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Electronic Supplementary Information

Iridium-Catalysed Dehydrocoupling of Aryl Phosphine-Borane Adducts: Synthesis and Characterisation of High-Molecular-Weight Poly(phosphinoboranes)

U. S. D. Paul, H. Braunschweig, U. Radius**

Ursula Sofia Désirée Paul, Prof. Dr. Holger Braunschweig, Prof. Dr. Udo Radius
Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany.
* Author for correspondence. E-mail: u.radius@uni-wuerzburg.de

The Supporting Information contents:

1. Additional Figures and Tables 2 - 11
2. Experimental Details 13 - 21
3. Crystallography 22 - 26
4. References 27

1. Additional Figures and Tables

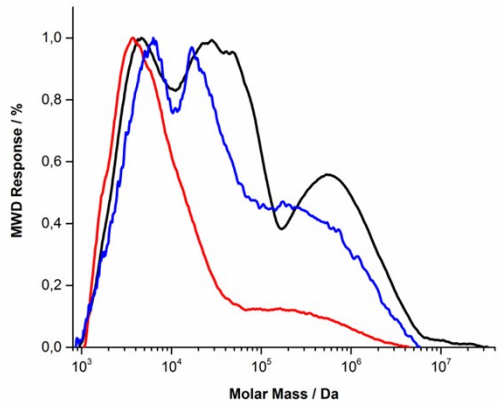

Figure S1. GPC trace in THF (**5 mol% 1a**, in 5 mL of **toluene**, **100 °C**, **24 h**) of ***blue***: [PhPH–BH_2]$_n$ (**3a**); ***red***: [^{p}TolPH–BH_2]$_n$ (**3b**); ***black***: [MesPH–BH_2]$_n$ (**3c**).

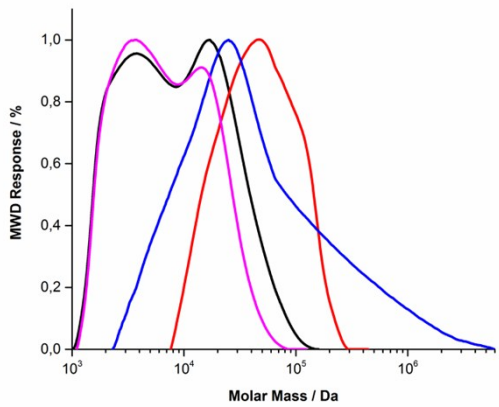

Figure S2. GPC trace in THF of [MesPH–BH_2]$_n$ (**3c**): ***black***: (**2.5 mol% 1a**, in 5 mL of toluene, 100 °C, 24 h); ***red***: (2.5 mol% **1a**, in 0.6 mL of **benzene**, **80 °C**, 24 h); ***blue***: (2.5 mol% **1a**, in 0.6 mL of benzene, 80 °C, **6 h**); ***magenta***: (**0.5 mol% 1a**, in 0.6 mL of benzene, 80 °C, 24 h).

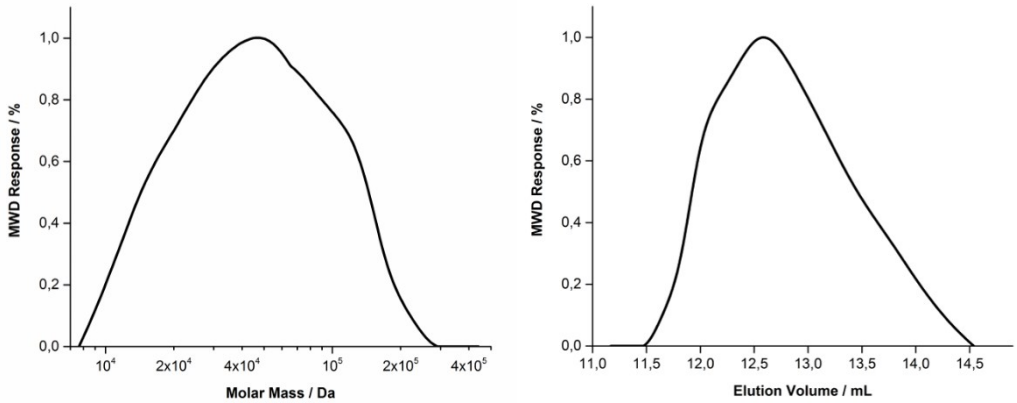

Figure S3. GPC trace (THF, vs. polystyrene standards) of [MesPH–BH_2]$_n$ (**3c**) (M_n = 33 000, M_w = 59 000, DP_w = 360, PDI = 1.8).

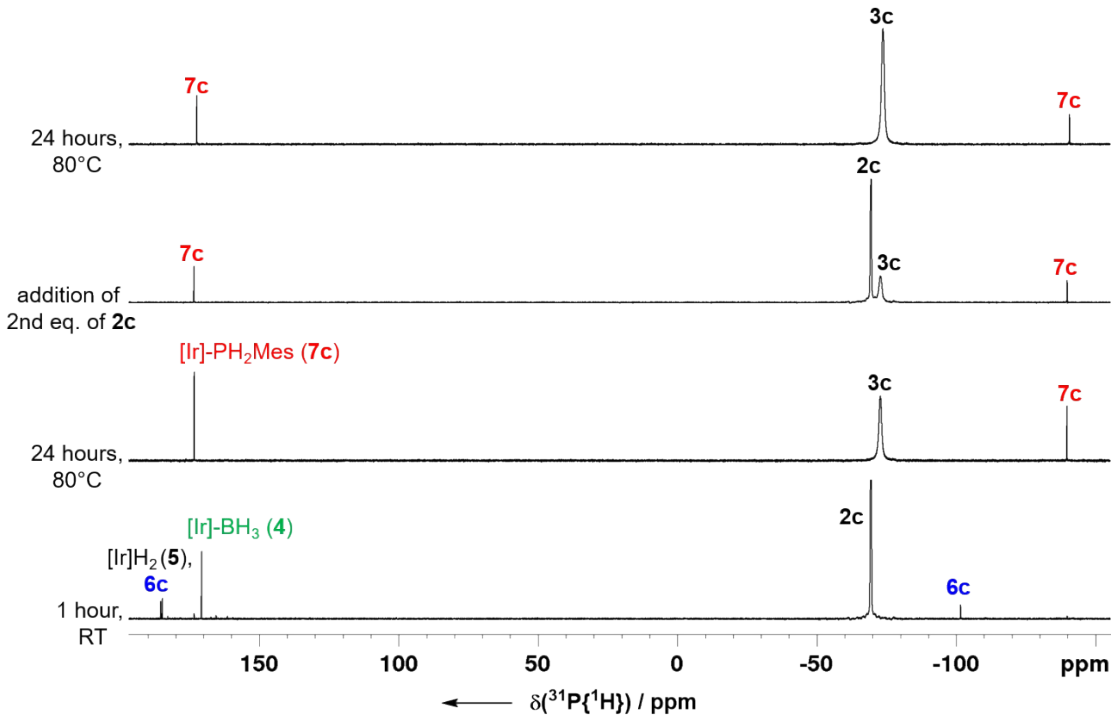

Figure S4. Time dependent ^{31}P NMR spectra (162 MHz, C_6D_6, 298 K) of the initial and resumed dehydrogenation reaction of $MesPH_2$–BH_3 (**2c**) with complex [(^{t}BuPOCOP)IrH_2] (**1a**) as catalyst (2.5 mol% **1a**, in 0.6 mL of benzene, RT to 80°C).

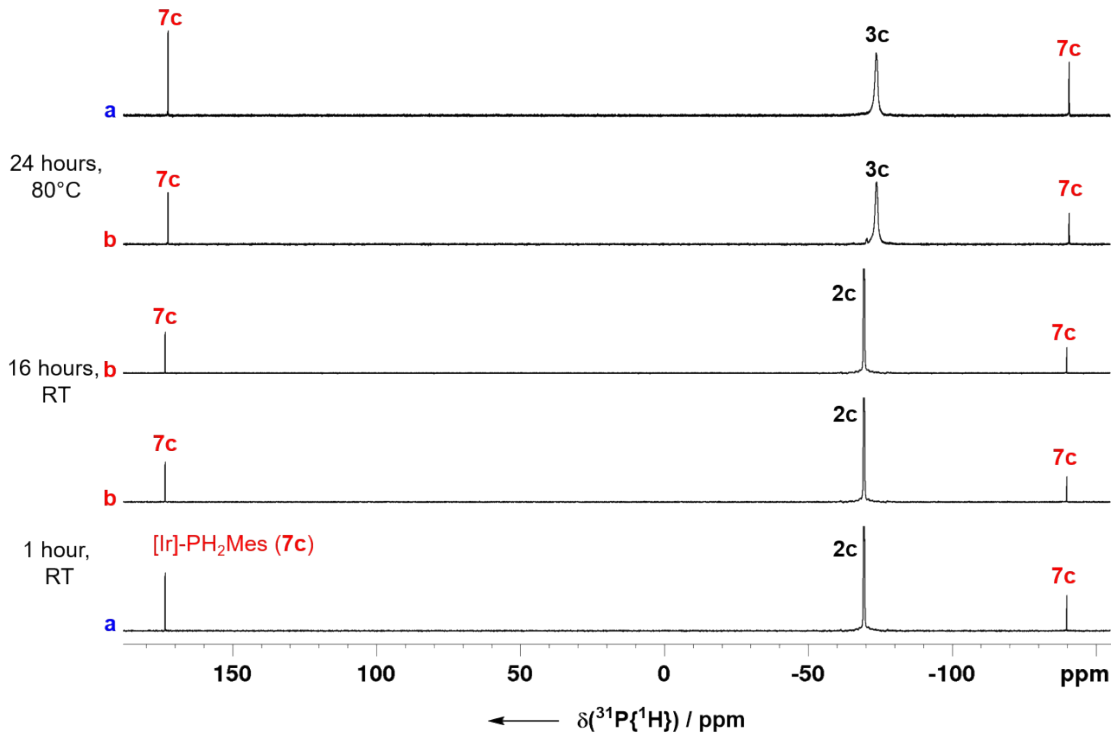

Figure S5. Time dependent ^{31}P NMR spectra (162 MHz, C_6D_6, 298 K) of the dehydrogenation reaction of adduct **2c** with complexes **a**: 2.5 mol% [(^{t}BuPOCOP)Ir(PH_2Mes)] (**6c**) and **b**: 2.5 mol% [(^{t}BuPOCOP)Ir$(H)_2$(PH_2Mes)] (**7c**) as catalyst (2.5 mol% catalyst, in 0.6 mL of benzene, RT to 80°C).

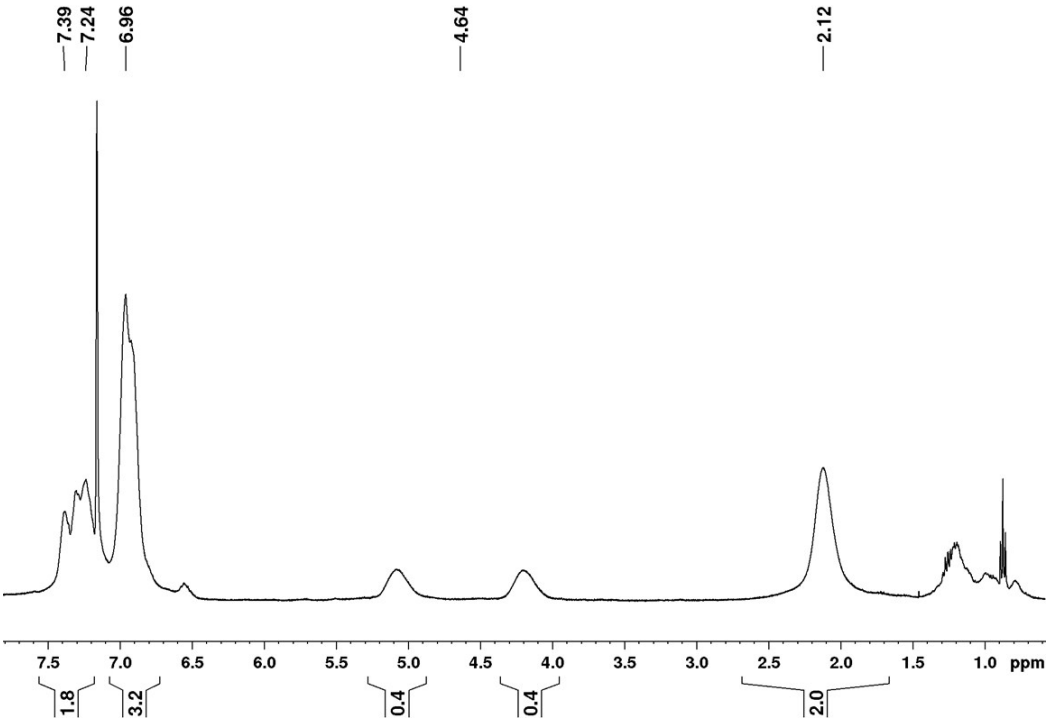

Figure S6. $^{1}H\{^{11}B\}$ NMR spectrum of $[PhPH–BH_2]_n$ (**3a**) in C_6D_6.

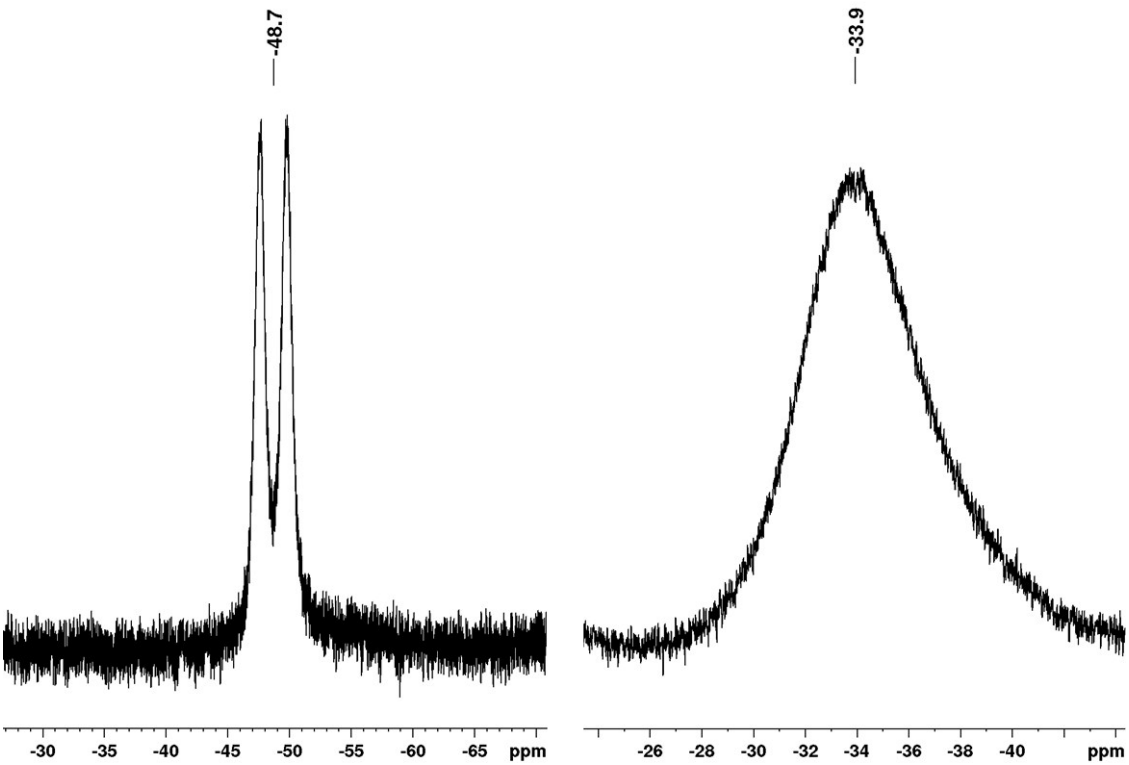

Figure S7. Segments of the ^{31}P (left) and ^{11}B (right) NMR spectra of $[PhPH–BH_2]_n$ (**3a**) in C_6D_6.

