Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPLEMENTARY INFORMATION

NO-binding in $\{Ru(NO)_2\}^8$-type $[Ru(NO)_2(PR_3)_2X]BF_4$ compounds

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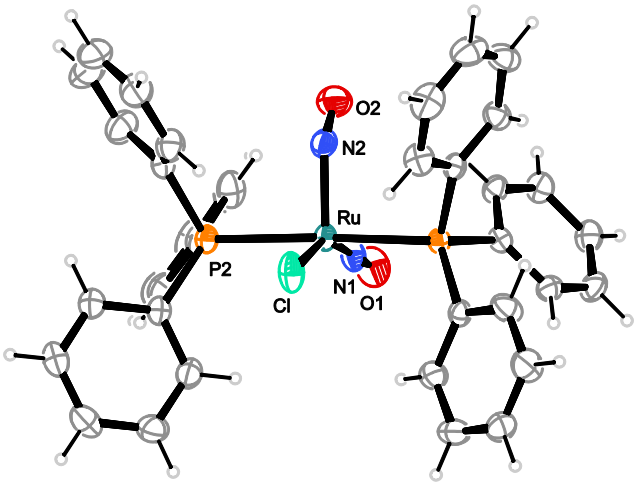

Fig. 5 (extended) Structure of the *vOC*-5-type complex cation in crystals of $[RuCl(NO)_2(PPh_3)_2]BF_4$ (**1**). Interatomic distances (Å) and angles (°): Ru–N1 1.746(2), Ru–N2 1.872(2), Ru–P1 2.4470(6), Ru–P2 2.4534(6), Ru–Cl 2.3523(6), O1–N1 1.155(3), O2–N2 1.162(3); O1–N1–Ru 178.9(2), O2–N2–Ru 134.78(19), N1–Ru–Cl 151.17(7), N1–Ru–P1 92.87(7), N1–Ru–P2 92.99(7), N1–Ru–N2 102.67(10), N2–Ru–Cl 106.14(7), N2–Ru–P1 92.21(6), N2–Ru–P2 90.15(6), Cl–Ru–P1 85.13(2), Cl–Ru–P2 87.93(2), P1–Ru–P2 173.05(2).

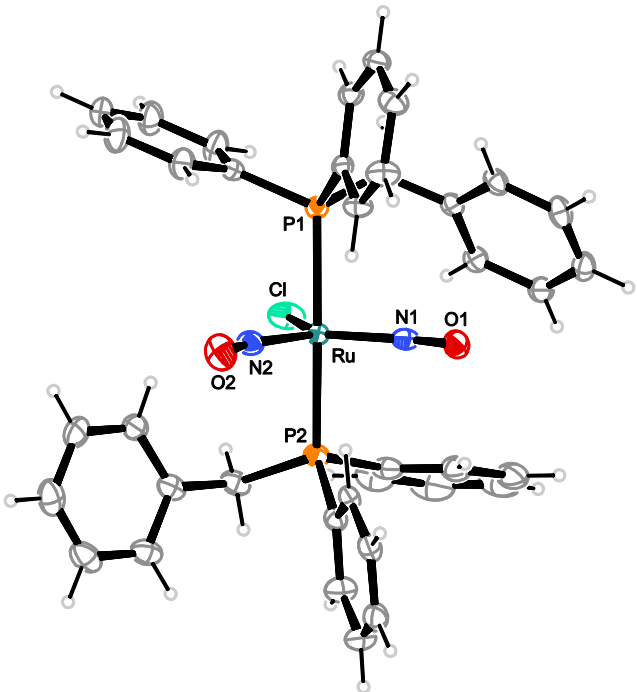

Fig. 6 (extended): Structure of the *TBPY*-5-type complex cation $[RuCl(NO)_2(PPh_2Bn)_2]^+$ in crystals of **3**. The thermal ellipsoids are drawn at 50% probability level. Interatomic distances (Å) and angles (°), the standard deviation of the last decimal place is given in parentheses: Ru–N1 1.781(2), Ru–N2 1.785(2), Ru–Cl 2.4122(7), Ru–P1 2.4110(7), Ru–P2 2.4168(7), O1–N1 1.156(3), O2–N2 1.145(3); O1–N1–Ru 167.2(2), O2–N2–Ru 164.0(2), N1–Ru–Cl 124.14(8), N1–Ru–P1 93.41(7), N1–Ru–P2 92.88(7), N1–Ru–N2 115.52(11), N2–Ru–Cl 120.34(8), N2–Ru–P1 95.58(7), N2–Ru–P2 95.83(7), Cl–Ru–P1 81.63(2), Cl–Ru–P2 81.85(2), P1–Ru–P2 163.10(2).

