Supplementary Material (ESI) for Dalton Transactions

Homo- and heterodinuclear complexes of the tetrakis(pyrazolyl)borate ligand

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Supplementary Information

Contents

Table 1 ^{1}H,^{13}C-{^{1}H}, ^{11}B and ^{31}P-{^{1}H} NMR spectroscopic data for rhodium and iridium homo- and hetero-dinuclear complexes.[a]

Complex		^{1}H	^{13}C-{^{1}H}	^{11}B	^{31}P-{^{1}H}
1^{+}	[(η-cod)Rh{μ-B(pz)$_4$}Rh(η-cod)]$^{+}$	7.68 (d, 4H, PzC*H*), J(H,H) = 1.6 Hz; 7.50 (d, 4H, PzC*H*), J(H,H) = 2.6 Hz; 6.62 (app. t,[b] 4H, PzC*H*), J(H,H) = 2.3 Hz; 4.08 (s, 8H, codC*H*); 2.34-2.38 (br m, 8H, codC*H*$_2$); 1.82-1.90 (br m, 8H, codC*H*$_2$)	143.8 (s, Pz*C*H); 137.5 (s, Pz*C*H); 108.0 (s, Pz*C*H); 83.2 (d, cod*C*H), J(Rh,C) = 12.7 Hz; 30. 3 (s, cod*C*H$_2$)	-0.7	
2^{+}	[(η-nbd)Rh{μ-B(pz)$_4$}Rh(η-nbd)]$^{+}$	7.37 (d, 4H, PzC*H*), J(H,H) = 2.3 Hz; 7.07 (s, 4H, PzC*H*); 6.50 (app. t,[b] 4H, PzC*H*), J(H,H) = 2.3 Hz; 4.11 (dd, 8H, nbdC*H*)[c], J(H,H) = 2.3 and 4.9 Hz; 3.89-3.95 (br m, 4H, nbdC*H*); 1.47 (t, 4H, nbdC*H*$_2$), J(H,H) = 1.7 Hz;	144.6 (s, Pz*C*H); 138.4 (s, Pz*C*H); 109.4 (s, Pz*C*H); 64.5 (d, nbd*C*H)[c], J(Rh,C) = 6.2 Hz; 60.3 (s, nbd*C*H$_2$); 52.3 (s, nbd*C*H)	-0.5	
3^{+}	[(η-cod)Ir{μ-B(pz)$_4$}Ir(η-cod)]$^{+}$	7.76 (d, 4H, PzC*H*), J(H,H) = 2.4 Hz; 7.45 (d, 4H, PzC*H*), J(H,H) = 2.5 Hz; 6.59 (app t,[b] 4H, PzC*H*), J(H,H) = 2.4 Hz; 3.79 (br, 8H, codC*H*); 2.13-2.17 (br m, 8H, codC*H*$_2$); 1.61-1.69 (br m, 8H, codC*H*$_2$)	145.6 (s, Pz*C*H); 139.7 (s, Pz*C*H); 110.1 (s, Pz*C*H); 69.5 (cod*C*H); 32.4 (cod*C*H$_2$)	-0.5	
4^{+}	[(CO)$_2$Rh{μ-B(pz)$_4$}Rh(CO)$_2$]$^{+}$	7.93 (d, 4H, PzC*H*), J(H,H) = 2.3 Hz; 7.39 (d, 4H, PzC*H*), J(H,H) = 2.3 Hz; 6.63 (app. t,[b] 4H, PzC*H*), J(H,H) = 2.3 Hz	182.9 (d, *C*O), J(Rh,C) = 72 Hz; 149.2 (s, pz*C*H); 138.1 (s, pz*C*H); 109.3 (s, pz*C*H)	-0.6	
