Supporting Information

for

Isolation of Heterometallic Cerium(III) Complexes with a Multidentate Nitrogen-Phosphorus Ligand

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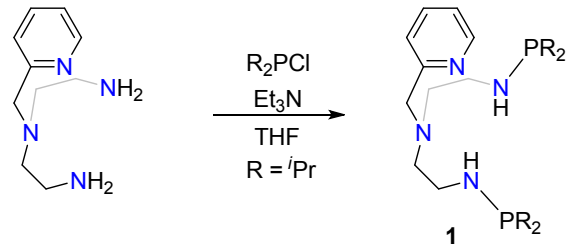
Contents

1. Experimental Procedures

General Procedures: All manipulations were performed under an N_2 atmosphere using standard Schlenk techniques or in a glovebox. Commercially available chemicals were used as received without further purification. The solvents were obtained by passing through a Solve Purer G5 (MIKROUNA) solvent purification system and further dried over 4 Å molecular sieves. Deuterated solvents (benzene-d_6 and THF-d_8) were dried over Na/K and stored under a N_2 atmosphere prior to use. Nuclear magnetic resonance spectroscopy was performed using a Bruker AVIII-400 (^{1}H 400 MHz; ^{13}C{^{1}H} 101 MHz; ^{31}P{^{1}H} 162 MHz) or a Bruker AVIII-500 (^{1}H 500 MHz; ^{13}C{^{1}H} 126 MHz; ^{31}P{^{1}H} 202 MHz) spectrometer at room temperature (RT). The ^{1}H and ^{13}C{^{1}H} NMR chemical shifts (δ) are relative to tetramethylsilane, and ^{31}P{^{1}H} NMR chemical shifts are relative to 85% H_3PO_4. Absolute values of the coupling constants are provided in Hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (br). Elemental analyses (C, H, N) were performed on a Vario EL III elemental analyzer at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. High-resolution mass spectroscopy (HRMS) was conducted using a Waters SYNAPT G2-Si system equipped with an ESI ionization source. UV-vis absorption spectra were obtained by using a Shimadzu UV-3600 absorption spectrophotometer. Powder X-ray diffraction (PXRD) was performed on a Bruker D8 Advance diffractometer with Cu Kα X-ray source (λ = 1.54056 Å) operated at 40 kV and 40 mA at 298 K. (2-NC_5H_4)$CH_2N(CH_2CH_2NH_2)_2$ and compound**1**wereprepared according to previously reported procedures.[1,2]

Synthesis of compound 1

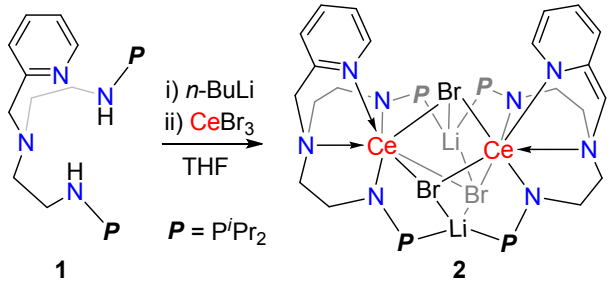


1

A solution of ^{i}Pr$_2$PCl (3.06 g, 20.0 mmol) in THF (20 mL) was added dropwise to a solution of (2-NC_5H_4)$CH_2N(CH_2CH_2NH_2)_2$ (1.94 g, 10.0 mmol) and Et_3N (11 mL, 80.0 mmol) in THF (30 mL),

resulting in the immediate formation of a white precipitate. The reaction mixture was stirred overnight before being dried *in vacuo*. The white solid was extracted with hexane and filtered through celite. The volatiles were removed under reduced pressure to give compound **1** as a pale yellow oil. Yield: 3.75 g (88%). ^{1}H NMR (C_6D_6, 500 MHz, 298K) δ 8.46 (d, $^{3}J_{HH}$= 5.0 Hz,1H, 6-C_5H_4N), 7.12-7.20 (m, 2H, 3,4-C_5H_4N), 6.64 (dd, $^{3}J_{HH}$=7.0Hz, 5.0Hz, 1H, 5-C_5H_4N), 3.07 (s, 2H, $C_5H_4NCH_2$), 2.99-3.04 (m, 4H, NCH_2CH_2-NP), 2.49 (t, $^{3}J_{HH}$= 6.5 Hz, 4H, NCH_2CH_2-NP), 1.48-1.53 (m, 4H, $CH(CH_3)_2$), 1.39-1.43 (m, 2H, N*H*),1.01-1.06 (m, 24H, $CH(CH_3)_2$). ^{13}C{^{1}H}NMR(C_6D_6, 101 MHz, 298K) δ 160.5 (2-C_5H_4N), 149.1 (6-C_5H_4N), 135.5 (4-C_5H_4N), 122.5 (3-C_5H_4N), 121.4 (5-C_5H_4N), 60.5 ($C_5H_4NCH_2$), 57.7 (NCH_2CH_2NP), 57.6 (NCH_2CH_2NP), 46.6 (NCH_2CH_2NP), 46.4 (NCH_2CH_2NP), 26.6 ($CH(CH_3)_2$), 26.5 ($CH(CH_3)_2$), 19.2 ($CH(CH_3)_2$), 19.0 ($CH(CH_3)_2$), 17.5 ($CH(CH_3)_2$), 17.4 ($CH(CH_3)_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz, 298K) δ 63.9. HRMS (ESI) calcd for $C_{22}H_{44}N_4P_2$ $[M+H]^+$ 427.3114, found 427.3118.

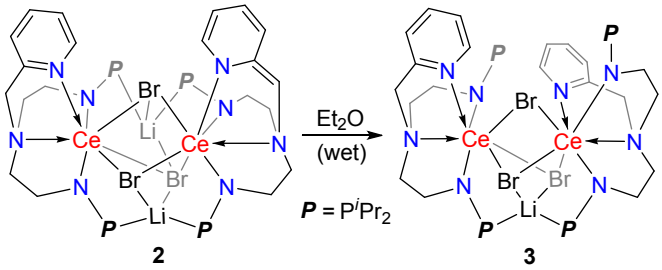
Synthesis of complex 2



A 2.4 M solution of *n*-BuLi in hexanes (2.5 mL, 6.0 mmol) was added dropwise to a solution of compound **1** (1.28 g, 3.0 mmol) in THF (20 mL) cooled at -30 °C. The mixture was allowed to warm to rt and stirred for a further 2 h, and was then added to the suspension of $CeBr_3$ (1.14 g, 3.0 mmol) in THF (10 mL). After stirring overnight at rt, the suspension became transparent. The solvents were removed under reduced pressure and the residues were extracted with toluene. The mixture was filtered through a sintered glass funnel and the filtrate was dried *in vacuo* to afford complex **2** (1.57 g, 76 %) as a red solid. Red crystals of **2** suitable for X-ray diffraction were obtained by placing the concentrated toluene solution at -30 °C for 3 days. ^{1}H NMR (C_6D_6, 400 MHz, 298K) δ 21.06 (s, 1H), 14.49 (s, 2H), 11.49 (s, 6H), 10.65 (s, 6H), 10.15 (s, 2H), 9.13 (s, 2H), 8.77 (s, 2H), 8.12 (m, 4H), 7.71 (s, 6H), 7.55 (s, 6H), 6.88 (m, 1H), 6.02 (s, 2H), 5.27 (m,

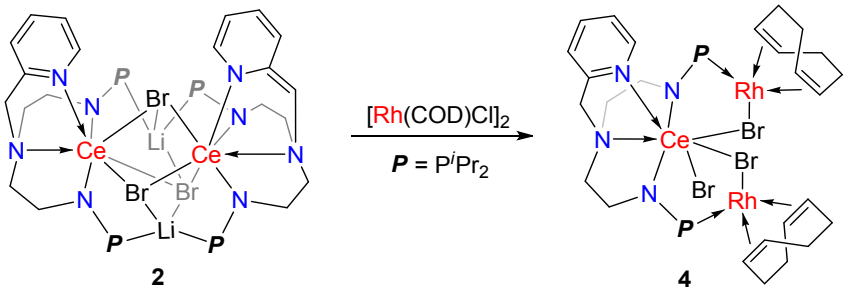
1H), 3.18 (s, 2H), 2.91 (m, 1H), 2.84 (m, 1H), 2.54 (s, 6H), 2.40 (m, 6H), 0.14 (m, 1H), -0.95 (s, 6H), -1.07 (m, 1H), -3.01 (s, 1H), -3.75 (s, 2H) -4.76 (s, 2H), -6.50 (s, 6H), -6.92 (s, 2H), -9.65 (s, 2H), -11.08 (s, 2H), -12.38 (s, 1H). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 162 MHz, 298K) δ 49.2, 33.0. Anal. Calcd. For $C_{44}H_{83}Br_3Ce_2Li_2N_8P_4$: C 38.24; H 6.05; N 8.11. Found: C 35.83; H 5.64; N 7.43.This complex consistently has low carbon content, possibly due to the high sensitivity.