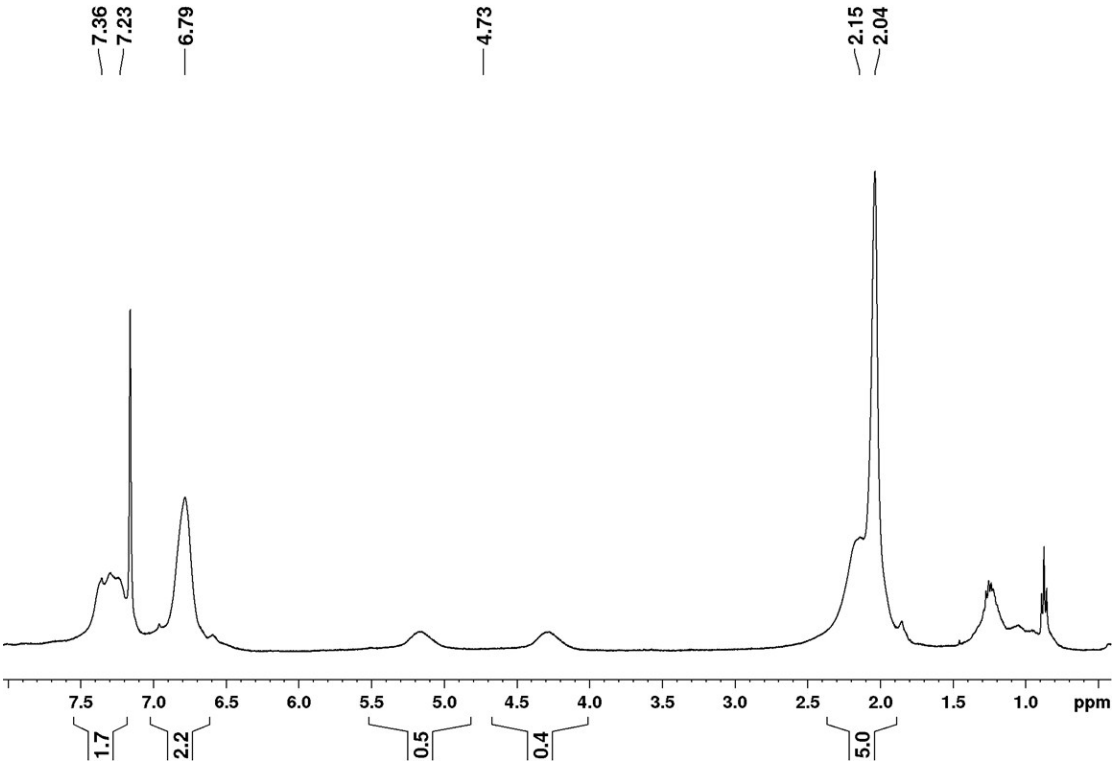

Figure S8. $^{1}H\{^{11}B\}$ NMR spectrum of $[^{p}TolPH–BH_2]_n$ (**3b**) in C_6D_6.

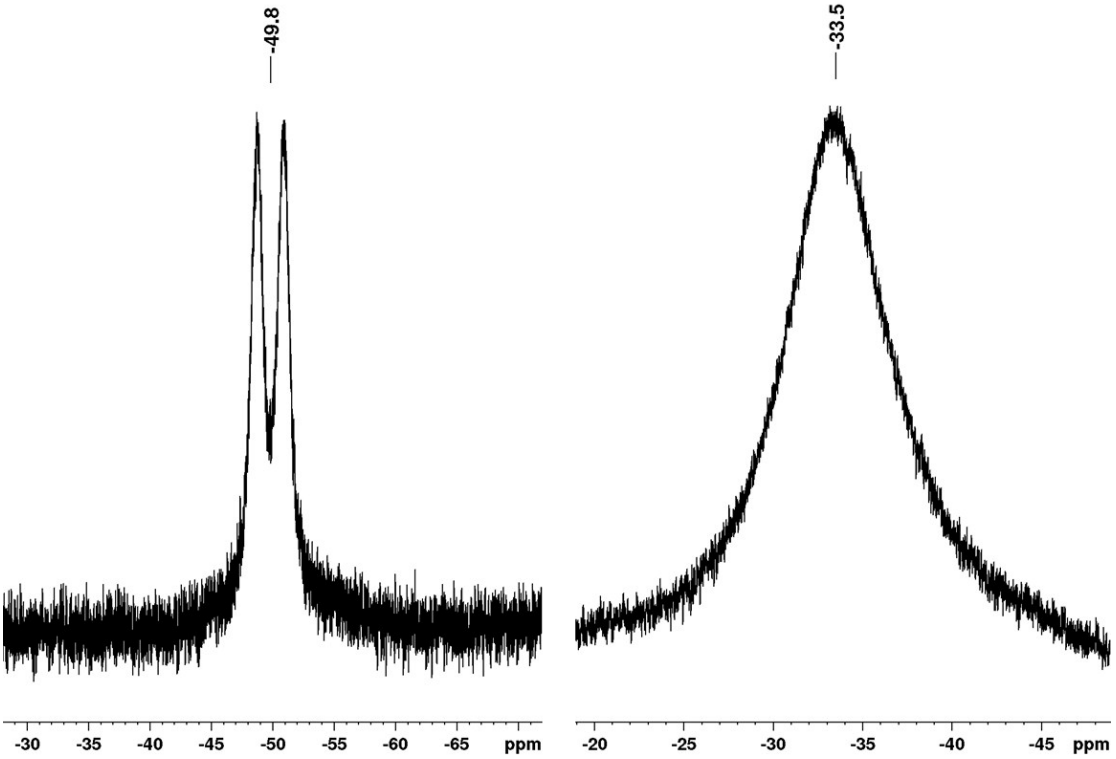

Figure S9. Segments of the ^{31}P (left) and ^{11}B (right) NMR spectra of $[^{p}TolPH–BH_2]_n$ (**3b**) in C_6D_6.

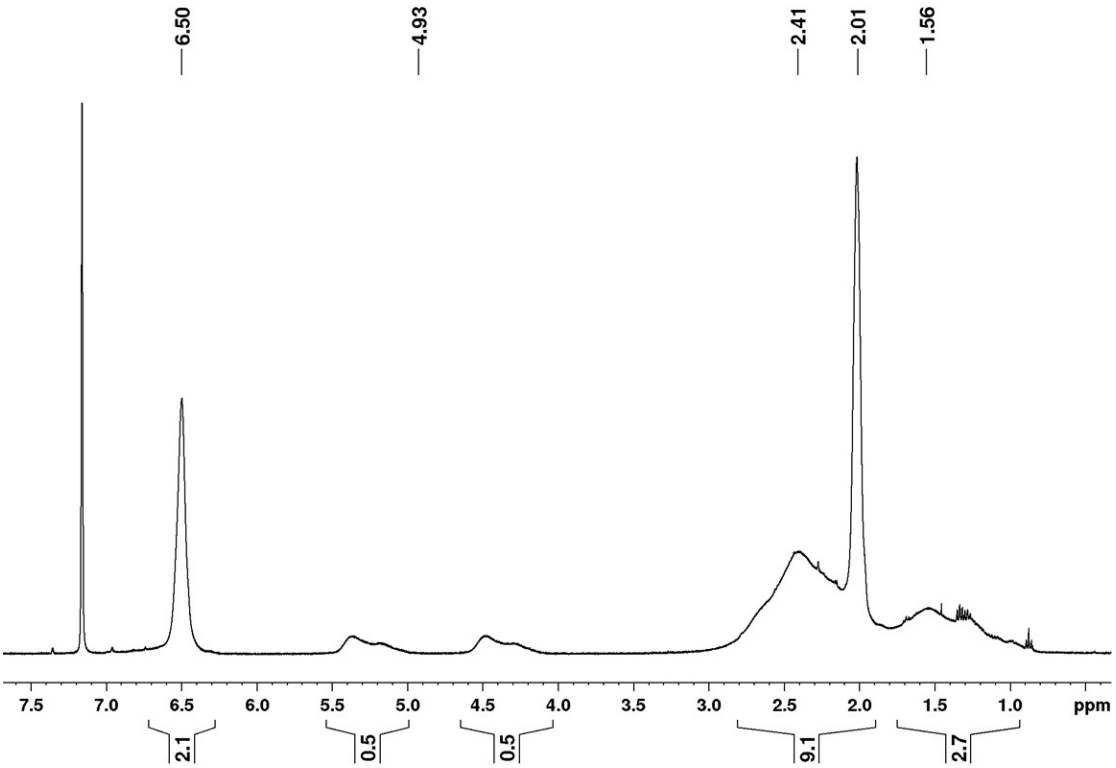

Figure S10. $^{1}H\{^{11}B\}$ NMR spectrum of $[MesPH–BH_2]_n$ (**3c**) in C_6D_6.

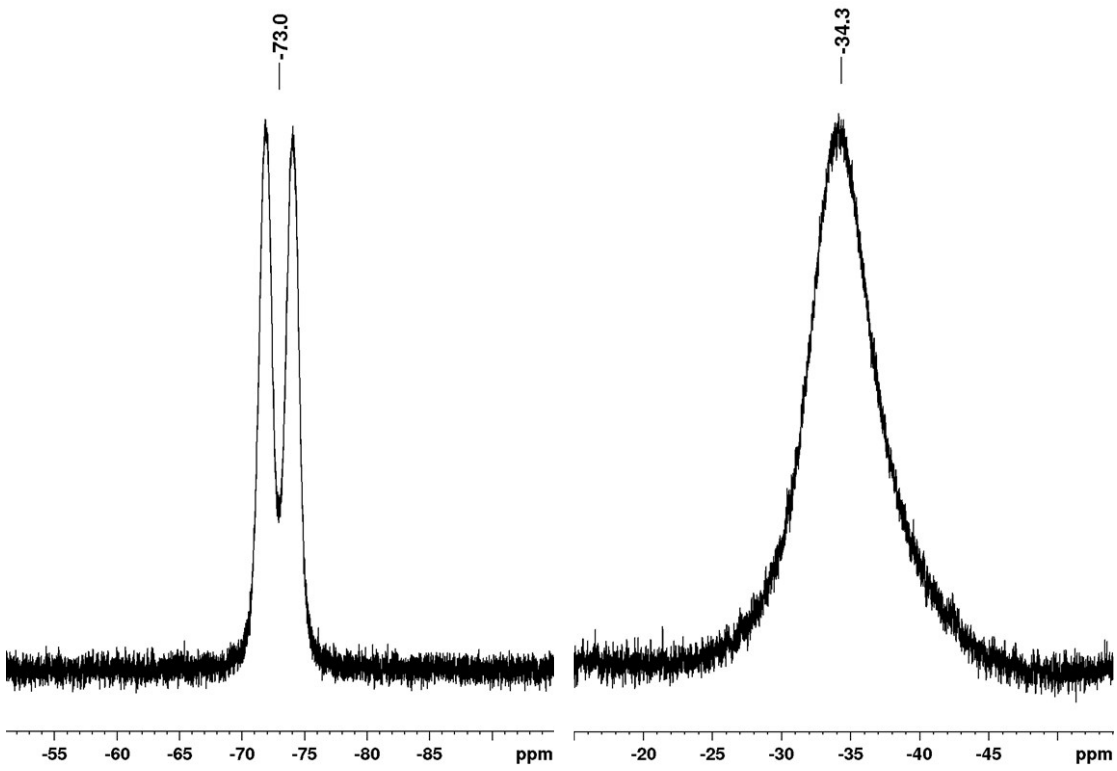

Figure S11. Segments of the ^{31}P (left) and ^{11}B (right) NMR spectra of $[MesPH–BH_2]_n$ (**3c**) in C_6D_6.

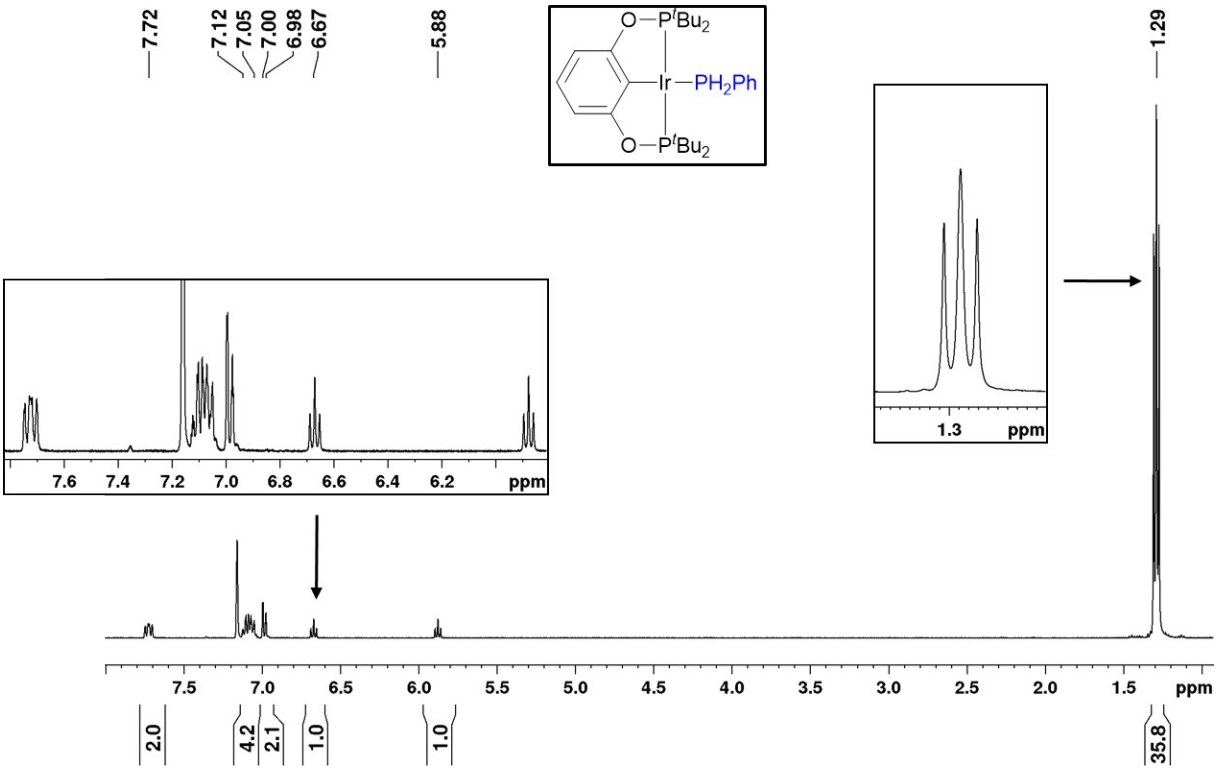

Figure S12. ^{1}H NMR spectrum of [(^{t}BuPOCOP)Ir(PH$_2$Ph)] **6a** in C_6D_6.

