Table S1. Crystallographic Experimental Details for $[RhIr(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**2**)

A. Crystal Data	
formula	$C_{54}H_{47}F_3IrO_5P_4RhS$
formula weight	1283.97
crystal dimensions (mm)	0.62 × 0.42 × 0.24
crystal system	monoclinic
space group	$P2_1/n$ (a non-standard setting of $P2_1/c$ [No. 14])
unit cell parameters[a]	
a (Å)	13.8579 (13)
b (Å)	15.6368 (13)
c (Å)	23.6710 (14)
β (deg)	96.525 (6)
V (Å^3)	5096.1 (7)
Z	4
ρ_{calcd} (g cm^{-3})	1.673
μ (mm^{-1})	9.661
B. Data Collection and Refinement Conditions	
diffractometer	Siemens P4/RA[b]
radiation (λ [Å])	graphite-monochromated Cu Kα (1.54178)
temperature (°C)	–60
scan type	θ–2θ
data collection 2θ limit (deg)	115.0
total data collected	7133 ($0 \le h \le 15$, $0 \le k \le 17$, $-23 \le l \le 23$)
independent reflections	6817
number of observations (*NO*)	6119 ($F_o^2 \ge 2\sigma(F_o^2)$)
structure solution method	direct methods/fragment search (*DIRDIF–96*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–93*[d])
absorption correction method	semiempirical (ψ scans)
range of transmission factors	0.9595–0.1741
data/restraints/parameters	6815 [$F_o^2 \ge -3\sigma(F_o^2)$] / 0 / 630
goodness-of-fit (S)[e]	1.087 [$F_o^2 \ge -3\sigma(F_o^2)$]
final R indices[f]	
$F_o^2 > 2\sigma(F_o^2)$	$\boldsymbol{R_1 = 0.0726}$, $wR_2 = 0.1910$
all data	$R_1 = 0.0781$, $\boldsymbol{wR_2 = 0.1980}$
largest difference peak and hole	2.474 and –3.664 e Å^{-3}

[a]Obtained from least-squares refinement of 33 reflections with $57.0° < 2\theta < 58.0°$.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Siemens.

(continued)

Table S1. (continued)

[c]Beurskens, P. T.; Beurskens, G.; Bosman, W.P.; de Gelder, R.; Garcia Granda, S.; Gould, R. O.; Israel, R; Smits, J M.M. (1996). The *DIRDIF-96* program system. Crystallography Laboratory, University of Nijmegen, The Netherlands.

[d]Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections except for 2 having $F_o^2 < -3\sigma(F_o^2)$. Weighted R-factors wR_2 and all goodnesses of fit S are based on F_o^2; conventional R-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. R-factors based on F_o^2 are statistically about twice as large as those based on F_o, and R-factors based on ALL data will be even larger.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.1404P)^2 + 22.2339P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Compound **2**

(a) 'inner-core' atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
Ir/Rh'	0.39568(4)	-0.25875(3)	0.01274(2)	0.0233(2)*
Rh/Ir'	0.24145(4)	-0.37255(3)	-0.02171(2)	0.0261(2)*
P(1)	0.4183(2)	-0.32061(15)	0.10219(10)	0.0231(5)*
P(2)	0.2582(2)	-0.4435(2)	0.06447(10)	0.0241(5)*
P(3)	0.3735(2)	-0.18216(15)	-0.07162(10)	0.0252(6)*
P(4)	0.2009(2)	-0.2944(2)	-0.10378(10)	0.0266(6)*
O(1)	0.4447(5)	-0.4230(5)	-0.0414(3)	0.040(2)*
O(3)	0.0773(16)	-0.4833(14)	-0.0578(9)	0.096(8)*
O(3')	0.5396(21)	-0.1287(13)	0.0523(12)	0.085(8)*
C(1)	0.4058(14)	-0.3729(11)	-0.0232(7)	0.016(4)
C(2)	0.4745(18)	-0.1524(18)	0.0513(11)	0.042(7)
C(3)	0.1375(17)	-0.4419(14)	-0.0449(9)	0.031(5)
C(1')	0.3724(23)	-0.3928(19)	-0.0309(12)	0.040(7)
C(2')	0.1068(20)	-0.4253(17)	-0.0367(11)	0.031(6)
C(3')	0.4821(17)	-0.1783(17)	0.0384(11)	0.026(6)
C(4)	0.3792(6)	-0.4328(6)	0.1033(4)	0.024(2)*
C(5)	0.3053(7)	-0.2411(6)	-0.1293(4)	0.029(2)*

(b) dppm phenyl carbons

Atom	*x*	*y*	*z*	U_{eq}, Å^2
C(11)	0.5456(7)	-0.3245(6)	0.1320(4)	0.026(2)*
C(12)	0.6071(8)	-0.3862(7)	0.1133(5)	0.041(3)*
C(13)	0.7041(8)	-0.3851(8)	0.1314(6)	0.046(3)*
C(14)	0.7410(8)	-0.3241(8)	0.1692(6)	0.048(3)*
C(15)	0.6829(8)	-0.2640(8)	0.1890(5)	0.046(3)*
C(16)	0.5858(8)	-0.2625(7)	0.1699(5)	0.036(3)*
C(21)	0.3587(6)	-0.2687(6)	0.1572(4)	0.022(2)*
C(22)	0.3731(8)	-0.2949(7)	0.2128(4)	0.037(3)*
C(23)	0.3273(8)	-0.2532(8)	0.2551(5)	0.042(3)*
C(24)	0.2692(9)	-0.1845(8)	0.2407(6)	0.052(3)*
C(25)	0.2505(9)	-0.1573(8)	0.1855(6)	0.057(4)*
C(26)	0.2962(8)	-0.1988(7)	0.1431(5)	0.039(3)*
C(31)	0.1730(7)	-0.4125(6)	0.1141(4)	0.030(2)*
C(32)	0.0911(9)	-0.3664(7)	0.0952(6)	0.052(3)*
C(33)	0.0221(12)	-0.3471(10)	0.1334(8)	0.085(6)*
C(34)	0.0402(12)	-0.3715(8)	0.1880(7)	0.067(5)*
C(35)	0.1198(11)	-0.4159(10)	0.2070(6)	0.063(4)*
C(36)	0.1899(8)	-0.4377(8)	0.1696(5)	0.046(3)*

Table S2. (continued)

Atom	*x*	*y*	*z*	U_{eq}, Å^2
C(41)	0.2410(7)	-0.5582(6)	0.0569(4)	0.027(2)*
C(42)	0.3020(8)	-0.6047(7)	0.0265(5)	0.041(3)*
C(43)	0.2848(11)	-0.6904(8)	0.0147(7)	0.070(5)*
C(44)	0.2070(11)	-0.7298(8)	0.0339(6)	0.057(4)*
C(45)	0.1464(11)	-0.6867(8)	0.0658(6)	0.063(4)*
C(46)	0.1630(8)	-0.5996(7)	0.0770(5)	0.044(3)*
C(51)	0.4869(7)	-0.1556(6)	-0.1006(4)	0.029(2)*
C(52)	0.5386(9)	-0.2200(8)	-0.1240(6)	0.048(3)*
C(53)	0.6269(9)	-0.2021(10)	-0.1425(6)	0.069(4)*
C(54)	0.6659(9)	-0.1194(9)	-0.1403(5)	0.055(4)*
C(55)	0.6131(9)	-0.0561(9)	-0.1169(5)	0.056(4)*
C(56)	0.5235(9)	-0.0735(7)	-0.0960(5)	0.043(3)*
C(61)	0.3111(7)	-0.0796(6)	-0.0700(4)	0.027(2)*
C(62)	0.2830(9)	-0.0488(7)	-0.0213(5)	0.041(3)*
C(63)	0.2405(10)	0.0324(8)	-0.0205(5)	0.059(4)*
C(64)	0.2177(10)	0.0766(7)	-0.0690(5)	0.053(3)*
C(65)	0.2449(11)	0.0451(7)	-0.1187(6)	0.055(3)*
C(66)	0.2908(10)	-0.0327(7)	-0.1196(5)	0.051(3)*
C(71)	0.1133(8)	-0.2100(6)	-0.0958(4)	0.034(2)*
C(72)	0.0759(9)	-0.1595(8)	-0.1406(5)	0.046(3)*
C(73)	0.0084(9)	-0.0958(8)	-0.1328(7)	0.061(4)*
C(74)	-0.0181(9)	-0.0828(8)	-0.0779(6)	0.056(4)*
C(75)	0.0215(9)	-0.1306(8)	-0.0324(6)	0.052(3)*
C(76)	0.0855(8)	-0.1947(7)	-0.0418(5)	0.042(3)*
C(81)	0.1509(7)	-0.3562(6)	-0.1647(4)	0.026(2)*
C(82)	0.0538(8)	-0.3557(7)	-0.1866(5)	0.037(3)*
C(83)	0.0207(8)	-0.4067(7)	-0.2320(5)	0.042(3)*
C(84)	0.0824(9)	-0.4612(7)	-0.2562(5)	0.044(3)*
C(85)	0.1785(9)	-0.4644(7)	-0.2343(4)	0.039(3)*
C(86)	0.2144(7)	-0.4130(6)	-0.1891(4)	0.032(2)*

