Supporting Information

Synthesis of Binuclear Complexes Bound in Enlarged Tetraphosphamacrocycle: Two Diphosphine Metal Units Linked in Front-to-Front Style

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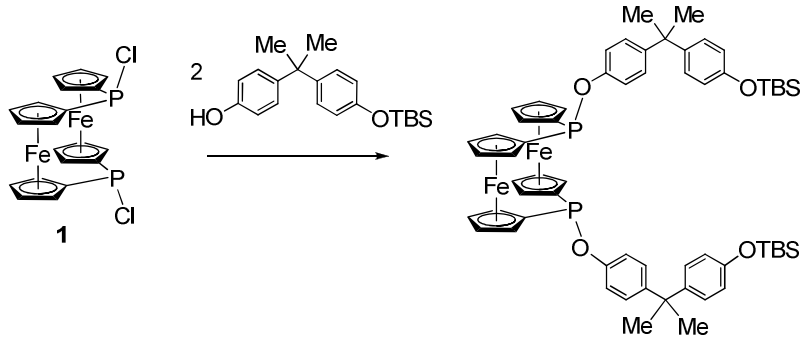
Experimental Details

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen using Schlenk tube techniques. All solvents were dried and distilled from sodium (for hexane and toluene), sodium/benzophenone (for ether and THF), or P_2O_5 (for CH_3CN, CH_2Cl_2 and $CHCl_3$). These purified solvents were stored under an N_2 atmosphere. PCl-bridged [1.1]ferrocenophane,[1] $Pt(PPh_3)_4$[2] and $Pt(PhC{\equiv}CPh)(PPh_3)_2$[3] were prepared according to methods in literatures. Other reagents were used as received.

NMR spectra were recorded on JEOL LA-300 spectrometer. ^1H and ^{13}C NMR chemical shifts were reported relative to Me_4Si and were determined by reference to the residual solvent peaks. ^{31}P NMR chemical shifts were reported relative to H_3PO_4 (85%) used as an external reference. Elemental analyses were performed with a Perkin-Elmer 2400CHN elemental analyzer. Preparative-scale GPC was performed with a recycling HPLC system (Japan Analytical Industry Model LC-908) with JAIGEL-1H (20 mm I. D. × 600 mm; exclusion limit: 1.0×10^3) and -2H (20 mm I. D. × 600 mm; exclusion limit: 5.0×10^3) columns.

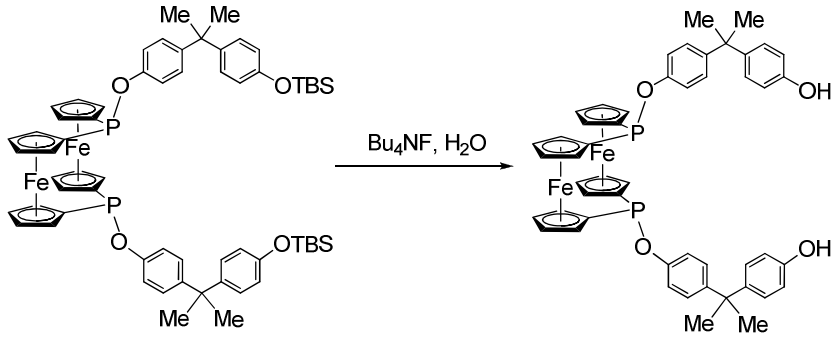
P(TBS-Bisphenol A)-bridged [1.1]ferrocenophane.



