Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Synthesis and Reactivity of Rhodium and Iridium Alkene, Alkyl and Silyl Complexes Supported by Phenyl-substituted PNP Pincer Ligand

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Contents:

For **2**: Crystals were grown from vapor diffusion heptane into a concentrated solution of **2** in *ortho*-dichlorobenzene at ambient temperature. The unit cell contained two molecules of *ortho*-dichlorobenzene, one of the molecules exhibited rotational disorder treated by utilizing a free variable for the occupancy and employing the SAME command.

Table S1. Crystal data and structure refinement for compound **2**.

Empirical formula	C58 H49 Cl5 Ir N P2	
Formula weight	1191.37	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.6344(14) Å	α= 88.097(4)°.
	b = 10.6886(15) Å	β= 81.884(4)°.
	c = 24.996(4) Å	γ = 80.357(4)°.
Volume	2512.1(6) $Å^3$	
Z	2	
Density (calculated)	1.575 g/cm^3	
Absorption coefficient	8.501 mm^{-1}	
F(000)	1192	
Crystal size	0.10 x 0.07 x 0.03 mm^3	
Theta range for data collection	4.20 to 68.57°.	
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -30 ≤ l ≤ 29	
Reflections collected	37973	
Independent reflections	8775 [R(int) = 0.0201]	
Completeness to theta = 68.57°	94.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7845 and 0.4836	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8775 / 54 / 642	
Goodness-of-fit on F^2	1.339	
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.1231	
R indices (all data)	R1 = 0.0361, wR2 = 0.1310	
Largest diff. peak and hole	1.962 and -1.426 e. $Å^{-3}$	

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

	x	y	z	U(eq)
Ir(1)	1320(1)	2444(1)	2682(1)	18(1)
P(1)	565(1)	2054(1)	1864(1)	18(1)
P(2)	1372(1)	612(1)	3195(1)	20(1)
N(1)	3330(3)	1493(3)	2278(1)	21(1)
Cl(1)	5959(1)	2237(1)	2650(1)	32(1)
C(1)	2131(5)	4189(4)	2504(2)	33(1)
C(2)	2450(5)	3720(4)	3018(2)	32(1)
C(3)	1667(6)	4435(5)	3526(2)	43(1)
C(4)	352(5)	3935(4)	3759(2)	34(1)
C(5)	-277(4)	3256(4)	3348(2)	26(1)
C(6)	-629(5)	3801(4)	2856(2)	29(1)
C(7)	-469(6)	5179(5)	2693(2)	35(1)
C(8)	1035(5)	5342(4)	2415(2)	42(1)
C(9)	-245(4)	716(3)	1679(2)	20(1)
C(10)	140(5)	-458(4)	1918(2)	27(1)
C(11)	-425(5)	-1511(4)	1789(2)	32(1)
C(12)	-1362(4)	-1397(4)	1417(2)	30(1)
C(13)	-1740(4)	-226(4)	1160(2)	28(1)
C(14)	-1190(4)	811(4)	1296(2)	25(1)
C(15)	-450(4)	3403(3)	1546(2)	19(1)
C(16)	179(4)	4290(4)	1218(2)	25(1)
C(17)	-674(5)	5339(4)	1018(2)	28(1)
C(18)	-2142(5)	5508(4)	1148(2)	28(1)
C(19)	-2765(4)	4655(4)	1489(2)	28(1)
C(20)	-1929(4)	3609(4)	1688(2)	24(1)
C(21)	3492(4)	1664(3)	1687(2)	21(1)
C(22)	2276(4)	1778(3)	1434(2)	19(1)
C(23)	2414(4)	1802(4)	868(2)	23(1)
C(24)	3742(4)	1777(4)	558(2)	25(1)
C(25)	4901(4)	1789(4)	828(2)	28(1)
C(26)	4795(4)	1720(4)	1387(2)	23(1)

C(27)	3883(5)	1831(4)	-58(2)	33(1)
C(28)	3708(4)	124(4)	2418(2)	20(1)
C(29)	2850(4)	-434(4)	2822(2)	23(1)
C(30)	3236(4)	-1711(4)	2955(2)	25(1)
C(31)	4468(4)	-2458(4)	2700(2)	25(1)
C(32)	5327(4)	-1851(4)	2316(2)	26(1)
C(33)	4967(4)	-602(4)	2170(2)	23(1)
C(34)	4848(5)	-3839(4)	2840(2)	33(1)
C(35)	1937(5)	661(4)	3859(2)	26(1)
C(36)	3371(5)	589(5)	3913(2)	33(1)
C(37)	3768(5)	691(5)	4420(2)	38(1)
C(38)	2775(5)	903(4)	4872(2)	34(1)
C(39)	1345(5)	1002(4)	4821(2)	32(1)
C(40)	931(5)	880(4)	4319(2)	28(1)
C(41)	-105(4)	-278(4)	3343(2)	23(1)
C(42)	-27(4)	-1358(4)	3683(2)	25(1)
C(43)	-1152(5)	-2029(4)	3769(2)	32(1)
C(44)	-2373(5)	-1619(5)	3541(2)	35(1)
C(45)	-2472(5)	-551(4)	3215(2)	33(1)
C(46)	-1347(4)	126(4)	3119(2)	25(1)
Cl(2)	3033(2)	3942(1)	5025(1)	48(1)
Cl(3)	2350(2)	6693(2)	4523(1)	70(1)
C(47)	3265(5)	5268(4)	5358(2)	35(1)
C(48)	2933(5)	6476(5)	5151(2)	40(1)
C(49)	3092(6)	7528(5)	5430(2)	43(1)
C(50)	3587(5)	7347(5)	5928(2)	39(1)
C(51)	3923(5)	6163(5)	6137(2)	39(1)
C(52)	3762(5)	5114(5)	5857(2)	40(1)
Cl(4A)	5831(2)	4999(1)	9210(1)	38(1)
Cl(5A)	6436(2)	2269(1)	8680(1)	37(1)
C(53A)	6933(10)	3754(5)	9469(3)	27(2)
C(54A)	7225(5)	2576(5)	9228(2)	24(1)
C(55A)	8148(5)	1596(5)	9438(2)	28(1)
C(56A)	8777(8)	1845(7)	9900(3)	25(2)
C(57A)	8494(5)	3027(5)	10123(2)	26(1)
C(58A)	7592(5)	3976(5)	9908(2)	25(1)

Cl(4B)	7185(14)	4708(13)	10000(5)	89(3)
Cl(5B)	8840(30)	1780(20)	9947(10)	124(9)
C(53B)	7270(40)	3740(20)	9447(11)	31(12)
C(54B)	7790(30)	2460(20)	9468(10)	62(8)
C(55B)	7750(60)	1690(30)	9034(15)	118(19)
C(56B)	7190(70)	2330(40)	8586(14)	130(20)
C(57B)	6270(30)	3450(20)	8652(9)	45(6)
C(58B)	6400(30)	4240(20)	9055(9)	47(6)

Table S3. Bond lengths [Å] and angles [°] for **2**.

Ir(1)-C(2)	2.141(4)	C(8)-H(8A)	0.9900
Ir(1)-C(1)	2.149(4)	C(8)-H(8B)	0.9900
Ir(1)-N(1)	2.159(3)	C(9)-C(10)	1.388(5)
Ir(1)-C(6)	2.172(4)	C(9)-C(14)	1.400(5)
Ir(1)-C(5)	2.196(4)	C(10)-C(11)	1.395(6)
Ir(1)-P(2)	2.3027(9)	C(10)-H(10A)	0.9500
Ir(1)-P(1)	2.3378(9)	C(11)-C(12)	1.375(7)
P(1)-C(22)	1.821(4)	C(11)-H(11A)	0.9500
P(1)-C(15)	1.827(4)	C(12)-C(13)	1.404(6)
P(1)-C(9)	1.840(4)	C(12)-H(12A)	0.9500
P(2)-C(29)	1.818(4)	C(13)-C(14)	1.377(6)
P(2)-C(35)	1.823(4)	C(13)-H(13A)	0.9500
P(2)-C(41)	1.829(4)	C(14)-H(14A)	0.9500
N(1)-C(21)	1.472(5)	C(15)-C(16)	1.391(5)
N(1)-C(28)	1.490(5)	C(15)-C(20)	1.401(5)
N(1)-H(1)	0.90(6)	C(16)-C(17)	1.398(6)
C(1)-C(2)	1.419(7)	C(16)-H(16A)	0.9500
C(1)-C(8)	1.515(6)	C(17)-C(18)	1.389(6)
C(1)-H(1A)	1.0000	C(17)-H(17A)	0.9500
C(2)-C(3)	1.538(6)	C(18)-C(19)	1.379(6)
C(2)-H(2A)	1.0000	C(18)-H(18A)	0.9500
C(3)-C(4)	1.492(7)	C(19)-C(20)	1.386(6)
C(3)-H(3A)	0.9900	C(19)-H(19A)	0.9500
C(3)-H(3B)	0.9900	C(20)-H(20A)	0.9500
C(4)-C(5)	1.523(6)	C(21)-C(26)	1.377(6)
C(4)-H(4A)	0.9900	C(21)-C(22)	1.393(5)
C(4)-H(4B)	0.9900	C(22)-C(23)	1.403(5)
C(5)-C(6)	1.404(6)	C(23)-C(24)	1.395(6)
C(5)-H(5A)	1.0000	C(23)-H(23A)	0.9500
C(6)-C(7)	1.541(6)	C(24)-C(25)	1.386(6)
C(6)-H(6A)	1.0000	C(24)-C(27)	1.526(5)
C(7)-C(8)	1.551(7)	C(25)-C(26)	1.388(6)
C(7)-H(7A)	0.9900	C(25)-H(25A)	0.9500
C(7)-H(7B)	0.9900	C(26)-H(26A)	0.9500

C(27)-H(27A)	0.9800	C(45)-H(45A)	0.9500
C(27)-H(27B)	0.9800	C(46)-H(46A)	0.9500
C(27)-H(27C)	0.9800	Cl(2)-C(47)	1.728(5)
C(28)-C(29)	1.396(6)	Cl(3)-C(48)	1.738(5)
C(28)-C(33)	1.401(6)	C(47)-C(48)	1.378(6)
C(29)-C(30)	1.395(6)	C(47)-C(52)	1.394(6)
C(30)-C(31)	1.398(6)	C(48)-C(49)	1.382(7)
C(30)-H(30A)	0.9500	C(49)-C(50)	1.392(7)
C(31)-C(32)	1.394(6)	C(49)-H(49A)	0.9500
C(31)-C(34)	1.502(5)	C(50)-C(51)	1.358(7)
C(32)-C(33)	1.373(6)	C(50)-H(50A)	0.9500
C(32)-H(32A)	0.9500	C(51)-C(52)	1.384(7)
C(33)-H(33A)	0.9500	C(51)-H(51A)	0.9500
C(34)-H(34A)	0.9800	C(52)-H(52A)	0.9500
C(34)-H(34B)	0.9800	Cl(4A)-C(53A)	1.726(7)
C(34)-H(34C)	0.9800	Cl(5A)-C(54A)	1.724(5)
C(35)-C(40)	1.394(6)	C(53A)-C(54A)	1.383(7)
C(35)-C(36)	1.396(6)	C(53A)-C(58A)	1.389(8)
C(36)-C(37)	1.388(6)	C(54A)-C(55A)	1.394(7)
C(36)-H(36A)	0.9500	C(55A)-C(56A)	1.430(8)
C(37)-C(38)	1.372(7)	C(56A)-C(57A)	1.367(9)
C(37)-H(37A)	0.9500	C(57A)-C(58A)	1.369(7)
C(38)-C(39)	1.387(7)	Cl(4B)-C(53B)	1.735(16)
C(38)-H(38A)	0.9500	Cl(5B)-C(54B)	1.740(15)
C(39)-C(40)	1.386(6)	C(53B)-C(54B)	1.379(15)
C(39)-H(39A)	0.9500	C(53B)-C(58B)	1.413(16)
C(40)-H(40A)	0.9500	C(54B)-C(55B)	1.395(16)
C(41)-C(46)	1.390(6)	C(55B)-C(56B)	1.413(17)
C(41)-C(42)	1.409(6)	C(56B)-C(57B)	1.366(18)
C(42)-C(43)	1.385(6)	C(57B)-C(58B)	1.374(16)
C(42)-H(42A)	0.9500		
C(43)-C(44)	1.378(7)	C(2)-Ir(1)-C(1)	38.62(18)
C(43)-H(43A)	0.9500	C(2)-Ir(1)-N(1)	88.43(15)
C(44)-C(45)	1.378(7)	C(1)-Ir(1)-N(1)	86.86(16)
C(44)-H(44A)	0.9500	C(2)-Ir(1)-C(6)	89.50(17)
C(45)-C(46)	1.390(6)	C(1)-Ir(1)-C(6)	79.90(18)