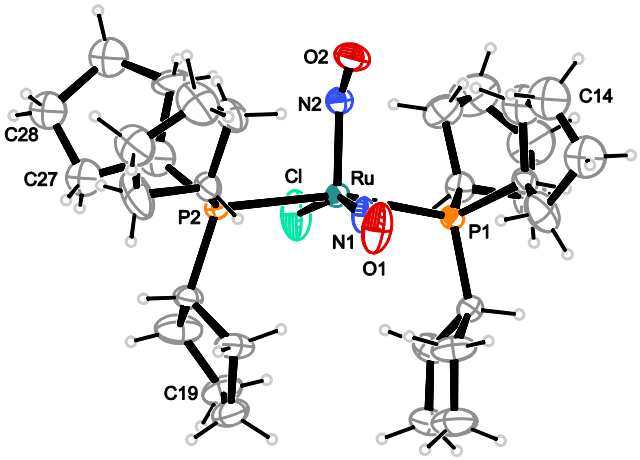

Fig. 7 (extended) Structure of the *vOC*-5-type complex cation $[RuCl(NO)_2(PCyp_3)_2]^+$ in crystals of **8a**. The thermal ellipsoids are drawn at 40% probability level. Some carbon atoms are disordered. The minor parts of C14 (44%), C19 (42%) and C27 and C28 (47%) are not shown. Interatomic distances (Å) and angles (°), the standard deviation of the last decimal place is given in parentheses: Ru–N1 1.758(3), Ru–N2 1.850 (4), Ru–Cl 2.3523(16), Ru–P1 2.4569(16), Ru–P2 2.4729(15), O1–N1 1.128(5), O2–N2 1.157(5), O1–N1–Ru 176.9(4), O2–N2–Ru 137.0(4), N1–Ru–N2 103.5(2), N1–Ru–Cl 157.42(15), N1–Ru–P1 92.77(13), N1–Ru–P2 90.01(13), N2–Ru–Cl 98.93(14), N2–Ru–P1 98.35(13), N2–Ru–P2 97.42(13), Cl–Ru–P1 86.20(6), Cl–Ru–P2 84.78(6), P1–Ru–P2 162.87(4). C13–15 and C26–29 were refined isotropically.

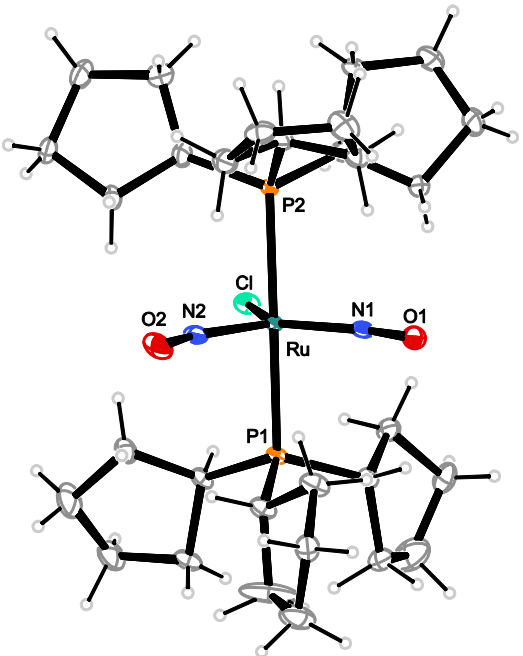

Fig. 8 (extended) Structure of the *TBPY*-5-type complex cation $[RuCl(NO)_2(PCyp_3)_2]^+$ in crystals of **8b**. The thermal ellipsoids are drawn at 50% probability level. Interatomic distances (Å) and angles (°), the standard deviation of the last decimal place is given in parentheses: Ru–N1 1.775(2), Ru–N2 1.783 (2), Ru–Cl 2.4185(7), Ru–P1 2.4470(7), Ru–P2 2.4480(7), O1–N1 1.154(3), O2–N2 1.153(3), O1–N1–Ru 168.1(2), O2–N2–Ru 164.4(2), N1–Ru–Cl 126.35(8), N1–Ru–P1 89.93(7), N1–Ru–P2 95.83(7), N1–Ru–N2 117.02(11), N2–Ru–Cl 116.60(8), N2–Ru–P1 91.74(7),

N2–Ru–P2 96.04(7), Cl–Ru–P1 86.72(2), Cl–Ru–P2 80.42(2), P1–Ru–P2 166.94(2).

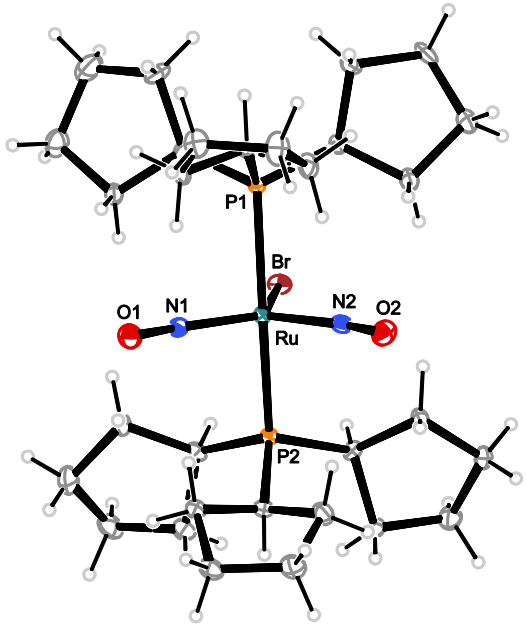

Fig. 9 (extended) Structure of the *TBPY*-5-type complex cation $[RuBr(NO)_2(PCyp_3)_2]^+$ in crystals of **9**. The thermal ellipsoids are drawn at 50% probability level. Interatomic distances (Å) and angles (°), the standard deviation of the last decimal place is given in parentheses: Ru–N1 1.779(3), Ru–N2 1.780(3), Ru–Br 2.5734(5), Ru–P1 2.4438(10), Ru–P2 2.4479(10), O1–N1 1.164(4), O2–N2 1.162(4), O1–N1–Ru 168.7(3), O2–N2–Ru 166.6(3), N1–Ru–Br 124.57(11), N1–Ru–P1 93.11(10), N1–Ru–P2 95.01(10), N1–Ru–N2 118.83(15), N2–Ru–Br 116.60(10), N2–Ru–P1 95.05(10), N2–Ru–P2 93.95(10), Br–Ru–P1 81.95(3), Br–Ru–P2 81.26(3), P1–Ru–P2 163.12(4).

