Nazarov Cyclization of Bis([2.2]paracyclophane-1,9-dienyl) Ketone: First Synthesis of a Bis([2.2]paracyclophane)-Annelated Cyclopenta-1,4-diene

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The annelation of five-membered rings onto the bridges of [2.2]paracyclophane-1,9-diene (**1**) can be achieved via Nazarov cyclization. Depending on the reaction conditions, bis([2.2]paracyclophane-1,9-dienyl) ketone (**4**) yielded the cyclopentenone **8** or the α-substituted cyclopentanones **3**–**7** with two annelated [2.2]paracyclophane units. The synthesis of 1:2-(1:2-[2.2]paracyclophane-1,9-dieno)-4:5-(9:10-[2.2]paracyclophane-1-eno)cyclopenta-1,4-diene (**10**) from **8** as a potential ligand for metallocene complexes and generation of its anion **11** is also described.

In the course of our studies probing the effects of electronic interactions between the benzene decks of a [2.2]paracyclophane unit and bridge-annelated cyclopentadienyl and indenyl transition metal complexes,[1][2] we explored various possibilities for the synthesis of appropriate precursors to sterically congested cyclopentadienyl ligands with [2.2]paracyclophane units fused along their C_2 bridges. Among other approaches,[1][2] we tested the annelation of a cyclopentenone moiety to one of the bridges of [2.2]paracyclophane-1,9-diene (**1**) by use of a Nazarov cyclization,[3] a cyclopentenone synthesis which has been well established with numerous examples in natural product syntheses.[3b][4] While the Pauson-Khand reaction, which we had previously used for the annelation of five-membered rings onto the skeleton of **1**,[1a] is limited to cases with only one substituent on the double bond of the resulting cyclopenta[2.2]paracyclophane, the Nazarov reaction, an acid catalyzed conrotatory cyclization[5] of a divinyl ketone, which is less sensitive to steric influences, could open up access to interesting highly congested cyclopentadienyl ligands with one or two [2.2]paracyclophane units attached.

The divinyl ketone **4** as a suitable precursor for the cyclization was accessed by connecting two [2.2]paracyclophane-1,9-diene units onto a C_1 fragment; this was achieved by reacting 1-lithio[2.2]paracyclophane-1,9-diene with ethyl formate.[1b][1c] The resulting 1,4-pentadienyl alcohol **2** (91%)[6] was oxidized with pyridinium dichromate in dichloromethane to the ketone **4** in 81% yield. As expected, **4** underwent rapid cyclization under acidic conditions, even under the influence of water on silica gel. However, the product was not the expected bis[2.2]paracyclophane-annelated cyclopentenone **8**, but the saturated α-hydroxycyclopentanone **3**. The formation of this unexpected product can be visualized as resulting from an addition of water to the hydroxycyclopentenyl cation intermediate,[7] winning over the usual deprotonation to give a cyclopentenone. The same product was obtained upon treating **4** with orthophosphoric acid in tetrahydrofuran (58%). The stability of the cyclization product **3** in strong acids is remarkable. Acyloins of type **3** have been discussed as intermediates in mechanistic studies of the Nazarov cyclization.[8][9] However, isolation had been successful only under special conditions.[7] When ketone **4** was treated with phosphoric acid in a 3:1 mixture of dichloromethane and tetrahydrofuran in the presence of methanol or ethanol as a nucleophile, the α-methoxy- and α-ethoxy-substituted bis[2.2]paracyclophane-annelated cyclopentanones **5** and **7** were isolated in 31 and 33% yield, respectively.

