Synthesis, Structure and Reactivity of Ruthenium(II) Carbonyl Complexes Containing Bis(pyrazol-1-yl)methane and Bis(*N*-methylimidazol-2-yl)methane

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A series of ruthenium(II) complexes with the pyrazolylalkane ligands bis(pyrazol-1-yl)methane (BPM) (**I**) and bis(3,5-dimethylpyrazol-1-yl)methane (dmBPM) (**II**), and the imidazolylalkane ligand bis(*N*-methylimidazol-2-yl)methane (BIM) (**III**) have been synthesised and characterised. The complexes $[Ru(N\text{-}N)(CO)_2X_2]$ [N-N = BPM, X = Cl (**1a**), Br (**1b**); N-N = dmBPM, X = Cl (**2**); N-N = BIM, X = Cl (**3**)] were prepared from the stoichiometric reaction of $[Ru(CO)_2X_2]_n$ and the bidentate N-donor ligand in refluxing methanol. The crystal structure of **2** showed the complex to have octahedral geometry about the ruthenium centre, with the carbonyl and chloride ligands being coordinated *cis* and *trans*, respectively. The complex $[Ru(BPM)_2(CO)(Cl)][BPh_4]$ (**4**) was prepared from the reaction of $RuCl_3$ and BPM in refluxing DMF, or from the decarbonylation of $[Ru(BPM)(CO)_2Cl_2]$ (**1a**) in the presence of BPM and $NaBPh_4$. The NMR spectra of **4** were fully assigned from 2D NMR experiments. The NOESY showed a *cis* coordination of the chloride and carbonyl ligands, and this was confirmed by single crystal X-ray diffraction studies.

Introduction

Organometallic ruthenium complexes are efficient catalysts for a variety of processes,[1] such as the coupling of pyridine, carbon monoxide and hexenes,[2] the coupling of aromatic carbon-hydrogen bonds with olefins,[3] and the intramolecular cyclisation of hydroxyenynes to form furan derivatives.[4,5] Catalytically active ruthenium complexes containing N-donor ligands are becoming more significant, leading to the development of new ruthenium complexes with N-donor ligands and suitable co-ligands for optimum catalytic activity. The preparation of a number of ruthenium carbonyl systems containing 2,2′-dipyridyl and its derivatives has been reported,[6−8] and in some cases these complexes are efficient catalysts for processes such as the reduction[9] and hydrogenation[10] of CO_2 and, in particular, the water-gas shift reaction, in both homogeneous[11−14] and heterogeneous environments.[15−17]

The sp^2-N donor poly(pyrazol-1-yl)methane and poly(imidazol-2-yl)methane ligands, such as bis(pyrazol-1-yl)methane (**I**) (BPM),[18] bis(3,5-dimethylpyrazol-1-yl)methane (**II**),[18] tris(pyrazol-1-yl)methane (**III**) (TPM),[18] bis(*N*-methylimidazol-2-yl)methane (**IV**) (BIM),[19] and tris(*N*-methylimidazol-2-yl)methanol (**V**; TIM) are neutral ligands closely related to the poly(pyrazolyl)borate ligands.[20] The basicity of the sp^2-N donor atoms of the five-membered heterocycles of BPM and BIM are considerably different to that of N-atoms of other ligands containing heterocycles, such as 2,2′-bipyridyl (BIPY), which has a significant effect on the relative degree of electron donation to the metal by the ligand.[21] A number of complexes containing poly(pyrazol-1-yl)methane ligands have been synthesised for metals in groups 5, 6, 9 and 10.[22] Only a limited number of poly(pyrazol-1-yl)methane complexes of metals of group 8 have been reported;[23,24] these include $[Ru(TPM)(OH_2)_3](p\text{-}CH_3C_6H_4SO_3)_2\cdot 1.5H_2O$[25] and [Ru(TPM)(COD)Cl]Cl (COD = 1,5-cyclooctadiene).[26] Group 8 metal complexes containing poly(imidazol-2-yl)methane ligands have also been reported and include $[Ru(BIM)(CO)(PPh_3)H]Cl$,[27] $[M(TIM)(CO)(PPh_3)H]Cl$ (M = Ru, Os)[28] and $[Fe(TIM)_2][FeCl_4]$.[29] We have recently reported a series of ruthenium(II) complexes with the pyrazolylalkane ligands TPM and BPM, $[RuCl(PPh_3)_2(TPM)]X$ (X = Cl, BF_4), $[Ru(CO)H(PPh_3)(BPM)_2]Cl$ and $[Ru(PPh_3)(BPM)(\mu\text{-}Cl)_3Ru(PPh_3)(BPM)]Cl$.[30]

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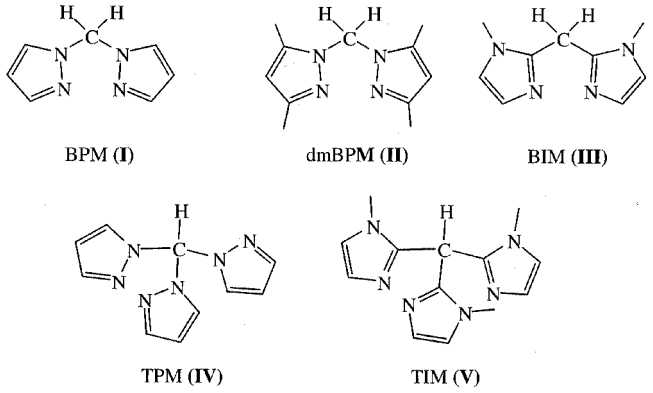
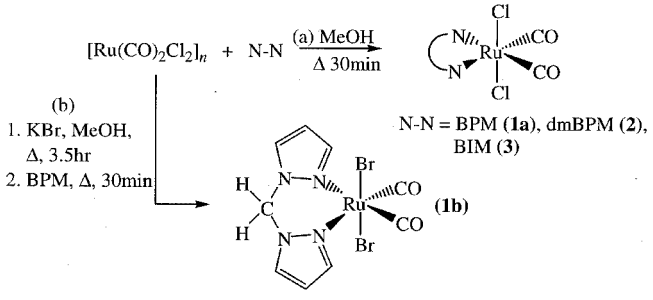


Herein we report the preparation of a series of neutral and charged ruthenium carbonyl complexes containing the N-donor ligands BPM, dmBPM, and BIM. These complexes are of interest for their possible application in hydrogenation catalysis. The complexes $[Ru(N\text{-}N)(CO)_2X_2]$ [N-N = BPM, X = Cl (**1a**), Br (**1b**); N-N = dmBPM, X = Cl (**2**); N-N = BIM, X = Cl (**3**)] were prepared from the stoichiometric reaction of $[Ru(CO)_2X_2]_n$ and the bidentate ligand in refluxing methanol. The ionic complex $[Ru(BPM)_2(CO)Cl][BPh_4]$ (**4**) was prepared from the reaction of $RuCl_3$ and BPM in refluxing DMF, and from the decarbonylation of $[Ru(BPM)(CO)_2Cl_2]$, followed by the addition of BPM and $NaBPh_4$.