N(1)-Ir(1)-C(6)	161.15(17)	C(8)-C(1)-Ir(1)	115.7(3)
C(2)-Ir(1)-C(5)	79.10(17)	C(2)-C(1)-H(1A)	113.1
C(1)-Ir(1)-C(5)	93.88(17)	C(8)-C(1)-H(1A)	113.1
N(1)-Ir(1)-C(5)	158.57(16)	Ir(1)-C(1)-H(1A)	113.1
C(6)-Ir(1)-C(5)	37.49(16)	C(1)-C(2)-C(3)	118.7(4)
C(2)-Ir(1)-P(2)	109.91(13)	C(1)-C(2)-Ir(1)	71.0(2)
C(1)-Ir(1)-P(2)	147.58(12)	C(3)-C(2)-Ir(1)	115.9(3)
N(1)-Ir(1)-P(2)	84.05(9)	C(1)-C(2)-H(2A)	114.7
C(6)-Ir(1)-P(2)	114.19(13)	C(3)-C(2)-H(2A)	114.7
C(5)-Ir(1)-P(2)	83.94(11)	Ir(1)-C(2)-H(2A)	114.7
C(2)-Ir(1)-P(1)	139.91(13)	C(4)-C(3)-C(2)	113.0(4)
C(1)-Ir(1)-P(1)	101.74(13)	C(4)-C(3)-H(3A)	109.0
N(1)-Ir(1)-P(1)	82.04(9)	C(2)-C(3)-H(3A)	109.0
C(6)-Ir(1)-P(1)	87.55(12)	C(4)-C(3)-H(3B)	109.0
C(5)-Ir(1)-P(1)	118.59(12)	C(2)-C(3)-H(3B)	109.0
P(2)-Ir(1)-P(1)	107.68(3)	H(3A)-C(3)-H(3B)	107.8
C(22)-P(1)-C(15)	104.22(17)	C(3)-C(4)-C(5)	113.5(4)
C(22)-P(1)-C(9)	101.32(16)	C(3)-C(4)-H(4A)	108.9
C(15)-P(1)-C(9)	102.36(17)	C(5)-C(4)-H(4A)	108.9
C(22)-P(1)-Ir(1)	99.58(12)	C(3)-C(4)-H(4B)	108.9
C(15)-P(1)-Ir(1)	116.46(12)	C(5)-C(4)-H(4B)	108.9
C(9)-P(1)-Ir(1)	129.16(12)	H(4A)-C(4)-H(4B)	107.7
C(29)-P(2)-C(35)	102.52(19)	C(6)-C(5)-C(4)	123.9(4)
C(29)-P(2)-C(41)	107.36(19)	C(6)-C(5)-Ir(1)	70.3(2)
C(35)-P(2)-C(41)	101.52(18)	C(4)-C(5)-Ir(1)	112.8(3)
C(29)-P(2)-Ir(1)	101.77(14)	C(6)-C(5)-H(5A)	114.1
C(35)-P(2)-Ir(1)	116.55(13)	C(4)-C(5)-H(5A)	114.1
C(41)-P(2)-Ir(1)	124.85(14)	Ir(1)-C(5)-H(5A)	114.1
C(21)-N(1)-C(28)	110.0(3)	C(5)-C(6)-C(7)	122.5(4)
C(21)-N(1)-Ir(1)	113.4(2)	C(5)-C(6)-Ir(1)	72.2(2)
C(28)-N(1)-Ir(1)	115.5(2)	C(7)-C(6)-Ir(1)	114.0(3)
C(21)-N(1)-H(1)	101(3)	C(5)-C(6)-H(6A)	113.8
C(28)-N(1)-H(1)	123(3)	C(7)-C(6)-H(6A)	113.8
Ir(1)-N(1)-H(1)	93(3)	Ir(1)-C(6)-H(6A)	113.8
C(2)-C(1)-C(8)	124.7(4)	C(6)-C(7)-C(8)	114.5(4)
C(2)-C(1)-Ir(1)	70.4(2)	C(6)-C(7)-H(7A)	108.6

C(8)-C(7)-H(7A)	108.6	C(16)-C(17)-H(17A)	119.8
C(6)-C(7)-H(7B)	108.6	C(19)-C(18)-C(17)	120.0(4)
C(8)-C(7)-H(7B)	108.6	C(19)-C(18)-H(18A)	120.0
H(7A)-C(7)-H(7B)	107.6	C(17)-C(18)-H(18A)	120.0
C(1)-C(8)-C(7)	111.5(4)	C(18)-C(19)-C(20)	120.1(4)
C(1)-C(8)-H(8A)	109.3	C(18)-C(19)-H(19A)	120.0
C(7)-C(8)-H(8A)	109.3	C(20)-C(19)-H(19A)	120.0
C(1)-C(8)-H(8B)	109.3	C(19)-C(20)-C(15)	120.6(4)
C(7)-C(8)-H(8B)	109.3	C(19)-C(20)-H(20A)	119.7
H(8A)-C(8)-H(8B)	108.0	C(15)-C(20)-H(20A)	119.7
C(10)-C(9)-C(14)	118.4(3)	C(26)-C(21)-C(22)	120.3(4)
C(10)-C(9)-P(1)	118.1(3)	C(26)-C(21)-N(1)	121.8(4)
C(14)-C(9)-P(1)	123.5(3)	C(22)-C(21)-N(1)	117.9(3)
C(9)-C(10)-C(11)	120.7(4)	C(21)-C(22)-C(23)	119.2(3)
C(9)-C(10)-H(10A)	119.6	C(21)-C(22)-P(1)	117.4(3)
C(11)-C(10)-H(10A)	119.6	C(23)-C(22)-P(1)	123.1(3)
C(12)-C(11)-C(10)	120.0(4)	C(24)-C(23)-C(22)	120.8(4)
C(12)-C(11)-H(11A)	120.0	C(24)-C(23)-H(23A)	119.6
C(10)-C(11)-H(11A)	120.0	C(22)-C(23)-H(23A)	119.6
C(11)-C(12)-C(13)	120.1(4)	C(25)-C(24)-C(23)	117.8(4)
C(11)-C(12)-H(12A)	119.9	C(25)-C(24)-C(27)	121.5(4)
C(13)-C(12)-H(12A)	119.9	C(23)-C(24)-C(27)	120.6(4)
C(14)-C(13)-C(12)	119.3(4)	C(24)-C(25)-C(26)	122.2(4)
C(14)-C(13)-H(13A)	120.4	C(24)-C(25)-H(25A)	118.9
C(12)-C(13)-H(13A)	120.4	C(26)-C(25)-H(25A)	118.9
C(13)-C(14)-C(9)	121.4(4)	C(21)-C(26)-C(25)	119.2(4)
C(13)-C(14)-H(14A)	119.3	C(21)-C(26)-H(26A)	120.4
C(9)-C(14)-H(14A)	119.3	C(25)-C(26)-H(26A)	120.4
C(16)-C(15)-C(20)	119.2(3)	C(24)-C(27)-H(27A)	109.5
C(16)-C(15)-P(1)	123.4(3)	C(24)-C(27)-H(27B)	109.5
C(20)-C(15)-P(1)	117.2(3)	H(27A)-C(27)-H(27B)	109.5
C(15)-C(16)-C(17)	119.8(4)	C(24)-C(27)-H(27C)	109.5
C(15)-C(16)-H(16A)	120.1	H(27A)-C(27)-H(27C)	109.5
C(17)-C(16)-H(16A)	120.1	H(27B)-C(27)-H(27C)	109.5
C(18)-C(17)-C(16)	120.3(4)	C(29)-C(28)-C(33)	119.0(4)
C(18)-C(17)-H(17A)	119.8	C(29)-C(28)-N(1)	120.3(4)

C(33)-C(28)-N(1)	120.6(3)	C(38)-C(39)-H(39A)	119.9
C(30)-C(29)-C(28)	119.4(4)	C(39)-C(40)-C(35)	120.8(4)
C(30)-C(29)-P(2)	123.5(3)	C(39)-C(40)-H(40A)	119.6
C(28)-C(29)-P(2)	116.8(3)	C(35)-C(40)-H(40A)	119.6
C(29)-C(30)-C(31)	122.2(4)	C(46)-C(41)-C(42)	118.7(4)
C(29)-C(30)-H(30A)	118.9	C(46)-C(41)-P(2)	119.3(3)
C(31)-C(30)-H(30A)	118.9	C(42)-C(41)-P(2)	121.9(3)
C(32)-C(31)-C(30)	116.6(4)	C(43)-C(42)-C(41)	119.9(4)
C(32)-C(31)-C(34)	122.0(4)	C(43)-C(42)-H(42A)	120.0
C(30)-C(31)-C(34)	121.4(4)	C(41)-C(42)-H(42A)	120.0
C(33)-C(32)-C(31)	122.6(4)	C(44)-C(43)-C(42)	120.5(4)
C(33)-C(32)-H(32A)	118.7	C(44)-C(43)-H(43A)	119.8
C(31)-C(32)-H(32A)	118.7	C(42)-C(43)-H(43A)	119.8
C(32)-C(33)-C(28)	120.1(4)	C(45)-C(44)-C(43)	120.1(4)
C(32)-C(33)-H(33A)	120.0	C(45)-C(44)-H(44A)	119.9
C(28)-C(33)-H(33A)	120.0	C(43)-C(44)-H(44A)	119.9
C(31)-C(34)-H(34A)	109.5	C(44)-C(45)-C(46)	120.2(4)
C(31)-C(34)-H(34B)	109.5	C(44)-C(45)-H(45A)	119.9
H(34A)-C(34)-H(34B)	109.5	C(46)-C(45)-H(45A)	119.9
C(31)-C(34)-H(34C)	109.5	C(45)-C(46)-C(41)	120.4(4)
H(34A)-C(34)-H(34C)	109.5	C(45)-C(46)-H(46A)	119.8
H(34B)-C(34)-H(34C)	109.5	C(41)-C(46)-H(46A)	119.8
C(40)-C(35)-C(36)	118.6(4)	C(48)-C(47)-C(52)	119.0(4)
C(40)-C(35)-P(2)	120.3(3)	C(48)-C(47)-Cl(2)	122.0(4)
C(36)-C(35)-P(2)	120.9(3)	C(52)-C(47)-Cl(2)	118.9(4)
C(37)-C(36)-C(35)	119.8(4)	C(47)-C(48)-C(49)	121.1(4)
C(37)-C(36)-H(36A)	120.1	C(47)-C(48)-Cl(3)	119.9(4)
C(35)-C(36)-H(36A)	120.1	C(49)-C(48)-Cl(3)	118.9(4)
C(38)-C(37)-C(36)	121.4(4)	C(48)-C(49)-C(50)	118.6(4)
C(38)-C(37)-H(37A)	119.3	C(48)-C(49)-H(49A)	120.7
C(36)-C(37)-H(37A)	119.3	C(50)-C(49)-H(49A)	120.7
C(37)-C(38)-C(39)	119.2(4)	C(51)-C(50)-C(49)	121.1(5)
C(37)-C(38)-H(38A)	120.4	C(51)-C(50)-H(50A)	119.5
C(39)-C(38)-H(38A)	120.4	C(49)-C(50)-H(50A)	119.5
C(40)-C(39)-C(38)	120.2(4)	C(50)-C(51)-C(52)	120.0(5)
C(40)-C(39)-H(39A)	119.9	C(50)-C(51)-H(51A)	120.0

C(52)-C(51)-H(51A)	120.0	C(56A)-C(57A)-C(58A)	120.1(5)
C(51)-C(52)-C(47)	120.0(4)	C(57A)-C(58A)-C(53A)	120.9(5)
C(51)-C(52)-H(52A)	120.0	C(54B)-C(53B)-C(58B)	120.7(16)
C(47)-C(52)-H(52A)	120.0	C(54B)-C(53B)-Cl(4B)	121.2(16)
C(54A)-C(53A)-C(58A)	120.1(6)	C(58B)-C(53B)-Cl(4B)	115.4(14)
C(54A)-C(53A)-Cl(4A)	121.2(5)	C(53B)-C(54B)-C(55B)	120.0(16)
C(58A)-C(53A)-Cl(4A)	118.6(4)	C(53B)-C(54B)-Cl(5B)	123.1(17)
C(53A)-C(54A)-C(55A)	120.0(5)	C(55B)-C(54B)-Cl(5B)	115.5(16)
C(53A)-C(54A)-Cl(5A)	121.4(4)	C(54B)-C(55B)-C(56B)	115(2)
C(55A)-C(54A)-Cl(5A)	118.6(4)	C(57B)-C(56B)-C(55B)	121(2)
C(54A)-C(55A)-C(56A)	118.5(5)	C(56B)-C(57B)-C(58B)	118(2)
C(57A)-C(56A)-C(55A)	120.3(5)	C(57B)-C(58B)-C(53B)	117.5(16)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	19(1)	19(1)	17(1)	-1(1)	-3(1)	-2(1)
P(1)	18(1)	18(1)	17(1)	-1(1)	-3(1)	-3(1)
P(2)	20(1)	23(1)	17(1)	1(1)	-2(1)	-3(1)
N(1)	20(2)	21(2)	22(2)	1(1)	-6(1)	-3(1)
Cl(1)	22(1)	41(1)	34(1)	2(1)	-7(1)	-10(1)
C(1)	30(2)	23(2)	49(3)	0(2)	-11(2)	-11(2)
C(2)	29(2)	35(2)	35(2)	-10(2)	-7(2)	-9(2)
C(3)	45(3)	48(3)	35(2)	-24(2)	-5(2)	-3(2)
C(4)	47(3)	30(2)	22(2)	-7(2)	-3(2)	-3(2)
C(5)	27(2)	25(2)	20(2)	-9(2)	10(2)	4(2)
C(6)	26(2)	27(2)	32(2)	-6(2)	-7(2)	5(2)
C(7)	40(2)	28(2)	34(2)	1(2)	-11(2)	4(2)
C(8)	44(3)	25(2)	58(3)	-1(2)	-13(2)	-9(2)
C(9)	23(2)	19(2)	18(2)	-4(1)	0(2)	-4(1)
C(10)	34(2)	27(2)	21(2)	-1(2)	-4(2)	-5(2)
C(11)	45(2)	22(2)	29(2)	3(2)	-2(2)	-5(2)
C(12)	30(2)	22(2)	39(2)	-6(2)	-2(2)	-9(2)
C(13)	22(2)	27(2)	35(2)	-5(2)	-9(2)	-4(2)
C(14)	27(2)	21(2)	27(2)	0(1)	-8(2)	-2(2)
C(15)	22(2)	15(2)	21(2)	-5(1)	-6(1)	4(1)
C(16)	26(2)	21(2)	27(2)	-1(2)	-4(2)	-3(2)
C(17)	36(2)	21(2)	28(2)	1(2)	-5(2)	-7(2)
C(18)	35(2)	19(2)	31(2)	-5(2)	-14(2)	6(2)
C(19)	28(2)	24(2)	34(2)	-7(2)	-12(2)	1(2)
C(20)	23(2)	26(2)	24(2)	-3(1)	-2(2)	-4(2)
C(21)	24(2)	22(2)	14(2)	-1(1)	2(2)	-1(1)
C(22)	20(2)	17(2)	19(2)	-1(1)	-3(1)	-2(1)
C(23)	27(2)	21(2)	21(2)	0(1)	-6(2)	-3(1)
C(24)	29(2)	24(2)	21(2)	1(1)	-1(2)	0(2)
C(25)	24(2)	28(2)	28(2)	7(2)	2(2)	-1(2)
C(26)	20(2)	25(2)	22(2)	1(1)	-2(2)	1(1)

