

Supporting Information

Iridium(I) and Rhodium(I) Cationic Complexes with Triphosphinocalix[6]arene Ligands: Dynamic Motion with Size-selective Molecular Encapsulation

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1. General

All reactions were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried and purified before use by the usual methods.¹ [RhCl(COD)]₂² and [IrCl(COD)]₂³ were prepared according to procedures in the literature. ¹H NMR (400.13 MHz), ¹³C{¹H}NMR (100.61 MHz), and ³¹P{¹H}NMR (161.98 MHz) spectra were recorded on a Bruker ARX 400 instrument. Simulation of ³¹P{¹H}NMR spectra at various temperatures were carried out with gNMR ver. 4.1 (Cherwell Scientific). Elemental analysis was performed at the Center for Instrumental Analysis of Hokkaido University. FD and ESI mass spectra were recorded on a JEOL JMS-SX102A instrument at the GC-MS & NMR Laboratory of Faculty of Agriculture, Hokkaido University. DFT molecular calculations were performed with Gaussian 98 program⁴ on a Super Server HP Exemplar V2500 at the Information Initiative Center, Hokkaido University.

2. X-ray Crystallographic Studies of Complexes **1**, **2a**, and **2c**.

Suitable crystals of **1a**, **2a**, and **2c** for diffraction studies were grown by slow diffusion of ethyl acetate/hexane (for **1a**), dichloromethane/Et₂O (for **2a**), and tetrachloroethane/hexane (for **2c**). The crystals of **2a** and **2c** appear to lose crystallinity very rapidly upon exposure to air. Data were collected with Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$) at -160°C on a Rigaku RAXIS RAPID imaging plate (for **1**) or a Rigaku Saturn CCD diffractometer (for **2a** and **2c**) area detector with graphite monochromated Mo-K α radiation to a maximum 2θ value of 55.0° . The structure of **1a**, **2a**, and **2c** were solved by direct methods using the program SIR92⁵ (for **1a** and **2c**), and SIR97⁶ (for **2a**), followed by expanded using Fourier techniques. For **1a**, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. For **2a**, some non-hydrogen atoms were refined anisotropically, while the rest were

refined isotropically. Hydrogen atoms were included in fixed positions. Neutral atom scattering factors were taken from Cromer and Waber.⁷ Anomalous dispersion effects were included in F_c .⁸ For **2c**, the atoms connecting scheme and inclusion of one 1,1,2,2-tetrachloroethane molecule into the cavity of **2c** have been confirmed. However, considerable disorder of solvents outside the cavity occurred. All calculations were performed using the CrystalStructure⁹ crystallographic software package (ver 3.6). The crystal data of **1a**, **2a**, and **2c** are listed in Table S1. The X-ray structure of **1a** and the cationic part of **2c** are shown in Figure S1 and S2.

Table S1.

Crystal data and structure refinements for complex **1a**, **2a**, and **2c**.

	1	2a	2c
Empirical formula	C ₁₀₈ H ₁₂₃ O ₆ P ₃	C ₂₄₀ H ₂₈₂ O ₁₂ - B ₃ F ₁₂ Ir ₃ P ₆ ·3CH ₂ Cl ₂	C ₂₄₀ H ₂₈₂ O ₁₂ - B ₃ F ₁₂ Rh ₃ P ₆ ·xCl ₂ CHCHCl ₂
Formula weight	1610.1	4636.5	—
Temperature (°C)	−160(1)	−160(1)	−160(1)
Wavelength (Å)	0.71070	0.71070	0.71070
Crystal system	monoclinic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ /n (#14)	<i>C</i> 2 (#5)	<i>P</i> ī(#2)
<i>a</i> (Å)	14.7596(3)	33.75(1)	20.95(3)
<i>b</i> (Å)	33.0204(5)	20.155(6)	21.80(3)
<i>c</i> (Å)	19.5277(4)	20.504(7)	36.40(6)
α (°)	—	—	83.30(2)
β (°)	98.6988(5)	117.045(3)	82.90(2)
γ (°)	—	—	86.90(2)
<i>V</i> (Å ³)	9407.7(3)	12422(7)	16371(4)
<i>Z</i>	4	2	2
<i>D</i> _{calc} (g cm ^{−3})	1.137	1.239	—
μ (cm ^{−1})	1.17	17.73	3.91
Crystal size (mm)	0.40 × 0.20 × 0.15	0.20 × 0.20 × 0.08	0.22 × 0.12 × 0.10
No. reflections collected	21938	50765	73805
No. observations	11138	10052	15071
Parameters	1055	1241	1873
Refinements on	<i>F</i> ²	<i>F</i>	<i>F</i>
<i>R</i>	0.073 ^a	0.062 ^c	0.129 ^c
<i>wR</i>	0.179 ^b	0.076 ^c	0.142 ^c
GOF	1.46	1.51	10.4

^aI > 2.0σ(I). ^bI > 1.5σ(I). ^cI > 3.0σ(I).

