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Supplementary Information

Tetrahedral Cage Complex with Planar Vertices: Selective Synthesis of Pt_4L_6 Cage Complexes Involving Halide Bindings Driven by Hydrogen Bonds

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General considerations

Ferrocene derivatives ($Fe(C_5H_4NCO)_2$,[S1] $Fe(C_5H_4NCS)_2$[S2]), platinum complexes ($Pt(PPh_3)_4$,[S3] *cis*-$PtCl_2(PPh_3)_2$,[S4] *cis*-$PtBr_2(PPh_3)_2$,[S5] *cis*-$PtI_2(PPh_3)_2$[S5]), $PhNHC(O)PPh_2$,[S6] lanthanum complex (La(a-dimethylbenzylamine)$_3$[S7]) and $HPPh_2$[S8] 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 N_2. NMR spectra (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, H-H COSY and DOSY) were recorded on a JNM AL-400 spectrometer. ^1H NMR and $^{13}C\{^1H\}$ NMR data were referenced to the residual peaks of the solvent, and $^{31}P\{^1H\}$ NMR spectrum was referenced to external 85% H_3PO_4. The $^{31}P\{^1H\}$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 1,1′-bis(diphenylphosphinecarboxamidyl)ferrocene (L)

A toluene (60 mL) solution of $Fe(C_5H_4NCO)_2$ (4.42 g, 16.5 mmol) and $HPPh_2$ (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 ^{n}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 ^{n}hexane into the CH_2Cl_2 solution of **L**. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.93 (s, 4H, C_5H_4), 4.29 (s, 4H, C_5H_4), 7.14 (s, 2H, NH), 7.38-7.40 (m, 12H, Ph), 7.55-7.60 (m, 8H, Ph). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$, δ, ppm): 63.67 (s, C_5H_4), 65.77 (s, C_5H_4), 94.50 (s, C_5H_4-*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). $^{31}P\{^1H\}$ NMR (161.7 MHz, $CDCl_3$, δ, ppm): -2.06 (s). ESI-MS: $[M]^+$ calcd for $C_{36}H_{30}FeN_2O_2P_2$: 640.1127; found: 640.1119. Elemental analysis (%) calcd for $C_{36}H_{30}FeN_2O_2P_2$: C, 67.52; H, 4.72; N, 4.37; found: C, 67.16; H, 4.83; N, 4.38.

Synthesis of 1,1′-bis(diphenylphosphinethiocarboyamidyl)ferrocene (L′)

A THF (3 mL) solution of $Fe(C_5H_4NCS)_2$ (150 mg, 0.50 mmol), $HPPh_2$ (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 ^{n}hexane (20 mL × 4) and dried in *vacuo* to give a brown powder of **L′** (68.7 mg, 0.10 mmol, 20%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.08 (s, 4H, C_5H_4), 4.71 (s, 4H, C_5H_4), 7.46 (s, 12H, Ph), 7.54 (s, 8H, Ph), 8.38 (s, 2H, NH). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$, δ, ppm): 64.86 (s, C_5H_4), 66.77 (s, C_5H_4), 96.69 (s, C_5H_4-*ipso*), 128.60 (br, Ph-*ipso*), 129.38 (s, Ph), 130.38 (s, Ph), 134.67 (br, Ph), 206.18 (br, CO). $^{31}P\{^1H\}$ NMR (161.7 MHz, $CDCl_3$, δ, ppm): 17.63 (s). ESI-MS: $[M]^+$ calcd for $C_{36}H_{30}FeN_2P_2S_2$: 672.0675; found: 672.0672. Elemental analysis (%) calcd for $C_{36}H_{30}FeN_2P_2S_2$: C, 64.29; H, 4.50; N, 4.17; found: C, 63.35; H, 4.88; N, 4.70.

Synthesis of PtL_2 (1)

A dichloromethane (5 mL) solution of **L** (128 mg, 0.20 mmol) and $Pt(PPh_3)_4$ (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 CH_2Cl_2 (5.0 mL × 3) and were dried in *vacuo* to give of **1** (101 mg, 0.068 mmol, 68%). Elemental analysis (%) calcd for $C_{72}H_{60}Fe_2N_4O_4P_4Pt$: 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 insolubility for water and organic solvent. In addition, we tried several times to obtain FAB-MS data, but could not get it.

Synthesis of [$CHCl_3 \subset$2a]

A ^{n}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 $PtCl_2(PPh_3)_2$ (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 $[CHCl_3 \subset \mathbf{2a}]$ were isolated by filtration.

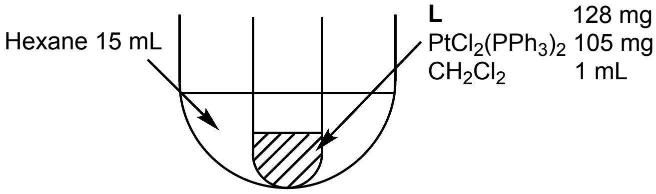


Fig. S1 Equipment diagram

Synthesis of 2a

A ^{n}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 $PtCl_2(PPh_3)_2$ (105 mg, 0.13 mmol) was vigorously 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 $[CHCl_3 \subset \mathbf{2a}]$ 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%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.83 (s, 4H, C_5H_4), 3.92 (s, 4H, C_5H_4), 4.28 (s, 4H, C_5H_4), 4.55 (s, 8H, C_5H_4), 4.73 (s, 4H, C_5H_4), 4.78 (s, 4H, C_5H_4), 5.13 (s, 4H, C_5H_4), 5.56 (s, 4H, C_5H_4), 5.62 (s, 4H, C_5H_4), 5.97 (s, 4H, C_5H_4), 6.29 (s, 4H, C_5H_4), 6.63 (t, J_{HH} = 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). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$, δ, ppm): 63.03 (s, C_5H_4), 64.14 (s, C_5H_4), 64.36 (s, C_5H_4), 64.42 (s, C_5H_4), 64.49 (s, C_5H_4), 65.20 (s, C_5H_4), 66.16 (s, C_5H_4), 66.95 (s, C_5H_4), 67.08 (s, C_5H_4), 67.17 (s, C_5H_4), 68.20 (s, C_5H_4), 69.02 (s, C_5H_4), 93.92 (d, J_{PC} = 11.63 Hz, C_5H_4-*ipso*), 94.74 (d, J_{PC} = 12.46 Hz, C_5H_4-*ipso*), 95.08 (d, J_{PC} = 12.46 Hz, C_5H_4-*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), 131.97 (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, 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, J_{PC} = 70.0 Hz, J_{PC} = 4.2 Hz, CO), 161.03 (d, J_{PC} = 57.1 Hz, CO), 163.19 (dd, J_{PC} = 74.1 Hz, J_{PC} = 3.53 Hz, CO). $^{31}P\{^1H\}$ NMR (161.7 MHz, $CDCl_3$, δ, ppm): -1.87 (dd, J_{PtP} = 3680.0 Hz, J_{PP} = 20.0 Hz, J_{PP} = 18.8 Hz), 0.33 (dd, J_{PtP} = 2496.0 Hz, J_{PP} = 368.0 Hz, J_{PP} = 18.8 Hz), 1.87 (dd, J_{PtP} = 2456.0 Hz, J_{PP} = 368.0 Hz, J_{PP} = 20.0 Hz). ESI-MS: $[M]^{2+}$ calcd for $C_{216}H_{180}Cl_8Fe_6N_{12}O_{12}P_{12}Pt_4$: 2453.1447; found: 2453.1386. Elemental analysis (%) calcd for $C_{216}H_{180}Cl_8Fe_6N_{12}O_{12}P_{12}Pt_4$: C, 52.88; H, 3.70; N, 3.43; found: C, 53.00; H, 4.10; N, 3.36.

Synthesis of $[CHCl_3 \subset \mathbf{2b}]$

A ^{n}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 to stand for overnight. The resulting crystals of [$CHCl_3$⊂**2b**] were isolated by filtration.