To a Schlenk tube charged with PCl-bridged [1.1]ferrocenophane **1** (0.23 g, 0.46 mmol) and toluene (30 mL) was added dropwise a toluene (15 mL) solution of TBS-bisphenol (0.32 g, 0.93 mmol) and NEt_3 (0.13 ml, 0.94 mmol). After the solution thus obtained was stirred overnight, it was filtered with celite. The solvent was removed under reduced pressure, and the residue was dried in vacuo. An orange wax thus obtained (0.50 g, 97 %) was used for the next step without purification. ^1H NMR (300.5 MHz,

C_6D_6): δ 0.16 (s, 12H, $SiMe_2$), 1.04 (s, 18H, CMe_3), 1.53 (s, 12H, Me), 4.11 (br, 4H, C_5H_4), 4.16 (br, 4H, C_5H_4), 4.59 (br, 4H, C_5H_4), 4.73 (br, 4H, C_5H_4), 6.83 (d, J_{HH} = 8.6 Hz, 4H, Ar), 7.05 (m, 8H, Ar), 7.08 (d, J_{HH} = 8.6 Hz, 4H, Ar). $^{13}C\{^1H\}$ NMR (75.6 MHz, C_6D_6): δ –4.3 (s, $SiMe_2$), 18.3 (s, C*Me*$_3$), 25.8 (s, *C*Me_3), 31.2 (s, Me), 42.0 (s, *C*Me_2), 71.9 (s, C_5H_4), 72.6 (t, J_{PC} = 4 Hz, C_5H_4), 73.5 (t, J_{PC} = 3 Hz, C_5H_4), 76.7 (t, J_{PC} = 13 Hz, C_5H_4), 78.4 (t, J_{PC} = 11 Hz, *ipso*-C_5H_4), 115.2 (s, Ar), 119.6 (s, Ar), 119.7 (t, J_{PC} = 5 Hz, Ar), 127.9 (s, Ar), 128.1 (s, Ar), 144.1 (s, *ipso*-Ar), 144.8 (s, *ipso*-Ar), 153.7 (s, *ipso*-Ar), 155.6 (t, J_{PC} = 2 Hz, *ipso*-Ar). $^{31}P\{^1H\}$ NMR (121.7 MHz, $CDCl_3$): δ 112.8 (s).

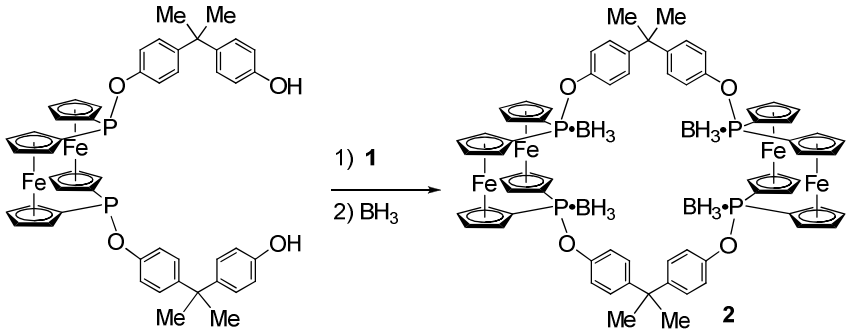
P(Bisphenol A)-bridged [1.1]ferrocenophane.



A Schlenk tube was charged with P(TBS-Bisphenol A)-bridged [1.1]ferrocenophane (0.63 g, 0.57 mmol) and THF (20 mL). To the solution cooled to –20 °C was added $^{n}Bu_4NF$ (1.0 M THF solution, 1.41 mL). The solution was kept under –10 °C for 45 min, and then water (40 mL) was added. The product was extracted repeatedly with CH_2Cl_2 until the extracts became colorless. The combined extracts were washed with water, and then dried with $MgSO_4$. After the mixture was filtered, the solvent was removed under reduced pressure. The residue was washed with hexane, and then dried in vacuo to give an orange powder of P(Bisphenol A)-bridged [1.1]ferrocenophane (0.41 g, 83 %), which was used for the next step as it was. ^1H NMR (300.5 MHz, C_6D_6): δ 1.51 (s, 12H, Me), 4.13 (br, 4H, C_5H_4), 4.17 (br, 4H, C_5H_4), 4.41 (br, 2H, OH), 4.59 (br, 4H, C_5H_4), 4.74 (br, 4H, C_5H_4), 6.54 (d, J_{HH} = 8.6 Hz, 4H, Ar), 7.00 (d, J_{HH} = 8.6 Hz, 4H, Ar), 7.05 (br, 8H, Ar). $^{13}C\{^1H\}$ NMR (75.6 MHz, C_6D_6): δ 31.2 (s, Me), 41.9 (s, *C*Me_2), 71.9 (s, C_5H_4), 72.7 (t, J_{PC} = 4 Hz, C_5H_4), 73.5 (t, J_{PC} = 3 Hz, C_5H_4), 76.7