Synthesis of complex 3



The complex **2** (138.2 mg, 0.1 mmol) was dissolved in wet Et_2O (2 mL) and the resulting red orange solution was filtered, concentrated to 1 mL, and evaporated slowly, yielding **3** as single orange crystals suitable for X-ray diffraction. Yield: 61.9 mg (45%). ^{1}H NMR (C_6D_6, 400 MHz, 298K) δ 18.40 (s, 2H), 17.71 (s, 2H), 11.60 (s, 10H), 11.29 (s, 2H), 10.69 (s, 2H), 9.83 (s, 6H), 6.39 (s, 6H), 6.16 (s, 6H), 5.02 (s, 2H), 3.03 (m, 2H), 2.76 (s, 2H), 2.51 (s, 2H), 2.28 (m, 8H), 0.71 (m, 2H), 0.47 (s, 2H), 0.30 (s, 2H), -1.25 (s, 2H), -1.52 (s, 2H), -3.16 (s, 6H), -3.82 (s, 2H), -4.97 (s, 6H) -7.52 (s, 2H), -7.60 (s, 6H). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 162 MHz, 298K) δ 169.4, 69.6. Anal. Calcd. For $C_{44}H_{84}Br_3Ce_2LiN_8P_4$: C 38.41; H 6.15; N 8.14. Found: C 38.70; H 6.25; N 8.01.

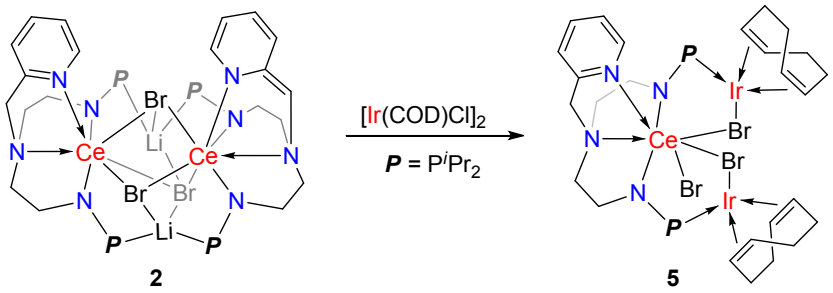
Synthesis of complex 4



Atoluene solution (2 mL) of $[Rh(COD)Cl]_2$ (49.3 mg, 0.1 mmol) was added to a stirred solution of **2** (138.2 mg, 0.1 mmol) in toluene (2 mL) at rt. The reaction was heated at 90 °C for 2 h, then the

mixture was filtered through a sintered glass funnel and the filtrate was concentrated to 2 mL. After the concentrated solution was placed at -30 °C for 12 h, yellow crystals of **4** suitable for X-ray diffraction were obtained (34.4 mg, 28%). ^{1}H NMR (THF-d_8, 400 MHz, 298K) δ 13.46, 12.51, 12.07, 10.95, 10.41, 9.24, 8.52, 7.99, 7.69, 7.46, 7.35, 7.19, 7.14, 6.14, 5.64, 5.37, 5.18, 4.27, 3.72, 3.60, 2.96, 2.55, 2.33, 2.02, 1.97, 1.92, 1.75, 1.32, 0.92, 0.14, 0.02, -0.39, -1.66, -3.32, -4.96, -7.44, -13.10. ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz, 298K) δ 85.2 (d, $^{1}J_{P-Rh}$ = 149.4 Hz), 81.6 (d, $^{1}J_{P-Rh}$ = 155.3 Hz). Anal. Calcd. For $C_{38}H_{66}Br_3CeRh_2N_4P_2$·1.5 toluene: C 42.68.10; H 5.76; N 4.11. Found: C 42.35; H 6.08; N 4.34.

Synthesis of complex 5



A solution in toluene (2 mL) of $[Ir(COD)Cl]_2$ (67.2 mg, 0.1 mmol) was added to a stirred solution of **2** (138.2mg, 0.1 mmol) in toluene (2 mL) at rt. The reaction was heated at 90 °C for 2 h. The mixture was filtered through a sintered glass funnel and the filtrate was concentrated to 2 mL. After the concentrated solution was placed at -30 °C for 12 h, orange crystals of **5** suitable for X-ray diffraction were obtained (47.8 mg, 34%). ^{1}H NMR (THF-d_8, 400 MHz, 298K) δ 14.32, 13.33, 11.71, 9.75, 8.54,7.70,7.47, 7.17, 7.16, 6.13, 5.76, 5.40, 5.22, 4.99, 3.90, 3.77, 3.62, 3.28, 3.02, 2.73, 2.71, 2.70, 2.68, 2.45, 2.35, 2.29, 2.27, 2.19, 2.15, 2.11, 1.91, 1.89, 1.77, 1.59, 1.57, 1.56, 1.33, 0.93, -0.25, -1.58, -5.30, -5.96, -13.17. ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz, 298K) δ 68.6, 64.7. Anal. Calcd. For $C_{38}H_{66}Br_3CeIr_2N_4P_2$·toluene: C 36.10; H 4.98; N 3.74.Found: C 36.10; H 5.33; N 3.45.

2. X-ray crystallographic analysis

Crystals suitable for X-ray diffraction were grown from a solution of the product in hexane at RT. The intensity data were collected using a Bruker APEX-II CCD area detector witha radiation source of Ga (Kα) (1.34139 Å) or Mo(Kα) (0.71073 Å). Multiscan or empirical absorption corrections (SADABS) were applied. The structures were solved using Patterson methods, expanded using difference Fourier syntheses, and refined using full-matrix least squares fitting on F^2 using the Bruker SHELXTL-2014 program package.[3] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms. The program SQUEEZEwasusedto handle the contribution of disordered solvents in a crystal structure refinement.[4] CCDC-1940013 (**2**), 1940015 (**3**), 1940016 (**4**), 1940017 (**5**) contain the crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data-request/cif). Details regarding the data collection and refinement for these complexes are given in Table S1.

Table S1. Crystal data and structural refinement for **2**, **3**, **4** and **5**.

