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The First Synthesis and Characterization of Both Diastereomers of a Di[2.2]paracyclophane: 4,4′-Bis(1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane)

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The synthesis and characterization of both diastereomers of a system comprised of two [2.2]-paracyclophane units linked through a single 4,4′ bond are described. Both the meso and d,l diastereomers of 4,4′-bis(octafluoro[2.2]paracyclophane) have been prepared via a palladium-catalyzed reductive homocoupling reaction by copper, producing a 3:2 ratio of meso and d,l diastereomers. A similar reductive homocoupling of pseudo-*o*-iodotrifluoromethyloctafluoro[2.2]-paracyclophane gave only the analogous meso diastereomer. Single-crystal X-ray structures were obtained for all of the diparacyclophane products.

Introduction

Although it has been 50 years since the first isolation of [2.2] paracyclophane (PCP),[1] the interest and scope of cyclophane chemistry continues to expand.[2] Recently, bridge-fluorinated cyclophanes have attracted attention with reports of the synthesis,[3] chemical reactivity,[4−6] and commercial applications[7] of 1,1,2,2,9,9,10,10-octafluoro-[2.2]paracyclophane (OFP). It has been clearly demonstrated that OFP displays not only all of the classic [2.2]paracyclophane phenomena[4,5] (e.g., thermal isomerization/racemisation, transannular communication, NMR substituent chemical shift additivity, and mass spectral (xylylene) fragmentation), but also some unusual reactivity characteristics that are apparently unique to fluorinated cyclophanes.[6]

As a consequence of their geometry and rigid molecular scaffold,[8] paracyclophanes exhibit planar chirality,[9] and they find numerous applications as chiral building blocks and ligands.[10,11] When two paracyclophane units are linked through a single aryl−aryl bond, such diparacyclophanes can exist as either meso or d,l diastereomers. The first synthesis of the parent hydrocarbon bis[2.2]-paracyclophane was reported in 1994,[12] with the crystal structure of the meso diastereomer appearing later.[13] Not being mentioned, it appears that the d,l diastereomer was not formed in this reaction. Unable to reproduce the above synthesis, Ernst and Wittkowski prepared a series of meso and d,l diparacyclophane structures, where the [2.2]paracyclophanyl groups are separated by various spacer groups such as carbonyl or methylene linkages, and the syntheses, diastereomeric ratios, separation, and NMR assignments of these compounds were reported along with several crystal structures.[14] Structurally novel diastereomers closely related to “dimers” of OFP were recently reported via reaction of OFP with a trifluoromethyl radical source.[6]

Results and Discussion

Our recent studies of the reactivity of OFP and its simple derivatives have provided building block compounds that can be used to create more elaborate or exotic systems that contain its signature bridge-fluorinated cyclophane skeleton.[4,5] One of the more versatile OFP derivatives is the iodo derivative, and it was recognized that reductive homocoupling of this compound could potentially generate bis(OFP) compounds.

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(1) Reviews: (a) Vogtle, F. *Cyclophane Chemistry*; Wiley: New York, 1993. (b) Boekelheide, V. Cyclophanes. I. *Top. Curr. Chem.* **1983**, *113*, 87. (c) Hopf, H.; Marquard, C. *Strain and Its Implications In Organic Chemistry*; Kluwer: Dordrecht, 1989.

(2) Brown, C. J.; Farthing, A. C. *Nature* **1949**, *164*, 915.

(3) (a) Dolbier, W. R., Jr.; Rong, X. X.; Xu, Y.; Beach, W. F. *J. Org. Chem.* **1997**, *62*, 7500. (b) Dolbier, W. R., Jr.; Asghar, M. A.; Pan, H.-Q.; Celewicz, L. *J. Org. Chem.* **1993**, *58*, 1827. (c) Dolbier, W. R., Jr.; Duan, J.-X.; Roche, A. J. USP 5,841,005, 1998. (d) Dolbier, W. R., Jr.; Duan, J.-X.; Roche, A. J. *Org. Lett.* **2000**, *2*(13), 1867.

