Figure S1 - *Plot of $\Sigma|F_o|/\Sigma|F_c|$ versus resolution for (top) [Rh(C$_7$H$_8$)(P^{t}Bu$_3$)Cl], **1**, (bottom) [Rh(C$_7$H$_8$)(PCy$_3$)Cl], **2** prior to multipole refinement.*
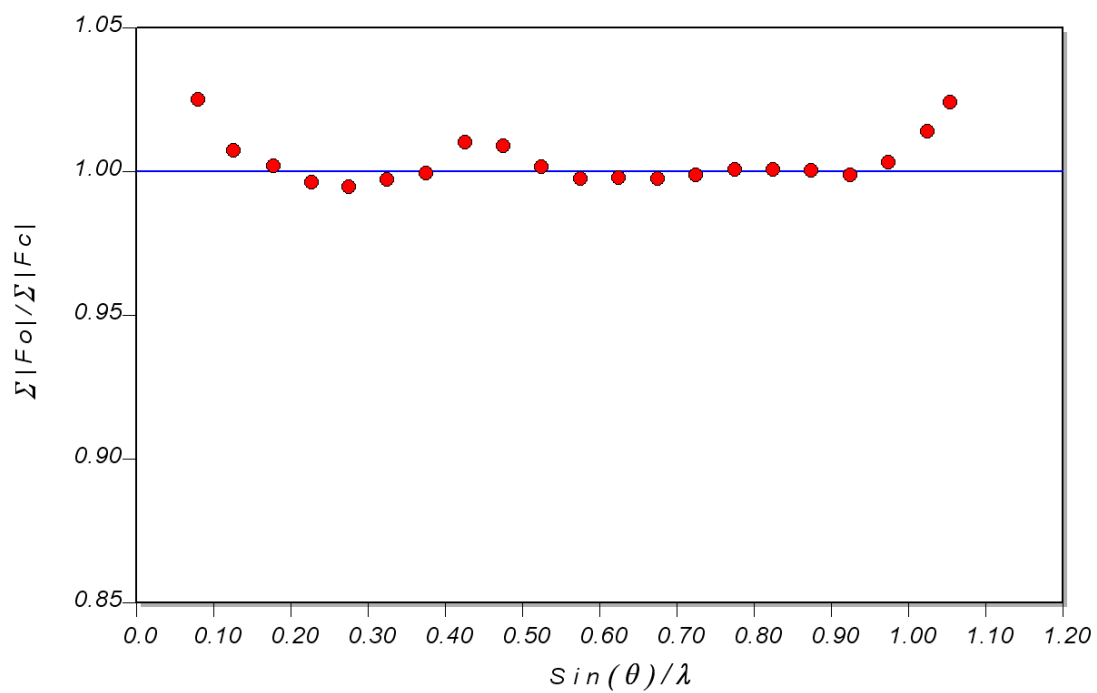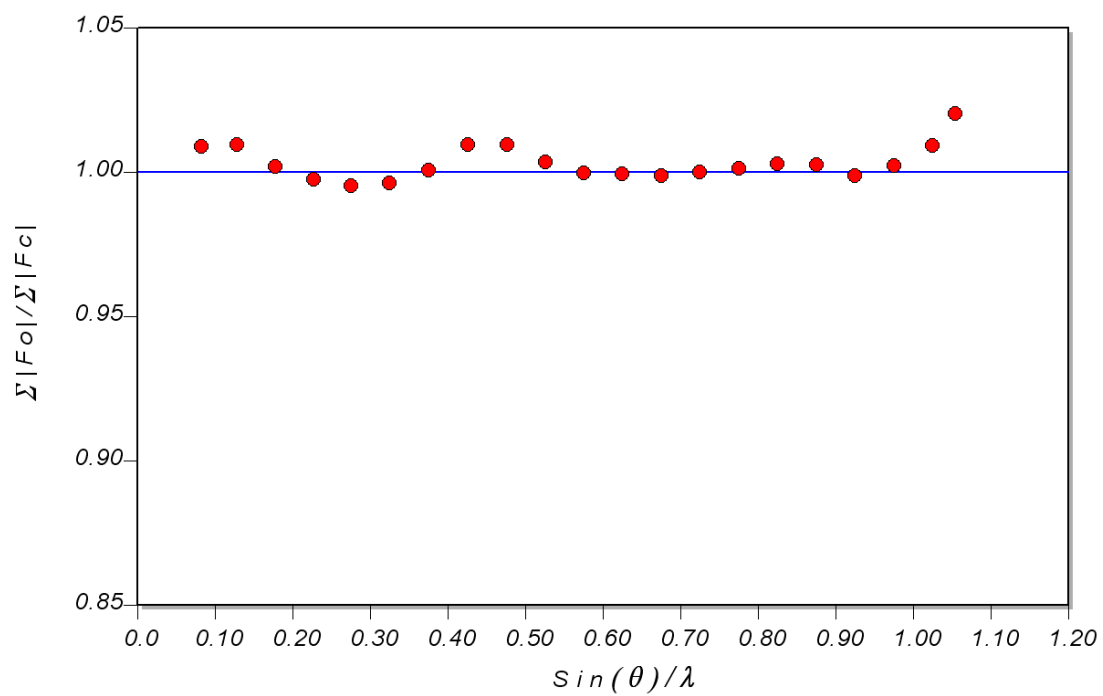
Figure S2 - *Plot of $\Sigma|F_o|/\Sigma|F_c|$ versus resolution for (top) [Rh(C₇H₈)(PᵗBu₃)Cl], **1**, (bottom) [Rh(C₇H₈)(PCy₃)Cl], **2** after multipole refinement.*
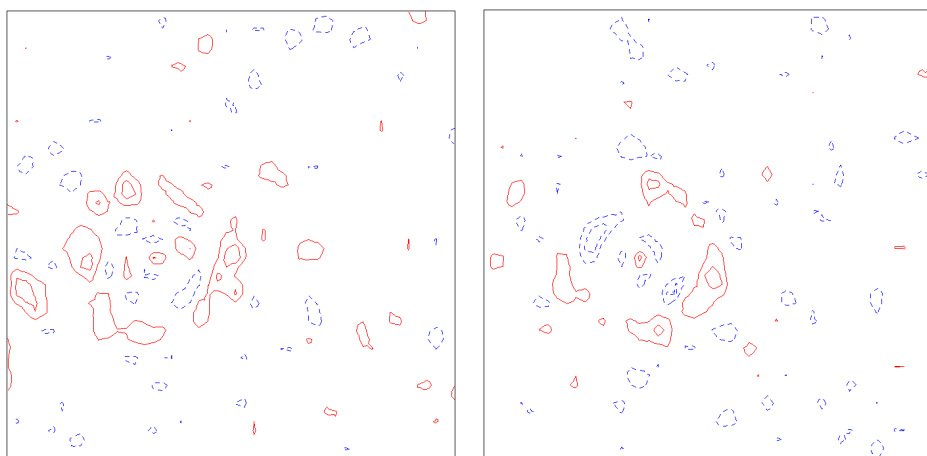
Figure S3 - *Residual density map for [Rh(C₇H₈)(PᵗBu₃)Cl],* **1,** *after multipole refinement for all data map calculated through (left) Rh1, C1 and C2, (right) Rh1, C4 and C5 . Contours are depicted at the 0.1 e Å⁻³ level, with positive contours as solid red lines and negative contours as blue dashed lines.*

