Table S–1. Crystallographic Experimental Details for **2b**

A. Crystal Data	
formula	$C_{54}H_{44}BF_4O_4P_4RhRu$
formula weight	1171.56
crystal dimensions (mm)	0.39 × 0.24 × 0.12
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters[a]	
a (Å)	11.5765 (6)
b (Å)	12.7577 (7)
c (Å)	17.4006 (10)
β (deg)	101.6645 (10)
V (Å^3)	2516.8 (2)
Z	2
ρ_{calcd} (g cm^{-3})	1.546
μ (mm^{-1})	0.815
B. Data Collection and Refinement Conditions	
diffractometer	Bruker PLATFORM/SMART 1000 CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–80
scan type	ω scans (0.2°) (25 s exposures)
data collection 2θ limit (deg)	52.76
total data collected	13316 ($-14 \le h \le 14$, $-12 \le k \le 15$, $-21 \le l \le 21$)
independent reflections	5141 (R_{int} = 0.0244)
number of observed reflections (*NO*)	4489 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–86*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–93*[d])
absorption correction method	empirical (*SADABS*)
range of transmission factors	0.9085–0.7416
data/restraints/parameters	5141 [$F_o^2 \ge -3\sigma(F_o^2)$] / 0 / 340
goodness-of-fit (*S*)[e]	1.028 [$F_o^2 \ge -3\sigma(F_o^2)$]
final *R* indices[f]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0255
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0690
largest difference peak and hole	0.593 and –0.358 e Å^{-3}

[a]Obtained from least-squares refinement of 4710 centered reflections.

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

(continued)

Table S–1. Crystallographic Experimental Details for **2b** (continued)

[c]Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

[d]Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). 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; $w = [\sigma^2(F_o^2) + (0.0368P)^2 + 1.1895P]^{-1}$ 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 S–2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **2b**

(a) 'inner-core' atoms of $[RhRu(CO)_4(dppm)_2]^+$

Atom	*x*	*y*	*z*	U_{eq}, Å^2
Rh/Ru[a]	0.094288(13)	-0.002639(11)	-0.038652(8)	0.02288(6)*
P(1)	0.20020(4)	-0.11951(4)	0.05260(3)	0.02239(11)*
P(2)	-0.00818(4)	-0.12006(4)	0.13246(3)	0.02159(11)*
O(1)	0.2966(2)	-0.01098(19)	-0.12337(15)	0.0798(8)*
O(2)	0.10482(18)	0.17554(14)	0.08966(10)	0.0590(5)*
C(1)	0.2209(2)	-0.00812(18)	-0.09170(14)	0.0409(6)*
C(2)[b]	0.0258(4)	0.1115(3)	0.0724(2)	0.0312(9)*
C(3)[b]	-0.1067(4)	-0.1074(3)	-0.0404(2)	0.0305(8)*
C(4)	0.10559(16)	-0.20039(15)	0.10147(11)	0.0241(4)*

(b) dppm phenyl carbons

Atom	*x*	*y*	*z*	U_{eq}, Å^2
C(11)	0.28286(16)	-0.21666(15)	0.00833(10)	0.0257(4)*
C(12)	0.22077(19)	-0.28753(16)	-0.04547(12)	0.0329(4)*
C(13)	0.2797(2)	-0.35885(18)	-0.08345(13)	0.0402(5)*
C(14)	0.4011(2)	-0.3591(2)	-0.06909(13)	0.0452(6)*
C(15)	0.4631(2)	-0.2891(2)	-0.01694(14)	0.0492(7)*
C(16)	0.40543(18)	-0.2170(2)	0.02248(12)	0.0379(5)*
C(21)	0.31039(16)	-0.06003(17)	0.12960(12)	0.0296(4)*
C(22)	0.3495(2)	-0.1088(2)	0.20145(13)	0.0422(5)*
C(23)	0.4357(2)	-0.0618(3)	0.25861(15)	0.0568(7)*
C(24)	0.4853(2)	0.0322(3)	0.24308(17)	0.0578(7)*
C(25)	0.4500(2)	0.0787(2)	0.17137(17)	0.0552(7)*
C(26)	0.3616(2)	0.0342(2)	0.11485(15)	0.0428(5)*
C(31)	-0.11634(16)	-0.21559(15)	0.15159(11)	0.0241(4)*
C(32)	-0.16145(16)	-0.28896(16)	0.09419(11)	0.0287(4)*
C(33)	-0.25024(18)	-0.35661(17)	0.10508(13)	0.0348(5)*
C(34)	-0.2956(2)	-0.3516(2)	0.17235(14)	0.0443(6)*
C(35)	-0.2518(2)	-0.2787(2)	0.22919(15)	0.0489(6)*
C(36)	-0.16270(19)	-0.21064(19)	0.21940(12)	0.0367(5)*
C(41)	0.06078(17)	-0.07102(17)	0.22903(11)	0.0289(4)*
C(42)	0.1227(2)	-0.1384(2)	0.28587(12)	0.0421(5)*
C(43)	0.1791(2)	-0.0989(3)	0.35822(13)	0.0575(8)*
C(44)	0.1718(3)	0.0056(3)	0.37513(16)	0.0629(9)*
C(45)	0.1083(3)	0.0709(3)	0.32057(17)	0.0602(8)*
C(46)	0.0529(2)	0.0339(2)	0.24721(14)	0.0416(5)*

Table S–2. Atomic Coordinates and Displacement Parameters for **2b** (continued)

(c) tetrafluoroborate ion atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
F(1)[b]	-0.1135(3)	0.5116(3)	-0.0035(4)	0.0937(15)*
F(2)[b]	0.0593(3)	0.5668(2)	0.0640(2)	0.0623(9)*
F(3)[b]	0.0340(3)	0.3962(2)	0.03663(16)	0.0502(7)*
F(4)[b]	0.0532(6)	0.5093(3)	-0.0583(3)	0.1017(17)*
B	0.0000	0.5000	0.0000	0.0479(10)*

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]Refined as a combination of 50% Rh/50% Ru. [b]Refined with an occupacy factor of 0.5.

Table S–3. Selected Interatomic Distances (Å) for **2b**

(a) within $[RhRu(CO)_4(dppm)_2]^+$

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Rh	Ru	2.7870(3)	Ru	C(3)	1.950(4)
Rh	P(1)	2.3368(5)	P(1)	P(2)	3.0176(6)†
Rh	P(2')	2.3346(5)	P(1)	C(4)	1.8342(19)
Rh	C(1)	1.885(2)	P(2)	C(4)	1.8337(19)
Rh	C(2)	2.665(4)†	O(1)	C(1)	1.126(3)
Rh	C(3)	2.678(4)†	O(2)	C(2)	1.218(4)
Ru	C(2)	1.969(4)	O(2')	C(3)	1.224(4)

Primed atoms are related to unprimed ones via the crystallographic inversion center (0, 0, 0).

†Nonbonded distance.

(b) involving dppm phenyl carbons

Atom1	Atom2	Distance	Atom1	Atom2	Distance
P(1)	C(11)	1.8285(19)	C(24)	C(25)	1.367(4)
P(1)	C(21)	1.8185(19)	C(25)	C(26)	1.389(3)
P(2)	C(31)	1.8255(19)	C(31)	C(32)	1.391(3)
P(2)	C(41)	1.8193(19)	C(31)	C(36)	1.393(3)
C(11)	C(12)	1.392(3)	C(32)	C(33)	1.384(3)
C(11)	C(16)	1.390(3)	C(33)	C(34)	1.378(3)
C(12)	C(13)	1.383(3)	C(34)	C(35)	1.378(4)
C(13)	C(14)	1.377(3)	C(35)	C(36)	1.385(3)
C(14)	C(15)	1.368(4)	C(41)	C(42)	1.394(3)
C(15)	C(16)	1.396(3)	C(41)	C(46)	1.383(3)
C(21)	C(22)	1.388(3)	C(42)	C(43)	1.390(3)
C(21)	C(26)	1.387(3)	C(43)	C(44)	1.371(4)
C(22)	C(23)	1.394(3)	C(44)	C(45)	1.362(5)
C(23)	C(24)	1.379(4)	C(45)	C(46)	1.390(3)

(c) within the tetrafluoroborate ion

Atom1	Atom2	Distance	Atom1	Atom2	Distance
F(1)	B	1.311(4)	F(3)	B	1.488(3)
F(2)	B	1.459(3)	F(4)	B	1.295(4)

Table S–4. Selected Interatomic Angles (deg) for **2b**

(a) within $[RhRu(CO)_4(dppm)_2]^+$

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Ru	Rh	P(1)	92.409(13)	P(2)	Ru	C(3)	88.32(12)
Ru	Rh	P(2')	93.203(13)	C(1')	Ru	C(2)	113.57(14)
Ru	Rh	C(1)	179.13(8)	C(1')	Ru	C(3)	114.73(15)
P(1)	Rh	P(2')	173.781(17)	C(2)	Ru	C(3)	131.69(17)
P(1)	Rh	C(1)	87.47(7)	Rh	P(1)	C(4)	113.17(6)
P(2')	Rh	C(1)	86.96(7)	Ru	P(2)	C(4)	113.56(6)
Rh	Ru	C(2)	65.56(12)	Rh	C(1)	O(1)	179.7(3)
Rh	Ru	C(3)	66.13(12)	Ru	C(2)	O(2)	175.3(3)
P(1')	Ru	C(2)	89.71(12)	Ru	C(3)	O(2')	174.8(3)
P(1')	Ru	C(3)	91.51(12)	P(1)	C(4)	P(2)	110.71(10)
P(2)	Ru	C(2)	95.05(12)				

Primed atoms are related to unprimed ones via the crystallographic inversion center (0, 0, 0).