Synthesis of 2b

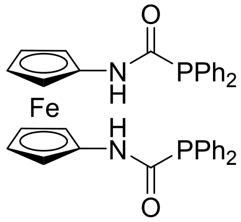
A ^{n}hexane (15 mL) and a vacant test tube were put in a 150 mL Schlenk tube under a dry nitrogen atmosphere. A chloroform (1.0 mL) solution of **L** (128 mg, 0.20 mmol) and $PtBr_2(PPh_3)_2$ (117 mg, 0.13 mmol) was stirred at ambient temperature for 5 min in the test tube, then it was left standing 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, $CDCl_3$, δ, ppm): 2.87 (s, 4H, C_5H_4), 3.90 (s, 4H, C_5H_4), 4.30 (s, 4H, C_5H_4), 4.45 (s, 4H, C_5H_4), 4.51 (s, 4H, C_5H_4), 4.72 (s, 4H, C_5H_4), 4.87 (s, 4H, C_5H_4), 5.18 (s, 4H, C_5H_4), 5.52 (s, 4H, C_5H_4), 5.84 (s, 4H, C_5H_4), 5.97 (s, 4H, C_5H_4), 6.19 (s, 4H, C_5H_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). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$, δ, ppm): 62.48 (s, C_5H_4), 63.50 (s, C_5H_4), 64.23 (s, C_5H_4), 64.53 (s, C_5H_4), 64.72 (s, C_5H_4), 65.13 (s, C_5H_4), 65.70 (s, C_5H_4), 66.65 (s, C_5H_4), 66.96 (s, C_5H_4), 67.17 (s, C_5H_4), 68.02 (s, C_5H_4), 69.48 (s, C_5H_4), 94.28 (d, J_{PC} = 11.65 Hz, C_5H_4-*ipso*), 94.69 (d, J_{PC} = 12.4 Hz, C_5H_4-*ipso*), 95.01 (d, J_{PC} = 12.4 Hz, C_5H_4-*ipso*), 126.28 (Ph), 126.87 (Ph), 126.99 (Ph), 127.32 (Ph), 127.44 (Ph), 127.54 (Ph), 127.68 (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), 128.86 (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), 137.29 (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). $^{31}P\{^1H\}$ NMR (161.7 MHz, $CDCl_3$, δ, ppm): -5.98 (dd, J_{PtP} = 2477.0 Hz, J_{PP} = 368.0 Hz, J_{PP} = 16.2 Hz), -4.11 (dd, J_{PtP} = 3606.0 Hz, J_{PP} = 16.7 Hz, J_{PP} = 16.2 Hz), 12.22 (dd, J_{PtP} = 2478.0 Hz, J_{PP} = 368.0 Hz, J_{PP} = 16.7 Hz). ESI-MS: $[M]^{2+}$ calcd for $C_{216}H_{180}Br_8Fe_6N_{12}O_{12}P_{12}Pt_4$: 2630.941; found: 2630.938. Elemental analysis (%) calcd for $C_{216}H_{180}Br_8Fe_6N_{12}O_{12}P_{12}Pt_4$: 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

$\times 10^{-3}$ 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 ^{n}hexane, collected by filtration, and dried in vacuo to give **3** (7.3 mg, 6.2×10^{-3} mmol, 93%). The crystals were obtained by vapor diffusion of ^{n}hexane into the Et_2O solution of **3**. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.89 (s, 4H, Ph), 7.10-8.03 (overlapping m, 41H, Ph), 11.84 (s, 2H, NH), 12.70 (s, 1H, NH). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, δ, ppm): 121.28 (s, N_{cis}Ph), 121.44 (s, N_{trans}Ph), 125.02 (s, N_{cis}Ph), 125.37 (s, P_{trans}Ph), 126.16 (t, $^{1}J_{PC}$ =28.3 Hz, P_{cis}Ph-*ipso*), 127.94 (d, $^{2}J_{PC}$ = 11.6 Hz, PPh), 128.22 (br, PPh and P_{cis}Ph-*ipso*), 128.82 (s, PPh), 131.33 (d, $^{4}J_{PC}$ = 2.4 Hz, NPh), 132.27 (d, $^{3}J_{PC}$ = 2.4 Hz, PPh), 135.52 ($^{2}J_{PC}$ = 10.8 Hz, NPh), 138.10 (d, $^{3}J_{PC}$ = 10.8 Hz, NPh-*ipso*), 138.31 (t, $^{3}J_{PC}$ = 5.0 Hz, NPh-*ipso*), 140.80 (d, $^{1,}J_{CP}$ = 72.2 Hz, CO), 163.66 (app. t, $^{1,3}J_{CP}$ = 36.0 Hz, CO). ^{31}P{^{1}H} NMR (161.7 MHz, $CDCl_3$, δ, ppm): 2.60 (t, J_{PtP} = 3671.9 Hz, J_{PP} = 16.5 Hz, P_{cis}), 14.36 (d, J_{PtP} = 2489.9 Hz, J_{PP} = 18.4 Hz, P_{trans}). ESI-MS: $[M-Cl]^{+}$ calcd for $C_{57}H_{48}FN_2ClN_3O_3P_2Pt$: 1145.2239; found: 1145.2237. Elemental analysis (%) calcd for $C_{57}H_{48}Cl_2N_3O_3P_3Pt$: C, 57.92; H, 4.09; N, 3.56; found: C, 57.73; H, 4.35; N, 3.35.

NMR spectra of L



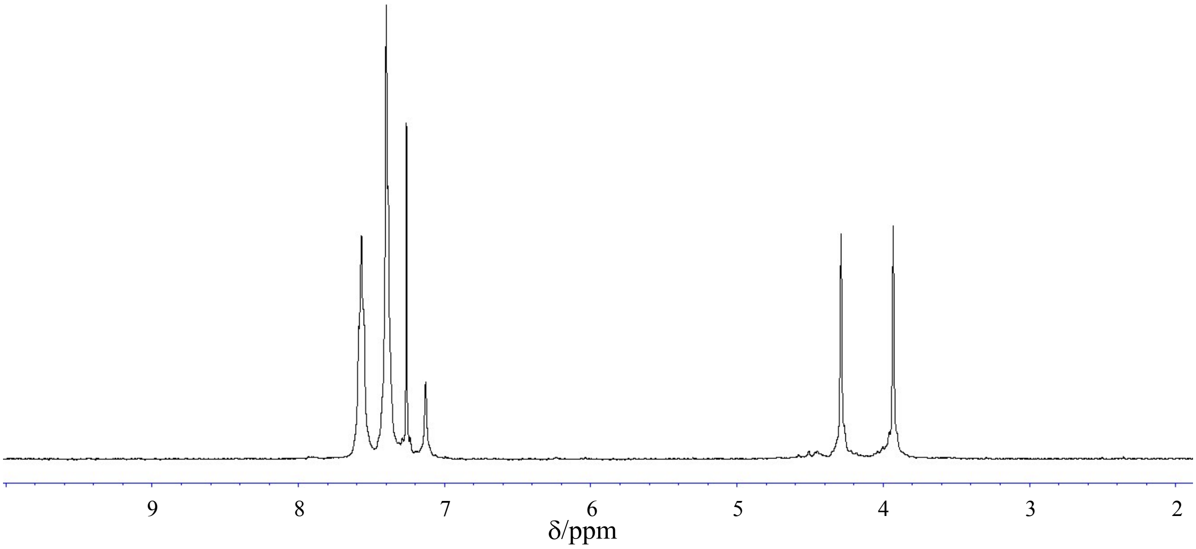


Fig. S2 ^{1}H NMR spectrum (CDCl$_3$, rt, 400 MHz) of **L**.

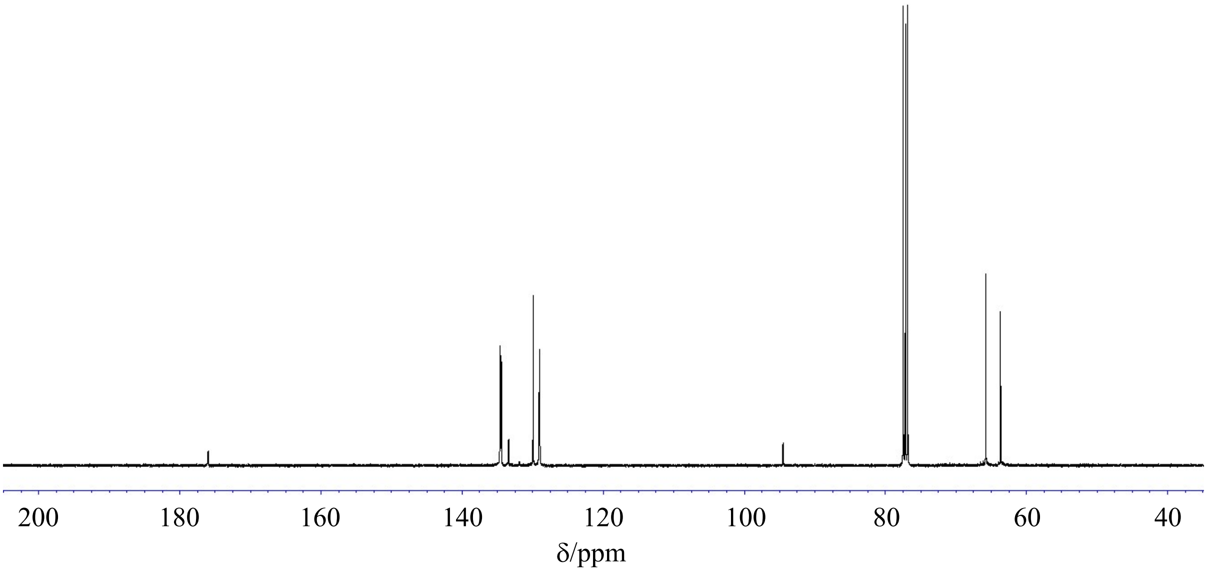


Fig. S3 ^{13}C{^{1}H} NMR spectrum (CDCl$_3$, rt, 100.4 MHz) of **L**.

