Supplementary Information

Tetrahedral Cage Complex with Planar Vertices: Selective Synthesis of Pt₄L₆ Cage Complexes Involving Halide Bindings Driven by Hydrogen Bonds

Masaki Ito, Masato Iseki, Masumi Itazaki, Hiroshi Nakazawa*

Department of Chemistry, Graduate School of Science, Osaka City University,
Sugimoto 3-3-138, Sumiyoshi-ku, Osaka 558-8585, Japan. *e-mail: nakazawa@sci.osaka-cu.ac.jp

Table of Contents

General considerations S1
Synthesis of 1,1ʹ-bis(diphenylphosphinecarboxamidyl)ferrocene (L) S2
Synthesis of 1,1ʹ-bis(diphenylphosphinethiocarboxamidyl)ferrocene (Lʹ) S2
Synthesis of PtL₂ (1) S2
Syntheses of [CHCl₃⊂2a], 2a S3
Syntheses of [CHCl₃⊂2b] and 2b S4
Synthesis of 3 S5
NMR spectra of L S6-S7
NMR spectra of Lʹ S7-S8
NMR and ESI-MS spectra of 2a S9-S11
NMR and ESI-MS spectra of 2b S12-S13
NMR spectra of 3 S14-S15
X-ray crystallography measurements S16-S18
References S19
General considerations
Ferrocene derivatives (Fe(C₅H₄NCO)₂S¹, Fe(C₅H₄NCS)₂S²), platinum complexes (Pt(PPh₃)₄S³ cis-PtCl₂(PPh₃)₂S⁴ cis-PtBr₂(PPh₃)₂S⁵ cis-PtI₂(PPh₃)₂S⁶), PhNHC(O)PPh₂S⁷ lanthanum complex (La(a-dimethylbenzylamine)₃S⁷) and HPPh₂S⁸ were prepared according to the literature methods. The other chemicals were commercially available. Solvents were purified employing a two-column solid-state purification system or were distilled from appropriate drying agents under N₂. NMR spectra (¹H, ¹³C{¹H}, ³¹P{¹H}, H-H COSY and DOSY) were recorded on a JNM AL-400 spectrometer. ¹H NMR and ¹³C{¹H} NMR data were referenced to the residual peaks of the solvent, and ³¹P{¹H} NMR spectrum was referenced to external 85% H₃PO₄. The ³¹P{¹H} NMR spectra were simulated using gNMR program (v.5.6.0.0) for Windows, Ivory Soft, 2006. ESI-MS imaging experiments were performed on a 7.0 T solariX FT-ICR MS (Bruker Daltonics) in positive-ion mode.
Synthesis of 1,1ʹ-bis(diphenylphosphinecarboxamidyl)ferrocene (L)

A toluene (60 mL) solution of Fe(C₅H₄NCO)₂ (4.42 g, 16.5 mmol) and HPPh₂ (5.70 mL, 32.8 mmol) was stirred at 100 °C for 1 h under a dry nitrogen atmosphere. The red solution was passed through a neutral alumina pad. After all volatile materials were removed under reduced pressure, the residue was washed with hexane (20 mL × 4) and dried in vacuo to give a yellow powder of L (6.67 g, 10.4 mmol, 63%). Suitable single crystals were obtained from slow diffusion of hexane into the CH₂Cl₂ solution of L.

¹H NMR (400 MHz, CDCl₃, δ, ppm): 3.93 (s, 4H, C₅H₄), 4.29 (s, 4H, C₅H₄), 7.14 (s, 2H, NH), 7.38–7.40 (m, 12H, Ph), 7.55–7.60 (m, 8H, Ph).

¹³C{¹H} NMR (100.4 MHz, CDCl₃, δ, ppm): 63.67 (s, C₅H₄), 65.77 (s, C₅H₄), 94.50 (s, C₅H₄–ipso), 129.03 (m, Ph), 129.94 (s, Ph), 133.42 (d, J_PC = 10.0 Hz, Ph–ipso), 134.53 (m, Ph), 176.00 (d, J_PC = 15.8 Hz, CO).

³¹P{¹H} NMR (161.7 MHz, CDCl₃, δ, ppm): -2.06 (s). ESI-MS: [M]+ calcd for C₃₆H₃₀FeN₂O₂P₂: 640.1127; found: 640.1119. Elemental analysis (%) calcd for C₃₆H₃₀FeN₂O₂P₂: C, 67.52; H, 4.72; N, 4.37; found: C, 67.16; H, 4.83; N, 4.38.