	2	**3**	**4**	**5**
empirical formula	$C_{44}H_{83}Br_3Ce_2Li_2$ N_8P_4	$C_{44}H_{84}Br_3Ce_2Li$ N_8P_4	$C_{76}H_{130}Br_6Ce_2$ $N_8P_4Rh_4$	$C_{76}H_{130}Br_6Ce_2$ $N_8P_4Ir_4$
formula weight	1381.91	1375.98	2545.24	2808.25
temperature, K	173(2)	193(2)	193(2)	193(2)
wavelength, Å	0.71073	1.34139	1.34139	1.34139
crystal system	Triclinic	Triclinic	Triclinic	Triclinic
space group	*P*-1	*P*-1	*P*-1	*P*-1
a, Å	14.0359(4)	12.4128(4)	14.3545(4)	14.3632(5)
b, Å	14.1167(4)	15.6235(5)	19.2818(5)	19.3199(7)
c, Å	17.7636(6)	17.6653(5)	21.2924(6)	21.3343(7)
α, °	70.333(1)	96.143(1)	91.396(1)	91.439(2)
β, °	81.160(1)	100.177(1)	105.106(1)	104.959(1)
γ, °	84.094(1)	102.728(1)	109.615(1)	109.739(1)

V, Å^3	3270.04(17)	3250.87(17)	5318.8(3)	5342.3(3)
Z	2	2	2	2
d_{calcd}, g cm^{-3}	1.403	1.400	1.531	1.747
$\mu(Mo_{K\alpha})$, mm^{-1}	3.337	9.295	9.845	13.149
F(000)	1380.0	1376.0	2416.0	2672.0
crystal size, mm	0.10 × 0.10 × 0.10	0.20 × 0.10 × 0.10	0.20 × 0.10 × 0.10	0.20× 0.10 × 0.10
θ_{max},°	25.000	53.919	53.878	53.847
reflns collected	24842	40061	67150	74998
indep reflns	11417 [R_{int}=0.0258, R_{sigma}=0.0389]	11631 [R_{int}=0.0470, R_{sigma}=0.0420]	19351 [R_{int}=0.0530, R_{sigma}=0.0491]	19372 [R_{int}=0.0469, R_{sigma}=0.0403]
data/restraints/params	11417/0/584	11631/264/576	19351/0/917	19372/0/917
goodness-of-fit on F^2	1.077	1.030	1.036	0.987
final R ($I > 2\sigma(I)$)	R_1 = 0.0252, wR_2 = 0.0664	R_1 = 0.0386, wR_2 = 0.1029	R_1 = 0.0671, wR_2 = 0.1983	R_1 =0.0481, wR_2 =0.1465
R indices (all data)	R_1 = 0.0321, wR_2 = 0.0684	R_1 = 0.0395, wR_2 = 0.1038	R_1 = 0.0750, wR_2 = 0.2056	R_1 =0.0552, wR_2 =0.1526
Residual electron density (e. Å^{-3}) max/min	0.46/-0.50	1.74/-1.10	2.67/-3.44	1.61/-3.81

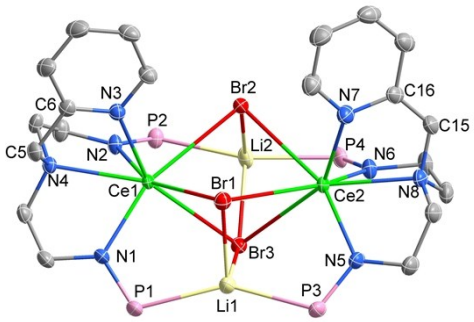


Figure S1. X-ray molecular structure of complex **2** drawn with 40% probability. Hydrogen atoms and isopropyl moieties in P^{i}Pr$_2$ are omitted for clarity.

Table S2. Selected bond distances (Å) and angles (deg) for **2**.

Ce1-Br1	3.1249(4)	Ce1-Br2	3.1516(3)
Ce1-Br3	3.1539(3)	Ce1-N1	2.348(2)
Ce1-N2	2.370(3)	Ce1-N3	2.645(3)
Ce1-N4	2.613(2)	Ce2-Br1	3.2034(4)
Ce2-Br2	3.1300(3)	Ce2-Br3	3.2903(4)
Ce2-N5	2.380(2)	Ce2-N6	2.393(3)
Ce2-N7	2.483(3)	Ce2-N8	2.584(2)
Br1-Li1	2.506(6)	Br2-Li2	2.504(6)
Br3-Li1	2.664(6)	Br3-Li2	2.598(5)
P1-N1	1.670(2)	P2-N2	1.667(3)
P3-N5	1.656(3)	P4-N6	1.656(3)
P1-Li1	2.523(5)	P2-Li2	2.540(6)
P3-Li1	2.512(5)	P4-Li2	2.497(5)
N3-C6	1.338(4)	N3-C10	1.345(4)
C6-C7	1.374(4)	C7-C8	1.358(5)
C9-C8	1.373(5)	C10-C9	1.370(4)
C6-C5	1.511(4)	N7-C16	1.410(4)
N7-C20	1.353(4)	C16-C17	1.444(4)

C17-C18	1.340(5)	C18-C19	1.402(5)
C20-C19	1.372(5)	C15-C16	1.348(4)
Br2-Ce1-Br3	73.084(8)	Br2-Ce1-Li2	42.99(10)
Br2-Ce1-Li1	93.69(8)	Br3-Ce1-Li2	44.73(9)
Br3-Ce1-Li1	45.76(10)	Br1-Ce1-Br2	72.914(9)
Br1-Ce1-Br3	75.330(10)	Br1-Ce1-Li2	96.21(10)
Br1-Ce1-Li1	42.92(10)	N3-Ce1-Br2	82.84(5)
N3-Ce1-Br3	148.42(6)	N3-Ce1-Br1	78.30(6)
N3-Ce1-Li2	123.10(11)	N3-Ce1-Li1	118.17(12)
Li2-Ce1-Li1	87.05(13)	Br2-Ce2-Br3	71.523(9)
Br2-Ce2-Br1	72.147(9)	Br2-Ce2-Li2	41.54(9)
Br2-Ce2-Li1	92.88(8)	Br3-Ce2-Li2	42.74(8)
Br3-Ce2-Li1	44.57(11)	Br1-Ce2-Br3	72.418(9)
Br1-Ce2-Li2	91.94(8)	Br1-Ce2-Li1	42.05(9)
N7-Ce2-Br2	82.71(6)	N7-Ce2-Br3	150.64(6)
N7-Ce2-Br1	86.69(6)	N7-Ce2-N8	67.02(9)
N7-Ce2-Li2	120.55(11)	N7-Ce2-Li1	126.04(12)
Li1-Ce2-Li2	83.95(13)		

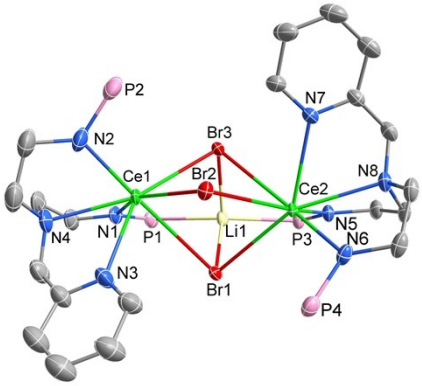


Figure S2. X-ray molecular structure of complex **3** drawn with 40% probability. Hydrogen atoms and isopropyl moieties in P^{i}Pr$_2$ are omitted for clarity.

Table S3. Selected bond distances (Å) and angles (deg) for **3**.

Ce1-Br1	3.2733(5)	Ce1-Br2	3.0797(5)
Ce1-Br3	3.0620(5)	Ce2-Br1	3.0941(5)
Ce2-Br2	3.0727(5)	Ce2-Br3	3.2923(5)
Ce1-N1	2.427(4)	Ce1-N2	2.330(4)
Ce1-N3	2.696(4)	Ce1-N4	2.665(4)
Ce1-Li1	3.679(8)	Ce2-N5	2.402(3)
Ce2-N6	2.329(3)	Ce2-N7	2.688(4)
Ce2-N8	2.664(4)	Ce2-Li1	3.673(7)
Br3-Li1	2.494(7)	Br1-Li1	2.508(8)
P1-Li1	2.498(7)	P3-Li1	2.490(7)
C6-C5	1.506(9)		
Br2-Ce1-Br1	74.773(12)	Br2-Ce1-Li1	95.77(10)
Br3-Ce1-Br2	78.060(13)	Br3-Ce1-Br1	72.612(12)
Br3-Ce1-Li1	42.21(12)	Br1-Ce1-Li1	41.79(12)
N1-Ce1-Br2	157.76(10)	N1-Ce1-Br3	89.35(10)
N1-Ce1-Br1	84.05(10)	N1-Ce1-N3	101.62(14)
N1-Ce1-N4	66.71(15)	N1-Ce1-Li1	63.21(14)
N3-Ce1-Br2	79.57(10)	N3-Ce1-Br3	144.29(10)
N3-Ce1-Br1	74.86(10)	N3-Ce1-Li1	114.06(16)
N2-Ce1-Br2	94.46(13)	N2-Ce1-Br3	108.65(14)
N2-Ce1-Br1	168.81(14)	N2-Ce1-N1	106.99(16)
N2-Ce1-N3	100.51(18)	N2-Ce1-N4	64.82(17)
N2-Ce1-Li1	145.17(19)	N4-Ce1-Br2	130.26(11)
N4-Ce1-Br3	149.95(11)	N4-Ce1-Br1	119.82(11)
N4-Ce1-N3	62.44(15)	N4-Ce1-Li1	127.65(15)

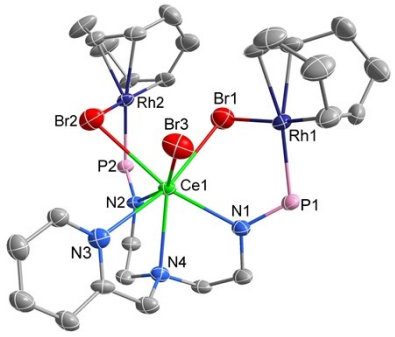


Figure S3. X-ray molecular structure of complex **4** drawn with 40% probability. Hydrogen atoms and isopropyl moieties in P^iPr_2 are omitted for clarity.