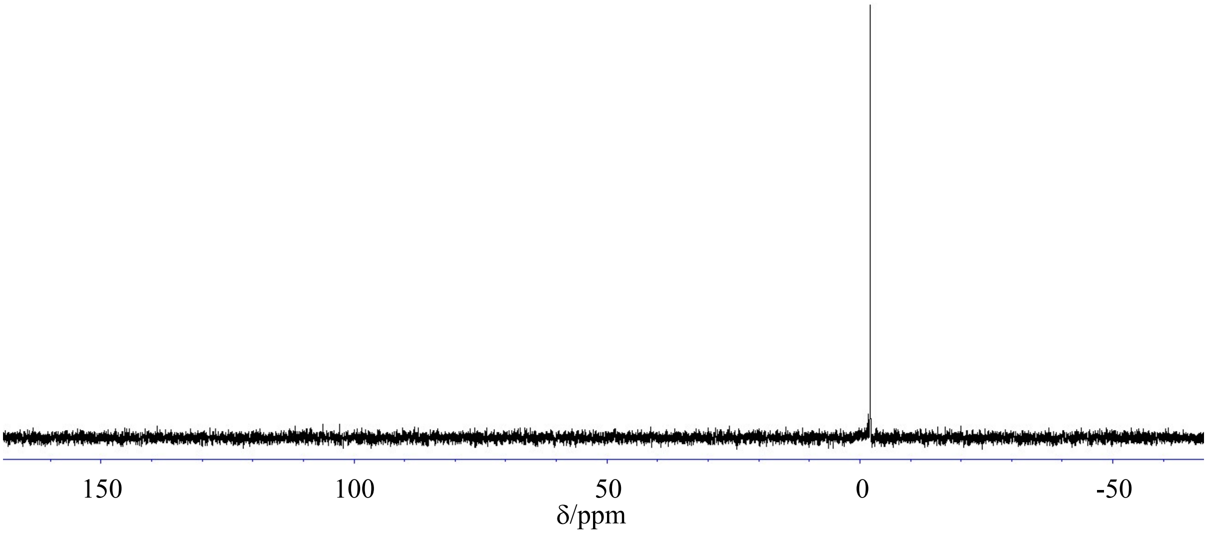
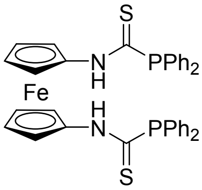


Fig. S4 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, rt, 161.7 MHz) of **L**.

NMR spectra of L′



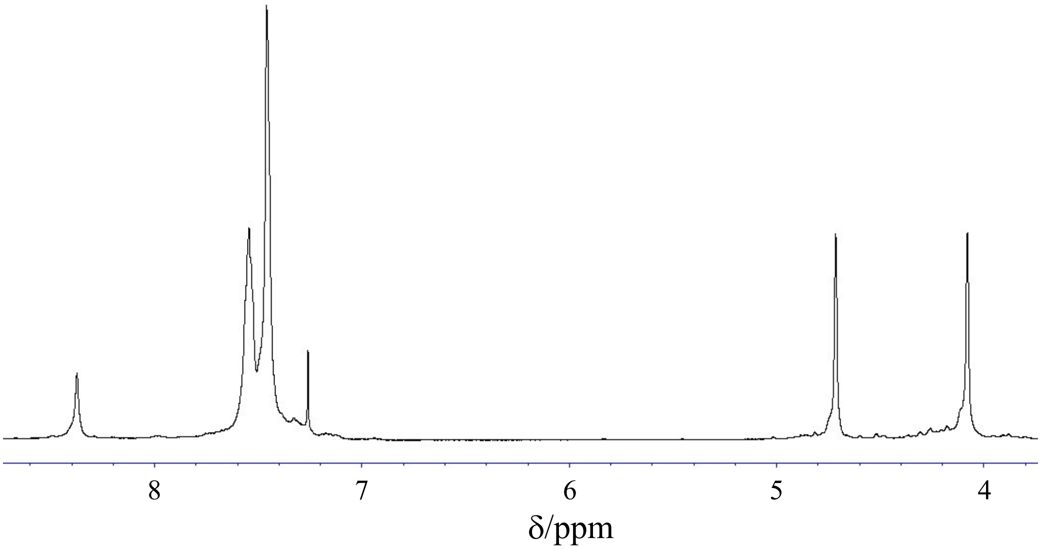


Fig. S5 ^{1}H NMR spectrum ($CDCl_3$, rt, 400 MHz) of **L′**.

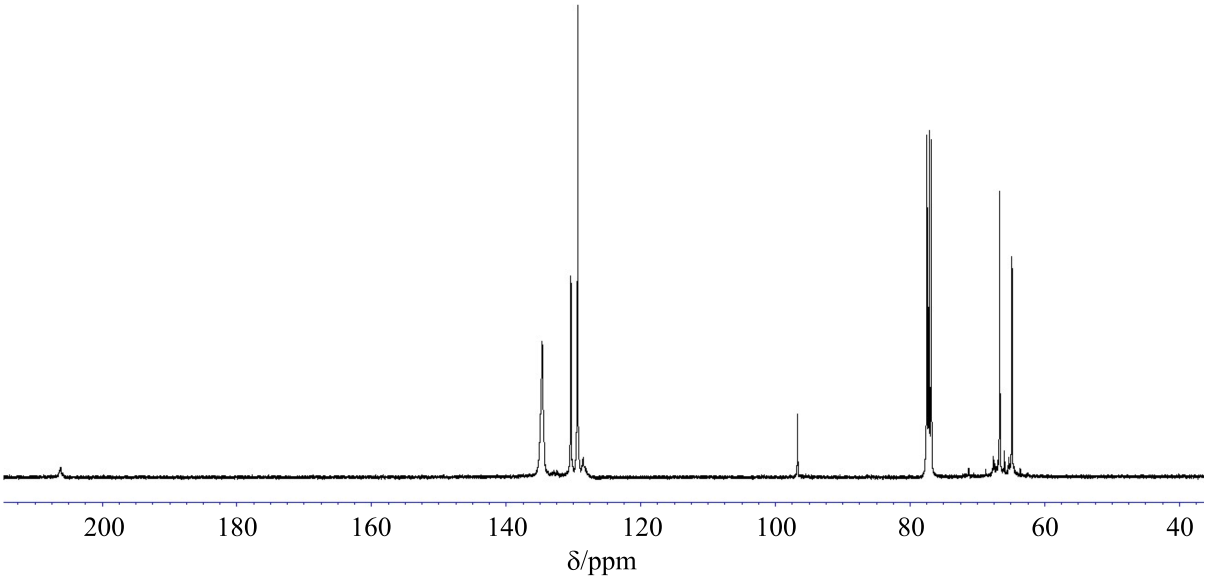


Fig. S6 $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, rt, 100.4 MHz) of **L′**.

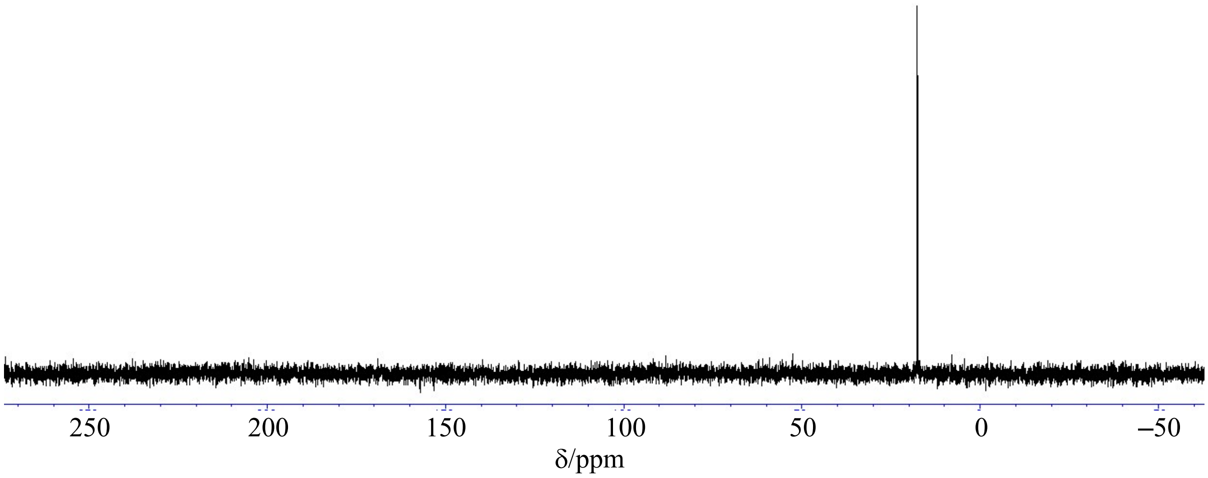
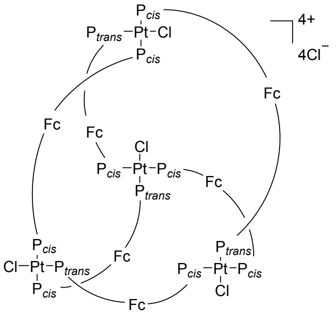


Fig. S7 $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$, rt, 161.7 MHz) of **L′**.

