution of this bis-pyridinium salt (2.01 g, 5 mmol) and *N,N*-dimethyl-*p*-nitrosoaniline (1.50 g, 10 mmol) in ethanol (20 ml), 10% aqueous sodium hydroxide solution (10 ml) was added at rt. After 90 min, 5N hydrochloric acid (15 ml)

was added at rt. The mixture was stirred for 30 min, then water (50 ml) was added to it. The mixture was extracted with dichloromethane (30 ml x 3) and the extract was washed with water, dried, and evaporated to afford the crude product which was purified by chromatography (hexane/ethyl acetate, 9/1) to yield **1c** (0.78 g, 3.56 mmol, 71%) as colorless plates (hexane): mp 87-88°C; IR 2960, 2850, 1684; ^{1}HNMR ($CDCl_3$) 1.36 (s, 9H), 4.07 (s, 3H), 8.14 (s, 2H), 10.42 (s, 2H); ^{13}CNMR ($CDCl_3$) 31.09, 34.84, 66.72, 129.47, 132.06, 148.34, 163.61, 188.77; MS *m/z* 220 (M^+); Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.60; H, 7.31.

2,5-Dimethoxybenzene-1,3-dicarboxaldehyde (1d) by $BaMnO_4$ mediated oxidation:[15] A mixture of 1,3-bis(hydroxymethyl)-2,5-dimethoxybenzene[16] (1.00 g, 5 mmol) and $BaMnO_4$ (10.0 g, 39 mmol) in dichloromethane (100 ml) was stirred at rt. The reaction was followed by TLC. After 8 h, the mixture was filtered and the filter cake was washed with dichloromethane (200 ml). Then the filtrates were combined and the solvent was evaporated to afford **1d** (0.93 g, 4.6 mmol, 93%) as colorless needles (hexane/ethyl acetate, 1/1): mp 115-117°C (lit.,[16] 113-115°C).

1,2-Bis(5-*tert*-butyl-3-formyl-2-methylphenyl)ethane (3). A solution of 1,2-bis(5-*tert*-butyl-3-chloromethyl-2-methylphenyl)ethane[17] (4.20 g, 10 mmol) in pyridine (180 ml) was heated under gentle reflux for 90 min. After the reaction mixture was cooled, the precipitates formed were filtered, washed several times with benzene, and dried to afford a quantitative yield of bis-pyridinium salt. To a stirred solution of this bis-pyridinium salt (2.90 g, 5 mmol) and *N,N*-dimethyl-*p*-nitrosoaniline (1.50 g, 10 mmol) in ethanol (20 ml), was added a solution of 10% aqueous sodium hydroxide (12 ml) at rt and the mixture was stirred for 90 min. Then, 5 N hydrochloric acid (15 ml) was added to it at rt and the mixture was stirred for 30 min. Water (50 ml) was added and the mixture was extracted with dichloromethane (30 ml x 3), washed with water, dried over $MgSO_4$ and evaporated *in vacuo* to yield the crude product which was purified by chromatography (hexane/ethyl acetate, 8/1) to afford **3** (1.45 g, 3.83 mmol, 77 %) as colorless needles (ethanol/H_2O): mp 87-88 °C; IR 2956, 1699; ^{1}HNMR ($CDCl_3$) 1.25 (s, 18H), 2.52 (s, 6H), 2.98 (s, 4H), 7.18 (d, J= 2 Hz, 2H), 7.67 (d, J= 2 Hz, 2H), 10.29 (s, 2H); ^{13}CNMR ($CDCl_3$) 13.66, 31.12, 34.07, 34.32, 127.24, 132.43, 134.36, 135.58, 140.54, 148.87, 193.40; MS *m/z* 378 (M^+). Anal. Calcd for $C_{26}H_{34}O_2$: C, 82.49; H, 9.05. Found: C, 82.29; H, 9.04.

