Electronic Supplementary Material (ESI) for Dalton Transactions.

From carbones to carbenes and ylides in the coordination sphere of iridium

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1. Experimental Procedures and Spectra

Materials and Methods

All experiments were carried out under an atmosphere of purified argon or nitrogen in the MBraun glove boxes LABmaster 130 and UNIlab or using standard Schlenk techniques.
THF was dried over Na/K alloy, dichloromethane and chloroform were dried over CaH_2. After drying, solvents were stored over appropriate molecular sieves. Deuterated solvents were degassed with freeze-pump-thaw cycles and stored over appropriate molecular sieves under argon atmosphere.
^{1}H, ^{13}C, ^{11}B and ^{31}P NMR spectra were recorded using Bruker Avance HD 250, 300 A, DRX 400, DRX 500 and Avance 500 NMR spectrometers at 300 K. ^{1}H and ^{13}C $\{^{1}H\}$, ^{13}C-APT (attached proton test) NMR chemical shifts are reported in ppm downfield from tetramethylsilane. The resonance of the residual protons in the deuterated solvent was used as internal standard for ^{1}H NMR spectra. The solvent peak of the deuterated solvent was used as internal standard for ^{13}C NMR spectra. The assignment of resonances in ^{1}H and ^{13}C NMR spectra was further supported by ^{1}H COSY and ^{1}H,^{13}C HMQC NMR spectra. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85 % solution of phosphoric acid in D_2O. The following abbreviations are used for the description of NMR data: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet).
FT-IR spectra were recorded by attenuated total reflection of the solid samples on a Bruker Tensor IF37 spectrometer. The intensity of the absorption band is indicated as w (weak), m (medium), s (strong), vs (very strong) and br (broad).
HR-ESI mass spectra were acquired with a LTQ-FT mass spectrometer (Thermo Fisher Scientific). The resolution was set to 100.000.
Bis(diphenylphosphino)methane (dppm) was synthesized following the procedure published by K. Sommer.[1] $[HC(dppm)_2]Cl$ was synthesized according to the literature by Peringer and coworkers.[2]

Synthesis of complex 2

Complex **2** was prepared according to a previously reported procedure.[3] $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2, 25 °C): δ = 1.9 (t, J_{PP} = 32.9 Hz, 2P), 25.7 (t, J_{PP} = 33.6 Hz, 2P) ppm. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = -23.95 (t, 1H, $^{2}J_{PH}$ = 12.6 Hz, Ir-*H*), 3.82 (dt, 2H, $^{2}J_{HH}$ = 13.6 Hz, $^{2}J_{PH}$ = 3.6 Hz, P-C*H*H-P), 4.16-4.33 (m, 2H, P-CH*H*-P), 6.91-7.07 (m, 8H, phenyl-*H*), 7.11-7.32 (m, 20H, phenyl-*H*), 7.33-7.40 (m superimposed, 4H, phenyl-*H*), 7.77-7.87 (m, 4H, phenyl-*H*), 7.95-8.06 (m, 4H, phenyl-*H*) ppm. Only resonances that are changing upon ^{31}P-decoupling are reported in the $^{1}H\{^{31}P\}$ NMR spectra. $^{1}H\{^{31}P\}$ NMR (300 MHz, CD_2Cl_2, 25 °C, o2p = 25.7 ppm): δ = 4.24 (dt, 2H, $^{2}J_{HH}$ = 13.5 Hz, $^{2}J_{PH}$ = 4.0 Hz, P-CH*H*-P) ppm. $^{1}H\{^{31}P\}$ NMR (300 MHz, CD_2Cl_2, 25 °C, o2p = 1.9 ppm): δ = -23.96 (s, 1H, Ir-*H*), 3.82 (d, 2H, $^{2}J_{HH}$ = 13.5 Hz, P-C*H*H-P), 4.17-4.30 (m, 2H, P-CH*H*-P), 7.79-7.84 (m, 4H, phenyl-*H*), 7.98-8.03 (m, 4H, phenyl-*H*) ppm. $^{13}C\{^{1}H\}$ NMR (125.7 MHz, CD2Cl2, 27 °C): δ = -31.4 (tt, $^{1}J_{PC}$ = 92.7 Hz, $^{2}J_{PC}$ = 3.1 Hz, P-C-P), 39.1 (m, P-CH2-P), 127.9-128.3 (superimposed, phenyl-C), 128.4 (t, J_{PC} = 5.8 Hz, phenyl-C), 130.1 (d, J_{PC} = 30.4 Hz, phenyl-C), 130.0 (s, phenyl-C), 130.3 (s, phenyl-C), 131.2 (s, phenyl-C), 131.4 (s, phenyl-C), 132.9 (t, JPC = 5.2 Hz, phenyl-C), 133.3 (t, J_{PC} = 4.9 Hz, phenyl-C), 133.9 (t, J_{PC} = 5.7 Hz, phenyl-C), 134.1 (t, J_{PC} = 7.1 Hz, phenyl-C) ppm. IR (ATR): $\tilde{\vartheta}$ = 3047 (w), 2960 (w), 2900 (w), 2240 (w), 1623 (m), 1578 (s), 1481 (w), 1432 (w), 1360 (w), 1312 (w), 1262 (w), 1189 (w), 1132 (s), 1097 (s), 1026 (m), 999 (m), 912 (w), 830 (m), 775 (s), 730 (s), 690 (s), 527 (m), 498 (s), 476 (s), 413 (w) cm^{-1}.HR-MS (LIFDI^{+}, CH_2Cl_2): m/z = 975.2265 $[\{(dppm)_2CH\}Ir(H)]^{+}$ measured; 975.2179 calculated, Δ = 8.82 ppm.

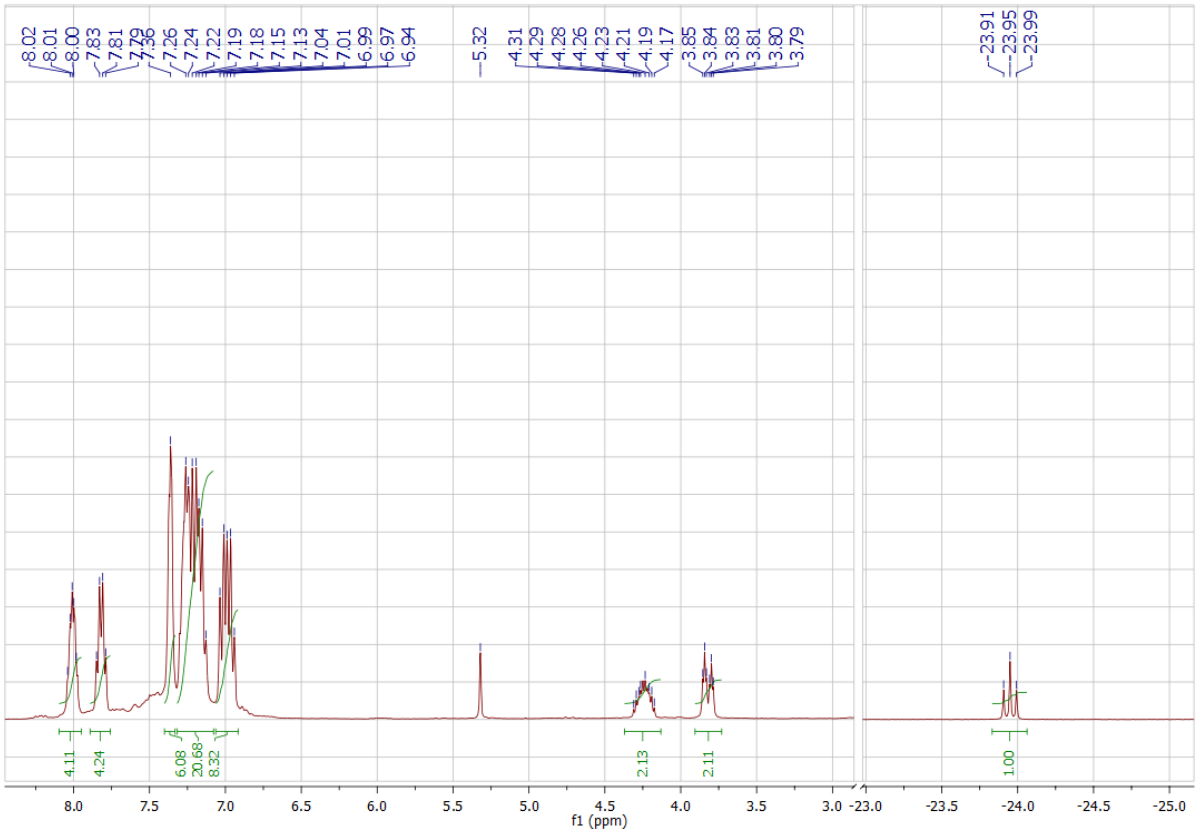

Figure 1 ^{1}H NMR spectrum of [({dppm}$_2$C)IrCl$_2$(H)] (**2**) in CD_2Cl_2.

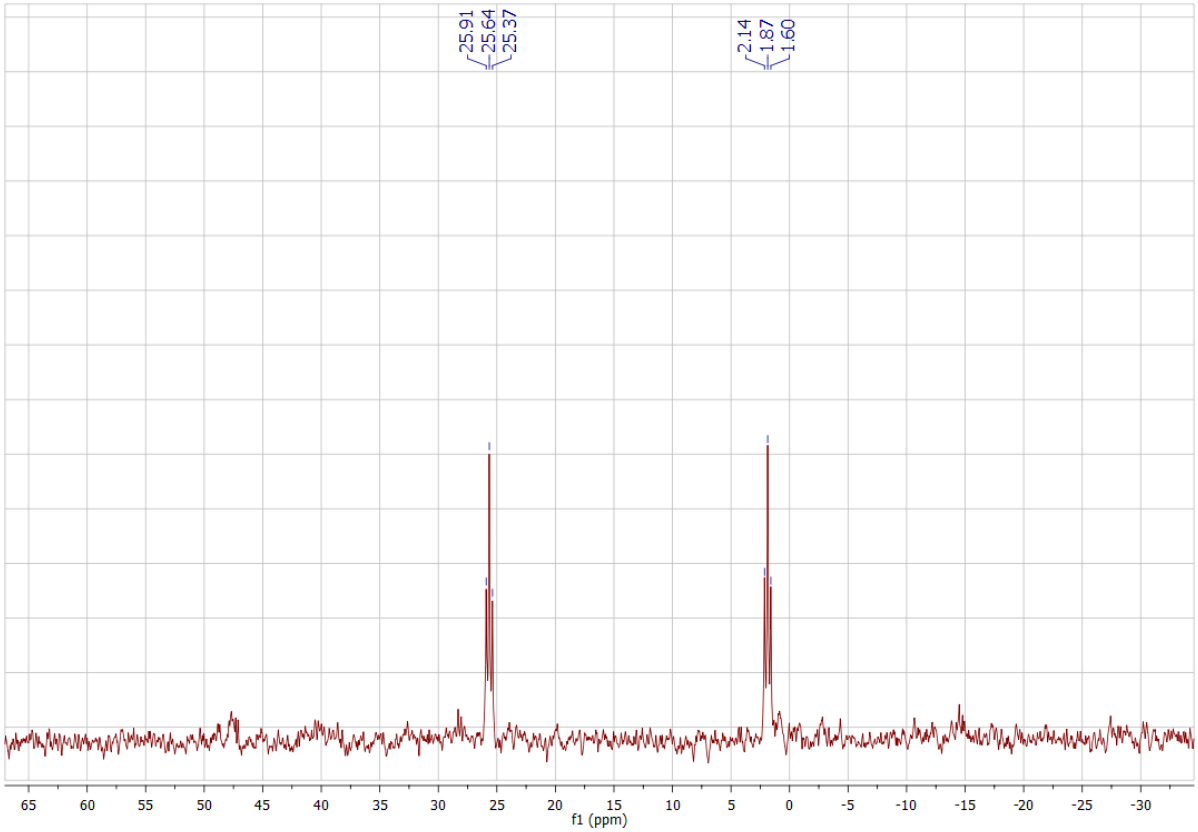

Figure 2 $^{31}P\{^{1}H\}$ NMR spectrum of [({dppm}$_2$C)IrCl$_2$(H)] (**2**) in CD_2Cl_2.

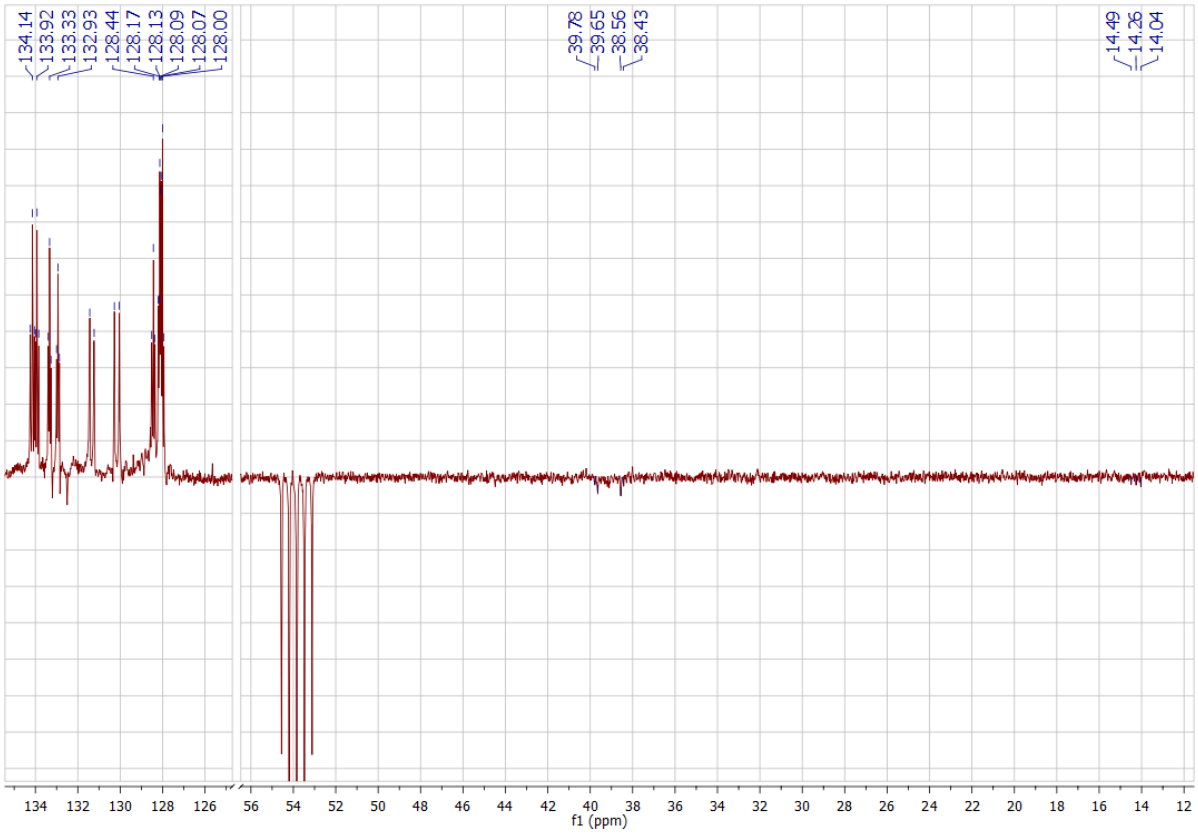

Figure 3 ^{13}C APT NMR spectrum of [({dppm}$_2$C)IrCl$_2$(H)] (**2**) in CD_2Cl_2.

Synthesis of Complex 3

50 mg of complex [({dppm}$_2$C)IrCl$_2$(H)] (**2**, 48 µmol) were dissolved in 8 mL $CHCl_3$ and heated to 55 °C for three hours. Continuous stirring at ambient temperature for further 2 days leads to full conversion of **2**, as indicated by ^{31}P{^{1}H} NMR spectroscopy. Removal of all volatiles *in vacuo* allowed for the isolation of 49 mg of [(Ph_2PCH_2P{Ph_2}CH_2)IrCl$_2$(dppm)]Cl (**3**, 45 µmol, 95% yield). Suitable single crystals for single crystal X-Ray diffraction were grown by recrystallization from THF. The assignment in the NMR spectra was confirmed by ^{1}H-COSY and ^{1}H,^{13}C-HSQC NMR spectra. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 25 °C): δ = -64.0 (dd, J_{PP} = 38.9 Hz, J_{PP} = 16.5 Hz, 1P), -63.9 (ddd, J_{PP} = 445.0 Hz, J_{PP} = 38.1 Hz, J_{PP} = 22.4 Hz, 1P), -2.2 (ddd, J_{PP} = 444.7 Hz, J_{PP} = 52.7 Hz, J_{PP} = 16.1 Hz, 1P), 47.8 (dd, J_{PP} = 52.4 Hz, J_{PP} = 22.4 Hz, 1P) ppm. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 2.36 (m, 1H, P-C*H*H-Ir), 2.88 (m, 1H, P-CH*H*-Ir), 3.90 (dt, 1H, $^2J_{HH}$ = 15.1 Hz, $^2J_{PH}$ = 10.0 Hz, P-C*H*^{1}H^2-P), 4.74 (dt, 1H, $^2J_{HH}$ = 16.2 Hz, $^2J_{PH}$ = 12.3 Hz, P-C*H*^{3}H^4-P), 5.37 (td superimposed, 1H, $^2J_{PH}$ = 15.4 Hz, $^2J_{HH}$ = 11.2 Hz, P-CH^1*H*^{2}-P), 6.06 (m, 1H, P-CH^3*H*^{4}-P), 6.89 (m, 4H, phenyl-*H*), 7.17-7.33 (m superimposed, 12 H, phenyl-*H*), 7.38-7.52 (m superimposed, 12 H, phenyl-*H*), 7.60 (br m, 4H, phenyl-*H*), 7.73 (dd, 2H, J_{PH} = 13.1 Hz, J_{HH} = 7.8 Hz, phenyl-*H*), 8.05 (m, 4H, phenyl-*H*), 8.24 (m, 2H, phenyl-*H*) ppm. Only resonances that are changing upon ^{31}P-decoupling are reported in the ^{1}H{^{31}P} NMR spectra. ^{1}H{^{31}P} NMR (300 MHz, CD_2Cl_2, 25 °C, o2p = 48 ppm): δ = 2.34 (dd, 1H, $^2J_{HH}$ = 13.9 Hz, $^2J_{PH}$ = 5.9 Hz, P-C*H*H-Ir), 2.89 (dt, 1H, $^2J_{HH}$ = 13.9 Hz, $^2J_{PH}$ = 6.0 Hz, P-CH*H*-Ir), 3.96 (dd, 1H, $^2J_{HH}$ = 15.4 Hz, $^2J_{PH}$ = 10.2 Hz, P-C*H*^{1}H^2-P), 5.51 (dd, 1H, $^2J_{HH}$ = 15.0 Hz, $^2J_{PH}$ = 10.6 Hz, P-CH^1*H*^{2}-P), 7.77 (d, 2H, J_{HH} = 7.7 Hz, phenyl-*H*) ppm. ^{1}H{^{31}P} NMR (300 MHz, CD_2Cl_2, 25 °C, o2p = 0 ppm): δ = 2.34 (m, 1H, P-C*H*H-Ir), 2.89 (m, 1H, P-CH*H*-Ir), 3.96 (dd, 1H, $^2J_{HH}$ = 15.1 Hz, $^2J_{PH}$ = 9.9 Hz, P-C*H*^{1}H^2-P), 5.51 (t, 1H, *J* = 14.7 Hz, P-CH^1*H*^{2}-P), 8.27 (d, 2H, $^3J_{HH}$ = 6.9 Hz, phenyl-*H*) ppm. ^{1}H{^{31}P} NMR (300 MHz, CD_2Cl_2, 25 °C, o2p = -64 ppm): δ = 2.34 (dd, 1H, $^2J_{HH}$ = 13.8 Hz, $^2J_{PH}$ = 11.0 Hz, P-C*H*H-Ir), 2.91 (td, 1H, *J* = 19.3 Hz, $^2J_{PH}$ = 6.1 Hz, P-CH*H*-Ir), 4.75 (d, 1H, $^2J_{HH}$ = 16.2 Hz, P-C*H*^{3}H^4-P), 6.07 (dd, 1H, $^2J_{HH}$ = 16.2 Hz, J_{PH} = 2.5 Hz, P-CH^3*H*^{4}-P), 6.91 (d, 4H, J_{HH} = 7.4 Hz, phenyl-*H*) ppm. ^{13}C APT NMR (125.8 MHz, CD_2Cl_2, 25