C(27)	39(2)	35(2)	21(2)	4(2)	-1(2)	-2(2)
C(28)	21(2)	21(2)	20(2)	2(1)	-8(2)	-3(1)
C(29)	24(2)	26(2)	20(2)	0(2)	-6(2)	-5(2)
C(30)	25(2)	27(2)	21(2)	4(2)	-1(2)	-4(2)
C(31)	24(2)	24(2)	26(2)	1(2)	-7(2)	-4(2)
C(32)	24(2)	26(2)	27(2)	-1(2)	-3(2)	0(2)
C(33)	21(2)	26(2)	23(2)	1(1)	-4(2)	-3(1)
C(34)	32(2)	25(2)	37(2)	4(2)	-2(2)	3(2)
C(35)	30(2)	30(2)	21(2)	3(2)	-7(2)	-9(2)
C(36)	28(2)	47(3)	25(2)	1(2)	-5(2)	-9(2)
C(37)	35(2)	54(3)	30(2)	3(2)	-11(2)	-17(2)
C(38)	51(3)	30(2)	28(2)	3(2)	-14(2)	-16(2)
C(39)	43(2)	34(2)	18(2)	0(2)	-4(2)	-6(2)
C(40)	28(2)	34(2)	20(2)	-4(2)	2(2)	-5(2)
C(41)	24(2)	27(2)	19(2)	-4(2)	3(2)	-5(2)
C(42)	24(2)	30(2)	18(2)	-4(2)	5(2)	-1(2)
C(43)	37(2)	26(2)	32(2)	-2(2)	1(2)	-9(2)
C(44)	33(2)	38(2)	37(2)	-7(2)	-2(2)	-15(2)
C(45)	25(2)	39(2)	36(2)	-7(2)	-6(2)	-7(2)
C(46)	22(2)	28(2)	22(2)	-4(2)	-1(2)	-2(2)
Cl(2)	60(1)	39(1)	47(1)	-7(1)	-8(1)	-15(1)
Cl(3)	99(1)	60(1)	53(1)	2(1)	-41(1)	11(1)
C(47)	32(2)	36(2)	35(2)	-3(2)	-2(2)	-3(2)
C(48)	42(2)	40(3)	37(3)	-2(2)	-10(2)	0(2)
C(49)	44(3)	31(2)	52(3)	8(2)	-7(2)	-1(2)
C(50)	41(2)	40(2)	33(2)	-8(2)	8(2)	-9(2)
C(51)	38(2)	46(3)	33(2)	-4(2)	-3(2)	-8(2)
C(52)	42(2)	42(3)	32(2)	5(2)	-3(2)	2(2)
Cl(4A)	35(1)	34(1)	45(1)	-1(1)	-20(1)	7(1)
Cl(5A)	35(1)	51(1)	27(1)	-15(1)	-11(1)	-4(1)
C(53A)	14(3)	32(4)	34(4)	3(2)	-3(2)	-3(2)
C(54A)	20(2)	33(3)	19(2)	-4(2)	1(2)	-7(2)
C(55A)	26(2)	34(3)	20(2)	-14(2)	5(2)	3(2)
C(56A)	26(3)	22(3)	22(3)	8(2)	-7(2)	9(2)
C(57A)	27(2)	37(3)	16(2)	2(2)	-3(2)	-8(2)
C(58A)	21(2)	20(2)	32(3)	1(2)	-2(2)	-1(2)

Table S5. Hydrogen bonds for **2** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...Cl(1)	0.90(6)	2.31(5)	3.051(3)	139(4)

Symmetry transformations used to generate equivalent atoms:

For **3**: Crystals were grown from vapor diffusion pentane into a concentrated solution of **3** in dichloromethane at -30 °C.

Table S6. Crystal data and structure refinement for complex **3**.

Empirical formula	C46 H44 Ir N P2	
Formula weight	864.96	
Temperature	144(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.230(2) Å	α= 88.76(3)°.
	b = 10.663(2) Å	β= 89.08(3)°.
	c = 17.091(3) Å	γ = 73.16(3)°.
Volume	1783.9(6) $Å^3$	
Z	2	
Density (calculated)	1.610 g/cm^3	
Absorption coefficient	3.868 mm^{-1}	
F(000)	868	
Crystal size	0.19 x 0.13 x 0.07 mm^3	
Crystal color/habit	yellow prism	
Theta range for data collection	3.27 to 24.73°	
Index ranges	-12 ≤ h ≤ 11, -12 ≤ k ≤ 12, -9 ≤ l ≤ 20	
Reflections collected	9035	
Independent reflections	5839 [R(int) = 0.0185]	
Completeness to theta = 24.73°	95.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7735 and 0.5269	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5839 / 0 / 453	
Goodness-of-fit on F^2	1.156	
Final R indices [I>2sigma(I)]	R1 = 0.0253, wR2 = 0.0581	
R indices (all data)	R1 = 0.0317, wR2 = 0.0598	
Largest diff. peak and hole	2.135 and -0.614 e. $Å^{-3}$	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	-171(1)	2468(1)	3121(1)	14(1)
P(1)	-499(1)	3492(1)	1923(1)	15(1)
P(2)	2111(1)	1156(1)	3194(1)	14(1)
N(1)	-228(3)	843(3)	2460(2)	15(1)
C(1)	-2059(4)	2343(4)	3588(2)	21(1)
C(2)	-982(4)	1643(4)	4102(2)	17(1)
C(3)	-798(4)	2190(4)	4891(2)	24(1)
C(4)	49(4)	3155(4)	4861(2)	22(1)
C(5)	186(4)	3708(4)	4047(2)	20(1)
C(6)	-960(4)	4409(4)	3620(2)	21(1)
C(7)	-2413(4)	4704(4)	3946(3)	32(1)
C(8)	-3081(4)	3637(4)	3803(3)	33(1)
C(9)	3453(4)	1053(4)	2449(2)	16(1)
C(10)	3054(4)	978(4)	1678(2)	18(1)
C(11)	3976(4)	889(4)	1064(2)	22(1)
C(12)	5287(4)	899(4)	1212(3)	25(1)
C(13)	5698(4)	975(4)	1973(3)	26(1)
C(14)	4790(4)	1042(4)	2592(2)	22(1)
C(15)	2933(4)	1154(4)	4133(2)	17(1)
C(16)	3549(4)	2128(4)	4279(2)	20(1)
C(17)	3999(4)	2280(4)	5024(2)	24(1)
C(18)	3795(4)	1479(4)	5634(2)	25(1)
C(19)	3184(4)	511(4)	5496(2)	22(1)
C(20)	2744(4)	349(4)	4749(2)	19(1)
C(21)	1831(4)	-447(4)	3092(2)	16(1)
C(22)	2721(4)	-1638(4)	3326(2)	18(1)
C(23)	2386(4)	-2797(4)	3275(2)	18(1)
C(24)	1104(4)	-2730(4)	2987(2)	20(1)
C(25)	211(4)	-1557(4)	2725(2)	19(1)
C(26)	584(4)	-388(4)	2742(2)	14(1)
C(27)	3350(4)	-4082(4)	3560(3)	26(1)

C(28)	-992(4)	2306(4)	1354(2)	16(1)
C(29)	-666(4)	1023(4)	1692(2)	15(1)
C(30)	-810(4)	34(4)	1199(2)	16(1)
C(31)	-1372(4)	326(4)	465(2)	18(1)
C(32)	-1824(4)	1608(4)	163(2)	20(1)
C(33)	-1585(4)	2576(4)	615(2)	18(1)
C(34)	-2526(4)	1917(4)	-617(2)	28(1)
C(35)	-1868(4)	5033(4)	1802(2)	17(1)
C(36)	-3223(4)	5013(4)	1825(2)	21(1)
C(37)	-4278(4)	6182(4)	1803(3)	25(1)
C(38)	-3991(4)	7371(4)	1772(3)	27(1)
C(39)	-2655(4)	7393(4)	1753(3)	27(1)
C(40)	-1589(4)	6235(4)	1761(2)	24(1)
C(41)	946(4)	3863(4)	1414(2)	17(1)
C(42)	1167(4)	3806(4)	614(2)	26(1)
C(43)	2348(4)	3988(4)	284(2)	27(1)
C(44)	3327(5)	4232(4)	751(3)	29(1)
C(45)	3108(4)	4305(4)	1553(3)	26(1)
C(46)	1938(4)	4118(4)	1881(2)	20(1)

Table S8. Bond lengths [Å] and angles [°] for **3**.

Ir(1)-N(1)	2.104(3)	C(8)-H(8B)	0.9900
Ir(1)-C(1)	2.116(4)	C(9)-C(14)	1.390(5)
Ir(1)-C(2)	2.142(4)	C(9)-C(10)	1.397(5)
Ir(1)-C(6)	2.179(4)	C(10)-C(11)	1.386(5)
Ir(1)-C(5)	2.185(4)	C(10)-H(10A)	0.9500
Ir(1)-P(1)	2.2827(12)	C(11)-C(12)	1.372(6)
Ir(1)-P(2)	2.3525(13)	C(11)-H(11A)	0.9500
P(1)-C(28)	1.799(4)	C(12)-C(13)	1.384(6)
P(1)-C(35)	1.835(4)	C(12)-H(12A)	0.9500
P(1)-C(41)	1.839(4)	C(13)-C(14)	1.386(6)
P(2)-C(15)	1.822(4)	C(13)-H(13A)	0.9500
P(2)-C(21)	1.826(4)	C(14)-H(14A)	0.9500
P(2)-C(9)	1.839(4)	C(15)-C(20)	1.391(6)
N(1)-C(29)	1.385(5)	C(15)-C(16)	1.391(5)
N(1)-C(26)	1.414(5)	C(16)-C(17)	1.389(6)
C(1)-C(2)	1.439(6)	C(16)-H(16A)	0.9500
C(1)-C(8)	1.518(6)	C(17)-C(18)	1.384(6)
C(1)-H(1A)	1.0000	C(17)-H(17A)	0.9500
C(2)-C(3)	1.515(5)	C(18)-C(19)	1.379(6)
C(2)-H(2A)	1.0000	C(18)-H(18A)	0.9500
C(3)-C(4)	1.525(6)	C(19)-C(20)	1.392(5)
C(3)-H(3A)	0.9900	C(19)-H(19A)	0.9500
C(3)-H(3B)	0.9900	C(20)-H(20A)	0.9500
C(4)-C(5)	1.519(6)	C(21)-C(22)	1.386(5)
C(4)-H(4A)	0.9900	C(21)-C(26)	1.403(5)
C(4)-H(4B)	0.9900	C(22)-C(23)	1.380(5)
C(5)-C(6)	1.400(6)	C(22)-H(22A)	0.9500
C(5)-H(5A)	1.0000	C(23)-C(24)	1.390(6)
C(6)-C(7)	1.526(6)	C(23)-C(27)	1.513(5)
C(6)-H(6A)	1.0000	C(24)-C(25)	1.388(5)
C(7)-C(8)	1.513(6)	C(24)-H(24A)	0.9500
C(7)-H(7A)	0.9900	C(25)-C(26)	1.405(5)
C(7)-H(7B)	0.9900	C(25)-H(25A)	0.9500
C(8)-H(8A)	0.9900	C(27)-H(27A)	0.9800

C(27)-H(27B)	0.9800	C(46)-H(46A)	0.9500
C(27)-H(27C)	0.9800		
C(28)-C(33)	1.398(5)	N(1)-Ir(1)-C(1)	84.58(14)
C(28)-C(29)	1.423(5)	N(1)-Ir(1)-C(2)	88.98(13)
C(29)-C(30)	1.405(5)	C(1)-Ir(1)-C(2)	39.51(15)
C(30)-C(31)	1.380(5)	N(1)-Ir(1)-C(6)	156.41(14)
C(30)-H(30A)	0.9500	C(1)-Ir(1)-C(6)	79.60(16)
C(31)-C(32)	1.400(6)	C(2)-Ir(1)-C(6)	89.85(15)
C(31)-H(31A)	0.9500	N(1)-Ir(1)-C(5)	163.37(13)
C(32)-C(33)	1.381(6)	C(1)-Ir(1)-C(5)	94.95(16)
C(32)-C(34)	1.508(5)	C(2)-Ir(1)-C(5)	80.36(15)
C(33)-H(33A)	0.9500	C(6)-Ir(1)-C(5)	37.42(15)
C(34)-H(34A)	0.9800	N(1)-Ir(1)-P(1)	82.25(9)
C(34)-H(34B)	0.9800	C(1)-Ir(1)-P(1)	109.91(12)
C(34)-H(34C)	0.9800	C(2)-Ir(1)-P(1)	149.14(11)
C(35)-C(40)	1.392(6)	C(6)-Ir(1)-P(1)	86.79(11)
C(35)-C(36)	1.392(5)	C(5)-Ir(1)-P(1)	113.29(11)
C(36)-C(37)	1.392(6)	N(1)-Ir(1)-P(2)	78.54(9)
C(36)-H(36A)	0.9500	C(1)-Ir(1)-P(2)	135.17(11)
C(37)-C(38)	1.381(6)	C(2)-Ir(1)-P(2)	98.53(11)
C(37)-H(37A)	0.9500	C(6)-Ir(1)-P(2)	124.90(11)
C(38)-C(39)	1.374(6)	C(5)-Ir(1)-P(2)	90.39(11)
C(38)-H(38A)	0.9500	P(1)-Ir(1)-P(2)	108.50(5)
C(39)-C(40)	1.390(6)	C(28)-P(1)-C(35)	105.87(18)
C(39)-H(39A)	0.9500	C(28)-P(1)-C(41)	107.57(18)
C(40)-H(40A)	0.9500	C(35)-P(1)-C(41)	102.23(18)
C(41)-C(42)	1.383(6)	C(28)-P(1)-Ir(1)	101.19(13)
C(41)-C(46)	1.392(6)	C(35)-P(1)-Ir(1)	119.39(13)
C(42)-C(43)	1.387(6)	C(41)-P(1)-Ir(1)	119.49(13)
C(42)-H(42A)	0.9500	C(15)-P(2)-C(21)	107.53(18)
C(43)-C(44)	1.375(6)	C(15)-P(2)-C(9)	105.63(18)
C(43)-H(43A)	0.9500	C(21)-P(2)-C(9)	100.37(17)
C(44)-C(45)	1.386(6)	C(15)-P(2)-Ir(1)	115.38(13)
C(44)-H(44A)	0.9500	C(21)-P(2)-Ir(1)	98.72(13)
C(45)-C(46)	1.378(6)	C(9)-P(2)-Ir(1)	126.34(13)
C(45)-H(45A)	0.9500	C(29)-N(1)-C(26)	121.4(3)