5^{+}	[(CO)(PPh$_3$)Rh{μ-B(pz)$_4$}Rh(CO)(PPh$_3$)]$^{+}$	8.01 (d, 2H, pzC*H*), J(H,H) = 2.3 Hz; 7.65 (d, 2H, pzC*H*), J(H,H) = 2.3 Hz; 7.49-7.27 (m, 30H, Ph*H*); 7.00 (d, 2H, pzC*H*), J(H,H) = 2.3 Hz; 6.72 (s, 2H, pzC*H*); 6.51 (app. t,[b] 2H, pzC*H*), J(H,H) = 2.2 Hz; 5.94 (t, 2H, pzC*H*) J(H,H) = 2.2 Hz	187.2 (dd, *C*O), J(Rh,C = 73 Hz, J(C,P) = 24 Hz; 149.3 (s, Pz*C*H); 147.8 (s, Pz*C*H); 139.2 (s, pz*C*H);); 138.5 (s, pz*C*H); 134.0-129.3 {m, P(C$_6$H$_5$)$_3$}; 110.7 (s, pz*C*H); 109.5 (s, pz*C*H)	-0.6	43.9 {d, J(Rh,P) =159 Hz}
6^{+}	[(CO)$_2$Ir{μ-B(pz)$_4$}Ir(CO)$_2$]$^{+}$	8.10 (d, 4H, PzC*H*), J(H,H) = 2.4 Hz; 7.49 (d, 4H, PzC*H*), J(H,H) = 2.4 Hz; 6.69 (app. t,[b] 4H, PzC*H*), J(H,H) = 2.4 Hz	185.3 (s, *C*O); 184.7 (s, *C*O); 151.2 (s, pz*C*H); 140.0 (s, pz*C*H); 110.9 (s, pz*C*H)	-0.5	
7^{+}	[(η-cod)Rh{μ-B(pz)$_4$}Rh(η-nbd)]$^{+}$			-0.7	
8^{+}	[(η-cod)Rh{μ-B(pz)$_4$}Ir(η-cod)]$^{+}$			-0.7	
9^{+}	[(η-cod)Rh{μ-B(pz)$_4$}Rh(CO)$_2$]$^{+}$			-0.6	
10	[(η-cod)Rh{μ-B(pz)$_4$}CoCl$_2$]	40.77 (br s, 2H, pzC*H*); 29.72 (br s, 2H, pzC*H*); 11.84 (br s, 2H, pzC*H*); 10.10 (s, 2H, pzC*H*); 8.95 (s, 2H, pzC*H*); 6.47 (s, 4H, codC*H*); 3.47 (s, 4H, codC*H*$_2$); 2.73 (s, 4H, codC*H*$_2$); -25.40 (br s, 2H, pzC*H*)	206.4 (s, pz*C*H); 148.2 (s, pz*C*H); 115.1 (s, pz*C*H); 86.7 (s, cod*C*H); 32.4 (s, cod*C*H$_2$)	-0.9; 27.8	
11	[(η-nbd)Rh{μ-B(pz)$_4$}CoCl$_2$]	42.44 (s, 2H, pzC*H*); 28.59 (s, 2H, pzC*H*); 14.32 (br s, 2H, pzC*H*); 9.88 (s, 2H, pzC*H*); 8.99 (s, 2H, pzC*H*); 6.23 (s, 4H, nbdC*H*)[c]; 5.07 (s, 2H, nbdC*H*); 2.29 (s, 2H, nbdC*H*$_2$); -24.00 (br s, 2H, pzC*H*)	148.5 (s, pz*C*H); 116.3 (s, pz*C*H); 65.2 (s, nbd*C*H$_2$); 62.0 (s, nbd*C*H)[c]; 52.1 (s, nbd*C*H)	-0.8; 21.4	
12	[(CO)$_2$Rh{μ-B(pz)$_4$}CoCl$_2$]	41.60 (s, 2H, pzC*H*); 30.00 (s, 2H, pzC*H*); 12.09 (br s, 2H, pzC*H*); 10.54 (s, 2H, pzC*H*); 9.30 (s, 2H, pzC*H*); -25.00 (br s, 2H, pzC*H*)	167.6 (s, pz*C*H); 132.5 (s, pz*C*H); 130.9 (s, pz*C*H); 128.8 (s, pz*C*H)	-0.8; 21.8	