°C): δ = -14.1 (d, $^1J_{PC}$ = 37.2 Hz, P-*C*H$_2$-Ir), 29.6 (dd, $^1J_{PC}$ = 60.9 Hz, $^1J_{PC}$ = 23.6 Hz, P-*C*H$_2$-P), 44.3 (dd, $^1J_{PC}$ = 34.1 Hz, $^1J_{PC}$ = 28.6 Hz, P-*C*H$_2$-P), 124.4 (d, J_{PC} = 3.6 Hz, phenyl-*C*), 125.0 (t, J_{PC} = 3.6 Hz, phenyl-*C*), 125.7 (d, J_{PC} = 3.6 Hz, phenyl-*C*), 126.5 (s, phenyl-*C*), 126.9 (s, phenyl-*C*), 127.4 (d, J_{PC} = 10.9 Hz, phenyl-*C*), 127.7 (d, J_{PC} = 10.9 Hz, phenyl-*C*), 127.9 (d, J_{PC} = 11.8 Hz, phenyl-*C*), 128.1 (d, J_{PC} = 10.9 Hz, phenyl-*C*), 128.5 (d, J_{PC} = 12.7 Hz, phenyl-*C*),128.6 (d, J_{PC} = 10.9 Hz, phenyl-*C*), 128.9 (dd, J_{PC} = 15.0 Hz, J_{PC} = 10.4 Hz, phenyl-*C*), 129.2 (d, J_{PC} = 8.2 Hz, phenyl-*C*), 129.6 (d, J_{PC} = 12.7 Hz, phenyl-*C*), 129.8 (d, J_{PC} = 10.0 Hz, phenyl-*C*), 130.1 (t, J_{PC} = 10.4 Hz, phenyl-*C*), 130.5 (d, J_{PC} = 9.1 Hz, phenyl-*C*), 130.7 (d, J_{PC} = 8.2 Hz, phenyl-*C*), 131.5 (d, J_{PC} = 9.1 Hz, phenyl-*C*), 131.6 (d, J_{PC} = 1.8 Hz, phenyl-*C*), 131.6 (d, J_{PC} = 1.8 Hz, phenyl-*C*), 131.8 (d, J_{PC} = 2.7 Hz, phenyl-*C*), 132.0 (d, J_{PC} = 2.7 Hz, phenyl-*C*), 132.1 (d, J_{PC} = 9.1 Hz, phenyl-*C*), 132.2 (d, J_{PC} = 9.9 Hz, phenyl-*C*), 132.7 (d, J_{PC} = 8.2 Hz, phenyl-*C*), 132.7 (d superimposed, J_{PC} = 9.9 Hz, phenyl-*C*), 132.9 (d, J_{PC} = 10.0 Hz, phenyl-*C*), 133.5 (d, J_{PC} = 7.3 Hz, phenyl-*C*), 133.7 (d, J_{PC} = 3.6 Hz, phenyl-*C*), 133.8 (d, J_{PC} = 2.7 Hz, phenyl-*C*), 134.4 (d, J_{PC} = 9.1 Hz, phenyl-*C*), 134.7 (d, J_{PC} = 10.0 Hz, phenyl-*C*), 134.9 (d, J_{PC} = 9.1 Hz, phenyl-*C*), 134.9 (d superimposed, J_{PC} = 10.0 Hz, phenyl-*C*), 136.9 (s, phenyl-*C*), 137.7 (s, phenyl-*C*),141.1 (s, phenyl-*C*),141.8 (s, phenyl-*C*) ppm. HR-MS (ESI$^+$, CH_2Cl_2): m/z = 1045.1551 [(dppm)(dppmCH$_2$)IrCl$_2$]$^+$ measured; 1045.1540 calculated, Δ = 1.05 ppm. IR (ATR): $\tilde{\vartheta}$ = 3050 (w), 2956 (w), 2920 (w), 2856 (w), 1628 (w), 1579 (w), 1481 (w), 1431 (m), 1357 (w), 1262 (w), 1157 (m), 1095 (s), 1025 (w), 999 (w), 952 (w), 834 (m), 731 (s), 688 (s), 508 (s), 479 (s), 435 (w) cm^{-1}.

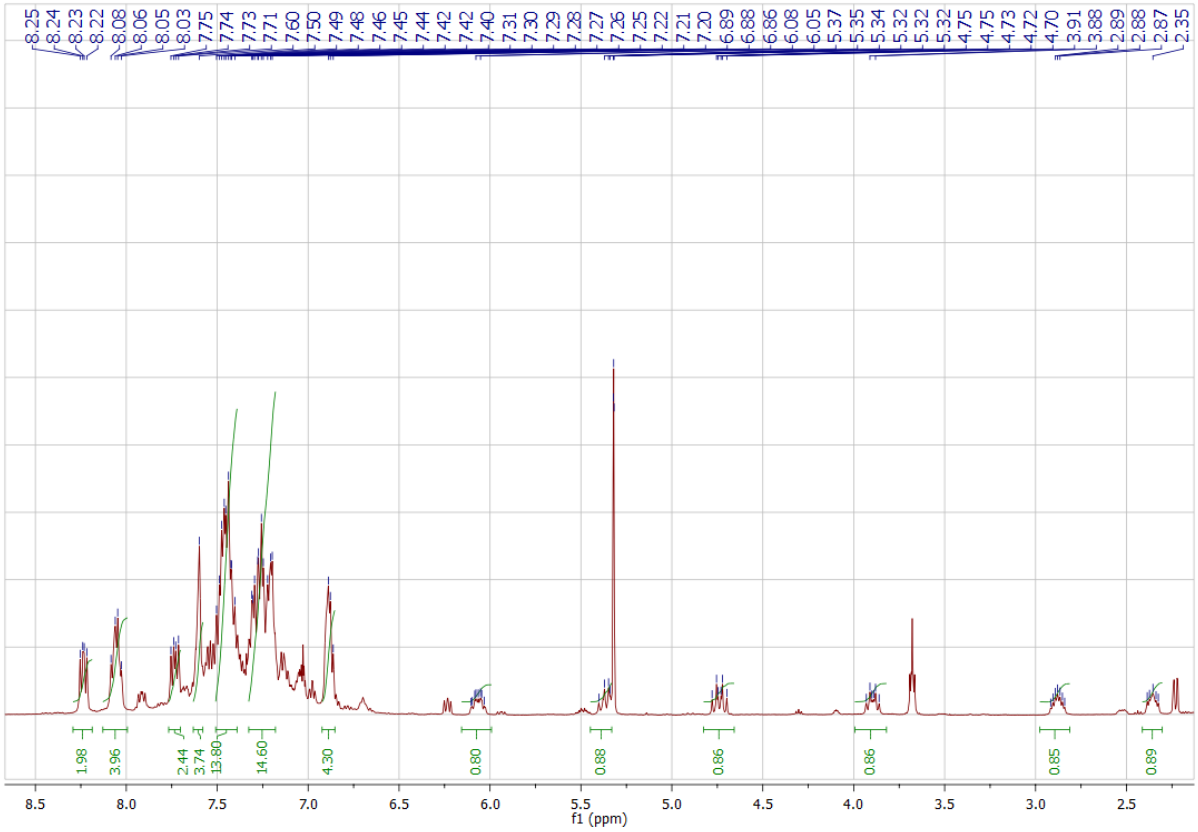

Figure 4 ^{1}H NMR spectrum of [(Ph$_2$PCH$_2$P{Ph$_2$}CH$_2$)IrCl$_2$(dppm)]Cl (**3**) in CD_2Cl_2.

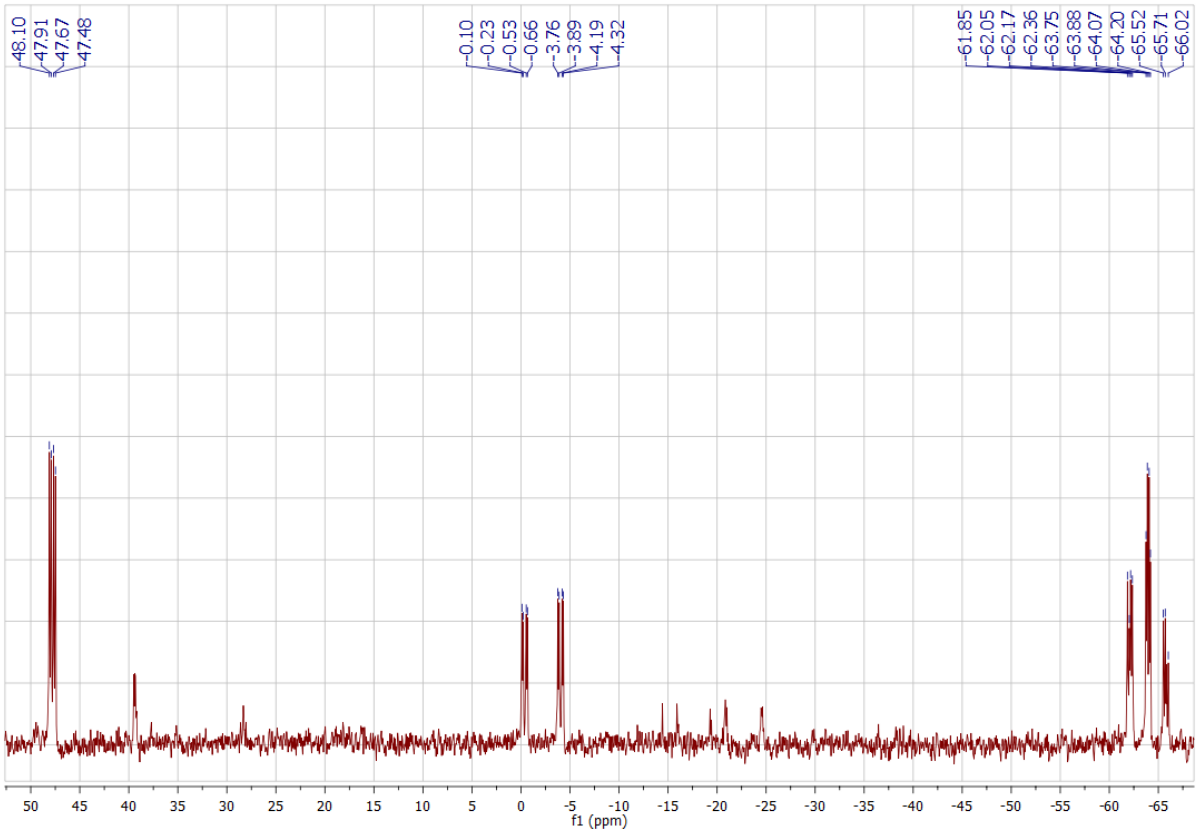

Figure 5 $^{31}P\{^{1}H\}$ NMR spectrum of $[(Ph_2PCH_2P\{Ph_2\}CH_2)IrCl_2(dppm)]Cl$ (**3**) in CD_2Cl_2.

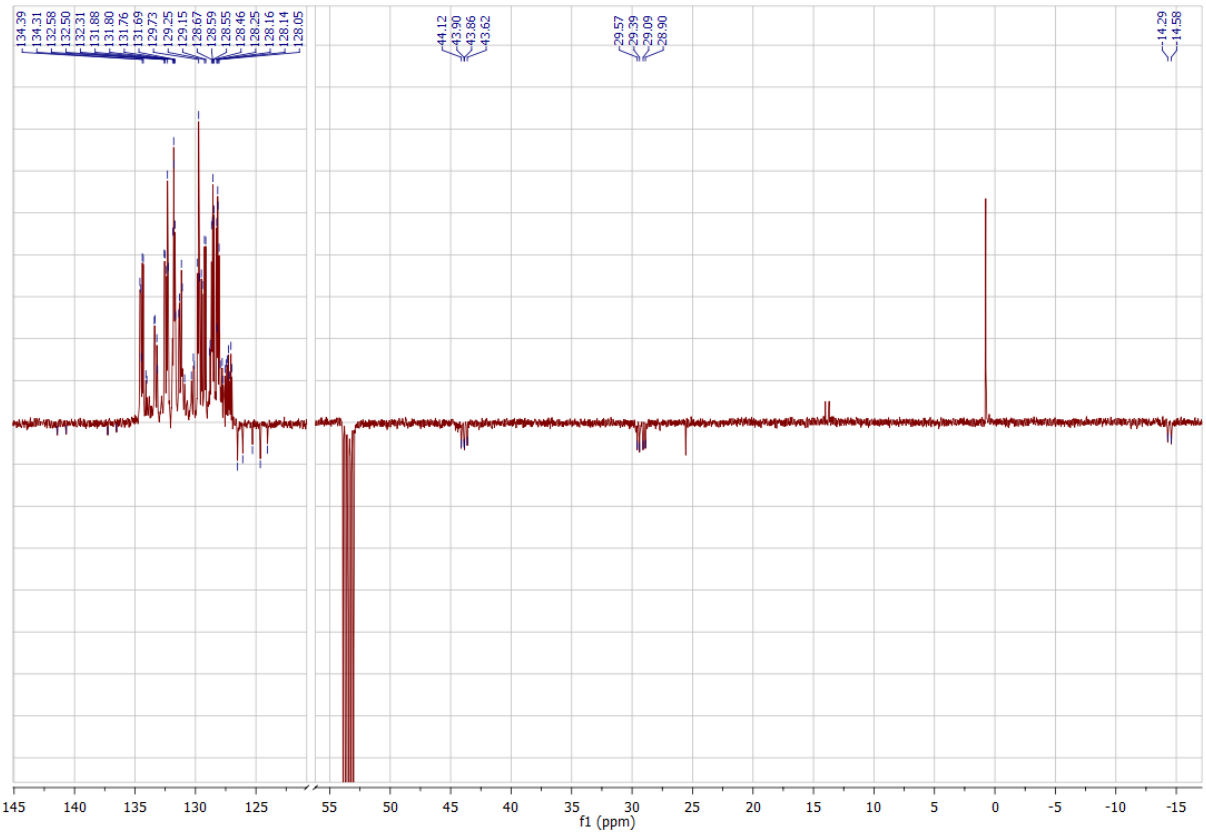

Figure 6 ^{13}C APT NMR spectrum of $[(Ph_2PCH_2P\{Ph_2\}CH_2)IrCl_2(dppm)]Cl$ (**3**) in CD_2Cl_2.

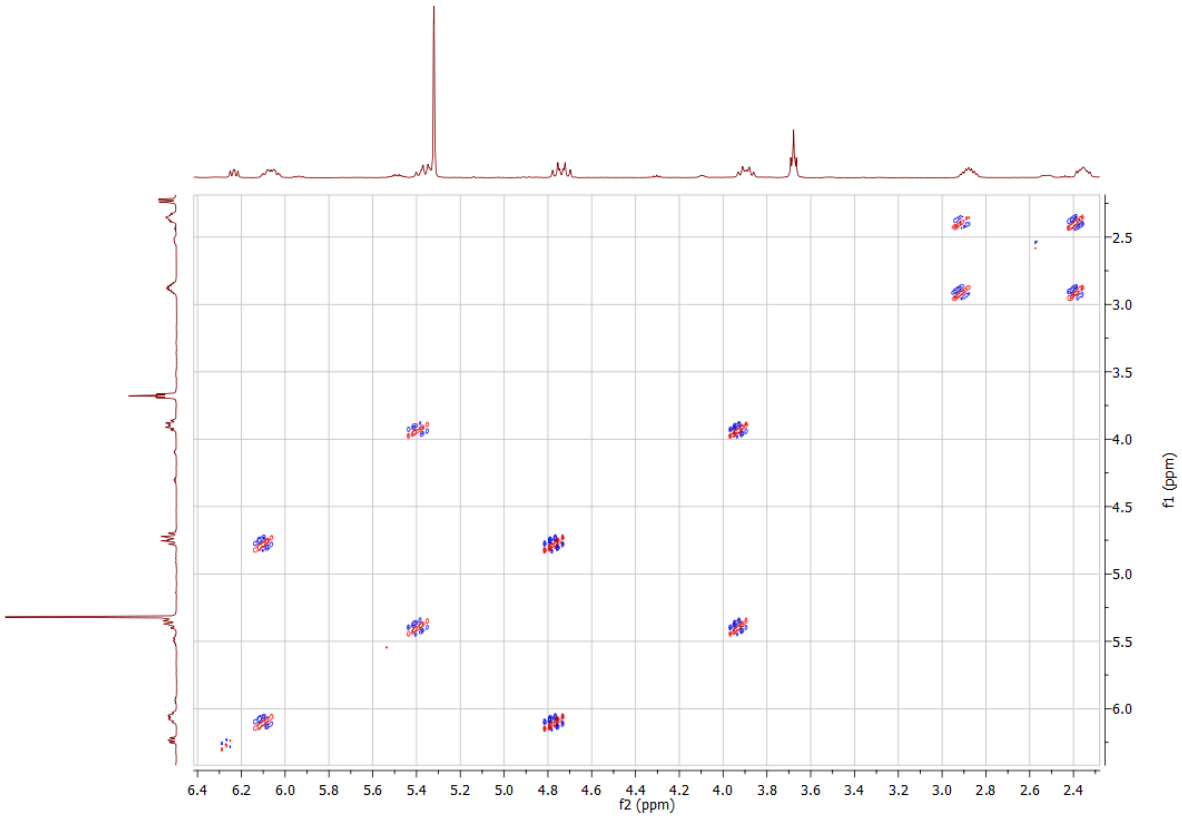

Figure 7 ^{1}H-COSY NMR spectrum of [($Ph_2PCH_2P\{Ph_2\}CH_2$)$IrCl_2$(dppm)]Cl (**3**) in CD_2Cl_2.