C(29)-N(1)-Ir(1)	119.9(2)	C(7)-C(6)-H(6A)	113.9
C(26)-N(1)-Ir(1)	115.6(2)	Ir(1)-C(6)-H(6A)	113.9
C(2)-C(1)-C(8)	122.7(4)	C(8)-C(7)-C(6)	113.9(3)
C(2)-C(1)-Ir(1)	71.2(2)	C(8)-C(7)-H(7A)	108.8
C(8)-C(1)-Ir(1)	115.7(3)	C(6)-C(7)-H(7A)	108.8
C(2)-C(1)-H(1A)	113.5	C(8)-C(7)-H(7B)	108.8
C(8)-C(1)-H(1A)	113.5	C(6)-C(7)-H(7B)	108.8
Ir(1)-C(1)-H(1A)	113.5	H(7A)-C(7)-H(7B)	107.7
C(1)-C(2)-C(3)	120.8(4)	C(7)-C(8)-C(1)	112.8(4)
C(1)-C(2)-Ir(1)	69.3(2)	C(7)-C(8)-H(8A)	109.0
C(3)-C(2)-Ir(1)	115.3(3)	C(1)-C(8)-H(8A)	109.0
C(1)-C(2)-H(2A)	114.6	C(7)-C(8)-H(8B)	109.0
C(3)-C(2)-H(2A)	114.6	C(1)-C(8)-H(8B)	109.0
Ir(1)-C(2)-H(2A)	114.6	H(8A)-C(8)-H(8B)	107.8
C(2)-C(3)-C(4)	114.1(3)	C(14)-C(9)-C(10)	119.0(3)
C(2)-C(3)-H(3A)	108.7	C(14)-C(9)-P(2)	125.9(3)
C(4)-C(3)-H(3A)	108.7	C(10)-C(9)-P(2)	115.2(3)
C(2)-C(3)-H(3B)	108.7	C(11)-C(10)-C(9)	120.6(4)
C(4)-C(3)-H(3B)	108.7	C(11)-C(10)-H(10A)	119.7
H(3A)-C(3)-H(3B)	107.6	C(9)-C(10)-H(10A)	119.7
C(5)-C(4)-C(3)	113.9(3)	C(12)-C(11)-C(10)	119.8(4)
C(5)-C(4)-H(4A)	108.8	C(12)-C(11)-H(11A)	120.1
C(3)-C(4)-H(4A)	108.8	C(10)-C(11)-H(11A)	120.1
C(5)-C(4)-H(4B)	108.8	C(11)-C(12)-C(13)	120.3(4)
C(3)-C(4)-H(4B)	108.8	C(11)-C(12)-H(12A)	119.8
H(4A)-C(4)-H(4B)	107.7	C(13)-C(12)-H(12A)	119.8
C(6)-C(5)-C(4)	121.6(4)	C(12)-C(13)-C(14)	120.3(4)
C(6)-C(5)-Ir(1)	71.1(2)	C(12)-C(13)-H(13A)	119.8
C(4)-C(5)-Ir(1)	112.7(3)	C(14)-C(13)-H(13A)	119.8
C(6)-C(5)-H(5A)	114.7	C(13)-C(14)-C(9)	120.0(4)
C(4)-C(5)-H(5A)	114.7	C(13)-C(14)-H(14A)	120.0
Ir(1)-C(5)-H(5A)	114.7	C(9)-C(14)-H(14A)	120.0
C(5)-C(6)-C(7)	122.7(4)	C(20)-C(15)-C(16)	118.9(4)
C(5)-C(6)-Ir(1)	71.5(2)	C(20)-C(15)-P(2)	120.9(3)
C(7)-C(6)-Ir(1)	114.2(3)	C(16)-C(15)-P(2)	119.2(3)
C(5)-C(6)-H(6A)	113.9	C(17)-C(16)-C(15)	120.8(4)

C(17)-C(16)-H(16A)	119.6	H(27A)-C(27)-H(27C)	109.5
C(15)-C(16)-H(16A)	119.6	H(27B)-C(27)-H(27C)	109.5
C(18)-C(17)-C(16)	119.7(4)	C(33)-C(28)-C(29)	121.1(4)
C(18)-C(17)-H(17A)	120.1	C(33)-C(28)-P(1)	123.8(3)
C(16)-C(17)-H(17A)	120.1	C(29)-C(28)-P(1)	115.0(3)
C(19)-C(18)-C(17)	120.0(4)	N(1)-C(29)-C(30)	125.6(3)
C(19)-C(18)-H(18A)	120.0	N(1)-C(29)-C(28)	118.6(3)
C(17)-C(18)-H(18A)	120.0	C(30)-C(29)-C(28)	115.8(3)
C(18)-C(19)-C(20)	120.3(4)	C(31)-C(30)-C(29)	121.4(4)
C(18)-C(19)-H(19A)	119.8	C(31)-C(30)-H(30A)	119.3
C(20)-C(19)-H(19A)	119.8	C(29)-C(30)-H(30A)	119.3
C(15)-C(20)-C(19)	120.2(4)	C(30)-C(31)-C(32)	122.7(4)
C(15)-C(20)-H(20A)	119.9	C(30)-C(31)-H(31A)	118.6
C(19)-C(20)-H(20A)	119.9	C(32)-C(31)-H(31A)	118.6
C(22)-C(21)-C(26)	120.8(4)	C(33)-C(32)-C(31)	116.4(4)
C(22)-C(21)-P(2)	125.8(3)	C(33)-C(32)-C(34)	121.7(4)
C(26)-C(21)-P(2)	113.4(3)	C(31)-C(32)-C(34)	121.9(4)
C(23)-C(22)-C(21)	121.9(4)	C(32)-C(33)-C(28)	122.0(4)
C(23)-C(22)-H(22A)	119.0	C(32)-C(33)-H(33A)	119.0
C(21)-C(22)-H(22A)	119.0	C(28)-C(33)-H(33A)	119.0
C(22)-C(23)-C(24)	117.4(4)	C(32)-C(34)-H(34A)	109.5
C(22)-C(23)-C(27)	121.2(4)	C(32)-C(34)-H(34B)	109.5
C(24)-C(23)-C(27)	121.3(4)	H(34A)-C(34)-H(34B)	109.5
C(25)-C(24)-C(23)	121.8(4)	C(32)-C(34)-H(34C)	109.5
C(25)-C(24)-H(24A)	119.1	H(34A)-C(34)-H(34C)	109.5
C(23)-C(24)-H(24A)	119.1	H(34B)-C(34)-H(34C)	109.5
C(24)-C(25)-C(26)	120.6(4)	C(40)-C(35)-C(36)	119.0(4)
C(24)-C(25)-H(25A)	119.7	C(40)-C(35)-P(1)	121.4(3)
C(26)-C(25)-H(25A)	119.7	C(36)-C(35)-P(1)	119.4(3)
C(21)-C(26)-C(25)	117.1(3)	C(37)-C(36)-C(35)	120.2(4)
C(21)-C(26)-N(1)	118.0(3)	C(37)-C(36)-H(36A)	119.9
C(25)-C(26)-N(1)	124.8(3)	C(35)-C(36)-H(36A)	119.9
C(23)-C(27)-H(27A)	109.5	C(38)-C(37)-C(36)	120.4(4)
C(23)-C(27)-H(27B)	109.5	C(38)-C(37)-H(37A)	119.8
H(27A)-C(27)-H(27B)	109.5	C(36)-C(37)-H(37A)	119.8
C(23)-C(27)-H(27C)	109.5	C(39)-C(38)-C(37)	119.5(4)

C(39)-C(38)-H(38A)	120.3	C(43)-C(42)-H(42A)	119.4
C(37)-C(38)-H(38A)	120.3	C(44)-C(43)-C(42)	120.4(4)
C(38)-C(39)-C(40)	120.9(4)	C(44)-C(43)-H(43A)	119.8
C(38)-C(39)-H(39A)	119.6	C(42)-C(43)-H(43A)	119.8
C(40)-C(39)-H(39A)	119.6	C(43)-C(44)-C(45)	119.0(4)
C(39)-C(40)-C(35)	120.0(4)	C(43)-C(44)-H(44A)	120.5
C(39)-C(40)-H(40A)	120.0	C(45)-C(44)-H(44A)	120.5
C(35)-C(40)-H(40A)	120.0	C(46)-C(45)-C(44)	120.6(4)
C(42)-C(41)-C(46)	118.1(4)	C(46)-C(45)-H(45A)	119.7
C(42)-C(41)-P(1)	124.9(3)	C(44)-C(45)-H(45A)	119.7
C(46)-C(41)-P(1)	116.8(3)	C(45)-C(46)-C(41)	120.8(4)
C(41)-C(42)-C(43)	121.1(4)	C(45)-C(46)-H(46A)	119.6
C(41)-C(42)-H(42A)	119.4	C(41)-C(46)-H(46A)	119.6

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	15(1)	13(1)	15(1)	0(1)	-1(1)	-4(1)
P(1)	17(1)	13(1)	15(1)	1(1)	-2(1)	-4(1)
P(2)	14(1)	13(1)	16(1)	0(1)	-1(1)	-4(1)
N(1)	20(2)	12(2)	13(2)	0(1)	-2(1)	-5(1)
C(1)	15(2)	28(2)	21(2)	-1(2)	4(2)	-9(2)
C(2)	18(2)	17(2)	16(2)	-1(2)	2(2)	-7(2)
C(3)	24(2)	26(2)	21(2)	3(2)	4(2)	-6(2)
C(4)	27(2)	20(2)	18(2)	-4(2)	-5(2)	-4(2)
C(5)	23(2)	15(2)	23(2)	-5(2)	-1(2)	-7(2)
C(6)	30(2)	14(2)	18(2)	-5(2)	4(2)	-5(2)
C(7)	28(3)	26(2)	32(3)	-9(2)	-3(2)	6(2)
C(8)	25(2)	32(3)	33(3)	10(2)	7(2)	5(2)
C(9)	15(2)	11(2)	24(2)	-1(2)	1(2)	-4(2)
C(10)	14(2)	17(2)	25(2)	0(2)	-1(2)	-6(2)
C(11)	26(2)	19(2)	19(2)	-1(2)	0(2)	-6(2)
C(12)	22(2)	24(2)	28(2)	-2(2)	9(2)	-4(2)
C(13)	14(2)	27(2)	36(3)	-3(2)	-1(2)	-5(2)
C(14)	19(2)	22(2)	23(2)	-2(2)	1(2)	-6(2)
C(15)	17(2)	17(2)	16(2)	-2(2)	-4(2)	-5(2)
C(16)	17(2)	20(2)	22(2)	-2(2)	1(2)	-4(2)
C(17)	21(2)	23(2)	30(3)	-5(2)	-2(2)	-8(2)
C(18)	20(2)	32(2)	21(2)	-5(2)	-5(2)	-5(2)
C(19)	21(2)	27(2)	16(2)	6(2)	-4(2)	-4(2)
C(20)	17(2)	18(2)	24(2)	-1(2)	-2(2)	-5(2)
C(21)	16(2)	16(2)	15(2)	0(2)	2(2)	-4(2)
C(22)	15(2)	22(2)	16(2)	0(2)	-2(2)	-6(2)
C(23)	23(2)	14(2)	15(2)	0(2)	1(2)	-3(2)
C(24)	27(2)	15(2)	19(2)	-2(2)	0(2)	-10(2)
C(25)	19(2)	19(2)	20(2)	-1(2)	-4(2)	-7(2)
C(26)	16(2)	14(2)	13(2)	-4(2)	1(2)	-4(2)
C(27)	31(2)	18(2)	26(2)	1(2)	-2(2)	0(2)

C(28)	13(2)	18(2)	18(2)	-1(2)	-2(2)	-5(2)
C(29)	8(2)	19(2)	18(2)	-1(2)	2(2)	-4(2)
C(30)	13(2)	19(2)	17(2)	-2(2)	0(2)	-6(2)
C(31)	13(2)	20(2)	22(2)	-7(2)	-1(2)	-5(2)
C(32)	16(2)	25(2)	17(2)	-1(2)	1(2)	-6(2)
C(33)	16(2)	19(2)	19(2)	3(2)	-2(2)	-3(2)
C(34)	31(3)	29(2)	24(2)	0(2)	-10(2)	-9(2)
C(35)	22(2)	17(2)	11(2)	-1(2)	-5(2)	-3(2)
C(36)	22(2)	17(2)	26(2)	2(2)	-1(2)	-9(2)
C(37)	19(2)	25(2)	33(3)	5(2)	-4(2)	-6(2)
C(38)	23(2)	19(2)	34(3)	3(2)	-8(2)	0(2)
C(39)	27(2)	15(2)	40(3)	-1(2)	-9(2)	-9(2)
C(40)	21(2)	23(2)	28(2)	3(2)	-8(2)	-9(2)
C(41)	21(2)	13(2)	17(2)	3(2)	1(2)	-4(2)
C(42)	27(2)	28(2)	22(2)	8(2)	-4(2)	-8(2)
C(43)	30(2)	28(2)	19(2)	8(2)	2(2)	-5(2)
C(44)	30(3)	25(2)	35(3)	5(2)	6(2)	-12(2)
C(45)	27(2)	22(2)	34(3)	0(2)	-2(2)	-14(2)
C(46)	26(2)	15(2)	20(2)	1(2)	0(2)	-9(2)

For **16**: Crystals were grown from vapor diffusion pentane into a concentrated solution of **16** in fluoorobenzene at -30 °C. The unit cell contained one molecule of fluorobenzene.

