Multinuclear Calixarene Synthons with Covalently Linked Aryl-Palladium(II) Complexes

Arjan W. Kleij, ^{*,§} Beatriz Souto, ^b César J. Pastor, ^b Pilar Prados ^a and Javier de Mendoza ^{*,#}

^aUniversidad Autónoma de Madrid, Departamento de Química Orgánica, Cantoblanco, E-28049 Madrid, Spain. [#]Current Address: Institute of Chemical Research of Catalonia (ICIQ), Avda. Països Catalans, s/n, E-43007 Tarragona, Spain. Tel: +34-977-920220; Fax: +34-977-920226; E-mail: jmendoza@iciq.es

^bUniversidad Autónoma de Madrid, Servicio Interdepartamental de Investigación (SIIdI), Cantoblanco, E-28049 Madrid, Spain.

[§]Current Address: van 't Hoff Institute for Molecular Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands. Fax: +31 205256422; Tel: +31 205256960; E-mail: kleij@science.uva.nl

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Experimental Section

General. Unless reported otherwise, all reactions were carried out under a dry and deoxygenated argon atmosphere. Solvents were freshly distilled and dried before use. All standard chemicals (including **6** and **18**, 4-iodobenzyl bromide, 4-cyanobenzyl bromide and 4-chloromethylpyridine hydrochloride) were commercially purchased and used without further purification. Compounds 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-27-tribenzoyloxy-28-hydroxycalix[4]arene (**1**)¹ and 25,26,27,28-tetrahydroxycalix[4]arene (**7**)² were prepared according to (modified) literature procedures. The NMR spectroscopic measurements (¹H, ¹³C{¹H}, ³¹P{¹H}, COSY (H,H), HETCOR (C,H) and NOESY experiments) were carried out at 200 (25), 300 (75) or 500 (125) MHz and reported chemical shifts (δ) are externally referenced to SiMe₄ and given in ppm. Mass spectra by FAB method were recorded on a VG AutoSpec spectrometer and by MALDI-TOF method on a REFLEX spectrometer. Elemental analyses, performed on a LECO CHN 932 micro-analyser and reported as percentage, indicated inclusion of solvent molecules for nearly all calixarene products and were supported by separate ¹H NMR studies. Reported melting points are uncorrected and were measured in open capillaries.

Crystallographic studies. For **2** (C₅₂H₆₃Cl₂IO₄) and **20** (C₈₆H₁₀₂Cl₆I₂O₆): For both compounds a colorless single crystal of approximate dimensions 0.07 × 0.04 × 0.02 mm (for **2**) and 0.14 × 0.04 × 0.02 mm (for **20**) with prismatic shape was mounted on a glass fiber and transferred to a Bruker SMART³ 6K CCD area-detector three-circle diffractometer with a MAC Science Co., Ltd. Rotating Anode (Cu K_α radiation, $\lambda = 1.54178$ Å) generator equipped with Goebel mirrors at settings of 50 kV and 120 mA (for **2**) and 90 mA (for **20**). X-Ray data were collected at 296K, with a combination of six runs at different ϕ and 2θ angles, 3600 frames. The quality of reflections for **2** was very poor. The data were collected using 0.3° wide ω scans (40 sec/frame at $2\theta = 40^\circ$ and 130 sec/frame at $2\theta = 100^\circ$ for compound **2**; 10 sec/frame at $2\theta = 40^\circ$ and 30 sec/frame at $2\theta = 100^\circ$ for compound **20**), crystal-to-

detector distance of 4.0 cm. The substantial redundancy in data allows empirical absorption corrections (SADABS)⁴ to be applied using multiple measurements of symmetry-equivalent reflections (for **2**, Ratio of minimum to maximum apparent transmission: 0.754602). A total number of 56395 reflections were collected for compound **2**, with 8652 independent reflections ($R_{\text{int}} = 0.0973$ and $R_{\text{sigma}} = 0.0682$) and the unit cell parameters were obtained by full-matrix least-squares refinements of 6938 reflections. In the case of **20**, a total number of 48930 reflections were collected, with 16178 independent reflections ($R_{\text{int}} = 0.0504$ and $R_{\text{sigma}} = 0.0486$) and the unit cell parameters were calculated and refined from the full data set. Crystallographic details for both compounds are reported in Table S3. The raw intensity data frames were integrated with the SAINT⁵ program, which also applied corrections for Lorentz and polarization effects. The software package SHELXTL⁶ version 6.10 was used for space group determination, structure solution and refinement. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods (SHELXS-97),⁷ completed with difference Fourier syntheses, and refined with full-matrix least-squares using SHELXL-97⁸ minimizing $\omega(F_o^2 - F_c^2)^2$. Weighted R factors (R_w) and all goodness of fit S are based on F^2 ; conventional R factors (R) are based on F . All non-hydrogen atoms were refined with anisotropic displacement parameters. All scattering factors and anomalous dispersions factors are contained in the SHELXTL 6.10 program library. For compound **2**, all hydrogen atoms were located by difference maps. After refinement, 32 of them showed abnormal behavior and were treated as idealized contributions. In this case, the hydrogen atom positions were calculated geometrically and were allowed to ride on their parent carbon atoms with fixed isotropic U . The rest of hydrogen atoms (31) were located by difference maps and refined isotropically. Crystallographic details are reported in Table S3. In the case of **20**, all hydrogen atoms were treated as idealized contributions. In the last difference Fourier map, the significant density residuals were $1.66 \text{ e}\text{\AA}^{-3}$ at $2.38 \text{ \AA}$ from the Cl(3) atom. Although the refinement of the structure converged, rather high values of residual electron density were observed, which is attributed to some

disorder in the solvent region.