13	[(CO)(PPh$_3$)Rh{μ-B(pz)$_4$}CoCl$_2$]	41.98 (br s, 2H, pzC*H*); 31.29 (br s, 2H, pzC*H*); 16.09 (br s, 2H, pzC*H*); 11.71 (s, 2H, pzC*H*); 10.20 (s, 2H, pzC*H*); 7.22-7.86 (br m, 15H, Ph*H*); -23.54 (br s, 2H, pzC*H*)		-0.8; 31.4	45.9 {d, J(Rh,P) = 162 Hz}; 29.9 {d, J(Rh,P) = 128 Hz}
14	[(η-cod)Rh{μ-B(pz)$_4$}ZnCl$_2$]	8.11 (d, 2H, pzC*H*), J(H,H) = 2.4; 7.68 (d, 2H, pzC*H*), J(H,H) = 2.4 Hz; 7.53 (d, 2H, pzC*H*), J(H,H) = 2.4 Hz; 7.19 (d, 2H, pzC*H*), J(H,H) = 2.4 Hz; 6.67 (app. t,[b] 2H, pzC*H*), J(H,H) = 2.2 Hz; 6.42 (app. t,[b] 2H, pzC*H*), J(H,H) = 2.2 Hz; 4.18 (s, 4H, codC*H*); 2.42-2.50 (br m, 4H, codC*H*$_2$); 1.94 (m, 4H, codC*H*$_2$)	146.8 (s, pz*C*H); 144.9 (s, pz*C*H); 143.2 (s, pz*C*H); 141.7 (s, pz*C*H); 137.8 (s, pz*C*H); 107.5 (s, pz*C*H); 83.2 (d, cod*C*H), J(Rh,C) = 12.0 Hz; 30.4 (s, cod*C*H$_2$)	-0.8	
15	[(η-nbd)Rh{μ-B(pz)$_4$}ZnCl$_2$]	8.07 (d, 2H, pzC*H*) J(H,H) = 2.4 Hz; 7.50 (d, 2H, pzC*H*), J(H,H) = 2.4 Hz; 7.24 (d, 2H, pzC*H*), J(H,H) = 2.4 Hz; 7.07 (d, 2H, pzC*H*), J(H,H) = 2.3 Hz; 6.62 (app. t,[b] 2H, pzC*H*), J(H,H) = 2.3 Hz) 6.38 (app. t,[b] 2H, pzC*H*), J(H,H) = 2.4 Hz; 4.11-4.13 (br m, 4H, nbdC*H*)[c]; 3.93 (s, 2H, nbdC*H*); 1.47 (br m, 2H, nbdC*H*$_2$)	145.3 (s, pz*C*H); 144.4 (s, pz*C*H); 142.7 (s, pz*C*H); 137.8 (s, pz*C*H); 137.3 (s, pz*C*H); 107.6 (s, pz*C*H); 62.9 (s, nbd*C*H$_2$); 58.8 (d, nbd*C*H)[c], J(Rh,C) = 11.0 Hz; 61.0 (s, nbd*C*H$_2$); 50.7 (s, nbd*C*H)	-0.8	
16	[(η-cod)Rh{μ-B(pz)$_4$}PdCl$_2$]	8.41 (d, 2H, pzC*H*), J(H,H) = 2.2 Hz; 7.61 (d, 2H, pzC*H*), J(H,H) = 2.2 Hz; 7.54 (s, 4H, pzC*H*); 6.57 (app. t,[b] 2H, pzC*H*), J(H,H) = 2.2 Hz; 6.51 (app. t,[b] 2H, pzC*H*), J(H,H) = 2.2 Hz; 4.19 (s, 4H, codC*H*); 2.40-2.46 (br m, 4H, codC*H*$_2$); 1.91-1.97 (br m, 4H, codC*H*$_2$)	147.1 (s, pz*C*H); 145.3 (s, pz*C*H); 143.8 (s, pz*C*H); 137.5 (s, pz*C*H); 136.2 (s, pz*C*H); 107.7 (s, pz*C*H); 83.7 (s, cod*C*H), J(Rh,C) = 12.2 Hz; 30.7 (s, cod*C*H$_2$)	-2.2	

