Supporting Information

For

Tuning PCP-Ir Complexes: The impact of an N-Heterocyclic Olefin

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General:

All experiments were carried out under an inert atmosphere by using standard Schlenk techniques. The solvents were dried by known procedures and distilled under argon prior to use or obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies). The starting complexes $[Ir(COD)(\mu\text{-}Cl)]_2$ was prepared according to the literature procedure.[1,2] All other chemicals were used as purchased from Sigma-Aldrich, Merck and J. T. Baker. H_2 gas (>99.5 %) was obtained from Infra. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^{19}F spectra were recorded either on a Bruker ARX 300 MHz or a Bruker Avance 400 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$) and to an external reference of $CFCl_3$ for ^{19}F and H_3PO_4 for $^{31}P\{^1H\}$. Coupling constants, *J*, are given in Hz. Spectral assignments were achieved by combination of ^1H-^1H COSY, ^{13}C APT and ^1H-^{13}C HSQC/HMBC experiments. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer.

Molecular Structure Determination for Complexes 1, 2 and 3. Intensity data were collected at 100 K on a Bruker APEX-II diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV and 40 mA. Data reduction of the diffraction images was performed using the APEX2 software.[3] All the structures were solved by direct methods and refined by full-matrix least-squares methods based on F^2 using the SHELXL-97 software.[4] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically in idealized positions and refined with isotropic displacement parameters according to the riding model, except for the hydrido ligands, which were observed in the difference Fourier map and refined without restraints. All distance and angle calculations were performed using the SHELXL-97 and WinGX programs.[4,5]

[1] Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth*. **1982**, *15*, 18-20.

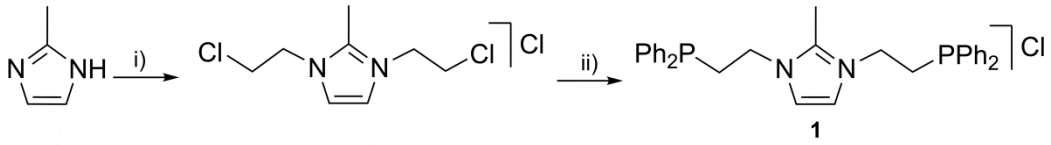
[2] Kelly, R. A.; Clavier, H.; Giudice, S.; Scott, N. M.; Stevens, E. D.; Bordner, J.; Samardjiev, I.; Hoff, C. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2008**, *27*, 202-210.

[3] APEX2 Bruker AXS Inc., Madison, Wisconsin, USA, **2011**.

[4] G. M. Sheldrick, SHELXS-97 and SHELXL-97; University of Göttingen, Germany, **1997**.

[5] L. J. Farrugia, *WinGX*; University of Glasgow, Great Britain, **1998**.

Preparation of 1,3-bis(2-(diphenylphosphino)ethyl)-2-methylimidazolium chloride (1)



1

i) Preparation of 1,3-bis(2-chloroethyl)-2-methylimidazolium chloride.

2-methylimidazole (3.3 g, 40 mmol) was added to a solution of tetrabutylammonium bromide (275 mg, 0.85 mmol), potassium hydroxide (14.96 g, 0.26 mmol), potassium carbonate (11.80 g, 0.085 mmol) and 1,2-dichloroethane (20 ml). This solution was stirred at 45 ºC for 5 hours. The mixture thus obtained was evaporated under reduced pressure. The product was extracted with acetonitrile, filtered and evaporated. The solid was dissolved in dichloromethane, washed with water (10 ml), dried with magnesium sulfate, filtered and evaporated. The resulting colorless oil was redissolved in 1,2-dichloroethane (10 ml) and refluxed 7 days at 80 ºC.