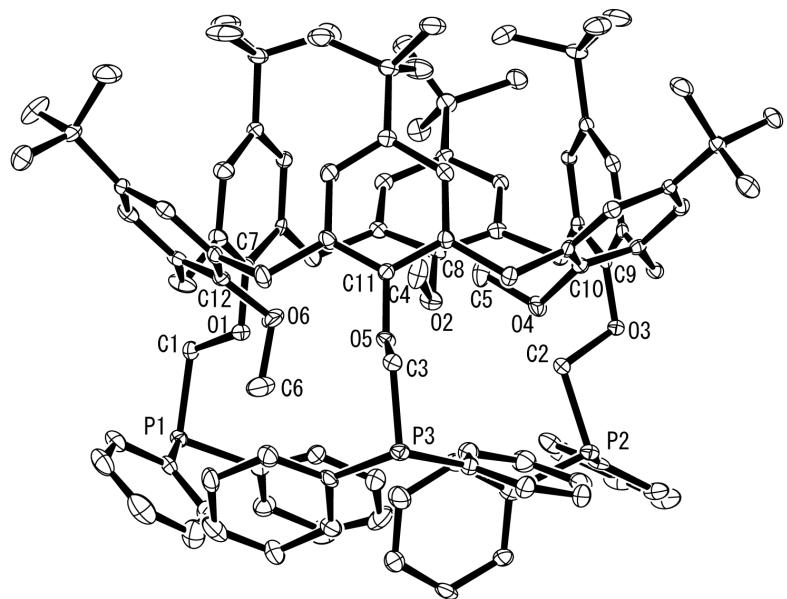


Figure S1. Perspective ORTEP drawing of the molecular structure of **1a**.
Thermal ellipsoids are shown at 30 % probability, and hydrogen atoms are deleted
for ease of viewing.

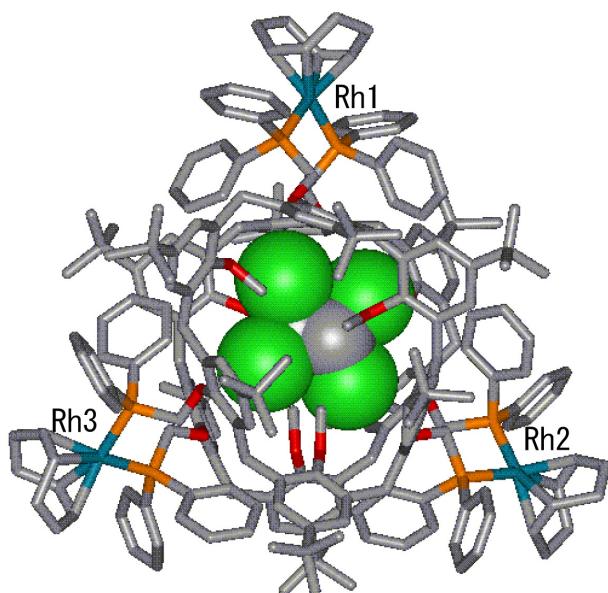


Figure S2. X-ray structure of cationic part of **2c**.
Hydrogen atoms are deleted for ease of viewing. Encapsulated $\text{Cl}_2\text{CHCHCl}_2$ is
denoted as space-filling model.

3. $^{31}\text{P}\{\text{H}\}$ NMR spectra of **2c** in CD_2Cl_2 and $\text{Cl}_2\text{CDCDCl}_2$.

The $^{31}\text{P}\{\text{H}\}$ NMR spectra of **2c** (10.3 mg, 2.5 μmol) in CD_2Cl_2 (0.5 mL) and $\text{Cl}_2\text{CDCDCl}_2$ (0.5 mL) were shown in Figure S3.

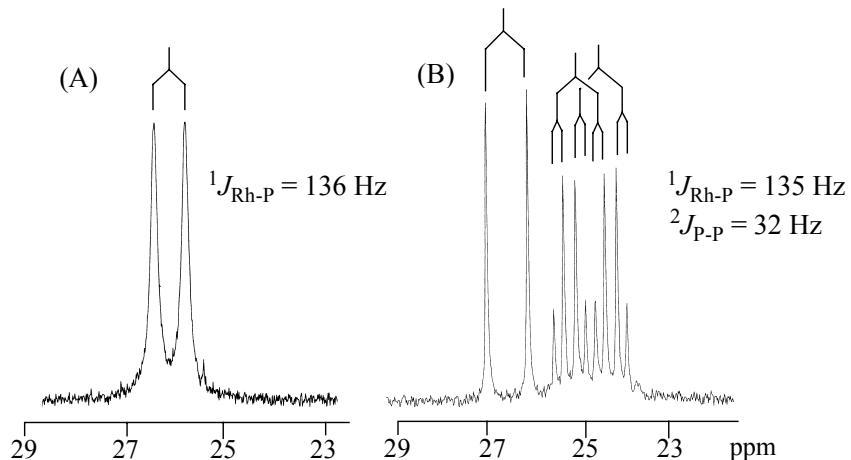


Figure S3. $^{31}\text{P}\{\text{H}\}$ NMR spectra of **2c** measured in (A) CD_2Cl_2 and (B) $\text{Cl}_2\text{CDCDCl}_2$.

