Supplementary Information

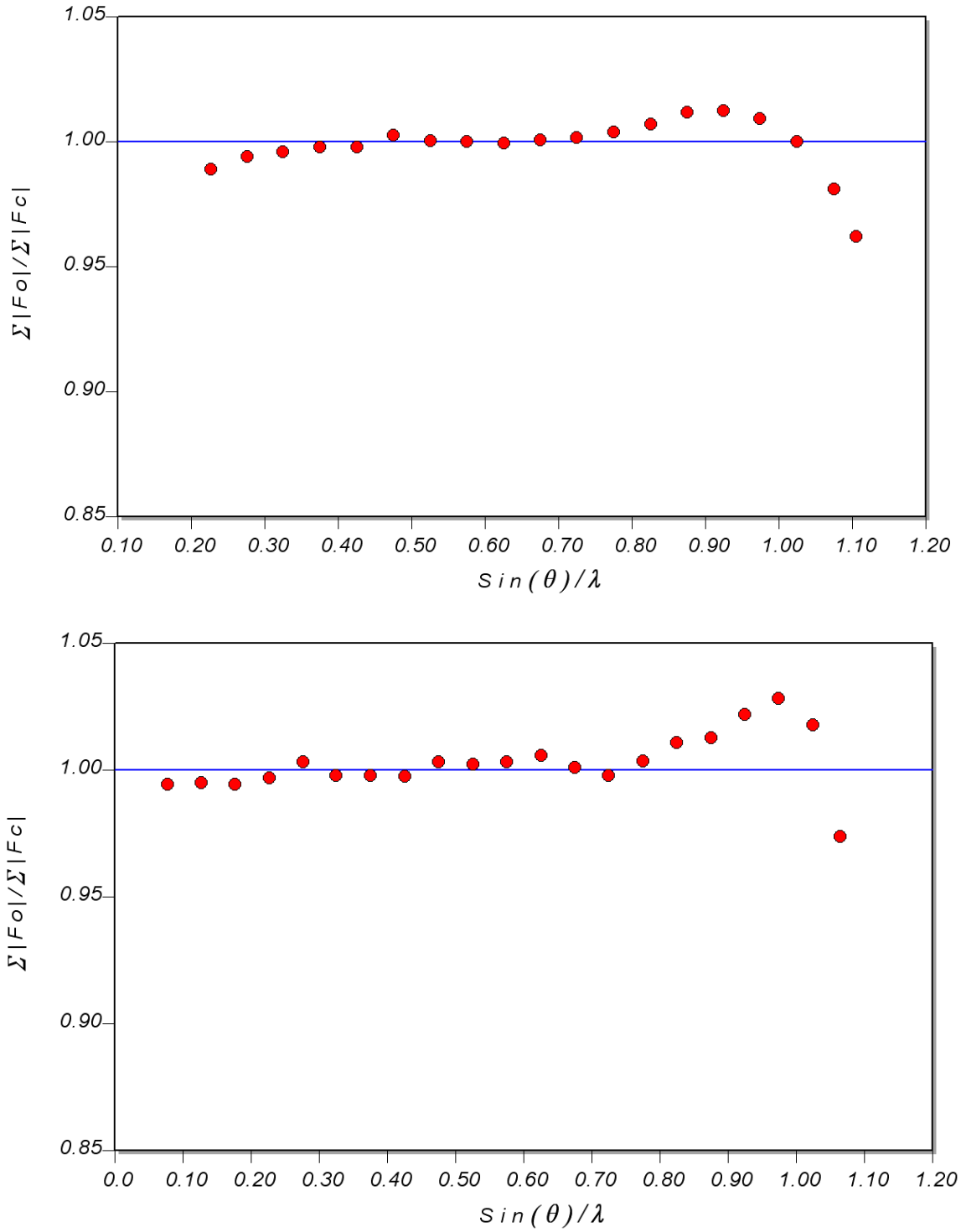

Figure S1 - *Plot of* $\sum|F_o|/\sum|F_c|$ *versus resolution for (top) collection 1, (bottom) collection 2.*