NMR and ESI-MS spectra of 2a



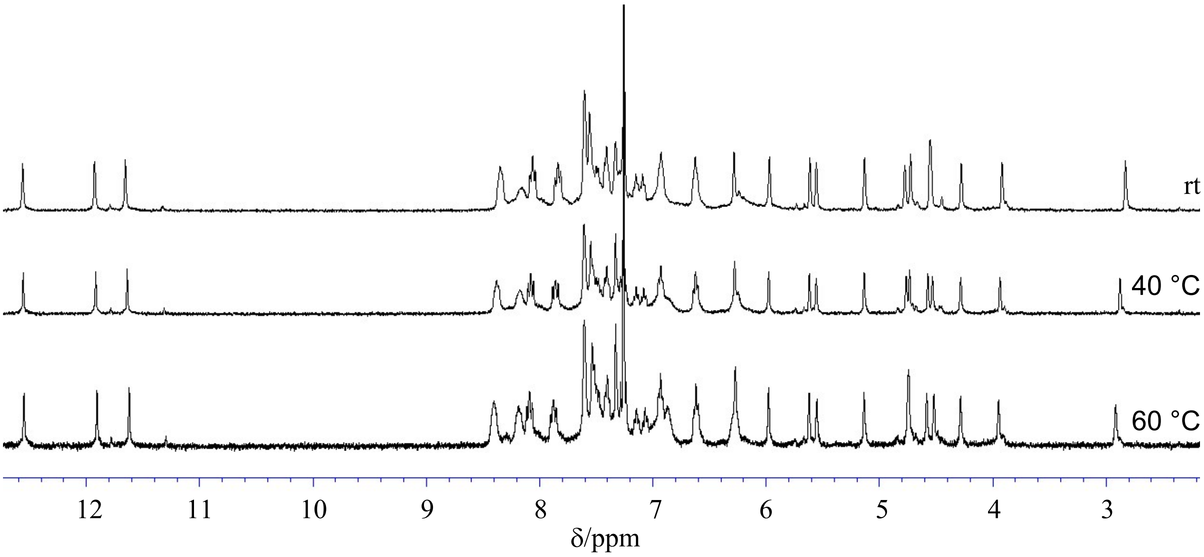


Fig. S8 ^{1}H NMR spectrum (CDCl$_3$, rt-60 °C, 400 MHz) of **2a**.

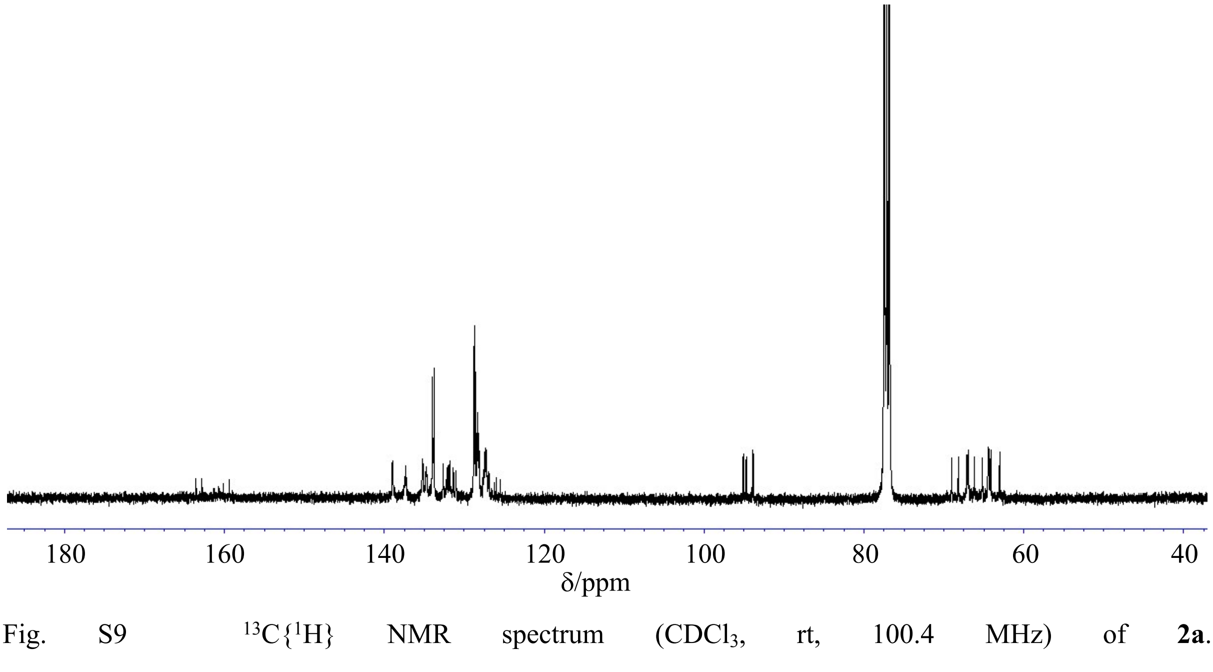


Fig. S9 ^{13}C{^{1}H} NMR spectrum (CDCl$_3$, rt, 100.4 MHz) of **2a**.

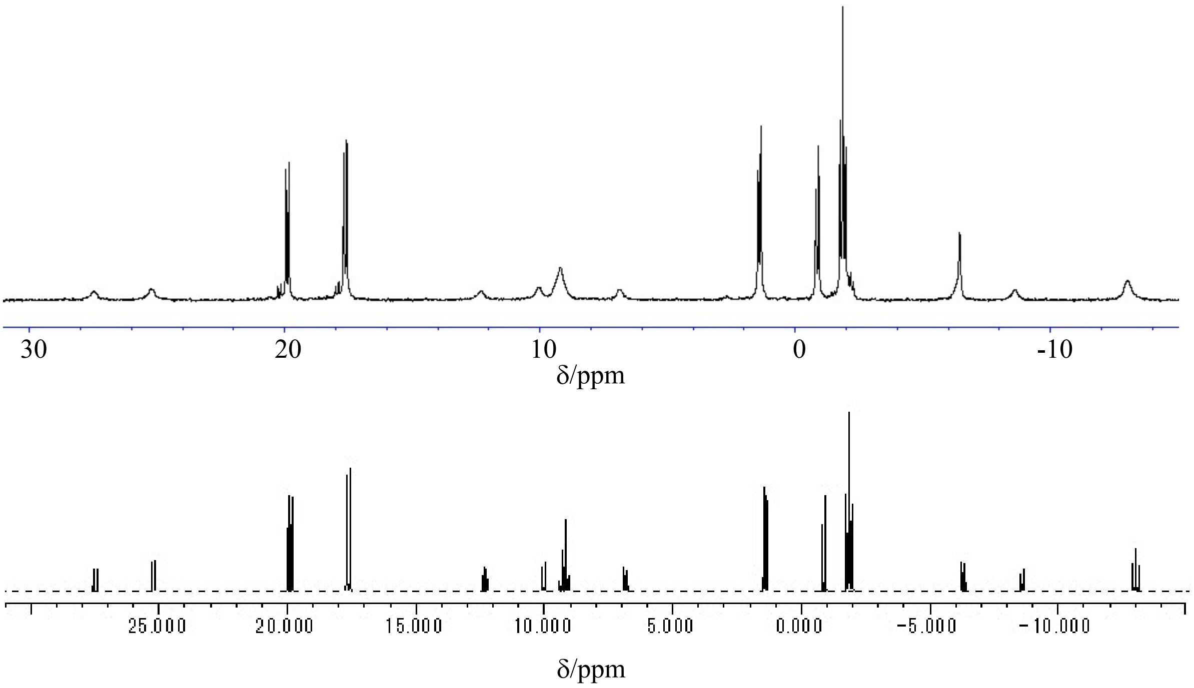


Fig. S10 $^{31}P\{^1H\}$ NMR spectrum of **2a** ($CDCl_3$, rt, 161.7 MHz) (top) and the computer-simulated spectrum using gNMR (bottom)