4. $^{31}\text{P}\{\text{H}\}$ NMR experiments of **2a** (Table 1) and **2c** (Table S1) with various molecules

In a ϕ 5 mm NMR tube, a 5 mM solution of **2a** or **2c** was prepared by dissolving **2a** (11.0 mg, 2.5 μmol) or **2c** (10.3 mg, 2.5 μmol) in a degassed mixture of CDCl_3 (0.35 mL) and the molecule (0.15 mL). The resulting mixture was left for 5 h at room temperature prior to the measurement at 25 °C. $^{31}\text{P}\{\text{H}\}$ NMR of **2c** with selected molecules in group A-C were shown in Table S1.

Table S1. $^{31}\text{P}\{\text{H}\}$ NMR of **2c** with various molecules^a

entry	molecule ^{31}P resonances at 25 °C /ppm	$V^b/\text{\AA}^3$	$A^c/\text{\AA}^2$
A 1	CHCl_3 , 26.7 (d, $\Delta\nu=58$ Hz, ${}^1\text{J}(\text{P},\text{Rh})=136$ Hz)	67.7	42.0
B 2	$\text{Cl}_2\text{CHCHCl}_2$ 25.6 (dd, ${}^1\text{J}(\text{P},\text{Rh})=135$ Hz, ${}^2\text{J}(\text{P},\text{P})=31$ Hz), 26.5 (dd), 27.8 (d, ${}^1\text{J}(\text{Rh},\text{P})=136$ Hz)	100.3	49.5
C 3	Cumene, 26.6 (d, $\Delta\nu=62$ Hz, ${}^1\text{J}(\text{P},\text{Rh})=136$ Hz)	123.1	68.1

^a**2c** (5 mM) in the presence of the molecule (30% v/v) in CDCl_3 at 25 °C. ^bConnolly solvent-excluded volume. ^c Maximum projection area of the solvent accessible surface.

5. Details of calculation of size of the molecules (V and A) listed in Table 1 and Table S1

Size of the molecules listed in Table 1 and Table S1 was calculated by the following two methods on structures optimized by B3LYP/6-31G(d,p).⁴ One is Connolly solvent-excluded volume^{10a} (V) which was calculated using Chem 3D Ultra (ver. 7, CambridgeSoft) with a solvent probe radius of 1.4 Å. The solvent-excluded volume represents the volume of space that the probe is excluded from by collisions with the atoms of the van der Waals surface.^{10a} The other method is Maximum projecting area (A) of the solvent accessible surface^{10b} on the same DFT optimized structure. Figure S4 shows the details of the calculation of the area with cumene as the example. First, the solvent accessible surface model was defined as the model made by the contact of the probe sphere center (radius = 1.4 Å) with the van der Waals surface (**I**). Then projection of the model to get maximum area was subjected and the area was calculated on 0.070 Å² gridded map (**II**). As for cumene, the value is 68.1 Å².