Results And Discussion

Synthesis of $[Ru(N\text{-}N)(CO)_2X_2]$ Complexes

Preparations of the complexes $[Ru(N\text{-}N)(CO)_2X_2]$ are outlined in Scheme 1. Treatment of $[Ru(CO)_2Cl_2]_n$ with the bidentate nitrogen ligands in refluxing methanol results in the isolation of $[Ru(N\text{-}N)(CO)_2Cl_2]$ [N-N = bis(pyrazol-1-yl)methane (BPM) (**1a**), bis(3,5-dimethylpyrazol-1-yl)methane (dmBPM) (**2**), bis(N-methylimidazol-2-yl)methane



Scheme 1. Preparation of neutral organoruthenium complexes **1(a,b)**, **2** and **3**

(BIM) (**3**)] in good yields as yellow solids (Scheme 1a). The preparation of $[Ru(BPM)(CO)_2Br_2]$ (**1b**) involved an initial halide exchange reaction between $[Ru(CO)_2Cl_2]_n$ and KBr, followed by the addition of BPM (Scheme 1b). This complex was isolated in fair yield as an orange solid. Attempts to prepare the complex $[Ru(BPM)(CO)_2I_2]$ from the reaction of $[Ru(CO)_2Cl_2]_n$ with NaI resulted in an orange solid. Unfortunately, residual NaI remained and a pure complex could not be obtained. CI mass spectra of the chloride complexes exhibit peaks corresponding to M^+ ions for all complexes, confirming the complexes to be monomeric. Subsequent loss of CO ligands are observed followed by peaks corresponding to the [M − 2CO − Cl] and [M − 2CO − 2Cl] ions. FAB mass spectra of the bromide complex show similar results, exhibiting peaks corresponding to the M^+ ions with subsequent loss of CO ligands.

The ^1H NMR spectra of **1(a, b)**, **2** and **3** exhibit resonances typical of symmetrical complexes containing such ligands. The protons of the two nitrogen-containing rings of each ligand are equivalent, with only one set of resonances observed for the aromatic protons of the pyrazolyl or imidazolyl rings. Broad singlets are observed for the methylene protons of the BPM and dmBPM ligands of **1(a, b)**, due to the fluxionality of the puckered six-membered ring containing the central Ru atom. At room temperature, the resonance due to the methylene protons of the dmBPM ligand of **2** is not observed, however, on reducing the temperature to −28 °C two resonances due to the two inequivalent protons of the methylene group of dmBPM are observed, where the six-membered ring is in a nonexchanging boat conformation. A similar ligand geometry was observed in the complex $[Ru(BPM)_2(PPh_3)Cl]Cl$.[30] The assignments are consistent with the *cis*-(CO), *trans*-(halide) structure of the complexes. The $^{13}C\{^1H\}$ NMR spectra for each of the complexes **1(a, b)** and **2** are also consistent with the ^{13}C nuclei of the two aromatic rings of the ligands being equivalent.

The IR spectra of these complexes in the ν(C≡O) region show two C≡O stretches at typical wavenumbers for terminal carbonyl ligands, indicating that the complexes have octahedral ruthenium centres with C_{2v} symmetry, and that the coordination sphere about the ruthenium centre is *cis*(CO)-*trans*(halide). The ν(C≡O) frequencies and $^{13}C\{^1H\}$ NMR carbonyl resonances are listed in Table 1. A shift in ν(C≡O) frequencies towards lower wavenumbers is observed in the order BPM > dmBPM > BIM, which is associated with a downfield shift for the ^{13}C CO resonance. The additional four electron-donating methyl groups on the dmBPM ligand give the ligand a better electron-donating ability than BPM. The trend also shows that the imidazolyl ligand is a better electron donor than pyrazolyl ligands. A marginal shift in ν(C≡O) frequencies to lower wavenumber

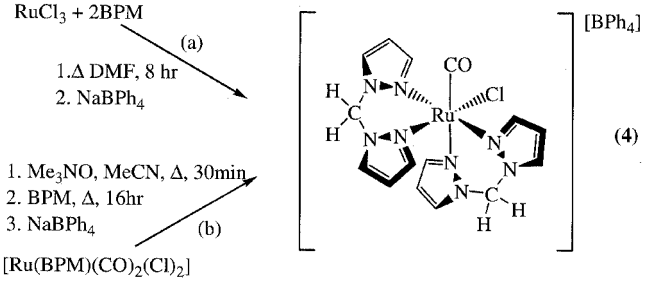
Table 1. Infrared ν(CO) absorptions and ^{13}C CO shifts of *cis*(CO)-*trans*(X)-$[Ru(N\text{-}N)(CO)_2X_2]$ complexes

Complex	ν(CO) (cm^{-1})	^{13}C (ppm)
$[Ru(BPM)(CO)_2Cl_2]$ (**1a**)	2064, 2011	196.4
$[Ru(BPM)(CO)_2Br_2]$ (**1b**)	2064, 2007	196.3
$[Ru(dmBPM)(CO)_2Cl_2]$ (**2**)	2061, 1998	197.1
$[Ru(BIM)(CO)_2Cl_2]$ (**3**)	2051, 1986	198.4
$[Ru(bipy)(CO)_2Cl_2]$	2066, 2003	196.3
$[Ru(bipy)(CO)_2Br_2]$	2062, 2004	197.2
$[Ru(bipy)(CO)_2I_2]$	2056, 2000	198.5

is also observed for the complexes $[Ru(BPM)(CO)_2X_2]$ (Cl > Br). This trend has been observed on a number of occasions for dipyridylruthenium complexes.[6,31,32]