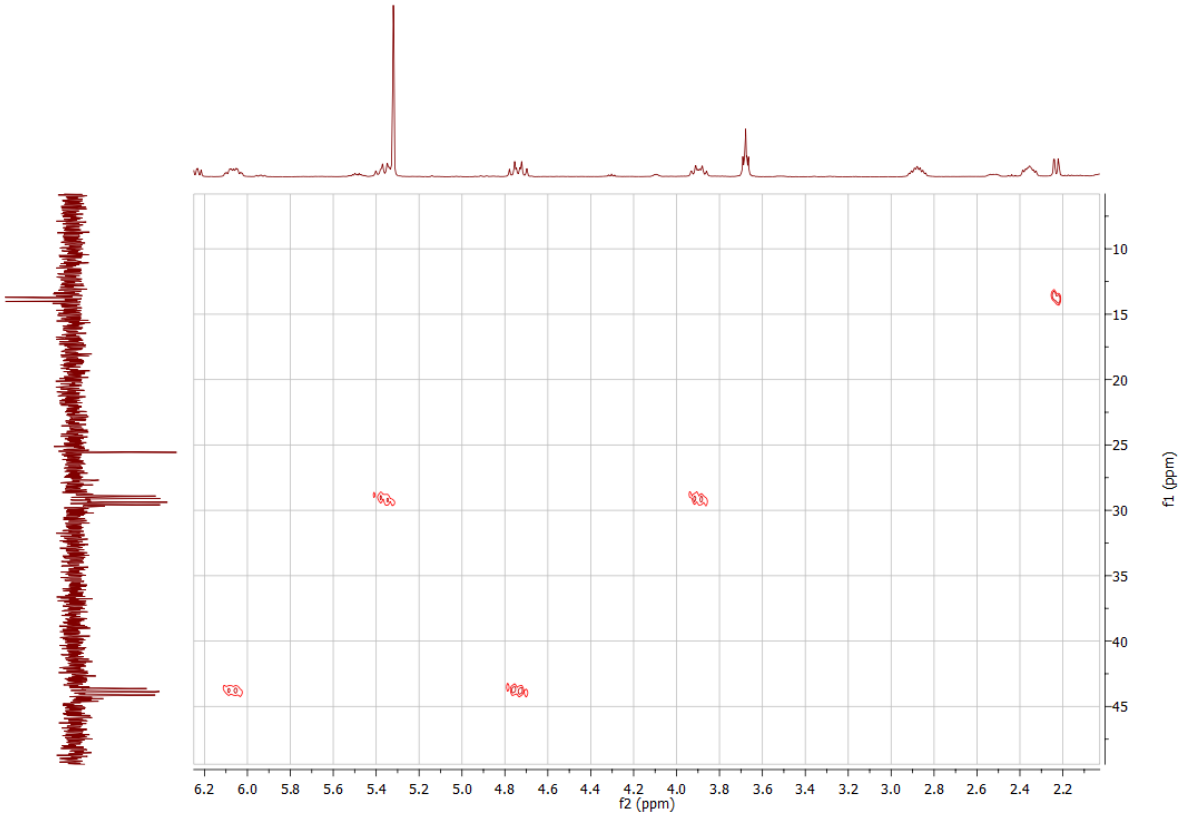

Figure 8 ^{1}H,^{13}C-HSQC NMR spectrum of [($Ph_2PCH_2P\{Ph_2\}CH_2$)$IrCl_2$(dppm)]Cl (**3**) in CD_2Cl_2.

Synthesis of complex 4

Complex **4** has been synthesized my modification of a previously reported procedure, using one equivalent of $HCl{\cdot}OEt_2$.[3] The identity of **4** was confirmed by multi-nuclear NMR spectroscopy: $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 25 °C): δ = -4.3 (td, J_{PP} = 47.1 Hz, J_{PP} = 3.0 Hz, 2P), 45.0 (t, J_{PP} = 30.7 Hz, 2P) ppm. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = -21.86 (t, 1H, $^2J_{PH}$ = 13.5 Hz, Ir-*H*), 4.37 (m, 2H, P-C*H*H-P), 5.04 (dt, 2H, *J* = 10.9 Hz, J_{PH} = 3.7 Hz, P-CH*H*-P), 5.39 (t, 1H, $^2J_{PH}$ = 19.0 Hz, P-C*H*-P), 7.13 (td, 4H, *J* = 7,6 Hz, *J* = 3.2 Hz, phenyl-*H*), 7.23-7.61 (m superimposed, 28H, phenyl-*H*), 7.94 (m, 8H, phenyl-*H*) ppm. Only resonances that are changing upon ^{31}P-decoupling are reported in the $^1H\{^{31}P\}$ NMR spectra.$^1H\{^{31}P\}$ NMR (300 MHz, CD_2Cl_2, 25 °C, o2p = 45 ppm): δ = 4.37 (dt, 2H, $^2J_{HH}$ = 15.2 Hz, $^2J_{PH}$ = 3.6 Hz, P-C*H*H-P), 5.04 (dt, 2H, $^2J_{HH}$ = 15.1 Hz, $^2J_{PH}$ = 3.1 Hz, P-CH*H*-P), 5.39 (s, 1H, P-C*H*-P), 7.13 (t, 4H, $^3J_{HH}$ = 7.7 Hz, phenyl-*H*), $^1H\{^{31}P\}$ NMR (300 MHz, CD_2Cl_2, 25 °C, o2p = -4 ppm): δ = -21.86 (s, 1H, Ir-*H*), 4.37 (dd, 2H, $^2J_{HH}$ = 14.8 Hz, J_{PH} = 12.7 Hz, P-C*H*H-P), 5.04 (dd, 2H, $^2J_{HH}$ = 15.0 Hz, J_{PH} = 6.3 Hz, P-CH*H*-P), 7.94 (br m, 8H, *J* = 6.8 Hz, phenyl-H) ppm.

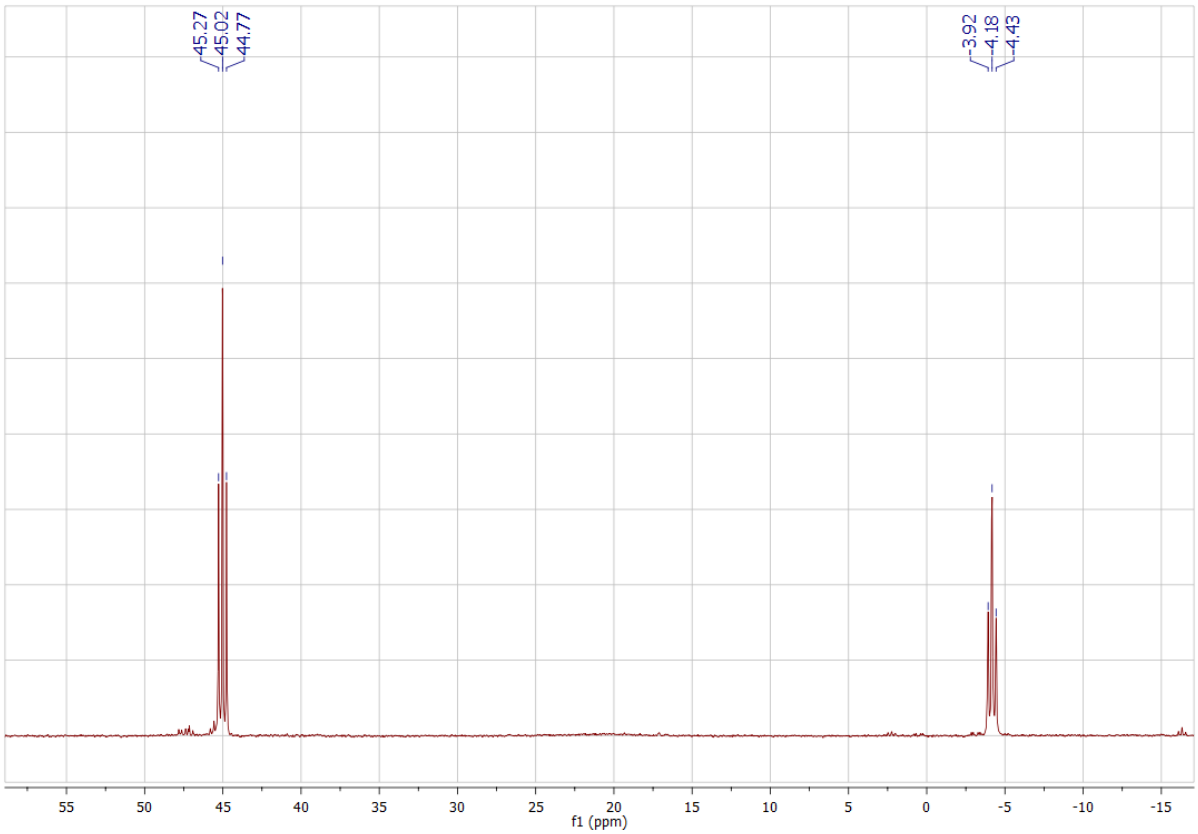

Figure 9 $^{31}P\{^1H\}$ NMR spectrum of of $[(\{dppm\}_2CH)IrCl_2(H)]Cl$ (**4**) in CD_2Cl_2.

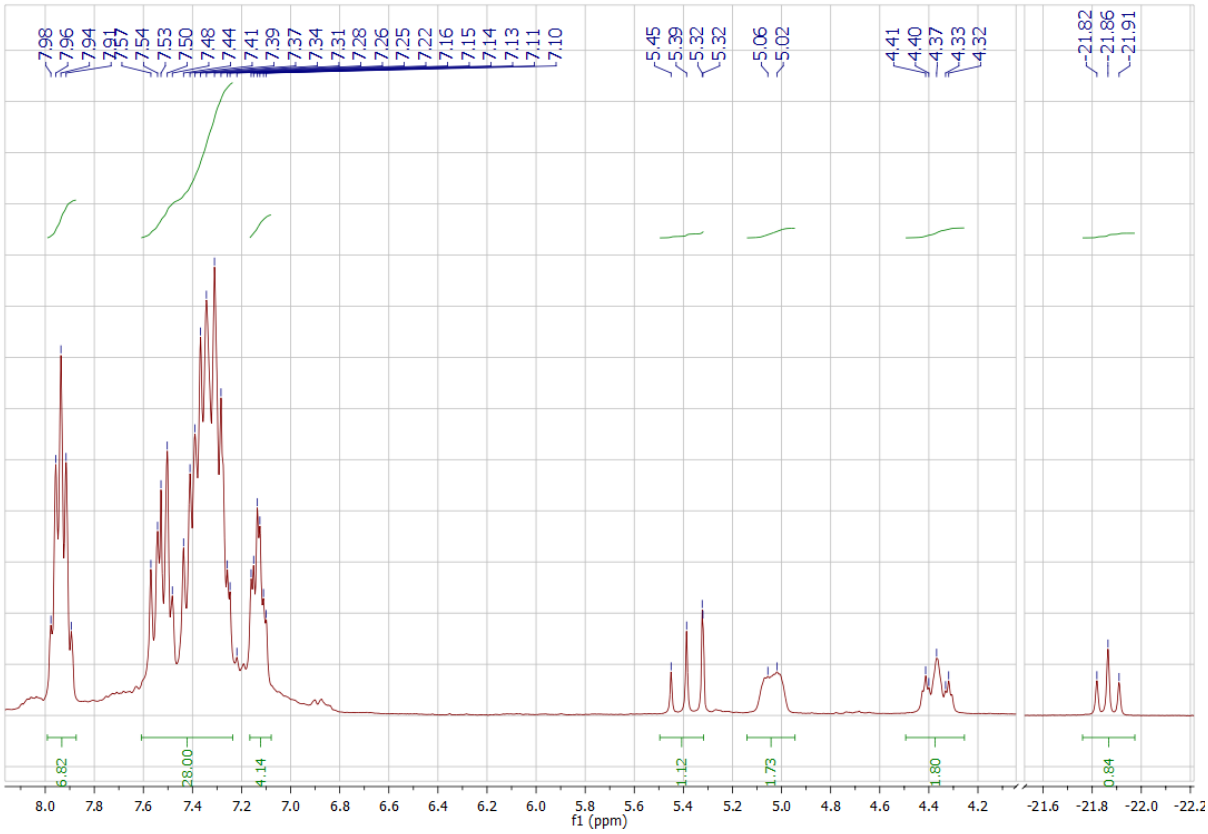

Figure 10 ^{1}H NMR spectrum of of [({dppm}$_2$CH)IrCl$_2$(H)]Cl (**4**) in CD_2Cl_2.

Formation of intermediate 5

The intermediate **5** was detected in a mixture with complex **3** after stirring complex **2** for days in CHCl3 at ambient temperature. It was analyzed in solution using multinuclear NMR spectroscopy. Assignments are based on ^{1}H-COSY and ^{1}H,^{13}C-HSQC NMR data. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = -66.6 (dd, J_{PP} = 30.9 Hz, J_{PP} = 16.4 Hz, 1P), -56.9 (dt, J_{PP} = 428.7 Hz, J_{PP} = 32.7 Hz, 1P), -6.2 (ddd, J_{PP} = 428.7 Hz, J_{PP} = 119.9 Hz, J_{PP} = 16.4 Hz, 1P), 45.1 (dd, J_{PP} = 119.9 Hz, J_{PP} = 34.5 Hz, 1P) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.97 (br dd, 1H, J_{PH} = 12.5 Hz, J_{PH} = 7.3 Hz, P-C*H*-P), 2.14 (br m, 1H, P-C*H*H-Ir), 2.55 (br m, 1H, P-CH*H*-Ir), 4.69 (dt, 1H, $^{2}J_{HH}$ = 15.7 Hz, $^{2}J_{PH}$ = 11.2 Hz, P-C*H*H-P), 5.37 (m superimposed, 1H, P-CH*H*-P), 6.71 (br m, 4H, phenyl-*H*), 6.83 (br m, 4H, phenyl-*H*), 7.06-7.24 (br m, 10H, phenyl-*H*), 7.30-7.57 (br m, 16H, phenyl-*H*), 7.81(dd br, 2H, J_{HH} = 10.5 Hz, J_{HH} = 7.8 Hz, phenyl-*H*), 8.14-8.30 (m br, 4H, phenyl-*H*) ppm. ^{13}C APT NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = -7.6 (d, $^{1}J_{PC}$ = 51.4 Hz, P-*C*H_2-Ir), 12.4 (dd, $^{1}J_{PC}$ = 128.9 Hz, $^{1}J_{PC}$ = 70.1 Hz, P-*C*H-P), 46.1 (dd, $^{1}J_{PC}$ = 32.5 Hz, $^{1}J_{PC}$ = 25.7 Hz, P-*C*H_2-P), 127.0 (t, J_{PC} = 9.6 Hz, phenyl-*C*), 127.7 (t, J_{PC} = 10.5 Hz, phenyl-*C*), 127.9-130.1 (superimposed, phenyl-*C*), 130.8-131.5 (superimposed, phenyl-*C*), 131.8 (d, J_{PC} = 10.2 Hz, phenyl-*C*), 132.1-132.5 (superimposed, phenyl-*C*), 133.0-133.6 (superimposed, phenyl-*C*), 134.1 (d, J_{PC} = 9.0 Hz, phenyl-*C*), 134.4 (d, J_{PC} = 1.7 Hz, phenyl-*C*), 134.6 (d, J_{PC} = 2.3 Hz, phenyl-*C*), 134.7 (d, J_{PC} = 10.2 Hz, phenyl-*C*), 138.2 (s, phenyl-*C*) ppm.

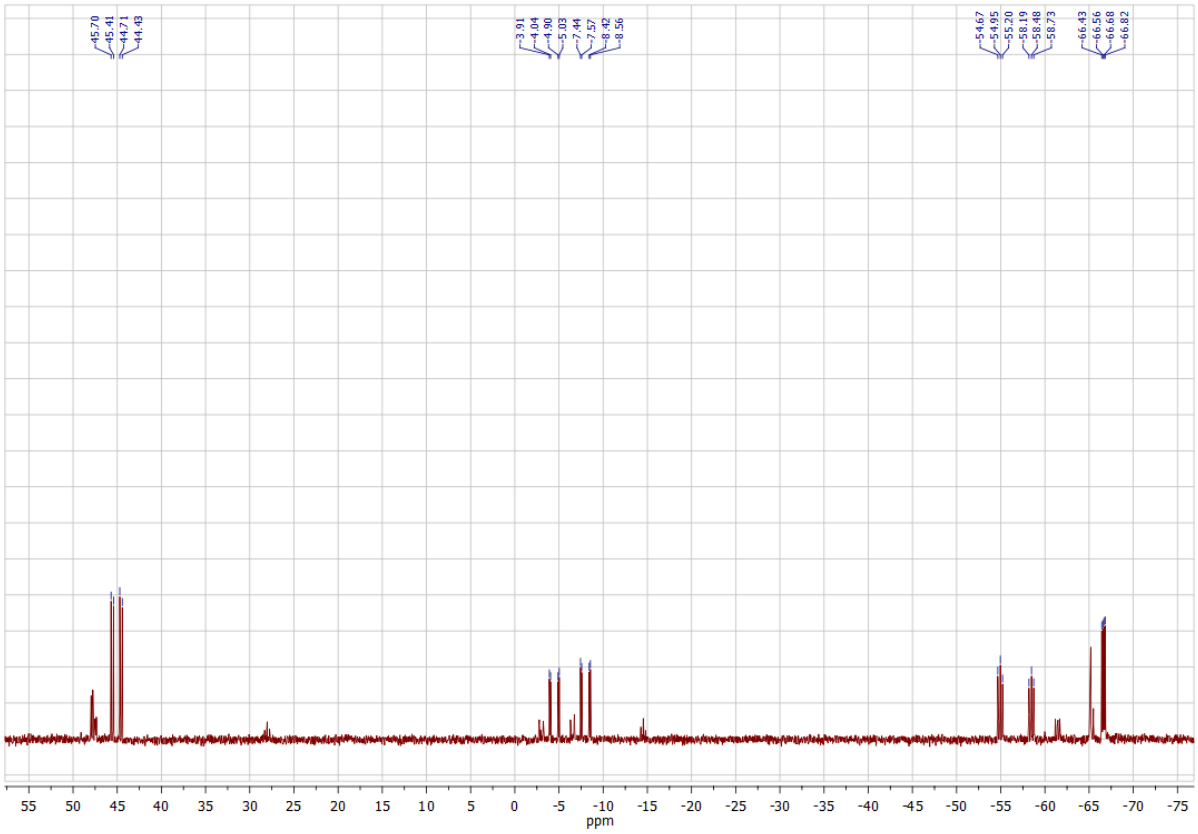

Figure 11 $^{31}P\{^{1}H\}$ NMR spectrum of $[(Ph_2PCHP\{Ph_2\}CH_2)IrCl_2(dppm)]$ (**5**) in $CDCl_3$.

