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ARTICLE TYPE

Tuning the depth of bowl-shaped phosphine hosts: capsule and pseudo-cage architectures in host-guest complexes with C_{60} fullerene

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Bowl-shaped phosphine molecules, whose bowl geometry can be controlled by a variation of the axial substituent, were synthesized, and used as host molecules to encapsulate C_{60}. Host molecules with relatively shallow bowls formed a chiral
10 **capsule, while hosts with a deeper bowls formed an achiral pseudo-cage.**

Bowl-shaped π-conjugated molecules, such as corannulene[1] and sumanene[2] have recently attracted considerable attention as molecular hosts, due to their ability to recognize and encapsulate
15 guest molecules on their concave surface.[3] In this context, the recognition of curved carbon materials such as fullerenes and single-walled carbon nanotubes by bowl-shaped hosts is an especially active area of research, not only due to the diverse applications of these carbon materials but also owing to the
20 unique architectures of the host-guest complexes resulting from such convex/concave interactions.[4] As a consequence of these efforts, the last two decades have seen significant progress in the development of bowl-shaped host molecules for such carbon materials.[5]
25 The depth and the surface area of bowl-shaped host molecules represent important structural parameters for the recognition of guest molecules, and the correlation between surface area and affinity towards guest molecules has been intensively investigated.[6] Conversely, the effect of the bowl depth on the
30 recognition still remains unclear, mostly because it is non-trivial to modify the bowl depth while keeping the bowl surface constant.[7]
Recently, we have reported the successful recognition of fullerenes[8] by using phosphorous-containing chiral host molecule
35 **1** with a unique bowl-shaped structure.[9] We were able to demonstrate that the incorporation of phenylacetylene groups into the bowl-shaped compound resulted in chiral induction as well as in a higher affinity towards a fullerene derivative. Subsequently, we envisioned that a modulation of the hybridization state of the
40 central phosphorus atom should induce a modification of the bowl geometry (Fig. 1). This assumption is supported by the Walsh diagram for tertiary phosphines, wherein the molecular phosphine orbital that contains the lone pair of electrons, is stabilized upon bending to form a more pyramidal shape.[10]
45 Accordingly, the depth of the bowl should increase with increasing contributions from the 3s orbital of the phosphorous atom. Herein, we would like to report the synthesis of bowl-shaped phosphine host molecules, containing different axial

substituents on the phosphorus atom. Varying the axial
50 substituent should affect the bowl structure of the host molecules, as the P–X bond should influence the hybridization of the phosphorous atom. A modification of the bowl geometry should thus lead to different assembly architectures in host-guest complexes with C_{60}.
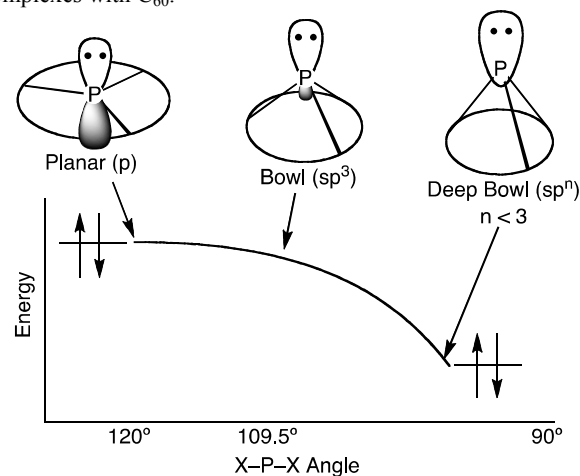

55 **Fig. 1.** Walsh diagram-based correlation between the bowl geometry of phosphorus-containing host molecules (planar, bowl, and deep bowl) and the hybridization of the molecular orbital on phosphorous that contains the lone pair of electrons