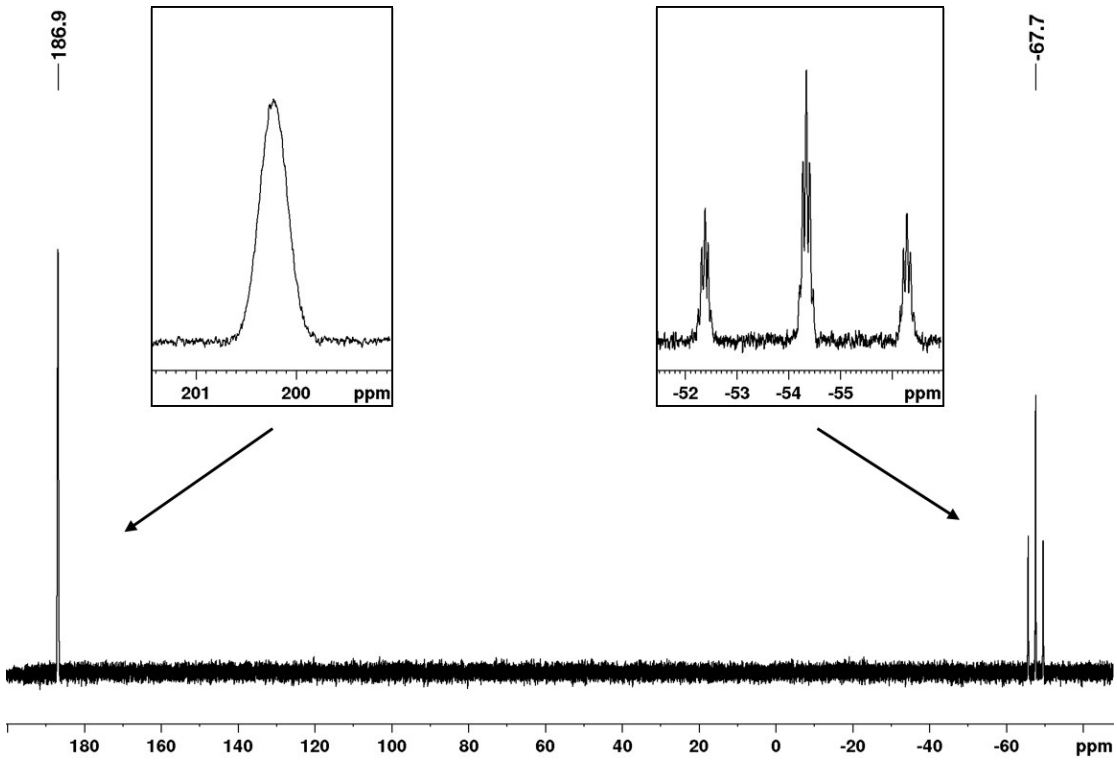

Figure S13. ^{31}P NMR spectrum of [(^{t}BuPOCOP)Ir(PH$_2$Ph)] **6a** in C_6D_6.

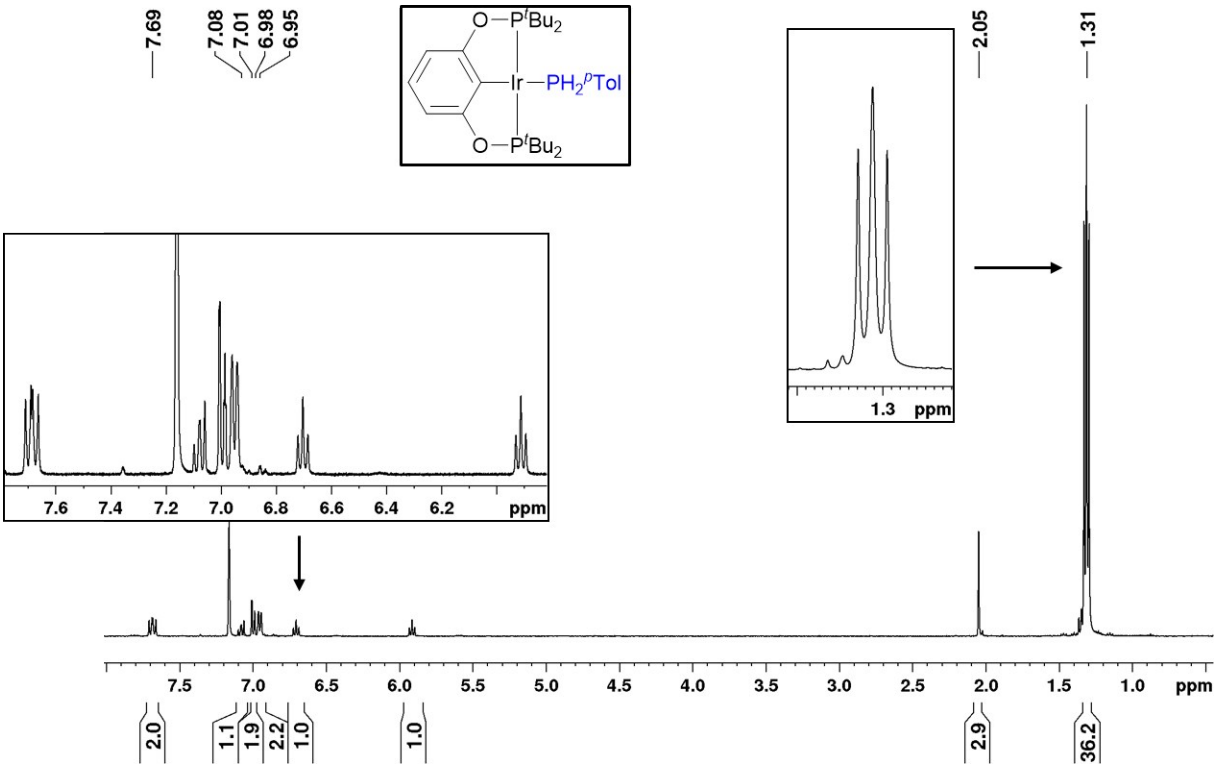

Figure S14. ^{1}H NMR spectrum of [(^{t}BuPOCOP)Ir(PH$_2$^{p}Tol)] **6b** in C_6D_6.

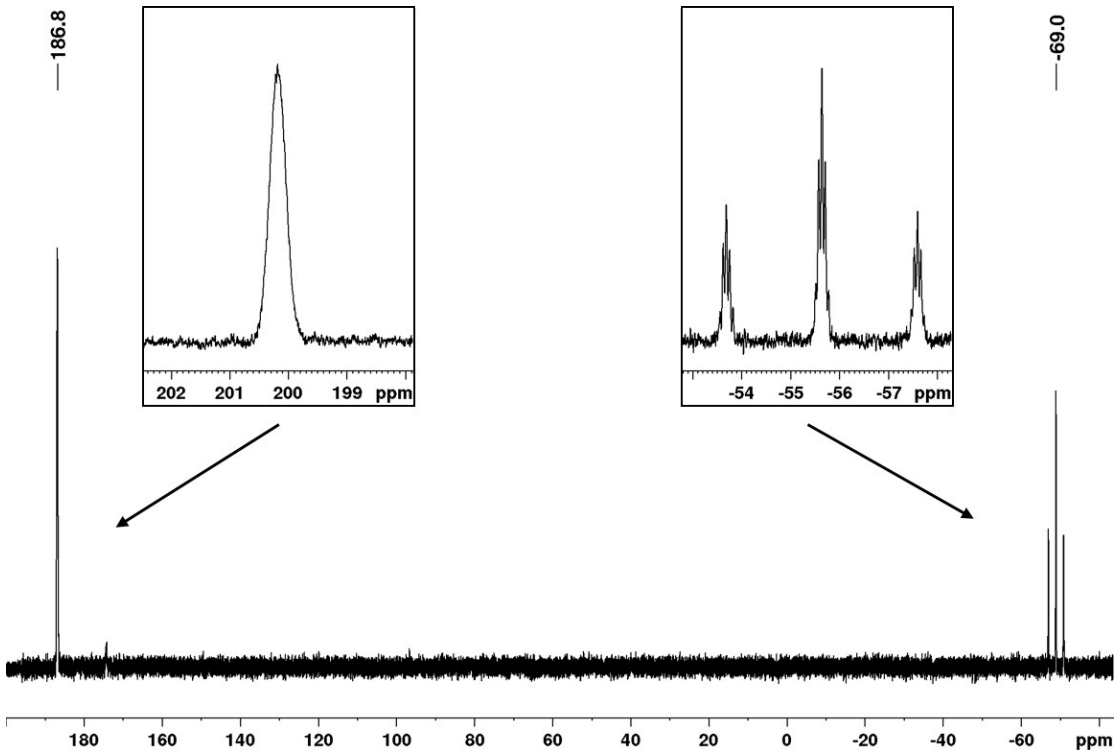

Figure S15. ^{31}P NMR spectrum of [(^{t}BuPOCOP)Ir(PH$_2$^{p}Tol)] **6b** in C_6D_6.

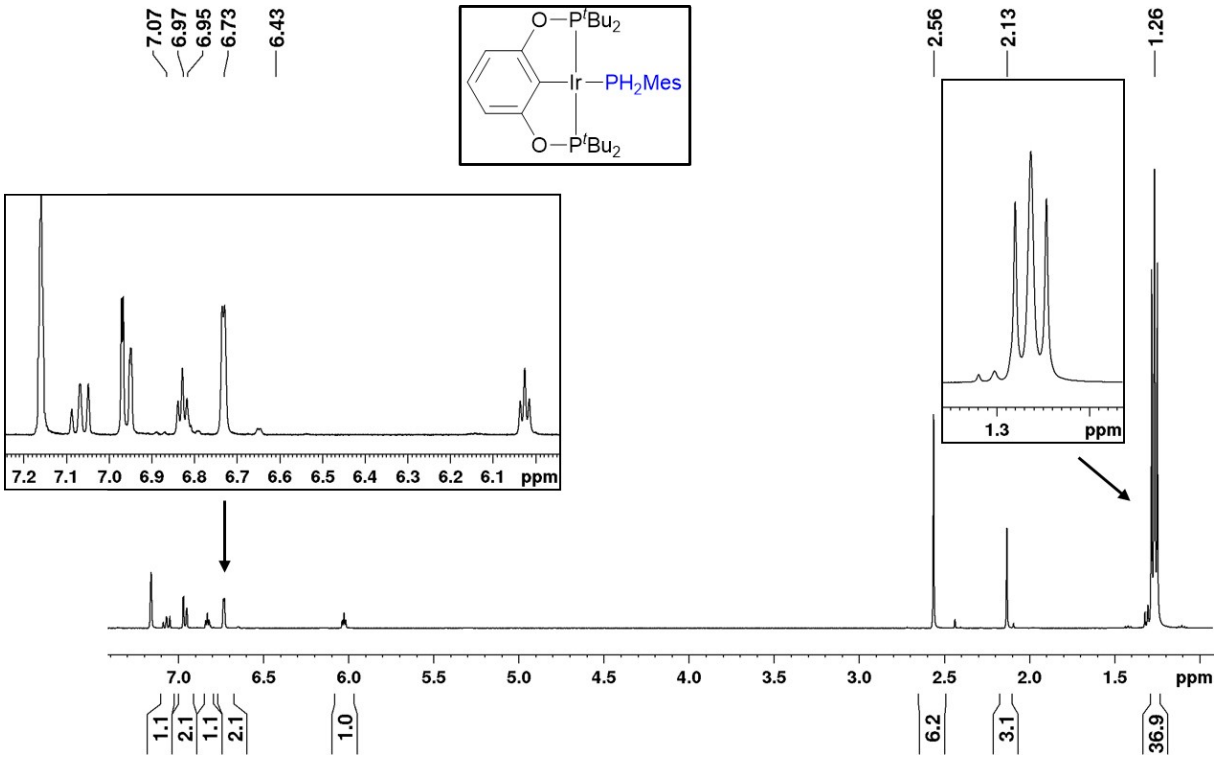

Figure S16. ^{1}H NMR spectrum of [(^{t}BuPOCOP)Ir(PH$_2$Mes)] **6c** in C_6D_6.

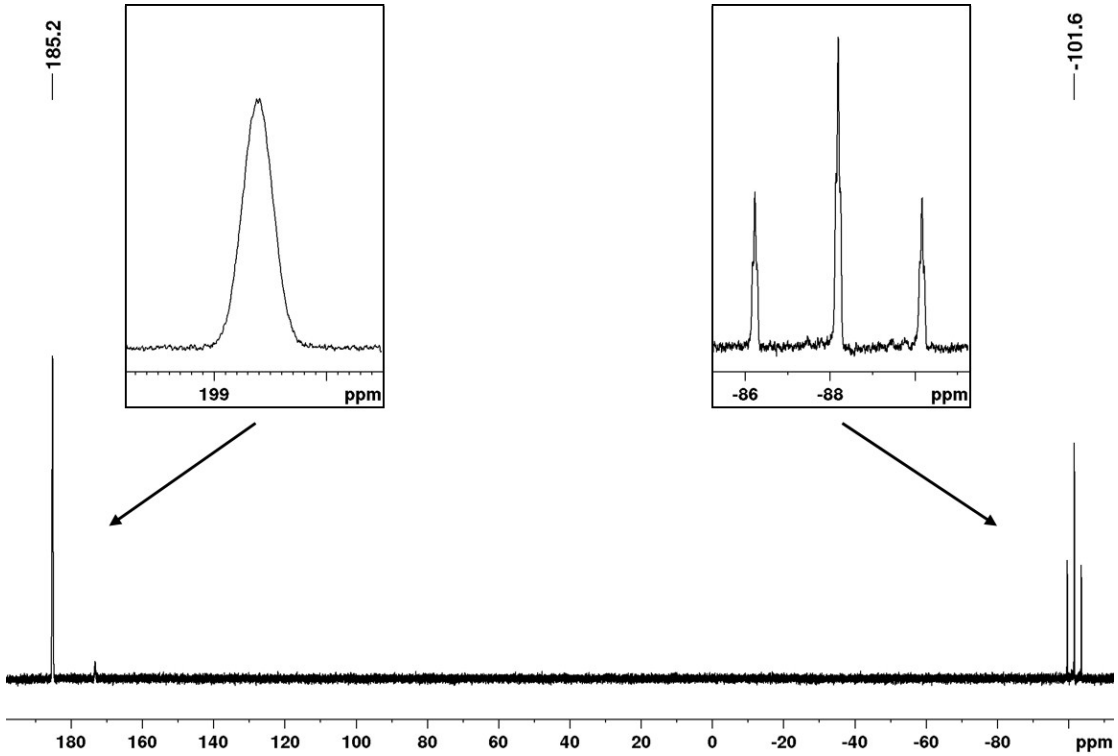

Figure S17. ^{31}P NMR spectrum of [(^{t}BuPOCOP)Ir(PH$_2$Mes)] **6c** in C_6D_6.

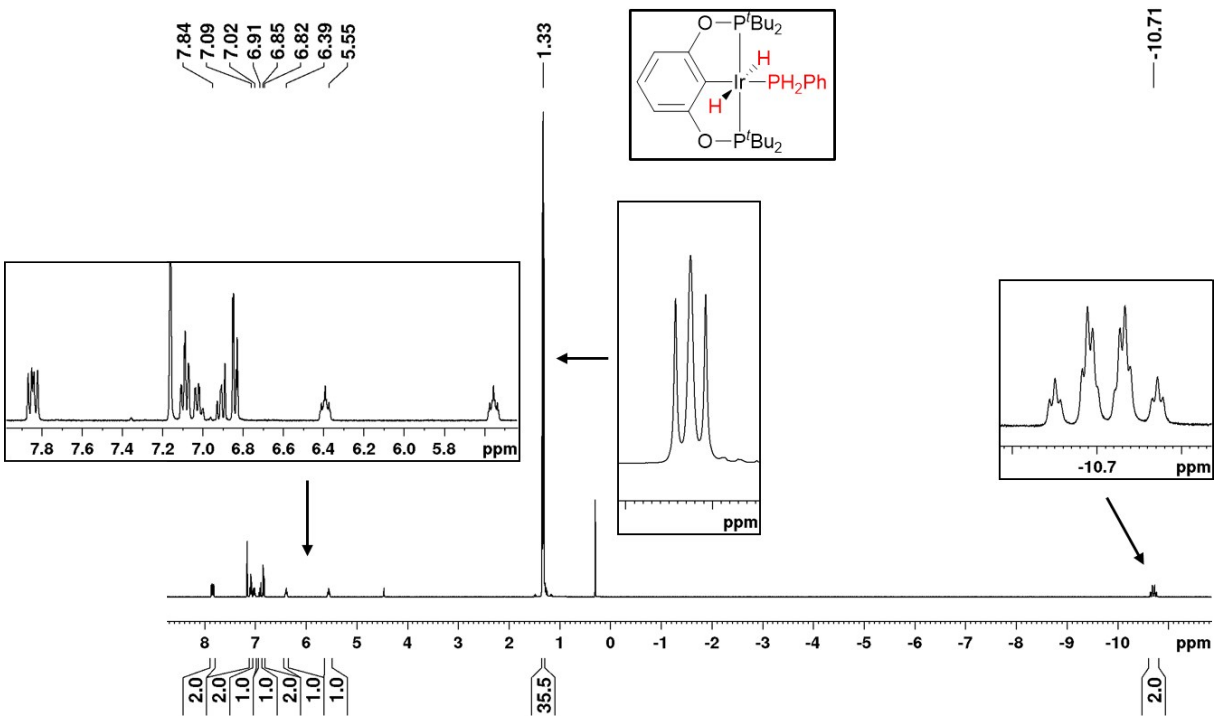

Figure S18. ^{1}H NMR spectrum of [(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$Ph)] **7a** in C_6D_6.

