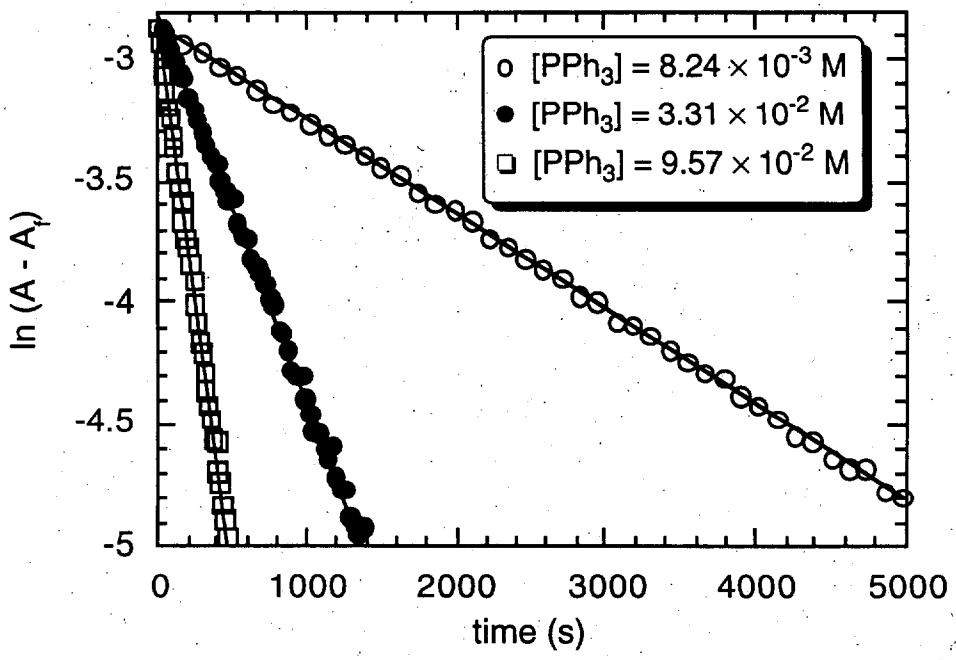

Figure S1. Kinetics of reduction of $[(HCpz_3)ReOCl_2]Cl$ ([**1**]Cl) by PPh_3 under pseudo-first-order conditions (CH_2Cl_2, 25.3° C). $[PPh_3] = 8.24 \times 10^{-3}$ M (open circles), 3.31×10^{-2} M (solid circles), 9.57×10^{-2} M (open squares).

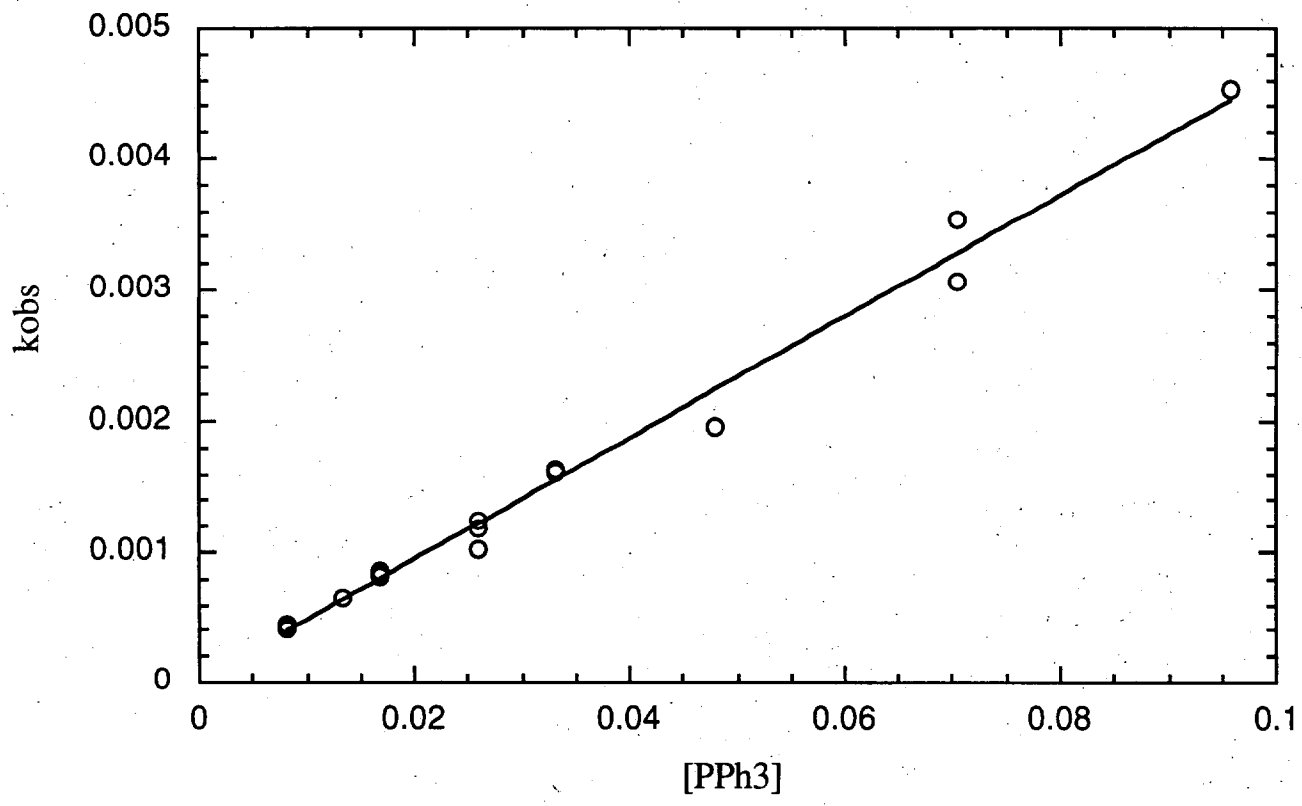

Figure S2. Kinetics of reduction of $[(HCpz_3)ReOCl_2]Cl$ (**[1]**Cl) by PPh_3 under pseudo-first-order conditions as a function of $[PPh_3]$ (CH_2Cl_2, 25.3° C).

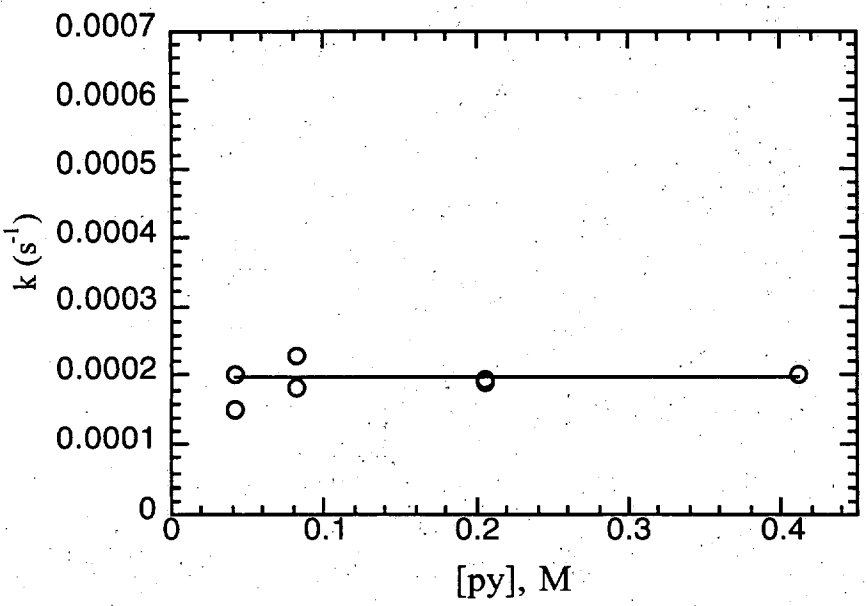

Figure S3a. Kinetics of ligand substution of $[(HCpz_3)ReOCl_2]BF_4$ ([**3**]BF_4) in 3% (v/v) CH_2Cl_2/1,2-dichlorobenzene as a function of [pyridine] at 73 °C.