Synthesis of $[Ru(BPM)_2(CO)Cl][BPh_4]$

The complex $[Ru(BPM)_2(CO)Cl][BPh_4]$ (**4**) was prepared by two methods (Scheme 2). Firstly, $RuCl_3{\cdot}xH_2O$ was allowed to react with two equivalents of BPM in refluxing DMF for 8 hours (Scheme 2a). After cooling, the solvent volume was reduced by distillation and $NaBPh_4$ was added. Et_2O was then added to the reaction to afford an off-white precipitate. This was recrystallised from acetone and diethyl ether to afford $[Ru(BPM)_2(CO)Cl][BPh_4]$ (**4**). This method is analogous to the preparation of $[Ru(BIPY)_2(CO)Cl][ClO_4]$.[33] Complex **4** was also prepared by the monodecarbonylation of $[Ru(BPM)(CO)_2Cl_2]$ **(1a)**. Complex **1a** was reacted with excess Me_3NO in refluxing MeCN after which one equivalent of BPM was added and the reaction refluxed for a further 16 hours. The addition of $NaBPh_4$ after this time resulted in the formation of compound **4** (Scheme 2b). This method proved to be the more efficient, with 37% yield obtained. The positive electrospray mass spectrum of the cation of **4** gave a M^+ ion mass of 460.9, consistent with the cation formula. Loss of CO is observed (432.9 $[M - CO]^+$) followed by loss of chlorine (396.9 $[M - CO - Cl]^+$). The infrared spectrum of $[Ru(BPM)_2(CO)Cl][BPh_4]$ exhibits a ν(CO) frequency of 1970 cm^{-1}. This is similar to the CO(str) frequency of $[Ru(BIPY)_2(CO)Cl][ClO_4]$,[33] again showing that the two ligands have similar electron-donating properties to the ruthenium centre.



Scheme 2. Preparation of $[Ru(BPM)_2(CO)Cl][BPh_4]$ (**4**)

Attempts to prepare the halogen-free compounds $[Ru(BPM)_2(CO)_2][BPh_4]_2$ and $[Ru(BIM)_2(CO)_2][BPh_4]_2$ by dechlorination with trifluoromethanesulfonic acid or silver triflate, followed by the addition of BPM and $NaBPh_4$, were unsuccessful. These methods have been reported for the preparation of $[Ru(BIPY)_2(CO)_2]^{2+}$. No product could be isolated from the reaction of $[Ru(BPM)(CO)_2Cl_2]$ or $[Ru(BIM)(CO)_2Cl_2]$ and silver triflate, while the reaction of $[Ru(BIM)(CO)_2Cl_2]$ with trifluoromethanesulfonic acid followed by the addition of $NaBPh_4$ resulted in the quantitative protonation of the BIM ligand affording an ionic compound (Figure 1). Important crystal data are given in Table 2 with important bond lengths and bond angles listed in Table 3. Figure 2 shows the dimeric nature of the cation through H-bonding.

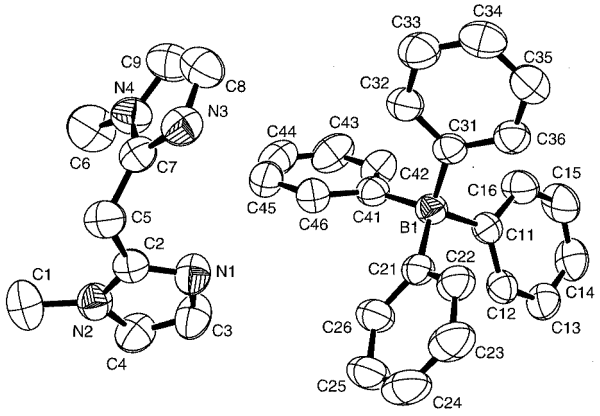


Figure 1. Molecular projection of the asymmetric unit of [HBIM][BPh_4], showing atom labelling scheme; thermal ellipsoids are drawn at the 50% probability level; H-atoms removed for clarity

NMR Spectroscopic Studies of $[Ru(BPM)_2(CO)(Cl)][BPh_4]$

The ^1H and $^{13}C\{^1H\}$ NMR spectra were completely assigned for $[Ru(BPM)_2(CO)Cl][BPh_4]$ (**4**) (at 250 K). At room temperature, rapid conformational exchange is observed, so that the resonances of the protons of the two BPM ligands are completely equivalent. At 250 K, the resonances of the protons of the four pyrazole rings of the ligands are found to be inequivalent, indicating that the two BPM ligands are mutually *cis*, and that the chloride and carbonyl ligands are mutually *cis*. It was not possible to distinguish the positions of the carbonyl and the chloride ligands. The NOESY spectrum shows the chelating ligands to be puckered and the six-membered chelate ring to have a boat conformation with only one methylene proton interacting with the closest protons of the pyrazole rings. A similar geometry is observed in the complex $[Ru(BPM)_2(PPh_3)Cl]Cl$, where the complete coordination sphere of the ruthenium centre could be determined because of strong NOESY interactions between the protons of the pyrazole rings and the triphenylphosphane ligand.[30] The atom labelling used for the assignment of NMR spectra of **4** is shown in Figure 3.

Structures of $[Ru(dmBPM)(CO)_2Cl_2]$ (2) and $[Ru(BPM)_2(CO)Cl][BPh_4]$ (4)

Important crystal data are listed in Table 2 with important bond lengths and bond angles of $[Ru(dmBPM)(CO)_2Cl_2]$ (**2**) and $[Ru(BPM)_2(CO)Cl][BPh_4]$ (**4**) listed in Table 4 and 5, respectively. Both compounds are noncentrosymmetric and crystallise in the $P\bar{1}$ (#2) space group. The ruthenium centres in both complexes have a distorted octahedral geometry, with the bis(pyrazol-1-yl)methane ligands chelating the ruthenium centres to form six-membered chelate rings with boat conformations. The structure of $[Ru(dmBPM)(CO)_2Cl_2]$ (Figure 4) shows the carbonyl and chloride ligands to have *cis* and *trans* arrangements, respectively. The structures of both *cis*(CO), *cis*(Cl)-

Table 1. Crystallographic data for [Ru(dmBPM)$(CO)_2Cl_2$] (**2**), [Ru$(BPM)_2$(CO)Cl][BPh_4] (**4**) and [HBIM][BPh_4]