Table S1. Selected inter-atomic distances (Å) and angles (deg) for mono-iodoarylated **2**.

Bond Lengths			
C(2)-O(2)	1.375 (7)	C(24)-O(4)	1.398 (7)
C(13)-O(3)	1.361 (8)	C(35)-O(1)	1.371 (8)
C(49)-I(1)	2.098 (7)		
Bond Angles			
C(14)-C(22)-C(23)	112.5 (5)	C(25)-C(33)-C(34)	111.8 (5)
C(12)-C(11)-C(3)	112.3 (5)	C(1)-C(44)-C(36)	113.4 (5)
Torsion Angles			
C(46)-C(45)-O(4)-C(24)	167.3 (6)	O(4)-C(45)-C(46)-C(47)	-113.9 (7)

Table S2. Selected inter-atomic distances (Å) and angles (deg) for calix[6]arene **20**.

Bond Lengths			
O(1)-C(8)	1.387(5)	O(4)-C(44)	1.393(6)
O(2)-C(24)	1.385(6)	O(5)-C(62)	1.390(6)
O(3)-C(32)	1.376(7)	O(6)-C(74)	1.370(6)
I(1)-C(1)	2.093(6)	I(2)-C(53)	2.099(6)
O(2)-C(25)	1.415(7)	O(5)-C(67)	1.414(7)
O(3)-C(37)	1.440(8)	O(6)-C(79)	1.438(7)
Bond Angles			
C(9)-C(18)-C(19)	110.2(6)	C(8)-O(1)-C(7)	114.4(3)
C(31)-C(30)-C(23)	113.5(5)	C(24)-O(2)-C(25)	115.2(5)
C(43)-C(42)-C(33)	116.4(5)	C(32)-O(3)-C(33)	114.3(5)
C(45)-C(60)-C(61)	109.3(4)	C(44)-O(4)-C(49)	113.6(4)
C(63)-C(72)-C(73)	114.1(5)	C(62)-O(5)-C(67)	116.0(4)
C(75)-C(84)-C(13)	115.9(4)	C(74)-O(6)-C(79)	115.1(5)
Torsion Angles			
C(8)-O(1)-C(7)-C(4)	171.8(4)	C(44)-O(4)-C(49)-C(50)	-171.0(4)

Table S3. Crystal data and structure refinement for compounds **2** and **20**.

	2·CH₂Cl₂	20·2CHCl₃^a
Empirical formula	C ₅₂ H ₆₃ Cl ₂ IO ₄	C ₈₆ H ₁₀₂ Cl ₆ I ₂ O ₆
Formula weight	949.82	1698.18
Temperature (K)	273(2)	297(2)
Wavelength (Å)	1.54178	1.54178
Crystal system	Orthorhombic	Monoclinic
Space group	Pbca	P2(1)/n
<i>a</i> (Å)	25.1927(7)	15.1582(6)
<i>b</i> (Å)	12.5759(4)	26.6443(8)
<i>c</i> (Å)	30.9084(9)	22.1283(7)
α , β , γ (°)	90	90, 101.198(2), 90
Volume (Å ³)	9792.4(5)	8767.0(5)
Z	8	4
Density (calculated) (mg/m ³)	1.289	1.287
Absorption coefficient (mm ⁻¹)	6.463	7.686
F(ooo)	3952	3496
Crystal size (mm)	0.07 × 0.04 × 0.02	0.14 × 0.04 × 0.02
θ range for data collection (°)	2.86 to 66.85	2.63 to 70.57
Index ranges (<i>h,k,l</i>)	-29:29, -14:14, -36:35	-17:17, -31:29, -25:27
Reflections collected	56395	48930
Independent reflections	8652 [R(int) = 0.0973]	16178 [R(int) = 0.0504]
Completeness ($\theta=66.85^\circ$) (%)	99.4	96.2
Absorption correction	Sadabs vers. 2.03	Sadabs vers. 2.03
Refinement method	Full-matr. least-sq. on F ²	Full-matr. least-sq. on F ²
Data / restraints / parameters	8652 / 0 / 666	16178 / 0 / 923
Goodness-of-fit on F ²	1.013	1.347
Final R / wR2 [<i>I</i> >2sigma(<i>I</i>)]	0.0668, 0.1710	0.1058, 0.3384
R / wR2 (all data)	0.1514, 0.2210	0.1360, 0.3762
Min/max resd. dens. (e/Å ³)	0.835 and -0.844	1.658 and -1.316

^a The structure comprises a disordered amount of solvent molecules

Figure S1. Selected part of the Variable Temperature ¹H NMR spectra at 500 MHz for compound **20**.

Figure S2. NOESY spectrum (500 MHz, 323 K) of compound **20**.

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