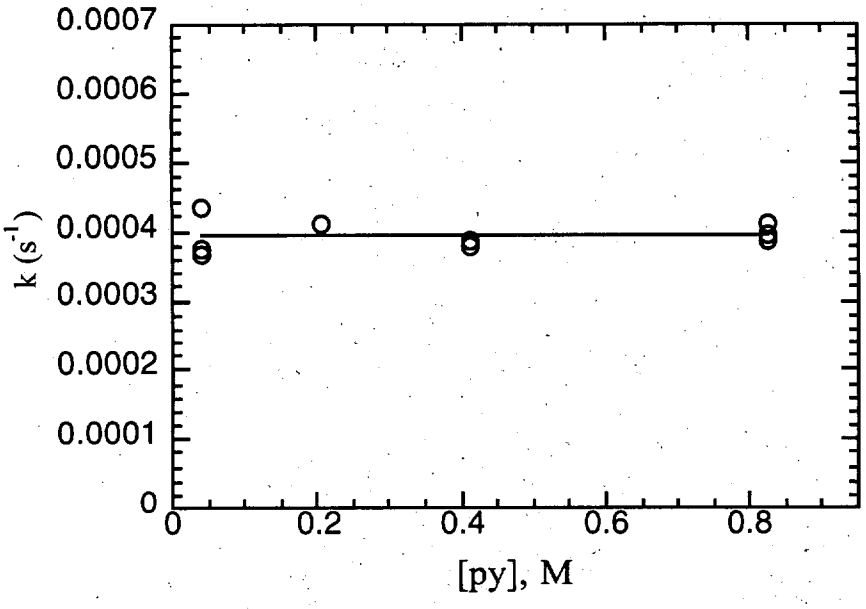

Figure S3b. Kinetics of ligand substution of $(HBpz_3)ReOCl_2$ (**4**) in 1,2-dichlorobenzene as a function of [pyridine] at 47 °C.

Table S1a. Kinetic Data for the Reduction of [**1**]Cl and **2** by PPh_3 in 1,2-dichlorobenzene

Complex	T (K)	k ($M^{-1}s^{-1}$)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
[**1**]Cl	289	0.026(6)	13.4(5)	-19(2)
	297	0.0534(4)		
	304	0.081(4)		
	312	0.160(7)		
	322	0.352(8)		
2	291	$3.95(9) \times 10^{-5}$	17.11(13)	-19.7(4)
	311	$3.25(5) \times 10^{-4}$		
	322	$7.73(13) \times 10^{-4}$		
	338	$2.94(8) \times 10^{-3}$		
	351	$7.7(5) \times 10^{-3}$		

Table S1b. Kinetic data for displacement of $OPPh_3$ by pyridine. The solvent is 1,2-dichlorobenzene for **4** and 3% (v/v) CH_2Cl_2/1,2-dichlorobenzene for [**3**]BF_4.

Complex	T (K)	k (s^{-1})	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
[**3**]BF_4	324	$1.1(2) \times 10^{-5}$	29.6(5)	10(2)
	335	$4.99(9) \times 10^{-5}$		
	345	$2.01(1) \times 10^{-4}$		
	353	$5.8(8) \times 10^{-4}$		
4	306	$3.38(1) \times 10^{-5}$	28.4(9)	14(3)
	313	$1.35(2) \times 10^{-4}$		
	320	$3.9(4) \times 10^{-4}$		
	328	$1.13(5) \times 10^{-3}$		
	337	$2.80(6) \times 10^{-3}$		

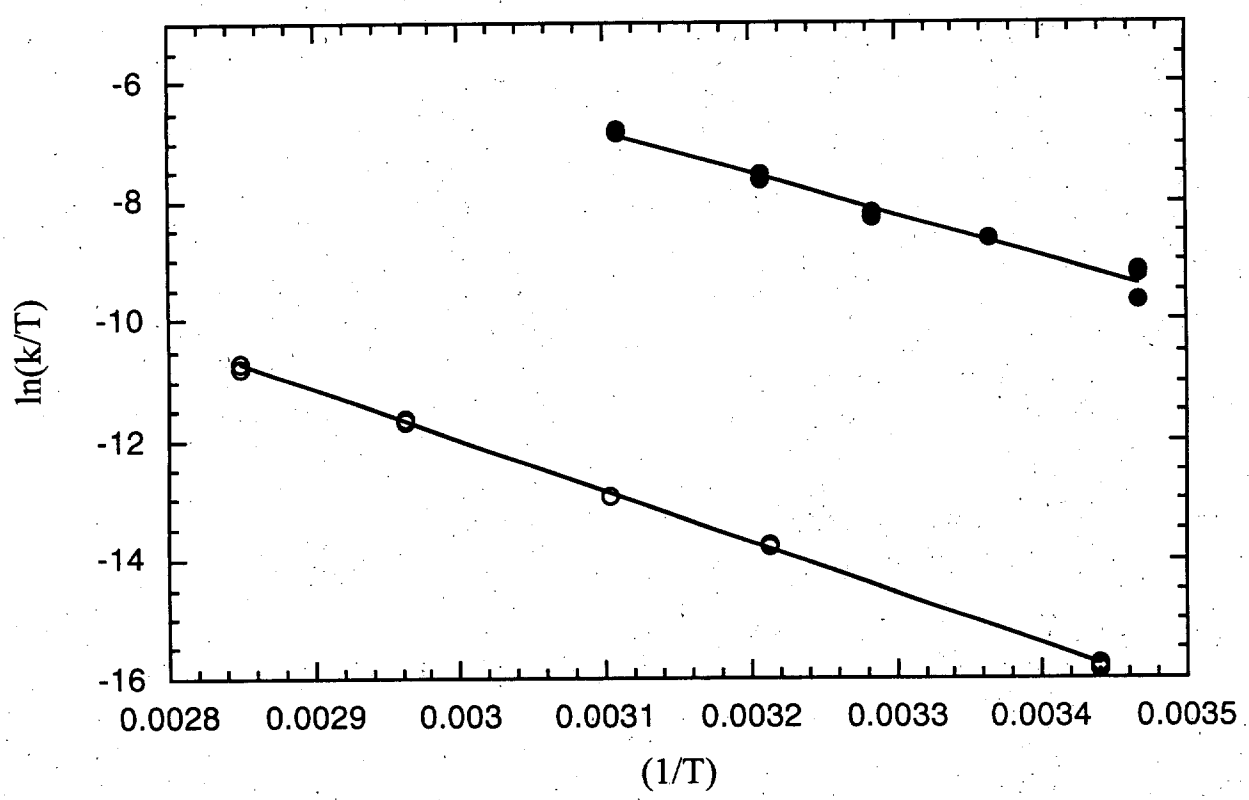

Figure S4a. Temperature effects on oxygen atom transfer to PPh_3 from [**1**]Cl (solid circles) and **2** (open circles) in 1,2-$C_6H_4Cl_2$.