60 Racemic (*rac*)-**1**, as well as enantiopure (*P*)- and (*M*)-**1** were prepared according to literature procedures.[8] Treatment of phosphine oxide (*rac*)-**1** with Lawesson's reagent readily afforded the corresponding sulfide (*rac*)-**2** (Scheme 1). Crystals
65 of (*rac*)-**2**, belonging to the centrosymmetric space group $P2_1/n$, were obtained after recrystallization from chloroform/hexane. The enantiopure sulfides (*P*)-**2** and (*M*)-**2** were obtained, under retention of the configuration,[11] from the corresponding enantiomers of **1**. The absolute configuration of (*M*)-**2** was
70 determined by single crystal X-ray diffraction analysis.[12] Circular dichroism (CD) spectra of (*M*)-**2** exhibited a positive Cotton effect in the lowest excitation state (Figure S7). Polarimetry measurements established a positive specific rotation of (*M*)-**2**. A comparison of the chiroptical properties of (*M*)-**2** with the
75 positive Cotton effect and the specific rotation of (*M*)-**1**, suggested that both compounds share an identical configuration. TD-DFT calculations at the M06-2X/6-31G(d,p) level of theory

on the rotatory strength supported a positive CD signal for (*M*)-**2** (Table S3). Accordingly, the absolute structure of (*M*)-**2** was supported by spectroscopic as well as crystallographic data.
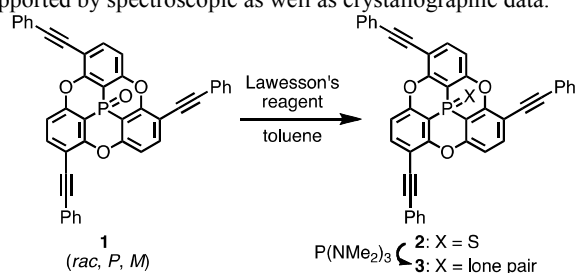
Scheme 1. Synthesis of bowl-shaped phosphine hosts **2** and **3**.

The desulfurized phosphine **3** was obtained, under retention of the configuration, from the reaction of **2** with P(NMe$_2$)$_3$ (Scheme 1). The absolute structure of enantiopure **3** was determined in a manner similar to **2**. Single crystals of (*rac*)-**3** belong to the space group *P*-3, contain a crystallographic *C*$_3$-axis, and exhibit a one-dimensional π-stacked structure (Fig. 2a). In these crystals, molecules of enantiopure (*M*)-**3** or (*P*)-**3** are stacked in a convex/concave way to form columns, in which all the molecules are related by translational symmetry along the *c*-axis (4.12 Å). The concave/convex interactions render these columns anisotropic, and the directional alignment of each (*M*)-**3** or (*P*)-**3** column is diametrically opposed to its neighboring column, which contains molecules of the other enantiomer. The distance between the centroids of the phenyl planes in the stacks of **3** (3.42 Å) is consistent with commonly encountered π-π stacking distances.[13] We also carried out a single-crystal X-ray diffraction analysis on enantiopure (*M*)-**3**, which provided a unit cell (*c* = 4.08 Å) similar to that of (*rac*)-**3**. Molecules of (*M*)-**3** are also aligned in convex/concave columnar stacks (Fig. 2b), but the packing structure of the (*M*)-**3** columns is different from that of (*rac*)-**3**: every column is surrounded by four columns orientated in opposite direction as well as by one column orientated in similar direction.
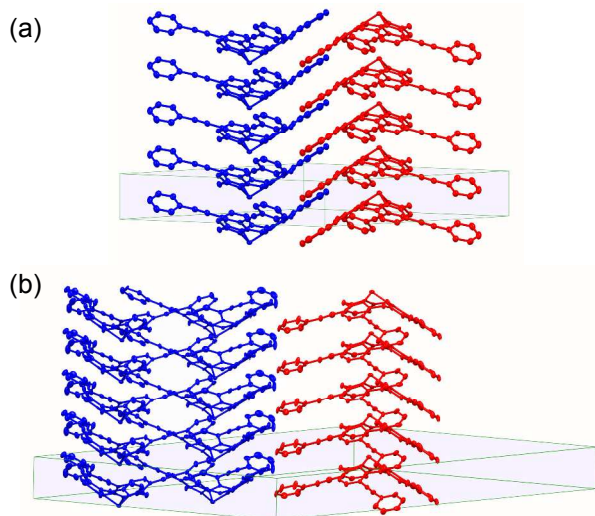

Fig. 2. *ORTEP* drawing of columnar π-π stacks of (*rac*)-**3** (a) and (*M*)-**3** (b); thermal ellipsoids were set at 50% probability and all hydrogen atoms omitted for clarity.