Evaporation of the volatiles afforded a beige oil that was washed with tetrahydrofurane (3 x 10 mL) and diethyl ether (3 x 10 mL) in an ultrasonic bath to give the product as an off-white solid (3.80 g, 16 mmol, yield = 30%). ^1H

NMR (400 MHz, dmso-d_6): δ 7.86 (s, 2H, CH_{im}), 4.62-4.59 (m, 4H, NCH_2), 4.10-4.07 (m, 4H, CH_2Cl), 2.72 (s, 3H, CH_3). ^{13}C NMR (101 MHz dmso-d_6): δ 145.5 (s, $NC_{im}N$), 121.8 (s, NCH), 48.8 (s, CH_2N), 43.0 (s, CH_2Cl), 9.8 (s, CH_3). HRMS (ESI) *m/z* calcd. for $C_8H_{13}Cl_3N_2$ ($M - Cl^-$) 207.0450, found 207.0450.

ii) Preparation of 1,3-bis(2-diphenylphosphylethyl)-2-methylimidazolium chloride (1).

A mixture of diphenylphospine (1.5 mL, 8.70 mmol) and potassium tert-butoxide (1.00 g, 8.90 mmol) in dry dimethylsulfoxide (5 mL) was stirred at 25 ºC for 2 hours. Subsequently, a solution of 1,3-bis-(2-chloroethyl)-2-imidazolium (1.05 g, 4.34 mmol) in 5 ml of dry dimethylsulfoxide was added dropwise and stirred for 48 hours at 25 ºC. The solvent was then evaporated under reduced pressure and the product extracted from the residue in dichloromethane and filtered through celite®. The solvent was evaporated *in vacuo* and the residue washed with diethyl ether (3 x 10 mL) in an ultrasonic bath to afford the title product as an pale yellow solid (1.20 g, 2.20 mmol, yield = 51%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 2H, CH_{im}), 7.41-7.28 (m, 20H, CH_{Ar}), 4.28-4.18 (m, 4H, NCH_2), 2.56 (t, $^3J_{HH}$ =7.3 Hz, 4H, PCH_2), 2.38 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.7 (s, $NC_{im}N$), 136.1 (d, $^1J_{C\text{-}P}$ = 11.5, $C_{Ar\text{-}ipso}$), 132.5 (d, $^2J_{C\text{-}P}$ = 18.61, $C_{Ar\text{-}orto}$), 129.3 (s, $C_{Ar\text{-}para}$), 128.9 (d, $^3J_{C\text{-}P}$ = 7.1, $C_{Ar\text{-}meta}$), 121.8 (s, NCH), 46.2 (d, $^2J_{C\text{-}P}$ = 22.5, CH_2N), 28.9 (d, $^1J_{C\text{-}P}$=16.0, CH_2P), 10.6 (s, CH3). ^{31}P NMR (121 MHz, $CDCl_3$): δ –22.2 (bs). HRMS (ESI) *m/z* calcd for $C_{32}H_{33}N_2P_2Cl$ ($M - Cl^-$) 507.2113, found 507.2113.

Preparation of [Ir(cod)(PCP)]Cl (2)