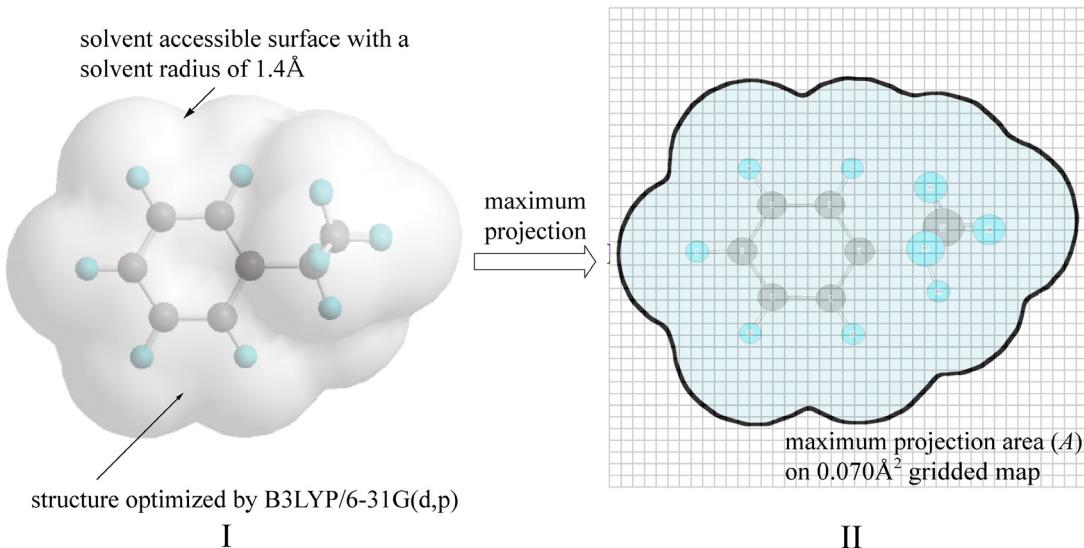
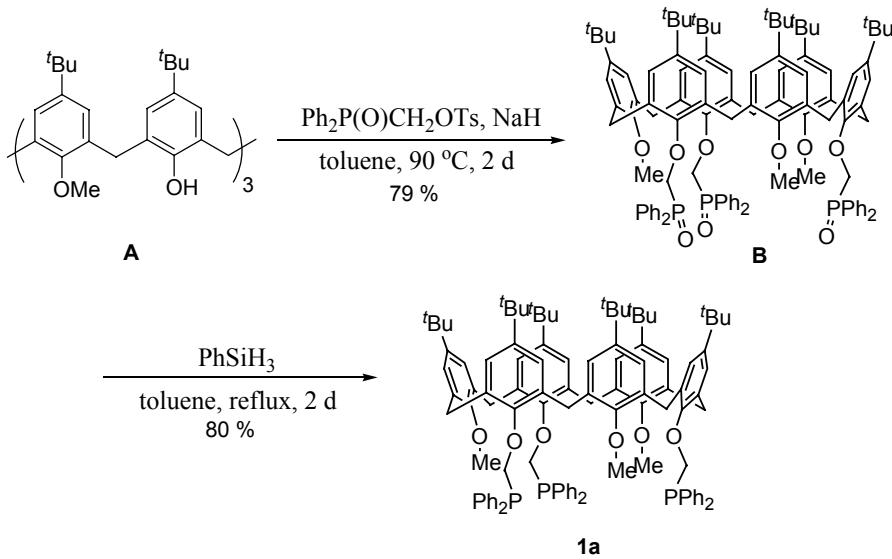


Figure S4. Calculation of maximum projection area (A) of the solvent accessible surface

6. Preparation of 1a



Scheme 1S

5,11,17,23,29,35-Hexa(*tert*-butyl)-37,39,41-tris(diphenylphosphinoylmethoxy)-38,40,42-trimethoxycalix[6]arene (**B**) (Scheme 1S)

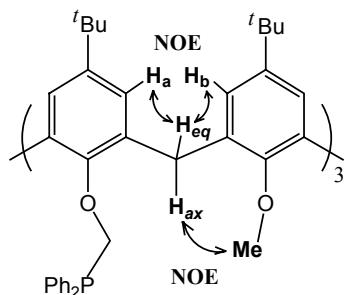
To a suspension of **A**¹¹ (5.08 g, 5.0 mmol) and NaH (3.60 g, 0.15 mol) in 120 mL of toluene was added tosyloxymethyldiphenylphosphine oxide¹² (6.57 g, 17.0 mmol). The reaction mixture was heated to 90 °C and stirred for 2 days. After cooling down, the excess NaH was carefully neutralized with 3% HCl aq. The crude product was extracted with chloroform and dried over MgSO₄. Analytically pure product was obtained by medium-pressure column chromatography with ethyl acetate as an eluent followed by recrystallization from ethyl acetate and *n*-hexane. Yield: 6.53 g, 79 %. Mp: 290–294 °C; FD-MS: *m/z* 1657 [M]⁺; ¹H NMR (CDCl₃): δ 0.71 (s, 27H), 1.32 (s, 27H), 2.02 (s, 9H, OCH₃), 3.18 (d, 6H, *J*(H,H) = 15 Hz, ArCH₂Ar), 4.17 (d, 6H, *J*(H,H) = 15 Hz, ArCH₂Ar), 4.72 (d, 6H, ²*J*(H,P) = 8 Hz, OCH₂P(O)Ph₂), 6.54 (s, 6H), 7.14 (s, 6H), 7.50–7.55 (m, 18H), 8.08–8.13 (m, 12H). ¹³C{¹H}NMR (CDCl₃): δ 29.41 (ArCH₂Ar), 30.99, 31.56, 33.91, 34.17, 59.70 (OCH₃), 70.22 (d, ¹*J*(C,P) = 85 Hz, OCH₂P(O)Ph₂), 123.8, 128.0, 128.8 (d, ³*J*(C,P) = 12 Hz), 130.8 (d, ¹*J*(C,P) = 100 Hz), 131.7 (d, ²*J*(C,P) = 9 Hz), 132.4, 132.6,

133.1, 145.7, 146.6, 151.6 (d, $^3J_{CP} = 12$ Hz), 154.2. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.7.