Compared to the C–P–C bond angles in triphenylphosphine (102°), those in **3** (93.8°) are extraordinarily narrow.[14] Phosphine **3** may accordingly be categorized as a highly restricted phosphine, such as *e.g.* phosphabarrelene[15] or phosphatriptycene[16], and the highly restricted structures of these phosphines is reflected in a high s-character of their lone pairs of electrons. In order to shed more light on the bowl-structures and the character of the P-X bond in **1-3**, theoretical structure optimizations were carried out using DFT calculations at the M062X/6-31G(d,p) level of theory. The thus obtained theoretically calculated structures in the gas phase are almost identical to the experimentally obtained crystal structures, except for the orientation of the terminal phenyl groups (Table S2). Due to the high levels of compliance, these DFT-optimized structures were subsequently used in order to avoid minor deviations arising from experimental values (Fig. 3). Two structural parameters were employed to examine the bowl structures of **1-3**: the bowl depth (*d*) and the cone angle (*θ*). The former is defined as the distance between the phosphorous atom and the centroid of the three terminal carbon atoms, while the latter is determined by the angle between the P–C and the P–centroid axes (Table 1). A summary of these and other DFT-derived parameters for **1-3** is presented in Table 1. The *d* values decrease in the order of **3** (2.463 Å) > **2** (2.232 Å) > **1** (2.215 Å), while the *θ* values increase in the same order. The observed cone angle difference between **1** (121.09°) and **3** (114.78°) reflects a significant substituent effect on the bowl structure of these phosphines.[17]
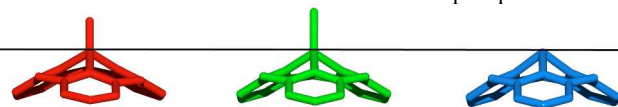

Fig. 3. DFT-optimized molecular structures for **1** (red), **2** (green), and **3** (blue); 4-phenylethynyl substituents as well as hydrogen atoms were omitted for clarity.

Table 1. Theoretically calculated structural and NBO parameters for **1-3**.

	d/Å[a]	*θ*/deg[b]	NBO charge[c]	Hybrid orbital[c], [d]
1: X = O	2.215	121.09	+2.09	s(31.2%) p(67.9%)
2: X = S	2.232	120.65	+1.45	s(32.1%) p(67.2%)
3: X = LP	2.463	114.78	+1.01	s(55.8%) p(44.2%)

[a]: The bowl depth "*d*" is defined as the distance between the phosphorus atom and the centroid of the plane consisting of the three terminal carbon atoms; [b]:The cone angle "*θ*" is defined as 2 × (C–P–Y) (Y: the centroid of the plane consisting of the three terminal carbon atoms); [c]:Calculated at the M06-2X/6-31G(d,p) level of theory; [d]: Percentage contribution of the 3s and 3p orbitals of phosphorous to the P–X bond.

In order to elucidate the relationship between the bowl geometry and the axial substituent on the phosphorus atom, a

natural bond orbital (NBO) analysis was carried out, which furnished a rough correlation between θ and the NBO charge. This result implied that bonding with an electron-withdrawing substituent such as S or O decreases the electron density on the phosphorus atom, which induces a more planar structure. The proportional contributions of the phosphorus 3s and 3p orbitals to the P–X bond were calculated by a natural hybrid orbital analysis, which revealed that the s-character of the P–O bond in **1** (31.2%) is slightly lower, but comparable to that of the P–S bond in **2** (32.1%). However, the s-character of the molecular orbital containing the lone pair in **3** is substantially higher (55.8%), even surpassing that of triphenylphosphine (48.9%). This result should most likely be ascribed to the constrained structure of **1**. The s-character of the P–X bond (*i.e.* the lone pair in **3**) is accordingly strongly correlated to the cone angle, θ. This can be feasibly interpreted on the basis of the diagram shown in Figure 1, which suggests an increased s-character for the lone pair upon deviation of the molecular structure from planarity. As **3** exhibits a narrow cone angle (114.78°), the s-character of the lone pair is correspondingly high. The formation of P–X (X = O, S) bonds induces a hybridization of the phosphorus atom under concomitantly higher contributions from the 3p orbital, which results in a widening of the cone angle.