A solution of potassium tert-butoxide (63 mg, 0.56 mmol) in dry tetrahydrofurane (5 ml) was added dropwise to a dry tetrahydrofurane solution of 1,3-bis(2-diphenylphosphylethyl)-2-methylimidazolium chloride (293 mg, 0.54 mmol) at –78 ºC. After 30 minutes, a solution of bis(1,5-cyclooctadiene)diiridium(I) dichloride (184 mg, 0.27 mmol) in dry tetrahydrofurane (5 ml) was added dropwise to the first solution and stirred for 3 hours at low temperature. The solvent was evaporated in vacuo and the resultant oil was dissolved in dichloromethane and filtered through celite®. After removing the solvent under reduced pressure, the product was obtained as a yellow solid (396 mg, 0.47 mmol, yield = 87%). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.50-7.35 (m, 10H, CH_{Ar}), 7.30-7.25 (m, 2H, CH_{Ar}), 7.19-7.13 (m, 4H, CH_{Ar}), 7.13-7.05 (m, 4H, CH_{Ar}), 6.50 (s, 2H, CH_{im}), 5.00-4.84 (m, 2H, NCH_2), 4.64-4.50 (m, 2H, NCH_2), 3.50-3.38 (m, 2H, CH_{COD}), 3.24-3.11 (m, 2H, CH_2P), 2.94-2.78 (m, 2H, CH_2P), 2.46-2.29 (m, 4H, CH_{COD}+$IrCH_2$), 1.84-1.69 (m, 2H, $CH_{2\ COD}$), 1.68-1.54 (m, 2H, $CH_{2\ COD}$), 1.11-0.98 (m, 4H, $CH_{2\ COD}$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.6 (t, $^2J_{C\text{-}P}$ = 3.4, CH_2Ir), 142.8 (d, $^3J_{C\text{-}P}$ = 42.1, $NC_{im}N$), 134.3 (d, $^2J_{C\text{-}P}$=13.9, $C_{Ar\text{-}orto}$), 133.7 (d, $^1J_{C\text{-}P}$ = 28.9, $C_{ipso}P$), 130.8 (s, $C_{Ar\text{-}para}$), 130.3 (d, $^3J_{C\text{-}P}$ = 8.9, $C_{Ar\text{-}meta}$), 129.0 (s, $C_{Ar\text{-}para}$), 128.6 (d, $^3J_{C\text{-}P}$ = 8.9, $C_{Ar\text{-}meta}$), 119.3 (s, NCH), 79.9 (s, CH_{COD}), 60.4 (d, $^2J_{C\text{-}P}$ = 32.0, CH_{COD}), 44.0 (s, $CH_{2\ COD}$), 33.7 (s, $CH_{2\ COD}$), 31.1 (d, $^3J_{C\text{-}P}$ = 4.9, CH_2N), 24.5 (d, $^3J_{C\text{-}P}$ = 22.1, CH_2P). ^{31}P NMR (121 MHz, $CDCl_3$): δ –23.3 (bs). HRMS (ESI) *m/z* calcd for $C_{40}H_{44}IrN_2P_2Cl$ ($M - Cl^-$) 807.2606, found 807.2623.

Preparation of [Ir(PCP)(cod)]PF_6 (3)

91 mg (0.36 mmol) of silver hexafluorophosphate was added to a solution of [Ir(COD)(PCP)]Cl (200 mg, 0.24 mmol) in dichloromethane (15 ml) and stirred at room temperature for 3 hours in absence of light. The mixture thus obtained was filtered through silica and evaporated to obtain the product as an off-white solid (180 mg, 0.19 mmol, yield = 79%). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.54-7.40 (m, 10H, CH_{Ar}), 7.38-7.30 (m, 2H, CH_{Ar}), 7.44-7.15 (m, 4H, CH_{Ar}), 7.15-7.06 (m, 4H, CH_{Ar}), 5.96 (s, 2H, CH_{im}), 4.69-4.54 (m, 2H, NCH_2), 4.41-4.24 (m, 2H, NCH_2), 3.54-3.41 (m, 2H, CH_{COD}), 3.24-3.10 (m, 2H, CH_2P), 2.91-2.75 (m, 2H, CH_2P), 2.51-2.29 (m, 4H, CH_{COD}+$IrCH_2$), 1.90-

1.74 (m, 2H, CH_{2COD}), 1.74-1.56 (m, 2H, CH_{2COD}), 1.14-0.94 (m, 4H, $CH_{2\ COD}$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 161.2 (t, $^2J_{C-P}$ = 3.4, CH_2Ir), 142.5 (d, $^3J_{C-P}$ = 42.3, $NC_{im}N$), 134.1 (d, $^2J_{C-P}$ = 14.0, $C_{Ar\text{-}orto}$), 133.6 (d, $^1J_{C-P}$ = 28.9, $C_{ipso}P$), 130.7 (s, $C_{Ar\text{-}para}$), 130.2 (d, $^3J_{C-P}$ = 8.9, $C_{Ar\text{-}meta}$), 129.9 (s, $C_{Ar\text{-}para}$), 128.5 (d, $^3J_{C-P}$ = 7.9, $C_{Ar\text{-}meta}$), 128.4 (d, $^3J_{C-P}$ = 9.0, $C_{Ar\text{-}meta}$), 118.5 (s, NCH), 80 (s, CH_{COD}), 60.6 (d, $^2J_{C-P}$ = 32.3, CH_{COD}), 44.0 (s, $CH_{2\ COD}$), 33.4 (s, $CH_{2\ COD}$), 30.9 (d, $^2J_{C-P}$ = 4.6, CH_2N), 24.0 (d, $^1J_{C-P}$ = 23.1, CH_2P). ^{31}P NMR (121 MHz, CD_2Cl_2): δ –24.4 (bs, PPh_2), –144.3 (sept, $^1J_{P-F}$ = 712, PF_6). ^{19}F NMR (282, CD_2Cl_2): δ –72.8 (d, $^1J_{P-F}$ = 712, PF_6). HRMS (ESI) *m/z* calcd. for $C_{40}H_{44}F_6IrN_2P_3$ (M – PF_6^-) 807.2606, found, 807.2751. Anal. Calcd. for $C_{40}H_{44}F_6IrN_2P_3$ (952.22 + CH_2Cl_2): C, 47.49; H, 4.63; N, 2.70. Found: C, 46.93; H, 4.63; N, 3.33.