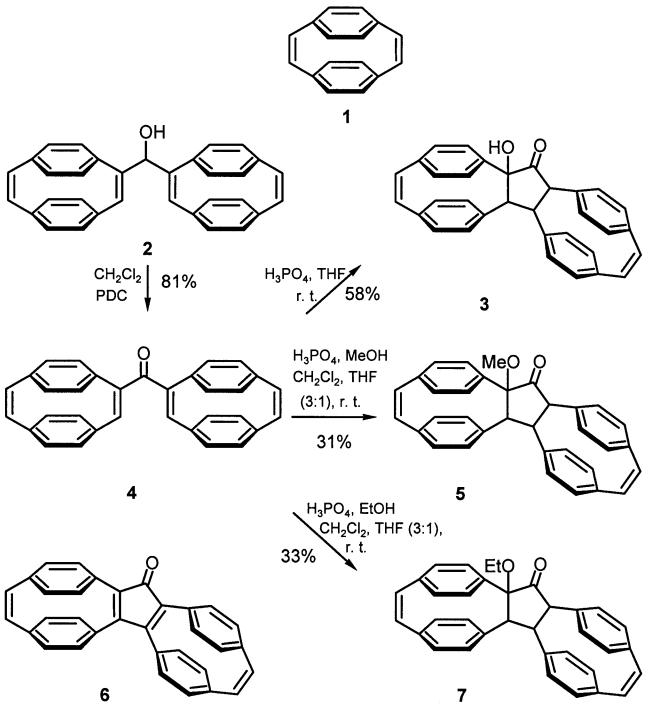
To direct the cyclization to the desired cyclopentenone **8** and avoid competition with the trapping of the intermediate hydroxycyclopentyl cation by nucleophiles, various Lewis acids like iron(III) chloride, aluminum(III) chloride, zinc(II) chloride and tin(IV) chloride under anhydrous conditions, were applied in dichloromethane.[10] The best result (61% yield) for the cyclization of **4** to cyclopentenone **8** was achieved with tin(IV) chloride, which had previously been reported to be favorable for the cyclization of sensitive compounds.[11]

An attempt to dehydrogenate cyclopentenone **8** to the tetracyclone analog cyclopentadiene-1-one **6** with two annelated [2.2]paracyclophane-9-ene units, was not successful.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/eurjoc or from the author.

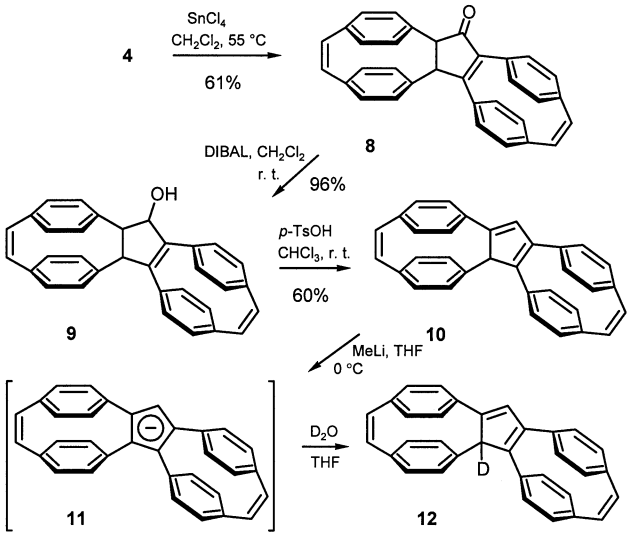
  1434–193X/98/1111–2301 $ 17.50+.50/0

Scheme 1



Although after prolonged heating of **8** with DDQ[12] in refluxing xylene, an increasing proportion of the derivative with two double bonds could be detected by mass spectrometry, **6** could not be isolated with any of the applied methods.

Scheme 2



Reduction of **8** with diisobutylaluminum hydride gave the alcohol **9** as the direct precursor to the bisannelated cyclopentadiene **10** in almost quantitative yield (96%). As expected from earlier studies on cyclopentenol-annelated [2.2]paracyclophanes,[1a] elimination of water from **9** to introduce the second double bond was difficult due to the acid sensitivity of the resulting diene. However, treatment of the alcohol **9** with a catalytic amount of *p*-toluenesulfonic acid in chloroform, led to 1:2-(1:2-[2.2]paracyclophane-1,9-dieno)-4:5-([2.2]paracyclophane-1-eno)cyclopenta-1,4-diene (**10**) in 60% yield. Deprotonation of **10** to the corresponding bis[2.2]paracyclophane-annelated cyclopentadienide anion **11** was achieved upon treatment of a solution of **10** in tetrahydrofuran at 0°C with methyllithium. The immediate development of a deep red color indicated formation of the cyclopentadienide anion **11**, which was characterized by quenching with D_2O to give exclusively the monodeuterated compound **12** as indicated by its mass spectrum.