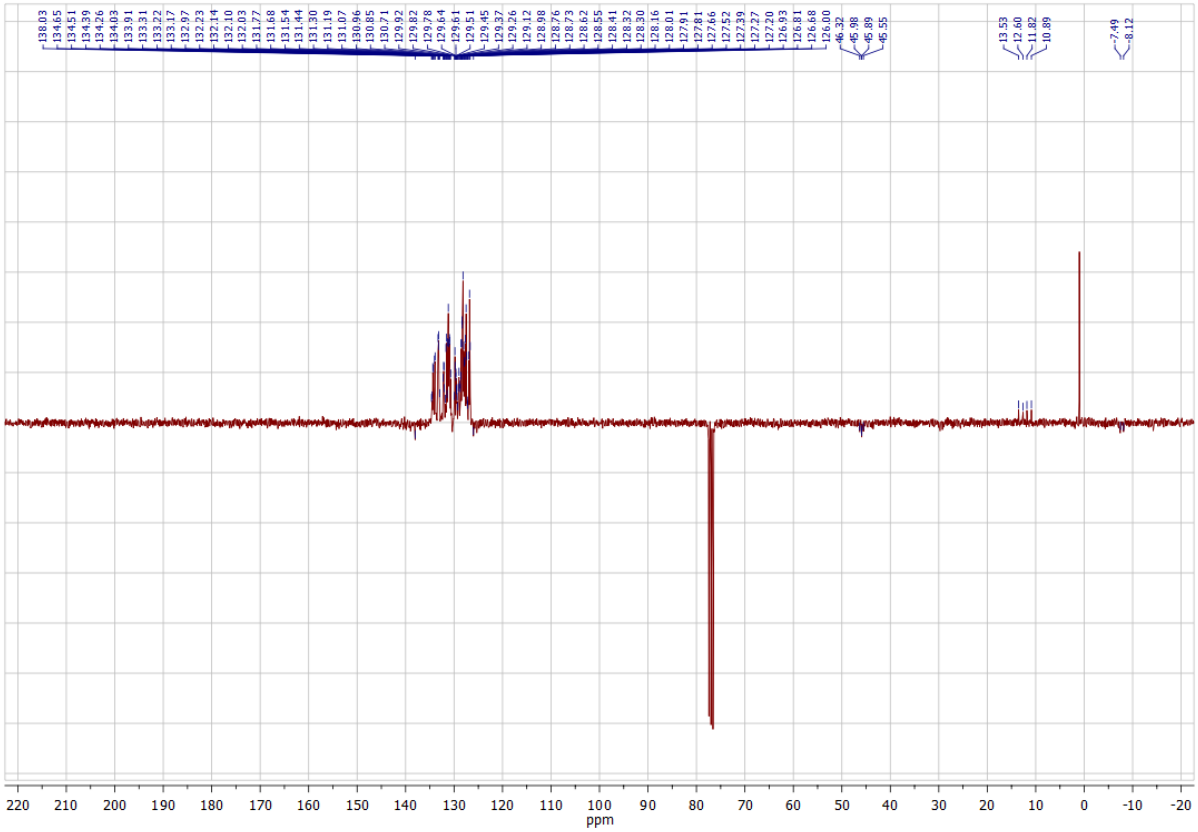

Figure 12 ^{13}C APT NMR spectrum of $[(Ph_2PCHP\{Ph_2\}CH_2)IrCl_2(dppm)]$ (**5**) in $CDCl_3$.

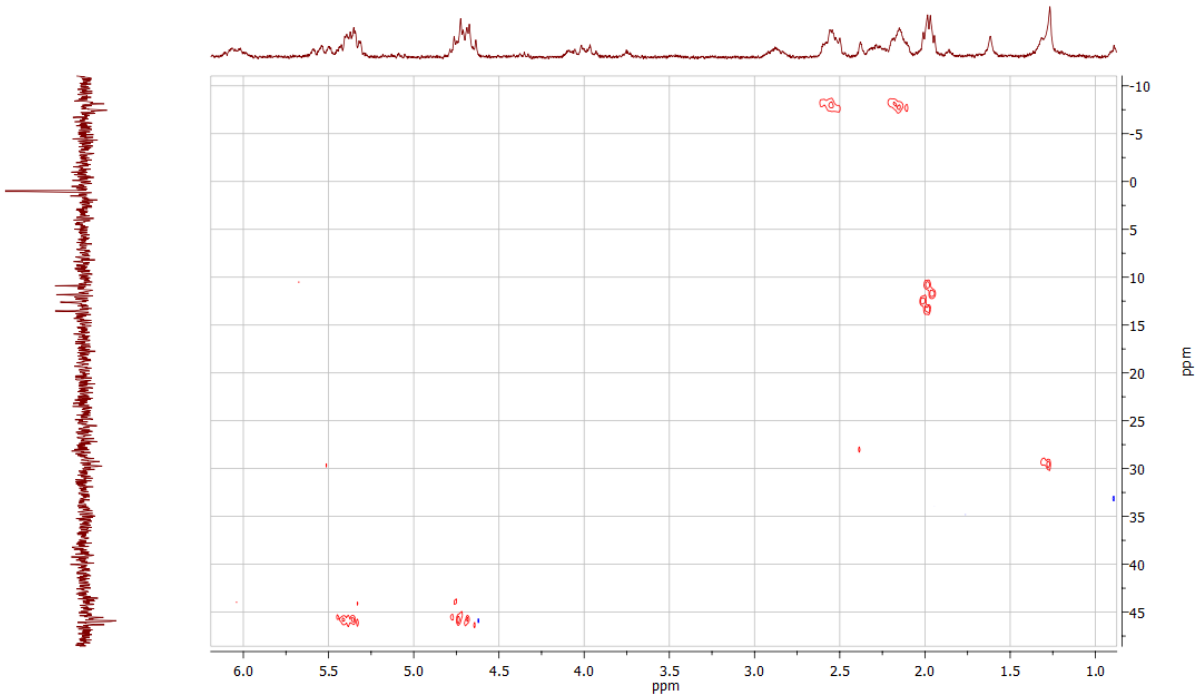

Figure 13 $^{1}H,^{13}C$-HSQC NMR spectrum of $[(Ph_2PCHP\{Ph_2\}CH_2)IrCl_2(dppm)]$ (**5**) in $CDCl_3$.

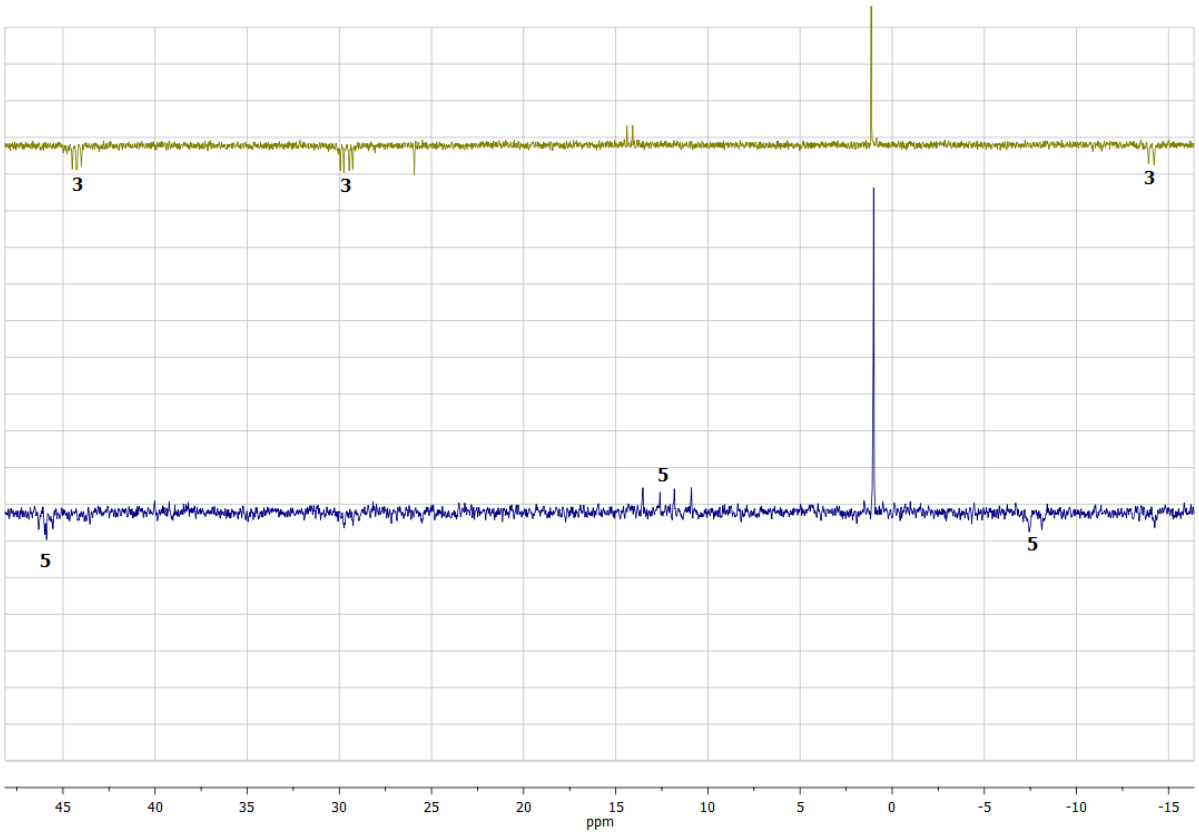

Figure 14 Comperison of diagnostic regions in the ^{13}C APT NMR spectrum of complex **3** (top) and **5** (bottom).

2. X-Ray Crystallography

The single crystal X-ray diffraction data for the structural analysis were collected using graphite-monochromated Mo-K_α-radiation ($\lambda_{MoK\alpha}$= 0.71073) on the pixel detector system Bruker Quest D8. The structures were solved with the Olex2 software by direct methods with SHELXT and refined against F^2 by full-matrix-least-square techniques using SHELXL.[4–7] Crystallographic data for **3** was deposited at Cambridge Crystallographic Data Centre (CCDC 2020037) and can be obtained free of charge via www.ccdc.cam.ac.uk/.

Table S1. Crystallographic data of complex **3**.

Complex	**3**
Formula	$C_{52}H_{47}Cl_4IrP_4$
M / g·mol^{-1}	1117.81
T/K	100(2)
Crystal System	monoclinic
Space Group	$P2_1/n$
a / Å	18.3814(10)
b / Å	13.5520(6)
c / Å	18.9756(9)
α / °	90
β / °	101.989(2)
γ / °	90
V / Å^3	4623.8(4)
Z	4
$\rho_{calc.}$ / g·cm^{-3}	1.623
μ / mm^{-1}	3.294
F(000)	2256
Θ_{min}/°	2.194
Θ_{max}/°	25.242
Measured Refl.	78757
Independent Refl.	9622 (R_{Int} = 0.1661)
Ind. Refl. (I>2σ(I))	7159
Parameters / Restraints	550/0
R_1	0.0626
R_1 (all data)	0.0895
wR_2	0.1584
wR_2 (all data)	0.1796
GooF	1.035
Max. peak + hole / e·Å^{-3}	2.695/-3.455
CCDC	2020037

3. Computational Details

All reported structures were optimized by the density functional theory (DFT)[8] with the M06-L functional[9] with def2svp basis sets[10,11] in the solvent phase. Frequency analysis calculations of optimized structures were performed at the same level of theory (M06-L/def2svp) to characterize the structures to be minima (no imaginary frequency) or transition states (one imaginary frequency). Intrinsic reaction coordinate (IRC) calculations were performed to confirm the connection between two correct minima for a transition state. Based on the M06-L/def2svp optimized geometries, the energy results were further refined by calculating the single point energy at the M06-L/def2tzvp level of theory. The bulky solvation effect of Chloroform (ε= 4.7) was simulated by SMD[12] continuum solvent mode at the M06-L/def2tzvp level of theory. The standard Gibbs free energy in solution is calculated by equation (1).

$$G^{\circ}_{(\mathrm{sol})} = G_{\mathrm{gas}} + \Delta G_{\mathrm{solv}} + RT\ln(24.5) \quad (1)$$

Where the G_{gas} is the gas-phase free energy, G_{solv} is the solvation free energy. The final term accounts for the free energy change from an ideal gas of 1 atm (24.5 L, 298.15 K) to 1M solution. All the calculations were performed with the Gaussian 09 program.[13]

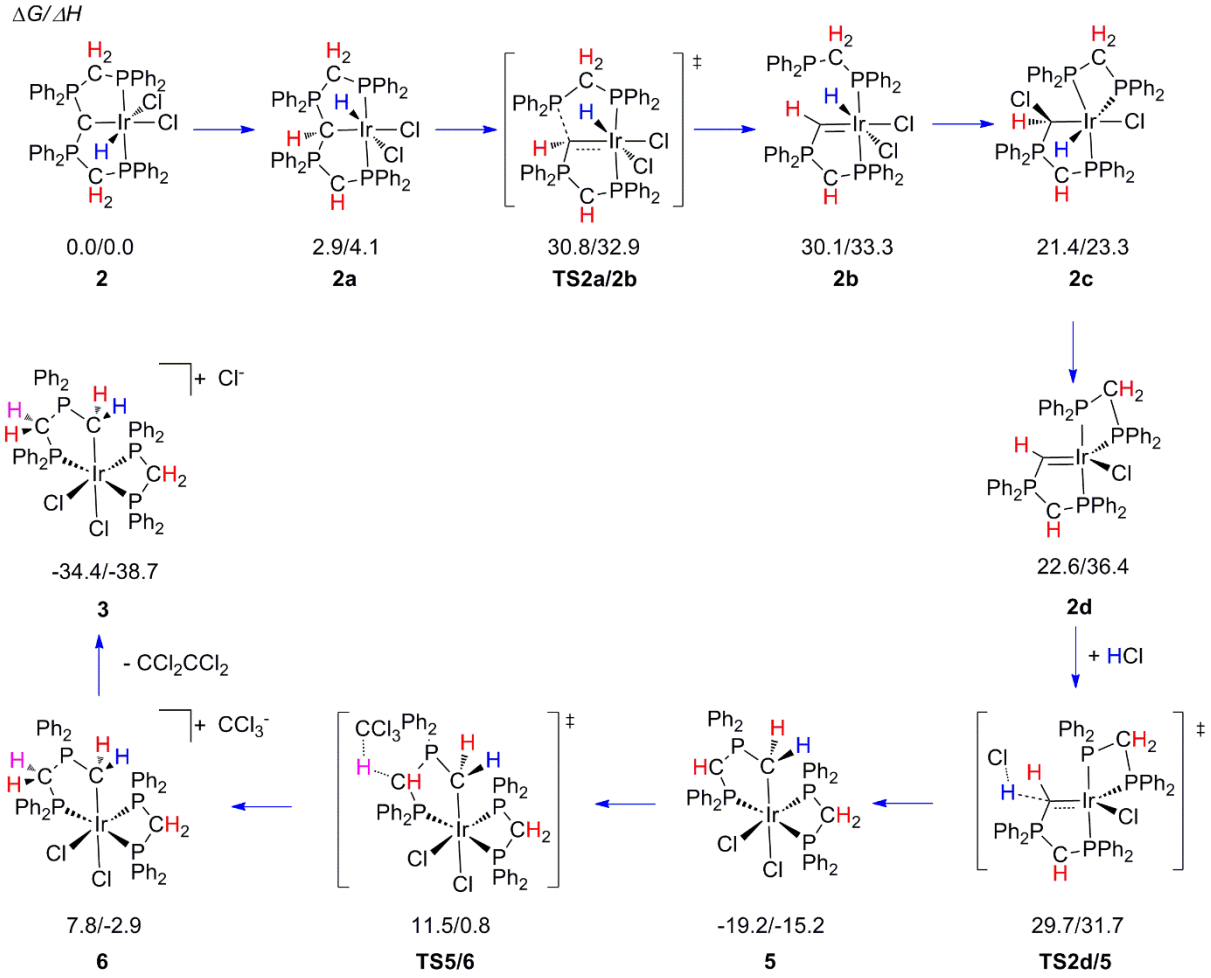

Figure 15 Details of the isomerisation-initiated mechanism leading to complex **3**.