[a] Chemical shift (δ) in ppm, *J* values in Hz, spectra in CD_2Cl_2 at 20 °C unless otherwise stated. [b] Apparent triplet (coincident dd). [c] Alkenic proton or carbon of nbd.

Table 2 Selected bond lengths (Å) and angles (°) for **1**$^+$[PF$_6$]$^-$·0.25CH$_2$Cl$_2$, **2**$^+$[PF$_6$]$^-$·CH$_2$Cl$_2$, **4**$^+$[PF$_6$]$^-$, **5**$^+$[PF$_6$]$^-$·3CH$_2$Cl$_2$, **10**, **11**·CH$_2$Cl$_2$, **14**·CH$_2$Cl$_2$ and **16**·CH$_3$CN.[a]

	Complex							
	1$^+$[PF$_6$]$^-$·0.25CH$_2$Cl$_2$	**2**$^+$[PF$_6$]$^-$·CH$_2$Cl$_2$	**4**$^+$[PF$_6$]$^-$	**5**$^+$[PF$_6$]$^-$·3CH$_2$Cl$_2$	**10**	**11**·CH$_2$Cl$_2$	**14**·CH$_2$Cl$_2$	**16**·CH$_3$CN
Rh(1)–N(1)	2.132(3)	2.075(7)	2.086(3)	2.103(3)	2.105(5)	2.083(3)	2.107(3)	2.114(3)
Rh(1)–N(3)	2.071(3)	2.056(8)	2.056(3)	2.087(3)	2.086(3)	2.065(3)	2.087(3)	2.068(3)
M–N(5)[b]	2.121(2)	2.073(8)	2.088(3)	2.103(3)	2.008(3)	1.997(3)	2.033(3)	2.043(3)
M–N(7)[b]	2.070(3)	2.055(7)	2.060(3)	2.084(3)	2.001(3)	1.985(3)	2.018(3)	2.017(3)
Rh(1)–X(1)[c]	2.022	2.027	-	-	2.019	1.992	2.024	2.027
Rh(1)–X(2)[c]	2.001	1.995	-	-	2.016	2.012	2.022	2.024
Rh(2)–X(3)[c]	2.033	2.011	-	-	-	-	-	-
Rh(2)–X(4)[c]	1.996	1.975	-	-	-	-	-	-
C(1)–C(2)	1.403(6)	1.399(14)	-	-	1.400(5)	1.386(5)	1.380(6)	1.406(6)
C(3)–C(4)	1.393(5)	1.371(15)	-	-	1.392(5)	1.377(5)	1.401(7)	1.398(6)
C(5)–C(6)	1.384(5)	1.396(13)	-	-	-	-	-	-
C(7)–C(8)	1.388(5)	1.412(13)	-	-	-	-	-	-
Rh(1)–C(1)	-	-	1.874(4)	1.830(4)	-	-	-	-
Rh(1)–C(2)	-	-	1.861(4)	-	-	-	-	-
Rh(2)–C(3)	-	-	1.865(4)	1.829(4)	-	-	-	-
Rh(2)–C(4)	-	-	1.859(4)	-	-	-	-	-
C(1)–O(1)	-	-	1.133(4)	1.141(5)	-	-	-	-
C(2)–O(2)	-	-	1.130(3)	1.139(5)	-	-	-	-
C(3)–O(3)	-	-	1.128(4)	-	-	-	-	-
C(4)–O(4)	-	-	1.136(4)	-	-	-	-	-
Rh(1)–P(1)	-	-	-	2.263(1)	-	-	-	-
Rh(2)–P(2)	-	-	-	2.262(1)	-	-	-	-
M–Cl(1)	-	-	-	-	2.233(1)	2.233(1)	2.225(1)	2.286(1)
M–Cl(2)	-	-	-	-	2.216(1)	2.243(1)	2.218(1)	2.292(1)
N(1)–Rh(1)–N(3)	86.2(1)	88.4(3)	88.7(1)	86.7(1)	87.6(1)	90.0(1)	88.2(1)	88.1(1)
N(5)–M–N(7)[b]	86.2(1)	91.5(3)	89.4(1)	84.7(1)	93.9(1)	94.3(1)	93.1(1)	91.2(1)
X(1)–Rh(1)–X(2)	87.3	72.0	-	-	87.0	71.7	86.8	87.2
X(3)–Rh(2)–X(4)	87.0	72.0	-	-	-	-	-	-
N(1)–Rh(1)–X(2)	173.3	169.8	-	-	171.0	169.2	178.9	172.4
N(3)–Rh(1)–X(1)	176.7	171.0	-	-	173.7	172.0	174.3	178.6
N(5)–Rh(2)–X(4)	174.1	170.1	-	-	-	-	-	-
N(7)–Rh(2)–X(3)	178.1	169.3	-	-	-	-	-	-
N(3)–Rh(1)–C(1)	-	-	178.1(1)	175.4(1)	-	-	-	-
Rh(1)–C(1)–O(1)	-	-	177.1(3)	178.8(3)	-	-	-	-
N(1)–Rh(1)–P(1)	-	-	-	174.2(1)	-	-	-	-
Cl(1)–M–Cl(2)[b]	-	-	-	-	111.5(1)	115.9(1)	114.6(1)	89.0(1)
Mplna(1)[d]	147.5	155.6	158.1	152.7	153.6	168.7	155.6	153.1
Mplna(2)[d]	147.4	176.8	162.9	146.5	166.3	170.4	175.0	160.0
Mplnb(1)[e]	135.9	143.1	139.7	141.1	142.4	141.5	145.3	142.1
Mplnb(2)[e]	135.6	143.6	139.3	141.0	141.1	147.2	144.7	141.4

[a] Non-bonded components and those involving centroids were not included in the refinement, and thus do not have an e.s.d. [b] M is Rh(2) for complexes **1**$^+$, **2**$^+$, **4**$^+$ and **5**$^+$, Co(1) for **10** and **11**, Zn(1) for **14** and Pd(1) for **16**. [c] X(1), X(2), X(3) and X(4) are the midpoints of the C(1)–C(2), C(3)–C(4), C(5)–C(6) and C(7)–C(8) bonds respectively. [d] Mplna(1) is the angle between the midpoints of N(2) and N(4), N(1) and N(3) and Rh(1); Mplna(2) is the angle between the midpoints of N(6) and N(8), N(5) and N(7) and M. [e] Mplnb(1) is the angle between the midpoints of N(1) and N(3), N(2) and N(4) and B; Mplnb(2) is the angle between the midpoints of N(5) and N(7), N(6) and N(8) and B.

Table 3 Crystal and refinement data for **1**$^+$[PF$_6$]$^-$·0.25CH$_2$Cl$_2$, **2**$^+$[PF$_6$]$^-$·CH$_2$Cl$_2$, **4**$^+$[PF$_6$]$^-$, **5**$^+$[PF$_6$]$^-$·3CH$_2$Cl$_2$, **10**, **11**·CH$_2$Cl$_2$, **14**·CH$_2$Cl$_2$ and **16**·CH$_3$CN.