(b) involving dppm phenyl carbons

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Rh	P(1)	C(11)	113.18(6)	C(21)	C(22)	C(23)	120.4(2)
Rh	P(1)	C(21)	115.34(7)	C(22)	C(23)	C(24)	120.0(2)
C(4)	P(1)	C(11)	103.09(9)	C(23)	C(24)	C(25)	119.7(2)
C(4)	P(1)	C(21)	106.79(9)	C(24)	C(25)	C(26)	120.7(3)
C(11)	P(1)	C(21)	104.15(9)	C(21)	C(26)	C(25)	120.3(2)
Ru	P(2)	C(31)	111.32(6)	P(2)	C(31)	C(32)	119.34(14)
Ru	P(2)	C(41)	117.44(7)	P(2)	C(31)	C(36)	121.34(15)
C(4)	P(2)	C(31)	103.91(8)	C(32)	C(31)	C(36)	119.06(18)
C(4)	P(2)	C(41)	104.87(9)	C(31)	C(32)	C(33)	120.17(18)
C(31)	P(2)	C(41)	104.49(9)	C(32)	C(33)	C(34)	120.6(2)
P(1)	C(11)	C(12)	118.72(15)	C(33)	C(34)	C(35)	119.5(2)
P(1)	C(11)	C(16)	121.98(16)	C(34)	C(35)	C(36)	120.7(2)
C(12)	C(11)	C(16)	119.14(19)	C(31)	C(36)	C(35)	120.0(2)
C(11)	C(12)	C(13)	120.7(2)	P(2)	C(41)	C(42)	120.67(17)
C(12)	C(13)	C(14)	119.9(2)	P(2)	C(41)	C(46)	120.49(17)
C(13)	C(14)	C(15)	119.9(2)	C(42)	C(41)	C(46)	118.8(2)
C(14)	C(15)	C(16)	121.2(2)	C(41)	C(42)	C(43)	120.0(3)
C(11)	C(16)	C(15)	119.2(2)	C(42)	C(43)	C(44)	120.6(3)
P(1)	C(21)	C(22)	121.93(17)	C(43)	C(44)	C(45)	119.6(2)
P(1)	C(21)	C(26)	119.20(16)	C(44)	C(45)	C(46)	121.1(3)
C(22)	C(21)	C(26)	118.8(2)	C(41)	C(46)	C(45)	120.0(3)

(c) within the tetrafluoroborate ion

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
F(1)	B	F(2)	106.4(2)	F(2)	B	F(3)	98.63(17)
F(1)	B	F(3)	107.2(3)	F(2)	B	F(4)	108.7(3)
F(1)	B	F(4)	125.7(4)	F(3)	B	F(4)	106.9(2)

Table S–5. Anisotropic Displacement Parameters (U_{ij}, Å^2) for **2b**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh/Ru	0.02340(10)	0.02251(10)	0.02312(9)	0.00135(5)	0.00562(6)	0.00299(6)
P(1)	0.0196(2)	0.0232(2)	0.0244(2)	-0.00058(19)	0.00441(17)	0.00158(19)
P(2)	0.0232(2)	0.0219(2)	0.0201(2)	-0.00106(18)	0.00561(17)	-0.00018(19)
O(1)	0.0667(14)	0.0997(18)	0.0913(16)	0.0472(13)	0.0593(13)	0.0433(12)
O(2)	0.0818(14)	0.0363(10)	0.0504(10)	-0.0043(8)	-0.0068(9)	-0.0108(10)
C(1)	0.0408(13)	0.0420(14)	0.0436(13)	0.0181(10)	0.0171(10)	0.0174(10)
C(2)	0.032(2)	0.029(2)	0.031(2)	0.0010(17)	0.0028(16)	-0.0010(17)
C(3)	0.035(2)	0.029(2)	0.0266(18)	-0.0018(16)	0.0049(16)	0.0025(17)
C(4)	0.0244(9)	0.0226(9)	0.0256(9)	0.0012(7)	0.0059(7)	0.0011(7)
C(11)	0.0265(9)	0.0269(10)	0.0252(9)	0.0067(8)	0.0089(7)	0.0071(8)
C(12)	0.0353(11)	0.0307(11)	0.0358(11)	-0.0011(9)	0.0144(9)	0.0022(9)
C(13)	0.0571(14)	0.0297(11)	0.0392(12)	0.0004(9)	0.0229(10)	0.0050(10)
C(14)	0.0579(15)	0.0444(14)	0.0392(12)	0.0071(11)	0.0238(11)	0.0242(12)
C(15)	0.0339(11)	0.0718(19)	0.0448(13)	0.0098(13)	0.0148(10)	0.0251(13)
C(16)	0.0287(10)	0.0506(14)	0.0344(10)	0.0023(10)	0.0062(8)	0.0109(10)
C(21)	0.0199(9)	0.0354(11)	0.0337(10)	-0.0069(9)	0.0056(8)	-0.0006(8)
C(22)	0.0349(11)	0.0542(15)	0.0347(11)	-0.0003(10)	0.0001(9)	-0.0065(11)
C(23)	0.0445(14)	0.083(2)	0.0373(13)	-0.0049(13)	-0.0053(11)	-0.0078(14)
C(24)	0.0380(13)	0.076(2)	0.0559(16)	-0.0279(15)	0.0004(12)	-0.0153(14)
C(25)	0.0451(14)	0.0513(16)	0.0664(17)	-0.0148(13)	0.0047(12)	-0.0168(12)
C(26)	0.0385(12)	0.0405(13)	0.0480(13)	-0.0043(11)	0.0055(10)	-0.0080(11)
C(31)	0.0224(9)	0.0237(9)	0.0267(9)	0.0045(7)	0.0057(7)	0.0018(7)
C(32)	0.0260(9)	0.0306(11)	0.0292(9)	0.0021(8)	0.0048(7)	0.0003(8)
C(33)	0.0299(10)	0.0313(11)	0.0408(11)	-0.0012(9)	0.0013(8)	-0.0041(9)
C(34)	0.0357(12)	0.0459(14)	0.0542(14)	0.0044(11)	0.0158(10)	-0.0109(10)
C(35)	0.0471(14)	0.0603(16)	0.0466(13)	-0.0023(12)	0.0269(11)	-0.0130(12)
C(36)	0.0381(11)	0.0429(13)	0.0320(10)	-0.0042(9)	0.0137(9)	-0.0079(10)
C(41)	0.0263(9)	0.0386(12)	0.0230(9)	-0.0073(8)	0.0075(7)	-0.0067(8)
C(42)	0.0418(12)	0.0577(16)	0.0258(10)	-0.0017(10)	0.0041(9)	0.0004(11)
C(43)	0.0370(13)	0.107(3)	0.0260(11)	-0.0019(14)	0.0010(9)	-0.0016(15)
C(44)	0.0427(15)	0.110(3)	0.0371(14)	-0.0365(16)	0.0103(12)	-0.0254(16)
C(45)	0.0588(17)	0.0677(19)	0.0574(17)	-0.0373(15)	0.0199(14)	-0.0215(15)
C(46)	0.0443(13)	0.0420(13)	0.0408(12)	-0.0155(11)	0.0139(10)	-0.0065(11)
F(1)	0.041(2)	0.090(3)	0.139(4)	-0.019(3)	-0.008(2)	0.0023(18)
F(2)	0.0534(18)	0.0426(17)	0.082(2)	-0.0211(16)	-0.0072(16)	0.0031(14)
F(3)	0.0690(19)	0.0347(15)	0.0484(16)	-0.0013(12)	0.0153(14)	0.0009(14)
F(4)	0.166(5)	0.081(3)	0.073(3)	0.010(2)	0.060(3)	0.009(3)
B	0.041(2)	0.048(2)	0.057(3)	-0.0069(18)	0.0154(19)	0.0052(17)

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 S–6. Derived Parameters for Hydrogen Atoms of **2b**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H(4A)	0.0676	-0.2557	0.0651	0.029
H(4B)	0.1543	-0.2350	0.1479	0.029
H(12)	0.1370	-0.2869	-0.0562	0.040
H(13)	0.2365	-0.4076	-0.1194	0.048
H(14)	0.4418	-0.4078	-0.0953	0.054
H(15)	0.5469	-0.2896	-0.0074	0.059
H(16)	0.4494	-0.1687	0.0585	0.045
H(22)	0.3174	-0.1747	0.2117	0.051
H(23)	0.4602	-0.0944	0.3083	0.068
H(24)	0.5438	0.0645	0.2821	0.069
H(25)	0.4863	0.1420	0.1601	0.066
H(26)	0.3362	0.0684	0.0659	0.051
H(32)	-0.1312	-0.2926	0.0474	0.034
H(33)	-0.2801	-0.4069	0.0658	0.042
H(34)	-0.3567	-0.3981	0.1795	0.053
H(35)	-0.2831	-0.2750	0.2756	0.059
H(36)	-0.1332	-0.1606	0.2589	0.044
H(42)	0.1264	-0.2112	0.2752	0.051
H(43)	0.2230	-0.1447	0.3963	0.069
H(44)	0.2109	0.0322	0.4246	0.075
H(45)	0.1017	0.1430	0.3328	0.072
H(46)	0.0097	0.0807	0.2096	0.050

Table S–7. Crystallographic Experimental Details for **3b**

A. Crystal Data	
formula	$C_{55}H_{46}BF_4O_4P_4RhRu$
formula weight	1185.59
crystal dimensions (mm)	0.63 × 0.13 × 0.08
crystal system	monoclinic
space group	*I*2/*a* (an alternate setting of *C*2/*c* [No. 15])
unit cell parameters[a]	
a (Å)	42.754 (5)
b (Å)	10.2403 (12)
c (Å)	23.590 (3)
β (deg)	90.455 (2)
V (Å^3)	10327 (2)
Z	8
ρ_{calcd} (g cm^{-3})	1.525
μ (mm^{-1})	0.796
B. Data Collection and Refinement Conditions	
diffractometer	Bruker PLATFORM/SMART 1000 CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–80
scan type	ω scans (0.2°) (25 s exposures)
data collection 2θ limit (deg)	52.82
total data collected	22827 ($-53 \le h \le 45$, $-10 \le k \le 12$, $-29 \le l \le 29$)
independent reflections	10526 (R_{int} = 0.0400)
number of observed reflections (*NO*)	8180 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–86*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–93*[d])
absorption correction method	empirical (*SADABS*)
range of transmission factors	0.9391–0.6340
data/restraints/parameters	10526 [$F_o^2 \ge -3\sigma(F_o^2)$] / 0 / 626
goodness-of-fit (*S*)[e]	1.010 [$F_o^2 \ge -3\sigma(F_o^2)$]
final *R* indices[f]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0415
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.1051
largest difference peak and hole	1.482 and –0.698 e Å^{-3}

[a]Obtained from least-squares refinement of 4386 centered reflections.

