Addition of C-C and C-H Bonds by Pincer-Iridium Complexes: a Combined Experimental and Computational Study

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Supporting Information

Part I: X-Ray Structure Determination

X-ray Structure Determination for 2-C1 co-crystal

X-ray diffraction data were collected on a Bruker Smart APEX CCD diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073Å) at 100 K. Crystals were immersed in Paratone oil, placed on a glass needle, and examined at 100 K. The data were corrected for Lorenz effects, polarization, and absorption, the latter by a multiscan (SADABS) method.[1] The structures were solved by direct methods (SHELXS86).[2] All non-hydrogen atoms were refined (SHELXL97)3 based upon Fobs.[2] All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97). Scattering factors (fo, f', f'') are as described in SHELXL97.

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. SHELX86, 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 2-C1 (**anti** and **syn** co-crystal)

Figure S-1. ORTEP Diagram of **2-C1-anti**

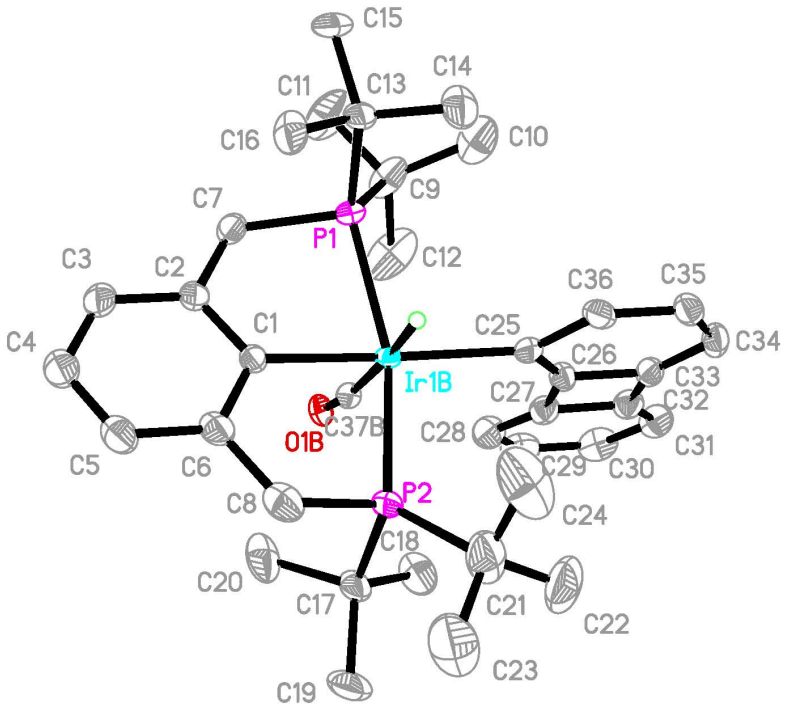

Figure S-1. ORTEP Diagram of **2-C1-syn**

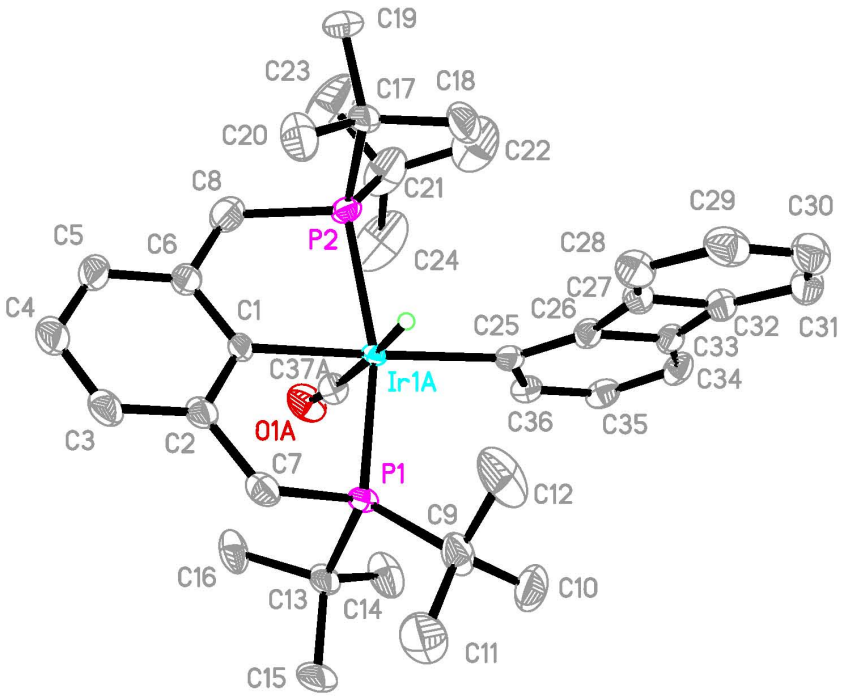

Table S-1. Crystal data and structure refinement for **2-C1** co-crystal

Identification code	biphenco_R3	
Empirical formula	C37.83 H53 Ir O P2	
Formula weight	777.94	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R -3 :H	
Unit cell dimensions	a = 29.294(7) Å	□= 90°.
	b = 29.294(7) Å	□= 90°.
	c = 21.131(7) Å	□ = 120°.
Volume	15703(9) $Å^3$	
Z	18	
Density (calculated)	1.481 Mg/m^3	
Absorption coefficient	3.946 mm^{-1}	
F(000)	7110	
Crystal size	0.440 x 0.370 x 0.090 mm^3	
Theta range for data collection	1.254 to 32.561°.	
Index ranges	-42<=h<=43, -44<=k<=43, -31<=l<=31	
Reflections collected	49815	
Independent reflections	12685 [R(int) = 0.0628]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7464 and 0.5832	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12685 / 562 / 410	
Goodness-of-fit on F^2	1.007	
Final R indices [I>2sigma(I)]	R1 = 0.0533, wR2 = 0.1219	
R indices (all data)	R1 = 0.0712, wR2 = 0.1295	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.598 and -1.850 $e.Å^{-3}$	

Table S-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2-C1** co-crystal. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1A)	2217(1)	1555(1)	3226(1)	14(1)
O(1A)	1387(2)	1463(2)	4167(3)	37(1)
C(37A)	1694(2)	1506(3)	3869(2)	26(1)
Ir(1B)	2320(1)	1580(1)	3105(1)	14(1)
O(1B)	2998(4)	1667(4)	1978(4)	21(2)
C(37B)	2787(4)	1624(5)	2390(4)	20(2)
P(1)	2567(1)	2458(1)	3003(1)	17(1)
P(2)	1762(1)	645(1)	3108(1)	21(1)
C(1)	1706(2)	1493(2)	2481(2)	22(1)
C(2)	1808(2)	1923(2)	2103(2)	25(1)
C(3)	1453(2)	1872(2)	1624(2)	32(1)
C(4)	996(2)	1391(2)	1525(3)	37(1)
C(5)	890(2)	962(2)	1896(3)	34(1)
C(6)	1243(2)	1013(2)	2375(2)	27(1)
C(7)	2314(2)	2436(2)	2200(2)	25(1)
C(8)	1132(2)	545(2)	2781(3)	32(1)
C(9)	3295(2)	2926(2)	2938(3)	35(1)
C(10)	3535(2)	3097(3)	3601(3)	50(2)
C(11)	3431(3)	3416(3)	2528(4)	54(2)
C(12)	3541(3)	2632(3)	2621(4)	55(2)
C(13)	2253(2)	2761(2)	3500(2)	26(1)
C(14)	2323(3)	2689(3)	4205(2)	42(1)
C(15)	2478(3)	3352(2)	3368(3)	43(1)
C(16)	1666(2)	2487(2)	3326(2)	33(1)
C(17)	2002(2)	349(2)	2498(2)	32(1)
C(18)	2586(3)	528(3)	2627(3)	44(1)
C(19)	1686(3)	-248(2)	2431(4)	58(2)
C(20)	1980(3)	587(3)	1847(3)	44(1)
C(21)	1565(3)	216(3)	3836(3)	50(2)
C(22)	2011(3)	142(3)	4069(4)	67(2)

C(23)	1063(3)	-319(3)	3731(4)	76(3)
C(24)	1428(3)	479(4)	4357(3)	72(2)
C(25)	2800(2)	1627(2)	3901(2)	20(1)
C(26)	3275(2)	1632(2)	3840(2)	21(1)
C(27)	3690(2)	1635(2)	3387(2)	23(1)
C(28)	3851(2)	1644(2)	2783(2)	30(1)
C(29)	4354(2)	1690(2)	2712(3)	36(1)
C(30)	4660(2)	1720(2)	3221(3)	35(1)
C(31)	4495(2)	1719(2)	3850(3)	32(1)
C(32)	4008(2)	1673(2)	3910(2)	26(1)
C(33)	3607(2)	1670(2)	4352(2)	22(1)
C(34)	3493(2)	1710(2)	4969(2)	26(1)
C(35)	3018(2)	1713(2)	5058(2)	25(1)
C(36)	2701(2)	1676(2)	4557(2)	24(1)
C(41A)	6108	2508	3626	100
C(42A)	6386	2994	3184	200
C(43A)	6339	3454	3479	200
C(44A)	6898	3900	3664	200
C(45A)	7284	3683	3630	200

Table S-3. Bond lengths [Å] and angles [°] for **2-C1** co-crystal.

Ir(1A)-C(37A)	1.9983(11)	C(8)-H(8B)	0.9900
Ir(1A)-C(1)	2.119(4)	C(9)-C(12)	1.527(9)
Ir(1A)-C(25)	2.153(4)	C(9)-C(10)	1.536(9)
Ir(1A)-P(2)	2.3220(13)	C(9)-C(11)	1.549(8)
Ir(1A)-P(1)	2.3604(12)	C(10)-H(10A)	0.9800
Ir(1A)-H(1A)	1.578(9)	C(10)-H(10B)	0.9800
O(1A)-C(37A)	1.053(5)	C(10)-H(10C)	0.9800
Ir(1B)-C(37B)	1.9994(11)	C(11)-H(11A)	0.9800
Ir(1B)-C(1)	2.142(4)	C(11)-H(11B)	0.9800
Ir(1B)-C(25)	2.152(4)	C(11)-H(11C)	0.9800
Ir(1B)-P(1)	2.3081(17)	C(12)-H(12A)	0.9800
Ir(1B)-P(2)	2.3885(17)	C(12)-H(12B)	0.9800
Ir(1B)-H(1B)	1.623(9)	C(12)-H(12C)	0.9800
O(1B)-C(37B)	1.039(7)	C(13)-C(14)	1.532(7)
P(1)-C(7)	1.839(5)	C(13)-C(16)	1.535(7)
P(1)-C(9)	1.876(5)	C(13)-C(15)	1.540(7)
P(1)-C(13)	1.885(4)	C(14)-H(14A)	0.9800
P(2)-C(8)	1.854(5)	C(14)-H(14B)	0.9800
P(2)-C(17)	1.875(5)	C(14)-H(14C)	0.9800
P(2)-C(21)	1.885(6)	C(15)-H(15A)	0.9800
C(1)-C(2)	1.391(6)	C(15)-H(15B)	0.9800
C(1)-C(6)	1.400(7)	C(15)-H(15C)	0.9800
C(2)-C(3)	1.404(7)	C(16)-H(16A)	0.9800
C(2)-C(7)	1.506(7)	C(16)-H(16B)	0.9800
C(3)-C(4)	1.392(8)	C(16)-H(16C)	0.9800
C(3)-H(3)	0.9500	C(17)-C(19)	1.522(8)
C(4)-C(5)	1.377(8)	C(17)-C(18)	1.542(8)
C(4)-H(4)	0.9500	C(17)-C(20)	1.558(8)
C(5)-C(6)	1.401(7)	C(18)-H(18A)	0.9800
C(5)-H(5)	0.9500	C(18)-H(18B)	0.9800
C(6)-C(8)	1.507(8)	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(20)-H(20A)	0.9800	C(30)-H(30)	0.9500
C(20)-H(20B)	0.9800	C(31)-C(32)	1.372(7)
C(20)-H(20C)	0.9800	C(31)-H(31)	0.9500
C(21)-C(24)	1.508(11)	C(32)-C(33)	1.498(7)
C(21)-C(22)	1.511(11)	C(33)-C(34)	1.364(7)
C(21)-C(23)	1.538(9)	C(34)-C(35)	1.409(7)
C(22)-H(22A)	0.9800	C(34)-H(34)	0.9500
C(22)-H(22B)	0.9800	C(35)-C(36)	1.376(6)
C(22)-H(22C)	0.9800	C(35)-H(35)	0.9500
C(23)-H(23A)	0.9800	C(36)-H(36)	0.9500
C(23)-H(23B)	0.9800	C(41A)-C(42A)	1.5514(3)
C(23)-H(23C)	0.9800	C(41A)-H(41A)	0.9800
C(24)-H(24A)	0.9800	C(41A)-H(41B)	0.9800
C(24)-H(24B)	0.9800	C(41A)-H(41C)	0.9800
C(24)-H(24C)	0.9800	C(42A)-C(43A)	1.5505(3)
C(25)-C(26)	1.390(6)	C(42A)-H(42A)	0.9900
C(25)-C(36)	1.438(6)	C(42A)-H(42B)	0.9900
C(26)-C(33)	1.421(6)	C(43A)-C(44A)	1.5499(3)
C(26)-C(27)	1.546(6)	C(43A)-H(43A)	0.9900
C(27)-C(28)	1.355(7)	C(43A)-H(43B)	0.9900
C(27)-C(32)	1.413(6)	C(44A)-C(45A)	1.5533(4)
C(28)-C(29)	1.418(7)	C(44A)-H(44A)	0.9900
C(28)-H(28)	0.9500	C(44A)-H(44B)	0.9900
C(29)-C(30)	1.373(8)	C(45A)-H(45A)	0.9800
C(29)-H(29)	0.9500	C(45A)-H(45B)	0.9800
C(30)-C(31)	1.412(8)	C(45A)-H(45C)	0.9800