(t, J_{PC} = 19 Hz, C_5H_4), 78.4 (t, J_{PC} = 11 Hz, *ipso*-C_5H_4), 115.0 (s, Ar), 119.8 (t, J_{PC} = 5 Hz, Ar), 127.9 (s, Ar), 128.2 (s, Ar), 143.0 (s, *ipso*-Ar), 145.0 (s, *ipso*-Ar), 154.2 (s, *ipso*-Ar), 155.7 (t, J_{PC} = 3 Hz, *ipso*-Ar). $^{31}P\{^1H\}$ NMR (121.7 MHz, $CDCl_3$): δ 113.4 (s).

BH_3 adduct of Macrocycle, 2·$(BH_3)_4$.



To the flask charged with PCl-bridged [1.1]ferrocenophane (0.22 g, 0.44 mmol) and CH_2Cl_2 (1.3 L) was added slowly (over 3 h) a CH_2Cl_2 solution of P(Bisphenol A)-bridged [1.1]ferrocenophane (0.37 g, 0.42 mmol) and NEt_3 (0.23 mL, 1.67 mmol). After stirring overnight, the solvent was removed. The residue thus obtained was extracted with toluene at 40–50 °C until extracts became colorless. The solvent was removed under reduced pressure, and the crude product was weighed. To the product dissolved in a minimum amount of THF was added an excess amount (ca. 8 equiv) of BH_3 (0.9 M THF solution). After the solvent was removed, the residue was dissolved in $CHCl_3$. The products were separated with a preparative-scale GPC equipment. A band containing **2**·$(BH_3)_4$ was collected, and the solvent was removed. The residue was dried in vacuo to give a red powder of **2**·$(BH_3)_4$ (0.11 g, 18 %). ^1H NMR (300.5 MHz, $CDCl_3$): δ 0.98 (br, 12H, BH_3), 1.55 (s, 12H, Me), 4.62 (br, 8H, C_5H_4), 4.72 (br, 8H, C_5H_4), 4.78 (br, 8H, C_5H_4), 5.20 (br, 8H, C_5H_4), 6.65 (d, J_{HH} = 8.5 Hz, 8H, Ar), 7.00 (d, J_{HH} = 8.6 Hz, 8H, Ar). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ 30.7 (s, Me), 42.0 (s, *C*Me_2), 72.5 (d, J_{PC} = 8 Hz, C_5H_4), 72.8 (br, C_5H_4), 72.8 (d, J_{PC} = 20 Hz, C_5H_4), 72.9 (d, J_{PC} = 69 Hz, *ipso*-C_5H_4), 75.6 (d, J_{PC} = 16 Hz, C_5H_4), 120.9 (d, J_{PC} = 3 Hz, Ar), 127.5 (s, Ar), 146.8 (s, *ipso*-Ar), 150.1 (d, J_{PC} = 10 Hz, *ipso*-Ar). $^{31}P\{^1H\}$ NMR (121.7 MHz, $CDCl_3$): δ 114.7. $^{11}B\{^1H\}$ NMR (96.4 MHz, $CDCl_3$): δ -35.3. Anal. Calcd for $C_{70}H_{72}B_4Fe_4O_4P_4$·$CHCl_3$: C, 57.34; H, 4.95. Found: C, 57.06; H, 5.04.