Complex	**1**$^+$[PF$_6$]$^-$·0.25CH$_2$Cl$_2$	**2**$^+$[PF$_6$]$^-$·CH$_2$Cl$_2$	**4**$^+$[PF$_6$]$^-$	**5**$^+$[PF$_6$]$^-$·3CH$_2$Cl$_2$	**10**	**11**·CH$_2$Cl$_2$	**14**·CH$_2$Cl$_2$	**16**·CH$_3$CN
Formula	$C_{28.25}H_{36.50}BN_8Rh_2PF_6Cl_{0.50}$	$C_{27}H_{30}BCl_2F_6N_8PRh_2$	$C_{16}H_{12}BF_6N_8O_4PRh_2$	$C_{53}H_{48}BCl_6F_6N_8O_2P_3Rh_2$	$C_{20}H_{24}BCl_2CoN_8Rh$	$C_{20}H_{22}BCl_4CoN_8Rh$	$C_{21}H_{26}BCl_4N_8RhZn$	$C_{22}H_{27}BCl_2N_9PdRh$
Formula weight	867.47	899.09	741.94	1465.23	620.02	688.91	711.39	708.55
Temperature / K	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	*C*2	*P*2(1)/*n*	*P*2(1)/*c*	*P*1	*P*-1	*P*2(1)/*c*	*P*2(1)/*c*	*P*-1
a/Å	28.003(7)	14.410(3)	11.397(2)	13.281(3)	9.780(1)	12.218(2)	12.943(19)	9.584(1)
b/Å	13.173(3)	11.036(2)	12.453(2)	13.380(3)	9.860(1)	19.578(4)	19.987(3)	11.856(1)
c/Å	17.663(4)	21.209(5)	17.059(3)	17.393(3)	13.492(2)	12.041(2)	12.152(1)	12.616(1)
α/°	90	90	90	84.36(3)	94.068(2)	90	90	73.114(2)
β/°	99.48(2)	108.51(1)	103.042(3)	74.524(16)	103.562(2)	116.14(3)	117.538(11)	86.102(2)
γ/°	90	90	90	84.84(3)	104.509(2)	90	90	74.047(2)
V/Å^3	6416(3)	3198.3(12)	2358.6(6)	2957.6(11)	1212.7(3)	2585.6(9)	2745.7(7)	1318.8(3)
Z	2	4	4	2	2	4	4	2
μ/mm^{-1}	1.191	1.319	1.558	0.977	1.610	1.720	1.891	1.541
Reflections collected	33881	16779	10391	34118	7977	29115	18789	10115
Independent reflections (R_{int})	14570 (0.0206)	5632 (0.1010)	3382 (0.0306)	13538 (0.0308)	5441 (0.0261)	5926 (0.0720)	5881 (0.0657)	5677 (0.0293)
Final $R1$ [I>2σ(I)]: R_1, wR_2	0.0235, 0.0547	0.0605, 0.1246	0.0240, 0.0499	0.0487, 0.1163	0.0353, 0.0625	0.0394, 0.0718	0.0339, 0.0706	0.0301, 0.0632

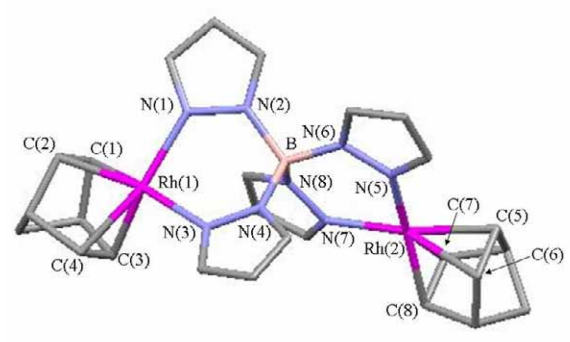

Fig. 1 The structure of [(η-nbd)Rh{μ-B(pz)$_4$}Rh(η-nbd)]$^+$ **2**$^+$.

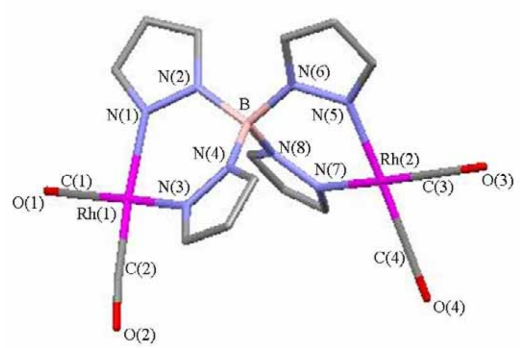

Fig. 2 The structure of [(CO)$_2$Rh{μ-B(pz)$_4$}Rh(CO)$_2$]$^+$ **4**$^+$.

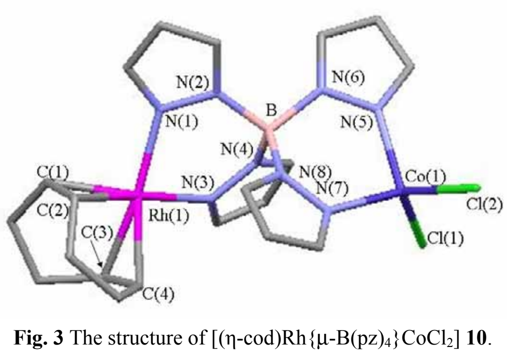

Fig. 3 The structure of [(η-cod)Rh{μ-B(pz)$_4$}CoCl$_2$] **10**.