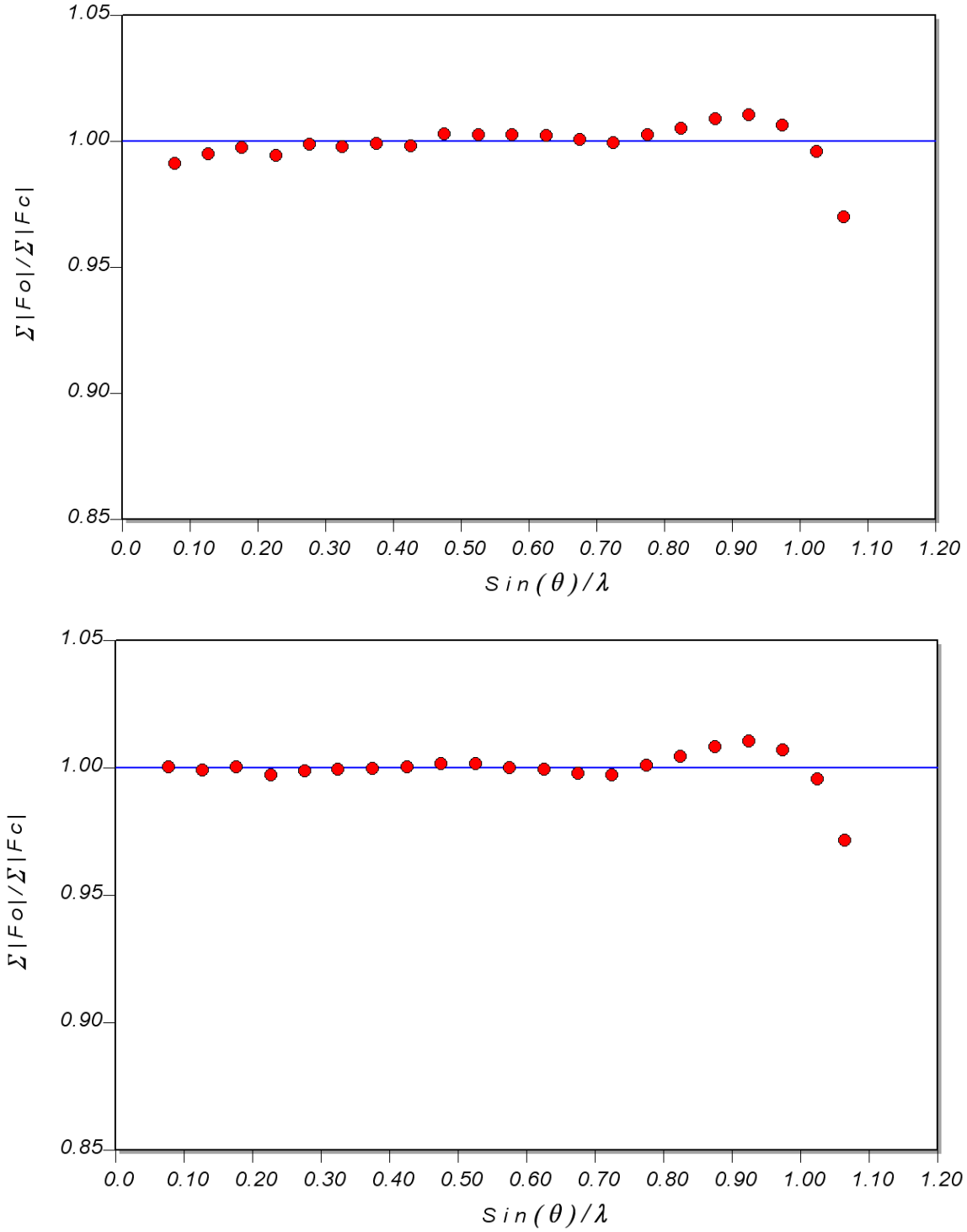

Figure S2 - *Plot of $\Sigma|F_o|/\Sigma|F_c|$ versus resolution for the merged data (top) before xd refinement (bottom) after multipole refinement in xd.*