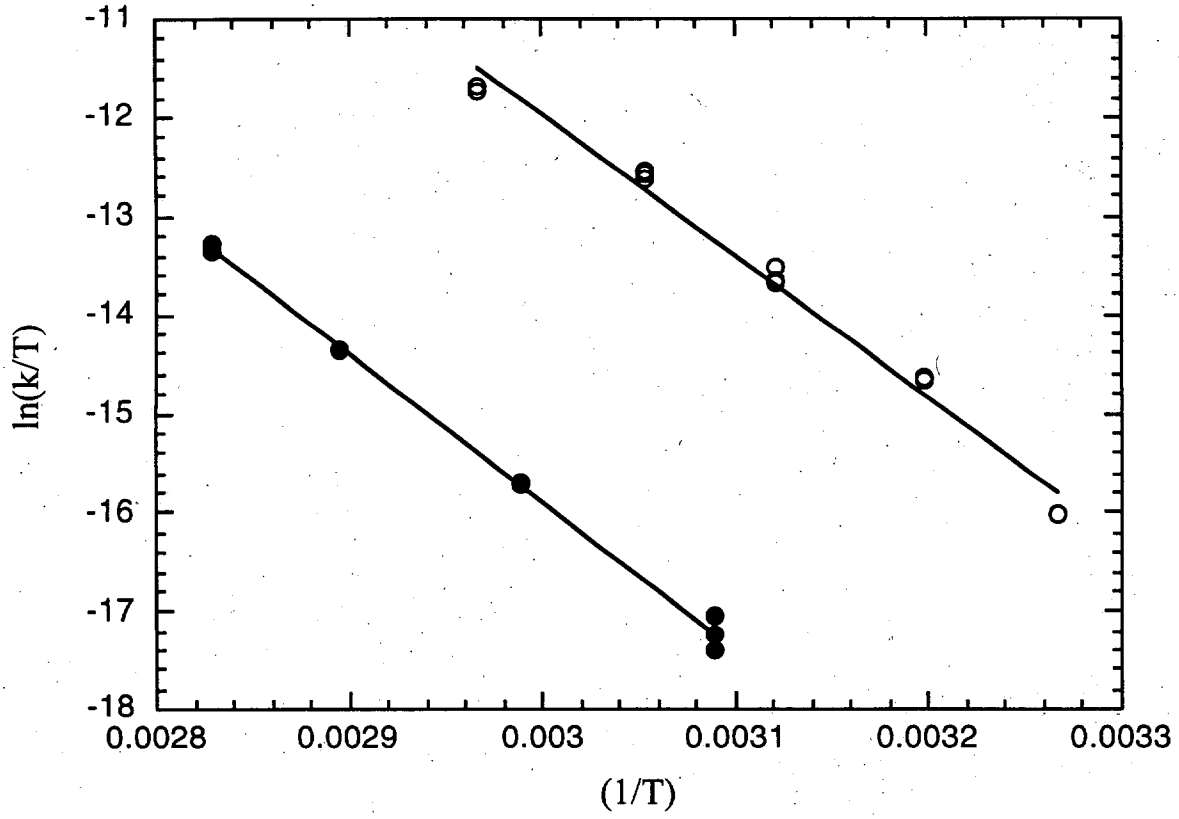

Figure S4b. Temperature effects on ligand substitution of [**3**]BF_4 in 3% (v/v) CH_2Cl_2/1,2-$C_6H_4Cl_2$ (solid circles) and **4** in 1,2-$C_6H_4Cl_2$ (open circles).

Table II.1. Crystal data and structure refinement for [(HCpz$_3$)Re(OPPh$_3$)Cl$_2$]Cl•0.5 CDCl$_3$ ([**3**]Cl•0.5 CDCl$_3$)

Empirical formula	$C_{28.5}H_{25}D_{0.5}Cl_{4.5}N_6OPRe$
Formula weight	845.75
Temperature	293(2) K
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 8.7612(11) Å α = 81.149(11) deg. b = 12.755(2) Å β = 85.397(9) deg. c = 14.418(2) Å γ = 81.243(12) deg.
Volume	1570.8(4) Å^3
Z	2
Density (calculated)	1.788 g/cm^3
Absorption coefficient	4.336 mm^{-1}
Absorption correction	Semi-empirical from psi-scans
Transmission	0.8166 to 0.9999
F(000)	826
Diffractometer	Enraf-Nonius CAD4
Radiation	graphite-monochromated MoKα (0.71073 Å)
Scan type	ω-2θ
Decay	0.2%, based on 3 standards measured every 7200 s exposure (180 reflections)
Crystal size	0.45 x 0.25 x 0.05 mm
Crystal habit	Plate
Crystal color	Orange
Theta range for data collection	2.01 to 24.98 deg.
Limiting indices	0<=h<=10, -14<=k<=15, -16<=l<=17
Reflections collected	5511
Independent reflections	5511
Structure solution method	Patterson

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5510 / 0 / 376
Goodness-of-fit on F^2	1.117
Final R indices [I>4sigma(I)]	R1 = 0.0301, wR2 = 0.0830
R indices (all data)	R1 = 0.0330, wR2 = 0.0866
Largest diff. peak and hole	1.241 and -1.135 $e \cdot Å^{-3}$