(c) triflate ion atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
S	0.0172(2)	0.0459(2)	-0.27153(12)	0.0416(7)*
F(91)	0.1110(6)	0.1775(5)	-0.2253(4)	0.082(3)*
F(92)	-0.0420(6)	0.1962(5)	-0.2443(3)	0.069(2)*
F(93)	0.0118(7)	0.1209(5)	-0.1729(3)	0.071(2)*
O(91)	-0.0797(6)	0.0156(6)	-0.2681(4)	0.061(2)*
O(92)	0.0939(7)	-0.0084(6)	-0.2458(4)	0.064(3)*

Table S2. (continued)

Atom	*x*	*y*	*z*	U_{eq}, Å^2
O(93)	0.0323(7)	0.0805(6)	-0.3262(4)	0.057(2)*
C(91)	0.0242(9)	0.1397(8)	-0.2262(6)	0.049(3)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$. Primed and unprimed atoms are related by a 55:45 disorder – see Figure 1 for explanation.

Table S3. Selected Interatomic Distances for Compound **2**

(a) involving 'inner-core' atoms

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ir	Rh	2.8290(7)	Rh'	C(1')	2.34(3)
Ir/Rh'	P(1)	2.317(2)	Rh'	C(3')	1.79(2)
Ir/Rh'	P(3)	2.319(2)	P(1)	C(4)	1.837(9)
Ir	C(1)	1.99(2)	P(2)	C(4)	1.826(9)
Ir	C(2)	2.14(3)	P(3)	C(5)	1.820(10)
Ir'	C(1')	1.88(3)	P(4)	C(5)	1.830(9)
Ir'	C(2')	2.03(3)	O(1)	C(1)	1.07(2)
Rh/Ir'	P(2)	2.311(2)	O(1)	C(1')	1.16(3)
Rh/Ir'	P(4)	2.310(3)	O(3)	C(3)	1.07(3)
Rh	C(1)	2.28(2)	O(3')	C(3')	1.13(3)
Rh	C(3)	1.84(2)			

(b) involving dppm phenyl carbons

Atom1	Atom2	Distance	Atom1	Atom2	Distance
P(1)	C(11)	1.826(10)	C(35)	C(36)	1.43(2)
P(1)	C(21)	1.811(9)	C(41)	C(42)	1.379(14)
P(2)	C(31)	1.824(9)	C(41)	C(46)	1.390(14)
P(2)	C(41)	1.815(10)	C(42)	C(43)	1.39(2)
P(3)	C(51)	1.831(10)	C(43)	C(44)	1.36(2)
P(3)	C(61)	1.825(10)	C(44)	C(45)	1.37(2)
P(4)	C(71)	1.819(10)	C(45)	C(46)	1.40(2)
P(4)	C(81)	1.808(10)	C(51)	C(52)	1.387(15)
C(11)	C(12)	1.392(14)	C(51)	C(56)	1.380(15)
C(11)	C(16)	1.392(14)	C(52)	C(53)	1.38(2)
C(12)	C(13)	1.36(2)	C(53)	C(54)	1.40(2)
C(13)	C(14)	1.37(2)	C(54)	C(55)	1.38(2)
C(14)	C(15)	1.35(2)	C(55)	C(56)	1.42(2)
C(15)	C(16)	1.37(2)	C(61)	C(62)	1.348(14)
C(21)	C(22)	1.370(15)	C(61)	C(66)	1.38(2)
C(21)	C(26)	1.411(14)	C(62)	C(63)	1.40(2)
C(22)	C(23)	1.41(2)	C(63)	C(64)	1.35(2)
C(23)	C(24)	1.36(2)	C(64)	C(65)	1.37(2)
C(24)	C(25)	1.37(2)	C(65)	C(66)	1.37(2)
C(25)	C(26)	1.40(2)	C(71)	C(72)	1.38(2)
C(31)	C(32)	1.38(2)	C(71)	C(76)	1.396(15)
C(31)	C(36)	1.37(2)	C(72)	C(73)	1.39(2)
C(32)	C(33)	1.42(2)	C(73)	C(74)	1.41(2)
C(33)	C(34)	1.34(2)	C(74)	C(75)	1.37(2)
C(34)	C(35)	1.34(2)	C(75)	C(76)	1.37(2)

Table S3. (continued)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
C(81)	C(82)	1.387(14)	C(83)	C(84)	1.38(2)
C(81)	C(86)	1.418(14)	C(84)	C(85)	1.37(2)
C(82)	C(83)	1.37(2)	C(85)	C(86)	1.386(15)

(c) within the triflate ion

Atom1	Atom2	Distance	Atom1	Atom2	Distance
S	O(91)	1.436(9)	F(91)	C(91)	1.338(14)
S	O(92)	1.440(10)	F(92)	C(91)	1.311(14)
S	O(93)	1.439(9)	F(93)	C(91)	1.32(2)
S	C(91)	1.813(12)			

Primed and unprimed atoms are related by a 55:45 disorder – see Figure 1 for explanation.

Table S4. Selected Interatomic Angles for Compound **2**

(a) involving 'inner-core' atoms

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Rh/Ir'	Ir/Rh'	P(1)	91.15(6)	P(4)	Rh	C(1)	97.8(4)
Rh/Ir'	Ir/Rh'	P(3)	93.15(6)	P(4)	Rh	C(3)	87.3(6)
Rh	Ir	C(1)	53.1(6)	C(1)	Rh	C(3)	138.1(9)
Rh	Ir	C(2)	161.0(7)	Ir'	Rh'	C(1')	41.3(8)
P(1)	Ir/Rh'	P(3)	173.57(8)	Ir'	Rh'	C(3')	172.7(9)
P(1)	Ir	C(1)	90.4(5)	P(1)	Rh'	C(1')	91.5(7)
P(1)	Ir	C(2)	85.7(7)	P(1)	Rh'	C(3')	88.1(8)
P(3)	Ir	C(1)	96.0(5)	P(3)	Rh'	C(1')	94.8(7)
P(3)	Ir	C(2)	88.7(7)	P(3)	Rh'	C(3')	87.0(8)
C(1)	Ir	C(2)	145.5(9)	C(1')	Rh'	C(3')	146.0(12)
Rh'	Ir'	C(1')	55.4(9)	Ir/Rh'	P(1)	C(4)	113.7(3)
Rh'	Ir'	C(2')	162.4(8)	Rh/Ir'	P(2)	C(4)	113.2(3)
P(2)	Ir'	C(1')	91.1(8)	Ir/Rh'	P(3)	C(5)	113.0(3)
P(2)	Ir'	C(2')	87.5(7)	Rh/Ir'	P(4)	C(5)	113.1(3)
P(4)	Ir'	C(1')	97.9(8)	Ir	C(1)	Rh	82.7(6)
P(4)	Ir'	C(2')	86.4(7)	Ir	C(1)	O(1)	153.2(16)
C(1')	Ir'	C(2')	142.2(13)	Rh	C(1)	O(1)	123.9(15)
Ir/Rh'	Rh/Ir'	P(2)	92.92(6)	Ir'	C(1')	Rh'	83.4(10)
Ir/Rh'	Rh/Ir'	P(4)	90.76(6)	Ir'	C(1')	O(1)	164.3(26)
Ir	Rh	C(1)	44.2(5)	Rh'	C(1')	O(1)	112.3(22)
Ir	Rh	C(3)	177.2(7)	Rh	C(3)	O(3)	178.9(19)
P(2)	Rh/Ir'	P(4)	170.77(8)	Rh'	C(3')	O(3')	176.3(30)
P(2)	Rh	C(1)	90.7(4)	P(1)	C(4)	P(2)	109.7(5)
P(2)	Rh	C(3)	88.7(6)	P(3)	C(5)	P(4)	110.3(5)