C(37A)-Ir(1A)-C(1)	90.9(2)	P(2)-Ir(1A)-P(1)	160.79(5)
C(37A)-Ir(1A)-C(25)	95.7(2)	C(37A)-Ir(1A)-H(1A)	177.2(4)
C(1)-Ir(1A)-C(25)	173.41(17)	C(1)-Ir(1A)-H(1A)	87.1(5)
C(37A)-Ir(1A)-P(2)	90.7(2)	C(25)-Ir(1A)-H(1A)	86.3(5)
C(1)-Ir(1A)-P(2)	81.21(12)	P(2)-Ir(1A)-H(1A)	87.1(2)
C(25)-Ir(1A)-P(2)	98.98(11)	P(1)-Ir(1A)-H(1A)	85.7(2)
C(37A)-Ir(1A)-P(1)	96.0(2)	O(1A)-C(37A)-Ir(1A)	173.6(7)
C(1)-Ir(1A)-P(1)	80.69(13)	C(37B)-Ir(1B)-C(1)	92.8(4)
C(25)-Ir(1A)-P(1)	98.26(11)	C(37B)-Ir(1B)-C(25)	100.5(4)

C(1)-Ir(1B)-C(25)	166.52(18)	C(6)-C(1)-Ir(1B)	123.5(3)
C(37B)-Ir(1B)-P(1)	92.0(4)	C(1)-C(2)-C(3)	120.3(5)
C(1)-Ir(1B)-P(1)	81.44(13)	C(1)-C(2)-C(7)	118.9(4)
C(25)-Ir(1B)-P(1)	99.89(12)	C(3)-C(2)-C(7)	120.7(4)
C(37B)-Ir(1B)-P(2)	97.4(4)	C(4)-C(3)-C(2)	120.1(5)
C(1)-Ir(1B)-P(2)	79.22(13)	C(4)-C(3)-H(3)	119.9
C(25)-Ir(1B)-P(2)	96.97(12)	C(2)-C(3)-H(3)	119.9
P(1)-Ir(1B)-P(2)	158.84(7)	C(5)-C(4)-C(3)	120.2(5)
C(37B)-Ir(1B)-H(1B)	176.2(6)	C(5)-C(4)-H(4)	119.9
C(1)-Ir(1B)-H(1B)	83.7(4)	C(3)-C(4)-H(4)	119.9
C(25)-Ir(1B)-H(1B)	83.0(4)	C(4)-C(5)-C(6)	119.8(5)
P(1)-Ir(1B)-H(1B)	86.1(2)	C(4)-C(5)-H(5)	120.1
P(2)-Ir(1B)-H(1B)	83.4(2)	C(6)-C(5)-H(5)	120.1
O(1B)-C(37B)-Ir(1B)	171.3(13)	C(1)-C(6)-C(5)	121.0(5)
C(7)-P(1)-C(9)	104.5(2)	C(1)-C(6)-C(8)	118.9(4)
C(7)-P(1)-C(13)	104.5(2)	C(5)-C(6)-C(8)	120.2(5)
C(9)-P(1)-C(13)	110.0(3)	C(2)-C(7)-P(1)	109.9(3)
C(7)-P(1)-Ir(1B)	98.62(16)	C(2)-C(7)-H(7A)	109.7
C(9)-P(1)-Ir(1B)	115.36(18)	P(1)-C(7)-H(7A)	109.7
C(13)-P(1)-Ir(1B)	121.11(17)	C(2)-C(7)-H(7B)	109.7
C(7)-P(1)-Ir(1A)	101.70(16)	P(1)-C(7)-H(7B)	109.7
C(9)-P(1)-Ir(1A)	122.06(17)	H(7A)-C(7)-H(7B)	108.2
C(13)-P(1)-Ir(1A)	112.00(17)	C(6)-C(8)-P(2)	109.0(3)
C(8)-P(2)-C(17)	104.2(2)	C(6)-C(8)-H(8A)	109.9
C(8)-P(2)-C(21)	104.5(3)	P(2)-C(8)-H(8A)	109.9
C(17)-P(2)-C(21)	108.4(3)	C(6)-C(8)-H(8B)	109.9
C(8)-P(2)-Ir(1A)	100.05(17)	P(2)-C(8)-H(8B)	109.9
C(17)-P(2)-Ir(1A)	118.17(19)	H(8A)-C(8)-H(8B)	108.3
C(21)-P(2)-Ir(1A)	119.1(2)	C(12)-C(9)-C(10)	108.3(5)
C(8)-P(2)-Ir(1B)	103.60(18)	C(12)-C(9)-C(11)	107.6(5)
C(17)-P(2)-Ir(1B)	109.20(19)	C(10)-C(9)-C(11)	110.2(5)
C(21)-P(2)-Ir(1B)	124.9(2)	C(12)-C(9)-P(1)	107.8(4)
C(2)-C(1)-C(6)	118.7(4)	C(10)-C(9)-P(1)	109.9(4)
C(2)-C(1)-Ir(1A)	121.8(3)	C(11)-C(9)-P(1)	112.9(4)
C(6)-C(1)-Ir(1A)	119.5(3)	C(9)-C(10)-H(10A)	109.5
C(2)-C(1)-Ir(1B)	117.2(3)	C(9)-C(10)-H(10B)	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)	110.0(5)
C(9)-C(11)-H(11B)	109.5	C(19)-C(17)-C(20)	107.1(5)
H(11A)-C(11)-H(11B)	109.5	C(18)-C(17)-C(20)	107.0(5)
C(9)-C(11)-H(11C)	109.5	C(19)-C(17)-P(2)	116.1(5)
H(11A)-C(11)-H(11C)	109.5	C(18)-C(17)-P(2)	109.2(3)
H(11B)-C(11)-H(11C)	109.5	C(20)-C(17)-P(2)	106.9(3)
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(9)-C(12)-H(12C)	109.5	C(17)-C(18)-H(18C)	109.5
H(12A)-C(12)-H(12C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(12B)-C(12)-H(12C)	109.5	H(18B)-C(18)-H(18C)	109.5
C(14)-C(13)-C(16)	110.7(5)	C(17)-C(19)-H(19A)	109.5
C(14)-C(13)-C(15)	108.6(4)	C(17)-C(19)-H(19B)	109.5
C(16)-C(13)-C(15)	106.4(4)	H(19A)-C(19)-H(19B)	109.5
C(14)-C(13)-P(1)	110.3(3)	C(17)-C(19)-H(19C)	109.5
C(16)-C(13)-P(1)	107.7(3)	H(19A)-C(19)-H(19C)	109.5
C(15)-C(13)-P(1)	113.1(4)	H(19B)-C(19)-H(19C)	109.5
C(13)-C(14)-H(14A)	109.5	C(17)-C(20)-H(20A)	109.5
C(13)-C(14)-H(14B)	109.5	C(17)-C(20)-H(20B)	109.5
H(14A)-C(14)-H(14B)	109.5	H(20A)-C(20)-H(20B)	109.5
C(13)-C(14)-H(14C)	109.5	C(17)-C(20)-H(20C)	109.5
H(14A)-C(14)-H(14C)	109.5	H(20A)-C(20)-H(20C)	109.5
H(14B)-C(14)-H(14C)	109.5	H(20B)-C(20)-H(20C)	109.5
C(13)-C(15)-H(15A)	109.5	C(24)-C(21)-C(22)	107.9(6)
C(13)-C(15)-H(15B)	109.5	C(24)-C(21)-C(23)	105.3(7)
H(15A)-C(15)-H(15B)	109.5	C(22)-C(21)-C(23)	110.8(7)
C(13)-C(15)-H(15C)	109.5	C(24)-C(21)-P(2)	109.0(5)
H(15A)-C(15)-H(15C)	109.5	C(22)-C(21)-P(2)	111.2(5)
H(15B)-C(15)-H(15C)	109.5	C(23)-C(21)-P(2)	112.3(5)
C(13)-C(16)-H(16A)	109.5	C(21)-C(22)-H(22A)	109.5
C(13)-C(16)-H(16B)	109.5	C(21)-C(22)-H(22B)	109.5

H(22A)-C(22)-H(22B)	109.5	C(32)-C(31)-C(30)	115.2(5)
C(21)-C(22)-H(22C)	109.5	C(32)-C(31)-H(31)	122.4
H(22A)-C(22)-H(22C)	109.5	C(30)-C(31)-H(31)	122.4
H(22B)-C(22)-H(22C)	109.5	C(31)-C(32)-C(27)	123.1(5)
C(21)-C(23)-H(23A)	109.5	C(31)-C(32)-C(33)	146.5(5)
C(21)-C(23)-H(23B)	109.5	C(27)-C(32)-C(33)	90.3(4)
H(23A)-C(23)-H(23B)	109.5	C(34)-C(33)-C(26)	123.3(4)
C(21)-C(23)-H(23C)	109.5	C(34)-C(33)-C(32)	145.0(4)
H(23A)-C(23)-H(23C)	109.5	C(26)-C(33)-C(32)	91.6(4)
H(23B)-C(23)-H(23C)	109.5	C(33)-C(34)-C(35)	114.3(4)
C(21)-C(24)-H(24A)	109.5	C(33)-C(34)-H(34)	122.9
C(21)-C(24)-H(24B)	109.5	C(35)-C(34)-H(34)	122.9
H(24A)-C(24)-H(24B)	109.5	C(36)-C(35)-C(34)	121.9(4)
C(21)-C(24)-H(24C)	109.5	C(36)-C(35)-H(35)	119.1
H(24A)-C(24)-H(24C)	109.5	C(34)-C(35)-H(35)	119.1
H(24B)-C(24)-H(24C)	109.5	C(35)-C(36)-C(25)	125.9(4)
C(26)-C(25)-C(36)	109.9(4)	C(35)-C(36)-H(36)	117.1
C(26)-C(25)-Ir(1B)	123.1(3)	C(25)-C(36)-H(36)	117.1
C(36)-C(25)-Ir(1B)	127.0(3)	C(42A)-C(41A)-H(41A)	109.5
C(26)-C(25)-Ir(1A)	132.9(3)	C(42A)-C(41A)-H(41B)	109.5
C(36)-C(25)-Ir(1A)	117.3(3)	H(41A)-C(41A)-H(41B)	109.5
C(25)-C(26)-C(33)	124.8(4)	C(42A)-C(41A)-H(41C)	109.5
C(25)-C(26)-C(27)	147.0(4)	H(41A)-C(41A)-H(41C)	109.5
C(33)-C(26)-C(27)	88.1(3)	H(41B)-C(41A)-H(41C)	109.5
C(28)-C(27)-C(32)	121.8(4)	C(43A)-C(42A)-C(41A)	108.757(16)
C(28)-C(27)-C(26)	148.0(4)	C(43A)-C(42A)-H(42A)	109.9
C(32)-C(27)-C(26)	90.0(4)	C(41A)-C(42A)-H(42A)	109.9
C(27)-C(28)-C(29)	115.8(5)	C(43A)-C(42A)-H(42B)	109.9
C(27)-C(28)-H(28)	122.1	C(41A)-C(42A)-H(42B)	109.9
C(29)-C(28)-H(28)	122.1	H(42A)-C(42A)-H(42B)	108.3
C(30)-C(29)-C(28)	122.4(5)	C(44A)-C(43A)-C(42A)	108.664(2)
C(30)-C(29)-H(29)	118.8	C(44A)-C(43A)-H(43A)	110.0
C(28)-C(29)-H(29)	118.8	C(42A)-C(43A)-H(43A)	110.0
C(29)-C(30)-C(31)	121.7(5)	C(44A)-C(43A)-H(43B)	110.0
C(29)-C(30)-H(30)	119.1	C(42A)-C(43A)-H(43B)	110.0
C(31)-C(30)-H(30)	119.1	H(43A)-C(43A)-H(43B)	108.3

