

Polypyrazolylmethane complexes of ruthenium†

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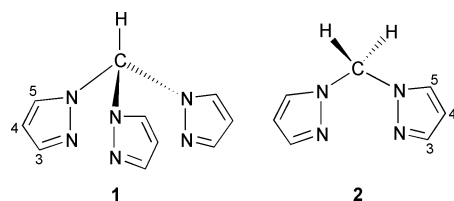
Received 11th October 2000, Accepted 2nd May 2001

First published as an Advance Article on the web 12th June 2001

A series of ruthenium(II) complexes with the pyrazolyl alkane ligands tris(1-pyrazolyl)methane **1** (TPM) and bis(1-pyrazolyl)methane **2** (BPM) have been synthesized and characterised. The complex $[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]^+\text{X}^-$ ($\text{X} = \text{Cl}$ **3a** or BF_4 **3b**) was formed by the reaction of TPM with $\text{RuCl}_2(\text{PPh}_3)_3$ and $[\text{Ru}(\text{CO})\text{H}(\text{PPh}_3)(\text{TPM})]^+\text{X}^-$ ($\text{X} = \text{Cl}$ **4a** or BF_4 **4b**) by the reaction of TPM with $\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3$. The complexes $[\text{RuCl}(\text{PPh}_3)(\text{BPM})_2]^+\text{Cl}^-$ **5** and $(\text{BPM})(\text{Ph}_3\text{P})\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{PPh}_3)(\text{BPM})]^+\text{Cl}^-$ **6** were synthesized by the reaction of BPM with $\text{RuCl}_2(\text{PPh}_3)_3$. Complexes **3–6** were characterised by multinuclear NMR spectroscopy, and **3a** and **6** by X-ray crystallography. $[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]^+\text{Cl}^-$ exhibits dynamic behaviour at low temperature and this is attributed to restricted rotation of the PPh_3 groups about the M–P bond.

Introduction

Transition metal complexes with ligand systems containing N-donors have been used successfully to promote the transformation of organic compounds,¹ and also to act as structural mimics of metalloenzymes.² Ruthenium complexes containing bidentate N-donor ligands with sp^2 hybridised nitrogen atoms such as 2,2'-bipyridyl,³ 1,10-phenanthroline,³ and bis(pyrazol-1-yl)methane⁴ have recently found use in catalytic hydrogenation. N-Donor poly(1-pyrazolyl)borate ligands are also well established as versatile polydentate N-donors and tris-(1-pyrazolyl)borate complexes of Ir,⁵ Rh⁶ and Re⁷ are sufficiently reactive species to undergo additions to C–H bonds in alkanes, alkenes and aromatic hydrocarbons. Polypyrazolylmethanes, such as tris(1-pyrazolyl)methane **1** (TPM)⁸ and bis(1-pyrazolyl)methane **2** (BPM),⁸ are neutral ligands which



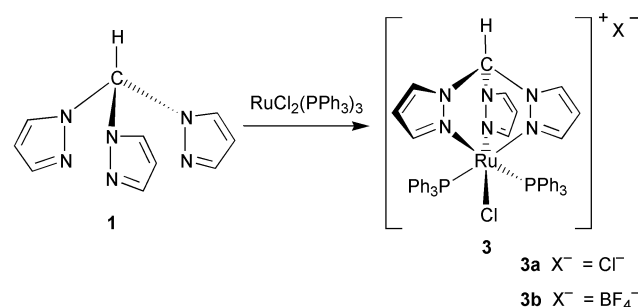
are isosteric and isoelectronic with polypyrazolylborates. Complexes of Ru,⁹ Rh and Ir,¹⁰ Pt,¹¹ Pd,¹² Fe,¹³ Cd and Hg,¹⁴ V,¹⁵ Mo and W,¹⁶ and Al¹⁷ of poly(1-pyrazolyl)methane ligands have been synthesized and studied. A limited number of poly-(1-pyrazolyl)methane complexes of metals of the iron triad have been reported,⁹ and these include $[\text{Ru}(\text{BPM})(\text{PMe}_3)_2(\text{CO})(\text{COMe})]^+\text{BPh}_4^-$,¹⁸ $[\text{Ru}(\text{TPM})(\text{OH}_2)_3][p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3]_2 \cdot 1.5\text{H}_2\text{O}$ ¹⁹ and $[\text{Ru}(\text{TPM})(\text{COD})\text{Cl}]^+\text{Cl}^-$.²⁰

In this paper we report the synthesis and characterisation of ruthenium(II) complexes containing the bidentate and tridentate (1-pyrazolyl)methane ligands **1** and **2**. The cation $[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]^+$ **3** was formed by the reaction of TPM **1** with $\text{RuCl}_2(\text{PPh}_3)_3$,²¹ and the cation $[\text{Ru}(\text{CO})\text{H}(\text{PPh}_3)(\text{TPM})]^+$ **4** by the reaction of TPM **1** with $\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3$.²² The

complex $[\text{RuCl}(\text{PPh}_3)(\text{BPM})_2]^+\text{Cl}^-$ **5** and a bimetallic complex $[(\text{BPM})(\text{Ph}_3\text{P})\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{PPh}_3)(\text{BPM})]^+\text{Cl}^-$ **6** were formed by the reaction of BPM **2** with $\text{RuCl}_2(\text{PPh}_3)_3$. Complexes **3–6** were characterised by multinuclear NMR spectroscopy and **3a** and **6** also by X-ray diffraction.

Results and discussion

Complex $[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]^+\text{Cl}^-$ **3a** was synthesized by displacement of triphenylphosphine and chloride from $\text{RuCl}_2(\text{PPh}_3)_3$ with TPM (Scheme 1). The reaction proceeded quickly



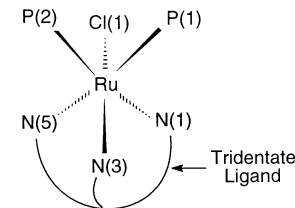
Scheme 1

in good yield to give **3a** as an air-stable yellow crystalline solid. Crystals of the complex were also formed with the tetrafluoroborate counter ion by slowly cooling a warm ethanolic solution containing equimolar quantities of **3** and Na^+BF_4^- to yield yellow-orange crystals of $[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]^+\text{BF}_4^-$ **3b**.