The 1:2,3:4-bis([2.2]paracyclophane-1,9-dieno)cyclopenta-1,4-dienide **11** would represent the sterically most demanding metallocene ligand known to date. It would therefore be interesting to see, whether complexes of the type Cp_2MX_2 (M = Ti, Zr, Hf) can be made and what their respective properties would be. The cyclopentadienide **11** is isoelectronic with the previously reported 1:2,4:5-bis-([2.2]paracyclophane-1,9-dieno)benzene.[13]

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Experimental Section

General: ^{1}H NMR: Bruker AW 250 (250 MHz), WM 270 (270 MHz), WM 400 (400 MHz); δ (ppm) = 0 for tetramethylsilane, 2.04 for [D_5]acetone, 2.49 for [D_5]DMSO, 3.30 for [D_3]methanol, 5.32 for $CHDCl_2$, 7.15 for [D_5]benzene, 7.24 for $CHCl_3$. Characterization of signal multiplicities: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, mc = centrosymmetric multiplet. − ^{13}C NMR: Bruker WM 250 (62.9 MHz), WM 270 (67.9 MHz); δ = 77.0 for $CDCl_3$, 128.0 for C_6D_6. Assignments of ^{13}C signals were supported by measurements applying the DEPT (distortionless enhancement by polarization transfer) puls sequence, results are reported as follows: + = primary or tertiary, − = secondary, C_{quat} = quaternary C atom. − IR: Perkin-Elmer 297, 399. − MS: Varian Mat CH7 with Varian Aerograph 1740, Varian Mat 311 A (high resolution). − Column chromatography: Merck silica gel 60 (70−230 mesh). − TLC: Merck silica gel 60 F_{254} on aluminum foil, detection by UV light of 254 nm. Attempts to obtain correct elemental analyses for the new compounds were met with difficulties in that samples could not be obtained analytically pure by column chromatography and were too small for several recrystallizations. In addition, [2.2]paracyclophanediene derivatives in general gave incomplete combustion in the automatic microanalyzer used.

Bis(1-[2.2]paracyclophane-1,9-dienyl) Ketone (**4**): A solution of 1.30 g (2.98 mmol) of **2** and 1.46 g (3.88 mmol) of pyridinium dichromate in 250 ml of dichloromethane was stirred for 48 h at room temperature. The mixture was passed through a column (45 × 1.5 cm) of celite (50 g), with a top layer of fluorisil (5 g). The obtained solution was washed with two portions (each 200 ml) of water and dried with Na_2SO_4. After the solvent had been evaporated under reduced pressure, 1.04 g (81%) of **4** were obtained. − IR (KBr): $\tilde{\nu}$ = 2984 cm^{-1}, 2884, 1735 (C=O), 1688, 1448, 1182,

1054, 867. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.58 (s, 8 H, [2.2]phane-aromatic-H), 6.55 and 6.67 (AB system, J_{AB} = 6.8 Hz, 8 H, [2.2]phane-aromatic-H), 7.24 [s, 4 H, 9(9′,10,10′)-H], 8.23 [s, 2 H, 2(2′)-H]. − MS (70 eV); *m/z* (%): 434 (100) [M^+]. − HRMS ($C_{33}H_{22}O$) calcd. 434.1670, found 434.1659.