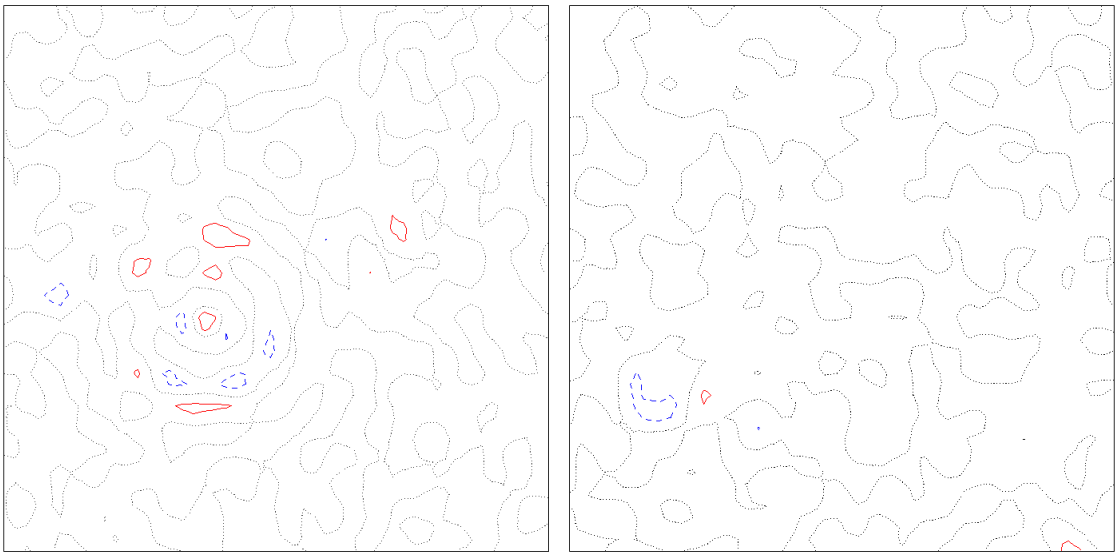

Figure S3 - *Residual density map for after multipole refinement for data sinθ/λ = 0.9 Å^{-1} (left) map calculated through Rh, C1 and C5 (right) map calculated through C8, C10 and C12. Contours are depicted at the 0.1 e Å^{-3} level, with positive contours as solid red lines, negative contours as blue dashed lines and the zero level is the dotted black line.*

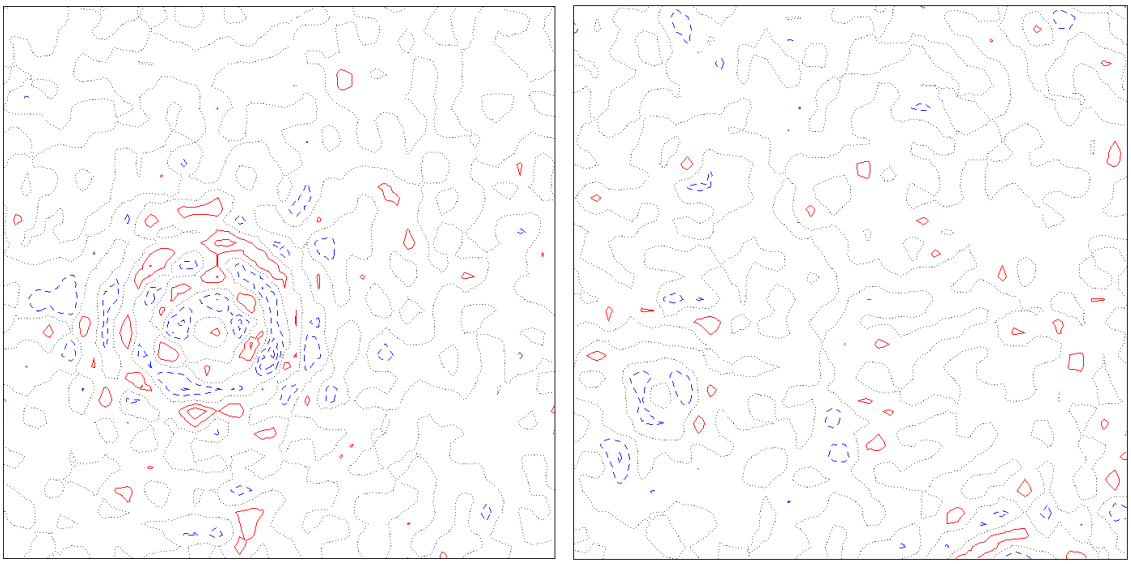

Figure S4 - *Residual density map for after multipole refinement for all data (left) map calculated through Rh, C1 and C5 (right) map calculated through C8, C10 and C12. Contours are depicted at the 0.1 e Å^{-3} level, with positive contours as solid red lines, negative contours as blue dashed lines and the zero level is the dotted black line.*