C(43A)-C(44A)-C(45A)	108.700(1)	C(44A)-C(45A)-H(45A)	109.5
C(43A)-C(44A)-H(44A)	109.9	C(44A)-C(45A)-H(45B)	109.5
C(45A)-C(44A)-H(44A)	109.9	H(45A)-C(45A)-H(45B)	109.5
C(43A)-C(44A)-H(44B)	109.9	C(44A)-C(45A)-H(45C)	109.5
C(45A)-C(44A)-H(44B)	109.9	H(45A)-C(45A)-H(45C)	109.5
H(44A)-C(44A)-H(44B)	108.3	H(45B)-C(45A)-H(45C)	109.5

Table S-4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2-C1** co-crystal. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1A)	15(1)	13(1)	16(1)	-2(1)	0(1)	8(1)
O(1A)	33(3)	41(3)	43(3)	6(2)	13(2)	25(2)
C(37A)	26(3)	26(3)	27(3)	-2(2)	-3(2)	14(2)
Ir(1B)	15(1)	13(1)	16(1)	-2(1)	0(1)	8(1)
O(1B)	24(4)	26(5)	13(4)	-1(3)	-1(3)	12(4)
C(37B)	22(4)	18(4)	21(4)	-2(3)	-6(3)	11(3)
P(1)	19(1)	14(1)	20(1)	1(1)	2(1)	9(1)
P(2)	22(1)	15(1)	22(1)	-2(1)	-3(1)	7(1)
C(1)	25(2)	25(2)	24(2)	-9(1)	-9(1)	19(2)
C(2)	35(2)	29(2)	21(2)	-8(2)	-6(2)	24(2)
C(3)	44(2)	40(2)	28(2)	-9(2)	-7(2)	33(2)
C(4)	43(2)	47(2)	39(2)	-17(2)	-14(2)	35(2)
C(5)	30(2)	40(2)	40(2)	-17(2)	-12(2)	24(2)
C(6)	25(2)	31(2)	31(2)	-11(2)	-6(2)	19(2)
C(7)	35(2)	28(2)	21(2)	1(2)	-1(2)	21(2)
C(8)	27(2)	33(2)	35(2)	-9(2)	-3(2)	13(2)
C(9)	20(2)	32(2)	51(3)	18(2)	4(2)	12(2)
C(10)	25(2)	37(3)	72(4)	11(3)	-16(3)	4(2)
C(11)	35(3)	40(3)	77(4)	33(3)	8(3)	11(2)
C(12)	37(3)	69(4)	75(4)	32(3)	31(3)	37(3)
C(13)	34(2)	30(2)	27(2)	-10(2)	-6(2)	24(2)
C(14)	55(3)	68(4)	27(2)	-14(2)	-7(2)	50(3)
C(15)	61(3)	31(2)	52(3)	-19(2)	-20(3)	35(3)
C(16)	32(2)	54(3)	27(2)	-5(2)	-2(2)	33(2)
C(17)	41(2)	33(2)	33(2)	-17(2)	-16(2)	28(2)
C(18)	48(3)	62(4)	47(3)	-24(3)	-18(2)	45(3)
C(19)	73(4)	35(3)	79(4)	-34(3)	-44(3)	38(3)
C(20)	54(3)	76(4)	26(2)	-20(2)	-11(2)	51(3)
C(21)	47(3)	43(3)	36(2)	12(2)	-5(2)	3(2)
C(22)	74(4)	52(4)	52(4)	26(3)	-18(3)	14(3)

C(23)	64(4)	51(4)	56(4)	19(3)	-13(3)	-15(3)
C(24)	55(4)	81(5)	35(3)	5(3)	15(3)	0(3)
C(25)	22(2)	15(2)	22(2)	0(1)	-3(1)	9(1)
C(26)	21(2)	20(2)	20(2)	0(1)	-3(1)	9(1)
C(27)	21(2)	21(2)	27(2)	2(2)	0(1)	10(2)
C(28)	32(2)	31(2)	29(2)	1(2)	2(2)	17(2)
C(29)	36(2)	32(2)	42(2)	2(2)	11(2)	19(2)
C(30)	25(2)	33(2)	49(2)	4(2)	8(2)	15(2)
C(31)	25(2)	29(2)	42(2)	2(2)	-4(2)	12(2)
C(32)	23(2)	22(2)	30(2)	1(2)	-3(2)	10(2)
C(33)	21(2)	19(2)	25(2)	1(1)	-6(1)	8(1)
C(34)	25(2)	22(2)	23(2)	3(2)	-7(2)	6(2)
C(35)	30(2)	21(2)	18(2)	0(1)	-1(2)	8(2)
C(36)	26(2)	21(2)	25(2)	-5(2)	-2(2)	12(2)

Table S-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **2-C1** co-crystal.

	x	y	z	U(eq)
H(1A)	2607(4)	1570(2)	2701(5)	21
H(1B)	1921(4)	1557(2)	3654(5)	21
H(3)	1525	2167	1367	38
H(4)	756	1358	1201	44
H(5)	579	633	1827	40
H(7A)	2250	2734	2139	30
H(7B)	2579	2468	1884	30
H(8A)	961	219	2524	39
H(8B)	891	508	3130	39
H(10A)	3436	2783	3861	75
H(10B)	3403	3311	3799	75
H(10C)	3920	3304	3567	75
H(11A)	3245	3591	2693	82
H(11B)	3322	3306	2090	82
H(11C)	3812	3661	2542	82
H(12A)	3923	2867	2584	83
H(12B)	3389	2516	2199	83
H(12C)	3470	2324	2877	83
H(14A)	2691	2924	4327	63
H(14B)	2230	2322	4284	63
H(14C)	2093	2773	4455	63
H(15A)	2279	3480	3611	64
H(15B)	2448	3405	2916	64
H(15C)	2849	3548	3494	64
H(16A)	1476	2573	3643	49
H(16B)	1521	2105	3316	49
H(16C)	1625	2609	2909	49
H(18A)	2614	362	3017	67
H(18B)	2786	912	2674	67
H(18C)	2729	423	2272	67

H(19A)	1811	-356	2062	87
H(19B)	1312	-360	2376	87
H(19C)	1730	-412	2813	87
H(20A)	2174	507	1531	66
H(20B)	2139	970	1887	66
H(20C)	1611	434	1713	66
H(22A)	2346	471	4013	101
H(22B)	2018	-140	3826	101
H(22C)	1959	47	4518	101
H(23A)	763	-265	3662	114
H(23B)	997	-543	4104	114
H(23C)	1110	-492	3359	114
H(24A)	1173	576	4198	108
H(24B)	1748	797	4496	108
H(24C)	1274	236	4714	108
H(28)	3641	1621	2429	36
H(29)	4484	1700	2298	43
H(30)	4991	1743	3149	42
H(31)	4706	1747	4205	39
H(34)	3715	1733	5310	32
H(35)	2915	1743	5475	30
H(36)	2387	1683	4654	29
H(41A)	6135	2215	3444	150
H(41B)	5736	2404	3671	150
H(41C)	6278	2597	4043	150
H(42A)	6762	3099	3133	240
H(42B)	6218	2906	2761	240
H(43A)	6179	3587	3170	240
H(43B)	6110	3328	3858	240
H(44A)	6893	4025	4098	240
H(44B)	7013	4202	3370	240
H(45A)	7639	3962	3746	300
H(45B)	7289	3563	3198	300
H(45C)	7168	3387	3924	300

Table S-6. Torsion angles [°] for **2-C1** co-crystal.

C(6)-C(1)-C(2)-C(3)	-0.3(7)	C(7)-P(1)-C(9)-C(10)	165.0(4)
Ir(1A)-C(1)-C(2)-C(3)	-178.1(3)	C(13)-P(1)-C(9)-C(10)	53.4(4)
Ir(1B)-C(1)-C(2)-C(3)	171.5(3)	Ir(1B)-P(1)-C(9)-C(10)	-87.9(4)
C(6)-C(1)-C(2)-C(7)	-178.1(4)	Ir(1A)-P(1)-C(9)-C(10)	-80.8(4)
Ir(1A)-C(1)-C(2)-C(7)	4.1(6)	C(7)-P(1)-C(9)-C(11)	41.6(5)
Ir(1B)-C(1)-C(2)-C(7)	-6.3(5)	C(13)-P(1)-C(9)-C(11)	-70.0(5)
C(1)-C(2)-C(3)-C(4)	0.0(7)	Ir(1B)-P(1)-C(9)-C(11)	148.7(4)
C(7)-C(2)-C(3)-C(4)	177.7(4)	Ir(1A)-P(1)-C(9)-C(11)	155.7(4)
C(2)-C(3)-C(4)-C(5)	0.0(8)	C(7)-P(1)-C(13)-C(14)	166.8(4)
C(3)-C(4)-C(5)-C(6)	0.3(8)	C(9)-P(1)-C(13)-C(14)	-81.6(4)
C(2)-C(1)-C(6)-C(5)	0.6(7)	Ir(1B)-P(1)-C(13)-C(14)	57.1(4)
Ir(1A)-C(1)-C(6)-C(5)	178.5(4)	Ir(1A)-P(1)-C(13)-C(14)	57.5(4)
Ir(1B)-C(1)-C(6)-C(5)	-170.7(4)	C(7)-P(1)-C(13)-C(16)	45.9(4)
C(2)-C(1)-C(6)-C(8)	179.5(4)	C(9)-P(1)-C(13)-C(16)	157.5(3)
Ir(1A)-C(1)-C(6)-C(8)	-2.5(6)	Ir(1B)-P(1)-C(13)-C(16)	-63.7(4)
Ir(1B)-C(1)-C(6)-C(8)	8.3(6)	Ir(1A)-P(1)-C(13)-C(16)	-63.3(4)
C(4)-C(5)-C(6)-C(1)	-0.6(7)	C(7)-P(1)-C(13)-C(15)	-71.3(4)
C(4)-C(5)-C(6)-C(8)	-179.6(5)	C(9)-P(1)-C(13)-C(15)	40.3(4)
C(1)-C(2)-C(7)-P(1)	-22.5(5)	Ir(1B)-P(1)-C(13)-C(15)	179.1(3)
C(3)-C(2)-C(7)-P(1)	159.7(4)	Ir(1A)-P(1)-C(13)-C(15)	179.5(3)
C(9)-P(1)-C(7)-C(2)	155.0(3)	C(8)-P(2)-C(17)-C(19)	-69.2(4)
C(13)-P(1)-C(7)-C(2)	-89.5(3)	C(21)-P(2)-C(17)-C(19)	41.7(5)
Ir(1B)-P(1)-C(7)-C(2)	35.9(3)	Ir(1A)-P(2)-C(17)-C(19)	-179.0(3)
Ir(1A)-P(1)-C(7)-C(2)	27.2(3)	Ir(1B)-P(2)-C(17)-C(19)	-179.3(4)
C(1)-C(6)-C(8)-P(2)	-22.9(5)	C(8)-P(2)-C(17)-C(18)	165.7(4)
C(5)-C(6)-C(8)-P(2)	156.0(4)	C(21)-P(2)-C(17)-C(18)	-83.4(5)
C(17)-P(2)-C(8)-C(6)	-89.3(4)	Ir(1A)-P(2)-C(17)-C(18)	55.9(4)
C(21)-P(2)-C(8)-C(6)	157.0(4)	Ir(1B)-P(2)-C(17)-C(18)	55.6(4)
Ir(1A)-P(2)-C(8)-C(6)	33.3(3)	C(8)-P(2)-C(17)-C(20)	50.3(4)
Ir(1B)-P(2)-C(8)-C(6)	24.9(4)	C(21)-P(2)-C(17)-C(20)	161.1(4)
C(7)-P(1)-C(9)-C(12)	-77.1(4)	Ir(1A)-P(2)-C(17)-C(20)	-59.6(4)
C(13)-P(1)-C(9)-C(12)	171.3(4)	Ir(1B)-P(2)-C(17)-C(20)	-59.9(4)
Ir(1B)-P(1)-C(9)-C(12)	30.0(5)	C(8)-P(2)-C(21)-C(24)	-75.6(5)
Ir(1A)-P(1)-C(9)-C(12)	37.1(5)	C(17)-P(2)-C(21)-C(24)	173.8(5)