*General Procedure for the Cyclization of **4** with a Protic Acid (GP 1):* A solution of **4** (5 ml of alcohol for synthesis of **5** and **7**) and 83% phosphoric acid in tetrahydrofuran [methylene chloride/THF (3:1) for the synthesis of **5** and **7**] was stirred under reflux for 48 h or sonicated for 10 h. The reaction mixture was neutralized with saturated sodium bicarbonate solution and extracted twice with 100 ml of water. After the organic layer had been dried with $MgSO_4$, the solvent was evaporated under reduced pressure and the remaining solid purified by column chromatography on 20 g of silica gel (petroleum ether/methylene chloride).

2:3,4:5-Bis(1,2-[2.2]paracyclophane-9-eno)-2-hydroxycyclopentanone (**3**): 100 mg (0.23 mmol) of **4** was reacted with 3 ml of phosphoric acid in 70 ml of tetrahydrofuran according to *GP 1* under sonication for 10 h. After work-up (chromatography with petroleum ether/methylene chloride 1:2; R_f = 0.18, petroleum ether/methylene chloride 3:1) 60 mg (58%) of **3** was obtained. − IR (KBr): $\tilde{\nu}$ = 3352 cm^{-1} (OH), 3008, 1732 (C=O), 1588, 1493, 1030, 986, 936, 903, 704. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.35 (s, 1 H, OH), 4.28 (d, ^3J = 5.4 Hz, 1 H, 3-H), 4.52 (dd, ^3J = 5.4, ^3J = 12.3 Hz, 1 H, 4-H), 4.69 (d, ^3J = 12.3 Hz, 1 H, 5-H), 6.41−7.13 (m, 16 H, [2.2]phane-aromatic-H), 7.30 and 7.31 [2s, 4 H, 9(9′,10,10′)-H]. − MS (70 eV); *m/z* (%): 452 (44) [M^+], 424 (100), 396 (56). − HRMS ($C_{33}H_{24}O_2$) calcd. 452.1776, found 452.1783.

2:3,4:5-Bis(1,2-[2.2]paracyclophane-9-eno)-2-methoxycyclopentanone (**5**): 230 mg (0.53 mmol) of **4** in the presence of 5 ml of methanol, in 40 ml of methylene chloride/tetrahydrofuran (3:1), was reacted with 5 ml of phosphoric acid for 48 h according to *GP 1*. After work-up and purification by column chromatography (petroleum ether/methylene chloride 3:1; R_f = 0.45, methylene chloride) 77 mg (31%) of **5** was obtained. − IR (KBr): $\tilde{\nu}$ = 3013 cm^{-1}, 2973, 1730 (C=O). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.63 (s, 3 H, OCH_3), 4.12 (d, ^3J = 11.3 Hz, 1 H, 3-H), 4.36 (d, ^3J = 4.1, ^3J = 11.3 Hz, 1 H, 4-H), 4.58 (d, ^3J = 11.3 Hz, 1 H, 5-H), 6.41−6.91 and 7.33 (m, 16 H, [2.2]phane-aromatic-H), 7.29 and 7.31 [2s, 4 H, 9(9′,10,10′)-H]. − ^{13}C NMR (62.5 MHz): δ = 53.98 (+), 54.37 (+), 64.51 (+), 65.20 (+), 93.85 (C_{quat}), 129.43 (+), 130.26 (+), 130.46 (+), 130.69 (+), 130.73 (+), 130.88 (+), 130.96 (+), 131.16 (+), 131.79 (+), 132.11 (+), 132.15 (+), 132.19 (+), 132.72 (+), 132.82 (+), 132.98 (+), 134.81 (C_{quat}), 137.45 (C_{quat}), 137.53 (+), 137.62 (+), 137.65 (+), 137.75 (+), 139.25 (C_{quat}), 139.45 (C_{quat}), 139.57 (C_{quat}), 140.18 (C_{quat}), 140.98 (C_{quat}), 142.83 (C_{quat}), 213.69 (C_{quat}). − MS (70 eV); *m/z* (%): 466 (100) [M^+], 451 (43), 396 (56). − HRMS ($C_{34}H_{26}O_2$) calcd. 466.1933, found 466.1944.