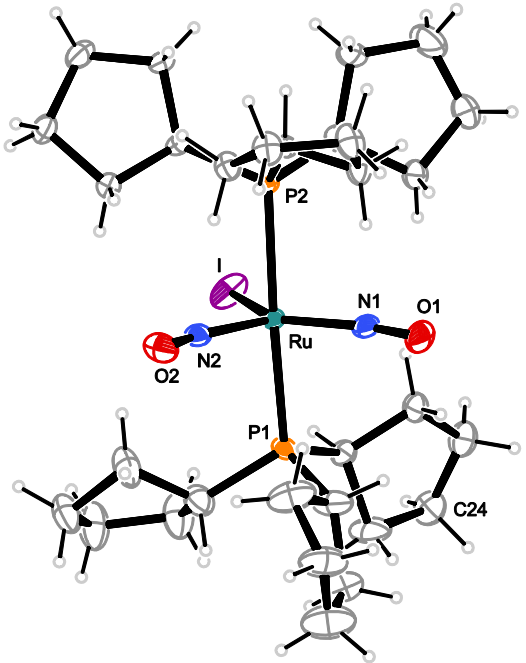

Fig. 12: Structure of the *TBPY*-5-type complex cation $[RuI(NO)_2(PCyp_3)_2]^+$ in crystals of **10**. The thermal ellipsoids are drawn at 50% probability level. C24 is disordered, the minor part (34%) is not shown. Interatomic distances (Å) and angles (°), the standard deviation of the last decimal place is given in parentheses: Ru–N1 1.779(4), Ru–N2 1.787(4), Ru–I 2.7301(5), Ru–P1 2.4584(11), Ru–P2 2.4583(11), O1–N1 1.148(5), O2–N2 1.152(5), O1–N1–Ru 168.9(4), O2–N2–Ru 165.5(4), N1–Ru–I 128.30(14), N1–Ru–P1 88.00(12), N1–Ru–P2 94.51(12), N1–Ru–N2 118.45(19), N2–Ru–I 113.18(13), N2–Ru–P1 95.78(12), N2–Ru–P2 94.14(12), I–Ru–P1 84.35(3), I–Ru–P2 84.18(3), P1–Ru–P2 167.10(4).

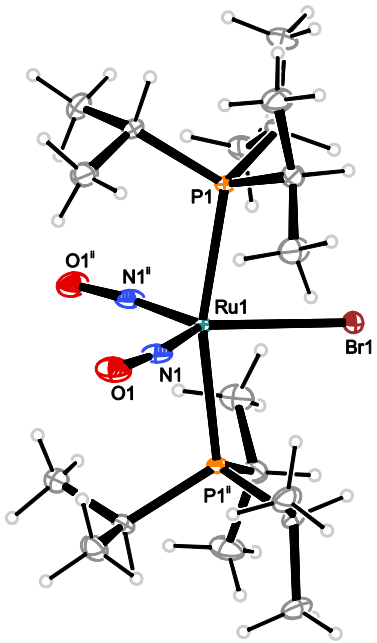

Fig. 11 (extended) Structure of the *TBPY*-5-type conformer **12b** of the complex cation $[RuBr(NO)_2(P^iPr_3)_2]^+$ in crystals of **12**. The thermal ellipsoids are drawn at 50% probability level. Interatomic distances (Å) and angles (°), the standard deviation of the last decimal place is given in parentheses: Ru–N1 1.785(3), Ru–Br 2.5502(6), Ru–P1 2.4592(8), O1–N1 1.138(4), O1–N1–Ru 165.34(3), N1–Ru–Br 123.54(10), N1–Ru–P1 93.18(9), N1–Ru–$P1^{ii}$ 95.19(9), N1–Ru–$N1^{ii}$ 112.9(2), Br–Ru–P1 82.41(2), P1–Ru–$P1^{ii}$ 164.82(4). Selected torsion angles: $N1^{ii}$–Ru1–N1–O1 4(1), Br1–Ru1–N1–O1 −176(1). Symmetry code: ^{ii} −x + 1, y, −z + ½.

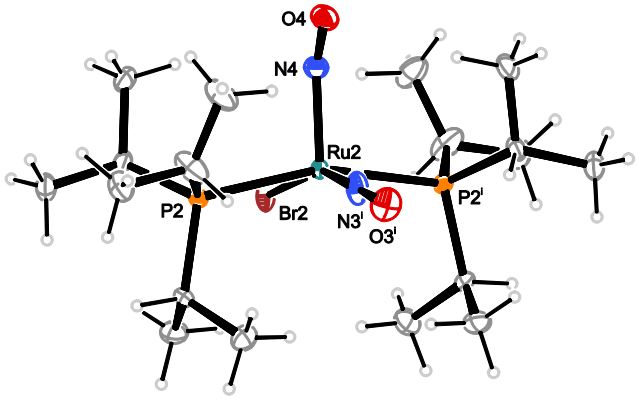

Fig. 12 (extended) Structure of the *vOC*-5-type conformer **12a** of the complex cation $[RuBr(NO)_2(P^iPr_3)_2]^+$ in crystals of **12**. The thermal ellipsoids are drawn at 50% probability level. Interatomic distances (Å) and angles (°), the standard deviation of the last decimal place is given in parentheses: Ru2–N3 1.72(1), Ru2–N4 1.860(5), Ru2–Br 2.4606(17), Ru2–P2 2.4705(9), O3–N3 1.22(1), O4–N4 1.060(6); O3–N3–Ru2 177(1), O4–N4–Ru2 150.8(3), N4–Ru2–Br 103.34(5), N4–Ru2–P2 99.14(2), N4–Ru2–N3 100.1(3), N3–Ru2–Br^i 156.5(3), N3–Ru2–P2 88.5(3), $Br2^i$–Ru–P2 89.16(4), P1–Ru–P2 161.72(4). Selected torsion angles: $N3^i$–Ru2–N4–O4 −2.1(7), Br2–Ru2–N4–O4 176.5(7). Symmetry code: ^{i} −x, y, −z + ½. The Ru–N distances and RuNO angles as well as the Ru–Br distance have to be viewed with caution, since the linear NO group and the Br ligand are disordered in such a way as to be superimposed onto each other. The bent NO group is also disordered in such a way to ensure that the O4 atom is always inclined to the linear NO group. This kind of disorder corresponds to crystallographic

*mm*2 site symmetry of the cations.