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

(continued)

Table S–7. Crystallographic Experimental Details for **3b** (continued)

[c]Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

[d]Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). 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; $w = [\sigma^2(F_o^2) + (0.0587P)^2 + 0.0587P]^{-1}$ 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 S–8. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **3b**

(a) 'inner-core' atoms of $[RhRu(CO)_3(\mu\text{–}CO)(\mu\text{–}CH_2)(dppm)_2]^+$

Atom	*x*	*y*	*z*	U_{eq}, Å^2
Rh	0.152142(6)	0.37777(3)	0.106435(12)	0.02588(8)*
Ru	0.084784(6)	0.41857(3)	0.109499(12)	0.02358(8)*
P(1)	0.16071(2)	0.49647(9)	0.02501(4)	0.0276(2)*
P(2)	0.08612(2)	0.52709(9)	0.02023(4)	0.02625(19)*
P(3)	0.15668(2)	0.32711(9)	0.20333(4)	0.02521(19)*
P(4)	0.08641(2)	0.32582(9)	0.20209(4)	0.02518(19)*
O(1)	0.20400(7)	0.1878(3)	0.07745(14)	0.0498(7)*
O(2)	0.11551(6)	0.1808(3)	0.04637(12)	0.0407(7)*
O(3)	0.02568(6)	0.2633(3)	0.07947(13)	0.0469(7)*
O(4)	0.04860(7)	0.6418(3)	0.16386(12)	0.0438(7)*
C(1)	0.18324(9)	0.2528(4)	0.08767(16)	0.0331(8)*
C(2)	0.11582(8)	0.2743(4)	0.07441(16)	0.0302(8)*
C(3)	0.04834(9)	0.3171(4)	0.08971(16)	0.0331(8)*
C(4)	0.06194(8)	0.5593(3)	0.14276(16)	0.0303(8)*
C(5)	0.12599(7)	0.5414(3)	0.12959(15)	0.0274(7)*
C(6)	0.12450(8)	0.5254(4)	-0.01575(15)	0.0306(8)*
C(7)	0.12146(7)	0.3722(3)	0.24273(15)	0.0263(7)*

(b) dppm phenyl carbons

Atom	*x*	*y*	*z*	U_{eq}, Å^2
C(11)	0.18144(9)	0.6499(4)	0.03479(18)	0.0377(9)*
C(12)	0.19963(10)	0.6636(4)	0.0836(2)	0.0499(11)*
C(13)	0.21777(13)	0.7730(6)	0.0907(3)	0.0771(18)*
C(14)	0.21746(14)	0.8710(5)	0.0518(4)	0.087(2)*
C(15)	0.19914(13)	0.8610(5)	0.0042(4)	0.087(2)*
C(16)	0.18147(11)	0.7471(5)	-0.0053(3)	0.0639(15)*
C(21)	0.18411(9)	0.4099(4)	-0.02777(15)	0.0320(8)*
C(22)	0.17327(10)	0.2903(4)	-0.04789(17)	0.0409(9)*
C(23)	0.19108(11)	0.2159(4)	-0.08426(17)	0.0457(10)*
C(24)	0.22008(11)	0.2597(5)	-0.1012(2)	0.0549(12)*
C(25)	0.23097(10)	0.3766(5)	-0.0813(2)	0.0571(13)*
C(26)	0.21327(9)	0.4523(4)	-0.04488(18)	0.0418(10)*
C(31)	0.06215(8)	0.4575(4)	-0.03694(15)	0.0315(8)*
C(32)	0.06274(10)	0.3226(4)	-0.04502(18)	0.0451(10)*
C(33)	0.04697(11)	0.2669(5)	-0.0900(2)	0.0539(12)*
C(34)	0.02962(11)	0.3430(5)	-0.12675(19)	0.0557(13)*
C(35)	0.02894(11)	0.4740(5)	-0.11922(18)	0.0543(12)*
C(36)	0.04524(10)	0.5329(4)	-0.07484(17)	0.0423(10)*

Table S–8. Atomic Coordinates and Displacement Parameters for **3b** (continued)

Atom	*x*	*y*	*z*	U_{eq}, Å^2
C(41)	0.07315(8)	0.6955(3)	0.02215(15)	0.0295(8)*
C(42)	0.04194(9)	0.7208(4)	0.03561(17)	0.0399(9)*
C(43)	0.03043(12)	0.8470(4)	0.0343(2)	0.0535(12)*
C(44)	0.04997(13)	0.9482(4)	0.0195(2)	0.0572(13)*
C(45)	0.08030(13)	0.9244(4)	0.0068(2)	0.0556(13)*
C(46)	0.09233(10)	0.8004(4)	0.00801(17)	0.0423(10)*
C(51)	0.18919(8)	0.4106(4)	0.23839(16)	0.0326(8)*
C(52)	0.21896(10)	0.3805(6)	0.2204(2)	0.0685(16)*
C(53)	0.24475(11)	0.4420(7)	0.2431(3)	0.0809(19)*
C(54)	0.24166(11)	0.5342(6)	0.2834(2)	0.0669(15)*
C(55)	0.21222(12)	0.5636(5)	0.3033(2)	0.0647(15)*
C(56)	0.18598(10)	0.5022(4)	0.2802(2)	0.0489(11)*
C(61)	0.16315(7)	0.1576(3)	0.22488(16)	0.0287(8)*
C(62)	0.16109(8)	0.0550(4)	0.18639(18)	0.0374(9)*
C(63)	0.16522(9)	-0.0721(4)	0.2048(2)	0.0489(11)*
C(64)	0.17084(10)	-0.0969(5)	0.2617(3)	0.0588(14)*
C(65)	0.17290(10)	0.0036(5)	0.2999(2)	0.0541(13)*
C(66)	0.16917(9)	0.1307(4)	0.28169(18)	0.0395(9)*
C(71)	0.08466(8)	0.1487(3)	0.20942(16)	0.0288(8)*
C(72)	0.08187(8)	0.0664(3)	0.16316(16)	0.0303(8)*
C(73)	0.08242(9)	-0.0676(4)	0.17069(18)	0.0379(9)*
C(74)	0.08609(9)	-0.1196(4)	0.22400(19)	0.0388(9)*
C(75)	0.08809(9)	-0.0382(4)	0.27091(18)	0.0395(9)*
C(76)	0.08743(8)	0.0943(4)	0.26415(17)	0.0350(9)*
C(81)	0.05382(8)	0.3805(4)	0.24558(16)	0.0325(8)*
C(82)	0.02425(9)	0.3291(4)	0.23401(19)	0.0414(10)*
C(83)	-0.00168(10)	0.3741(5)	0.2628(2)	0.0570(14)*
C(84)	0.00141(11)	0.4706(5)	0.3029(2)	0.0639(15)*
C(85)	0.03047(12)	0.5214(5)	0.3149(2)	0.0596(13)*
C(86)	0.05696(10)	0.4775(4)	0.28628(18)	0.0431(10)*

(c) tetrafluoroborate ion atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
F(1)	0.12126(6)	0.6617(2)	0.30170(10)	0.0495(6)*
F(2A)[a]	0.13042(16)	0.5640(6)	0.3865(3)	0.0804(19)
F(3A)[a]	0.08757(13)	0.7022(5)	0.3728(2)	0.0741(14)
F(4A)[a]	0.13571(15)	0.7749(6)	0.3792(3)	0.0852(16)
B(1A)[a,b]	0.1172(2)	0.6670(11)	0.3586(5)	0.0478(18)
F(2B)[c]	0.11817(18)	0.5388(7)	0.3796(3)	0.0541(19)

Table S–8. Atomic Coordinates and Displacement Parameters for **3b** (continued)

Atom	*x*	*y*	*z*	U_{eq}, Å^2
B(1B)[b,c]	0.1261(4)	0.6720(17)	0.3623(8)	0.0478(18)
F(3B)[c]	0.1052(2)	0.7579(9)	0.3840(4)	0.086(2)
F(4B)[c]	0.1540(3)	0.7174(11)	0.3739(5)	0.109(3)

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$. [a]Refined with an occupancy factor of 0.6. [b]The boron atoms were refined with a common isotropic displacement parameter. [c]Refined with an occupancy factor of 0.4.

Table S–9. Selected Interatomic Distances (Å) for **3b**

(a) involving 'inner-core' atoms of $[RhRu(CO)_3(\mu\text{–}CO)(\mu\text{–}CH_2)(dppm)_2]^+$

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Rh	Ru	2.9114(5)	Ru	C(5)	2.213(3)
Rh	P(1)	2.3047(10)	P(1)	P(2)	3.2052(13)†
Rh	P(3)	2.3505(10)	P(1)	C(6)	1.840(3)
Rh	C(1)	1.900(4)	P(2)	C(6)	1.853(4)
Rh	C(2)	2.021(3)	P(3)	P(4)	3.0042(12)†
Rh	C(5)	2.089(3)	P(3)	C(7)	1.835(3)
Ru	P(2)	2.3821(10)	P(4)	C(7)	1.835(3)
Ru	P(4)	2.3822(10)	O(1)	C(1)	1.137(4)
Ru	C(2)	2.155(4)	O(2)	C(2)	1.164(4)
Ru	C(3)	1.927(4)	O(3)	C(3)	1.139(4)
Ru	C(4)	1.913(4)	O(4)	C(4)	1.136(4)

†Nonbonded distance.

(b) involving dppm phenyl carbons

Atom1	Atom2	Distance	Atom1	Atom2	Distance
P(1)	C(11)	1.818(4)	C(34)	C(35)	1.353(7)
P(1)	C(21)	1.832(4)	C(35)	C(36)	1.390(6)
P(2)	C(31)	1.832(3)	C(41)	C(42)	1.398(5)
P(2)	C(41)	1.813(3)	C(41)	C(46)	1.393(5)
P(3)	C(51)	1.824(4)	C(42)	C(43)	1.383(6)
P(3)	C(61)	1.829(4)	C(43)	C(44)	1.378(7)
P(4)	C(71)	1.824(3)	C(44)	C(45)	1.355(7)
P(4)	C(81)	1.825(4)	C(45)	C(46)	1.371(6)
C(11)	C(12)	1.391(6)	C(51)	C(52)	1.380(6)
C(11)	C(16)	1.372(6)	C(51)	C(56)	1.368(5)
C(12)	C(13)	1.372(6)	C(52)	C(53)	1.375(6)
C(13)	C(14)	1.360(9)	C(53)	C(54)	1.346(7)
C(14)	C(15)	1.369(9)	C(54)	C(55)	1.380(7)
C(15)	C(16)	1.406(7)	C(55)	C(56)	1.393(6)
C(21)	C(22)	1.392(5)	C(61)	C(62)	1.391(5)
C(21)	C(26)	1.383(5)	C(61)	C(66)	1.390(5)
C(22)	C(23)	1.381(6)	C(62)	C(63)	1.383(6)
C(23)	C(24)	1.381(6)	C(63)	C(64)	1.385(7)
C(24)	C(25)	1.366(6)	C(64)	C(65)	1.371(7)
C(25)	C(26)	1.387(6)	C(65)	C(66)	1.379(6)
C(31)	C(32)	1.395(6)	C(71)	C(72)	1.383(5)
C(31)	C(36)	1.381(5)	C(71)	C(76)	1.410(5)
C(32)	C(33)	1.376(6)	C(72)	C(73)	1.384(5)
C(33)	C(34)	1.378(7)	C(73)	C(74)	1.374(6)

Table S–9. Selected Interatomic Distances for **3b** (continued)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
C(74)	C(75)	1.387(6)	C(82)	C(83)	1.384(6)
C(75)	C(76)	1.367(5)	C(83)	C(84)	1.373(8)
C(81)	C(82)	1.394(5)	C(84)	C(85)	1.374(7)
C(81)	C(86)	1.388(6)	C(85)	C(86)	1.397(6)

(c) within the teterafluoroborate ion

Atom1	Atom2	Distance	Atom1	Atom2	Distance
F(1)	B(1A)	1.357(12)	F(4A)	B(1A)	1.440(13)
F(1)	B(1B)	1.446(18)	F(2B)	B(1B)	1.465(19)
F(2A)	B(1A)	1.363(13)	F(3B)	B(1B)	1.36(2)
F(3A)	B(1A)	1.362(12)	F(4B)	B(1B)	1.307(18)

Table S–10. Selected Interatomic Angles (deg) for **3b**

(a) involving 'inner-core' atoms of $[RhRu(CO)_3(\mu\text{–}CO)(\mu\text{–}CH_2)(dppm)_2]^+$

