Combined Experimental and Computational Studies on Carbon-Carbon Reductive Elimination from Bis(hydrocarbyl) Complexes of (PCP)Ir

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Supporting Information Part II: Crystal Structure Data

X-ray Structure Determinations. Data were collected on a Bruker Smart APEX CCD diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073Å) at 100K. The data were corrected for Lorenz effects and polarization, and absorption, the latter by a multi-scan (SADABS)[1] method. The structures were solved by Patterson or direct methods (SHELXS86).[2] All non-hydrogen atoms were refined (SHELXL97)[3] based upon F_{obs}^2. All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97), except for the hydride in complex **3** which was located from the difference Fourier map and restrained at an Ir-H distance of 1.60Å. Scattering factors (f_o, f', f'') are as described in SHELXL97. Crystal data for the structures have been deposited in the Cambridge Crystallogaphic Data Center with numbers (compound numbers) CCDC-610458 (**1**), CCDC-611507 (**3**), CCDC-611508 (**4-CO**), CCDC-611509 (**5-CO**), CCDC-611510 (**5**), CCDC-611511 (**6-Ar-CO**), CCDC-611512 (**7a**), CCDC-611513 (**8-CO**).

References

(1) Bruker-AXS. SADABS, Bruker area detector scaling and absorption correction, v2.05, Bruker-AXS Inc., Madison, Wisconsin, 2003; SAINTplus, Bruker area detector data reduction program, v6.45, Bruker-AXS Inc., Madison, Wisconsin, 2003.

(2) Sheldrick, G. M. SHELXS86, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1986.

(3) Sheldrick, G. M. SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.

I. Structural Data for (PCP)Ir(CCPh)$_2$(CO)

Figure S-1 : ORTEP Diagram of **(PCP)Ir(CCPh)$_2$(CO)**

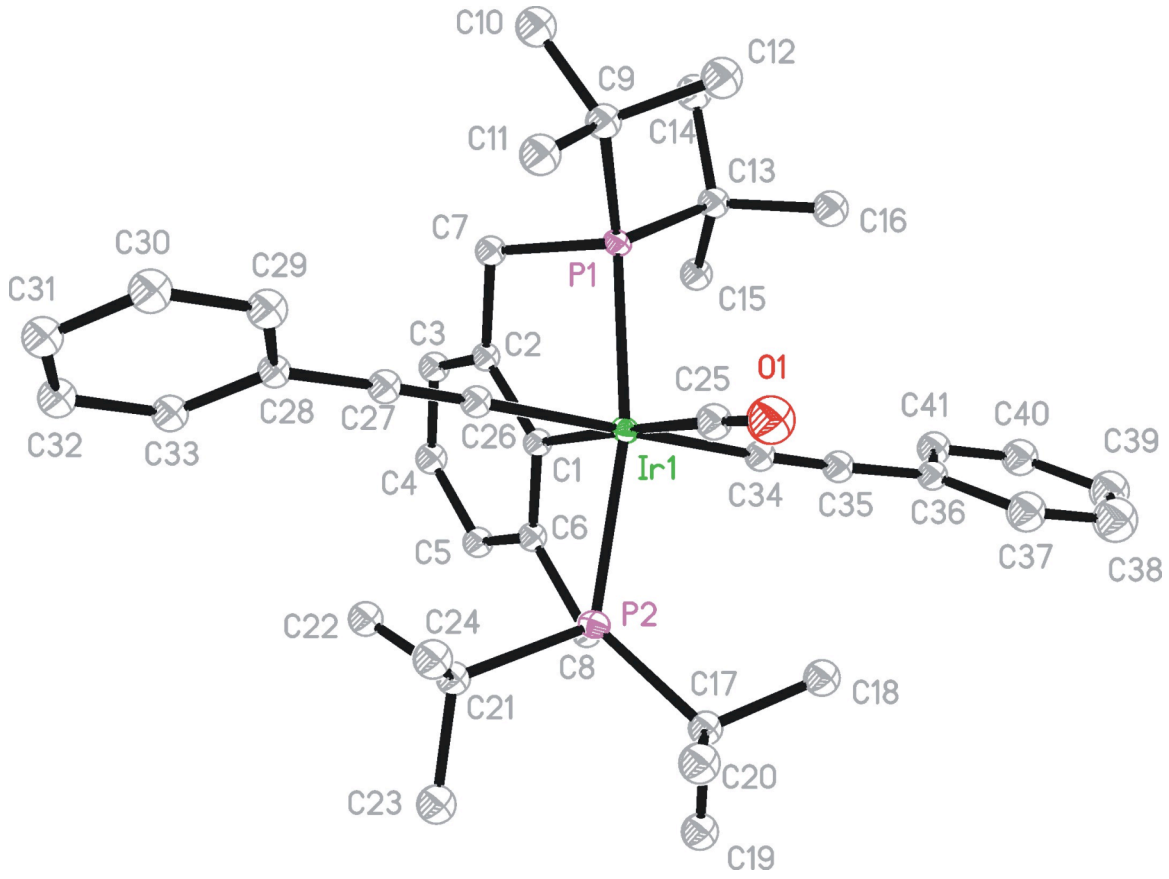

Table S1. Crystal data and structure refinement for **(PCP)Ir(CCPh)$_2$(CO)**

Identification code	ircoccp2	
Empirical formula	C41 H53 Ir O P2	
Formula weight	815.97	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.7586(7) Å	α= 92.034(1)°.
	b = 12.5994(8) Å	β= 94.130(1)°.
	c = 13.1209(8) Å	γ = 108.557(1)°.
Volume	1834.5(2) Å^3	
Z	2	
Density (calculated)	1.477 Mg/m^3	
Absorption coefficient	3.757 mm^{-1}	
F(000)	828	
Crystal size	0.15 x 0.12 x 0.08 mm^3	
Theta range for data collection	1.83 to 30.72°.	
Index ranges	-16<=h<=16, -17<=k<=18, -18<=l<=18	
Reflections collected	22702	
Independent reflections	11197 [R(int) = 0.0264]	
Completeness to theta = 30.72°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9999 and 0.6816	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11197 / 0 / 418	
Goodness-of-fit on F^2	1.007	
Final R indices [I>2sigma(I)]	R1 = 0.0276, wR2 = 0.0721	
R indices (all data)	R1 = 0.0306, wR2 = 0.0740	
Largest diff. peak and hole	3.566 and -2.732 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(PCP)Ir(CCPh)$_2$(CO)**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	4666(1)	2479(1)	2414(1)	11(1)
P(1)	3107(1)	2478(1)	1120(1)	13(1)
P(2)	6316(1)	3168(1)	3706(1)	13(1)
C(1)	4874(2)	4186(2)	2458(2)	13(1)
C(2)	4439(2)	4662(2)	1628(2)	13(1)
C(3)	4578(2)	5804(2)	1660(2)	17(1)
C(4)	5169(2)	6493(2)	2517(2)	18(1)
C(5)	5621(2)	6044(2)	3344(2)	17(1)
C(6)	5467(2)	4893(2)	3320(2)	14(1)
C(7)	3804(2)	3899(2)	698(2)	15(1)
C(8)	5961(2)	4391(2)	4210(2)	14(1)
C(9)	2778(2)	1489(2)	-72(2)	19(1)
C(10)	2367(3)	2012(3)	-1017(2)	25(1)
C(11)	3899(2)	1198(3)	-337(2)	24(1)
C(12)	1813(3)	378(2)	112(2)	24(1)
C(13)	1612(2)	2509(2)	1560(2)	16(1)
C(14)	730(2)	2622(3)	671(2)	22(1)
C(15)	1855(2)	3562(2)	2287(2)	18(1)
C(16)	976(2)	1451(2)	2114(2)	21(1)
C(17)	6453(2)	2322(2)	4845(2)	17(1)
C(18)	5191(3)	1609(2)	5125(2)	20(1)
C(19)	7062(3)	3077(2)	5812(2)	21(1)
C(20)	7133(3)	1497(2)	4603(2)	23(1)
C(21)	7870(2)	3771(2)	3235(2)	17(1)
C(22)	7866(2)	4757(2)	2567(2)	18(1)
C(23)	8875(2)	4276(3)	4106(2)	23(1)
C(24)	8208(3)	2860(3)	2621(2)	21(1)
C(25)	4508(2)	911(2)	2404(2)	18(1)
O(1)	4435(2)	-13(2)	2425(2)	31(1)
C(26)	5798(2)	2738(2)	1266(2)	14(1)
C(27)	6489(2)	2880(2)	604(2)	16(1)

C(28)	7330(2)	2992(2)	-158(2)	14(1)
C(29)	7278(3)	2062(2)	-807(2)	20(1)
C(30)	8086(3)	2164(2)	-1549(2)	24(1)
C(31)	8963(3)	3184(3)	-1663(2)	21(1)
C(32)	9018(2)	4116(2)	-1030(2)	20(1)
C(33)	8213(2)	4019(2)	-283(2)	18(1)
C(34)	3530(2)	2319(2)	3556(2)	15(1)
C(35)	2822(2)	2186(2)	4204(2)	17(1)
C(36)	1948(2)	1938(2)	4946(2)	15(1)
C(37)	1783(3)	991(3)	5518(2)	27(1)
C(38)	941(4)	732(3)	6232(3)	36(1)
C(39)	236(3)	1416(3)	6393(2)	31(1)
C(40)	391(3)	2356(3)	5837(2)	25(1)
C(41)	1228(3)	2616(2)	5116(2)	20(1)

Table S3. Bond lengths [Å] and angles [°] for **(PCP)Ir(CCPh)$_2$(CO)**.

Ir(1)-C(25)	1.924(3)	C(13)-C(14)	1.545(4)
Ir(1)-C(26)	2.049(2)	C(17)-C(20)	1.537(4)
Ir(1)-C(34)	2.050(3)	C(17)-C(19)	1.542(4)
Ir(1)-C(1)	2.085(2)	C(17)-C(18)	1.548(4)
Ir(1)-P(2)	2.3961(6)	C(21)-C(23)	1.543(4)
Ir(1)-P(1)	2.4073(6)	C(21)-C(22)	1.546(4)
P(1)-C(7)	1.839(3)	C(21)-C(24)	1.548(4)
P(1)-C(9)	1.901(3)	C(25)-O(1)	1.140(3)
P(1)-C(13)	1.901(3)	C(26)-C(27)	1.211(4)
P(2)-C(8)	1.834(2)	C(27)-C(28)	1.437(3)
P(2)-C(17)	1.893(3)	C(28)-C(33)	1.401(4)
P(2)-C(21)	1.900(3)	C(28)-C(29)	1.406(4)
C(1)-C(2)	1.403(3)	C(29)-C(30)	1.390(4)
C(1)-C(6)	1.405(3)	C(30)-C(31)	1.389(4)
C(2)-C(3)	1.395(3)	C(31)-C(32)	1.394(4)
C(2)-C(7)	1.516(3)	C(32)-C(33)	1.393(4)
C(3)-C(4)	1.391(4)	C(34)-C(35)	1.212(4)
C(4)-C(5)	1.390(4)	C(35)-C(36)	1.437(3)
C(5)-C(6)	1.402(3)	C(36)-C(37)	1.400(4)
C(6)-C(8)	1.513(3)	C(36)-C(41)	1.403(4)
C(9)-C(12)	1.536(4)	C(37)-C(38)	1.384(4)
C(9)-C(11)	1.536(4)	C(38)-C(39)	1.393(5)
C(9)-C(10)	1.543(4)	C(39)-C(40)	1.382(5)
C(13)-C(16)	1.542(4)	C(40)-C(41)	1.387(4)
C(13)-C(15)	1.543(4)		
C(25)-Ir(1)-C(26)	92.06(11)	C(34)-Ir(1)-P(2)	87.85(7)
C(25)-Ir(1)-C(34)	91.47(11)	C(1)-Ir(1)-P(2)	79.89(7)
C(26)-Ir(1)-C(34)	176.44(9)	C(25)-Ir(1)-P(1)	101.61(8)
C(25)-Ir(1)-C(1)	178.40(10)	C(26)-Ir(1)-P(1)	86.59(7)
C(26)-Ir(1)-C(1)	88.11(10)	C(34)-Ir(1)-P(1)	92.23(7)
C(34)-Ir(1)-C(1)	88.38(9)	C(1)-Ir(1)-P(1)	79.99(7)
C(25)-Ir(1)-P(2)	98.51(8)	P(2)-Ir(1)-P(1)	159.87(2)
C(26)-Ir(1)-P(2)	92.10(7)	C(7)-P(1)-C(9)	106.39(12)

C(7)-P(1)-C(13)	103.87(12)	C(15)-C(13)-P(1)	108.25(17)
C(9)-P(1)-C(13)	108.03(12)	C(14)-C(13)-P(1)	112.84(17)
C(7)-P(1)-Ir(1)	98.00(8)	C(20)-C(17)-C(19)	110.3(2)
C(9)-P(1)-Ir(1)	120.31(9)	C(20)-C(17)-C(18)	106.7(2)
C(13)-P(1)-Ir(1)	117.68(8)	C(19)-C(17)-C(18)	105.8(2)
C(8)-P(2)-C(17)	106.04(11)	C(20)-C(17)-P(2)	111.09(18)
C(8)-P(2)-C(21)	104.70(12)	C(19)-C(17)-P(2)	112.07(19)
C(17)-P(2)-C(21)	108.01(12)	C(18)-C(17)-P(2)	110.55(17)
C(8)-P(2)-Ir(1)	98.63(8)	C(23)-C(21)-C(22)	105.5(2)
C(17)-P(2)-Ir(1)	120.80(9)	C(23)-C(21)-C(24)	107.8(2)
C(21)-P(2)-Ir(1)	116.37(8)	C(22)-C(21)-C(24)	110.9(2)
C(2)-C(1)-C(6)	118.4(2)	C(23)-C(21)-P(2)	113.47(18)
C(2)-C(1)-Ir(1)	121.01(18)	C(22)-C(21)-P(2)	108.29(17)
C(6)-C(1)-Ir(1)	120.64(18)	C(24)-C(21)-P(2)	110.77(19)
C(3)-C(2)-C(1)	120.9(2)	O(1)-C(25)-Ir(1)	178.0(2)
C(3)-C(2)-C(7)	120.8(2)	C(27)-C(26)-Ir(1)	178.2(2)
C(1)-C(2)-C(7)	118.2(2)	C(26)-C(27)-C(28)	176.4(3)
C(4)-C(3)-C(2)	120.1(2)	C(33)-C(28)-C(29)	118.3(2)
C(5)-C(4)-C(3)	120.1(2)	C(33)-C(28)-C(27)	121.5(2)
C(4)-C(5)-C(6)	120.0(2)	C(29)-C(28)-C(27)	120.2(2)
C(5)-C(6)-C(1)	120.6(2)	C(30)-C(29)-C(28)	120.5(3)
C(5)-C(6)-C(8)	120.6(2)	C(31)-C(30)-C(29)	120.8(3)
C(1)-C(6)-C(8)	118.7(2)	C(30)-C(31)-C(32)	119.3(2)
C(2)-C(7)-P(1)	108.43(16)	C(33)-C(32)-C(31)	120.3(3)
C(6)-C(8)-P(2)	107.88(16)	C(32)-C(33)-C(28)	120.8(2)
C(12)-C(9)-C(11)	106.7(2)	C(35)-C(34)-Ir(1)	177.1(2)
C(12)-C(9)-C(10)	110.0(2)	C(34)-C(35)-C(36)	175.5(3)
C(11)-C(9)-C(10)	106.7(2)	C(37)-C(36)-C(41)	118.0(2)
C(12)-C(9)-P(1)	109.97(18)	C(37)-C(36)-C(35)	120.2(2)
C(11)-C(9)-P(1)	111.54(18)	C(41)-C(36)-C(35)	121.8(2)
C(10)-C(9)-P(1)	111.8(2)	C(38)-C(37)-C(36)	121.2(3)
C(16)-C(13)-C(15)	109.8(2)	C(37)-C(38)-C(39)	120.1(3)
C(16)-C(13)-C(14)	108.0(2)	C(40)-C(39)-C(38)	119.4(3)
C(15)-C(13)-C(14)	105.8(2)	C(39)-C(40)-C(41)	120.7(3)
C(16)-C(13)-P(1)	111.93(18)	C(40)-C(41)-C(36)	120.6(3)

Table S4. Torsion angles [°] for **(PCP)Ir(CCPh)$_2$(CO)**.

C(25)-Ir(1)-P(1)-C(7)	-151.13(12)	P(1)-Ir(1)-C(1)-C(2)	-20.85(18)
C(26)-Ir(1)-P(1)-C(7)	-59.72(11)	C(25)-Ir(1)-C(1)-C(6)	-17(4)
C(34)-Ir(1)-P(1)-C(7)	116.92(11)	C(26)-Ir(1)-C(1)-C(6)	-113.3(2)
C(1)-Ir(1)-P(1)-C(7)	28.96(10)	C(34)-Ir(1)-C(1)-C(6)	67.3(2)
P(2)-Ir(1)-P(1)-C(7)	27.09(11)	P(2)-Ir(1)-C(1)-C(6)	-20.83(18)
C(25)-Ir(1)-P(1)-C(9)	-36.79(13)	P(1)-Ir(1)-C(1)-C(6)	159.8(2)
C(26)-Ir(1)-P(1)-C(9)	54.62(12)	C(6)-C(1)-C(2)-C(3)	-0.7(4)
C(34)-Ir(1)-P(1)-C(9)	-128.74(12)	Ir(1)-C(1)-C(2)-C(3)	179.91(18)
C(1)-Ir(1)-P(1)-C(9)	143.30(12)	C(6)-C(1)-C(2)-C(7)	179.8(2)
P(2)-Ir(1)-P(1)-C(9)	141.43(11)	Ir(1)-C(1)-C(2)-C(7)	0.5(3)
C(25)-Ir(1)-P(1)-C(13)	98.57(13)	C(1)-C(2)-C(3)-C(4)	0.8(4)
C(26)-Ir(1)-P(1)-C(13)	-170.03(12)	C(7)-C(2)-C(3)-C(4)	-179.7(2)
C(34)-Ir(1)-P(1)-C(13)	6.61(12)	C(2)-C(3)-C(4)-C(5)	0.0(4)
C(1)-Ir(1)-P(1)-C(13)	-81.35(12)	C(3)-C(4)-C(5)-C(6)	-0.8(4)
P(2)-Ir(1)-P(1)-C(13)	-83.22(11)	C(4)-C(5)-C(6)-C(1)	0.9(4)
C(25)-Ir(1)-P(2)-C(8)	-150.82(11)	C(4)-C(5)-C(6)-C(8)	179.6(2)
C(26)-Ir(1)-P(2)-C(8)	116.78(11)	C(2)-C(1)-C(6)-C(5)	-0.1(4)
C(34)-Ir(1)-P(2)-C(8)	-59.66(11)	Ir(1)-C(1)-C(6)-C(5)	179.23(18)
C(1)-Ir(1)-P(2)-C(8)	29.08(10)	C(2)-C(1)-C(6)-C(8)	-178.8(2)
P(1)-Ir(1)-P(2)-C(8)	30.95(11)	Ir(1)-C(1)-C(6)-C(8)	0.5(3)
C(25)-Ir(1)-P(2)-C(17)	-36.25(13)	C(3)-C(2)-C(7)-P(1)	-151.3(2)
C(26)-Ir(1)-P(2)-C(17)	-128.65(12)	C(1)-C(2)-C(7)-P(1)	28.1(3)
C(34)-Ir(1)-P(2)-C(17)	54.91(12)	C(9)-P(1)-C(7)-C(2)	-162.11(17)
C(1)-Ir(1)-P(2)-C(17)	143.65(12)	C(13)-P(1)-C(7)-C(2)	84.00(18)
P(1)-Ir(1)-P(2)-C(17)	145.52(10)	Ir(1)-P(1)-C(7)-C(2)	-37.19(17)
C(25)-Ir(1)-P(2)-C(21)	97.97(12)	C(5)-C(6)-C(8)-P(2)	-150.9(2)
C(26)-Ir(1)-P(2)-C(21)	5.57(12)	C(1)-C(6)-C(8)-P(2)	27.8(3)
C(34)-Ir(1)-P(2)-C(21)	-170.87(12)	C(17)-P(2)-C(8)-C(6)	-162.68(17)
C(1)-Ir(1)-P(2)-C(21)	-82.13(12)	C(21)-P(2)-C(8)-C(6)	83.24(18)
P(1)-Ir(1)-P(2)-C(21)	-80.26(11)	Ir(1)-P(2)-C(8)-C(6)	-37.05(17)
C(25)-Ir(1)-C(1)-C(2)	162(3)	C(7)-P(1)-C(9)-C(12)	-159.62(19)
C(26)-Ir(1)-C(1)-C(2)	66.0(2)	C(13)-P(1)-C(9)-C(12)	-48.6(2)
C(34)-Ir(1)-C(1)-C(2)	-113.4(2)	Ir(1)-P(1)-C(9)-C(12)	90.52(19)
P(2)-Ir(1)-C(1)-C(2)	158.5(2)	C(7)-P(1)-C(9)-C(11)	82.2(2)

C(13)-P(1)-C(9)-C(11)	-166.8(2)	P(2)-Ir(1)-C(25)-O(1)	14(8)
Ir(1)-P(1)-C(9)-C(11)	-27.7(2)	P(1)-Ir(1)-C(25)-O(1)	-166(8)
C(7)-P(1)-C(9)-C(10)	-37.1(2)	C(25)-Ir(1)-C(26)-C(27)	-58(7)
C(13)-P(1)-C(9)-C(10)	73.9(2)	C(34)-Ir(1)-C(26)-C(27)	130(7)
Ir(1)-P(1)-C(9)-C(10)	-147.00(16)	C(1)-Ir(1)-C(26)-C(27)	121(7)
C(7)-P(1)-C(13)-C(16)	-170.41(18)	P(2)-Ir(1)-C(26)-C(27)	41(7)
C(9)-P(1)-C(13)-C(16)	76.9(2)	P(1)-Ir(1)-C(26)-C(27)	-159(7)
Ir(1)-P(1)-C(13)-C(16)	-63.5(2)	Ir(1)-C(26)-C(27)-C(28)	30(11)
C(7)-P(1)-C(13)-C(15)	-49.27(19)	C(26)-C(27)-C(28)-C(33)	-127(4)
C(9)-P(1)-C(13)-C(15)	-161.98(17)	C(26)-C(27)-C(28)-C(29)	54(5)
Ir(1)-P(1)-C(13)-C(15)	57.66(19)	C(33)-C(28)-C(29)-C(30)	0.2(4)
C(7)-P(1)-C(13)-C(14)	67.5(2)	C(27)-C(28)-C(29)-C(30)	179.7(3)
C(9)-P(1)-C(13)-C(14)	-45.2(2)	C(28)-C(29)-C(30)-C(31)	0.3(5)
Ir(1)-P(1)-C(13)-C(14)	174.44(16)	C(29)-C(30)-C(31)-C(32)	-0.8(5)
C(8)-P(2)-C(17)-C(20)	-161.79(19)	C(30)-C(31)-C(32)-C(33)	0.9(4)
C(21)-P(2)-C(17)-C(20)	-50.0(2)	C(31)-C(32)-C(33)-C(28)	-0.5(4)
Ir(1)-P(2)-C(17)-C(20)	87.5(2)	C(29)-C(28)-C(33)-C(32)	-0.1(4)
C(8)-P(2)-C(17)-C(19)	-37.8(2)	C(27)-C(28)-C(33)-C(32)	-179.6(2)
C(21)-P(2)-C(17)-C(19)	74.0(2)	C(25)-Ir(1)-C(34)-C(35)	-53(5)
Ir(1)-P(2)-C(17)-C(19)	-148.51(16)	C(26)-Ir(1)-C(34)-C(35)	119(4)
C(8)-P(2)-C(17)-C(18)	80.0(2)	C(1)-Ir(1)-C(34)-C(35)	129(5)
C(21)-P(2)-C(17)-C(18)	-168.23(17)	P(2)-Ir(1)-C(34)-C(35)	-151(5)
Ir(1)-P(2)-C(17)-C(18)	-30.7(2)	P(1)-Ir(1)-C(34)-C(35)	49(5)
C(8)-P(2)-C(21)-C(23)	68.1(2)	Ir(1)-C(34)-C(35)-C(36)	30(8)
C(17)-P(2)-C(21)-C(23)	-44.6(2)	C(34)-C(35)-C(36)-C(37)	45(4)
Ir(1)-P(2)-C(21)-C(23)	175.77(16)	C(34)-C(35)-C(36)-C(41)	-134(3)
C(8)-P(2)-C(21)-C(22)	-48.64(19)	C(41)-C(36)-C(37)-C(38)	-0.3(5)
C(17)-P(2)-C(21)-C(22)	-161.33(17)	C(35)-C(36)-C(37)-C(38)	-179.6(3)
Ir(1)-P(2)-C(21)-C(22)	59.01(18)	C(36)-C(37)-C(38)-C(39)	0.1(6)
C(8)-P(2)-C(21)-C(24)	-170.51(18)	C(37)-C(38)-C(39)-C(40)	-0.3(6)
C(17)-P(2)-C(21)-C(24)	76.8(2)	C(38)-C(39)-C(40)-C(41)	0.7(5)
Ir(1)-P(2)-C(21)-C(24)	-62.9(2)	C(39)-C(40)-C(41)-C(36)	-0.9(5)
C(26)-Ir(1)-C(25)-O(1)	107(8)	C(37)-C(36)-C(41)-C(40)	0.7(4)
C(34)-Ir(1)-C(25)-O(1)	-74(8)	C(35)-C(36)-C(41)-C(40)	-180.0(3)
C(1)-Ir(1)-C(25)-O(1)	11(10)		

II. Structural Data for (PCP)Ir(CCPh)(Me)(CO)

Figure S-2 : ORTEP Diagram of **(PCP)Ir(CCPh)(Me)(CO)**

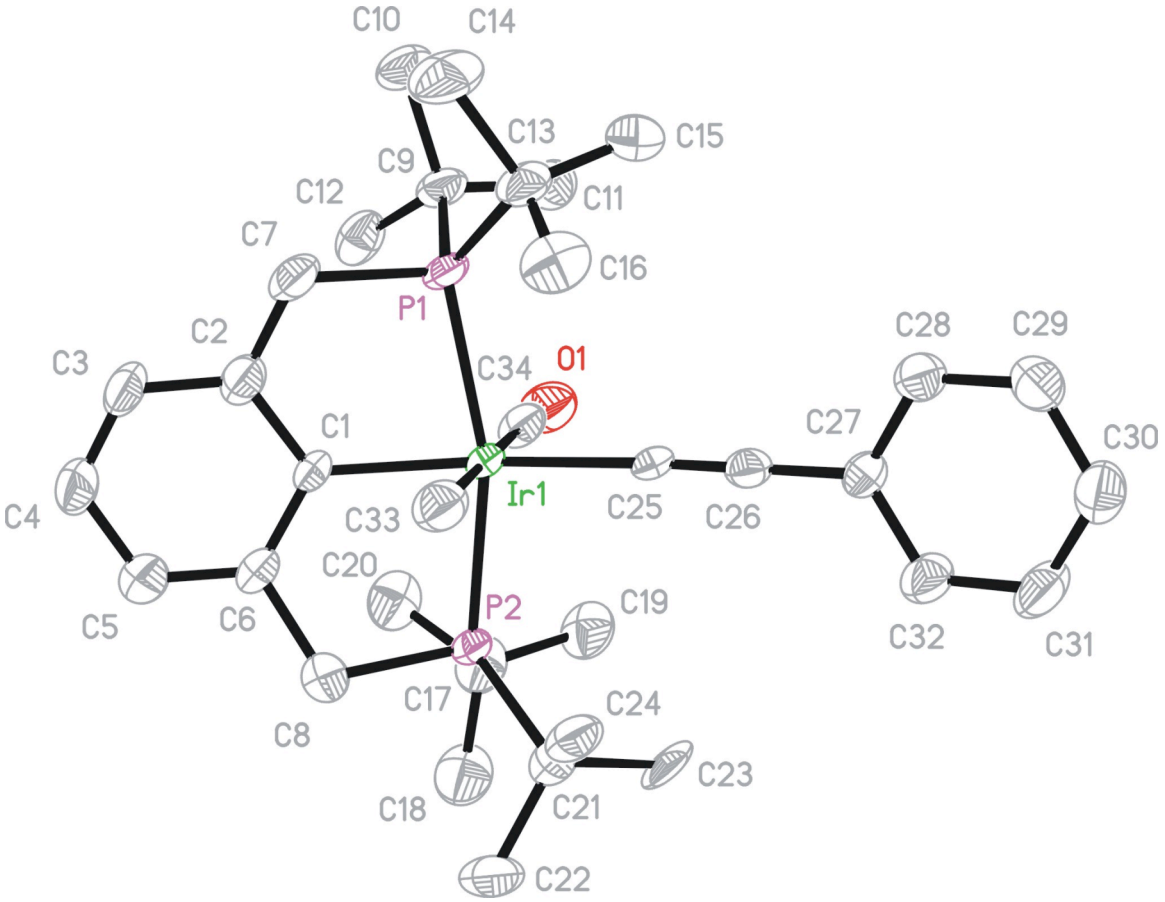

Table S5. Crystal data and structure refinement for **(PCP)Ir(CCPh)(Me)(CO)**.