Figures S1–S6 show the structures of the complex cations of **2**, **4**, **5**, **6**, **7** and **11**. Tables 2 and 5 enlist the crystallographic data for the measurements of **3** and **9** at different temperatures, performed for the investigation of the temperature dependence of the atomic displacement parameters. Tables 1, 3, 4 and 6 enlist crystallographic data for **1**–**12**.

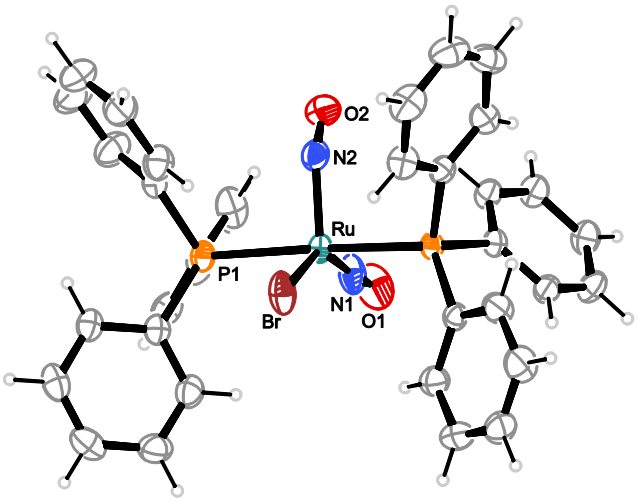

Fig. S1 Structure of the *vOC*-5-type complex cation $[RuBr(NO)_2(PPh_3)_2]^+$ in crystals of **2**. The thermal ellipsoids are drawn at 50% probability level. Interatomic distances (Å) and angles (°), the standard deviation of the lastdecimal place is given in parentheses: Ru–N1 1.753(2), Ru–N2 1.854(2), Ru–P1 2.4537(6), Ru–P2 2.4470(6), Ru–Br 2.5062(3), O1–N1 1.1352(29), O2–N2 1.148(3); O1–N1–Ru 175.3(3), O2–N2–Ru 143.1(2), N1–Ru–Br 142.03(9), N1–Ru–P1 93.50(7), N1–Ru–P2 92.21(7), N1–Ru–N2 105.75(11), N2–Ru–Br 112.20(7), N2–Ru–P1 90.11(6), N2–Ru–P2 92.59(7), Br–Ru–P1 87.71(2), Br–Ru–P2 85.06(2), P1–Ru–P2 172.78(2). Selected torsion angles: N1–Ru1–N2–O2 4.4(3), Br1–Ru1–N2–O2 −176.8(3).

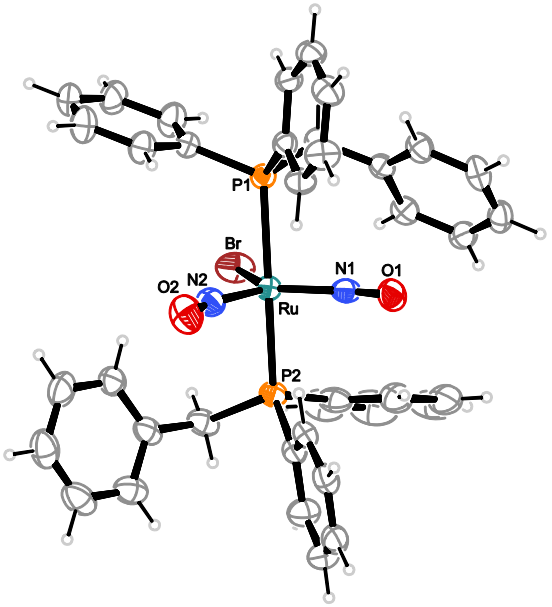

Fig. S2 Structure of the coordination cation $[RuBr(NO)_2(PPh_2Bn)_2]^+$ in crystals of **4**. The thermal ellipsoids are drawn at 50% probability level. Interatomic distances (Å) and angles (°), the standard deviation of the last decimal place is given in parentheses: Ru–N1 1.776(3), Ru–N2 1.781(3), Ru–Br 2.5446(5), Ru–P1 2.4224(9), Ru–P2 2.4225(10), O1–N1 1.153(4), O2–N2 1.158(4), O1–N1–Ru 168.3(3), O2–N2–Ru 162.4(3), N1–Ru–Br 125.51(11), N1–Ru–P1 93.45(10), N1–Ru–P2 92.06(10), N1–Ru–N2 115.53(15), N2–Ru–Br 118.95(11), N2–Ru–P1 95.96(11), N2–Ru–P2 95.46(11), Br–Ru–P1 81.83(3), Br–Ru–P2 82.49(3), P1–Ru–P2 163.72(3).