Table S10. Crystal data and structure refinement for complex **16**.

Empirical formula	C62 H47 F Ir N P2 Si	
Formula weight	1107.24	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/ c	
Unit cell dimensions	a = 13.1135(8) Å	α= 90°.
	b = 15.3247(9) Å	β= 98.463(4)°.
	c = 25.2279(16) Å	γ = 90°.
Volume	5014.6(5) Å^3	
Z	4	
Density (calculated)	1.467 g/cm^3	
Absorption coefficient	6.334 mm^{-1}	
F(000)	2224	
Crystal size	0.20 x 0.15 x 0.04 mm^3	
Crystal color/habit	orange plate	
Theta range for data collection	3.38 to 67.70°.	
Index ranges	$-15 \leq h \leq 15$, $-17 \leq k \leq 14$, $-30 \leq l \leq 30$	
Reflections collected	46231	
Independent reflections	8821 [R(int) = 0.0675]	
Completeness to theta = 67.70°	97.1 %	
Absorption correction	Analytical	
Max. and min. transmission	0.7857 and 0.3640	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8821 / 30 / 580	
Goodness-of-fit on F^2	1.192	
Final R indices [I>2sigma(I)]	R1 = 0.0382, wR2 = 0.0918	
R indices (all data)	R1 = 0.0562, wR2 = 0.0987	
Largest diff. peak and hole	2.035 and -0.973 e. Å^{-3}	

Table S11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **16**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	3293(1)	9045(1)	8442(1)	12(1)
Si(1)	2362(1)	8986(1)	9156(1)	14(1)
P(1)	2385(1)	10104(1)	7943(1)	14(1)
P(2)	4449(1)	7932(1)	8670(1)	13(1)
N(1)	3302(3)	8495(3)	7694(2)	13(1)
C(1)	2699(3)	9846(3)	7281(2)	14(1)
C(2)	2533(3)	10414(3)	6843(2)	16(1)
C(3)	2816(4)	10199(4)	6352(2)	19(1)
C(4)	3291(4)	9384(3)	6318(2)	19(1)
C(5)	3444(4)	8809(3)	6741(2)	18(1)
C(6)	3134(3)	9019(3)	7235(2)	16(1)
C(7)	3540(3)	7594(3)	7659(2)	14(1)
C(8)	4141(3)	7200(3)	8099(2)	14(1)
C(9)	5750(3)	8342(3)	8650(2)	14(1)
C(10)	6034(4)	9142(3)	8884(2)	19(1)
C(11)	7040(4)	9441(4)	8920(2)	22(1)
C(12)	7754(4)	8943(4)	8703(2)	25(1)
C(13)	7469(4)	8161(4)	8449(2)	28(1)
C(14)	6468(4)	7851(4)	8425(2)	19(1)
C(15)	4625(4)	7213(3)	9256(2)	19(1)
C(16)	5483(5)	7291(4)	9642(2)	26(1)
C(17)	5610(5)	6754(4)	10092(2)	36(2)
C(18)	4887(5)	6146(4)	10154(2)	39(2)
C(19)	4022(5)	6059(5)	9774(3)	50(2)
C(20)	3893(4)	6595(5)	9326(3)	39(2)
C(21)	4403(4)	6319(3)	8085(2)	20(1)
C(22)	4055(4)	5802(3)	7642(2)	20(1)
C(23)	4349(4)	4861(4)	7610(2)	29(1)
C(24)	3411(4)	6199(3)	7216(2)	19(1)
C(25)	3153(3)	7071(4)	7223(2)	19(1)

C(26)	2643(5)	10803(4)	5878(2)	30(1)
C(27)	2739(4)	11237(3)	8079(2)	19(1)
C(28)	2287(5)	11711(4)	8451(2)	28(1)
C(29)	2607(5)	12554(4)	8582(2)	35(2)
C(30)	3379(5)	12948(4)	8341(2)	39(2)
C(31)	3854(4)	12460(4)	7983(2)	28(1)
C(32)	3542(4)	11620(4)	7853(2)	19(1)
C(33)	979(4)	10047(4)	7829(2)	20(1)
C(34)	327(4)	10766(4)	7754(2)	30(1)
C(35)	-731(5)	10642(5)	7673(2)	39(2)
C(36)	-1139(4)	9826(6)	7651(2)	45(2)
C(37)	-501(4)	9101(5)	7710(3)	42(2)
C(38)	563(4)	9212(4)	7804(2)	27(1)
C(39)	3118(4)	8701(3)	9842(2)	18(1)
C(40)	2651(5)	8220(4)	10206(2)	31(1)
C(41)	3162(5)	8051(4)	10720(2)	37(2)
C(42)	4144(5)	8346(4)	10881(2)	31(1)
C(43)	4625(4)	8819(4)	10523(2)	26(1)
C(44)	4111(4)	8993(4)	10012(2)	22(1)
C(45)	1350(4)	8100(3)	9007(2)	17(1)
C(46)	478(4)	8067(4)	9271(2)	23(1)
C(47)	-216(4)	7382(4)	9188(2)	30(1)
C(48)	-60(4)	6711(4)	8843(3)	35(2)
C(49)	775(4)	6730(4)	8578(2)	31(1)
C(50)	1469(4)	7414(4)	8656(2)	22(1)
C(51)	1643(4)	10016(4)	9309(2)	19(1)
C(52)	2149(4)	10654(4)	9650(2)	24(1)
C(53)	1671(4)	11421(4)	9765(2)	32(1)
C(54)	654(5)	11574(4)	9537(2)	35(2)
C(55)	126(4)	10957(4)	9202(2)	32(1)
C(56)	618(4)	10184(4)	9091(2)	21(1)
C(57)	1051(10)	4407(10)	9071(6)	127(5)
C(58)	336(11)	4203(9)	8664(5)	124(5)
C(59)	-567(10)	3805(9)	8765(5)	117(5)
C(60)	-784(9)	3776(9)	9277(6)	109(4)
C(61)	-57(14)	4045(13)	9689(6)	219(10)

C(62)	896(12)	4280(12)	9583(6)	176(8)
F(1)	2010(9)	4728(7)	8986(4)	197(4)

Table S12. Bond lengths [Å] and angles [°] for **16**.

Ir(1)-N(1)	2.067(4)	C(12)-C(13)	1.385(8)
Ir(1)-P(1)	2.2800(12)	C(12)-H(12A)	0.9500
Ir(1)-P(2)	2.2978(12)	C(13)-C(14)	1.389(7)
Ir(1)-Si(1)	2.3220(13)	C(13)-H(13A)	0.9500
Si(1)-C(45)	1.897(5)	C(14)-H(14A)	0.9500
Si(1)-C(51)	1.907(6)	C(15)-C(20)	1.379(8)
Si(1)-C(39)	1.913(5)	C(15)-C(16)	1.382(7)
P(1)-C(27)	1.816(5)	C(16)-C(17)	1.390(8)
P(1)-C(1)	1.823(5)	C(16)-H(16A)	0.9500
P(1)-C(33)	1.825(5)	C(17)-C(18)	1.355(9)
P(2)-C(8)	1.824(5)	C(17)-H(17A)	0.9500
P(2)-C(9)	1.825(5)	C(18)-C(19)	1.381(10)
P(2)-C(15)	1.830(5)	C(18)-H(18A)	0.9500
N(1)-C(6)	1.402(6)	C(19)-C(20)	1.387(8)
N(1)-C(7)	1.421(6)	C(19)-H(19A)	0.9500
C(1)-C(2)	1.396(7)	C(20)-H(20A)	0.9500
C(1)-C(6)	1.402(7)	C(21)-C(22)	1.392(7)
C(2)-C(3)	1.385(7)	C(21)-H(21A)	0.9500
C(2)-H(2A)	0.9500	C(22)-C(24)	1.404(7)
C(3)-C(4)	1.404(7)	C(22)-C(23)	1.497(7)
C(3)-C(26)	1.502(7)	C(23)-H(23A)	0.9800
C(4)-C(5)	1.375(7)	C(23)-H(23B)	0.9800
C(4)-H(4A)	0.9500	C(23)-H(23C)	0.9800
C(5)-C(6)	1.404(7)	C(24)-C(25)	1.380(7)
C(5)-H(5A)	0.9500	C(24)-H(24A)	0.9500
C(7)-C(25)	1.395(7)	C(25)-H(25A)	0.9500
C(7)-C(8)	1.400(6)	C(26)-H(26A)	0.9800
C(8)-C(21)	1.395(7)	C(26)-H(26B)	0.9800
C(9)-C(10)	1.388(7)	C(26)-H(26C)	0.9800
C(9)-C(14)	1.389(7)	C(27)-C(28)	1.387(7)
C(10)-C(11)	1.386(7)	C(27)-C(32)	1.399(7)
C(10)-H(10A)	0.9500	C(28)-C(29)	1.384(8)
C(11)-C(12)	1.382(8)	C(28)-H(28A)	0.9500
C(11)-H(11A)	0.9500	C(29)-C(30)	1.393(9)

C(29)-H(29A)	0.9500	C(49)-C(50)	1.384(8)
C(30)-C(31)	1.388(8)	C(49)-H(49A)	0.9500
C(30)-H(30A)	0.9500	C(50)-H(50A)	0.9500
C(31)-C(32)	1.375(8)	C(51)-C(56)	1.399(6)
C(31)-H(31A)	0.9500	C(51)-C(52)	1.404(7)
C(32)-H(32A)	0.9500	C(52)-C(53)	1.382(8)
C(33)-C(38)	1.388(8)	C(52)-H(52A)	0.9500
C(33)-C(34)	1.391(7)	C(53)-C(54)	1.393(8)
C(34)-C(35)	1.385(8)	C(53)-H(53A)	0.9500
C(34)-H(34A)	0.9500	C(54)-C(55)	1.383(9)
C(35)-C(36)	1.359(10)	C(54)-H(54A)	0.9500
C(35)-H(35A)	0.9500	C(55)-C(56)	1.398(8)
C(36)-C(37)	1.385(10)	C(55)-H(55A)	0.9500
C(36)-H(36A)	0.9500	C(56)-H(56A)	0.9500
C(37)-C(38)	1.391(8)	C(57)-C(58)	1.323(11)
C(37)-H(37A)	0.9500	C(57)-C(62)	1.350(12)
C(38)-H(38A)	0.9500	C(57)-F(1)	1.395(13)
C(39)-C(44)	1.384(7)	C(58)-C(59)	1.389(11)
C(39)-C(40)	1.388(8)	C(59)-C(60)	1.362(11)
C(40)-C(41)	1.392(7)	C(60)-C(61)	1.367(12)
C(40)-H(40A)	0.9500	C(61)-C(62)	1.363(12)
C(41)-C(42)	1.369(9)		
C(41)-H(41A)	0.9500	N(1)-Ir(1)-P(1)	81.90(11)
C(42)-C(43)	1.380(8)	N(1)-Ir(1)-P(2)	80.46(11)
C(42)-H(42A)	0.9500	P(1)-Ir(1)-P(2)	159.81(4)
C(43)-C(44)	1.389(7)	N(1)-Ir(1)-Si(1)	140.04(11)
C(43)-H(43A)	0.9500	P(1)-Ir(1)-Si(1)	99.49(4)
C(44)-H(44A)	0.9500	P(2)-Ir(1)-Si(1)	100.33(5)
C(45)-C(50)	1.398(7)	C(45)-Si(1)-C(51)	106.3(2)
C(45)-C(46)	1.406(7)	C(45)-Si(1)-C(39)	105.7(2)
C(46)-C(47)	1.385(8)	C(51)-Si(1)-C(39)	102.2(2)
C(46)-H(46A)	0.9500	C(45)-Si(1)-Ir(1)	107.79(16)
C(47)-C(48)	1.381(8)	C(51)-Si(1)-Ir(1)	117.11(16)
C(47)-H(47A)	0.9500	C(39)-Si(1)-Ir(1)	116.71(16)
C(48)-C(49)	1.365(8)	C(27)-P(1)-C(1)	107.1(2)
C(48)-H(48A)	0.9500	C(27)-P(1)-C(33)	107.5(2)