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

	Chemical shift / ppm	Coupling constant / Hz		
P_{trans}	–1.87	$J_{Pt\text{-}P}$ = 3608.0	$J_{Pcis1\text{-}P}$ = 18.8	$J_{Pcis2\text{-}P}$ = 20.0
P_{cis1}	0.33	$J_{Pt\text{-}P}$ = 2496.0	$J_{Ptrans\text{-}P}$ = 18.8	$J_{Pcis2\text{-}P}$ = 368.0
P_{cis2}	18.68	$J_{Pt\text{-}P}$ = 2456.0	$J_{Ptrans\text{-}P}$ = 20.0	$J_{Pcis1\text{-}P}$ = 368.0

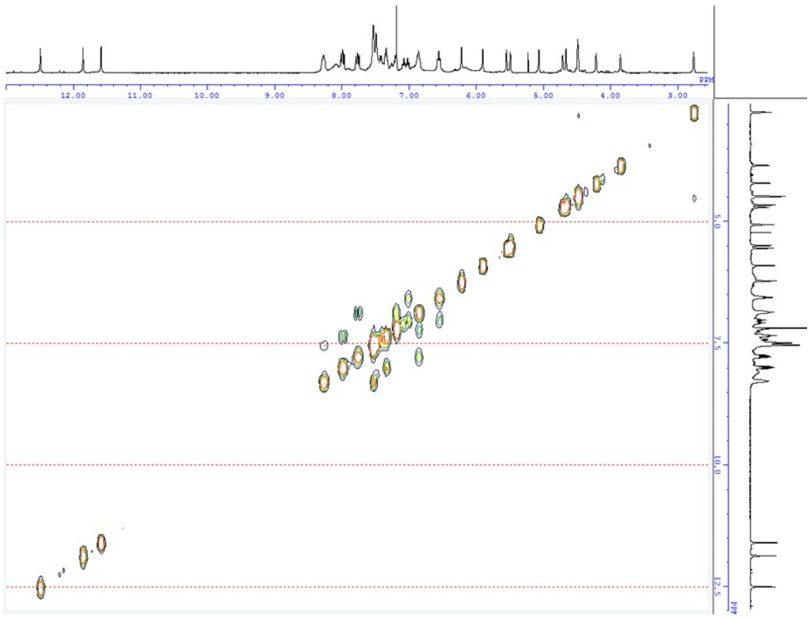


Fig. S11 H-H COSY spectrum of **2a** ($CDCl_3$, rt, 400 MHz)

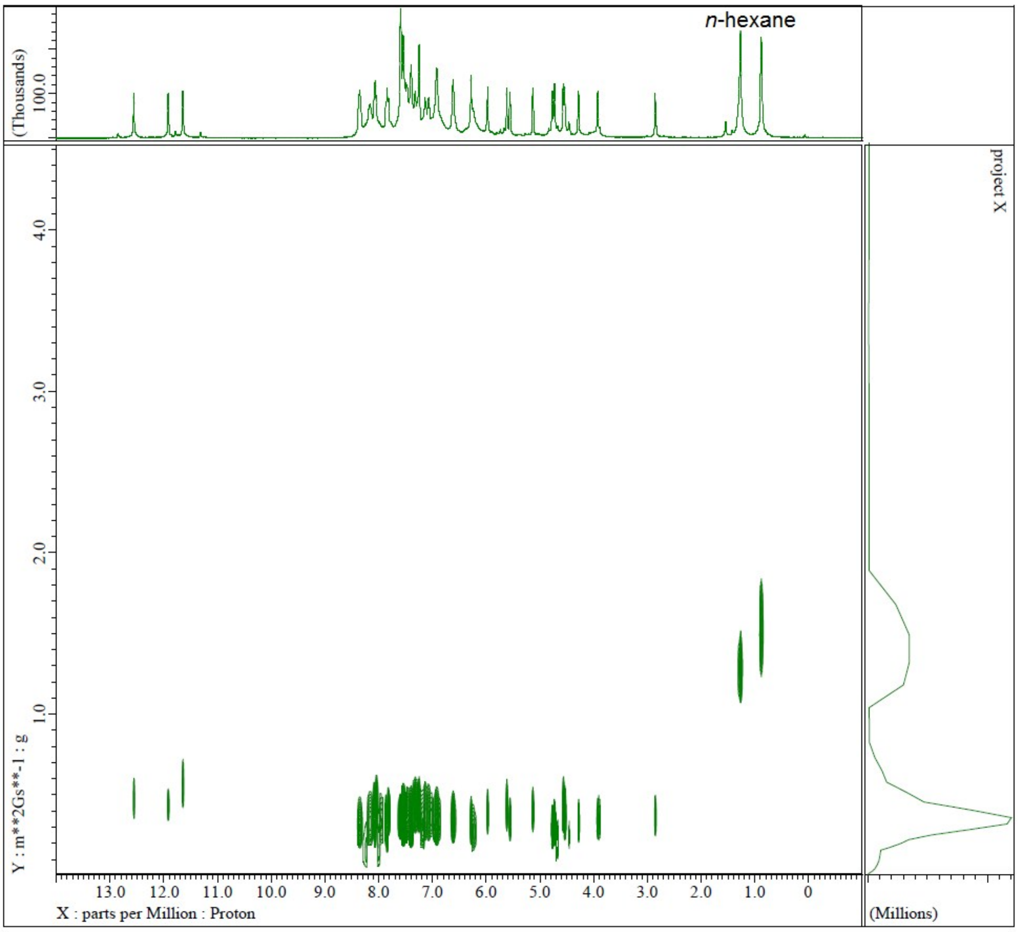


Fig. S12 DOSY spectrum of **2a** ($CDCl_3$, 400 MHz, 30°C, D = 100 ms, d = 2.3 ms, G = 0.3 T/m).

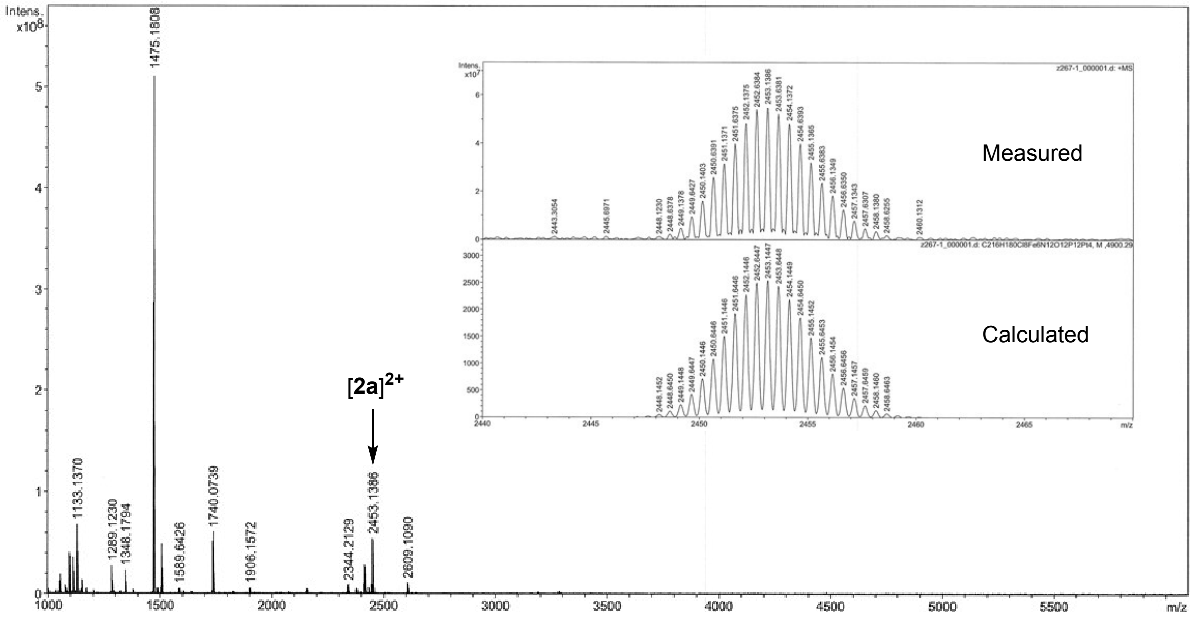
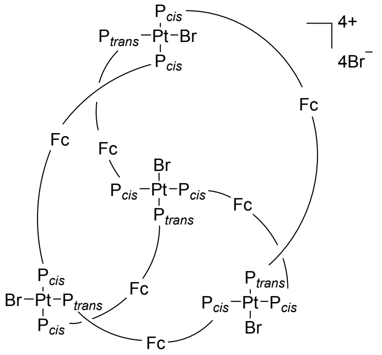