1,2-Bis[2-methyl-3-formyl-5-*tert*-butylphenyl]ethane-1,2-diol (4 as a *dl*- and *meso*-isomer). Prepared by pinacol coupling reaction of **1b**: To a mixture of **1b** (1.02 g, 5 mmol), methanol (15 ml) and aluminium powder (150 mesh, 0.45 g, 16.7 mmol), aqueous 10% sodium hydroxide solution (6.7 ml) was added dropwise at rt under mechanical stirring. After 90 min of total reaction time, the mixture was filtered and the filtrate was extracted with ethyl acetate (40 ml x 3). The extract was washed with water, dried over $MgSO_4$ and evaporated *in vacuo*, giving a mixture of **4-*dl*** and **4-*meso*** . The mixture was chromatographed (hexane/ethyl acetate, 4/1) to give **4-*dl*** (0.45 g, 44%) and crude **4-*meso*** (0.13 g, 13%) which was contaminated by a small amount of higher oligomers and could not be purified further.

Diol **4-*dl*** : A colorless solid; mp 72-77°C; IR 3440, 2960, 1685; ^{1}HNMR (DMSO-d_6) 1.21 (s, 18H), 2.09 (s, 6H), 4.99 (s, 2H), 5.63 (s, 2H), 7.64 (s, 4H), 10.13 (s, 2H); ^{13}CNMR (DMSO-d_6) 12.99, 30.69, 33.96, 73.58, 127.13, 130.87, 133.42, 134.61, 141.27, 147.26, 193.74; FAB-MS *m/z* 411 ($M+H^+$). Anal. Calcd for ($C_{26}H_{34}O_4$ + 1/4 H_2O): C, 75.24; H, 8.38. Found: C, 75.43; H, 8.40.

Diol **4-*meso*** : ^{1}HNMR (DMSO-d_6) 1.15 (s, 18H), 2.17 (s, 6H), 5.15 (d, J= 2.80 Hz, 2H), 5.47 (d, J= 2.80 Hz, 2H), 7.49 (d, J= 2.31 Hz, 2H), 7.66 (d, J=2.31 Hz, 2H), 10.35 (s, 2H).

Aluminium-mediated Pinacol Coupling Reaction. General procedure. To a mixture of dialdehyde **1** (5 mmol), aluminium powder (0.55 g, 20 mmol) and methanol (22 ml) was added 10% aqueous sodium hydroxide solution (10 ml) under mechanical stirring. After being stirred for 3 h, the mixture was filtered. The filtrate was extracted with ethyl acetate (40 ml x 3), washed with water, dried over $MgSO_4$, evaporated *in vacuo*, and column chromatographed.

1,2,9,10-(all-*endo*)-Tetrahydroxy-5,13-di-*tert*-butyl-8,16-dimethoxy[2.2]metacyclophane (2c): A mixture of stereoisomers; colorless solid; mp >248°C (dec); ^{1}HNMR (DMSO-d_6) of the major isomer (>95%) 1.27 (s, 18H), 2.86 (s, 6H), 4.16 (s, 4H), 5.29 (s, 4H), 7.37 (s, 4H); MS *m/z* 444 (M^+). Anal. Calcd for $C_{26}H_{36}O_6$: C, 70.25; H, 8.16. Found: C, 70.07; H 8.13.

1,2,9,10-(all-*endo*)-Tetrahydroxy-5,8,13,16-tetramethoxy[2.2]metacyclophane (2d): A mixture of stereoisomers; colorless solid (ethyl acetate); mp >219°C (dec); ^{1}HNMR ($CDCl_3$) of the major isomer (>90%) 2.86 (s, 6H), 3.69 (s, 6H), 4.20 (s, 4H), 5.39 (s, 4H), 6.89 (s, 4H); MS *m/z* 392(M^+). Anal. Calcd for ($C_{20}H_{24}O_8$ + 1/4H_2O): C, 60.52; H, 6.22. Found: C, 60.77; H, 6.13.