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Ru	Rh	P(1)	96.24(2)	P(2)	Ru	C(5)	84.23(10)
Ru	Rh	P(3)	94.68(2)	P(4)	Ru	C(2)	93.74(10)
Ru	Rh	C(1)	142.80(11)	P(4)	Ru	C(3)	91.42(11)
Ru	Rh	C(2)	47.73(10)	P(4)	Ru	C(4)	86.31(11)
Ru	Rh	C(5)	49.24(9)	P(4)	Ru	C(5)	90.74(10)
P(1)	Rh	P(3)	156.12(3)	C(2)	Ru	C(3)	92.09(14)
P(1)	Rh	C(1)	92.58(12)	C(2)	Ru	C(4)	172.67(14)
P(1)	Rh	C(2)	95.25(10)	C(2)	Ru	C(5)	88.87(13)
P(1)	Rh	C(5)	83.32(10)	C(3)	Ru	C(4)	95.23(15)
P(3)	Rh	C(1)	91.45(12)	C(3)	Ru	C(5)	177.57(14)
P(3)	Rh	C(2)	107.76(10)	C(4)	Ru	C(5)	83.80(14)
P(3)	Rh	C(5)	87.88(10)	Rh	P(1)	C(6)	112.45(12)
C(1)	Rh	C(2)	95.56(15)	Ru	P(2)	C(6)	115.35(12)
C(1)	Rh	C(5)	167.91(14)	Rh	P(3)	C(7)	112.04(12)
C(2)	Rh	C(5)	96.14(14)	Ru	P(4)	C(7)	113.18(12)
Rh	Ru	P(2)	90.82(2)	Rh	C(1)	O(1)	173.0(3)
Rh	Ru	P(4)	86.78(2)	Rh	C(2)	Ru	88.33(14)
Rh	Ru	C(2)	43.94(9)	Rh	C(2)	O(2)	130.4(3)
Rh	Ru	C(3)	135.61(11)	Ru	C(2)	O(2)	141.1(3)
Rh	Ru	C(4)	128.80(10)	Ru	C(3)	O(3)	175.7(3)
Rh	Ru	C(5)	45.65(9)	Ru	C(4)	O(4)	178.2(3)
P(2)	Ru	P(4)	174.72(3)	Rh	C(5)	Ru	85.12(12)
P(2)	Ru	C(2)	87.76(10)	P(1)	C(6)	P(2)	120.4(2)
P(2)	Ru	C(3)	93.58(11)	P(3)	C(7)	P(4)	109.89(18)
P(2)	Ru	C(4)	91.55(11)				

(b) involving dppm phenyl carbons

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Rh	P(1)	C(11)	115.51(14)	Rh	P(3)	C(61)	119.40(12)
Rh	P(1)	C(21)	113.73(12)	C(7)	P(3)	C(51)	106.12(17)
C(6)	P(1)	C(11)	109.54(18)	C(7)	P(3)	C(61)	102.77(16)
C(6)	P(1)	C(21)	100.63(17)	C(51)	P(3)	C(61)	101.88(16)
C(11)	P(1)	C(21)	103.65(17)	Ru	P(4)	C(71)	118.85(13)
Ru	P(2)	C(31)	116.88(12)	Ru	P(4)	C(81)	112.10(12)
Ru	P(2)	C(41)	114.35(12)	C(7)	P(4)	C(71)	104.00(16)
C(6)	P(2)	C(31)	98.70(17)	C(7)	P(4)	C(81)	104.53(17)
C(6)	P(2)	C(41)	107.01(17)	C(71)	P(4)	C(81)	102.68(16)
C(31)	P(2)	C(41)	102.66(17)	P(1)	C(11)	C(12)	117.5(3)
Rh	P(3)	C(51)	113.21(13)	P(1)	C(11)	C(16)	122.9(4)

Table S–10. Selected Interatomic Angles for **3b** (continued)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C(12)	C(11)	C(16)	119.5(4)	P(3)	C(51)	C(56)	124.6(3)
C(11)	C(12)	C(13)	119.8(5)	C(52)	C(51)	C(56)	118.2(4)
C(12)	C(13)	C(14)	121.1(6)	C(51)	C(52)	C(53)	121.1(5)
C(13)	C(14)	C(15)	120.1(5)	C(52)	C(53)	C(54)	120.9(5)
C(14)	C(15)	C(16)	119.7(6)	C(53)	C(54)	C(55)	119.2(4)
C(11)	C(16)	C(15)	119.8(5)	C(54)	C(55)	C(56)	120.2(5)
P(1)	C(21)	C(22)	118.4(3)	C(51)	C(56)	C(55)	120.4(4)
P(1)	C(21)	C(26)	123.0(3)	P(3)	C(61)	C(62)	121.8(3)
C(22)	C(21)	C(26)	118.4(4)	P(3)	C(61)	C(66)	118.8(3)
C(21)	C(22)	C(23)	120.9(4)	C(62)	C(61)	C(66)	119.3(4)
C(22)	C(23)	C(24)	120.1(4)	C(61)	C(62)	C(63)	120.0(4)
C(23)	C(24)	C(25)	119.3(4)	C(62)	C(63)	C(64)	119.8(4)
C(24)	C(25)	C(26)	121.1(4)	C(63)	C(64)	C(65)	120.6(4)
C(21)	C(26)	C(25)	120.2(4)	C(64)	C(65)	C(66)	119.8(5)
P(2)	C(31)	C(32)	118.4(3)	C(61)	C(66)	C(65)	120.4(4)
P(2)	C(31)	C(36)	123.1(3)	P(4)	C(71)	C(72)	122.3(3)
C(32)	C(31)	C(36)	118.4(3)	P(4)	C(71)	C(76)	118.4(3)
C(31)	C(32)	C(33)	120.4(4)	C(72)	C(71)	C(76)	119.2(3)
C(32)	C(33)	C(34)	120.6(4)	C(71)	C(72)	C(73)	120.1(4)
C(33)	C(34)	C(35)	119.3(4)	C(72)	C(73)	C(74)	120.2(4)
C(34)	C(35)	C(36)	121.2(4)	C(73)	C(74)	C(75)	120.2(4)
C(31)	C(36)	C(35)	120.1(4)	C(74)	C(75)	C(76)	120.1(4)
P(2)	C(41)	C(42)	118.3(3)	C(71)	C(76)	C(75)	120.0(4)
P(2)	C(41)	C(46)	123.1(3)	P(4)	C(81)	C(82)	118.0(3)
C(42)	C(41)	C(46)	118.5(4)	P(4)	C(81)	C(86)	122.6(3)
C(41)	C(42)	C(43)	120.5(4)	C(82)	C(81)	C(86)	119.2(4)
C(42)	C(43)	C(44)	119.5(5)	C(81)	C(82)	C(83)	120.5(5)
C(43)	C(44)	C(45)	120.2(4)	C(82)	C(83)	C(84)	120.3(4)
C(44)	C(45)	C(46)	121.4(4)	C(83)	C(84)	C(85)	119.7(4)
C(41)	C(46)	C(45)	119.8(4)	C(84)	C(85)	C(86)	120.9(5)
P(3)	C(51)	C(52)	117.2(3)	C(81)	C(86)	C(85)	119.3(4)

(c) within the teterafluoroborate ion

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
F(1)	B(1A)	F(2A)	113.0(9)	F(1)	B(1B)	F(2B)	100.1(11)
F(1)	B(1A)	F(3A)	112.4(8)	F(1)	B(1B)	F(3B)	109.3(12)
F(1)	B(1A)	F(4A)	106.9(8)	F(1)	B(1B)	F(4B)	110.9(13)
F(2A)	B(1A)	F(3A)	118.0(9)	F(2B)	B(1B)	F(3B)	110.1(13)
F(2A)	B(1A)	F(4A)	101.9(8)	F(2B)	B(1B)	F(4B)	119.1(14)
F(3A)	B(1A)	F(4A)	102.9(8)	F(3B)	B(1B)	F(4B)	107.1(14)

Table S–11. Anisotropic Displacement Parameters (U_{ij}, Å^2) for **3b**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh	0.02247(15)	0.03061(15)	0.02458(16)	0.00004(11)	0.00110(11)	0.00120(10)
Ru	0.01961(14)	0.02574(15)	0.02536(16)	0.00036(11)	-0.00213(11)	-0.00238(10)
P(1)	0.0231(5)	0.0331(5)	0.0266(5)	0.0006(4)	0.0006(4)	-0.0027(4)
P(2)	0.0227(4)	0.0292(5)	0.0269(5)	0.0008(4)	-0.0032(4)	-0.0027(3)
P(3)	0.0185(4)	0.0318(5)	0.0253(5)	-0.0009(4)	-0.0013(4)	-0.0004(3)
P(4)	0.0175(4)	0.0308(5)	0.0272(5)	0.0014(4)	0.0001(4)	0.0005(3)
O(1)	0.0407(17)	0.0480(17)	0.061(2)	0.0018(14)	0.0099(15)	0.0144(14)
O(2)	0.0360(15)	0.0346(15)	0.0517(18)	-0.0129(13)	0.0049(13)	-0.0061(11)
O(3)	0.0278(15)	0.0521(18)	0.061(2)	-0.0064(14)	-0.0078(14)	-0.0123(13)
O(4)	0.0488(17)	0.0364(16)	0.0462(18)	-0.0038(13)	0.0019(14)	0.0075(13)
C(1)	0.033(2)	0.035(2)	0.032(2)	0.0020(15)	0.0025(16)	0.0000(16)
C(2)	0.0227(18)	0.036(2)	0.032(2)	0.0031(16)	0.0012(15)	-0.0051(14)
C(3)	0.034(2)	0.0329(19)	0.033(2)	0.0030(15)	-0.0017(17)	0.0004(16)
C(4)	0.0282(19)	0.0308(19)	0.032(2)	0.0042(15)	-0.0035(16)	-0.0042(15)
C(5)	0.0207(17)	0.0324(18)	0.0291(19)	0.0004(14)	-0.0010(14)	-0.0020(14)
C(6)	0.0257(18)	0.038(2)	0.028(2)	0.0041(15)	-0.0022(15)	-0.0005(15)
C(7)	0.0202(17)	0.0329(18)	0.0257(19)	-0.0019(14)	-0.0017(14)	-0.0005(13)
C(11)	0.0271(19)	0.035(2)	0.051(3)	-0.0050(18)	0.0085(18)	-0.0063(15)
C(12)	0.045(3)	0.054(3)	0.051(3)	-0.013(2)	0.003(2)	-0.021(2)
C(13)	0.065(4)	0.079(4)	0.088(4)	-0.038(3)	0.011(3)	-0.036(3)
C(14)	0.057(4)	0.050(3)	0.156(7)	-0.023(4)	0.029(4)	-0.022(3)
C(15)	0.051(3)	0.047(3)	0.162(7)	0.031(4)	0.016(4)	-0.008(2)
C(16)	0.038(3)	0.055(3)	0.099(4)	0.025(3)	-0.001(3)	-0.009(2)
C(21)	0.032(2)	0.040(2)	0.0246(19)	0.0037(15)	-0.0015(16)	0.0036(15)
C(22)	0.045(2)	0.046(2)	0.032(2)	0.0007(17)	0.0075(18)	-0.0004(18)
C(23)	0.056(3)	0.051(2)	0.030(2)	-0.0070(18)	-0.004(2)	0.009(2)
C(24)	0.050(3)	0.073(3)	0.041(3)	-0.007(2)	0.007(2)	0.016(2)
C(25)	0.030(2)	0.083(4)	0.058(3)	-0.009(3)	0.011(2)	0.000(2)
C(26)	0.028(2)	0.058(3)	0.040(2)	-0.0038(19)	0.0010(18)	-0.0001(17)
C(31)	0.0261(19)	0.044(2)	0.0246(19)	-0.0024(15)	-0.0033(15)	-0.0086(15)
C(32)	0.049(3)	0.047(2)	0.039(2)	-0.0078(19)	-0.006(2)	-0.0071(19)
C(33)	0.059(3)	0.056(3)	0.047(3)	-0.018(2)	-0.002(2)	-0.014(2)
C(34)	0.047(3)	0.087(4)	0.033(3)	-0.018(2)	-0.003(2)	-0.021(2)
C(35)	0.043(3)	0.089(4)	0.030(2)	0.002(2)	-0.012(2)	-0.001(2)
C(36)	0.041(2)	0.052(2)	0.034(2)	0.0024(18)	-0.0081(19)	-0.0017(19)
C(41)	0.033(2)	0.0268(18)	0.029(2)	0.0020(14)	-0.0082(16)	0.0014(14)
C(42)	0.036(2)	0.042(2)	0.042(2)	0.0063(18)	-0.0045(18)	0.0034(17)
C(43)	0.053(3)	0.054(3)	0.053(3)	0.000(2)	-0.010(2)	0.019(2)
C(44)	0.089(4)	0.033(2)	0.050(3)	-0.0016(19)	-0.012(3)	0.014(2)
C(45)	0.080(4)	0.031(2)	0.055(3)	-0.005(2)	-0.002(3)	-0.011(2)