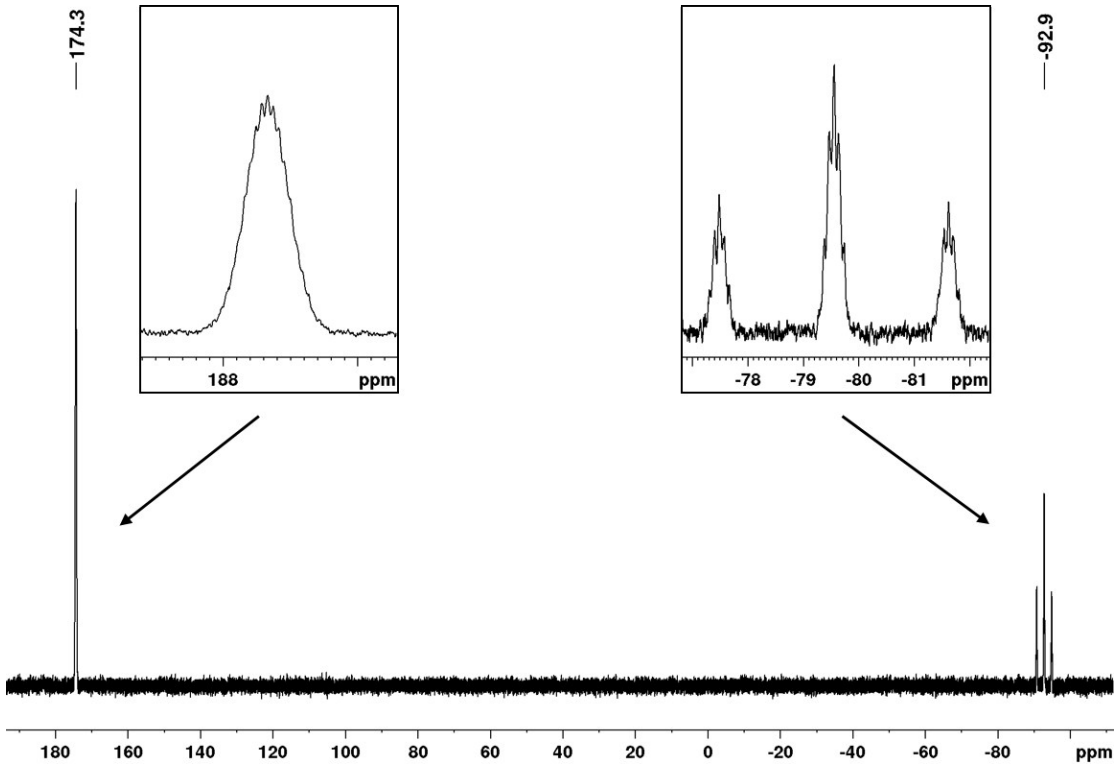

Figure S19. ^{31}P NMR spectrum of [(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$Ph)] **7a** in C_6D_6.

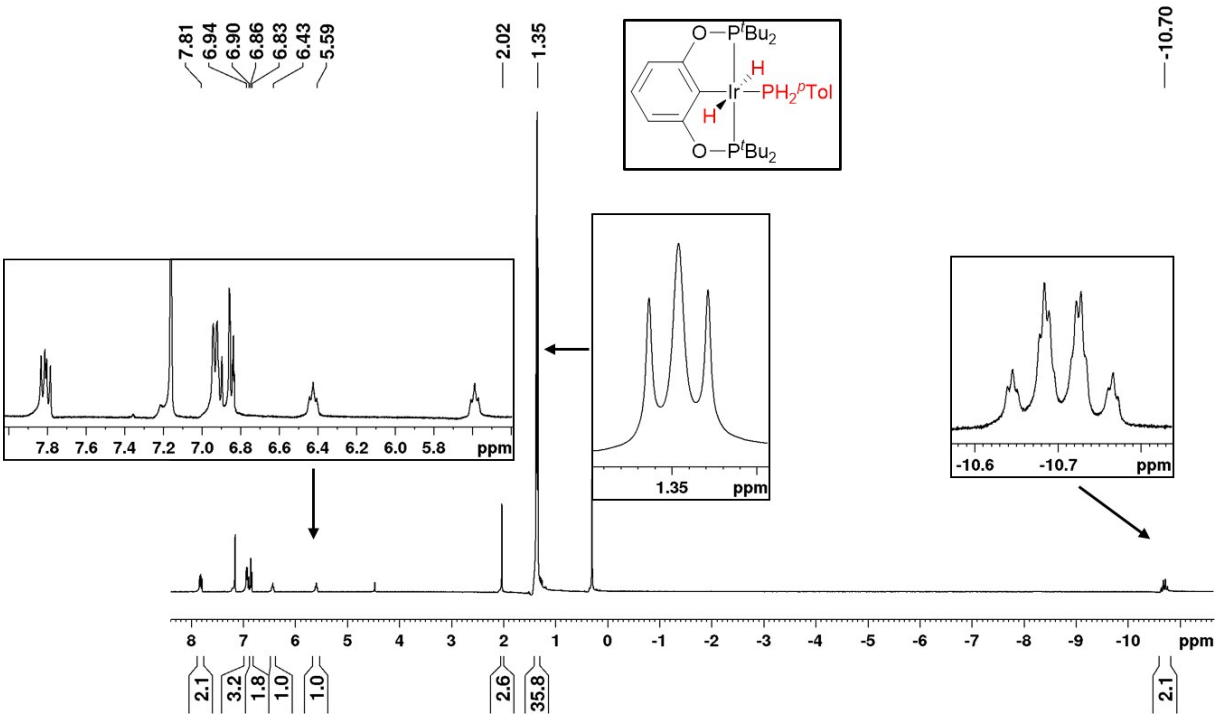

Figure S20. ^{1}H NMR spectrum of [(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$^{p}Tol)] **7b** in C_6D_6.

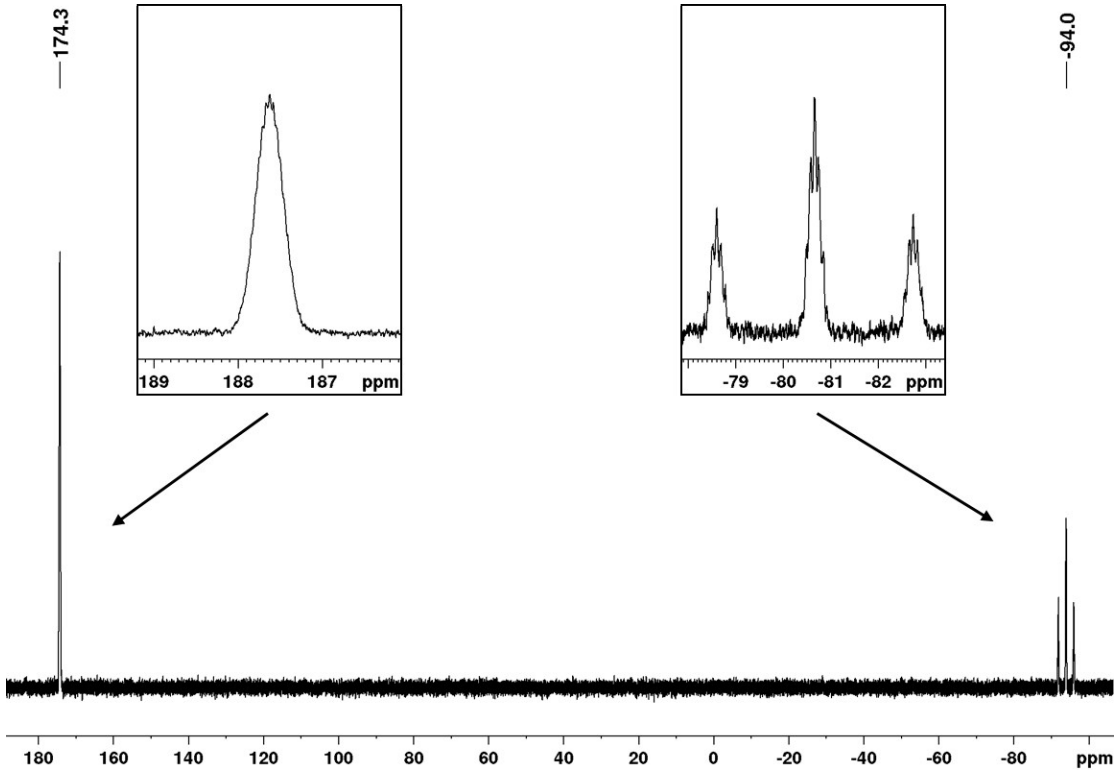

Figure S21. ^{31}P NMR spectrum of [(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$^{p}Tol)] **7b** in C_6D_6.

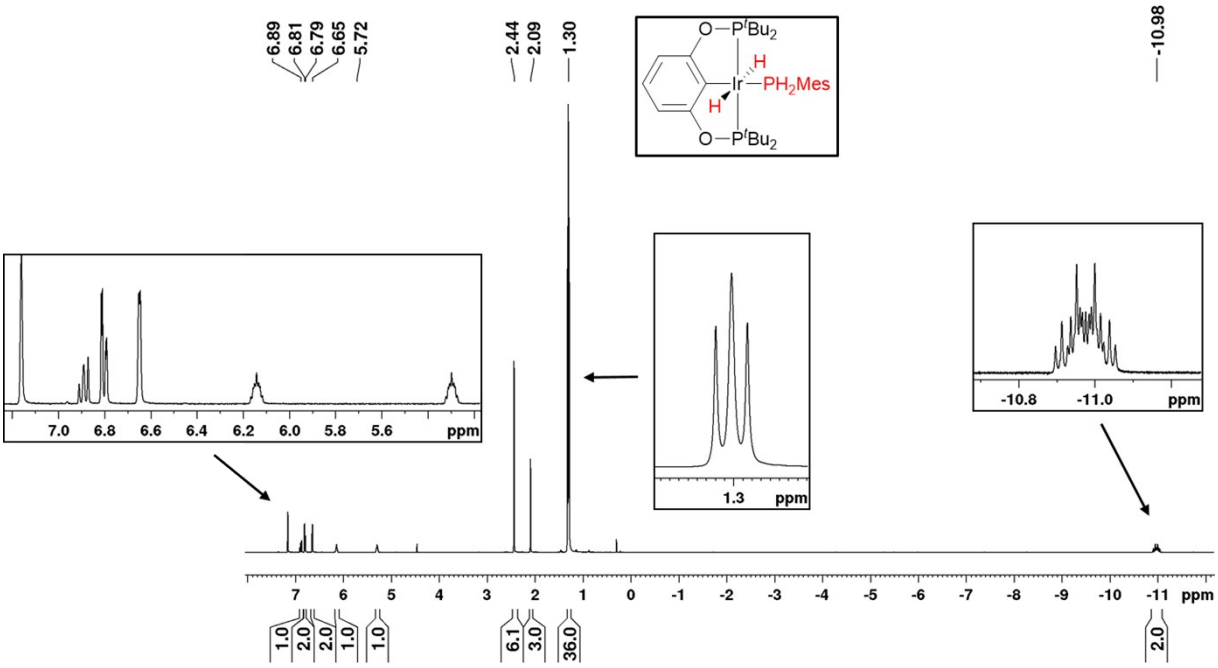

Figure S22. ^{1}H NMR spectrum of [(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$Mes)] **7c** in C_6D_6.

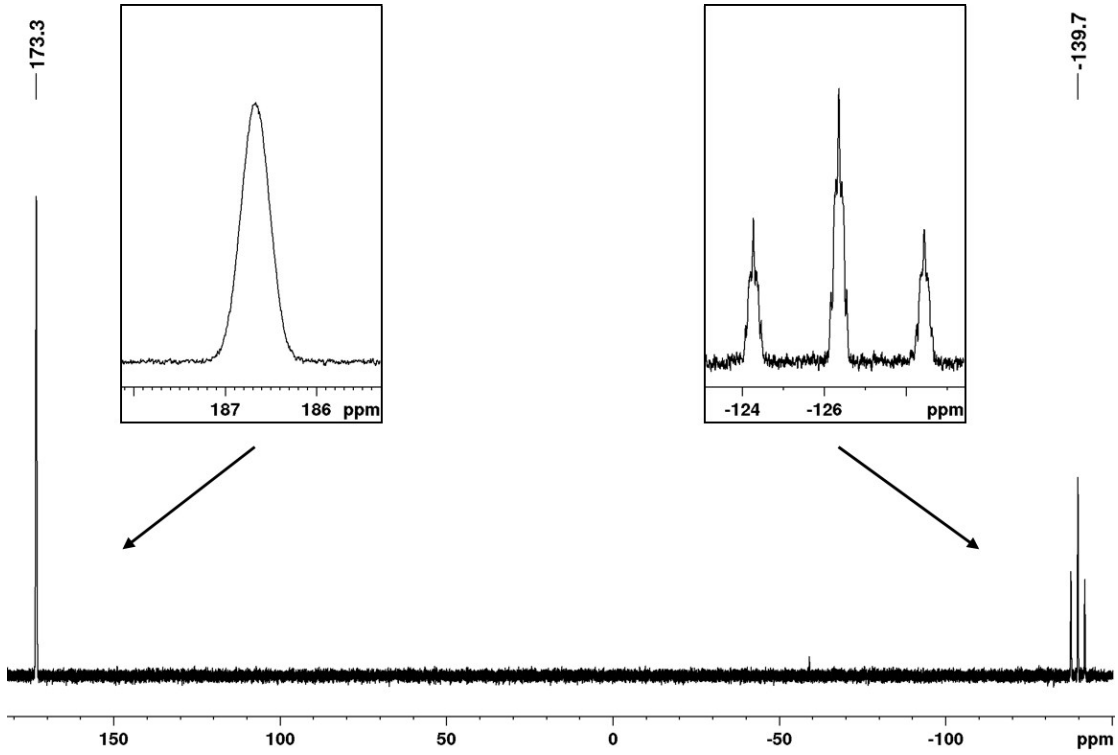

Figure S23. ^{31}P NMR spectrum of [(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$Mes)] **7c** in C_6D_6.

2. Experimental Details

General Considerations.