Fig. S13 ESI-MS spectrum of **2a** in CH_2Cl_2/IPA (9:1, v:v)

NMR and ESI-MS spectra of 2b



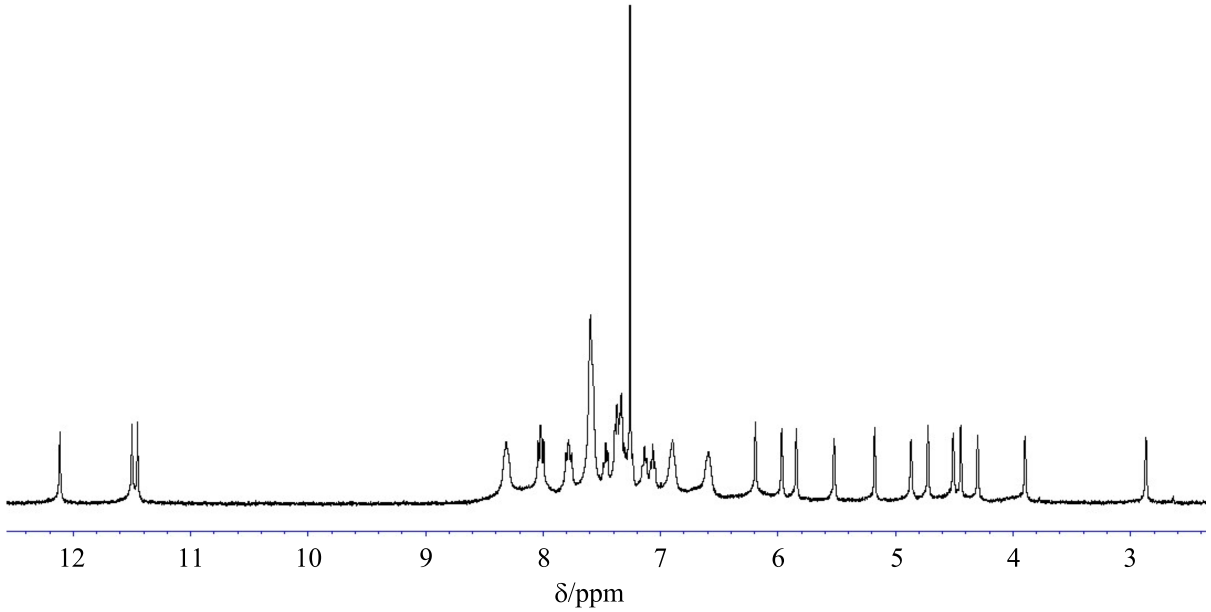


Fig. S14 ^{1}H NMR spectrum ($CDCl_3$, rt, 400 MHz) of **2b**.

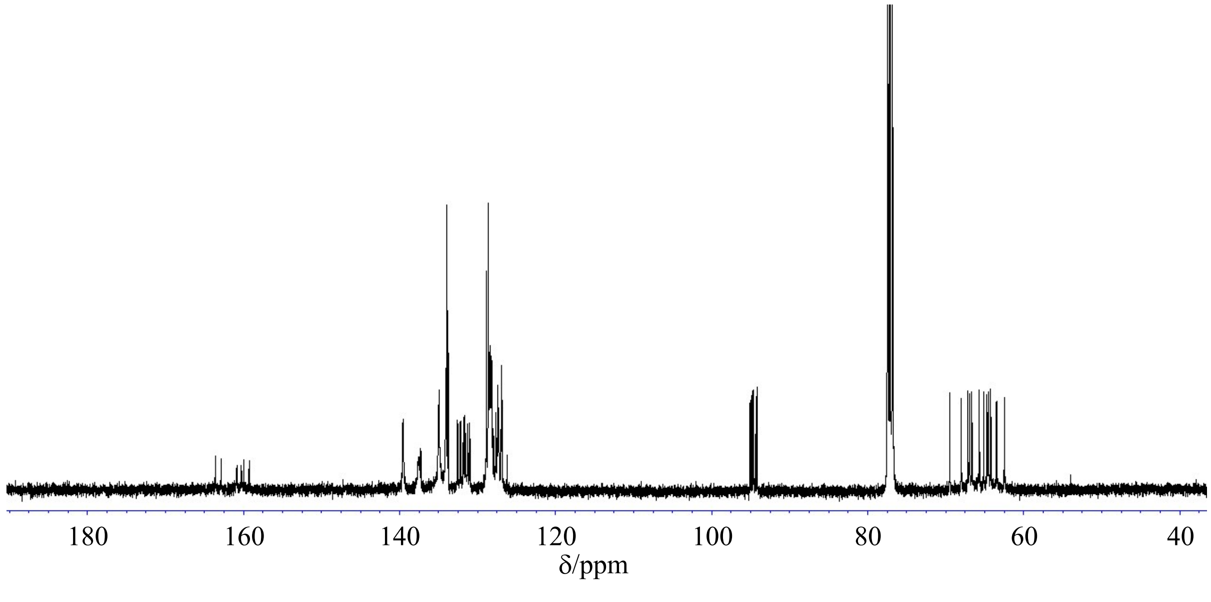


Fig. S15 $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, rt, 100.4 MHz) of **2b**.

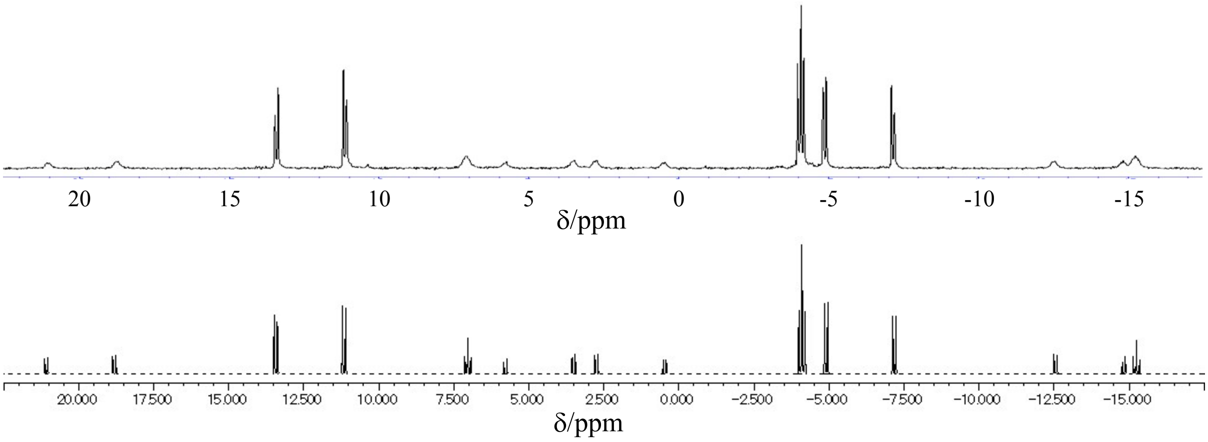


Fig. S16 $^{31}P\{^1H\}$ NMR spectrum of **2b** ($CDCl_3$, rt, 161.7 MHz) (top) and the computer-simulated spectrum using gNMR (bottom)

Table S2 gNMR simulation of $^{31}P\{^1H\}$ NMR spectrum

	Chemical shift / ppm	Coupling constant / Hz		
P_{trans}	–4.11	$J_{Pt\text{-}P}$ = 3606.0	$J_{Pcis1\text{-}P}$ = 16.2	$J_{Pcis2\text{-}P}$ = 16.7
P_{cis1}	–5.98	$J_{Pt\text{-}P}$ = 2477.0	$J_{Ptrans\text{-}P}$ = 16.2	$J_{Pcis2\text{-}P}$ = 368.0
P_{cis2}	12.22	$J_{Pt\text{-}P}$ = 2478.0	$J_{Ptrans\text{-}P}$ = 16.7	$J_{Pcis1\text{-}P}$ = 368.0