Synthesis of 1,1ʹ-bis(diphenylphosphinethiocarboyamidyl)ferrocene (Lʹ)

A THF (3 mL) solution of Fe(C₅H₄NCS)₂ (150 mg, 0.50 mmol), HPPh₂ (0.20 mL, 1.18 mmol) and La(α-dimethylbenzylamine)₃ (30 mg, 0.050 mmol) was stirred at ambient temperature for 15 h under a dry nitrogen atmosphere. The solution was passed through a neutral alumina pad. After all volatile materials were removed under reduced pressure, the residue was washed with hexane (20 mL × 4) and dried in vacuo to give a brown powder of Lʹ (68.7 mg, 0.10 mmol, 20%).

¹H NMR (400 MHz, CDCl₃, δ, ppm): 4.08 (s, 4H, C₅H₄), 4.71 (s, 4H, C₅H₄), 7.46 (s, 12H, Ph), 7.54 (s, 8H, Ph), 8.38 (s, 2H, NH).

¹³C{¹H} NMR (100.4 MHz, CDCl₃, δ, ppm): 64.86 (s, C₅H₄), 66.77 (s, C₅H₄), 96.69 (s, C₅H₄–ipso), 128.60 (br, Ph–ipso), 129.38 (s, Ph), 130.38 (s, Ph), 134.67 (br, Ph), 206.18 (br, CO).

³¹P{¹H} NMR (161.7 MHz, CDCl₃, δ, ppm): 17.63 (s). ESI-MS: [M]+ calcd for C₃₆H₃₀FeN₂O₂P₂S₂: 672.0675; found: 672.0672. Elemental analysis (%) calcd for C₃₆H₃₀FeN₂O₂P₂S₂: C, 67.52; H, 4.72; N, 4.37; found: C, 67.16; H, 4.83; N, 4.38.

Synthesis of PtL₂ (1)

A dichloromethane (5 mL) solution of L (128 mg, 0.20 mmol) and Pt(PPh₃)₄ (124 mg, 0.10 mmol) was stirred at ambient temperature for 1 h under a dry nitrogen atmosphere, poorly soluble yellow crystals were formed and were filtered. The obtained crystals were washed with CH₂Cl₂ (5.0 mL × 3) and were dried in vacuo to give of I (101 mg, 0.068 mmol, 68%). Elemental analysis (%) calcd for C₇₂H₆₀Fe₂N₄O₄P₄Pt: C, 58.59; H, 4.10; N, 3.80; found: C, 58.25; H, 4.16; N, 3.91. No ESI-MS was recorded because of sample insolvability for water and organic solvent. In addition, we tried several times to obtain FAB-MS data, but could not get it.

Synthesis of [CHCl₃c2a]
A hexane (15 mL) and a vacant test tube were put in a 150 mL Schlenk tube under a dry nitrogen atmosphere. A chloroform (1.0 mL) solution of L (128 mg, 0.2 mmol) and PtCl₂(PPh₃)₂ (105 mg, 0.13 mmol) was vigorously stirred at ambient temperature for 5 min in the test tube, then it was left to stand for overnight. The resulting red crystals of [CHCl₃–2a] were isolated by filtration.