Table S4. Selected bond distances (Å) and angles (deg) for **4**.

Ce1-Br1	2.9139(14)	Ce1-Br2	3.0509(14)
Ce1-Br3	2.9448(13)	Ce1-N1	2.453(8)
Ce1-N2	2.466(7)	Ce1-N3	2.676(8)
Ce1-N4	2.630(7)	Rh1-Br1	2.4891(17)
Rh1-P1	2.350(2)	Rh2-Br2	2.4787(13)
Rh2-P2	2.338(2)	P1-N1	1.636(8)
P2-N2	1.649(7)		
Br3-Ce1-Br2	82.65(4)	Br1-Ce1-Br3	88.37(4)
Br1-Ce1-Br2	84.94(4)	N2-Ce1-Br3	158.57(17)
N2-Ce1-Br2	76.61(16)	N2-Ce1-Br1	95.07(16)
N2-Ce1-N4	67.2(2)	N2-Ce1-N3	93.5(2)
N4-Ce1-Br3	123.34(15)	N4-Ce1-Br2	126.06(16)
N4-Ce1-Br1	135.18(16)	N4-Ce1-N3	62.5(2)
N1-Ce1-Br3	93.05(18)	N1-Ce1-Br2	165.67(17)
N1-Ce1-Br1	81.26(17)	N1-Ce1-N2	108.4(2)
N1-Ce1-N4	67.6(2)	N1-Ce1-N3	110.5(2)
N3-Ce1-Br3	78.16(17)	N3-Ce1-Br2	82.06(17)

N3-Ce1-Br1	162.33(17)		

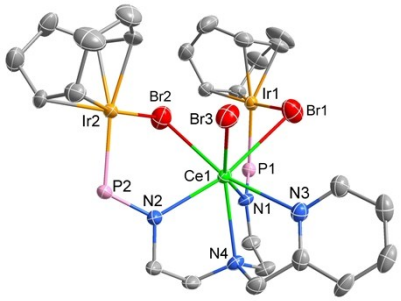


Figure S4. X-ray molecular structure of complex **5** drawn with 40% probability. Hydrogen atoms and isopropyl moieties in P^{i}Pr$_2$ are omitted for clarity.

Table S5. Selected bond distances (Å) and angles (deg) for **5**.

Ce1-Br1	3.0742(14)	Ce1-Br2	2.9215(14)
Ce1-Br3	2.9440(12)	Ir1-Br1	2.4547(13)
Ir1-P1	2.343(2)	Ir2-Br2	2.4432(14)
Ir2-P2	2.340(2)	Ce1-N1	2.445(7)
Ce1-N2	2.447(7)	Ce1-N3	2.671(7)
Ce1-N4	2.624(7)	P1-N1	1.659(7)
P2-N2	1.652(7)		
Br3-Ce1-Br1	81.59(4)	Br2-Ce1-Br3	88.60(4)
Br2-Ce1-Br1	87.42(4)	P1-Ir1-Br1	92.21(6)
P2-Ir2-Br2	91.91(6)	N1-Ce1-Br3	157.25(18)
N1-Ce1-Br1	76.01(17)	N1-Ce1-Br2	94.23(15)
N1-Ce1-N2	108.1(2)	N1-Ce1-N3	94.6(2)
N1-Ce1-N4	67.6(2)	N2-Ce1-Br3	94.66(17)
N2-Ce1-Br1	167.29(16)	N2-Ce1-Br2	80.33(16)

N2-Ce1-N3	110.7(2)	N2-Ce1-N4	67.9(2)
N3-Ce1-Br3	77.70(17)	N3-Ce1-Br1	80.53(17)
N3-Ce1-Br2	162.89(17)	N4-Ce1-Br3	124.32(15)
N4-Ce1-Br1	124.14(16)	N4-Ce1-Br2	134.63(15)
N4-Ce1-N3	62.5(2)		

3. NMR Spectra and powder X-ray diffraction patterns

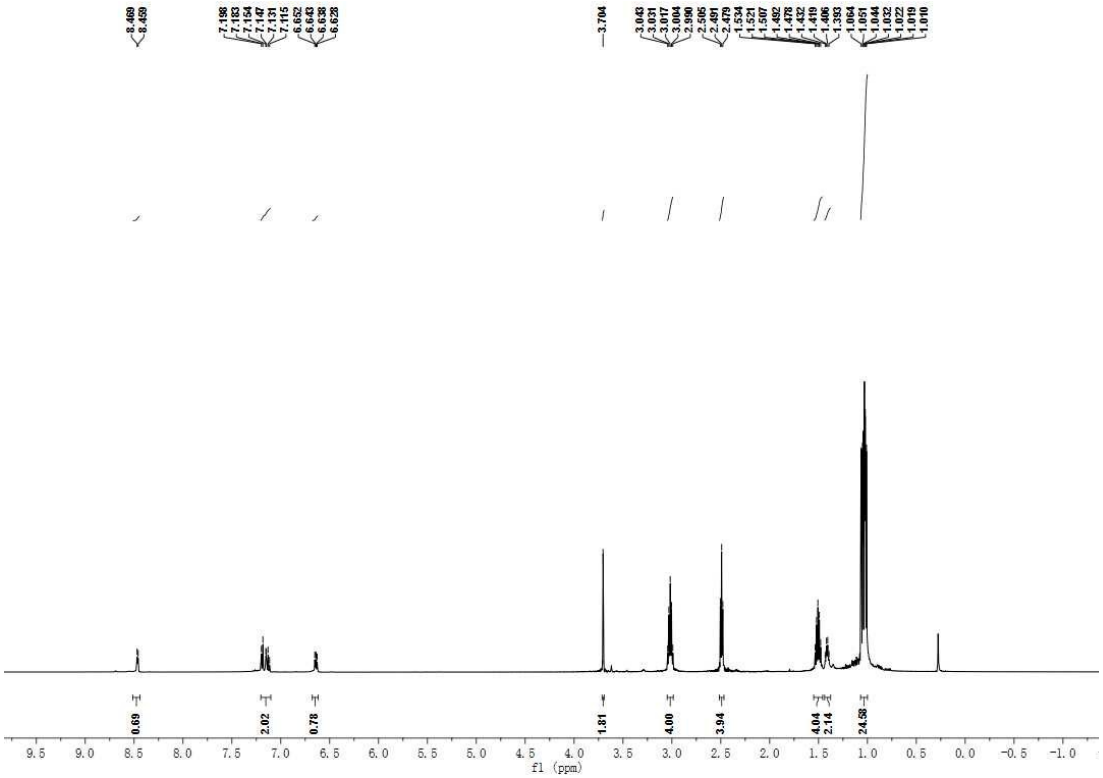


Figure S5. The ^{1}H NMR (500 MHz) spectrum of compound **1** in C_6D_6.