Identification code	irpccph	
Empirical formula	C34 H51 Ir O P2	
Formula weight	729.89	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.375(1) Å	α= 90°.
	b = 11.371(1) Å	β= 91.821(2)°.
	c = 22.904(2) Å	γ = 90°.
Volume	3221.3(5) $Å^3$	
Z	4	
Density (calculated)	1.505 Mg/m^3	
Absorption coefficient	4.268 mm^{-1}	
F(000)	1480	
Crystal size	0.12 x 0.07 x 0.02 mm^3	
Theta range for data collection	2.39 to 28.28°.	
Index ranges	-16<=h<=16, -15<=k<=15, -30<=l<=30	
Reflections collected	32119	
Independent reflections	7992 [R(int) = 0.0404]	
Completeness to theta = 28.28°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9195 and 0.6284	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7992 / 444 / 356	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0495, wR2 = 0.1221	
R indices (all data)	R1 = 0.0618, wR2 = 0.1297	
Largest diff. peak and hole	4.453 and -2.516 e.$Å^{-3}$	

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(PCP)Ir(CCPh)(Me)(CO)**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	2703(1)	388(1)	1390(1)	27(1)
P(1)	3556(1)	-1456(1)	1510(1)	28(1)
P(2)	1425(1)	1914(1)	1273(1)	27(1)
C(1)	1321(5)	-659(5)	1307(3)	34(1)
C(2)	1419(6)	-1903(6)	1254(3)	37(1)
C(3)	489(6)	-2592(6)	1173(3)	46(2)
C(4)	-523(7)	-2100(7)	1126(4)	53(2)
C(5)	-618(7)	-885(7)	1103(4)	55(2)
C(6)	304(6)	-199(6)	1166(4)	43(1)
C(7)	2501(6)	-2438(5)	1210(3)	38(1)
C(8)	220(6)	1105(7)	999(3)	44(2)
C(9)	3721(6)	-1971(6)	2295(3)	37(1)
C(10)	4176(7)	-3246(6)	2345(4)	50(2)
C(11)	4502(6)	-1158(7)	2649(3)	41(2)
C(12)	2600(6)	-2009(7)	2555(3)	43(2)
C(13)	4839(6)	-1805(6)	1121(3)	38(1)
C(14)	4941(7)	-3157(7)	991(4)	57(2)
C(15)	5818(6)	-1394(7)	1479(3)	46(2)
C(16)	4828(7)	-1184(7)	533(3)	47(2)
C(17)	942(6)	2553(7)	1978(4)	49(2)
C(18)	36(7)	3470(8)	1907(4)	61(2)
C(19)	1891(7)	3153(7)	2331(4)	52(2)
C(20)	450(7)	1521(8)	2322(4)	53(2)
C(21)	1633(6)	3148(6)	746(3)	44(2)
C(22)	545(7)	3642(8)	489(4)	58(2)
C(23)	2319(6)	4122(5)	1061(4)	45(2)
C(24)	2259(6)	2712(6)	220(3)	42(2)
C(25)	4057(5)	1395(5)	1254(3)	27(1)
C(26)	4820(5)	1951(5)	1105(3)	30(1)
C(27)	5733(5)	2575(5)	873(3)	29(1)
C(28)	6720(5)	2021(6)	797(3)	35(1)

C(29)	7572(6)	2600(6)	550(3)	39(1)
C(30)	7459(6)	3771(7)	387(3)	45(2)
C(31)	6487(6)	4335(6)	463(4)	47(2)
C(32)	5640(6)	3748(6)	710(3)	40(1)
C(33)	2581(6)	68(6)	459(3)	40(2)
C(34)	2830(6)	671(6)	2205(3)	36(1)
O(1)	2944(5)	892(5)	2692(2)	52(1)

Table S7. Bond lengths [Å] and angles [°] for **(PCP)Ir(CCPh)(Me)(CO)**.

Ir(1)-C(34)	1.896(6)	C(9)-C(11)	1.547(9)
Ir(1)-C(25)	2.062(6)	C(9)-C(10)	1.558(9)
Ir(1)-C(1)	2.088(6)	C(13)-C(15)	1.515(10)
Ir(1)-C(33)	2.162(7)	C(13)-C(16)	1.519(10)
Ir(1)-P(2)	2.3570(15)	C(13)-C(14)	1.571(10)
Ir(1)-P(1)	2.3605(14)	C(17)-C(18)	1.537(12)
P(1)-C(7)	1.835(7)	C(17)-C(20)	1.549(11)
P(1)-C(13)	1.887(7)	C(17)-C(19)	1.562(11)
P(1)-C(9)	1.897(6)	C(21)-C(24)	1.534(10)
P(2)-C(8)	1.844(7)	C(21)-C(22)	1.557(10)
P(2)-C(21)	1.875(7)	C(21)-C(23)	1.558(10)
P(2)-C(17)	1.885(8)	C(25)-C(26)	1.194(8)
C(1)-C(6)	1.392(10)	C(26)-C(27)	1.450(8)
C(1)-C(2)	1.425(9)	C(27)-C(32)	1.390(9)
C(2)-C(3)	1.400(9)	C(27)-C(28)	1.390(9)
C(2)-C(7)	1.477(10)	C(28)-C(29)	1.380(9)
C(3)-C(4)	1.372(11)	C(29)-C(30)	1.389(10)
C(4)-C(5)	1.388(11)	C(30)-C(31)	1.378(11)
C(5)-C(6)	1.386(10)	C(31)-C(32)	1.379(10)
C(6)-C(8)	1.534(10)	C(34)-O(1)	1.148(8)
C(9)-C(12)	1.528(10)		

C(34)-Ir(1)-C(25)	90.7(3)	C(1)-Ir(1)-P(1)	82.28(18)
C(34)-Ir(1)-C(1)	103.2(3)	C(33)-Ir(1)-P(1)	88.98(19)
C(25)-Ir(1)-C(1)	166.1(2)	P(2)-Ir(1)-P(1)	164.43(6)
C(34)-Ir(1)-C(33)	179.2(3)	C(7)-P(1)-C(13)	107.1(3)
C(25)-Ir(1)-C(33)	88.7(3)	C(7)-P(1)-C(9)	102.8(3)
C(1)-Ir(1)-C(33)	77.5(3)	C(13)-P(1)-C(9)	108.4(3)
C(34)-Ir(1)-P(2)	91.2(2)	C(7)-P(1)-Ir(1)	100.7(2)
C(25)-Ir(1)-P(2)	96.88(15)	C(13)-P(1)-Ir(1)	120.8(2)
C(1)-Ir(1)-P(2)	82.23(18)	C(9)-P(1)-Ir(1)	114.8(2)
C(33)-Ir(1)-P(2)	89.2(2)	C(8)-P(2)-C(21)	106.3(3)
C(34)-Ir(1)-P(1)	90.7(2)	C(8)-P(2)-C(17)	102.0(4)
C(25)-Ir(1)-P(1)	98.53(15)	C(21)-P(2)-C(17)	108.5(4)

C(8)-P(2)-Ir(1)	101.8(2)	C(15)-C(13)-P(1)	110.5(5)
C(21)-P(2)-Ir(1)	121.3(2)	C(16)-C(13)-P(1)	109.7(5)
C(17)-P(2)-Ir(1)	114.6(3)	C(14)-C(13)-P(1)	111.6(5)
C(6)-C(1)-C(2)	115.6(6)	C(18)-C(17)-C(20)	105.7(7)
C(6)-C(1)-Ir(1)	122.6(5)	C(18)-C(17)-C(19)	107.0(7)
C(2)-C(1)-Ir(1)	120.2(5)	C(20)-C(17)-C(19)	111.6(7)
C(3)-C(2)-C(1)	119.7(7)	C(18)-C(17)-P(2)	114.9(6)
C(3)-C(2)-C(7)	120.3(6)	C(20)-C(17)-P(2)	106.5(5)
C(1)-C(2)-C(7)	119.6(6)	C(19)-C(17)-P(2)	111.1(5)
C(4)-C(3)-C(2)	121.8(7)	C(24)-C(21)-C(22)	105.8(6)
C(3)-C(4)-C(5)	119.0(7)	C(24)-C(21)-C(23)	108.2(6)
C(6)-C(5)-C(4)	119.2(8)	C(22)-C(21)-C(23)	111.8(6)
C(5)-C(6)-C(1)	123.2(7)	C(24)-C(21)-P(2)	110.3(5)
C(5)-C(6)-C(8)	118.0(7)	C(22)-C(21)-P(2)	112.3(5)
C(1)-C(6)-C(8)	118.4(6)	C(23)-C(21)-P(2)	108.5(5)
C(2)-C(7)-P(1)	111.1(5)	C(26)-C(25)-Ir(1)	172.0(5)
C(6)-C(8)-P(2)	110.5(5)	C(25)-C(26)-C(27)	174.9(7)
C(12)-C(9)-C(11)	111.9(6)	C(32)-C(27)-C(28)	117.9(6)
C(12)-C(9)-C(10)	106.0(6)	C(32)-C(27)-C(26)	120.6(6)
C(11)-C(9)-C(10)	107.4(6)	C(28)-C(27)-C(26)	121.5(6)
C(12)-C(9)-P(1)	107.8(4)	C(29)-C(28)-C(27)	121.4(6)
C(11)-C(9)-P(1)	111.1(5)	C(28)-C(29)-C(30)	119.7(7)
C(10)-C(9)-P(1)	112.6(5)	C(31)-C(30)-C(29)	119.6(7)
C(15)-C(13)-C(16)	108.7(6)	C(30)-C(31)-C(32)	120.3(7)
C(15)-C(13)-C(14)	109.7(6)	C(31)-C(32)-C(27)	121.1(7)
C(16)-C(13)-C(14)	106.6(6)	O(1)-C(34)-Ir(1)	176.2(6)

Table S8. Torsion angles [°] for **(PCP)Ir(CCPh)(Me)(CO)**.

C(34)-Ir(1)-P(1)-C(7)	121.0(3)	C(34)-Ir(1)-C(1)-C(2)	-99.2(6)
C(25)-Ir(1)-P(1)-C(7)	-148.2(3)	C(33)-Ir(1)-C(1)-C(2)	80.5(6)
C(1)-Ir(1)-P(1)-C(7)	17.8(3)	P(2)-Ir(1)-C(1)-C(2)	171.4(6)
C(33)-Ir(1)-P(1)-C(7)	-59.7(3)	P(1)-Ir(1)-C(1)-C(2)	-10.2(5)
P(2)-Ir(1)-P(1)-C(7)	23.7(3)	C(6)-C(1)-C(2)-C(3)	-11.5(10)
C(34)-Ir(1)-P(1)-C(13)	-121.5(3)	Ir(1)-C(1)-C(2)-C(3)	-177.2(5)
C(25)-Ir(1)-P(1)-C(13)	-30.7(3)	C(6)-C(1)-C(2)-C(7)	160.8(6)
C(1)-Ir(1)-P(1)-C(13)	135.3(3)	Ir(1)-C(1)-C(2)-C(7)	-4.8(9)
C(33)-Ir(1)-P(1)-C(13)	57.8(3)	C(1)-C(2)-C(3)-C(4)	1.9(11)
P(2)-Ir(1)-P(1)-C(13)	141.2(3)	C(7)-C(2)-C(3)-C(4)	-170.4(7)
C(34)-Ir(1)-P(1)-C(9)	11.3(3)	C(2)-C(3)-C(4)-C(5)	6.3(13)
C(25)-Ir(1)-P(1)-C(9)	102.1(3)	C(3)-C(4)-C(5)-C(6)	-4.3(14)
C(1)-Ir(1)-P(1)-C(9)	-91.9(3)	C(4)-C(5)-C(6)-C(1)	-6.2(14)
C(33)-Ir(1)-P(1)-C(9)	-169.4(3)	C(4)-C(5)-C(6)-C(8)	166.1(8)
P(2)-Ir(1)-P(1)-C(9)	-85.9(3)	C(2)-C(1)-C(6)-C(5)	13.9(12)
C(34)-Ir(1)-P(2)-C(8)	-117.7(3)	Ir(1)-C(1)-C(6)-C(5)	179.2(7)
C(25)-Ir(1)-P(2)-C(8)	151.4(3)	C(2)-C(1)-C(6)-C(8)	-158.4(7)
C(1)-Ir(1)-P(2)-C(8)	-14.6(3)	Ir(1)-C(1)-C(6)-C(8)	6.8(10)
C(33)-Ir(1)-P(2)-C(8)	62.9(3)	C(3)-C(2)-C(7)-P(1)	-165.8(5)
P(1)-Ir(1)-P(2)-C(8)	-20.5(3)	C(1)-C(2)-C(7)-P(1)	22.0(8)
C(34)-Ir(1)-P(2)-C(21)	124.8(4)	C(13)-P(1)-C(7)-C(2)	-152.5(5)
C(25)-Ir(1)-P(2)-C(21)	34.0(3)	C(9)-P(1)-C(7)-C(2)	93.3(5)
C(1)-Ir(1)-P(2)-C(21)	-132.1(3)	Ir(1)-P(1)-C(7)-C(2)	-25.4(5)
C(33)-Ir(1)-P(2)-C(21)	-54.6(4)	C(5)-C(6)-C(8)-P(2)	167.0(7)
P(1)-Ir(1)-P(2)-C(21)	-138.0(3)	C(1)-C(6)-C(8)-P(2)	-20.3(9)
C(34)-Ir(1)-P(2)-C(17)	-8.5(3)	C(21)-P(2)-C(8)-C(6)	149.7(5)
C(25)-Ir(1)-P(2)-C(17)	-99.3(3)	C(17)-P(2)-C(8)-C(6)	-96.7(6)
C(1)-Ir(1)-P(2)-C(17)	94.6(3)	Ir(1)-P(2)-C(8)-C(6)	21.9(6)
C(33)-Ir(1)-P(2)-C(17)	172.1(3)	C(7)-P(1)-C(9)-C(12)	-51.0(5)
P(1)-Ir(1)-P(2)-C(17)	88.7(3)	C(13)-P(1)-C(9)-C(12)	-164.2(5)
C(34)-Ir(1)-C(1)-C(6)	96.2(6)	Ir(1)-P(1)-C(9)-C(12)	57.4(5)
C(33)-Ir(1)-C(1)-C(6)	-84.2(6)	C(7)-P(1)-C(9)-C(11)	-173.9(5)
P(2)-Ir(1)-C(1)-C(6)	6.8(6)	C(13)-P(1)-C(9)-C(11)	72.8(5)
P(1)-Ir(1)-C(1)-C(6)	-174.8(6)	Ir(1)-P(1)-C(9)-C(11)	-65.6(5)

C(7)-P(1)-C(9)-C(10)	65.6(6)	C(21)-P(2)-C(17)-C(19)	-75.4(6)
C(13)-P(1)-C(9)-C(10)	-47.7(6)	Ir(1)-P(2)-C(17)-C(19)	63.6(6)
Ir(1)-P(1)-C(9)-C(10)	173.9(4)	C(8)-P(2)-C(21)-C(24)	-83.6(6)
C(7)-P(1)-C(13)-C(15)	-158.8(5)	C(17)-P(2)-C(21)-C(24)	167.4(5)
C(9)-P(1)-C(13)-C(15)	-48.5(6)	Ir(1)-P(2)-C(21)-C(24)	31.7(6)
Ir(1)-P(1)-C(13)-C(15)	86.9(5)	C(8)-P(2)-C(21)-C(22)	34.2(7)
C(7)-P(1)-C(13)-C(16)	81.4(5)	C(17)-P(2)-C(21)-C(22)	-74.9(7)
C(9)-P(1)-C(13)-C(16)	-168.3(5)	Ir(1)-P(2)-C(21)-C(22)	149.4(5)
Ir(1)-P(1)-C(13)-C(16)	-32.8(6)	C(8)-P(2)-C(21)-C(23)	158.2(5)
C(7)-P(1)-C(13)-C(14)	-36.5(6)	C(17)-P(2)-C(21)-C(23)	49.1(6)
C(9)-P(1)-C(13)-C(14)	73.8(6)	Ir(1)-P(2)-C(21)-C(23)	-86.6(5)
Ir(1)-P(1)-C(13)-C(14)	-150.8(5)	C(32)-C(27)-C(28)-C(29)	-2.0(10)
C(8)-P(2)-C(17)-C(18)	-65.7(7)	C(26)-C(27)-C(28)-C(29)	176.7(6)
C(21)-P(2)-C(17)-C(18)	46.2(7)	C(27)-C(28)-C(29)-C(30)	1.8(10)
Ir(1)-P(2)-C(17)-C(18)	-174.8(5)	C(28)-C(29)-C(30)-C(31)	-1.4(11)
C(8)-P(2)-C(17)-C(20)	50.9(6)	C(29)-C(30)-C(31)-C(32)	1.4(12)
C(21)-P(2)-C(17)-C(20)	162.9(5)	C(30)-C(31)-C(32)-C(27)	-1.7(12)
Ir(1)-P(2)-C(17)-C(20)	-58.1(6)	C(28)-C(27)-C(32)-C(31)	2.0(10)
C(8)-P(2)-C(17)-C(19)	172.7(6)	C(26)-C(27)-C(32)-C(31)	-176.8(7)

III. Structural Data for [(PCP)Ir(H_2O)(Me)]+[BF_4]-·THF

Figure S-3 : ORTEP Diagram of **[(PCP)Ir(H_2O)(Me)]+[BF_4]-·THF**

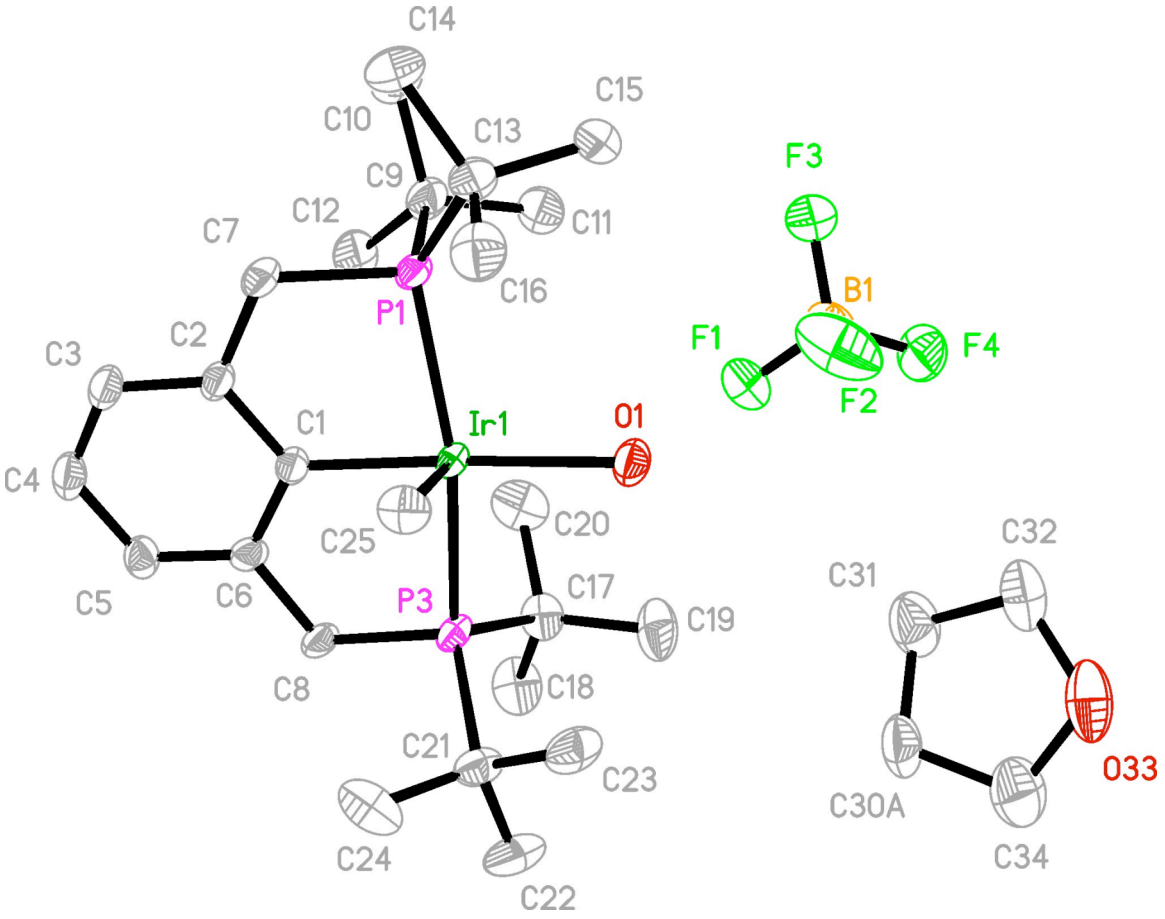

Table S9. Crystal data and structure refinement for **[(PCP)Ir(H_2O)(Me)]+[BF_4]-·THF**.

Identification code	irmei	
Empirical formula	C29 H56 B F4 Ir O2 P2	
Formula weight	777.69	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.7947(6) Å	α= 106.138(2)°.
	b = 11.3126(6) Å	β= 97.056(1)°.
	c = 15.4888(8) Å	γ = 110.110(1)°.
Volume	1655.36(15) $Å^3$	
Z	2	
Density (calculated)	1.560 Mg/m^3	
Absorption coefficient	4.176 mm^{-1}	
F(000)	788	
Crystal size	0.28 x 0.10 x 0.07 mm^3	
Theta range for data collection	2.04 to 30.60°.	
Index ranges	-15<=h<=15, -16<=k<=16, -22<=l<=21	
Reflections collected	20485	
Independent reflections	10029 [R(int) = 0.0194]	
Completeness to theta = 30.60°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7500 and 0.6556	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10029 / 0 / 393	
Goodness-of-fit on F^2	1.000	
Final R indices [I>2sigma(I)]	R1 = 0.0275, wR2 = 0.0630	
R indices (all data)	R1 = 0.0303, wR2 = 0.0641	
Largest diff. peak and hole	1.922 and -1.105 e.$Å^{-3}$	

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **[(PCP)Ir(H_2O)(Me)]+[BF_4]-·THF**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1A)	3273(1)	7484(1)	2494(1)	18(1)
P(1A)	5138(1)	8872(1)	2112(1)	22(1)
P(2A)	1094(1)	6070(1)	2456(1)	20(1)
Ir(1B)	3435	7175	2183	39(1)
P(1B)	5150(30)	8740(30)	1883(15)	39(7)
P(2B)	1298(18)	5802(18)	2309(13)	34(5)
O(1)	4331(2)	6519(2)	3209(2)	31(1)
C(1)	2291(3)	8388(3)	1911(2)	25(1)
C(2)	3015(3)	9610(3)	1786(2)	27(1)
C(3)	2335(3)	10290(3)	1432(2)	31(1)
C(4)	923(3)	9769(3)	1187(2)	33(1)
C(5)	191(3)	8574(3)	1296(2)	29(1)
C(6)	849(3)	7889(3)	1657(2)	26(1)
C(7)	4554(3)	10191(3)	2043(2)	31(1)
C(8)	15(3)	6573(3)	1750(2)	35(1)
C(9)	5228(4)	8057(3)	892(2)	34(1)
C(10)	6370(4)	8955(4)	573(3)	52(1)
C(11)	5415(4)	6741(4)	795(2)	41(1)
C(12)	3870(4)	7719(4)	243(2)	43(1)
C(13)	6897(3)	9779(3)	2905(2)	34(1)
C(14)	7749(4)	11048(4)	2725(4)	56(1)
C(15)	7649(3)	8834(4)	2833(3)	40(1)
C(16)	6757(4)	10227(3)	3899(3)	42(1)
C(17)	863(3)	4360(3)	1675(2)	35(1)
C(18)	-605(4)	3407(4)	1157(3)	48(1)
C(19)	1500(4)	3676(3)	2209(3)	48(1)
C(20)	1696(4)	4724(4)	976(3)	50(1)
C(21)	449(3)	5998(3)	3512(2)	33(1)
C(22)	-791(4)	4705(4)	3338(3)	48(1)
C(23)	1610(4)	6121(4)	4264(2)	41(1)

C(24)	21(4)	7177(4)	3857(3)	49(1)
C(25)	3560(3)	8937(3)	3740(2)	33(1)
B(1)	5907(4)	4465(4)	2263(3)	41(1)
F(1)	4636(2)	4378(3)	1860(2)	62(1)
F(2)	6291(3)	5335(3)	3174(2)	79(1)
F(3)	6854(2)	5007(3)	1801(2)	61(1)
F(4)	5857(2)	3237(2)	2231(2)	55(1)
O(2)	5797(3)	7667(3)	4974(2)	61(1)
C(26)	5197(4)	6921(4)	5539(3)	53(1)
C(27)	6368(4)	6951(5)	6211(3)	58(1)
C(28A)	7627(10)	8054(11)	6147(7)	49(1)
C(28B)	7436(7)	7110(7)	5645(5)	49(1)
C(29)	7243(5)	8009(5)	5172(3)	64(1)

Table S11. Bond lengths [Å] and angles [°] for **[(PCP)Ir(H_2O)(Me)]+[BF_4]-·TH**.

Ir(1A)-C(1)	2.002(3)	C(11)-H(11A)	0.9800
Ir(1A)-C(25)	2.065(3)	C(11)-H(11B)	0.9800
Ir(1A)-O(1)	2.223(2)	C(11)-H(11C)	0.9800
Ir(1A)-P(2A)	2.328(1)	C(12)-H(12A)	0.9800
Ir(1A)-P(1A)	2.346(1)	C(12)-H(12B)	0.9800
P(1A)-C(7)	1.831(3)	C(12)-H(12C)	0.9800
P(1A)-C(13)	1.885(3)	C(13)-C(16)	1.525(5)
P(1A)-C(9)	1.890(3)	C(13)-C(14)	1.537(5)
P(2A)-C(8)	1.835(3)	C(13)-C(15)	1.539(5)
P(2A)-C(21)	1.867(3)	C(14)-H(14A)	0.9800
P(2A)-C(17)	1.886(3)	C(14)-H(14B)	0.9800
O(1)-H(1A)	0.92(4)	C(14)-H(14C)	0.9800
O(1)-H(1B)	0.87(4)	C(15)-H(15A)	0.9800
C(1)-C(2)	1.414(4)	C(15)-H(15B)	0.9800
C(1)-C(6)	1.421(4)	C(15)-H(15C)	0.9800
C(2)-C(3)	1.398(4)	C(16)-H(16A)	0.9800
C(2)-C(7)	1.514(4)	C(16)-H(16B)	0.9800
C(3)-C(4)	1.390(5)	C(16)-H(16C)	0.9800
C(3)-H(3)	0.9500	C(17)-C(19)	1.529(5)
C(4)-C(5)	1.380(4)	C(17)-C(18)	1.533(5)
C(4)-H(4)	0.9500	C(17)-C(20)	1.544(5)
C(5)-C(6)	1.392(4)	C(18)-H(18A)	0.9800
C(5)-H(5)	0.9500	C(18)-H(18B)	0.9800
C(6)-C(8)	1.510(4)	C(18)-H(18C)	0.9800
C(7)-H(7A)	0.9900	C(19)-H(19A)	0.9800
C(7)-H(7B)	0.9900	C(19)-H(19B)	0.9800
C(8)-H(8A)	0.9900	C(19)-H(19C)	0.9800
C(8)-H(8B)	0.9900	C(20)-H(20A)	0.9800
C(9)-C(12)	1.531(5)	C(20)-H(20B)	0.9800
C(9)-C(10)	1.537(5)	C(20)-H(20C)	0.9800
C(9)-C(11)	1.539(4)	C(21)-C(22)	1.532(5)
C(10)-H(10A)	0.9800	C(21)-C(24)	1.538(5)
C(10)-H(10B)	0.9800	C(21)-C(23)	1.540(4)
C(10)-H(10C)	0.9800	C(22)-H(22A)	0.9800

C(22)-H(22B)	0.9800	O(2)-C(26)	1.440(6)
C(22)-H(22C)	0.9800	O(2)-C(29)	1.442(6)
C(23)-H(23A)	0.9800	C(26)-C(27)	1.519(5)
C(23)-H(23B)	0.9800	C(26)-H(26A)	0.9900
C(23)-H(23C)	0.9800	C(26)-H(26B)	0.9900
C(24)-H(24A)	0.9800	C(27)-C(28A)	1.533(12)
C(24)-H(24B)	0.9800	C(27)-H(27A)	0.9900
C(24)-H(24C)	0.9800	C(27)-H(27B)	0.9900
C(25)-H(25A)	1.07(4)	C(28A)-C(29)	1.499(10)
C(25)-H(25B)	1.06(4)	C(28A)-H(28A)	0.9900
C(25)-H(25C)	1.11(4)	C(28A)-H(28B)	0.9900
B(1)-F(4)	1.358(4)	C(28B)-H(28C)	0.994(7)
B(1)-F(3)	1.388(5)	C(28B)-H(28D)	0.987(7)
B(1)-F(2)	1.391(5)	C(29)-H(29A)	0.9900
B(1)-F(1)	1.395(5)	C(29)-H(29B)	0.9900

C(1)-Ir(1A)-C(25)	86.53(13)	C(21)-P(2A)-Ir(1A)	123.80(11)
C(1)-Ir(1A)-O(1)	176.97(10)	C(17)-P(2A)-Ir(1A)	104.92(11)
C(25)-Ir(1A)-O(1)	90.80(12)	Ir(1A)-O(1)-H(1A)	107(3)
C(1)-Ir(1A)-P(2A)	83.84(8)	Ir(1A)-O(1)-H(1B)	125(3)
C(25)-Ir(1A)-P(2A)	96.28(9)	H(1A)-O(1)-H(1B)	112(4)
O(1)-Ir(1A)-P(2A)	95.04(6)	C(2)-C(1)-C(6)	116.8(2)
C(1)-Ir(1A)-P(1A)	82.90(8)	C(2)-C(1)-Ir(1A)	120.9(2)
C(25)-Ir(1A)-P(1A)	93.18(10)	C(6)-C(1)-Ir(1A)	122.2(2)
O(1)-Ir(1A)-P(1A)	98.69(7)	C(3)-C(2)-C(1)	121.2(3)
P(2A)-Ir(1A)-P(1A)	163.20(4)	C(3)-C(2)-C(7)	119.5(3)
C(7)-P(1A)-C(13)	105.25(15)	C(1)-C(2)-C(7)	119.3(2)
C(7)-P(1A)-C(9)	104.66(15)	C(4)-C(3)-C(2)	120.3(3)
C(13)-P(1A)-C(9)	110.26(16)	C(4)-C(3)-H(3)	119.8
C(7)-P(1A)-Ir(1A)	99.62(11)	C(2)-C(3)-H(3)	119.8
C(13)-P(1A)-Ir(1A)	123.47(12)	C(5)-C(4)-C(3)	119.6(3)
C(9)-P(1A)-Ir(1A)	111.14(12)	C(5)-C(4)-H(4)	120.2
C(8)-P(2A)-C(21)	108.08(16)	C(3)-C(4)-H(4)	120.2
C(8)-P(2A)-C(17)	103.65(16)	C(4)-C(5)-C(6)	120.9(3)
C(21)-P(2A)-C(17)	111.98(15)	C(4)-C(5)-H(5)	119.6
C(8)-P(2A)-Ir(1A)	102.33(10)	C(6)-C(5)-H(5)	119.6