**Synthesis of 2a**
A hexane (15 mL) and a vacant test tube were put in a 150 mL Schlenk tube under a dry nitrogen atmosphere. A chloroform (1.0 mL) solution of L (128 mg, 0.2 mmol) and PtCl₂(PPh₃)₂ (105 mg, 0.13 mmol) was vigorously stirred at ambient temperature for 5 min in the test tube, then it was left to stand for overnight without stirring. The resulting red crystals of [CHCl₃–2a] were isolated by filtration and rinsed with chloroform (0.5 mL). The crystals were dried in vacuo to give orange powder of 2a (150 mg, 0.031 mmol, 93%). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 2.83 (s, 4H, C₆H₄), 3.92 (s, 4H, C₂H₅), 4.28 (s, 4H, C₂H₅), 4.55 (s, 8H, C₆H₄), 4.73 (s, 4H, C₂H₅), 4.78 (s, 4H, C₂H₅), 5.13 (s, 4H, C₂H₅), 5.56 (s, 4H, C₂H₅), 5.62 (s, 4H, C₂H₅), 5.97 (s, 4H, C₂H₅), 6.29 (s, 4H, C₂H₅), 6.63 (t, J₃₄ = 7.8 Hz, 8H, Ph), 6.93 (br, 8H, Ph), 7.07-7.17 (overlapping m, 8H, Ph), 7.27-7.60 (overlapping m, 68H, Ph), 7.81-7.87 (m, 8H, Ph), 8.04-8.08 (m, 8H, Ph), 8.16 (br, 4H, Ph), 8.33-8.37 (m, 8H, Ph), 11.66 (s, 4H, NH), 11.93 (s, 4H, NH), 12.56 (s, 4H, NH). ¹³C [¹H] NMR (100.4 MHz, CDCl₃, δ, ppm): 63.03 (s, C₆H₄), 64.14 (s, C₂H₅), 64.36 (s, C₂H₅), 64.42 (s, C₂H₅), 64.49 (s, C₂H₅), 65.20 (s, C₂H₅), 66.16 (s, C₂H₅), 66.95 (s, C₂H₅), 67.08 (s, C₂H₅), 67.17 (s, C₂H₅), 68.20 (s, C₂H₅), 69.02 (s, C₂H₅), 93.92 (d, JPC = 11.63 Hz, C₆H₄-ipso), 94.74 (d, JPC = 12.46 Hz, C₆H₄-ipso), 95.08 (d, JPC = 12.46 Hz, C₆H₄-ipso), 125.52 (Ph), 126.02 (Ph), 126.20 (Ph), 126.86 (Ph), 126.95 (Ph), 127.19 (Ph), 127.30 (Ph), 127.37 (Ph), 127.49 (Ph), 127.62 (Ph), 128.11 (Ph), 128.23 (Ph), 128.33 (Ph), 128.42 (Ph), 128.60 (Ph), 128.67 (Ph), 128.78 (Ph), 128.85 (Ph), 131.03 (Ph), 131.37 (Ph), 131.38 (Ph), 131.81 (Ph), 131.95 (Ph), 132.16 (Ph), 132.20 (Ph), 132.64 (Ph), 132.65 (Ph), 133.79 (Ph), 133.90 (Ph), 133.98 (Ph), 134.70 (Ph), 134.7 (br, 134.7 (Ph), 135.17 (Ph), 135.26 (Ph), 137.26 (Ph), 137.37 (Ph), 137.47 (Ph), 138.91 (Ph), 139.01 (Ph), 159.79 (dd, JPC = 70.0 Hz, JPC = 4.2 Hz, CO), 161.03 (d, JPC = 57.1 Hz, CO), 163.19 (dd, JPC = 74.1 Hz, JPC = 3.53 Hz, CO). ³¹P [¹H] NMR (161.7 MHz, CDCl₃, δ, ppm): -1.87 (dd, JpP = 3680.0 Hz, Jpp = 20.0 Hz, Jpp = 18.8 Hz), 0.33 (dd, JpP = 2496.0 Hz, Jpp = 368.0 Hz, Jpp = 18.8 Hz), 1.87 (dd, JpP = 2456.0 Hz, Jpp = 368.0 Hz, Jpp = 20.0 Hz). ESI-MS: [M]+ calc for C₂₁₆H₁₸₄Cl₂Fe₂N₁₂O₁₂P₁₂Pt₄: 2453.1447; found: 2453.1386. Elemental analysis (%) calcd for C₂₁₆H₁₸₄Cl₂Fe₂N₁₂O₁₂P₁₂Pt₄: C, 52.88; H, 3.70; N, 3.43; found: C, 53.00; H, 4.10; N, 3.36.

**Synthesis of [CHCl₃–2b]**
A hexane (15 mL) and a vacant test tube were put in a 150 mL Schlenk tube under a dry nitrogen atmosphere. A chloroform (1.0 mL) solution of L (128 mg, 0.2 mmol) and PtCl₂(PPh₃)₂ (105 mg, 0.13 mmol) was vigorously stirred at ambient temperature for 5 min in the test tube, then it was left to stand for overnight without stirring. The resulting red crystals of [CHCl₃–2b] were isolated by filtration.