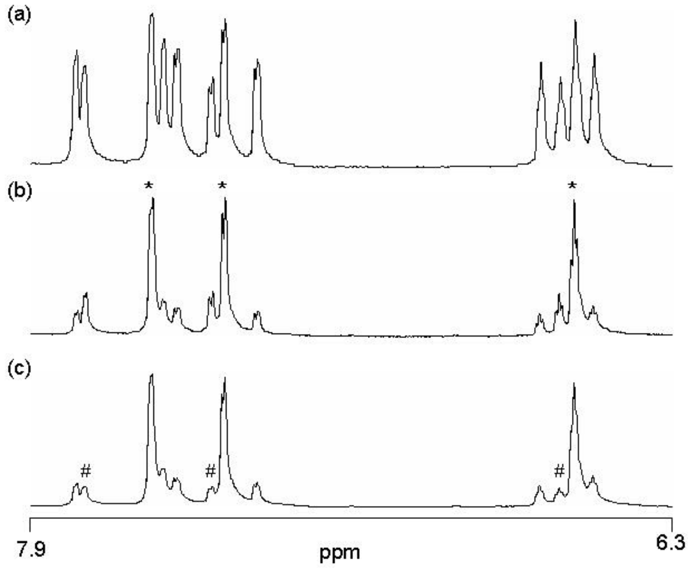

Fig. 4 ^{1}H NMR spectra of the pyrazolyl region of: (a) [(η-cod)Rh{μ-B(pz)$_4$}Ir(η-cod)]$^+$ **8**$^+$; (b) 1:1 mixture of **8**$^+$ and [(η-cod)Rh{μ-B(pz)$_4$}Rh(η-cod)]$^+$ **1**$^+$; (c) 1:1:0.38 mixture of **8**$^+$, [(η-cod)Rh{μ-B(pz)$_4$}Rh(η-cod)]$^+$ **1**$^+$ and [(η-cod)Ir{μ-B(pz)$_4$}Ir(η-cod)]$^+$ **3**$^+$. [* = peaks due to **1**$^+$. # = peaks due to **3**$^+$].

Table 3 Data for the pyrazolyl region of the ^{1}H NMR spectra of samples including [(η-cod)Rh{μ-B(pz)$_4$}Ir(η-cod)]$^+$ **8**$^+$.[a]

Sample	Chemical Shift (δ) (ppm)
Sample of [(η-cod)Rh{μ-B(pz)$_4$}Ir(η-cod)]$^+$ **8**$^+$	7.87 {d, 1H, J(H,H) = 2.2 Hz, pzC*H* **8**$^+$}, 7.85 {d, 1H, J(H,H) = 2.2 Hz, pzC*H* **3**$^+$}, 7.68 {d, 1H, J(H,H) = 1.7 Hz pzC*H* **1**$^+$}, 7.65 (d, 1H, J(H,H) = 1.8 Hz, pzC*H* **8**$^+$}, 7.62 (d, 1H, J(H,H) = 2.2 Hz, pzC*H* **8**$^+$}, 7.53 {d, 1H, J(H,H) = 2.5 Hz, pzC*H* **3**$^+$}, 7.50 {d, 1H, J(H,H) = 2.7 Hz, pzC*H* **1**$^+$}, 7.42 {d, 1H, J(H,H) = 2.5 Hz, pzC*H* **8**$^+$}, 6.71 {t, 1H, J(H,H) = 2.4 Hz, pzC*H* **8**$^+$}, 6.66 {t, 1H, J(H,H) = 2.5 Hz, pzC*H* **3**$^+$}, 6.62 {t, 1H, J(H,H) = 2.4 Hz, pzC*H* **1**$^+$}, 6.57 {t, 1H, J(H,H) = 2.6 Hz, pzC*H* **8**$^+$}
1:1 mixture of [(η-cod)Rh{μ-B(pz)$_4$}Rh(η-cod)]$^+$ **1**$^+$ and [(η-cod)Rh{μ-B(pz)$_4$}Ir(η-cod)]$^+$ **8**$^+$	7.87 {d, 1H, J(H,H) = 2.1 Hz, pzC*H* **8**$^+$}, 7.85 {d, 1H, J(H,H) = 2.1 Hz, pzC*H* **3**$^+$}; 7.68 {d, 4H, J(H,H) = 1.7 Hz, pzC*H* **1**$^+$}, 7.65 {d, 1H, J(H,H) = 1.7 Hz, pzC*H* **8**$^+$}, 7.62 {d, 1H, J(H,H) = 2.2 Hz, pzC*H* **8**$^+$}, 7.53 {d, 1H, J(H,H) = 2.5 Hz, pzC*H* **3**$^+$}, 7.50 (d, 4H, J(H,H) = 2.6 Hz, pzC*H* **1**$^+$), 7.42 {d, 1H, J(H,H) = 2.5 Hz, pzC*H* **8**$^+$}, 6.71 {t, 1H, J(H,H) = 2.2 Hz, pzC*H* **8**$^+$}, 6.66 {t, 1H, J(H,H) = 2.5 Hz, pzC*H* **3**$^+$}; 6.62 {t, 4H, J(H,H) = 2.2 Hz, pzC*H* **1**$^+$}, 6.57 {t, 1H, J(H,H) = 2.6 Hz, pzC*H* **8**$^+$}
0.38:1:1 mixture of [(η-cod)Ir{μ-B(pz)$_4$}Ir(η-cod)]$^+$ **3**$^+$, [(η-cod)Rh{μ-B(pz)$_4$}Rh(η-cod)]$^+$ **1**$^+$ and [(η-cod)Rh{μ-B(pz)$_4$}Ir(η-cod)]$^+$ **8**$^+$	7.87 {d, 1H, J(H,H) = 2.2 Hz, pzC*H* **8**$^+$}, 7.85 {d, 2.14H, J(H,H) = 2.2 Hz, pzC*H* **3**$^+$}, 7.68 {d, 4H, J(H,H) = 1.9 Hz, pzC*H* **1**$^+$}, 7.65 {d, 1H, J(H,H) = 1.8 Hz, pzC*H* **8**$^+$}, 7.62 {d, 1H, J(H,H) = 2.2 Hz, pzC*H* **8**$^+$}, 7.53 {d, 2.14H, J(H,H) = 2.4 Hz, pzC*H* **3**$^+$}, 7.50 {d, 4H, J(H,H) = 2.5 Hz, pzC*H* **1**$^+$}, 7.42 {d, 1H, J(H,H) = 2.5 Hz, pzC*H* **8**$^+$}, 6.71 {t, 1H, J(H,H) = 2.4 Hz, pzC*H* **8**$^+$}; 6.66 {t, 2.14H, J(H,H) = 2.4 Hz, pzC*H* **3**$^+$}, 6.62 {t, 4H, J(H,H) = 2.2 Hz, pzC*H* **1**$^+$}, 6.57 {t, 1H, J(H,H) = 2.6 Hz pzC*H* **8**$^+$}