(4) Roche, A. J.; Dolbier, W. R., Jr. *J. Org. Chem.* **1999**, *64*, 9137.

(5) Roche, A. J.; Dolbier, W. R., Jr. *J. Org. Chem.* **2000**, *65*, 5282.

(6) Dolbier, W. R., Jr.; Duan, J.-X.; Abboud, K.; Ameduri, B. *J. Am. Chem. Soc.* **2000**, *122*, 12083.

(7) (a) Beach, W. F.; Lee, C.; Basset, D. R.; Austin, T. M.; Olson, A. R. Xylylene Polymers. In *Wiley Encyclopaedia of Polymer Science and Technology*; Wiley: New York, 1989; Vol. 17, p 990. (b) Majid, N.; Dabral, S.; McDonald, J. F. *J. Electron. Mater.* **1989**, *18*, 301. (c) Williams, K. R. *J. Thermal Anal.* **1997**, *49*, 589.

(8) Hope, H.; Bernstein, J.; Trueblood, K. N. *Acta Crystallogr. B* **1972**, *28*, 1733.

(9) For a clarification of *R* and *S* for complex cyclophanes, see: Pye, P. J.; Rossen, K. *Tetrahedron*: *Asymmetry* **1998**, 9, 539. Otherwise, see: Cahn, R. S.; Ingold, C. K.; Prelog, V. *Experimentia* **1956**, *12*, 81. Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385. Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994.

(10) Selected recent examples of chiral monosubstituted PCP ligands include: (a) Tanji, S.; Ohno, A.; Sato, I.; Soai, K. *Org. Lett.* **2001**, *3*, 287. (b) Bolm, C.; Kuhn, T *Synlett.* **2000**, 899. (c) Masterson, D. S.; Glatzhofer, D. T. *J. Mol. Catal. A* **2000**, *161*, 65.

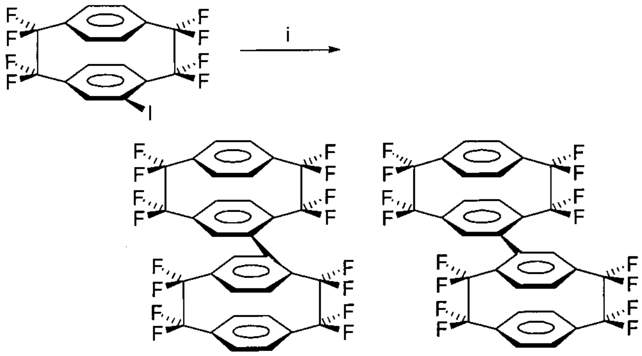
(11) Selected recent examples of chiral di-substituted PCP ligands include: (a) Hou, X. L.; Wu, X. W.; Dai, L. X.; Cao, B. X.; Sun, J. *Chem. Commun.* **2000**, 1195. (b) Vetter, A. H.; Berkessel, A. *Tetrahedron Lett.* **1998**, *39*, 1741. (c) Belokon, Y.; Moscalenko, M.; Ikonnikov, N.; Yashkina, L.; Antonov, D.; Vorontsov, E.; Rozenberg, V. *Tetrahedron*: *Asymmetry* **1997**, *8*, 3245. (d) Pye, P. J.; Rossen, K.; Reamer, R. A.; Volante, R. P.; Reider, P. J. *Tetrahedron Lett.* **1998**, *39*, 4441.

(12) Kus, P. *Pol. J. Chem.* **1994**, *68*, 1983.

(13) Jones, P. G.; Kus, P. *Pol. J. Chem.* **1998**, *72*, 1106.

(14) (a) Ernst, L.; Wittkowski, L. *Eur. J. Org. Chem.* **1999**, *1653*, 3. (b) Jones, G. J.; Ernst, L.; Dix, I.; Wittkowski, L. *Acta Crystallogr.* **2000**, *C56*, 239.

10.1021/jo0157775 CCC: $20.00



***d,l*-bis-OFP**
(30%)

***meso*-bis-OFP**
(44%)

i = Cu, 80°C, PdCl$_2$.dppf, DMF, 8hrs.