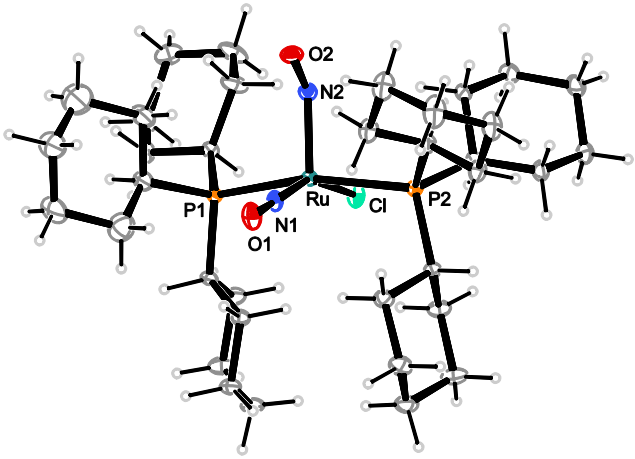

Fig. S3 Structure of the *vOC*-5-type complex cation $[RuCl(NO)_2(PCy_3)_2]^+$ in crystals of **5**. The thermal ellipsoids are drawn at 50% probability level. Interatomic distances (Å) and angles (°), the standard deviation of the last decimal place is given in parentheses: Ru–N1 1.739(3), Ru–N2 1.870(3), Ru–Cl 2.3738(7), Ru–P1 2.4558(8), Ru–P2 2.4792(8), O1–N1 1.162(3), O2–N2 1.159(3), O1–N1–Ru 179.9(3), O2–N2–Ru 136.5(2), N1–Ru–Cl 154.52(9), N1–Ru–P1 92.69(8), N1–Ru–P2 92.11(8), N1–Ru–N2 103.64(12), N2–Ru–Cl 101.80(8), N2–Ru–P1 99.06(8), N2–Ru–P2 95.06(8), Cl–Ru–P1 81.97(3), Cl–Ru–P2 86.98(3), P1–Ru–P2 163.58(3).

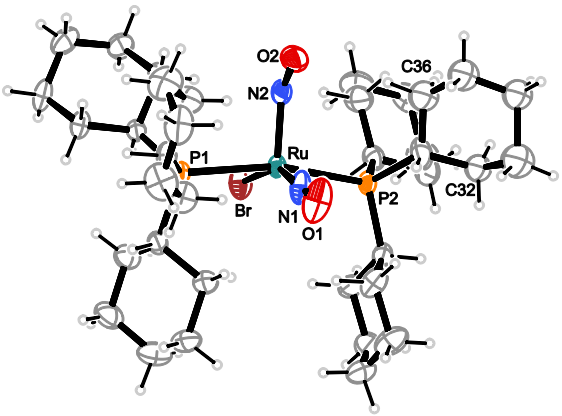

Fig. S4 Structure of the coordination cation $[RuBr(NO)_2(PCy_3)_2]^+$ in crystals of **6**. The thermal ellipsoids are drawn at 50% probability level. Carbon atoms C32–C36 are disordered, the minor part is not shown (40%). Interatomic distances (Å) and angles (°), the standard deviation of the last decimal place is given in parentheses: Ru–N1 1.756(6), Ru–N2 1.846(6), Ru–Br 2.5092(12), Ru–P1 2.4585(17), Ru–P2 2.4769(18), O1–N1 1.120(8), O2–N2 1.151(7), O1–N1–Ru 177.3(6), O2–N2–Ru 139.3(6), N1–Ru–Br 153.0(2), N1–Ru–P1 94.64(18), N1–Ru–P2 89.75(18), N1–Ru–N2 104.1(3), N2–Ru–Br 102.83(19), N2–Ru–P1 96.68(16), N2–Ru–P2 97.16(16), Br–Ru–P1 82.27(5), Br–Ru–P2 86.84(5), P1–Ru–P2 163.99(5). Atoms C32–C36 were refined isotropically.

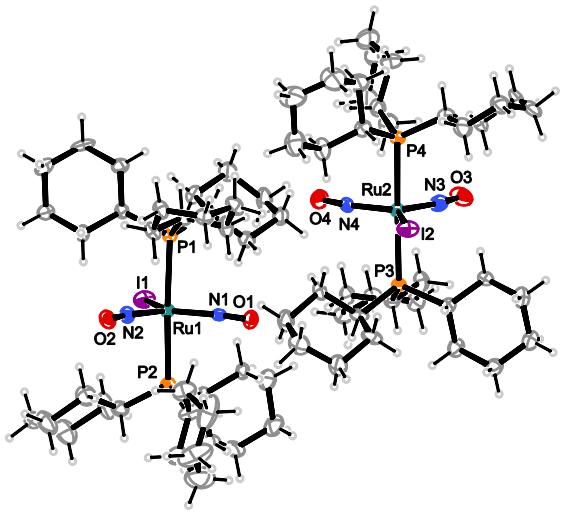

Fig. S5 Structures of the two crystallographic independent coordination cations $[RuI(NO)_2(PCy_3)_2]^+$ in the asymmetric unit in crystals of **7**. The thermal ellipsoids are drawn at 50% probability level. Interatomic distances (Å) and angles (°), the standard deviation of the last decimal place is given in parentheses: Ru1–N1 1.773(8), Ru1–N2 1.789(9), Ru1–I1 2.7231(10), Ru1–P1 2.475(2), Ru1–P2 2.479(3), O1–N1 1.16(1), O2–N2 1.16(1), O1–N1–Ru1 170.9(8), O2–N2–Ru1 165.9(8), N1–Ru1–I1 121.9(3), N1–Ru1–P1 92.2(2), N1–Ru1–P2 88.1(2), N1–Ru1–N2 122.3(4), N2–Ru1–I1 115.8(3), N2–Ru1–P1 93.9(3), N2–Ru1–P2 93.9(3), I1–Ru1–P1 83.93(6), I1–Ru1–P2 86.71(6), P1–Ru1–P2 169.16(9); Ru2–N3 1.791(9), Ru2–N4 1.790(7), Ru2–I2 2.7301(10), Ru2–P3 2.466(2), Ru2–P4 2.485(3), O3–N3 1.15(1), O4–N4 1.15 (1), O3–N3–Ru2 170.3(9), O4–N4–Ru2 163.1(8), N3–Ru2–I2 122.9(3), N3–Ru2–P3 93.0(3), N3–Ru2–P4 92.6(3), N3–Ru2–N4 118.8(4), N4–Ru2–I2 118.3(3), N4–Ru2–P3 94.7(3), N4–Ru2–P4 89.7(3), I2–Ru2–P3 82.56(6), I2–Ru2–P4 87.56(7), P3–Ru2–P4 170.12(9).