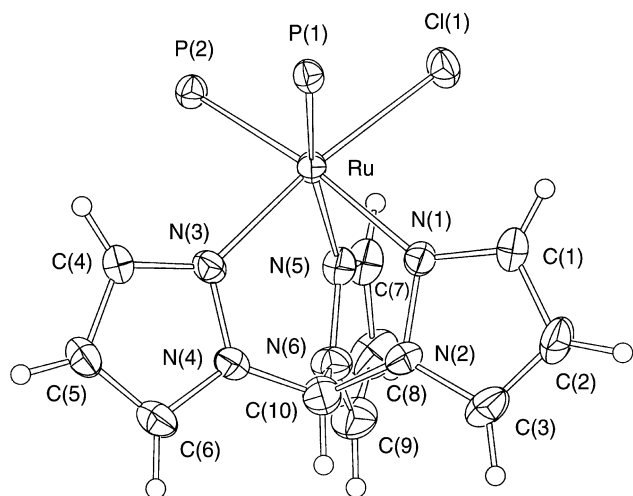
Crystal structure of $[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]\text{Cl} \cdot \text{PPh}_3 \cdot 2\text{CH}_3\text{CH}_2\text{OH}$ **3a**

$[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]^+\text{Cl}^-$ **3a** forms air-stable yellow prisms as the ethanol solvate with TPP (PPh_3) cocrystallised when crystallised from an ethanolic solution. A perspective view of the cation **3a** is shown in Fig. 1 and selected bond lengths and angles for the inner coordination sphere are listed in the electronic supplementary information (ESI). The geometry about the ruthenium centre is essentially octahedral with the three nitrogen atoms of the pyrazolyl groups, a chlorine atom and the phosphorus atoms of the two triphenylphosphine ligands as

† Electronic supplementary information (ESI) available: selected bond lengths and angles for complexes **3a** and **6**, NMR data for complexes **3–5**. See <http://www.rsc.org/suppdata/dt/b1/b103939n/>

Table 1 Comparison of selected bond lengths (Å) and bond angles (deg) in compounds related to $[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]^+\text{Cl}^- \mathbf{3a}^a$


Atoms	$[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]^+\text{Cl}^-$	$\text{RuCl}(\text{PPh}_3)_2(\text{TPB})^{24}$	$\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)^{25}$	$[\text{RuCl}(\text{PPh}_3)_2((\text{mim})_3\text{COH})]^+\text{Cl}^-^{26}$	$\text{Ru}(\text{TPM})(\text{OH}_2)_3^{2+ 19}$
Ru–Cl(1)	2.402(2)	2.409(3)	2.453(2)	2.420(1)	2.121(1) ^{Ru–O}
Ru–P(1)	2.351(2)	2.349(3)	2.337(1)	2.344(1)	2.134(1) ^{Ru–O}
Ru–P(2)	2.374(2)	2.332(3)	2.335(1)	2.371(1)	2.139(1) ^{Ru–O}
Ru–N(1)	2.117(6)	2.104(7)	—	2.123(3)	2.008(2)
Ru–N(2)	2.126(6)	2.126(7)	—	2.137(4)	2.028(2)
Ru–N(3)	2.083(6)	2.085(8)	—	2.062(3)	2.006(2)
P(1)–Ru–P(2)	103.9(1)	101.9(1)	103.99(4)	102.4(0)	89.34(7) ^{O–Ru–O}
P(1)–Ru–Cl(1)	89.9(1)	96.0(1)	89.05(3)	91.6(0)	89.89(8) ^{O–Ru–O}
P(2)–Ru–Cl(1)	94.8(1)	89.0(1)	90.41(4)	95.9(0)	88.15(7) ^{O–Ru–O}
N(1)–Ru–N(5)	78.4(2)	79.9(3)	—	79.4(1)	86.49(8)
N(3)–Ru–N(5)	86.4(2)	87.7(3)	—	86.0(1)	87.46(8)
N(1)–Ru–N(3)	87.2(2)	87.3(3)	—	85.7(1)	87.09(8)

^a Atoms from references have been renumbered to a common numbering scheme.**Fig. 1** An ORTEP²³ plot of $[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]\text{Cl} \cdot \text{PPh}_3 \cdot 2\text{CH}_3\text{CH}_2\text{OH} \mathbf{3a}$ with numbering. The molecule is oriented with the Ru–apical carbon axis vertical. Only the P atoms of the two triphenylphosphine ligands are shown.

ligating atoms. There is some distortion from ideal octahedral geometry about the metal centre, and this is probably the result of the constraints imposed on the three pyrazolyl nitrogen donor atoms by the TPM architecture. The pyrazolyl rings within the TPM ligand are essentially planar.