C(1)-P(1)-C(33)	101.8(2)	C(7)-C(8)-P(2)	113.2(4)
C(27)-P(1)-Ir(1)	118.59(16)	C(10)-C(9)-C(14)	119.7(4)
C(1)-P(1)-Ir(1)	100.46(16)	C(10)-C(9)-P(2)	119.0(4)
C(33)-P(1)-Ir(1)	119.06(18)	C(14)-C(9)-P(2)	121.2(4)
C(8)-P(2)-C(9)	106.7(2)	C(11)-C(10)-C(9)	120.9(5)
C(8)-P(2)-C(15)	104.7(2)	C(11)-C(10)-H(10A)	119.5
C(9)-P(2)-C(15)	102.9(2)	C(9)-C(10)-H(10A)	119.5
C(8)-P(2)-Ir(1)	101.37(15)	C(12)-C(11)-C(10)	119.0(5)
C(9)-P(2)-Ir(1)	108.83(16)	C(12)-C(11)-H(11A)	120.5
C(15)-P(2)-Ir(1)	130.49(16)	C(10)-C(11)-H(11A)	120.5
C(6)-N(1)-C(7)	121.0(4)	C(11)-C(12)-C(13)	120.6(5)
C(6)-N(1)-Ir(1)	120.0(3)	C(11)-C(12)-H(12A)	119.7
C(7)-N(1)-Ir(1)	118.9(3)	C(13)-C(12)-H(12A)	119.7
C(2)-C(1)-C(6)	121.0(5)	C(12)-C(13)-C(14)	120.3(5)
C(2)-C(1)-P(1)	124.0(4)	C(12)-C(13)-H(13A)	119.8
C(6)-C(1)-P(1)	114.9(4)	C(14)-C(13)-H(13A)	119.8
C(3)-C(2)-C(1)	121.9(5)	C(13)-C(14)-C(9)	119.3(5)
C(3)-C(2)-H(2A)	119.1	C(13)-C(14)-H(14A)	120.3
C(1)-C(2)-H(2A)	119.1	C(9)-C(14)-H(14A)	120.3
C(2)-C(3)-C(4)	116.5(5)	C(20)-C(15)-C(16)	118.6(5)
C(2)-C(3)-C(26)	122.5(5)	C(20)-C(15)-P(2)	120.7(4)
C(4)-C(3)-C(26)	121.0(5)	C(16)-C(15)-P(2)	120.7(4)
C(5)-C(4)-C(3)	122.6(5)	C(15)-C(16)-C(17)	120.7(6)
C(5)-C(4)-H(4A)	118.7	C(15)-C(16)-H(16A)	119.6
C(3)-C(4)-H(4A)	118.7	C(17)-C(16)-H(16A)	119.6
C(4)-C(5)-C(6)	120.9(5)	C(18)-C(17)-C(16)	120.0(6)
C(4)-C(5)-H(5A)	119.6	C(18)-C(17)-H(17A)	120.0
C(6)-C(5)-H(5A)	119.6	C(16)-C(17)-H(17A)	120.0
N(1)-C(6)-C(1)	117.8(4)	C(17)-C(18)-C(19)	120.2(6)
N(1)-C(6)-C(5)	124.9(5)	C(17)-C(18)-H(18A)	119.9
C(1)-C(6)-C(5)	117.1(5)	C(19)-C(18)-H(18A)	119.9
C(25)-C(7)-C(8)	118.3(5)	C(18)-C(19)-C(20)	119.9(7)
C(25)-C(7)-N(1)	123.4(4)	C(18)-C(19)-H(19A)	120.0
C(8)-C(7)-N(1)	118.2(4)	C(20)-C(19)-H(19A)	120.0
C(21)-C(8)-C(7)	120.6(5)	C(15)-C(20)-C(19)	120.5(6)
C(21)-C(8)-P(2)	126.1(4)	C(15)-C(20)-H(20A)	119.8

C(19)-C(20)-H(20A)	119.8	C(29)-C(30)-H(30A)	120.8
C(22)-C(21)-C(8)	121.3(5)	C(32)-C(31)-C(30)	120.9(6)
C(22)-C(21)-H(21A)	119.4	C(32)-C(31)-H(31A)	119.5
C(8)-C(21)-H(21A)	119.4	C(30)-C(31)-H(31A)	119.5
C(21)-C(22)-C(24)	117.2(5)	C(31)-C(32)-C(27)	120.7(5)
C(21)-C(22)-C(23)	122.3(5)	C(31)-C(32)-H(32A)	119.6
C(24)-C(22)-C(23)	120.5(5)	C(27)-C(32)-H(32A)	119.6
C(22)-C(23)-H(23A)	109.5	C(38)-C(33)-C(34)	119.6(5)
C(22)-C(23)-H(23B)	109.5	C(38)-C(33)-P(1)	115.7(4)
H(23A)-C(23)-H(23B)	109.5	C(34)-C(33)-P(1)	124.7(5)
C(22)-C(23)-H(23C)	109.5	C(35)-C(34)-C(33)	119.6(6)
H(23A)-C(23)-H(23C)	109.5	C(35)-C(34)-H(34A)	120.2
H(23B)-C(23)-H(23C)	109.5	C(33)-C(34)-H(34A)	120.2
C(25)-C(24)-C(22)	122.0(5)	C(36)-C(35)-C(34)	120.8(6)
C(25)-C(24)-H(24A)	119.0	C(36)-C(35)-H(35A)	119.6
C(22)-C(24)-H(24A)	119.0	C(34)-C(35)-H(35A)	119.6
C(24)-C(25)-C(7)	120.4(5)	C(35)-C(36)-C(37)	120.4(5)
C(24)-C(25)-H(25A)	119.8	C(35)-C(36)-H(36A)	119.8
C(7)-C(25)-H(25A)	119.8	C(37)-C(36)-H(36A)	119.8
C(3)-C(26)-H(26A)	109.5	C(36)-C(37)-C(38)	119.7(7)
C(3)-C(26)-H(26B)	109.5	C(36)-C(37)-H(37A)	120.2
H(26A)-C(26)-H(26B)	109.5	C(38)-C(37)-H(37A)	120.2
C(3)-C(26)-H(26C)	109.5	C(33)-C(38)-C(37)	119.9(6)
H(26A)-C(26)-H(26C)	109.5	C(33)-C(38)-H(38A)	120.1
H(26B)-C(26)-H(26C)	109.5	C(37)-C(38)-H(38A)	120.1
C(28)-C(27)-C(32)	118.5(5)	C(44)-C(39)-C(40)	116.8(5)
C(28)-C(27)-P(1)	120.4(4)	C(44)-C(39)-Si(1)	123.1(4)
C(32)-C(27)-P(1)	120.8(4)	C(40)-C(39)-Si(1)	120.0(4)
C(29)-C(28)-C(27)	120.4(6)	C(39)-C(40)-C(41)	121.1(6)
C(29)-C(28)-H(28A)	119.8	C(39)-C(40)-H(40A)	119.5
C(27)-C(28)-H(28A)	119.8	C(41)-C(40)-H(40A)	119.5
C(28)-C(29)-C(30)	120.9(6)	C(42)-C(41)-C(40)	121.2(6)
C(28)-C(29)-H(29A)	119.5	C(42)-C(41)-H(41A)	119.4
C(30)-C(29)-H(29A)	119.5	C(40)-C(41)-H(41A)	119.4
C(31)-C(30)-C(29)	118.4(6)	C(41)-C(42)-C(43)	118.6(5)
C(31)-C(30)-H(30A)	120.8	C(41)-C(42)-H(42A)	120.7

C(43)-C(42)-H(42A)	120.7	C(56)-C(51)-Si(1)	123.2(4)
C(42)-C(43)-C(44)	120.1(5)	C(52)-C(51)-Si(1)	119.8(4)
C(42)-C(43)-H(43A)	119.9	C(53)-C(52)-C(51)	122.1(5)
C(44)-C(43)-H(43A)	119.9	C(53)-C(52)-H(52A)	118.9
C(39)-C(44)-C(43)	122.2(5)	C(51)-C(52)-H(52A)	118.9
C(39)-C(44)-H(44A)	118.9	C(52)-C(53)-C(54)	119.6(6)
C(43)-C(44)-H(44A)	118.9	C(52)-C(53)-H(53A)	120.2
C(50)-C(45)-C(46)	116.6(5)	C(54)-C(53)-H(53A)	120.2
C(50)-C(45)-Si(1)	121.6(4)	C(55)-C(54)-C(53)	120.0(6)
C(46)-C(45)-Si(1)	121.7(4)	C(55)-C(54)-H(54A)	120.0
C(47)-C(46)-C(45)	121.3(5)	C(53)-C(54)-H(54A)	120.0
C(47)-C(46)-H(46A)	119.4	C(54)-C(55)-C(56)	119.8(5)
C(45)-C(46)-H(46A)	119.4	C(54)-C(55)-H(55A)	120.1
C(48)-C(47)-C(46)	120.2(5)	C(56)-C(55)-H(55A)	120.1
C(48)-C(47)-H(47A)	119.9	C(55)-C(56)-C(51)	121.5(5)
C(46)-C(47)-H(47A)	119.9	C(55)-C(56)-H(56A)	119.3
C(49)-C(48)-C(47)	119.8(6)	C(51)-C(56)-H(56A)	119.3
C(49)-C(48)-H(48A)	120.1	C(58)-C(57)-C(62)	121.3(9)
C(47)-C(48)-H(48A)	120.1	C(58)-C(57)-F(1)	121.0(13)
C(48)-C(49)-C(50)	120.3(6)	C(62)-C(57)-F(1)	117.7(13)
C(48)-C(49)-H(49A)	119.8	C(57)-C(58)-C(59)	119.1(9)
C(50)-C(49)-H(49A)	119.8	C(60)-C(59)-C(58)	119.5(9)
C(49)-C(50)-C(45)	121.8(5)	C(59)-C(60)-C(61)	119.4(9)
C(49)-C(50)-H(50A)	119.1	C(62)-C(61)-C(60)	119.2(10)
C(45)-C(50)-H(50A)	119.1	C(57)-C(62)-C(61)	119.8(10)
C(56)-C(51)-C(52)	117.0(5)		

Symmetry transformations used to generate equivalent atoms:

Table S13. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **16**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	12(1)	14(1)	10(1)	0(1)	0(1)	2(1)
Si(1)	14(1)	20(1)	8(1)	-1(1)	0(1)	2(1)
P(1)	14(1)	16(1)	12(1)	2(1)	1(1)	5(1)
P(2)	12(1)	15(1)	12(1)	1(1)	-1(1)	2(1)
N(1)	13(2)	15(2)	10(2)	-2(2)	-2(1)	1(2)
C(1)	14(2)	18(3)	12(2)	0(2)	2(2)	-1(2)
C(2)	18(2)	13(3)	18(2)	0(2)	2(2)	2(2)
C(3)	23(2)	21(3)	14(2)	2(2)	2(2)	-3(2)
C(4)	19(2)	24(3)	14(2)	-4(2)	4(2)	1(2)
C(5)	18(2)	20(3)	15(2)	-5(2)	1(2)	-1(2)
C(6)	13(2)	20(3)	14(2)	-3(2)	-1(2)	-1(2)
C(7)	12(2)	14(3)	17(2)	-2(2)	4(2)	-3(2)
C(8)	12(2)	15(3)	16(2)	-2(2)	3(2)	2(2)
C(9)	12(2)	15(3)	13(2)	4(2)	-2(2)	1(2)
C(10)	20(2)	21(3)	13(2)	1(2)	-3(2)	4(2)
C(11)	24(2)	19(3)	20(3)	-2(2)	-5(2)	-5(2)
C(12)	16(2)	29(3)	28(3)	5(2)	-3(2)	-3(2)
C(13)	20(2)	26(3)	38(3)	-6(3)	7(2)	0(2)
C(14)	20(2)	18(3)	20(2)	-3(2)	4(2)	4(2)
C(15)	25(2)	17(3)	16(2)	1(2)	6(2)	8(2)
C(16)	42(3)	22(3)	14(2)	-2(2)	-1(2)	4(3)
C(17)	57(4)	35(4)	14(3)	3(3)	-3(3)	13(3)
C(18)	53(4)	41(4)	27(3)	19(3)	19(3)	29(3)
C(19)	39(3)	51(5)	62(5)	34(4)	17(3)	8(3)
C(20)	26(3)	47(4)	42(4)	23(3)	7(3)	3(3)
C(21)	16(2)	18(3)	23(3)	3(2)	-4(2)	3(2)
C(22)	15(2)	11(3)	32(3)	-3(2)	2(2)	-1(2)
C(23)	22(2)	20(3)	42(3)	-4(3)	-5(2)	0(2)
C(24)	15(2)	19(3)	23(3)	-2(2)	-1(2)	-3(2)
C(25)	16(2)	21(3)	18(2)	1(2)	-1(2)	-1(2)
C(26)	48(3)	28(4)	13(2)	6(2)	6(2)	5(3)

C(27)	21(2)	18(3)	17(2)	1(2)	-1(2)	3(2)
C(28)	42(3)	25(3)	20(3)	2(2)	11(2)	8(3)
C(29)	68(4)	18(3)	22(3)	-3(2)	16(3)	5(3)
C(30)	70(4)	21(3)	28(3)	2(3)	14(3)	-7(3)
C(31)	31(3)	29(3)	22(3)	2(2)	-3(2)	-1(2)
C(32)	17(2)	26(3)	14(2)	1(2)	-1(2)	6(2)
C(33)	19(2)	33(3)	10(2)	1(2)	4(2)	6(2)
C(34)	26(3)	40(4)	24(3)	9(3)	6(2)	13(3)
C(35)	25(3)	62(5)	30(3)	17(3)	7(2)	19(3)
C(36)	14(2)	87(6)	31(3)	15(4)	-1(2)	5(3)
C(37)	24(3)	59(5)	39(4)	2(3)	-1(3)	-5(3)
C(38)	23(3)	38(4)	21(3)	0(3)	3(2)	2(2)
C(39)	23(2)	14(3)	17(2)	-2(2)	2(2)	5(2)
C(40)	40(3)	35(4)	16(3)	0(3)	-4(2)	-4(3)
C(41)	55(4)	35(4)	18(3)	7(3)	-3(3)	-6(3)
C(42)	51(3)	26(3)	13(3)	2(2)	-8(2)	13(3)
C(43)	26(3)	27(3)	21(3)	-11(2)	-6(2)	12(2)
C(44)	26(2)	27(3)	13(2)	-4(2)	2(2)	7(2)
C(45)	18(2)	18(3)	15(2)	0(2)	-2(2)	-1(2)
C(46)	20(2)	32(3)	17(2)	-5(2)	5(2)	-2(2)
C(47)	26(3)	34(4)	31(3)	-5(3)	8(2)	-7(2)
C(48)	24(3)	43(4)	38(3)	-16(3)	8(2)	-12(3)
C(49)	27(3)	35(4)	30(3)	-18(3)	2(2)	-6(3)
C(50)	22(2)	30(3)	15(2)	-2(2)	3(2)	1(2)
C(51)	18(2)	32(3)	6(2)	3(2)	3(2)	1(2)
C(52)	29(3)	27(3)	17(3)	1(2)	1(2)	7(2)
C(53)	34(3)	37(4)	26(3)	-5(3)	4(2)	11(3)
C(54)	47(3)	38(4)	23(3)	2(3)	14(3)	22(3)
C(55)	29(3)	46(4)	22(3)	4(3)	7(2)	21(3)
C(56)	20(2)	32(3)	13(2)	1(2)	6(2)	3(2)

For **18**: Crystals were grown out of a vapor diffusion of pentane into toluene at -30 °C. Badly disordered toluene was treated by Platon SQUEEZE (see cif for details).