All reactions and subsequent manipulations involving organometallic reagents were performed under an argon atmosphere using standard Schlenk techniques as reported previously. [S1] Elemental analyses were performed in the microanalytical laboratory of the authors department with an Elementar vario micro cube. NMR spectra were recorded on a Bruker Avance 200 (^{1}H, 200.1 MHz; ^{13}C, 50.3 MHz; ^{31}P, 80.9 MHz; ^{11}B, 64.14 MHz), Bruker DPX-400 (^{1}H, 400.40 MHz; ^{13}C, 100.68 MHz; ^{31}P, 162.08 MHz; ^{11}B, 128.46 MHz) and a Bruker Avance 500 (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{31}P, 202.5 MHz; ^{11}B, 160.46 MHz) at 298 °K, using C_6D_6 and toluene-d_8 as the solvent. Assignment of the ^{1}H and ^{13}C NMR data was supported by ^{1}H,^{1}H and ^{13}C,^{1}H correlation experiments. ^{13}C NMR spectra were broad-band proton-decoupled (^{13}C{^{1}H}). NMR data are listed in parts per million (ppm) and are reported relative to Tetramethylsilane. Coupling constants are quoted in Hertz (Hz). Spectra are referenced internally to residual protio-solvent resonances (^{1}H: C_6D_5H 7.16 ppm, d_7-toluene 2.08 ppm) or natural abundance carbon resonances (^{13}C: C_6D_6 128.1 ppm, d_8-toluene 20.43 ppm). Infrared spectra were recorded on a Bruker Alpha FT-IR spectrometer as solids by using an ATR unit and are reported in cm^{-1}. The gel permeation chromatography (GPC) experiments for polymers **3a-c** were performed on an Agilent SECcurity GPC System (1260 Infinity) with light scattering, refractive index, and viscometer detector. The eluent was THF with a flow rate of 1.0 mL·min^{-1}. All molecular weights are reported relative to a monodisperse polystyrene standard. The columns were contained within an oven (35 °C) and consisted of styrene/divinylbenzene gels with pore sizes ranging from 500 to 100 000 Å. Samples were dissolved in the eluent (1 mg·mL^{-1}) and filtered with a Ministart SRP 15 filter (polytetrafluoroethylene membrane of 0.45 µm pore size) before analysis. The Iridium complexes [(^{t}BuPOCOP)IrH$_2$] (**1a**) and [(^{t}BuPOCOP)IrHPh] (**1b**) [S2], the adducts PhPH$_2$–BH$_3$ (**2a**) [S3a], MesPH$_2$–BH$_3$ (**2c**) [S3b] and Mes$_2$PH–BH$_3$ [S3c] and the phosphines PhPH$_2$ (**8a**) [S4a], ^{p}TolPH$_2$ (**8b**) [S4b] and MesPH$_2$ (**8c**) [S4c] were prepared according to literature procedures. All other reagents have been obtained from commercial sources and have been used as received.

Synthesis of phosphine-borane adduct ^{p}TolPH$_2$–BH$_3$ (2b)

In a Schlenk flask BH$_3$–THF (0.70 M in thf, 5.7 mL, 4.00 mmol) was added dropwise to a solution of ^{p}TolPH$_2$ (**8b**) (0.50 mL, 1.0 equiv.) in 5 mL of THF. After stirring the solution for 16 hours at room temperature all volatile material was removed *in vacuo*, the residue suspended in 5 mL of hexane and the resulting precipitate filtered and dried *in vacuo* to afford ^{p}TolPH$_2$–BH$_3$ (**2b**) as colorless solid.

^{p}TolPH$_2$–BH$_3$ (2b): yield 260 mg (1.90 mmol, 48 %) of a colorless solid.

^{1}H NMR (400.40 MHz, C_6D_6, 298 K, ppm) δ 7.17 (dd, $^3J_{PH}$ = 11.9 Hz, $^3J_{HH}$ = 7.8 Hz, 2H, CH^{ortho}, PH$_2$Tol), 6.75 (d, $^3J_{HH}$ = 7.3 Hz, 2H, CH^{meta}, PH$_2$Tol), 4.65 (dq, $^1J_{PH}$ = 370.5 Hz, $^3J_{HH}$=7.9 Hz, 2H, P*H*$_2$Tol), 1.91 (s, 3H, CH$_3^{para}$, PH$_2$Tol), 1.67 (vbr q, $^1J_{BH}$ = 101.8 Hz, 3H, B*H*$_3$); **^{1}H{^{11}B} NMR** (400.40 MHz, C_6D_6, 298 K, ppm) δ 7.17 (dd, $^3J_{PH}$ = 11.9 Hz, $^3J_{HH}$ = 7.8 Hz, 2H, CH^{ortho}, PH$_2$Tol), 6.75 (d, $^3J_{HH}$ = 7.3 Hz, 2H, CH^{meta}, PH$_2$Tol), 4.65 (dq, $^1J_{PH}$ = 370.5 Hz, $^3J_{HH}$=7.9 Hz, 2H, P*H*$_2$Tol), 1.91 (s, 3H, CH$_3^{para}$, PH$_2$Tol), 1.67 (dt, $^2J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.9 Hz, 3H, B*H*$_3$).

^{31}P NMR (162.08 MHz, C_6D_6, 298 K, ppm) δ -50.5 (t, $^1J_{PH}$ = 370.5 Hz), **^{31}P{^{1}H} NMR** (162.08 MHz, C_6D_6, 298 K, ppm) δ -50.5 (q, $^1J_{PB}$ = 33.1 Hz).

^{11}B NMR (128.46 MHz, C_6D_6, 298 K, ppm) δ -39.7 (dq, $^1J_{PB}$ = 33.1 Hz, $^1J_{BH}$ = 101.8 Hz).

^{13}C{^{1}H} NMR (100.68 MHz, C_6D_6, 298 K, ppm) δ 142.1 (d, $^4J_{CP}$ = 2.7 Hz, C$^{q\ para}$, PH$_2$Tol), 133.9 (d, $^2J_{CP}$ = 9.2 Hz, CH^{ortho}, PH$_2$Tol), 129.8 (d, $^3J_{CP}$ = 10.7 Hz, CH^{meta}, PH$_2$Tol), 117.2 (d, $^1J_{CP}$ = 57.7 Hz, C$^{q\ ipso}$, PH$_2$Tol), 21.2 (d, $^5J_{CP}$ = 1.2 Hz, CH$_3^{para}$, PH$_2$Tol).

Anal. calcd. (found) for $C_7H_{12}BP$ [137.96 gmol^{-1}]: C, 60.94 (60.52); H, 8.77 (8.77).

Spectroscopic data of the primary phosphine boranes 2a and 2c

PhPH$_2$–BH$_3$ (2a)

^{1}H NMR (400.40 MHz, C_6D_6, 298 K, ppm) δ 7.19 (dd, $^3J_{PH}$ = 12.3 Hz, $^3J_{HH}$ = 7.1 Hz, 2H, CH^{ortho}, PH$_2$Ph), 6.96 (tm, $^3J_{HH}$ = 7.5 Hz, 1H, CH^{para}, PH$_2$Ph), 6.88 (tm, $^3J_{HH}$ = 7.4 Hz, 2H, CH^{meta}, PH$_2$Ph), 4.58 (dq, $^1J_{PH}$ = 370.6 Hz, $^3J_{HH}$=7.9 Hz, 2H, P*H*$_2$Ph), 1.63 (vbr q, $^1J_{BH}$ = 101.5 Hz, 3H, B*H*$_3$); **^{1}H{^{11}B} NMR** (400.40 MHz, C_6D_6, 298 K, ppm) δ 7.19 (dd, $^3J_{PH}$ = 12.3 Hz, $^3J_{HH}$ = 7.1 Hz, 2H, CH^{ortho}, PH$_2$Ph), 6.96 (tm, $^3J_{HH}$ = 7.5 Hz, 1H, CH^{para}, PH$_2$Ph), 6.88 (tm, $^3J_{HH}$ = 7.4 Hz, 2H, CH^{meta}, PH$_2$Ph), 4.58 (dq, $^1J_{PH}$ = 370.6 Hz, $^3J_{HH}$=7.9 Hz, 2H, P*H*$_2$Ph), 1.63 (dt, $^2J_{PH}$ = 15.7 Hz, $^3J_{HH}$ = 7.9 Hz, 3H, B*H*$_3$).

^{31}P NMR (162.08 MHz, C_6D_6, 298 K, ppm) δ -49.5 (t, $^1J_{PH}$ = 370.6 Hz); **^{31}P{^{1}H} NMR** (162.08 MHz, C_6D_6, 298 K, ppm) δ -49.5 (q, $^1J_{PB}$ = 32.5 Hz); reference: -46.9. [S3a]

^{11}B NMR (128.46 MHz, C_6D_6, 298 K, ppm) δ -41.4 (dq, $^1J_{PB}$ = 32.5 Hz, $^3J_{HH}$ = 101.5 Hz); reference: -42.2. [S3a]

^{13}C{^{1}H} NMR (100.68 MHz, C_6D_6, 298 K, ppm) δ 133.8 (d, $^2J_{CP}$ = 9.0 Hz, CH ^{ortho}, PH$_2$Ph), 131.5 (d, $^4J_{CP}$ = 2.7 Hz, CH^{para}, PH$_2$Ph), 129.0 (d, $^3J_{CP}$ = 10.4 Hz, CH^{meta}, PH$_2$Ph), 131.5 (d, $^1J_{CP}$ = 56.4 Hz, C$^{q\ ipso}$, PH$_2$Ph).

$MesPH_2$–BH_3 (2c)

^{1}H NMR (400.40 MHz, C_6D_6, 298 K, ppm) δ 6.47 (d, $^4J_{PH}$ = 3.1 Hz, 2H, CH^{meta}, PH_2Mes), 4.74 (dq, $^1J_{PH}$ = 368.4 Hz, $^3J_{HH}$ = 7.9 Hz 2H, P*H*$_2$Mes), 2.04 (s, 6H, CH_3^{ortho}, PH_2Mes), 1.94 (s, 3H, CH_3^{para}, PH_2Mes), 1.65 (vbr q, $^1J_{BH}$ = 101.2 Hz, 3H, B*H*$_3$); **^{1}H{^{11}B} NMR** (400.40 MHz, C_6D_6, 298 K, ppm) δ 6.47 (d, $^4J_{PH}$ = 3.1 Hz, 2H, CH^{meta}, PH_2Mes), 4.74 (dq, $^1J_{PH}$ = 368.4 Hz, $^3J_{HH}$ = 7.9 Hz 2H, P*H*$_2$Mes), 2.04 (s, 6H, CH_3^{ortho}, PH_2Mes), 1.94 (s, 3H, CH_3^{para}, PH_2Mes), 1.65 (dt, $^2J_{PH}$ = 15.2 Hz, $^3J_{HH}$ = 7.9 Hz, 3H, B*H*$_3$).

^{31}P NMR (162.08 MHz, C_6D_6, 298 K, ppm) δ -69.5 (t, $^1J_{PH}$ = 368.4 Hz); reference: -68.8. [S3b]

^{11}B NMR (128.46 MHz, C_6D_6, 298 K, ppm) δ -39.7 (dq, $^1J_{PB}$ = 30.5 Hz, $^1J_{BH}$ = 101.2 Hz).

^{13}C{^{1}H} NMR (100.68 MHz, C_6D_6, 298 K, ppm) δ 140.9 (d, *J* = 7.9 Hz, $C^{q\ ortho}$, PH_2Mes), 140.8 (d, $^4J_{CP}$ = 2.3 Hz, $C^{q\ para}$, PH_2Mes), 129.5 (d, $^3J_{CP}$ = 8.2 Hz, CH^{meta}, PH_2Mes), 123.5 (d, $^1J_{CP}$ = 56.4 Hz, $C^{q\ ipso}$, PH_2Mes), 22.6 (d, $^3J_{CP}$ = 8.4 Hz, CH_3^{ortho}, PH_2Mes), 21.0 (d, $^5J_{CP}$ = 1.0 Hz, CH_3^{para}, PH_2Mes).

General procedures for the Iridium-promoted dehydrogenative coupling of phosphine-borane adducts

A Schlenk tube (**method A**) / an NMR tube (**method B**) was charged with 0.5-5 mol% of the precatalyst **1a,b** and a solution of the respective phosphine-borane adduct **2a-c** (0.40 mmol) in 5 mL of toluene (**A**) / 0.6 mL of benzene (**B**). The mixture was heated to100 °C (**A**) / 80 °C (**B**) for 24 hours (unless stated otherwise) and the reaction was monitored by ^{31}P NMR spectroscopy. The polymeric products were purified by precipitation into cold (-78 °C) hexane. After filtration the solid was washed with cold hexane (2x5 mL) and dried *in vacuo* to yield the respective poly(phosphinoborane) $[ArPH–BH_2]_n$ **3a-c** as colorless to pale yellow solid.

$[PhPH–BH_2]_n$ 3a: yield 20.0 mg (18 µmol, 88 %) of a pale yellow solid.

^{1}H{^{11}B} NMR (400.40 MHz, C_6D_6, 298 K, ppm) δ 7.39-7.24 (br m, 2H, CH^{ortho}, PHPh), 6.96 (br s, 3H, $CH^{meta/para}$, PHPh), 4.64 (br d, $^1J_{PH}$ = 351.5 Hz, 1H, P*H*Ph), 2.12 (br s, 2H, B*H*$_2$).

^{31}P NMR (162.08 MHz, C_6D_6, 298 K, ppm) δ -48.7 (br d, $^1J_{PH}$ = 351.5 Hz); reference: -48.9. [S5]

^{11}B NMR (128.46 MHz, C_6D_6, 298 K, ppm) δ -33.9 (vbr s); reference: -34.7. [S5]

^{13}C{^{1}H} NMR (100.68 MHz, C_6D_6, 298 K, ppm) δ 133.1 (m, CH^{ortho}, PHPh), 129.6 (m, CH^{para}, PHPh), 128.7 (br m, CH^{meta}/$C^{q\ ipso}$, PHPh).

IR (ATR, cm^{-1}) $\tilde{\nu}$ = 2424 (vs, BH), 2382 (vs, PH).

GPC: 5 mol% precatalyst (**1a**) and **method A**: M_n = 10 000, M_w = 216 000, DP_w = 17, PDI = 21.6.

[^{p}TolPH–BH$_2$]$_n$ 3b: yield 21.0 mg (18 µmol, 88 %) of a pale yellow solid.

^{1}H{^{11}B} NMR (400.40 MHz, C_6D_6, 298 K, ppm) δ 7.36-7.23 (br m, 2H, CH^{ortho}, PHTol), 6.79 (br s, 2H, CH^{meta}, PHTol), 4.73 (br d, $^1J_{PH}$ = 352.9 Hz, 1H, P*H*Tol), 2.15 (vbr s, 2H, B*H*$_2$), 2.04 (s, 3H, CH$_3^{para}$, PHTol).

^{31}P NMR (162.08 MHz, C_6D_6, 298 K, ppm) δ -49.8 (br d, $^1J_{PH}$ = 352.9 Hz).

^{11}B NMR (128.46 MHz, C_6D_6, 298 K, ppm) δ -33.5 (vbr s).

^{13}C{^{1}H} NMR (100.68 MHz, C_6D_6, 298 K, ppm) δ 139.3 (m, C$^{q\ para}$, PHTol), 133.1 (m, CH^{ortho}, PHTol), 129.5 (m, CH^{meta}, PHTol), 125.7 (br m, C$^{q\ ipso}$, PHTol), 21.4 (s, CH$_3^{para}$, PHTol).

Anal. calcd. (found) for $C_7H_{10}BP$ [135.94 gmol^{-1}]: C, 61.85 (59.22); H, 7.41 (7.92).

IR (ATR, cm^{-1}) $\tilde{\nu}$ = 2411 (vs, BH), 2386 (vs, PH).

GPC: 5 mol% precatalyst (**1a**) and **method A**: M_n = 5 000, M_w = 66 000, DP_w = 486, PDI = 13.2.

[MesPH–BH$_2$]$_n$ 3c: yield 25.0 mg (18 µmol, 88 %) of a pale yellow solid.

^{1}H{^{11}B} NMR (400.40 MHz, C_6D_6, 298 K, ppm) δ 6.50 (br s, 2H, CH^{meta}, PHMes), 4.93 (br dm, $^1J_{PH}$ = 355.7 Hz, 1H, P*H*Mes), 2.41 (vbr s, 6H, CH$_3^{ortho}$, PHMes), 2.01 (s, 3H, CH$_3^{para}$, PHMes), 1.56 (vbr s, 2H, B*H*$_2$).

^{31}P NMR (162.08 MHz, C_6D_6, 298 K, ppm) δ -73.0 (br d, $^1J_{PH}$ = 355.7 Hz).