Table S–11. Anisotropic Displacement Parameters for **3b** (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(46)	0.048(2)	0.038(2)	0.040(2)	-0.0026(17)	-0.001(2)	-0.0107(18)
C(51)	0.0244(18)	0.040(2)	0.033(2)	0.0006(16)	-0.0034(16)	-0.0053(15)
C(52)	0.024(2)	0.107(4)	0.074(4)	-0.046(3)	0.004(2)	-0.012(2)
C(53)	0.022(2)	0.134(5)	0.087(4)	-0.037(4)	0.006(3)	-0.016(3)
C(54)	0.039(3)	0.085(4)	0.076(4)	-0.020(3)	-0.014(3)	-0.021(2)
C(55)	0.052(3)	0.065(3)	0.077(4)	-0.029(3)	-0.020(3)	-0.004(2)
C(56)	0.031(2)	0.050(3)	0.065(3)	-0.020(2)	-0.012(2)	0.0034(18)
C(61)	0.0144(16)	0.0345(19)	0.037(2)	0.0032(15)	-0.0001(14)	0.0015(13)
C(62)	0.0257(19)	0.038(2)	0.049(3)	0.0018(17)	0.0029(17)	-0.0010(15)
C(63)	0.031(2)	0.038(2)	0.078(4)	0.002(2)	0.008(2)	-0.0017(17)
C(64)	0.030(2)	0.050(3)	0.097(4)	0.033(3)	0.000(2)	0.0016(19)
C(65)	0.031(2)	0.068(3)	0.063(3)	0.029(3)	-0.008(2)	-0.002(2)
C(66)	0.031(2)	0.045(2)	0.042(2)	0.0085(18)	-0.0061(18)	-0.0031(17)
C(71)	0.0162(16)	0.0315(19)	0.039(2)	0.0092(15)	0.0003(15)	-0.0024(13)
C(72)	0.0248(18)	0.0342(19)	0.032(2)	0.0051(15)	-0.0047(15)	-0.0049(14)
C(73)	0.032(2)	0.034(2)	0.048(3)	-0.0019(17)	-0.0048(18)	-0.0082(16)
C(74)	0.029(2)	0.033(2)	0.055(3)	0.0106(18)	-0.0071(18)	-0.0028(15)
C(75)	0.031(2)	0.045(2)	0.043(2)	0.0159(18)	-0.0017(18)	-0.0037(17)
C(76)	0.0263(19)	0.042(2)	0.037(2)	0.0063(16)	-0.0003(16)	-0.0019(15)
C(81)	0.0249(18)	0.039(2)	0.034(2)	0.0122(16)	0.0076(16)	0.0092(15)
C(82)	0.0238(19)	0.054(2)	0.047(3)	0.0196(19)	0.0018(17)	0.0036(17)
C(83)	0.026(2)	0.073(3)	0.072(4)	0.034(3)	0.009(2)	0.013(2)
C(84)	0.037(3)	0.074(3)	0.081(4)	0.032(3)	0.031(3)	0.031(2)
C(85)	0.061(3)	0.054(3)	0.064(3)	0.005(2)	0.024(3)	0.024(2)
C(86)	0.037(2)	0.045(2)	0.048(3)	0.0009(19)	0.0110(19)	0.0076(18)
F(1)	0.0597(16)	0.0454(14)	0.0435(15)	-0.0104(11)	0.0018(12)	0.0024(11)

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 S–12. Derived Parameters for Hydrogen Atoms of **3b**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H(5A)	0.1286	0.6179	0.1044	0.033
H(5B)	0.1280	0.5661	0.1700	0.033
H(6A)	0.1234	0.4578	-0.0457	0.037
H(6B)	0.1268	0.6105	-0.0351	0.037
H(7A)	0.1214	0.4676	0.2497	0.032
H(7B)	0.1215	0.3273	0.2799	0.032
H(12)	0.1995	0.5975	0.1118	0.060
H(13)	0.2308	0.7803	0.1234	0.093
H(14)	0.2300	0.9465	0.0577	0.105
H(15)	0.1984	0.9306	-0.0224	0.104
H(16)	0.1696	0.7375	-0.0392	0.077
H(22)	0.1533	0.2594	-0.0364	0.049
H(23)	0.1834	0.1344	-0.0976	0.055
H(24)	0.2323	0.2091	-0.1265	0.066
H(25)	0.2510	0.4064	-0.0926	0.069
H(26)	0.2212	0.5335	-0.0316	0.050
H(32)	0.0741	0.2688	-0.0193	0.054
H(33)	0.0481	0.1752	-0.0958	0.065
H(34)	0.0183	0.3040	-0.1571	0.067
H(35)	0.0171	0.5266	-0.1447	0.065
H(36)	0.0447	0.6251	-0.0706	0.051
H(42)	0.0285	0.6507	0.0458	0.048
H(43)	0.0092	0.8637	0.0434	0.064
H(44)	0.0422	1.0350	0.0182	0.069
H(45)	0.0935	0.9953	-0.0031	0.067
H(46)	0.1137	0.7859	-0.0008	0.051
H(52)	0.2217	0.3161	0.1919	0.082
H(53)	0.2650	0.4192	0.2302	0.097
H(54)	0.2595	0.5785	0.2979	0.080
H(55)	0.2098	0.6258	0.3328	0.078
H(56)	0.1657	0.5241	0.2935	0.059
H(62)	0.1569	0.0722	0.1475	0.045
H(63)	0.1642	-0.1422	0.1784	0.059
H(64)	0.1733	-0.1844	0.2743	0.071
H(65)	0.1769	-0.0142	0.3388	0.065
H(66)	0.1707	0.2004	0.3082	0.047
H(72)	0.0796	0.1020	0.1262	0.036
H(73)	0.0803	-0.1238	0.1389	0.046
H(74)	0.0873	-0.2116	0.2288	0.047
H(75)	0.0899	-0.0747	0.3078	0.047

Table S–12. Derived Parameters for Hydrogen Atoms of **3b** (continued)

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H(76)	0.0888	0.1498	0.2963	0.042
H(82)	0.0219	0.2628	0.2062	0.050
H(83)	-0.0217	0.3381	0.2548	0.068
H(84)	-0.0165	0.5021	0.3223	0.077
H(85)	0.0326	0.5872	0.3431	0.072
H(86)	0.0769	0.5138	0.2946	0.052

Table S–13. Crystallographic Experimental Details for **5b**

A. Crystal Data	
formula	$C_{59}H_{59}BCl_4F_4O_3P_5RhRu$
formula weight	1403.50
crystal dimensions (mm)	0.38 × 0.16 × 0.07
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters[a]	
a (Å)	20.3808 (13)
b (Å)	12.7481 (9)
c (Å)	23.2397 (14)
β (deg)	91.4953 (16)
V (Å^3)	6036.0 (7)
Z	4
ρ_{calcd} (g cm^{-3})	1.544
μ (mm^{-1})	0.889
B. Data Collection and Refinement Conditions	
diffractometer	Bruker P4/RA/SMART 1000 CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–80
scan type	ϕ rotations (0.3°) / ω scans (0.3°) (30 s exposures)
data collection 2θ limit (deg)	52.82
total data collected	29512 (-25 ≤ h ≤ 22, -15 ≤ k ≤ 15, -29 ≤ l ≤ 14)
independent reflections	12333
number of observations (*NO*)	7751 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–86*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–93*[d])
absorption correction method	*SADABS*
range of transmission factors	0.9562–0.7304
data/restraints/parameters	12333 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 703
goodness-of-fit (S)[e]	0.951 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices[f]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0506
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.1200
largest difference peak and hole	1.205 and –1.097 e Å^{-3}

[a]Obtained from least-squares refinement of 6861 centered reflections.