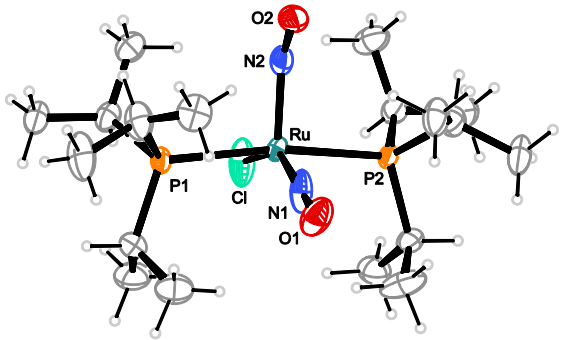

Fig. S6 Structure of the complex cation $[RuCl(NO)_2(P^iPr_3)_2]^+$ in crystals of **11**. The thermal ellipsoids are drawn at 50% probability level. Interatomic distances (Å) and angles (°), the standard deviation of the last decimal place is given in parentheses: Ru–N1 1.740(8), Ru–N2 1.831(8), Ru–Cl 2.380(2), Ru–P1 2.456(2), Ru–P2 2.459(2), O1–N1 1.12(1), O2–N2 1.131 (9), O1–N1–Ru 178.0(9), O2–N2–Ru 149.2(8), N1–Ru–Cl 143.7(3), N1–Ru–P1 91.4(2), N1–Ru–P2 91.7(2), N1–Ru–N2 109.0(4), N2–Ru–Cl 107.2(3), N2–Ru–P1 95.6(2), N2–Ru–P2 94.8(2), Cl–Ru–P1 85.88(8), Cl–Ru–P2 84.53(8), P1–Ru–P2 167.53(7).

Table 1 Crystallographic data for $[RuCl(NO)_2(PPh_3)_2]BF_4$ (**1**), $[RuBr(NO)_2(PPh_3)_2]BF_4$ (**2**) and $[RuCl(NO)_2(PPh_2Bn)_2]BF_4$ (**3**).

Compound reference	**1**	**2**	**3** (103K)[a]
Chemical formula	$C_{36}H_{30}BClF_4N_2O_2P_2Ru$	$C_{36}H_{30}BBrF_4N_2O_2P_2Ru$	$C_{38}H_{34}BClF_4N_2O_2P_2Ru$
Formula Mass	807.89	852.35	835.94
Crystal system	monoclinic	monoclinic	monoclinic
a/Å	19.2204(3)	19.2932(3)	12.9469(4)
b/Å	9.9060(2)	9.96620(10)	20.7987(6)
c/Å	20.6933(4)	20.7107(3)	13.6465(4)
α/°	90.00	90.00	90.00
β/°	117.6270(10)	116.9370(10)	91.274(3)
γ/°	90.00	90.00	90.00
Unit cell volume/Å^3	3490.73(11)	3550.20(8)	3673.80(19)
Temperature/K	173(2)	173(2)	103(2)
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
No. of formula units per unit cell, *Z*	4	4	4
No. of reflections measured	22356	28118	21238
No. of independent reflections	7924	8113	8425
R_{int}	0.0357	0.0359	0.0435
Final R_1 values ($I > 2\sigma(I)$)	0.0347	0.0303	0.0384
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0726	0.0684	0.0908
Final R_1 values (all data)	0.0552	0.0453	0.0516
Final $wR(F^2)$ values (all data)	0.0809	0.0745	0.1009
Goodness of fit on F^2	1.045	1.013	1.060
CCDC number	985278	985280	985283

5

Table 2 Crystallographic data for $[RuCl(NO)_2(PPh_2Bn)_2]BF_4$ (**3**) at different temperatures.

Compound reference	**3** (153 K)	**3** (203 K)	**3** (248 K)	**3** (293 K)
Chemical formula	$C_{38}H_{34}BClF_4N_2O_2P_2Ru$	$C_{38}H_{34}BClF_4N_2O_2P_2Ru$	$C_{38}H_{34}BClF_4N_2O_2P_2Ru$	$C_{38}H_{34}BClF_4N_2O_2P_2Ru$
Formula Mass	835.94	835.94	835.94	835.94
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
a/Å	12.9805(4)	13.0423(4)	13.1114(9)	13.1197(13)
b/Å	20.8824(7)	20.9379(8)	20.9350(16)	21.006(2)
c/Å	13.7090(5)	13.7807(5)	13.8377(12)	13.8668(13)
α/°	90.00	90.00	90.00	90.00
β/°	91.563(4)	91.718(3)	91.974(8)	91.774(9)
γ/°	90.00	90.00	90.00	90.00
Unit cell volume/Å^3	3714.6(2)	3761.5(2)	3796.0(5)	3819.8(6)
Temperature/K	153(2)	203(2)	248(2)	293(2)
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
No. of formula units per unit cell, *Z*	4	4	4	4
No. of reflections measured	29144	24559	23872	17610
No. of independent reflections	8618	12185	12329	8667
R_{int}	0.0449	0.0380	0.0411	0.0400
Final R_1 values ($I > 2\sigma(I)$)	0.0357	0.0468	0.0569	0.0484
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0815	0.0880	0.1114	0.0970
Final R_1 values (all data)	0.0502	0.0867	0.1121	0.0900
Final $wR(F^2)$ values (all data)	0.0915	0.1084	0.1443	0.1237
Goodness of fit on F^2	1.068	1.037	1.043	1.048

Table 3 Crystallographic data for $[RuBr(NO)_2(PPh_2Bn)_2]BF_4$ (**4**), $[RuCl(NO)_2(PCy_3)_2]BF_4$ (**5**) $[RuBr(NO)_2(PCy_3)_2]BF_4$ (**6**).