2:3,4:5-Bis(1,2-[2.2]paracyclophane-9-eno)-2-ethoxycyclopentanone (**7**): 230 mg (0.53 mmol) of **4** in the presence of 5 ml of ethanol, in 40 ml of methylene chloride/tetrahydrofuran (3:1), were reacted with 5 ml of phosphoric acid for 48 h according to *GP 1*. After work-up and purification by column chromatography (petroleum ether/methylene chloride 3:1; R_f = 0.42, methylene chloride) 83 mg (33%) of **7** were obtained. − IR (KBr): $\tilde{\nu}$ = 3011 cm^{-1}, 2976, 1726 (C=O). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.85 (m, 5 H, OCH_2CH_3), 4.16 (d, ^3J = 4.3 Hz, 1 H, 3-H), 4.39 (dd, ^3J = 4.3, ^3J = 11.5 Hz, 1 H, 4-H), 4.61 (d, ^3J = 11.5 Hz, 1 H, 5-H), 6.43−6.92 and 7.42 (m, 16 H, [2.2]phane-aromatic-H), 7.29 and 7.31 [2s, 4 H, 9(9′,10,10′)-H]. − MS (70 eV); *m/z* (%): 480 (100) [M^+], 452 (31), 451 (43).

2:3,4:5-Bis(1,2-[2.2]paracyclophane-1,9-dieno)cyclopent-2-enone (**8**): A solution of 180 mg (0.41 mmol) of **4** and 0.16 ml of $SnCl_4$ in 60 ml of methylene chloride was stirred and heated under reflux for 3 d. After cooling to room temp., the mixture was diluted with 100 ml of methylene chloride and extracted twice with cold 5% aqueous HCl (50 ml each). The organic layer was neutralized with sodium bicarbonate solution, extracted with 20 ml of water and dried with magnesium sulfate. After the solvent had been evaporated under reduced pressure, the remaining solid was purified by column chromatography on silica gel [20 × 1.5 cm, petroleum ether/methylene chloride (3:5); R_f = 0.56, methylene chloride], yield 109 mg (61%) of **8**. − IR (KBr): $\tilde{\nu}$ = 3004 cm^{-1}, 1693 (C=O), 1588, 1347, 1103, 902, 704. − ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 4.57 (d, ^3J = 6.6 Hz, 1 H, 3-H), 5.03 (d, ^3J = 6.6 Hz, 1 H, 2-H), 6.41−6.80 (m, 16 H, [2.2]phane-aromatic-H), 7.26 and 7.28 (2s, 2 H, olefin-bridge-H), 7.33 (s, 2 H, olefin-bridge-H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 58.17 (+), 60.32 (+), 128.64 (+), 129.80 (+), 129.95 (+), 130.99 (+), 131.10 (+), 131.15 (+), 131.22 (+), 131.38 (+), 131.46 (+), 131.49 (+), 132.13 (+), 132.21 (+), 132.38 (+), 132.67 (C_{quat}), 133.26 (+), 135.97 (C_{quat}), 136.14 (C_{quat}), 136.75 (+), 137.29 (+), 137.56 (+), 137.99 (+), 138.92 (C_{quat}), 139.27 (C_{quat}), 139.47 (C_{quat}), 140.38 (C_{quat}), 152.58 (C_{quat}), 178.26 (C_{quat}), 203.26 (C_{quat}, CO). − MS (70 eV); *m/z* (%): 434 (70) [M^+], 406 (100). − HRMS ($C_{33}H_{22}O$) calcd. 434.1670, found 434.1668. − HRMS ($C_{32}H_{22}$) calcd. 406.1722, found 406.1725.