Of the various methods employed (summarized in Table 1), the most successful employed copper and PdCl$_2$•dppf in DMF at 80 °C overnight (entry 7), which produced bis(OFP) in 74% isolated yield; the only other fluorine-containing product was OFP (11% isolated yield) resulting from reduction of the starting iodo compound. The diastereomeric ratio was calculated as 3:2 as determined from ^{19}F NMR and GC analyses. The diastereomers could not be separated from each other by column chromatography on silica gel but could be enriched by fractional crystallization.

By working at much higher concentrations (6×) and temperatures (120−140 °C), it was possible to carry out the coupling reaction in moderate yield (and at higher scale) without the use of the Pd catalyst (Table 1, entry 10).

GC analysis of the product formed with Pd catalysis showed two compounds in a 3:2 ratio. The GCMS analysis of the two components produced identical spectra, with both compounds having prominent M$^+$ ions of mass 702 along with the fragmentation pattern expected for such bis-cyclophane structures.

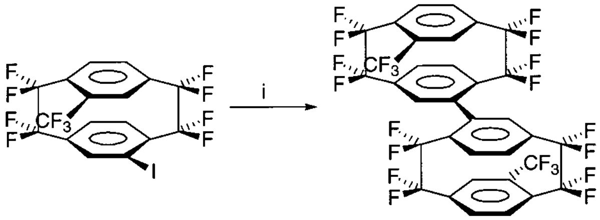
However, the ^{19}F NMR was more complex than anticipated on the basis of our previous experience with OFP derivatives and their ^{19}F and ^{1}H NMR.[4,5] Each diastereomer has eight chemically different fluorine atoms, and since each fluorine will couple strongly with its neighbor attached to the same carbon ($^2J_{F-F} \sim 240$ Hz), it was predicted that each diastereomer would display eight doublets (four AB quartet patterns) in the ^{19}F NMR.

Unexpectedly, the ^{19}F NMR of the mixture (that by GC showed only the presence of the two diastereomers) exhibited more than 16 doublets, and some of the peaks showed significant line broadening (Figure 1). This was taken to be an indication of restricted molecular rotation, observable on the NMR time scale. This was confirmed by warming the NMR sample to 150 °C, whereupon all of the lines became sharp, with 16 doublets being observed. Through integration of the signals it was confirmed that the two diastereomers were formed in a 3:2 ratio (which agreed well with the GC analysis). Indeed, knowledge of this 3:2 ratio aided in the assignment of peaks to one or the other diastereomer.

Examination of the ^{19}F NMR at lower temperatures allowed the observation of both rotameric forms of the diastereomer. As the temperature was lowered, the peak broadening decreased and more peaks appeared, and at −60 °C, a total of 24 doublets could be observed, indicating the presence of three bis(OFP) isomers (spectra can be found in the Supporting Information). Integration showed the ratio of isomers to be 2:1.5:1.5. As expected, the ^{19}F NMR signals of the major isomer at the lower temperature were consistent with it being the minor diastereomer at the higher temperature. Thus, the major structural diastereomer is able, at low temperatures, to be detected in two different rotameric forms (which are themselves present in a 1:1 ratio).

The assignment of meso and d,l to each compound was made on the basis of single-crystal X-ray analysis. It is noteworthy that this is the first time that *both* diastereomers of a di[2.2]paracyclophane system have been prepared, isolated, and characterized.

When an analogous homocoupling reaction was performed using pseudo-*o*-iodotrifluoromethyl OFP, NMR and GC analysis indicated that *only one* diastereomer was produced! The GCMS data was entirely consistent with a bis(OFP)-type structure bearing two trifluoromethyl groups as indicated by the observed parent ion (838). Furthermore, the trifluoromethyl groups were shown to be on the "outer" layers of the structure by observation of a fragment of mass 244, which is consistent with a trifluoromethyl-substituted tetrafluoroxylylene fragment.



i = Cu, 80°C, PdCl$_2$.dppf, DMF, 8hrs.