Table II.2. Atomic coordinates and equivalent isotropic displacement parameters for [($HCpz_3$)Re($OPPh_3$)Cl_2]Cl•0.5 $CDCl_3$ ([**3**]Cl•0.5 $CDCl_3$). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Re	0.05774(2)	0.382107(14)	0.248442(11)	0.03023(8)
Cl1	0.2920(2)	0.31667(12)	0.32296(10)	0.0492(3)
Cl2	0.1731(2)	0.50509(12)	0.13446(10)	0.0510(3)
Cl3	-0.4399(2)	0.3841(2)	0.6058(2)	0.0882(7)
P	0.06313(14)	0.17769(11)	0.11232(9)	0.0363(3)
O	0.1074(4)	0.2652(3)	0.1582(3)	0.0463(9)
N12	-0.0092(5)	0.4954(3)	0.3371(3)	0.0352(9)
N22	-0.1616(5)	0.4349(3)	0.1967(3)	0.0362(9)
N32	-0.0558(5)	0.2811(3)	0.3499(3)	0.0375(9)
N11	-0.1559(5)	0.5018(3)	0.3787(3)	0.0369(9)
N21	-0.2848(5)	0.4493(4)	0.2590(3)	0.0386(9)
N31	-0.1966(5)	0.3208(3)	0.3878(3)	0.0396(9)
C1	-0.2606(5)	0.4315(4)	0.3588(3)	0.0376(11)
C13	0.0555(6)	0.5706(4)	0.3671(4)	0.0424(12)
C14	-0.0482(7)	0.6261(5)	0.4262(4)	0.0506(13)
C15	-0.1812(7)	0.5797(4)	0.4340(4)	0.0457(12)
C23	-0.2186(7)	0.4579(4)	0.1129(4)	0.0448(12)
C24	-0.3777(7)	0.4865(5)	0.1219(4)	0.055(2)
C25	-0.4169(6)	0.4805(5)	0.2150(4)	0.0495(13)
C33	-0.0246(8)	0.1827(5)	0.3940(4)	0.0522(14)
C34	-0.1433(9)	0.1574(5)	0.4575(5)	0.065(2)
C35	-0.2514(8)	0.2471(5)	0.4525(5)	0.061(2)
C41	0.1693(6)	0.1753(4)	0.0005(4)	0.0387(11)
C42	0.2653(6)	0.0843(5)	-0.0211(4)	0.0487(13)
C43	0.3510(8)	0.0894(6)	-0.1062(5)	0.063(2)
C44	0.3400(8)	0.1826(6)	-0.1687(4)	0.066(2)
C45	0.2418(9)	0.2710(5)	-0.1483(5)	0.064(2)
C46	0.1585(7)	0.2689(5)	-0.0635(4)	0.0541(14)
C51	-0.1402(6)	0.1934(4)	0.0959(4)	0.0441(12)
C52	-0.2401(7)	0.1865(5)	0.1768(5)	0.056(2)
C53	-0.3966(8)	0.2076(6)	0.1689(7)	0.078(2)
C54	-0.4561(8)	0.2346(6)	0.0829(8)	0.089(3)
C55	-0.3598(9)	0.2398(6)	0.0026(7)	0.080(2)
C56	-0.2014(7)	0.2192(5)	0.0093(5)	0.059(2)
C61	0.1143(6)	0.0504(4)	0.1813(4)	0.0436(12)
C62	0.0356(9)	-0.0352(5)	0.1779(5)	0.066(2)
C63	0.0829(12)	-0.1345(6)	0.2283(6)	0.091(3)
C64	0.2089(11)	-0.1483(6)	0.2814(5)	0.081(2)
C65	0.2870(8)	-0.0648(7)	0.2861(5)	0.076(2)
C66	0.2405(7)	0.0351(6)	0.2371(4)	0.059(2)
Cl4	0.648(2)	-0.0951(7)	0.4407(10)	0.245(7)
C4	0.5000	0.0000	0.5000	0.179(9)

Table II.3. Bond lengths [Å] and angles [deg] for [(HCpz$_3$)Re(OPPh$_3$)Cl$_2$]Cl•0.5 CDCl$_3$ ([**3**]Cl•0.5 CDCl$_3$).

Re-N12	2.063(4)
Re-N32	2.089(4)
Re-N22	2.094(4)
Re-O	2.101(4)
Re-Cl2	2.3676(13)
Re-Cl1	2.3703(13)
P-O	1.494(4)
P-C61	1.783(6)
P-C51	1.792(5)
P-C41	1.797(5)
N12-C13	1.326(7)
N12-N11	1.370(6)
N22-C23	1.319(7)
N22-N21	1.357(6)
N32-C33	1.317(7)
N32-N31	1.365(6)
N11-C15	1.349(6)
N11-C1	1.449(6)
N21-C25	1.342(7)
N21-C1	1.449(6)
N31-C35	1.334(7)
N31-C1	1.449(7)
C13-C14	1.386(8)
C14-C15	1.375(8)
C23-C24	1.387(8)
C24-C25	1.353(9)
C33-C34	1.372(8)
C34-C35	1.366(9)
C41-C42	1.387(7)
C41-C46	1.388(8)
C42-C43	1.384(8)
C43-C44	1.373(10)
C44-C45	1.366(10)
C45-C46	1.371(8)
C51-C56	1.373(9)
C51-C52	1.401(8)
C52-C53	1.366(9)
C53-C54	1.358(13)
C54-C55	1.376(13)
C55-C56	1.381(10)
C61-C62	1.386(9)
C61-C66	1.392(8)
C62-C63	1.382(10)
C63-C64	1.368(12)
C64-C65	1.363(12)
C65-C66	1.379(10)
Cl4-C4	1.881(14)
C4-Cl4#1	1.881(14)
N12-Re-N32	84.8(2)
N12-Re-N22	83.8(2)
N32-Re-N22	85.2(2)
N12-Re-O	175.46(14)
N32-Re-O	92.6(2)

N22-Re-O	92.3(2)
N12-Re-Cl2	92.59(12)
N32-Re-Cl2	176.40(12)
N22-Re-Cl2	92.01(12)
O-Re-Cl2	89.84(12)
N12-Re-Cl1	93.24(12)
N32-Re-Cl1	89.04(13)
N22-Re-Cl1	173.76(11)
O-Re-Cl1	90.44(11)
Cl2-Re-Cl1	93.60(5)
O-P-C61	110.7(2)
O-P-C51	112.8(2)
C61-P-C51	107.6(3)
O-P-C41	108.8(2)
C61-P-C41	107.3(2)
C51-P-C41	109.6(2)
P-O-Re	151.6(2)
C13-N12-N11	105.8(4)
C13-N12-Re	135.9(4)
N11-N12-Re	118.2(3)
C23-N22-N21	105.6(4)
C23-N22-Re	135.8(4)
N21-N22-Re	118.7(3)
C33-N32-N31	105.3(4)
C33-N32-Re	136.1(4)
N31-N32-Re	118.5(3)
C15-N11-N12	110.8(4)
C15-N11-C1	129.1(4)
N12-N11-C1	120.1(4)
C25-N21-N22	111.4(4)
C25-N21-C1	129.3(4)
N22-N21-C1	119.4(4)
C35-N31-N32	110.8(5)
C35-N31-C1	129.7(5)
N32-N31-C1	119.4(4)
N31-C1-N21	110.1(4)
N31-C1-N11	109.9(4)
N21-C1-N11	109.5(4)
N12-C13-C14	110.4(5)
C15-C14-C13	106.4(5)
N11-C15-C14	106.6(5)
N22-C23-C24	110.0(5)
C25-C24-C23	106.8(5)
N21-C25-C24	106.3(5)
N32-C33-C34	110.9(6)
C35-C34-C33	106.0(5)
N31-C35-C34	106.9(5)
C42-C41-C46	119.9(5)
C42-C41-P	121.7(4)
C46-C41-P	118.3(4)
C43-C42-C41	119.0(6)
C44-C43-C42	120.6(6)
C45-C44-C43	120.2(6)
C44-C45-C46	120.3(6)
C45-C46-C41	120.0(6)
C56-C51-C52	119.2(5)
C56-C51-P	123.3(5)
C52-C51-P	117.3(5)

C53-C52-C51	120.0(7)
C54-C53-C52	120.4(7)
C53-C54-C55	120.4(6)
C54-C55-C56	120.0(8)
C51-C56-C55	120.0(7)
C62-C61-C66	119.0(6)
C62-C61-P	121.7(5)
C66-C61-P	119.2(5)
C63-C62-C61	120.5(7)
C64-C63-C62	119.6(8)
C65-C64-C63	120.7(7)
C64-C65-C66	120.5(7)
C65-C66-C61	119.7(7)