The steric bulk of the two triphenylphosphine ligands causes the P–Ru–P bond angle (103.9°) to exceed the expected 90° of perfect octahedral symmetry. In addition, the pyrazolyl rings located between a triphenylphosphine ligand and chlorine are displaced away from the triphenylphosphine ligands, with the angle between the plane containing the Ru atom and N donors and the plane of the pyrazole ring less than 180°. Both P–Ru–Cl bond angles (89.9(1), 94.8(1)°) are smaller than the P–Ru–P angle. Comparison with similar compounds $\text{RuCl}(\text{PPh}_3)_2(\text{TPB})^{24}$ [TPB = hydrotris(pyrazolyl)borate] and $\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)^{25}$ reveals the same distortion with large P–Ru–P angles (*ca.* 102°) and similar P–Ru–Cl angles (*ca.* 89 and 95° respectively) (Table 1). The other source of distortion from perfect octahedral symmetry is likely to arise from constraints imposed by the tridentate ligand, with the N–Ru–N angles

(78.4(2), 86.4(2), 87.2(2)°) being smaller than the ideal 90° (Table 1). Diminished N–Ru–N bond angles have also been noted in related complexes including $[\text{Ru}(\text{TPM})(\text{OH}_2)_3][p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3] \cdot 1.5\text{H}_2\text{O}^{19}$ (86.49(8), 87.46(8), 87.09(9)°), $[\text{Ru}(\text{TPM})(\text{COD})\text{Cl}]^+\text{Cl}^-^{20}$ (86.6(2), 83.9(2), 79.9(2)°), and $[\text{RuCl}(\text{PPh}_3)_2((\text{mim})_3\text{COH})]^+\text{Cl}^-^{26}$ (79.4(1), 85.7(1), 86.0(1)°) (mim = *N*-methylimidazolyl).

In complex **3a** both Ru–P bond lengths (2.374(2), 2.351(2) Å) are shorter than the Ru–Cl bond (2.402(2) Å). Similar Ru–Cl bond lengths are found in $\text{RuCl}(\text{PPh}_3)_2(\text{TPB})^{24}$ (2.409(3) Å), $[\text{Ru}(\text{TPM})(\text{COD})\text{Cl}]^+\text{Cl}^-^{20}$ (2.424(2) Å), and $\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)^{25}$ (2.453(2) Å) (Table 1). Similar Ru–P bond lengths are found in $\text{RuCl}(\text{PPh}_3)_2(\text{TPB})^{24}$ (2.332(3), 2.349(3) Å), and $\text{RuCl}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)^{25}$ (2.337(1), 2.335(1) Å) (Table 1). Both Ru–N bond lengths *trans* to the phosphorus ligands are longer (2.117(6), 2.126(6) Å) than Ru–N bond lengths *trans* to the chloro ligand (2.083(6) Å). The equivalent $\text{RuCl}(\text{PPh}_3)_2(\text{TPB})^{24}$ and $[\text{RuCl}(\text{PPh}_3)_2((\text{mim})_3\text{COH})]^+\text{Cl}^-^{26}$ complexes display the same lengthening of the Ru–N bonds.

NMR Studies of $[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]^+\text{Cl}^- \mathbf{3a}$

By NMR at room temperature the two triphenylphosphine ligands of **3** are equivalent, as are the two pyrazolyl rings *trans* to the triphenylphosphine ligands. Only one ³¹P resonance is observed, and in the proton spectrum at room temperature two sets of resonances are observed for the TPM ligand protons, with intensities in the ratio of 2 : 1 (rings A and B, Fig. 2). However, at 185 K (600 MHz), the phosphorus resonance is clearly split into two signals, and the proton resonances of the TPM ligand split to give three sets of resonances indicating three non-equivalent pyrazolyl rings. The proton resonances of the phenyl groups of the PPh₃ groups also show some broadening near 185 K. The dynamic behaviour is consistent with a slowing of the rotation of the triphenylphosphine groups about the M–P bonds. The motion of the triphenylphosphine ligands must freeze to conformations where the PPh₃ groups are non-equivalent, and this probably involves interleaving or “cog-wheeling” of the phenyl substituents on the phosphorus donors²⁷ (Fig. 2).

The kinetics of interconversion between the two conformations, observed at low temperature, was calculated by line shape analysis of the two exchanging phosphorus resonances and the

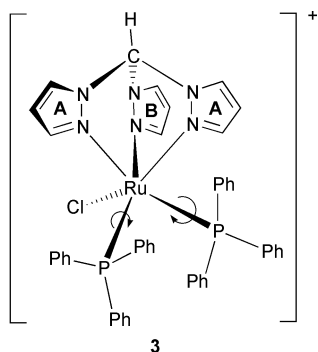
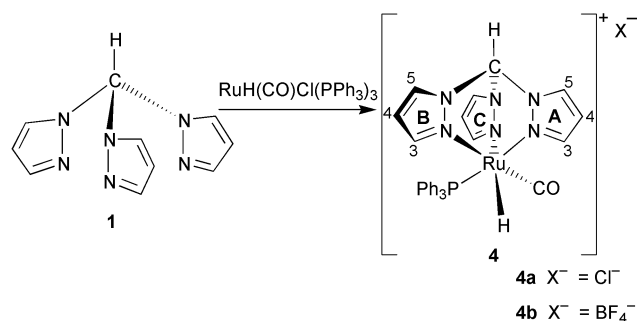


Fig. 2 Restricted rotation of bulky triphenylphosphine ligands in *cis*-coordination sites in $[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]^+ \mathbf{3}$.

rate of exchange is approximately 1150 s^{-1} at 205 K. Restricted rotation is not unexpected with two bulky triphenylphosphine substituents in adjacent coordination sites.

$[\text{Ru}(\text{CO})\text{H}(\text{PPh}_3)(\text{TPM})]^+\text{Cl}^- \mathbf{4a}$

Complex $[\text{Ru}(\text{CO})\text{H}(\text{PPh}_3)(\text{TPM})]^+\text{X}^-$ ($\text{X}^- = \text{Cl}^-$, **4a**; BF_4^- , **4b**) was prepared by the reaction of TPM with $\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3$ (Scheme 2). The complex **4a** was obtained as an air-stable



Scheme 2

cream powder and **4b** by exchange of the counter ion by treatment with a methanolic solution of NaBF_4 .