***meso*-bis-(CF$_3$OFP)**
(58%)

The ^{19}F NMR of this diparacyclophane displayed the expected eight doublets (four AB quartets) between −107 and −118 ppm, plus a trifluoromethyl signal (−59 ppm). (the spectrum can be found in Figure 3 in the Supporting Information.) At room temperature, again the ^{19}F NMR showed line broadening consistent with restricted rotational motion. On warming to 50 °C, the lines sharpened sufficiently to resolve the peaks clearly, which also allowed the observation of the recently reported characteristic through-space coupling of the trifluoromethyl group with the proximate bridge fluorines ($^5J_{FF} = 26.8$ Hz and $^6J_{FF} = 19.5$ Hz).[4,5] The question of whether this was the meso or d,l diastereomer was answered by a single-crystal X-ray structure of the product, and it was shown to be the meso diastereomer.

It is interesting to note that of all the other related diparacyclophane systems,[7,12,14] none were reported to exhibit such restricted rotational motion on the basis of their NMR spectra. They also showed no diastereoselectivity (ratio of 1:1) in their formation, except for the case of the fluorinated radical addition "dimers", and in this reaction, the d,l diastereomer was reported to be the major product in a 57:43 ratio.[6]

The homocoupling of iodo-OFP is only 60% diastereoselective, giving the meso isomer as the major product, whereas the pseudo-*o*-iodotrifluoromethyl (OFP) homocoupling reaction gives completely selective meso isomer formation (no d,l by NMR or GC). These observations are consistent with the recent observation by Soai and coworkers[10a] that pseudo-ortho-disubstituted PCPs give