C(5)-C(6)-C(1)	121.0(3)	C(9)-C(12)-H(12C)	109.5
C(5)-C(6)-C(8)	119.4(3)	H(12A)-C(12)-H(12C)	109.5
C(1)-C(6)-C(8)	119.6(2)	H(12B)-C(12)-H(12C)	109.5
C(2)-C(7)-P(1A)	109.21(19)	C(16)-C(13)-C(14)	106.9(3)
C(2)-C(7)-H(7A)	109.8	C(16)-C(13)-C(15)	107.7(3)
P(1A)-C(7)-H(7A)	109.8	C(14)-C(13)-C(15)	110.2(3)
C(2)-C(7)-H(7B)	109.8	C(16)-C(13)-P(1A)	108.2(2)
P(1A)-C(7)-H(7B)	109.8	C(14)-C(13)-P(1A)	113.0(3)
H(7A)-C(7)-H(7B)	108.3	C(15)-C(13)-P(1A)	110.6(2)
C(6)-C(8)-P(2A)	110.1(2)	C(13)-C(14)-H(14A)	109.5
C(6)-C(8)-H(8A)	109.6	C(13)-C(14)-H(14B)	109.5
P(2A)-C(8)-H(8A)	109.6	H(14A)-C(14)-H(14B)	109.5
C(6)-C(8)-H(8B)	109.6	C(13)-C(14)-H(14C)	109.5
P(2A)-C(8)-H(8B)	109.6	H(14A)-C(14)-H(14C)	109.5
H(8A)-C(8)-H(8B)	108.2	H(14B)-C(14)-H(14C)	109.5
C(12)-C(9)-C(10)	108.1(3)	C(13)-C(15)-H(15A)	109.5
C(12)-C(9)-C(11)	108.2(3)	C(13)-C(15)-H(15B)	109.5
C(10)-C(9)-C(11)	108.7(3)	H(15A)-C(15)-H(15B)	109.5
C(12)-C(9)-P(1A)	107.5(2)	C(13)-C(15)-H(15C)	109.5
C(10)-C(9)-P(1A)	113.8(3)	H(15A)-C(15)-H(15C)	109.5
C(11)-C(9)-P(1A)	110.5(2)	H(15B)-C(15)-H(15C)	109.5
C(9)-C(10)-H(10A)	109.5	C(13)-C(16)-H(16A)	109.5
C(9)-C(10)-H(10B)	109.5	C(13)-C(16)-H(16B)	109.5
H(10A)-C(10)-H(10B)	109.5	H(16A)-C(16)-H(16B)	109.5
C(9)-C(10)-H(10C)	109.5	C(13)-C(16)-H(16C)	109.5
H(10A)-C(10)-H(10C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(10B)-C(10)-H(10C)	109.5	H(16B)-C(16)-H(16C)	109.5
C(9)-C(11)-H(11A)	109.5	C(19)-C(17)-C(18)	109.5(3)
C(9)-C(11)-H(11B)	109.5	C(19)-C(17)-C(20)	109.3(3)
H(11A)-C(11)-H(11B)	109.5	C(18)-C(17)-C(20)	109.7(3)
C(9)-C(11)-H(11C)	109.5	C(19)-C(17)-P(2A)	110.9(2)
H(11A)-C(11)-H(11C)	109.5	C(18)-C(17)-P(2A)	115.6(2)
H(11B)-C(11)-H(11C)	109.5	C(20)-C(17)-P(2A)	101.5(2)
C(9)-C(12)-H(12A)	109.5	C(17)-C(18)-H(18A)	109.5
C(9)-C(12)-H(12B)	109.5	C(17)-C(18)-H(18B)	109.5
H(12A)-C(12)-H(12B)	109.5	H(18A)-C(18)-H(18B)	109.5

C(17)-C(18)-H(18C)	109.5	C(21)-C(24)-H(24C)	109.5
H(18A)-C(18)-H(18C)	109.5	H(24A)-C(24)-H(24C)	109.5
H(18B)-C(18)-H(18C)	109.5	H(24B)-C(24)-H(24C)	109.5
C(17)-C(19)-H(19A)	109.5	Ir(1A)-C(25)-H(25A)	109(2)
C(17)-C(19)-H(19B)	109.5	Ir(1A)-C(25)-H(25B)	106(2)
H(19A)-C(19)-H(19B)	109.5	H(25A)-C(25)-H(25B)	108(3)
C(17)-C(19)-H(19C)	109.5	Ir(1A)-C(25)-H(25C)	104(2)
H(19A)-C(19)-H(19C)	109.5	H(25A)-C(25)-H(25C)	117(3)
H(19B)-C(19)-H(19C)	109.5	H(25B)-C(25)-H(25C)	112(3)
C(17)-C(20)-H(20A)	109.5	F(4)-B(1)-F(3)	109.8(3)
C(17)-C(20)-H(20B)	109.5	F(4)-B(1)-F(2)	110.9(4)
H(20A)-C(20)-H(20B)	109.5	F(3)-B(1)-F(2)	108.2(3)
C(17)-C(20)-H(20C)	109.5	F(4)-B(1)-F(1)	110.7(3)
H(20A)-C(20)-H(20C)	109.5	F(3)-B(1)-F(1)	109.5(3)
H(20B)-C(20)-H(20C)	109.5	F(2)-B(1)-F(1)	107.7(3)
C(22)-C(21)-C(24)	107.4(3)	C(26)-O(2)-C(29)	109.6(3)
C(22)-C(21)-C(23)	109.4(3)	O(2)-C(26)-C(27)	106.5(4)
C(24)-C(21)-C(23)	109.5(3)	O(2)-C(26)-H(26A)	110.4
C(22)-C(21)-P(2A)	113.2(2)	C(27)-C(26)-H(26A)	110.4
C(24)-C(21)-P(2A)	109.0(2)	O(2)-C(26)-H(26B)	110.4
C(23)-C(21)-P(2A)	108.2(2)	C(27)-C(26)-H(26B)	110.4
C(21)-C(22)-H(22A)	109.5	H(26A)-C(26)-H(26B)	108.6
C(21)-C(22)-H(22B)	109.5	C(26)-C(27)-C(28A)	104.5(5)
H(22A)-C(22)-H(22B)	109.5	C(26)-C(27)-H(27A)	110.9
C(21)-C(22)-H(22C)	109.5	C(28A)-C(27)-H(27A)	110.9
H(22A)-C(22)-H(22C)	109.5	C(26)-C(27)-H(27B)	110.9
H(22B)-C(22)-H(22C)	109.5	C(28A)-C(27)-H(27B)	110.9
C(21)-C(23)-H(23A)	109.5	H(27A)-C(27)-H(27B)	108.9
C(21)-C(23)-H(23B)	109.5	C(29)-C(28A)-C(27)	102.4(6)
H(23A)-C(23)-H(23B)	109.5	C(29)-C(28A)-H(28A)	111.3
C(21)-C(23)-H(23C)	109.5	C(27)-C(28A)-H(28A)	111.3
H(23A)-C(23)-H(23C)	109.5	C(29)-C(28A)-H(28B)	111.3
H(23B)-C(23)-H(23C)	109.5	C(27)-C(28A)-H(28B)	111.3
C(21)-C(24)-H(24A)	109.5	H(28A)-C(28A)-H(28B)	109.2
C(21)-C(24)-H(24B)	109.5	H(28C)-C(28B)-H(28D)	108.7(6)
H(24A)-C(24)-H(24B)	109.5	O(2)-C(29)-C(28A)	105.4(5)

O(2)-C(29)-H(29A)	110.7	C(28A)-C(29)-H(29B)	110.7
C(28A)-C(29)-H(29A)	110.7	H(29A)-C(29)-H(29B)	108.8
O(2)-C(29)-H(29B)	110.7		

Table S12. Torsion angles [°] for **[(PCP)Ir(H$_2$O)(Me)]+[BF$_4$]-·THF**.

C(1)-Ir(1A)-P(1A)-C(7)	23.0(1)	C(1)-C(2)-C(3)-C(4)	-0.5(4)
C(25)-Ir(1A)-P(1A)-C(7)	-63.1(1)	C(7)-C(2)-C(3)-C(4)	179.6(3)
O(1)-Ir(1A)-P(1A)-C(7)	-154.4(1)	C(2)-C(3)-C(4)-C(5)	0.1(5)
P(2A)-Ir(1A)-P(1A)-C(7)	61.2(2)	C(3)-C(4)-C(5)-C(6)	0.6(5)
C(1)-Ir(1A)-P(1A)-C(13)	138.6(2)	C(4)-C(5)-C(6)-C(1)	-0.9(4)
C(25)-Ir(1A)-P(1A)-C(13)	52.5(2)	C(4)-C(5)-C(6)-C(8)	-178.9(3)
O(1)-Ir(1A)-P(1A)-C(13)	-38.8(2)	C(2)-C(1)-C(6)-C(5)	0.5(4)
P(2A)-Ir(1A)-P(1A)-C(13)	176.8(2)	Ir(1A)-C(1)-C(6)-C(5)	176.7(2)
C(1)-Ir(1A)-P(1A)-C(9)	-86.9(1)	C(2)-C(1)-C(6)-C(8)	178.5(3)
C(25)-Ir(1A)-P(1A)-C(9)	-173.0(2)	Ir(1A)-C(1)-C(6)-C(8)	-5.3(4)
O(1)-Ir(1A)-P(1A)-C(9)	95.7(1)	C(3)-C(2)-C(7)-P(1A)	-161.5(2)
P(2A)-Ir(1A)-P(1A)-C(9)	-48.7(2)	C(1)-C(2)-C(7)-P(1A)	18.6(3)
C(1)-Ir(1A)-P(2A)-C(8)	9.4(2)	C(13)-P(1A)-C(7)-C(2)	-156.0(2)
C(25)-Ir(1A)-P(2A)-C(8)	95.2(2)	C(9)-P(1A)-C(7)-C(2)	87.8(2)
O(1)-Ir(1A)-P(2A)-C(8)	-173.4(1)	Ir(1A)-P(1A)-C(7)-C(2)	-27.2(2)
P(1A)-Ir(1A)-P(2A)-C(8)	-28.6(2)	C(5)-C(6)-C(8)-P(2A)	-168.2(2)
C(1)-Ir(1A)-P(2A)-C(21)	-112.5(2)	C(1)-C(6)-C(8)-P(2A)	13.7(4)
C(25)-Ir(1A)-P(2A)-C(21)	-26.7(2)	C(21)-P(2A)-C(8)-C(6)	117.9(2)
O(1)-Ir(1A)-P(2A)-C(21)	64.7(2)	C(17)-P(2A)-C(8)-C(6)	-123.1(2)
P(1A)-Ir(1A)-P(2A)-C(21)	-150.6(2)	Ir(1A)-P(2A)-C(8)-C(6)	-14.2(3)
C(1)-Ir(1A)-P(2A)-C(17)	117.4(1)	C(7)-P(1A)-C(9)-C(12)	-50.3(3)
C(25)-Ir(1A)-P(2A)-C(17)	-156.8(2)	C(13)-P(1A)-C(9)-C(12)	-163.0(2)
O(1)-Ir(1A)-P(2A)-C(17)	-65.4(1)	Ir(1A)-P(1A)-C(9)-C(12)	56.3(2)
P(1A)-Ir(1A)-P(2A)-C(17)	79.3(2)	C(7)-P(1A)-C(9)-C(10)	69.3(3)
C(25)-Ir(1A)-C(1)-C(2)	75.4(2)	C(13)-P(1A)-C(9)-C(10)	-43.4(3)
P(2A)-Ir(1A)-C(1)-C(2)	172.1(2)	Ir(1A)-P(1A)-C(9)-C(10)	176.0(2)
P(1A)-Ir(1A)-C(1)-C(2)	-18.2(2)	C(7)-P(1A)-C(9)-C(11)	-168.1(2)
C(25)-Ir(1A)-C(1)-C(6)	-100.6(2)	C(13)-P(1A)-C(9)-C(11)	79.2(3)
P(2A)-Ir(1A)-C(1)-C(6)	-3.9(2)	Ir(1A)-P(1A)-C(9)-C(11)	-61.5(3)
P(1A)-Ir(1A)-C(1)-C(6)	165.7(2)	C(7)-P(1A)-C(13)-C(16)	76.5(2)
C(6)-C(1)-C(2)-C(3)	0.2(4)	C(9)-P(1A)-C(13)-C(16)	-171.1(2)
Ir(1A)-C(1)-C(2)-C(3)	-176.0(2)	Ir(1A)-P(1A)-C(13)-C(16)	-36.3(3)
C(6)-C(1)-C(2)-C(7)	-179.9(3)	C(7)-P(1A)-C(13)-C(14)	-41.6(3)
Ir(1A)-C(1)-C(2)-C(7)	3.8(4)	C(9)-P(1A)-C(13)-C(14)	70.8(3)

Ir(1A)-P(1A)-C(13)-C(14)	-154.4(2)	C(17)-P(2A)-C(21)-C(22)	-33.5(3)
C(7)-P(1A)-C(13)-C(15)	-165.7(2)	Ir(1A)-P(2A)-C(21)-C(22)	-160.7(2)
C(9)-P(1A)-C(13)-C(15)	-53.3(3)	C(8)-P(2A)-C(21)-C(24)	-39.4(3)
Ir(1A)-P(1A)-C(13)-C(15)	81.5(3)	C(17)-P(2A)-C(21)-C(24)	-152.9(2)
C(8)-P(2A)-C(17)-C(19)	-170.2(3)	Ir(1A)-P(2A)-C(21)-C(24)	79.9(2)
C(21)-P(2A)-C(17)-C(19)	-54.0(3)	C(8)-P(2A)-C(21)-C(23)	-158.4(2)
Ir(1A)-P(2A)-C(17)-C(19)	82.8(3)	C(17)-P(2A)-C(21)-C(23)	88.0(3)
C(8)-P(2A)-C(17)-C(18)	-44.8(3)	Ir(1A)-P(2A)-C(21)-C(23)	-39.2(3)
C(21)-P(2A)-C(17)-C(18)	71.5(3)	C(29)-O(2)-C(26)-C(27)	7.2(4)
Ir(1A)-P(2A)-C(17)-C(18)	-151.8(2)	O(2)-C(26)-C(27)-C(28A)	14.4(6)
C(8)-P(2A)-C(17)-C(20)	73.7(2)	C(26)-C(27)-C(28A)-C(29)	-29.4(7)
C(21)-P(2A)-C(17)-C(20)	-170.0(2)	C(26)-O(2)-C(29)-C(28A)	-26.6(6)
Ir(1A)-P(2A)-C(17)-C(20)	-33.2(2)	C(27)-C(28A)-C(29)-O(2)	34.2(7)
C(8)-P(2A)-C(21)-C(22)	80.1(3)		

Table S13. Hydrogen bonds for **[(PCP)Ir(H_2O)(Me)]+[BF_4]-·THF.**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1B)...O(2)	0.87(4)	1.83(4)	2.686(4)	167(4)
O(1)-H(1A)...F(1)	0.92(4)	1.99(4)	2.872(4)	158(4)
O(1)-H(1A)...F(2)	0.92(4)	2.27(4)	2.866(4)	122(3)

IV. Structural Data for (Br-PCP)Ir(CO)(Ph)(Br)

Figure S-4 : ORTEP Diagram of **(Br-PCP)Ir(CO)(Ph)(Br)**

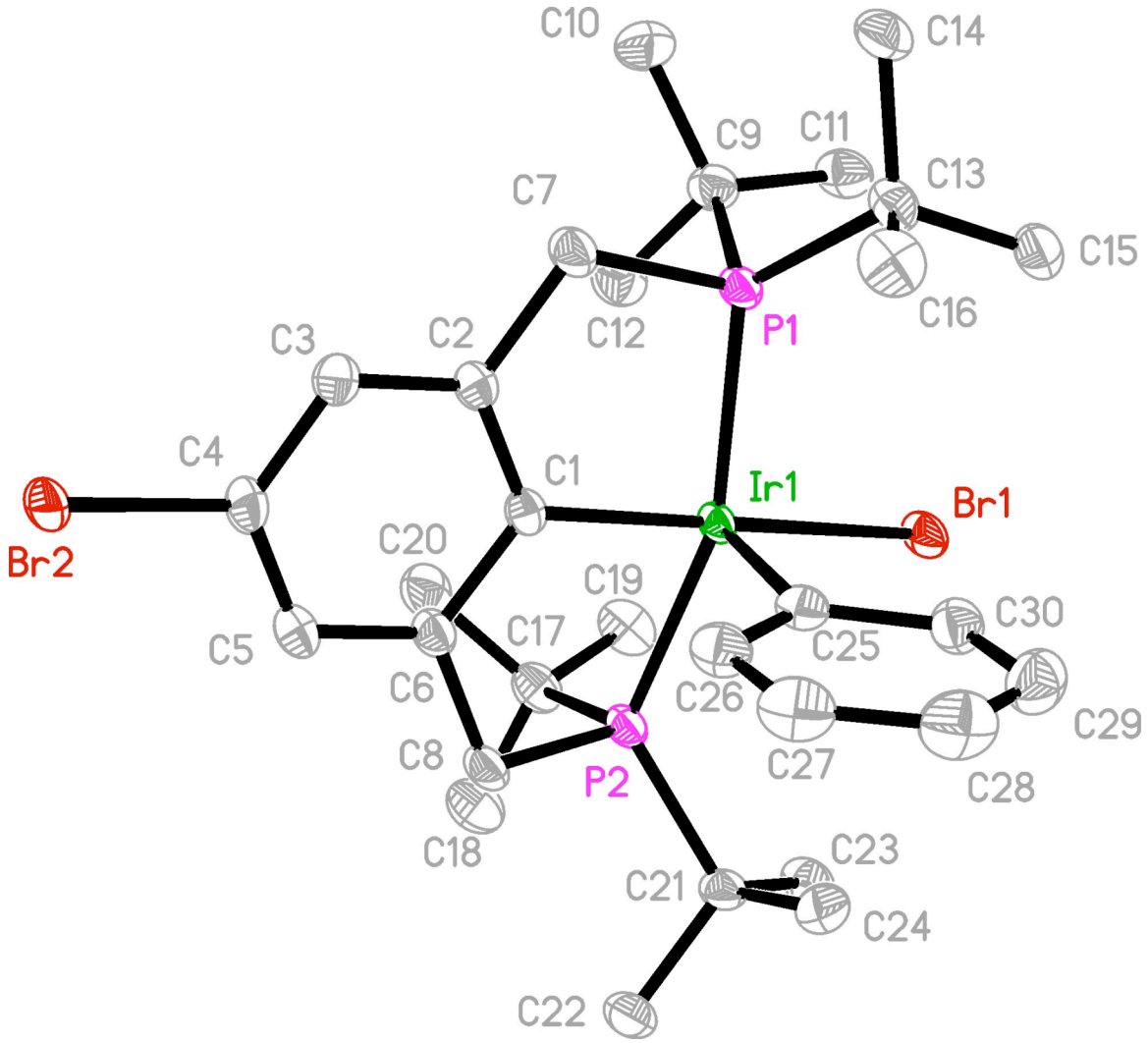

Table S14. Crystal data and structure refinement for **(Br-PCP)Ir(Ph)(Br)**.

Identification code	irphbr_abc	
Empirical formula	C30 H47.26 Br1.74 Ir P2	
Formula weight	800.92	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 17.5108(10) Å	α= 90°.
	b = 17.3197(10) Å	β= 90°.
	c = 20.0351(11) Å	γ = 90°.
Volume	6076.3(6) $Å^3$	
Z	8	
Density (calculated)	1.751 Mg/m^3	
Absorption coefficient	6.803 mm^{-1}	
F(000)	3161	
Crystal size	0.35 x 0.23 x 0.08 mm^3	
Theta range for data collection	1.94 to 30.54°.	
Index ranges	-25<=h<=24, -24<=k<=24, -28<=l<=28	
Reflections collected	69218	
Independent reflections	9296 [R(int) = 0.0306]	
Completeness to theta = 30.54°	99.9 %	
Absorption correction	Integration	
Max. and min. transmission	0.6121 and 0.1993	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9296 / 0 / 329	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0236, wR2 = 0.0561	
R indices (all data)	R1 = 0.0315, wR2 = 0.0595	
Largest diff. peak and hole	2.207 and -0.455 e.$Å^{-3}$	

Table S15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(Br-PCP)Ir(Ph)(Br)**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	1833(1)	3752(1)	2846(1)	16(1)
P(1)	1183(1)	4492(1)	3640(1)	18(1)
P(2)	2119(1)	2822(1)	2031(1)	19(1)
Br(1)	2452(1)	4863(1)	2168(1)	23(1)
C(1)	1239(1)	2865(1)	3257(1)	19(1)
C(2)	738(2)	2970(1)	3801(1)	20(1)
C(3)	358(2)	2347(2)	4094(1)	22(1)
C(4)	479(2)	1604(2)	3855(1)	25(1)
Br(2)	-6(1)	745(1)	4264(1)	28(1)
C(5)	965(2)	1475(2)	3322(1)	23(1)
C(6)	1344(2)	2094(1)	3029(1)	20(1)
C(7)	633(2)	3763(1)	4106(1)	25(1)
C(8)	1928(2)	1935(1)	2494(1)	22(1)
C(9)	428(2)	5050(2)	3169(1)	24(1)
C(10)	-324(2)	5213(2)	3542(2)	33(1)
C(11)	744(2)	5812(2)	2895(1)	28(1)
C(12)	242(2)	4517(2)	2576(2)	31(1)
C(13)	1638(2)	5110(2)	4301(1)	24(1)
C(14)	1039(2)	5577(2)	4688(2)	30(1)
C(15)	2224(2)	5655(2)	3978(2)	29(1)
C(16)	2062(2)	4592(2)	4804(2)	32(1)
C(17)	1376(2)	2825(2)	1346(1)	26(1)
C(18)	1509(2)	2199(2)	814(2)	35(1)
C(19)	1331(2)	3613(2)	993(2)	32(1)
C(20)	594(2)	2656(2)	1670(2)	30(1)
C(21)	3100(2)	2669(2)	1671(1)	23(1)
C(22)	3220(2)	1840(2)	1407(2)	29(1)
C(23)	3258(2)	3248(2)	1110(2)	29(1)
C(24)	3679(2)	2820(2)	2228(2)	29(1)
C(25)	2701(2)	3486(2)	3477(1)	22(1)
C(26)	2722(2)	2844(2)	3905(1)	26(1)

C(27)	3328(2)	2733(2)	4346(2)	33(1)
C(28)	3922(2)	3246(2)	4378(2)	38(1)
C(29)	3922(2)	3880(2)	3954(2)	33(1)
C(30)	3326(2)	3999(2)	3508(2)	26(1)

Table S16. Bond lengths [Å] and angles [°] for **(Br-PCP)Ir(Ph)(Br)**.

Ir(1)-C(1)	2.029(2)	C(6)-C(8)	1.506(4)
Ir(1)-C(25)	2.030(3)	C(9)-C(11)	1.531(4)
Ir(1)-P(1)	2.3382(6)	C(9)-C(12)	1.539(4)
Ir(1)-P(2)	2.3480(6)	C(9)-C(10)	1.540(4)
Ir(1)-Br(1)	2.5947(3)	C(13)-C(14)	1.535(4)
P(1)-C(7)	1.842(3)	C(13)-C(15)	1.537(4)
P(1)-C(13)	1.880(3)	C(13)-C(16)	1.541(4)
P(1)-C(9)	1.890(3)	C(17)-C(19)	1.538(4)
P(2)-C(8)	1.826(3)	C(17)-C(18)	1.539(4)
P(2)-C(21)	1.882(3)	C(17)-C(20)	1.543(4)
P(2)-C(17)	1.891(3)	C(21)-C(24)	1.531(4)
C(1)-C(2)	1.410(3)	C(21)-C(23)	1.532(4)
C(1)-C(6)	1.424(3)	C(21)-C(22)	1.544(4)
C(2)-C(3)	1.397(3)	C(25)-C(26)	1.404(4)
C(2)-C(7)	1.515(3)	C(25)-C(30)	1.412(4)
C(3)-C(4)	1.388(4)	C(26)-C(27)	1.395(4)
C(4)-C(5)	1.384(4)	C(27)-C(28)	1.369(5)
C(4)-Br(2)	1.900(3)	C(28)-C(29)	1.388(5)
C(5)-C(6)	1.391(3)	C(29)-C(30)	1.388(4)
C(1)-Ir(1)-C(25)	87.67(10)	C(13)-P(1)-Ir(1)	125.78(9)
C(1)-Ir(1)-P(1)	83.66(7)	C(9)-P(1)-Ir(1)	106.34(9)
C(25)-Ir(1)-P(1)	93.78(7)	C(8)-P(2)-C(21)	104.10(12)
C(1)-Ir(1)-P(2)	82.70(7)	C(8)-P(2)-C(17)	104.19(13)
C(25)-Ir(1)-P(2)	96.76(7)	C(21)-P(2)-C(17)	110.49(13)
P(1)-Ir(1)-P(2)	162.37(2)	C(8)-P(2)-Ir(1)	100.64(9)
C(1)-Ir(1)-Br(1)	171.28(7)	C(21)-P(2)-Ir(1)	123.92(9)
C(25)-Ir(1)-Br(1)	100.47(8)	C(17)-P(2)-Ir(1)	110.87(9)
P(1)-Ir(1)-Br(1)	98.785(17)	C(2)-C(1)-C(6)	116.7(2)
P(2)-Ir(1)-Br(1)	93.156(18)	C(2)-C(1)-Ir(1)	122.35(17)
C(7)-P(1)-C(13)	104.77(13)	C(6)-C(1)-Ir(1)	120.83(18)
C(7)-P(1)-C(9)	103.80(13)	C(3)-C(2)-C(1)	121.4(2)
C(13)-P(1)-C(9)	110.92(12)	C(3)-C(2)-C(7)	118.3(2)
C(7)-P(1)-Ir(1)	102.89(9)	C(1)-C(2)-C(7)	120.2(2)

C(4)-C(3)-C(2)	119.8(2)	C(16)-C(13)-P(1)	109.55(19)
C(5)-C(4)-C(3)	120.7(2)	C(19)-C(17)-C(18)	108.4(2)
C(5)-C(4)-Br(2)	118.77(19)	C(19)-C(17)-C(20)	108.5(2)
C(3)-C(4)-Br(2)	120.5(2)	C(18)-C(17)-C(20)	106.9(2)
C(4)-C(5)-C(6)	119.6(2)	C(19)-C(17)-P(2)	111.8(2)
C(5)-C(6)-C(1)	121.7(2)	C(18)-C(17)-P(2)	113.4(2)
C(5)-C(6)-C(8)	118.8(2)	C(20)-C(17)-P(2)	107.74(19)
C(1)-C(6)-C(8)	119.3(2)	C(24)-C(21)-C(23)	107.7(2)
C(2)-C(7)-P(1)	110.73(18)	C(24)-C(21)-C(22)	108.5(2)
C(6)-C(8)-P(2)	109.34(17)	C(23)-C(21)-C(22)	109.4(2)
C(11)-C(9)-C(12)	108.5(2)	C(24)-C(21)-P(2)	107.51(18)
C(11)-C(9)-C(10)	109.0(2)	C(23)-C(21)-P(2)	110.80(19)
C(12)-C(9)-C(10)	107.7(2)	C(22)-C(21)-P(2)	112.72(18)
C(11)-C(9)-P(1)	111.54(19)	C(26)-C(25)-C(30)	116.9(3)
C(12)-C(9)-P(1)	103.10(18)	C(26)-C(25)-Ir(1)	125.4(2)
C(10)-C(9)-P(1)	116.6(2)	C(30)-C(25)-Ir(1)	117.7(2)
C(14)-C(13)-C(15)	110.2(2)	C(27)-C(26)-C(25)	121.0(3)
C(14)-C(13)-C(16)	107.7(2)	C(28)-C(27)-C(26)	121.2(3)
C(15)-C(13)-C(16)	108.1(2)	C(27)-C(28)-C(29)	119.0(3)
C(14)-C(13)-P(1)	111.5(2)	C(28)-C(29)-C(30)	120.8(3)
C(15)-C(13)-P(1)	109.70(18)	C(29)-C(30)-C(25)	121.1(3)

Table S17. Torsion angles [°] for **(Br-PCP)Ir(Ph)(Br)**.