[Fig. S1 Equipment diagram]
atmosphere. A chloroform (1.0 mL) solution of L (128 mg, 0.20 mmol) and PtBr$_2$(PPh$_3$)$_2$ (117 mg, 0.13 mmol) was stirred at ambient temperature for 5 min in the test tube, then it was left to stand for overnight. The resulting crystals of [CHCl$_3$·2b] were isolated by filtration.

**Synthesis of 2b**

A hexane (15 mL) and a vacant test tube were put in a 150 mL Schlenk tube under a dry nitrogen atmosphere. A chloroform (1.0 mL) solution of L (128 mg, 0.20 mmol) and PtBr$_2$(PPh$_3$)$_2$ (117 mg, 0.13 mmol) was stirred at ambient temperature for 5 min in the test tube, then it was left standing for overnight without stirring. The resulting red crystals of [CHCl$_3$·2b] were isolated by filtration and rinsed with chloroform (0.5 ml). The crystals were dried in vacuo to give orange powder of 2b (136 mg, 0.026 mmol, 78%).

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$, ppm): 2.87 (s, 4H, C$_5$H$_4$), 3.90 (s, 4H, C$_5$H$_4$), 4.30 (s, 4H, C$_5$H$_4$), 4.45 (s, 4H, C$_5$H$_4$), 4.51 (s, 4H, C$_5$H$_4$), 4.72 (s, 4H, C$_5$H$_4$), 4.87 (s, 4H, C$_5$H$_4$), 5.18 (s, 4H, C$_5$H$_4$), 5.45 (s, 4H, C$_5$H$_4$), 5.52 (s, 4H, C$_5$H$_4$), 5.84 (s, 4H, C$_5$H$_4$), 5.97 (s, 4H, C$_5$H$_4$), 6.19 (s, 4H, C$_5$H$_4$), 6.59 (br, 8H, Ph), 6.90 (br, 8H, Ph), 7.05-7.16 (overlapping m, 8H, Ph), 7.27-7.39 (overlapping m, 26H, Ph), 7.45-7.49 (m, 8H, Ph), 7.59 (br, 30, Ph), 7.78 (m, 8H, Ph), 8.02 (m, 12H, Ph), 8.31 (br, 12H, Ph), 11.45 (s, 4H, NH), 11.50 (s, 4H, NH), 12.11 (s, 4H, NH).

$^{13}$C{$^1$H} NMR (100.4 MHz, CDCl$_3$, $\delta$, ppm): 62.48 (s, C$_5$H$_4$), 63.50 (s, C$_5$H$_4$), 64.23 (s, C$_5$H$_4$), 64.53 (s, C$_5$H$_4$), 64.72 (s, C$_5$H$_4$), 65.13 (s, C$_5$H$_4$), 65.70 (s, C$_5$H$_4$), 66.65 (s, C$_5$H$_4$), 66.96 (s, C$_5$H$_4$), 67.17 (s, C$_5$H$_4$), 68.02 (s, C$_5$H$_4$), 69.48 (s, C$_5$H$_4$), 94.28 (d, $J_{PC} = 11.65$ Hz, C$_5$H$_4$-ipso), 94.69 (d, $J_{PC} = 12.4$ Hz, C$_5$H$_4$-ipso), 95.01 (d, $J_{PC} = 12.4$ Hz, C$_5$H$_4$-ipso), 126.28 (Ph), 126.87 (Ph), 126.99 (Ph), 127.32 (Ph), 127.44 (Ph), 127.54 (Ph), 127.93 (Ph), 128.08 (Ph), 128.19 (Ph), 128.29 (Ph), 128.37 (Ph), 128.47 (Ph), 128.55 (Ph), 128.60 (Ph), 128.67 (Ph), 131.03 (Ph), 131.28 (Ph), 131.64 (Ph), 131.83 (Ph), 132.21 (Ph), 132.59 (Ph), 133.79 (Ph), 133.99 (Ph), 134.06 (Ph), 134.98 (Ph), 135.06 (Ph), 135.29 (Ph), 137.40 (Ph), 137.5 (br, Ph), 139.52 (Ph), 139.62 (Ph), 159.64 (dd, $J_{PC} = 72.2$ Hz, $J_{PC} = 4.1$ Hz, CO), 160.60 (ddd, $J_{PC} = 55.6$ Hz, $J_{PC} = 7.5$ Hz, $J_{PC} = 1.7$ Hz, CO), 163.25 (dd, $J_{PC} = 75.5$ Hz, $J_{PC} = 4.7$ Hz, CO).