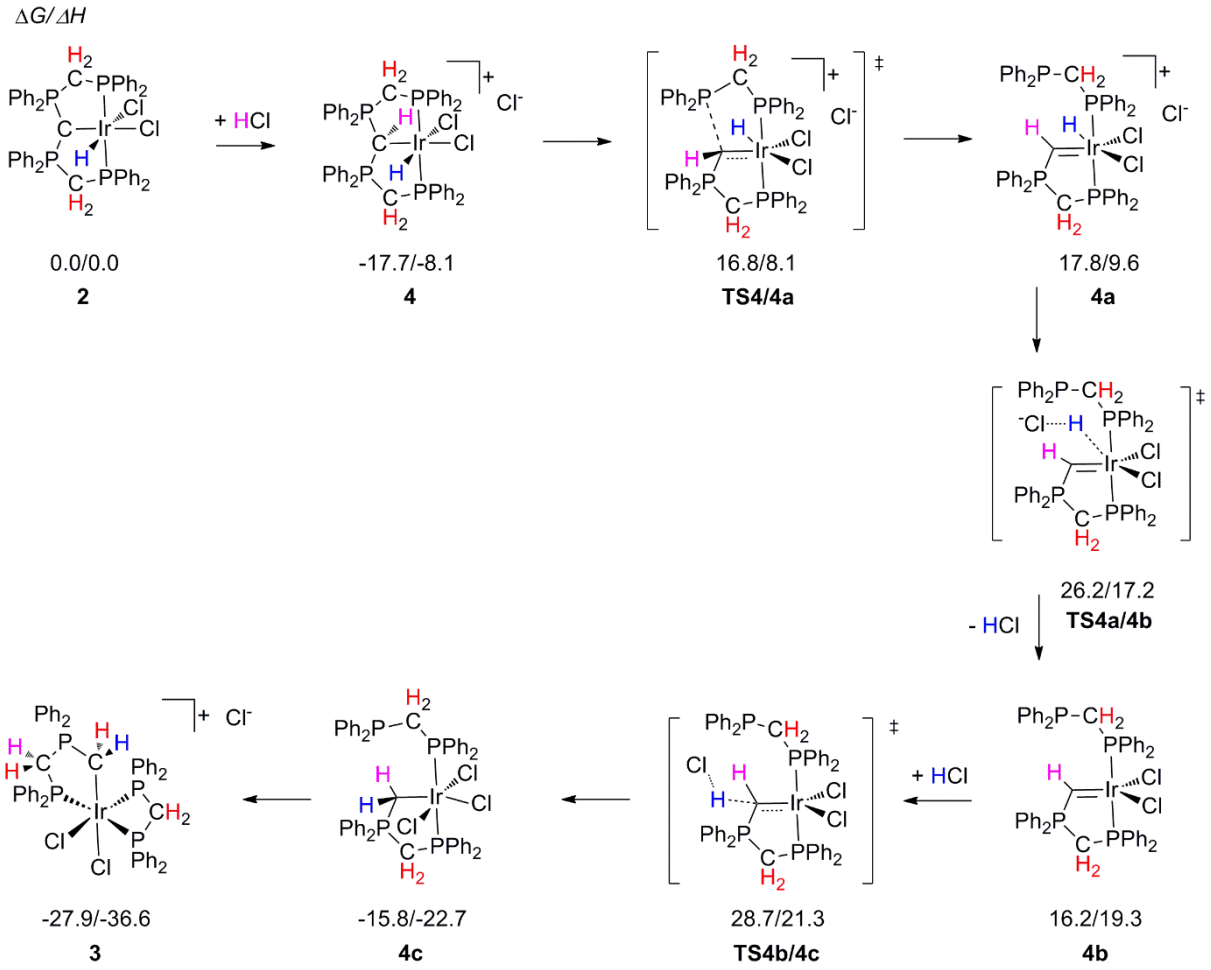

Figure 16 Details of the protonation-initiated mechanism leading to complex **3**.

4. Cartesian coordinates of all DFT-optimized geometries

Complex **2**

Ir	-0.636876	1.151441	0.095968
P	-2.660375	0.014802	-0.115131
Cl	-0.690457	1.640757	-2.505973
P	1.472274	2.134554	0.035029
C	0.383873	-0.678406	-0.333462
C	-2.230135	-1.668919	-0.733832
C	-3.912917	0.580037	-1.325379
C	-3.644963	-0.302577	1.400008
C	1.623977	3.837181	-0.588999
C	2.580764	2.110723	1.493410
C	2.366405	1.087540	-1.187355
P	-0.573513	-2.059862	-0.079328
P	2.025649	-0.650404	-0.787538
H	-2.973434	-2.448611	-0.510162
H	-2.122029	-1.589015	-1.826737
C	-4.111265	1.955551	-1.502151
C	-4.688104	-0.326520	-2.061632
C	-3.345466	0.396782	2.574549
C	-4.711546	-1.214034	1.398764
C	1.448469	4.889897	0.321748
C	1.823196	4.129673	-1.943625
C	3.818004	2.771807	1.463210
C	2.231844	1.367427	2.625561
H	3.435614	1.311219	-1.317070
H	1.837313	1.254049	-2.142039
C	-0.045372	-3.603006	-0.886805
C	-0.887077	-2.508059	1.667866
C	2.432743	-1.583752	-2.299936
C	3.283071	-1.180267	0.437604
H	-3.490582	2.662617	-0.942156
C	-5.080539	2.410932	-2.393986
H	-4.542226	-1.404788	-1.950059
C	-5.653672	0.135421	-2.955656
H	-2.529833	1.125470	2.570914
C	-4.087257	0.170342	3.734532
H	-4.970942	-1.758979	0.485108
C	-5.449009	-1.438814	2.558125
C	1.494612	6.211426	-0.112651
H	1.274413	4.674236	1.379633
H	1.932588	3.326071	-2.674866
C	1.869619	5.455911	-2.373733
H	4.102352	3.364439	0.587758
C	4.690378	2.679946	2.544666
C	3.111508	1.266341	3.703450
H	1.256399	0.873531	2.655391

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C -0.149073 -3.713277 -2.281720
C -0.149050 -1.875992 2.672614
C -1.855167 -3.459329 2.018529
C 3.393496 -2.599484 -2.348101
C 1.710457 -1.250587 -3.456891
C 2.978493 -2.274044 1.256391
C 4.523766 -0.546514 0.589673
C -5.852712 1.505469 -3.121687
H -5.224290 3.485910 -2.528568
H -6.249140 -0.580904 -3.527446
H -3.843893 0.721305 4.646417
C -5.135764 -0.747066 3.730072
H -6.275122 -2.154377 2.546567
H 1.357877 7.021949 0.607287
C 1.708586 6.497481 -1.461440
H 2.029746 5.673416 -3.432610
C 4.340830 1.921706 3.664556
H 5.649815 3.202662 2.514606
H 2.830594 0.675826 4.579556
H 0.583093 -4.596101 0.934945
C 0.965073 -5.805928 -0.808870
H -0.569263 -2.891493 -2.868203
C 0.296949 -4.861889 -2.929785
C -0.370452 -2.187549 4.013521
H 0.602943 -1.135701 2.385228
H -2.441596 -3.963561 1.243380
C -2.075300 -3.771177 3.358232
H 3.960159 -2.869206 -1.452061
C 3.628995 -3.278551 -3.545023
C 1.964214 -1.918089 -4.651008
H 0.935976 -0.472973 -3.403756
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C 3.882893 -2.725544 2.214018
C 5.425112 -0.989276 1.557842
H 4.797287 0.302941 -0.041407
H -6.606623 1.867794 -3.825310
H -5.715080 -0.923212 4.639996
H 1.743820 7.535250 -1.802264
H 5.029034 1.848174 4.510505
H 1.400247 -6.623430 -0.229328
C 0.857541 -5.908132 -2.195062
H 0.212460 -4.936350 -4.016648
H 0.208223 -1.683436 4.791856
C -1.334605 -3.134267 4.356454
H -2.833232 -4.511276 3.626698
C 2.920604 -2.936162 -4.695494
H 4.372978 -4.078495 -3.575934

H 1.406227 -1.649584 -5.551600
H 3.626570 -3.582769 2.841673
C 5.107504 -2.076989 2.371432
H 6.382261 -0.475426 1.678580
H 1.210834 -6.807080 -2.706133
H -1.514251 -3.376899 5.406786
H 3.112028 -3.465928 -5.632215
H 5.815628 -2.419181 3.130087
Cl -1.732305 3.314236 0.738603
H -0.575684 0.836801 1.641366

Complex **3**
Ir -0.333504 -0.130343 -0.797546
P 1.873832 -0.972029 -1.165343
Cl 0.201174 1.679488 -2.465941
P -2.518767 0.633480 -0.299693
C 0.622991 1.135303 0.621062
C 2.917700 0.558022 -1.096819
C 2.342923 -1.698813 -2.771540
C 2.582854 -2.091548 0.083852
C -2.698916 2.129334 0.719357
C -3.797963 0.843322 -1.576208
C -2.943361 -0.870929 0.655508
P 2.237296 1.729673 0.115075
P -1.227452 -1.493346 0.845971
H 3.989600 0.356418 -0.952642
H 2.782723 1.003507 -2.093446
C 1.695842 -1.236359 -3.927211
C 3.358250 -2.660263 -2.883041
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C -3.458475 1.259824 -2.867396
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H 0.902071 -0.490273 -3.840553
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H 3.873445 -3.030867 -1.992757
C 3.721352 -3.149399 -4.136764
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C -1.665303 -3.982766 2.014403
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C 3.079498 -2.683385 -5.283808
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C -5.799434 1.254207 -3.473445
H -7.182735 0.662212 -1.919760
H -4.196981 1.788103 -4.821728
H 3.577283 2.998607 -2.223337
C 3.054405 5.082175 -2.099383
H 0.974984 4.140772 1.045862
C 1.595058 5.721225 -0.283270
C 5.606275 1.954976 2.428593
H 5.140518 2.003042 0.326797
H 1.781032 1.631546 3.035483
C 3.731686 1.745506 3.938320
H -2.476062 0.036587 3.081634
C -1.000466 0.069783 4.641856
C 0.999438 -1.230443 4.271740
H 1.131305 -2.249892 2.377637
H -1.851255 -3.417009 2.931773
C -1.798678 -5.369479 2.025611
C -1.263105 -5.445562 -0.326607
H -0.890074 -3.541331 -1.280001
H 3.365510 -3.069715 -6.265252
H 3.805923 -4.546825 2.854695
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C 5.104513 1.856933 3.727984
H 3.333527 1.680244 4.953644
C 0.234459 -0.394445 5.089580
H -1.623052 0.695705 5.286365
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H 0.597008 -0.118720 6.083432
H -1.693838 -7.191804 0.870762
H 0.008927 2.015075 0.873262
Cl -1.454060 -1.478193 -2.590709
H 0.805717 0.598841 1.564648
Cl -4.976845 -0.674057 3.364357

Complex **4**
Ir 1.204768 0.122311 -0.273655
P 0.691425 2.344391 -0.839416
Cl 1.270385 -0.187160 -2.943795
P 1.666249 -2.089553 0.216266
C -0.839029 -0.424528 -0.655852
C -0.934955 2.182586 -1.699051
C 1.753850 3.228684 -2.029663
C 0.450167 3.587989 0.472557
C 2.687549 -2.997425 -0.992607
C 2.392384 -2.528679 1.830713
C 0.049918 -3.014923 0.199313
P -1.945569 0.990182 -0.786687
P -1.393768 -1.911607 0.192839
H -1.484567 3.117997 -1.885472
H -0.684956 1.694909 -2.656200
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C 2.914405 3.832553 -1.523055
C 0.989284 3.359194 1.741811
C -0.242485 4.781703 0.215510
C 4.062316 -3.135878 -0.755259
C 2.156614 -3.443605 -2.210602
C 2.608521 -3.879758 2.153403
C 2.689510 -1.536294 2.769169
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H -0.021410 -3.616659 -0.719149

C -3.403277 0.588499 -1.781337
C -2.486091 1.724344 0.765524
C -2.673812 -2.814454 -0.721493
C -1.969119 -1.608263 1.868171
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C 3.790293 4.496058 -2.378004
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C 0.824884 4.309628 2.750798
H -0.653974 4.980662 -0.779389
C -0.405186 5.725024 1.225933
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H 2.386649 -4.663659 1.421378
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H 5.950839 -3.848875 -1.504428
C 4.340424 -4.216910 -2.898502
H 2.551022 -4.411105 -4.094179
C 3.391452 -3.231565 4.344478
H 3.276735 -5.279081 3.648819
H 3.364672 -1.103964 4.759032
H -4.640624 0.098246 -0.068267
C -5.642219 -0.327670 -1.926035
H -2.426702 0.960178 -3.689559
C -4.409952 0.171671 -3.943216
C -2.103497 2.293993 3.084980
H -0.775348 1.055277 1.958618
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C -4.032107 3.181215 1.926258

H -3.427548 -3.861300 1.025106
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C -3.672190 -3.459018 -2.831412
H -2.100789 -2.001358 -2.656675
H -4.075039 -1.503795 1.323141
C -3.759433 -1.077066 3.407182
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H 4.204325 5.090346 -4.413768
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H 4.983561 -4.697810 -3.639575
H 3.774521 -3.508211 5.330319
H -6.544558 -0.696164 -1.432637
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H -4.346686 0.198341 -5.033133
H -1.454190 2.200728 3.961979
C -3.264192 3.065544 3.087033
H -4.935242 3.795885 1.921496
C -4.513217 -4.348479 -2.163272
H -5.067723 -5.195736 -0.253941
H -3.731179 -3.354552 -3.917102
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H -3.163000 -0.701446 5.449364
Cl 3.597232 0.630914 -0.019483
H 1.044342 0.365264 1.278290
H -0.724915 -0.725029 -1.719690
Cl 1.003976 1.023950 4.196906

Complex **5**
Ir -0.435602 0.380517 -0.630405
P -0.162623 -1.966451 -0.897708
Cl 0.793203 0.800699 -2.751695
P -0.752333 2.653230 -0.042017
C 1.493540 0.436995 0.217452
C 1.417268 -2.382932 -0.289344
C -0.354388 -2.665807 -2.594690
C -1.406652 -2.989967 -0.017041
C 0.645454 3.456825 0.797352
C -1.439295 3.921135 -1.146641
C -2.012557 2.237016 1.234550
P 2.465359 -1.070469 -0.003685
P -1.608653 0.436003 1.353831
C -0.953063 -1.957585 -3.642311

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C -2.742024 -2.969819 -0.450736
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C 1.672397 3.983041 -0.003234
C 0.808173 3.434808 2.187713
C -1.909251 5.135345 -0.623657
C -1.487924 3.685494 -2.525839
H -2.993626 2.325807 0.742632
H -2.047794 2.828686 2.162441
C 3.723637 -0.795140 -1.307919
C 3.464322 -1.303672 1.511999
C -0.675084 0.191352 2.902699
C -3.193317 -0.406330 1.736915
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C -1.072631 -2.542016 -4.904922
H 0.579065 -4.539131 -2.021664
C -0.003087 -4.546242 -4.093625
H -3.033568 -2.307814 -1.273336
C -3.692577 -3.777286 0.167421
H -0.008277 -3.819355 1.400012
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C 2.835516 4.477752 0.580708
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H -1.866145 5.325134 0.453697
C -2.430223 6.104317 -1.477467
C -2.003216 4.665717 -3.374514
H -1.119528 2.734813 -2.921828
C 3.594602 -1.473271 -2.524489
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C 3.767105 -2.598072 1.953732
C 3.905742 -0.204813 2.262901
C -0.955830 0.935634 4.056938
C 0.278639 -0.831917 2.962933
C -3.255418 -1.374897 2.750309
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C -0.598073 -3.832018 -5.135562
H -1.540175 -1.978126 -5.716383
H 0.367172 -5.560734 -4.263251
H -4.729992 -3.754749 -0.176719
C -3.324520 -4.610166 1.227180
H -1.714019 -5.264477 2.510069
H 3.627047 4.884593 -0.053022
C 2.992556 4.448208 1.968284
H 2.089610 3.903677 3.856016
C -2.476082 5.869327 -2.853492
H -2.799225 7.048054 -1.068713

H -2.038341 4.482808 -4.451000
H 2.751249 -2.155342 -2.671781
C 4.518840 -1.265228 -3.547184
H 4.904068 0.640034 -0.184963
C 5.705872 0.312435 -2.155684
C 4.501809 -2.790919 3.122715
H 3.414902 -3.463691 1.385165
H 3.667353 0.814347 1.941602
C 4.635412 -0.400169 3.435382
H -1.721200 1.717573 4.039358
C -0.267667 0.679887 5.241441
C 0.957209 -1.094539 4.152481
H 0.490618 -1.428636 2.067508
H -2.356885 -1.661724 3.301957
C -4.467556 -1.983981 3.070453
C -5.574693 -0.686550 1.367731
H -4.335319 0.657589 0.232313
H -0.691536 -4.284224 -6.126333
H -4.072516 -5.245655 1.708900
H 3.907594 4.833690 2.424270
H -2.882437 6.632040 -3.522393
H 4.407811 -1.798109 -4.494577
C 5.574012 -0.372044 -3.365062
H 6.529887 1.015258 -2.010110
H 4.733037 -3.805381 3.456633
C 4.934744 -1.692382 3.866877
H 4.965521 0.463657 4.017710
C 0.691255 -0.333844 5.290293
H -0.487420 1.270432 6.134130
H 1.703076 -1.893391 4.183595
H -4.496401 -2.737639 3.861431
C -5.630359 -1.641130 2.383528
H -6.479768 -0.413916 0.819620
H 6.296637 -0.206542 -4.167999
H 5.504392 -1.844846 4.786833
H 1.230007 -0.532325 6.220073
H -6.579888 -2.119221 2.636752
H 2.052379 1.253018 -0.267884
Cl -2.692717 0.521483 -1.819612
H 1.478348 0.653173 1.297224
H 1.834008 -3.384440 -0.440736

Complex **2a**
Ir 1.214866 0.113003 -0.041920
P 0.826560 2.362658 -0.509783
Cl 1.498716 -0.155240 -2.662633
P 1.495029 -2.193439 0.301830
C -0.809505 -0.345524 -0.570602