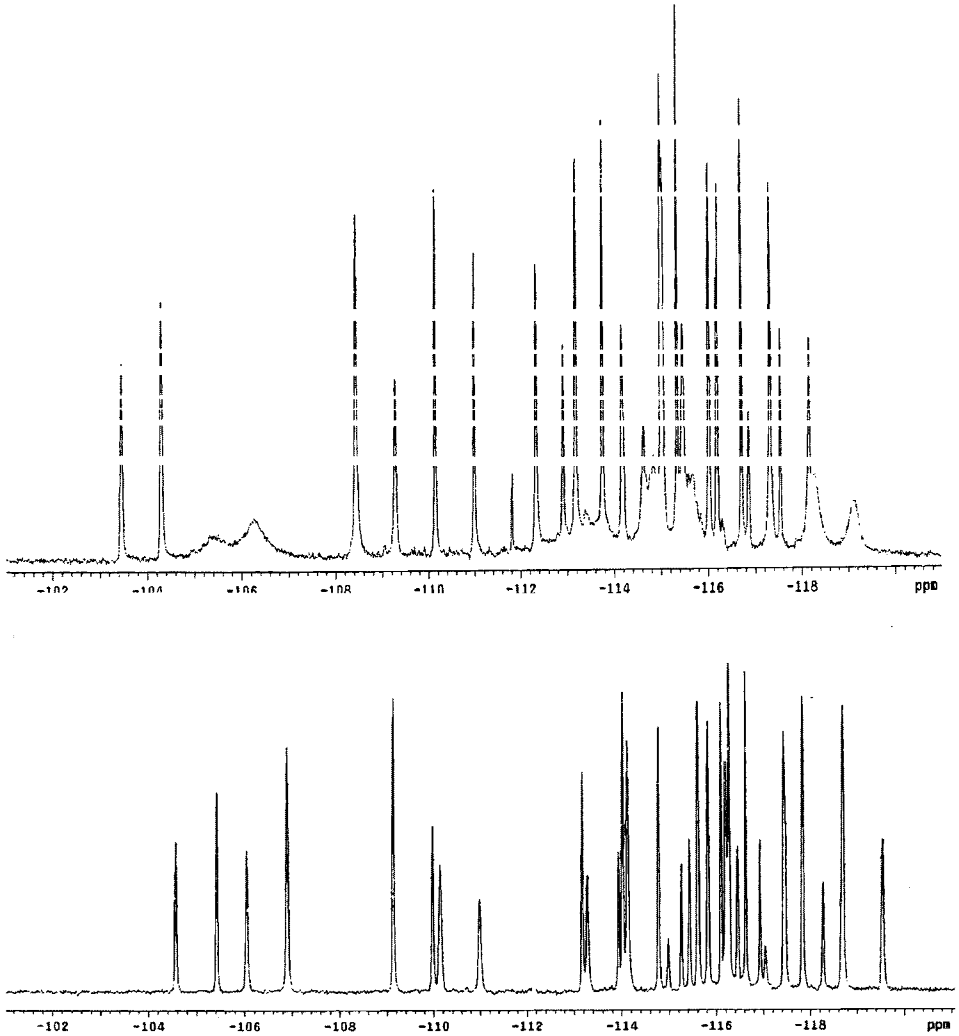


Figure 1. ^{19}F NMR of bis(OFP) mixture at room temperature (on top) and 150 °C (bottom).

Table 1. Preparation of 4,4′-Bis(1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane)

no.	starting material	reducing agent	catalyst (equiv)	solvent (*T*/°C, time/h)	bis(OFP) (%) (meso/d,l)	OFP (%)
1	OFP-I	Cu		DMF (25, 24)	0	0
2	OFP-I	Cu		DMF (140, 24)	4	90
3	OFP-I	Cu	$PdCl_2$ (1.0)	DMF (90,8)	40 (3:2)	55
4	OFP-I	Cu	$PdCl_2$ (0.2)	DMF (80, 8)	36 (3:2)	50
5	OFP-I	Cu	$PdCl_2$ (0.4)	DMF (80,8)	35 (3:2)	50
6	OFP-I	Cu	$PdCl_2$ (0.5)	THF (65, 8)	0	0
7	OFP-I	Cu	$PdCl_2$·dppf (0.2)	DMF (80,8)	74 (3:2)	11
8	OFP-I		$Ni(Ph_3P)_4$ (1.0)	DMF (70, 8)	0	23
9	OFP-I	Cu	$NiCl_2(PPH_3)_2$ (0.2)	DMF (70,8)	0	77
10	OFP-I	Cu		DMF (130, 6)	40 (1:0.8)	55
11	OFP-Br	Cu	$PdCl_2$·dppf (0.1)	DMF (80, 8)	0	0
12	OFP-Br	Zn	$PdCl_2$·dppf (0.3)	DMF (25,8)	0	96
13	OFP-Cl	Cu	$PdCl_2$·dppf (0.1)	DMF (80, 8)	0	0
14	OFP-Cl	Zn	$PdCl_2$·dppf (0.1)	DMF (80,8)	3	94

much higher enantioselectivities when used as chiral ligands, when compared to similar monosubstituted PCP derivatives. In light of the impressive diastereoselectivity displayed by the pseudo-ortho-disubstituted OFP derivative in this coupling reaction, it indicates that appropriately substituted bridge fluorinated paracyclophanes should be ideal candidates for chiral ligands, especially since it has already been demonstrated that the bridge fluorines prevents racemization (via bibenzyl radicals) up to temperatures of over 300 °C.[5] Work to prepare and test such compounds is currently in progress.

Conclusions

For the first time, the synthesis and characterization of both diastereomers of a system consisting of two [2.2] PCP units linked through a single 4,4′ bond are reported. The 3:2 ratio of meso/d,l bis(OFP) diastereomers was calculated directly from GC and ^{19}F NMR analyses of the crude products. Moreover, the meso diastereomer was shown to exist in two rotameric forms, which could be resolved at −50 °C by ^{19}F NMR. Crystal structures of the d,l and both rotamers of the meso compound are presented. When an analogous reductive homocoupling reaction of pseudo-*o*-iodotrifluoromethyl OFP was performed, only one diastereomer was produced. This also exhibited restricted rotational motion in its ^{19}F NMR spectrum at room temperature, and a crystal structure confirmed it to be the meso diastereomer.

Experimental Section

All NMR spectra were obtained on a Varian 300 MHz Gemini at the specified temperature with a variable-temperature control module. Deuterated acetone was used unless indicated otherwise, and TMS and $CFCl_3$ were used as references for ^{1}H and ^{19}F, respectively. All reagents, unless otherwise specified, were used as purchased from Aldrich or Fisher. Column chromatography was performed using chromatographic silica gel 200−425 mesh, as supplied by Fisher. Melting points are uncorrected. Mass spectrometric analyses were obtained at an ionizing potential of 70 eV.