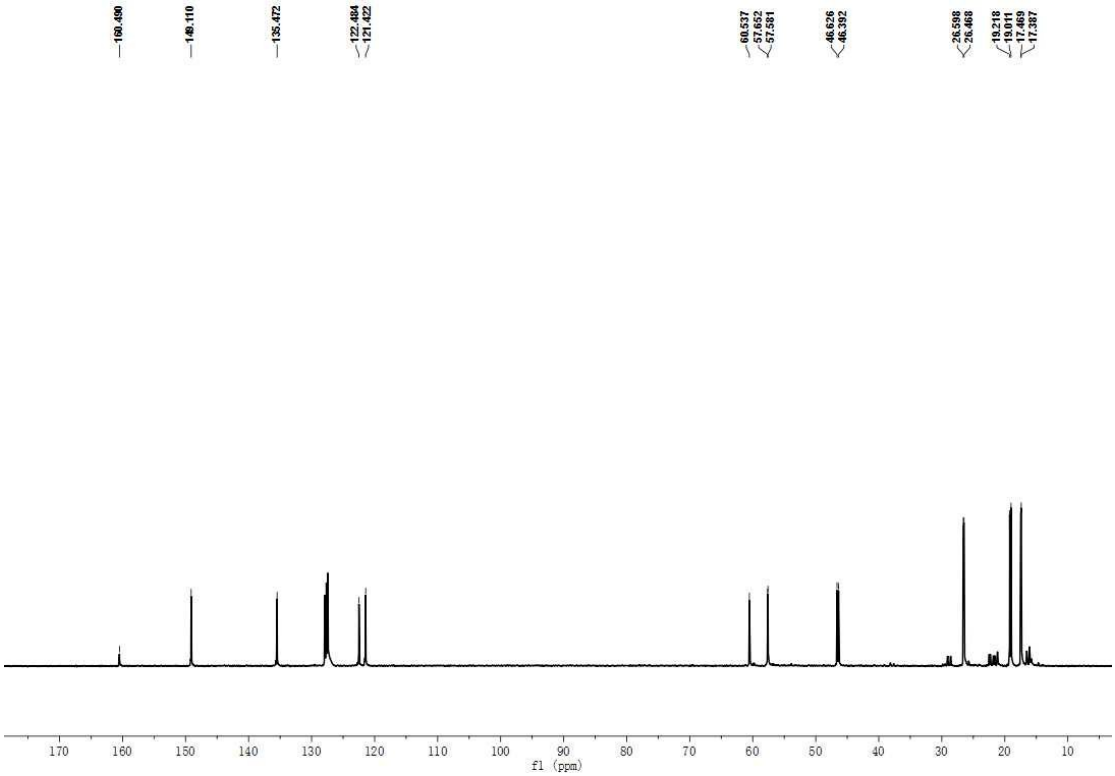


Figure S6. The $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of compound **1** in C_6D_6.

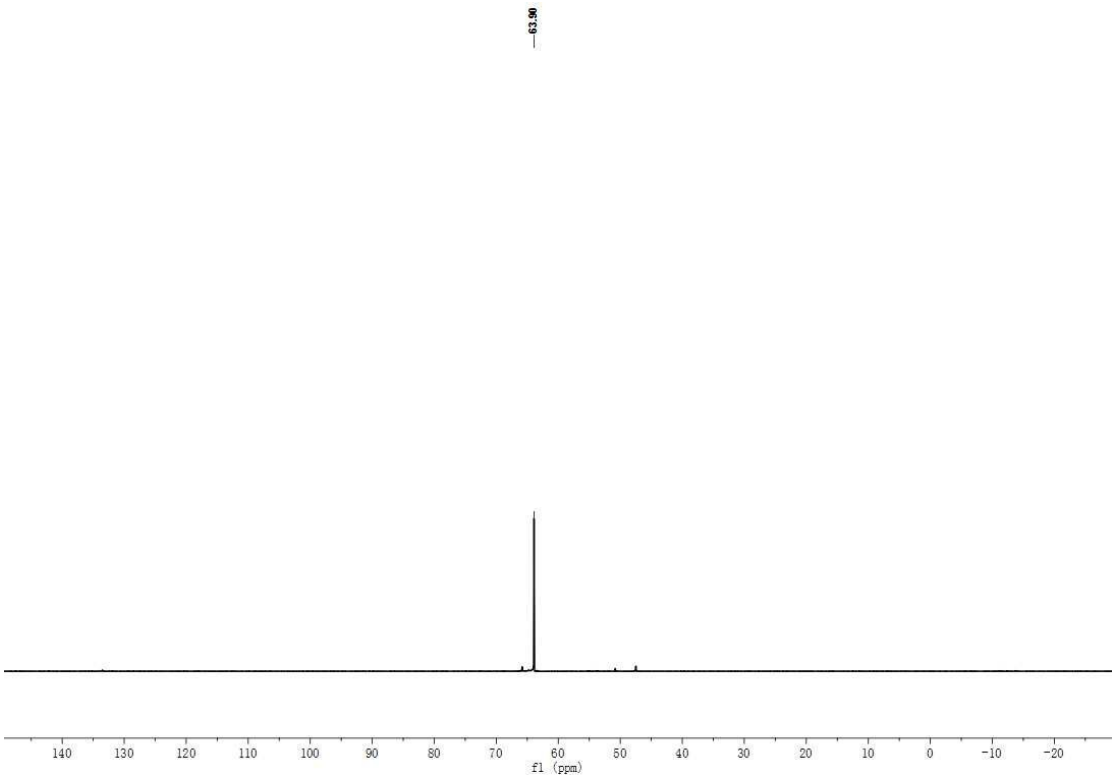


Figure S7. The $^{31}P\{^{1}H\}$ NMR (202 MHz) spectrum of compound **1** in C_6D_6.

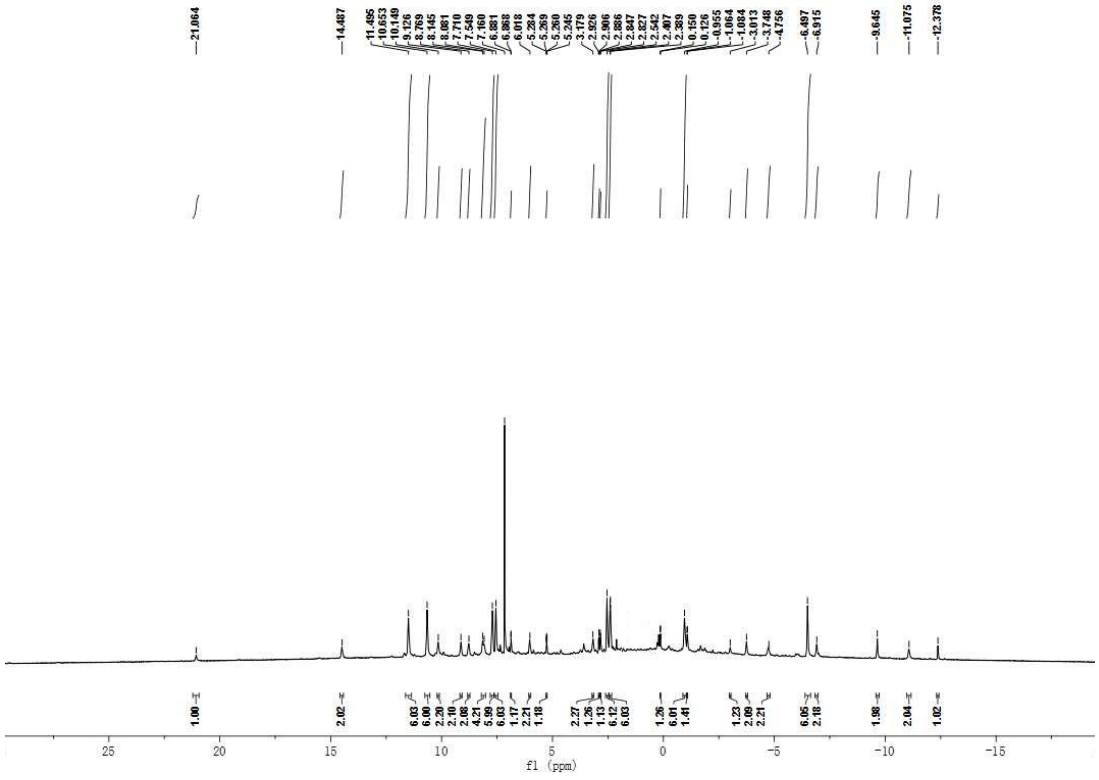


Figure S8. The ^{1}H NMR (400 MHz) spectrum of complex **2** in C_6D_6.