$^{31}$P{$^1$H} NMR (161.7 MHz, CDCl$_3$, $\delta$, ppm): -5.98 (dd, $J_{PP} = 2477.0$ Hz, $J_{PP} = 368.0$ Hz, $J_{PP} = 16.2$ Hz), -4.11 (dd, $J_{PP} = 3606.0$ Hz, $J_{PP} = 16.7$ Hz, $J_{PP} = 16.2$ Hz), 12.22 (dd, $J_{PP} = 2478.0$ Hz, $J_{PP} = 368.0$ Hz, $J_{PP} = 16.7$ Hz). ESI-MS: [M]+ calcd for C$_{216}$H$_{180}$Br$_8$Fe$_6$N$_{12}$O$_{12}$P$_{12}$Pt$_4$: 2630.941; found: 2630.938.

Elemental analysis (%) calcd for C$_{216}$H$_{180}$Br$_8$Fe$_6$N$_{12}$O$_{12}$P$_{12}$Pt$_4$: C, 49.30; H, 3.45; N, 3.19; found: C, 48.87; H, 3.56; N, 3.27.

**Synthesis of 3**

A chloroform (1.0 mL) solution of PhNHC(O)PPh$_2$ (6.1 mg, 0.020 mmol) and PtCl$_2$(PPh$_3$)$_2$ (5.3 mg, 6.7
\times 10^{-3} \text{ mmol}) was stirred at ambient temperature for 5 min under air. Removal of the volatile materials under reduced pressure caused the formation of a pale yellow solid. The solid was washed with a large amount of \textsuperscript{4}hexane, collected by filtration, and dried in vacuo to give 3 (7.3 mg, 6.2 \times 10^{-3} \text{ mmol, 93\%}). The crystals were obtained by vapor diffusion of \textsuperscript{4}hexane into the Et\textsubscript{2}O solution of 3. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, \delta, ppm): 6.89 (s, 4H, Ph), 7.10-8.03 (overlapping m, 41H, Ph), 11.84 (s, 2H, NH), 12.70 (s, 1H, NH). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100.4 MHz, CDCl\textsubscript{3}, \delta, ppm): 121.28 (s, N\textsubscript{cis}Ph), 121.44 (s, N\textsubscript{trans}Ph), 125.02 (s, N\textsubscript{cis}Ph), 125.37 (s, P\textsubscript{trans}Ph), 126.16 (t, \textsubscript{1}J\textsubscript{PC} =28.3 Hz, P\textsubscript{cis}Ph-ipso), 127.94 (d, \textsubscript{2}J\textsubscript{PC} = 11.6 Hz, PPh), 128.22 (br, PPh and P\textsubscript{cis}Ph-ipso), 128.82 (s, PPh), 131.33 (d, \textsubscript{4}J\textsubscript{PC} = 2.4 Hz, NPh), 132.27 (d, \textsubscript{3}J\textsubscript{PC} = 2.4 Hz, PPh), 135.52 (\textsubscript{2}J\textsubscript{PC} = 10.8 Hz, NPh), 138.10 (d, \textsubscript{3}J\textsubscript{PC} = 10.8 Hz, NPh-ipso), 138.31 (t, \textsubscript{3}J\textsubscript{PC} = 5.0 Hz, NPh-ipso), 140.80 (d, \textsubscript{1}J\textsubscript{CP} = 72.2 Hz, CO), 163.66 (app. t, \textsubscript{1,3}J\textsubscript{CP} = 36.0 Hz, CO). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (161.7 MHz, CDCl\textsubscript{3}, \delta, ppm): 2.60 (t, \textsubscript{JPP} = 3671.9 Hz, \textsubscript{JPP} = 16.5 Hz, P\textsubscript{cis}), 14.36 (d, \textsubscript{JPP} = 2489.9 Hz, \textsubscript{JPP} = 18.4 Hz, P\textsubscript{trans}).

ESI-MS: [M-Cl]\textsuperscript{+} calcd for C\textsubscript{57}H\textsubscript{48}FN\textsubscript{3}ClN\textsubscript{3}O\textsubscript{3}P\textsubscript{2}Pt: 1145.2239; found: 1145.2237. Elemental analysis (%) calcd for C\textsubscript{57}H\textsubscript{48}Cl\textsubscript{2}N\textsubscript{3}O\textsubscript{3}P\textsubscript{2}Pt: C, 57.92; H, 4.09; N, 3.56; found: C, 57.73; H, 4.35; N, 3.35.
NMR spectra of L

Fig. S2 ¹H NMR spectrum (CDCl₃, rt, 400 MHz) of L.

