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Supporting Information

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

Masaki Yamamura,^a* Kimiya Sukegawa,^a Tatsuya Nabeshima^a*

^a Graduate School of Pure and Applied Sciences, Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), University of Tsukuba 1-1-1, Tennodai, Tsukuba, Ibaraki 305-8571, Japan

E-mail: myama@chem.tsukuba.ac.jp

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(1) General methods

All chemicals were reagent grade, and used without further purification. All reactions were performed under a nitrogen atmosphere. Racemic mixture, P-isomer, and M-isomer of 1 were synthesized according to literature procedure. Chromatography was performed using SiO₂-60N (0.063-0.212 mm; Kanto). A recycling preparative HPLC was performed using a JAI LC-908 equipped with JAIGEL-1H and -2H columns (GPC) using CHCl₃ as an eluent. A preparative chiral resolution was performed using a JAI LC-9201 equipped with a DAICEL CHIRALPAK IA columns using 1:4 hexane/CHCl₃ as an eluent. Melting points were determined using a Yanaco melting point The ¹H, ¹³C, and ³¹P NMR spectra were recorded by Bruker apparatus and are uncorrected. AVANCE400 (400 MHz) spectrometer. Deuterated solvents were purchased from Cambridge Isotope Laboratories or Aldrich and used as received. In the NMR measurements, tetramethylsilane was used as the internal standard (0 ppm) for ¹H and ¹³C NMR and phosphorous acid was used as the external standard (0 ppm) for ³¹P NMR. MALDI-TOF mass spectra were recorded by an AB Sciex TOF/TOF5800. UV-vis absorption spectra were recorded by JASCO Ubest V-660. Circular dichroism spectra were recorded by a JASCO J-720W. Specific rotation ([□]_D) was measured at 17 °C in chloroform by a JASCO DIP-1000.

(2) Synthetic procedure

Synthesis of phosphine sulfide 2

To a toluene solution (3 mL) of (rac)-1 (20.1 mg, 32.4 µmol) was added Lawesson's reagent (11.2 mg, 27.7 µmol) and then the mixture was refluxed for 12 hours. The reaction mixture was separated by silica-gel column chromatography to give colorless powder of (rac)-2 (20.3 mg, 31.9 µmol, 98%). Enantiopure (*M*)-2 and (*P*)-2 were prepared from (*M*)-1 and (*P*)-1 in 86% and 93% yield, respectively.

2: colorless powder, mp > 300 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.30 dd, J = 8.8 4.8 Hz, 3H), 7.39-7.41 (m, 9H), 7.60-7.63 (m, 6H), 7.65 (d, J = 8.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 82.3 (d, $J_{C-P} = 2.0$ Hz), 95.7, 110.3 (d, $J_{C-P} = 85.1$ Hz), 111.9 (d, $J_{C-P} = 6.8$ Hz), 116.0 (d, $J_{C-P} = 5.9$ Hz), 122.7, 128.4, 128.9, 131.8, 136.2, 157.9, 158.0; ³¹P NMR (162 MHz, CDCl₃) δ - 52.2 MALDI-TOF MS m/z 637.17 [**2**+H]⁺; Anal. Calcd for C₄₂H₂₁O₃PS·H₂O: C, 77.05; H, 3.54. Found: C, 76.87; H, 3.74; [α]_D for *M*-**2**: +1132 (CHCl₃, c = 0.078, 17 °C).

To a toluene solution (5 mL) of (*rac*)-2 (16.0 mg, 25.1 μ mol) was added hexamethylphosphorus triamide (10 μ L, 55 μ mol) and then the mixture was refluxed for 24 hours. The reaction mixture was separated by silica-gel column chromatography to give colorless powder of (*rac*)-3 (10.7 mg, 17.7 μ mol, 70%). Enantiopure (*M*)-3 and (*P*)-3 were prepared from (*M*)-2 and (*P*)-2 in 88% and 97% yield, respectively.