^{11}B NMR (128.46 MHz, C_6D_6, 298 K, ppm) δ -34.3 (vbr s).

^{13}C{^{1}H} NMR (100.68 MHz, C_6D_6, 298 K, ppm) δ 142.4 (br d, *J* = 148.9 Hz, C$^{q\ ortho}$, PHMes), 138.9 (m, $^4J_{CP}$ = 1.9 Hz, C$^{q\ para}$, PHMes), 129.6 (s, CH^{meta}, PHMes), 123.5 (m, C$^{q\ ipso}$, PHMes), 22.6 (m, CH$_3^{ortho}$, PHMes), 21.0 (s, CH$_3^{para}$, PHMes).

IR (ATR, cm^{-1}) $\tilde{\nu}$ = 2443 (vs, BH), 2390 (vs, PH).

Anal. calcd. (found) for $C_9H_{14}BP$ [163.99 gmol^{-1}]: C, 65.92 (64.17); H, 8.61 (8.65).

GPC: 5 mol% precatalyst (**1a**) and **method A**: M_n = 10 000, M_w = 300 000, DP_w = 1829, PDI = 30.0; 2.5 mol% precatalyst (**1a**) and **method A**: M_n = 5 000, M_w = 13 000, DP_w = 79, PDI = 2.6; 2.5 mol% precatalyst (**1a**) and **method B**: M_n = 33 000, M_w = 59 000, DP_w = 360, PDI = 1.8; 2.5 mol% precatalyst (**1a**) and **method B** after **6 hours**: M_n = 20 000, M_w = 116 000, DP_w = 707, PDI = 5.8; 2.5 mol% precatalyst (**1a**) and **method B** (after dehydrocoupling of second equivalent of adduct **2c**): M_n = 99 000, M_w = 314 000, DP_w = 1891, PDI = 3.2; 2.5 mol% precatalyst (**1b**) and **method B**: M_n = 34 000, M_w = 71 000, DP_w = 432, PDI = 2.1; 2.5 mol% precatalyst (**7c**) and **method B**: M_n = 67 000, M_w = 233 000, DP_w = 1404, PDI = 3.5; 0.5 mol% precatalyst and **method B**: M_n = 5 000, M_w = 10 000, DP_w = 61, PDI = 2.0.

Attempted Iridium-promoted dehydrogenative coupling of $Mes_2PH–BH_3$ with 2.5 mol% of 1a

An NMR tube was charged with 2.5 mol% of the precatalyst **1a** and a solution of the phosphine-borane adduct $Mes_2PH–BH_3$ (11.0 mg, 0.40 mmol) in 0.6 mL of benzene / 0.6 mL of toluene. The reaction mixture was heated to 80 °C for 24 hours and monitored by ^{31}P NMR spectroscopy. No formation of polymeric products could be detected.

Synthesis of Iridium(I)phosphine complexes 6a-c

In an NMR tube 13.0 mg (20.0 µmol) [(^{t}BuPOCOP)IrHPh] (**1b**) were dissolved in 0.60 mL of C_6D_6 and one equivalent (20.0 µmol) of the respective phosphine **8a-c** was added. The color of the solution immediately turned from red to orange and quantitative conversion to the phosphine complexes **6a-c** was detected via NMR spectroscopy. The resulting mixture was transferred into a Schlenk flask, all volatiles removed *in vacuo*, the residue washed with small amounts of cold pentane and dried *in vacuo* to yield the [(^{t}BuPOCOP)Ir(PH_2Ar)] complexes (**6a-c**) as orange powders. Single crystals suitable for X-ray diffraction have been obtained by cooling saturated pentane solutions of the products to -30 °C.

[(^{t}BuPOCOP)Ir(PH_2Ph)] 6a: yield 12.0 mg (17.1 µmol, 86 %) of an orange solid.

^{1}H NMR (400.40 MHz, C_6D_6, 298 K, ppm) δ 7.72 (dd, $^3J_{PH}$ = 10.7 Hz, $^3J_{HH}$ = 6.5 Hz, 2H, CH^{ortho}, PH_2Ph), 7.12-7.05 (m, 4H, $CH^{meta/para}$, PH_2Ph/POCOP), 7.00-6.98 (m, 2H, CH^{meta}, POCOP) 6.27 (dt, $^1J_{PH}$ = 317.8 Hz, $^3J_{PH}$=7.2 Hz, 2H, P*H*$_2$Ph), 1.29 (vt, $^3J_{PH}$=6.9 Hz, 36H, P^{t}Bu$_2$); **^{1}H{^{31}P} NMR** (199.93 MHz, C_6D_6, 298 K, pppm) δ 7.75-7.70 (m, 2H, CH^{ortho}, PH_2Ph), 7.11-7.03 (m, 4H, $CH^{meta/para}$, PH_2Ph/POCOP), 6.99-6.94 (m, 2H, CH^{meta}, POCOP) 6.28 (m, 2H, P*H*$_2$Ph), 1.29 (m, 36H, P^{t}Bu$_2$).

^{31}P NMR (162.08 MHz, C_6D_6, 298 K, ppm) δ 186.9 (br s, P^{t}Bu$_2$), -67.7 (tm, $^1J_{PH}$ = 317.8 Hz, PH_2Ph); **^{31}P{^{1}H} NMR** (162.08 MHz, C_6D_6, 298 K) δ 186.9 (d, $^2J_{PP}$ = 10.8 Hz, P^{t}Bu$_2$), -67.7 (t, $^2J_{PP}$ = 10.8 Hz, PH_2Ph); **^{31}P{^{1}H} NMR** (80.93 MHz, C_6D_6, 298 K) δ 186.8 (d, $^2J_{PP}$ = 10.8 Hz, P^{t}Bu$_2$), -67.8 (t, $^2J_{PP}$ = 10.8 Hz, PH_2Ph).

^{13}C{^{1}H} NMR (100.68 MHz, C_6D_6, 298 K, ppm) δ 167.9 (dt, $^4J_{CP}$ = 1.8 Hz, $^2J_{CP}$ = 8.5 Hz, $C^{q\,ortho}$, POCOP), 146.9 (m, $C^{q\,ipso}$, POCOP), 135.0 (d, $^2J_{CP}$ = 10.0 Hz, CH^{ortho}, PH_2Ph), 131.8 (m, $C^{q\,ipso}$, PH_2Ph), 129.6 (d, $^4J_{CP}$ = 1.9 Hz, CH^{para}, PH_2Ph), 128.4 (d, $^3J_{CP}$ = 8.9 Hz, CH^{meta}, PH_2Ph), 126.5 (s, CH^{para}, POCOP), 103.8 (dt, $^4J_{CP}$ = 1.3 Hz, $^3J_{CP}$ = 6.0 Hz, CH^{meta}, POCOP), 41.9 (t, $^1J_{CP}$ = 12.0 Hz, C^q, P^{t}Bu$_2$), 28.8 (t, $^2J_{CP}$ = 3.2 Hz, CH_3, P^{t}Bu$_2$).

Anal. calcd. (found) for $C_{28}H_{46}IrO_2P_3$ [699.80 gmol^{-1}]: C, 48.06 (48.47); H, 6.63 (6.82).

[(^{t}BuPOCOP)Ir(PH$_2$^{p}Tol)] 6b: yield 10.0 mg (14 µmol, 70 %) of an orange solid.

^{1}H NMR (400.40 MHz, C_6D_6, 298 K, ppm) δ 7.69 (dd, $^3J_{PH}$ = 10.9 Hz, $^3J_{HH}$ = 8.1 Hz, 2H, CH^{ortho}, PH$_2$Tol), 7.08 (t, $^3J_{HH}$ = 8.0 Hz, 1H, CH^{para}, POCOP), 7.01-6.98 (m, 2H, CH^{meta}, POCOP) 6.95 (d, $^3J_{HH}$ = 7.7 Hz, 2H, CH^{meta}, PH$_2$Tol), 6.31 (dt, $^1J_{PH}$ = 316.8 Hz, $^3J_{PH}$=7.3 Hz, 2H, P*H*$_2$Tol), 2.05 (s, 3H, CH$_3^{para}$, PH$_2$Tol), 1.31 (vt, $^3J_{PH}$=6.8 Hz, 36H, P^{t}Bu$_2$); **^{1}H{^{31}P} NMR** (199.93 MHz, C_6D_6, 298 K, ppm) δ 7.69 (d, $^3J_{HH}$ = 8.1 Hz, 2H, CH^{ortho}, PH$_2$Tol), 7.12-6.94 (m, 5H, CH$^{para/meta}$, POCOP/PH$_2$Tol) 6.31 (m, 2H, P*H*$_2$Tol), 2.05 (s, 3H, CH$_3^{para}$, PH$_2$Tol), 1.31 (m, 36H, P^{t}Bu$_2$).

^{31}P NMR (162.08 MHz, C_6D_6, 298 K, ppm) δ 186.8 (br s, P^{t}Bu$_2$), -69.0 (tm, $^1J_{PH}$ = 316.8 Hz, PH$_2$Tol); **^{31}P{^{1}H} NMR** (162.08 MHz, C_6D_6, 298 K, ppm) δ 186.8 (d, $^2J_{PP}$ = 10.9 Hz, P^{t}Bu$_2$), -69.0 (t, $^2J_{PP}$ = 10.9 Hz, PH$_2$Tol); **^{31}P{^{1}H} NMR** (80.93 MHz, C_6D_6, 298 K, ppm) δ 186.8 (d, $^2J_{PP}$ = 10.7 Hz, P^{t}Bu$_2$), -69.1 (t, $^2J_{PP}$ = 10.7 Hz, PH$_2$Tol).

^{13}C{^{1}H} NMR (100.68 MHz, C_6D_6, 298 K, ppm) δ 167.9 (dt, $^4J_{CP}$ = 1.5 Hz, $^2J_{CP}$ = 8.5 Hz, C$^{q\ ortho}$, POCOP), 146.5 (m, C$^{q\ ipso}$, POCOP), 139.6 (d, $^4J_{CP}$ = 2.0 Hz, C$^{q\ para}$, PH$_2$Tol), 135.3 (d, $^2J_{CP}$ = 10.2 Hz, CH^{ortho}, PH$_2$Tol), 129.2 (d, $^3J_{CP}$ = 9.4 Hz, CH^{meta}, PH$_2$Tol), 128.7 (m, C$^{q\ ipso}$, PH$_2$Tol), 126.5 (s, CH^{para}, POCOP), 103.8 (dt, $^4J_{CP}$ = 1.0 Hz, $^3J_{CP}$ = 5.6 Hz, CH^{meta}, POCOP), 41.9 (t, $^1J_{CP}$ = 12.0 Hz, C^q, P^{t}Bu$_2$), 28.9 (t, $^2J_{CP}$ = 3.2 Hz, CH$_3$, P^{t}Bu$_2$), 21.2 (s, CH$_3^{para}$, PH$_2$Tol).

Anal. calcd. (found) for $C_{29}H_{48}IrO_2P_3$ [713.83 gmol^{-1}]: C, 48.79 (48.72); H, 6.78 (7.08).

[(^{t}BuPOCOP)Ir(PH$_2$Mes)] 6c: yield 14.0 mg (18.9 µmol, 95 %) of an orange solid.

^{1}H NMR (400.40 MHz, C_6D_6, 298 K, ppm) δ 7.07 (t, $^3J_{HH}$ = 7.7 Hz, 1H, CH^{para}, POCOP), 6.97-6.95 (m, 2H, CH^{meta}, POCOP) 6.73 (d, $^4J_{PH}$ = 2.2 Hz, 2H, CH^{meta}, PH$_2$Mes), 6.43 (dt, $^1J_{PH}$ = 320.9 Hz, $^3J_{PH}$=4.4 Hz, 2H, P*H*$_2$Mes), 2.56 (s, 6H, CH$_3^{ortho}$, PH$_2$Mes), 2.13 (s, 3H, CH$_3^{para}$, PH$_2$Mes), 1.26 (vt, $^3J_{PH}$=6.8 Hz, 36H, P^{t}Bu$_2$); **^{1}H{^{31}P} NMR** (199.93 MHz, C_6D_6, 298 K, ppm) δ 7.07 (dd, $^3J_{HH}$ = 9.0 Hz, $^3J_{HH}$ = 6.3 Hz, 1H, CH^{para}, POCOP), 6.96-6.92 (m, 2H, CH^{meta}, POCOP) 6.74 (s, 2H, CH^{meta}, PH$_2$Mes), 6.44 (br s, 2H, P*H*$_2$Mes), 2.58 (s, 6H, CH$_3^{ortho}$, PH$_2$Mes), 2.13 (s, 3H, CH$_3^{para}$, PH$_2$Mes), 1.27 (br s, 36H, P^{t}Bu$_2$).

^{31}P NMR (162.08 MHz, C_6D_6, 298 K, ppm) δ 185.2 (br s, P^{t}Bu$_2$), -101.6 (tm, $^1J_{PH}$ = 320.9 Hz, PH$_2$Mes); **^{31}P{^{1}H} NMR** (162.08 MHz, C_6D_6, 298 K, ppm) δ 185.2 (d, $^2J_{PP}$ = 9.2 Hz, P^{t}Bu$_2$), -101.6 (t, $^2J_{PP}$ = 9.2 Hz, PH$_2$Mes); **^{31}P{^{1}H} NMR** (80.93 MHz, C_6D_6, 298 K, ppm) δ 185.2 (d, $^2J_{PP}$ = 9.1 Hz, P^{t}Bu$_2$), -101.7 (t, $^2J_{PP}$ = 9.1 Hz, PH$_2$Mes).

^{13}C{^{1}H} NMR (100.68 MHz MHz, C_6D_6, 298 K, ppm) δ 167.4 (dt, $^4J_{CP}$ = 1.3 Hz, $^2J_{CP}$ = 8.3 Hz, C$^{q\ ortho}$, POCOP), 144.8 (m, C$^{q\ ipso}$, POCOP), 140.6 (d, $^2J_{CP}$ = 7.7 Hz, C$^{q\ ortho}$, PH$_2$Mes), 138.5 (d, $^4J_{CP}$ = 1.5 Hz, C$^{q\ para}$, PH$_2$Mes), 129.6 (d, $^3J_{CP}$ = 6.3 Hz, CH^{meta}, PH$_2$Mes), 128.7 (m, C$^{q\ ipso}$, PH$_2$Mes), 125.8 (s, CH^{para}, POCOP), 103.7 (dt, $^4J_{CP}$ = 1.3 Hz, $^3J_{CP}$ = 6.0 Hz, CH^{meta}, POCOP), 41.3 (dt, $^3J_{CP}$ = 1.2 Hz, $^1J_{CP}$ = 12.1 Hz, C^q, P^{t}Bu$_2$), 28.7 (t, $^2J_{CP}$ = 3.4 Hz, CH$_3$, P^{t}Bu$_2$), 23.3 (d, $^2J_{CP}$ = 8.8 Hz, CH$_3^{ortho}$, PH$_2$Mes), 20.9 (s, CH$_3^{para}$, PH$_2$Mes).

Anal. calcd. (found) for $C_{31}H_{52}IrO_2P_3$ [741.88 gmol^{-1}]: C, 50.19 (50.24); H, 7.06 (6.84).

Synthesis of Iridium(III)phosphine complexes 7a-c

In a Schlenk flask 20.0 µmol of the respective Iridium(I)phosphine complex **6a-c** were dissolved in 5 mL of toluene. After being degassed by three freeze-pump cycles the flask was pressurised with 1 atm dihydrogen and the solution stirred for 16 h while becoming light yellow. All volatile material was removed *in vacuo*, the residue washed with small amounts of cold pentane and dried *in vacuo* to yield the [(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$Ar)] complexes **7a-c** as yellow powders. Single crystals suitable for X-ray diffraction have been obtained by cooling saturated pentane solutions of the products to -30 °C.

[(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$Ph)] 7a: yield 10.0 mg (13.4 µmol, 67 %) of a yellow powder.