Compound reference	**4**	**5**	**6** · 0.5 H_2O · EtOH
Chemical formula	$C_{38}H_{34}BBrF_4N_2O_2P_2Ru$	$C_{36}H_{66}BClF_4N_2O_2P_2Ru$	$C_{38}H_{73}BBrF_4N_2O_{3.5}P_2Ru$
Formula Mass	880.40	844.18	943.71
Crystal system	monoclinic	triclinic	triclinic
a/Å	13.1175(2)	10.1237(3)	10.152(4)
b/Å	20.7878(3)	13.1351(4)	13.095(5)
c/Å	13.6911(2)	16.2864(4)	18.857(7)
α/°	90.00	80.7850(10)	95.262(14)
β/°	92.1940(10)	85.1250(10)	102.251(18)
γ/°	90.00	68.7460(10)	109.874(19)
Unit cell volume/Å^3	3730.61(10)	1991.49(10)	2267.0(15)
Temperature/K	173(2)	100(2)	293(2)
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
No. of formula units per unit cell, *Z*	4	2	2
No. of reflections measured	29667	35930	60091
No. of independent reflections	8530	9180	8641
R_{int}	0.0445	0.0533	0.0861
Final R_1 values ($I > 2\sigma(I)$)	0.0447	0.0431	0.0656
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1048	0.1021	0.1685
Final R_1 values (all data)	0.0679	0.0608	0.0977
Final $wR(F^2)$ values (all data)	0.1163	0.1106	0.1868
Goodness of fit on F^2	1.037	1.042	1.064
CCDC number	985281	985288	986284

Table 4 Crystallographic data for, $[RuI(NO)_2(PCy_3)_2]BF_4$ (**7**), $[RuCl(NO)_2(PCyp_3)_2]BF_4$ (**8**) and $[RuBr(NO)_2(PCyp_3)_2]BF_4$ (**9**).

Compound reference	**7**	**8a**	**8b**	**9** (113 K)[a]
Chemical formula	$C_{36}H_{66}BF_4IN_2O_2P_2Ru$	$C_{30}H_{54}BClF_4N_2O_2P_2Ru$	$C_{30}H_{54}BClF_4N_2O_2P_2Ru$	$C_{30}H_{54}BBrF_4N_2O_2P_2Ru$
Formula Mass	935.63	760.02	760.02	804.47
Crystal system	orthorhombic	monoclinic	monoclinic	triclinic
a/Å	29.645(3)	14.3483(8)	12.664(6)	10.8145(7)
b/Å	14.4732(9)	12.5016(7)	19.479(9)	12.3066(9)
c/Å	20.678(3)	19.4893(12)	14.921(7)	13.8538(9)
α/°	90.00	90.00	90.00	104.889(6)
β/°	90.00	106.688(2)	111.23(2)	91.394(5)
γ/°	90.00	90.00	90.00	108.105(6)
Unit cell volume/Å^3	8872.1(17)	3348.7(3)	3431(3)	1682.7(2)
Temperature/K	173(2)	100(2)	293(2)	113(2)
Space group	$Pca2_1$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
No. of formula units per unit cell, *Z*	8	4	4	2
No. of reflections measured	29769	126341	77101	7909
No. of independent reflections	11453	9061	7892	5780
R_{int}	0.0402	0.0634	0.0914	0.0315
Final R_1 values ($I > 2\sigma(I)$)	0.0557	0.0415	0.0570	0.0388
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1532	0.0985	0.1155	0.0715
Final R_1 values (all data)	0.0684	0.0567	0.1217	0.0543
Final $wR(F^2)$ values (all data)	0.1667	0.1059	0.1413	0.0816
Goodness of fit on F^2	1.062	1.052	1.020	1.060
CCDC number	986283	985289	985285	985284

Table 5 Crystallographic data for $[RuBr(NO)_2(PCyp_3)_2]BF_4$ (**9**) at different temperatures.

Compound reference	**9** (153 K)	**9** (193 K)	**9** (233 K)	**9** (273 K)
Chemical formula	$C_{30}H_{54}BBrF_4N_2O_2P_2Ru$	$C_{30}H_{54}BBrF_4N_2O_2P_2Ru$	$C_{30}H_{54}BBrF_4N_2O_2P_2Ru$	$C_{30}H_{54}BBrF_4N_2O_2P_2Ru$
Formula Mass	804.47	804.47	804.47	804.47
Crystal system	triclinic	triclinic	triclinic	triclinic
a/Å	10.7881(7)	10.6634(6)	10.6061(5)	10.5646(5)
b/Å	12.3342(9)	12.3972(8)	12.4576(7)	12.4979(7)
c/Å	13.8933(9)	14.0285(8)	14.1425(9)	14.1969(8)
α/°	104.916(6)	104.851(5)	104.826(5)	104.825(5)
β/°	91.354(6)	91.200(5)	91.111(4)	90.938(4)
γ/°	107.901(6)	107.314(5)	106.940(4)	106.823(4)
Unit cell volume/Å^3	1689.3(2)	1701.80(17)	1719.06(16)	1726.24(15)
Temperature/K	153(2)	193(2)	233(2)	273(2)
Space group	*P*−1	*P*−1	*P*−1	*P*−1
No. of formula units per unit cell, *Z*	2	2	2	2
No. of reflections measured	8660	8635	9397	9186
No. of independent reflections	6102	6138	5330	6255
R_{int}	0.0317	0.0241	0.0268	0.0220
Final R_1 values ($I > 2\sigma(I)$)	0.0407	0.0525	0.0496	0.0463
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0790	0.1174	0.1131	0.1121
Final R_1 values (all data)	0.0592	0.0655	0.0609	0.0566
Final $wR(F^2)$ values (all data)	0.0919	0.1288	0.1224	0.1207
Goodness of fit on F^2	1.039	1.029	1.035	1.037

Table 6 Crystallographic data for $[RuI(NO)_2(PCyp_3)_2]BF_4$ (**10**), $[RuCl(NO)_2(P^iPr_3)_2]BF_4$ (**11**) and $[RuBr(NO)_2(P^iPr_3)_2]BF_4$ (**12**).