Fig. S3 ¹³C{¹H} NMR spectrum (CDCl₃, rt, 100.4 MHz) of L.
Fig. S4  $^{31}$P{$^1$H} NMR spectrum (CDCl$_3$, rt, 161.7 MHz) of L.

NMR spectra of L'

Fig. S5  $^1$H NMR spectrum (CDCl$_3$, rt, 400 MHz) of L'.
Fig. S6 $^{13}$C\{\textsuperscript{1}H\} NMR spectrum (CDCl\textsubscript{3}, rt, 100.4 MHz) of L'.

Fig. S7 $^{31}$P\{\textsuperscript{1}H\} NMR spectrum (CDCl\textsubscript{3}, rt, 161.7 MHz) of L'.
NMR and ESI-MS spectra of 2a

Fig. S8 $^1$H NMR spectrum (CDCl$_3$, rt-60 °C, 400 MHz) of 2a.

Fig. S9 $^{13}$C{$^1$H} NMR spectrum (CDCl$_3$, rt, 100.4 MHz) of 2a.
Fig. S10  $^{31}$P{$^1$H} NMR spectrum of 2a (CDCl$_3$, rt, 161.7 MHz) (top) and the computer-simulated spectrum using gNMR (bottom)

Table S1  gNMR simulation of $^{31}$P{$^1$H} NMR spectrum

<table>
<thead>
<tr>
<th>Chemical shift / ppm</th>
<th>Coupling constant / Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{trans}$</td>
<td>$-1.87$</td>
</tr>
<tr>
<td>$J_{P_{trans}-P}$</td>
<td>$3608.0$</td>
</tr>
<tr>
<td>$J_{P_{trans}-P}^{cis}$</td>
<td>$18.8$</td>
</tr>
<tr>
<td>$J_{P_{trans}-P}^{cis}$</td>
<td>$20.0$</td>
</tr>
<tr>
<td>$P_{cis1}$</td>
<td>$0.33$</td>
</tr>
<tr>
<td>$J_{P_{cis1}-P}$</td>
<td>$2496.0$</td>
</tr>
<tr>
<td>$J_{P_{trans}-P}^{cis}$</td>
<td>$18.8$</td>
</tr>
<tr>
<td>$J_{P_{trans}-P}^{cis}$</td>
<td>$368.0$</td>
</tr>
<tr>
<td>$P_{cis2}$</td>
<td>$18.68$</td>
</tr>
<tr>
<td>$J_{P_{cis2}-P}$</td>
<td>$2456.0$</td>
</tr>
<tr>
<td>$J_{P_{trans}-P}^{cis}$</td>
<td>$20.0$</td>
</tr>
<tr>
<td>$J_{P_{cis1}-P}$</td>
<td>$368.0$</td>
</tr>
</tbody>
</table>

Fig. S11  H-H COSY spectrum of 2a (CDCl$_3$, rt, 400 MHz)
Fig. S12  DOSY spectrum of 2a (CDCl₃, 400 MHz, 30°C, D = 100 ms, d = 2.3 ms, G = 0.3 T/m).

Fig. S13  ESI-MS spectrum of 2a in CH₂Cl₂/IPA (9:1, v:v)
NMR and ESI-MS spectra of 2b

Fig. S14  $^1$H NMR spectrum (CDCl$_3$, rt, 400 MHz) of 2b.