The ^1H NMR spectrum of $[\text{Ru}(\text{CO})\text{H}(\text{PPh}_3)(\text{TPM})]^+ \mathbf{4}$ contained a doublet due to the phosphorus-coupled metal hydride as well as nine inequivalent pyrazolyl protons. The stereospecific assignment of the ^1H spectra was achieved using a combination of ^1H NOESY and ^1H COSY experiments. The two pyrazolyl rings closest to the metal bound hydride exhibit strong NOESY crosspeaks between the hydride resonances and the protons of two of the pyrazolyl rings (labelled H_A^3 and H_B^3 in **4**, Scheme 2). The NOESY crosspeaks $\{\text{hydride} \leftrightarrow \text{H}_\text{A}^3\}$ and $\{\text{hydride} \leftrightarrow \text{H}_\text{B}^3\}$ are approximately equal in intensity, which indicates that the hydride is located approximately symmetrically between the two pyrazolyl rings, consistent with the octahedral geometry of the system. Additional interactions between the phenyl protons of the triphenylphosphine ligand and the protons of the pyrazolyl rings allowed the stereochemistry about the metal centre fully to be assigned. The infrared spectrum of **4a** contained a band at 1934 cm^{-1} attributed to the CO stretching mode.²⁸

Analogues of **4**, $[\text{Ru}(\text{CO})\text{H}(\text{TPB})(\text{PPh}_3)]^{28}$ and $[\text{Ru}(\text{PPh}_3)(\text{CO})\text{H}(\text{mim})_3\text{COH}]^+\text{Cl}^-$,²⁶ have also been reported.

Bis[bis(1-pyrazolyl)methane]chloro(triphenylphosphine)-ruthenium(II) chloride $[\text{RuCl}(\text{PPh}_3)(\text{BPM})_2]^+\text{Cl}^- \mathbf{5}$

The air-stable glassy green solid $[\text{RuCl}(\text{PPh}_3)(\text{BPM})_2]^+\text{Cl}^- \mathbf{5}$ was formed by the addition of BPM to a THF solution of $\text{RuCl}_2(\text{PPh}_3)_3$ in a 1 : 2 ratio (Scheme 3). The structure of the complex is evident from its NMR spectra. The ^{31}P NMR spectrum contains one resonance due to bound triphenyl-

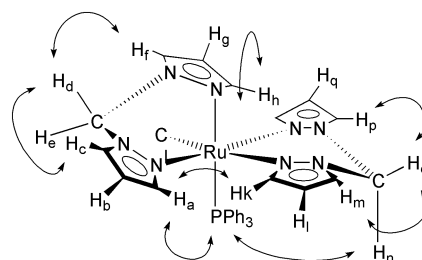
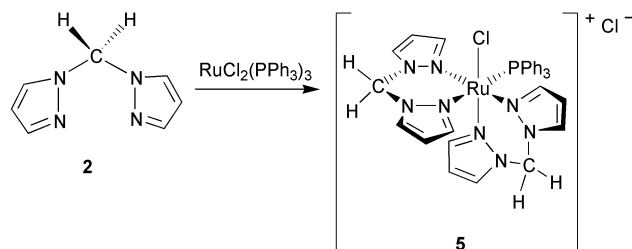


Fig. 3 Structure of $[\text{RuCl}(\text{PPh}_3)(\text{BPM})_2]^+\text{Cl}^- \mathbf{5}$ indicating the strong NOESY interactions observed.



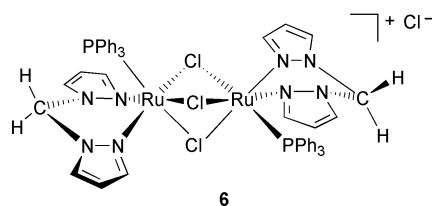
Scheme 3

phosphine and the ^1H NMR spectrum contains peaks due to one bound triphenylphosphine and two inequivalent BPM ligands, indicating that the triphenylphosphine and chloride ligands are mutually *cis*. The neutral bis(1-pyrazolyl)borate (BPB) analogue $\text{Ru}(\text{BPB})_2(\text{PPh}_3)_2$ ²⁹ possesses a similar geometry with the two PPh_3 ligands mutually *cis*.

Resonances in the ^1H NMR spectrum of $[\text{RuCl}(\text{PPh}_3)(\text{BPM})_2]^+\text{Cl}^- \mathbf{5}$ were assigned by a combination of ^1H COSY and ^1H NOESY NMR experiments. The NOESY spectrum demonstrates that the two methylene protons of each ligand interacts with the closest protons of the pyrazolyl rings. There is also a strong NOESY interaction between the protons of the pyrazolyl rings and the protons of the triphenylphosphine ligand (Fig. 3). Boat geometries have been observed for the ligands of similar bis(1-pyrazolyl)methane complexes involving ruthenium,²⁰ rhodium,^{10a} and palladium.³⁰

Bis[bis(1-pyrazolyl)methane]tri- μ -chloro-bis(triphenylphosphine)-diruthenium(II) chloride $[(\text{BPM})(\text{Ph}_3\text{P})\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{PPh}_3)(\text{BPM})]^+\text{Cl}^- \mathbf{6}$

Addition of BPM to a dichloromethane solution of $\text{RuCl}_2(\text{PPh}_3)_3$, in a 2 : 1 ratio, formed the highly insoluble triply bridged dinuclear product $[(\text{BPM})(\text{Ph}_3\text{P})\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{PPh}_3)(\text{BPM})]^+\text{Cl}^- \mathbf{6}$. The air stable deep red crystals were character-



ised by ^1H NMR and single crystal X-ray diffraction analysis. The mononuclear species $[\text{RuCl}(\text{PPh}_3)(\text{BPM})_2]^+\text{Cl}^- \mathbf{5}$ was also isolated from the reaction mixture. Investigation of the dinuclear species **6** by ^1H NMR spectroscopy reveals that the two BPM ligands are chemically equivalent and the two pyrazolyl rings of each of ligand are chemically non-equivalent.