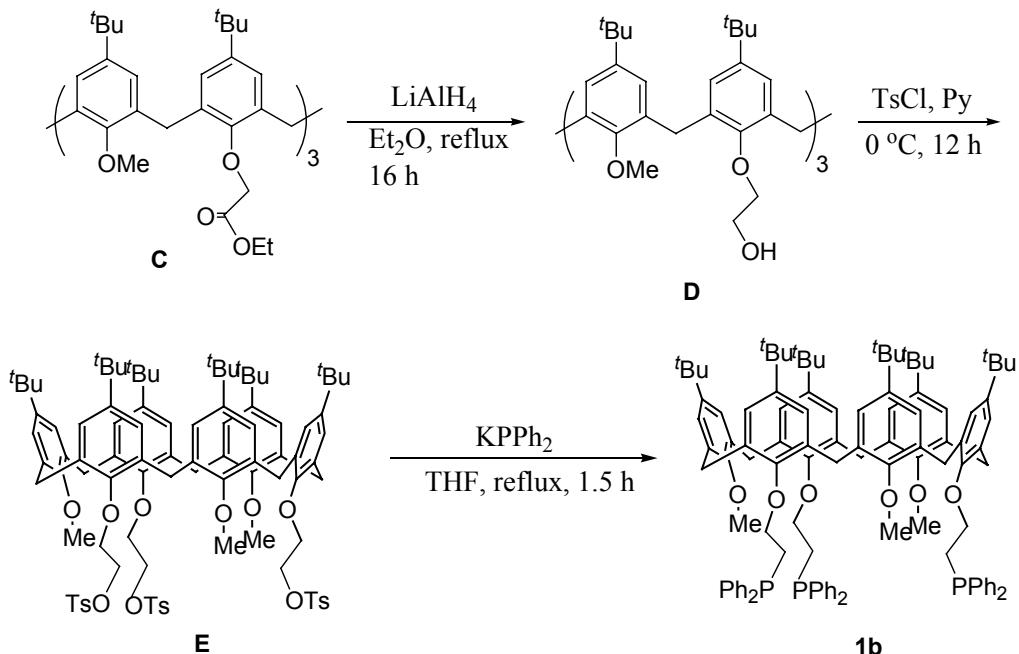
5,11,17,23,29,35-Hexa(*tert*-butyl)-37,39,41-tris(diphenylphosphinomethoxy)-38,40,42-trimethoxycalix[6]arene (1a)

To a solution of **B** (1.0 g, 0.603 mmol) in 15 mL of toluene was added $PhSiH_3$ (1.96 g, 18.1 mmol). The reaction mixture was refluxed for 2 days and then cooled down. After evaporation, analytically pure product was obtained by medium-pressure column chromatography with ethyl acetate/*n*-hexane (1:25) as an eluent. Yield: 0.78 g, 80%. Mp: 254–255 °C; FD-MS: m/z 1609 [M] $^+$; 1H NMR ($CDCl_3$): δ 0.75 (s, 27H), 1.34 (s, 27H), 2.12 (s, 9H, OCH_3), 3.30 (d, 6H, $J(H,H) = 15$ Hz, $ArCH_2Ar$), 4.42 (d, 6H, $J(H,H) = 15$ Hz, $ArCH_2Ar$), 4.72 (d, 6H, $^2J(H,P) = 4$ Hz, OCH_2PPh_2), 6.59 (s, 6H), 7.19 (s, 6H), 7.31–7.37 (m, 18H), 7.60–7.64 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.22 ($ArCH_2Ar$), 31.31, 31.70, 34.23, 34.44, 60.24 (OCH_3), 74.44 (d, $^1J(C,P) = 11$ Hz, OCH_2PPh_2), 124.0, 128.3, 128.9 (d, $^3J(C,P) = 7$ Hz), 129.3, 133.3, 133.5 (d, $^2J(C,P) = 18.5$ Hz), 133.8, 136.7 (d, $^1J(C,P) = 12$ Hz), 146.0, 146.3, 153.1 (d, $^3J(C,P) = 6$ Hz), 154.8. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ –17.1. Anal. Calcd for $C_{108}H_{123}O_6P_3$: C, 80.57; H, 7.70. Found: C, 80.64; H, 7.71.

2D-ROESY experiments of **1a** showed NOE correlation of the aromatic protons with the equatorial protons on the bridging methylene and not with the distant axial protons.