Macrocycle, 2. A Schlenk tube was charged with **2**·$(BH_3)_4$ (0.17 g, 0.124 mmol), THF (20 mL), and an excess amount of $NHEt_2$ (0.1 mL, 0.994mmol). The solution was stirred for 8 h at 55 °C. The solvent was removed under reduced pressure. The residue was washed with ether, and dried in vacuo to give an orange powder of macrocycle (0.15 g, 91 %). ^{1}H NMR (300.5 MHz, $CDCl_3$): δ 1.52 (s, 12H, Me), 4.59 (br, 8H, C_5H_4), 4.61 (br, 8H, C_5H_4), 4.78 (br, 8H, C_5H_4), 4.85 (br, 8H, C_5H_4), 6.79 (d, J_{HH} = 8.6 Hz, 8H, Ar), 6.98 (d, J_{HH} = 8.6 Hz, 8H, Ar). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): δ 31.0 (s, Me), 41.9 (s, *C*Me_2), 72.0 (s, C_5H_4), 72.5 (t, J_{PC} = 4 Hz, C_5H_4), 73.0 (br, C_5H_4), 76.4 (t, J_{PC} = 19 Hz, C_5H_4), 77.9 (t, J_{PC} = 10 Hz, *ipso*-C_5H_4), 119.1 (t, J_{PC} = 5 Hz, Ar), 127.5 (s, Ar), 144.7 (s, *ipso*-Ar), 155.2 (t, J_{PC} = 5 Hz, *ipso*-Ar). ^{31}P{^{1}H} NMR (121.7 MHz, $CDCl_3$): δ 116.3. Anal. Calcd for $C_{70}H_{60}Fe_4O_4P_4$·1.5$CHCl_3$·0.5C_7H_{16}: C, 58.43; H, 4.54. Found: C, 58.46; H, 4.15.

[Ag_2(2)](BF_4)$_2$. A THF solution (5 mL) of $AgBF_4$ (8.8 mg, 0.045 mmol) was added to a THF solution (8 mL) of macrocycle **2** (29.7 mg, 0.022 mmol). After the solution was stirred for 30 min, the solvent was removed under reduced pressure. The residue was washed with ether, dried, and extracted with MeCN. After MeCN was removed under reduced pressure, the product was dried in vacuo to give an orange powder (32 mg, 83 %). The ^{1}H NMR (300.5 MHz, CD_3CN): δ 1.55 (s, 12H, Me), 4.81 (br, 16H, C_5H_4), 4.92 (br, 8H, C_5H_4), 5.11 (br, 8H, C_5H_4), 6.90 (d, J_{HH} = 8.6 Hz, 8H, Ar), 7.20 (d, J_{HH} = 8.6 Hz, 8H, Ar). ^{31}P{^{1}H} NMR (121.7 MHz, CD_3CN, –40 °C): δ 111.9 (dd, J_{107AgP} = 396 Hz, J_{109AgP} = 458 Hz). Anal. Calcd for $C_{70}H_{60}Ag_2B_2F_8Fe_4O_4P_4$·0.5$CH_3CN$: C, 49.51; H, 3.60; N, 0.41. Found: C, 49.48; H, 3.57; N, 0.35.

μ-2-[Pt(PhC≡CPh)]$_2$. A THF solution (10 mL) of Pt(PhC≡CPh)(PPh_3)$_2$ (71 mg, 0.079 mmol) was added to a THF solution (10 mL) of macrocycle **2** (49 mg, 0.037 mmol). After the solution was stirred for 2 h, it was filtered, and the solvent was removed under reduced pressure. The residue was washed with ether, and dried in vacuo to give an orange powder (32 mg, 83 %). ^{1}H NMR (300.5 MHz, C_6D_6): δ 1.36 (s, 12H, Me), 4.39 (br, 8H, C_5H_4), 4.49 (br, 8H, C_5H_4), 4.83 (br, 8H, C_5H_4), 4.98 (br, 8H, C_5H_4),

6.47 (d, J_{HH} = 8.4 Hz, 8H, Ar), 6.64 (d, J_{HH} = 8.1 Hz, 8H, Ar), 7.08 (t, J_{HH} = 7.0 Hz, 4H, *p*-Ph), 7.23 (t, J_{HH} = 8.0 Hz, 8H, *m*-Ph), 7.95 (t, J_{HH} = 7.7 Hz, 8H, *o*-Ph). $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6): δ 133.6 (s, J_{195PtP} = 4053 Hz). Anal. Calcd for $C_{98}H_{80}Fe_4O_4P_4Pt_2 \cdot 2C_6H_6$: C, 59.64; H, 4.19. Found: C, 59.44; H, 4.09.