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

(continued)

Table S–13. Crystallographic Experimental Details for **5b** (continued)

[c]Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

[d]Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). 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; $w = [\sigma^2(F_o^2) + (0.0527P)^2]^{-1}$ 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 S–14. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **5b**

(a) 'inner-core' atoms of $[RhRu(CO)_3(PMe_3)(\mu\text{–}CH_2)(dppm)_2]^+$

Atom	*x*	*y*	*z*	U_{eq}, Å^2
Rh	0.229375(19)	0.56397(3)	0.402432(15)	0.01869(10)*
Ru	0.330725(19)	0.54563(3)	0.318010(16)	0.01892(11)*
P(1)	0.26559(6)	0.73469(10)	0.42214(5)	0.0209(3)*
P(2)	0.35624(6)	0.72543(10)	0.32250(5)	0.0204(3)*
P(3)	0.21936(6)	0.38342(10)	0.39229(5)	0.0198(3)*
P(4)	0.29099(6)	0.38207(10)	0.28343(5)	0.0203(3)*
P(5)	0.11416(7)	0.59800(11)	0.38930(6)	0.0259(3)*
O(1)	0.2463(2)	0.5324(3)	0.53142(14)	0.0425(11)*
O(2)	0.44516(17)	0.4754(3)	0.39701(15)	0.0361(9)*
O(3)	0.40926(19)	0.5478(3)	0.20941(16)	0.0433(10)*
C(1)	0.2406(2)	0.5418(4)	0.4829(2)	0.0269(12)*
C(2)	0.4029(2)	0.4996(4)	0.3675(2)	0.0231(11)*
C(3)	0.3783(3)	0.5476(4)	0.2508(2)	0.0264(12)*
C(4)	0.2310(2)	0.5916(4)	0.31129(18)	0.0226(11)*
C(5)	0.2962(2)	0.8050(4)	0.35949(19)	0.0215(11)*
C(6)	0.2146(2)	0.3411(4)	0.31704(18)	0.0205(11)*
C(7)	0.0709(3)	0.5249(4)	0.3324(2)	0.0333(13)*
C(8)	0.0872(3)	0.7296(4)	0.3691(3)	0.0474(17)*
C(9)	0.0640(3)	0.5705(5)	0.4506(2)	0.0409(15)*

(b) dppm phenyl carbons of $[RhRu(CO)_3(PMe_3)(\mu\text{–}CH_2)(dppm)_2]^+$

Atom	*x*	*y*	*z*	U_{eq}, Å^2
C(11)	0.3334(2)	0.7479(4)	0.47596(19)	0.0237(12)*
C(12)	0.3801(2)	0.6692(4)	0.4818(2)	0.0304(13)*
C(13)	0.4338(3)	0.6829(5)	0.5190(2)	0.0402(15)*
C(14)	0.4401(3)	0.7725(5)	0.5518(2)	0.0476(17)*
C(15)	0.3926(3)	0.8496(5)	0.5474(2)	0.0468(17)*
C(16)	0.3398(3)	0.8384(4)	0.5093(2)	0.0340(14)*
C(21)	0.2059(2)	0.8262(4)	0.4506(2)	0.0239(11)*
C(22)	0.1755(3)	0.7994(4)	0.5017(2)	0.0296(13)*
C(23)	0.1275(3)	0.8653(4)	0.5243(2)	0.0360(14)*
C(24)	0.1108(3)	0.9573(4)	0.4957(3)	0.0390(15)*
C(25)	0.1409(3)	0.9836(4)	0.4453(3)	0.0418(15)*
C(26)	0.1881(3)	0.9202(4)	0.4230(2)	0.0293(12)*
C(31)	0.3569(2)	0.7915(4)	0.25210(19)	0.0222(11)*
C(32)	0.4100(3)	0.8462(4)	0.2328(2)	0.0294(12)*
C(33)	0.4073(3)	0.8989(4)	0.1799(2)	0.0389(15)*
C(34)	0.3507(3)	0.8970(5)	0.1464(2)	0.0451(16)*
C(35)	0.2972(3)	0.8425(5)	0.1654(2)	0.0531(19)*

Table S–14. Atomic Coordinates and Displacement Parameters (continued)

Atom	*x*	*y*	*z*	U_{eq}, Å^2
C(36)	0.2992(3)	0.7897(5)	0.2174(2)	0.0420(16)*
C(41)	0.4367(2)	0.7634(4)	0.3521(2)	0.0249(12)*
C(42)	0.4480(3)	0.8555(4)	0.3839(2)	0.0331(13)*
C(43)	0.5116(3)	0.8863(5)	0.3982(2)	0.0390(15)*
C(44)	0.5648(3)	0.8274(5)	0.3818(2)	0.0430(16)*
C(45)	0.5543(3)	0.7349(5)	0.3518(2)	0.0360(14)*
C(46)	0.4906(3)	0.7032(4)	0.3366(2)	0.0307(13)*
C(51)	0.1479(2)	0.3223(4)	0.4251(2)	0.0218(11)*
C(52)	0.0976(2)	0.2718(4)	0.3943(2)	0.0299(13)*
C(53)	0.0459(3)	0.2267(4)	0.4227(3)	0.0373(14)*
C(54)	0.0438(3)	0.2292(4)	0.4819(3)	0.0392(15)*
C(55)	0.0940(3)	0.2769(4)	0.5127(2)	0.0382(14)*
C(56)	0.1456(3)	0.3229(4)	0.4856(2)	0.0313(13)*
C(61)	0.2826(2)	0.2995(4)	0.4251(2)	0.0222(11)*
C(62)	0.2765(3)	0.1910(4)	0.4191(2)	0.0299(13)*
C(63)	0.3229(3)	0.1244(5)	0.4427(2)	0.0401(15)*
C(64)	0.3762(3)	0.1639(5)	0.4738(2)	0.0386(15)*
C(65)	0.3821(3)	0.2720(5)	0.4817(2)	0.0374(14)*
C(66)	0.3356(2)	0.3388(4)	0.4576(2)	0.0275(12)*
C(71)	0.3446(2)	0.2671(4)	0.29071(19)	0.0232(11)*
C(72)	0.4118(3)	0.2804(4)	0.2983(2)	0.0267(12)*
C(73)	0.4528(3)	0.1936(4)	0.3037(2)	0.0322(13)*
C(74)	0.4273(3)	0.0941(4)	0.3000(2)	0.0370(14)*
C(75)	0.3610(3)	0.0797(4)	0.2910(3)	0.0409(15)*
C(76)	0.3196(3)	0.1648(4)	0.2872(2)	0.0325(13)*
C(81)	0.2671(2)	0.3829(4)	0.20593(19)	0.0244(12)*
C(82)	0.2560(3)	0.4776(5)	0.1773(2)	0.0370(14)*
C(83)	0.2375(3)	0.4789(6)	0.1197(2)	0.0537(19)*
C(84)	0.2315(3)	0.3867(6)	0.0897(3)	0.058(2)*
C(85)	0.2422(3)	0.2929(6)	0.1168(3)	0.058(2)*
C(86)	0.2603(3)	0.2902(5)	0.1754(2)	0.0468(17)*

(c) tetrafluoroborate ion atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
F(1)	0.1662(2)	0.0937(3)	0.32112(16)	0.0645(11)*
F(2)	0.1745(3)	0.0688(5)	0.2269(2)	0.132(2)*
F(3)	0.1629(4)	-0.0671(4)	0.2848(2)	0.147(3)*
F(4)	0.0827(3)	0.0361(6)	0.2649(3)	0.160(3)*
B	0.1463(5)	0.0347(6)	0.2750(4)	0.059(2)*

Table S–14. Atomic Coordinates and Displacement Parameters (continued)

(d) solvent dichloromethane atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
Cl(1S)	0.06541(13)	0.1949(2)	-0.28284(10)	0.1101(9)*
Cl(2S)	0.03740(17)	0.0610(2)	-0.38195(10)	0.1278(11)*
C(1S)	0.0449(7)	0.0717(8)	-0.3132(4)	0.165(6)*
Cl(3S)	0.10087(12)	-0.39010(18)	-0.39001(9)	0.0882(7)*
Cl(4S)	0.12002(12)	-0.2072(2)	-0.31660(9)	0.0932(7)*
C(2S)	0.0939(5)	-0.3351(8)	-0.3225(3)	0.110(4)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Table S–15. Selected Interatomic Distances (Å) for **5b**

(a) involving 'inner-core' atoms of $[RhRu(CO)_3(PMe_3)(\mu\text{–}CH_2)(dppm)_2]^+$

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Rh	Ru	2.8952(6)	P(1)	C(5)	1.833(5)
Rh	P(1)	2.3396(13)	P(2)	C(5)	1.822(5)
Rh	P(3)	2.3221(13)	P(3)	P(4)	2.9537(18)†
Rh	P(5)	2.3996(14)	P(3)	C(6)	1.830(4)
Rh	C(1)	1.900(5)	P(4)	C(6)	1.836(5)
Rh	C(4)	2.148(4)	P(5)	C(7)	1.826(5)
Ru	P(2)	2.3520(13)	P(5)	C(8)	1.822(5)
Ru	P(4)	2.3697(13)	P(5)	C(9)	1.809(6)
Ru	C(2)	1.934(5)	O(1)	C(1)	1.136(6)
Ru	C(3)	1.860(5)	O(2)	C(2)	1.130(5)
Ru	C(4)	2.117(5)	O(3)	C(3)	1.164(6)
P(1)	P(2)	3.0022(19)†			

†Nonbonded distance.

(b) involving dppm phenyl carbons of $[RhRu(CO)_3(PMe_3)(\mu\text{–}CH_2)(dppm)_2]^+$

Atom1	Atom2	Distance	Atom1	Atom2	Distance
P(1)	C(11)	1.847(5)	C(33)	C(34)	1.376(7)
P(1)	C(21)	1.822(5)	C(34)	C(35)	1.375(8)
P(2)	C(31)	1.841(5)	C(35)	C(36)	1.383(7)
P(2)	C(41)	1.826(5)	C(41)	C(42)	1.404(7)
P(3)	C(51)	1.834(5)	C(41)	C(46)	1.394(7)
P(3)	C(61)	1.826(5)	C(42)	C(43)	1.387(7)
P(4)	C(71)	1.833(5)	C(43)	C(44)	1.380(8)
P(4)	C(81)	1.853(5)	C(44)	C(45)	1.384(8)
C(11)	C(12)	1.387(7)	C(45)	C(46)	1.396(7)
C(11)	C(16)	1.394(7)	C(51)	C(52)	1.394(6)
C(12)	C(13)	1.388(7)	C(51)	C(56)	1.408(7)
C(13)	C(14)	1.377(8)	C(52)	C(53)	1.383(7)
C(14)	C(15)	1.382(8)	C(53)	C(54)	1.380(8)
C(15)	C(16)	1.382(7)	C(54)	C(55)	1.374(7)
C(21)	C(22)	1.395(7)	C(55)	C(56)	1.372(7)
C(21)	C(26)	1.403(7)	C(61)	C(62)	1.395(7)
C(22)	C(23)	1.402(7)	C(61)	C(66)	1.395(6)
C(23)	C(24)	1.386(8)	C(62)	C(63)	1.375(7)
C(24)	C(25)	1.378(8)	C(63)	C(64)	1.383(7)
C(25)	C(26)	1.369(7)	C(64)	C(65)	1.395(8)
C(31)	C(32)	1.371(7)	C(65)	C(66)	1.382(7)
C(31)	C(36)	1.410(7)	C(71)	C(72)	1.387(7)
C(32)	C(33)	1.400(7)	C(71)	C(76)	1.402(7)

Table S–15. Selected Interatomic Distances for **5b** (continued)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
C(72)	C(73)	1.391(7)	C(81)	C(86)	1.384(7)
C(73)	C(74)	1.373(7)	C(82)	C(83)	1.382(7)
C(74)	C(75)	1.375(8)	C(83)	C(84)	1.370(9)
C(75)	C(76)	1.375(7)	C(84)	C(85)	1.367(9)
C(81)	C(82)	1.394(7)	C(85)	C(86)	1.402(8)