3: colorless powder, mp 234 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.16 (dd, J = 8.4, 1.6 Hz, 3H), 7.36-7.40 (m, 9H), 7.49 (dd, J = 8.4, 1.6 Hz, 3H), 7.58-7.62 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 83.4, 94.5, 111.4 (d, $J_{C-P} = 1.8$ Hz), 113.9 (d, $J_{C-P} = 15$ Hz), 115.4, 123.2, 128.4, 128.5, 131.7, 133.6, 155.3 (d, $J_{C-P} = 6.8$ Hz), 155.4 (d, $J_{C-P} = 6.6$ Hz); ³¹P NMR (162 MHz, CDCl₃) δ –132.3; MALDI-TOF MS *m*/*z* 604.14 [M]; Anal. Calcd for C₄₂H₂₁O₃P·0.2H₂O: C, 82.94; H, 3.55. Found: C, 82.90; H, 3.95; [α]_D for *P*-**3**: –1751 (CHCl₃, *c* = 0.083, 17 °C).



Figure S1. ¹H NMR spectrum of (*rac*)-2 (400 MHz, CDCl₃).



Figure S2. ¹³C NMR spectrum of (*rac*)-2 (100 MHz, CDCl₃)



Figure S3. ³¹P NMR spectrum of (*rac*)-2 (162 MHz, CDCl₃)



Figure S4. ¹H NMR spectrum of (*rac*)-3 (400 MHz, CDCl₃)



Figure S5. ¹³C NMR spectrum of (*rac*)-3 (100 MHz, CDCl₃)



Figure S6. ³¹P NMR spectrum of (*rac*)-3 (162 MHz, CDCl₃)

(4) UV-vis absorption and circular dichroism spectra



Figure S7. UV-vis absorption (bottom) and CD (top) spectra of (P)- (red) and (M)-2 (black) in chloroform.



Figure S8. UV-vis absorption (bottom) and CD (top) spectra of (P)- (red) and (M)-3 (black) in chloroform.

(5) MALDI-TOF MS



Figure S9. MALDI-TOF MS (negative) of $[(P)-2]_4 \supset C_{60}$. Inset shows ion peas for $[2 \supset C_{60}]^-$ with isotope simulation.



Figure S10. MALDI-TOF MS (negative) of $[(M)-3][(P)-3] \supset C_{60}$. Insets show ion peas for $[3 \supset C_{60}]^-$ and $[(3)_2 \supset C_{60}]^-$ with isotope simulation.

(6) X-ray crystallographic analysis

X-ray diffraction measurements were performed using a Bruker APEXII ULTRA. The X-ray diffraction intensities were collected on a CCD diffractometer at 120 K using MoK α (graphite-monochromated, $\lambda = 0.71073$ Å) radiation. The data were integrated with SAINT (Bruker, 2004), and an empirical absorption correction (SADABS) was applied. The structure was solved by the direct method of SHELXS-97 or SHELXD-2014 and refined using the SHELXL-97 or SHELXL-2014 program.^{1,2} All of the positional parameters and thermal parameters of non-hydrogen atoms were anisotropically refined on F^2 by the full-matrix least-squares method. Hydrogen atoms were placed at the calculated positions and refined riding on their corresponding carbon atoms. The crystallographic data for (*rac*)-2, (*M*)-2, (*rac*)-3, (*M*)-3, [(*P*)-2]₄ \supset C₆₀, and [(*M*)-3][(*P*)-3] \supset C₆₀ were deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC 1060806–1060809, 1060816, and 1060817. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).



Figure S11. *ORTEP* drawing of (*rac*)-2, top (left) and side (right) views; thermal ellipsoids set at 50% probability. One of the enantiomers is shown.



Figure S13. *ORTEP* drawing of (*M*)-**2**, top (left) and side (right) views; thermal ellipsoids set at 50% probability.



Figure S12. *ORTEP* drawing of (*rac*)-**3**, top (left) and side (right) views; thermal ellipsoids set at 50% probability. One of the enantiomers is shown.



Figure S14. *ORTEP* drawing of (*M*)-**3**, top (left) and side (right) views; thermal ellipsoids set at 50% probability.



Figure S15. *ORTEP* drawing of $[(M)-3][(P)-3] \supset C_{60}$, top (left) and side (right) views; thermal ellipsoids set at 50% probability.



Figure S16. *ORTEP* drawing of $[(P)-2]_4 \supset C_{60}$; thermal ellipsoids set at 50% probability.