Figure S4 - *Residual density map for [Rh(C₇H₈)(PCy₃)Cl],* **2,** *after multipole refinement for all data map calculated through (left) Rh1, C1 and C2, (right) Rh1, C4 and C5. Contours are depicted at the 0.1 e Å⁻³ level, with positive contours as solid red lines and negative contours as blue dashed lines.*

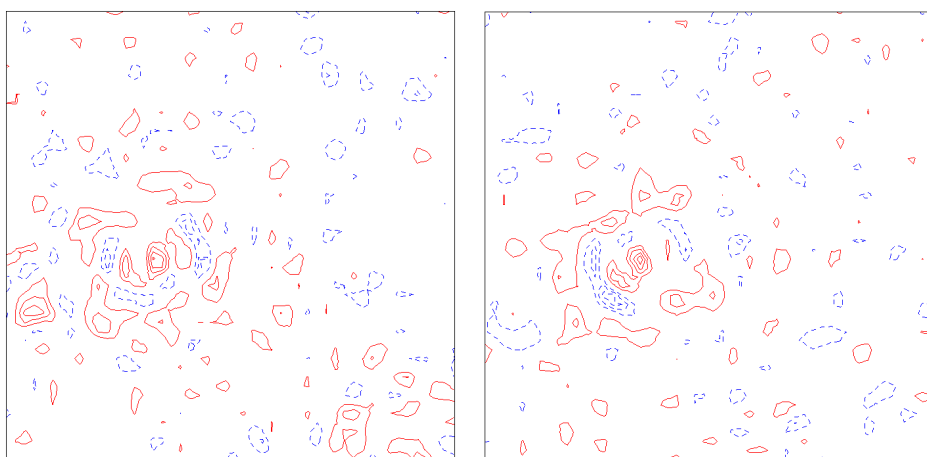Table S1 - *Crystal data for the two datasets of [Rh(C$_7$H$_8$)(PCy$_3$)Cl], **2**.*