Table S14. Crystal data and structure refinement for complex **18**.

Empirical formula	C56 H48 N P2 Rh Si	
Formula weight	927.89	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/ c	
Unit cell dimensions	a = 13.1126(5) Å	α= 90°.
	b = 15.3957(6) Å	β= 98.327(2)°.
	c = 25.2088(10) Å	γ = 90°.
Volume	5035.4(3) $Å^3$	
Z	4	
Density (calculated)	1.224 g/cm^3	
Absorption coefficient	3.834 mm^{-1}	
F(000)	1920	
Crystal size	0.18 x 0.12 x 0.10 mm^3	
Crystal color/habit	orange block	
Theta range for data collection	3.37 to 68.08°.	
Index ranges	$-15 \leq h \leq 15$, $-18 \leq k \leq 18$, $-29 \leq l \leq 27$	
Reflections collected	25446	
Independent reflections	8114 [R(int) = 0.0487]	
Completeness to theta = 68.08°	88.1 %	
Absorption correction	Analytical	
Max. and min. transmission	0.7004 and 0.5453	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8114 / 0 / 555	
Goodness-of-fit on F^2	0.969	
Final R indices [I>2sigma(I)]	R1 = 0.0348, wR2 = 0.0773	
R indices (all data)	R1 = 0.0511, wR2 = 0.0823	
Largest diff. peak and hole	0.481 and -0.292 e.$Å^{-3}$	

Table S15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **18**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(1)	6706(1)	947(1)	1552(1)	18(1)
Si(1)	7613(1)	988(1)	830(1)	20(1)
P(1)	7609(1)	-110(1)	2054(1)	20(1)
P(2)	5549(1)	2056(1)	1323(1)	19(1)
N(1)	6675(2)	1496(2)	2298(1)	18(1)
C(1)	6861(2)	1288(2)	149(1)	24(1)
C(2)	7333(3)	1760(2)	-221(2)	41(1)
C(3)	6826(4)	1936(3)	-728(2)	51(1)
C(4)	5834(3)	1646(2)	-882(2)	41(1)
C(5)	5350(3)	1185(2)	-525(1)	36(1)
C(6)	5862(2)	1001(2)	-18(1)	30(1)
C(7)	8334(2)	-26(2)	677(1)	24(1)
C(8)	9365(2)	-191(2)	898(1)	29(1)
C(9)	9856(3)	-960(2)	782(2)	39(1)
C(10)	9336(3)	-1575(2)	447(2)	40(1)
C(11)	8323(3)	-1424(2)	220(2)	36(1)
C(12)	7841(3)	-663(2)	331(1)	29(1)
C(13)	8620(2)	1875(2)	995(1)	25(1)
C(14)	9492(2)	1915(2)	736(1)	31(1)
C(15)	10192(3)	2591(2)	829(2)	38(1)
C(16)	10047(3)	3234(3)	1189(2)	43(1)
C(17)	9207(3)	3203(3)	1458(2)	41(1)
C(18)	8503(3)	2526(2)	1366(1)	33(1)
C(19)	5872(2)	2780(2)	1892(1)	20(1)
C(20)	6844(2)	973(2)	2757(1)	22(1)
C(21)	7287(2)	149(2)	2713(1)	21(1)
C(22)	7471(2)	-405(2)	3152(1)	26(1)
C(23)	7195(3)	-194(2)	3646(1)	28(1)
C(24)	7404(3)	-786(2)	4125(2)	42(1)
C(25)	6710(3)	605(2)	3680(1)	29(1)

C(26)	6541(2)	1175(2)	3255(1)	24(1)
C(27)	7237(2)	-1236(2)	1921(1)	23(1)
C(28)	7685(3)	-1706(2)	1543(2)	34(1)
C(29)	7360(3)	-2545(2)	1414(2)	44(1)
C(30)	6580(3)	-2922(2)	1657(2)	43(1)
C(31)	6134(3)	-2454(2)	2020(2)	37(1)
C(32)	6449(2)	-1620(2)	2153(1)	28(1)
C(33)	9012(2)	-78(2)	2169(1)	26(1)
C(34)	9442(3)	756(2)	2208(1)	36(1)
C(35)	10508(3)	859(3)	2304(2)	50(1)
C(36)	11139(3)	137(3)	2350(2)	54(1)
C(37)	10718(3)	-682(3)	2310(2)	53(1)
C(38)	9656(3)	-793(3)	2227(2)	39(1)
C(39)	6453(2)	2383(2)	2338(1)	22(1)
C(40)	6830(2)	2912(2)	2770(1)	24(1)
C(41)	6576(2)	3782(2)	2773(1)	26(1)
C(42)	5958(2)	4177(2)	2347(1)	26(1)
C(43)	5617(2)	3667(2)	1903(1)	24(1)
C(44)	5667(3)	5116(2)	2379(2)	34(1)
C(45)	4261(2)	1644(2)	1358(1)	20(1)
C(46)	3968(2)	840(2)	1129(1)	23(1)
C(47)	2970(2)	548(2)	1102(1)	27(1)
C(48)	2251(2)	1045(2)	1312(1)	31(1)
C(49)	2534(2)	1826(2)	1561(2)	32(1)
C(50)	3527(2)	2136(2)	1577(1)	26(1)
C(51)	5339(2)	2759(2)	736(1)	24(1)
C(52)	4457(3)	2699(2)	364(1)	36(1)
C(53)	4318(3)	3234(3)	-81(2)	44(1)
C(54)	5052(3)	3826(2)	-167(2)	42(1)
C(55)	5936(3)	3881(3)	189(2)	53(1)
C(56)	6091(3)	3357(2)	640(2)	45(1)

Table S16. Bond lengths [Å] and angles [°] for **18**.

Rh(1)-N(1)	2.069(2)	C(10)-C(11)	1.387(5)
Rh(1)-P(1)	2.2844(8)	C(10)-H(10A)	0.9500
Rh(1)-P(2)	2.3017(8)	C(11)-C(12)	1.379(4)
Rh(1)-Si(1)	2.3148(8)	C(11)-H(11A)	0.9500
Rh(1)-H(1)	1.49(3)	C(12)-H(12A)	0.9500
Si(1)-C(7)	1.893(3)	C(13)-C(18)	1.394(4)
Si(1)-C(13)	1.903(3)	C(13)-C(14)	1.397(4)
Si(1)-C(1)	1.908(3)	C(14)-C(15)	1.385(5)
Si(1)-H(1)	1.83(3)	C(14)-H(14A)	0.9500
P(1)-C(21)	1.818(3)	C(15)-C(16)	1.374(5)
P(1)-C(27)	1.819(3)	C(15)-H(15A)	0.9500
P(1)-C(33)	1.821(3)	C(16)-C(17)	1.375(5)
P(2)-C(19)	1.817(3)	C(16)-H(16A)	0.9500
P(2)-C(45)	1.819(3)	C(17)-C(18)	1.391(5)
P(2)-C(51)	1.820(3)	C(17)-H(17A)	0.9500
N(1)-C(20)	1.401(4)	C(18)-H(18A)	0.9500
N(1)-C(39)	1.402(4)	C(19)-C(39)	1.405(4)
C(1)-C(6)	1.389(4)	C(19)-C(43)	1.407(4)
C(1)-C(2)	1.395(5)	C(20)-C(26)	1.404(4)
C(2)-C(3)	1.379(5)	C(20)-C(21)	1.407(4)
C(2)-H(2A)	0.9500	C(21)-C(22)	1.389(4)
C(3)-C(4)	1.377(6)	C(22)-C(23)	1.384(4)
C(3)-H(3A)	0.9500	C(22)-H(22A)	0.9500
C(4)-C(5)	1.371(5)	C(23)-C(25)	1.394(4)
C(4)-H(4A)	0.9500	C(23)-C(24)	1.507(5)
C(5)-C(6)	1.384(5)	C(24)-H(24A)	0.9800
C(5)-H(5A)	0.9500	C(24)-H(24B)	0.9800
C(6)-H(6A)	0.9500	C(24)-H(24C)	0.9800
C(7)-C(12)	1.406(5)	C(25)-C(26)	1.378(5)
C(7)-C(8)	1.409(4)	C(25)-H(25A)	0.9500
C(8)-C(9)	1.399(5)	C(26)-H(26A)	0.9500
C(8)-H(8A)	0.9500	C(27)-C(32)	1.391(4)
C(9)-C(10)	1.382(5)	C(27)-C(28)	1.393(4)
C(9)-H(9A)	0.9500	C(28)-C(29)	1.384(5)

C(28)-H(28A)	0.9500	C(48)-C(49)	1.383(5)
C(29)-C(30)	1.393(5)	C(48)-H(48A)	0.9500
C(29)-H(29A)	0.9500	C(49)-C(50)	1.382(4)
C(30)-C(31)	1.362(5)	C(49)-H(49A)	0.9500
C(30)-H(30A)	0.9500	C(50)-H(50A)	0.9500
C(31)-C(32)	1.376(5)	C(51)-C(52)	1.382(5)
C(31)-H(31A)	0.9500	C(51)-C(56)	1.396(4)
C(32)-H(32A)	0.9500	C(52)-C(53)	1.382(5)
C(33)-C(38)	1.382(5)	C(52)-H(52A)	0.9500
C(33)-C(34)	1.400(5)	C(53)-C(54)	1.365(5)
C(34)-C(35)	1.392(5)	C(53)-H(53A)	0.9500
C(34)-H(34A)	0.9500	C(54)-C(55)	1.361(6)
C(35)-C(36)	1.382(6)	C(54)-H(54A)	0.9500
C(35)-H(35A)	0.9500	C(55)-C(56)	1.384(5)
C(36)-C(37)	1.375(6)	C(55)-H(55A)	0.9500
C(36)-H(36A)	0.9500	C(56)-H(56A)	0.9500
C(37)-C(38)	1.388(5)		
C(37)-H(37A)	0.9500	N(1)-Rh(1)-P(1)	82.22(7)
C(38)-H(38A)	0.9500	N(1)-Rh(1)-P(2)	79.98(7)
C(39)-C(40)	1.391(4)	P(1)-Rh(1)-P(2)	159.68(3)
C(40)-C(41)	1.380(4)	N(1)-Rh(1)-Si(1)	141.65(7)
C(40)-H(40A)	0.9500	P(1)-Rh(1)-Si(1)	99.82(3)
C(41)-C(42)	1.389(5)	P(2)-Rh(1)-Si(1)	100.22(3)
C(41)-H(41A)	0.9500	N(1)-Rh(1)-H(1)	166.1(11)
C(42)-C(43)	1.386(5)	P(1)-Rh(1)-H(1)	94.1(12)
C(42)-C(44)	1.500(4)	P(2)-Rh(1)-H(1)	100.9(12)
C(43)-H(43A)	0.9500	Si(1)-Rh(1)-H(1)	52.2(11)
C(44)-H(44A)	0.9800	C(7)-Si(1)-C(13)	106.55(14)
C(44)-H(44B)	0.9800	C(7)-Si(1)-C(1)	102.98(14)
C(44)-H(44C)	0.9800	C(13)-Si(1)-C(1)	105.95(14)
C(45)-C(46)	1.396(4)	C(7)-Si(1)-Rh(1)	117.79(10)
C(45)-C(50)	1.399(4)	C(13)-Si(1)-Rh(1)	105.49(10)
C(46)-C(47)	1.376(4)	C(1)-Si(1)-Rh(1)	117.14(10)
C(46)-H(46A)	0.9500	C(7)-Si(1)-H(1)	95.3(9)
C(47)-C(48)	1.378(4)	C(13)-Si(1)-H(1)	145.5(9)
C(47)-H(47A)	0.9500	C(1)-Si(1)-H(1)	94.3(10)