Preparation of $[Ir(PCP)(CO)_2]PF_6$ (4)

A dichloromethane solution of **3** (20 mg, 0.024 mmol) was placed under a carbon monoxide atmosphere for 1 h at room temperature in a Young NMR tube. The characterization of the product was carried out *in situ* as the isolation of the product was not possible due to loss of a CO ligand. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.99-7.90 (m, 2H, CH_{Ar}), 7.73-7.50 (m, 10H, CH_{Ar}), 7.44-7.37 (m, 8H, CH_{Ar}), 6.83 (s, 2H, CH_{im}), 4.65-4.45 (m, 2H, NCH_2), 4.03-3.88 (m, 2H, NCH_2), 3.13-3.04 (m, 2H, CH_2P), 2.60-2.50 (m, 4H, CH_2P+$IrCH_2$). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 159.5 (s, CH_2Ir), 135.7 (t, J_{C-P} = 28.8, $NC_{im}N$), 134.4 (t, J_{C-P} = 7.1, C_{Ar}), 132.3 (s, C_{Ar}), 130.9 (s, C_{Ar}), 130.7 (d, J_{C-P} = 6.5 C_{Ar}), 129.7 (d, J_{C-P} = 5.6, C_{Ar}), 128.9 (d, J_{C-P} = 5.2, C_{Ar}), 128.5 (s, C_{Ar}), 126.6 (d, $^1J_{C-P}$ = 28.9, $C_{ipso}P$), 118.4 (s, NCH), 42.4 (s, CH_2N), 22.5 (app. t, $^1J_{C-P}$ = 18.7, CH_2P).^{31}P NMR (121 MHz, CD_2Cl_2): δ –8.97 (bs, PPh_2), –144.3 (sept, $^1J_{P-F}$ = 712, PF_6). ^{19}F NMR (282, CD_2Cl_2): δ –72.8 (d, $^1J_{P-F}$ = 712, PF_6). IR: ν_{CO} = 1968 (ν_s) and 1924 (ν_{as}) cm^{-1}.

Preparation of $[Ir(PCP)(CO)]PF_6$ (5)