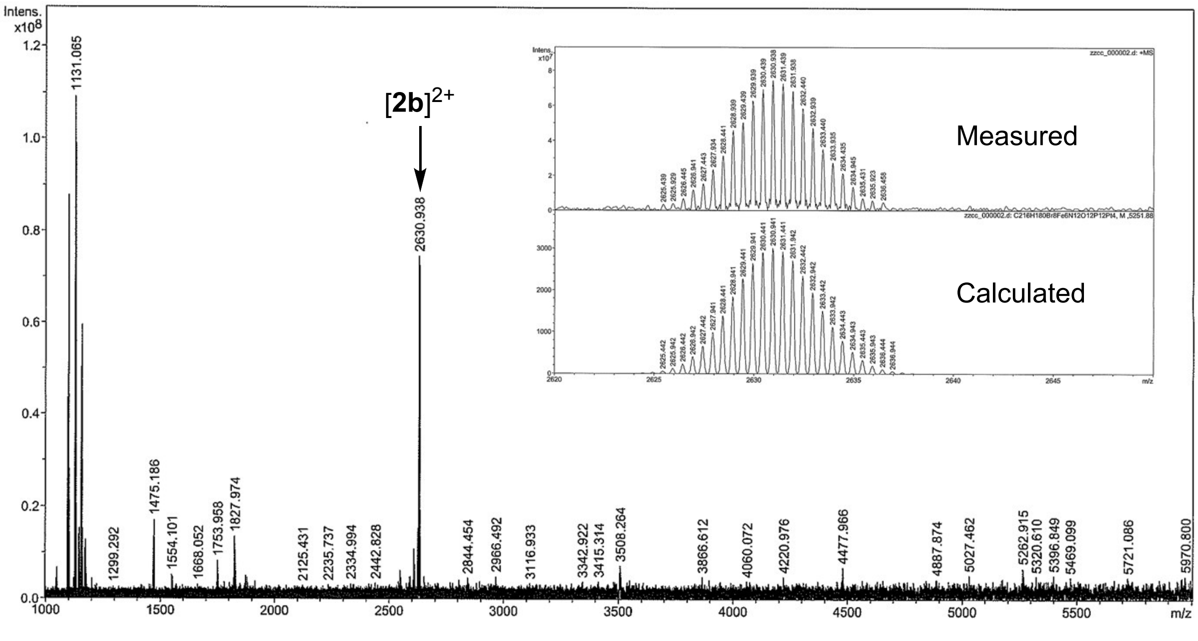
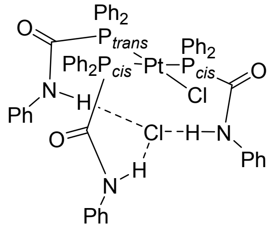


Fig. S17 ESI-MS spectrum of **2b** in CH_2Cl_2/IPA (9:1, v:v)

NMR spectra of 3



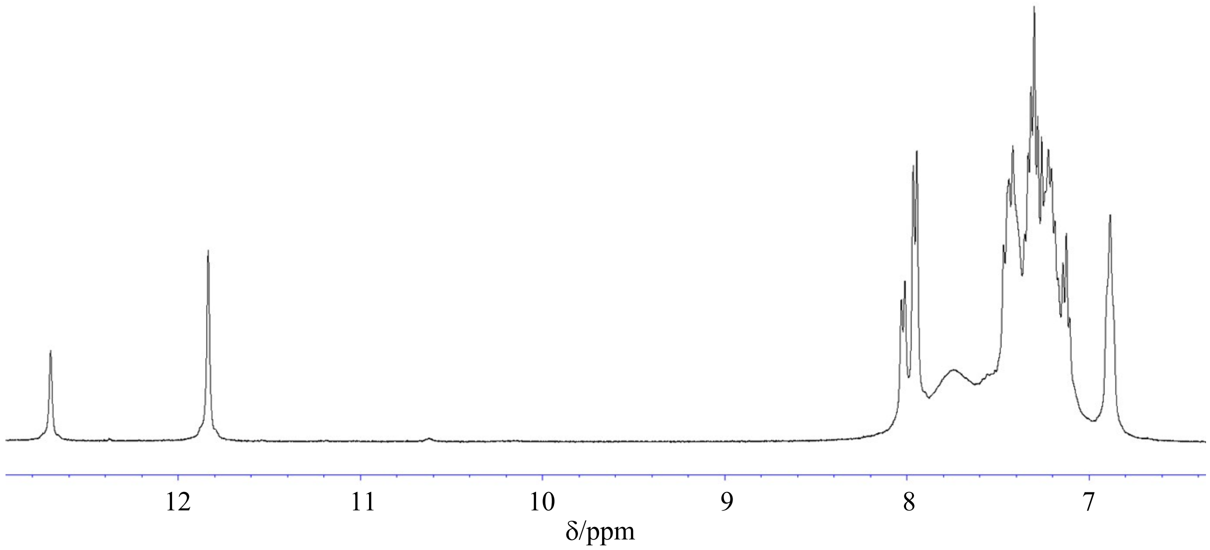


Fig. S18 ^{1}H NMR spectrum (CDCl$_3$, rt, 400 MHz) of **3**.

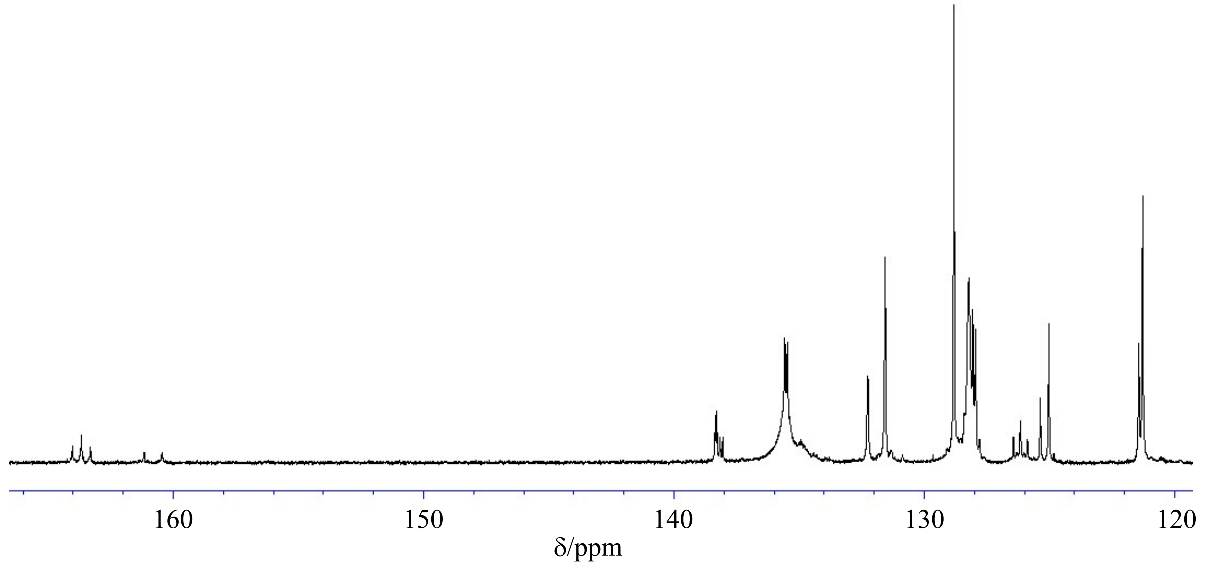


Fig. S19 ^{13}C{^{1}H} NMR spectrum (CDCl$_3$, rt, 100.4 MHz) of **3**.

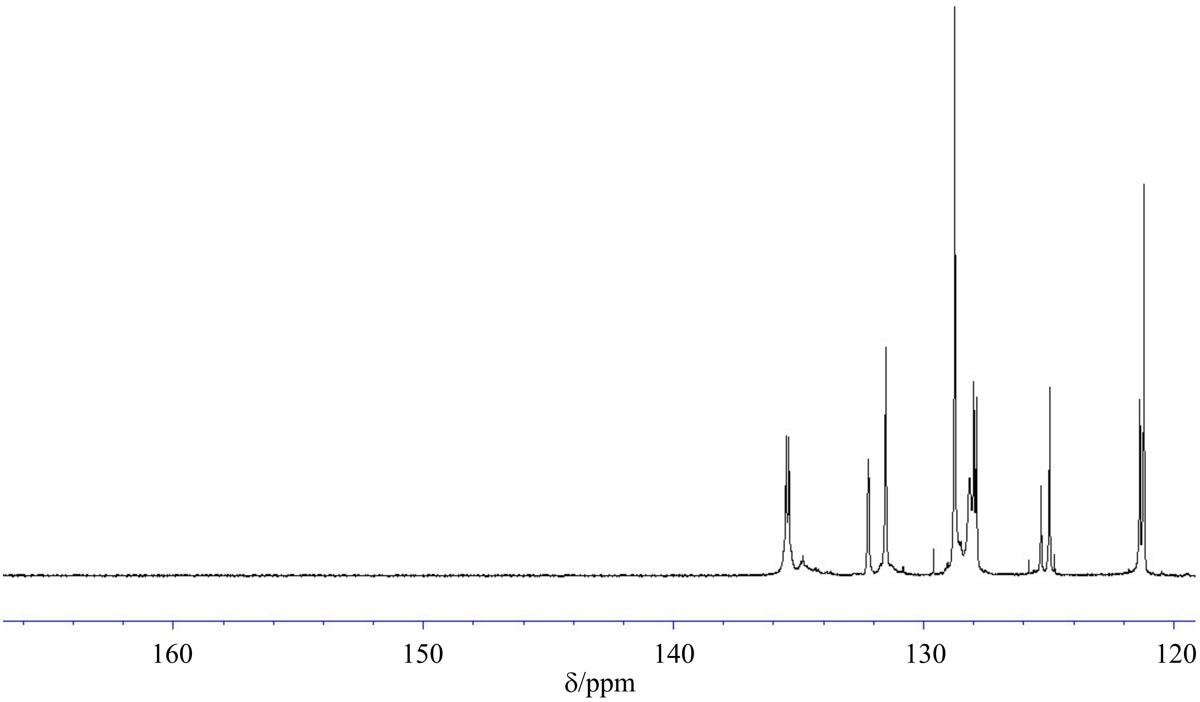


Fig. S20 135DEPT $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, rt, 100.4 MHz) of **3**.