Table II.4. Anisotropic displacement parameters for [(HCpz$_3$)Re(OPPh$_3$)Cl$_2$]Cl•0.5 CDCl$_3$ ([**3**]Cl•0.5 CDCl$_3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Re	0.02750(12)	0.03691(12)	0.02699(12	-0.00958(8)	0.00222(7)	-0.00381(8)
Cl1	0.0338(6)	0.0637(8)	0.0487(7)	-0.0096(6)	-0.0062(5)	0.0012(6)
Cl2	0.0498(8)	0.0607(8)	0.0410(7)	0.0016(6)	0.0055(6)	-0.0166(6)
Cl3	0.0516(9)	0.105(2)	0.114(2)	-0.0650(13)	-0.0240(10)	0.0273(9)
P	0.0311(6)	0.0413(7)	0.0385(7)	-0.0162(5)	0.0010(5)	-0.0024(5)
O	0.038(2)	0.054(2)	0.053(2)	-0.030(2)	0.003(2)	-0.008(2)
N12	0.034(2)	0.039(2)	0.034(2)	-0.009(2)	-0.003(2)	-0.005(2)
N22	0.036(2)	0.039(2)	0.033(2)	-0.008(2)	-0.002(2)	-0.001(2)
N32	0.038(2)	0.042(2)	0.032(2)	-0.008(2)	0.007(2)	-0.008(2)
N11	0.031(2)	0.047(2)	0.036(2)	-0.017(2)	0.001(2)	-0.003(2)
N21	0.029(2)	0.051(2)	0.040(2)	-0.020(2)	-0.002(2)	-0.005(2)
N31	0.036(2)	0.046(2)	0.038(2)	-0.010(2)	0.009(2)	-0.009(2)
C1	0.029(2)	0.049(3)	0.037(3)	-0.017(2)	0.003(2)	-0.005(2)
C13	0.039(3)	0.044(3)	0.048(3)	-0.012(2)	-0.009(2)	-0.008(2)
C14	0.055(3)	0.047(3)	0.056(3)	-0.027(3)	-0.009(3)	-0.002(3)
C15	0.049(3)	0.049(3)	0.040(3)	-0.024(2)	-0.003(2)	0.007(2)
C23	0.052(3)	0.049(3)	0.035(3)	-0.014(2)	-0.009(2)	-0.002(2)
C24	0.046(3)	0.068(4)	0.053(3)	-0.021(3)	-0.023(3)	0.002(3)
C25	0.032(3)	0.059(3)	0.061(4)	-0.020(3)	-0.012(2)	-0.002(2)
C33	0.064(4)	0.051(3)	0.041(3)	-0.011(2)	0.003(3)	-0.005(3)
C34	0.085(5)	0.045(3)	0.061(4)	-0.003(3)	0.024(4)	-0.014(3)
C35	0.064(4)	0.064(4)	0.055(4)	-0.011(3)	0.025(3)	-0.022(3)
C41	0.035(2)	0.046(3)	0.040(3)	-0.021(2)	0.001(2)	-0.008(2)
C42	0.042(3)	0.050(3)	0.055(3)	-0.021(3)	0.001(2)	0.002(2)
C43	0.056(4)	0.074(4)	0.062(4)	-0.037(3)	0.009(3)	0.003(3)
C44	0.069(4)	0.091(5)	0.044(3)	-0.027(3)	0.019(3)	-0.024(4)
C45	0.084(5)	0.057(4)	0.050(3)	-0.009(3)	0.010(3)	-0.014(3)
C46	0.064(4)	0.050(3)	0.048(3)	-0.013(3)	0.008(3)	-0.005(3)
C51	0.034(3)	0.044(3)	0.057(3)	-0.018(2)	-0.001(2)	-0.006(2)
C52	0.042(3)	0.065(4)	0.068(4)	-0.029(3)	0.007(3)	-0.013(3)
C53	0.038(3)	0.077(5)	0.130(7)	-0.053(5)	0.020(4)	-0.019(3)
C54	0.028(3)	0.073(5)	0.177(10)	-0.047(6)	-0.018(5)	-0.004(3)
C55	0.065(5)	0.073(5)	0.109(6)	-0.023(4)	-0.041(5)	-0.004(4)
C56	0.047(3)	0.059(4)	0.073(4)	-0.019(3)	-0.014(3)	-0.005(3)
C61	0.042(3)	0.051(3)	0.037(3)	-0.012(2)	0.000(2)	-0.001(2)
C62	0.081(5)	0.055(4)	0.065(4)	-0.004(3)	-0.020(4)	-0.018(3)
C63	0.134(8)	0.055(4)	0.082(5)	0.002(4)	-0.023(5)	-0.015(5)
C64	0.111(7)	0.063(5)	0.060(4)	0.001(4)	-0.005(4)	0.013(4)
C65	0.056(4)	0.106(6)	0.054(4)	-0.005(4)	-0.016(3)	0.020(4)
C66	0.045(3)	0.071(4)	0.058(4)	-0.014(3)	-0.005(3)	0.002(3)
Cl4	0.289(13)	0.137(7)	0.34(2)	-0.043(8)	-0.208(12)	-0.017(7)
C4	0.22(3)	0.14(2)	0.19(2)	-0.05(2)	-0.02(2)	-0.03(2)

Table II.5. Hydrogen coordinates and isotropic displacement parameters for [(HCpz$_3$)Re(OPPh$_3$)Cl$_2$]Cl•0.5 CDCl$_3$ ([**3**]Cl•0.5 CDCl$_3$).

	x	y	z	U(eq)
H1	-0.3600(5)	0.4476(4)	0.3937(3)	0.038
H13	0.1563(6)	0.5841(4)	0.3507(4)	0.042
H14	-0.0312(7)	0.6834(5)	0.4550(4)	0.051
H15	-0.2711(7)	0.5984(4)	0.4703(4)	0.046
H23	-0.1606(7)	0.4553(4)	0.0562(4)	0.045
H24	-0.4445(7)	0.5061(5)	0.0732(4)	0.055
H25	-0.5158(6)	0.4950(5)	0.2430(4)	0.050
H33	0.0659(8)	0.1364(5)	0.3834(4)	0.052
H34	-0.1490(9)	0.0924(5)	0.4961(5)	0.065
H35	-0.3452(8)	0.2552(5)	0.4876(5)	0.061
H42	0.2720(6)	0.0209(5)	0.0209(4)	0.049
H43	0.4167(8)	0.0291(6)	-0.1212(5)	0.063
H44	0.3996(8)	0.1856(6)	-0.2252(4)	0.066
H45	0.2314(9)	0.3330(5)	-0.1920(5)	0.064
H46	0.0949(7)	0.3301(5)	-0.0489(4)	0.054
H52	-0.2000(7)	0.1676(5)	0.2358(5)	0.056
H53	-0.4626(8)	0.2034(6)	0.2227(7)	0.078
H54	-0.5627(8)	0.2498(6)	0.0783(8)	0.089
H55	-0.4014(9)	0.2572(6)	-0.0561(7)	0.080
H56	-0.1362(7)	0.2229(5)	-0.0450(5)	0.059
H62	-0.0496(9)	-0.0258(5)	0.1414(5)	0.066
H63	0.0293(12)	-0.1916(6)	0.2262(6)	0.091
H64	0.2417(11)	-0.2154(6)	0.3146(5)	0.081
H65	0.3723(8)	-0.0753(7)	0.3227(5)	0.076
H66	0.2932(7)	0.0921(6)	0.2412(4)	0.059