	[Ru(dmBPM)$(CO)_2Cl_2$]	[Ru$(BPM)_2$(CO)Cl][BPh_4]	[HBIM][BPh_4]
Formula	$C_{13}H_{16}N_4O_2RuCl_2$	$C_{39}H_{36}N_8OBRuCl$	$C_{33}H_{33}BN_4$
M	432.27	780.09	496.45
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P2_1/c$ (#14)
a/ Å	7.9834(6)	13.167(3)	10.5867(4)
b/ Å	8.8530(6)	15.354(3)	14.9348(6)
c/ Å	12.4069(9)	9.952(2)	18.2777(7)
α/°	98.9100(10)	106.188(4)	90.00
β/°	90.4100(10)	98.774(4)	105.9330(10)
γ/°	94.1650(10)	89.101(4)	90.00
V/ Å^3	863.86(11)	1908.8(7)	2778.87(19)
D_c/mg cm^{-3}	1.662	1.357	1.187
Z	2	2	4
F(000)	432	444	1056
μ/mm^{-1}	1.227	0.5223	0.070
$T^*_{(min, max)}$	0.830, 1.000	0.85370, 0.96303	0.980, 0.993
$2\theta_{max}$/°	56.54	56.40	56.56
No. unique reflections	4020	8483	6695
No. observed data [$I_o < 2(I)$]	3497	5241	2914
R[a]	3.15	5.16	3.97
R′[a]	7.42	14.67	8.41
GooF	1.027	1.262	1.064
Absorption Correction	Empirical	Gaussian	Gaussian

[a] *R* and *R′* defined as residual factor and weighted residual factor, respectively, for observed reflections satisfying $F_0^2 \geq 2\sigma F^2$. (w = 1/[$\sigma^2(F_0^2)$ + (0.0332P)^2 + 0.6217*P*] (**2**), w = 1/[$\sigma^2(F_0^2)$ + (0.0550*P*)^2] (**4**), (w = 1/[$\sigma^2(F_0^2)$ + (0.0300*P*)^2] ([HBIM][BPh_4], where *P* = (F_0^2 + 2F_c^2)/3).

Table 2. Selected bond lengths and angles for [HBIM][BPh_4]

Bond lengths (Å)			
N(1)−C(2)	1.3167(18)	N(3)−C(7)	1.3259(19)
N(1)−C(3)	1.3683(19)	N(3)−C(8)	1.369(2)
N(2)−C(2)	1.3493(18)	N(4)−C(7)	1.3294(18)
N(2)−C(4)	1.3619(19)	N(4)−C(9)	1.371(2)
N(2)−C(1)	1.4618(19)	N(4)−C(6)	1.4627(19)
C(2)−C(5)	1.494(2)	C(5)−C(7)	1.483(2)
C(3)−C(4)	1.337(2)	C(8)−C(9)	1.331(2)
Bond angles (°)			
C(2)−N(1)−C(3)	105.33(14)	C(7)−N(3)−C(8)	109.10(16)
C(2)−N(2)−C(4)	107.05(13)	C(7)−N(4)−C(9)	108.84(15)
C(2)−N(2)−C(1)	127.58(15)	C(7)−N(4)−C(6)	125.60(15)
C(4)−N(2)−C(1)	125.36(15)	C(9)−N(4)−C(6)	125.56(16)
N(1)−C(2)−N(2)	110.93(14)	N(3)−C(7)−N(4)	107.60(15)
N(1)−C(2)−C(5)	123.61(15)	N(3)−C(7)−C(5)	126.13(15)
N(2)−C(2)−C(5)	125.46(15)	N(4)−C(7)−C(5)	126.23(16)
C(4)−C(3)−N(1)	110.29(16)	C(9)−C(8)−N(3)	107.18(17)
C(3)−C(4)−N(2)	106.40(16)	C(8)−C(9)−N(4)	107.28(16)

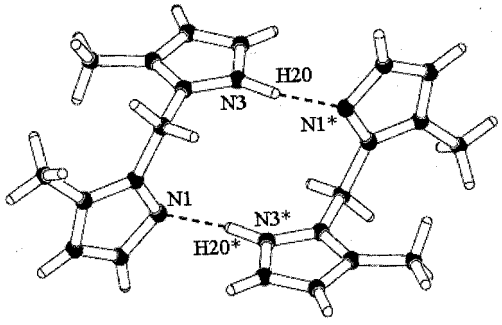


Figure 2. Molecular projection of [$(HBIM)_2$]$^{2+}$, showing dimeric nature through H-bonding

[Ru(BIPY)$(CO)_2Cl_2$] and *cis*(CO), *trans*(Cl)-[Ru(BIPY)-$(CO)_2Cl_2$] have been reported previously.[34] The structure of the [Ru$(BPM)_2$(CO)Cl]$^+$ cation (Figure 5) shows the carbonyl and chloride ligands to have *cis* coordination with respect to each other, as was observed for the complex in solution at low temperatures using NMR spectroscopy.

The Ru−N distances for **2** [2.165(2) and 2.167(2) Å] are significantly longer than those seen in the analogous bipyridine complexes *cis*(CO), *cis*(Cl)-[Ru(BIPY)$(CO)_2Cl_2$] and *cis*(CO), *trans*(Cl)-[Ru(BIPY)$(CO)_2Cl_2$] [2.117(8) and 2.090(8), 2.112(12) and 2.102(9) Å, respectively],[34] where the longer Ru−N bond length corresponds to the bond *trans* to the carbonyl ligand in the *cis*(CO), *cis*(Cl)-[Ru(BIPY)$(CO)_2Cl_2$] structure. The Ru−N bond lengths of **2** are also considerably longer than those in the cation of **4** [2.076(4)−2.140(4) Å] and can be attributed to the increased steric interaction caused by the methyl substituents present on the pyrazolyl rings. The Ru−Cl bond lengths [2.3941(7), 2.4155(7) Å] are similar, as would be expected for a *cis*(CO), *trans*(Cl) geometry. Both distances are similar to those of *cis*(CO), *trans*(Cl)-[Ru(BIPY)$(CO)_2Cl_2$] [2.391(5), 2.390(5) Å (Ru−Cl); 1.85(17), 1.817(8) Å (Ru−C)].[34] The distortion in the octahedral geometry about the ruthenium centre is evident by the slight deviation from ideal bond angles about the ruthenium centre. The