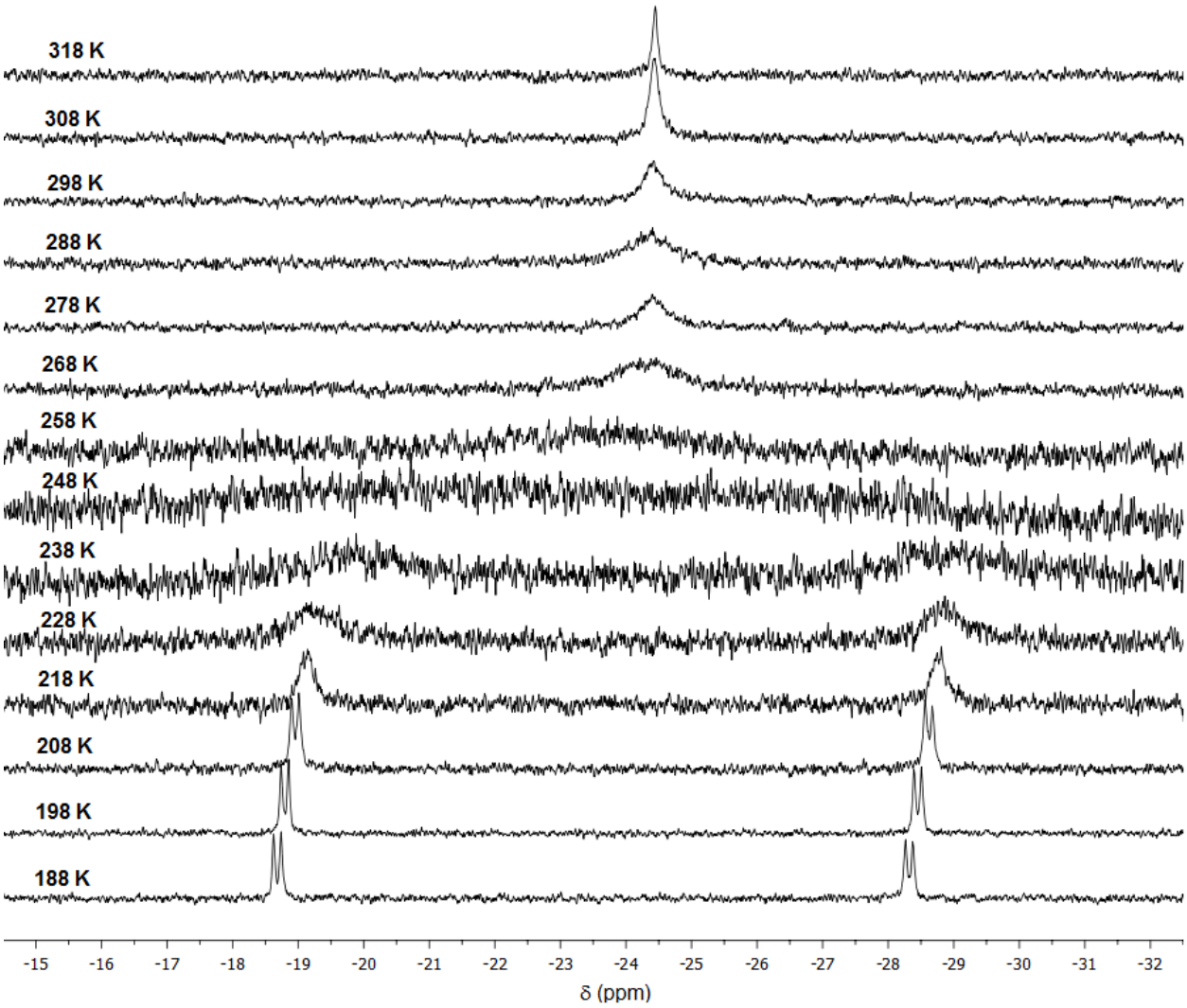
A dichloromethane solution of **3** (200 mg, 0.24 mmol) was placed under a carbon monoxide atmosphere for 1 h at room temperature. The thus obtained complex **4** was placed under an Ar atmosphere, leading to loss of a carbonyl ligand and concomitant formation of the title compound as a brown solid after evaporation the solvent and washing of the resulting solid with diethyl ether (3 x 5 ml) (165 mg, 0.19 mmol, yield = 80%).^1H NMR (300 MHz, CD_2Cl_2): δ 8.11-8.00 (m, 4H, CH_{Ar}), 7.73-7.65 (m, 5H, CH_{Ar}), 7.59-7.49 (m, 2H, CH_{Ar}), 7.36-7.30 (m, 5H, CH_{Ar}), 7.26-7.18 (m, 4H, CH_{Ar}), 7.05 (s, 2H, CH_{im}), 4.60-4.40 (m, 2H, NCH_2), 4.00-3.84 (m, 2H, NCH_2), 3.04-2.93 (m, 2H, CH_2P), 2.73-2.60 (m, 2H, CH_2P), 2.32 (t, $^3J_{H-P}$ = 11, 2H, $IrCH_2$). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 181.8 (s, CO), 153.1 (s, CH_2Ir), 136.5 (t, J_{C-P} = 6.8, C_{Ar}), 136.1 (s, $NC_{im}N$), 132.9 (s, C_{Ar}), 130.8 (t, J_{C-P} = 5.7, C_{Ar}), 130.1 (t, J_{C-P} = 5.1, C_{Ar}), 129.1 (d, J_{C-P} = 5.5, C_{Ar}), 128.5 (t, J_{C-P} = 25.5, C_{Ar}), 119.4 (s, NCH), 43.5 (s, CH_2N), 25.2 (app. t, $^1J_{C-P}$ = 15.6, CH_2P). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 8.28 (bs, PPh_2), –144.3 (sept, $^1J_{P-F}$ = 712, PF_6). ^{19}F NMR (282, CD_2Cl_2): δ –72.8 (d, $^1J_{P-F}$ = 712, PF_6). IR: ν_{CO} = 1978 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{33}H_{32}F_6IrN_2OP_3$ (M – PF_6^-) 727.1619, found 727.1615.