Crystal structure of $[(\text{BPM})(\text{Ph}_3\text{P})\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{PPh}_3)(\text{BPM})]^+\text{Cl}^- \mathbf{6}$

The compound was crystallised as an air-stable red solid. It has pseudo twofold symmetry and the two ruthenium atoms, which

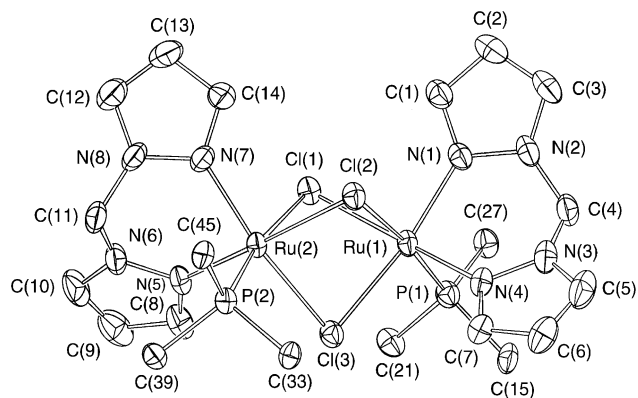


Fig. 4 Structure of $[(\text{BPM})(\text{Ph}_3\text{P})\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{PPh}_3)(\text{BPM})]^+\text{Cl}^-$ **6** indicating the atom numbering scheme. The molecule is oriented with the Ru–apical carbon axis horizontal. For clarity, only the P and three attached C atoms are shown for the triphenylphosphine ligands.

lack perfect octahedral coordination, are linked by three bridging chlorine atoms. A perspective view of **6** is shown in Fig. 4, and the bond lengths and angles for the inner coordination sphere are listed in the electronic supplementary information.

The distortion from octahedral geometry at the two metal centres is seen in the small Ru–Cl–Ru bond angles (80–84°) and the small Cl–Ru–Cl bond angles (80–84°). The N–Ru–N bond angles comply with octahedral restraints, partly due to the structural properties of the ligand itself. However, the P–Ru–N bond angles (99.5(2), 92.3(2) and 99.7(2), 95.1(2)°) exceed the value expected for perfect octahedral symmetry, which is likely to be due to steric crowding by the triphenylphosphine ligand. The pyrazolyl rings are essentially planar and the six-membered metallocycle Ru(N–N)₂C units of the bound BPM ligands adopt pseudo-boat conformations. The dihedral angles between the planes of the pyrazolyl subunits (44.04 and 47.48°) are similar to the values found for the structurally similar Rh(N–N)₂C metallocycle of the [Rh(COD)(BPM)]⁺ClO₄ complex (47.1°).^{10a}

The relatively large Ru...Ru separation of 3.208 Å indicates that there is no significant metal-metal interaction.³¹ Similar dinuclear ruthenium complexes containing a tri-μ-chloro bridge and triphenylphosphine ligands with a confacial bioctahedral structure have been reported: (Buⁿ₃P)₂ClRu(μ-Cl)₃Ru(PBuⁿ)₂Cl,³² (Et₂PhP)₃Ru(μ-Cl)₃Ru(PEt₂Ph)₂Cl,³¹ and [(Me₂PhP)₃-Ru(μ-Cl)₃Ru(PMe₂Ph)₃]⁺Cl⁻.³³ The Ru-μ-Cl bonds in **6** *trans* to the triphenylphosphine ligands are longer than the other Ru-μ-Cl bonds. Related dinuclear complexes³¹⁻³³ also exhibit lengthening of the Ru-Cl bonds *trans* to the Ru-P bonds, compression of the Cl-Ru-Cl and Ru-Cl-Ru bond angles, and consequent distortion of the bioctahedral symmetry.

Conclusion

Novel ruthenium complexes containing the TPM and BPM ligands were synthesized and characterised. The complex cation $[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]^+$ **3** has a structure which is analogous to those of neutral ruthenium complexes containing tris-(1-pyrazolyl)borate ligands. With two triphenylphosphine groups in *cis* coordination sites, it exhibits dynamic behaviour in solution and this is consistent with restricted rotation about the Ru–P bonds. The complex $[\text{Ru}(\text{CO})\text{H}(\text{PPh}_3)(\text{TPM})]^+$ **4** was prepared by the reaction of TPM with $\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3$ and the structure and stereochemistry were fully assigned using NMR experiments.

The complexes $[\text{RuCl}(\text{PPh}_3)(\text{BPM})_2]^+\text{Cl}^-$ **5** and $(\text{BPM})-(\text{Ph}_3\text{P})\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{PPh}_3)(\text{BPM})^+\text{Cl}^-$ **6** were synthesized by reaction of the bidentate ligand BPM **2** with $\text{RuCl}_2(\text{PPh}_3)_3$. The NMR studies of the mononuclear complex **5** showed that the conformation of the BPM ligands was fixed in solution at room temperature, and that both BPM ligands were in boat con-

formations. The two metal centres in the dinuclear complex **6** are too far apart to show any significant bonding interaction.

Experimental

The synthesis and manipulation of all ligands and metal complexes were performed under an inert atmosphere of argon or nitrogen unless otherwise stated using a Vacuum Atmosphere dry box or standard Schlenk techniques.

¹H, ³¹P, and ¹³C NMR spectra were recorded on Bruker AMX400, AMX600 or AC200 spectrometers. ³¹P NMR spectra were acquired with broadband ¹H decoupling. ¹H NMR chemical shifts are referenced to residual solvent resonances or using TMS as an internal reference, ³¹P NMR to external, neat trimethyl phosphite, taken as δ 140.85 at the temperature quoted. Uncertainties in the chemical shifts are typically ± 0.005 ppm for ¹H and ± 0.05 ppm for ³¹P NMR. Coupling constants (*J*) are given in Hz. Spectra were acquired at 300 K, unless otherwise stated. DQF (double quantum filtered) COSY³⁴ and NOESY³⁵ spectra were acquired with ³¹P decoupling in both ω_1 and ω_2 . Typically 640 slices in ω_1 of 2048 points in ω_2 were acquired, with a total acquisition time of approximately 8 hours. For the NOESY experiments mixing times, τ_m , of 1.6 seconds were used. Total acquisition times were typically 8 hours.