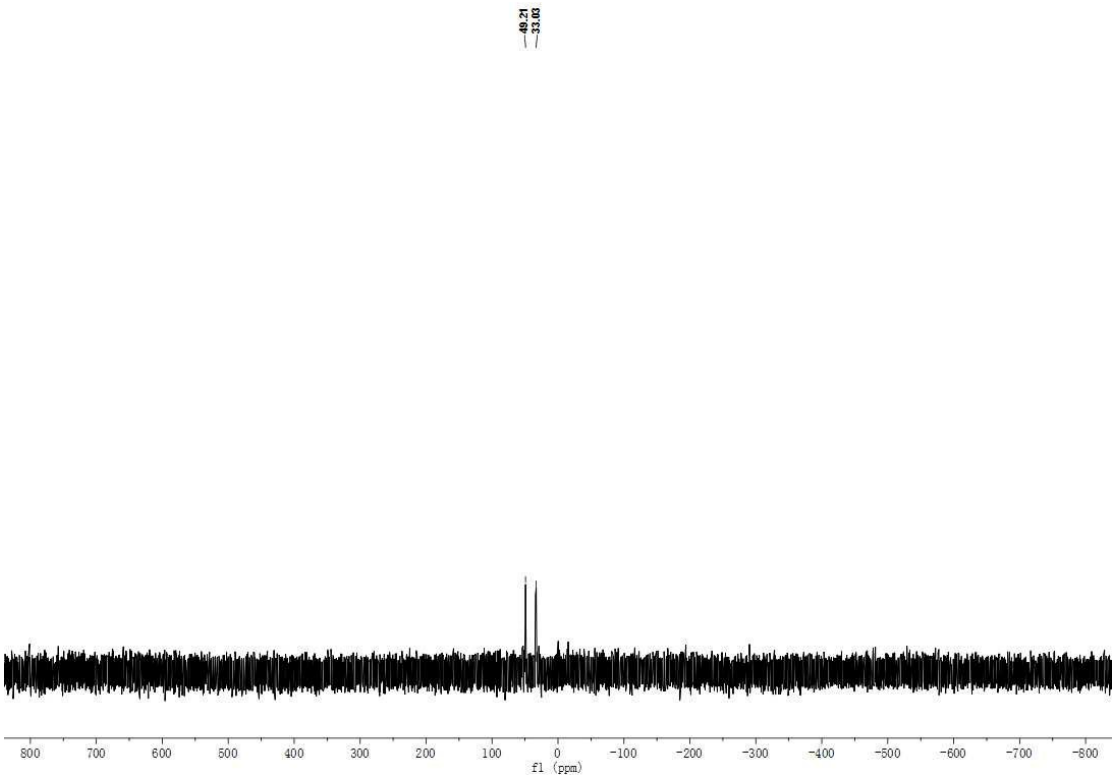


Figure S9. The $^{31}P\{^{1}H\}$ NMR (162 MHz) spectrum of complex **2** in C_6D_6.

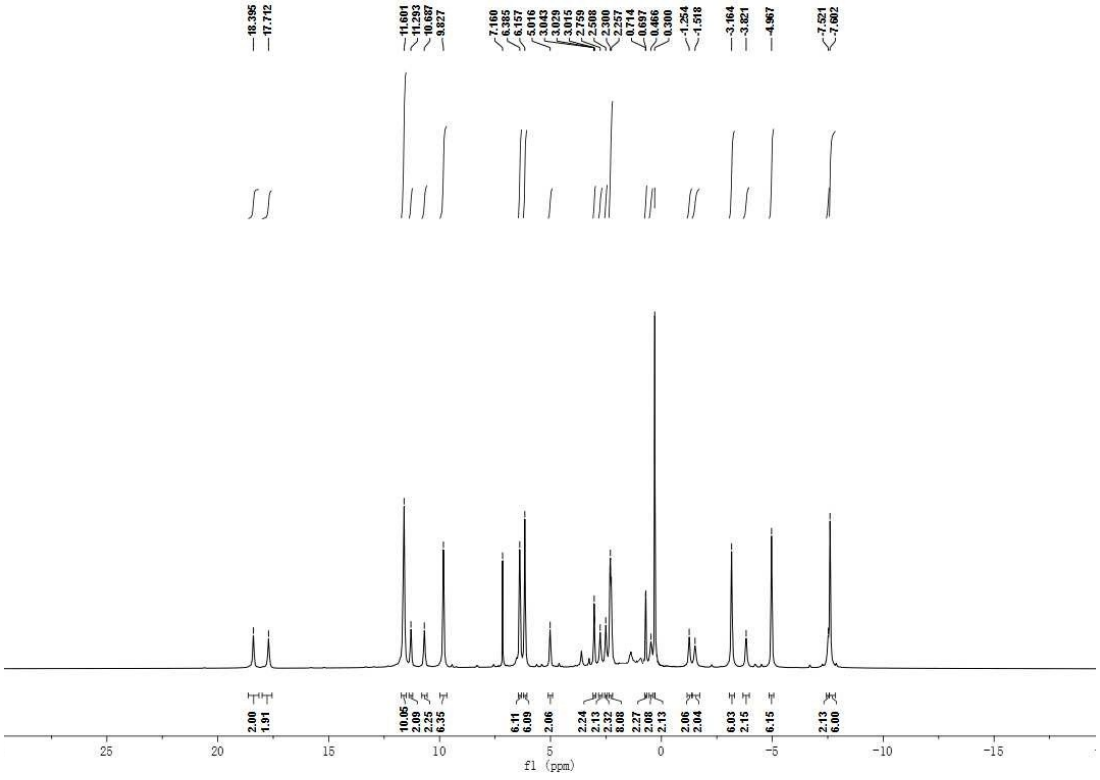


Figure S10. The ^{1}H NMR (400 MHz) spectrum of complex **3** in C_6D_6.

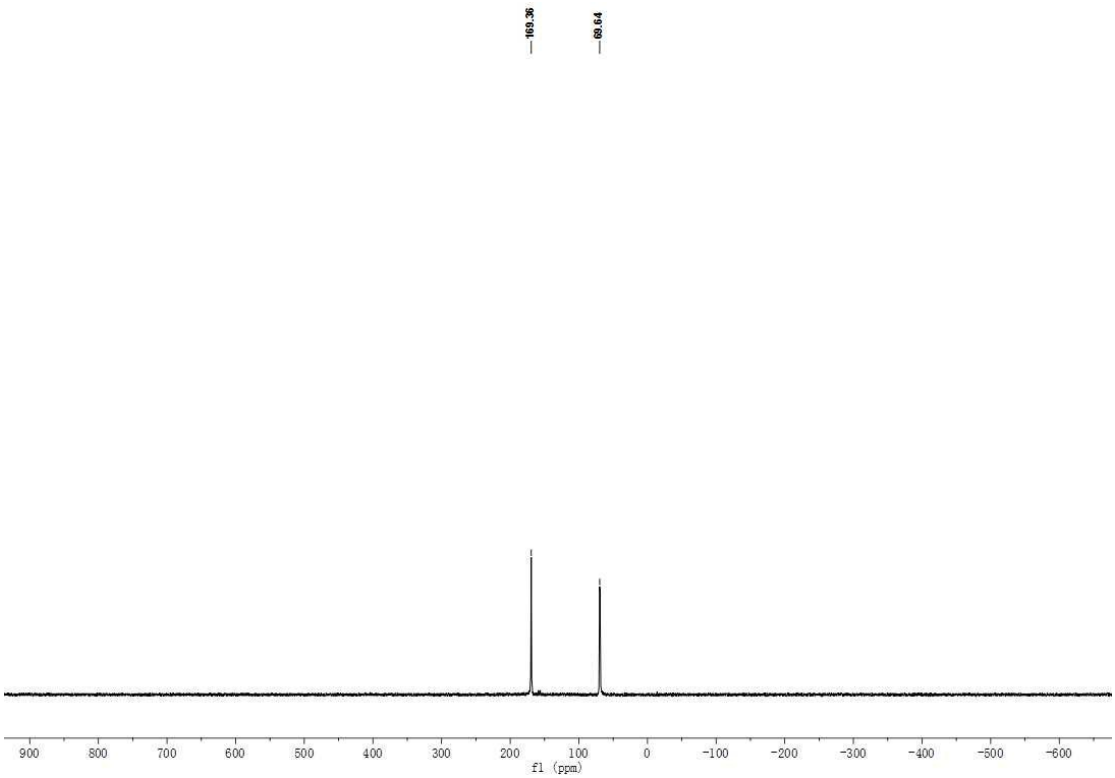


Figure S11. The $^{31}P\{^{1}H\}$ NMR (162 MHz) spectrum of complex **3** in C_6D_6.