C -0.858734 2.366001 -1.270732
C 1.893394 3.250612 -1.692818
C 0.671001 3.588954 0.844426
C 2.835233 -2.959231 -0.679270
C 1.957410 -2.697669 2.015454
C 0.009854 -2.988339 -0.153319
P -1.828888 1.108725 -0.389266
P -1.393208 -2.039024 -0.201378
H -1.372560 3.339526 -1.284749
H -0.773532 2.002581 -2.307726
C 1.625387 3.330383 -3.064458
C 3.074335 3.819241 -1.191477
C 0.979222 3.234518 2.160948
C 0.261063 4.901351 0.563099
C 4.156529 -2.939714 -0.211521
C 2.565030 -3.507777 -1.938431
C 1.779396 -4.032985 2.407345
C 2.429554 -1.773827 2.954714
C -3.418103 0.997141 -1.255736
C -2.084668 1.703879 1.293400
C -2.478826 -2.548357 -1.581701
C -2.423652 -2.054211 1.313272
H 0.728588 2.871273 -3.485259
C 2.511734 3.989570 -3.915345
H 3.305167 3.750748 -0.125174
C 3.960450 4.468820 -2.046811
H 1.311394 2.214189 2.375884
C 0.866820 4.176308 3.185410
H 0.039732 5.196952 -0.467931
C 0.140503 5.835848 1.587615
C 5.184745 -3.476520 -0.983265
H 4.382510 -2.494353 0.761468
H 1.537048 -3.507146 -2.311866
C 3.594684 -4.048955 -2.706377
H 1.413347 -4.767389 1.681905
C 2.049249 -4.432399 3.714337
C 2.701206 -2.174932 4.264767
H 2.597839 -0.737548 2.646283
C -4.652054 1.216553 -0.629654
C -3.381632 0.604008 -2.603083
C -1.640013 0.986276 2.410069
C -2.691520 2.958273 1.466547
C -3.783674 -3.033807 -1.438155
C -1.917167 -2.463678 -2.867434
C -3.685142 -1.445746 1.390994
C -1.867997 -2.616311 2.469568
C 3.679234 4.559314 -3.409972
H 2.289147 4.049683 -4.983493

H 4.877743 4.904690 -1.643569
H 1.110559 3.890333 4.211853
C 0.443381 5.473204 2.902063
H -0.182121 6.854880 1.359530
H 6.211484 -3.455227 -0.608894
C 4.906115 -4.035882 -2.230871
H 3.371824 -4.479946 -3.686170
C 2.506397 -3.500488 4.648988
H 1.903133 -5.476005 4.005952
H 3.071016 -1.444137 4.988919
H -4.693153 1.512110 0.422284
C -5.835330 1.031968 -1.343492
H -2.422416 0.431659 -3.103386
C -4.566960 0.421171 -3.308782
C -1.832832 1.503122 3.689171
H -1.126535 0.032431 2.282341
H -3.018426 3.539763 0.598150
C -2.870974 3.473239 2.747326
H -4.228151 -3.150702 -0.447336
C -4.529166 -3.390109 -2.563547
C -2.663488 -2.820609 -3.985868
H -0.885908 -2.109096 -2.988417
H -4.140891 -1.005454 0.500384
C -4.370558 -1.390318 2.602057
C -2.553762 -2.558624 3.682522
H -0.882250 -3.089199 2.412702
H 4.373825 5.071190 -4.080622
H 0.353911 6.208691 3.705575
H 5.713096 -4.458676 -2.835102
H 2.715501 -3.811255 5.676039
H -6.794999 1.198940 -0.849010
C -5.794361 0.631525 -2.678250
H -4.530955 0.110153 -4.355213
H -1.487614 0.933607 4.555338
C -2.450852 2.740898 3.859170
H -3.337598 4.452397 2.876847
C -3.975195 -3.277444 -3.836659
H -5.547885 -3.765681 -2.439172
H -2.217010 -2.745564 -4.980458
H -5.351187 -0.909233 2.649005
C -3.802936 -1.942437 3.751566
H -2.106106 -2.996835 4.578114
H -6.724389 0.481950 -3.231769
H -2.592616 3.147168 4.863665
H -4.561546 -3.556225 -4.715756
H -4.338434 -1.894207 4.703059
Cl 3.604489 0.608721 0.429610
H 0.952760 0.285655 1.507581

H -0.694113 -0.380642 -1.674794
H -0.097771 -4.078002 -0.191962

Complex **2b**
Ir 0.999086 0.789480 -0.180051
P 2.929997 -0.432897 0.536972
Cl 0.447016 1.235072 2.263465
P -1.042637 1.887510 -0.811838
C 0.151458 -0.867704 -0.414311
C 2.333467 -2.031356 0.901768
C 3.783456 0.192283 2.021653
C 4.297475 -0.520180 -0.691523
C -0.983020 3.702330 -0.939168
C -1.815665 1.300224 -2.361439
C -2.337711 1.626691 0.470764
P 0.869301 -2.442085 0.155341
P -2.672154 -0.160887 0.853494
C 4.781834 1.169097 1.903901
C 3.403840 -0.253166 3.293589
C 4.397477 0.374118 -1.762934
C 5.257683 -1.534300 -0.557084
C -1.212460 4.384836 -2.139033
C -0.631548 4.424048 0.212262
C -3.138222 1.656556 -2.673038
C -1.109267 0.476987 -3.247491
H -3.257340 2.178105 0.213702
H -1.921251 2.080095 1.383216
C -0.342516 -3.235591 1.252429
C 0.939970 -3.399115 -1.399364
C -3.496564 -0.055970 2.487996
C -4.087117 -0.501556 -0.273085
H 5.079306 1.532109 0.916416
C 5.392239 1.687805 3.043542
H 2.618655 -1.008175 3.386252
C 4.022065 0.262935 4.430833
H 3.668270 1.183778 -1.857790
C 5.435953 0.250359 -2.688120
H 5.190376 -2.240442 0.277483
C 6.293156 -1.655749 -1.480276
C -1.118869 5.776224 -2.180278
H -1.462941 3.833498 -3.049183
H -0.401344 3.888163 1.139168
C -0.549439 5.812258 0.166473
H -3.704387 2.313345 -2.005568
C -3.739715 1.186723 -3.837292
C -1.716552 0.000418 -4.409800
H -0.074347 0.203795 -3.025402
C -1.056709 -4.395277 0.932079

C -0.588115 -2.575539 2.467820
C -0.201828 -3.593998 -2.193263
C 2.186590 -3.827489 -1.870287
C -4.636540 -0.827506 2.768218
C -2.900548 0.665608 3.534814
C -5.237701 0.302133 -0.303849
C -3.999026 -1.585982 -1.153707
C 5.014846 1.235397 4.308215
H 6.167623 2.451146 2.942136
H 3.721919 -0.092694 5.419880
H 5.504980 0.955904 -3.520088
C 6.382568 -0.763147 -2.550509
H 7.035464 -2.449767 -1.364702
H -1.300963 6.302506 -3.120616
C -0.795269 6.491060 -1.028511
H -0.278964 6.367925 1.067471
C -3.032117 0.352079 -4.704750
H -4.769398 1.471554 -4.067296
H -1.152718 -0.645956 -5.086958
H -0.861785 -4.927543 -0.002947
C -2.022661 -4.880997 1.814574
H -0.040477 -1.655435 2.703934
C -1.550279 -3.067728 3.344088
C -0.095331 -4.223670 -3.430814
H -1.179807 -3.248583 -1.844588
H 3.080219 -3.646404 -1.264450
C 2.287866 -4.465821 -3.105911
H -5.108668 -1.416617 1.976449
C -5.178575 -0.853757 4.052242
C -3.450738 0.642812 4.814814
H -1.982333 1.232626 3.352202
H -5.332461 1.144485 0.389581
C -6.264145 0.035818 -1.205327
C -5.025170 -1.852099 -2.062714
H -3.110583 -2.225383 -1.130008
H 5.494971 1.643888 5.201301
H 7.193515 -0.858782 -3.277067
H -0.725287 7.581049 -1.062500
H -3.508502 -0.021435 -5.614710
H -2.579976 -5.786506 1.562748
C -2.273697 -4.215878 3.013997
H -1.747697 -2.543265 4.282590
H -0.987550 -4.368908 -4.044591
C 1.149163 -4.663601 -3.885769
H 3.263665 -4.802251 -3.463967
C -4.591495 -0.115849 5.079991
H -6.070017 -1.455227 4.249100
H -2.976221 1.218225 5.613867

H -7.154319 0.670061 -1.219441
C -6.156876 -1.039569 -2.090971
H -4.937799 -2.695705 -2.752187
H -3.036071 -4.595678 3.699045
H 1.231692 -5.156248 -4.857647
H -5.019101 -0.135306 6.085509
H -6.960828 -1.243960 -2.802695
H -0.739882 -1.048240 -1.043424
Cl 2.345612 2.908815 -0.222689
H 1.476419 0.756833 -1.694406
H 2.930298 -2.788487 1.418751

Complex **2c**
Ir -0.410265 0.080021 -0.762664
P 0.466559 -2.083910 -0.580131
P -1.508172 2.200257 -0.601583
C 1.360911 0.811340 0.042880
C 1.995069 -1.967121 0.254716
C 0.699643 -3.011524 -2.155606
C -0.556668 -3.272329 0.374944
C -0.663817 3.645415 0.130882
C -2.443525 2.886738 -2.000984
C -2.711847 1.652102 0.693472
P 2.719728 -0.428976 0.248283
P -1.875301 0.091448 1.245322
C 0.296565 -2.483060 -3.387082
C 1.355988 -4.251762 -2.128863
C -1.749472 -3.775623 -0.167963
C -0.165579 -3.680436 1.655786
C -0.370137 4.788592 -0.623423
C -0.185058 3.559411 1.446080
C -3.492626 3.795827 -1.805409
C -2.069292 2.526452 -3.300311
H -3.652521 1.382542 0.189039
H -2.949925 2.387291 1.478377
C 3.979556 -0.207179 -1.055048
C 3.570839 -0.032258 1.810686
C -1.122021 0.450912 2.870322
C -3.247592 -1.047774 1.668704
H -0.230011 -1.524942 -3.412330
C 0.554143 -3.178075 -4.570387
H 1.672605 -4.681999 -1.172624
C 1.614546 -4.942183 -3.310163
H -2.072694 -3.451695 -1.161906
C -2.525793 -4.675831 0.558502
H 0.761603 -3.285353 2.083961
C -0.940301 -4.590724 2.375918
C 0.390301 5.818594 -0.071216

H -0.723654 4.872446 -1.655017
H -0.397252 2.674748 2.051410
C 0.578800 4.586417 1.993763
H -3.787901 4.084081 -0.791288
C -4.156175 4.340687 -2.902463
C -2.729986 3.081267 -4.395238
H -1.262173 1.801324 -3.441654
C 3.609480 -0.576049 -2.356707
C 5.277504 0.254640 -0.813340
C 3.980920 -1.061551 2.666486
C 3.791874 1.302915 2.181411
C -1.758444 1.219600 3.856254
C 0.159937 -0.055336 3.117510
C -3.205834 -1.826992 2.834264
C -4.342940 -1.184146 0.800346
C 1.214010 -4.405133 -4.535658
H 0.230736 -2.756841 -5.525935
H 2.130707 -5.905280 -3.275686
H -3.456190 -5.057639 0.129386
C -2.120211 -5.091128 1.828479
H -0.617439 -4.910663 3.370641
H 0.613546 6.704633 -0.670724
C 0.872992 5.718733 1.233596
H 0.947392 4.495513 3.019496
C -3.772064 3.986449 -4.197364
H -4.974427 5.048252 -2.747700
H -2.433846 2.798338 -5.408143
H 2.594914 -0.942681 -2.549302
C 4.521615 -0.471456 -3.402061
H 5.582681 0.542849 0.196469
C 6.193772 0.345575 -1.861901
C 4.618026 -0.761353 3.870042
H 3.790874 -2.103828 2.393605
H 3.478141 2.116577 1.519350
C 4.415349 1.598491 3.392473
H -2.766984 1.608830 3.683765
C -1.106395 1.499075 5.055208
C 0.808871 0.220356 4.321647
H 0.653674 -0.668503 2.353488
H -2.359381 -1.746211 3.522309
C -4.244135 -2.709172 3.131154
C -5.376944 -2.066046 1.103601
H -4.376681 -0.614495 -0.130150
H 1.416030 -4.947442 -5.462999
H -2.730183 -5.801339 2.393394
H 1.475746 6.524962 1.658770
H -4.291742 4.417834 -5.056629
H 4.220961 -0.754816 -4.413781

C 5.817897 -0.014309 -3.154912
H 7.209066 0.698669 -1.664588
H 4.941286 -1.570665 4.529328
C 4.834120 0.567768 4.234771
H 4.577676 2.641108 3.676841
C 0.180097 1.005700 5.286105
H -1.604462 2.105584 5.815743
H 1.813720 -0.172657 4.498637
H -4.196820 -3.307896 4.044547
C -5.333435 -2.829607 2.269915
H -6.223082 -2.157137 0.417893
H 6.538429 0.057778 -3.973415
H 5.329549 0.801000 5.180630
H 0.691602 1.232116 6.225101
H -6.147607 -3.519575 2.506026
Cl -2.496082 -0.698704 -1.991352
H 2.636112 -2.847823 0.377535
H 1.215697 1.242534 1.049284
H 0.341618 0.285752 -2.179070
Cl 2.091585 2.251139 -0.879717

Complex **2d**
Ir -0.244728 -0.046118 0.738237
P -0.150883 2.214323 0.036040
P -0.367832 -2.363123 1.153046
C 1.633010 -0.095911 0.356822
C 1.331083 2.432863 -0.856147
C -0.204512 3.413047 1.432191
C -1.567461 2.758848 -0.983342
C 0.877989 -3.382935 0.297412
C -0.534219 -3.155523 2.787727
C -1.979407 -2.570280 0.276848
P 2.458975 1.180954 -0.568814
P -1.965886 -0.938407 -0.597292
C 0.113397 2.987573 2.729408
C -0.433360 4.777800 1.203203
C -2.821635 2.920669 -0.371959
C -1.441278 2.980450 -2.358688
C 2.111332 -3.590187 0.937178
C 0.710218 -3.842093 -1.015083
C -0.686744 -4.546284 2.898211
C -0.515680 -2.365123 3.942894
H -2.762434 -2.541462 1.050660
H -2.134621 -3.476997 -0.331169
C 3.936587 1.707737 0.375167
C 3.167169 0.473784 -2.105593
C -1.372392 -1.326435 -2.282425
C -3.714269 -0.471581 -0.866198

H 0.276457 1.920702 2.914004
C 0.215843 3.909159 3.770728
H -0.689873 5.126966 0.197226
C -0.332622 5.698092 2.245334
H -2.929909 2.713475 0.698355
C -3.921467 3.322622 -1.123787
H -0.464068 2.842520 -2.834491
C -2.548590 3.379457 -3.110799
C 3.146131 -4.252529 0.280218
H 2.264011 -3.227380 1.959018
H -0.234627 -3.683499 -1.540762
C 1.749558 -4.502490 -1.671133
H -0.696306 -5.169828 1.998374
C -0.819028 -5.135976 4.152669
C -0.646922 -2.961974 5.197311
H -0.412939 -1.280282 3.851222
C 3.777186 2.706377 1.345970
C 5.189103 1.100964 0.212878
C 3.442191 1.320190 -3.188703
C 3.408526 -0.900307 -2.234486
C -2.029456 -2.307127 -3.042253
C -0.239928 -0.696644 -2.807213
C -4.140617 0.023239 -2.108538
C -4.634756 -0.531624 0.193456
C -0.005435 5.265830 3.531509
H 0.461635 3.564092 4.778598
H -0.512054 6.759248 2.052765
H -4.894439 3.441713 -0.639364
C -3.786349 3.559162 -2.493770
H -2.440498 3.558041 -4.184098
H 4.098631 -4.409335 0.792625
C 2.968089 -4.710722 -1.026016
H 1.600828 -4.856021 -2.695034
C -0.798031 -4.343660 5.302893
H -0.936065 -6.219385 4.234487
H -0.631228 -2.341363 6.096316
H 2.800763 3.188417 1.463758
C 4.852303 3.087201 2.145762
H 5.328673 0.326222 -0.547200
C 6.263962 1.485551 1.013813
C 3.965393 0.804162 -4.372845
H 3.239709 2.392896 -3.106529
H 3.178894 -1.579738 -1.407196
C 3.929515 -1.415415 -3.422401
H -2.922752 -2.800485 -2.645138
C -1.545515 -2.664686 -4.297269
C 0.236803 -1.048450 -4.070901
H 0.270990 0.070512 -2.215596

H -3.436552 0.103554 -2.941219
C -5.463487 0.418941 -2.295385
C -5.954822 -0.131857 0.000437
H -4.310214 -0.870514 1.179209
H 0.071806 5.987630 4.348829
H -4.651810 3.873831 -3.083265
H 3.780853 -5.228941 -1.541025
H -0.899124 -4.809500 6.286367
H 4.718156 3.866914 2.899747
C 6.096748 2.476205 1.981872
H 7.238555 1.009418 0.879619
H 4.179921 1.474079 -5.209304
C 4.212629 -0.565027 -4.490499
H 4.111196 -2.489781 -3.512266
C -0.407645 -2.037909 -4.811691
H -2.057433 -3.436421 -4.877558
H 1.122278 -0.547092 -4.471429
H -5.779529 0.796879 -3.271320
C -6.375537 0.338555 -1.244417
H -6.661510 -0.189019 0.832129
H 6.940446 2.776491 2.608283
H 4.621428 -0.969425 -5.419930
H -0.027915 -2.320400 -5.796946
H -7.413764 0.646755 -1.391972
Cl -2.211532 0.408520 2.371506
H 1.662697 3.420946 -1.193413
H 2.274586 -0.988792 0.467856

Transition State **$TS_{2a/2b}$**
Ir -1.027064 0.827341 0.007782
P -2.892196 -0.641480 -0.212326
Cl -0.565335 0.548701 -2.505931
P 0.958338 2.157342 0.193863
C -0.040993 -0.663872 0.618501
C -2.212368 -2.244382 -0.181376
C -3.873321 -0.496448 -1.742742
C -4.169237 -0.445018 1.099272
C 0.827842 3.916464 -0.249329
C 1.812607 2.106875 1.810962
C 2.217886 1.517830 -0.985020
P -0.644899 -2.386549 0.447338
P 2.543207 -0.292767 -0.761506
C -4.924899 0.425596 -1.831710
C -3.543478 -1.272836 -2.860183
C -4.334126 0.761241 1.790521
C -4.993821 -1.533153 1.420999
C 0.980690 4.938054 0.695711
C 0.474166 4.240621 -1.568239