Rh(1)-Si(1)-H(1)	40.0(9)	C(8)-C(7)-Si(1)	123.1(3)
C(21)-P(1)-C(27)	106.56(14)	C(9)-C(8)-C(7)	120.9(3)
C(21)-P(1)-C(33)	102.14(14)	C(9)-C(8)-H(8A)	119.5
C(27)-P(1)-C(33)	107.08(15)	C(7)-C(8)-H(8A)	119.5
C(21)-P(1)-Rh(1)	100.37(10)	C(10)-C(9)-C(8)	120.4(3)
C(27)-P(1)-Rh(1)	118.27(11)	C(10)-C(9)-H(9A)	119.8
C(33)-P(1)-Rh(1)	119.99(11)	C(8)-C(9)-H(9A)	119.8
C(19)-P(2)-C(45)	106.63(13)	C(9)-C(10)-C(11)	119.8(3)
C(19)-P(2)-C(51)	105.54(14)	C(9)-C(10)-H(10A)	120.1
C(45)-P(2)-C(51)	102.42(14)	C(11)-C(10)-H(10A)	120.1
C(19)-P(2)-Rh(1)	100.78(10)	C(12)-C(11)-C(10)	119.8(4)
C(45)-P(2)-Rh(1)	108.14(10)	C(12)-C(11)-H(11A)	120.1
C(51)-P(2)-Rh(1)	131.42(10)	C(10)-C(11)-H(11A)	120.1
C(20)-N(1)-C(39)	120.7(2)	C(11)-C(12)-C(7)	122.4(3)
C(20)-N(1)-Rh(1)	119.64(19)	C(11)-C(12)-H(12A)	118.8
C(39)-N(1)-Rh(1)	119.7(2)	C(7)-C(12)-H(12A)	118.8
C(6)-C(1)-C(2)	116.9(3)	C(18)-C(13)-C(14)	117.3(3)
C(6)-C(1)-Si(1)	122.6(2)	C(18)-C(13)-Si(1)	121.4(2)
C(2)-C(1)-Si(1)	120.4(3)	C(14)-C(13)-Si(1)	121.3(3)
C(3)-C(2)-C(1)	121.4(4)	C(15)-C(14)-C(13)	121.5(3)
C(3)-C(2)-H(2A)	119.3	C(15)-C(14)-H(14A)	119.2
C(1)-C(2)-H(2A)	119.3	C(13)-C(14)-H(14A)	119.2
C(4)-C(3)-C(2)	120.4(4)	C(16)-C(15)-C(14)	120.0(3)
C(4)-C(3)-H(3A)	119.8	C(16)-C(15)-H(15A)	120.0
C(2)-C(3)-H(3A)	119.8	C(14)-C(15)-H(15A)	120.0
C(5)-C(4)-C(3)	119.4(4)	C(15)-C(16)-C(17)	120.0(3)
C(5)-C(4)-H(4A)	120.3	C(15)-C(16)-H(16A)	120.0
C(3)-C(4)-H(4A)	120.3	C(17)-C(16)-H(16A)	120.0
C(4)-C(5)-C(6)	120.1(4)	C(16)-C(17)-C(18)	120.2(3)
C(4)-C(5)-H(5A)	119.9	C(16)-C(17)-H(17A)	119.9
C(6)-C(5)-H(5A)	119.9	C(18)-C(17)-H(17A)	119.9
C(5)-C(6)-C(1)	121.7(3)	C(17)-C(18)-C(13)	121.1(3)
C(5)-C(6)-H(6A)	119.1	C(17)-C(18)-H(18A)	119.5
C(1)-C(6)-H(6A)	119.1	C(13)-C(18)-H(18A)	119.5
C(12)-C(7)-C(8)	116.7(3)	C(39)-C(19)-C(43)	120.6(3)
C(12)-C(7)-Si(1)	120.2(2)	C(39)-C(19)-P(2)	113.8(2)

C(43)-C(19)-P(2)	125.6(2)	C(29)-C(30)-H(30A)	120.3
N(1)-C(20)-C(26)	125.4(3)	C(30)-C(31)-C(32)	121.0(3)
N(1)-C(20)-C(21)	118.1(3)	C(30)-C(31)-H(31A)	119.5
C(26)-C(20)-C(21)	116.3(3)	C(32)-C(31)-H(31A)	119.5
C(22)-C(21)-C(20)	121.1(3)	C(31)-C(32)-C(27)	120.6(3)
C(22)-C(21)-P(1)	123.9(2)	C(31)-C(32)-H(32A)	119.7
C(20)-C(21)-P(1)	115.0(2)	C(27)-C(32)-H(32A)	119.7
C(23)-C(22)-C(21)	122.3(3)	C(38)-C(33)-C(34)	119.3(3)
C(23)-C(22)-H(22A)	118.9	C(38)-C(33)-P(1)	125.6(3)
C(21)-C(22)-H(22A)	118.9	C(34)-C(33)-P(1)	115.1(2)
C(22)-C(23)-C(25)	116.4(3)	C(35)-C(34)-C(33)	120.0(4)
C(22)-C(23)-C(24)	122.6(3)	C(35)-C(34)-H(34A)	120.0
C(25)-C(23)-C(24)	121.0(3)	C(33)-C(34)-H(34A)	120.0
C(23)-C(24)-H(24A)	109.5	C(36)-C(35)-C(34)	119.8(4)
C(23)-C(24)-H(24B)	109.5	C(36)-C(35)-H(35A)	120.1
H(24A)-C(24)-H(24B)	109.5	C(34)-C(35)-H(35A)	120.1
C(23)-C(24)-H(24C)	109.5	C(37)-C(36)-C(35)	120.2(4)
H(24A)-C(24)-H(24C)	109.5	C(37)-C(36)-H(36A)	119.9
H(24B)-C(24)-H(24C)	109.5	C(35)-C(36)-H(36A)	119.9
C(26)-C(25)-C(23)	122.4(3)	C(36)-C(37)-C(38)	120.5(4)
C(26)-C(25)-H(25A)	118.8	C(36)-C(37)-H(37A)	119.8
C(23)-C(25)-H(25A)	118.8	C(38)-C(37)-H(37A)	119.8
C(25)-C(26)-C(20)	121.3(3)	C(33)-C(38)-C(37)	120.1(4)
C(25)-C(26)-H(26A)	119.3	C(33)-C(38)-H(38A)	119.9
C(20)-C(26)-H(26A)	119.3	C(37)-C(38)-H(38A)	119.9
C(32)-C(27)-C(28)	118.7(3)	C(40)-C(39)-N(1)	124.9(3)
C(32)-C(27)-P(1)	121.6(2)	C(40)-C(39)-C(19)	117.5(3)
C(28)-C(27)-P(1)	119.5(2)	N(1)-C(39)-C(19)	117.4(3)
C(29)-C(28)-C(27)	120.0(3)	C(41)-C(40)-C(39)	120.9(3)
C(29)-C(28)-H(28A)	120.0	C(41)-C(40)-H(40A)	119.5
C(27)-C(28)-H(28A)	120.0	C(39)-C(40)-H(40A)	119.5
C(28)-C(29)-C(30)	120.4(3)	C(40)-C(41)-C(42)	122.3(3)
C(28)-C(29)-H(29A)	119.8	C(40)-C(41)-H(41A)	118.8
C(30)-C(29)-H(29A)	119.8	C(42)-C(41)-H(41A)	118.8
C(31)-C(30)-C(29)	119.3(3)	C(43)-C(42)-C(41)	117.3(3)
C(31)-C(30)-H(30A)	120.3	C(43)-C(42)-C(44)	122.4(3)

C(41)-C(42)-C(44)	120.3(3)	C(50)-C(49)-H(49A)	119.9
C(42)-C(43)-C(19)	121.2(3)	C(48)-C(49)-H(49A)	119.9
C(42)-C(43)-H(43A)	119.4	C(49)-C(50)-C(45)	120.0(3)
C(19)-C(43)-H(43A)	119.4	C(49)-C(50)-H(50A)	120.0
C(42)-C(44)-H(44A)	109.5	C(45)-C(50)-H(50A)	120.0
C(42)-C(44)-H(44B)	109.5	C(52)-C(51)-C(56)	118.0(3)
H(44A)-C(44)-H(44B)	109.5	C(52)-C(51)-P(2)	121.7(2)
C(42)-C(44)-H(44C)	109.5	C(56)-C(51)-P(2)	120.3(3)
H(44A)-C(44)-H(44C)	109.5	C(53)-C(52)-C(51)	120.6(3)
H(44B)-C(44)-H(44C)	109.5	C(53)-C(52)-H(52A)	119.7
C(46)-C(45)-C(50)	118.7(3)	C(51)-C(52)-H(52A)	119.7
C(46)-C(45)-P(2)	119.4(2)	C(54)-C(53)-C(52)	120.9(4)
C(50)-C(45)-P(2)	121.8(2)	C(54)-C(53)-H(53A)	119.6
C(47)-C(46)-C(45)	120.9(3)	C(52)-C(53)-H(53A)	119.6
C(47)-C(46)-H(46A)	119.6	C(55)-C(54)-C(53)	119.3(4)
C(45)-C(46)-H(46A)	119.6	C(55)-C(54)-H(54A)	120.3
C(46)-C(47)-C(48)	119.9(3)	C(53)-C(54)-H(54A)	120.3
C(46)-C(47)-H(47A)	120.1	C(54)-C(55)-C(56)	121.0(4)
C(48)-C(47)-H(47A)	120.1	C(54)-C(55)-H(55A)	119.5
C(47)-C(48)-C(49)	120.2(3)	C(56)-C(55)-H(55A)	119.5
C(47)-C(48)-H(48A)	119.9	C(55)-C(56)-C(51)	120.2(4)
C(49)-C(48)-H(48A)	119.9	C(55)-C(56)-H(56A)	119.9
C(50)-C(49)-C(48)	120.3(3)	C(51)-C(56)-H(56A)	119.9

Symmetry transformations used to generate equivalent atoms:

Table S17. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **18**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh(1)	16(1)	22(1)	16(1)	0(1)	5(1)	2(1)
Si(1)	20(1)	26(1)	16(1)	-1(1)	5(1)	0(1)
P(1)	18(1)	25(1)	17(1)	2(1)	6(1)	4(1)
P(2)	18(1)	21(1)	19(1)	0(1)	4(1)	1(1)
N(1)	18(1)	24(1)	14(1)	-4(1)	4(1)	2(1)
C(1)	29(2)	26(1)	18(2)	-2(1)	2(1)	4(1)
C(2)	53(2)	43(2)	25(2)	6(2)	0(2)	-11(2)
C(3)	75(3)	50(2)	27(2)	12(2)	1(2)	-7(2)
C(4)	61(3)	42(2)	18(2)	1(2)	-3(2)	18(2)
C(5)	34(2)	46(2)	26(2)	-11(2)	-4(2)	13(2)
C(6)	30(2)	37(2)	23(2)	-5(2)	4(1)	8(2)
C(7)	25(2)	31(2)	17(2)	4(2)	10(1)	3(1)
C(8)	25(2)	43(2)	22(2)	0(2)	8(1)	2(2)
C(9)	30(2)	50(2)	38(2)	8(2)	13(2)	17(2)
C(10)	51(2)	43(2)	31(2)	-1(2)	19(2)	19(2)
C(11)	38(2)	41(2)	32(2)	-5(2)	9(2)	11(2)
C(12)	28(2)	36(2)	25(2)	-1(2)	8(1)	4(2)
C(13)	22(2)	35(2)	19(2)	2(2)	4(1)	-1(2)
C(14)	29(2)	37(2)	30(2)	0(2)	10(1)	-2(2)
C(15)	30(2)	47(2)	40(2)	-4(2)	15(2)	-10(2)
C(16)	31(2)	53(2)	47(3)	-13(2)	7(2)	-18(2)
C(17)	39(2)	47(2)	38(2)	-17(2)	7(2)	-12(2)
C(18)	28(2)	42(2)	31(2)	-7(2)	9(2)	-4(2)
C(19)	17(1)	26(1)	18(2)	-1(1)	6(1)	0(1)
C(20)	16(1)	30(2)	19(2)	-4(2)	4(1)	-4(1)
C(21)	17(1)	26(1)	22(2)	-2(1)	6(1)	0(1)
C(22)	26(2)	29(2)	23(2)	-3(2)	5(1)	-1(1)
C(23)	35(2)	31(2)	20(2)	2(2)	8(1)	-4(2)
C(24)	63(3)	40(2)	25(2)	8(2)	15(2)	4(2)
C(25)	32(2)	37(2)	20(2)	-8(2)	11(1)	-3(2)
C(26)	26(2)	26(2)	22(2)	-5(1)	6(1)	-3(1)

C(27)	27(2)	25(1)	18(2)	3(1)	4(1)	4(1)
C(28)	45(2)	30(2)	31(2)	2(2)	16(2)	0(2)
C(29)	66(3)	34(2)	35(2)	-4(2)	16(2)	2(2)
C(30)	62(3)	31(2)	35(2)	-2(2)	8(2)	-10(2)
C(31)	39(2)	41(2)	30(2)	4(2)	2(2)	-11(2)
C(32)	26(2)	36(2)	21(2)	1(2)	1(1)	4(2)
C(33)	20(2)	45(2)	16(2)	4(2)	7(1)	4(2)
C(34)	28(2)	52(2)	28(2)	3(2)	6(1)	1(2)
C(35)	32(2)	77(3)	42(2)	-1(2)	5(2)	-16(2)
C(36)	18(2)	98(4)	48(3)	16(3)	5(2)	4(2)
C(37)	32(2)	84(3)	43(3)	20(2)	11(2)	23(2)
C(38)	29(2)	56(2)	36(2)	12(2)	11(2)	15(2)
C(39)	16(1)	28(2)	23(2)	-4(2)	8(1)	-2(1)
C(40)	20(2)	30(2)	23(2)	-2(2)	3(1)	-4(1)
C(41)	20(2)	30(2)	28(2)	-10(2)	6(1)	-7(1)
C(42)	21(2)	26(2)	33(2)	-7(2)	9(1)	-3(1)
C(43)	19(2)	25(1)	29(2)	-2(2)	6(1)	-1(1)
C(44)	28(2)	24(2)	47(2)	-9(2)	1(2)	2(2)
C(45)	19(1)	26(1)	17(2)	5(1)	5(1)	0(1)
C(46)	24(2)	24(1)	22(2)	2(1)	4(1)	3(1)
C(47)	29(2)	31(2)	21(2)	2(2)	0(1)	-5(2)
C(48)	20(2)	37(2)	35(2)	9(2)	2(1)	-4(2)
C(49)	23(2)	32(2)	42(2)	-2(2)	10(2)	1(2)
C(50)	25(2)	29(2)	24(2)	-2(2)	6(1)	3(1)
C(51)	29(2)	23(1)	22(2)	-2(1)	11(1)	4(1)
C(52)	46(2)	42(2)	18(2)	7(2)	2(2)	-2(2)
C(53)	48(2)	56(2)	28(2)	7(2)	1(2)	10(2)
C(54)	58(3)	41(2)	31(2)	13(2)	15(2)	19(2)
C(55)	58(3)	50(2)	53(3)	28(2)	20(2)	-2(2)
C(56)	34(2)	49(2)	51(3)	18(2)	5(2)	-5(2)