(b) involving dppm phenyl carbons

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Ir/Rh'	P(1)	C(11)	113.1(3)	C(5)	P(3)	C(51)	103.2(4)
Ir/Rh'	P(1)	C(21)	116.4(3)	C(5)	P(3)	C(61)	104.7(5)
C(4)	P(1)	C(11)	103.7(4)	C(51)	P(3)	C(61)	103.7(4)
C(4)	P(1)	C(21)	104.9(4)	Rh/Ir'	P(4)	C(71)	113.5(3)
C(11)	P(1)	C(21)	103.7(4)	Rh/Ir'	P(4)	C(81)	115.0(3)
Rh/Ir'	P(2)	C(31)	115.7(4)	C(5)	P(4)	C(71)	105.4(5)
Rh/Ir'	P(2)	C(41)	112.9(3)	C(5)	P(4)	C(81)	103.0(4)
C(4)	P(2)	C(31)	106.0(5)	C(71)	P(4)	C(81)	105.7(5)
C(4)	P(2)	C(41)	104.1(4)	P(1)	C(11)	C(12)	120.0(8)
C(31)	P(2)	C(41)	103.9(4)	P(1)	C(11)	C(16)	121.6(8)
Ir/Rh'	P(3)	C(51)	113.9(3)	C(12)	C(11)	C(16)	118.2(10)
Ir/Rh'	P(3)	C(61)	116.9(3)	C(11)	C(12)	C(13)	120.5(10)

Table S4. (continued)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C(12)	C(13)	C(14)	119.7(10)	C(52)	C(51)	C(56)	120.3(10)
C(13)	C(14)	C(15)	121.1(11)	C(51)	C(52)	C(53)	119.9(11)
C(14)	C(15)	C(16)	119.9(11)	C(52)	C(53)	C(54)	122.0(12)
C(11)	C(16)	C(15)	120.4(10)	C(53)	C(54)	C(55)	117.1(11)
P(1)	C(21)	C(22)	121.8(8)	C(54)	C(55)	C(56)	121.8(11)
P(1)	C(21)	C(26)	119.7(7)	C(51)	C(56)	C(55)	118.8(11)
C(22)	C(21)	C(26)	118.5(9)	P(3)	C(61)	C(62)	121.1(8)
C(21)	C(22)	C(23)	121.1(11)	P(3)	C(61)	C(66)	119.9(8)
C(22)	C(23)	C(24)	119.3(12)	C(62)	C(61)	C(66)	119.0(10)
C(23)	C(24)	C(25)	121.7(11)	C(61)	C(62)	C(63)	119.9(10)
C(24)	C(25)	C(26)	119.1(12)	C(62)	C(63)	C(64)	120.8(11)
C(21)	C(26)	C(25)	120.2(11)	C(63)	C(64)	C(65)	119.2(11)
P(2)	C(31)	C(32)	120.0(8)	C(64)	C(65)	C(66)	120.3(11)
P(2)	C(31)	C(36)	119.3(8)	C(61)	C(66)	C(65)	120.5(11)
C(32)	C(31)	C(36)	120.6(9)	P(4)	C(71)	C(72)	122.2(8)
C(31)	C(32)	C(33)	119.6(13)	P(4)	C(71)	C(76)	118.4(9)
C(32)	C(33)	C(34)	119.1(14)	C(72)	C(71)	C(76)	119.3(10)
C(33)	C(34)	C(35)	121.9(12)	C(71)	C(72)	C(73)	120.5(11)
C(34)	C(35)	C(36)	120.5(13)	C(72)	C(73)	C(74)	118.4(12)
C(31)	C(36)	C(35)	118.3(12)	C(73)	C(74)	C(75)	121.6(11)
P(2)	C(41)	C(42)	119.4(8)	C(74)	C(75)	C(76)	118.6(11)
P(2)	C(41)	C(46)	121.6(8)	C(71)	C(76)	C(75)	121.6(12)
C(42)	C(41)	C(46)	118.8(9)	P(4)	C(81)	C(82)	124.2(8)
C(41)	C(42)	C(43)	120.8(10)	P(4)	C(81)	C(86)	117.4(7)
C(42)	C(43)	C(44)	119.7(12)	C(82)	C(81)	C(86)	118.3(9)
C(43)	C(44)	C(45)	121.3(12)	C(81)	C(82)	C(83)	120.8(10)
C(44)	C(45)	C(46)	119.0(12)	C(82)	C(83)	C(84)	121.1(11)
C(41)	C(46)	C(45)	120.3(10)	C(83)	C(84)	C(85)	119.1(10)
P(3)	C(51)	C(52)	119.3(8)	C(84)	C(85)	C(86)	121.2(10)
P(3)	C(51)	C(56)	120.3(8)	C(81)	C(86)	C(85)	119.5(10)

(c) within the triflate ion

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
O(91)	S	O(92)	115.5(6)	S	C(91)	F(91)	110.8(9)
O(91)	S	O(93)	114.1(6)	S	C(91)	F(92)	111.3(9)
O(91)	S	C(91)	102.8(5)	S	C(91)	F(93)	112.4(9)
O(92)	S	O(93)	115.2(5)	F(91)	C(91)	F(92)	107.5(10)
O(92)	S	C(91)	103.8(6)	F(91)	C(91)	F(93)	107.3(11)
O(93)	S	C(91)	103.0(6)	F(92)	C(91)	F(93)	107.4(10)

Primed and unprimed atoms are related by a 55:45 disorder – see Figure 1 for explanation.

Table S5. Anisotropic Displacement Parameters for Compound **2**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir/Rh'	0.0268(3)	0.0220(3)	0.0211(4)	-0.0003(2)	0.0034(2)	-0.0052(2)
Rh/Ir'	0.0200(3)	0.0345(4)	0.0236(4)	0.0048(2)	0.0020(2)	-0.0084(2)
P(1)	0.0247(12)	0.0225(12)	0.0230(13)	-0.0012(10)	0.0067(10)	-0.0014(10)
P(2)	0.0203(12)	0.0267(13)	0.0265(13)	0.0009(10)	0.0086(10)	-0.0040(10)
P(3)	0.0303(13)	0.0246(13)	0.0228(13)	0.0004(10)	0.0117(10)	-0.0026(10)
P(4)	0.0221(12)	0.0354(14)	0.0231(13)	-0.0002(11)	0.0058(10)	-0.0024(10)
O(1)	0.037(4)	0.036(4)	0.048(5)	-0.016(4)	0.015(3)	-0.001(3)
O(3)	0.089(15)	0.105(16)	0.083(14)	0.029(12)	-0.038(12)	-0.078(13)
O(3')	0.111(21)	0.044(13)	0.092(19)	0.017(12)	-0.022(15)	-0.056(13)
C(4)	0.011(4)	0.027(5)	0.035(6)	0.001(4)	0.008(4)	-0.005(4)
C(5)	0.026(5)	0.037(6)	0.027(6)	0.007(4)	0.009(4)	-0.003(4)
C(11)	0.025(5)	0.028(5)	0.027(5)	0.006(4)	0.010(4)	-0.001(4)
C(12)	0.046(7)	0.030(6)	0.049(7)	-0.013(5)	0.014(6)	0.001(5)
C(13)	0.022(6)	0.048(7)	0.071(9)	-0.004(6)	0.015(6)	0.006(5)
C(14)	0.025(6)	0.053(7)	0.065(8)	0.003(6)	0.000(6)	-0.006(5)
C(15)	0.030(6)	0.063(8)	0.045(7)	-0.014(6)	0.002(5)	-0.013(6)
C(16)	0.031(6)	0.039(6)	0.037(7)	-0.011(5)	-0.003(5)	-0.002(5)
C(21)	0.014(4)	0.026(5)	0.027(6)	-0.002(4)	0.010(4)	-0.005(4)
C(22)	0.034(6)	0.050(7)	0.030(6)	-0.012(5)	0.010(5)	-0.004(5)
C(23)	0.035(6)	0.059(8)	0.035(7)	-0.014(5)	0.015(5)	-0.013(6)
C(24)	0.046(7)	0.053(8)	0.064(9)	-0.025(7)	0.037(7)	-0.008(6)
C(25)	0.046(8)	0.047(7)	0.081(11)	-0.012(7)	0.022(7)	0.014(6)
C(26)	0.035(6)	0.038(6)	0.046(7)	-0.002(5)	0.019(5)	0.008(5)
C(31)	0.028(5)	0.036(6)	0.031(6)	-0.008(4)	0.023(4)	-0.010(4)
C(32)	0.049(7)	0.049(7)	0.065(9)	0.010(6)	0.045(7)	0.014(6)
C(33)	0.074(11)	0.065(10)	0.128(16)	0.025(10)	0.067(11)	0.039(8)
C(34)	0.083(11)	0.050(8)	0.081(11)	-0.010(7)	0.059(9)	0.004(7)
C(35)	0.067(9)	0.079(10)	0.047(8)	-0.011(7)	0.026(7)	-0.035(8)
C(36)	0.029(6)	0.068(8)	0.042(7)	-0.007(6)	0.011(5)	-0.012(6)
C(41)	0.024(5)	0.026(5)	0.032(6)	0.001(4)	0.004(4)	0.000(4)
C(42)	0.031(6)	0.041(6)	0.057(7)	-0.003(5)	0.023(5)	-0.007(5)
C(43)	0.083(10)	0.035(7)	0.102(12)	-0.022(7)	0.055(9)	-0.002(7)
C(44)	0.076(10)	0.034(7)	0.059(9)	-0.013(6)	0.005(7)	-0.004(6)
C(45)	0.073(10)	0.044(7)	0.079(10)	-0.014(7)	0.038(8)	-0.025(7)
C(46)	0.036(6)	0.035(6)	0.065(8)	-0.022(6)	0.020(6)	-0.012(5)
C(51)	0.026(5)	0.038(6)	0.022(5)	-0.005(4)	0.004(4)	-0.003(4)
C(52)	0.043(7)	0.042(7)	0.063(8)	-0.016(6)	0.020(6)	-0.009(5)
C(53)	0.040(7)	0.089(11)	0.083(11)	-0.038(9)	0.034(7)	-0.003(7)
C(54)	0.040(7)	0.083(10)	0.046(8)	-0.015(7)	0.022(6)	-0.014(7)
C(55)	0.046(7)	0.068(9)	0.053(8)	0.004(7)	0.006(6)	-0.033(7)