(c) within the tetrafluoroborate ion

Atom1	Atom2	Distance	Atom1	Atom2	Distance
F(1)	B	1.363(8)	F(3)	B	1.359(9)
F(2)	B	1.341(10)	F(4)	B	1.312(10)

(d) within the solvent dichloromethane molecules

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Cl(1S)	C(1S)	1.768(9)	Cl(3S)	C(2S)	1.727(9)
Cl(2S)	C(1S)	1.606(9)	Cl(4S)	C(2S)	1.720(9)

Table S–16. Selected Interatomic Angles (deg) for **5b**

(a) involving 'inner-core' atoms of $[RhRu(CO)_3(PMe_3)(\mu\text{–}CH_2)(dppm)_2]^+$

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Ru	Rh	P(1)	88.90(4)	P(2)	Ru	C(4)	86.80(14)
Ru	Rh	P(3)	85.04(4)	P(4)	Ru	C(2)	100.51(15)
Ru	Rh	P(5)	129.91(4)	P(4)	Ru	C(3)	84.74(15)
Ru	Rh	C(1)	125.83(15)	P(4)	Ru	C(4)	84.25(13)
Ru	Rh	C(4)	46.81(13)	C(2)	Ru	C(3)	95.6(2)
P(1)	Rh	P(3)	165.55(5)	C(2)	Ru	C(4)	147.30(19)
P(1)	Rh	P(5)	99.17(5)	C(3)	Ru	C(4)	117.08(19)
P(1)	Rh	C(1)	85.21(15)	Rh	P(1)	C(5)	114.29(16)
P(1)	Rh	C(4)	91.57(13)	Ru	P(2)	C(5)	114.38(17)
P(3)	Rh	P(5)	94.77(5)	Rh	P(3)	C(6)	113.05(16)
P(3)	Rh	C(1)	87.72(15)	Ru	P(4)	C(6)	113.10(16)
P(3)	Rh	C(4)	93.80(14)	Rh	P(5)	C(7)	116.92(18)
P(5)	Rh	C(1)	104.15(16)	Rh	P(5)	C(8)	119.1(2)
P(5)	Rh	C(4)	83.40(13)	Rh	P(5)	C(9)	115.82(18)
C(1)	Rh	C(4)	172.2(2)	C(7)	P(5)	C(8)	98.4(3)
Rh	Ru	P(2)	92.99(4)	C(7)	P(5)	C(9)	101.5(3)
Rh	Ru	P(4)	93.28(4)	C(8)	P(5)	C(9)	102.0(3)
Rh	Ru	C(2)	99.59(15)	Rh	C(1)	O(1)	177.2(5)
Rh	Ru	C(3)	164.77(15)	Ru	C(2)	O(2)	178.1(5)
Rh	Ru	C(4)	47.71(12)	Ru	C(3)	O(3)	178.5(5)
P(2)	Ru	P(4)	161.04(4)	Rh	C(4)	Ru	85.48(16)
P(2)	Ru	C(2)	96.05(15)	P(1)	C(5)	P(2)	110.5(2)
P(2)	Ru	C(3)	84.53(16)	P(3)	C(6)	P(4)	107.3(2)

(b) involving dppm phenyl carbons of $[RhRu(CO)_3(PMe_3)(\mu\text{–}CH_2)(dppm)_2]^+$

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Rh	P(1)	C(11)	116.36(17)	C(6)	P(3)	C(61)	104.2(2)
Rh	P(1)	C(21)	117.15(17)	C(51)	P(3)	C(61)	97.9(2)
C(5)	P(1)	C(11)	103.2(2)	Ru	P(4)	C(71)	118.33(16)
C(5)	P(1)	C(21)	102.7(2)	Ru	P(4)	C(81)	113.76(17)
C(11)	P(1)	C(21)	101.0(2)	C(6)	P(4)	C(71)	104.1(2)
Ru	P(2)	C(31)	114.43(16)	C(6)	P(4)	C(81)	102.2(2)
Ru	P(2)	C(41)	118.05(17)	C(71)	P(4)	C(81)	103.6(2)
C(5)	P(2)	C(31)	100.7(2)	P(1)	C(11)	C(12)	120.0(4)
C(5)	P(2)	C(41)	106.4(2)	P(1)	C(11)	C(16)	120.7(4)
C(31)	P(2)	C(41)	100.7(2)	C(12)	C(11)	C(16)	119.3(4)
Rh	P(3)	C(51)	116.57(16)	C(11)	C(12)	C(13)	119.9(5)
Rh	P(3)	C(61)	118.64(16)	C(12)	C(13)	C(14)	120.6(6)
C(6)	P(3)	C(51)	104.4(2)	C(13)	C(14)	C(15)	119.6(5)

Table S–16. Selected Interatomic Angles for **5b** (continued)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C(14)	C(15)	C(16)	120.3(6)	C(51)	C(52)	C(53)	120.5(5)
C(11)	C(16)	C(15)	120.2(6)	C(52)	C(53)	C(54)	120.7(5)
P(1)	C(21)	C(22)	117.9(4)	C(53)	C(54)	C(55)	119.3(5)
P(1)	C(21)	C(26)	123.2(4)	C(54)	C(55)	C(56)	121.2(5)
C(22)	C(21)	C(26)	118.9(5)	C(51)	C(56)	C(55)	120.2(5)
C(21)	C(22)	C(23)	120.1(5)	P(3)	C(61)	C(62)	118.6(4)
C(22)	C(23)	C(24)	119.5(5)	P(3)	C(61)	C(66)	122.9(4)
C(23)	C(24)	C(25)	120.3(5)	C(62)	C(61)	C(66)	118.4(4)
C(24)	C(25)	C(26)	120.7(5)	C(61)	C(62)	C(63)	120.9(5)
C(21)	C(26)	C(25)	120.5(5)	C(62)	C(63)	C(64)	120.5(5)
P(2)	C(31)	C(32)	123.2(4)	C(63)	C(64)	C(65)	119.5(5)
P(2)	C(31)	C(36)	118.4(4)	C(64)	C(65)	C(66)	120.0(5)
C(32)	C(31)	C(36)	118.3(5)	C(61)	C(66)	C(65)	120.7(5)
C(31)	C(32)	C(33)	121.3(5)	P(4)	C(71)	C(72)	119.9(4)
C(32)	C(33)	C(34)	120.0(5)	P(4)	C(71)	C(76)	121.6(4)
C(33)	C(34)	C(35)	119.2(5)	C(72)	C(71)	C(76)	118.5(5)
C(34)	C(35)	C(36)	121.4(5)	C(71)	C(72)	C(73)	120.2(5)
C(31)	C(36)	C(35)	119.8(5)	C(72)	C(73)	C(74)	120.3(5)
P(2)	C(41)	C(42)	123.6(4)	C(73)	C(74)	C(75)	120.2(5)
P(2)	C(41)	C(46)	117.6(4)	C(74)	C(75)	C(76)	120.2(5)
C(42)	C(41)	C(46)	118.5(5)	C(71)	C(76)	C(75)	120.6(5)
C(41)	C(42)	C(43)	120.1(5)	P(4)	C(81)	C(82)	120.3(4)
C(42)	C(43)	C(44)	121.1(6)	P(4)	C(81)	C(86)	120.9(4)
C(43)	C(44)	C(45)	119.4(5)	C(82)	C(81)	C(86)	118.9(4)
C(44)	C(45)	C(46)	120.3(6)	C(81)	C(82)	C(83)	120.6(6)
C(41)	C(46)	C(45)	120.6(5)	C(82)	C(83)	C(84)	120.1(6)
P(3)	C(51)	C(52)	124.4(4)	C(83)	C(84)	C(85)	120.3(5)
P(3)	C(51)	C(56)	117.4(4)	C(84)	C(85)	C(86)	120.3(6)
C(52)	C(51)	C(56)	118.1(5)	C(81)	C(86)	C(85)	119.8(6)

(c) within the tetrafluoroborate ion

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
F(1)	B	F(2)	110.6(7)	F(2)	B	F(3)	109.8(8)
F(1)	B	F(3)	109.1(6)	F(2)	B	F(4)	106.8(7)
F(1)	B	F(4)	113.9(8)	F(3)	B	F(4)	106.5(7)

(d) within the solvent dichloromethane molecules

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Cl(1S)	C(1S)	Cl(2S)	119.2(5)	Cl(3S)	C(2S)	Cl(4S)	115.2(4)