	(<i>rac</i>)- 2	(M)- 2	[(<i>P</i>)-2]₄⊃C ₆₀
Composite	$C_{42}H_{21}O_3PS\cdot CHCl_3$	$C_{42}H_{21}O_3PS$	$(C_{42}H_{21}O_3PS)_4 \cdot C_{60} \cdot (CHCl_3)_3$
Formula	$C_{43}H_{22}O_3PSCl_3$	$C_{42}H_{21}O_3PS$	$C_{231}H_{87}O_{12}P_4S_4Cl_9$
Formula weight	755.98	636.62	3625.17
Crystal size (mm ³)	$0.20\times0.05\times0.02$	$0.20 \times 0.10 \times 0.05$	$0.20\times0.02\times0.01$
Crystal system	monoclinic	monoclinic	tetragonal
Space group	$P2_{1}/n$	$P2_1$	$P4_1$
<i>a</i> (Å)	14.036(5)	10.913(3)	31.8140(15)
<i>b</i> (Å)	16.260(6)	16.970(4)	31.8140(15)
<i>c</i> (Å)	16.551(6)	17.246(4)	16.4344(9)
α (deg)	90	90	90
$\beta(\text{deg})$	109.896(3)	100.936(3)	90
$\gamma(\text{deg})$	90	90	90
$V(Å^3)$	3552(2)	3135.8(13)	16633.8(18)
Ζ	4	4	4
$D_{ m calcd}(m g\cdot m cm^{-3})$	1.414	1.348	1.448
Collected/Unique	33137/7145	34659/14143	144715/24006
<i>R</i> _{int}	0.0681	0.0557	0.1100
$\theta_{\rm max}({\rm deg})$	26.34	27.61	23.32
F_{000}	1544	1312	7384
μ (MoK α) (mm ⁻¹)	0.403	0.196	0.312
Limiting indices	$-17 \le h \le 16$	$-14 \le h \le 14$	$-29 \le h \le 35$
	$-20 \le k \le 20$	$-22 \le k \le 21$	$-34 \le k \le 35$
	$-18 \le l \le 20$	$-22 \le l \le 22$	$-18 \le l \le 18$
Parameters/restraints	481/0	847/0	2341/1
Goodness of fit (F^2)	0.987	1.032	1.147
$R_1 (I > 2\sigma(I))$	0.0924	0.0501	0.1104
wR_2 (all date)	0.2138	0.1086	0.2503
	-	-0.04(6)	0.16(3)

 Table S1. Crystallographic data.

 $\overline{R_1 = \sum ||F_0| - |F_c| / \sum |F_0|}, \quad wR_2 = \{\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2] \}^{1/2}$

	(<i>rac</i>)- 3	(M) -3	[(<i>M</i>)- 3][(<i>P</i>)- 3]⊃C ₆₀
Composite	$C_{42}H_{21}O_3P{\cdot}H_2O$	$C_{42}H_{21}O_3P$	$(C_{42}H_{21}O_3P)_2 \cdot C_{60}$
Formula	$C_{42}H_{23}O_4P$	$C_{42}H_{21}O_3P$	$C_{144}H_{42}O_6P_2$
Formula weight	622.57	604.56	1929.71
Crystal size (mm ³)	$0.10\times0.03\times0.03$	$0.40 \times 0.01 \times 0.01$	$0.05\times0.05\times0.05$
Crystal system	trigonal	orthorhombic	trigonal
Space group	<i>P</i> -3	$P2_{1}2_{1}2$	<i>R</i> -3
<i>a</i> (Å)	20.785(7)	30.262(14)	19.058(12)
<i>b</i> (Å)	20.785(7)	51.48(2)	19.058(12)
<i>c</i> (Å)	4.1189(15)	4.0818(19)	20.787(14)
α (deg)	90	90	90
$\beta(\text{deg})$	90	90	90
$\gamma(\text{deg})$	120	90	120
$V(Å^3)$	1541.1(11)	6359(5)	6539(9)
Ζ	2	8	3
$D_{\text{calcd}}(\text{g}\cdot\text{cm}^{-3})$	1.342	1.263	1.470
Collected/Unique	8681/2351	33744/9120	11604/3025
$R_{ m int}$	0.0331	0.1595	0.0926
$\theta_{\max}(\deg)$	27.51	23.23	26.50
F_{000}	644	2496	2952
μ (MoK α) (mm ⁻¹)	0.135	0.126	0.124
Limiting indices	$-27 \le h \le 26$	$-33 \le h \le 32$	$-23 \le h \le 18$
	$-22 \le k \le 27$	$-55 \le k \le 57$	$-23 \le k \le 23$
	$-5 \le l \le 4$	$-4 \le l \le 4$	$-24 \le l \le 26$
Parameters/restraints	143/0	819/0	229/0
Goodness of fit (F^2)	1.084	1.084	1.097
$R_1 (I > 2\sigma(I))$	0.0523	0.0901	0.0498
wR_2 (all date)	0.1255	0.1854	0.1198
	_	-0.09(16)	_