Table S5. (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(56)	0.048(7)	0.040(6)	0.043(7)	0.002(5)	0.015(5)	-0.018(5)
C(61)	0.032(5)	0.023(5)	0.025(5)	0.001(4)	0.001(4)	0.000(4)
C(62)	0.053(7)	0.044(7)	0.028(6)	-0.005(5)	0.008(5)	0.012(5)
C(63)	0.088(11)	0.055(8)	0.038(8)	-0.016(6)	0.024(7)	0.021(7)
C(64)	0.080(9)	0.029(6)	0.049(8)	-0.001(6)	-0.002(7)	0.020(6)
C(65)	0.089(10)	0.030(6)	0.045(8)	0.013(5)	0.003(7)	0.008(6)
C(66)	0.076(9)	0.033(6)	0.045(8)	0.001(5)	0.013(6)	0.007(6)
C(71)	0.038(6)	0.031(6)	0.035(6)	-0.006(5)	0.014(5)	-0.001(5)
C(72)	0.045(7)	0.047(7)	0.048(8)	0.014(6)	0.016(6)	0.010(6)
C(73)	0.048(8)	0.049(8)	0.087(11)	0.025(7)	0.018(7)	0.012(6)
C(74)	0.045(7)	0.038(7)	0.091(11)	-0.007(7)	0.026(7)	0.006(6)
C(75)	0.045(7)	0.055(8)	0.065(9)	-0.014(7)	0.038(7)	-0.004(6)
C(76)	0.046(7)	0.045(7)	0.039(7)	-0.002(5)	0.018(5)	-0.008(5)
C(81)	0.017(5)	0.037(5)	0.026(5)	0.006(4)	0.002(4)	-0.006(4)
C(82)	0.033(6)	0.043(6)	0.036(6)	-0.004(5)	0.013(5)	0.002(5)
C(83)	0.031(6)	0.049(7)	0.045(7)	-0.003(6)	-0.002(5)	-0.003(5)
C(84)	0.056(8)	0.042(7)	0.035(7)	-0.008(5)	0.002(6)	-0.012(6)
C(85)	0.051(7)	0.038(6)	0.031(6)	-0.010(5)	0.013(5)	0.005(5)
C(86)	0.029(5)	0.039(6)	0.027(6)	0.000(5)	0.004(4)	0.004(4)
S	0.043(2)	0.046(2)	0.037(2)	-0.0083(12)	0.0096(12)	-0.0091(13)
F(91)	0.058(5)	0.071(5)	0.117(7)	-0.027(5)	0.004(5)	-0.024(4)
F(92)	0.066(5)	0.056(5)	0.082(6)	-0.011(4)	-0.003(4)	0.025(4)
F(93)	0.090(6)	0.074(5)	0.049(5)	-0.024(4)	0.009(4)	0.000(4)
O(91)	0.053(5)	0.076(6)	0.057(6)	-0.018(5)	0.011(4)	-0.030(5)
O(92)	0.082(7)	0.054(5)	0.058(6)	-0.001(4)	0.023(5)	0.018(5)
O(93)	0.066(6)	0.061(5)	0.046(5)	0.006(4)	0.013(4)	-0.001(4)
C(91)	0.034(7)	0.047(7)	0.064(9)	-0.011(6)	0.002(6)	-0.002(6)

The form of the anisotropic displacement parameter is:

$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$

Primed and unprimed atoms are related by a 55:45 disorder – see Figure 1 for explanation.

Table S6. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for Compound **2**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H(2A)[a]	0.4449	-0.0996	0.0365	0.050
H(2B)[a]	0.5413	-0.1549	0.0428	0.050
H(2C)[a]	0.4732	-0.1545	0.0922	0.050
H(2A')[b]	0.0583	-0.3802	-0.0404	0.037
H(2B')[b]	0.0955	-0.4624	-0.0052	0.037
H(2C')[b]	0.1023	-0.4584	-0.0715	0.037
H(4A)	0.4252	-0.4689	0.0857	0.029
H(4B)	0.3780	-0.4516	0.1427	0.029
H(5A)	0.3475	-0.2838	-0.1442	0.035
H(5B)	0.2828	-0.2017	-0.1602	0.035
H(12)	0.5815	-0.4290	0.0880	0.049
H(13)	0.7455	-0.4262	0.1180	0.055
H(14)	0.8079	-0.3238	0.1817	0.058
H(15)	0.7091	-0.2234	0.2157	0.056
H(16)	0.5461	-0.2194	0.1824	0.043
H(22)	0.4144	-0.3416	0.2227	0.045
H(23)	0.3366	-0.2725	0.2930	0.051
H(24)	0.2412	-0.1550	0.2694	0.063
H(25)	0.2078	-0.1115	0.1761	0.068
H(26)	0.2850	-0.1800	0.1052	0.046
H(32)	0.0809	-0.3478	0.0572	0.062
H(33)	-0.0354	-0.3176	0.1206	0.101
H(34)	-0.0045	-0.3571	0.2135	0.081
H(35)	0.1297	-0.4329	0.2453	0.075
H(36)	0.2462	-0.4685	0.1828	0.055
H(42)	0.3561	-0.5778	0.0135	0.050
H(43)	0.3265	-0.7214	-0.0064	0.084
H(44)	0.1947	-0.7876	0.0250	0.068
H(45)	0.0945	-0.7152	0.0800	0.076
H(46)	0.1211	-0.5690	0.0982	0.053
H(52)	0.5134	-0.2758	-0.1271	0.058
H(53)	0.6622	-0.2467	-0.1571	0.083
H(54)	0.7254	-0.1074	-0.1542	0.066
H(55)	0.6375	0.0001	-0.1147	0.067
H(56)	0.4894	-0.0300	-0.0793	0.051
H(62)	0.2918	-0.0817	0.0121	0.049
H(63)	0.2278	0.0564	0.0143	0.071
H(64)	0.1836	0.1285	-0.0687	0.064
H(65)	0.2322	0.0768	-0.1525	0.066
H(66)	0.3085	-0.0543	-0.1540	0.061

Table S6. (continued)

Atom	x	y	z	U_{eq}, Å^2
H(72)	0.0961	-0.1681	-0.1768	0.055
H(73)	-0.0187	-0.0622	-0.1636	0.073
H(74)	-0.0640	-0.0404	-0.0722	0.068
H(75)	0.0052	-0.1197	0.0044	0.063
H(76)	0.1113	-0.2291	-0.0112	0.051
H(82)	0.0100	-0.3200	-0.1702	0.044
H(83)	-0.0452	-0.4043	-0.2467	0.051
H(84)	0.0590	-0.4957	-0.2873	0.053
H(85)	0.2206	-0.5022	-0.2504	0.047
H(86)	0.2804	-0.4158	-0.1746	0.038

[a]Included with an occupancy factor of 0.55. [b]Included with an occupancy factor of 0.45.