C(1)-Ir(1)-P(1)-C(7)	2.80(12)	C(1)-C(2)-C(3)-C(4)	0.7(4)
C(25)-Ir(1)-P(1)-C(7)	-84.43(13)	C(7)-C(2)-C(3)-C(4)	-175.9(3)
P(2)-Ir(1)-P(1)-C(7)	42.26(13)	C(2)-C(3)-C(4)-C(5)	-0.9(4)
Br(1)-Ir(1)-P(1)-C(7)	174.36(10)	C(2)-C(3)-C(4)-Br(2)	178.0(2)
C(1)-Ir(1)-P(1)-C(13)	121.96(13)	C(3)-C(4)-C(5)-C(6)	0.9(4)
C(25)-Ir(1)-P(1)-C(13)	34.72(13)	Br(2)-C(4)-C(5)-C(6)	-178.0(2)
P(2)-Ir(1)-P(1)-C(13)	161.42(12)	C(4)-C(5)-C(6)-C(1)	-0.9(4)
Br(1)-Ir(1)-P(1)-C(13)	-66.49(11)	C(4)-C(5)-C(6)-C(8)	174.1(3)
C(1)-Ir(1)-P(1)-C(9)	-105.98(12)	C(2)-C(1)-C(6)-C(5)	0.8(4)
C(25)-Ir(1)-P(1)-C(9)	166.79(12)	Ir(1)-C(1)-C(6)-C(5)	177.4(2)
P(2)-Ir(1)-P(1)-C(9)	-66.52(12)	C(2)-C(1)-C(6)-C(8)	-174.2(2)
Br(1)-Ir(1)-P(1)-C(9)	65.57(9)	Ir(1)-C(1)-C(6)-C(8)	2.4(3)
C(1)-Ir(1)-P(2)-C(8)	-20.45(12)	C(3)-C(2)-C(7)-P(1)	-180.0(2)
C(25)-Ir(1)-P(2)-C(8)	66.32(12)	C(1)-C(2)-C(7)-P(1)	3.3(3)
P(1)-Ir(1)-P(2)-C(8)	-60.00(12)	C(13)-P(1)-C(7)-C(2)	-136.7(2)
Br(1)-Ir(1)-P(2)-C(8)	167.26(9)	C(9)-P(1)-C(7)-C(2)	106.8(2)
C(1)-Ir(1)-P(2)-C(21)	-135.60(13)	Ir(1)-P(1)-C(7)-C(2)	-3.9(2)
C(25)-Ir(1)-P(2)-C(21)	-48.83(13)	C(5)-C(6)-C(8)-P(2)	163.1(2)
P(1)-Ir(1)-P(2)-C(21)	-175.16(11)	C(1)-C(6)-C(8)-P(2)	-21.8(3)
Br(1)-Ir(1)-P(2)-C(21)	52.11(11)	C(21)-P(2)-C(8)-C(6)	156.17(19)
C(1)-Ir(1)-P(2)-C(17)	89.34(12)	C(17)-P(2)-C(8)-C(6)	-88.0(2)
C(25)-Ir(1)-P(2)-C(17)	176.11(12)	Ir(1)-P(2)-C(8)-C(6)	26.9(2)
P(1)-Ir(1)-P(2)-C(17)	49.79(13)	C(7)-P(1)-C(9)-C(11)	165.07(19)
Br(1)-Ir(1)-P(2)-C(17)	-82.95(10)	C(13)-P(1)-C(9)-C(11)	53.1(2)
C(25)-Ir(1)-C(1)-C(2)	92.4(2)	Ir(1)-P(1)-C(9)-C(11)	-86.79(19)
P(1)-Ir(1)-C(1)-C(2)	-1.6(2)	C(7)-P(1)-C(9)-C(12)	-78.7(2)
P(2)-Ir(1)-C(1)-C(2)	-170.4(2)	C(13)-P(1)-C(9)-C(12)	169.29(18)
C(25)-Ir(1)-C(1)-C(6)	-84.0(2)	Ir(1)-P(1)-C(9)-C(12)	29.4(2)
P(1)-Ir(1)-C(1)-C(6)	-178.1(2)	C(7)-P(1)-C(9)-C(10)	39.0(2)
P(2)-Ir(1)-C(1)-C(6)	13.1(2)	C(13)-P(1)-C(9)-C(10)	-73.0(2)
C(6)-C(1)-C(2)-C(3)	-0.7(4)	Ir(1)-P(1)-C(9)-C(10)	147.13(19)
Ir(1)-C(1)-C(2)-C(3)	-177.3(2)	C(7)-P(1)-C(13)-C(14)	-67.4(2)
C(6)-C(1)-C(2)-C(7)	175.9(2)	C(9)-P(1)-C(13)-C(14)	44.0(2)
Ir(1)-C(1)-C(2)-C(7)	-0.7(3)	Ir(1)-P(1)-C(13)-C(14)	174.28(15)

C(7)-P(1)-C(13)-C(15)	170.3(2)	Ir(1)-P(2)-C(21)-C(23)	-82.8(2)
C(9)-P(1)-C(13)-C(15)	-78.3(2)	C(8)-P(2)-C(21)-C(22)	40.7(2)
Ir(1)-P(1)-C(13)-C(15)	52.0(2)	C(17)-P(2)-C(21)-C(22)	-70.6(2)
C(7)-P(1)-C(13)-C(16)	51.7(2)	Ir(1)-P(2)-C(21)-C(22)	154.19(16)
C(9)-P(1)-C(13)-C(16)	163.14(19)	C(1)-Ir(1)-C(25)-C(26)	6.1(2)
Ir(1)-P(1)-C(13)-C(16)	-66.6(2)	P(1)-Ir(1)-C(25)-C(26)	89.6(2)
C(8)-P(2)-C(17)-C(19)	167.6(2)	P(2)-Ir(1)-C(25)-C(26)	-76.3(2)
C(21)-P(2)-C(17)-C(19)	-81.1(2)	Br(1)-Ir(1)-C(25)-C(26)	-170.8(2)
Ir(1)-P(2)-C(17)-C(19)	60.2(2)	C(1)-Ir(1)-C(25)-C(30)	-171.6(2)
C(8)-P(2)-C(17)-C(18)	-69.5(2)	P(1)-Ir(1)-C(25)-C(30)	-88.2(2)
C(21)-P(2)-C(17)-C(18)	41.7(2)	P(2)-Ir(1)-C(25)-C(30)	106.0(2)
Ir(1)-P(2)-C(17)-C(18)	-177.01(19)	Br(1)-Ir(1)-C(25)-C(30)	11.5(2)
C(8)-P(2)-C(17)-C(20)	48.6(2)	C(30)-C(25)-C(26)-C(27)	1.2(4)
C(21)-P(2)-C(17)-C(20)	159.86(18)	Ir(1)-C(25)-C(26)-C(27)	-176.6(2)
Ir(1)-P(2)-C(17)-C(20)	-58.88(19)	C(25)-C(26)-C(27)-C(28)	0.0(5)
C(8)-P(2)-C(21)-C(24)	-78.8(2)	C(26)-C(27)-C(28)-C(29)	-0.9(5)
C(17)-P(2)-C(21)-C(24)	169.85(18)	C(27)-C(28)-C(29)-C(30)	0.6(5)
Ir(1)-P(2)-C(21)-C(24)	34.7(2)	C(28)-C(29)-C(30)-C(25)	0.7(5)
C(8)-P(2)-C(21)-C(23)	163.8(2)	C(26)-C(25)-C(30)-C(29)	-1.5(4)
C(17)-P(2)-C(21)-C(23)	52.4(2)	Ir(1)-C(25)-C(30)-C(29)	176.4(2)

V. Structural Data for (PCP)Ir(CO)(Ph)$_2$

Figure S-5 : ORTEP Diagram of **(PCP)Ir(CO)(Ph)$_2$**

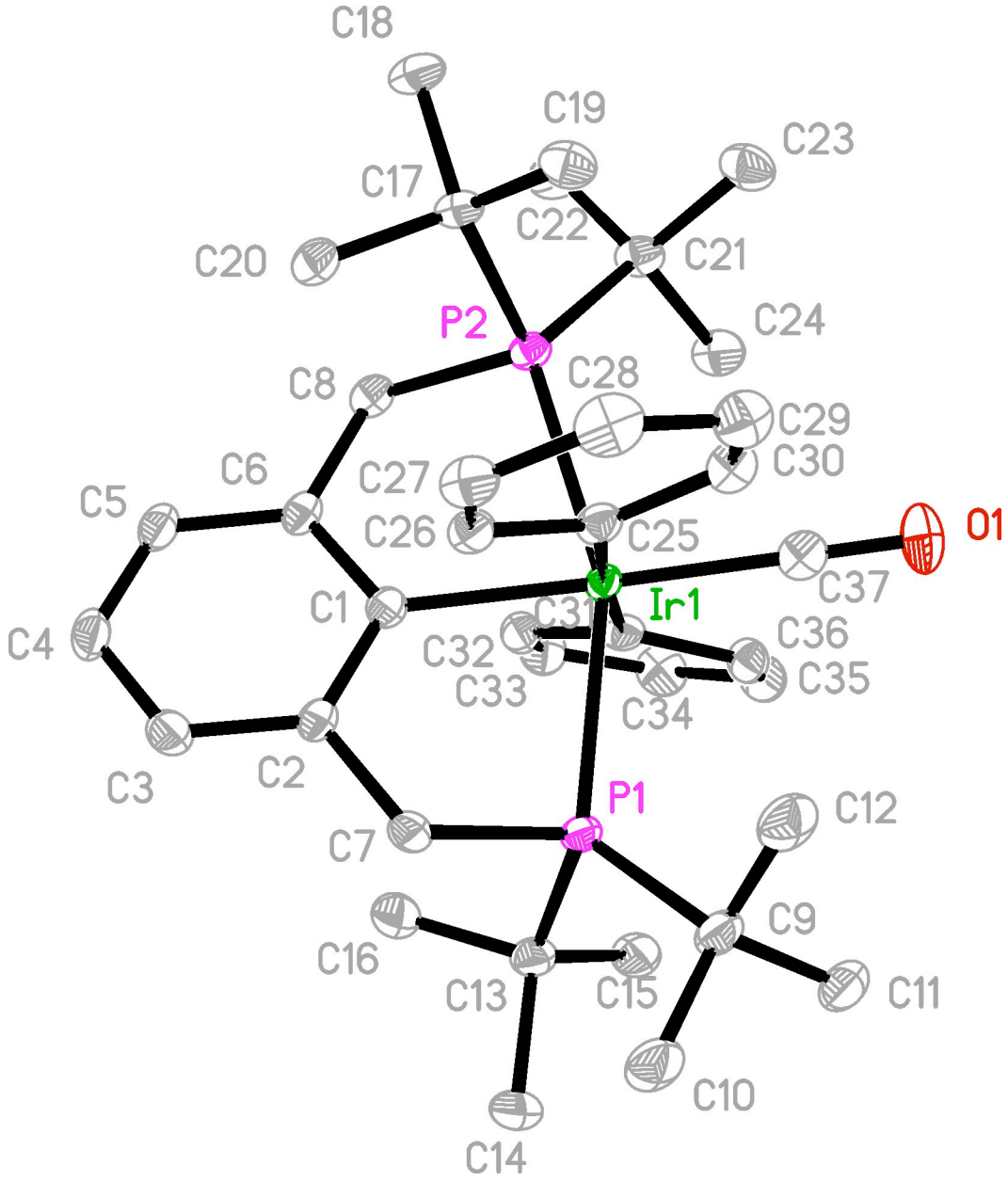

Table S18. Crystal data and structure refinement for **(PCP)Ir(CO)(Ph)$_2$**.

Identification code	irph2	
Empirical formula	C37 H53 Ir O P2	
Formula weight	767.93	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 9.9228(4) Å	α= 90°.
	b = 16.8100(7) Å	β= 99.890(1)°.
	c = 10.3137(4) Å	γ = 90°.
Volume	1694.78(12) Å^3	
Z	2	
Density (calculated)	1.505 Mg/m^3	
Absorption coefficient	4.061 mm^{-1}	
F(000)	780	
Crystal size	0.38 x 0.07 x 0.07 mm^3	
Theta range for data collection	2.00 to 30.56°.	
Index ranges	-14<=h<=14, -23<=k<=24, -14<=l<=14	
Reflections collected	19031	
Independent reflections	9506 [R(int) = 0.0169]	
Completeness to theta = 30.56°	98.4 %	
Absorption correction	Numerical	
Max. and min. transmission	0.7642 and 0.3075	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9506 / 0 / 381	
Goodness-of-fit on F^2	0.882	
Final R indices [I>2sigma(I)]	R1 = 0.0169, wR2 = 0.0419	
R indices (all data)	R1 = 0.0177, wR2 = 0.0419	
Absolute structure parameter	0.017(3)	
Largest diff. peak and hole	1.690 and -0.865 e.Å^{-3}	

Table S19. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(PCP)Ir(CO)(Ph)$_2$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	2351(1)	0(1)	3933(1)	13(1)
P(1)	907(1)	-525(1)	1998(1)	17(1)
P(2)	4357(1)	134(1)	5608(1)	15(1)
O(1)	459(2)	1178(1)	4981(2)	30(1)
C(1)	3681(2)	-787(1)	3237(2)	16(1)
C(2)	3484(2)	-994(2)	1895(3)	18(1)
C(3)	4413(3)	-1478(2)	1408(3)	23(1)
C(4)	5551(2)	-1776(1)	2234(2)	23(1)
C(5)	5757(2)	-1597(1)	3562(2)	21(1)
C(6)	4837(2)	-1106(1)	4069(2)	17(1)
C(7)	2238(2)	-673(1)	997(2)	19(1)
C(8)	5088(2)	-861(1)	5509(2)	18(1)
C(9)	-407(2)	151(1)	994(2)	23(1)
C(10)	-602(2)	11(4)	-502(2)	31(1)
C(11)	-1785(2)	91(2)	1483(2)	28(1)
C(12)	74(3)	1022(2)	1203(3)	29(1)
C(13)	130(2)	-1578(1)	1940(2)	22(1)
C(14)	-658(3)	-1774(2)	553(3)	29(1)
C(15)	-841(2)	-1714(2)	2931(3)	25(1)
C(16)	1279(2)	-2202(2)	2217(3)	26(1)
C(17)	5895(2)	772(1)	5373(2)	18(1)
C(18)	7058(2)	740(2)	6582(2)	25(1)
C(19)	5535(3)	1650(1)	5083(2)	22(1)
C(20)	6548(2)	437(1)	4232(2)	20(1)
C(21)	4110(2)	298(1)	7379(2)	19(1)
C(22)	5211(2)	-112(3)	8401(2)	28(1)
C(23)	4043(3)	1196(2)	7642(2)	26(1)
C(24)	2736(2)	-33(3)	7624(2)	25(1)
C(25)	3076(2)	973(1)	2832(2)	16(1)
C(26)	3960(2)	904(2)	1911(2)	18(1)
C(27)	4433(3)	1553(2)	1264(3)	21(1)

C(28)	3991(3)	2320(2)	1485(3)	27(1)
C(29)	3102(2)	2418(2)	2369(2)	24(1)
C(30)	2676(2)	1767(1)	3026(2)	20(1)
C(31)	1534(2)	-901(1)	5073(2)	18(1)
C(32)	2131(2)	-1644(1)	5428(2)	20(1)
C(33)	1627(3)	-2176(1)	6274(3)	25(1)
C(34)	468(3)	-1991(2)	6792(3)	27(1)
C(35)	-190(3)	-1283(2)	6427(3)	25(1)
C(36)	314(2)	-754(1)	5585(2)	21(1)
C(37)	1170(3)	740(2)	4578(3)	21(1)

Table S20. Bond lengths [Å] and angles [°] for **(PCP)Ir(CO)(Ph)$_2$**.

Ir(1)-C(37)	1.906(3)	C(9)-C(10)	1.539(3)
Ir(1)-C(1)	2.081(2)	C(13)-C(15)	1.538(3)
Ir(1)-C(31)	2.159(2)	C(13)-C(16)	1.539(3)
Ir(1)-C(25)	2.183(2)	C(13)-C(14)	1.543(3)
Ir(1)-P(2)	2.4120(5)	C(17)-C(19)	1.536(3)
Ir(1)-P(1)	2.4151(5)	C(17)-C(20)	1.545(3)
P(1)-C(7)	1.827(2)	C(17)-C(18)	1.548(3)
P(1)-C(9)	1.897(2)	C(21)-C(24)	1.533(3)
P(1)-C(13)	1.927(2)	C(21)-C(23)	1.538(3)
P(2)-C(8)	1.833(2)	C(21)-C(22)	1.544(3)
P(2)-C(21)	1.904(2)	C(25)-C(26)	1.403(3)
P(2)-C(17)	1.915(2)	C(25)-C(30)	1.416(3)
O(1)-C(37)	1.145(3)	C(26)-C(27)	1.401(4)
C(1)-C(2)	1.407(3)	C(27)-C(28)	1.394(4)
C(1)-C(6)	1.415(3)	C(28)-C(29)	1.383(4)
C(2)-C(3)	1.387(4)	C(29)-C(30)	1.391(3)
C(2)-C(7)	1.512(3)	C(31)-C(32)	1.403(3)
C(3)-C(4)	1.386(4)	C(31)-C(36)	1.423(3)
C(4)-C(5)	1.383(3)	C(32)-C(33)	1.401(3)
C(5)-C(6)	1.397(3)	C(33)-C(34)	1.384(3)
C(6)-C(8)	1.519(3)	C(34)-C(35)	1.379(4)
C(9)-C(11)	1.540(3)	C(35)-C(36)	1.395(3)
C(9)-C(12)	1.543(4)		

C(37)-Ir(1)-C(1)	178.52(10)	C(37)-Ir(1)-P(1)	102.39(8)
C(37)-Ir(1)-C(31)	87.54(9)	C(1)-Ir(1)-P(1)	78.70(7)
C(1)-Ir(1)-C(31)	93.51(9)	C(31)-Ir(1)-P(1)	88.22(6)
C(37)-Ir(1)-C(25)	88.27(10)	C(25)-Ir(1)-P(1)	92.64(6)
C(1)-Ir(1)-C(25)	90.68(9)	P(2)-Ir(1)-P(1)	157.760(19)
C(31)-Ir(1)-C(25)	175.81(9)	C(7)-P(1)-C(9)	105.57(10)
C(37)-Ir(1)-P(2)	99.78(8)	C(7)-P(1)-C(13)	100.48(11)
C(1)-Ir(1)-P(2)	79.18(7)	C(9)-P(1)-C(13)	107.43(10)
C(31)-Ir(1)-P(2)	90.91(7)	C(7)-P(1)-Ir(1)	97.62(7)
C(25)-Ir(1)-P(2)	89.84(6)	C(9)-P(1)-Ir(1)	119.12(7)

C(13)-P(1)-Ir(1)	122.59(8)	C(16)-C(13)-P(1)	109.91(15)
C(8)-P(2)-C(21)	107.62(10)	C(14)-C(13)-P(1)	111.15(17)
C(8)-P(2)-C(17)	99.93(10)	C(19)-C(17)-C(20)	108.39(18)
C(21)-P(2)-C(17)	106.08(10)	C(19)-C(17)-C(18)	107.89(18)
C(8)-P(2)-Ir(1)	99.24(7)	C(20)-C(17)-C(18)	104.39(18)
C(21)-P(2)-Ir(1)	118.33(7)	C(19)-C(17)-P(2)	113.54(16)
C(17)-P(2)-Ir(1)	122.64(7)	C(20)-C(17)-P(2)	109.90(14)
C(2)-C(1)-C(6)	117.6(2)	C(18)-C(17)-P(2)	112.26(15)
C(2)-C(1)-Ir(1)	120.46(17)	C(24)-C(21)-C(23)	105.1(2)
C(6)-C(1)-Ir(1)	121.85(16)	C(24)-C(21)-C(22)	105.7(2)
C(3)-C(2)-C(1)	120.9(2)	C(23)-C(21)-C(22)	111.4(2)
C(3)-C(2)-C(7)	120.8(2)	C(24)-C(21)-P(2)	111.71(15)
C(1)-C(2)-C(7)	118.4(2)	C(23)-C(21)-P(2)	109.13(16)
C(4)-C(3)-C(2)	120.7(3)	C(22)-C(21)-P(2)	113.47(17)
C(3)-C(4)-C(5)	119.8(2)	C(26)-C(25)-C(30)	113.4(2)
C(4)-C(5)-C(6)	120.3(2)	C(26)-C(25)-Ir(1)	126.18(17)
C(5)-C(6)-C(1)	120.7(2)	C(30)-C(25)-Ir(1)	120.46(16)
C(5)-C(6)-C(8)	121.16(19)	C(27)-C(26)-C(25)	123.9(2)
C(1)-C(6)-C(8)	118.04(19)	C(28)-C(27)-C(26)	120.1(3)
C(2)-C(7)-P(1)	107.26(16)	C(29)-C(28)-C(27)	118.2(2)
C(6)-C(8)-P(2)	107.53(14)	C(28)-C(29)-C(30)	120.6(2)
C(11)-C(9)-C(12)	106.6(2)	C(29)-C(30)-C(25)	123.8(2)
C(11)-C(9)-C(10)	110.63(18)	C(32)-C(31)-C(36)	114.0(2)
C(12)-C(9)-C(10)	105.5(3)	C(32)-C(31)-Ir(1)	125.82(16)
C(11)-C(9)-P(1)	110.35(17)	C(36)-C(31)-Ir(1)	120.16(18)
C(12)-C(9)-P(1)	108.97(14)	C(33)-C(32)-C(31)	123.4(2)
C(10)-C(9)-P(1)	114.3(2)	C(34)-C(33)-C(32)	120.5(2)
C(15)-C(13)-C(16)	107.7(2)	C(33)-C(34)-C(35)	118.3(2)
C(15)-C(13)-C(14)	107.97(19)	C(34)-C(35)-C(36)	121.1(2)
C(16)-C(13)-C(14)	105.6(2)	C(35)-C(36)-C(31)	122.6(2)
C(15)-C(13)-P(1)	114.11(16)	O(1)-C(37)-Ir(1)	179.0(2)

Table S21. Torsion angles [°] for **(PCP)Ir(CO)(Ph)$_2$**.

C(37)-Ir(1)-P(1)-C(7)	146.22(11)	C(31)-Ir(1)-C(1)-C(6)	-70.21(19)
C(1)-Ir(1)-P(1)-C(7)	-32.75(10)	C(25)-Ir(1)-C(1)-C(6)	109.76(18)
C(31)-Ir(1)-P(1)-C(7)	-126.69(10)	P(2)-Ir(1)-C(1)-C(6)	20.05(16)
C(25)-Ir(1)-P(1)-C(7)	57.42(10)	P(1)-Ir(1)-C(1)-C(6)	-157.69(18)
P(2)-Ir(1)-P(1)-C(7)	-38.63(10)	C(6)-C(1)-C(2)-C(3)	-1.5(3)
C(37)-Ir(1)-P(1)-C(9)	33.61(11)	Ir(1)-C(1)-C(2)-C(3)	175.9(2)
C(1)-Ir(1)-P(1)-C(9)	-145.36(10)	C(6)-C(1)-C(2)-C(7)	178.8(2)
C(31)-Ir(1)-P(1)-C(9)	120.70(11)	Ir(1)-C(1)-C(2)-C(7)	-3.8(3)
C(25)-Ir(1)-P(1)-C(9)	-55.20(10)	C(1)-C(2)-C(3)-C(4)	0.6(4)
P(2)-Ir(1)-P(1)-C(9)	-151.24(9)	C(7)-C(2)-C(3)-C(4)	-179.7(2)
C(37)-Ir(1)-P(1)-C(13)	-106.13(12)	C(2)-C(3)-C(4)-C(5)	0.8(4)
C(1)-Ir(1)-P(1)-C(13)	74.90(11)	C(3)-C(4)-C(5)-C(6)	-1.2(4)
C(31)-Ir(1)-P(1)-C(13)	-19.04(11)	C(4)-C(5)-C(6)-C(1)	0.3(3)
C(25)-Ir(1)-P(1)-C(13)	165.07(11)	C(4)-C(5)-C(6)-C(8)	-176.3(2)
P(2)-Ir(1)-P(1)-C(13)	69.02(10)	C(2)-C(1)-C(6)-C(5)	1.0(3)
C(37)-Ir(1)-P(2)-C(8)	152.26(10)	Ir(1)-C(1)-C(6)-C(5)	-176.32(16)
C(1)-Ir(1)-P(2)-C(8)	-28.80(9)	C(2)-C(1)-C(6)-C(8)	177.7(2)
C(31)-Ir(1)-P(2)-C(8)	64.60(10)	Ir(1)-C(1)-C(6)-C(8)	0.4(3)
C(25)-Ir(1)-P(2)-C(8)	-119.52(9)	C(3)-C(2)-C(7)-P(1)	151.7(2)
P(1)-Ir(1)-P(2)-C(8)	-22.93(9)	C(1)-C(2)-C(7)-P(1)	-28.6(3)
C(37)-Ir(1)-P(2)-C(21)	36.41(12)	C(9)-P(1)-C(7)-C(2)	163.47(16)
C(1)-Ir(1)-P(2)-C(21)	-144.65(10)	C(13)-P(1)-C(7)-C(2)	-84.95(17)
C(31)-Ir(1)-P(2)-C(21)	-51.25(11)	Ir(1)-P(1)-C(7)-C(2)	40.31(16)
C(25)-Ir(1)-P(2)-C(21)	124.62(10)	C(5)-C(6)-C(8)-P(2)	148.36(18)
P(1)-Ir(1)-P(2)-C(21)	-138.79(9)	C(1)-C(6)-C(8)-P(2)	-28.4(2)
C(37)-Ir(1)-P(2)-C(17)	-99.57(11)	C(21)-P(2)-C(8)-C(6)	160.93(14)
C(1)-Ir(1)-P(2)-C(17)	79.37(11)	C(17)-P(2)-C(8)-C(6)	-88.54(15)
C(31)-Ir(1)-P(2)-C(17)	172.77(11)	Ir(1)-P(2)-C(8)-C(6)	37.14(15)
C(25)-Ir(1)-P(2)-C(17)	-11.36(11)	C(7)-P(1)-C(9)-C(11)	160.51(18)
P(1)-Ir(1)-P(2)-C(17)	85.24(10)	C(13)-P(1)-C(9)-C(11)	53.9(2)
C(31)-Ir(1)-C(1)-C(2)	112.53(18)	Ir(1)-P(1)-C(9)-C(11)	-91.27(18)
C(25)-Ir(1)-C(1)-C(2)	-67.51(19)	C(7)-P(1)-C(9)-C(12)	-82.71(18)
P(2)-Ir(1)-C(1)-C(2)	-157.21(19)	C(13)-P(1)-C(9)-C(12)	170.71(17)
P(1)-Ir(1)-C(1)-C(2)	25.05(17)	Ir(1)-P(1)-C(9)-C(12)	25.5(2)

C(7)-P(1)-C(9)-C(10)	35.0(3)	C(1)-Ir(1)-C(25)-C(26)	8.0(2)
C(13)-P(1)-C(9)-C(10)	-71.5(2)	P(2)-Ir(1)-C(25)-C(26)	87.13(19)
Ir(1)-P(1)-C(9)-C(10)	143.3(2)	P(1)-Ir(1)-C(25)-C(26)	-70.76(19)
C(7)-P(1)-C(13)-C(15)	167.84(17)	C(37)-Ir(1)-C(25)-C(30)	7.85(19)
C(9)-P(1)-C(13)-C(15)	-82.03(19)	C(1)-Ir(1)-C(25)-C(30)	-171.11(17)
Ir(1)-P(1)-C(13)-C(15)	61.69(19)	P(2)-Ir(1)-C(25)-C(30)	-91.94(17)
C(7)-P(1)-C(13)-C(16)	46.77(18)	P(1)-Ir(1)-C(25)-C(30)	110.17(17)
C(9)-P(1)-C(13)-C(16)	156.90(16)	C(30)-C(25)-C(26)-C(27)	1.4(3)
Ir(1)-P(1)-C(13)-C(16)	-59.38(18)	Ir(1)-C(25)-C(26)-C(27)	-177.7(2)
C(7)-P(1)-C(13)-C(14)	-69.78(18)	C(25)-C(26)-C(27)-C(28)	-2.3(4)
C(9)-P(1)-C(13)-C(14)	40.36(19)	C(26)-C(27)-C(28)-C(29)	1.1(4)
Ir(1)-P(1)-C(13)-C(14)	-175.93(13)	C(27)-C(28)-C(29)-C(30)	0.6(4)
C(8)-P(2)-C(17)-C(19)	166.50(16)	C(28)-C(29)-C(30)-C(25)	-1.4(4)
C(21)-P(2)-C(17)-C(19)	-81.77(17)	C(26)-C(25)-C(30)-C(29)	0.4(3)
Ir(1)-P(2)-C(17)-C(19)	58.69(18)	Ir(1)-C(25)-C(30)-C(29)	179.56(17)
C(8)-P(2)-C(17)-C(20)	44.92(16)	C(37)-Ir(1)-C(31)-C(32)	-162.4(2)
C(21)-P(2)-C(17)-C(20)	156.65(15)	C(1)-Ir(1)-C(31)-C(32)	16.6(2)
Ir(1)-P(2)-C(17)-C(20)	-62.89(17)	P(2)-Ir(1)-C(31)-C(32)	-62.6(2)
C(8)-P(2)-C(17)-C(18)	-70.79(18)	P(1)-Ir(1)-C(31)-C(32)	95.1(2)
C(21)-P(2)-C(17)-C(18)	40.95(19)	C(37)-Ir(1)-C(31)-C(36)	14.8(2)
Ir(1)-P(2)-C(17)-C(18)	-178.59(13)	C(1)-Ir(1)-C(31)-C(36)	-166.19(19)
C(8)-P(2)-C(21)-C(24)	-86.0(2)	P(2)-Ir(1)-C(31)-C(36)	114.60(18)
C(17)-P(2)-C(21)-C(24)	167.8(2)	P(1)-Ir(1)-C(31)-C(36)	-87.63(19)
Ir(1)-P(2)-C(21)-C(24)	25.3(2)	C(36)-C(31)-C(32)-C(33)	-3.6(3)
C(8)-P(2)-C(21)-C(23)	158.27(16)	Ir(1)-C(31)-C(32)-C(33)	173.73(18)
C(17)-P(2)-C(21)-C(23)	52.01(18)	C(31)-C(32)-C(33)-C(34)	1.2(4)
Ir(1)-P(2)-C(21)-C(23)	-90.47(16)	C(32)-C(33)-C(34)-C(35)	1.7(4)
C(8)-P(2)-C(21)-C(22)	33.4(2)	C(33)-C(34)-C(35)-C(36)	-1.7(4)
C(17)-P(2)-C(21)-C(22)	-72.9(2)	C(34)-C(35)-C(36)-C(31)	-1.0(4)
Ir(1)-P(2)-C(21)-C(22)	144.63(18)	C(32)-C(31)-C(36)-C(35)	3.6(3)
C(37)-Ir(1)-C(25)-C(26)	-173.1(2)	Ir(1)-C(31)-C(36)-C(35)	-173.98(18)

VI. Structural Data for (PCP)Ir(CO)(CH=CHPh)(Ph)

Figure S-6 : ORTEP Diagram of **(PCP)Ir(CO)(CH=CHPh)(Ph)**

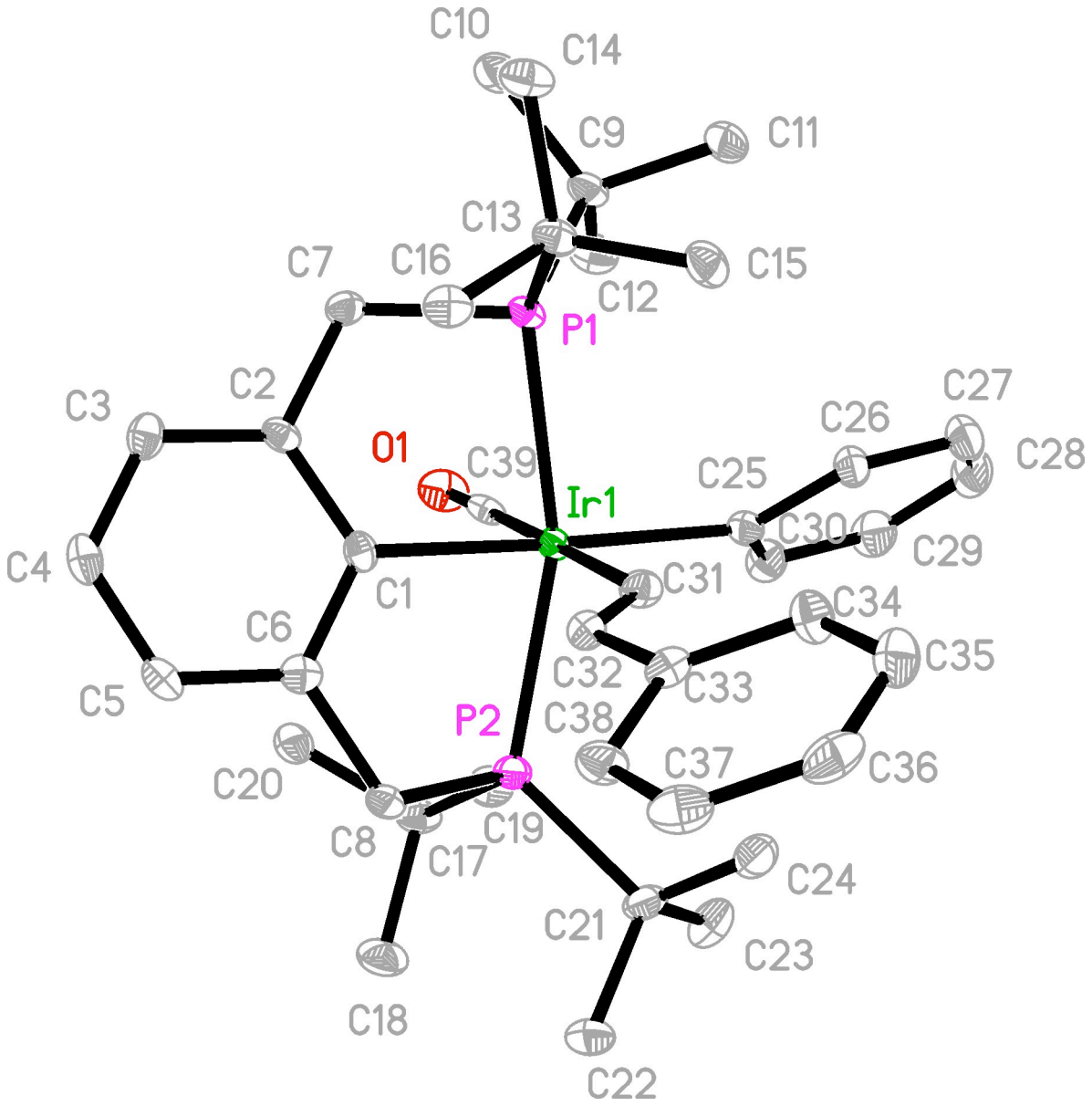

Table S22. Crystal data and structure refinement for **(PCP)Ir(CO)(CH=CHPh)(Ph)**.