Table III.1. Crystal data and structure refinement for $(HBpz_3)Re(OPPh_3)Cl_2 \cdot C_6H_6$ (**4**$\cdot C_6H_6$)

Empirical formula	$C_{33}H_{31}BCl_2N_6OPRe$
Formula weight	826.52
Temperature	293(2) K
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 8.867(2) Å α = 84.22(3) deg. b = 11.288(2) Å β = 85.08(3) deg. c = 16.881(3) Å γ = 89.35(3) deg.
Volume	1674.8(6) $Å^3$
Z	2
Density (calculated)	1.639 g/cm^3
Absorption coefficient	3.872 mm^{-1}
Absorption correction	Semi-empirical from psi-scans
Transmission	0.2240 to 0.3078
F(000)	816
Diffractometer	Enraf-Nonius CAD4
Radiation	graphite-monochromated MoKα (0.71073 Å)
Scan type	ω-2θ
Decay	<2%, based on 3 standards measured every 7200 s exposure (350 reflections)
Crystal size	0.38 x 0.22 x 0.12 mm
Crystal habit	Prism
Crystal color	Yellow
Theta range for data collection	2.08 to 25.01 deg.
Limiting indices	0<=h<=10, -13<=k<=13, -19<=l<=20
Reflections collected	5890
Independent reflections	5890
Structure solution method	Patterson

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5890 / 0 / 506
Goodness-of-fit on F^2	1.076
Final R indices [I>4sigma(I)]	R1 = 0.0180, wR2 = 0.0452
R indices (all data)	R1 = 0.0197, wR2 = 0.0462
Largest diff. peak and hole	0.468 and -0.498 $e \cdot Å^{-3}$

Table III.2. Atomic coordinates and equivalent isotropic displacement parameters for $(HBpz_3)Re(OPPh_3)Cl_2 \cdot C_6H_6$ (**4**$\cdot C_6H_6$). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Re	-0.196408(11)	-0.351246(8)	-0.276219(6)	0.02589(4)
Cl2	-0.04348(9)	-0.47926(7)	-0.19515(5)	0.0481(2)
Cl1	0.01998(9)	-0.25386(7)	-0.34701(5)	0.0460(2)
P	-0.29347(8)	-0.15017(6)	-0.13645(4)	0.02840(14)
O	-0.2034(2)	-0.2263(2)	-0.19156(11)	0.0337(4)
N11	-0.3535(3)	-0.4916(2)	-0.38446(14)	0.0367(5)
N12	-0.2134(3)	-0.4701(2)	-0.36012(14)	0.0331(5)
N31	-0.4671(3)	-0.2915(2)	-0.3681(2)	0.0388(6)
N32	-0.3389(3)	-0.2436(2)	-0.34455(14)	0.0343(5)
N21	-0.5090(3)	-0.4565(2)	-0.2589(2)	0.0372(5)
N22	-0.3881(3)	-0.4364(2)	-0.21774(14)	0.0327(5)
C13	-0.1148(4)	-0.5365(3)	-0.4006(2)	0.0423(7)
C14	-0.1895(4)	-0.6015(3)	-0.4501(2)	0.0502(8)
C15	-0.3379(4)	-0.5710(3)	-0.4382(2)	0.0465(8)
C33	-0.3418(4)	-0.1262(3)	-0.3683(2)	0.0421(7)
C34	-0.4724(4)	-0.0995(3)	-0.4058(2)	0.0536(9)
C35	-0.5472(4)	-0.2036(3)	-0.4046(2)	0.0512(9)
C23	-0.4271(4)	-0.4748(3)	-0.1413(2)	0.0415(7)
C24	-0.5722(4)	-0.5188(3)	-0.1332(2)	0.0511(9)
C25	-0.6209(4)	-0.5056(3)	-0.2078(2)	0.0479(8)
C51	-0.4905(3)	-0.1891(2)	-0.1184(2)	0.0342(6)
C52	-0.5781(4)	-0.1841(3)	-0.1831(2)	0.0418(7)
C53	-0.7262(4)	-0.2198(3)	-0.1727(2)	0.0540(9)
C54	-0.7899(4)	-0.2581(4)	-0.0973(3)	0.0643(11)
C55	-0.7064(4)	-0.2601(4)	-0.0321(2)	0.0593(10)
C56	-0.5561(4)	-0.2267(3)	-0.0426(2)	0.0432(7)
C61	-0.2870(3)	0.0033(2)	-0.1764(2)	0.0332(6)
C62	-0.4000(4)	0.0826(3)	-0.1539(2)	0.0476(8)
C63	-0.3906(5)	0.2000(3)	-0.1843(2)	0.0606(10)
C64	-0.2713(5)	0.2398(3)	-0.2362(2)	0.0599(10)
C65	-0.1589(5)	0.1622(3)	-0.2586(2)	0.0579(10)
C66	-0.1656(4)	0.0439(3)	-0.2286(2)	0.0439(7)
C41	-0.2157(3)	-0.1651(3)	-0.0412(2)	0.0337(6)
C42	-0.2110(4)	-0.0716(4)	0.0055(2)	0.0551(9)
C43	-0.1551(6)	-0.0913(5)	0.0804(3)	0.0794(14)
C44	-0.1050(5)	-0.2025(5)	0.1073(2)	0.0756(14)
C45	-0.1082(4)	-0.2944(4)	0.0605(2)	0.0619(11)
C46	-0.1628(4)	-0.2768(3)	-0.0138(2)	0.0434(7)
B	-0.4949(4)	-0.4258(3)	-0.3500(2)	0.0412(8)
C1	0.1347(7)	-0.9007(10)	-0.4249(6)	0.144(4)
C2	0.1650(7)	-0.7832(10)	-0.4519(3)	0.122(3)
C3	0.2464(7)	-0.7208(5)	-0.4105(5)	0.105(2)
C4	0.3001(6)	-0.7657(6)	-0.3447(4)	0.100(2)
C5	0.2748(7)	-0.8772(6)	-0.3176(3)	0.098(2)
C6	0.1936(7)	-0.9454(4)	-0.3555(6)	0.111(3)
H0	-0.593(4)	-0.451(3)	-0.376(2)	0.038(8)
H13	-0.021(4)	-0.532(3)	-0.388(2)	0.035(8)

H14	-0.147(4)	-0.657(3)	-0.482(2)	0.045(9)
H15	-0.422(4)	-0.593(3)	-0.460(2)	0.048(10)
H33	-0.254(4)	-0.076(3)	-0.359(2)	0.036(8)
H34	-0.507(4)	-0.027(4)	-0.423(2)	0.065(12)
H35	-0.633(4)	-0.220(3)	-0.420(2)	0.040(9)
H23	-0.364(3)	-0.471(3)	-0.104(2)	0.031(8)
H24	-0.633(5)	-0.544(4)	-0.086(3)	0.082(14)
H25	-0.710(4)	-0.521(3)	-0.227(2)	0.048(9)
H52	-0.538(4)	-0.157(3)	-0.233(2)	0.049(10)
H53	-0.786(4)	-0.217(3)	-0.217(2)	0.059(11)
H54	-0.885(6)	-0.277(4)	-0.093(3)	0.10(2)
H55	-0.750(5)	-0.286(4)	0.021(3)	0.072(12)
H56	-0.498(4)	-0.225(3)	0.000(2)	0.044(9)
H62	-0.482(4)	0.055(3)	-0.121(2)	0.033(8)
H63	-0.455(5)	0.250(4)	-0.171(3)	0.075(14)
H64	-0.269(4)	0.315(4)	-0.257(2)	0.061(11)
H65	-0.088(5)	0.189(4)	-0.294(3)	0.071(13)
H66	-0.094(4)	-0.005(3)	-0.245(2)	0.042(9)
H42	-0.240(4)	0.005(3)	-0.014(2)	0.058(11)
H43	-0.138(6)	-0.032(4)	0.109(3)	0.10(2)
H44	-0.070(6)	-0.217(4)	0.157(3)	0.10(2)
H45	-0.072(5)	-0.367(4)	0.079(3)	0.082(14)
H46	-0.162(4)	-0.341(3)	-0.047(2)	0.049(10)