Preparation of $[Ir(PCP)(CO)(H)_2]PF_6$ (6)

A dichloromethane solution (10 mL) of **4** (180mg, 0.18 mmol) was placed under a carbon monoxide atmosphere for 1 h at room temperature. The CO atmosphere was replaced by a hydrogen atmosphere and stirred for 3 h at room temperature. Subsequently, the hydrogen atmosphere was removed and the solvent was evaporated *in vacuo*. The solid was washed with diethyl ether (3 x 5 mL) and the product was obtained as a yellow solid (134 mg, 0.15 mmol,

yield = 83%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.76-7.71 (m, 5H, CH_{Ar}), 7.63-7.58 (m, 5H, CH_{Ar}), 7.49-7.44 (m, 5H, CH_{Ar}), 7.41-7.37 (m, 5H, CH_{Ar}), 6.91 (s, 2H, CH_{im}), 4.55-4.49 (m, 2H, NCH_2), 4.15-4.03 (m, 2H, NCH_2), 2.96-2.88 (m, 2H, CH_2P), 2.72 (app. dt, J = 6, J' = 3 , 2H, CH_2Ir), 2.16-2.05 (m, 2H, CH_2P), –11.03 (t, $^{2}J_{H-P}$ = 23.0, 1H), –13.91 (t, $^{2}J_{H-P}$ = 14.0, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 162.8 (s, $NC_{im}N$), 147.8 (bs, $IrCH_2$), 132.8 (t, J_{C-P} = 6.8, C_{Ar}), 132.3 (s, C_{Ar}), 131.6 (t, J_{C-P} = 6.2, C_{Ar}), 130.7 (s, C_{Ar}), 130.2 (t, J_{C-P} = 4.6, C_{Ar}), 129.5 (t, J_{C-P} = 5.3, C_{Ar}), 129.3 (t, J_{C-P} = 5.1, C_{Ar}), 128.5 (s, J_{C-P} = 5.3, C_{Ar}), 118.3 (s, NCH), 42.3 (s, CH_2N), 27.3 (t, J_{C-P} = 19.3, CH_2P). ^{31}P NMR (121 MHz, CD_2Cl_2): δ –18.0 (s, PPh_2), –144.3 (sept, $^{1}J_{P-F}$ = 712, PF_6). ^{19}F NMR (282, CD_2Cl_2): δ –72.8 (d, $^{1}J_{P-F}$ = 712, PF_6). IR: ν_{CO} = 2066 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{33}H_{32}F_6IrN_2OP_3$ ($M - H_2 - PF_6^-$) 727.1619, found 727.1665. Anal. Calcd. for $C_{33}H_{32}F_6IrN_2OP_3$ (874.14 + 1/2 CH_2Cl_2): C, 43.92; H, 3.85; N, 3.06. Found: C, 43.63; H, 3.99; N, 3.36.

Variable temperature ^{31}P NMR spectra of 3



All calculations have been carried out at the DFT level using the Gaussian 09.D1 package.[6] The B3LYP-D3[7,8] functional has been used with Becke-Johnson damping[9] and the "ultrafine" grid in combination with the def2-SVP basis set[10] for all atoms..

[6] Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

[7] a) Lee, C.; Yang, W.; Parr, W, R. G. Phys. Rev. B 1988, 37, 785-789. b) Becke, A. D. J. Chem. Phys. 1993, 98, 1372-1377. c) Becke, A. D. J. Chem. Phys. 1993, 98, 5648-5652.

[8] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. J. Chem. Phys. 2010, 132, 154104.