Ir(1A)-P(2)-C(21)-C(24)	34.9(6)
Ir(1B)-P(2)-C(21)-C(24)	42.9(6)
C(8)-P(2)-C(21)-C(22)	165.6(5)
C(17)-P(2)-C(21)-C(22)	55.0(6)
Ir(1A)-P(2)-C(21)-C(22)	-83.9(6)
Ir(1B)-P(2)-C(21)-C(22)	-75.9(6)
C(8)-P(2)-C(21)-C(23)	40.8(7)
C(17)-P(2)-C(21)-C(23)	-69.9(7)
Ir(1A)-P(2)-C(21)-C(23)	151.3(6)
Ir(1B)-P(2)-C(21)-C(23)	159.3(6)
C(36)-C(25)-C(26)-C(33)	0.9(6)
Ir(1B)-C(25)-C(26)-C(33)	179.0(3)
Ir(1A)-C(25)-C(26)-C(33)	-178.2(3)
C(36)-C(25)-C(26)-C(27)	-174.9(6)
Ir(1B)-C(25)-C(26)-C(27)	3.2(9)
Ir(1A)-C(25)-C(26)-C(27)	6.0(10)
C(25)-C(26)-C(27)-C(28)	2.0(13)
C(33)-C(26)-C(27)-C(28)	-174.5(8)
C(25)-C(26)-C(27)-C(32)	176.5(7)
C(33)-C(26)-C(27)-C(32)	-0.1(4)
C(32)-C(27)-C(28)-C(29)	0.6(7)
C(26)-C(27)-C(28)-C(29)	174.1(7)
C(27)-C(28)-C(29)-C(30)	0.3(8)
C(28)-C(29)-C(30)-C(31)	-1.4(9)
C(29)-C(30)-C(31)-C(32)	1.4(8)
C(30)-C(31)-C(32)-C(27)	-0.5(7)
C(30)-C(31)-C(32)-C(33)	-175.3(7)
C(28)-C(27)-C(32)-C(31)	-0.5(7)
C(26)-C(27)-C(32)-C(31)	-177.1(5)
C(28)-C(27)-C(32)-C(33)	176.6(5)
C(26)-C(27)-C(32)-C(33)	0.1(3)
C(25)-C(26)-C(33)-C(34)	-0.3(7)
C(27)-C(26)-C(33)-C(34)	177.5(4)
C(25)-C(26)-C(33)-C(32)	-177.7(4)
C(27)-C(26)-C(33)-C(32)	0.1(3)
C(31)-C(32)-C(33)-C(34)	-0.6(13)
C(27)-C(32)-C(33)-C(34)	-176.3(7)
C(31)-C(32)-C(33)-C(26)	175.6(8)
C(27)-C(32)-C(33)-C(26)	-0.1(4)
C(26)-C(33)-C(34)-C(35)	-0.5(7)
C(32)-C(33)-C(34)-C(35)	175.0(6)
C(33)-C(34)-C(35)-C(36)	0.5(7)
C(34)-C(35)-C(36)-C(25)	0.3(7)
C(26)-C(25)-C(36)-C(35)	-1.0(6)
Ir(1B)-C(25)-C(36)-C(35)	-178.9(4)
Ir(1A)-C(25)-C(36)-C(35)	178.3(4)
C(41A)-C(42A)-C(43A)-C(44A)	114.204(12)
C(42A)-C(43A)-C(44A)-C(45A)	-12.571(4)

X-ray Structure Determination for 4

Data collection:
A crystal (0.32 x 0.26 x 0.18 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD platform diffractometer for a data collection at 100.0(5) K.[1] A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoK□ radiation (graphite monochromator) with a frame time of 10 seconds and a detector distance of 4.04 cm. A randomly oriented region of reciprocal space was surveyed: four major sections of frames were collected with 0.50º steps in □ at four different □ settings and a detector position of -38º in 2□. The intensity data were corrected for absorption.[2] Final cell constants were calculated from the xyz centroids of 3879 strong reflections from the actual data collection after integration.[3] See Table 1 for additional crystal and refinement information.

Structure solution and refinement:
The structure was solved using SIR2011[4] and refined using SHELXL-2014.[5] The space group $P2_1/n$ was determined based on systematic absences. The data are truly monoclinic, despite a β angle of approximately 90º, and no significant twinning was observed. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0284$ (F^2, $I > 2\sigma(I)$) and $wR2 = 0.0519$ (F^2, all data).

Structure description:
The structure is the one suggested. The asymmetric unit contains one molecule in a general position.

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W.

Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

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1 *APEX2*, version 2013.10-0; Bruker AXS: Madison, WI, 2013.

2 Sheldrick, G. M. *SADABS*, version 2012/1; University of Göttingen: Göttingen, Germany, 2012.

3 *SAINT*, version 8.34A; Bruker AXS: Madison, WI, 2013.

4 Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G.; Spagna, R. *SIR2011: a new package for crystal structure determination and refinement*, version 1.0; Istituto di Cristallografia: Bari, Italy, 2012.

5 Sheldrick, G. M. *SHELXL-2014/3*; University of Göttingen: Göttingen, Germany, 2014.

Some equations of interest:

$$R_{int} = \Box\ |F_o^2 - < F_o^2 >| \ / \ \Box |F_o\ ^2|$$

$$R1 = \Box||F_o|-|F_c|| \ / \ \Box|F_o|$$

$$wR2 = [\Box[w(F_o^2-F_c\ ^2)^2] \ / \ \Box\ [w(F_o^2\ )^2]]^{1/2}$$

where $w = 1 \ / \ [\Box^2\ (F_o^2) + (aP\ )^2 + bP]$ and

$$P = 1/3 \text{ max } (0, F_o^2) + 2/3\ F_c^2$$

$$\text{GOF} = S = [\Box[w(F_o^2-F_c\ ^2)^2] \ / \ (m-n\ )]^{1/2}$$

where m = number of reflections and n = number of parameters

II. Structural Data for 4

Figure S-3. ORTEP Diagram of **4**

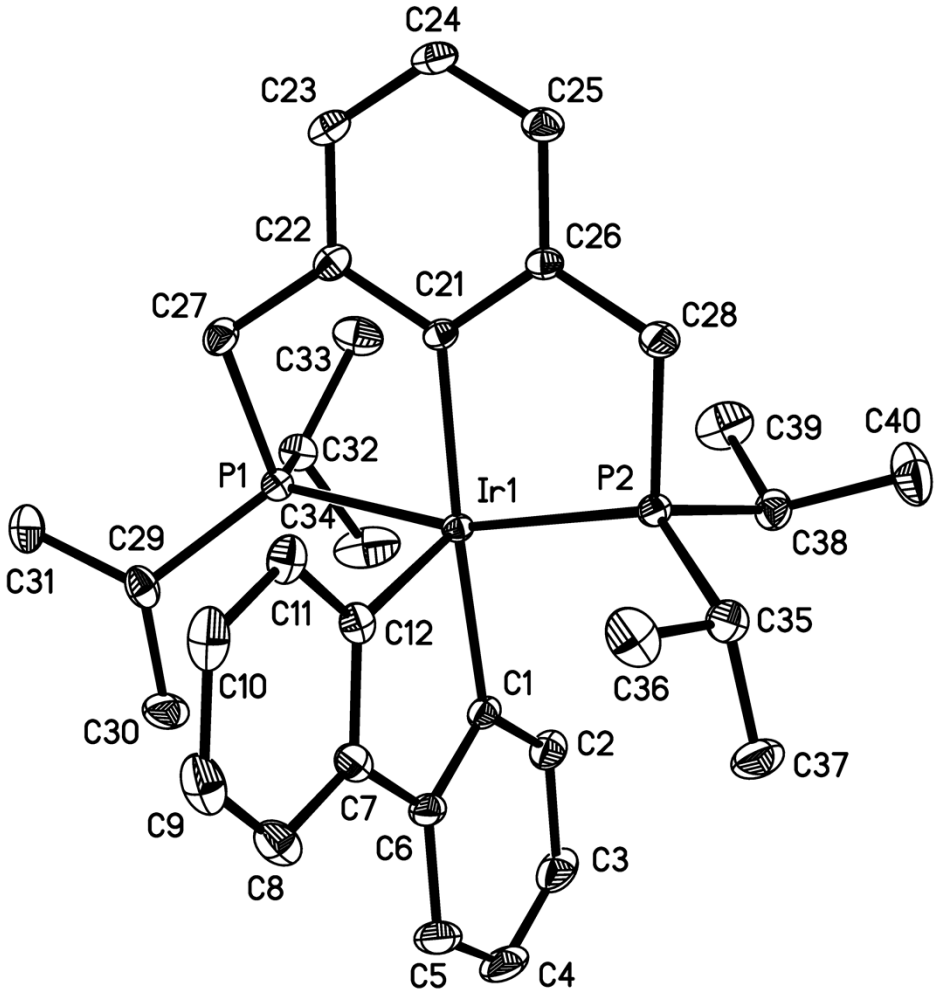

Table S-7. Crystal data and structure refinement for **4**.

Identification code	jonmm04	
Empirical formula	C32 H43 Ir P2	
Formula weight	681.80	
Temperature	100.0(5) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.5407(12) Å	□ = 90°
	b = 25.531(3) Å	□ = 90.086(2)°
	c = 10.8527(12) Å	□ = 90°
Volume	2920.7(6) Å^3	
Z	4	
Density (calculated)	1.551 Mg/m^3	
Absorption coefficient	4.700 mm^{-1}	
F(000)	1368	
Crystal color, morphology	dark orange, block	
Crystal size	0.32 x 0.26 x 0.18 mm^3	
Theta range for data collection	2.039 to 38.485°	
Index ranges	-18 □ h □ 18, -43 □ k □ 43, -18 □ l □ 18	
Reflections collected	70917	
Independent reflections	15707 [R(int) = 0.0368]	
Observed reflections	13214	
Completeness to theta = 37.785°	98.7%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.4403 and 0.2588	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15707 / 0 / 324	
Goodness-of-fit on F^2	1.136	
Final R indices [I>2sigma(I)]	R1 = 0.0284, wR2 = 0.0497	
R indices (all data)	R1 = 0.0398, wR2 = 0.0519	
Largest diff. peak and hole	1.652 and -2.917 e.Å^{-3}	

Table S-8. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2 x\ 10^3$) for **4**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ir1	2253(1)	1377(1)	2664(1)	10(1)
P1	4069(1)	1876(1)	2539(1)	11(1)
P2	207(1)	1099(1)	2992(1)	12(1)
C1	3058(2)	628(1)	2733(2)	14(1)
C2	3397(2)	333(1)	3769(2)	19(1)
C3	3926(2)	-166(1)	3671(2)	26(1)
C4	4117(2)	-389(1)	2518(3)	30(1)
C5	3781(2)	-112(1)	1461(2)	25(1)
C6	3255(2)	391(1)	1568(2)	16(1)
C7	2881(2)	724(1)	530(2)	16(1)
C8	2994(2)	596(1)	-721(2)	22(1)
C9	2589(2)	942(1)	-1626(2)	26(1)
C10	2061(2)	1420(1)	-1303(2)	23(1)
C11	1953(2)	1561(1)	-63(2)	18(1)
C12	2359(2)	1215(1)	860(2)	14(1)
C21	1398(2)	2116(1)	2694(2)	11(1)
C22	2119(2)	2583(1)	2549(2)	14(1)
C23	1584(2)	3077(1)	2766(2)	17(1)
C24	319(2)	3117(1)	3120(2)	18(1)
C25	-425(2)	2671(1)	3211(2)	16(1)
C26	97(2)	2177(1)	2978(2)	13(1)
C27	3467(2)	2526(1)	2092(2)	16(1)
C28	-757(2)	1698(1)	2935(2)	16(1)
C29	5270(2)	1734(1)	1355(2)	17(1)
C30	5965(2)	1212(1)	1557(2)	27(1)
C31	6217(2)	2180(1)	1157(2)	21(1)
C32	4944(2)	1986(1)	3997(2)	16(1)
C33	4213(2)	2345(1)	4871(2)	24(1)
C34	5236(3)	1468(1)	4650(2)	34(1)
C35	-674(2)	609(1)	2082(2)	18(1)

C36	-689(2)	741(1)	704(2)	26(1)
C37	-128(2)	59(1)	2304(2)	27(1)
C38	87(2)	871(1)	4600(2)	18(1)
C39	758(3)	1267(1)	5428(2)	30(1)
C40	-1273(2)	764(1)	5043(2)	33(1)

Table S-9. Bond lengths [Å] and angles [°] for **4**.