^{1}H NMR (400.40 MHz, C_6D_6, 298 K, ppm) δ 7.84 (dd, $^3J_{PH}$ = 11.9 Hz, $^3J_{HH}$ = 7.2 Hz, 2H, CH^{ortho}, PH$_2$Ph), 7.09 (dt, $^4J_{PH}$ = 1.7 Hz, $^3J_{HH}$ = 7.4 Hz, 2H, CH^{meta}, PH$_2$Ph), 7.02 (dt, $^5J_{PH}$ = 2.1 Hz, $^3J_{HH}$ = 7.4 Hz, 1H, CH^{para}, PH$_2$Ph), 6.91 (t, $^3J_{HH}$ = 7.7 Hz, 1H, CH^{para}, POCOP), 6.84-6.82 (m, 2H, CH^{meta}, POCOP), 5.97 (dm, $^1J_{PH}$ = 335.2 Hz, 2H, P*H*$_2$Ph), 1.32 (vt, $^3J_{PH}$=7.0 Hz, 36H, P^{t}Bu$_2$), -10.70 (dtm, $^2J_{PH}$ = 16.6 Hz, $^2J_{PH}$ = 15.5 Hz, 2H, Ir(*H*)$_2$); **^{1}H{^{31}P} NMR** (400.40 MHz, C_6D_6, 298 K, ppm) δ 7.84 (d, $^3J_{HH}$ = 7.0 Hz, 2H, CH^{ortho}, PH$_2$Ph), 7.09 (t, $^3J_{HH}$ = 7.3 Hz, 2H, CH^{meta}, PH$_2$Ph), 7.02 (t, $^3J_{HH}$ = 7.4 Hz, 1H, CH^{para}, PH$_2$Ph), 6.91 (t, $^3J_{HH}$ = 7.4 Hz, 1H, CH^{para}, POCOP), 6.84-6.82 (m, 2H, CH^{meta}, POCOP) 5.97 (m, 2H, P*H*$_2$Ph), 1.32 (vt, $^3J_{PH}$=6.9 Hz, 36H, P^{t}Bu$_2$), -10.71 (tm, $^2J_{PH}$ = 15.3 Hz, 2H, Ir(*H*)$_2$); **^{1}H{^{31}P} NMR** (199.93 MHz, C_6D_6, 298 K, pppm) δ 7.85 (dm, $^3J_{HH}$ = 8.0 Hz, 2H, CH^{ortho}, PH$_2$Ph), 7.14-6.80 (m, 6H, CH$^{meta/para}$, PH$_2$Ph/POCOP), 5.98 (m, 2H, P*H*$_2$Ph), 1.33 (s, 36H, P^{t}Bu$_2$), -10.71 (m, 2H, Ir(*H*)$_2$).

^{31}P NMR (162.08 MHz, C_6D_6, 298 K, ppm) δ 174.3 (br s, P^{t}Bu$_2$), -92.9 (tm, $^1J_{PH}$ = 335.2 Hz, PH$_2$Ph); **^{31}P{^{1}H} NMR** (162.08 MHz, C_6D_6, 298 K, ppm) δ 174.3 (d, $^2J_{PP}$ = 13.1 Hz, P^{t}Bu$_2$), -92.9 (t, $^2J_{PP}$ = 13.1 Hz, PH$_2$Ph); **^{31}P{^{1}H} NMR** (80.93 MHz, C_6D_6, 298 K, ppm) δ 174.3 (d, $^2J_{PP}$ = 13.0 Hz, P^{t}Bu$_2$), -93.1 (t, $^2J_{PP}$ = 13.0 Hz, PH$_2$Ph).

^{13}C{^{1}H} NMR (100.68 MHz, C_6D_6, 298 K, ppm) δ 163.3 (t, $^2J_{CP}$ = 6.2 Hz, C$^{q\ ortho}$, POCOP), 134.9 (d, $^2J_{CP}$ = 10.5 Hz, CH ^{ortho}, PH$_2$Ph), 129.6 (d, $^4J_{CP}$ = 2.1 Hz, CH^{para}, PH$_2$Ph), 128.6 (d, $^3J_{CP}$ = 9.8 Hz, CH^{meta}, PH$_2$Ph), 126.9 (dm, $^2J_{CP}$ = 69.0 Hz, C$^{q\ ipso}$, POCOP), 126.8 (dm, $^1J_{CP}$ = 44.7 Hz, C$^{q\ ipso}$, PH$_2$Ph), 123.8 (s, CH^{para}, POCOP), 104.2 (t, $^3J_{CP}$ = 5.4 Hz, CH^{meta}, POCOP), 40.7 (t, $^1J_{CP}$ = 13.6 Hz, C^q, P^{t}Bu$_2$), 28.5 (t, $^2J_{CP}$ = 2.7 Hz, CH$_3$, P^{t}Bu$_2$).

Anal. calcd. (found) for $C_{28}H_{48}IrO_2P_3$ [701.82 gmol^{-1}]: C, 47.92 (48.31); H, 6.89 (6.43).

[(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$^{p}Tol)] 7b: yield 11 mg (15.4 µmol, 77 %) of a yellow powder.

^{1}H NMR (400.40 MHz, C_6D_6, 298 K, ppm) δ 7.81 (dd, $^3J_{PH}$ = 11.6 Hz, $^3J_{HH}$ = 7.7 Hz, 2H, CH^{ortho}, PH$_2$Tol), 6.94-6.90 (m, 3H, CH$^{meta/para}$, PH$_2$Tol/POCOP), 6.86-6.83 (m, 2H, CH^{meta}, POCOP), 6.01 (dm, $^1J_{PH}$ = 334.6 Hz, 2H, P*H*$_2$Tol), 2.02 (s, 3H, CH$_3^{para}$, PH$_2$Tol), 1.35 (vt, $^3J_{PH}$=7.0 Hz, 36H, P^{t}Bu$_2$), -10.70 (dtm, $^2J_{PH}$ = 16.5 Hz, $^2J_{PH}$ = 15.4 Hz, 2H, Ir(*H*)$_2$); **^{1}H{^{31}P} NMR** (400.40 MHz, C_6D_6, 298 K, ppm) δ 7.80 (d, $^3J_{HH}$ = 7.8 Hz, 2H, CH^{ortho}, PH$_2$Tol), 6.94-6.89 (m, 3H, CH$^{meta/para}$, PH$_2$Tol/POCOP), 6.85-6.83 (m, 2H, CH^{meta}, POCOP), 6.01 (m, 2H, P*H*$_2$Tol), 2.02 (s, 3H, CH$_3^{para}$, PH$_2$Tol), 1.35 (vt, $^3J_{PH}$=6.9 Hz, 36H, P^{t}Bu$_2$), -10.71 (tm, $^2J_{PH}$ = 15.3 Hz, 2H, Ir(*H*)$_2$); **^{1}H{^{31}P} NMR** (199.93 MHz, C_6D_6, 298 K, ppm) δ 7.21 (d, $^3J_{HH}$ = 8.0 Hz, 2H, CH^{ortho}, PH$_2$Tol), 6.95-6.80 (m, 5H, CH$^{para/meta}$, POCOP/PH$_2$Tol) 6.01 (br s, 2H, P*H*$_2$Tol), 2.03 (s, 3H, CH$_3^{para}$, PH$_2$Tol), 1.34 (s, 36H, P^{t}Bu$_2$)), -10.71 (m, 2H, Ir(*H*)$_2$).

^{31}P NMR (162.08 MHz, C_6D_6, 298 K, ppm) δ 174.3 (br s, P^{t}Bu$_2$), -94.0 (tm, $^1J_{PH}$ = 334.6 Hz, PH$_2$Tol). **^{31}P{^{1}H} NMR** (162.08 MHz, C_6D_6, 298 K, ppm) δ 174.3 (d, $^2J_{PP}$ = 13.1 Hz, P^{t}Bu$_2$), -94.0 (t, $^2J_{PP}$ = 13.1 Hz, PH$_2$Tol); **^{31}P{^{1}H} NMR** (80.93 MHz, C_6D_6, 298 K, ppm) δ 174.2 (d, $^2J_{PP}$ = 13.2 Hz, P^{t}Bu$_2$), -94.2 (t, $^2J_{PP}$ = 13.2 Hz, PH$_2$Tol).

^{13}C{^{1}H} NMR (100.68 MHz, C_6D_6, 298 K, ppm) δ 163.3 (t, $^2J_{CP}$ = 6.3 Hz, C$^{q\ ortho}$, POCOP), 140.3 (d, $^4J_{CP}$ = 2.1 Hz, C$^{q\ para}$, PH$_2$Tol), 135.1 (d, $^2J_{CP}$ = 10.7 Hz, CH^{ortho}, PH$_2$Tol), 129.5 (d, $^3J_{CP}$ = 10.0 Hz, CH^{meta}, PH$_2$Tol), 127.0 (dm, $^2J_{CP}$ = 68.4 Hz, C$^{q\ ipso}$, POCOP), 123.8 (s, CH^{para}, POCOP), 122.9 (dm, $^1J_{CP}$ = 46.2 Hz, C$^{q\ ipso}$, PH$_2$Tol), 104.2 (t, $^3J_{CP}$ = 5.5 Hz, CH^{meta}, POCOP), 40.8 (t, $^1J_{CP}$ = 13.6 Hz, C^q, P^{t}Bu$_2$), 28.5 (t, $^2J_{CP}$ = 3.0 Hz, CH$_3$, P^{t}Bu$_2$), 21.1 (s, CH$_3^{para}$, PH$_2$Tol). Anal. calcd. (found) for $C_{29}H_{50}IrO_2P_3$ [715.84 gmol^{-1}]: C, 48.66 (48.66); H, 7.04 (7.04).

[(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$Mes)] 7c: yield 15 mg (18 µmol, 91 %) of a yellow powder.

^{1}H NMR (400.40 MHz, C_6D_6, 298 K, ppm) δ 6.89 (t, $^3J_{HH}$ = 7.8 Hz, 1H, CH^{para}, POCOP), 6.81-6.79 (m, 2H, CH^{meta}, POCOP) 6.64 (d, $^4J_{PH}$ = 3.1 Hz, 2H, CH^{meta}, PH$_2$Mes), 5.72 (dm, $^1J_{PH}$ = 338.7 Hz, 2H, P*H*$_2$Mes), 2.44 (s, 6H, CH$_3^{ortho}$, PH$_2$Mes), 2.09 (s, 3H, CH$_3^{para}$, PH$_2$Mes), 1.30 (vt, $^3J_{PH}$=7.0 Hz, 36H, P^{t}Bu$_2$), -10.98 (dm, $^2J_{PH}$ = 19.1 Hz, 2H, Ir(*H*)$_2$); **^{1}H{^{31}P} NMR** (400.40 MHz, C_6D_6, 298 K, ppm) δ 6.89 (t, $^3J_{HH}$ = 7.8 Hz, 1H, CH^{para}, POCOP), 6.81-6.79 (m, 2H, CH^{meta}, POCOP) 6.64 (s, 2H, CH^{meta}, PH$_2$Mes), 5.72 (m, 2H, P*H*$_2$Mes), 2.44 (s, 6H, CH$_3^{ortho}$, PH$_2$Mes), 2.09 (s, 3H, CH$_3^{para}$, PH$_2$Mes), 1.30 (vt, $^3J_{PH}$=6.9 Hz, 36H, P^{t}Bu$_2$), -10.98 (m, 2H, Ir(*H*)$_2$); **^{1}H{^{31}P} NMR** (199.93 MHz, C_6D_6, 298 K, ppm) δ 6.88 (dd, $^3J_{HH}$ = 9.1 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, CH^{para}, POCOP), 6.80-6.76 (m, 2H, CH^{meta}, POCOP) 6.65 (s, 2H, CH^{meta}, PH$_2$Mes), 5.73 (m, 2H, P*H*$_2$Mes), 2.44 (s, 6H, CH$_3^{ortho}$, PH$_2$Mes), 2.09 (s, 3H, CH$_3^{para}$, PH$_2$Mes), 1.30 (s, 36H, P^{t}Bu$_2$), -10.98 (m, 2H, Ir(*H*)$_2$).

^{31}P NMR (162.08 MHz, C_6D_6, 298 K, ppm) δ 173.3 (br s, P^{t}Bu$_2$), -139.7 (tm, $^1J_{PH}$ = 338.7 Hz, PH$_2$Mes); **^{31}P{^{1}H} NMR** (162.08 MHz, C_6D_6, 298 K, ppm) δ 173.3 (d, $^2J_{PP}$ = 11.9 Hz, P^{t}Bu$_2$), -139.7 (t, $^2J_{PP}$ = 11.9 Hz, PH$_2$Mes); **^{31}P{^{1}H} NMR** (80.93 MHz, C_6D_6, 298 K, ppm) δ 173.3 (d, $^2J_{PP}$ = 11.9 Hz, P^{t}Bu$_2$), -139.9 (t, $^2J_{PP}$ = 11.9 Hz, PH$_2$Mes).

^{13}C{^{1}H} NMR (100.68 MHz, C_6D_6, 298 K, ppm) δ 162.9 (t, $^2J_{CP}$ = 6.2 Hz, C$^{q\ ortho}$, POCOP), 140.8 (d, $^2J_{CP}$ = 7.9 Hz, C$^{q\ ortho}$, PH$_2$Mes), 139.1 (d, $^4J_{CP}$ = 1.9 Hz, C$^{q\ para}$, PH$_2$Mes), 129.5 (d, $^3J_{CP}$ = 6.9 Hz, CH^{meta}, PH$_2$Mes), 125.6 (dt, $^2J_{CP}$ = 69.8 Hz, $^2J_{CP}$ = 6.4 Hz, C$^{q\ ipso}$, POCOP), 125.2 (dt, $^1J_{CP}$ = 40.2 Hz, $^3J_{CP}$ = 3.8 Hz, C$^{q\ ipso}$, PH$_2$Mes), 123.7 (s, CH^{para}, POCOP), 104.0 (t, $^3J_{CP}$ = 5.8 Hz, CH^{meta}, POCOP), 40.1 (t, $^1J_{CP}$ = 13.8 Hz, C^q, P^{t}Bu$_2$), 28.5 (t, $^2J_{CP}$ = 3.1 Hz, CH$_3$, P^{t}Bu$_2$), 21.9 (d, $^2J_{CP}$ = 8.8 Hz, CH$_3^{ortho}$, PH$_2$Mes), 20.9 (s, CH$_3^{para}$, PH$_2$Mes).

Anal. calcd. (found) for $C_{31}H_{54}IrO_2P_3$ [743.90 gmol^{-1}]: C, 50.05 (50.63); H, 7.32 (7.26).

3. Crystallography

Crystal data collection and processing parameters are given below. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Bruker X8 Apex-2 diffractometer with CCD area detector and mirror-monochromated Mo-Kα radiation equipped with a Bruker Kryoflex[2] low-temperature device. Data were collected at 162 K. The images were processed with the Bruker software packages and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed if necessary and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were included in calculated positions and refined using a riding model. Extinction corrections were applied as required. Crystallographic calculations were performed using the SHELXTL software package. [S6] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factors calculations. All hydrogen atoms were assigned to idealized positions, except those bound to iridium and phosphorus. Positions of these atoms were also refined. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1472599 to 1472604. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Structure Determination of [(^{t}BuPOCOP)Ir(PH$_2$Ph)] 6a: $C_{28}H_{46}IrO_2P_3$, M_r = 699.76, orange block, 0.20 × 0.10 × 0.09 mm, monoclinic space group $P2_1/c$, a = 12.8054(14) Å, b = 12.7662(14) Å, c = 20.774(2), α = 90 °, β = 104.821(2) °, γ = 90 °, V = 3283.1(6) Å^3, T = 162(2) K, Z = 4, $\rho_{calcd.}$ = 1.416 g·cm^{-3}, μ = 4.233 mm^{-1}, F(000) = 1408, 67001 reflections in h(–15/15), k(–15/15), l(–25/25) measured in the range 1.645° < θ < 26.173°, completeness 99.8 %, 6565 independent reflections, 5939 observed reflections ($I > 2\sigma(I)$), 328 parameters, 0 restraints; *all data:* R_1 = 0.0199 and wR_2 = 0.0463, $I > 2\sigma(I)$: R_1 = 0.0243 and wR_2 = 0.0485, *Goof* 1.069, largest difference peak/hole 0.770/–0.309 e·Å^{-3}. For the molecular structure of **6a** one pentane solvent molecule could not be refined properly and was subsequently removed from the model using the PLATON/SQUEEZE routine.