C 3.104551 2.642367 1.948456
C 1.203801 1.508706 2.920802
H 3.148005 2.107128 -0.934195
H 1.779591 1.658470 -1.983230
C 0.449116 -3.417465 -0.578301
C -0.474474 -2.983893 2.165586
C 3.317954 -0.788887 -2.341437
C 3.976613 -0.232062 0.391735
H -5.181074 1.046835 -0.969583
C -5.640647 0.558652 -3.019464
H -2.714056 -1.982387 -2.793923
C -4.265259 -1.140849 -4.044581
H -3.705599 1.618954 1.532501
C -5.307792 0.876675 2.784056
H -4.872566 -2.483597 0.890694
C -5.962721 -1.416839 2.415795
C 0.811246 6.269913 0.318073
H 1.230106 4.697599 1.732505
H 0.296318 3.444083 -2.298256
C 0.314536 5.572081 -1.939940
H 3.593895 3.126295 1.097333
C 3.771692 2.566769 3.167168
C 1.877967 1.426536 4.139755
H 0.191636 1.105227 2.830743
C 1.059124 -4.591539 -0.122963
C 0.606699 -3.023629 -1.917355
C 0.786914 -3.091306 2.771929
C -1.625772 -3.200570 2.929969
C 4.363807 -1.727055 -2.340884
C 2.785124 -0.372975 -3.571242
C 5.188966 0.383266 0.039358
C 3.842317 -0.765545 1.678422
C -5.314237 -0.225193 -4.127127
H -6.458603 1.280916 -3.080759
H -4.003742 -1.755045 -4.910057
H -5.428720 1.824569 3.314868
C -6.120737 -0.210597 3.100643
H -6.598269 -2.272567 2.658389
H 0.934428 7.061289 1.061427
C 0.485442 6.589169 -0.998845
H 0.040408 5.816403 -2.968930
C 3.161661 1.953041 4.263548
H 4.776907 2.985378 3.260944
H 1.391373 0.951248 4.995091
H 0.924105 -4.922947 0.909573
C 1.833475 -5.358114 -0.995564
H 0.133262 -2.099310 -2.270953
C 1.381551 -3.792294 -2.780390

C 0.892426 -3.409654 4.122971
H 1.692049 -2.927875 2.178549
H -2.608559 -3.095284 2.458999
C -1.517421 -3.534167 4.280166
H 4.778197 -2.086959 -1.394115
C 4.883313 -2.209823 -3.540241
C 3.314226 -0.852641 -4.768527
H 1.930788 0.309843 -3.595104
H 5.313750 0.807860 -0.962069
C 6.237323 0.455697 0.952691
C 4.891738 -0.692700 2.594952
H 2.898557 -1.231189 1.976978
H -5.878519 -0.120109 -5.057400
H -6.880094 -0.119364 3.881492
H 0.353923 7.633756 -1.291938
H 3.691325 1.888498 5.217471
H 2.303371 -6.276464 -0.635226
C 1.996997 -4.958802 -2.320364
H 1.511689 -3.474485 -3.818051
H 1.877785 -3.486899 4.589386
C -0.261393 -3.634110 4.877324
H -2.420483 -3.708193 4.869948
C 4.366208 -1.768709 -4.758809
H 5.701475 -2.934517 -3.520497
H 2.894222 -0.508996 -5.717235
H 7.175636 0.937013 0.665079
C 6.091760 -0.085340 2.232548
H 4.765897 -1.109047 3.597855
H 2.606061 -5.559631 -3.000671
H -0.179482 -3.885207 5.937676
H 4.777088 -2.144901 -5.698913
H 6.915844 -0.027894 2.948198
H 0.787584 -0.613237 1.346652
Cl -2.494954 2.793936 -0.516775
H -1.428447 1.170155 1.503919
H -2.777238 -3.138149 -0.462614

Transition State **$TS_{2d/5}$**
Ir -0.344144 0.192475 -0.662155
P -0.041597 -2.187139 -0.505294
Cl 2.595337 1.372610 -2.821789
P -0.610162 2.542656 -0.471432
C 1.545340 0.285074 -0.115679
C 1.369404 -2.449373 0.474180
C 0.151438 -2.996980 -2.148868
C -1.374115 -3.177086 0.281213
C 0.578119 3.440926 0.582157
C -0.912979 3.698298 -1.847260

C -2.183062 2.387767 0.475577
P 2.413040 -1.108380 0.584511
P -2.088303 0.566103 0.788625
C -0.656638 -2.634185 -3.235783
C 1.140486 -3.972722 -2.333058
C -1.570542 -3.014810 1.661296
C -2.206405 -4.056926 -0.422813
C 1.779552 3.871543 -0.005718
C 0.384541 3.638884 1.955020
C -1.359798 4.998557 -1.569773
C -0.684184 3.306991 -3.170503
H -3.009558 2.553097 -0.233625
H -2.327376 3.047569 1.344478
C 3.987260 -1.337020 -0.328531
C 2.955060 -0.746425 2.291861
C -1.608241 0.335521 2.542894
C -3.824442 0.006849 0.702581
H -1.420513 -1.859279 -3.109912
C -0.481609 -3.245437 -4.477691
H 1.792642 -4.245447 -1.497583
C 1.313542 -4.582003 -3.575034
H -0.898906 -2.356264 2.222762
C -2.593383 -3.695981 2.316917
H -2.066369 -4.206649 -1.496958
C -3.223184 -4.747437 0.238674
C 2.758344 4.492475 0.766136
H 1.955766 3.709427 -1.074064
H -0.538047 3.311453 2.440114
C 1.370308 4.256542 2.725410
H -1.534421 5.309856 -0.534529
C -1.577315 5.898191 -2.609685
C -0.895788 4.216222 -4.207287
H -0.345682 2.290321 -3.383457
C 5.260378 -1.298135 0.252469
C 3.870468 -1.637297 -1.694408
C 3.578702 0.471713 2.598700
C 2.751338 -1.688398 3.306190
C -2.516210 -0.093020 3.522808
C -0.273502 0.560914 2.909797
C -4.819286 0.769804 1.332428
C -4.179124 -1.163877 0.027775
C 0.502164 -4.219397 -4.650823
H -1.115019 -2.951038 -5.318586
H 2.089931 -5.340799 -3.703890
H -2.736555 -3.554383 3.391736
C -3.425432 -4.562997 1.605848
H -3.861879 -5.435252 -0.321791
H 3.685976 4.825138 0.294221

C 2.557272 4.685557 2.133977
H 1.203856 4.404343 3.795537
C -1.342450 5.507038 -3.929373
H -1.926984 6.909921 -2.389915
H -0.712697 3.909705 -5.239875
H 5.376092 -1.079070 1.317365
C 6.394555 -1.552309 -0.520996
H 2.877457 -1.678259 -2.153814
C 5.001411 -1.885150 -2.464623
C 4.000225 0.736541 3.900540
H 3.752779 1.211506 1.810309
H 2.236126 -2.625697 3.073479
C 3.189966 -1.429318 4.604703
H -3.553124 -0.315615 3.262098
C -2.098367 -0.269488 4.841218
C 0.133149 0.412162 4.232668
H 0.458457 0.839127 2.145466
H -4.558227 1.696309 1.854576
C -6.147660 0.348338 1.306697
C -5.507448 -1.584851 0.007992
H -3.413256 -1.732183 -0.501836
H 0.640793 -4.692617 -5.626384
H -4.224903 -5.102016 2.120467
H 3.326774 5.172310 2.738224
H -1.509081 6.215324 -4.744824
H 7.383194 -1.524409 -0.055772
C 6.268248 -1.843501 -1.877891
H 4.893624 -2.110912 -3.528641
H 4.485905 1.688350 4.131377
C 3.815345 -0.218865 4.902913
H 3.037572 -2.175284 5.388882
C -0.776657 -0.009623 5.202316
H -2.814452 -0.617183 5.589945
H 1.175111 0.610831 4.498214
H -6.916128 0.947195 1.801570
C -6.491521 -0.833279 0.649293
H -5.773916 -2.501668 -0.523942
H 7.157813 -2.042683 -2.480691
H 4.155425 -0.014615 5.921371
H -0.453099 -0.145326 6.237431
H -7.533221 -1.162652 0.628537
H 1.989643 1.220928 0.270750
Cl -2.379582 0.392822 -2.316888
H 2.024481 0.744018 -1.674493
H 1.716958 -3.459040 0.714282

Complex **6**
Ir 1.101976 0.155424 -0.685337

P -0.917557 1.401333 -0.489364
Cl 0.384534 -0.891855 -2.816106
P 3.162016 -1.011762 -0.553036
C 0.143687 -1.514010 0.174786
C -2.144026 0.327050 0.372237
C -1.749512 1.973142 -2.013524
C -0.866542 2.955055 0.471768
C 3.091101 -2.671051 0.189733
C 4.371438 -1.147694 -1.899878
C 3.825471 0.150154 0.711944
P -1.651196 -1.403732 0.291849
P 2.208628 0.890565 1.209402
C -1.022325 2.112872 -3.201105
C -3.103196 2.343130 -1.973675
C 0.003568 3.943017 -0.019604
C -1.678594 3.240814 1.575695
C 2.776894 -3.754313 -0.646820
C 3.193235 -2.882436 1.570108
C 5.670363 -1.588377 -1.603566
C 4.019873 -0.830067 -3.216719
H 4.388389 0.916476 0.157051
H 4.482753 -0.244672 1.501326
C -2.493011 -2.187457 -1.099799
C -2.162660 -2.250869 1.808720
C 1.767439 0.151626 2.821233
C 2.550993 2.628779 1.665948
H 0.033408 1.832732 -3.225051
C -1.650654 2.608835 -4.343125
H -3.686696 2.250386 -1.051921
C -3.724541 2.825986 -3.122755
H 0.648980 3.719287 -0.876264
C 0.052116 5.195756 0.581586
H -2.394442 2.508343 1.958410
C -1.615572 4.498185 2.180705
C 2.567903 -5.020491 -0.105258
H 2.679326 -3.600690 -1.726352
H 3.437257 -2.057242 2.241534
C 2.976765 -4.150496 2.108939
H 5.943852 -1.842668 -0.574330
C 6.612973 -1.706363 -2.620903
C 4.969595 -0.960359 -4.230876
H 3.006383 -0.483796 -3.437687
C -3.078212 -1.419298 -2.112559
C -2.576400 -3.585787 -1.146488
C -3.282548 -1.846461 2.547861
C -1.405162 -3.353722 2.231888
C 2.749968 -0.114092 3.785869
C 0.426115 -0.092648 3.134011

C 1.921986 3.196191 2.784869
C 3.451504 3.406451 0.922162
C -2.999892 2.958056 -4.308036
H -1.079570 2.715341 -5.268702
H -4.781894 3.097858 -3.087375
H 0.729986 5.957118 0.187758
C -0.756525 5.476225 1.684222
H -2.258515 4.714999 3.037192
H 2.323972 -5.856244 -0.765177
C 2.662343 -5.220970 1.273723
H 3.055352 -4.295960 3.189441
C 6.260945 -1.393926 -3.935660
H 7.625065 -2.045822 -2.387807
H 4.695337 -0.716501 -5.259859
H -3.026874 -0.330089 -2.092401
C -3.750316 -2.046751 -3.157798
H -2.128610 -4.197908 -0.357725
C -3.248762 -4.205976 -2.196208
C -3.629482 -2.544318 3.704928
H -3.889982 -0.995529 2.222861
H -0.529327 -3.673115 1.659956
C -1.762056 -4.046531 3.384828
H 3.801972 0.103310 3.577698
C 2.395237 -0.654035 5.019759
C 0.069099 -0.627815 4.370759
H -0.348998 0.148709 2.401681
H 1.207707 2.617589 3.376612
C 2.203037 4.507722 3.160597
C 3.729238 4.716419 1.305983
H 3.929714 2.997414 0.030778
H -3.490224 3.339030 -5.207720
H -0.716633 6.460751 2.157380
H 2.492722 -6.214540 1.695446
H 7.000831 -1.491186 -4.733985
H -4.212723 -1.437656 -3.937953
C -3.840356 -3.436799 -3.198836
H -3.317103 -5.295650 -2.225667
H -4.503040 -2.228395 4.279676
C -2.874147 -3.640656 4.122903
H -1.166783 -4.904274 3.706569
C 1.055926 -0.920309 5.310641
H 3.169683 -0.862816 5.761507
H -0.983280 -0.818535 4.595874
H 1.704764 4.935407 4.034188
C 3.110234 5.269616 2.426283
H 4.438220 5.307677 0.721535
H -4.376093 -3.925886 -4.015920
H -3.154643 -4.183096 5.029013

H 0.780517 -1.347409 6.277799
H 3.333282 6.296934 2.724809
H 0.357335 -2.393015 -0.454449
Cl 2.388357 1.947000 -1.935160
H 0.516992 -1.739031 1.185394
H -3.205438 0.407650 -0.002690
H -2.172005 0.597798 1.437311
C -5.207632 0.174475 -0.165751
Cl -5.471587 1.142195 1.474164
Cl -6.436537 0.922301 -1.339894
Cl -5.881411 -1.527266 0.200170

Transition State **$TS_{5/6}$**
Ir 1.027398 0.133296 -0.711506
P -1.016512 1.324609 -0.459736
Cl 0.298007 -0.959682 -2.816363
P 3.118432 -0.986060 -0.606431
C 0.119539 -1.532716 0.201293
C -2.261463 0.242161 0.306762
C -1.793239 2.038353 -1.957960
C -0.910121 2.825309 0.584774
C 3.095243 -2.642564 0.147015
C 4.315039 -1.104037 -1.967487
C 3.772921 0.195309 0.645772
P -1.680811 -1.432025 0.364069
P 2.148918 0.916719 1.152706
C -1.116771 2.108090 -3.180777
C -3.076231 2.591678 -1.840927
C -0.202979 3.909132 0.035340
C -1.494749 2.967554 1.848521
C 2.795113 -3.740311 -0.675773
C 3.213710 -2.838783 1.528090
C 5.627327 -1.519536 -1.694840
C 3.934066 -0.793380 -3.277996
H 4.313638 0.971431 0.081703
H 4.447640 -0.179799 1.430548
C -2.488584 -2.373874 -0.958136
C -2.124724 -2.212038 1.942942
C 1.711818 0.190670 2.770803
C 2.505255 2.658436 1.600726
H -0.113247 1.687452 -3.266348
C -1.726616 2.722247 -4.275430
H -3.612787 2.548672 -0.887208
C -3.679615 3.199587 -2.938122
H 0.273424 3.803721 -0.944977
C -0.104028 5.111005 0.726870
H -2.053881 2.149730 2.310540
C -1.393764 4.177769 2.538775

C 2.614698 -5.004645 -0.119726
H 2.683739 -3.599520 -1.755641
H 3.445923 -2.001500 2.188347
C 3.026428 -4.105189 2.081791
H 5.923668 -1.769330 -0.670816
C 6.553833 -1.618127 -2.728856
C 4.868013 -0.903072 -4.309024
H 2.909045 -0.468850 -3.478851
C -2.967756 -1.706100 -2.092023
C -2.660392 -3.759023 -0.843513
C -3.182688 -1.756378 2.740392
C -1.356054 -3.305340 2.371528
C 2.688018 -0.109665 3.730887
C 0.363123 -0.002131 3.089287
C 2.000031 3.200208 2.791758
C 3.331525 3.451827 0.788234
C -3.005025 3.266654 -4.157334
H -1.194195 2.774338 -5.228547
H -4.684529 3.616419 -2.837100
H 0.445941 5.944717 0.283119
C -0.707360 5.251636 1.977878
H -1.867712 4.278854 3.518389
H 2.380007 -5.851235 -0.769133
C 2.724346 -5.189784 1.260340
H 3.117714 -4.238372 3.162961
C 6.172888 -1.310730 -4.036806
H 7.576429 -1.938084 -2.514558
H 4.571275 -0.663694 -5.332879
H -2.844040 -0.625475 -2.197174
C -3.621151 -2.418243 -3.093848
H -2.302735 -4.291333 0.042797
C -3.312647 -4.466359 -1.851018
C -3.460258 -2.389439 3.952056
H -3.800450 -0.913849 2.417210
H -0.523775 -3.664699 1.758821
C -1.639053 -3.933108 3.581206
H 3.746645 0.065426 3.516794
C 2.318940 -0.631693 4.968769
C -0.007321 -0.514485 4.331416
H -0.405801 0.259021 2.354384
H 1.348424 2.609781 3.440364
C 2.331491 4.499520 3.171301
C 3.657363 4.749631 1.174172
H 3.708781 3.059592 -0.157947
H -3.478844 3.745060 -5.018549
H -0.634231 6.198717 2.518678
H 2.576754 -6.182001 1.693445
H 6.900761 -1.391919 -4.847946

H -4.003577 -1.885740 -3.967645
C -3.797193 -3.796139 -2.974154
H -3.451036 -5.545527 -1.752366
H -4.286778 -2.030456 4.569726
C -2.691814 -3.475287 4.373170
H -1.030588 -4.780664 3.905643
C 0.971796 -0.842544 5.267668
H 3.088654 -0.870564 5.706483
H -1.065460 -0.668015 4.560228
H 1.930461 4.904534 4.103930
C 3.163547 5.276145 2.368096
H 4.306309 5.352662 0.534559
H -4.319566 -4.350334 -3.757708
H -2.914742 -3.967070 5.323221
H 0.683959 -1.255329 6.237588
H 3.426639 6.293018 2.670090
H 0.332230 -2.423985 -0.411130
Cl 2.216763 1.959177 -2.018353
H 0.519607 -1.725481 1.208964
H -3.498517 0.248295 -0.195916
H -2.479442 0.568858 1.331782
C -5.000224 0.227188 -0.303595
Cl -5.424496 1.425491 1.048630
Cl -5.950194 0.709471 -1.771750
Cl -5.629329 -1.405178 0.230026

Complex **4a**
Ir 0.767399 1.096223 -0.184410
P 2.804885 0.169731 0.608949
Cl 0.274033 1.275973 2.340501
P -1.399629 1.940756 -0.725843
C 0.084109 -0.656469 -0.456636
C 2.192813 -1.409788 1.311046
C 3.728663 0.978334 1.950310
C 4.080648 -0.194247 -0.638200
C -1.560458 3.751262 -0.718831
C -2.176305 1.347022 -2.261897
C -2.560426 1.412029 0.597930
P 0.983444 -2.130951 0.151634
P -2.634322 -0.428809 0.814055
H 2.972858 -2.139139 1.575364
H 1.653280 -1.115079 2.224610
C 4.579315 2.040242 1.609939
C 3.604084 0.598446 3.292263
C 4.126924 0.601667 -1.789764
C 5.042066 -1.196180 -0.446207
C -1.900688 4.483509 -1.862136
C -1.263142 4.426859 0.474536