Ir(1)-C(12)	2.0041(17)	C(22)-C(23)	1.400(3)
Ir(1)-C(21)	2.0909(16)	C(22)-C(27)	1.512(3)
Ir(1)-C(1)	2.0942(17)	C(23)-C(24)	1.393(3)
Ir(1)-P(2)	2.2989(5)	C(23)-H(23A)	0.9500
Ir(1)-P(1)	2.3023(5)	C(24)-C(25)	1.387(3)
P(1)-C(29)	1.8413(19)	C(24)-H(24A)	0.9500
P(1)-C(27)	1.8416(18)	C(25)-C(26)	1.400(2)
P(1)-C(32)	1.8521(18)	C(25)-H(25A)	0.9500
P(2)-C(28)	1.8373(18)	C(26)-C(28)	1.518(3)
P(2)-C(35)	1.8440(19)	C(27)-H(27A)	0.9900
P(2)-C(38)	1.8441(19)	C(27)-H(27B)	0.9900
C(1)-C(2)	1.398(3)	C(28)-H(28A)	0.9900
C(1)-C(6)	1.417(3)	C(28)-H(28B)	0.9900
C(2)-C(3)	1.396(3)	C(29)-C(31)	1.529(3)
C(2)-H(2A)	0.9500	C(29)-C(30)	1.536(3)
C(3)-C(4)	1.389(4)	C(29)-H(29A)	1.0000
C(3)-H(3A)	0.9500	C(30)-H(30A)	0.9800
C(4)-C(5)	1.393(3)	C(30)-H(30B)	0.9800
C(4)-H(4A)	0.9500	C(30)-H(30C)	0.9800
C(5)-C(6)	1.404(3)	C(31)-H(31A)	0.9800
C(5)-H(5A)	0.9500	C(31)-H(31B)	0.9800
C(6)-C(7)	1.464(3)	C(31)-H(31C)	0.9800
C(7)-C(8)	1.402(3)	C(32)-C(33)	1.528(3)
C(7)-C(12)	1.416(3)	C(32)-C(34)	1.532(3)
C(8)-C(9)	1.389(3)	C(32)-H(32A)	1.0000
C(8)-H(8A)	0.9500	C(33)-H(33A)	0.9800
C(9)-C(10)	1.387(3)	C(33)-H(33B)	0.9800
C(9)-H(9A)	0.9500	C(33)-H(33C)	0.9800
C(10)-C(11)	1.398(3)	C(34)-H(34A)	0.9800
C(10)-H(10A)	0.9500	C(34)-H(34B)	0.9800
C(11)-C(12)	1.402(3)	C(34)-H(34C)	0.9800
C(11)-H(11A)	0.9500	C(35)-C(36)	1.532(3)
C(21)-C(26)	1.415(2)	C(35)-C(37)	1.537(3)
C(21)-C(22)	1.423(2)	C(35)-H(35A)	1.0000

C(36)-H(36A)	0.9800	C(38)-P(2)-Ir(1)	108.05(6)
C(36)-H(36B)	0.9800	C(2)-C(1)-C(6)	116.80(16)
C(36)-H(36C)	0.9800	C(2)-C(1)-Ir(1)	128.54(14)
C(37)-H(37A)	0.9800	C(6)-C(1)-Ir(1)	114.65(13)
C(37)-H(37B)	0.9800	C(3)-C(2)-C(1)	122.1(2)
C(37)-H(37C)	0.9800	C(3)-C(2)-H(2A)	119.0
C(38)-C(39)	1.525(3)	C(1)-C(2)-H(2A)	119.0
C(38)-C(40)	1.537(3)	C(4)-C(3)-C(2)	120.0(2)
C(38)-H(38A)	1.0000	C(4)-C(3)-H(3A)	120.0
C(39)-H(39A)	0.9800	C(2)-C(3)-H(3A)	120.0
C(39)-H(39B)	0.9800	C(3)-C(4)-C(5)	119.82(19)
C(39)-H(39C)	0.9800	C(3)-C(4)-H(4A)	120.1
C(40)-H(40A)	0.9800	C(5)-C(4)-H(4A)	120.1
C(40)-H(40B)	0.9800	C(4)-C(5)-C(6)	119.7(2)
C(40)-H(40C)	0.9800	C(4)-C(5)-H(5A)	120.1
C(12)-Ir(1)-C(21)	103.06(7)	C(6)-C(5)-H(5A)	120.1
C(12)-Ir(1)-C(1)	79.84(7)	C(5)-C(6)-C(1)	121.48(19)
C(21)-Ir(1)-C(1)	176.63(7)	C(5)-C(6)-C(7)	124.94(18)
C(12)-Ir(1)-P(2)	98.11(5)	C(1)-C(6)-C(7)	113.57(15)
C(21)-Ir(1)-P(2)	82.63(5)	C(8)-C(7)-C(12)	119.01(18)
C(1)-Ir(1)-P(2)	95.32(5)	C(8)-C(7)-C(6)	125.95(18)
C(12)-Ir(1)-P(1)	90.52(5)	C(12)-C(7)-C(6)	115.05(16)
C(21)-Ir(1)-P(1)	81.99(5)	C(9)-C(8)-C(7)	120.71(19)
C(1)-Ir(1)-P(1)	99.79(5)	C(9)-C(8)-H(8A)	119.6
P(2)-Ir(1)-P(1)	163.724(16)	C(7)-C(8)-H(8A)	119.6
C(29)-P(1)-C(27)	103.27(9)	C(10)-C(9)-C(8)	120.27(18)
C(29)-P(1)-C(32)	106.51(9)	C(10)-C(9)-H(9A)	119.9
C(27)-P(1)-C(32)	105.02(9)	C(8)-C(9)-H(9A)	119.9
C(29)-P(1)-Ir(1)	120.35(6)	C(9)-C(10)-C(11)	120.3(2)
C(27)-P(1)-Ir(1)	103.13(6)	C(9)-C(10)-H(10A)	119.9
C(32)-P(1)-Ir(1)	116.55(6)	C(11)-C(10)-H(10A)	119.9
C(28)-P(2)-C(35)	105.57(9)	C(10)-C(11)-C(12)	119.98(19)
C(28)-P(2)-C(38)	104.81(9)	C(10)-C(11)-H(11A)	120.0
C(35)-P(2)-C(38)	104.95(9)	C(12)-C(11)-H(11A)	120.0
C(28)-P(2)-Ir(1)	104.88(6)	C(11)-C(12)-C(7)	119.73(16)
C(35)-P(2)-Ir(1)	126.75(7)	C(11)-C(12)-Ir(1)	123.39(14)

C(7)-C(12)-Ir(1)	116.87(13)	P(1)-C(29)-H(29A)	106.1
C(26)-C(21)-C(22)	116.78(15)	C(29)-C(30)-H(30A)	109.5
C(26)-C(21)-Ir(1)	121.32(12)	C(29)-C(30)-H(30B)	109.5
C(22)-C(21)-Ir(1)	121.63(12)	H(30A)-C(30)-H(30B)	109.5
C(23)-C(22)-C(21)	121.35(17)	C(29)-C(30)-H(30C)	109.5
C(23)-C(22)-C(27)	121.44(16)	H(30A)-C(30)-H(30C)	109.5
C(21)-C(22)-C(27)	117.14(15)	H(30B)-C(30)-H(30C)	109.5
C(24)-C(23)-C(22)	119.94(17)	C(29)-C(31)-H(31A)	109.5
C(24)-C(23)-H(23A)	120.0	C(29)-C(31)-H(31B)	109.5
C(22)-C(23)-H(23A)	120.0	H(31A)-C(31)-H(31B)	109.5
C(25)-C(24)-C(23)	120.06(17)	C(29)-C(31)-H(31C)	109.5
C(25)-C(24)-H(24A)	120.0	H(31A)-C(31)-H(31C)	109.5
C(23)-C(24)-H(24A)	120.0	H(31B)-C(31)-H(31C)	109.5
C(24)-C(25)-C(26)	120.32(17)	C(33)-C(32)-C(34)	109.38(18)
C(24)-C(25)-H(25A)	119.8	C(33)-C(32)-P(1)	111.75(13)
C(26)-C(25)-H(25A)	119.8	C(34)-C(32)-P(1)	111.28(14)
C(25)-C(26)-C(21)	121.32(16)	C(33)-C(32)-H(32A)	108.1
C(25)-C(26)-C(28)	119.80(16)	C(34)-C(32)-H(32A)	108.1
C(21)-C(26)-C(28)	118.74(15)	P(1)-C(32)-H(32A)	108.1
C(22)-C(27)-P(1)	108.97(12)	C(32)-C(33)-H(33A)	109.5
C(22)-C(27)-H(27A)	109.9	C(32)-C(33)-H(33B)	109.5
P(1)-C(27)-H(27A)	109.9	H(33A)-C(33)-H(33B)	109.5
C(22)-C(27)-H(27B)	109.9	C(32)-C(33)-H(33C)	109.5
P(1)-C(27)-H(27B)	109.9	H(33A)-C(33)-H(33C)	109.5
H(27A)-C(27)-H(27B)	108.3	H(33B)-C(33)-H(33C)	109.5
C(26)-C(28)-P(2)	109.92(12)	C(32)-C(34)-H(34A)	109.5
C(26)-C(28)-H(28A)	109.7	C(32)-C(34)-H(34B)	109.5
P(2)-C(28)-H(28A)	109.7	H(34A)-C(34)-H(34B)	109.5
C(26)-C(28)-H(28B)	109.7	C(32)-C(34)-H(34C)	109.5
P(2)-C(28)-H(28B)	109.7	H(34A)-C(34)-H(34C)	109.5
H(28A)-C(28)-H(28B)	108.2	H(34B)-C(34)-H(34C)	109.5
C(31)-C(29)-C(30)	110.75(16)	C(36)-C(35)-C(37)	110.92(18)
C(31)-C(29)-P(1)	113.70(14)	C(36)-C(35)-P(2)	112.25(14)
C(30)-C(29)-P(1)	113.47(14)	C(37)-C(35)-P(2)	110.31(14)
C(31)-C(29)-H(29A)	106.1	C(36)-C(35)-H(35A)	107.7
C(30)-C(29)-H(29A)	106.1	C(37)-C(35)-H(35A)	107.7

P(2)-C(35)-H(35A)	107.7	C(39)-C(38)-H(38A)	107.3
C(35)-C(36)-H(36A)	109.5	C(40)-C(38)-H(38A)	107.3
C(35)-C(36)-H(36B)	109.5	P(2)-C(38)-H(38A)	107.3
H(36A)-C(36)-H(36B)	109.5	C(38)-C(39)-H(39A)	109.5
C(35)-C(36)-H(36C)	109.5	C(38)-C(39)-H(39B)	109.5
H(36A)-C(36)-H(36C)	109.5	H(39A)-C(39)-H(39B)	109.5
H(36B)-C(36)-H(36C)	109.5	C(38)-C(39)-H(39C)	109.5
C(35)-C(37)-H(37A)	109.5	H(39A)-C(39)-H(39C)	109.5
C(35)-C(37)-H(37B)	109.5	H(39B)-C(39)-H(39C)	109.5
H(37A)-C(37)-H(37B)	109.5	C(38)-C(40)-H(40A)	109.5
C(35)-C(37)-H(37C)	109.5	C(38)-C(40)-H(40B)	109.5
H(37A)-C(37)-H(37C)	109.5	H(40A)-C(40)-H(40B)	109.5
H(37B)-C(37)-H(37C)	109.5	C(38)-C(40)-H(40C)	109.5
C(39)-C(38)-C(40)	111.45(19)	H(40A)-C(40)-H(40C)	109.5
C(39)-C(38)-P(2)	108.44(14)	H(40B)-C(40)-H(40C)	109.5
C(40)-C(38)-P(2)	114.69(14)		