Mass spectra of the ligands were recorded on an AEI model MS902 double focussing mass spectrometer with an accelerating voltage of 8000 V and using Electron Impact (EI) ionisation with an electron energy of 70 eV. The sample was inserted through a solid direct insertion probe with a source temperature of 200 °C. FAB mass spectra were acquired of the metal complexes using a Finnigan MAT TSQ 46 mass spectrometer (San Jose, CA, USA) which is fitted with an Electron Impact/Chemical Ionisation (EI/CI) source and a Fast Atom Bombardment (FAB) 8 kV potential gun (ION TECH, Fast Atom Gun, Middlesex, UK). The FAB mass spectra were acquired using a magic bullet matrix [a 5 : 1 (w/w) mixture of dithiothreitol (DTT) (98%) and dithioerythritol (DTE)(98%)],³⁶ a source temperature of 50 °C, and a manifold temperature of 80 °C. Both the CI and EI mass spectra were acquired using a source temperature of 140 °C and a manifold temperature of 115 °C. The spectra are quoted in the form $x(y)$ where x is the mass to charge ratio and y the percentage abundance relative to the base peak.

Infrared spectra (cm^{-1}) were recorded either on a Perkin-Elmer 1600 series FTIR instrument using KBr disks or by using diffuse reflectance techniques on a Bio-Rad FTS-40 using powdered KBr as the matrix. Melting points were recorded on a Reichert heating stage and are uncorrected.

Tetrahydrofuran (THF), benzene, toluene, and hexane were pre-dried over sodium and distilled under nitrogen from sodium-benzophenone over sodium wire immediately prior to use. Absolute ethanol and methanol were refluxed with magnesium turnings and iodine and distilled under an atmosphere of nitrogen. Acetone was dried over and distilled from anhydrous calcium sulfate. Dichloromethane (DCM) was washed sequentially with concentrated H_2SO_4 , water, 5% K_2CO_3 solution, water and distilled from CaCl_2 . All solvents used in reactions of air sensitive compounds were deaerated prior to use by saturation with nitrogen or degassed by four to five freeze-pump-thaw cycles. All compressed gases were obtained from Commonwealth Industrial Gases (C.I.G.). Argon (>99.99%), nitrogen (>99.5%), and hydrogen (>99.999%) were used as received.

Microanalyses were carried out at the Micro Analysis Facility in the University of New South Wales and at the Department of Chemical Engineering in the University of Sydney.

Pyrazole was obtained from Aldrich and used without further purification. Tris(1-pyrazolyl)methane (TPM) and bis(1-pyrazolyl)methane (BPM) were prepared using the

methods developed by Julia, *et al.*⁸ $\text{RuCl}_2(\text{PPh}_3)_3$ ²¹ and $\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3$ ²² were synthesized using literature methods.

Preparations

Chlorobis(triphenylphosphine)[tris(1-pyrazolyl)methane]-ruthenium(II) chloride 3a and tetrafluoroborate 3b $[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]^+\text{X}^-$ ($\text{X} = \text{Cl}$ **3a** or BF_4 **3b**). $[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]^+\text{Cl}^-$ **3a**. A solution of TPM (180 mg, 0.84 mmol) and $\text{RuCl}_2(\text{PPh}_3)_3$ **7** (0.79 g, 0.82 mmol) in THF (100 mL) was stirred under an atmosphere of nitrogen for 90 minutes. The mixture was filtered and the solvent removed *in vacuo* to give the crude product. Recrystallisation from ethanol (40 mL) afforded chlorobis(triphenylphosphine)[tris(1-pyrazolyl)methane]ruthenium(II) chloride **3a** as yellow plates (0.40 g, 53%), mp 139–143 °C. Found: C, 60.6; H, 4.9; N, 8.8. $\text{C}_{46}\text{H}_{40}\text{Cl}_2\text{N}_6\text{P}_2\text{Ru}$ requires C, 60.65; H, 4.4; N, 9.2%. IR $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (KBr disc): 3415b, 3099m, 3056m, 1623w, 1480m, 1433s, 1293s, 1091s, 853m, 797m, 745s, 698s, 614m, 522s, 468m. δ_{H} (400 MHz; solvent MeOD) 9.82 [1H, s, H_{apical}], 8.61 [1H, d, H_{B}^5], 8.49 [2H, d, $^3J_{\text{HA5-HA4}} = 2.8$, H_{A}^5], 7.55 [6H, m, $\text{H}_{\text{Ph}}^{\text{para}}$], 7.38 [12H, s(b), $\text{H}_{\text{Ph}}^{\text{ortho}}$], 7.35 [12H, m, $\text{H}_{\text{Ph}}^{\text{meta}}$], 7.12 [2H, d, $^3J_{\text{HA3-HA4}} = 2.1$ Hz, H_{A}^3], 6.28 [2H, dd, $^3J_{\text{HA4-HA3}} = ^3J_{\text{HA4-HA5}} = 2.5$, H_{A}^4], 5.93 [1H, dd, $^3J_{\text{HB4-HB3}} = ^3J_{\text{HB4-HB5}} = 2.7$, H_{B}^4], 5.46 [1H, d, $^3J_{\text{HB3-HB4}} = 2.3$ Hz, H_{B}^3]. $\delta_{\text{P}}(1\text{H})$ (162 MHz; solvent MeOD) 39.3. $\delta_{13\text{C}}(1\text{H})$ (150 MHz; solvent MeOD) 152.1 [C_{B}^5], 149.6 [C_{A}^3], 136.6 [C_{B}^5], 135.9 [dd, $^3J_{\text{CP}} = 4.4$, 4.9, $\text{C}_{\text{Ph}}^{\text{ortho}}$], 134.9 [d, $^3J_{\text{CP}} = 40.3$, $\text{C}_{\text{Ph}}^{\text{ipso}}$], 134.8 [C_{A}^5], 131.5 [s, $\text{C}_{\text{Ph}}^{\text{para}}$], 129.5 [dd, $^3J_{\text{CP}} = 4.4$, 4.9 Hz, $\text{C}_{\text{Ph}}^{\text{meta}}$], 109.6 [C_{A}^4], 109.3 [C_{B}^4], 77.6 [C_{apical}]. Mass spectrum (FAB): m/z 875 (M^+ , 10%, $\text{C}_{46}\text{H}_{40}\text{ClN}_6\text{P}_2\text{Ru}$), 840 (6, $\text{M} - \text{Cl}$), 731 (5), 641 (3, $\text{M} - \text{PPh}_3 + \text{N}_2$), 625 (14, $\text{M} - \text{TPM} - \text{Cl}$), 613 (100, $\text{M} - \text{PPh}_3$), 607 (16).