[a] Spectra in CD_2Cl_2 at 25 °C. Integrations are relative to those of the spectrum of [(η-cod)Rh{μ-B(pz)$_4$}Ir(η-cod)]$^+$ **8**$^+$.

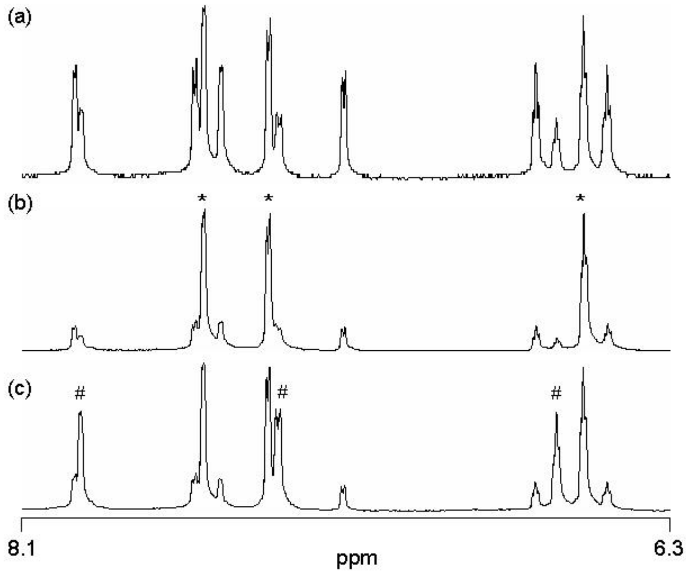

Fig. 5 ^{1}H NMR spectra of the pyrazolyl region of: (a) [(η-cod)Rh{μ-B(pz)$_4$}Rh(CO)$_2$]$^+$ **9**$^+$; (b) 1:1 mixture of **9**$^+$ and [(η-cod)Rh{μ-B(pz)$_4$}Rh(η-cod)]$^+$ **1**$^+$; (c) 1:1:0.78 mixture of **9**$^+$, [(η-cod)Rh{μ-B(pz)$_4$}Rh(η^{4}cod)]$^+$ **1**$^+$ and [(CO)$_2$Rh{μ-B(pz)$_4$}Rh(CO)$_2$]$^+$ **4**$^+$. [* = peaks due to **1**$^+$. # = peaks due to **4**$^+$].