5,13-Di-*tert*-butyl-1,2-(all-*endo*)-dihydroxy-8,16-dimethyl[2,2]metacyclophane (5): Colorless needles (hexane); mp >200°C (dec); IR 3430, 2954, 1478; ^{1}H NMR (DMSO-d_6) 0.47 (s, 6H), 1.24 (s, 18H), 2.63 (d, J= 9.9 Hz, 2H), 2.86 (d, J= 9.9 Hz, 2H), 4.33 (s, 2H), 5.47 (s, 2H), 7.13 (d, J= 1.98 Hz, 2H), 7.50 (d, J= 1.98 Hz, 2H); ^{13}C NMR (DMSO-d_6) 13.64, 31.10, 33.69, 35.31, 78.56, 120.00, 124.54, 135.81, 136.01, 137.05, 144.85; MS *m/z* 380 (M^+). Anal. Calcd for $C_{26}H_{36}O_2$: C, 82.06; H, 9.54. Found: C, 81.84; H, 9.54.

1,2,9,10-(all-*endo*)-Tetramethoxy-8,16-dimethyl[2.2]metacyclophane (6). To a mixture of dimethylsulfoxide (4 ml) and powdered potassium hydroxide (1.57 g, 28 mmol), the crude pinacol coupling product **2a** of **1a** (0.51 g) was added, followed by immediate addition of methyliodide (1.99 g, 0.87ml, 14 mmol) under vigorous stirring. After the mixture was stirred at rt for 30 min, it was poured into water (40 ml) and extracted with ethyl acetate (30 ml x 3). The extract was washed with water, dried over $MgSO_4$, and evaporated *in vacuo*, and chromatographed (hexane/ethyl acetate, 2/1, 1/1, 0/1) to give **6** (0.036 g, 4% yield from **1a**) as colorless plates (hexane/ AcOEt, 1/1): mp 217-218°C; IR 2928, 1446, 1096; ^{1}HNMR ($CDCl_3$) 0.75 (s, 6H), 3.54 (s, 12H), 4.27 (s, 4H), 7.03 (t, J= 7.6 Hz, 2H), 7.54 (d, J= 7.6 Hz, 4H); ^{13}CNMR ($CDCl_3$) 15.06, 57.81, 86.92, 123.65, 125.80, 134.21, 143.54; MS *m/z* 356 (M^+). Anal. Calcd for ($C_{22}H_{28}O_4$ + 1/8H_2O): C, 73.66; H, 7.94. Found: C, 73.71; H, 7.96.

*Pinacol Coupling of **1b** by Using Samarium Diiodide.*[10] A blue solution of samarium diiodide was prepared by refluxing a mixture of samarium (1.00 g, 6.7 mmol) and iodine (1.52 g, 6.0 mmol) in dry tetrahydrofuran (60 ml) for 12 h under argon. To it, a solution of **1b** (0.51 g, 2.5 mmol) in dry tetrahydrofuran (15 ml) was added dropwise during a period of 30 min at rt under argon. After the mixture was stirred at rt for 30 min, 0.1N hydrochloric acid (35 ml) was added to it and the mixture was extracted with ether (30 ml x 3). The extract was

treated with 10% sodium thiosulfate solution (40 ml), washed with water, dried over $MgSO_4$, and evaporated *in vacuo* to leave a residue, which was column chromatographed (hexane/ethyl acetate, 4/1) to afford **2b** (0.14 g, 28%).

Pinacol Coupling of **1b** *by Using the Mukaiyama Reagent.*[11] To a solution of **1b** (0.51 g, 2.5 mmol) in dry tetrahydrofuran (40 ml) cooled at -10°C under argon, titanium(IV) chloride (1.2 ml, 11.3 mmol) was added slowly and then a suspension of zinc powder (1.47 g, 22.5 mmol) in tetrahydrofuran (15 ml) was added dropwise. The resultant mixture was stirred for 2 h at 0°C, quenched with a 10% aqueous potassium carbonate solution (50 ml), and extracted with ether (30 ml x 3). The extract was washed with water, dried over $MgSO_4$, and evaporated *in vacuo* to afford a mixture of unidentified acyclic polypinacols.