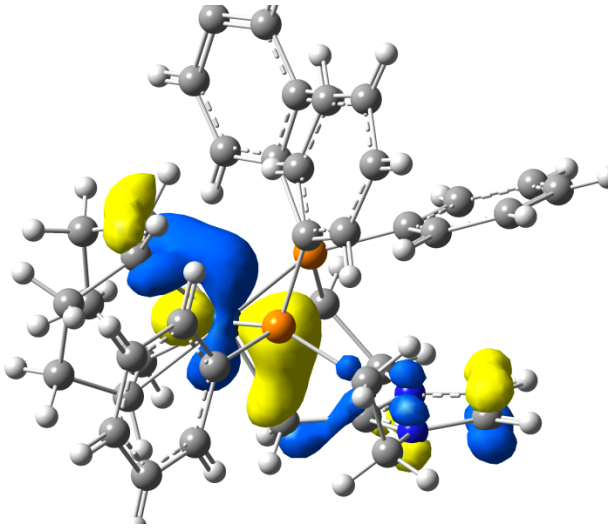
[9] Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comp. Chem*. **2011**, *32*, 1456–1465.

[10] Weigend, F.; Ahlrichs, R. Phys. Chem. Chem. Phys. 2005, 7, 3297-3305.

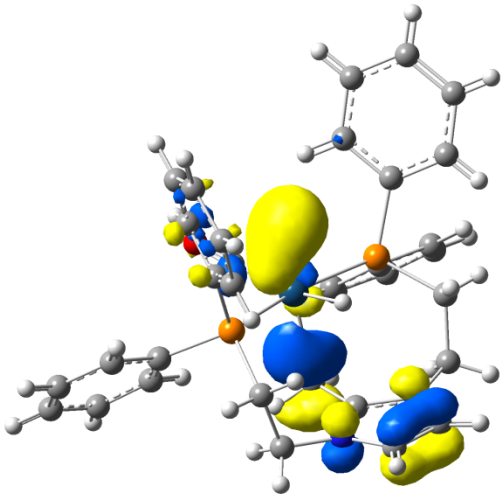
Comparison between experimental (x-ray) and DFT calculated geometrical parameters:

	complex 3		complex 6	
	x-ray	DFT	x-ray	DFT
dIr-C1	2.144	2.182	2.233	2.317
dIr-C2	3.073	3.078	2.936	2.951
Angle-Ir-C1_C2	116.5	114.5	103.9	101.2
dC1-C2	3.073	1.446	1.443	1.431
dihedHC1C2H	116.5	118.6	121.4	124.9

Complex **3**, MO 170 (HOMO-2)



Complex **6**, MO 150 (HOMO)



Cartesian coordinates for the DFT optimized complexes **3** and **6**

Complex **3**, E= -2446.12998868 a.u.

77 -0.456643 0.886234 -0.602186

15 1.917927 0.420341 -0.323250

7 1.804751 -1.282247 -2.880960

15 -1.591910 -1.083287 0.221758

6 0.465738 -1.174481 -2.694631

7 -0.004023 -2.434058 -2.541518

6 1.045631 -3.342265 -2.630088

1 0.893372 -4.411532 -2.523894

6 2.174879 -2.621325 -2.847287

1 3.208785 -2.933936 -2.949791

6 2.736710 -0.164931 -3.057907

1 2.523806 0.313047 -4.026323

1 3.726623 -0.628892 -3.138306

6 2.746519 0.894941 -1.935576

1 2.226126 1.803430 -2.264963

1 3.789470 1.176783 -1.737281

6 -0.301341 0.048816 -2.611495

1 -1.321940 -0.120634 -2.973520

1 0.160176 0.814041 -3.247013

6 -1.372189 -2.772025 -2.164869

1 -1.576732 -3.776588 -2.561991

1 -2.057491 -2.082989 -2.674730

6 -1.568143 -2.761006 -0.651120

1 -0.778494 -3.369096 -0.186845

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1 5.778706 -2.747514 -0.086149

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6 2.824382 1.464244 0.885662

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6 3.011357 0.982274 2.193032

1 2.709360 -0.035653 2.447585

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8 -0.000367 0.284314 -3.108004