μ-2-[Pt(PPh$_3$)]$_2$. A THF solution (10 mL) of $Pt(PPh_3)_4$ (55 mg, 0.044 mmol) was added to a THF solution (5 mL) of macrocycle **2** (23 mg, 0.018 mmol). After the solution was stirred for 2 h, it was filtered, and the solvent was removed under reduced pressure. The residue was washed with ether, and dried in vacuo to give a brown powder (32 mg, 83 %). ^1H NMR (300.5 MHz, C_6D_6): δ 1.31 (s, 12H, Me), 4.15 (br, 8H, C_5H_4), 4.30 (br, 8H, C_5H_4), 5.16 (br, 8H, C_5H_4), 5.25 (br, 8H, C_5H_4), 6.63 (d, J_{HH} = 8.6 Hz, 8H, Ar), 7.15—7.29 (26H, Ar), 7.99 (t, $J_{HH\ and\ HP}$ = 9.0 Hz, 4H, *o*-Ar). $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6): δ 58.1 (t, J_{PP} = 146 Hz, J_{195PtP} = 4538 Hz), 162.1 (d, J_{PP} = 147 Hz, J_{195PtP} = 5064 Hz).

X-ray crystallogray. Suitable crystals of **2**, **3**, and **5** were mounted separately on glass fibers. The measurements were made on a Mac Science DIP2030 imaging plate area detector at 200 K. Cell parameters and intensities for the reflection were estimated using the program packages of HKL.[4] The structures were solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms except those of disordered solvents were refined anisotropically. Hydrogen atoms were located at ideal positions. All calculations were performed using a SHELXL-97 crystallographic software package.[5] In the crystals of **2**, considerably disordered solvent molecules incorporated were refined as molecules having rigid ideal structures. In the crystals of **3** considerably disordered BF_4^- anion as well as CH_3CN were refined as molecules having rigid ideal structures. The molecular structures were depicted in Figures S1-S3 for **2**, **3**, and **5**, respectively. Details of data collection and refinement for these crystals were listed in Table S1 and in CIF files which include bond distances and angles, atomic coordinates, and anisotropic thermal parameters.