Table III.3. Bond lengths [Å] and angles [deg] for $(HBpz_3)Re(OPPh_3)Cl_2 \cdot C_6H_6$ (**4**$\cdot C_6H_6$).

Re-N12	2.062(2)
Re-N32	2.083(2)
Re-N22	2.084(2)
Re-O	2.103(2)
Re-Cl2	2.3824(11)
Re-Cl1	2.3891(11)
P-O	1.503(2)
P-C61	1.794(3)
P-C41	1.795(3)
P-C51	1.799(3)
N11-C15	1.336(4)
N11-N12	1.373(3)
N11-B	1.550(4)
N12-C13	1.334(4)
N31-C35	1.343(4)
N31-N32	1.370(3)
N31-B	1.535(4)
N32-C33	1.346(4)
N21-C25	1.344(4)
N21-N22	1.360(3)
N21-B	1.536(5)
N22-C23	1.337(4)
C13-C14	1.380(5)
C14-C15	1.360(5)
C33-C34	1.383(5)
C34-C35	1.353(6)
C23-C24	1.375(5)
C24-C25	1.359(5)
C51-C56	1.388(4)
C51-C52	1.389(4)
C52-C53	1.370(5)
C53-C54	1.378(6)
C54-C55	1.376(6)
C55-C56	1.381(5)
C61-C66	1.383(4)
C61-C62	1.390(4)
C62-C63	1.373(5)
C63-C64	1.364(6)
C64-C65	1.373(6)
C65-C66	1.380(5)
C41-C42	1.382(5)
C41-C46	1.390(4)
C42-C43	1.392(5)
C43-C44	1.373(7)
C44-C45	1.367(7)
C45-C46	1.379(5)
C1-C6	1.372(11)
C1-C2	1.380(10)
C2-C3	1.305(9)
C3-C4	1.300(8)
C4-C5	1.310(8)
C5-C6	1.309(9)
N12-Re-N32	85.16(9)

N12-Re-N22	85.02(9)
N32-Re-N22	88.34(10)
N12-Re-O	173.98(8)
N32-Re-O	90.20(9)
N22-Re-O	91.01(9)
N12-Re-Cl2	94.47(7)
N32-Re-Cl2	177.33(7)
N22-Re-Cl2	88.99(7)
O-Re-Cl2	89.98(6)
N12-Re-Cl1	93.68(7)
N32-Re-Cl1	90.40(7)
N22-Re-Cl1	178.26(6)
O-Re-Cl1	90.19(6)
Cl2-Re-Cl1	92.26(4)
O-P-C61	110.73(13)
O-P-C41	108.96(13)
C61-P-C41	109.28(13)
O-P-C51	114.29(12)
C61-P-C51	106.47(14)
C41-P-C51	106.95(13)
P-O-Re	149.72(12)
C15-N11-N12	108.5(3)
C15-N11-B	131.4(3)
N12-N11-B	120.1(2)
C13-N12-N11	106.7(2)
C13-N12-Re	134.6(2)
N11-N12-Re	118.7(2)
C35-N31-N32	108.6(3)
C35-N31-B	132.3(3)
N32-N31-B	119.1(2)
C33-N32-N31	106.9(2)
C33-N32-Re	133.5(2)
N31-N32-Re	119.4(2)
C25-N21-N22	109.1(3)
C25-N21-B	132.4(3)
N22-N21-B	118.5(2)
C23-N22-N21	106.6(2)
C23-N22-Re	133.1(2)
N21-N22-Re	120.2(2)
N12-C13-C14	110.1(3)
C15-C14-C13	105.3(3)
N11-C15-C14	109.4(3)
N32-C33-C34	109.1(3)
C35-C34-C33	106.3(3)
N31-C35-C34	109.2(3)
N22-C23-C24	110.0(3)
C25-C24-C23	105.8(3)
N21-C25-C24	108.6(3)
C56-C51-C52	119.3(3)
C56-C51-P	122.1(2)
C52-C51-P	118.6(2)
C53-C52-C51	120.5(3)
C52-C53-C54	119.8(4)
C55-C54-C53	120.6(3)
C54-C55-C56	119.7(4)
C55-C56-C51	120.1(3)
C66-C61-C62	119.5(3)
C66-C61-P	119.5(2)

C62-C61-P	121.0(2)
C63-C62-C61	119.7(4)
C64-C63-C62	120.7(4)
C63-C64-C65	120.1(3)
C64-C65-C66	120.3(4)
C65-C66-C61	119.7(3)
C42-C41-C46	119.9(3)
C42-C41-P	122.6(2)
C46-C41-P	117.4(2)
C41-C42-C43	119.3(4)
C44-C43-C42	120.2(4)
C45-C44-C43	120.3(4)
C44-C45-C46	120.4(4)
C45-C46-C41	119.7(4)
N31-B-N21	108.5(3)
N31-B-N11	107.9(3)
N21-B-N11	107.6(3)
C6-C1-C2	117.4(6)
C3-C2-C1	119.0(6)
C4-C3-C2	122.2(6)
C3-C4-C5	120.6(6)
C6-C5-C4	120.9(6)
C5-C6-C1	120.0(6)