Table S1 - *Crystal data for the two datasets*

	Collection 1	**Collection 2**
Empirical formula	C_{25} H_{23} Cl P Rh	C_{25} H_{23} Cl P Rh
Formula weight	492.76	492.76
λ (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.2438(2)	10.2430(1)
b (Å)	10.3994(3)	10.4042(1)
c (Å)	11.4076(3)	11.4078(1)
α (°)	99.235(2)	99.213(1)
β (°)	103.112(2)	103.131(1)
γ (°)	115.0660(10)	115.080(1)
V (Å^3)	1025.74(4)	1026.010(17)
Z	2	2
T(K)	100(2)	100(2)
D_c Mg/m^3	1.595	1.595
μ (mm^{-1})	1.049	1.049
F(000)	500	500
Crystal size (mm^3)	0.20 x 0.26 x 0.30	0.25 x 0.20 x 0.15
θ range for data collection (°)	8.18 to 52.16	1.92 to 50.14
Ranges of *h*, *k*, *l*	-22<=h<=22, -23<=k<=23, -25<=l<=23	-22<=h<=22, -22<=k<=22, -24<=l<=24
Reflections collected	168964	209634
Independent reflections	23403	21645
R_{int}	0.0317	0.0397
Absorption coefficients min/max	0.666/0.711	0.719/0.770
Spherical Atom Refinement		
No. of data in refinement	23403	21645
No. of refined parameters	253	345
GOF (F^2)	1.031	1.074
Final R_1 [$F^2 > 2\sigma(F)$] (all data)	0.0187(0.0216)	0.0240 (0.0302)
wR_2 [$F^2 > 2\sigma(F)$] (all data)	0.0475(0.0484)	0.0514 (0.0529)
Largest diff. peak/hole (e Å^{-3})	0.685/-1.270	0.765/-0.972

Table S2 - *Hirshfeld analysis for **1***

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

Table S3 - *Radial parameters and net atomic charge for **1** after multipole refinement.*

Atom	Kappa	Kappa'	Net Charge
Rh(1)	0.971	0.974	+0.143

Cl(1)	0.978	0.952	-0.548
P(1)	0.983	0.941	-0.095
C(1)	0.985	0.987	-0.242
C(2)	0.985	0.987	-0.211
C(3)	0.985	0.987	-0.134
C(4)	0.985	0.987	-0.243
C(5)	0.985	0.987	-0.236
C(6)	0.985	0.987	-0.062
C(7)	0.985	0.987	-0.231
C(8)	0.985	0.987	-0.153
C(9)	0.985	0.987	-0.130
C(10)	0.985	0.987	-0.108
C(11)	0.985	0.987	-0.078
C(12)	0.985	0.987	-0.108
C(13)	0.985	0.987	-0.130
C(14)	0.985	0.987	-0.153
C(15)	0.985	0.987	-0.130
C(16)	0.985	0.987	-0.108
C(17)	0.985	0.987	-0.078
C(18)	0.985	0.987	-0.108
C(19)	0.985	0.987	-0.130
C(20)	0.985	0.987	-0.153
C(21)	0.985	0.987	-0.130
C(22)	0.985	0.987	-0.108
C(23)	0.985	0.987	-0.078
C(24)	0.985	0.987	-0.108
C(25)	0.985	0.987	-0.130
H(1)	1.183	1.200	+0.190
H(2)	1.183	1.200	+0.190
H(3)	1.183	1.200	+0.185
H(4)	1.183	1.200	+0.190
H(5)	1.183	1.200	+0.190
H(6)	1.183	1.200	+0.185
H(7B)	1.183	1.200	+0.158
H(7A)	1.183	1.200	+0.158
H(9)	1.183	1.200	+0.169
H(10)	1.183	1.200	+0.169
H(11)	1.183	1.200	+0.169
H(12)	1.183	1.200	+0.169
H(13)	1.183	1.200	+0.169
H(15)	1.183	1.200	+0.169
H(16)	1.183	1.200	+0.169
H(17)	1.183	1.200	+0.169
H(18)	1.183	1.200	+0.169
H(19)	1.183	1.200	+0.169
H(21)	1.183	1.200	+0.169
H(22)	1.183	1.200	+0.169
H(23)	1.183	1.200	+0.169
H(24)	1.183	1.200	+0.169
H(25)	1.183	1.200	+0.169