Table S-10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir1	9(1)	9(1)	11(1)	0(1)	-1(1)	1(1)
P1	10(1)	12(1)	12(1)	0(1)	-2(1)	0(1)
P2	11(1)	11(1)	14(1)	0(1)	-1(1)	0(1)
C1	10(1)	10(1)	21(1)	2(1)	-1(1)	1(1)
C2	14(1)	16(1)	26(1)	5(1)	-1(1)	1(1)
C3	19(1)	16(1)	42(1)	11(1)	0(1)	3(1)
C4	22(1)	11(1)	56(2)	0(1)	4(1)	3(1)
C5	19(1)	15(1)	40(1)	-9(1)	4(1)	0(1)
C6	11(1)	12(1)	25(1)	-3(1)	2(1)	-1(1)
C7	12(1)	18(1)	19(1)	-6(1)	1(1)	-4(1)
C8	17(1)	28(1)	21(1)	-12(1)	1(1)	-5(1)
C9	22(1)	39(1)	16(1)	-8(1)	2(1)	-11(1)
C10	22(1)	34(1)	14(1)	2(1)	-3(1)	-12(1)
C11	17(1)	20(1)	15(1)	1(1)	-3(1)	-6(1)
C12	12(1)	18(1)	12(1)	-2(1)	-1(1)	-3(1)
C21	13(1)	10(1)	11(1)	1(1)	-2(1)	1(1)
C22	15(1)	13(1)	13(1)	2(1)	-3(1)	0(1)
C23	23(1)	11(1)	17(1)	2(1)	-2(1)	0(1)
C24	24(1)	12(1)	17(1)	0(1)	-2(1)	4(1)
C25	18(1)	15(1)	16(1)	2(1)	0(1)	5(1)
C26	14(1)	11(1)	13(1)	1(1)	-1(1)	2(1)
C27	16(1)	14(1)	17(1)	4(1)	-1(1)	0(1)
C28	12(1)	14(1)	21(1)	1(1)	-1(1)	2(1)
C29	12(1)	24(1)	15(1)	-3(1)	1(1)	-3(1)
C30	16(1)	20(1)	46(1)	-10(1)	7(1)	-1(1)
C31	16(1)	26(1)	21(1)	3(1)	1(1)	-4(1)
C32	16(1)	18(1)	14(1)	-2(1)	-4(1)	0(1)
C33	30(1)	26(1)	17(1)	-7(1)	-4(1)	5(1)
C34	53(2)	25(1)	25(1)	-2(1)	-20(1)	12(1)
C35	13(1)	19(1)	23(1)	-5(1)	-2(1)	-3(1)

C36	19(1)	38(1)	21(1)	-9(1)	-4(1)	-4(1)
C37	21(1)	15(1)	43(1)	-7(1)	-2(1)	-2(1)
C38	17(1)	18(1)	18(1)	4(1)	1(1)	1(1)
C39	42(1)	27(1)	20(1)	-2(1)	-8(1)	1(1)
C40	23(1)	45(1)	30(1)	16(1)	8(1)	3(1)

Table S-11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **4**.

	x	y	z	U(eq)
H2A	3263	478	4565	23
H3A	4155	-354	4394	31
H4A	4476	-729	2451	35
H5A	3907	-263	670	30
H8A	3352	269	-952	26
H9A	2673	851	-2471	31
H10A	1771	1653	-1926	28
H11A	1604	1892	155	21
H23A	2084	3384	2672	20
H24A	-35	3451	3299	21
H25A	-1294	2700	3433	19
H27A	4008	2802	2455	19
H27B	3488	2563	1184	19
H28A	-1266	1703	2167	19
H28B	-1348	1705	3643	19
H29A	4796	1696	561	20
H30A	6441	1121	813	41
H30B	5344	937	1734	41
H30C	6552	1247	2254	41
H31A	6796	2088	486	32
H31B	6705	2236	1915	32
H31C	5758	2501	944	32
H32A	5769	2159	3794	19
H33A	4701	2393	5632	37
H33B	3391	2187	5065	37
H33C	4079	2686	4476	37
H34A	5779	1535	5367	51
H34B	5674	1232	4080	51
H34C	4441	1306	4922	51
H35A	-1572	609	2377	22

H36A	-1265	501	274	39
H36B	169	703	369	39
H36C	-980	1102	589	39
H37A	-549	-192	1757	40
H37B	-271	-42	3164	40
H37C	785	62	2135	40
H38A	566	534	4660	21
H39A	734	1144	6283	45
H39B	329	1607	5369	45
H39C	1642	1304	5165	45
H40A	-1251	635	5894	49
H40B	-1668	500	4511	49
H40C	-1768	1089	5008	49

Table S-12. Torsion angles [°] for **4**.

C6-C1-C2-C3	1.2(3)	C24-C25-C26-C21	2.6(3)
Ir1-C1-C2-C3	179.78(15)	C24-C25-C26-C28	-172.93(17)
C1-C2-C3-C4	-0.8(3)	C22-C21-C26-C25	-5.5(2)
C2-C3-C4-C5	0.1(3)	Ir1-C21-C26-C25	168.61(13)
C3-C4-C5-C6	0.2(3)	C22-C21-C26-C28	170.08(15)
C4-C5-C6-C1	0.2(3)	Ir1-C21-C26-C28	-15.8(2)
C4-C5-C6-C7	179.06(19)	C23-C22-C27-P1	155.72(14)
C2-C1-C6-C5	-0.9(3)	C21-C22-C27-P1	-27.16(19)
Ir1-C1-C6-C5	-179.67(14)	C29-P1-C27-C22	153.07(12)
C2-C1-C6-C7	-179.85(16)	C32-P1-C27-C22	-95.49(13)
Ir1-C1-C6-C7	1.35(19)	Ir1-P1-C27-C22	27.05(13)
C5-C6-C7-C8	-0.4(3)	C25-C26-C28-P2	-166.29(14)
C1-C6-C7-C8	178.55(17)	C21-C26-C28-P2	18.1(2)
C5-C6-C7-C12	179.41(18)	C35-P2-C28-C26	-148.10(13)
C1-C6-C7-C12	-1.7(2)	C38-P2-C28-C26	101.38(14)
C12-C7-C8-C9	-0.7(3)	Ir1-P2-C28-C26	-12.31(14)
C6-C7-C8-C9	179.08(18)	C27-P1-C29-C31	49.84(16)
C7-C8-C9-C10	-0.2(3)	C32-P1-C29-C31	-60.49(16)
C8-C9-C10-C11	1.1(3)	Ir1-P1-C29-C31	163.96(11)
C9-C10-C11-C12	-1.1(3)	C27-P1-C29-C30	177.60(14)
C10-C11-C12-C7	0.2(3)	C32-P1-C29-C30	67.27(16)
C10-C11-C12-Ir1	179.85(14)	Ir1-P1-C29-C30	-68.28(15)
C8-C7-C12-C11	0.7(3)	C29-P1-C32-C33	152.98(15)
C6-C7-C12-C11	-179.09(16)	C27-P1-C32-C33	43.87(16)
C8-C7-C12-Ir1	-178.98(14)	Ir1-P1-C32-C33	-69.52(15)
C6-C7-C12-Ir1	1.2(2)	C29-P1-C32-C34	-84.41(18)
C26-C21-C22-C23	4.5(2)	C27-P1-C32-C34	166.48(16)
Ir1-C21-C22-C23	-169.56(13)	Ir1-P1-C32-C34	53.09(18)
C26-C21-C22-C27	-172.61(15)	C28-P2-C35-C36	68.84(16)
Ir1-C21-C22-C27	13.3(2)	C38-P2-C35-C36	179.27(14)
C21-C22-C23-C24	-0.6(3)	Ir1-P2-C35-C36	-53.90(17)
C27-C22-C23-C24	176.38(17)	C28-P2-C35-C37	-166.91(14)
C22-C23-C24-C25	-2.5(3)	C38-P2-C35-C37	-56.48(16)
C23-C24-C25-C26	1.5(3)	Ir1-P2-C35-C37	70.35(16)

C28-P2-C38-C39	-67.16(16)
C35-P2-C38-C39	-178.14(15)
Ir1-P2-C38-C39	44.28(16)
C28-P2-C38-C40	58.12(18)
C35-P2-C38-C40	-52.86(18)
Ir1-P2-C38-C40	169.56(15)

X-ray Structure Determination for 4-CO

Data collection:
A crystal (0.25 x 0.25 x 0.22 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD platform diffractometer for a data collection at 100.0(5) K.[1] A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoK□ radiation (graphite monochromator) with a frame time of 25 seconds and a detector distance of 4.00 cm. A randomly oriented region of reciprocal space was surveyed: six major sections of frames were collected with 0.50º steps in □ at six different □ settings and a detector position of -38º in 2□. The intensity data were corrected for absorption.[2] Final cell constants were calculated from the xyz centroids of 3886 strong reflections from the actual data collection after integration.[3] See Table 1 for additional crystal and refinement information.

Structure solution and refinement:
The structure was solved using SIR2011[4] and refined using SHELXL-2014.[5] The space group $P2_1/n$ was determined based on systematic absences. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0227$ (F^2, $I > 2\sigma(I)$) and $wR2 = 0.0494$ (F^2, all data).

Structure description:
The structure is the one suggested. The asymmetric unit contains one molecule in a general position.

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray

Crystallographic Facility of the Department of Chemistry at the University of Rochester.

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1 *APEX2*, version 2013.10-0; Bruker AXS: Madison, WI, 2013.

2 Sheldrick, G. M. *SADABS*, version 2012/1; University of Göttingen: Göttingen, Germany, 2012.

3 *SAINT*, version 8.34A; Bruker AXS: Madison, WI, 2013.

4 Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G.; Spagna, R. *SIR2011: a new package for crystal structure determination and refinement*, version 1.0; Istituto di Cristallografia: Bari, Italy, 2012.

5 Sheldrick, G. M. *SHELXL-2014/3*; University of Göttingen: Göttingen, Germany, 2014.

Some equations of interest:

$$R_{int} = \Box\ |F_o^2 - < F_o^2 >| \ / \ \Box |F_o\ ^2|$$

$$R1 = \Box ||F_o| - |F_c|| \ / \ \Box |F_o|$$

$$wR2 = [\Box [w(F_o^2 - F_c\ ^2)^2] \ / \ \Box\ [w(F_o^2\ )^2]]^{1/2}$$

where $w = 1 \ / \ [\Box^2\ (F_o^2) + (aP\ )^2 + bP]$ and

$$P = 1/3 \text{ max } (0, F_o^2) + 2/3\ F_c^2$$

$$\text{GOF} = S = [\Box [w(F_o^2 - F_c\ ^2)^2] \ / \ (m-n\ )]^{1/2}$$

where m = number of reflections and n = number of parameters

II. Structural Data for 4-CO

Figure S-4. ORTEP Diagram of **4-CO**

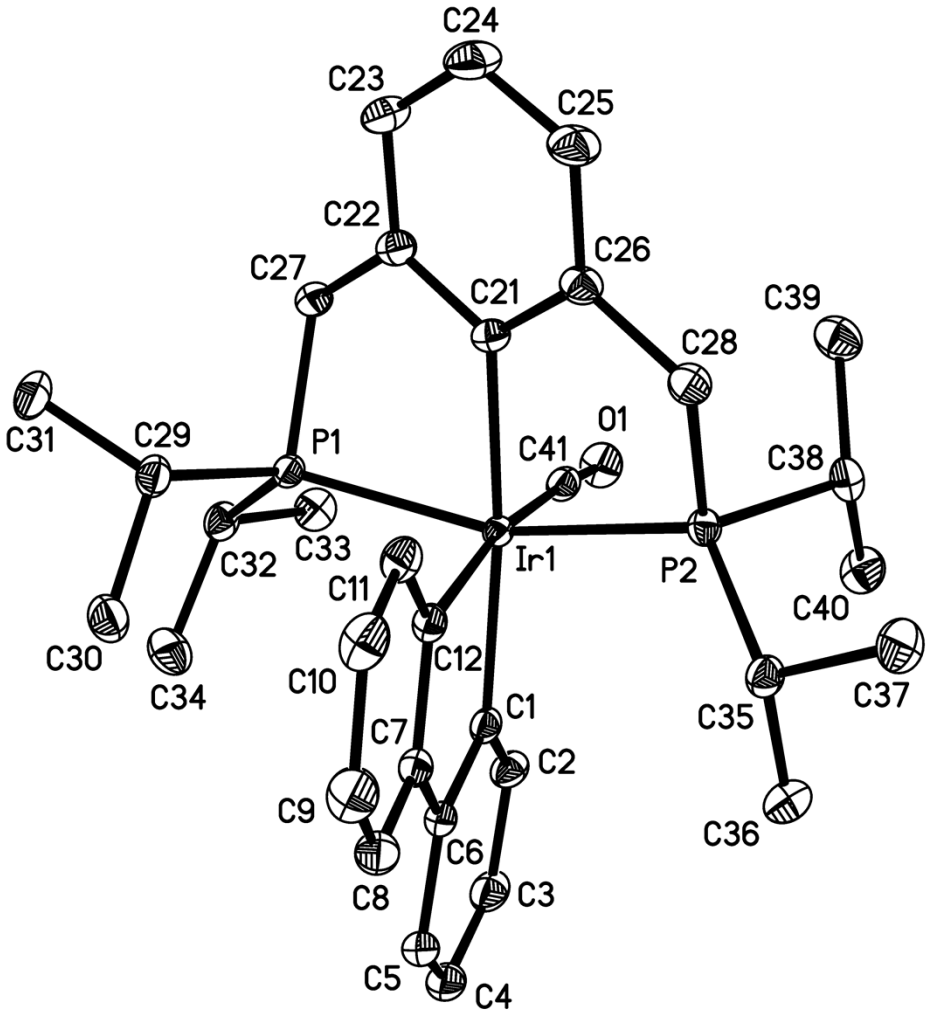

Table S-13. Crystal data and structure refinement for **4-CO**

Identification code	jonmm06	
Empirical formula	C33 H43 Ir O P2	
Formula weight	709.81	
Temperature	100.0(5) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 13.587(8) Å	□ = 90°
	b = 15.483(9) Å	□ = 96.765(11)°
	c = 13.932(8) Å	□ = 90°
Volume	2910(3) Å^3	
Z	4	
Density (calculated)	1.620 Mg/m^3	
Absorption coefficient	4.722 mm^{-1}	
F(000)	1424	
Crystal color, morphology	colorless, block	
Crystal size	0.25 x 0.25 x 0.22 mm^3	
Theta range for data collection	1.974 to 38.768°	
Index ranges	-23 □ h □ 23, -26 □ k □ 26, -24 □ l □ 24	
Reflections collected	108479	
Independent reflections	16157 [R(int) = 0.0413]	
Observed reflections	13591	
Completeness to theta = 37.785°	100.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.4405 and 0.3478	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16157 / 0 / 342	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0227, wR2 = 0.0466	
R indices (all data)	R1 = 0.0322, wR2 = 0.0494	
Largest diff. peak and hole	1.794 and -0.869 e.Å^{-3}	

Table S-14. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2 x 10^3$) for **4-CO**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ir1	5017(1)	2315(1)	6990(1)	10(1)
P1	5731(1)	3667(1)	7408(1)	13(1)
P2	4000(1)	1107(1)	7072(1)	13(1)
O1	6966(1)	1353(1)	7452(1)	21(1)
C1	5217(1)	2336(1)	5507(1)	14(1)
C2	6047(1)	2063(1)	5075(1)	17(1)
C3	6103(1)	2170(1)	4091(1)	22(1)
C4	5319(2)	2548(1)	3499(1)	23(1)
C5	4482(1)	2814(1)	3904(1)	20(1)
C6	4422(1)	2710(1)	4890(1)	15(1)
C7	3562(1)	2967(1)	5372(1)	15(1)
C8	2669(1)	3277(1)	4884(1)	21(1)
C9	1881(1)	3497(1)	5383(1)	24(1)
C10	1991(1)	3440(1)	6382(1)	22(1)
C11	2884(1)	3153(1)	6879(1)	17(1)
C12	3677(1)	2891(1)	6393(1)	13(1)
C21	4669(1)	2442(1)	8429(1)	14(1)
C22	5211(1)	3022(1)	9071(1)	16(1)
C23	4984(1)	3130(1)	10012(1)	21(1)
C24	4218(1)	2659(1)	10339(1)	25(1)
C25	3680(1)	2075(1)	9723(1)	22(1)
C26	3901(1)	1969(1)	8775(1)	16(1)
C27	6061(1)	3497(1)	8710(1)	16(1)
C28	3301(1)	1357(1)	8090(1)	17(1)
C29	4875(1)	4597(1)	7380(1)	17(1)
C30	4425(1)	4887(1)	6365(1)	22(1)
C31	5323(2)	5379(1)	7955(1)	24(1)
C32	6886(1)	4062(1)	6978(1)	17(1)
C33	7675(1)	3348(1)	7050(1)	21(1)
C34	6728(1)	4422(1)	5948(1)	25(1)

C35	3013(1)	863(1)	6075(1)	16(1)
C36	3420(1)	603(1)	5139(1)	21(1)
C37	2266(1)	192(1)	6349(1)	25(1)
C38	4595(1)	61(1)	7411(1)	17(1)
C39	5107(1)	56(1)	8456(1)	23(1)
C40	5308(1)	-231(1)	6702(1)	23(1)
C41	6231(1)	1722(1)	7318(1)	15(1)

Table S-15. Bond lengths [Å] and angles [°] for **4-CO**.

Ir(1)-C(41)	1.8966(17)	C(21)-C(26)	1.406(2)
Ir(1)-C(12)	2.1086(17)	C(21)-C(22)	1.412(2)
Ir(1)-C(1)	2.1156(18)	C(22)-C(23)	1.392(2)
Ir(1)-C(21)	2.1220(18)	C(22)-C(27)	1.506(2)
Ir(1)-P(2)	2.3360(11)	C(23)-C(24)	1.390(3)
Ir(1)-P(1)	2.3512(12)	C(23)-H(23)	0.9500
P(1)-C(27)	1.8356(18)	C(24)-C(25)	1.393(3)
P(1)-C(29)	1.8487(17)	C(24)-H(24)	0.9500
P(1)-C(32)	1.8491(17)	C(25)-C(26)	1.398(2)
P(2)-C(28)	1.8383(17)	C(25)-H(25)	0.9500
P(2)-C(38)	1.8469(18)	C(26)-C(28)	1.513(2)
P(2)-C(35)	1.8534(17)	C(27)-H(27A)	0.9900
O(1)-C(41)	1.1470(19)	C(27)-H(27B)	0.9900
C(1)-C(2)	1.405(2)	C(28)-H(28A)	0.9900
C(1)-C(6)	1.422(2)	C(28)-H(28B)	0.9900
C(2)-C(3)	1.392(2)	C(29)-C(31)	1.537(2)
C(2)-H(2)	0.9500	C(29)-C(30)	1.541(2)
C(3)-C(4)	1.397(3)	C(29)-H(29)	1.0000
C(3)-H(3)	0.9500	C(30)-H(30A)	0.9800
C(4)-C(5)	1.390(3)	C(30)-H(30B)	0.9800
C(4)-H(4)	0.9500	C(30)-H(30C)	0.9800
C(5)-C(6)	1.396(2)	C(31)-H(31A)	0.9800
C(5)-H(5)	0.9500	C(31)-H(31B)	0.9800
C(6)-C(7)	1.470(2)	C(31)-H(31C)	0.9800
C(7)-C(8)	1.403(2)	C(32)-C(34)	1.531(2)
C(7)-C(12)	1.416(2)	C(32)-C(33)	1.534(2)
C(8)-C(9)	1.386(3)	C(32)-H(32)	1.0000
C(8)-H(8)	0.9500	C(33)-H(33A)	0.9800
C(9)-C(10)	1.386(3)	C(33)-H(33B)	0.9800
C(9)-H(9)	0.9500	C(33)-H(33C)	0.9800
C(10)-C(11)	1.396(2)	C(34)-H(34A)	0.9800
C(10)-H(10)	0.9500	C(34)-H(34B)	0.9800
C(11)-C(12)	1.398(2)	C(34)-H(34C)	0.9800
C(11)-H(11)	0.9500	C(35)-C(36)	1.529(2)

C(35)-C(37)	1.531(2)	C(29)-P(1)-Ir(1)	116.62(7)
C(35)-H(35)	1.0000	C(32)-P(1)-Ir(1)	123.75(5)
C(36)-H(36A)	0.9800	C(28)-P(2)-C(38)	103.74(8)
C(36)-H(36B)	0.9800	C(28)-P(2)-C(35)	103.13(8)
C(36)-H(36C)	0.9800	C(38)-P(2)-C(35)	105.60(7)
C(37)-H(37A)	0.9800	C(28)-P(2)-Ir(1)	103.41(6)
C(37)-H(37B)	0.9800	C(38)-P(2)-Ir(1)	118.12(6)
C(37)-H(37C)	0.9800	C(35)-P(2)-Ir(1)	120.45(5)
C(38)-C(40)	1.532(2)	C(2)-C(1)-C(6)	117.04(14)
C(38)-C(39)	1.537(2)	C(2)-C(1)-Ir(1)	128.04(11)
C(38)-H(38)	1.0000	C(6)-C(1)-Ir(1)	114.86(11)
C(39)-H(39A)	0.9800	C(3)-C(2)-C(1)	121.81(16)
C(39)-H(39B)	0.9800	C(3)-C(2)-H(2)	119.1
C(39)-H(39C)	0.9800	C(1)-C(2)-H(2)	119.1
C(40)-H(40A)	0.9800	C(2)-C(3)-C(4)	120.26(16)
C(40)-H(40B)	0.9800	C(2)-C(3)-H(3)	119.9
C(40)-H(40C)	0.9800	C(4)-C(3)-H(3)	119.9
C(41)-Ir(1)-C(12)	170.43(6)	C(5)-C(4)-C(3)	119.25(15)
C(41)-Ir(1)-C(1)	91.96(6)	C(5)-C(4)-H(4)	120.4
C(12)-Ir(1)-C(1)	79.18(6)	C(3)-C(4)-H(4)	120.4
C(41)-Ir(1)-C(21)	95.85(6)	C(4)-C(5)-C(6)	120.74(16)
C(12)-Ir(1)-C(21)	93.19(6)	C(4)-C(5)-H(5)	119.6
C(1)-Ir(1)-C(21)	171.72(6)	C(6)-C(5)-H(5)	119.6
C(41)-Ir(1)-P(2)	95.91(6)	C(5)-C(6)-C(1)	120.90(15)
C(12)-Ir(1)-P(2)	82.53(6)	C(5)-C(6)-C(7)	124.10(14)
C(1)-Ir(1)-P(2)	101.84(4)	C(1)-C(6)-C(7)	115.00(13)
C(21)-Ir(1)-P(2)	80.14(4)	C(8)-C(7)-C(12)	120.10(14)
C(41)-Ir(1)-P(1)	92.85(6)	C(8)-C(7)-C(6)	124.02(14)
C(12)-Ir(1)-P(1)	91.90(5)	C(12)-C(7)-C(6)	115.87(13)
C(1)-Ir(1)-P(1)	97.54(4)	C(9)-C(8)-C(7)	121.06(15)
C(21)-Ir(1)-P(1)	79.35(4)	C(9)-C(8)-H(8)	119.5
P(2)-Ir(1)-P(1)	158.399(18)	C(7)-C(8)-H(8)	119.5
C(27)-P(1)-C(29)	102.26(7)	C(10)-C(9)-C(8)	119.28(15)
C(27)-P(1)-C(32)	104.45(7)	C(10)-C(9)-H(9)	120.4
C(29)-P(1)-C(32)	106.95(8)	C(8)-C(9)-H(9)	120.4
C(27)-P(1)-Ir(1)	99.38(5)	C(9)-C(10)-C(11)	120.23(15)