Table III.4. Anisotropic displacement parameters for $(HBpz_3)Re(OPPh_3)Cl_2 \cdot C_6H_6$ (**4**$\cdot C_6H_6$). The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} * U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Re	0.02511(6)	0.02566(6)	0.02710(6)	-0.00288(4)	-0.00320(4)	0.00101(4)
Cl2	0.0447(4)	0.0430(4)	0.0571(5)	0.0045(4)	-0.0185(4)	0.0096(3)
Cl1	0.0380(4)	0.0553(5)	0.0436(4)	-0.0032(3)	0.0035(3)	-0.0137(3)
P	0.0305(4)	0.0278(3)	0.0273(3)	-0.0044(3)	-0.0029(3)	0.0003(3)
O	0.0332(10)	0.0330(10)	0.0360(10)	-0.0098(8)	-0.0023(8)	0.0015(8)
N11	0.0366(13)	0.0391(13)	0.0367(13)	-0.0122(11)	-0.0062(10)	-0.0021(10)
N12	0.0326(12)	0.0339(12)	0.0330(12)	-0.0060(10)	-0.0001(10)	0.0017(10)
N31	0.0340(13)	0.0456(14)	0.0392(14)	-0.0089(11)	-0.0122(11)	0.0093(11)
N32	0.0379(13)	0.0353(13)	0.0302(12)	-0.0040(10)	-0.0045(10)	0.0051(10)
N21	0.0290(12)	0.0385(13)	0.0455(14)	-0.0120(11)	-0.0012(11)	-0.0035(10)
N22	0.0330(12)	0.0308(12)	0.0342(13)	-0.0043(10)	-0.0011(10)	-0.0030(10)
C13	0.043(2)	0.041(2)	0.043(2)	-0.0105(14)	0.0032(14)	0.0047(14)
C14	0.060(2)	0.045(2)	0.047(2)	-0.020(2)	0.004(2)	0.004(2)
C15	0.057(2)	0.046(2)	0.040(2)	-0.0164(14)	-0.009(2)	-0.002(2)
C33	0.057(2)	0.037(2)	0.032(2)	0.0011(12)	-0.0027(14)	0.006(2)
C34	0.066(2)	0.052(2)	0.041(2)	0.004(2)	-0.008(2)	0.025(2)
C35	0.048(2)	0.064(2)	0.044(2)	-0.009(2)	-0.017(2)	0.019(2)
C23	0.049(2)	0.035(2)	0.038(2)	-0.0022(13)	0.005(2)	-0.0036(14)
C24	0.053(2)	0.042(2)	0.056(2)	-0.006(2)	0.018(2)	-0.013(2)
C25	0.031(2)	0.044(2)	0.069(2)	-0.015(2)	0.008(2)	-0.0085(14)
C51	0.032(2)	0.0319(14)	0.039(2)	-0.0079(12)	-0.0014(12)	0.0015(11)
C52	0.038(2)	0.048(2)	0.040(2)	-0.0071(14)	-0.0059(14)	0.0045(14)
C53	0.037(2)	0.063(2)	0.066(2)	-0.021(2)	-0.011(2)	0.005(2)
C54	0.031(2)	0.080(3)	0.084(3)	-0.025(2)	0.007(2)	-0.009(2)
C55	0.045(2)	0.069(2)	0.060(2)	-0.010(2)	0.019(2)	-0.008(2)
C56	0.038(2)	0.049(2)	0.041(2)	-0.0057(14)	0.0038(14)	-0.0016(14)
C61	0.042(2)	0.0276(14)	0.0308(14)	-0.0034(11)	-0.0064(12)	-0.0004(12)
C62	0.057(2)	0.036(2)	0.049(2)	-0.0051(14)	0.004(2)	0.004(2)
C63	0.087(3)	0.034(2)	0.061(2)	-0.006(2)	-0.013(2)	0.018(2)
C64	0.088(3)	0.032(2)	0.059(2)	0.006(2)	-0.014(2)	-0.006(2)
C65	0.067(2)	0.047(2)	0.056(2)	0.008(2)	-0.003(2)	-0.015(2)
C66	0.044(2)	0.041(2)	0.046(2)	-0.0015(14)	-0.002(2)	-0.002(2)
C41	0.0284(14)	0.044(2)	0.0285(14)	-0.0020(12)	-0.0026(11)	-0.0032(12)
C42	0.064(2)	0.062(2)	0.044(2)	-0.017(2)	-0.016(2)	0.005(2)
C43	0.089(3)	0.111(4)	0.047(2)	-0.030(3)	-0.021(2)	-0.009(3)
C44	0.066(3)	0.123(4)	0.038(2)	0.004(2)	-0.019(2)	-0.010(3)
C45	0.044(2)	0.087(3)	0.050(2)	0.024(2)	-0.012(2)	-0.002(2)
C46	0.035(2)	0.051(2)	0.042(2)	0.005(2)	-0.0043(13)	-0.0041(14)
B	0.032(2)	0.047(2)	0.047(2)	-0.015(2)	-0.008(2)	0.002(2)
C1	0.059(3)	0.216(9)	0.181(8)	-0.155(8)	0.000(5)	-0.006(5)
C2	0.070(4)	0.245(10)	0.047(3)	-0.005(4)	0.001(2)	0.057(5)
C3	0.087(4)	0.074(3)	0.138(6)	0.035(4)	0.023(4)	0.013(3)
C4	0.091(4)	0.090(4)	0.129(5)	-0.045(4)	-0.025(4)	0.002(3)
C5	0.100(4)	0.112(5)	0.076(3)	0.012(3)	0.000(3)	0.035(4)
C6	0.077(4)	0.048(3)	0.199(8)	-0.021(4)	0.053(4)	-0.009(3)

Table III.5. Hydrogen coordinates and isotropic displacement parameters for $(HBpz_3)Re(OPPh_3)Cl_2 \cdot C_6H_6$ (**4**$\cdot C_6H_6$).

	x	y	z	U(eq)
H1	0.0766(7)	-0.9477(10)	-0.4527(6)	0.144
H2	0.1279(7)	-0.7490(10)	-0.4988(3)	0.122
H3	0.2667(7)	-0.6416(5)	-0.4287(5)	0.105
H4	0.3571(6)	-0.7183(6)	-0.3167(4)	0.100
H5	0.3150(7)	-0.9082(6)	-0.2707(3)	0.098
H6	0.1759(7)	-1.0242(4)	-0.3354(6)	0.111
H0	-0.593(4)	-0.451(3)	-0.376(2)	0.038(8)
H13	-0.021(4)	-0.532(3)	-0.388(2)	0.035(8)
H14	-0.147(4)	-0.657(3)	-0.482(2)	0.045(9)
H15	-0.422(4)	-0.593(3)	-0.460(2)	0.048(10)
H33	-0.254(4)	-0.076(3)	-0.359(2)	0.036(8)
H34	-0.507(4)	-0.027(4)	-0.423(2)	0.065(12)
H35	-0.633(4)	-0.220(3)	-0.420(2)	0.040(9)
H23	-0.364(3)	-0.471(3)	-0.104(2)	0.031(8)
H24	-0.633(5)	-0.544(4)	-0.086(3)	0.082(14)
H25	-0.710(4)	-0.521(3)	-0.227(2)	0.048(9)
H52	-0.538(4)	-0.157(3)	-0.233(2)	0.049(10)
H53	-0.786(4)	-0.217(3)	-0.217(2)	0.059(11)
H54	-0.885(6)	-0.277(4)	-0.093(3)	0.10(2)
H55	-0.750(5)	-0.286(4)	0.021(3)	0.072(12)
H56	-0.498(4)	-0.225(3)	0.000(2)	0.044(9)
H62	-0.482(4)	0.055(3)	-0.121(2)	0.033(8)
H63	-0.455(5)	0.250(4)	-0.171(3)	0.075(14)
H64	-0.269(4)	0.315(4)	-0.257(2)	0.061(11)
H65	-0.088(5)	0.189(4)	-0.294(3)	0.071(13)
H66	-0.094(4)	-0.005(3)	-0.245(2)	0.042(9)
H42	-0.240(4)	0.005(3)	-0.014(2)	0.058(11)
H43	-0.138(6)	-0.032(4)	0.109(3)	0.10(2)
H44	-0.070(6)	-0.217(4)	0.157(3)	0.10(2)
H45	-0.072(5)	-0.367(4)	0.079(3)	0.082(14)
H46	-0.162(4)	-0.341(3)	-0.047(2)	0.049(10)