Table S4 - *Atomic charge for **1** after multipole refinement.*

Atom	**Q**	**L**
Rh(1)	+0.331	-6.4×10^{-4}
Cl(1)	-0.633	-6.5×10^{-4}
P(1)	+0.913	-1.9×10^{-3}

C(1)	-0.329	$-3.5x10^{-3}$
C(2)	-0.255	$-3.7x10^{-3}$
C(3)	-0.125	$-3.7x10^{-3}$
C(4)	-0.277	$-5.3x10^{-3}$
C(5)	-0.281	$-3.2x10^{-3}$
C(6)	-0.044	$-1.2x10^{-2}$
C(7)	-0.199	$-1.3x10^{-4}$
C(8)	-0.462	$-3.6x10^{-3}$
C(9)	-0.131	$-4.2x10^{-3}$
C(10)	-0.103	$-1.8x10^{-3}$
C(11)	-0.072	$-9.9x10^{-4}$
C(12)	-0.096	$-2.1x10^{-3}$
C(13)	-0.112	$-2.0x10^{-3}$
C(14)	-0.466	$-4.1x10^{-4}$
C(15)	-0.127	$-1.6x10^{-3}$
C(16)	-0.102	$-2.0x10^{-3}$
C(17)	-0.075	$-2.7x10^{-3}$
C(18)	-0.098	$-1.2x10^{-3}$
C(19)	-0.116	$-6.7x10^{-4}$
C(20)	-0.458	$-6.9x10^{-3}$
C(21)	-0.120	$-3.4x10^{-3}$
C(22)	-0.103	$-2.0x10^{-3}$
C(23)	-0.071	$-1.1x10^{-3}$
C(24)	-0.103	$-1.2x10^{-3}$
C(25)	-0.118	$-3.4x10^{-3}$
H(1)	+0.221	$-1.1x10^{-5}$
H(2)	+0.224	$-5.5x10^{-5}$
H(3)	+0.177	$-1.3x10^{-5}$
H(4)	+0.208	$-2.4x10^{-4}$
H(5)	+0.201	$-1.5x10^{-4}$
H(6)	+0.178	$-3.5x10^{-5}$
H(7B)	+0.137	$-1.5x10^{-6}$
H(7A)	+0.139	$-2.4x10^{-5}$
H(9)	+0.158	$-3.5x10^{-5}$
H(10)	+0.168	$-5.7x10^{-5}$
H(11)	+0.158	$-1.5x10^{-5}$
H(12)	+0.168	$-5.0x10^{-5}$
H(13)	+0.154	$-3.5x10^{-4}$
H(15)	+0.145	$-1.0x10^{-4}$
H(16)	+0.168	$-8.9x10^{-7}$
H(17)	+0.158	$-1.4x10^{-6}$
H(18)	+0.168	$-3.6x10^{-5}$
H(19)	+0.148	$-1.1x10^{-3}$
H(21)	+0.157	$-9.7x10^{-5}$
H(22)	+0.168	$-2.6x10^{-5}$
H(23)	+0.158	$-3.3x10^{-5}$
H(24)	+0.168	$-6.5x10^{-6}$
H(25)	+0.145	$-2.3x10^{-5}$

Table S5 - *d-orbital populations for Rh(1).*

$d(z^2)$	d(xz)	d(yz)	$d(x^2-y^2)$	d(xy)	P_v
1.546(13)	1.814(13)	1.650(13)	1.368(13)	1.479(13)	7.857

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
-0.382(19)	-0.101(19)	0.464(19)	-0.107(19)	-0.262(19)	0.259(19)	0.093(19)	0.455(19)	0.063(19)	0.064(19)