C(9)-C(10)-H(10)	119.9	P(2)-C(28)-H(28B)	109.8
C(11)-C(10)-H(10)	119.9	H(28A)-C(28)-H(28B)	108.3
C(10)-C(11)-C(12)	121.74(15)	C(31)-C(29)-C(30)	109.84(13)
C(10)-C(11)-H(11)	119.1	C(31)-C(29)-P(1)	113.17(12)
C(12)-C(11)-H(11)	119.1	C(30)-C(29)-P(1)	115.26(11)
C(11)-C(12)-C(7)	117.50(13)	C(31)-C(29)-H(29)	105.9
C(11)-C(12)-Ir(1)	127.59(11)	C(30)-C(29)-H(29)	105.9
C(7)-C(12)-Ir(1)	114.79(10)	P(1)-C(29)-H(29)	105.9
C(26)-C(21)-C(22)	117.79(13)	C(29)-C(30)-H(30A)	109.5
C(26)-C(21)-Ir(1)	122.21(10)	C(29)-C(30)-H(30B)	109.5
C(22)-C(21)-Ir(1)	120.00(11)	H(30A)-C(30)-H(30B)	109.5
C(23)-C(22)-C(21)	121.14(14)	C(29)-C(30)-H(30C)	109.5
C(23)-C(22)-C(27)	121.31(14)	H(30A)-C(30)-H(30C)	109.5
C(21)-C(22)-C(27)	117.53(13)	H(30B)-C(30)-H(30C)	109.5
C(24)-C(23)-C(22)	120.13(15)	C(29)-C(31)-H(31A)	109.5
C(24)-C(23)-H(23)	119.9	C(29)-C(31)-H(31B)	109.5
C(22)-C(23)-H(23)	119.9	H(31A)-C(31)-H(31B)	109.5
C(23)-C(24)-C(25)	119.88(15)	C(29)-C(31)-H(31C)	109.5
C(23)-C(24)-H(24)	120.1	H(31A)-C(31)-H(31C)	109.5
C(25)-C(24)-H(24)	120.1	H(31B)-C(31)-H(31C)	109.5
C(24)-C(25)-C(26)	120.17(15)	C(34)-C(32)-C(33)	110.12(13)
C(24)-C(25)-H(25)	119.9	C(34)-C(32)-P(1)	113.13(11)
C(26)-C(25)-H(25)	119.9	C(33)-C(32)-P(1)	110.70(11)
C(25)-C(26)-C(21)	120.90(14)	C(34)-C(32)-H(32)	107.6
C(25)-C(26)-C(28)	120.67(14)	C(33)-C(32)-H(32)	107.6
C(21)-C(26)-C(28)	118.42(13)	P(1)-C(32)-H(32)	107.6
C(22)-C(27)-P(1)	107.00(10)	C(32)-C(33)-H(33A)	109.5
C(22)-C(27)-H(27A)	110.3	C(32)-C(33)-H(33B)	109.5
P(1)-C(27)-H(27A)	110.3	H(33A)-C(33)-H(33B)	109.5
C(22)-C(27)-H(27B)	110.3	C(32)-C(33)-H(33C)	109.5
P(1)-C(27)-H(27B)	110.3	H(33A)-C(33)-H(33C)	109.5
H(27A)-C(27)-H(27B)	108.6	H(33B)-C(33)-H(33C)	109.5
C(26)-C(28)-P(2)	109.23(11)	C(32)-C(34)-H(34A)	109.5
C(26)-C(28)-H(28A)	109.8	C(32)-C(34)-H(34B)	109.5
P(2)-C(28)-H(28A)	109.8	H(34A)-C(34)-H(34B)	109.5
C(26)-C(28)-H(28B)	109.8	C(32)-C(34)-H(34C)	109.5

H(34A)-C(34)-H(34C)	109.5	C(40)-C(38)-C(39)	111.06(14)
H(34B)-C(34)-H(34C)	109.5	C(40)-C(38)-P(2)	112.64(11)
C(36)-C(35)-C(37)	110.58(13)	C(39)-C(38)-P(2)	112.48(11)
C(36)-C(35)-P(2)	112.99(11)	C(40)-C(38)-H(38)	106.7
C(37)-C(35)-P(2)	113.21(11)	C(39)-C(38)-H(38)	106.7
C(36)-C(35)-H(35)	106.5	P(2)-C(38)-H(38)	106.7
C(37)-C(35)-H(35)	106.5	C(38)-C(39)-H(39A)	109.5
P(2)-C(35)-H(35)	106.5	C(38)-C(39)-H(39B)	109.5
C(35)-C(36)-H(36A)	109.5	H(39A)-C(39)-H(39B)	109.5
C(35)-C(36)-H(36B)	109.5	C(38)-C(39)-H(39C)	109.5
H(36A)-C(36)-H(36B)	109.5	H(39A)-C(39)-H(39C)	109.5
C(35)-C(36)-H(36C)	109.5	H(39B)-C(39)-H(39C)	109.5
H(36A)-C(36)-H(36C)	109.5	C(38)-C(40)-H(40A)	109.5
H(36B)-C(36)-H(36C)	109.5	C(38)-C(40)-H(40B)	109.5
C(35)-C(37)-H(37A)	109.5	H(40A)-C(40)-H(40B)	109.5
C(35)-C(37)-H(37B)	109.5	C(38)-C(40)-H(40C)	109.5
H(37A)-C(37)-H(37B)	109.5	H(40A)-C(40)-H(40C)	109.5
C(35)-C(37)-H(37C)	109.5	H(40B)-C(40)-H(40C)	109.5
H(37A)-C(37)-H(37C)	109.5	O(1)-C(41)-Ir(1)	175.54(13)
H(37B)-C(37)-H(37C)	109.5		

Table S-16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4-CO**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir1	11(1)	10(1)	10(1)	-1(1)	2(1)	0(1)
P1	14(1)	12(1)	13(1)	-1(1)	2(1)	-1(1)
P2	12(1)	12(1)	14(1)	0(1)	2(1)	-1(1)
O1	16(1)	22(1)	26(1)	0(1)	0(1)	4(1)
C1	15(1)	12(1)	14(1)	-2(1)	3(1)	-4(1)
C2	19(1)	18(1)	16(1)	-4(1)	5(1)	-3(1)
C3	28(1)	21(1)	18(1)	-4(1)	10(1)	-6(1)
C4	36(1)	20(1)	14(1)	-1(1)	7(1)	-6(1)
C5	30(1)	16(1)	13(1)	1(1)	0(1)	-4(1)
C6	19(1)	12(1)	13(1)	-1(1)	2(1)	-3(1)
C7	17(1)	12(1)	15(1)	0(1)	-1(1)	-1(1)
C8	23(1)	18(1)	19(1)	0(1)	-5(1)	0(1)
C9	20(1)	22(1)	29(1)	-1(1)	-7(1)	5(1)
C10	15(1)	20(1)	29(1)	-5(1)	0(1)	4(1)
C11	16(1)	15(1)	20(1)	-3(1)	2(1)	1(1)
C12	13(1)	11(1)	15(1)	-1(1)	0(1)	0(1)
C21	14(1)	15(1)	11(1)	-1(1)	2(1)	1(1)
C22	16(1)	17(1)	14(1)	-1(1)	2(1)	1(1)
C23	24(1)	25(1)	14(1)	-5(1)	3(1)	-1(1)
C24	28(1)	33(1)	16(1)	-4(1)	8(1)	-1(1)
C25	22(1)	28(1)	17(1)	0(1)	9(1)	-2(1)
C26	16(1)	18(1)	15(1)	1(1)	5(1)	1(1)
C27	17(1)	16(1)	13(1)	-1(1)	0(1)	-2(1)
C28	16(1)	18(1)	17(1)	0(1)	6(1)	-2(1)
C29	19(1)	13(1)	19(1)	-1(1)	3(1)	1(1)
C30	23(1)	17(1)	24(1)	3(1)	-2(1)	0(1)
C31	32(1)	15(1)	25(1)	-6(1)	0(1)	2(1)
C32	17(1)	16(1)	19(1)	-2(1)	4(1)	-5(1)
C33	15(1)	24(1)	24(1)	-1(1)	5(1)	-2(1)
C34	26(1)	24(1)	26(1)	6(1)	9(1)	-2(1)

C35	15(1)	15(1)	18(1)	-1(1)	0(1)	-2(1)
C36	20(1)	24(1)	19(1)	-5(1)	1(1)	-2(1)
C37	19(1)	26(1)	28(1)	1(1)	-1(1)	-10(1)
C38	18(1)	13(1)	21(1)	2(1)	2(1)	-1(1)
C39	24(1)	24(1)	22(1)	4(1)	1(1)	4(1)
C40	22(1)	20(1)	25(1)	-2(1)	2(1)	6(1)
C41	15(1)	14(1)	14(1)	-2(1)	2(1)	-3(1)

Table S-17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **4-CO**.

	x	y	z	U(eq)
H2	6584	1799	5464	21
H3	6677	1984	3820	26
H4	5357	2624	2828	27
H5	3945	3069	3505	24
H8	2604	3337	4201	25
H9	1271	3686	5043	29
H10	1458	3596	6731	26
H11	2955	3136	7565	20
H23	5353	3527	10433	25
H24	4063	2734	10981	30
H25	3162	1748	9948	26
H27A	6678	3152	8830	19
H27B	6169	4058	9046	19
H28A	2659	1627	7847	20
H28B	3164	818	8434	20
H29	4305	4402	7718	20
H30A	3759	5120	6398	33
H30B	4384	4391	5925	33
H30C	4845	5334	6126	33
H31A	4840	5852	7909	37
H31B	5924	5568	7689	37
H31C	5491	5216	8635	37
H32	7147	4543	7415	21
H33A	8298	3584	6873	31
H33B	7451	2876	6610	31
H33C	7780	3130	7715	31
H34A	7371	4562	5734	37
H34B	6321	4945	5936	37
H34C	6390	3988	5514	37
H35	2634	1411	5933	19

H36A	2894	654	4596	32
H36B	3655	5	5191	32
H36C	3971	985	5030	32
H37A	1712	153	5832	37
H37B	2016	366	6952	37
H37C	2591	-372	6437	37
H38	4053	-379	7379	21
H39A	5368	-523	8617	35
H39B	4626	213	8898	35
H39C	5653	473	8518	35
H40A	5531	-822	6860	34
H40B	5882	157	6750	34
H40C	4967	-215	6042	34

Table S-18. Torsion angles [°] for **4-CO**.

C6-C1-C2-C3	1.5(2)	C24-C25-C26-C21	0.4(3)
Ir1-C1-C2-C3	-175.54(12)	C24-C25-C26-C28	-178.10(16)
C1-C2-C3-C4	-0.7(2)	C22-C21-C26-C25	0.4(2)
C2-C3-C4-C5	-0.2(2)	Ir1-C21-C26-C25	-179.12(12)
C3-C4-C5-C6	0.3(2)	C22-C21-C26-C28	178.90(14)
C4-C5-C6-C1	0.5(2)	Ir1-C21-C26-C28	-0.61(19)
C4-C5-C6-C7	-179.50(14)	C23-C22-C27-P1	-149.80(13)
C2-C1-C6-C5	-1.3(2)	C21-C22-C27-P1	32.01(16)
Ir1-C1-C6-C5	176.05(11)	C29-P1-C27-C22	78.90(12)
C2-C1-C6-C7	178.64(13)	C32-P1-C27-C22	-169.75(10)
Ir1-C1-C6-C7	-3.97(16)	Ir1-P1-C27-C22	-41.15(10)
C5-C6-C7-C8	5.8(2)	C25-C26-C28-P2	-162.17(13)
C1-C6-C7-C8	-174.21(14)	C21-C26-C28-P2	19.31(17)
C5-C6-C7-C12	-173.85(14)	C38-P2-C28-C26	97.67(12)
C1-C6-C7-C12	6.18(19)	C35-P2-C28-C26	-152.37(11)
C12-C7-C8-C9	-1.3(2)	Ir1-P2-C28-C26	-26.18(11)
C6-C7-C8-C9	179.11(15)	C27-P1-C29-C31	54.53(13)
C7-C8-C9-C10	2.4(3)	C32-P1-C29-C31	-54.92(14)
C8-C9-C10-C11	-0.7(3)	Ir1-P1-C29-C31	161.72(10)
C9-C10-C11-C12	-2.0(3)	C27-P1-C29-C30	-177.87(11)
C10-C11-C12-C7	3.1(2)	C32-P1-C29-C30	72.67(13)
C10-C11-C12-Ir1	-172.77(12)	Ir1-P1-C29-C30	-70.69(12)
C8-C7-C12-C11	-1.4(2)	C27-P1-C32-C34	-168.19(12)
C6-C7-C12-C11	178.22(13)	C29-P1-C32-C34	-60.27(13)
C8-C7-C12-Ir1	174.97(11)	Ir1-P1-C32-C34	79.82(13)
C6-C7-C12-Ir1	-5.41(16)	C27-P1-C32-C33	67.67(12)
C26-C21-C22-C23	-0.9(2)	C29-P1-C32-C33	175.59(11)
Ir1-C21-C22-C23	178.66(12)	Ir1-P1-C32-C33	-44.32(13)
C26-C21-C22-C27	177.33(13)	C28-P2-C35-C36	-178.18(11)
Ir1-C21-C22-C27	-3.16(18)	C38-P2-C35-C36	-69.62(12)
C21-C22-C23-C24	0.6(3)	Ir1-P2-C35-C36	67.41(12)
C27-C22-C23-C24	-177.54(16)	C28-P2-C35-C37	-51.51(13)
C22-C23-C24-C25	0.2(3)	C38-P2-C35-C37	57.06(13)
C23-C24-C25-C26	-0.7(3)	Ir1-P2-C35-C37	-165.92(10)

C28-P2-C38-C40	-174.29(12)
C35-P2-C38-C40	77.59(13)
Ir1-P2-C38-C40	-60.63(13)
C28-P2-C38-C39	-47.84(13)
C35-P2-C38-C39	-155.97(12)
Ir1-P2-C38-C39	65.82(13)