$[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]^+\text{BF}_4^-$ **3b**. A solution of NaBF_4 (10 mg, 0.88 mmol) in ethanol (5 mL) was added to a solution of $[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]^+\text{Cl}^-$ **3a** (100 mg, 0.11 mmol) in ethanol (5 mL). The mixture was heated and then allowed to cool. The product was isolated and recrystallised from methanol. Chlorobis(triphenylphosphine)[tris(1-pyrazolyl)methane]ruthenium(II) tetrafluoroborate **3b** was obtained as small yellow crystals (95 mg, 90%), mp decomposes at 176 °C. Found: C, 55.4; H, 4.2; N, 8.7. $\text{C}_{46}\text{H}_{40}\text{N}_6\text{P}_2\text{BF}_4\text{Ru} + 3\text{MeOH}$ requires C, 55.6; H, 4.95; N, 7.9%. IR $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (KBr disc): 3415b, 3137w, 3059w, 2966w, 1622w, 1481m, 1434s, 1289m, 1092s, 1055s, 858w, 796m, 748s, 698s, 604w, 522s. Mass spectrum (FAB): m/z 875 (M^+ , 15%, $\text{C}_{46}\text{H}_{40}\text{ClN}_6\text{P}_2\text{Ru}$), 841 (6, $\text{M} - \text{Cl}$), 731 (9), 641 (5, $\text{M} - \text{PPh}_3 + \text{N}_2$), 625 (22, $\text{M} - \text{TPM} - \text{Cl}$), 613 (100, $\text{M} - \text{PPh}_3$), 607 (17). Complete NMR data have been deposited as electronic supplementary material.

Carbonylhydrido(triphenylphosphine)[tris(1-pyrazolyl)methane]ruthenium(II) chloride 4a and tetrafluoroborate 4b $[\text{Ru}(\text{CO})(\text{H})(\text{PPh}_3)_2(\text{TPM})]^+\text{X}^-$ ($\text{X} = \text{Cl}$ **4a** or BF_4 **4b**). $[\text{Ru}(\text{CO})(\text{H})(\text{PPh}_3)_2(\text{TPM})]^+\text{Cl}^-$ **4a**. A mixture of $\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3$ (573 mg, 601 mmol) and TPM (142 mg, 661 mmol) was refluxed vigorously in toluene (25 mL) for 3 hours. The crude product precipitated and was isolated by filtration and washed with hot toluene. $[\text{Ru}(\text{CO})(\text{H})(\text{PPh}_3)_2(\text{TPM})]^+\text{Cl}^-$ **4a** was obtained as a cream coloured powder (176 mg, 43%), mp decomposes at 163 °C. Found: C, 53.5; H, 4.1; N, 12.45. $\text{C}_{29}\text{H}_{26}\text{ClN}_6\text{OPRu}$ requires C, 54.2; H, 4.1; N, 13.1%. IR $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (KBr powder): 1934vs (CO), δ_{H} (400 MHz; solvent MeOD) 9.82 [1H, s, H_{apical}], 8.58 [1H, d, H_{C}^5], 8.49 [1H, d, H_{A}^5], 8.45 [1H, d, H_{B}^5], 8.24 [1H, d, H_{A}^3], 7.69 [3H, m, $\text{H}_{\text{Ph}}^{\text{para}}$], 7.59 [6H, m, $\text{H}_{\text{Ph}}^{\text{ortho}}$], 7.55 [6H, m, $\text{H}_{\text{Ph}}^{\text{meta}}$], 7.07 [1H, d, H_{C}^3], 6.78 [1H, d, H_{B}^3], 6.71 [1H, dd, 3.1 Hz, H_{A}^4], 6.57 [1H, dd, H_{C}^4], 6.30 [1H, dd, H_{B}^4], -12.12 [1H, d, $\text{H}_{\text{hydride}}$]. $\delta_{\text{P}}(1\text{H})$ (162 MHz; solvent MeOD) 63.5. $\delta_{13\text{C}}(1\text{H})$ (100 MHz; solvent MeOD) 206.3 [d, $^3J_{\text{C-Ru-P}} = 18.1$, Ru–CO], 149.1 [C_{B}^3], 149.0 [C_{A}^3], 147.4 [C_{C}^3], 134.8 [d, $^3J_{\text{CP}} = 10.7$, $\text{C}_{\text{Ph}}^{\text{meta}}$], 135.2 [C_{C}^5], 135.0 [C_{B}^5], 134.5 [C_{A}^5], 132.2 [d,

$^3J_{\text{CP}} = 2.2$, $\text{C}_{\text{Ph}}^{\text{para}}$], 130.0 [d, $^3J_{\text{CP}} = 9.9$ Hz, $\text{C}_{\text{Ph}}^{\text{ortho}}$], 109.7 [C_{A}^4], 109.5 [C_{C}^4], 109.3 [C_{B}^4], 69.1 [C_{apical}]. Complete NMR data have been deposited as electronic supplementary information. Mass spectrum (CI, CH_4): m/z 607 (M^+ , 44%, $\text{C}_{29}\text{H}_{26}\text{N}_6\text{OPRu}$), 409 (100, $\text{M} - \text{TPM} + \text{CH}_4$).