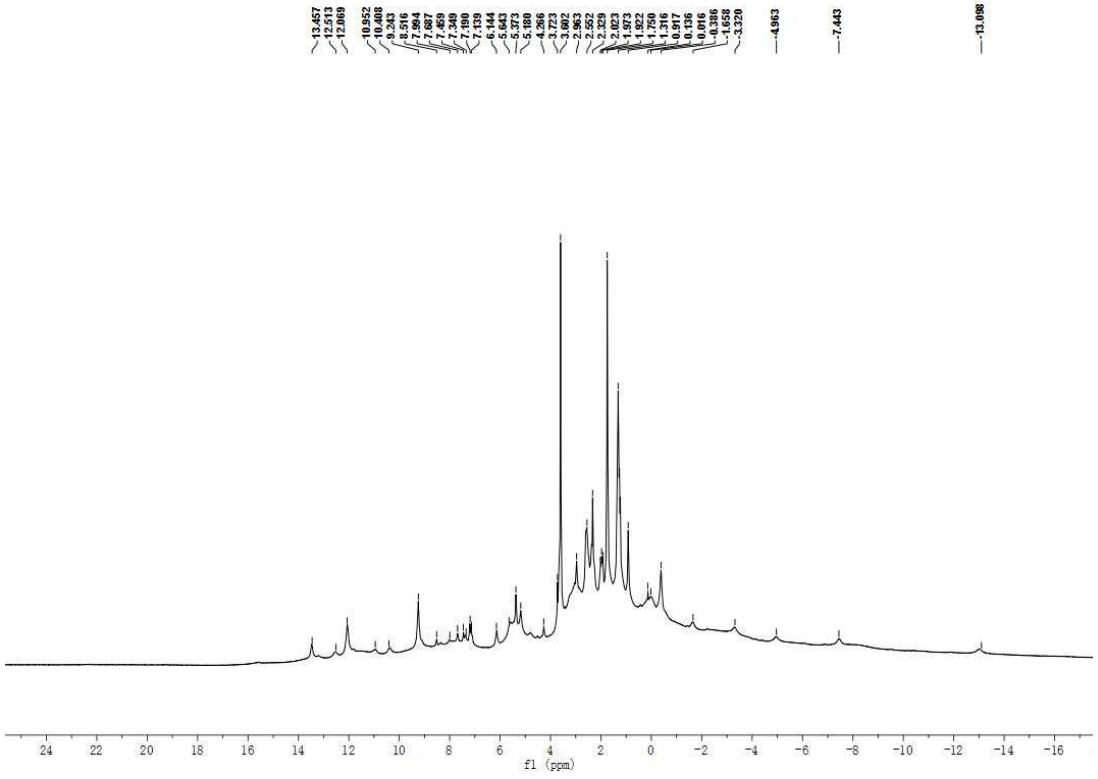


Figure S12. The ^{1}H NMR (400 MHz) spectrum of complex **4** in THF-d_8.

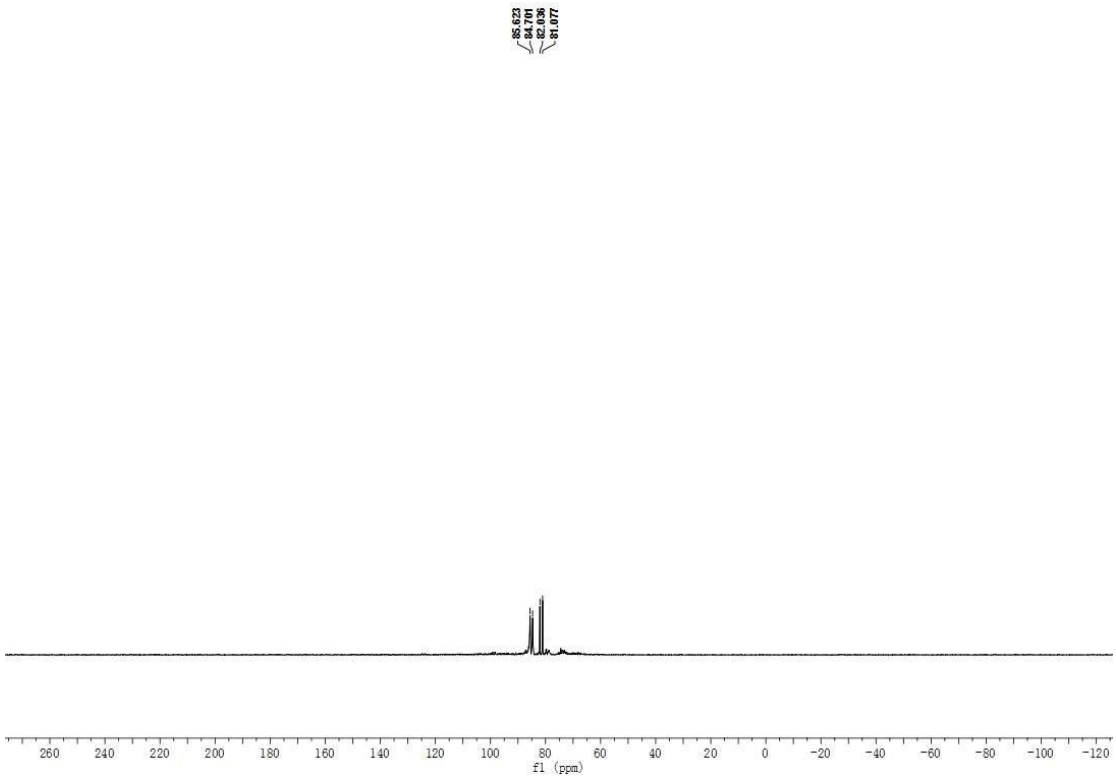


Figure S13. The $^{31}P\{^{1}H\}$ NMR (162 MHz) spectrum of complex **4** in THF-d_8.