Fig. S15  $^{13}$C($^1$H) NMR spectrum (CDCl$_3$, rt, 100.4 MHz) of 2b.
**Table S2** gNMR simulation of $^{31}$P{^1}H NMR spectrum

<table>
<thead>
<tr>
<th></th>
<th>Chemical shift / ppm</th>
<th>Coupling constant / Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{trans}}$</td>
<td>-4.11</td>
<td>$J_{P_1-P} = 3606.0$</td>
</tr>
<tr>
<td>$P_{\text{cis1}}$</td>
<td>-5.98</td>
<td>$J_{P_1-P} = 2477.0$, $J_{P_{\text{trans}}-P} = 16.2$, $J_{P_{\text{cis2}}-P} = 16.7$</td>
</tr>
<tr>
<td>$P_{\text{cis2}}$</td>
<td>12.22</td>
<td>$J_{P_1-P} = 2478.0$, $J_{P_{\text{trans}}-P} = 16.7$, $J_{P_{\text{cis1}}-P} = 368.0$</td>
</tr>
</tbody>
</table>

**Fig. S16**  $^{31}$P{^1}H NMR spectrum of 2b (CDCl$_3$, rt, 161.7 MHz) (top) and the computer-simulated spectrum using gNMR (bottom)

**Fig. S17** ESI-MS spectrum of 2b in CH$_2$Cl$_2$/IPA (9:1, v:v)
NMR spectra of 3

**Fig. S18** ¹H NMR spectrum (CDCl₃, rt, 400 MHz) of 3.

**Fig. S19** ¹³C{¹H} NMR spectrum (CDCl₃, rt, 100.4 MHz) of 3.
Fig. S20  135DEPT ¹³C{¹H} NMR spectrum (CDCl₃, rt, 100.4 MHz) of 3.

Fig. S21  ³¹P{¹H} NMR spectrum (CDCl₃, rt, 161.7 MHz) of 3.
X-ray crystallography measurements

X-ray intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation. Calculations were performed with the CrystalClear software package of Molecular Structure Corporation. The structures were solved by direct methods and expanded using Fourier techniques. The structures were refined by full matrix least-squares technique using the program ShelXL-97\textsuperscript{9} or ShelXL-2014\textsuperscript{10}. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. For [CHCl\textsubscript{3}2b], the solvent molecules within the lattice were significantly disordered. Therefore the SQUEEZE function of PLATON was employed to account for the highly disordered solvent molecules.

Table S3  Crystallographic data and details of structure refinement of L, I and [CHCl\textsubscript{3}2a].

<table>
<thead>
<tr>
<th></th>
<th>L</th>
<th>I</th>
<th>[CHCl\textsubscript{3}2a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C\textsubscript{36}H\textsubscript{30}FeN\textsubscript{2}O\textsubscript{2}P\textsubscript{2}</td>
<td>C\textsubscript{76}H\textsubscript{68}Cl\textsubscript{8}Fe\textsubscript{2}N\textsubscript{4}O\textsubscript{4}P\textsubscript{2}Pt</td>
<td>C\textsubscript{224}H\textsubscript{188}Cl\textsubscript{32}Fe\textsubscript{6}N\textsubscript{12}O\textsubscript{12}P\textsubscript{12}Pt\textsubscript{4}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>640.41</td>
<td>1815.61</td>
<td>5861.35</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>200(2)</td>
<td>200(2)</td>
<td>200(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P\textsubscript{2}/c</td>
<td>C\textsubscript{2}/c</td>
<td>Error!</td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>13.7346(13)</td>
<td>29.1376(18)</td>
<td>21.3085(7)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>11.8880(10)</td>
<td>15.0037(8)</td>
<td>22.6838(7)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>9.9583(10)</td>
<td>18.0317(12)</td>
<td>31.6313(6)</td>
</tr>
<tr>
<td>(\alpha) (°)</td>
<td>Error!</td>
<td>Error!</td>
<td>90.2849(10)</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>104.743(5)°</td>
<td>109.950(2)°</td>
<td>90.4102(6)</td>
</tr>
<tr>
<td>(\gamma) (°)</td>
<td>117.1817(13)</td>
<td>117.1817(13)</td>
<td>117.1817(13)</td>
</tr>
<tr>
<td>Volume (Å\textsuperscript{3})</td>
<td>1572.4(3)</td>
<td>7409.9(8)</td>
<td>13599.8(7)</td>
</tr>
<tr>
<td>(Z)</td>
<td>2</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>(\rho_{\text{calc}}) (Mg m\textsuperscript{-3})</td>
<td>1.353</td>
<td>1.627</td>
<td>1.431</td>
</tr>
<tr>
<td>(\mu) (mm\textsuperscript{-1})</td>
<td>0.616</td>
<td>2.697</td>
<td>2.795</td>
</tr>
<tr>
<td>(F(000))</td>
<td>664</td>
<td>3640</td>
<td>5808</td>
</tr>
<tr>
<td>Crystal size (mm\textsuperscript{3})</td>
<td>0.07 (\times) 0.05 (\times) 0.03</td>
<td>0.13 (\times) 0.10 (\times) 0.10</td>
<td>0.200 (\times) 0.080 (\times) 0.070</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>15425</td>
<td>28446</td>
<td>133682</td>
</tr>
<tr>
<td>Independent reflections (R(int))</td>
<td>3596 (0.0407)</td>
<td>8452 (0.0437)</td>
<td>47664 (0.0459)</td>
</tr>
<tr>
<td>(R1) (1 &gt; 2(\sigma(I)))</td>
<td>0.0433</td>
<td>0.0424</td>
<td>0.0801</td>
</tr>
<tr>
<td>(wR2) (all data)</td>
<td>0.0997</td>
<td>0.0931</td>
<td>0.2603</td>
</tr>
<tr>
<td>Goodness-of-fit</td>
<td>1.067</td>
<td>1.065</td>
<td>1.058</td>
</tr>
<tr>
<td>CCDC</td>
<td>1405347</td>
<td>1405343</td>
<td>1405344</td>
</tr>
</tbody>
</table>
Table S4  Crystallographic data and details of structure refinement of [CHCl₃­­­­­­­­­₂b] and 3.