Table S–17. Anisotropic Displacement Parameters (U_{ij}, Å^2) for **5b**

Atom	$U_{11)}$	$U_{22)}$	$U_{33)}$	$U_{23)}$	$U_{13)}$	U_{12}
Rh	0.0228(2)	0.0149(2)	0.01821(19)	-0.00041(16)	-0.00240(15)	-0.00004(17)
Ru	0.0223(2)	0.0146(2)	0.0198(2)	-0.00008(17)	-0.00119(16)	-0.00042(17)
P(1)	0.0263(8)	0.0156(7)	0.0207(6)	-0.0022(5)	-0.0017(5)	-0.0001(6)
P(2)	0.0259(7)	0.0145(7)	0.0207(6)	0.0014(5)	-0.0020(5)	-0.0014(6)
P(3)	0.0238(7)	0.0150(7)	0.0204(6)	0.0007(5)	-0.0016(5)	-0.0004(5)
P(4)	0.0253(7)	0.0153(7)	0.0202(6)	-0.0024(5)	-0.0011(5)	-0.0014(6)
P(5)	0.0266(8)	0.0209(7)	0.0300(7)	-0.0030(6)	-0.0049(6)	0.0026(6)
O(1)	0.067(3)	0.043(3)	0.0173(19)	0.0021(17)	-0.0077(18)	-0.008(2)
O(2)	0.030(2)	0.041(3)	0.038(2)	0.0046(19)	-0.0061(17)	0.0051(18)
O(3)	0.051(3)	0.040(3)	0.039(2)	-0.007(2)	0.019(2)	-0.011(2)
C(1)	0.029(3)	0.020(3)	0.031(3)	-0.002(2)	-0.002(2)	-0.001(2)
C(2)	0.021(3)	0.019(3)	0.030(3)	-0.003(2)	0.003(2)	0.001(2)
C(3)	0.031(3)	0.017(3)	0.031(3)	-0.001(2)	0.000(2)	-0.006(2)
C(4)	0.029(3)	0.023(3)	0.016(2)	0.001(2)	0.000(2)	-0.013(2)
C(5)	0.021(3)	0.015(3)	0.029(3)	0.000(2)	-0.001(2)	0.004(2)
C(6)	0.021(3)	0.021(3)	0.020(2)	-0.005(2)	-0.001(2)	-0.004(2)
C(7)	0.027(3)	0.031(3)	0.041(3)	-0.010(3)	-0.012(2)	0.002(2)
C(8)	0.044(4)	0.025(3)	0.072(4)	-0.004(3)	-0.021(3)	0.006(3)
C(9)	0.031(3)	0.053(4)	0.039(3)	-0.002(3)	0.008(3)	0.006(3)
C(11)	0.026(3)	0.027(3)	0.019(2)	0.000(2)	-0.004(2)	-0.006(2)
C(12)	0.030(3)	0.036(3)	0.025(3)	-0.004(2)	-0.003(2)	-0.003(3)
C(13)	0.032(3)	0.051(4)	0.038(3)	0.009(3)	-0.007(3)	0.001(3)
C(14)	0.039(4)	0.066(5)	0.037(3)	0.002(3)	-0.016(3)	-0.012(3)
C(15)	0.053(4)	0.047(4)	0.039(3)	-0.012(3)	-0.011(3)	-0.018(3)
C(16)	0.042(4)	0.030(3)	0.030(3)	-0.002(3)	-0.004(2)	-0.005(3)
C(21)	0.026(3)	0.019(3)	0.026(3)	-0.004(2)	-0.003(2)	-0.003(2)
C(22)	0.039(3)	0.024(3)	0.026(3)	-0.006(2)	0.001(2)	0.000(3)
C(23)	0.039(4)	0.038(4)	0.032(3)	-0.005(3)	0.007(3)	-0.004(3)
C(24)	0.040(4)	0.026(3)	0.051(4)	-0.013(3)	0.008(3)	0.003(3)
C(25)	0.044(4)	0.022(3)	0.059(4)	0.003(3)	0.004(3)	0.007(3)
C(26)	0.032(3)	0.023(3)	0.033(3)	-0.004(2)	0.006(2)	0.002(2)
C(31)	0.033(3)	0.014(3)	0.019(2)	-0.002(2)	0.000(2)	0.003(2)
C(32)	0.037(3)	0.023(3)	0.028(3)	0.002(2)	0.000(2)	0.003(2)
C(33)	0.045(4)	0.034(4)	0.038(3)	0.013(3)	0.010(3)	-0.001(3)
C(34)	0.052(4)	0.050(4)	0.032(3)	0.021(3)	0.003(3)	0.000(3)
C(35)	0.049(4)	0.070(5)	0.040(3)	0.023(3)	-0.016(3)	-0.002(4)
C(36)	0.045(4)	0.049(4)	0.031(3)	0.007(3)	-0.004(3)	-0.010(3)
C(41)	0.029(3)	0.024(3)	0.022(2)	0.006(2)	-0.003(2)	-0.006(2)
C(42)	0.037(3)	0.028(3)	0.034(3)	-0.001(3)	-0.005(3)	-0.005(3)
C(43)	0.044(4)	0.036(4)	0.036(3)	-0.002(3)	-0.010(3)	-0.010(3)
C(44)	0.042(4)	0.051(4)	0.036(3)	0.003(3)	-0.009(3)	-0.020(3)
C(45)	0.026(3)	0.043(4)	0.039(3)	0.010(3)	-0.001(3)	-0.007(3)
C(46)	0.033(3)	0.032(3)	0.027(3)	-0.002(2)	-0.002(2)	0.000(3)

Table S–17. Anisotropic Displacement Parameters for **5b** (continued)

Atom	$U_{11)}$	$U_{22)}$	$U_{33)}$	$U_{23)}$	$U_{13)}$	U_{12}
C(51)	0.025(3)	0.011(2)	0.030(3)	0.005(2)	0.006(2)	0.004(2)
C(52)	0.026(3)	0.022(3)	0.041(3)	0.001(3)	-0.003(2)	-0.002(2)
C(53)	0.034(4)	0.025(3)	0.053(4)	-0.002(3)	-0.001(3)	0.000(3)
C(54)	0.032(4)	0.024(3)	0.062(4)	0.010(3)	0.009(3)	0.001(3)
C(55)	0.044(4)	0.035(4)	0.036(3)	0.009(3)	0.011(3)	0.003(3)
C(56)	0.030(3)	0.031(3)	0.033(3)	0.001(3)	0.003(2)	-0.004(3)
C(61)	0.024(3)	0.021(3)	0.022(2)	0.004(2)	0.001(2)	0.002(2)
C(62)	0.037(3)	0.023(3)	0.029(3)	0.001(2)	-0.008(2)	0.000(2)
C(63)	0.056(4)	0.025(3)	0.039(3)	0.005(3)	-0.004(3)	0.008(3)
C(64)	0.040(4)	0.037(4)	0.039(3)	0.007(3)	-0.002(3)	0.015(3)
C(65)	0.032(3)	0.038(4)	0.042(3)	0.007(3)	-0.011(3)	0.005(3)
C(66)	0.030(3)	0.024(3)	0.029(3)	0.001(2)	-0.002(2)	-0.001(2)
C(71)	0.030(3)	0.020(3)	0.020(2)	0.001(2)	0.001(2)	0.002(2)
C(72)	0.033(3)	0.018(3)	0.029(3)	-0.002(2)	0.001(2)	0.000(2)
C(73)	0.036(3)	0.031(3)	0.030(3)	-0.001(3)	0.001(2)	0.007(3)
C(74)	0.044(4)	0.024(3)	0.043(3)	0.007(3)	0.011(3)	0.011(3)
C(75)	0.046(4)	0.016(3)	0.062(4)	-0.003(3)	0.020(3)	0.000(3)
C(76)	0.032(3)	0.021(3)	0.045(3)	-0.003(3)	0.007(3)	-0.003(2)
C(81)	0.026(3)	0.028(3)	0.019(2)	-0.005(2)	-0.002(2)	-0.004(2)
C(82)	0.045(4)	0.036(4)	0.029(3)	-0.003(3)	-0.010(3)	-0.005(3)
C(83)	0.066(5)	0.063(5)	0.032(3)	0.017(3)	-0.014(3)	-0.003(4)
C(84)	0.051(4)	0.096(6)	0.025(3)	-0.009(4)	-0.012(3)	-0.007(4)
C(85)	0.067(5)	0.068(5)	0.039(4)	-0.021(4)	-0.015(3)	-0.002(4)
C(86)	0.068(5)	0.036(4)	0.035(3)	-0.009(3)	-0.015(3)	-0.003(3)
F(1)	0.088(3)	0.045(2)	0.060(2)	-0.015(2)	0.007(2)	-0.019(2)
F(2)	0.209(6)	0.132(5)	0.055(3)	-0.001(3)	0.014(3)	-0.081(5)
F(3)	0.310(8)	0.050(3)	0.076(3)	-0.019(3)	-0.086(4)	0.034(4)
F(4)	0.066(4)	0.199(7)	0.212(7)	-0.041(6)	-0.034(4)	-0.023(4)
B	0.085(7)	0.034(5)	0.058(5)	-0.004(4)	-0.017(5)	-0.013(4)
Cl(1S)	0.128(2)	0.0917(18)	0.1070(18)	0.0082(15)	-0.0692(16)	-0.0094(16)
Cl(2S)	0.216(3)	0.101(2)	0.0668(15)	-0.0056(14)	0.0245(18)	0.034(2)
C(1S)	0.326(18)	0.090(8)	0.076(7)	0.027(6)	-0.085(9)	-0.087(10)
Cl(3S)	0.1047(18)	0.0778(16)	0.0819(14)	0.0152(12)	0.0008(13)	-0.0020(13)
Cl(4S)	0.1093(19)	0.0932(18)	0.0758(14)	0.0068(13)	-0.0230(13)	0.0036(14)
C(2S)	0.159(9)	0.117(9)	0.053(5)	0.035(5)	-0.010(5)	-0.057(7)

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 S–18. Derived Parameters for Hydrogen Atoms of **5b**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H(4A)	0.2027	0.5437	0.2880	0.027
H(4B)	0.2241	0.6658	0.3000	0.027
H(5A)	0.2591	0.8217	0.3327	0.026
H(5B)	0.3167	0.8717	0.3721	0.026
H(6A)	0.1763	0.3739	0.2970	0.025
H(6B)	0.2097	0.2639	0.3148	0.025
H(7A)	0.0937	0.5336	0.2962	0.040
H(7B)	0.0259	0.5516	0.3279	0.040
H(7C)	0.0697	0.4504	0.3427	0.040
H(8A)	0.1115	0.7533	0.3356	0.057
H(8B)	0.0955	0.7776	0.4014	0.057
H(8C)	0.0401	0.7285	0.3594	0.057
H(9A)	0.0825	0.6064	0.4847	0.049
H(9B)	0.0633	0.4947	0.4576	0.049
H(9C)	0.0192	0.5955	0.4428	0.049
H(12)	0.3753	0.6061	0.4605	0.036
H(13)	0.4665	0.6300	0.5219	0.048
H(14)	0.4769	0.7812	0.5773	0.057
H(15)	0.3961	0.9107	0.5707	0.056
H(16)	0.3079	0.8925	0.5058	0.041
H(22)	0.1873	0.7363	0.5211	0.035
H(23)	0.1067	0.8471	0.5590	0.043
H(24)	0.0785	1.0024	0.5110	0.047
H(25)	0.1286	1.0464	0.4257	0.050
H(26)	0.2090	0.9401	0.3886	0.035
H(32)	0.4493	0.8482	0.2556	0.035
H(33)	0.4447	0.9361	0.1672	0.047
H(34)	0.3485	0.9330	0.1106	0.054
H(35)	0.2581	0.8411	0.1423	0.064
H(36)	0.2618	0.7522	0.2296	0.050
H(42)	0.4119	0.8969	0.3957	0.040
H(43)	0.5187	0.9489	0.4196	0.047
H(44)	0.6082	0.8501	0.3911	0.052
H(45)	0.5905	0.6928	0.3414	0.043
H(46)	0.4839	0.6401	0.3155	0.037
H(52)	0.0988	0.2683	0.3535	0.036
H(53)	0.0114	0.1937	0.4011	0.045
H(54)	0.0082	0.1982	0.5013	0.047
H(55)	0.0929	0.2780	0.5536	0.046
H(56)	0.1798	0.3553	0.5077	0.038

le S–18. Derived Parameters for Hydrogen Atoms of **5b** (continued)

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H(62)	0.2397	0.1628	0.3984	0.036
H(63)	0.3184	0.0508	0.4376	0.048
H(64)	0.4085	0.1177	0.4896	0.046
H(65)	0.4180	0.2996	0.5037	0.045
H(66)	0.3398	0.4123	0.4632	0.033
H(72)	0.4299	0.3491	0.2998	0.032
H(73)	0.4987	0.2032	0.3099	0.039
H(74)	0.4556	0.0351	0.3036	0.044
H(75)	0.3437	0.0107	0.2875	0.049
H(76)	0.2737	0.1541	0.2821	0.039
H(82)	0.2611	0.5419	0.1976	0.044
H(83)	0.2291	0.5438	0.1008	0.064
H(84)	0.2197	0.3880	0.0499	0.069
H(85)	0.2374	0.2293	0.0959	0.070
H(86)	0.2679	0.2248	0.1941	0.056
H(1SA)	0.0788	0.0209	-0.3000	0.198
H(1SB)	0.0029	0.0490	-0.2967	0.198
H(2SA)	0.0474	-0.3385	-0.3116	0.132
H(2SB)	0.1196	-0.3782	-0.2945	0.132