Table 4 Data for the pyrazolyl region of the ^{1}H NMR spectra of samples including [(η-cod)Rh{μ-B(pz)$_4$}Rh(CO)$_2$]$^+$ **9**$^+$.[a]

Sample	Chemical Shift (ppm)
[(η-cod)Rh{μ-B(pz)$_4$}Rh(CO)$_2$]$^+$ **9**$^+$.	8.04 {d, 1H, J(H,H) = 2.2 Hz, pzC*H* **9**$^+$}, 8.02 {d, 1H, J(H,H) = 2.1 Hz, pzC*H* **4**$^+$}, 7.70 {d, 1H, J(H,H) = 2.5 Hz, pzC*H* **9**$^+$}, 7.68 {d, 1H, J(H,H) = 1.8 Hz, pzC*H* **1**$^+$}, 7.63 {d, 1H, J(H,H) = 1.8 Hz, pzC*H* **9**$^+$}, 7.50 {d, 1H, J(H,H) = 2.6 Hz, pzC*H* **1**$^+$}, 7.47 {d, 1H, J(H,H) = 2.7 Hz, pzC*H* **4**$^+$}, 7.29 {d, 1H, J(H,H) = 2.6 Hz, pzC*H* **9**$^+$}, 6.76 {t, 1H, J(H,H) = 2.4 Hz, pzC*H* **9**$^+$}, 6.70 {t, 1H, J(H,H) = 2.5 Hz, pzC*H* **4**$^+$}, 6.62 {t, 1H, J(H,H) = 2.3 Hz, pzC*H* **1**$^+$}, 6.56 {t, 1H, J(H,H) = 2.3 Hz, pzC*H* **9**$^+$}
1:1 mixture of [(η-cod)Rh{μ-B(pz)$_4$}Rh(η-cod)]$^+$ **1**$^+$ and [(η-cod)Rh{μ-B(pz)$_4$}Rh(CO)$_2$]$^+$ **9**$^+$.	8.04 {d, 1H, J(H,H) = 1.8 Hz, pzC*H* **9**$^+$}, 8.02 {d, 1H, J(H,H) = 1.8 Hz, pzC*H* **4**$^+$}, 7.70 {d, 1H, J(H,H) = 2.8 Hz, pzC*H* **9**$^+$}, 7.68 {d, 4H, J(H,H) = 1.7 Hz, pzC*H* **1**$^+$}, 7.63 {d, 1H, J(H,H) = 1.9 Hz, pzC*H* **9**$^+$}, 7.50 {d, 4H, J(H,H) = 2.5 Hz, pzC*H* **1**$^+$}, 7.47 {d, 1H, J(H,H) = 2.8 Hz, pzC*H* **4**$^+$}, 7.29 {d, 1H, J(H,H) = 2.6 Hz, pzC*H* **9**$^+$}, 6.76 {t, 1H, J(H,H) = 2.3 Hz, pzC*H* **9**$^+$}, 6.70 {t, 1H, J(H,H) = 2.3 Hz, pzC*H* **4**$^+$}, 6.62 {t, 4H, J(H,H) = 2.2 Hz, pzC*H* **1**$^+$}, 6.56 {t, 1H, J(H,H) = 2.3 Hz, pzC*H* **9**$^+$}
0.78:1:1 mixture of [(CO)$_2$Rh{μ-B(pz)$_4$}Rh(CO)$_2$]$^+$ **4**$^+$, [(η-cod)Rh{μ-B(pz)$_4$}Rh(η-cod)]$^+$ **1**$^+$ and [(η-cod)Rh{μ-B(pz)$_4$}Rh(CO)$_2$]$^+$ **9**$^+$.	8.04 {d, 1H, J(H,H) = 2.0 Hz, pzC*H* **9**$^+$}, 8.02 {d, 3.34H, J(H,H) = 2.1 Hz, pzC*H* **4**$^+$}; 7.70 {d, 1H, J(H,H) = 2.8 Hz, pzC*H* **9**$^+$}, 7.68 {d, 4H, J(H,H) = 1.8 Hz, pzC*H* **1**$^+$}, 7.63 {d, 1H, J(H,H) = 1.9 Hz, pzC*H* **9**$^+$}, 7.50 {d, 4H, J(H,H) = 2.5 Hz, pzC*H* **1**$^+$}, 7.47 {d, 3.34H, J(H,H) = 2.8 Hz, pzC*H* **4**$^+$}, 7.29 {d, 1H, J(H,H) = 2.7 Hz, pzC*H* **9**$^+$}, 6.76 {t, 1H, J(H,H) = 2.4 Hz, pzC*H* **9**$^+$}, 6.70 {t, 3.34H, J(H,H) = 2.3 Hz, pzC*H* **4**$^+$}, 6.62 {t, 4H, J(H,H) = 2.2 Hz, pzC*H* **1**$^+$}, 6.56 {t, 1H, J(H,H) = 2.3 Hz, pzC*H* **9**$^+$}

[a] Spectra in CD_2Cl_2 at 25 °C. Integrations are relative to those of the spectrum of [(η-cod)Rh{μ-B(pz)$_4$}Rh(CO)$_2$]$^+$ **9**$^+$.