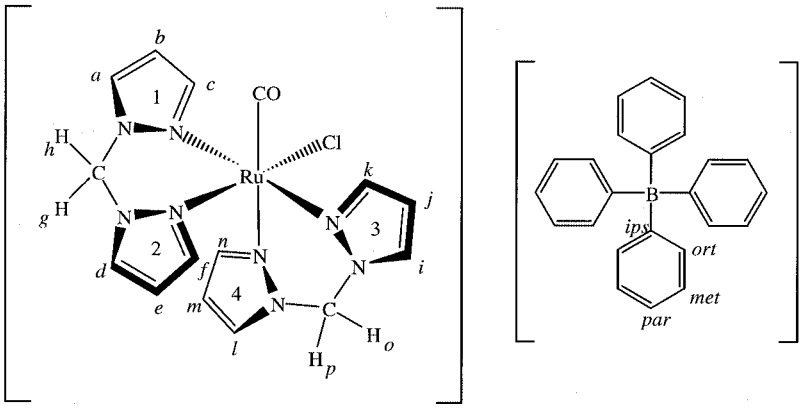


Figure 3. Atom labelling scheme of $[Ru(BPM)_2(CO)Cl][BPh_4]$ (**4**) for NMR spectra

Table 4. Selected bond lengths and angles for $[Ru(dmBPM)(CO)_2Cl_2]$ (**2**)

Bond lengths (Å)			
Ru−N(2	2.165(2)	Ru−C(2)	1.868(3)
Ru−N(4)	2.167(2)	Ru−Cl(3)	2.3941(7)
Ru−C(1)	1.869(3)	Ru−Cl(2)	2.4155(7)
Bond Angles (°)			
N(2)−Ru−N(4)	86.38(8)	Cl(3)−Ru−C(2)	91.95(10)
N(2)−Ru−C(2)	94.94(11)	Cl(3)−Ru−C(1)	91.23(10)
N(2)−Ru−C(1)	178.27(11)	Cl(2)−Ru−C(2	88.55(10)
N(4)−Ru−C(1)	94.44(11)	Cl(2)−Ru−C(1)	89.33(10)
N(4)−Ru−C(2)	178.68(10)	Cl(3)−Ru−N(2)	87.27(6)
C(1)−Ru−C(2)	84.24(13)	Cl(3)−Ru−N(4)	88.12(6)
Cl(3)−Ru−Cl(2)	179.28(3)	Cl(2)−Ru−N(2)	92.17(6)
Cl(2)−Ru−N(4)	91.38(6)		

Table 5. Selected bond lengths and angles of $[Ru(BPM)_2(CO)Cl][BPh_4]$ (**4**)

Bond lengths (Å)			
Ru−N(4)	2.071(4)	Ru−N(6)	2.095(4)
Ru−N(2)	2.090(4)	Ru−N(8)	2.142(4)
Ru−C(15)	1.930(5)	Ru−Cl(1)	2.3986(16)
Bond angles (°)			
N(4)−Ru−N(6)	173.88(15)	N(4)−Ru−N(2)	88.66(15)
N(6)−Ru−N(2)	88.44(15)	N(4)−Ru−N(8)	87.35(15)
N(6)−Ru−N(8)	87.01(14)	N(2)−Ru−N(8)	84.54(15)
N(4)−Ru−C(15)	91.50(17)	N(6)−Ru−C(15)	94.19(17)
Cl−Ru−N(4)	90.81(12)	Cl−Ru−N(6)	91.63(12)
N(2)−Ru−C(15)	96.72(18)	N(8)−Ru−C(15)	178.27(19)
Cl−Ru−N(2)	175.26(11)	Cl−Ru−N(8)	90.73(11)
Cl−Ru−C(15)	88.00(15)		

bite angle of the dmBPM ligand [86.38(8)°] is similar to that in *trans*-$[Ru(BPM)(CO)(PMe_3)_2(COMe)]^+$ [84.3(5)°][35] and $[Ru_2(PPh_3)_2(BPM)_2(\mu\text{-}Cl)_3]Cl$ [88.4(3)°].[30]

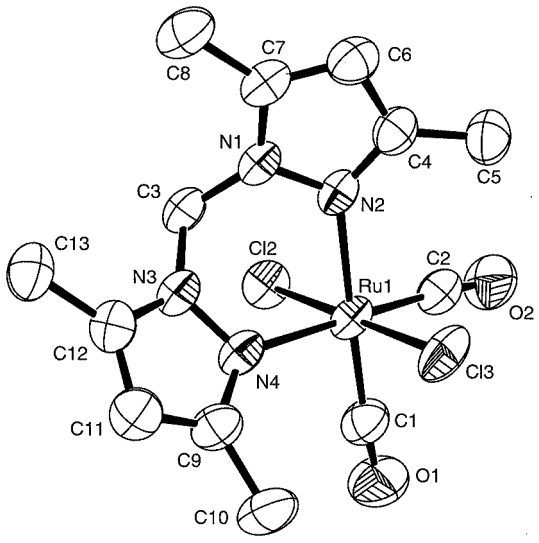


Figure 4. Molecular projection of $[Ru(dmBPM)(CO)_2Cl_2]$ (**2**) showing atom labelling scheme; thermal ellipsoids are drawn at the 50% probability level; H-atoms removed for clarity

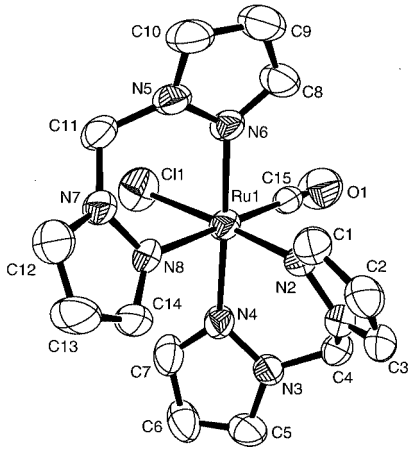


Figure 5. Molecular projection of $[Ru(BPM)_2(CO)Cl][BPh_4]$ (**4**) showing atom labelling scheme; thermal ellipsoids are drawn at the 50% probability level; H-atoms removed for clarity

The structure of the cation of **4** shows the CO and Cl ligands to have *cis* coordination with respect to each other. The Ru−N bond lengths are shorter than those of the neutral complex **2** because of the absence of the methyl moieties on the pyrazolyl rings of the ligands, but are similar to those of $[Ru(BIPY)_2(CO)Cl]^+$ [mean value 2.10(2) Å].[33] Similar to $[Ru(BIPY)_2(CO)Cl]^+$, three Ru−N bond lengths of **4** are similar, ranging from 2.071(4) to 2.095(4) Å, with one longer bond [2.140(4) Å], corresponding to the Ru−N bond *trans* to the carbonyl ligand; this is in accordance with the increased *trans* influence, CO > N_{ligand} > Cl. The Ru−Cl and Ru−C bond lengths in **4** of 2.3986(16) and 1.930(5) Å, respectively, are also similar to those reported for $[Ru(BIPY)_2(CO)Cl]^+$.[33] The slightly distorted octahedral geometry about the ruthenium centre in **4** is not unlike related structures, with the bite angle of the ligands being 88.66(15) and 87.01(14)°, similar to those in the compounds described above.