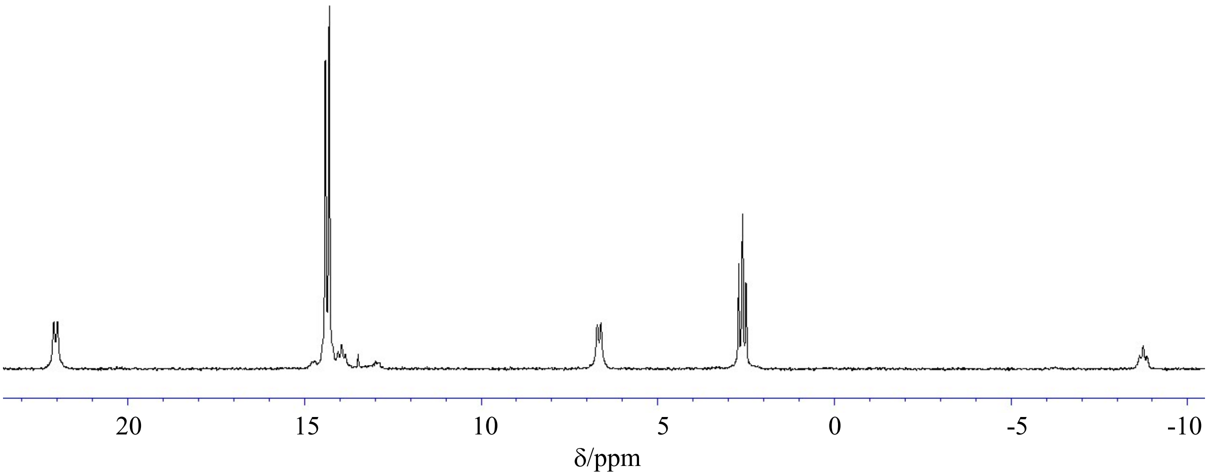


Fig. S21 $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, rt, 161.7 MHz) of **3**.

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[S9] or ShelXL-2014[S10]. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. For [$CHCl_3$⊂**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**, **1** and [$CHCl_3$⊂**2a**].

	L	**1**	[$CHCl_3$⊂**2a**]
Empirical formula	$C_{36}H_{30}FeN_2O_2P_2$	$C_{76}H_{68}Cl_8Fe_2N_4O_4P_4Pt$	$C_{224}H_{188}Cl_{32}Fe_6N_{12}O_{12}P_{12}Pt_4$
Formula weight	640.41	1815.61	5861.35
Temperature (K)	200(2)	200(2)	200(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1$/c	$C2$/c	**Error!**$_1$
a (Å)	13.7346(13)	29.1376(18)	21.3085(7)
b (Å)	11.8880(10)	15.0037(8)	22.6838(7)
c (Å)	9.9583(10)	18.0317(12)	31.6313(6)
α (°)			90.2849(10)
β (°)	104.743(5)°	109.950(2)°	90.4102(6)
γ (°)			117.1817(13)
Volume (Å^3)	1572.4(3)	7409.9(8)	13599.8(7)
Z	2	4	2
ρ_{calcd} (Mg m^{-3})	1.353	1.627	1.431
μ (mm^{-1})	0.616	2.697	2.795
F(000)	664	3640	5808
Crystal size (mm^3)	0.07 × 0.05 × 0.03	0.13 × 0.10 × 0.10	0.200 × 0.080 × 0.070
Reflections collected	15425	28446	133682
Independent reflections (R(int))	3596 (0.0407)	8452 (0.0437)	47664 (0.0459)
$R1$ ($I > 2\sigma(I)$)	0.0433	0.0424	0.0801
w$R2$ (all data)	0.0997	0.0931	0.2603
Goodness-of-fit	1.067	1.065	1.058
CCDC	1405347	1405343	1405344

Table S4 Crystallographic data and details of structure refinement of [$CHCl_3 \subset$ **2b**] and **3**.

	[$CHCl_3 \subset$ **2b**]	**3**
Empirical formula	$C_{237}H_{201}Br_8Cl_{63}Fe_6N_{12}O_{12}P_{12}Pt_4$	$C_{61}H_{58}Cl_2N_3O_4P_3Pt$
Formula weight	7768.82	1256.00
Temperature (K)	200(2)	200(2)
Crystal system	triclinic	triclinic
Space group	**Error!**$_{1}$	**Error!**$_{1}$
a (Å)	21.46830(10)	11.79990(10)
b (Å)	23.59400(10)	12.6886(2)
c (Å)	32.9537(8)	19.4168(2)
α (°)	88.034(3)	83.953(3)
β (°)	89.129(3)	73.888(3)
γ (°)	65.458(2)	87.375(2)
Volume (Å^3)	15174.8(5)	2777.02(6)
Z	2	2
ρ_{calcd} (Mg m^{-3})	1.700	1.502
μ (mm^{-1})	3.839	2.759
F(000)	7604	1268
Crystal size (mm^3)	0.30 × 0.25 × 0.25	0.30 × 0.23 × 0.15
Reflections collected	75372	31987
Independent reflections (R(int))	45899(0.0327)	12208 (0.0243)
$R1$ (I > 2σ(I))	0.0700	0.0301
wR2	0.2063	0.0674
Goodness-of-fit	1.070	1.102
CCDC	1405345	1405346

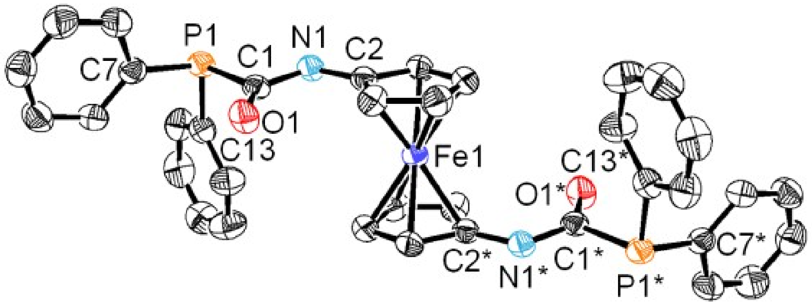


Fig. S22 ORTEP drawing of **L** (thermal ellipsoids at 50% probability). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å): O1–C1 = 1.225(2), N1–C1 = 1.343(3), P1–C1 = 1.886(2).

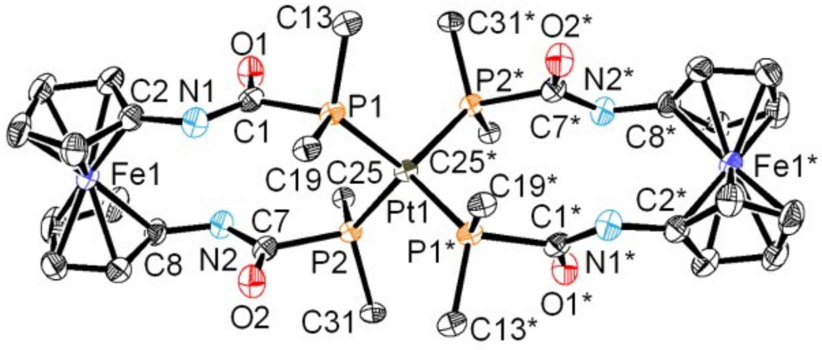


Fig. S23 ORTEP drawing of **1** (thermal ellipsoids at 50% probability). All hydrogen atoms, solvent molecules, and Ph rings (except *ipso*-C) are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt1–P1 = 2.2890(9), Pt1–P2 = 2.3004(9), O1–C1 = 1.216(4), O2–C7 = 1.216(5), N1–C1 = 1.350(5),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

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