Table S7. Crystallographic Experimental Details for $[RhIr(CH_3)(CO)_2(PMe_3)(dppm)_2][CF_3SO_3]$ (**4a**)

A. Crystal Data	
formula	$C_{65}H_{72}F_3IrO_7P_5RhS$
formula weight	1504.25
crystal dimensions (mm)	0.36 × 0.21 × 0.08
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters[a]	
a (Å)	16.431 (2)
b (Å)	23.117 (3)
c (Å)	17.851 (2)
β (deg)	93.410 (14)
V (Å^3)	6768.4 (13)
Z	4
ρ_{calcd} (g cm^{-3})	1.476
μ (mm^{-1})	2.414
B. Data Collection and Refinement Conditions	
diffractometer	Enraf-Nonius CAD4[b]
radiation (λ [Å])	Mo Kα (0.71073)
monochromator	incident-beam, graphite crystal
temperature (°C)	–50
scan type	θ–2θ
data collection 2θ limit (deg)	50.0
total data collected	12274 ($-19 \le h \le 19$, $0 \le k \le 27$, $0 \le l \le 21$)
independent reflections	11867
number of observations (*NO*)	4211 ($F_o^2 \ge 2\sigma(F_o^2)$)
structure solution method	direct methods (*SHELXS–86*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–93*[d])
absorption correction method	*DIFABS*[e]
range of absorption correction factors	1.217–0.619
data/restraints/parameters	11858 [$F_o^2 \ge -3\sigma(F_o^2)$]/39[f]/647
goodness-of-fit (S)[g]	0.998 [$F_o^2 \ge -3\sigma(F_o^2)$]
final R indices[h]	
$F_o^2 > 2\sigma(F_o^2)$	$\boldsymbol{R_1 = 0.0915}$, $wR_2 = 0.2258$
all data	$R_1 = 0.3217$, $\boldsymbol{wR_2 = 0.3249}$
largest difference peak and hole	1.761 and –2.362 e Å^{-3}

[a]Obtained from least-squares refinement of 24 reflections with $20.0° < 2\theta < 23.9°$.

[b]Programs for diffractometer operation and data collection were those supplied by Enraf-Nonius.

(continued)

Table S7. (continued)

[c]Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[d]Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections except for 9 having $F_o^2 < -3\sigma(F_o^2)$. Weighted *R*-factors wR_2 and all goodnesses of fit *S* are based on F_o^2; conventional *R*-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. *R*-factors based on F_o^2 are statistically about twice as large as those based on F_o, and *R*-factors based on ALL data will be even larger.

[e]Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158–166.

[f]Restraints were applied to fix the geometries of the triflate group (S–C(91) = 1.80 ± 0.01 Å; S–O(91) = S–O(92) = S–O(93) = 1.45 ± 0.01 Å; F(91)–C(91) = F(92)–C(91) = F93–C(91) = 1.35 ± 0.01 Å; F(91)–F(92) = F(91)–F(93) = F(92)–F(93) = 2.20 ± .01 Å; O(91)–O(92) = O(91)–O(93) = O(92)–O(93) = 2.20 ± .01 Å; F(91)–O(91) = F(91)–O(92) = F(92)–O(91) = F(92)–O(93) = F(93)–O(92) = F(93)–O(93) = 3.04 ± 0.01 Å) and the THF rings (all bond distances 1.50 ± 0.01 Å; all 1,3 distances [e.g. C(101)–C(103)] 2.45 ± 0.01 Å).

[g]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.1435P)^2]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[h]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S8. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **4a**

(a) 'inner-core' atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
Ir	0.14213(6)	-0.22037(5)	0.06246(5)	0.0363(3)*
Rh	0.04284(11)	-0.22603(9)	-0.07443(10)	0.0379(5)*
P(1)	0.2373(4)	-0.2517(3)	-0.0204(4)	0.040(2)*
P(2)	0.1486(4)	-0.1908(3)	-0.1419(4)	0.041(2)*
P(3)	0.0148(4)	-0.1943(3)	0.1022(3)	0.0351(15)*
P(4)	-0.0625(4)	-0.2680(3)	-0.0147(3)	0.037(2)*
P(5)	0.2287(4)	-0.2083(4)	0.1755(4)	0.054(2)*
O(1)	0.1098(16)	-0.3434(12)	0.1025(14)	0.113(9)*
O(3)	-0.0609(11)	-0.2219(12)	-0.2151(11)	0.090(7)*
C(1)	0.1241(18)	-0.2967(12)	0.0875(24)	0.085(13)*
C(2)	0.1743(14)	-0.1251(14)	0.0372(14)	0.085(12)*
C(3)	-0.0217(14)	-0.2209(14)	-0.1610(14)	0.056(7)*
C(4)	0.3309(14)	-0.1860(11)	0.1683(13)	0.055(8)*
C(5)	0.2403(22)	-0.2741(15)	0.2281(17)	0.108(14)*
C(6)	0.2003(17)	-0.1639(16)	0.2462(14)	0.098(13)*
C(7)	0.2496(13)	-0.1977(10)	-0.0924(12)	0.037(6)*
C(8)	-0.0582(15)	-0.2557(11)	0.0879(12)	0.048(7)*

(b) dppm phenyl carbons

Atom	*x*	*y*	*z*	U_{eq}, Å^2
C(11)	0.3420(15)	-0.2641(11)	0.0161(14)	0.045(7)*
C(12)	0.4070(16)	-0.2277(11)	0.0043(14)	0.051(6)*
C(13)	0.4850(15)	-0.2393(11)	0.0360(16)	0.050(7)*
C(14)	0.4961(14)	-0.2861(14)	0.0761(14)	0.058(8)*
C(15)	0.4353(16)	-0.3238(12)	0.0869(16)	0.062(8)*
C(16)	0.3583(13)	-0.3141(11)	0.0552(15)	0.050(7)*
C(21)	0.2193(15)	-0.3164(11)	-0.0762(14)	0.047(7)*
C(22)	0.2803(16)	-0.3373(14)	-0.1250(15)	0.070(9)*
C(23)	0.2669(25)	-0.3838(14)	-0.1693(17)	0.095(12)*
C(24)	0.1986(22)	-0.4184(14)	-0.1637(21)	0.095(13)*
C(25)	0.1415(16)	-0.4023(12)	-0.1146(19)	0.068(9)*
C(26)	0.1468(15)	-0.3524(11)	-0.0712(14)	0.048(7)*
C(31)	0.1620(13)	-0.2263(12)	-0.2295(13)	0.040(6)*
C(32)	0.1237(16)	-0.2781(13)	-0.2459(16)	0.064(8)*
C(33)	0.1399(20)	-0.3118(13)	-0.3150(17)	0.069(10)*
C(34)	0.1913(19)	-0.2846(16)	-0.3649(17)	0.073(11)*
C(35)	0.2206(22)	-0.2335(20)	-0.3464(22)	0.103(14)*
C(36)	0.2128(14)	-0.2024(12)	-0.2809(13)	0.052(8)*
C(41)	0.1412(16)	-0.1147(12)	-0.1695(14)	0.051(7)*

Table S8. (continued)