Crystal Structure Determination of [(^{t}BuPOCOP)Ir(PH$_2$^{p}Tol)] 6b: $C_{29}H_{48}IrO_2P_3$, M_r = 699.76, orange plate, 0.15 × 0.15 × 0.05 mm, triclinic space group $P\bar{1}$, a = 10.2215(11) Å, b = 11.8640(13) Å, c = 16.0253(18), α = 103.712(2) °, β = 100.633(2) °, γ = 93.622(2) °, V = 1843.9(4) Å^3, T = 168(2) K, Z = 2, $\rho_{calcd.}$ = 1.286 g·cm^{-3}, μ = 3.770 mm^{-1}, F(000) = 720, 38408 reflections in h(–12/12), k(–14/14), l(–19/19) measured in the range 1.778° < θ < 26.102°, completeness 100 %, 7343 independent reflections, 6843 observed reflections ($I > 2\sigma(I)$), 358

parameters, 0 restraints; *all data:* R_1 = 0.0247 and wR_2 = 0.0541, $I > 2\sigma(I)$: R_1 = 0.0218 and wR_2 = 0.0524, *Goof* 1.067, largest difference peak/hole 0.963/–0.314 e·Å^{-3}. For the molecular structure of **6b** one pentane solvent molecule could not be refined properly and was subsequently removed from the model using the PLATON/SQUEEZE routine.

Crystal Structure Determination of [(^{t}BuPOCOP)Ir(PH$_2$Mes)] 6c: $C_{31}H_{52}IrO_2P_3$, M_r = 741.83, orange plate, 0.12 × 0.10 × 0.08 mm, monoclinic space group *C*2/c, *a* = 10.5197(11) Å, *b* = 20.993(2) Å, *c* = 30.334(3), α = 90 °, β = 99.463(2) °, *γ* = 90 °, *V* = 6607.8(12) Å^3, *T* = 168(2) K, *Z* = 8, $\rho_{calcd.}$ = 1.491 g·cm^{-3}, *μ* = 4.211 mm^{-1}, *F*(000) = 3008, 63757 reflections in *h*(–13/13), *k*(–26/25), *l*(–37/37) measured in the range 1.940° < *θ* < 26.159°, completeness 99.8 %, 6601 independent reflections, 5882 observed reflections ($I > 2\sigma(I)$), 378 parameters, 18 restraints; *all data:* R_1 = 0.0394 and wR_2 = 0.0700, $I > 2\sigma(I)$: R_1 = 0.0328 and wR_2 = 0.0676, *Goof* 1.212, largest difference peak/hole 1.370/–1.178 e·Å^{-3}. The U_{ii} displacement parameters of atoms C13 to C14 and C53 to C54 of **6c** were restrained with the SIMU and DELU keywords.

Crystal Structure Determination of [(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$Ph)] 7a: $C_{28}H_{48}IrO_2P_3$, M_r = 701.77, yellow block, 0.20 × 0.20 × 0.20 mm, monoclinic space group $P2_1$/c, *a* = 12.8121(12) Å, *b* = 12.7747(12) Å, *c* = 20.771(2), α = 90 °, β = 104.5730(10) °, *γ* = 90 °, *V* = 3290.2(5) Å^3, *T* = 168(2) K, *Z* = 4, $\rho_{calcd.}$ = 1.417 g·cm^{-3}, *μ* = 4.224 mm^{-1}, *F*(000) = 1416, 75363 reflections in *h*(–15/15), *k*(–15/15), *l*(–25/25) measured in the range 1.889° < *θ* < 26.141°, completeness 99.7 %, 6554 independent reflections, 6052 observed reflections ($I > 2\sigma(I)$), 335 parameters, 2 restraints; *all data:* R_1 = 0.0185 and wR_2 = 0.0404, $I > 2\sigma(I)$: R_1 = 0.0161 and wR_2 = 0.0397, *Goof* 1.050, largest difference peak/hole 0.797/–0.356 e·Å^{-3}. The distances between atoms H101, H102 and Ir1 were kept during refinement at the value of 1.400 Å using the DFIX restraint. For the molecular structure of **7a** one pentane solvent molecule could not be refined properly and was subsequently removed from the model using the PLATON/SQUEEZE routine.

Crystal Structure Determination of [(^{t}BuPOCOP)Ir(H)$_2$(PH$_2$^{p}Tol)] 7b: $C_{29}H_{50}IrO_2P_3$, M_r = 715.80, yellow block, 0.20 × 0.20 × 0.20 mm, triclinic space group $P\bar{1}$, *a* = 10.2300(9) Å, *b* = 11.9105(10) Å, *c* = 15.9818(14), α = 103.7350(10) °, β = 100.9570(10) °, *γ* = 93.7140(10) °, *V* = 1844.8(3) Å^3, *T* = 168(2) K, *Z* = 2, $\rho_{calcd.}$ = 1.289 g·cm^{-3}, *μ* = 3.768 mm^{-1}, *F*(000) = 724, 43200 reflections in *h*(–12/12), *k*(–14/14), *l*(–19/19) measured in the range 1.342° < *θ* < 26.150°, completeness 99.7 %, 7352 independent reflections, 6968 observed reflections ($I > 2\sigma(I)$), 345 parameters, 2 restraints; *all data:* R_1 = 0.0204 and wR_2 = 0.0482, $I > 2\sigma(I)$: R_1 = 0.0187 and wR_2 = 0.0474, *Goof* 1.068, largest difference peak/hole 1.200/–0.503 e·Å^{-3}. The distances between atoms H101, H102 and Ir1 were kept during refinement at the value of 1.400 Å using the DFIX restraint. For the molecular structure of **7b** one pentane solvent molecule could not

be refined properly and was subsequently removed from the model using the PLATON/SQUEEZE routine.

Crystal Structure Determination of [(ᵗBuPOCOP)Ir(H)$_2$(PH$_2$Mes)] 7c: $C_{31}H_{54}IrO_2P_3 \cdot C_5H_{12}$, M_r = 815.99, yellow plate, 0.15 × 0.15 × 0.05 mm, triclinic space group $P\bar{1}$, a = 10.9010(13) Å, b = 12.6860(15) Å, c = 15.2272(17), α = 78.1840(10) °, β = 72.9730(10) °, γ = 73.4180(2) °, V = 1912.8(4) Å^3, T = 168(2) K, Z = 2, $\rho_{calcd.}$ = 1.417 g·cm^{-3}, μ = 3.644 mm^{-1}, F(000) = 840, 40878 reflections in h(–13/13), k(–15/15), l(–18/18) measured in the range 1.690° < θ < 26.221°, completeness 99.9 %, 7704 independent reflections, 7383 observed reflections ($I > 2\sigma(I)$), 460 parameters, 140 restraints; *all data:* R_1 = 0.0189 and wR_2 = 0.0418, $I > 2\sigma(I)$: R_1 = 0.0176 and wR_2 = 0.0421, *Goof* 1.069, largest difference peak/hole 0.531/–0.421 e·Å^{-3}. The U_{ii} displacement parameters of atoms C1_1 to C5_1 and C11_1 to C15_1 of the pentane solvent molecule were restrained with the SIMU and DELU keywords.

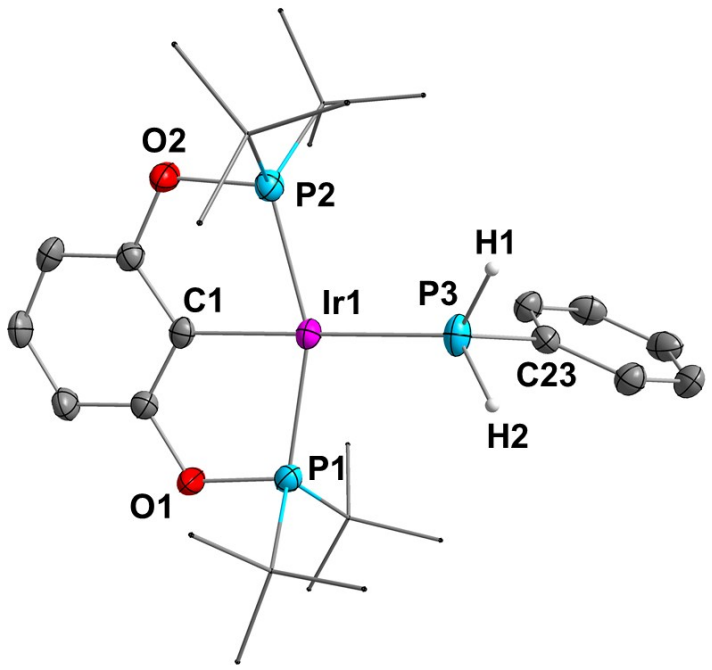

Figure S24. Molecular structure of **6a** with thermal ellipsoids drawn at the 50% probability level; some hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Ir1–C1 203.9(2), Ir1–P1 227.40(7), Ir1–P2 226.66(7), Ir1–P3 226.08(7), P1–O1 166.35(19), P2–O2 166.47(18), P3–C23 183.1(3); C1-Ir1-P3 179.88(8), P1-Ir1-P2 157.31(2), P1-Ir1-C1 78.69(7), Ir1-P3-C23 122.60(9).

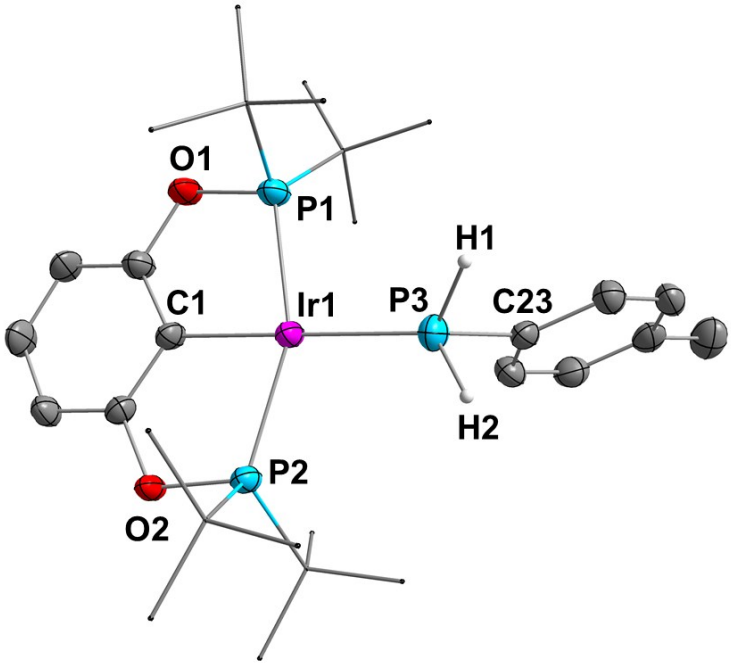

Figure S25. Molecular structure of **6b** with thermal ellipsoids drawn at the 50% probability level; some hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Ir1–C1 204.4(3), Ir1–P1 227.40(7), Ir1–P2 227.84(7), Ir1–P3 226.90(7), P1–O1 165.92(19), P2–O2 166.47(18), P3–C23 182.4(3); C1-Ir1-P3 178.33(8), P1-Ir1-P2 157.05(3), P1-Ir1-C1 78.77(8), Ir1-P3-C23 121.23(9).

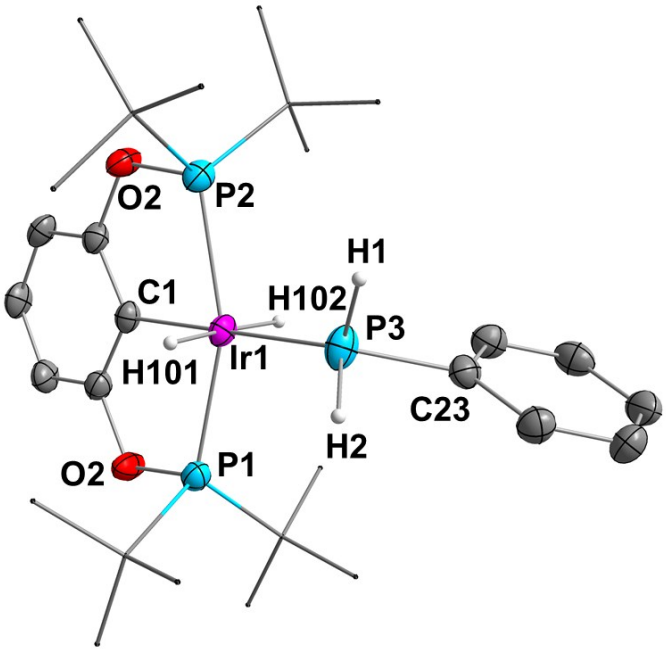

Figure S26. Molecular structure of **7a** with thermal ellipsoids drawn at the 50% probability level; some hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Ir1–C1 204.30(19), Ir1–P1 227.96(6), Ir1–P2 227.36(6), Ir1–P3 226.53(6), P1–O1 165.78(15), P2–O2 165.78(15), P3–C23 182.9(2); C1-Ir1-P3 179.84(6), P1-Ir1-P2 157.158(19), P1-Ir1-C1 78.68(6), Ir1-P3-C23 122.97(7).

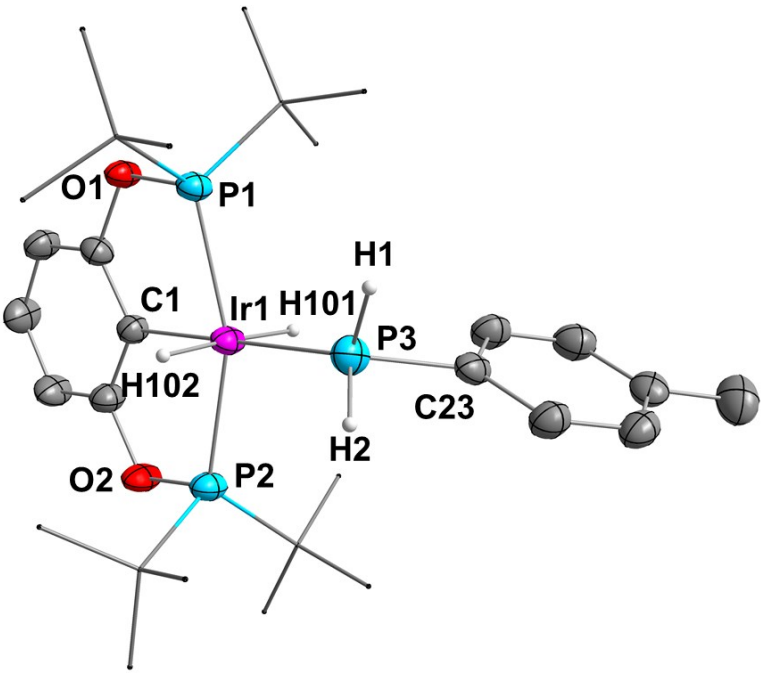

Figure S27. Molecular structure of **7b** with thermal ellipsoids drawn at the 50% probability level; some hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Ir1–C1 205.2(2), Ir1–P1 228.17(6), Ir1–P2 228.67(6), Ir1–P3 227.57(6), P1–O1 165.99(16), P2–O2 165.99(17), P3–C23 182.3(2); C1-Ir1-P3 178.48(6), P1-Ir1-P2 157.05(2), P1-Ir1-C1 78.94(6), Ir1-P3-C23 121.75(8).

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