X-ray Experimental Data. *meso*-CF3: $a = 15.745(2)$ Å, $b = 8.770(1)$ Å, $c = 21.155(3)$ Å, $\beta = 94.572(2)°$, $V = 2911.9(6)$ Å^3, R1 = 3.24, wR2 = 7.80, monoclinic $P2_1/c$, $Z = 4$, $T = 173$ K. Meso only: $a = 7.2046(5)$ Å, $b = 21.865(1)$ Å, $c = 17.051(1)$ Å, $\beta = 100.848(1)°$, $V = 2638.1(3)$ Å^3, R1 = 3.55, wR2 = 7.55, monoclinic Cc, $Z = 4$, $T = 173$ K. d/l + meso in one crystal: $a = 20.133(2)$ Å, $b = 12.6261(9)$ Å, $c = 23.175(2)$ Å, $\beta = 115.629(1)°$, $V = 5311.4(7)$ Å^3, R1 = 6.81, wR2 = 14.61, monoclinic $P2_1/c$ $Z = 8$, $T = 173$ K. The structures were solved by the direct methods in SHELXTL5[15] and refined using full-matrix least-squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. *All three structures* have disorders in some of the F atoms of the CF2 or CF3 groups. The most significant disorder is in *d/l + meso in one crystal*. This is because both meso and d/l structures crystallize where one-half of the molecule is the same in both but the other is disordered in in a way to give both stereoisomers in the same molecular position.

4,4′-Bis(1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane). A degassed DMF solution (2 mL) containing 4-iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane[4] (120 mg, 0.251 mmol), copper powder (50 mg, 0.78 mmol), and palladium dichloride complex with bis(diphenylphosphinyl) ferrocene (40 mg, 0.05 mmol) was stirred vigorously at 80 °C overnight under an atmosphere of nitrogen. The reaction was cooled to room temperature and then added to ice−water (30 mL). The solids thus produced were filtered and chromatographed on silica gel (hexane/diethyl ether 9/1) to give (R_f = 0.45) 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (10 mg, 11%) and (R_f = 0.26) **4,4′-bis(1,1,2,2,9,9,10,10-octafluoro[2.2]-paracyclophane)** (65 mg, 74%): MS *m/z* 702 (M^+, 49), 526 (23), 350 (13), 281 (100), 176 (87). Anal. Calcd for $C_{32}H_{14}F_{16}$: C, 54.70; H, 1.99. Found: C, 54.39; H, 1.77.

GC analysis of the product using a J&W DB-5ms column (Fisher) indicated a ratio of diastereomers of 3:2. (Retention times of 24.0. and 26.5 min for d,l and meso, respectively.)

***meso*-4,4′-Bis(1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane):** 150 °C, DMSO-d_6; ^{1}H NMR δ 7.637 (d, 1/2 AB, ^3J = 8.40 Hz, 1H), 7.566−7.500 (m, 2H), 7.418 (s, 1H), 7.240 (d, 1/2 AB, ^3J = 8.40 Hz, 1H), 7.189−7.166 (m, 2H); ^{19}F NMR δ −106.602 (d, ^2J = 239.90 Hz, 1F), −109.435 (d, ^2J = 239.90 Hz, 1F), −113.721 (d, ^2J = 239.62 Hz, 1F), −113.910 (d, ^2J = 239.62 Hz, 1F), −115.995 (d, ^2J = 239.62 Hz, 1F), −116.101 (d, ^2J = 239.62 Hz, 1F), −118.015 (d, ^2J = 239.62 Hz, 1F), −119.110 (d, ^2J = 239.62 Hz, 1F).