It was thus possible to modulate the bowl geometry of these phosphorus-containing host molecules by a judicious choice of the axial substituent. Subsequently, we investigated the formation of host-guest complexes between these phosphines and C_{60} fullerene as the convex guest. Previously, we reported the formation of co-crystals of $[(P)\text{-}\mathbf{1}]_4 \supset C_{60}$, in which C_{60} is encapsuled in the chiral cavity formed by four enantiopure molecules of (P)-**1**. A similar co-crystallization was attempted by slow evaporation of a toluene/chloroform solution of C_{60} and (P)-**2**, and the X-ray crystallographic analysis of the obtained single crystals revealed the formation of a comparable 4:1 host-guest complex, $[(P)\text{-}\mathbf{2}]_4 \supset C_{60}$ (Fig. 4a). Structurally, $[(P)\text{-}\mathbf{2}]_4 \supset C_{60}$ is very similar to $[(P)\text{-}\mathbf{1}]_4 \supset C_{60}$, and both host-guest complexes can be categorized as capsules.[18]

Co-crystals of C_{60} with (rac)-**1** or (rac)-**2** were obtained in a similar fashion and exhibited almost identical lattice parameters to those of enantiopure $[(P)\text{-}\mathbf{1}]_4 \supset C_{60}$ and $[(P)\text{-}\mathbf{2}]_4 \supset C_{60}$. This result strongly suggested a racemic twining of homochiral single crystals, as crystallization of C_{60} with (rac)-**3** from a toluene solution resulted, in contrast, in the formation of the 2:1 host-guest complex $[(M)\text{-}\mathbf{3}][(P)\text{-}\mathbf{3}] \supset C_{60}$ (Fig. 4b), in which the two molecules (M)-**3** and (P)-**3** form an achiral cavity. This complex may accordingly be categorized as a pseudo-cage with a large aperture.[19]
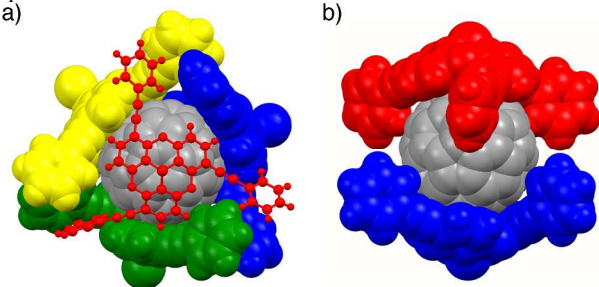
$\mathbf{2}]_4 \supset C_{60}$ and (b) $[(M)\text{-}\mathbf{3}][(P)\text{-}\mathbf{3}] \supset C_{60}$ ((P)-**2**, (P)-**3**, and (M)-**3**: colored; C_{60}: grey). One of the four molecules of (P)-**2** is drawn in a ball-and-stick representation to show the encapsuled C_{60}.

Within the cavities of $[(P)\text{-}\mathbf{1}]_4$, $[(P)\text{-}\mathbf{2}]_4$, and $[(M)\text{-}\mathbf{3}][(P)\text{-}\mathbf{3}]$, no disorder was observed for C_{60} (Figure S15 and S16), which suggested that the interactions between C_{60} and the cavity are sufficiently strong in order to consolidate a particular orientation of the guest. The host-guest complexes could also be detected by MALDI-TOF mass spectrometry measurements, which supports the formation of the complexes even in gas phase.[20] The C_3-axes of the C_{60} guests are almost identical with the pseudo-C_3-axes of the host molecules. However, the four (P)-**2** molecules in $[(P)\text{-}\mathbf{2}]_4 \supset C_{60}$ are crystallographically independent, and accordingly, the C_3-axes of the host and guest were slightly misaligned. Conversely, the C_3-axes of the host and guest in $[(M)\text{-}\mathbf{3}][(P)\text{-}\mathbf{3}] \supset C_{60}$ are aligned precisely with the crystallographic rotation axis of the R-3 space group. Accordingly, $[(M)\text{-}\mathbf{3}][(P)\text{-}\mathbf{3}] \supset C_{60}$ belongs to an S_6 point group.

The estimated π-π distance between the host and guest in $[(M)\text{-}\mathbf{3}][(P)\text{-}\mathbf{3}] \supset C_{60}$ (3.74 Å)[21] is comparable to the closest π-π distance reported for curved host-fullerene complexes based on convex/concave interaction (3.68-3.87 Å).[22] Similar π-π distances of 3.51-3.89 and 3.63-3.96 Å were observed for $[(P)\text{-}\mathbf{1}]_4 \supset C_{60}$ and $[(P)\text{-}\mathbf{2}]_4 \supset C_{60}$, respectively. However, the dihedral angles between the adjoined benzene rings in the host and guest in $[(M)\text{-}\mathbf{3}][(P)\text{-}\mathbf{3}] \supset C_{60}$ (10.4°) is lower than that in $[(P)\text{-}\mathbf{1}]_4 \supset C_{60}$ (18.8°) or $[(P)\text{-}\mathbf{2}]_4 \supset C_{60}$ (21.1°). These structural parameters suggest a stronger binding between C_{60} and **3** compared to **1** and **2**, which most likely arises from a more efficient π-π contact.