Reactivity of $[Ru(N\text{-}N)(CO)_2Cl_2]$ Compounds

The catalytic activity of the $[Ru(N\text{-}N)(CO)_2Cl_2]$ compounds was investigated. The analogous dipyridylruthenium compounds are active in the water-gas shift reaction as well as a number of other catalytic processes. The processes we investigated included hydrogenation, hydrosilylation, intramolecular cyclisation of unsaturated carboxylic acids to form lactones, and intermolecular coupling reactions. All reactions were conducted at 60 °C over several days. All coupling reactions were unsuccessful, as were the hydrogenation reactions. The activity of the complexes toward H_2 was monitored using *para*-hydrogen NMR experiments (4 atm H_2). No activation of H_2 by the ruthenium compounds was observed, at various temperatures or under photolytic conditions.

Conclusions

A series of organoruthenium compounds containing the bidentate ligands bis(*N*-methylimidazol-1-yl)methane and bis(pyrazol-1-yl)methane ligands have been prepared that are free of phosphane coligands. Structural elucidation of $[Ru(dmBPM)(CO)_2Cl_2]$ (**2**) shows it to be a mononuclear compound with *cis*(CO), *trans*(Cl) coordination in a distorted octahedral geometry. All other prepared analogous compounds are assigned with the same coordination environment based on spectral similarities. The ionic compound $[Ru(BPM)_2(CO)Cl][BPh_4]$ (**4**) was prepared by two routes. Structural elucidation of $[Ru(BPM)_2(CO)Cl][BPh_4]$ (**4**) shows it to have a *cis* arrangement of the two bis(pyrazol-1-yl)methane ligands. This was also confirmed by NOESY and COSY NMR spectroscopy and is similar to the previously reported $[Ru(BPM)_2(PPh_3)Cl]Cl$.[14] We were unable to prepare the halide-free compound $[Ru(BPM)_2(CO)_2][BPh_4]$. The activation of small molecules by the ruthenium compounds was investigated, with the ruthenium compounds described herein having quite different reactivity to that of $[Ru(BIPY)(CO)_2Cl_2]$.

Experimental Section

All reactions were performed under nitrogen gas using standard Schlenk techniques. Ruthenium(III) trichloride hydrate was obtained from Johnson−Matthey, and used without purification. The ruthenium complex $[Ru(CO)_2Cl_2]_n$ [36] and the ligands bis(pyrazol-1-yl)methane (BPM),[18] bis(3,5-dimethylpyrazol-1-yl)methane (dmBPM)[18] and bis(*N*-methylimidazol-1-yl)methane (BIM)[19] were prepared according to literature procedures. All solvents were degassed prior to use. DMF was freshly distilled under reduced pressure from $MgSO_4$ prior to use.

The positive electrospray mass spectra of the complexes were recorded on a Finnigan/MAT TSQ7000 LCMS mass spectrometer. CI mass spectra were recorded on a Finnigan PolarisQ GCMS/MS ion trap mass spectrometer and LSIMS mass spectra were recorded on a Kratos Analytical Concept ISQ mass spectrometer using an mnba matrix. Infrared spectra (cm^{-1}) were recorded using an ATI Mattson *Genesis Series* FTIR Spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker DPX300, DPX400, DPX500 or Varian Gemini 200 spectrometers at 300 K unless otherwise stated. Chemical shifts are internally referenced to residual solvent.

$[Ru(BPM)(CO)_2Cl_2]$ (1a): $[Ru(CO)_2Cl_2]_n$ (99 mg, 0.43 mmol) and BPM (70 mg, 0.44 mmol) were refluxed in MeOH (40 mL) for 30 mins. The yellow solution was cooled to room temperature and the volume reduced in vacuo (to about 5 mL) to afford a pale yellow precipitate. The solid was collected and washed with Et_2O (yield 90 mg, 55%). Recrystallisation by vapour diffusion of $MeNO_2$ and Et_2O at −30 °C afforded pale yellow block crystals. ^1H NMR (200 MHz, [D$_6$]acetone): δ = 6.63 (t, $^3J_{H\text{-}H}$ = 2.50 Hz, 2 H, pz-H), 7.26 (br. s, 2 H, CH_2), 8.16 (d, $^3J_{H\text{-}H}$ = 2.30 Hz, 4 H, pz-H), 8.24 (d, $^3J_{H\text{-}H}$ = 2.20 Hz, 4 H, pz-H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]acetone): δ = 63.4 (CH_2), 108.5 (C4), 135.3 (C5), 147.2 (C3), 196.4 (CO) ppm. CI-MS: *m*/*z* = 376 [M^+; $^{101}Ru(^{12}C_7N_4H_9)(^{12}CO)_2{}^{35}Cl_2$], 348 [M − CO; $^{101}Ru(^{12}C_7N_4H_9)(^{12}CO)^{35}Cl_2$], 320 [$M^+$ − 2CO; $^{101}Ru(^{12}C_7N_4H_9)^{35}Cl_2$], 285 [$M^+$ − 2CO-Cl; $^{101}Ru(^{12}C_7N_4H_9)^{35}Cl$], 250 [$M^+$ − 2CO − 2Cl; $^{101}Ru(^{12}C_7N_4H_9)$] 148 (L). $C_9H_8Cl_2N_4O_2Ru$ (376.18) calcd. C 28.74, H 2.14, N 14.90; found C 28.95, H 2.04, N 14.89.