Atom	*x*	*y*	*z*	U_{eq}, Å^2
C(42)	0.2089(19)	-0.0809(12)	-0.1734(17)	0.069(9)*
C(43)	0.2046(20)	-0.0241(12)	-0.1988(17)	0.074(10)*
C(44)	0.1305(19)	0.0014(13)	-0.2163(19)	0.076(11)*
C(45)	0.0631(27)	-0.0357(16)	-0.2163(18)	0.109(15)*
C(46)	0.0665(21)	-0.0920(15)	-0.1877(19)	0.091(11)*
C(51)	-0.0424(14)	-0.1342(10)	0.0602(12)	0.040(6)*
C(52)	-0.0185(15)	-0.1007(9)	0.0009(14)	0.041(6)*
C(53)	-0.0646(16)	-0.0571(12)	-0.0254(18)	0.065(9)*
C(54)	-0.1416(17)	-0.0467(12)	0.0014(19)	0.067(10)*
C(55)	-0.1684(20)	-0.0808(14)	0.0593(20)	0.083(11)*
C(56)	-0.1182(15)	-0.1217(13)	0.0863(16)	0.067(9)*
C(61)	0.0060(14)	-0.1804(11)	0.2063(14)	0.043(7)*
C(62)	-0.0024(14)	-0.2244(13)	0.2509(13)	0.051(7)*
C(63)	-0.0075(16)	-0.2150(13)	0.3309(13)	0.062(8)*
C(64)	-0.0031(14)	-0.1586(13)	0.3541(13)	0.052(8)*
C(65)	0.0044(16)	-0.1146(12)	0.3034(14)	0.056(8)*
C(66)	0.0075(15)	-0.1241(13)	0.2290(16)	0.061(8)*
C(71)	-0.1633(14)	-0.2457(11)	-0.0456(13)	0.040(6)*
C(72)	-0.2325(14)	-0.2830(12)	-0.0419(13)	0.052(6)*
C(73)	-0.3124(15)	-0.2633(14)	-0.0561(14)	0.057(9)*
C(74)	-0.3293(16)	-0.2100(13)	-0.0802(13)	0.053(8)*
C(75)	-0.2645(16)	-0.1730(12)	-0.0852(15)	0.059(8)*
C(76)	-0.1843(15)	-0.1891(11)	-0.0657(14)	0.048(7)*
C(81)	-0.0693(13)	-0.3457(10)	-0.0265(15)	0.040(6)*
C(82)	-0.0696(16)	-0.3691(13)	-0.0987(20)	0.076(10)*
C(83)	-0.0864(22)	-0.4281(14)	-0.1019(23)	0.101(13)*
C(84)	-0.0868(23)	-0.4636(14)	-0.0416(31)	0.108(17)*
C(85)	-0.0894(30)	-0.4407(20)	0.0191(26)	0.132(20)*
C(86)	-0.0748(17)	-0.3831(12)	0.0315(17)	0.065(9)*

(c) triflate ion atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
S	0.0505(10)	0.3854(7)	-0.2927(10)	0.224(8)
F(91)[a]	-0.0038(23)	0.4542(14)	-0.1926(17)	0.412(19)
F(92)[a]	0.1146(19)	0.4777(11)	-0.2365(22)	0.412(19)
F(93)[a]	0.0010(23)	0.4906(9)	-0.3061(21)	0.412(19)
O(91)[b]	0.0908(20)	0.3479(10)	-0.2362(16)	0.348(18)
O(92)[b]	-0.0310(13)	0.3615(11)	-0.3115(20)	0.348(18)
O(93)[b]	0.0956(19)	0.3866(13)	-0.3591(14)	0.348(18)
C(91)	0.0398(16)	0.4565(8)	-0.2540(15)	0.460(66)

Table S8. (continued)

(d) solvent THF atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
C(101)[c]	0.1653(34)	0.0128(29)	0.2100(31)	0.116(13)
C(102)[c]	0.2557(32)	0.0081(29)	0.2298(35)	0.116(13)
C(103)[c]	0.2749(27)	0.0437(31)	0.2995(35)	0.116(13)
C(104)[c]	0.1964(38)	0.0704(28)	0.3225(30)	0.116(13)
C(105)[c]	0.1305(25)	0.0560(30)	0.2629(37)	0.116(13)
C(111)[c]	0.1790(46)	-0.0538(34)	0.4760(31)	0.148(16)
C(112)[c]	0.1469(47)	0.0046(26)	0.4982(40)	0.148(16)
C(113)[c]	0.1109(45)	-0.0022(29)	0.5737(41)	0.148(16)
C(114)[c]	0.1358(50)	-0.0610(34)	0.6042(31)	0.148(16)
C(115)[c]	0.1784(49)	-0.0927(23)	0.5440(45)	0.148(16)

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$. [a]The triflate fluorine atoms (F(91), F(92), F(93)) were refined with a common displacement parameter. [b]The triflate oxygen atoms (O(91), O(92), O(93)) were refined with a common displacement parameter. *c*The THF rings were modelled to contain five carbon atoms (C(101)–C(105) and C(111)–C(115)) that were refined with a common displacement parameter for each ring.

Table S9. Selected Interatomic Distances for **4a**

(a) involving 'inner-core' atoms

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ir	Rh	2.859(2)	P(1)	C(7)	1.81(2)
Ir	P(1)	2.331(7)	P(2)	C(7)	1.84(2)
Ir	P(3)	2.328(6)	P(3)	C(8)	1.87(2)
Ir	P(5)	2.414(7)	P(4)	C(8)	1.85(2)
Ir	C(1)	1.85(3)	P(5)	C(4)	1.77(2)
Ir	C(2)	2.31(3)	P(5)	C(5)	1.79(3)
Rh	P(2)	2.320(7)	P(5)	C(6)	1.71(3)
Rh	P(4)	2.299(6)	O(1)	C(1)	1.14(3)
Rh	C(3)	1.83(3)	O(3)	C(3)	1.13(3)

(b) involving dppm phenyl carbons

Atom1	Atom2	Distance	Atom1	Atom2	Distance
P(1)	C(11)	1.83(3)	C(42)	C(43)	1.39(3)
P(1)	C(21)	1.81(3)	C(43)	C(44)	1.37(4)
P(2)	C(31)	1.79(3)	C(44)	C(45)	1.40(4)
P(2)	C(41)	1.83(3)	C(45)	C(46)	1.40(4)
P(3)	C(51)	1.81(2)	C(51)	C(52)	1.39(3)
P(3)	C(61)	1.90(3)	C(51)	C(56)	1.39(3)
P(4)	C(71)	1.79(2)	C(52)	C(53)	1.33(3)
P(4)	C(81)	1.81(2)	C(53)	C(54)	1.40(4)
C(11)	C(12)	1.39(3)	C(54)	C(55)	1.39(4)
C(11)	C(16)	1.37(3)	C(55)	C(56)	1.33(4)
C(12)	C(13)	1.40(3)	C(61)	C(62)	1.30(3)
C(13)	C(14)	1.30(3)	C(61)	C(66)	1.36(3)
C(14)	C(15)	1.35(3)	C(62)	C(63)	1.45(3)
C(15)	C(16)	1.37(3)	C(63)	C(64)	1.37(3)
C(21)	C(22)	1.45(3)	C(64)	C(65)	1.37(3)
C(21)	C(26)	1.46(3)	C(65)	C(66)	1.35(3)
C(22)	C(23)	1.34(4)	C(71)	C(72)	1.43(3)
C(23)	C(24)	1.39(4)	C(71)	C(76)	1.39(3)
C(24)	C(25)	1.37(4)	C(72)	C(73)	1.40(3)
C(25)	C(26)	1.39(3)	C(73)	C(74)	1.33(3)
C(31)	C(32)	1.38(3)	C(74)	C(75)	1.37(3)
C(31)	C(36)	1.39(3)	C(75)	C(76)	1.39(3)
C(32)	C(33)	1.50(4)	C(81)	C(82)	1.40(4)
C(33)	C(34)	1.41(4)	C(81)	C(86)	1.35(3)
C(34)	C(35)	1.31(4)	C(82)	C(83)	1.39(4)
C(35)	C(36)	1.38(4)	C(83)	C(84)	1.35(5)
C(41)	C(42)	1.36(3)	C(84)	C(85)	1.21(5)
C(41)	C(46)	1.36(4)	C(85)	C(86)	1.37(5)

Table S10. Selected Interatomic Angles for **4a**

(a) involving 'inner-core' atoms

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Rh	Ir	P(1)	79.2(2)	P(2)	Rh	C(3)	87.3(8)
Rh	Ir	P(3)	78.2(2)	P(2)	Rh	P(4)	174.9(2)
Rh	Ir	P(5)	175.7(2)	P(4)	Rh	C(3)	90.3(8)
Rh	Ir	C(1)	94.1(12)	Ir	P(1)	C(7)	110.1(8)
Rh	Ir	C(2)	90.1(6)	Rh	P(2)	C(7)	113.7(7)
P(1)	Ir	P(3)	157.3(2)	Ir	P(3)	C(8)	110.1(9)
P(1)	Ir	P(5)	100.5(2)	Rh	P(4)	C(8)	114.1(8)
P(1)	Ir	C(1)	88.9(11)	Ir	P(5)	C(4)	119.2(8)
P(1)	Ir	C(2)	90.2(6)	Ir	P(5)	C(5)	112.2(10)
P(3)	Ir	P(5)	102.2(2)	Ir	P(5)	C(6)	120.9(9)
P(3)	Ir	C(1)	90.8(10)	C(4)	P(5)	C(5)	102.3(14)
P(3)	Ir	C(2)	91.9(6)	C(4)	P(5)	C(6)	100.4(13)
P(5)	Ir	C(1)	90.2(12)	C(5)	P(5)	C(6)	98.5(16)
P(5)	Ir	C(2)	85.5(6)	Ir	C(1)	O(1)	177.4(30)
C(1)	Ir	C(2)	175.4(12)	Rh	C(3)	O(3)	174.9(32)
Ir	Rh	P(2)	91.2(2)	P(1)	C(7)	P(2)	105.4(11)
Ir	Rh	P(4)	91.7(2)	P(3)	C(8)	P(4)	103.8(12)
Ir	Rh	C(3)	173.6(10)				