<table>
<thead>
<tr>
<th></th>
<th>[CHCl₃­­­­­­­­­₂b]</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₂₃₇H₂₀₁Br₃Cl₆₃Fe₆N₁₂O₁₂P₁₂Pt₄</td>
<td>C₆₁H₅₉Cl₂N₆O₇P₃Pt</td>
</tr>
<tr>
<td>Formula weight</td>
<td>7768.82</td>
<td>1256.00</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>200(2)</td>
<td>200(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Error!</td>
<td>Error!</td>
</tr>
<tr>
<td>a (Å)</td>
<td>21.46830(10)</td>
<td>11.79990(10)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>23.59400(10)</td>
<td>12.6886(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>32.9537(8)</td>
<td>19.4168(2)</td>
</tr>
<tr>
<td>α (°)</td>
<td>88.034(3)</td>
<td>83.953(3)</td>
</tr>
<tr>
<td>β (°)</td>
<td>89.129(3)</td>
<td>73.888(3)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>65.458(2)</td>
<td>87.375(2)</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>15174.8(5)</td>
<td>2777.02(6)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>ρ_calcd (Mg m⁻³)</td>
<td>1.700</td>
<td>1.502</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>3.839</td>
<td>2.759</td>
</tr>
<tr>
<td>F(000)</td>
<td>7604</td>
<td>1268</td>
</tr>
<tr>
<td>Crystal size (mm³)</td>
<td>0.30 × 0.25 × 0.25</td>
<td>0.30 × 0.23 × 0.15</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>75372</td>
<td>31987</td>
</tr>
<tr>
<td>Independent reflections (R(int))</td>
<td>45899(0.0327)</td>
<td>12208 (0.0243)</td>
</tr>
<tr>
<td>R1 (I &gt; 2σ(I))</td>
<td>0.0700</td>
<td>0.0301</td>
</tr>
<tr>
<td>wR2</td>
<td>0.2063</td>
<td>0.0674</td>
</tr>
<tr>
<td>Goodness-of-fit</td>
<td>1.070</td>
<td>1.102</td>
</tr>
<tr>
<td>CCDC</td>
<td>1405345</td>
<td>1405346</td>
</tr>
</tbody>
</table>
Fig. S22  ORTEP drawing of L (thermal ellipsoids at 50% probability). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å): O1–C1 = 1.225(2), N1–C1 = 1.343(3), P1–C1 = 1.886(2).

Fig. S23  ORTEP drawing of 1 (thermal ellipsoids at 50% probability). All hydrogen atoms, solvent molecules, and Ph rings (except ipso-C) are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt1–P1 = 2.2890(9), Pt1–P2 = 2.3004(9), O1–C1 = 1.216(4), O2–C7 = 1.216(5), N1–C1 = 1.350(5), N1–C2 = 1.345(5), P1–C1 = 1.882(4), P2–C7 = 1.887(4); P1–Pt1–P1* = 106.62(5), P2–Pt1–P2* = 107.47(4), P1–Pt1–P2 = 108.48(3), P1–Pt1–P2* = 112.94(3).
References