Compound reference	**10**	**11**	**12**
Chemical formula	$C_{30}H_{54}BF_4IN_2O_2P_2Ru$	$C_{18}H_{42}BClF_4N_2O_2P_2Ru$	$C_{18}H_{42}BBrF_4N_2O_2P_2Ru$
Formula Mass	851.47	603.81	648.27
Crystal system	triclinic	triclinic	monoclinic
a/Å	10.4351(3)	8.0664(6)	25.5181(9)
b/Å	12.4604(4)	12.7931(9)	15.9734(6)
c/Å	14.3846(4)	14.3849(11)	14.3915(5)
α/°	105.9226(12)	114.416(4)	90.00
β/°	90.8080(13)	91.746(5)	115.204(2)
γ/°	106.6948(13)	91.295(5)	90.00
Unit cell volume/Å^3	1714.00(9)	1350.04(17)	5307.7(3)
Temperature/K	200(2)	100(2)	100(2)
Space group	*P*−1	*P*−1	*C*2/*c*
No. of formula units per unit cell, *Z*	2	2	8
No. of reflections measured	31009	42763	43688
No. of independent reflections	7837	4583	6131
R_{int}	0.0272	0.0964	0.0697
Final R_1 values ($I > 2\sigma(I)$)	0.0474	0.0724	0.0393
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1136	0.1837	0.0878
Final R_1 values (all data)	0.0600	0.1002	0.0555
Final $wR(F^2)$ values (all data)	0.1229	0.2042	0.0949
Goodness of fit on F^2	1.050	1.059	1.046
CCDC number	985286	985279	985287

Table 7 τ_5 values and continuous shape measures (CShM; the value closest to the respective conformer is printed boldface).

	PR_3/X	τ_5-value		CShM(exp.)			CShM(calc.)		
		exp.	calc.	*vOC*-5	*TBPY*-5	*SPY*-5	*vOC*-5	*TBPY*-5	*SPY*-5
1	PPh_3/Cl	0.36	0.30	2.118	4.428	2.500	**2.588**	3.899	3.613
2	PPh_3/Br	0.51	0.41	2.849	3.616	3.035	3.730	**3.096**	4.312
3	PPh_2Bn/Cl	0.65	0.64	6.041	1.958	5.170	5.464	**2.124**	4.616
4	PPh_2Bn/Br	0.64	0.68	5.792	1.976	5.060	5.419	**2.153**	4.618
5	PCy_3/Cl	0.15	0.21	2.101	4.829	2.517	**1.804**	2.292	2.292
6	PCy_3/Br	0.19	0.16	1.891	5.369	2.337	**1.851**	5.325	2.383
7a	PCy_3/I	0.79	0.76	6.547	2.247	6.000	6.205	**2.110**	5.467
7b	PCy_3/I	0.78	0.76	6.547	2.247	6.000	6.731	**2.193**	6.360
8a	$PCyp_3$/Cl	0.09	0.10	1.666	5.923	2.213	**1.555**	6.236	2.167
8b	$PCyp_3$/Cl	0.68	0.71	5.778	2.242	5.224	5.495	**2.075**	4.518
9	$PCyp_3$/Br	0.66	0.63	6.078	2.327	5.369	5.618	**2.023**	4.955
10	$PCyp_3$/I	0.65	0.68	5.832	2.430	5.302	4.941	**2.464**	4.518
11	P^iPr_3/Cl	0.26	0.27	2.325	4.493	2.714	**2.170**	4.590	2.454
12a	P^iPr_3/Br	0.09	0.11	1.689	6.138	2.135	**1.999**	6.638	2.400
12b	P^iPr_3/Br	0.69	0.68	6.558	2.244	5.756	6.518	**2.303**	4.975

Experimental Section (standard procedures)

Mass spectrometry

Mass spectra were recorded on a Thermo Finnigan MAT 95 (FAB) and Thermo Finnigan LTQ FT with IonMax (ion source with ESI head). The highest measured value of a molecule peak can deviate from the calculated one in two mass units, depending on the halide isotope measured.

IR spectroscopy at room temperature

Measurements of IR spectra were performed using a Jasco FT/IR-460 plus device equipped with a single reflection ATR diamond plate (solid samples). Liquid samples were measured within an NaCl cell.

NMR spectroscopy

NMR spectra were recorded at room temperature on Jeol Eclipse 270 (^{1}H: 270 MHz, ^{31}P: 109 MHz).

Crystal structure determination and refinement

Crystals suitable for single-crystal X-ray diffraction were selected with the aid of a polarisation microscope. For subsequent measurement the crystals were mounted on either the tip of a glass fibre, a micro mount or a loop and investigated on a Nonius KappaCCD, an Oxford XCalibur, a Bruker d8Venture or a Bruker d8Quest. All X-ray devices worked with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by either direct or Patterson methods (SHELXS-97) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97).[1] Anisotropic displacement parameters were refined for all non-hydrogen atoms. Structure plots were made using ORTEP; thermal ellipsoids are drawn at 50% probability except otherwise stated.[2] For the distances and angles given in the captions of the structure plots, the standard deviation of the last decimal is given in parentheses. Crystallographic data are listed in the supplementary information.

1 G. Sheldrick, *Acta Crystallogr., Sect. A,*, 2008, **64**, 112–122.

2 L. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.