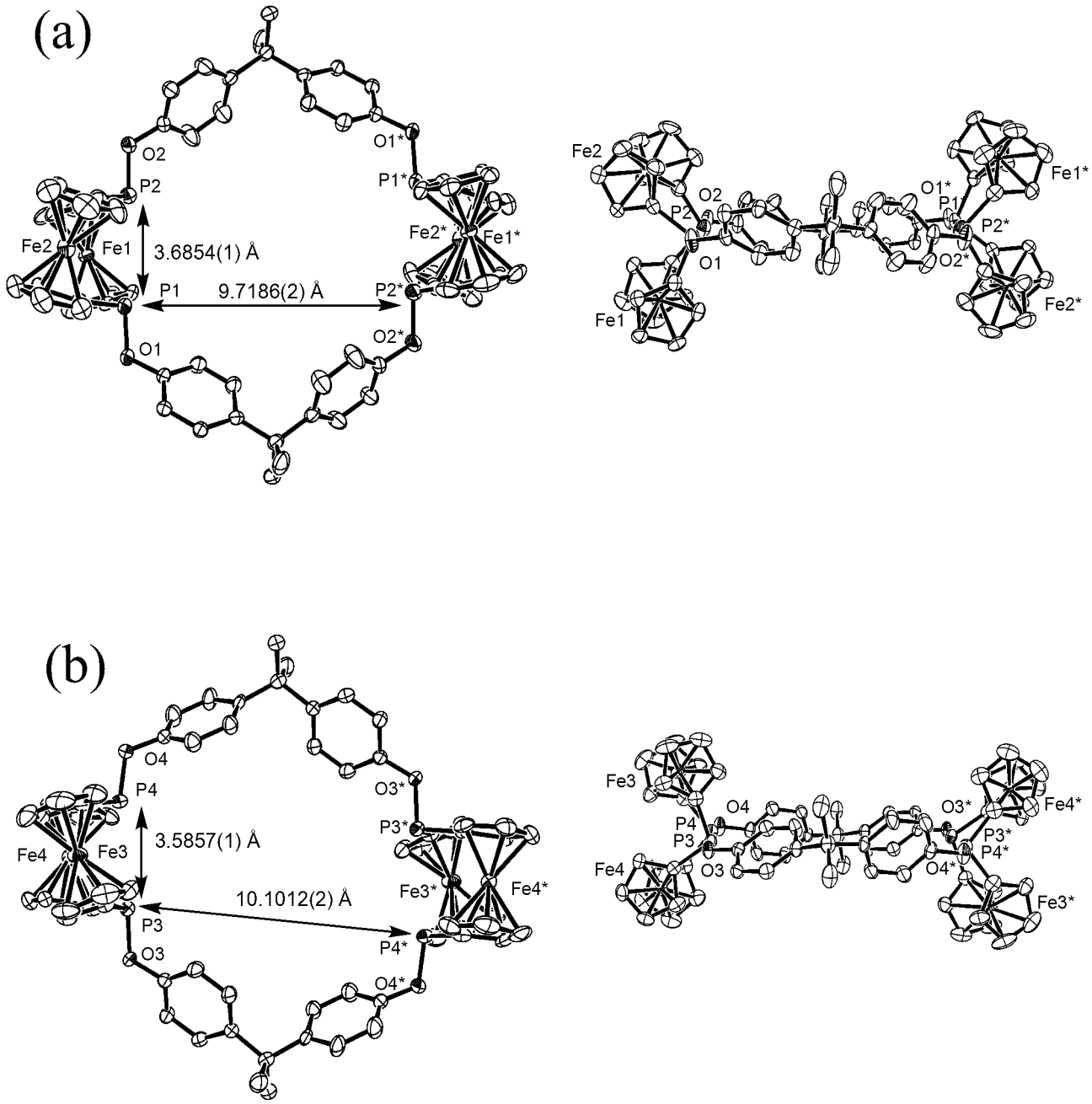


Figure S1. Orthogonal drawings of the molecular structures of **2**. Two independent molecules, (a) and (b), are drawn with the 50% probability level. Solvents and hydrogen atoms are omitted for clarity.