Identification code	ircovph	
Empirical formula	C39 H55 Ir O P2	
Formula weight	793.97	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 11.7237(10) Å	α= 90°.
	b = 20.4723(18) Å	β= 90°.
	c = 29.491(3) Å	γ = 90°.
Volume	7078.3(11) $Å^3$	
Z	8	
Density (calculated)	1.490 Mg/m^3	
Absorption coefficient	3.892 mm^{-1}	
F(000)	3232	
Crystal size	0.28 x 0.10 x 0.05 mm^3	
Theta range for data collection	1.99 to 28.34°.	
Index ranges	-15<=h<=15, 0<=k<=27, 0<=l<=39	
Reflections collected	16750	
Independent reflections	8802 [R(int) = 0.0278]	
Completeness to theta = 28.34°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9999 and 0.6118	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8802 / 0 / 400	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0385, wR2 = 0.1010	
R indices (all data)	R1 = 0.0506, wR2 = 0.1076	
Largest diff. peak and hole	2.847 and -2.500 $e.Å^{-3}$	

Table S23. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(PCP)Ir(CO)(CH=CHPh)(Ph)**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	1851(1)	1323(1)	1135(1)	10(1)
P(1)	549(1)	1805(1)	602(1)	11(1)
P(2)	3313(1)	645(1)	1443(1)	13(1)
C(1)	2380(4)	841(2)	539(2)	12(1)
C(2)	2149(4)	1111(2)	114(2)	13(1)
C(3)	2521(4)	818(2)	-284(2)	15(1)
C(4)	3176(4)	249(2)	-260(2)	17(1)
C(5)	3441(4)	-22(2)	157(2)	16(1)
C(6)	3028(4)	265(2)	558(2)	14(1)
C(7)	1471(4)	1743(2)	97(2)	14(1)
C(8)	3333(4)	-17(2)	1017(2)	16(1)
C(9)	178(4)	2710(2)	645(2)	16(1)
C(10)	35(4)	3029(2)	174(2)	20(1)
C(11)	-911(4)	2818(2)	924(2)	22(1)
C(12)	1135(4)	3084(2)	886(2)	21(1)
C(13)	-782(4)	1353(2)	419(2)	15(1)
C(14)	-1500(4)	1717(2)	64(2)	21(1)
C(15)	-1551(4)	1194(2)	825(2)	19(1)
C(16)	-416(4)	710(2)	187(2)	16(1)
C(17)	4835(4)	965(2)	1395(2)	17(1)
C(18)	5742(4)	463(3)	1545(2)	24(1)
C(19)	5034(4)	1591(2)	1672(2)	21(1)
C(20)	5091(4)	1109(2)	891(2)	18(1)
C(21)	3162(4)	230(2)	2021(2)	19(1)
C(22)	3748(5)	-447(2)	2029(2)	24(1)
C(23)	3645(5)	674(3)	2393(2)	26(1)
C(24)	1901(4)	124(3)	2133(2)	22(1)
C(25)	1231(4)	1828(2)	1729(2)	15(1)
C(26)	71(4)	1847(2)	1849(2)	19(1)
C(27)	-352(5)	2261(2)	2187(2)	24(1)
C(28)	378(5)	2672(2)	2423(2)	28(1)

C(29)	1529(5)	2659(2)	2324(2)	24(1)
C(30)	1938(4)	2244(2)	1987(2)	21(1)
C(31)	725(4)	552(2)	1279(2)	15(1)
C(32)	582(4)	-39(2)	1094(2)	15(1)
C(33)	-238(4)	-545(2)	1242(2)	14(1)
C(34)	-1217(4)	-409(2)	1491(2)	19(1)
C(35)	-1956(4)	-904(2)	1626(2)	22(1)
C(36)	-1727(4)	-1548(2)	1511(2)	23(1)
C(37)	-767(5)	-1691(2)	1261(2)	24(1)
C(38)	-26(4)	-1198(2)	1129(2)	19(1)
O(1)	3502(3)	2427(2)	935(1)	22(1)
C(39)	2869(4)	2018(2)	1020(2)	15(1)

Table S24. Bond lengths [Å] and angles [°] for **(PCP)Ir(CO)(CH=CHPh)(Ph)**.

Ir(1)-C(39)	1.887(5)	C(13)-C(14)	1.537(6)
Ir(1)-C(31)	2.101(4)	C(13)-C(16)	1.545(6)
Ir(1)-C(1)	2.107(4)	C(17)-C(19)	1.537(7)
Ir(1)-C(25)	2.160(5)	C(17)-C(18)	1.543(6)
Ir(1)-P(2)	2.3850(11)	C(17)-C(20)	1.545(7)
Ir(1)-P(1)	2.4040(11)	C(21)-C(24)	1.531(7)
P(1)-C(7)	1.843(5)	C(21)-C(23)	1.532(7)
P(1)-C(13)	1.892(5)	C(21)-C(22)	1.548(7)
P(1)-C(9)	1.907(4)	C(25)-C(26)	1.405(7)
P(2)-C(8)	1.848(5)	C(25)-C(30)	1.411(7)
P(2)-C(17)	1.906(5)	C(26)-C(27)	1.399(7)
P(2)-C(21)	1.914(5)	C(27)-C(28)	1.387(8)
C(1)-C(2)	1.396(6)	C(28)-C(29)	1.382(8)
C(1)-C(6)	1.404(6)	C(29)-C(30)	1.394(7)
C(2)-C(3)	1.389(6)	C(31)-C(32)	1.339(6)
C(2)-C(7)	1.519(6)	C(32)-C(33)	1.479(6)
C(3)-C(4)	1.398(6)	C(33)-C(34)	1.390(6)
C(4)-C(5)	1.385(7)	C(33)-C(38)	1.400(6)
C(5)-C(6)	1.406(6)	C(34)-C(35)	1.391(7)
C(6)-C(8)	1.517(6)	C(35)-C(36)	1.387(7)
C(9)-C(12)	1.533(7)	C(36)-C(37)	1.376(8)
C(9)-C(11)	1.533(7)	C(37)-C(38)	1.389(7)
C(9)-C(10)	1.546(6)	O(1)-C(39)	1.148(6)
C(13)-C(15)	1.532(7)		

C(39)-Ir(1)-C(31)	178.66(19)	C(25)-Ir(1)-P(2)	102.24(12)
C(39)-Ir(1)-C(1)	90.98(18)	C(39)-Ir(1)-P(1)	88.54(14)
C(31)-Ir(1)-C(1)	90.11(17)	C(31)-Ir(1)-P(1)	92.40(13)
C(39)-Ir(1)-C(25)	89.87(18)	C(1)-Ir(1)-P(1)	80.41(12)
C(31)-Ir(1)-C(25)	89.08(18)	C(25)-Ir(1)-P(1)	96.88(12)
C(1)-Ir(1)-C(25)	177.14(17)	P(2)-Ir(1)-P(1)	160.81(4)
C(39)-Ir(1)-P(2)	93.04(14)	C(7)-P(1)-C(13)	102.7(2)
C(31)-Ir(1)-P(2)	86.39(13)	C(7)-P(1)-C(9)	104.8(2)
C(1)-Ir(1)-P(2)	80.44(12)	C(13)-P(1)-C(9)	107.8(2)

C(7)-P(1)-Ir(1)	97.30(15)	C(14)-C(13)-P(1)	114.1(3)
C(13)-P(1)-Ir(1)	120.60(14)	C(16)-C(13)-P(1)	108.3(3)
C(9)-P(1)-Ir(1)	119.97(15)	C(19)-C(17)-C(18)	107.4(4)
C(8)-P(2)-C(17)	100.9(2)	C(19)-C(17)-C(20)	108.7(4)
C(8)-P(2)-C(21)	106.3(2)	C(18)-C(17)-C(20)	105.7(4)
C(17)-P(2)-C(21)	107.7(2)	C(19)-C(17)-P(2)	112.9(3)
C(8)-P(2)-Ir(1)	100.24(15)	C(18)-C(17)-P(2)	113.3(3)
C(17)-P(2)-Ir(1)	116.40(14)	C(20)-C(17)-P(2)	108.6(3)
C(21)-P(2)-Ir(1)	122.10(16)	C(24)-C(21)-C(23)	106.7(4)
C(2)-C(1)-C(6)	118.2(4)	C(24)-C(21)-C(22)	107.4(4)
C(2)-C(1)-Ir(1)	120.4(3)	C(23)-C(21)-C(22)	111.0(4)
C(6)-C(1)-Ir(1)	121.3(3)	C(24)-C(21)-P(2)	110.1(3)
C(3)-C(2)-C(1)	121.8(4)	C(23)-C(21)-P(2)	109.9(3)
C(3)-C(2)-C(7)	120.3(4)	C(22)-C(21)-P(2)	111.7(3)
C(1)-C(2)-C(7)	117.9(4)	C(26)-C(25)-C(30)	114.6(4)
C(2)-C(3)-C(4)	119.4(4)	C(26)-C(25)-Ir(1)	122.9(3)
C(5)-C(4)-C(3)	120.1(4)	C(30)-C(25)-Ir(1)	121.9(4)
C(4)-C(5)-C(6)	120.1(4)	C(27)-C(26)-C(25)	122.6(5)
C(1)-C(6)-C(5)	120.4(4)	C(28)-C(27)-C(26)	120.5(5)
C(1)-C(6)-C(8)	118.9(4)	C(29)-C(28)-C(27)	119.0(5)
C(5)-C(6)-C(8)	120.7(4)	C(28)-C(29)-C(30)	119.8(5)
C(2)-C(7)-P(1)	109.8(3)	C(29)-C(30)-C(25)	123.5(5)
C(6)-C(8)-P(2)	108.9(3)	C(32)-C(31)-Ir(1)	132.5(4)
C(12)-C(9)-C(11)	106.8(4)	C(31)-C(32)-C(33)	126.4(4)
C(12)-C(9)-C(10)	106.6(4)	C(34)-C(33)-C(38)	117.6(4)
C(11)-C(9)-C(10)	109.3(4)	C(34)-C(33)-C(32)	123.5(4)
C(12)-C(9)-P(1)	110.4(3)	C(38)-C(33)-C(32)	118.8(4)
C(11)-C(9)-P(1)	111.4(3)	C(33)-C(34)-C(35)	121.3(4)
C(10)-C(9)-P(1)	112.0(3)	C(36)-C(35)-C(34)	120.1(5)
C(15)-C(13)-C(14)	108.2(4)	C(37)-C(36)-C(35)	119.5(4)
C(15)-C(13)-C(16)	109.1(4)	C(36)-C(37)-C(38)	120.5(5)
C(14)-C(13)-C(16)	105.3(4)	C(37)-C(38)-C(33)	121.1(5)
C(15)-C(13)-P(1)	111.6(3)	O(1)-C(39)-Ir(1)	177.3(4)

Table S25. Torsion angles [°] for **(PCP)Ir(CO)(CH=CHPh)(Ph)**.

C(39)-Ir(1)-P(1)-C(7)	62.3(2)	P(1)-Ir(1)-C(1)-C(2)	22.0(3)
C(31)-Ir(1)-P(1)-C(7)	-118.62(19)	C(39)-Ir(1)-C(1)-C(6)	109.8(4)
C(1)-Ir(1)-P(1)-C(7)	-28.91(18)	C(31)-Ir(1)-C(1)-C(6)	-69.5(4)
C(25)-Ir(1)-P(1)-C(7)	152.03(18)	C(25)-Ir(1)-C(1)-C(6)	-143(3)
P(2)-Ir(1)-P(1)-C(7)	-32.71(19)	P(2)-Ir(1)-C(1)-C(6)	16.9(3)
C(39)-Ir(1)-P(1)-C(13)	171.9(2)	P(1)-Ir(1)-C(1)-C(6)	-161.9(4)
C(31)-Ir(1)-P(1)-C(13)	-9.1(2)	C(6)-C(1)-C(2)-C(3)	1.3(6)
C(1)-Ir(1)-P(1)-C(13)	80.6(2)	Ir(1)-C(1)-C(2)-C(3)	177.6(3)
C(25)-Ir(1)-P(1)-C(13)	-98.5(2)	C(6)-C(1)-C(2)-C(7)	-178.6(4)
P(2)-Ir(1)-P(1)-C(13)	76.8(2)	Ir(1)-C(1)-C(2)-C(7)	-2.3(5)
C(39)-Ir(1)-P(1)-C(9)	-49.4(2)	C(1)-C(2)-C(3)-C(4)	-2.0(7)
C(31)-Ir(1)-P(1)-C(9)	129.6(2)	C(7)-C(2)-C(3)-C(4)	177.9(4)
C(1)-Ir(1)-P(1)-C(9)	-140.7(2)	C(2)-C(3)-C(4)-C(5)	0.5(7)
C(25)-Ir(1)-P(1)-C(9)	40.2(2)	C(3)-C(4)-C(5)-C(6)	1.6(7)
P(2)-Ir(1)-P(1)-C(9)	-144.50(19)	C(2)-C(1)-C(6)-C(5)	0.8(6)
C(39)-Ir(1)-P(2)-C(8)	-114.9(2)	Ir(1)-C(1)-C(6)-C(5)	-175.4(3)
C(31)-Ir(1)-P(2)-C(8)	66.3(2)	C(2)-C(1)-C(6)-C(8)	177.2(4)
C(1)-Ir(1)-P(2)-C(8)	-24.40(19)	Ir(1)-C(1)-C(6)-C(8)	1.0(6)
C(25)-Ir(1)-P(2)-C(8)	154.6(2)	C(4)-C(5)-C(6)-C(1)	-2.3(7)
P(1)-Ir(1)-P(2)-C(8)	-20.6(2)	C(4)-C(5)-C(6)-C(8)	-178.6(4)
C(39)-Ir(1)-P(2)-C(17)	-7.1(2)	C(3)-C(2)-C(7)-P(1)	153.3(4)
C(31)-Ir(1)-P(2)-C(17)	174.1(2)	C(1)-C(2)-C(7)-P(1)	-26.8(5)
C(1)-Ir(1)-P(2)-C(17)	83.3(2)	C(13)-P(1)-C(7)-C(2)	-86.9(3)
C(25)-Ir(1)-P(2)-C(17)	-97.7(2)	C(9)-P(1)-C(7)-C(2)	160.6(3)
P(1)-Ir(1)-P(2)-C(17)	87.1(2)	Ir(1)-P(1)-C(7)-C(2)	36.9(3)
C(39)-Ir(1)-P(2)-C(21)	128.4(2)	C(1)-C(6)-C(8)-P(2)	-24.6(5)
C(31)-Ir(1)-P(2)-C(21)	-50.4(2)	C(5)-C(6)-C(8)-P(2)	151.8(4)
C(1)-Ir(1)-P(2)-C(21)	-141.2(2)	C(17)-P(2)-C(8)-C(6)	-87.7(3)
C(25)-Ir(1)-P(2)-C(21)	37.8(2)	C(21)-P(2)-C(8)-C(6)	160.0(3)
P(1)-Ir(1)-P(2)-C(21)	-137.4(2)	Ir(1)-P(2)-C(8)-C(6)	32.0(3)
C(39)-Ir(1)-C(1)-C(2)	-66.4(4)	C(7)-P(1)-C(9)-C(12)	-83.0(4)
C(31)-Ir(1)-C(1)-C(2)	114.4(4)	C(13)-P(1)-C(9)-C(12)	168.0(3)
C(25)-Ir(1)-C(1)-C(2)	41(3)	Ir(1)-P(1)-C(9)-C(12)	24.7(4)
P(2)-Ir(1)-C(1)-C(2)	-159.3(4)	C(7)-P(1)-C(9)-C(11)	158.4(3)

C(13)-P(1)-C(9)-C(11)	49.5(4)
Ir(1)-P(1)-C(9)-C(11)	-93.9(3)
C(7)-P(1)-C(9)-C(10)	35.6(4)
C(13)-P(1)-C(9)-C(10)	-73.4(4)
Ir(1)-P(1)-C(9)-C(10)	143.3(3)
C(7)-P(1)-C(13)-C(15)	165.7(3)
C(9)-P(1)-C(13)-C(15)	-84.0(3)
Ir(1)-P(1)-C(13)-C(15)	59.1(3)
C(7)-P(1)-C(13)-C(14)	-71.3(4)
C(9)-P(1)-C(13)-C(14)	39.0(4)
Ir(1)-P(1)-C(13)-C(14)	-177.9(3)
C(7)-P(1)-C(13)-C(16)	45.5(3)
C(9)-P(1)-C(13)-C(16)	155.9(3)
Ir(1)-P(1)-C(13)-C(16)	-61.0(3)
C(8)-P(2)-C(17)-C(19)	172.4(3)
C(21)-P(2)-C(17)-C(19)	-76.3(4)
Ir(1)-P(2)-C(17)-C(19)	65.1(4)
C(8)-P(2)-C(17)-C(18)	-65.3(4)
C(21)-P(2)-C(17)-C(18)	46.0(4)
Ir(1)-P(2)-C(17)-C(18)	-172.6(3)
C(8)-P(2)-C(17)-C(20)	51.8(3)
C(21)-P(2)-C(17)-C(20)	163.0(3)
Ir(1)-P(2)-C(17)-C(20)	-55.5(3)
C(8)-P(2)-C(21)-C(24)	-87.3(4)
C(17)-P(2)-C(21)-C(24)	165.2(3)
Ir(1)-P(2)-C(21)-C(24)	26.4(4)
C(8)-P(2)-C(21)-C(23)	155.4(4)
C(17)-P(2)-C(21)-C(23)	47.9(4)
Ir(1)-P(2)-C(21)-C(23)	-90.8(4)
C(8)-P(2)-C(21)-C(22)	31.9(4)
C(17)-P(2)-C(21)-C(22)	-75.7(4)
Ir(1)-P(2)-C(21)-C(22)	145.6(3)
C(39)-Ir(1)-C(25)-C(26)	139.5(4)
C(31)-Ir(1)-C(25)-C(26)	-41.4(4)
C(1)-Ir(1)-C(25)-C(26)	32(3)
P(2)-Ir(1)-C(25)-C(26)	-127.5(4)
P(1)-Ir(1)-C(25)-C(26)	50.9(4)
C(39)-Ir(1)-C(25)-C(30)	-31.0(4)
C(31)-Ir(1)-C(25)-C(30)	148.2(4)
C(1)-Ir(1)-C(25)-C(30)	-138(3)
P(2)-Ir(1)-C(25)-C(30)	62.1(4)
P(1)-Ir(1)-C(25)-C(30)	-119.5(4)
C(30)-C(25)-C(26)-C(27)	2.2(7)
Ir(1)-C(25)-C(26)-C(27)	-168.9(4)
C(25)-C(26)-C(27)-C(28)	-0.8(8)
C(26)-C(27)-C(28)-C(29)	-0.8(8)
C(27)-C(28)-C(29)-C(30)	0.9(8)
C(28)-C(29)-C(30)-C(25)	0.6(8)
C(26)-C(25)-C(30)-C(29)	-2.1(7)
Ir(1)-C(25)-C(30)-C(29)	169.1(4)
C(39)-Ir(1)-C(31)-C(32)	-136(8)
C(1)-Ir(1)-C(31)-C(32)	9.3(5)
C(25)-Ir(1)-C(31)-C(32)	-173.5(5)
P(2)-Ir(1)-C(31)-C(32)	-71.2(5)
P(1)-Ir(1)-C(31)-C(32)	89.7(5)
Ir(1)-C(31)-C(32)-C(33)	178.1(3)
C(31)-C(32)-C(33)-C(34)	22.4(8)
C(31)-C(32)-C(33)-C(38)	-157.7(5)
C(38)-C(33)-C(34)-C(35)	0.7(7)
C(32)-C(33)-C(34)-C(35)	-179.3(5)
C(33)-C(34)-C(35)-C(36)	-0.5(8)
C(34)-C(35)-C(36)-C(37)	-0.1(8)
C(35)-C(36)-C(37)-C(38)	0.6(8)
C(36)-C(37)-C(38)-C(33)	-0.4(8)
C(34)-C(33)-C(38)-C(37)	-0.2(7)
C(32)-C(33)-C(38)-C(37)	179.8(4)
C(31)-Ir(1)-C(39)-O(1)	143(9)
C(1)-Ir(1)-C(39)-O(1)	-2(9)
C(25)-Ir(1)-C(39)-O(1)	-179(100)
P(2)-Ir(1)-C(39)-O(1)	78(9)
P(1)-Ir(1)-C(39)-O(1)	-82(9)

VII. Structural Data for (PCP)Ir(Me)(CO)(CH=CHPh)

Figure S-7 : ORTEP Diagram of **(PCP)Ir(Me)(CO)(CH=CHPh)**

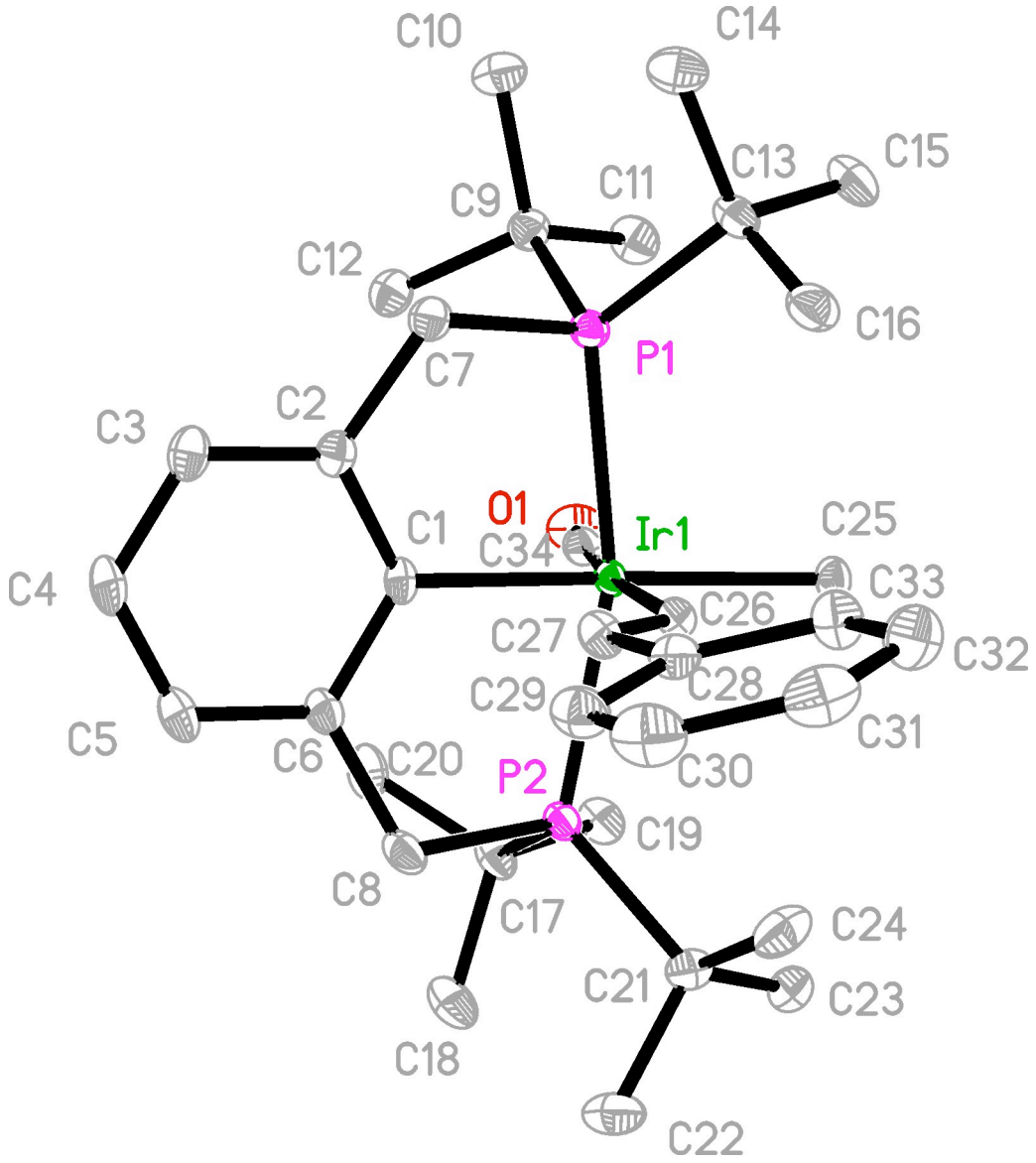

Table S26. Crystal data and structure refinement for **(PCP)Ir(Me)(CO)(CH=CHPh)**.

Identification code	irvinkt	
Empirical formula	C34 H53 Ir O P2	
Formula weight	731.90	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.3065(6) Å	α= 90°.
	b = 16.6734(9) Å	β= 93.327(1)°.
	c = 17.1406(9) Å	γ = 90°.
Volume	3225.9(3) $Å^3$	
Z	4	
Density (calculated)	1.507 Mg/m^3	
Absorption coefficient	4.263 mm^{-1}	
F(000)	1488	
Crystal size	0.36 x 0.23 x 0.055 mm^3	
Theta range for data collection	1.71 to 30.51°.	
Index ranges	-16<=h<=15, -23<=k<=23, -24<=l<=24	
Reflections collected	38989	
Independent reflections	9836 [R(int) = 0.0325]	
Completeness to theta = 30.51°	99.9 %	
Absorption correction	Integration	
Max. and min. transmission	0.7938 and 0.3484	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9836 / 0 / 357	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0250, wR2 = 0.0626	
R indices (all data)	R1 = 0.0289, wR2 = 0.0650	
Largest diff. peak and hole	4.069 and -1.203 e.$Å^{-3}$	

Table S27. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(PCP)Ir(Me)(CO)(CH=CHPh)**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	8514(1)	5994(1)	2345(1)	11(1)
P(1)	7027(1)	5648(1)	3211(1)	14(1)
P(2)	9910(1)	6715(1)	1633(1)	13(1)
C(1)	8099(2)	7164(1)	2721(1)	14(1)
C(2)	7163(2)	7301(1)	3214(1)	16(1)
C(3)	6899(2)	8073(1)	3472(1)	19(1)
C(4)	7529(2)	8729(1)	3212(2)	20(1)
C(5)	8362(2)	8618(1)	2663(2)	20(1)
C(6)	8626(2)	7845(1)	2406(1)	16(1)
C(7)	6328(2)	6622(1)	3372(1)	17(1)
C(8)	9357(2)	7748(1)	1699(2)	18(1)
C(9)	7623(2)	5353(1)	4231(1)	17(1)
C(10)	6665(2)	5222(2)	4818(2)	23(1)
C(11)	8366(2)	4575(2)	4218(2)	22(1)
C(12)	8369(2)	6069(2)	4558(2)	20(1)
C(13)	5745(2)	4960(1)	2918(1)	18(1)
C(14)	4651(2)	5105(2)	3393(2)	24(1)
C(15)	6132(2)	4079(1)	2995(2)	23(1)
C(16)	5358(2)	5100(2)	2058(2)	22(1)
C(17)	11436(2)	6766(1)	2142(2)	19(1)
C(18)	12317(2)	7303(2)	1725(2)	26(1)
C(19)	11990(2)	5922(1)	2223(2)	21(1)
C(20)	11300(2)	7165(2)	2942(2)	23(1)
C(21)	10109(2)	6553(2)	559(1)	19(1)
C(22)	10535(3)	7316(2)	149(2)	27(1)
C(23)	10984(2)	5867(2)	435(2)	22(1)
C(24)	8918(2)	6320(2)	150(2)	26(1)
C(25)	8700(2)	4811(1)	1805(1)	16(1)
C(26)	7194(2)	6245(1)	1464(1)	14(1)
C(27)	6487(2)	6880(1)	1306(1)	16(1)

C(28)	5547(2)	6916(1)	674(1)	16(1)
C(29)	5054(2)	7660(2)	453(2)	21(1)
C(30)	4145(2)	7717(2)	-128(2)	26(1)
C(31)	3690(2)	7030(2)	-491(2)	26(1)
C(32)	4159(2)	6290(2)	-276(2)	24(1)
C(33)	5071(2)	6233(2)	297(2)	20(1)
C(34)	9718(2)	5635(1)	3068(1)	16(1)
O(1)	10449(2)	5362(1)	3481(1)	25(1)

Table S28. Bond lengths [Å] and angles [°] for **(PCP)Ir(Me)(CO)(CH=CHPh)**.