2:3,4:5-Bis(1,2-[2.2]paracyclophane-1,9-dieno)cyclopent-2-enol (**9**): To a solution of 120 mg (0.28 mmol) of **8** in 25 ml of methylene chloride kept at 0°C, was dropped 0.4 ml (0.4 mmol) of a 1 M solution of DIBAL in hexane. After the reaction mixture had been stirred for 1 h at room temp., 1 ml of saturated potassium sodium tartrate solution was added and the mixture stirred for an additional 20 min. After filtration the solution was extracted twice with saturated ammonium chloride solution (10 ml each) and once with 10 ml of water. The organic layer was dried with $MgSO_4$ and the solvent evaporated under reduced pressure yielding 117 mg (96%) of **9**. − IR (KBr): $\tilde{\nu}$ = 3463 cm^{-1}, 3003, 1588, 1491, 1102, 1063, 718. − ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 2.29 (d, ^3J = 5.1 Hz, 1 H, OH), 4.47 (dd, ^3J = 2.4, ^3J = 9 Hz, 1 H, 5-H), 4.96 (dd, ^3J = 2.4, ^3J = 9 Hz, 1 H, 4-H), 5.68 (m, 1 H, 1-H), 6.35−6.70 (m, 12 H, [2.2]phane-aromatic-H), 6.81−6.90 (m, 2 H, [2.2]phane-aromatic-H), 6.97−7.18 (m, 2 H, [2.2]phane-aromatic-H), 7.22 and 7.24 (2s, 2 H, olefin-bridge-H), 7.29 (s, 2 H, olefin-bridge-H). − ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 57.39 (+), 60.49 (+), 129.62 (+), 129.79 (+), 130.41 (+), 130.76 (+), 131.37 (+), 131.68 (+), 131.90 (+), 132.33 (+), 132.84 (+), 133.04 (+), 133.26 (+), 137.06 (+), 137.63 (+), 137.87 (+), 138.63 (C_{quat}), 138.88 (C_{quat}), 139.00 (C_{quat}), 140.11 (C_{quat}). − MS (70 eV); *m/z* (%): 436 (100) [M^+]. − HRMS ($C_{33}H_{24}O$) calcd. 436.1827, found 436.1829.

1:2-(1,2-[2.2]Paracyclophane-1,9-dieno)-4:5-(9:10-[2.2]paracyclophane-1-eno)cyclopenta-1,4-diene (**10**): A solution of 117 mg (0.27 mmol) of **9** and 5 mg of *p*-toluenesulfonic acid in 25 ml of chloroform was stirred at room temp. for 30 h. The reaction mixture was extracted with two portions (each 20 ml) of water and dried with $MgSO_4$. The solvent was evaporated under reduced pressure and the remaining solid purified by column chromatography on 10 g of alumina B [activity III, 15 × 0.5 cm, petroleum ether/methylene chloride (10:1); R_f = 0.27, petroleum ether/methylene chloride (3:1)], yield 68 mg (60%) of **10**. − ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 4.53 (d, ^4J = 1.9 Hz, 1 H, 3-H), 6.09 (AB system, δ_A = 6.03, δ_B = 6.16, ^3J = 8.1 Hz, 2 H, [2.2]phane-aromatic-H), 6.34, 6.53−6.80, 7.0, and 7.1 (m, 14 H, [2.2]phane-aromatic-H), 6.82 (d, ^4J = 1.9 Hz, 1 H, 1-H), 7.21 and 7.22 (2s, 2 H, olefin-bridge-H), 7.29 (s, 2 H, olefin-bridge-H). − ^{13}C NMR (62.5 MHz,

CD_2Cl_2): δ = 65.63, 128.41, 129.41, 130.37, 130.96, 131.29, 131.33, 131.65, 131.96, 132.04, 132.13, 132.39, 132.42, 132.49, 132.67, 133.44, 133.72, 134.21, 136.38, 136.51, 137.38, 137.92, 138.01, 138.27, 139.07, 139.20, 140.28, 142.40, 147.73, 153.51. − MS (70 eV); *m/z* (%): 418 (100) [M^+]. − $C_{33}H_{22}$ (418.5) calcd. C 94.70, H 5.30; found C 94.49, H 5.53. − HRMS ($C_{33}H_{22}$) calcd. 418.1722, found 418.1729.

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