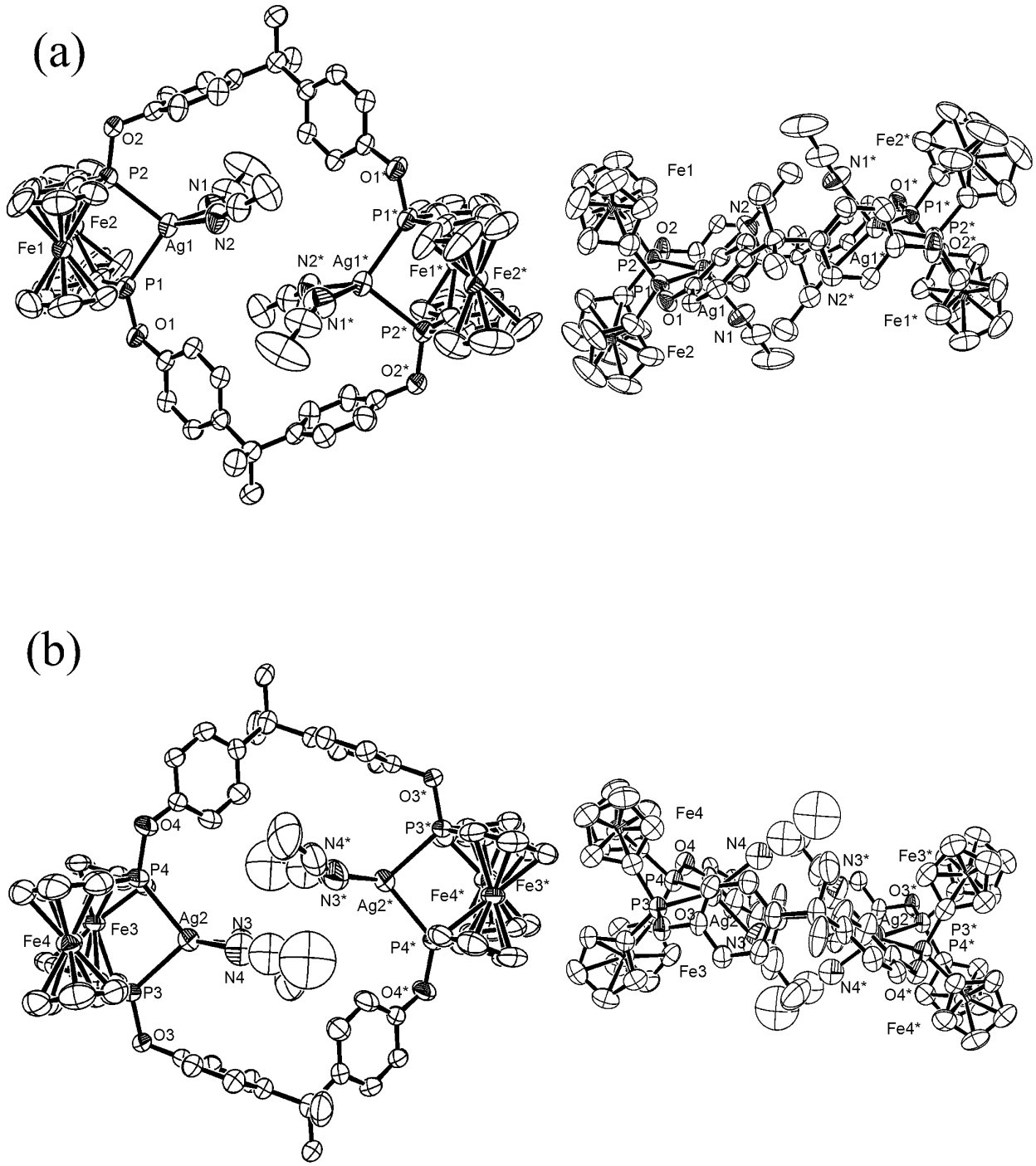


Figure S2. Orthogonal drawings of the molecular structures of **3**. Two independent molecules, (a) and (b), are drawn with the 50% probability level. Solvent, counterion, and hydrogen atoms are omitted for clarity.