Ir(1)-C(34)	1.884(2)	C(9)-C(12)	1.547(3)
Ir(1)-C(26)	2.103(2)	C(9)-C(11)	1.546(3)
Ir(1)-C(1)	2.115(2)	C(13)-C(16)	1.531(3)
Ir(1)-C(25)	2.194(2)	C(13)-C(15)	1.535(3)
Ir(1)-P(1)	2.3779(6)	C(13)-C(14)	1.539(3)
Ir(1)-P(2)	2.3769(6)	C(17)-C(20)	1.540(4)
P(1)-C(7)	1.833(2)	C(17)-C(19)	1.543(3)
P(1)-C(13)	1.894(2)	C(17)-C(18)	1.544(4)
P(1)-C(9)	1.902(2)	C(21)-C(24)	1.531(4)
P(2)-C(8)	1.837(2)	C(21)-C(23)	1.536(4)
P(2)-C(21)	1.887(2)	C(21)-C(22)	1.543(4)
P(2)-C(17)	1.890(2)	C(26)-C(27)	1.344(3)
C(1)-C(6)	1.405(3)	C(27)-C(28)	1.474(3)
C(1)-C(2)	1.411(3)	C(28)-C(29)	1.402(3)
C(2)-C(3)	1.399(3)	C(28)-C(33)	1.403(3)
C(2)-C(7)	1.508(3)	C(29)-C(30)	1.391(4)
C(3)-C(4)	1.392(4)	C(30)-C(31)	1.389(4)
C(4)-C(5)	1.383(4)	C(31)-C(32)	1.384(4)
C(5)-C(6)	1.399(3)	C(32)-C(33)	1.386(3)
C(6)-C(8)	1.514(3)	C(34)-O(1)	1.151(3)
C(9)-C(10)	1.537(3)		

C(34)-Ir(1)-C(26)	172.32(9)	C(1)-Ir(1)-P(2)	81.68(7)
C(34)-Ir(1)-C(1)	104.89(9)	C(25)-Ir(1)-P(2)	98.96(6)
C(26)-Ir(1)-C(1)	82.79(9)	P(1)-Ir(1)-P(2)	163.30(2)
C(34)-Ir(1)-C(25)	84.77(9)	C(7)-P(1)-C(13)	104.33(11)
C(26)-Ir(1)-C(25)	87.55(9)	C(7)-P(1)-C(9)	102.90(11)
C(1)-Ir(1)-C(25)	170.32(9)	C(13)-P(1)-C(9)	108.16(11)
C(34)-Ir(1)-P(1)	91.28(7)	C(7)-P(1)-Ir(1)	101.89(8)
C(26)-Ir(1)-P(1)	89.89(6)	C(13)-P(1)-Ir(1)	122.66(8)
C(1)-Ir(1)-P(1)	81.71(7)	C(9)-P(1)-Ir(1)	114.25(8)
C(25)-Ir(1)-P(1)	97.70(6)	C(8)-P(2)-C(21)	104.78(11)
C(34)-Ir(1)-P(2)	91.33(7)	C(8)-P(2)-C(17)	103.55(11)
C(26)-Ir(1)-P(2)	89.72(6)	C(21)-P(2)-C(17)	107.40(11)

C(8)-P(2)-Ir(1)	101.77(8)	C(16)-C(13)-P(1)	109.54(16)
C(21)-P(2)-Ir(1)	123.30(8)	C(15)-C(13)-P(1)	110.34(17)
C(17)-P(2)-Ir(1)	113.64(8)	C(14)-C(13)-P(1)	112.98(17)
C(6)-C(1)-C(2)	116.6(2)	C(20)-C(17)-C(19)	112.0(2)
C(6)-C(1)-Ir(1)	121.49(16)	C(20)-C(17)-C(18)	105.2(2)
C(2)-C(1)-Ir(1)	121.29(16)	C(19)-C(17)-C(18)	107.5(2)
C(3)-C(2)-C(1)	121.3(2)	C(20)-C(17)-P(2)	107.15(17)
C(3)-C(2)-C(7)	119.1(2)	C(19)-C(17)-P(2)	110.85(16)
C(1)-C(2)-C(7)	119.0(2)	C(18)-C(17)-P(2)	114.11(18)
C(4)-C(3)-C(2)	120.0(2)	C(24)-C(21)-C(23)	107.7(2)
C(5)-C(4)-C(3)	119.6(2)	C(24)-C(21)-C(22)	106.9(2)
C(4)-C(5)-C(6)	120.3(2)	C(23)-C(21)-C(22)	109.3(2)
C(5)-C(6)-C(1)	121.4(2)	C(24)-C(21)-P(2)	109.31(17)
C(5)-C(6)-C(8)	119.1(2)	C(23)-C(21)-P(2)	110.84(17)
C(1)-C(6)-C(8)	118.9(2)	C(22)-C(21)-P(2)	112.61(18)
C(2)-C(7)-P(1)	110.99(16)	C(27)-C(26)-Ir(1)	133.63(18)
C(6)-C(8)-P(2)	110.72(16)	C(26)-C(27)-C(28)	125.1(2)
C(10)-C(9)-C(12)	105.3(2)	C(29)-C(28)-C(33)	117.2(2)
C(10)-C(9)-C(11)	107.1(2)	C(29)-C(28)-C(27)	119.7(2)
C(12)-C(9)-C(11)	111.5(2)	C(33)-C(28)-C(27)	123.1(2)
C(10)-C(9)-P(1)	114.41(17)	C(30)-C(29)-C(28)	121.4(2)
C(12)-C(9)-P(1)	106.84(16)	C(29)-C(30)-C(31)	120.2(2)
C(11)-C(9)-P(1)	111.58(16)	C(32)-C(31)-C(30)	119.3(2)
C(16)-C(13)-C(15)	107.0(2)	C(33)-C(32)-C(31)	120.6(3)
C(16)-C(13)-C(14)	107.0(2)	C(32)-C(33)-C(28)	121.4(2)
C(15)-C(13)-C(14)	109.8(2)	O(1)-C(34)-Ir(1)	174.9(2)

Table S29. Torsion angles [°] for **(PCP)Ir(Me)(CO)(CH=CHPh)**.

C(34)-Ir(1)-P(1)-C(7)	119.25(11)	C(34)-Ir(1)-C(1)-C(2)	-94.34(19)
C(26)-Ir(1)-P(1)-C(7)	-68.33(10)	C(26)-Ir(1)-C(1)-C(2)	85.73(19)
C(1)-Ir(1)-P(1)-C(7)	14.40(10)	P(1)-Ir(1)-C(1)-C(2)	-5.21(17)
C(25)-Ir(1)-P(1)-C(7)	-155.85(10)	P(2)-Ir(1)-C(1)-C(2)	176.50(19)
P(2)-Ir(1)-P(1)-C(7)	20.31(11)	C(6)-C(1)-C(2)-C(3)	-9.7(3)
C(34)-Ir(1)-P(1)-C(13)	-124.93(11)	Ir(1)-C(1)-C(2)-C(3)	179.02(17)
C(26)-Ir(1)-P(1)-C(13)	47.48(11)	C(6)-C(1)-C(2)-C(7)	161.7(2)
C(1)-Ir(1)-P(1)-C(13)	130.21(11)	Ir(1)-C(1)-C(2)-C(7)	-9.6(3)
C(25)-Ir(1)-P(1)-C(13)	-40.04(11)	C(1)-C(2)-C(3)-C(4)	3.2(4)
P(2)-Ir(1)-P(1)-C(13)	136.13(10)	C(7)-C(2)-C(3)-C(4)	-168.2(2)
C(34)-Ir(1)-P(1)-C(9)	9.07(11)	C(2)-C(3)-C(4)-C(5)	3.9(4)
C(26)-Ir(1)-P(1)-C(9)	-178.52(10)	C(3)-C(4)-C(5)-C(6)	-4.0(4)
C(1)-Ir(1)-P(1)-C(9)	-95.79(10)	C(4)-C(5)-C(6)-C(1)	-3.0(4)
C(25)-Ir(1)-P(1)-C(9)	93.97(10)	C(4)-C(5)-C(6)-C(8)	168.3(2)
P(2)-Ir(1)-P(1)-C(9)	-89.87(11)	C(2)-C(1)-C(6)-C(5)	9.6(3)
C(34)-Ir(1)-P(2)-C(8)	-119.85(11)	Ir(1)-C(1)-C(6)-C(5)	-179.11(17)
C(26)-Ir(1)-P(2)-C(8)	67.75(10)	C(2)-C(1)-C(6)-C(8)	-161.7(2)
C(1)-Ir(1)-P(2)-C(8)	-15.00(10)	Ir(1)-C(1)-C(6)-C(8)	9.6(3)
C(25)-Ir(1)-P(2)-C(8)	155.23(10)	C(3)-C(2)-C(7)-P(1)	-165.54(18)
P(1)-Ir(1)-P(2)-C(8)	-20.92(12)	C(1)-C(2)-C(7)-P(1)	22.8(3)
C(34)-Ir(1)-P(2)-C(21)	123.48(12)	C(13)-P(1)-C(7)-C(2)	-151.59(16)
C(26)-Ir(1)-P(2)-C(21)	-48.91(11)	C(9)-P(1)-C(7)-C(2)	95.55(17)
C(1)-Ir(1)-P(2)-C(21)	-131.66(11)	Ir(1)-P(1)-C(7)-C(2)	-23.06(17)
C(25)-Ir(1)-P(2)-C(21)	38.57(11)	C(5)-C(6)-C(8)-P(2)	165.09(18)
P(1)-Ir(1)-P(2)-C(21)	-137.58(11)	C(1)-C(6)-C(8)-P(2)	-23.4(3)
C(34)-Ir(1)-P(2)-C(17)	-9.21(11)	C(21)-P(2)-C(8)-C(6)	153.21(17)
C(26)-Ir(1)-P(2)-C(17)	178.39(10)	C(17)-P(2)-C(8)-C(6)	-94.34(18)
C(1)-Ir(1)-P(2)-C(17)	95.64(10)	Ir(1)-P(2)-C(8)-C(6)	23.79(17)
C(25)-Ir(1)-P(2)-C(17)	-94.13(10)	C(7)-P(1)-C(9)-C(10)	63.9(2)
P(1)-Ir(1)-P(2)-C(17)	89.72(11)	C(13)-P(1)-C(9)-C(10)	-46.2(2)
C(34)-Ir(1)-C(1)-C(6)	94.80(19)	Ir(1)-P(1)-C(9)-C(10)	173.43(15)
C(26)-Ir(1)-C(1)-C(6)	-85.13(19)	C(7)-P(1)-C(9)-C(12)	-52.20(18)
P(1)-Ir(1)-C(1)-C(6)	-176.07(18)	C(13)-P(1)-C(9)-C(12)	-162.22(16)
P(2)-Ir(1)-C(1)-C(6)	5.64(17)	Ir(1)-P(1)-C(9)-C(12)	57.37(17)

C(7)-P(1)-C(9)-C(11)	-174.37(17)	Ir(1)-P(2)-C(21)-C(24)	32.2(2)
C(13)-P(1)-C(9)-C(11)	75.61(19)	C(8)-P(2)-C(21)-C(23)	158.47(17)
Ir(1)-P(1)-C(9)-C(11)	-64.80(18)	C(17)-P(2)-C(21)-C(23)	48.8(2)
C(7)-P(1)-C(13)-C(16)	79.01(19)	Ir(1)-P(2)-C(21)-C(23)	-86.33(18)
C(9)-P(1)-C(13)-C(16)	-171.95(17)	C(8)-P(2)-C(21)-C(22)	35.6(2)
Ir(1)-P(1)-C(13)-C(16)	-35.6(2)	C(17)-P(2)-C(21)-C(22)	-74.1(2)
C(7)-P(1)-C(13)-C(15)	-163.45(18)	Ir(1)-P(2)-C(21)-C(22)	150.82(15)
C(9)-P(1)-C(13)-C(15)	-54.4(2)	C(1)-Ir(1)-C(26)-C(27)	-0.9(2)
Ir(1)-P(1)-C(13)-C(15)	81.94(19)	C(25)-Ir(1)-C(26)-C(27)	178.5(2)
C(7)-P(1)-C(13)-C(14)	-40.1(2)	P(1)-Ir(1)-C(26)-C(27)	80.8(2)
C(9)-P(1)-C(13)-C(14)	68.90(19)	P(2)-Ir(1)-C(26)-C(27)	-82.5(2)
Ir(1)-P(1)-C(13)-C(14)	-154.75(14)	Ir(1)-C(26)-C(27)-C(28)	-175.81(18)
C(8)-P(2)-C(17)-C(20)	51.32(19)	C(26)-C(27)-C(28)-C(29)	-165.5(2)
C(21)-P(2)-C(17)-C(20)	161.85(17)	C(26)-C(27)-C(28)-C(33)	17.4(4)
Ir(1)-P(2)-C(17)-C(20)	-58.22(18)	C(33)-C(28)-C(29)-C(30)	-1.1(4)
C(8)-P(2)-C(17)-C(19)	173.77(18)	C(27)-C(28)-C(29)-C(30)	-178.4(2)
C(21)-P(2)-C(17)-C(19)	-75.7(2)	C(28)-C(29)-C(30)-C(31)	1.2(4)
Ir(1)-P(2)-C(17)-C(19)	64.23(19)	C(29)-C(30)-C(31)-C(32)	-0.7(4)
C(8)-P(2)-C(17)-C(18)	-64.7(2)	C(30)-C(31)-C(32)-C(33)	0.1(4)
C(21)-P(2)-C(17)-C(18)	45.8(2)	C(31)-C(32)-C(33)-C(28)	-0.1(4)
Ir(1)-P(2)-C(17)-C(18)	-174.27(16)	C(29)-C(28)-C(33)-C(32)	0.6(4)
C(8)-P(2)-C(21)-C(24)	-83.0(2)	C(27)-C(28)-C(33)-C(32)	177.7(2)
C(17)-P(2)-C(21)-C(24)	167.34(18)		

VIII. Structural Data for (PCP)Ir(CO)(Ph)(CCPh)

Figure S-8 : ORTEP Diagram of **(PCP)Ir(CO)(Ph)(CCPh)**

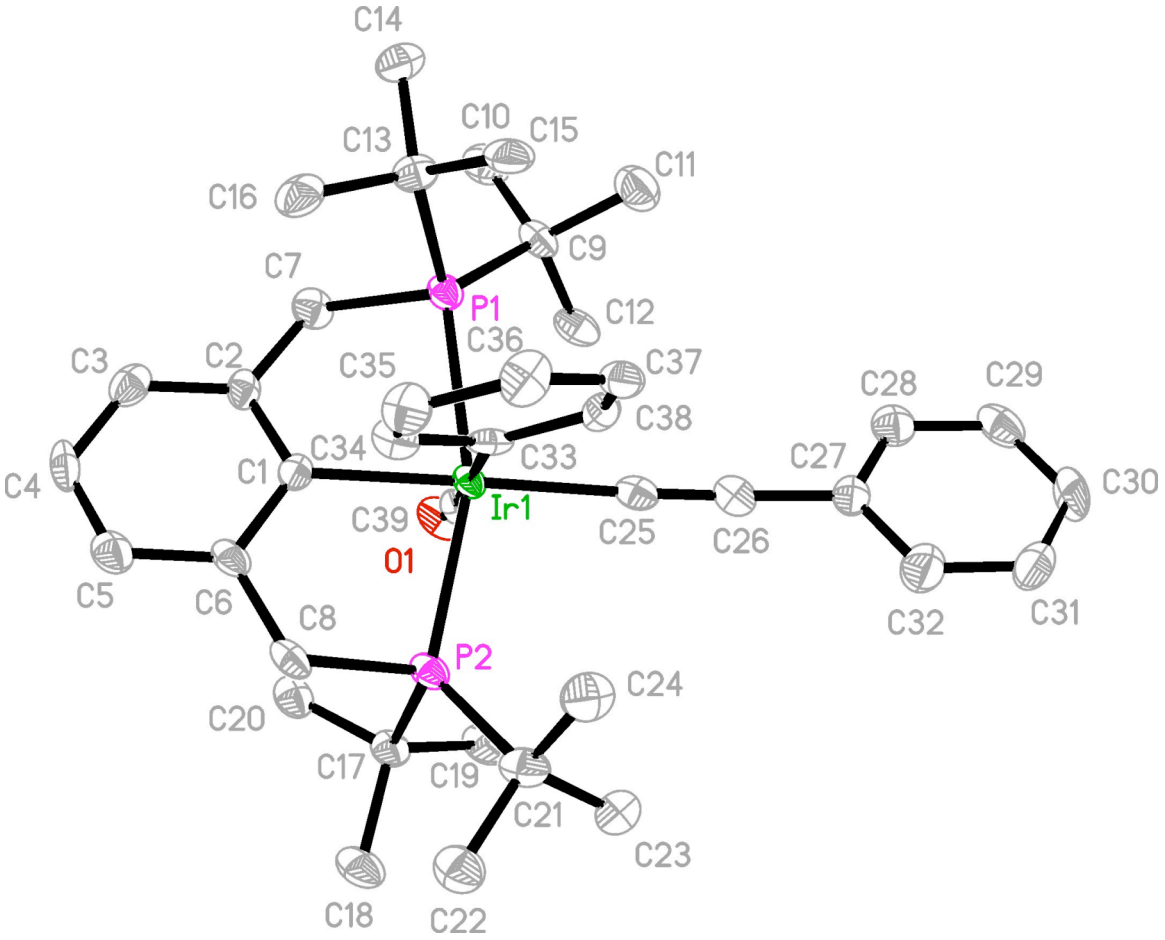

Table S30. Crystal data and structure refinement for **(PCP)Ir(CO)(Ph)(CCPh)**.

Identification code	irccpp	
Empirical formula	C39 H53 Ir O P2	
Formula weight	791.95	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.4658(10) Å	α= 90°.
	b = 24.540(3) Å	β= 96.002(2)°.
	c = 15.3058(16) Å	γ = 90°.
Volume	3535.9(6) $Å^3$	
Z	4	
Density (calculated)	1.488 Mg/m^3	
Absorption coefficient	3.895 mm^{-1}	
F(000)	1608	
Crystal size	0.08 x 0.06 x 0.005 mm^3	
Theta range for data collection	2.13 to 26.45°.	
Index ranges	-11<=h<=11, -26<=k<=30, -19<=l<=19	
Reflections collected	22726	
Independent reflections	7252 [R(int) = 0.0925]	
Completeness to theta = 26.45°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9999 and 0.7695	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7252 / 0 / 400	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.0704	
R indices (all data)	R1 = 0.0922, wR2 = 0.0798	
Largest diff. peak and hole	1.225 and -0.667 e.$Å^{-3}$	

Table S31. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(PCP)Ir(CO)(Ph)(CCPh)**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	-230(1)	1005(1)	2875(1)	17(1)
P(1)	-2022(2)	846(1)	1675(1)	20(1)
P(2)	1110(2)	1428(1)	4090(1)	20(1)
C(1)	-1377(7)	1736(3)	2917(4)	19(2)
C(2)	-2769(7)	1760(3)	2557(4)	20(2)
C(3)	-3566(7)	2230(3)	2621(4)	28(2)
C(4)	-2938(8)	2679(3)	3053(4)	28(2)
C(5)	-1564(8)	2666(3)	3421(4)	28(2)
C(6)	-748(7)	2194(3)	3368(4)	21(2)
C(7)	-3441(7)	1251(3)	2119(4)	26(2)
C(8)	732(7)	2149(3)	3818(4)	23(2)
C(9)	-2709(7)	115(3)	1532(4)	26(2)
C(10)	-4291(7)	74(3)	1225(4)	34(2)
C(11)	-1831(8)	-184(3)	895(4)	35(2)
C(12)	-2494(7)	-193(3)	2397(4)	29(2)
C(13)	-2008(7)	1157(3)	537(4)	23(2)
C(14)	-3314(6)	999(3)	-87(4)	29(2)
C(15)	-676(7)	1010(3)	95(4)	33(2)
C(16)	-2057(7)	1779(3)	620(4)	32(2)
C(17)	330(7)	1346(3)	5188(4)	23(2)
C(18)	1180(7)	1643(3)	5943(4)	33(2)
C(19)	318(8)	730(3)	5421(4)	32(2)
C(20)	-1159(7)	1588(3)	5116(4)	26(2)
C(21)	3093(7)	1352(3)	4305(4)	27(2)
C(22)	3826(7)	1852(3)	4752(4)	33(2)
C(23)	3476(7)	833(3)	4833(4)	33(2)
C(24)	3730(7)	1282(3)	3430(4)	34(2)
C(25)	902(7)	291(3)	2854(4)	21(2)
C(26)	1518(7)	-141(3)	2824(4)	24(2)
C(27)	2265(7)	-652(3)	2749(4)	23(2)
C(28)	1527(8)	-1116(3)	2444(4)	29(2)

C(29)	2247(8)	-1603(3)	2370(4)	33(2)
C(30)	3675(9)	-1634(3)	2602(4)	33(2)
C(31)	4405(8)	-1179(3)	2901(5)	38(2)
C(32)	3703(8)	-697(3)	2988(5)	37(2)
C(33)	1137(6)	1342(3)	1984(4)	20(2)
C(34)	1190(7)	1895(3)	1768(4)	24(2)
C(35)	2072(7)	2115(3)	1192(4)	28(2)
C(36)	2956(7)	1773(3)	779(4)	29(2)
C(37)	2918(7)	1224(3)	951(4)	24(2)
C(38)	2041(6)	1014(3)	1542(3)	22(1)
C(39)	-1485(7)	693(3)	3624(4)	23(2)
O(1)	-2299(5)	519(2)	4064(3)	31(1)

Table S32. Bond lengths [Å] and angles [°] for **(PCP)Ir(CO)(Ph)(CCPh)**.

Ir(1)-C(39)	1.896(7)	C(13)-C(16)	1.532(9)
Ir(1)-C(25)	2.056(7)	C(13)-C(15)	1.536(8)
Ir(1)-C(1)	2.102(6)	C(17)-C(20)	1.524(9)
Ir(1)-C(33)	2.142(6)	C(17)-C(18)	1.523(9)
Ir(1)-P(2)	2.3760(17)	C(17)-C(19)	1.552(9)
Ir(1)-P(1)	2.3988(17)	C(21)-C(23)	1.530(9)
P(1)-C(7)	1.856(6)	C(21)-C(22)	1.536(9)
P(1)-C(13)	1.902(6)	C(21)-C(24)	1.535(8)
P(1)-C(9)	1.914(7)	C(25)-C(26)	1.214(9)
P(2)-C(8)	1.845(7)	C(26)-C(27)	1.450(9)
P(2)-C(21)	1.881(7)	C(27)-C(32)	1.376(9)
P(2)-C(17)	1.916(6)	C(27)-C(28)	1.391(9)
C(1)-C(2)	1.375(8)	C(28)-C(29)	1.384(9)
C(1)-C(6)	1.417(9)	C(29)-C(30)	1.363(9)
C(2)-C(3)	1.388(9)	C(30)-C(31)	1.367(9)
C(2)-C(7)	1.525(9)	C(31)-C(32)	1.370(9)
C(3)-C(4)	1.388(9)	C(33)-C(34)	1.399(9)
C(4)-C(5)	1.363(9)	C(33)-C(38)	1.399(8)
C(5)-C(6)	1.399(9)	C(34)-C(35)	1.386(8)
C(6)-C(8)	1.499(9)	C(35)-C(36)	1.383(9)
C(9)-C(12)	1.519(9)	C(36)-C(37)	1.373(9)
C(9)-C(10)	1.525(9)	C(37)-C(38)	1.390(8)
C(9)-C(11)	1.533(9)	C(39)-O(1)	1.157(7)
C(13)-C(14)	1.532(8)		

C(39)-Ir(1)-C(25)	91.5(3)	C(33)-Ir(1)-P(2)	91.23(16)
C(39)-Ir(1)-C(1)	88.2(3)	C(39)-Ir(1)-P(1)	87.68(19)
C(25)-Ir(1)-C(1)	179.1(2)	C(25)-Ir(1)-P(1)	100.20(18)
C(39)-Ir(1)-C(33)	177.6(3)	C(1)-Ir(1)-P(1)	80.58(18)
C(25)-Ir(1)-C(33)	88.2(2)	C(33)-Ir(1)-P(1)	90.03(16)
C(1)-Ir(1)-C(33)	92.2(2)	P(2)-Ir(1)-P(1)	161.28(6)
C(39)-Ir(1)-P(2)	91.19(19)	C(7)-P(1)-C(13)	101.3(3)
C(25)-Ir(1)-P(2)	98.51(18)	C(7)-P(1)-C(9)	107.0(3)
C(1)-Ir(1)-P(2)	80.71(18)	C(13)-P(1)-C(9)	107.9(3)

C(7)-P(1)-Ir(1)	96.5(2)	C(16)-C(13)-P(1)	108.7(4)
C(13)-P(1)-Ir(1)	124.3(2)	C(15)-C(13)-P(1)	113.1(4)
C(9)-P(1)-Ir(1)	116.4(2)	C(20)-C(17)-C(18)	106.2(5)
C(8)-P(2)-C(21)	107.5(3)	C(20)-C(17)-C(19)	111.6(6)
C(8)-P(2)-C(17)	102.5(3)	C(18)-C(17)-C(19)	108.0(5)
C(21)-P(2)-C(17)	107.7(3)	C(20)-C(17)-P(2)	109.5(4)
C(8)-P(2)-Ir(1)	99.6(2)	C(18)-C(17)-P(2)	113.2(5)
C(21)-P(2)-Ir(1)	122.4(2)	C(19)-C(17)-P(2)	108.5(4)
C(17)-P(2)-Ir(1)	114.7(2)	C(23)-C(21)-C(22)	111.0(5)
C(2)-C(1)-C(6)	119.9(6)	C(23)-C(21)-C(24)	106.0(6)
C(2)-C(1)-Ir(1)	120.0(5)	C(22)-C(21)-C(24)	106.1(5)
C(6)-C(1)-Ir(1)	120.0(5)	C(23)-C(21)-P(2)	110.6(5)
C(1)-C(2)-C(3)	120.8(6)	C(22)-C(21)-P(2)	113.3(5)
C(1)-C(2)-C(7)	118.7(6)	C(24)-C(21)-P(2)	109.5(4)
C(3)-C(2)-C(7)	120.5(6)	C(26)-C(25)-Ir(1)	177.2(6)
C(2)-C(3)-C(4)	119.1(6)	C(25)-C(26)-C(27)	177.5(6)
C(5)-C(4)-C(3)	121.4(7)	C(32)-C(27)-C(28)	118.2(7)
C(4)-C(5)-C(6)	120.3(7)	C(32)-C(27)-C(26)	121.6(7)
C(5)-C(6)-C(1)	118.6(6)	C(28)-C(27)-C(26)	120.2(6)
C(5)-C(6)-C(8)	122.0(6)	C(29)-C(28)-C(27)	119.9(7)
C(1)-C(6)-C(8)	119.3(6)	C(30)-C(29)-C(28)	120.7(7)
C(2)-C(7)-P(1)	108.4(4)	C(29)-C(30)-C(31)	119.5(7)
C(6)-C(8)-P(2)	108.9(4)	C(30)-C(31)-C(32)	120.3(7)
C(12)-C(9)-C(10)	105.9(5)	C(31)-C(32)-C(27)	121.2(7)
C(12)-C(9)-C(11)	106.5(6)	C(34)-C(33)-C(38)	113.9(6)
C(10)-C(9)-C(11)	110.7(6)	C(34)-C(33)-Ir(1)	124.3(5)
C(12)-C(9)-P(1)	110.8(4)	C(38)-C(33)-Ir(1)	121.8(5)
C(10)-C(9)-P(1)	114.0(5)	C(35)-C(34)-C(33)	124.5(6)
C(11)-C(9)-P(1)	108.7(5)	C(36)-C(35)-C(34)	119.2(7)
C(14)-C(13)-C(16)	106.0(6)	C(37)-C(36)-C(35)	118.5(6)
C(14)-C(13)-C(15)	108.1(5)	C(36)-C(37)-C(38)	121.3(6)
C(16)-C(13)-C(15)	107.7(6)	C(37)-C(38)-C(33)	122.5(7)
C(14)-C(13)-P(1)	112.8(4)	O(1)-C(39)-Ir(1)	176.9(6)

Table S33. Torsion angles [°] for **(PCP)Ir(CO)(Ph)(CCPh)**.