	Collection 1	**Collection 2**
Empirical formula	C$_{19}$ H$_{35}$ Cl P Rh	C$_{19}$ H$_{35}$ Cl P Rh
Formula weight	432.80	432.80
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P\,2_1/n$	$P\,2_1/n$
a (Å)	10.2135(1)	10.2104(1)
b (Å)	15.8217(1)	15.8292(1)
c (Å)	14.6417(1)	14.6392(1)
β (°)	97.787(1)	97.765(1)
V (Å^3)	2344.21(3)	2344.33(3)
Z	4	4
T(K)	100(2)	100(2)
D_c Mg/m^3	1.448	1.448
μ (mm^{-1})	0.922	0.922
F(000)	1072	1072
Crystal size (mm^3)	0.20 x 0.24 x 0.38	0.20 x 0.24 x 0.34
θ range for data collection (°)	2.57-49.12	2.63-49.12
Ranges of h, k, l	-21<=h<=21,	-21<=h<=21,
	-33<=k<=33,	-33<=k<=33,
	-31<=l<=31	-31<=l<=31
Reflections collected	105430	194653
Independent reflections	23636	23633
R_{int}	0.0408	0.0465
Absorption coefficients min/max	0.911/1.00	0.801/0.860
Spherical Atom Refinement		
No. of data in refinement	17090	16863
No. of refined parameters	417	417
GOF (F^2)	0.710	0.809
Final R_1 [$F^2 > 2\sigma(F)$] (all data)	0.0216(0.0372)	0.0211(0.0393)
wR_2 [$F^2 > 2\sigma(F)$] (all data)	0.0419(0.0437)	0.0387(0.0401)
Largest diff. peak/hole (e Å^{-3})	-0.54/1.16	-0.73/1.22

Table S2 - *Hirshfeld analysis for [Rh(C₇H₈)(PᵗBu₃)Cl], 1.*

Atoms	DMSDA (x 10⁴ Å²)
Rh(1)-C(1)	22
Rh(1)-C(2)	23
Rh(1)-C(4)	23
Rh(1)-C(5)	22
Rh(1)-P(1)	1
Rh(1)-Cl(1)	16
P(1)-C(8)	10
P(1)-C(12)	11
P(1)-C(16)	8
C(1)-C(2)	0
C(1)-C(6)	0
C(2)-C(3)	1
C(3)-C(4)	0
C(3)-C(7)	1
C(4)-C(5)	-1
C(5)-C(6)	0
C(6)-C(7)	0
C(8)-C(9)	1
C(8)-C(10)	1
C(8)-C(11)	3
C(12)-C(13)	2
C(12)-C(14)	-1
C(12)-C(15)	-1
C(16)-C(17)	5
C(16)-C(18)	0
C(16)-C(19)	1

Table S3 - *Hirshfeld analysis for [Rh(C₇H₈)(PCy₃)Cl], 2.*

Atoms	DMSDA (x 10⁴ Å²)
Rh(1)-C(1)	23
Rh(1)-C(2)	24
Rh(1)-C(4)	19
Rh(1)-C(5)	18
Rh(1)-P(1)	3
Rh(1)-Cl(1)	11
P(1)-C(8)	9
P(1)-C(14)	10
P(1)-C(20)	7
C(1)-C(2)	0
C(1)-C(6)	-5
C(2)-C(3)	2
C(3)-C(4)	0
C(3)-C(7)	3
C(4)-C(5)	1
C(5)-C(6)	-1
C(6)-C(7)	1
C(8)-C(9)	-2
C(8)-C(13)	0
C(9)-C(10)	1
C(10)-C(11)	-1
C(11)-C(12)	-2
C(12)-C(13)	-2
C(14)-C(15)	1
C(14)-C(19)	0
C(15)-C(16)	3
C(16)-C(17)	-2
C(17)-C(18)	3
C(18)-C(19)	0
C(20)-C(21)	2
C(20)-C(25)	4
C(21)-C(22)	3
C(22)-C(23)	1
C(23)-C(24)	-3
C(24)-C(25)	-3

Table S4 - *d-orbital populations for Rh(1) in [Rh(C₇H₈)(P'Bu₃)Cl], 1.*

$d(z^2)$	$d(xz)$	$d(yz)$	$d(x^2-y^2)$	$d(xy)$	P_v
1.250(15)	1.774(15)	1.502(15)	1.667(15)	1.687(15)	7.880

Mixing terms

dz^2/xz	dz^2/yz	dz^2/x^2-y^2	dz^2/xy	dxz/yz	dxz/x^2-y^2	dxz/xy	dyz/x^2-y^2	dyz/xy	dx^2-y^2/xy
-0.380(21)	-0.153(22)	0.240(21)	-0.187(21)	-0.183(21)	0.115(21)	-0.170(22)	0.563(22)	-0.007(21)	0.154(21)

Table S5 - *d-orbital populations for Rh(1) in [Rh(C₇H₈)(PCy₃)Cl], 2.*

$d(z^2)$	$d(xz)$	$d(yz)$	$d(x^2-y^2)$	$d(xy)$	P_v
1.378(18)	1.678(18)	1.526(18)	1.565(18)	1.519(18)	7.667

Mixing terms

dz^2/xz	dz^2/yz	dz^2/x^2-y^2	dz^2/xy	dxz/yz	dxz/x^2-y^2	dxz/xy	dyz/x^2-y^2	dyz/xy	dx^2-y^2/xy
-0.240(26)	0.103(26)	0.183(26)	-0.040(26)	0.085(26)	0.208(26)	0.305(26)	0.268(25)	-0.052(26)	0.167(26)