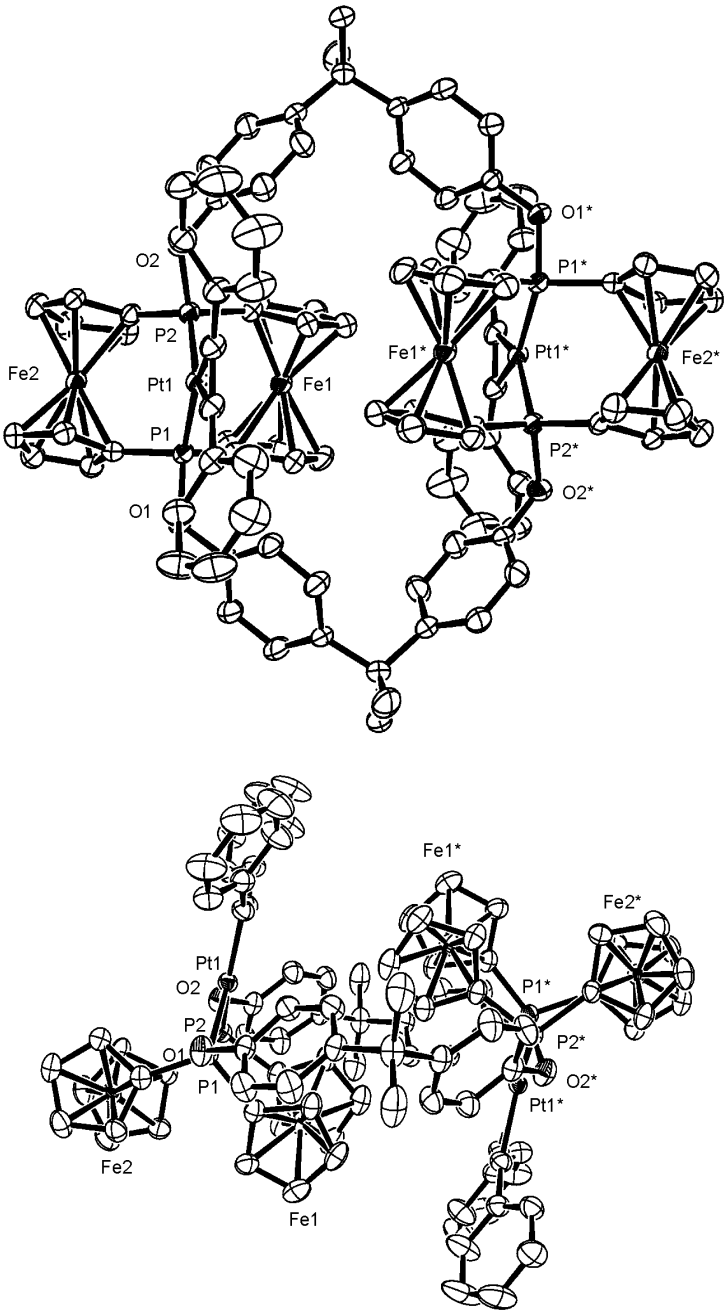


Figure S3. Orthogonal drawing of the molecular structure of **5** with the 50% probability level. Solvent and hydrogen atoms are omitted for clarity.

Table S1. Crystallographic Data

	2·$(C_6H_4Cl_2)_2(C_7H_{16})_{0.5}$	μ-**2**-$[Ag(NCCH_3)_2]_2$ ·$(CH_3CN)_2$ **3**	μ-**2**-$[Pt(PhCCPh)]_2$ ·$(C_6H_6)_7$ **5**
formula	$C_{91.50}H_{80}Cl_6Fe_4O_4P_4$	$C_{82}H_{78}Ag_2B_2F_8Fe_4N_6O_4P_4$	$C_{140}H_{122}Fe_4O_4P_4Pt_2$
cryst color, habit	orange, stick	yellow, block	yellow, block
cryst syst	triclinic	trigonal	monoclinic
space group	*P*-1 (No. 2)	*R-3* (No. 148)	*C*2/*c* (No. 15)
a /Å	16.8980(4)	32.2330(4)	26.7500(2)
b /Å	17.2740(4)	32.2330	14.9490(2)
c /Å	17.3800(5)	47.9690(7)	30.4060(3)
α /deg	69.996(1)	90.0	90.0
β /deg	69.621(1)	120.0	111.8310(10)
γ / deg	62.037(1)	90.0	90.0
V /Å^3	4101.3(2)	43161.1(8)	11286.9(2)
Z	2	18	4
temp/K	200	200	200
μ(Mo Kα)/mm^{-1}	1.019	1.117	3.084
diffractometer	MacScience DIP2030 imaging plate	MacScience DIP2030 imaging plate	MacScience DIP2030 imaging plate
no. of rflns measd	17508	16854	12233
obsd (I > 2.00σ(*I*))	11006 (2θ < 55°)	13776 (2θ < 50°)	11527 (2θ < 55°)
R1 (*I* > 2σ(*I*))	0.0707	0.0708	0.0460
wR2 [a]	0.1572	0.1762	0.1217
GOF	1.059	1.098	1.062
a/*b*[a]	0.0594/17.1277	0.0831 / 383.7046	0.0829/46.5226

[a]wR2=$\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(ap)^2+bp]$; $p = (F_o^2 + 2F_c^2)/3$.

References

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