C(39)-Ir(1)-P(1)-C(7)	58.1(3)	C(39)-Ir(1)-C(1)-C(6)	110.3(5)
C(25)-Ir(1)-P(1)-C(7)	149.2(3)	C(25)-Ir(1)-C(1)-C(6)	44(17)
C(1)-Ir(1)-P(1)-C(7)	-30.4(3)	C(33)-Ir(1)-C(1)-C(6)	-72.1(5)
C(33)-Ir(1)-P(1)-C(7)	-122.6(3)	P(2)-Ir(1)-C(1)-C(6)	18.8(4)
P(2)-Ir(1)-P(1)-C(7)	-28.7(3)	P(1)-Ir(1)-C(1)-C(6)	-161.8(5)
C(39)-Ir(1)-P(1)-C(13)	166.5(3)	C(6)-C(1)-C(2)-C(3)	0.7(9)
C(25)-Ir(1)-P(1)-C(13)	-102.4(3)	Ir(1)-C(1)-C(2)-C(3)	176.5(4)
C(1)-Ir(1)-P(1)-C(13)	78.0(3)	C(6)-C(1)-C(2)-C(7)	-176.7(5)
C(33)-Ir(1)-P(1)-C(13)	-14.2(3)	Ir(1)-C(1)-C(2)-C(7)	-1.0(8)
P(2)-Ir(1)-P(1)-C(13)	79.7(3)	C(1)-C(2)-C(3)-C(4)	0.1(9)
C(39)-Ir(1)-P(1)-C(9)	-54.5(3)	C(7)-C(2)-C(3)-C(4)	177.5(6)
C(25)-Ir(1)-P(1)-C(9)	36.6(3)	C(2)-C(3)-C(4)-C(5)	-0.5(10)
C(1)-Ir(1)-P(1)-C(9)	-143.1(3)	C(3)-C(4)-C(5)-C(6)	0.1(10)
C(33)-Ir(1)-P(1)-C(9)	124.7(3)	C(4)-C(5)-C(6)-C(1)	0.8(9)
P(2)-Ir(1)-P(1)-C(9)	-141.4(3)	C(4)-C(5)-C(6)-C(8)	-175.6(6)
C(39)-Ir(1)-P(2)-C(8)	-114.1(3)	C(2)-C(1)-C(6)-C(5)	-1.2(9)
C(25)-Ir(1)-P(2)-C(8)	154.3(3)	Ir(1)-C(1)-C(6)-C(5)	-176.9(4)
C(1)-Ir(1)-P(2)-C(8)	-26.1(3)	C(2)-C(1)-C(6)-C(8)	175.3(5)
C(33)-Ir(1)-P(2)-C(8)	65.9(3)	Ir(1)-C(1)-C(6)-C(8)	-0.4(8)
P(1)-Ir(1)-P(2)-C(8)	-27.8(3)	C(1)-C(2)-C(7)-P(1)	-29.3(7)
C(39)-Ir(1)-P(2)-C(21)	128.0(3)	C(3)-C(2)-C(7)-P(1)	153.3(5)
C(25)-Ir(1)-P(2)-C(21)	36.3(3)	C(13)-P(1)-C(7)-C(2)	-88.1(5)
C(1)-Ir(1)-P(2)-C(21)	-144.0(3)	C(9)-P(1)-C(7)-C(2)	159.0(4)
C(33)-Ir(1)-P(2)-C(21)	-52.0(3)	Ir(1)-P(1)-C(7)-C(2)	38.8(4)
P(1)-Ir(1)-P(2)-C(21)	-145.7(3)	C(5)-C(6)-C(8)-P(2)	151.4(5)
C(39)-Ir(1)-P(2)-C(17)	-5.5(3)	C(1)-C(6)-C(8)-P(2)	-24.9(7)
C(25)-Ir(1)-P(2)-C(17)	-97.1(3)	C(21)-P(2)-C(8)-C(6)	162.0(4)
C(1)-Ir(1)-P(2)-C(17)	82.5(3)	C(17)-P(2)-C(8)-C(6)	-84.6(4)
C(33)-Ir(1)-P(2)-C(17)	174.5(3)	Ir(1)-P(2)-C(8)-C(6)	33.5(4)
P(1)-Ir(1)-P(2)-C(17)	80.8(3)	C(7)-P(1)-C(9)-C(12)	-82.2(5)
C(39)-Ir(1)-C(1)-C(2)	-65.4(5)	C(13)-P(1)-C(9)-C(12)	169.5(5)
C(25)-Ir(1)-C(1)-C(2)	-132(17)	Ir(1)-P(1)-C(9)-C(12)	24.3(5)
C(33)-Ir(1)-C(1)-C(2)	112.2(5)	C(7)-P(1)-C(9)-C(10)	37.1(5)
P(2)-Ir(1)-C(1)-C(2)	-156.9(5)	C(13)-P(1)-C(9)-C(10)	-71.2(5)
P(1)-Ir(1)-C(1)-C(2)	22.5(4)	Ir(1)-P(1)-C(9)-C(10)	143.6(4)

C(7)-P(1)-C(9)-C(11)	161.1(5)	Ir(1)-C(25)-C(26)-C(27)	83(21)
C(13)-P(1)-C(9)-C(11)	52.8(5)	C(25)-C(26)-C(27)-C(32)	93(17)
Ir(1)-P(1)-C(9)-C(11)	-92.4(5)	C(25)-C(26)-C(27)-C(28)	-89(17)
C(7)-P(1)-C(13)-C(14)	-72.1(5)	C(32)-C(27)-C(28)-C(29)	-1.4(9)
C(9)-P(1)-C(13)-C(14)	40.1(6)	C(26)-C(27)-C(28)-C(29)	179.7(6)
Ir(1)-P(1)-C(13)-C(14)	-178.1(4)	C(27)-C(28)-C(29)-C(30)	0.6(10)
C(7)-P(1)-C(13)-C(16)	45.2(5)	C(28)-C(29)-C(30)-C(31)	-0.8(11)
C(9)-P(1)-C(13)-C(16)	157.4(5)	C(29)-C(30)-C(31)-C(32)	1.7(11)
Ir(1)-P(1)-C(13)-C(16)	-60.8(5)	C(30)-C(31)-C(32)-C(27)	-2.5(11)
C(7)-P(1)-C(13)-C(15)	164.8(5)	C(28)-C(27)-C(32)-C(31)	2.3(10)
C(9)-P(1)-C(13)-C(15)	-83.0(5)	C(26)-C(27)-C(32)-C(31)	-178.8(6)
Ir(1)-P(1)-C(13)-C(15)	58.8(6)	C(39)-Ir(1)-C(33)-C(34)	110(6)
C(8)-P(2)-C(17)-C(20)	47.7(5)	C(25)-Ir(1)-C(33)-C(34)	-168.6(5)
C(21)-P(2)-C(17)-C(20)	160.9(5)	C(1)-Ir(1)-C(33)-C(34)	10.6(5)
Ir(1)-P(2)-C(17)-C(20)	-59.1(5)	P(2)-Ir(1)-C(33)-C(34)	-70.1(5)
C(8)-P(2)-C(17)-C(18)	-70.5(5)	P(1)-Ir(1)-C(33)-C(34)	91.2(5)
C(21)-P(2)-C(17)-C(18)	42.7(6)	C(39)-Ir(1)-C(33)-C(38)	-68(7)
Ir(1)-P(2)-C(17)-C(18)	-177.4(4)	C(25)-Ir(1)-C(33)-C(38)	13.2(5)
C(8)-P(2)-C(17)-C(19)	169.7(5)	C(1)-Ir(1)-C(33)-C(38)	-167.5(5)
C(21)-P(2)-C(17)-C(19)	-77.1(5)	P(2)-Ir(1)-C(33)-C(38)	111.7(5)
Ir(1)-P(2)-C(17)-C(19)	62.8(5)	P(1)-Ir(1)-C(33)-C(38)	-87.0(5)
C(8)-P(2)-C(21)-C(23)	160.3(4)	C(38)-C(33)-C(34)-C(35)	-1.7(9)
C(17)-P(2)-C(21)-C(23)	50.6(5)	Ir(1)-C(33)-C(34)-C(35)	-179.9(5)
Ir(1)-P(2)-C(21)-C(23)	-85.6(5)	C(33)-C(34)-C(35)-C(36)	1.1(10)
C(8)-P(2)-C(21)-C(22)	35.0(5)	C(34)-C(35)-C(36)-C(37)	0.5(10)
C(17)-P(2)-C(21)-C(22)	-74.8(5)	C(35)-C(36)-C(37)-C(38)	-1.6(10)
Ir(1)-P(2)-C(21)-C(22)	149.0(4)	C(36)-C(37)-C(38)-C(33)	1.0(10)
C(8)-P(2)-C(21)-C(24)	-83.2(5)	C(34)-C(33)-C(38)-C(37)	0.6(9)
C(17)-P(2)-C(21)-C(24)	167.0(5)	Ir(1)-C(33)-C(38)-C(37)	178.9(4)
Ir(1)-P(2)-C(21)-C(24)	30.9(6)	C(25)-Ir(1)-C(39)-O(1)	-152(11)
C(39)-Ir(1)-C(25)-C(26)	63(11)	C(1)-Ir(1)-C(39)-O(1)	28(11)
C(1)-Ir(1)-C(25)-C(26)	130(16)	C(33)-Ir(1)-C(39)-O(1)	-71(14)
C(33)-Ir(1)-C(25)-C(26)	-115(11)	P(2)-Ir(1)-C(39)-O(1)	109(11)
P(2)-Ir(1)-C(25)-C(26)	154(11)	P(1)-Ir(1)-C(39)-O(1)	-52(11)
P(1)-Ir(1)-C(25)-C(26)	-25(11)		

IX. Structural Data for (PCP)Ir(CO)(Me)$_2$

Figure S-9 : ORTEP Diagram of **(PCP)Ir(CO)(Me)$_2$**

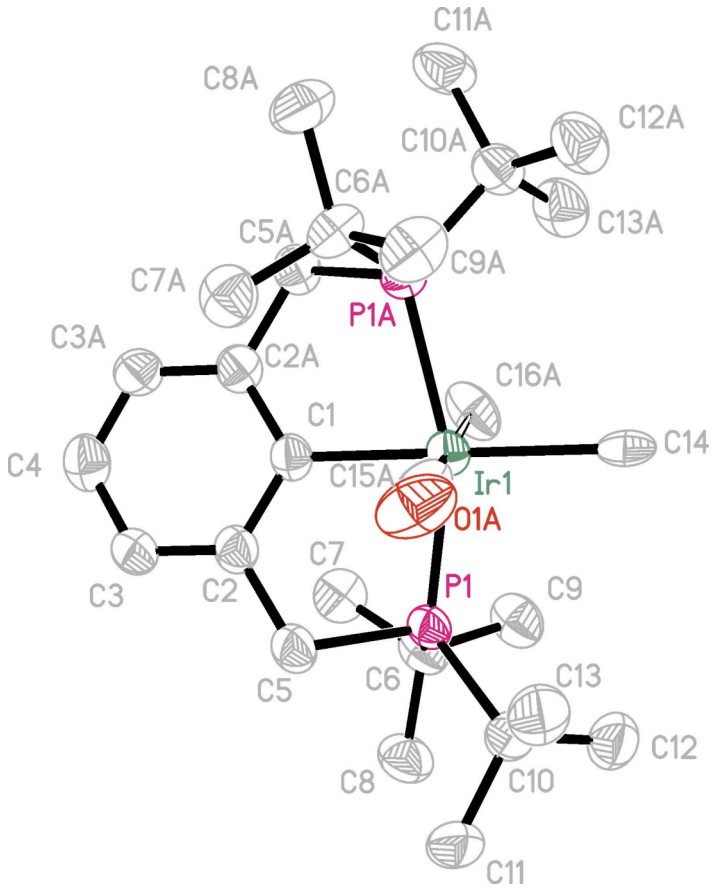

Table S34. Crystal data and structure refinement for **(PCP)Ir(CO)(Me)$_2$**

.

Identification code	irme2co	
Empirical formula	C29 H53.666667 Ir O P2	
Formula weight	672.53	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	P 61 2 2	
Unit cell dimensions	a = 16.2384(4) Å	α= 90°.
	b = 16.2384(4) Å	β= 90°.
	c = 20.0680(10) Å	γ = 120°.
Volume	4582.7(3) Å^3	
Z	6	
Density (calculated)	1.462 Mg/m^3	
Absorption coefficient	4.493 mm^{-1}	
F(000)	2056	
Crystal size	0.12 x 0.06 x 0.04 mm^3	
Theta range for data collection	1.77 to 28.28°.	
Index ranges	-21<=h<=21, -21<=k<=21, -26<=l<=26	
Reflections collected	45979	
Independent reflections	3816 [R(int) = 0.0672]	
Completeness to theta = 28.28°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.83 and 0.64	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3816 / 20 / 173	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0298, wR2 = 0.0690	
R indices (all data)	R1 = 0.0396, wR2 = 0.0724	
Absolute structure parameter	-0.03(2)	
Largest diff. peak and hole	0.895 and -0.571 e.Å^{-3}	

Table S35. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(PCP)Ir(CO)(Me)$_2$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	-1601(1)	4199(1)	833	31(1)
P(1)	-1896(2)	5350(2)	334(1)	35(1)
C(1)	-3084(8)	3458(4)	833	35(3)
C(2)	-3599(7)	3698(8)	392(5)	39(2)
C(3)	-4588(7)	3207(8)	394(5)	43(2)
C(4)	-5077(11)	2461(5)	833	50(3)
C(5)	-3042(7)	4535(7)	-71(5)	43(2)
C(6)	-2219(7)	6089(7)	898(6)	46(2)
C(7)	-3109(8)	5433(9)	1291(6)	53(3)
C(8)	-2453(9)	6772(9)	509(7)	58(3)
C(9)	-1395(8)	6708(8)	1383(6)	54(3)
C(10)	-1082(8)	6164(8)	-341(5)	46(2)
C(11)	-1584(9)	6489(8)	-847(6)	61(3)
C(12)	-231(9)	7033(8)	-25(6)	58(3)
C(13)	-655(9)	5659(9)	-751(6)	59(3)
C(14)	37(10)	5018(5)	833	39(3)
C(15A)	-1600(90)	3730(100)	-30(30)	54(4)
O(1A)	-1484(15)	3436(13)	-507(8)	70(5)
C(16B)	-1630(90)	3670(100)	-150(30)	54(4)
C(101)	-710(30)	-470(20)	-1188(2)	150(20)
C(102)	110(30)	210(50)	-729(2)	150(20)
C(103)	-180(30)	0	0	150(20)
C(104)	620(20)	670(30)	479(1)	150(20)
C(105)	330(30)	460(20)	1208(1)	150(20)
C(106)	1144(18)	1144(18)	1667	150(20)

Table S36. Bond lengths [Å] and angles [°] for **(PCP)Ir(CO)(Me)$_2$**.

Ir(1)-C(15A)#1	1.888(9)	C(10)-C(13)	1.547(16)
Ir(1)-C(15A)	1.888(9)	C(10)-C(11)	1.550(15)
Ir(1)-C(1)	2.085(12)	C(11)-H(11A)	0.9800
Ir(1)-C(16B)	2.138(9)	C(11)-H(11B)	0.9800
Ir(1)-C(16B)#1	2.138(9)	C(11)-H(11C)	0.9800
Ir(1)-C(14)	2.303(14)	C(12)-H(12A)	0.9800
Ir(1)-P(1)	2.370(3)	C(12)-H(12B)	0.9800
Ir(1)-P(1)#1	2.370(3)	C(12)-H(12C)	0.9800
P(1)-C(5)	1.848(10)	C(13)-H(13A)	0.9800
P(1)-C(10)	1.893(11)	C(13)-H(13B)	0.9800
P(1)-C(6)	1.905(11)	C(13)-H(13C)	0.9800
C(1)-C(2)	1.401(11)	C(14)-H(14A)	0.9800
C(1)-C(2)#1	1.401(11)	C(14)-H(14B)	0.9800
C(2)-C(3)	1.390(14)	C(14)-H(14C)	0.9800
C(2)-C(5)	1.516(14)	C(15A)-O(1A)	1.131(9)
C(3)-C(4)	1.383(13)	C(16B)-H(16A)	0.9800
C(3)-H(3)	0.9500	C(16B)-H(16B)	0.9800
C(4)-C(3)#1	1.383(13)	C(16B)-H(16C)	0.9800
C(4)-H(4)	0.9500	C(101)-C(102)	1.5364(19)
C(5)-H(5A)	0.9900	C(101)-H(10A)	0.9800
C(5)-H(5B)	0.9900	C(101)-H(10B)	0.9800
C(6)-C(7)	1.518(16)	C(101)-H(10C)	0.9800
C(6)-C(8)	1.551(14)	C(102)-C(103)	1.5206(18)
C(6)-C(9)	1.552(14)	C(102)-H(10D)	0.9900
C(7)-H(7A)	0.9800	C(102)-H(10E)	0.9900
C(7)-H(7B)	0.9800	C(103)-C(104)	1.5373(17)
C(7)-H(7C)	0.9800	C(103)-H(10F)	0.9900
C(8)-H(8A)	0.9800	C(103)-H(10G)	0.9900
C(8)-H(8B)	0.9800	C(104)-C(105)	1.5204(18)
C(8)-H(8C)	0.9800	C(104)-H(10H)	0.9900
C(9)-H(9A)	0.9800	C(104)-H(10I)	0.9900
C(9)-H(9B)	0.9800	C(105)-C(106)	1.5371(19)
C(9)-H(9C)	0.9800	C(105)-H(10J)	0.9900
C(10)-C(12)	1.535(15)	C(105)-H(10K)	0.9900

C(106)-H(10L)	0.9800	C(106)-H(10N)	0.9800
C(106)-H(10M)	0.9800		

C(15A)#1-Ir(1)-C(15A)	180(6)	C(6)-P(1)-Ir(1)	118.3(3)
C(15A)#1-Ir(1)-C(1)	90(4)	C(2)-C(1)-C(2)#1	117.7(12)
C(15A)-Ir(1)-C(1)	90(4)	C(2)-C(1)-Ir(1)	121.2(6)
C(15A)#1-Ir(1)-C(16B)	179(5)	C(2)#1-C(1)-Ir(1)	121.2(6)
C(15A)-Ir(1)-C(16B)	1(5)	C(3)-C(2)-C(1)	121.2(10)
C(1)-Ir(1)-C(16B)	89(3)	C(3)-C(2)-C(5)	121.1(9)
C(15A)#1-Ir(1)-C(16B)#1	1(6)	C(1)-C(2)-C(5)	117.7(9)
C(15A)-Ir(1)-C(16B)#1	179(5)	C(4)-C(3)-C(2)	119.8(11)
C(1)-Ir(1)-C(16B)#1	89(3)	C(4)-C(3)-H(3)	120.1
C(16B)-Ir(1)-C(16B)#1	178(7)	C(2)-C(3)-H(3)	120.1
C(15A)#1-Ir(1)-C(14)	90(4)	C(3)-C(4)-C(3)#1	120.3(14)
C(15A)-Ir(1)-C(14)	90(4)	C(3)-C(4)-H(4)	119.8
C(1)-Ir(1)-C(14)	180.0(4)	C(3)#1-C(4)-H(4)	119.8
C(16B)-Ir(1)-C(14)	91(3)	C(2)-C(5)-P(1)	108.0(7)
C(16B)#1-Ir(1)-C(14)	91(3)	C(2)-C(5)-H(5A)	110.1
C(15A)#1-Ir(1)-P(1)	92(4)	P(1)-C(5)-H(5A)	110.1
C(15A)-Ir(1)-P(1)	88(4)	C(2)-C(5)-H(5B)	110.1
C(1)-Ir(1)-P(1)	79.93(6)	P(1)-C(5)-H(5B)	110.1
C(16B)-Ir(1)-P(1)	87(3)	H(5A)-C(5)-H(5B)	108.4
C(16B)#1-Ir(1)-P(1)	92(4)	C(7)-C(6)-C(8)	106.0(9)
C(14)-Ir(1)-P(1)	100.07(6)	C(7)-C(6)-C(9)	109.8(10)
C(15A)#1-Ir(1)-P(1)#1	88(4)	C(8)-C(6)-C(9)	107.0(9)
C(15A)-Ir(1)-P(1)#1	92(4)	C(7)-C(6)-P(1)	109.4(7)
C(1)-Ir(1)-P(1)#1	79.93(6)	C(8)-C(6)-P(1)	113.3(8)
C(16B)-Ir(1)-P(1)#1	92(4)	C(9)-C(6)-P(1)	111.2(7)
C(16B)#1-Ir(1)-P(1)#1	87(3)	C(6)-C(7)-H(7A)	109.5
C(14)-Ir(1)-P(1)#1	100.07(6)	C(6)-C(7)-H(7B)	109.5
P(1)-Ir(1)-P(1)#1	159.87(12)	H(7A)-C(7)-H(7B)	109.5
C(5)-P(1)-C(10)	106.7(5)	C(6)-C(7)-H(7C)	109.5
C(5)-P(1)-C(6)	102.4(5)	H(7A)-C(7)-H(7C)	109.5
C(10)-P(1)-C(6)	107.5(5)	H(7B)-C(7)-H(7C)	109.5
C(5)-P(1)-Ir(1)	98.6(3)	C(6)-C(8)-H(8A)	109.5
C(10)-P(1)-Ir(1)	120.5(4)	C(6)-C(8)-H(8B)	109.5

H(8A)-C(8)-H(8B)	109.5	H(14A)-C(14)-H(14B)	109.5
C(6)-C(8)-H(8C)	109.5	Ir(1)-C(14)-H(14C)	109.5
H(8A)-C(8)-H(8C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(8B)-C(8)-H(8C)	109.5	H(14B)-C(14)-H(14C)	109.5
C(6)-C(9)-H(9A)	109.5	O(1A)-C(15A)-Ir(1)	169(8)
C(6)-C(9)-H(9B)	109.5	Ir(1)-C(16B)-H(16A)	109.5
H(9A)-C(9)-H(9B)	109.5	Ir(1)-C(16B)-H(16B)	109.5
C(6)-C(9)-H(9C)	109.5	H(16A)-C(16B)-H(16B)	109.5
H(9A)-C(9)-H(9C)	109.5	Ir(1)-C(16B)-H(16C)	109.5
H(9B)-C(9)-H(9C)	109.5	H(16A)-C(16B)-H(16C)	109.5
C(12)-C(10)-C(13)	105.7(10)	H(16B)-C(16B)-H(16C)	109.5
C(12)-C(10)-C(11)	110.1(9)	C(102)-C(101)-H(10A)	109.5
C(13)-C(10)-C(11)	106.5(9)	C(102)-C(101)-H(10B)	109.5
C(12)-C(10)-P(1)	109.8(8)	H(10A)-C(101)-H(10B)	109.5
C(13)-C(10)-P(1)	110.6(8)	C(102)-C(101)-H(10C)	109.5
C(11)-C(10)-P(1)	113.8(8)	H(10A)-C(101)-H(10C)	109.5
C(10)-C(11)-H(11A)	109.5	H(10B)-C(101)-H(10C)	109.5
C(10)-C(11)-H(11B)	109.5	C(103)-C(102)-C(101)	111.07(17)
H(11A)-C(11)-H(11B)	109.5	C(103)-C(102)-H(10D)	109.4
C(10)-C(11)-H(11C)	109.5	C(101)-C(102)-H(10D)	109.4
H(11A)-C(11)-H(11C)	109.5	C(103)-C(102)-H(10E)	109.4
H(11B)-C(11)-H(11C)	109.5	C(101)-C(102)-H(10E)	109.4
C(10)-C(12)-H(12A)	109.5	H(10D)-C(102)-H(10E)	108.0
C(10)-C(12)-H(12B)	109.5	C(102)-C(103)-C(104)	112.90(17)
H(12A)-C(12)-H(12B)	109.5	C(102)-C(103)-H(10F)	109.0
C(10)-C(12)-H(12C)	109.5	C(104)-C(103)-H(10F)	109.0
H(12A)-C(12)-H(12C)	109.5	C(102)-C(103)-H(10G)	109.0
H(12B)-C(12)-H(12C)	109.5	C(104)-C(103)-H(10G)	109.0
C(10)-C(13)-H(13A)	109.5	H(10F)-C(103)-H(10G)	107.8
C(10)-C(13)-H(13B)	109.5	C(105)-C(104)-C(103)	112.91(17)
H(13A)-C(13)-H(13B)	109.5	C(105)-C(104)-H(10H)	109.0
C(10)-C(13)-H(13C)	109.5	C(103)-C(104)-H(10H)	109.0
H(13A)-C(13)-H(13C)	109.5	C(105)-C(104)-H(10I)	109.0
H(13B)-C(13)-H(13C)	109.5	C(103)-C(104)-H(10I)	109.0
Ir(1)-C(14)-H(14A)	109.5	H(10H)-C(104)-H(10I)	107.8
Ir(1)-C(14)-H(14B)	109.5	C(104)-C(105)-C(106)	111.01(17)

C(104)-C(105)-H(10J)	109.4	C(105)-C(106)-H(10M)	109.5
C(106)-C(105)-H(10J)	109.4	H(10L)-C(106)-H(10M)	109.5
C(104)-C(105)-H(10K)	109.4	C(105)-C(106)-H(10N)	109.5
C(106)-C(105)-H(10K)	109.4	H(10L)-C(106)-H(10N)	109.5
H(10J)-C(105)-H(10K)	108.0	H(10M)-C(106)-H(10N)	109.5
C(105)-C(106)-H(10L)	109.5		

Symmetry transformations used to generate equivalent atoms:

#1 x,x-y+1,-z+1/6

Table S37. Torsion angles [°] for **(PCP)Ir(CO)(Me)$_2$**.

C(15A)#1-Ir(1)-P(1)-C(5)	-119(4)	P(1)#1-Ir(1)-C(1)-C(2)#1	22.1(5)
C(15A)-Ir(1)-P(1)-C(5)	61(4)	Ir(1)-C(1)-C(2)-C(3)	-179.7(7)
C(1)-Ir(1)-P(1)-C(5)	-29.6(3)	C(2)#1-C(1)-C(2)-C(5)	178.2(10)
C(16B)-Ir(1)-P(1)-C(5)	60(4)	Ir(1)-C(1)-C(2)-C(5)	-1.8(10)
C(16B)#1-Ir(1)-P(1)-C(5)	-118(3)	C(5)-C(2)-C(3)-C(4)	-178.4(8)
C(14)-Ir(1)-P(1)-C(5)	150.4(3)	C(3)-C(2)-C(5)-P(1)	150.8(9)
P(1)#1-Ir(1)-P(1)-C(5)	-29.6(3)	C(1)-C(2)-C(5)-P(1)	-27.0(10)
C(15A)#1-Ir(1)-P(1)-C(10)	125(3)	C(10)-P(1)-C(5)-C(2)	163.0(7)
C(15A)-Ir(1)-P(1)-C(10)	-55(4)	C(6)-P(1)-C(5)-C(2)	-84.1(8)
C(1)-Ir(1)-P(1)-C(10)	-144.8(4)	Ir(1)-P(1)-C(5)-C(2)	37.4(7)
C(16B)-Ir(1)-P(1)-C(10)	-55(4)	C(5)-P(1)-C(6)-C(7)	48.5(8)
C(16B)#1-Ir(1)-P(1)-C(10)	126(3)	C(10)-P(1)-C(6)-C(7)	160.7(7)
C(14)-Ir(1)-P(1)-C(10)	35.2(4)	Ir(1)-P(1)-C(6)-C(7)	-58.6(8)
P(1)#1-Ir(1)-P(1)-C(10)	-144.8(4)	C(5)-P(1)-C(6)-C(8)	-69.6(9)
C(15A)#1-Ir(1)-P(1)-C(6)	-10(4)	C(10)-P(1)-C(6)-C(8)	42.7(9)
C(15A)-Ir(1)-P(1)-C(6)	170(4)	Ir(1)-P(1)-C(6)-C(8)	-176.6(7)
C(1)-Ir(1)-P(1)-C(6)	79.6(4)	C(5)-P(1)-C(6)-C(9)	169.9(8)
C(16B)-Ir(1)-P(1)-C(6)	169(4)	C(10)-P(1)-C(6)-C(9)	-77.9(9)
C(16B)#1-Ir(1)-P(1)-C(6)	-9(3)	Ir(1)-P(1)-C(6)-C(9)	62.9(8)
C(14)-Ir(1)-P(1)-C(6)	-100.4(4)	C(5)-P(1)-C(10)-C(12)	163.7(8)
P(1)#1-Ir(1)-P(1)-C(6)	79.6(4)	C(6)-P(1)-C(10)-C(12)	54.4(9)
C(15A)#1-Ir(1)-C(1)-C(2)	114(4)	Ir(1)-P(1)-C(10)-C(12)	-85.3(9)
C(15A)-Ir(1)-C(1)-C(2)	-66(4)	C(5)-P(1)-C(10)-C(13)	-80.0(9)
C(16B)-Ir(1)-C(1)-C(2)	-65(4)	C(6)-P(1)-C(10)-C(13)	170.7(7)
C(16B)#1-Ir(1)-C(1)-C(2)	115(4)	Ir(1)-P(1)-C(10)-C(13)	31.0(9)
P(1)-Ir(1)-C(1)-C(2)	22.2(5)	C(5)-P(1)-C(10)-C(11)	39.8(10)
P(1)#1-Ir(1)-C(1)-C(2)	-157.8(5)	C(6)-P(1)-C(10)-C(11)	-69.5(9)
C(15A)#1-Ir(1)-C(1)-C(2)#1	-66(4)	Ir(1)-P(1)-C(10)-C(11)	150.8(7)
C(15A)-Ir(1)-C(1)-C(2)#1	114(4)	C(101)-C(102)-C(103)-C(104)	180.0(4)
C(16B)-Ir(1)-C(1)-C(2)#1	115(4)	C(102)-C(103)-C(104)-C(105)	-180.0(5)
C(16B)#1-Ir(1)-C(1)-C(2)#1	-65(4)	C(103)-C(104)-C(105)-C(106)	-179.8(6)
P(1)-Ir(1)-C(1)-C(2)#1	-157.9(5)		

Symmetry transformations used to generate equivalent atoms:

#1 x,x-y+1,-z+1/6

X. Structural Data for (PCP)Ir(CO)(Me)(Ph)

Figure S-10 : ORTEP Diagram of **(PCP)Ir(CO)(Me)(Ph)**

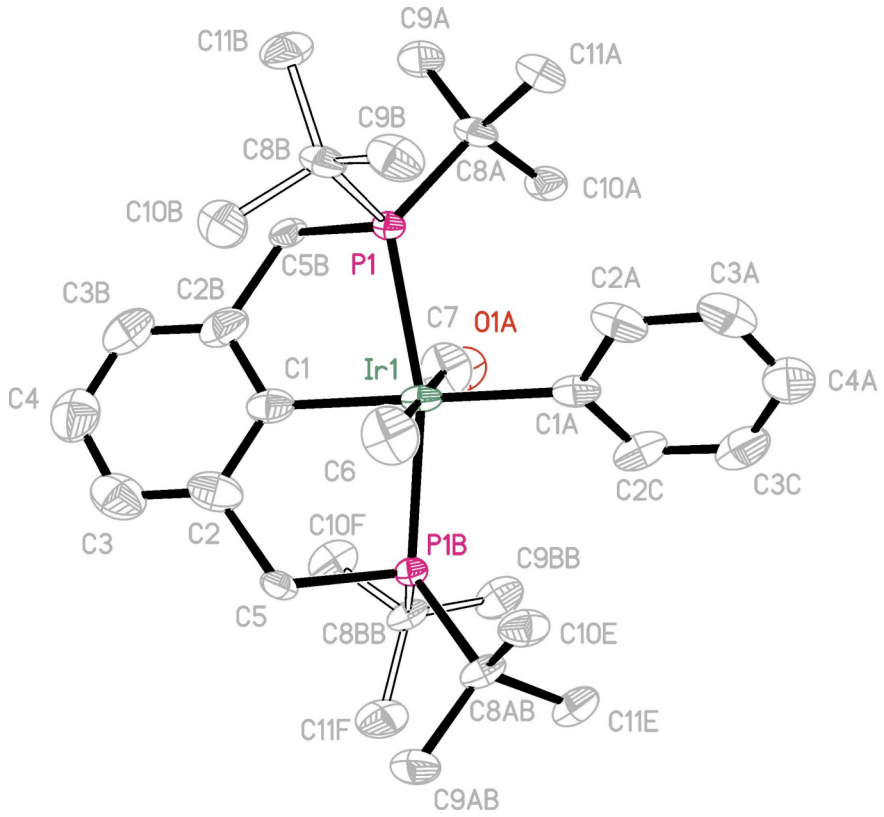

Table S38. Crystal data and structure refinement for **(PCP)Ir(CO)(Me)(Ph)**.