$[Ru(dmBPM)(CO)_2Cl_2]$ (2): Procedure as above using dmBPM (yield 54 mg, 30%). Recrystallisation by vapour diffusion of $MeNO_2$ and Et_2O at −30 °C afforded pale yellow block crystals. ^1H NMR (500 MHz, [D$_8$]THF, −28 °C): δ = 2.48 (s, 6 H, pz-CH_3), 2.63 (s, 6 H, pz-CH_3), 6.15 (s, 2 H, pz-H), 6.20 (d, $^2J_{H\text{-}H}$ = 15.09 Hz, 1 H, CH_2), 7.53 (d, $^2J_{H\text{-}H}$ = 15.09 Hz, 1 H, CH_2) ppm. ^1H NMR (500 MHz, [D$_8$]THF, 27 °C): δ = 2.46 (s, 6 H, pz-CH_3), 2.63 (s, 6 H, pz-CH_3), 6.09 (s, 2 H, pz-H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, [D$_8$]THF, 27 °C): δ = 10.8, 15.5, 56.3, 108.8, 142.7, 155.3, 197.1 (C≡O) ppm. CI MS: *m*/*z* = 431 [M^+; $^{101}Ru(^{12}C_{11}N_4H_{16})(^{12}CO)_2{}^{35}Cl_2$], 403 [$M^+$ − CO; $^{101}Ru(^{12}C_{11}N_4H_{16})(^{12}CO)^{35}Cl_2$], 375 [$M^+$ − 2CO; $^{101}Ru(^{12}C_{11}N_4H_{16})^{35}Cl_2$], 340 [$M^+$ − 2CO − Cl; $^{101}Ru(^{12}C_{11}N_4H_{16})^{35}Cl$], 305 [$M^+$ − 2CO − 2Cl; $^{101}Ru(^{12}C_{11}N_4H_{16})$], 204 [L; $^{12}C_{11}N_4H_{16}$]. $C_{13}H_{16}Cl_2N_4O_2Ru$ (432.27): calcd. C 36.11, H 3.73, N 12.97; found C 36.04, H 3.76, N 12.86.

$[Ru(BIM)(CO)_2Cl_2]$ (3): Procedure as above using BIM (yield 197 mg, 55%). Recrystallisation from $MeNO_2$ at −30 °C afforded pale yellow block crystals. ^1H NMR (300 MHz, CD_3NO_2, 27 °C): δ = 6.16 (s, 6 H, CH_3), 6.77 (s, 2 H, CH_2), 8.65 (d, $^3J_{H\text{-}H}$ = 1.11 Hz, 2 H, mim-H), 8.81 (d, $^3J_{H\text{-}H}$ = 1.50 Hz, 2 H, mim-H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_3NO_2, 27 °C): δ = 23.9, 34.6, 123.8, 130.7, 144.1, 198.4 ppm. CI-MS: *m*/*z* = 375 [M^+ − CO;

$^{101}Ru(^{12}C_9N_4H_{12})(CO)^{35}Cl_2]$, 347 [$M^+$ − 2CO; $^{101}Ru(^{12}C_9N_4H_{12})^{35}Cl_2]$, 312 [$M^+$ − 2CO − Cl; $^{101}Ru(^{12}C_9N_4H_{12})^{35}Cl]$, 176 [$M^+$ − 2CO − 2Cl − Ru; $^{12}C_9N_4H_{12}$]. $C_{11}H_{12}Cl_2N_4O_2Ru$ (404.22): calcd. C 32.69, H 2.99, N 13.86; found C 32.76, H 2.90, N 13.80.

[Ru(BPM)(CO)$_2$Br$_2$] (1b): $[Ru(CO)_2Cl_2]_n$ (202 mg, 0.87 mmol) and KBr (1.0 g, 8.40 mmol) were refluxed in degassed MeOH (40 mL) for 3.5 hours. BPM (147 mg, 0.99 mmol) was then added to the orange solution and the reaction was refluxed for a further 30 mins. The orange solution was cooled to room temperature affording a colourless precipitate which was collected by filtration. The solvent of the filtrate was removed in vacuo and the resulting orange solid was isolated and washed with MeOH (184 mg, 50%). ^{1}H NMR (200 MHz, [D$_6$]acetone, 27 °C): δ = 6.64 (t, $^3J_{H\text{-}H}$ = 2.58 Hz, 2 H, pz-H), 7.29 (br. s, 2 H, CH_2), 8.20 (d, $^3J_{H\text{-}H}$ = 2.34 Hz, 4 H, pz-H), 8.25 (d, $^3J_{H\text{-}H}$ = 2.06 Hz, 4 H, pz-H) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, [D$_6$]acetone, 27 °C): δ = 64.19 (CH_2), 108.83 (C4), 135.76 (C5),148.45 (C3), 197.72 (CO) ppm. LSIMS: *m*/*z* = 466 [M^+; $^{101}Ru(^{12}C_7N_4H_9)(^{12}CO)_2{}^{80}Br_2]$, 438 [$M^+$ − CO; $^{101}Ru(^{12}C_7N_4H_9)(^{12}CO)^{80}Br_2]$, 410 [$M^+$ − 2CO) [$^{101}Ru(^{12}C_7N_4H_9)^{80}Br_2$ 410], 386 [M^+ − Br; $^{101}Ru(^{12}C_7N_4H_9)(^{12}CO)_2{}^{80}Br_2]$, 358 [$M^+$ − CO − Br; $^{101}Ru(^{12}C_7N_4H_9)(^{12}CO)^{80}Br]$. $C_9H_8Br_2N_4O_2Ru$ (465.06): calcd. C 23.24, H 1.73, N 12.05; found C 23.44, H 1.78, N 12.01.