Pinacol Coupling of **1b** *by Using Titanocene Chloride.*[12] A mixture consisting of titanocene dichloride (0.997 g, 4 mmol), zinc powder (0.71 g, 11 mmol) and dry tetrahydrofuran (20 ml) was stirred under argon at rt for 15 min. The mixture was immersed in an acetone bath (-60 °C) and to it, a solution of **1b** (0.20 g, 1 mmol) in dry tetrahydrofuran (10 ml) was added dropwise. The mixture was stirred for 5 min at -60°C, and then it was allowed to warm to rt within 1 h. 5N sodium hydroxide solution (10 ml) was added to the mixture and it was extracted with ethyl acetate (30 ml x 3). The extract was washed with water, dried over $MgSO_4$, and evaporated *in vacuo* to leave a residue which was analyzed by ^1H NMR. No cyclophane compound was present.

Methylation of **2c**. To a mixture of dimethylsulfoxide (2 ml) and powdered potassium hydroxide (0.25 g, 4.4 mmol), **2c** (0.12 g, 0.27 mmol) was added, followed by immediate addition of methyliodide (0.31 g, 0.14 ml, 2.2 mmol) under vigorous stirring. After the mixture was stirred at rt for 30 min, it was poured into water (20 ml) and extracted with dichloromethane (30 ml x 3). The extract was washed with water, dried over magnesium sulfate, evaporated *in vacuo*, and chromatographed (hexane/ethyl acetate, 1/1) to afford **1,2,9,10-(all-*endo*)-8,16-hexamethoxy-5,13-di-*tert*-butyl[2.2]metacyclophane (7)** (0.076 g, 56%) as colorless plates (hexane/ethyl acetate, 1/1): mp >223°C (dec); IR 2956, 1477, 1461, 1117; ^{1}HNMR ($CDCl_3$) 1.34 (s, 18H), 3.02 (s, 6H), 3.52 (s, 12H), 4.16 (s, 4H), 7.40 (s, 4H); ^{13}CNMR ($CDCl_3$) 31.58, 34.38, 57.58, 60.48, 85.46, 124.87, 127.77, 145.97, 157.91; MS *m/z* 500 (M^+). Anal. Calc. for ($C_{30}H_{44}O_6$ + 1/4 H_2O): C, 71.33; H, 8.88. Found: C, 71.13; H, 8.76.

Crystallographic Data of 7: Colorless plates, $C_{15}H_{22}O_3$, F. W.= 250.33, monoclinic, a= 10.339(2), b= 17.403 (2), c= 8.6930 (10) Å, α= 90.00, β= 112.460 (10), γ= 90.00 (10)°, V= 1445.483 (4) Å^3, Z= 4, D_C= 1.150 g cm^{-3}, space group $P2_1/n$.

Single crystal X-ray diffraction analysis of 7. All crystallographic measurements were carried out at 296 K on a Enraf-Nonius FR-590 diffractometer operating in the ω-2θ scan mode using graphite monochromated Cu Kα-radiation (λ = 1.54184 Å). Of 3108 independent reflections collected in the range $2 < \theta < 65°$, 2949 with $I_0 > 2\sigma(I_0)$ were taken as observed. The crystal did not show any significant decay during the data collection. Positional parameters were determined by direct methods using SIR 97[18] and were reflected by full-matrix least-squares calculations with nonhydrogen atoms treated anisotropically using the scheme $w = 1/[\sigma^2(F_0^2)+(0.2000P)^2+0.000P]$ were $P=(F_0^2+2F_c^2)/3$. All hydrogen atoms were located at ideal positions (SHELXL-97) and were included in the refinement, but restrained to ride on the atom to which they are bonded.

Isotropic thermal factors of H atoms were held fixed to 1.3 times U(eq) of the riding atoms. Final residuals R= 0.0649, R_w= 0.2696%. The supplementary data has been deposited at the Cambridge Crystallographic Data Center.

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