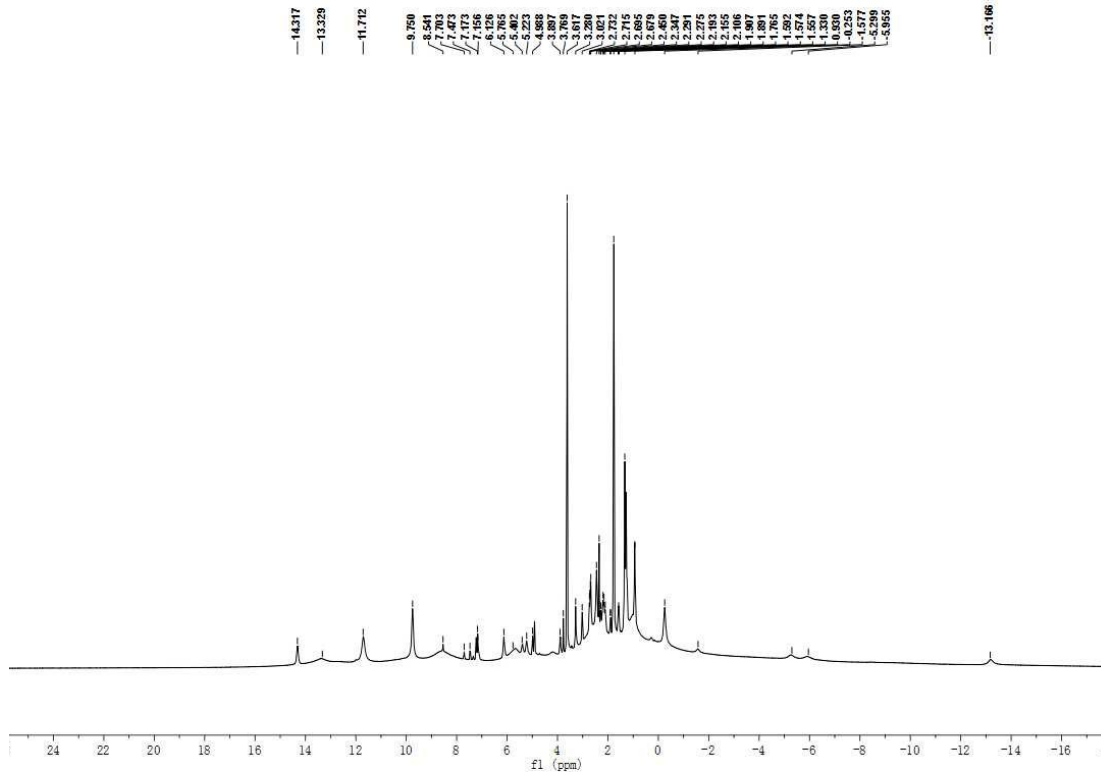


Figure S14. The ^{1}H NMR (400 MHz) spectrum of complex **5** in THF-d_8.

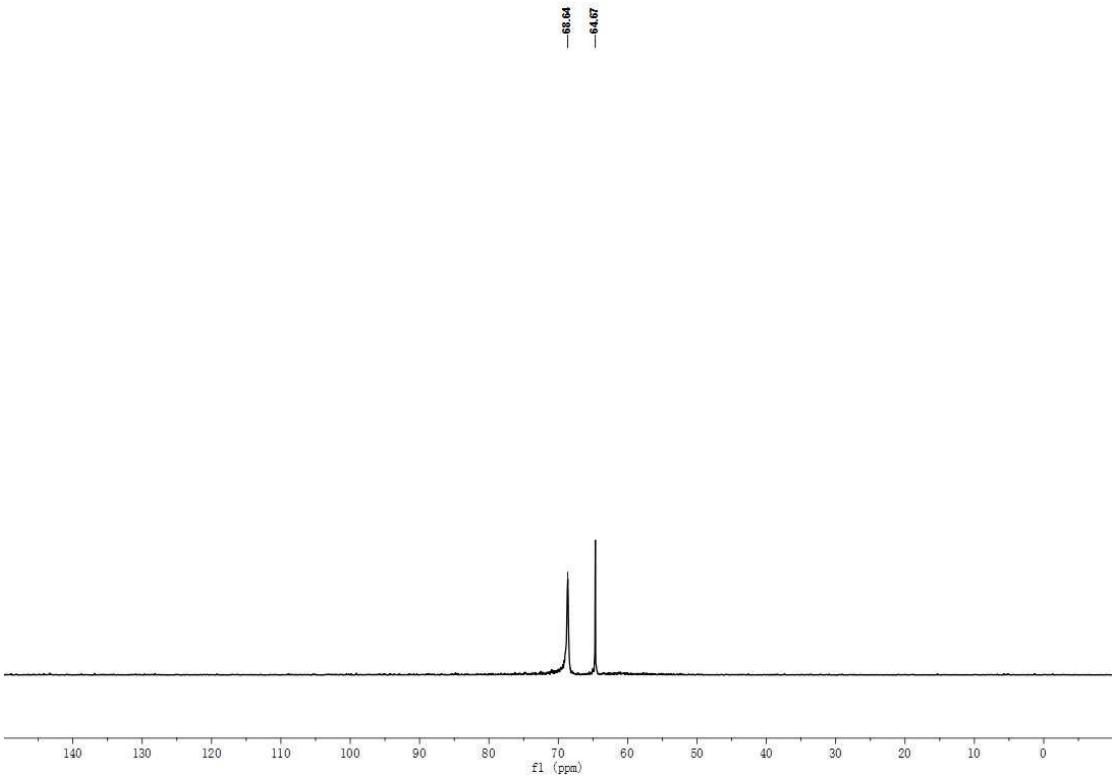


Figure S15. The $^{31}P\{^{1}H\}$ NMR (162 MHz) spectrum of complex **5** in THF-d_8.

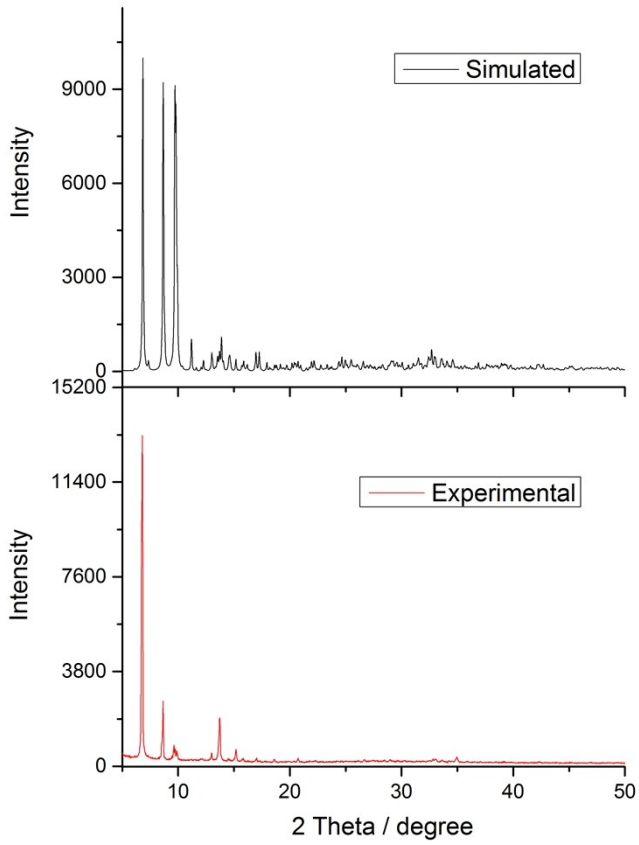


Figure S16. Experimental and calculated powder X-ray diffraction patterns for **4**.

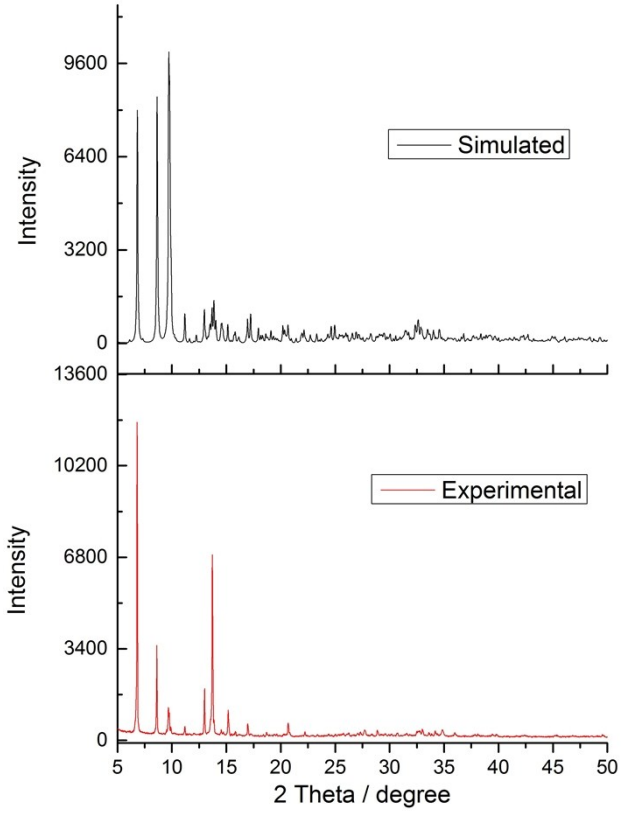


Figure S17. Experimental and calculated powder X-ray diffraction patterns for **5**.

4. References

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