7. Preparation of **1b**



Scheme 2S

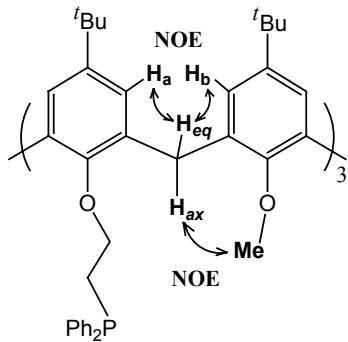
5,11,17,23,29,35-Hexa(tert-butyl)-37,39,41-tris(hydroxyethoxy)-38,40,42-trimethoxy calix[6]arene (D**) (Scheme 2)** A mixture of **C**¹³ (2.5 g, 1.96 mmol) and ether (50 mL) was added dropwise at room temperature to LiAlH_4 (0.89 g, 23.6 mmol) in ether (20 mL). The reaction mixture was refluxed for 16 h and quenched with 1N HCl at 0°C . The product was extracted with CHCl_3 and the solution was washed with water. The organic layer was dried over MgSO_4 . Removal of solvents afforded the product in pure form. Yield: 2.1 g, 93%. FD-MS: m/z 1146 [M]⁺; ¹H NMR (CDCl_3): δ 0.97 (s, 27H), 1.28 (s, 27H), 3.17 (br s, 3H), 3.36 (t, 6H, $J(\text{H,H}) = 4$ Hz), 3.43 (s, 9H), 3.47 (t, 6H, $J = 4$ Hz), 3.94 (s, 12H), 6.73 (s, 6H), 7.11(s, 6H). ¹³C{¹H}NMR (CDCl_3): δ 30.73 (Ar CH_2 Ar), 31.18, 31.45, 33.95, 34.12, 60.13 (OCH_3), 61.55, 75.02, 124.2, 127.0, 132.9, 133.0, 145.6, 146.0, 153.0, 153.2. Anal. Calcd for $\text{C}_{75}\text{H}_{102}\text{O}_9$: C, 78.49; H 8.96. Found: C, 78.58; H, 8.85.

5,11,17,23,29,35-Hexa(tert-butyl)-37,39,41-tris(*p*-tolylsulfonyloxyethoxy)-38,40,42-trimethoxycalix[6]arene (E**)** To a mixture of **D** (0.35 g, 0.305 mmol) and pyridine (6

mL) was added *p*-toluenesulfonyl chloride (0.70 g, 3.66 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 12 h and then poured into 1N HCl (60 mL). The white precipitate was collected, washed with water, and extracted with CH₂Cl₂. The organic layer was dried and concentrated to yield a white solid, which was reprecipitated by CH₂Cl₂/MeOH. Yield: 0.38 g, 77%. FD-MS: *m/z* 1609 [M]⁺; ¹H NMR (CDCl₃): δ 0.80 (s, 27H), 1.37 (s, 27H), 2.07 (s, 9H), 2.36 (s, 9H), 3.28 (d, 6H, *J*(H,H) = 15 Hz, ArCH₂Ar), 4.11 (t, 6H, *J*(H,H) = 5 Hz, OCH₂CH₂OTs), 4.38–4.42 (m, 12H, overlap of ArCH₂Ar and OCH₂CH₂OTs), 6.58 (s, 6H), 7.21 (s, 6H), 7.27(d, 6H, *J*(H,H) = 8 Hz, ArH on tosyl group), 7.81 (d, 6H, *J*(H,H) = 8 Hz, ArH on tosyl group); ¹³C{¹H}NMR (CDCl₃): δ 21.60, 29.54, 31.03, 31.60, 33.91, 34.21, 59.91 (OCH₃), 68.81, 69.99, 123.5, 127.96, 128.00, 129.9, 132.8, 133.3, 145.0, 145.8, 146.1, 150.9, 154.3.

5,11,17,23,29,35-Hexa(*tert*-butyl)-37,39,41-tris(diphenylphosphinoethoxy)-38,40,42-trimethoxycalix[6]arene (1b) Potassium diphenylphosphide (0.5 M in THF, 0.75 mmol) was added dropwise to a solution of **E** (0.30 g, 0.186 mmol) in THF (6 mL) at 0 °C. The reaction mixture was then refluxed for 1.5 h and cooled down. After quenching with water, THF was removed. The white solid was dissolved in dichloromethane and washed with water. After dried over MgSO₄, the product was purified by recrystallization from CH₂Cl₂/MeOH. Yield: 0.24 g, 79%. Mp: 219.0–222.0 °C. FD-MS: *m/z* 1652 [M]⁺; ¹H NMR (CDCl₃): δ 0.75 (s, 27H), 1.39 (s, 27H), 2.05 (s, 9H, OCH₃), 2.77 (t, 6H, *J*(H,H) = 8 Hz, OCH₂CH₂PPh₂), 3.29 (d, 6H, *J*(H,H) = 15 Hz, ArCH₂Ar), 4.03 (td, 6H, *J*(H,H) = 8 Hz, ³J(H,P) = 8 Hz, OCH₂CH₂PPh₂), 4.53 (d, 6H, *J*(H,H) = 15 Hz, ArCH₂Ar), 6.60 (s, 6H), 7.26 (s, 6H), 7.32–7.38 (m, 18H), 7.49–7.53 (m, 12H); ¹³C{¹H}NMR (CDCl₃): δ 29.53 (d, ¹J(C,P) = 13.6 Hz, OCH₂CH₂PPh₂), 29.89 (ArCH₂Ar), 31.28, 31.72, 34.20, 34.45, 60.29 (OCH₃), 70.48 (d, ²J(C,P) = 26 Hz, OCH₂CH₂PPh₂), 123.8, 128.4, 128.9 (d, ³J_{PC} = 7 Hz), 129.0, 133.0 (d, ²J(C,P) = 19 Hz),

133.3, 133.9, 138.8 (d, $^1J(C,P) = 13$ Hz), 146.0, 151.9, 154.7. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ –22.5. Anal. Calcd for $C_{111}H_{129}O_6P_3$: C, 80.70; H 7.87. Found: C, 80.62; H 7.74. 2D-ROESY experiments of **1b** showed NOE correlation of the aromatic protons with the equatorial protons on the bridging methylene and not with the distant axial protons.