 $R_1 = \sum ||F_0| - |F_c| / \sum |F_0|, \quad wR_2 = \{\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2] \}^{1/2}$

(7) Computational methods.

All computations were performed using the Gaussian09 packages³ with the M06-2X functional.⁴ The basis set 6-31G(d,p) was used for the geometry optimizations and NBO analysis, and time-dependent calculations.

		1	2	3
P-X bond length/Å	exp (rac)	1.475(3)	1.929(2)	_
	exp (chiral)	1.466(4)	1.928(2)	_
	calc	1.485	1.939	_
C-P-X bond angles/deg	exp (rac)	119.2	120.0	_
	exp (chiral)	119.0	119.6	_
	calc	120.1	120.4	_
C–P–C bond angles/deg ^a	exp (rac)	98.3	97.1	93.8
	exp (chiral)	98.4	97.7	94.0
	calc	97.1	96.7	92.4
Bowl depth /Å (height) ^b	exp (rac)	2.089	2.183	2.400
	exp (chiral)	2.087	2.112	2.453
	calc	2.215	2.232	2.463
Bowl depth /Å (center) c	exp (rac)	2.089	2.184	2.400
	exp (chiral)	2.087	2.112	2.453
	calc	2.215	2.232	2.463
Generatrix length/Å d	exp (rac)	4.44	4.47	4.537
	exp (chiral)	4.47	4.47	4.54
	calc	4.505	4.509	4.570

Table S2. Comparison of experimental and calculated structure parameters of 1-3.

 $a \ 2 \times \ \ \ C - P - Y$ (Y: the centroid of the plane consisting of the three terminal carbon atoms); *b* a height from the bottom to the P atom; *c* distance between the P atom and the center of the bottom plane; *d* an averaged distance between the P atom and the terminal carbon atom.



Table S3. Singlet electronic excitation of (*M*)-1, (*M*)-2, and (*M*)-3 based on TD DFT calculation.

excited	avaited state	wave function ^{<i>a</i>}	λ / nm	f	<i>R</i> / 10 ⁻⁴⁰ cgs
	exciled state				(velocity)
	S ₁ (E)	$0.50 \times H - 1 \rightarrow L$	297	1.267	541.23
(<i>M</i>)-1	$S_2(E)$	$0.50 \times H \rightarrow L$	297	1.267	541.08
	S ₃ (E)	$0.42 \times H \rightarrow L+3$	279	0.329	198.17
	$\mathbf{S}_{1}\left(\mathbf{E}\right)$	$0.47 \times H - 1 \rightarrow L$	295	1.346	618.56
(<i>M</i>)-2	$S_2(E)$	$0.47 \times H \rightarrow L$	295	1.346	618.56
	S (E)	$0.42 \times H \rightarrow L + 0.36$	279	0.047	71.19
	5 3 (E)	\times H \rightarrow L+3			
(M)- 3	S ₁ (E)	$0.37 \times H-1 \rightarrow L$	290	1.502	776.10
	$S_2(E)$	$0.37 \times H \rightarrow L$	290	1.502	776.10
	S ₃ (A) $0.42 \times H \rightarrow L^{-1} \rightarrow L^{-1}$ $0.42 \times H \rightarrow L^{-1}$	$0.42 \times H \rightarrow L + 1 +$	280	0.126	-1212.05
		$0.42 \times H \rightarrow L+2$			1215.05

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