***d,l*-4,4′-Bis(1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane):** 150 °C, DMSO-d_6; ^{1}H NMR δ 7.763 (s, 1H), 7.566−7.500 (m, 5H), 7.418 (d, 1/2 AB, ^3J = 8.40 Hz, 1H); ^{19}F NMR δ −105.017 (d, ^2J = 242.16 Hz, 1F), −110.210 (d, ^2J = 242.16 Hz, 1F), −114.353 (d, ^2J = 239.62 Hz, 1F), −115.596 (d, ^2J = 237.36 Hz, 1F), −115.680 (d, ^2J = 239.90 Hz, 1F), −116.523 (d, ^2J = 237.36 Hz, 1F), −116.980 (d, ^2J = 239.90 Hz, 1F), −117.804 (d, ^2J = 239.62 Hz, 1F).

Preparation of Bis-OFP Diastereomers without Pd Catalyst. Into a 100 mL, three-necked, round-bottomed flask containing 20 mL of DMF was added 5 g (10.4 mmol) of iodo-OFP and 2 g (31.2 mmol) of Cu powder. The mixture was heated to 120−140 °C and stirred under N_2 for 6 h, after which time the reaction was cooled and 100 mL of Et_2O added. The mixture was filtered to remove solids, and the filtrate was washed with brine (3 × 30 mL) and then dried over Na_2SO_4. After removal of the solvent by rotary evaporation, the residue was subjected to flash chromatography (silica gel) using hexan/EtOAc (10:0.05) as eluent to obtain pure bis-OFP as a 1:0.8 mixture of meso and dl isomers, as estimated by ^{19}F NMR.

4,4′-Bis(12-trifluoromethyl-1,1,2,2,9,9,10,10-octafluoro-[2.2]paracyclophane). A degassed DMF solution (2 mL) containing pseudo-*o*-iodotrifluoromethyl-1,1,2,2,9,9,10,10-octafluoro-[2.2]paracyclophane[5] (0.50 g, 0.92 mmol), copper powder (0.09 g, 1.4 mmol), and palladium dichloride complex with bis(diphenylphosphinyl)ferrocene (0.15 g, 0.18 mmol) was stirred vigorously at 80 °C overnight under an atmosphere of nitrogen. The reaction was cooled to room temperature and then added to ice−water (100 mL). The solids thus produced were filtered and chromatographed (hexane/diethyl ether, 8/2) to give (R_f = 0.53) 4-trifluoromethyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane[4] (0.100 g, 26%) and (R_f = 0.17) **4,4′-bis(12-trifluoromethyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane)** (0.224 g, 58%): mp >250 °C; ^{1}H NMR (50 °C) δ 7.920 (d, ? AB, ^3J = 8.70 Hz, 1H), 7.835−7.866 (m, 2H), 7.675 (d, 1/2 AB, ^3J = 8.40 Hz, 1H), 7.612 (s, 1H), 7.074 (s, 1H); ^{19}F NMR (50 °C) δ −59.025 (dd, ^5J = 26.81 Hz, ^6J = 19.47 Hz, 3F), −108.507 (d, ^2J = 237.36 Hz, 1F), −109.900 (d, ^2J = 237.36 Hz, 1F), −109.915 (d, ^2J = 242.16 Hz, 1F), −112.223 (d, ^2J = 237.36 Hz, 1F), −113.676 (d, ^2J = 242.16 Hz, 1F), −114.281 (dq, ^2J = 242.16 Hz, ^5J = 26.81 Hz, 1F), −116.433 (dq, ^2J = 237.36 Hz, ^6J = 19.47 Hz, 1F), −116.673 (d, ^2J = 242.16 Hz, 1F); MS *m/z* 838 (M^+, 57), 594 (72), 350 (9), 281 (100), 244 (40). Anal. Calcd for $C_{34}H_{12}F_{22}$: C, 48.69; H, 1.43. Found: C, 48.60; H, 1.26. The product was shown to be a single diastereomer by GC analysis using a J&W DB-5ms column (Fisher), and single-crystal X-ray crystallography confirmed it as the meso diastereomer.

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Supporting Information Available: NMR spectra (two figures), ORTEP drawings, and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Sheldrick, G. M. *SHELXTL5*; Bruker-AXS: Madison, WI, 1998.