C -3.528910 1.634611 -2.515480
C -1.463730 0.559025 -3.171551
H -3.562213 1.833603 0.414447
H -2.173935 1.852307 1.528752
C -0.030486 -3.284007 1.097995
C 2.045947 -2.935654 -1.071375
C -3.363463 -0.618730 2.484134
C -4.065327 -0.850081 -0.262180
H 4.672654 2.355171 0.567729
C 5.298812 2.704700 2.599234
H 2.938646 -0.216268 3.584961
C 4.332285 1.264227 4.277011
H 3.385952 1.395358 -1.927450
C 5.121033 0.392535 -2.744268
H 5.024056 -1.814981 0.456249
C 6.027542 -1.406489 -1.407883
C -1.974515 5.875363 -1.801662
H -2.108624 3.968533 -2.803953
H -0.940995 3.862046 1.355152
C -1.347757 5.814307 0.530266
H -4.101150 2.256686 -1.819915
C -4.149197 1.133705 -3.654877
C -2.094232 0.041145 -4.302558
H -0.409977 0.336039 -2.989898
C -0.385108 -4.540655 0.592704
C -0.504751 -2.862509 2.349725
C 2.226552 -2.383804 -2.345472
C 2.794749 -4.048481 -0.671284
C -4.290670 -1.650474 2.711727
C -2.935027 0.152369 3.575745
C -5.312497 -0.224233 -0.092060
C -3.909755 -1.805245 -1.271366
C 5.178229 2.317379 3.933691
H 5.955261 3.533283 2.323813
H 4.232161 0.957636 5.320842
H 5.153972 1.020182 -3.637765
C 6.067573 -0.613462 -2.556831
H 6.768413 -2.196279 -1.261129
H -2.241963 6.441466 -2.697192
C -1.705976 6.540700 -0.606822
H -1.118382 6.333778 1.463720
C -3.434602 0.327023 -4.544501
H -5.201193 1.361637 -3.843697
H -1.531975 -0.602528 -4.982163
H -0.058980 -4.834478 -0.407624
C -1.196244 -5.377617 1.357313
H -0.273637 -1.862799 2.731086
C -1.318182 -3.705655 3.100976

C 3.154842 -2.947425 -3.213482
H 1.631632 -1.522981 -2.658158
H 2.663510 -4.478430 0.326654
C 3.707160 -4.621559 -1.558362
H -4.620590 -2.280377 1.880488
C -4.801195 -1.879265 3.987291
C -3.451736 -0.077900 4.850094
H -2.178779 0.929966 3.435717
H -5.453542 0.518154 0.701002
C -6.381029 -0.547928 -0.922934
C -4.985257 -2.123760 -2.104759
H -2.940876 -2.297593 -1.429006
H 5.743701 2.840060 4.708904
H 6.843628 -0.780362 -3.307771
H -1.765439 7.630923 -0.562925
H -3.930558 -0.083828 -5.427534
H -1.476419 -6.358256 0.966008
C -1.662417 -4.963190 2.605584
H -1.690424 -3.369607 4.071722
H 3.299144 -2.511241 -4.204620
C 3.889445 -4.070035 -2.825103
H 4.278117 -5.501485 -1.253241
C -4.388809 -1.089989 5.061244
H -5.530107 -2.679352 4.139900
H -3.116549 0.542075 5.685531
H -7.347392 -0.056409 -0.781914
C -6.218239 -1.499993 -1.933579
H -4.845039 -2.865489 -2.895931
H -2.304439 -5.623260 3.194024
H 4.610027 -4.515406 -3.515341
H -4.792988 -1.265540 6.061279
H -7.058440 -1.752349 -2.586111
H -0.698761 -0.984535 -1.161866
Cl 1.849728 3.351525 -0.162490
H 1.169673 1.163383 -1.715857
Cl -0.856977 -3.095974 -2.352802

Complex **4b**
Ir -0.502211 -0.968432 0.106072
P -2.508552 -0.198345 0.971594
Cl 0.172022 -2.248134 2.225887
P 1.647869 -1.591177 -0.662050
C -0.273334 0.734320 -0.722777
C -2.354589 1.644933 0.969908
C -2.998324 -0.633977 2.666754
C -4.038181 -0.438582 -0.009695
C 2.023888 -3.379427 -0.680590
C 2.062697 -1.072157 -2.370284

C 2.989237 -0.879938 0.375927
P -1.457236 2.039430 -0.549990
P 3.163861 0.978841 0.238308
C -3.169547 -1.999425 2.941708
C -3.188978 0.306915 3.684803
C -3.959220 -0.961830 -1.305352
C -5.278832 -0.022592 0.494114
C 1.662279 -4.155152 -1.790341
C 2.609104 -4.006171 0.427315
C 3.375827 -0.777236 -2.761307
C 1.035807 -0.988521 -3.321392
H 3.950159 -1.349359 0.112935
H 2.762776 -1.175805 1.412641
C -0.717772 3.683471 -0.393343
C -2.636202 2.093376 -1.924975
C 2.718624 1.542920 1.927539
C 4.999482 1.136381 0.274988
H -2.990093 -2.734511 2.150049
C -3.547703 -2.409920 4.216494
H -3.054399 1.374833 3.491307
C -3.559202 -0.112300 4.963634
H -2.991031 -1.301052 -1.685342
C -5.108176 -1.055055 -2.090750
H -5.352774 0.377047 1.511149
C -6.423309 -0.113566 -0.295449
C 1.899933 -5.527351 -1.799788
H 1.185550 -3.684649 -2.655034
H 2.869686 -3.425903 1.314745
C 2.847954 -5.379509 0.413095
H 4.196420 -0.843515 -2.040772
C 3.654694 -0.396198 -4.072869
C 1.318098 -0.619852 -4.636409
H 0.006231 -1.212857 -3.019268
C -1.081447 4.750514 -1.225321
C 0.282360 3.862241 0.574983
C -2.230114 1.597859 -3.170817
C -3.933578 2.597869 -1.762888
C 3.255024 2.742758 2.426686
C 1.719285 0.897168 2.670100
C 5.783776 0.642807 1.329856
C 5.635732 1.770775 -0.800190
C -3.742253 -1.468082 5.228995
H -3.678240 -3.474527 4.424845
H -3.706675 0.627868 5.753990
H -5.039803 -1.462916 -3.102577
C -6.337939 -0.628776 -1.589990
H -7.386662 0.214857 0.102869
H 1.614499 -6.119822 -2.672617

C 2.496681 -6.142902 -0.699380
H 3.308764 -5.855375 1.282415
C 2.626614 -0.316557 -5.012489
H 4.682440 -0.160880 -4.361190
H 0.509275 -0.563336 -5.369822
H -1.852750 4.618513 -1.988682
C -0.453774 5.987045 -1.081150
H 0.579026 3.026512 1.216673
C 0.904085 5.099995 0.711605
C -3.115032 1.610656 -4.246374
H -1.221918 1.190992 -3.293125
H -4.262862 2.986697 -0.794802
C -4.815014 2.602655 -2.841285
H 4.033119 3.270319 1.864399
C 2.806049 3.273291 3.635384
C 1.268298 1.434599 3.876125
H 1.278732 -0.043750 2.325937
H 5.301529 0.150359 2.180754
C 7.169511 0.778423 1.303857
C 7.025231 1.905928 -0.826987
H 5.033673 2.163986 -1.625578
H -4.032456 -1.794022 6.231019
H -7.236300 -0.702379 -2.208367
H 2.683653 -7.219658 -0.707395
H 2.846606 -0.018960 -6.040775
H -0.740319 6.817058 -1.730978
C 0.535264 6.163327 -0.114162
H 1.682834 5.232700 1.466206
H -2.795307 1.222203 -5.216125
C -4.406775 2.110105 -4.081671
H -5.829871 2.985498 -2.709460
C 1.804431 2.626406 4.362802
H 3.241332 4.203403 4.011639
H 0.495070 0.901118 4.437703
H 7.770157 0.390405 2.130633
C 7.792768 1.409973 0.224483
H 7.507662 2.403315 -1.672302
H 1.025218 7.133825 -0.005235
H -5.103491 2.110250 -4.923379
H 1.453290 3.045699 5.309182
H 8.880427 1.515168 0.206727
H -3.302030 2.195066 1.073069
H -1.684710 1.932427 1.796512
Cl -1.513062 -3.220815 -0.411286
H 0.541761 1.033519 -1.407062

Complex **4c**
Ir -0.622196 -0.724056 -0.180846

P -2.752044 -0.550736 0.808839
Cl 0.186621 -1.381869 2.027485
P 1.555525 -1.020778 -1.117998
C -0.190828 1.258439 0.407002
C -2.821523 1.166455 1.515296
C -3.157092 -1.630598 2.229940
C -4.270004 -0.697098 -0.201311
C 1.661118 -2.539678 -2.125382
C 2.292079 0.227149 -2.250691
C 2.872786 -1.257730 0.136437
P -1.659821 2.240952 0.635236
P 3.215122 0.246224 1.180800
C -3.807890 -2.843137 1.960261
C -2.808437 -1.325839 3.551728
C -4.245417 -1.367846 -1.429135
C -5.483733 -0.182801 0.281021
C 1.148046 -2.512019 -3.428459
C 2.157083 -3.741753 -1.609566
C 3.567130 -0.017704 -2.788108
C 1.626660 1.406345 -2.601523
H 3.793769 -1.630927 -0.341115
H 2.503602 -2.041972 0.810562
C -1.356998 3.705558 1.663692
C -2.357568 2.815801 -0.921300
C 4.091648 -0.542964 2.595157
C 4.621284 0.986749 0.245182
H -4.064323 -3.108044 0.931315
C -4.126744 -3.718081 2.996342
H -2.267271 -0.408623 3.792976
C -3.137937 -2.199220 4.586434
H -3.310377 -1.807679 -1.781984
C -5.417102 -1.484219 -2.179126
H -5.526964 0.311117 1.256971
C -6.648046 -0.299116 -0.473099
C 1.142418 -3.666673 -4.206000
H 0.735174 -1.581829 -3.828729
H 2.537669 -3.791948 -0.586381
C 2.152805 -4.895975 -2.392874
H 4.099822 -0.942079 -2.540779
C 4.164659 0.903602 -3.643354
C 2.230686 2.332054 -3.454512
H 0.611745 1.578210 -2.241383
C -2.044591 4.905270 1.432079
C -0.417535 3.633239 2.703481
C -1.510547 3.509188 -1.798069
C -3.679092 2.551190 -1.292429
C 5.223212 0.055791 3.173984
C 3.556497 -1.684900 3.212827

C 5.794385 0.279311 -0.060304
C 4.498227 2.308191 -0.201410
C -3.800620 -3.394873 4.312911
H -4.637223 -4.657407 2.770694
H -2.866858 -1.943123 5.613520
H -5.390719 -2.007207 -3.138283
C -6.613089 -0.943849 -1.711262
H -7.586992 0.107731 -0.089605
H 0.737740 -3.633974 -5.220626
C 1.646390 -4.861979 -3.690677
H 2.542704 -5.829773 -1.979924
C 3.498354 2.085489 -3.974737
H 5.157523 0.698626 -4.051809
H 1.697274 3.247264 -3.725464
H -2.775283 4.974399 0.621586
C -1.788535 6.019965 2.228144
H 0.132172 2.706885 2.893816
C -0.168057 4.751644 3.494955
C -1.979918 3.909061 -3.044356
H -0.477038 3.726698 -1.509211
H -4.354128 2.019413 -0.618978
C -4.141615 2.948885 -2.545291
H 5.656344 0.953402 2.721647
C 5.812113 -0.485813 4.316138
C 4.148812 -2.225725 4.352037
H 2.653900 -2.154168 2.812357
H 5.913603 -0.752396 0.287555
C 6.813743 0.877305 -0.796575
C 5.517972 2.909457 -0.941858
H 3.587159 2.871666 0.027356
H -4.057529 -4.077694 5.126578
H -7.525946 -1.034678 -2.305538
H 1.640128 -5.768673 -4.300851
H 3.967904 2.809141 -4.646004
H -2.323988 6.953181 2.039296
C -0.850750 5.944664 3.257347
H 0.569465 4.690119 4.298100
H -1.316737 4.441767 -3.729616
C -3.292495 3.619194 -3.423003
H -5.170340 2.723002 -2.835723
C 5.280970 -1.631758 4.907998
H 6.697335 -0.007904 4.744575
H 3.715905 -3.119551 4.809028
H 7.721982 0.313748 -1.026467
C 6.675754 2.194522 -1.241071
H 5.404027 3.939882 -1.289023
H -0.646870 6.822210 3.875335
H -3.653536 3.921540 -4.408884

H 5.746064 -2.057922 5.800535
H 7.475277 2.663204 -1.820690
H 0.282160 1.200229 1.403035
Cl -1.399334 -0.027007 -2.385545
H 0.497033 1.842585 -0.226997
H -3.828688 1.603912 1.582068
H -2.429080 1.133355 2.543902
Cl -1.246831 -3.108617 -0.701128

Transition State **$TS_{4/4a}$**
Ir 0.782437 1.114630 -0.202592
P 2.790444 0.105111 0.561678
Cl 0.353257 1.284305 2.350703
P -1.361997 2.027254 -0.667875
C 0.010251 -0.619681 -0.457294
C 2.126515 -1.445643 1.289570
C 3.780593 0.876208 1.880087
C 4.031662 -0.322902 -0.700173
C -1.487117 3.837465 -0.592394
C -2.222467 1.495778 -2.182438
C -2.477723 1.461332 0.680800
P 0.869123 -2.112080 0.155593
P -2.519261 -0.380321 0.836218
C 4.662712 1.903817 1.515569
C 3.685120 0.494920 3.223849
C 4.085395 0.457301 -1.861988
C 4.960872 -1.355459 -0.512330
C -1.814808 4.614163 -1.709720
C -1.156601 4.465420 0.617916
C -3.574656 1.836751 -2.362290
C -1.585818 0.697500 -3.138574
H -3.492314 1.865926 0.535881
H -2.072231 1.880783 1.611994
C -0.174711 -3.255396 1.079517
C 1.866694 -2.959605 -1.093391
C -3.172615 -0.667559 2.520952
C -3.976235 -0.793116 -0.204339
H 4.736109 2.219076 0.471834
C 5.440643 2.533610 2.482817
H 2.997790 -0.294537 3.534688
C 4.472268 1.125192 4.186319
H 3.367871 1.272642 -1.997490
C 5.055841 0.203883 -2.829981
H 4.936250 -1.963561 0.397310
C 5.921609 -1.610904 -1.487828
C -1.841990 6.004904 -1.606889
H -2.047407 4.134676 -2.664438
H -0.844005 3.863059 1.477159

C -1.194760 5.852614 0.715749
H -4.088496 2.462336 -1.625604
C -4.269595 1.382651 -3.477211
C -2.291512 0.228783 -4.247137
H -0.534076 0.428310 -3.014573
C -0.710080 -4.392765 0.460829
C -0.491543 -2.956286 2.413571
C 2.068077 -2.410019 -2.365393
C 2.550174 -4.119467 -0.709120
C -4.034795 -1.756784 2.733218
C -2.761546 0.094012 3.624928
C -5.228070 -0.203152 0.046177
C -3.842404 -1.696327 -1.261440
C 5.348905 2.144599 3.819129
H 6.121516 3.335523 2.188375
H 4.394768 0.817094 5.231633
H 5.094552 0.819125 -3.731815
C 5.969691 -0.832369 -2.646472
H 6.636994 -2.424475 -1.344410
H -2.099639 6.606065 -2.482123
C -1.539949 6.624250 -0.395413
H -0.939014 6.336133 1.661568
C -3.629483 0.570902 -4.417703
H -5.321179 1.650769 -3.606697
H -1.789137 -0.421009 -4.966463
H -0.498906 -4.585521 -0.594881
C -1.548319 -5.233301 1.191737
H -0.115428 -2.045984 2.888946
C -1.322996 -3.808516 3.133222
C 2.954680 -3.022114 -3.244986
H 1.524479 -1.512688 -2.667080
H 2.402033 -4.550798 0.285976
C 3.421979 -4.737615 -1.605905
H -4.346586 -2.379435 1.889293
C -4.501761 -2.052007 4.011385
C -3.232918 -0.205206 4.902243
H -2.053925 0.916551 3.492151
H -5.352033 0.497652 0.878880
C -6.322086 -0.512673 -0.756651
C -4.944838 -2.002185 -2.063956
H -2.873392 -2.160324 -1.490098
H 5.961948 2.638808 4.576709
H 6.726420 -1.035051 -3.408290
H -1.562242 7.714020 -0.318414
H -4.183365 0.199200 -5.283398
H -1.971708 -6.118514 0.711474
C -1.849777 -4.947953 2.523633
H -1.569664 -3.570300 4.170655

H 3.113676 -2.589931 -4.235575
C 3.625437 -4.187571 -2.870450
H 3.943361 -5.651226 -1.311288
C -4.107320 -1.273912 5.100584
H -5.180280 -2.896836 4.155294
H -2.913046 0.406609 5.749524
H -7.291172 -0.048553 -0.554831
C -6.182095 -1.414170 -1.815963
H -4.817130 -2.702724 -2.894097
H -2.507831 -5.612697 3.088969
H 4.312900 -4.669450 -3.570004
H -4.476016 -1.503548 6.103366
H -7.043277 -1.654431 -2.445220
H -0.722687 -0.925497 -1.224468
Cl 1.951187 3.320748 -0.212365
H 1.140958 1.136547 -1.745249
H 2.880086 -2.208353 1.536737
H 1.625492 -1.122561 2.214836
Cl -0.976474 -2.937247 -2.643019

Transition State **$TS_{4a/4b}$**
Ir 0.809483 0.985512 0.093685
P 2.799035 -0.165918 0.782979
Cl -0.025283 0.100610 2.851325
P -1.320780 1.943675 -0.315244
C 0.117633 -0.649695 -0.531975
C 2.137066 -1.856580 1.130883
C 3.730917 0.268314 2.294462
C 4.091411 -0.409016 -0.481878
C -1.427154 3.724850 0.039021
C -2.118169 1.752203 -1.948545
C -2.532774 1.190858 0.848797
P 0.887376 -2.231348 -0.115930
P -2.712515 -0.641548 0.646831
H 2.886524 -2.657222 1.210955
H 1.619508 -1.748467 2.097986
C 5.013652 -0.264766 2.493282
C 3.177739 1.119148 3.260280
C 4.454904 0.706993 -1.247400
C 4.723617 -1.638869 -0.719244
C -1.232221 4.655125 -0.989950
C -1.580616 4.175819 1.355933
C -3.422886 2.236604 -2.133262
C -1.468784 1.112483 -3.008917
H -3.501471 1.717127 0.801022
H -2.093962 1.330115 1.848519
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C 1.704241 -2.812751 -1.618103

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