Identification code	ircomph	
Empirical formula	C32 H49 Ir O P2	
Formula weight	703.85	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Fddd	
Unit cell dimensions	a = 12.9330(9) Å	α= 90°.
	b = 19.0074(14) Å	β= 90°.
	c = 24.7240(18) Å	γ = 90°.
Volume	6077.7(8) $Å^3$	
Z	8	
Density (calculated)	1.538 Mg/m^3	
Absorption coefficient	4.522 mm^{-1}	
F(000)	2848	
Crystal size	0.14 x 0.08 x 0.02 mm^3	
Theta range for data collection	2.08 to 30.50°.	
Index ranges	-18<=h<=18, -27<=k<=27, -34<=l<=35	
Reflections collected	17366	
Independent reflections	2326 [R(int) = 0.0402]	
Completeness to theta = 30.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.915 and 0.555	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2326 / 124 / 134	
Goodness-of-fit on F^2	1.075	
Final R indices [I>2sigma(I)]	R1 = 0.0271, wR2 = 0.0612	
R indices (all data)	R1 = 0.0312, wR2 = 0.0627	
Largest diff. peak and hole	1.283 and -1.319 $e.Å^{-3}$	

Table S39. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(PCP)Ir(CO)(Me)(Ph)**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	6250	6250	6250	22(1)
C(1)	6250	5140(3)	6250	31(1)
C(2)	7034(3)	4758(2)	6506(2)	41(1)
C(3)	7047(3)	4030(2)	6500(2)	50(1)
C(4)	6250	3660(3)	6250	53(1)
C(5)	7950(4)	5239(3)	6728(2)	25(1)
C(6)	6250	6250	7105(3)	46(1)
C(7)	6250	6250	5475(3)	46(1)
O(1A)	6440(30)	6250(20)	5019(5)	43(5)
O(1B)	6030(30)	6040(14)	5054(6)	43(5)
P(1)	4447(1)	6095(1)	6123(1)	18(1)
C(8A)	3632(4)	6671(3)	5653(3)	29(1)
C(9A)	2866(5)	6230(4)	5318(3)	37(1)
C(10A)	4325(5)	7073(4)	5257(3)	32(1)
C(11A)	3021(5)	7235(4)	5964(3)	37(2)
C(8B)	3604(4)	5860(3)	6734(3)	29(1)
C(9B)	3533(6)	6472(4)	7139(3)	39(2)
C(10B)	4086(6)	5226(4)	7024(3)	40(2)
C(11B)	2512(5)	5632(4)	6569(3)	44(2)

Table S40. Bond lengths [Å] and angles [°] for **(PCP)Ir(CO)(Me)(Ph)**.

Ir(1)-C(7)	1.916(7)	C(8A)-C(11A)	1.538(7)
Ir(1)-C(1)	2.110(5)	C(8A)-C(9A)	1.540(7)
Ir(1)-C(6)	2.113(8)	C(9A)-H(9A1)	0.9800
Ir(1)-P(1)#1	2.3714(14)	C(9A)-H(9A2)	0.9800
Ir(1)-P(1)	2.3714(14)	C(9A)-H(9A3)	0.9800
C(1)-C(2)	1.399(4)	C(10A)-H(10A)	0.9800
C(1)-C(2)#1	1.399(4)	C(10A)-H(10B)	0.9800
C(2)-C(3)	1.386(6)	C(10A)-H(10C)	0.9800
C(2)-C(5)	1.593(7)	C(11A)-H(11A)	0.9800
C(3)-C(4)	1.393(6)	C(11A)-H(11B)	0.9800
C(3)-H(3)	0.9500	C(11A)-H(11C)	0.9800
C(4)-C(3)#1	1.393(6)	C(8B)-C(11B)	1.532(7)
C(4)-H(4)	0.9500	C(8B)-C(10B)	1.534(7)
C(5)-P(1)#1	1.849(6)	C(8B)-C(9B)	1.537(7)
C(5)-H(5A)	0.9900	C(9B)-H(9B1)	0.9800
C(5)-H(5B)	0.9900	C(9B)-H(9B2)	0.9800
C(6)-H(6A)	0.936(8)	C(9B)-H(9B3)	0.9800
C(6)-H(6B)	0.951(7)	C(10B)-H(10D)	0.9800
C(6)-H(6C)	0.951(7)	C(10B)-H(10E)	0.9800
C(7)-O(1B)	1.153(10)	C(10B)-H(10F)	0.9800
C(7)-O(1A)	1.154(9)	C(11B)-H(11D)	0.9800
P(1)-C(8A)	1.912(7)	C(11B)-H(11E)	0.9800
P(1)-C(8B)	1.916(7)	C(11B)-H(11F)	0.9800
C(8A)-C(10A)	1.532(6)		

C(7)-Ir(1)-C(1)	90.000(1)	P(1)#1-Ir(1)-P(1)	165.75(6)
C(7)-Ir(1)-C(6)	180.000(2)	C(2)-C(1)-C(2)#1	117.5(5)
C(1)-Ir(1)-C(6)	90.0	C(2)-C(1)-Ir(1)	121.2(2)
C(7)-Ir(1)-P(1)#1	97.62(3)	C(2)#1-C(1)-Ir(1)	121.2(2)
C(1)-Ir(1)-P(1)#1	82.87(3)	C(3)-C(2)-C(1)	121.5(4)
C(6)-Ir(1)-P(1)#1	82.38(3)	C(3)-C(2)-C(5)	124.6(4)
C(7)-Ir(1)-P(1)	82.38(3)	C(1)-C(2)-C(5)	113.5(4)
C(1)-Ir(1)-P(1)	82.87(3)	C(2)-C(3)-C(4)	120.0(4)
C(6)-Ir(1)-P(1)	97.62(3)	C(2)-C(3)-H(3)	120.0

C(4)-C(3)-H(3)	120.0	H(10B)-C(10A)-H(10C)	109.5
C(3)-C(4)-C(3)#1	119.4(6)	C(8A)-C(11A)-H(11A)	109.5
C(3)-C(4)-H(4)	120.3	C(8A)-C(11A)-H(11B)	109.5
C(3)#1-C(4)-H(4)	120.3	H(11A)-C(11A)-H(11B)	109.5
C(2)-C(5)-P(1)#1	113.4(3)	C(8A)-C(11A)-H(11C)	109.5
C(2)-C(5)-H(5A)	108.9	H(11A)-C(11A)-H(11C)	109.5
P(1)#1-C(5)-H(5A)	108.9	H(11B)-C(11A)-H(11C)	109.5
C(2)-C(5)-H(5B)	108.9	C(11B)-C(8B)-C(10B)	106.1(5)
P(1)#1-C(5)-H(5B)	108.9	C(11B)-C(8B)-C(9B)	109.3(5)
H(5A)-C(5)-H(5B)	107.7	C(10B)-C(8B)-C(9B)	108.3(5)
O(1B)-C(7)-Ir(1)	154.7(16)	C(11B)-C(8B)-P(1)	112.4(4)
O(1A)-C(7)-Ir(1)	167.6(18)	C(10B)-C(8B)-P(1)	108.7(4)
C(8A)-P(1)-C(8B)	107.4(2)	C(9B)-C(8B)-P(1)	111.8(4)
C(8A)-P(1)-Ir(1)	123.48(19)	C(8B)-C(9B)-H(9B1)	109.5
C(8B)-P(1)-Ir(1)	118.96(18)	C(8B)-C(9B)-H(9B2)	109.5
C(10A)-C(8A)-C(11A)	105.7(5)	H(9B1)-C(9B)-H(9B2)	109.5
C(10A)-C(8A)-C(9A)	107.7(5)	C(8B)-C(9B)-H(9B3)	109.5
C(11A)-C(8A)-C(9A)	108.5(5)	H(9B1)-C(9B)-H(9B3)	109.5
C(10A)-C(8A)-P(1)	110.6(4)	H(9B2)-C(9B)-H(9B3)	109.5
C(11A)-C(8A)-P(1)	112.3(4)	C(8B)-C(10B)-H(10D)	109.5
C(9A)-C(8A)-P(1)	111.8(4)	C(8B)-C(10B)-H(10E)	109.5
C(8A)-C(9A)-H(9A1)	109.5	H(10D)-C(10B)-H(10E)	109.5
C(8A)-C(9A)-H(9A2)	109.5	C(8B)-C(10B)-H(10F)	109.5
H(9A1)-C(9A)-H(9A2)	109.5	H(10D)-C(10B)-H(10F)	109.5
C(8A)-C(9A)-H(9A3)	109.5	H(10E)-C(10B)-H(10F)	109.5
H(9A1)-C(9A)-H(9A3)	109.5	C(8B)-C(11B)-H(11D)	109.5
H(9A2)-C(9A)-H(9A3)	109.5	C(8B)-C(11B)-H(11E)	109.5
C(8A)-C(10A)-H(10A)	109.5	H(11D)-C(11B)-H(11E)	109.5
C(8A)-C(10A)-H(10B)	109.5	C(8B)-C(11B)-H(11F)	109.5
H(10A)-C(10A)-H(10B)	109.5	H(11D)-C(11B)-H(11F)	109.5
C(8A)-C(10A)-H(10C)	109.5	H(11E)-C(11B)-H(11F)	109.5
H(10A)-C(10A)-H(10C)	109.5		

Symmetry transformations used to generate equivalent atoms:

#1 -x+5/4,y,-z+5/4

Table S41. Torsion angles [°] for **(PCP)Ir(CO)(Me)(Ph)**.

C(7)-Ir(1)-C(1)-C(2)	121.98(18)	C(6)-Ir(1)-P(1)-C(8A)	130.2(2)
C(6)-Ir(1)-C(1)-C(2)	-58.02(18)	P(1)#1-Ir(1)-P(1)-C(8A)	-140.7(2)
P(1)#1-Ir(1)-C(1)-C(2)	24.30(18)	C(7)-Ir(1)-P(1)-C(8B)	169.4(2)
P(1)-Ir(1)-C(1)-C(2)	-155.70(18)	C(1)-Ir(1)-P(1)-C(8B)	78.5(2)
C(7)-Ir(1)-C(1)-C(2)#1	-58.02(18)	C(6)-Ir(1)-P(1)-C(8B)	-10.6(2)
C(6)-Ir(1)-C(1)-C(2)#1	121.98(18)	P(1)#1-Ir(1)-P(1)-C(8B)	78.5(2)
P(1)#1-Ir(1)-C(1)-C(2)#1	-155.70(18)	C(8B)-P(1)-C(8A)-C(10A)	161.7(5)
P(1)-Ir(1)-C(1)-C(2)#1	24.30(18)	Ir(1)-P(1)-C(8A)-C(10A)	17.1(5)
C(2)#1-C(1)-C(2)-C(3)	1.1(3)	C(8B)-P(1)-C(8A)-C(11A)	43.9(5)
Ir(1)-C(1)-C(2)-C(3)	-178.9(3)	Ir(1)-P(1)-C(8A)-C(11A)	-100.7(4)
C(2)#1-C(1)-C(2)-C(5)	173.6(4)	C(8B)-P(1)-C(8A)-C(9A)	-78.3(5)
Ir(1)-C(1)-C(2)-C(5)	-6.4(4)	Ir(1)-P(1)-C(8A)-C(9A)	137.1(4)
C(1)-C(2)-C(3)-C(4)	-2.1(5)	C(8A)-P(1)-C(8B)-C(11B)	45.2(5)
C(5)-C(2)-C(3)-C(4)	-173.8(4)	Ir(1)-P(1)-C(8B)-C(11B)	-168.3(4)
C(2)-C(3)-C(4)-C(3)#1	1.0(3)	C(8A)-P(1)-C(8B)-C(10B)	162.4(5)
C(3)-C(2)-C(5)-P(1)#1	149.2(4)	Ir(1)-P(1)-C(8B)-C(10B)	-51.2(5)
C(1)-C(2)-C(5)-P(1)#1	-23.1(5)	C(8A)-P(1)-C(8B)-C(9B)	-78.2(4)
C(7)-Ir(1)-P(1)-C(8A)	-49.8(2)	Ir(1)-P(1)-C(8B)-C(9B)	68.3(4)
C(1)-Ir(1)-P(1)-C(8A)	-140.7(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+5/4,y,-z+5/4

XI. Structural Data for (PCP)IrI(CCPh)

Figure S-11 : ORTEP Diagram of **(PCP)IrI(CCPh)**

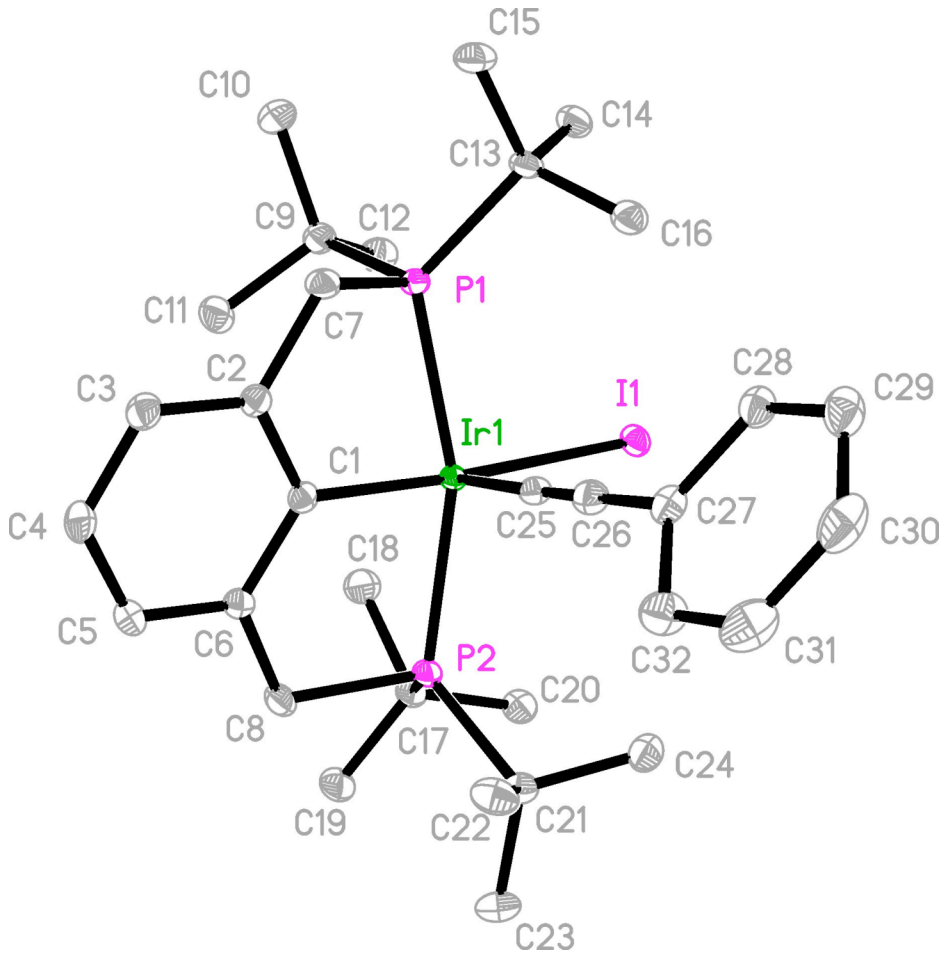

Table S42. Crystal data and structure refinement for **(PCP)IrI(CCPh)**

Identification code	iriccph	
Empirical formula	C32 H48 I Ir P2	
Formula weight	813.74	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.2440(6) Å	α= 90°.
	b = 15.2021(7) Å	β= 110.383(1)°.
	c = 16.7996(8) Å	γ = 90°.
Volume	3170.6(3) $Å^3$	
Z	4	
Density (calculated)	1.705 Mg/m^3	
Absorption coefficient	5.305 mm^{-1}	
F(000)	1600	
Crystal size	0.20 x 0.18 x 0.10 mm^3	
Theta range for data collection	1.86 to 30.55°.	
Index ranges	-18<=h<=18, -21<=k<=21, -23<=l<=24	
Reflections collected	38358	
Independent reflections	9666 [R(int) = 0.0191]	
Completeness to theta = 30.55°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9999 and 0.8237	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9666 / 0 / 337	
Goodness-of-fit on F^2	0.998	
Final R indices [I>2sigma(I)]	R1 = 0.0171, wR2 = 0.0384	
R indices (all data)	R1 = 0.0190, wR2 = 0.0390	
Largest diff. peak and hole	1.253 and -0.330 e.$Å^{-3}$	

Table S43. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(PCP)IrI(CCPh)**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	3080(1)	3295(1)	1240(1)	10(1)
I(1)	3893(1)	1656(1)	1780(1)	14(1)
P(1)	3450(1)	3223(1)	-22(1)	12(1)
P(2)	2201(1)	3591(1)	2218(1)	13(1)
C(1)	2443(1)	4485(1)	754(1)	12(1)
C(2)	2713(1)	4873(1)	90(1)	13(1)
C(3)	2275(2)	5680(1)	-254(1)	16(1)
C(4)	1583(2)	6130(1)	62(1)	17(1)
C(5)	1307(1)	5762(1)	715(1)	15(1)
C(6)	1728(1)	4949(1)	1058(1)	13(1)
C(7)	3478(1)	4401(1)	-248(1)	15(1)
C(8)	1354(2)	4542(1)	1723(1)	17(1)
C(9)	2242(1)	2754(1)	-885(1)	16(1)
C(10)	2347(2)	2787(1)	-1767(1)	22(1)
C(11)	1249(2)	3307(1)	-931(1)	21(1)
C(12)	2030(2)	1803(1)	-671(1)	20(1)
C(13)	4730(1)	2788(1)	-129(1)	14(1)
C(14)	4682(2)	1793(1)	-298(1)	18(1)
C(15)	4996(2)	3270(1)	-838(1)	20(1)
C(16)	5652(1)	2963(1)	710(1)	18(1)
C(17)	1170(1)	2716(1)	2163(1)	15(1)
C(18)	803(2)	2382(1)	1239(1)	21(1)
C(19)	174(2)	3050(1)	2345(1)	20(1)
C(20)	1674(2)	1948(1)	2762(1)	18(1)
C(21)	2979(2)	3920(1)	3340(1)	16(1)
C(22)	3465(2)	4833(1)	3303(1)	22(1)
C(23)	2287(2)	3992(1)	3907(1)	22(1)
C(24)	3901(2)	3263(1)	3715(1)	20(1)
C(25)	4382(1)	3943(1)	1803(1)	14(1)
C(26)	5205(2)	4347(1)	2145(1)	16(1)
C(27)	6219(1)	4774(1)	2578(1)	15(1)

C(28)	7165(1)	4492(1)	2463(1)	17(1)
C(29)	8147(2)	4894(1)	2890(1)	23(1)
C(30)	8206(2)	5583(2)	3446(1)	27(1)
C(31)	7280(2)	5870(2)	3567(1)	28(1)
C(32)	6293(2)	5473(1)	3137(1)	22(1)

Table S44. Bond lengths [Å] and angles [°] for **(PCP)IrI(CCPh)**.

Ir(1)-C(25)	1.9236(18)	C(9)-C(12)	1.538(3)
Ir(1)-C(1)	2.0417(17)	C(9)-C(11)	1.541(3)
Ir(1)-P(1)	2.3397(4)	C(13)-C(16)	1.533(2)
Ir(1)-P(2)	2.3643(4)	C(13)-C(14)	1.536(2)
Ir(1)-I(1)	2.74175(16)	C(13)-C(15)	1.542(2)
P(1)-C(7)	1.8338(18)	C(17)-C(20)	1.534(3)
P(1)-C(13)	1.8850(17)	C(17)-C(19)	1.539(2)
P(1)-C(9)	1.8858(18)	C(17)-C(18)	1.543(3)
P(2)-C(8)	1.8404(18)	C(21)-C(24)	1.533(3)
P(2)-C(21)	1.8733(18)	C(21)-C(23)	1.538(3)
P(2)-C(17)	1.8859(18)	C(21)-C(22)	1.541(3)
C(1)-C(6)	1.411(2)	C(25)-C(26)	1.208(2)
C(1)-C(2)	1.414(2)	C(26)-C(27)	1.440(2)
C(2)-C(3)	1.394(2)	C(27)-C(32)	1.399(3)
C(2)-C(7)	1.504(2)	C(27)-C(28)	1.400(3)
C(3)-C(4)	1.389(3)	C(28)-C(29)	1.388(3)
C(4)-C(5)	1.391(2)	C(29)-C(30)	1.388(3)
C(5)-C(6)	1.395(2)	C(30)-C(31)	1.382(3)
C(6)-C(8)	1.505(2)	C(31)-C(32)	1.391(3)
C(9)-C(10)	1.536(3)		
C(25)-Ir(1)-C(1)	85.29(7)	C(7)-P(1)-Ir(1)	99.59(6)
C(25)-Ir(1)-P(1)	92.00(5)	C(13)-P(1)-Ir(1)	125.56(6)
C(1)-Ir(1)-P(1)	82.37(5)	C(9)-P(1)-Ir(1)	108.96(6)
C(25)-Ir(1)-P(2)	97.75(5)	C(8)-P(2)-C(21)	106.26(9)
C(1)-Ir(1)-P(2)	82.79(5)	C(8)-P(2)-C(17)	102.36(8)
P(1)-Ir(1)-P(2)	161.484(16)	C(21)-P(2)-C(17)	111.86(8)
C(25)-Ir(1)-I(1)	96.97(5)	C(8)-P(2)-Ir(1)	101.88(6)
C(1)-Ir(1)-I(1)	176.07(5)	C(21)-P(2)-Ir(1)	121.24(6)
P(1)-Ir(1)-I(1)	94.320(11)	C(17)-P(2)-Ir(1)	110.82(6)
P(2)-Ir(1)-I(1)	100.042(11)	C(6)-C(1)-C(2)	117.60(15)
C(7)-P(1)-C(13)	103.87(8)	C(6)-C(1)-Ir(1)	122.25(12)
C(7)-P(1)-C(9)	106.50(8)	C(2)-C(1)-Ir(1)	120.14(12)
C(13)-P(1)-C(9)	110.17(8)	C(3)-C(2)-C(1)	120.76(16)

C(3)-C(2)-C(7)	120.07(15)	C(20)-C(17)-C(19)	109.15(15)
C(1)-C(2)-C(7)	119.17(15)	C(20)-C(17)-C(18)	108.76(15)
C(4)-C(3)-C(2)	120.65(16)	C(19)-C(17)-C(18)	108.47(15)
C(3)-C(4)-C(5)	119.55(16)	C(20)-C(17)-P(2)	111.23(12)
C(4)-C(5)-C(6)	120.37(16)	C(19)-C(17)-P(2)	114.46(13)
C(5)-C(6)-C(1)	121.04(16)	C(18)-C(17)-P(2)	104.51(12)
C(5)-C(6)-C(8)	118.87(15)	C(24)-C(21)-C(23)	110.61(16)
C(1)-C(6)-C(8)	119.98(15)	C(24)-C(21)-C(22)	108.62(15)
C(2)-C(7)-P(1)	108.87(12)	C(23)-C(21)-C(22)	107.96(15)
C(6)-C(8)-P(2)	110.57(12)	C(24)-C(21)-P(2)	108.68(12)
C(10)-C(9)-C(12)	110.03(15)	C(23)-C(21)-P(2)	113.87(13)
C(10)-C(9)-C(11)	107.25(15)	C(22)-C(21)-P(2)	106.91(13)
C(12)-C(9)-C(11)	107.60(16)	C(26)-C(25)-Ir(1)	178.89(16)
C(10)-C(9)-P(1)	113.01(13)	C(25)-C(26)-C(27)	176.16(19)
C(12)-C(9)-P(1)	110.53(12)	C(32)-C(27)-C(28)	117.93(17)
C(11)-C(9)-P(1)	108.20(12)	C(32)-C(27)-C(26)	121.09(17)
C(16)-C(13)-C(14)	108.06(15)	C(28)-C(27)-C(26)	120.97(17)
C(16)-C(13)-C(15)	107.74(15)	C(29)-C(28)-C(27)	121.10(18)
C(14)-C(13)-C(15)	109.34(15)	C(28)-C(29)-C(30)	120.19(19)
C(16)-C(13)-P(1)	107.85(12)	C(31)-C(30)-C(29)	119.47(18)
C(14)-C(13)-P(1)	112.47(12)	C(30)-C(31)-C(32)	120.6(2)
C(15)-C(13)-P(1)	111.20(12)	C(31)-C(32)-C(27)	120.72(19)

Table S45. Torsion angles [°] for **(PCP)IrI(CCPh)**

C(25)-Ir(1)-P(1)-C(7)	-60.61(8)	C(6)-C(1)-C(2)-C(7)	179.65(15)
C(1)-Ir(1)-P(1)-C(7)	24.37(7)	Ir(1)-C(1)-C(2)-C(7)	-0.3(2)
P(2)-Ir(1)-P(1)-C(7)	61.33(8)	C(1)-C(2)-C(3)-C(4)	1.6(3)
I(1)-Ir(1)-P(1)-C(7)	-157.76(6)	C(7)-C(2)-C(3)-C(4)	-178.85(17)
C(25)-Ir(1)-P(1)-C(13)	54.21(9)	C(2)-C(3)-C(4)-C(5)	-1.5(3)
C(1)-Ir(1)-P(1)-C(13)	139.19(8)	C(3)-C(4)-C(5)-C(6)	0.6(3)
P(2)-Ir(1)-P(1)-C(13)	176.15(8)	C(4)-C(5)-C(6)-C(1)	0.2(3)
I(1)-Ir(1)-P(1)-C(13)	-42.94(7)	C(4)-C(5)-C(6)-C(8)	-175.91(17)
C(25)-Ir(1)-P(1)-C(9)	-171.86(8)	C(2)-C(1)-C(6)-C(5)	-0.1(2)
C(1)-Ir(1)-P(1)-C(9)	-86.89(8)	Ir(1)-C(1)-C(6)-C(5)	179.85(13)
P(2)-Ir(1)-P(1)-C(9)	-49.93(8)	C(2)-C(1)-C(6)-C(8)	175.98(15)
I(1)-Ir(1)-P(1)-C(9)	90.99(6)	Ir(1)-C(1)-C(6)-C(8)	-4.1(2)
C(25)-Ir(1)-P(2)-C(8)	95.54(8)	C(3)-C(2)-C(7)-P(1)	-155.94(14)
C(1)-Ir(1)-P(2)-C(8)	11.32(8)	C(1)-C(2)-C(7)-P(1)	23.6(2)
P(1)-Ir(1)-P(2)-C(8)	-25.60(9)	C(13)-P(1)-C(7)-C(2)	-161.53(12)
I(1)-Ir(1)-P(2)-C(8)	-165.92(7)	C(9)-P(1)-C(7)-C(2)	82.14(13)
C(25)-Ir(1)-P(2)-C(21)	-22.01(9)	Ir(1)-P(1)-C(7)-C(2)	-31.04(12)
C(1)-Ir(1)-P(2)-C(21)	-106.22(8)	C(5)-C(6)-C(8)-P(2)	-169.20(13)
P(1)-Ir(1)-P(2)-C(21)	-143.14(8)	C(1)-C(6)-C(8)-P(2)	14.6(2)
I(1)-Ir(1)-P(2)-C(21)	76.54(7)	C(21)-P(2)-C(8)-C(6)	111.62(13)
C(25)-Ir(1)-P(2)-C(17)	-156.16(8)	C(17)-P(2)-C(8)-C(6)	-130.92(13)
C(1)-Ir(1)-P(2)-C(17)	119.62(8)	Ir(1)-P(2)-C(8)-C(6)	-16.22(14)
P(1)-Ir(1)-P(2)-C(17)	82.70(8)	C(7)-P(1)-C(9)-C(10)	66.09(15)
I(1)-Ir(1)-P(2)-C(17)	-57.62(6)	C(13)-P(1)-C(9)-C(10)	-45.95(15)
C(25)-Ir(1)-C(1)-C(6)	-104.39(14)	Ir(1)-P(1)-C(9)-C(10)	172.67(12)
P(1)-Ir(1)-C(1)-C(6)	162.95(14)	C(7)-P(1)-C(9)-C(12)	-170.11(12)
P(2)-Ir(1)-C(1)-C(6)	-5.95(13)	C(13)-P(1)-C(9)-C(12)	77.86(14)
I(1)-Ir(1)-C(1)-C(6)	130.3(6)	Ir(1)-P(1)-C(9)-C(12)	-63.52(13)
C(25)-Ir(1)-C(1)-C(2)	75.57(14)	C(7)-P(1)-C(9)-C(11)	-52.52(14)
P(1)-Ir(1)-C(1)-C(2)	-17.09(12)	C(13)-P(1)-C(9)-C(11)	-164.55(12)
P(2)-Ir(1)-C(1)-C(2)	174.01(13)	Ir(1)-P(1)-C(9)-C(11)	54.07(13)
I(1)-Ir(1)-C(1)-C(2)	-49.8(7)	C(7)-P(1)-C(13)-C(16)	82.51(13)
C(6)-C(1)-C(2)-C(3)	-0.8(2)	C(9)-P(1)-C(13)-C(16)	-163.77(12)
Ir(1)-C(1)-C(2)-C(3)	179.25(13)	Ir(1)-P(1)-C(13)-C(16)	-30.29(15)

C(7)-P(1)-C(13)-C(14)	-158.44(13)	Ir(1)-P(2)-C(21)-C(23)	-173.98(11)
C(9)-P(1)-C(13)-C(14)	-44.72(15)	C(8)-P(2)-C(21)-C(22)	-48.46(14)
Ir(1)-P(1)-C(13)-C(14)	88.76(13)	C(17)-P(2)-C(21)-C(22)	-159.39(12)
C(7)-P(1)-C(13)-C(15)	-35.42(14)	Ir(1)-P(2)-C(21)-C(22)	66.87(13)
C(9)-P(1)-C(13)-C(15)	78.30(14)	C(1)-Ir(1)-C(25)-C(26)	-93(9)
Ir(1)-P(1)-C(13)-C(15)	-148.22(10)	P(1)-Ir(1)-C(25)-C(26)	-11(9)
C(8)-P(2)-C(17)-C(20)	-163.68(13)	P(2)-Ir(1)-C(25)-C(26)	-175(100)
C(21)-P(2)-C(17)-C(20)	-50.30(15)	I(1)-Ir(1)-C(25)-C(26)	84(9)
Ir(1)-P(2)-C(17)-C(20)	88.33(12)	Ir(1)-C(25)-C(26)-C(27)	-88(9)
C(8)-P(2)-C(17)-C(19)	-39.38(15)	C(25)-C(26)-C(27)-C(32)	-123(3)
C(21)-P(2)-C(17)-C(19)	74.00(15)	C(25)-C(26)-C(27)-C(28)	56(3)
Ir(1)-P(2)-C(17)-C(19)	-147.37(12)	C(32)-C(27)-C(28)-C(29)	0.0(3)
C(8)-P(2)-C(17)-C(18)	79.13(13)	C(26)-C(27)-C(28)-C(29)	-179.00(17)
C(21)-P(2)-C(17)-C(18)	-167.49(12)	C(27)-C(28)-C(29)-C(30)	0.4(3)
Ir(1)-P(2)-C(17)-C(18)	-28.86(13)	C(28)-C(29)-C(30)-C(31)	-0.4(3)
C(8)-P(2)-C(21)-C(24)	-165.54(13)	C(29)-C(30)-C(31)-C(32)	0.0(3)
C(17)-P(2)-C(21)-C(24)	83.53(14)	C(30)-C(31)-C(32)-C(27)	0.4(3)
Ir(1)-P(2)-C(21)-C(24)	-50.20(14)	C(28)-C(27)-C(32)-C(31)	-0.4(3)
C(8)-P(2)-C(21)-C(23)	70.68(15)	C(26)-C(27)-C(32)-C(31)	178.56(19)
C(17)-P(2)-C(21)-C(23)	-40.25(16)		