8. Preparation of **2a**

$AgBF_4$ (9.1 mg, 0.047 mmol, dissolved in 0.3 mL of THF) was added to $[IrCl(COD)]_2$ (0.024 mmol) in dichloromethane (2 mL). Supernatant over $AgCl$ was taken carefully with syringe and added dropwise to **1a** (0.031 mmol) in dichloromethane (6 mL). The mixture was stirred at room temperature for 3 h. Removal of the solvent gave the crude product as light red powder, which was purified by reprecipitation with CH_2Cl_2/Et_2O . Yield: 92 %. ESI-MS: m/z 2103 [**2a**– $2(BF_4^-)$] $^{2+}$; 1H NMR (CD_2Cl_2 , 25 °C): δ 0.68 (s, 54H), 1.27 (s, 54H), 1.87 (br s, 24H, methylene-H(cod)), 2.11 (br s, 12H, Ar CH_2 Ar), 2.29 (br s, 18H, OCH₃), 3.49 (br s, 12H, Ar CH_2 Ar), 4.30 (s, 12H, OCH₂PPh₂), 5.05 (br s, 12H, olefin-H(cod)), 6.35 (br s, 12H), 6.70–8.80 ppm (m, 72H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 25 °C, δ = 16.3; –60 °C, 15.6 (d, $^2J(P,P) = 17$ Hz), 17.3 (s), 18.5 (d, $^2J(P,P) = 17$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 17.2. 1H NMR ($Cl_2CDCDCl_2$, 25 °C): δ 0.51 (s, 18H), 0.64 (s, 18H), 0.70 (s, 18H), 1.16 (s, 18H), 1.21 (s, 6H), 1.34 (s, 18H), 1.68 (s, 18H), 1.74–2.12 (m, 24H), 2.20–2.50 (m, 12H), 2.62–2.80 (m, 6H), 2.95 (d, 2H, $J(H,H) = 15$ Hz), 3.35 (d, 2H, $J(H,H) = 15$ Hz), 3.42–3.60 (m, 6H), 3.67 (d, 2H, $J(H,H) = 15$ Hz), 4.12 (br s, 6H), 4.27 (br s, 6H),

4.52-4.73 (m, 6H), 4.84-4.96 (m, 2H), 5.00-5.10 (m, 2H), 5.12-5.22 (m, 2H), 6.07 (s, 2H), 6.14 (s, 2H), 6.23 (s, 2H), 6.34 (s, 2H), 6.43 (s, 2H), 6.46-6.54 (m, 8H), 6.56-6.70 (m, 4H), 6.73 (s, 2H), 6.90-7.28 (m, 24H), 7.32-7.70 (m, 26H), 7.80-7.90 (m, 2H), 7.92-8.02 (m, 2H), 8.10-8.32 (m, 4H), 8.40-8.52 (m, 2H), 8.72-8.92 (m, 6H). ^{13}C NMR ($\text{Cl}_2\text{CDCCDCl}_2$, 25 °C): twelve kinds of *t*-Bu (δ 30.83, 30.92, 31.01, 31.55, 31.82, 32.05, 33.84, 33.87, 33.89, 34.10, 34.38, 34.81). $^{31}\text{P}\{\text{H}\}$ NMR ($\text{Cl}_2\text{CDCCDCl}_2$, 25 °C): δ 15.3 (d, $^2J(\text{P,P}) = 18$ Hz), 15.9 (d, $^2J(\text{P,P}) = 18$ Hz), 16.4 (s). Anal. Calcd for $\text{C}_{240}\text{H}_{282}\text{B}_3\text{F}_{12}\text{Ir}_3\text{O}_{12}\text{P}_6 \cdot 3\text{CH}_2\text{Cl}_2$: C, 62.95; H, 6.26. Found: C, 62.45; H, 6.37.

9. Preparation of 2b

In the similar manner as synthesis of **2a**, **2b** was prepared from $[\text{IrCl}(\text{COD})]_2$ (0.024 mmol), NaBPh_4 (0.047 mmol), and **1a** (0.031 mmol) as light red solid. Yield: 68 %. ^1H NMR (CD_2Cl_2 , 25 °C): δ 0.70 (s, 54H), 1.38 (s, 54H), 1.56 (s, 18H), 1.80-2.50 (m, 24H), 3.54 (br s, 24H), 4.17 (br s, 6H), 4.29 (br s, 6H), 5.02 (br s, 12H), 6.20-8.42 (m, 144H). $^{31}\text{P}\{\text{H}\}$ NMR (CD_2Cl_2 , 25 °C): δ 17.4. $^{31}\text{P}\{\text{H}\}$ NMR ($\text{Cl}_2\text{CDCCDCl}_2$, 25 °C): δ 15.5 (d, $^2J(\text{P,P}) = 17$ Hz), 16.1 (d, $^2J(\text{P,P}) = 17$ Hz), 16.6 (s). Anal. Calcd for $\text{C}_{312}\text{H}_{342}\text{B}_3\text{Ir}_3\text{O}_{12}\text{P}_6 \cdot \text{CH}_2\text{Cl}_2$: C, 72.80; H, 6.71. Found: C, 72.43; H, 6.87.