(b) involving dppm phenyl carbons

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Ir	P(1)	C(11)	118.4(8)	C(8)	P(4)	C(81)	105.3(12)
Ir	P(1)	C(21)	120.8(9)	C(71)	P(4)	C(81)	101.5(11)
C(7)	P(1)	C(11)	102.6(11)	P(1)	C(11)	C(16)	117.8(19)
C(7)	P(1)	C(21)	101.5(11)	P(1)	C(11)	C(12)	124.6(20)
C(11)	P(1)	C(21)	100.7(11)	C(12)	C(11)	C(16)	117.5(23)
Rh	P(2)	C(31)	115.2(8)	C(11)	C(12)	C(13)	121.2(25)
Rh	P(2)	C(41)	115.9(9)	C(12)	C(13)	C(14)	118.5(25)
C(7)	P(2)	C(31)	103.0(10)	C(13)	C(14)	C(15)	122.3(25)
C(7)	P(2)	C(41)	104.9(11)	C(14)	C(15)	C(16)	120.5(26)
C(31)	P(2)	C(41)	102.4(12)	C(11)	C(16)	C(15)	119.7(24)
Ir	P(3)	C(51)	121.7(9)	P(1)	C(21)	C(22)	120.7(20)
Ir	P(3)	C(61)	117.6(7)	P(1)	C(21)	C(26)	123.0(19)
C(8)	P(3)	C(51)	102.3(11)	C(22)	C(21)	C(26)	116.2(24)
C(8)	P(3)	C(61)	100.1(11)	C(21)	C(22)	C(23)	121.7(28)
C(51)	P(3)	C(61)	102.0(11)	C(22)	C(23)	C(24)	121.6(31)
Rh	P(4)	C(71)	116.4(9)	C(23)	C(24)	C(25)	118.5(28)
Rh	P(4)	C(81)	114.1(8)	C(24)	C(25)	C(26)	123.9(28)
C(8)	P(4)	C(71)	103.9(11)	C(21)	C(26)	C(25)	117.7(24)

Table S10. (continued)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
P(2)	C(31)	C(32)	120.5(19)	P(3)	C(61)	C(62)	118.8(20)
P(2)	C(31)	C(36)	120.1(21)	P(3)	C(61)	C(66)	116.8(21)
C(32)	C(31)	C(36)	119.4(26)	C(62)	C(61)	C(66)	124.3(27)
C(31)	C(32)	C(33)	121.8(29)	C(61)	C(62)	C(63)	119.8(28)
C(32)	C(33)	C(34)	115.6(28)	C(62)	C(63)	C(64)	115.9(26)
C(33)	C(34)	C(35)	117.8(32)	C(63)	C(64)	C(65)	120.7(22)
C(34)	C(35)	C(36)	129.1(39)	C(64)	C(65)	C(66)	122.6(26)
C(31)	C(36)	C(35)	116.0(31)	C(61)	C(66)	C(65)	116.6(26)
P(2)	C(41)	C(42)	121.5(22)	P(4)	C(71)	C(72)	122.4(21)
P(2)	C(41)	C(46)	118.8(23)	P(4)	C(71)	C(76)	124.0(17)
C(42)	C(41)	C(46)	119.7(28)	C(72)	C(71)	C(76)	113.1(23)
C(41)	C(42)	C(43)	122.1(29)	C(71)	C(72)	C(73)	122.4(27)
C(42)	C(43)	C(44)	120.6(30)	C(72)	C(73)	C(74)	122.4(27)
C(43)	C(44)	C(45)	115.3(29)	C(73)	C(74)	C(75)	116.8(25)
C(44)	C(45)	C(46)	123.8(33)	C(74)	C(75)	C(76)	122.9(26)
C(41)	C(46)	C(45)	117.7(34)	C(71)	C(76)	C(75)	122.0(24)
P(3)	C(51)	C(52)	125.4(19)	P(4)	C(81)	C(82)	119.1(22)
P(3)	C(51)	C(56)	118.2(21)	P(4)	C(81)	C(86)	123.4(22)
C(52)	C(51)	C(56)	116.2(23)	C(82)	C(81)	C(86)	117.5(26)
C(51)	C(52)	C(53)	120.7(26)	C(81)	C(82)	C(83)	114.0(32)
C(52)	C(53)	C(54)	121.2(30)	C(82)	C(83)	C(84)	124.9(38)
C(53)	C(54)	C(55)	119.2(26)	C(83)	C(84)	C(85)	116.8(39)
C(54)	C(55)	C(56)	117.2(32)	C(84)	C(85)	C(86)	123.7(51)
C(51)	C(56)	C(55)	125.2(33)	C(81)	C(86)	C(85)	121.0(33)

Table S11. Anisotropic Displacement Parameters for **4a**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir	0.0347(5)	0.0384(6)	0.0358(5)	0.0014(6)	0.0025(3)	0.0026(6)
Rh	0.0381(10)	0.0411(13)	0.0342(10)	0.0010(11)	0.0008(8)	-0.0038(11)
P(1)	0.035(4)	0.041(4)	0.045(4)	0.002(3)	0.006(3)	0.005(3)
P(2)	0.046(4)	0.040(4)	0.039(4)	0.004(3)	0.005(3)	-0.002(3)
P(3)	0.036(3)	0.037(4)	0.032(3)	0.001(3)	0.003(3)	0.000(3)
P(4)	0.036(3)	0.036(4)	0.039(3)	-0.005(3)	0.002(3)	-0.001(3)
P(5)	0.043(4)	0.080(7)	0.040(4)	-0.007(4)	0.000(3)	0.010(4)
O(1)	0.134(23)	0.107(22)	0.100(20)	-0.017(18)	0.020(17)	-0.006(19)
O(3)	0.052(12)	0.157(23)	0.060(13)	0.004(16)	-0.011(10)	-0.014(15)
C(1)	0.049(19)	0.019(17)	0.187(41)	-0.010(21)	-0.002(21)	-0.017(13)
C(2)	0.024(13)	0.177(35)	0.053(18)	-0.063(20)	0.004(12)	0.033(18)
C(3)	0.037(13)	0.088(21)	0.043(15)	-0.022(18)	0.015(11)	0.003(17)
C(4)	0.059(18)	0.066(20)	0.039(15)	0.007(14)	-0.014(13)	-0.024(15)
C(5)	0.135(31)	0.116(32)	0.065(21)	0.037(22)	-0.054(21)	-0.034(27)
C(6)	0.068(21)	0.186(39)	0.035(17)	0.004(21)	-0.036(15)	-0.044(23)
C(7)	0.050(15)	0.029(14)	0.034(13)	0.008(11)	0.023(11)	0.003(11)
C(8)	0.058(16)	0.066(19)	0.018(12)	0.013(12)	-0.014(11)	-0.004(14)
C(11)	0.047(15)	0.050(20)	0.040(14)	-0.003(13)	0.017(12)	0.004(13)
C(12)	0.062(15)	0.043(16)	0.047(14)	0.003(15)	-0.002(12)	0.002(16)
C(13)	0.031(14)	0.037(18)	0.081(21)	0.001(14)	-0.007(13)	-0.004(11)
C(14)	0.033(13)	0.093(26)	0.047(15)	-0.014(17)	0.000(11)	-0.004(17)
C(15)	0.057(18)	0.041(17)	0.085(22)	0.010(16)	-0.036(16)	-0.006(14)
C(16)	0.022(13)	0.049(18)	0.077(20)	0.008(15)	-0.012(13)	-0.005(12)
C(21)	0.043(15)	0.051(18)	0.047(15)	0.021(13)	-0.004(12)	0.013(13)
C(22)	0.051(17)	0.098(26)	0.063(20)	-0.029(19)	0.030(15)	-0.025(18)
C(23)	0.162(37)	0.057(23)	0.070(23)	-0.050(19)	0.029(23)	0.026(24)
C(24)	0.113(30)	0.050(22)	0.128(33)	-0.060(22)	0.042(25)	-0.033(21)
C(25)	0.039(16)	0.049(20)	0.115(28)	-0.008(19)	-0.009(17)	0.007(14)
C(26)	0.052(16)	0.041(17)	0.053(16)	0.001(13)	0.018(13)	0.000(13)
C(31)	0.032(12)	0.046(16)	0.043(14)	0.014(14)	0.006(10)	0.000(13)
C(32)	0.054(17)	0.057(19)	0.080(20)	-0.010(19)	0.001(14)	0.016(18)
C(33)	0.097(25)	0.046(20)	0.059(20)	-0.026(16)	-0.036(18)	0.029(17)
C(34)	0.083(25)	0.079(27)	0.056(20)	-0.001(21)	0.001(18)	0.059(22)
C(35)	0.086(26)	0.140(42)	0.085(27)	0.009(28)	0.025(21)	0.054(28)
C(36)	0.033(13)	0.084(23)	0.040(15)	-0.006(14)	0.000(11)	0.034(14)
C(41)	0.054(17)	0.052(18)	0.048(16)	0.005(14)	0.020(13)	-0.008(15)
C(42)	0.082(22)	0.041(19)	0.088(23)	0.023(17)	0.025(18)	0.014(17)
C(43)	0.098(25)	0.041(19)	0.087(24)	0.030(17)	0.033(20)	0.009(17)
C(44)	0.072(22)	0.032(18)	0.130(31)	0.035(19)	0.046(21)	0.010(16)
C(45)	0.176(42)	0.077(27)	0.070(24)	0.027(21)	-0.030(26)	0.064(28)