[Ru(BPM)$_2$(CO)Cl][BPh$_4$] (4): Method 1. $RuCl_3{\cdot}3H_2O$ (100 mg, 0.48 mmol) and BPM (123 mg, 0.83 mmol) were refluxed in DMF for 8 hours. The reaction mixture was cooled, $NaBH_4$ (2.62 mg, 0.77 mmol) was added and the reaction stirred for 1 hour. The solution was then cooled and the volume of solvent reduced to about 5 mL. Et_2O was then added to the solution resulting in an off-white precipitate which was collected and washed with Et_2O. The off-white compound was recrystallised from acetone and Et_2O (89 mg, 15%). NMR assignments refer to the numbering given in Figure 3. ^{1}H NMR (500 MHz, [D$_6$]acetone, −23 °C): δ = 5.92 (d, $^3J_{H\text{-}H}$ = 2.36 Hz, H*r*), 6.25 (d, $^3J_{H\text{-}H}$ = 2.13 Hz, H*h*), 6.29 (d, $^3J_{H\text{-}H}$ = 2.52, $^3J_{H\text{-}H}$ = 2.60 Hz, H*q*), 6.40 (t, $^3J_{H\text{-}H}$ = 2.36 Hz, H*g*), 6.63 (d, $^3J_{H\text{-}H}$ = 14.66 Hz, H*n*), 6.70 (t, $^3J_{H\text{-}H}$ = 2.60 Hz, H*l*), 6.71 (t, $^3J_{H\text{-}H}$ = 2.44 Hz, H*b*), 6.77 (t, BPh_4), 6.92 (t, BPh_4), 7.11 (d, $^3J_{H\text{-}H}$ = 13.79 Hz, H*d*), 7.24 (d, $^3J_{H\text{-}H}$ = 14.98 Hz, H*o*), 7.32 (t, BPh_4), 7.63 (d, $^3J_{H\text{-}H}$ = 13.87 Hz, H*e*), 8.09 (d, $^3J_{H\text{-}H}$ = 2.21 Hz, H*a*), 8.14 (d, $^3J_{H\text{-}H}$ = 2.13 Hz, H*k*), 8.23 (d, $^3J_{H\text{-}H}$ = 3.00 Hz, H*p*), 8.29 (t, $^3J_{H\text{-}H}$ = 2.68, $^3J_{H\text{-}H}$ = 3.00 Hz, H*f*), 8.38 (d, $^3J_{H\text{-}H}$ = 2.68 Hz, H*m*), 8.41 (d, $^3J_{H\text{-}H}$ = 2.84 Hz, H*c*) ppm. ^{13}C NMR (125 MHz, [D$_6$]acetone, −23 °C): δ = 64.1 (C*d,e*), 64.7 (C*o,n*), 109.1 (C*g*), 109.3 (C*l*), 109.6 (C*q*), 110.0 (C*b*), 122.9 (BPh_4), 126.6 (BPh_4), 135.8 (C*f*), 136.8 (C*p*), 137.4 (BPh_4), 137.4 (C*m*), 137.7 (C*c*), 144.0 (C*h*), 145.7 (C*r*), 147.2 (C*k*), 149.5 (C*a*) ppm. IR (nujol): $\tilde{\nu}$ = 1970 cm^{-1} (C≡O str). $^+$ES MS: *m*/*z* = 460.9 [M^+; $^{101}Ru(^{12}C_7N_4H_9)_2(^{12}CO)^{35}Cl]$. $C_{39}H_{36}BClN_8ORu$ (780.13): calcd. C 60.04, H 4.65, N 14.37; found C 60.16, H 4.99, N 14.07.

Method 2. A mixture of $[Ru(BPM)(CO)_2Cl_2]$ (103 mg, 0.452 mmol) and Me_3NO (90 mg, 2.00 mmol) in MeCN was refluxed for 30 mins. BPM (150 mg, 1.01 mmol) was then added to the reaction mixture which was then refluxed for a further 16 hours. The yellow solution was allowed to cool slightly, after which $NaBPh_4$ (459 mg, 1.34 mmol) was added. A pale yellow precipitate was formed on cooling, which was collected and washed with Et_2O (132 mg, 37%). Suitable crystals for X-ray diffraction were grown from $MeNO_2/Et_2O$.

Catalysis Reactions

Coupling of HC≡CPh and HSiEt$_3$: *Typical reaction*. Phenylacetylene (25 mg, 0.25 mmol), triethylsilane (29 mg, 0.25 mmol), [Ru(BIM)(CO)$_2$Cl$_2$] (5.3 mg, 14.1 μmol) and [D$_3$]$MeNO_2$ were sealed in an NMR tube. The mixture was heated to 60 °C and the reaction was monitored using NMR spectroscopy. After one week, no coupling product was observed.

Coupling of Acetophenone and 1-Pentene: *Typical reaction*. Acetophenone (35 mg, 0.29 mmol), 1-pentene (17 mg, 0.25 mmol), [Ru(dmBPM)(CO)$_2$Cl$_2$] (5.7 mg, 12.9 μmol) and [D$_8$]THF were sealed in an NMR tube. The mixture was heated to 60 °C and the reaction was monitored using NMR spectroscopy. After one week, no coupling product was observed.

Cyclisation of *cis*-3-Methyl-2-pentene-4-yn-1-ol to 2,3-Dimethylfuran: *Typical reaction*. *cis*-3-Methyl-2-pentene-4-yn-1-ol (63 mg, 0.66 mmol), [Ru(BIM)(CO)$_2$Cl$_2$] (2.8 mg, 6.9 μmol) and [D$_8$]THF were sealed in an NMR tube. The mixture was heated to 60 °C and the reaction was monitored using NMR spectroscopy. After one week, no cyclisation product was observed.

Cyclisation of 4-Pentynoic acid to γ-Methylene-γ-butyrolactone: *Typical reaction*. 4-Pentynoic acid (58 mg, 0.59 mmol), [Ru(BIM)(CO)$_2$Cl$_2$] (2.4 mg, 5.9 μmol) and [D$_8$]THF were sealed in an NMR tube. The mixture was heated to 60 °C and the reaction was monitored using NMR spectroscopy. After one week, no cyclisation product was observed.

Parahydrogen Experiments: Hydrogen enriched in the *para* spin state was prepared by cooling H_2 to 77 K over a paramagnetic catalyst. An atmosphere of H_2 equivalent to ca. 3 atm. pressure at 298 K was introduced into the resealable NMR tube on a high vacuum line already containing the sample and deuterated solvent. The samples were thawed immediately prior to use and introduced into the NMR spectrometer at the pre-set temperature.

X-ray diffraction studies

Data collection used a Bruker SMART 1000 CCD diffractometer equipped with an Oxford System Cryostream low-temperature attachment, with graphite monochromated Mo-K_α radiation (λ_{max} = 0.71073 Å), *T* = 173 K ([Ru(dmBPM)(CO)$_2$Cl$_2$]) or 293 K ([HBIM][BPh$_4$] and [Ru(BPM)$_2$(CO)Cl][BPh$_4$]). Data integration and reduction were performed with SAINT and XPREP.[37] A Gaussian absorption correction was applied to the data of [Ru(BPM)$_2$(CO)Cl][BPh$_4$] and [HBIM][BPh$_4$].[37,38] A semi-empirical correction was determined with SADABS[39] for [Ru(dmBPM)(CO)$_2$Cl$_2$]. Molecular projections of all structures were generated with Ortep-3.[40] All structures were solved by direct methods using SHELXS-97[41] and structure refinement was done using SHELXL-97.[42] All non-hydrogen sites for the three structures were treated anisotropically. All hydrogen atoms were calculated and refined isotropically. H(20) in [HBIM][BPh$_4$] was modelled with isotropic displacement parameters.

CCDC-184163 (**2**), -184164 (**4**) and -184165 ([HBIM][BPh$_4$]) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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