10. Preparation of 2c

AgBF_4 (9.1 mg, 0.047 mmol, dissolved in 0.3 mL of THF) was added to $[\text{RhCl}(\text{COD})]_2$ (0.024 mmol) in dichloromethane (2 mL). Supernatant over AgCl was taken carefully with syringe and added dropwise to **1a** (0.031 mmol) in dichloromethane (6 mL). The mixture was stirred at room temperature for 3 h. Removal of the solvent gave the crude product, which was purified by reprecipitation with $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. Yellow solid. Yield: 84 %. ESI-MS: m/z 1970 [**2c**-2(BF_4^-)] $^{2+}$, 1284 [**2c**-3(BF_4^-)] $^{3+}$. ^1H NMR (CD_2Cl_2 , 25 °C): δ 0.68 (s, 54H), 1.35 (s, 54H), 2.02 (br s, 24H, methylene-H(cod)), 2.32 (br s, 12H, ArCH_2Ar), 2.46 (br s, 18H, OCH_3), 3.50 (br s,

12H, ArCH₂Ar), 4.68 (br s, 12H, OCH₂PPh₂), 5.06 (br s, 12H, olefin-H(cod)), 6.34 (s, 12H), 6.70–8.80 (m, 72H). -60 °C, six peaks of singlet at the range of *t*-Bu (δ =0.40, 0.53, 0.67, 1.09, 1.30, 1.63). ¹³C{¹H}NMR (CD₂Cl₂, 25 °C): four kinds of *t*-Bu (δ = 30.32, 30.93, 33.30, 33.70). ³¹P{¹H}NMR (CD₂Cl₂, 25 °C) : δ 26.0 (d, ¹J(P,Rh) = 136 Hz); -60 °C, δ = 24.7 (dd, ¹J(P,Rh) = 135 Hz, ²J(P,P) = 33 Hz), 27.3 (d, ¹J(P,Rh) = 135 Hz), 27.7 (dd, ¹J(P,Rh) = 135 Hz, ²J(P,P) = 33 Hz). ¹H NMR (Cl₂CDCDCl₂, 25 °C): δ 0.51 (s, 18H), 0.64 (s, 18H), 0.70 (s, 18H), 1.15 (s, 18H), 1.22 (s, 6H), 1.34 (s, 18H), 1.69 (s, 18H), 1.88-2.30 (m, 24H), 2.38-2.60 (m, 12H), 2.64-2.83 (m, 6H), 3.00 (d, 2H, *J*(H,H) = 15 Hz), 3.36 (d, 2H, *J*(H,H) = 15 Hz), 3.42-3.60 (m, 6H), 3.70 (d, 2H, *J*(H,H) = 15 Hz), 4.50 (br s, 6H), 4.56-4.82 (m, 12H), 4.87-4.98 (m, 2H), 5.02-5.12 (m, 2H), 5.14-5.24 (m, 2H), 6.06 (s, 2H), 6.14 (s, 2H), 6.23 (s, 2H), 6.33 (s, 2H), 6.42 (s, 2H), 6.44-6.56 (m, 8H), 6.58-6.68 (m, 4H), 6.73 (s, 2H), 6.88-6.94 (m, 2H), 6.95-7.02 (m, 2H), 7.04-7.23 (m, 20H), 7.32-7.66 (m, 26H), 7.82-7.92 (m, 2H), 7.94-8.06 (m, 2H), 8.23-8.44 (m, 4H), 8.58-8.88 (m, 8H). ¹³C{¹H}NMR (Cl₂CDCDCl₂, 25 °C): twelve kinds of *t*-Bu (δ 30.83, 30.93, 31.01, 31.55, 31.82, 32.06, 33.83, 33.86, 33.88, 34.09, 34.37, 34.81). ³¹P{¹H}NMR (Cl₂CDCDCl₂, 25 °C): δ 24.8 (dd, ¹J(P,Rh) = 135 Hz, ²J(P,P) = 32 Hz), 25.0 (dd, ¹J(P,Rh) = 135 Hz, ²J(P,P) = 32 Hz), 26.6 (d, ¹J(P,Rh) = 135 Hz). Anal. Calcd for C₂₄₀H₂₈₂B₃F₁₂O₁₂P₆Rh₃·CH₂Cl₂: C, 68.94; H, 6.82. Found: C, 69.21; H, 6.71.

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