For $[(P)\text{-}\mathbf{1}]_4 \supset C_{60}$, $[(P)\text{-}\mathbf{2}]_4 \supset C_{60}$, and $[(M)\text{-}\mathbf{3}][(P)\text{-}\mathbf{3}] \supset C_{60}$, distances of 7.58, 7.62, and 7.89 Å, respectively, were measured between the phosphorus atom and the centroid of the C_{60} guest. This trend in distances is linearly correlated to the bowl depth of the corresponding host molecule (Table 1). In all complexes, these structural parameters are indicative of a nearly equivalent distance between the bottom of the central phosphangulene units and the centroid of C_{60} (Fig. 5). However, the distance between the centroid of the terminal benzene ring in the side chains of $[(M)\text{-}\mathbf{3}][(P)\text{-}\mathbf{3}] \supset C_{60}$ and the centroid of C_{60} is shorter (9.41 Å) compared to those in $[(P)\text{-}\mathbf{1}]_4 \supset C_{60}$ (9.88 Å) and $[(P)\text{-}\mathbf{2}]_4 \supset C_{60}$ (10.3 Å). A close inspection of the molecular structures led us to the conclusion that the different stoichiometry of the host-guest complexes should arise from the different spatial arrangement of the side chains, ultimately leading to differing degrees of contact or repulsion.
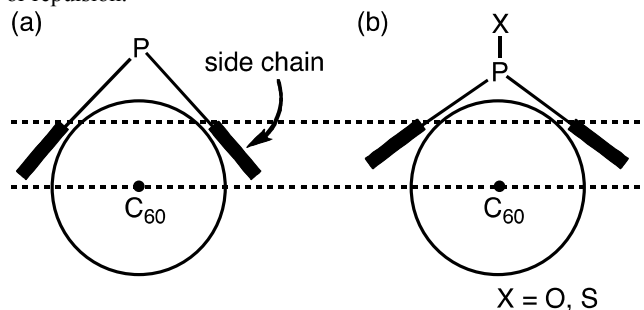

Fig. 4. Space-filling model of the crystal structures of (a) $[(P)$-

Fig. 5. Location of the C_{60} guest molecules in co-crystals with (a) deep or (b) shallow bowl-shaped phosphine hosts.

In conclusion, we disclosed the synthesis of phosphorus-containing bowl-shaped host molecules with different axial substituents on the central phosphorus atom. X-ray crystallographic analyses revealed that the axial substituent (O, S, or LP) has a significant effect on the bowl geometry, both with respect to the depth of the bowl as well as to its cone angle. An NBO analysis performed on the basis of DFT-calculated optimized structures indicated that the bonding properties of the P–X bonds should play an important role in tuning the geometry of the bowl. Although all host molecules encapsulated C_{60} as a guest molecule in co-crystals, the structures of the host-guest complexes are significantly different, depending on the bowl geometry of the host molecule. Hosts **1** and **2**, with relatively shallow bowls, afforded chiral cavities composed of four host molecules, while host **3**, with a deeper bowl, afforded an achiral cavity composed of two molecules. This study thus provides a strategy for the design of bowl-shaped phosphine host molecules with tunable bowl geometries. The control over the bowl geometry afforded control over the assembly architectures in co-crystals with C_{60} fullerene, and resulted in the formation of chiral capsules or an achiral pseudo-cage. This modulation approach should hence allow the induction of specific supramolecular architectures that may be used in order to control the electrochemical and/or photochemical properties of fullerenes.

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19   The host part in [(*M*)-**3**][(*P*)-**3**]⊃C_{60} is a "pseudo-cage" rather than a "cage" because the two host molecules are not connected to each other.

20   In our previous work, an NMR titration study of **1** with C_{60} exhibited negligible spectral change, indicating very weak interaction in solution, see reference 8.

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