Table S11. (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(46)	0.080(25)	0.096(29)	0.099(28)	0.045(23)	0.008(20)	0.016(21)
C(51)	0.044(14)	0.042(16)	0.031(13)	-0.015(12)	-0.023(11)	0.014(12)
C(52)	0.053(16)	0.019(14)	0.050(15)	-0.002(12)	-0.006(13)	0.014(12)
C(53)	0.055(18)	0.043(19)	0.092(24)	-0.017(17)	-0.030(17)	-0.004(15)
C(54)	0.067(21)	0.039(18)	0.089(24)	-0.015(17)	-0.050(18)	0.036(16)
C(55)	0.076(23)	0.084(27)	0.087(26)	-0.019(22)	-0.017(20)	0.042(21)
C(56)	0.045(16)	0.084(23)	0.069(20)	-0.013(17)	-0.023(15)	0.036(16)
C(61)	0.033(13)	0.040(17)	0.053(16)	-0.011(14)	-0.018(12)	0.009(12)
C(62)	0.052(15)	0.062(19)	0.039(14)	0.008(16)	-0.006(11)	-0.002(16)
C(63)	0.074(18)	0.082(23)	0.026(13)	0.007(16)	-0.016(12)	0.025(19)
C(64)	0.051(16)	0.083(23)	0.021(13)	-0.040(14)	-0.003(11)	-0.003(15)
C(65)	0.084(21)	0.052(19)	0.031(15)	-0.007(14)	-0.008(14)	0.017(16)
C(66)	0.049(17)	0.068(22)	0.063(20)	0.031(17)	-0.004(14)	-0.001(15)
C(71)	0.030(13)	0.046(16)	0.045(15)	-0.015(13)	0.007(11)	-0.017(12)
C(72)	0.052(15)	0.051(17)	0.054(15)	-0.012(16)	0.008(12)	0.002(16)
C(73)	0.033(14)	0.107(29)	0.034(14)	0.007(16)	0.017(11)	0.003(16)
C(74)	0.052(17)	0.073(25)	0.030(14)	-0.016(14)	-0.022(12)	-0.008(16)
C(75)	0.059(18)	0.054(19)	0.061(18)	-0.018(15)	-0.019(15)	0.041(16)
C(76)	0.053(17)	0.030(16)	0.058(17)	0.003(13)	-0.015(13)	-0.012(13)
C(81)	0.024(12)	0.028(15)	0.068(18)	0.003(14)	-0.005(12)	-0.013(11)
C(82)	0.065(20)	0.056(21)	0.111(28)	-0.042(20)	0.037(19)	-0.002(16)
C(83)	0.137(34)	0.031(20)	0.136(36)	-0.039(23)	0.022(27)	-0.018(21)
C(84)	0.098(29)	0.011(18)	0.218(54)	0.033(27)	0.019(34)	0.013(18)
C(85)	0.181(48)	0.091(39)	0.121(42)	-0.037(30)	-0.016(36)	0.025(33)
C(86)	0.095(23)	0.027(16)	0.072(21)	0.003(15)	-0.018(17)	-0.027(16)

The form of the anisotropic displacement parameter is:

$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$

Table S12. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for **4a**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H(2A)	0.1682	-0.1018	0.0817	0.102
H(2B)	0.1379	-0.1108	-0.0034	0.102
H(2C)	0.2302	-0.1229	0.0228	0.102
H(4A)	0.3553	-0.2081	0.1293	0.066
H(4B)	0.3613	-0.1924	0.2158	0.066
H(4C)	0.3322	-0.1451	0.1559	0.066
H(5A)	0.2568	-0.3050	0.1954	0.129
H(5B)	0.1888	-0.2842	0.2486	0.129
H(5C)	0.2815	-0.2689	0.2687	0.129
H(6A)	0.1440	-0.1716	0.2564	0.118
H(6B)	0.2058	-0.1238	0.2312	0.118
H(6C)	0.2350	-0.1712	0.2911	0.118
H(7A)	0.2903	-0.2103	-0.1270	0.044
H(7B)	0.2670	-0.1608	-0.0700	0.044
H(8A)	-0.0383	-0.2902	0.1152	0.057
H(8B)	-0.1120	-0.2455	0.1047	0.057
H(12)	0.3984	-0.1945	-0.0256	0.061
H(13)	0.5285	-0.2139	0.0286	0.060
H(14)	0.5484	-0.2938	0.0982	0.069
H(15)	0.4457	-0.3570	0.1164	0.075
H(16)	0.3170	-0.3418	0.0602	0.060
H(22)	0.3305	-0.3179	-0.1257	0.084
H(23)	0.3047	-0.3931	-0.2049	0.114
H(24)	0.1916	-0.4520	-0.1929	0.114
H(25)	0.0961	-0.4265	-0.1100	0.082
H(26)	0.1052	-0.3421	-0.0398	0.058
H(32)	0.0864	-0.2928	-0.2128	0.077
H(33)	0.1172	-0.3486	-0.3246	0.083
H(34)	0.2042	-0.3026	-0.4100	0.087
H(35)	0.2511	-0.2154	-0.3826	0.123
H(36)	0.2402	-0.1671	-0.2717	0.063
H(42)	0.2601	-0.0965	-0.1583	0.083
H(43)	0.2528	-0.0031	-0.2042	0.089
H(44)	0.1253	0.0410	-0.2274	0.092
H(45)	0.0127	-0.0220	-0.2366	0.131
H(46)	0.0187	-0.1134	-0.1814	0.110
H(52)	0.0308	-0.1089	-0.0210	0.049
H(53)	-0.0451	-0.0328	-0.0625	0.078
H(54)	-0.1749	-0.0170	-0.0195	0.081
H(55)	-0.2199	-0.0752	0.0784	0.100

Table S12. (continued)

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H(56)	-0.1355	-0.1440	0.1265	0.081
H(62)	-0.0051	-0.2622	0.2313	0.061
H(63)	-0.0135	-0.2457	0.3646	0.074
H(64)	-0.0053	-0.1498	0.4054	0.062
H(65)	0.0076	-0.0764	0.3211	0.067
H(66)	0.0105	-0.0935	0.1947	0.073
H(72)	-0.2239	-0.3221	-0.0295	0.062
H(73)	-0.3557	-0.2887	-0.0483	0.069
H(74)	-0.3830	-0.1982	-0.0931	0.063
H(75)	-0.2747	-0.1352	-0.1026	0.071
H(76)	-0.1431	-0.1609	-0.0662	0.057
H(82)	-0.0594	-0.3469	-0.1413	0.091
H(83)	-0.0983	-0.4445	-0.1495	0.121
H(84)	-0.0852	-0.5040	-0.0468	0.130
H(85)	-0.1021	-0.4638	0.0602	0.158
H(86)	-0.0684	-0.3692	0.0810	0.078