$[\text{Ru}(\text{CO})(\text{H})(\text{PPh}_3)_2(\text{TPM})]^+\text{BF}_4^-$ **4b**. A mixture of $\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3$ (238 mg, 0.25 mmol) and TPM (54 mg, 0.25 mmol) was refluxed vigorously in toluene (25 mL) for 3 hours. The toluene solvent was removed under reduced pressure and the product taken up in methanol (25 mL) containing NaBF_4 (40 mg, 0.36 mmol). The reaction mixture was stirred well for 3 hours and the product, $[\text{Ru}(\text{CO})(\text{H})(\text{PPh}_3)_2(\text{TPM})]^+\text{BF}_4^-$ **4b**, isolated by filtration as a pale grey powder (88 mg, 48%), mp decomposes at 225 °C (from MeOH). IR $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (KBr powder): 1984m (Ru–H), 1944vs (CO). Complete NMR data have been deposited as electronic supplementary information.

Bis[bis(1-pyrazolyl)methane]chloro(triphenylphosphine)-ruthenium(II) chloride $[\text{RuCl}(\text{PPh}_3)(\text{BPM})_2]^+\text{Cl}^-$ 5. A solution of BPM (170 mg, 1.1 mmol) and $\text{RuCl}_2(\text{PPh}_3)_3$ (540 mg, 0.57 mmol) in THF (150 mL) was stirred for 1 hour at room temperature then heated for 30 minutes with stirring. The solvent was removed *in vacuo* to yield the crude product as a deep green residue. The residue was washed with hexane to remove free PPh_3 after which methanol (150 mL) was added. The solution was heated and stirred fully to dissolve the residue. After 24 hours the solution was filtered to remove the dark yellow crystals from the clear olive-green filtrate. The filtrate was reduced *in vacuo* to give the air stable product $[\text{RuCl}(\text{PPh}_3)(\text{BPM})_2]^+\text{Cl}^-$ **5** as a clear green glassy residue (0.3 g, ca. 73% based on unsolvated $[\text{RuCl}(\text{PPh}_3)(\text{BPM})_2]^+\text{Cl}^-$ **5**), mp 188–191 °C (from MeOH). Found: C, 52.3; H, 4.65; N, 14.4. $\text{C}_{32}\text{H}_{31}\text{Cl}_2\text{N}_8\text{PRu} + 1\text{MeOH}$ requires C, 52.0; H, 4.6; N, 14.7%. IR $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (KBr disc): 3406b, 3105w, 3054w, 3001w, 1623w, 1516w, 1480m, 1434s, 1281s, 1184m, 1092s, 997w, 749s, 696s, 603w, 529s, 503m. δ_{H} (400 MHz; solvent MeOD) 8.46 [1H, d, H^7], 8.43 [1H, dd, H^7], 8.25 [1H, dd, H^7], 8.23 [1H, d, H^6], 8.21 [1H, dd, H^6], 8.17 [1H, dd, H^6], 7.55–7.21 [15H, m, aromatics], 7.54 [1H, d, H^4], 6.99 [1H, d, H^4], 6.74 [1H, dd, H^4], 6.69 [1H, d, H^4], 6.52 [1H, dd, H^4], 6.47 [1H, dd, H^4], 6.41 [1H, dt, H^4], 6.04 [1H, d, H^4], 5.86 [1H, d, H^4], 5.72 [1H, d, H^4]. $\delta_{\text{P}}(1\text{H})$ (162 MHz; solvent MeOD) 50.8. $\delta_{13\text{C}}(1\text{H})$ (100 MHz; solvent MeOD) 151.6 [C^4], 148.8 [C^7], 147.1 [C^4], 144.2 [C^6], 137.0 [C^7], 136.4 [C^6], 136.0 [C^7], 134.6 [C^7], 134.6–128.8 [PPh_3], 110.0 [C^7], 109.4 [C^4], 109.1 [C^6], 108.9 [C^7], 64.3 [C^4], 63.4 [C^6]. Complete NMR data have been deposited as electronic supplementary material. Mass spectrum (FAB): m/z 695 (M^+ , 100%, $\text{C}_{32}\text{H}_{31}\text{ClN}_8\text{PRu}$), 660 (3.81, $\text{M} - \text{Cl}$).

Bis[bis(1-pyrazolyl)methane]tri- μ -chlorobis(triphenylphosphine)diruthenium(II)chloride $[(\text{BPM})(\text{Ph}_3\text{P})\text{Ru}(\mu\text{-Cl})_3\text{-Ru}(\text{PPh}_3)(\text{BPM})]^+\text{Cl}^-$ 6. A solution of BPM (160 mg, 1.0 mmol) and $\text{RuCl}_2(\text{PPh}_3)_3$ (530 mg, 0.55 mmol) in DCM (40 mL) was stirred for 2 hours, then filtered and the orange residue discarded. The clear amber filtrate was reduced in volume and unchanged $\text{RuCl}_2(\text{PPh}_3)_3$ precipitated. The mixture was filtered and the solvent removed to give a yellow powder, which was recrystallised from methanol at room temperature to give the product bis[bis(1-pyrazolyl)methane]tri- μ -chlorobis(triphenylphosphine)diruthenium(II) chloride **6** as red crystals from a yellow solution. δ_{H} (400 MHz; solvent d_6 -DMSO) 8.40 [2H, d, $^3J = 2.5$], 8.02 [2H, d, $^3J = 2.5$], 7.84 [2H, d, $^3J = 2.5$], 7.49–7.29 [30H, m, aromatics], 7.19 [2H, d, $^3J = 2.5$], 6.68 [2H, t, $^3J = 14.2$], 6.39 [2H, t, $^3J = 2.52$], 4.85 [4H, d, $^3J = 14.2$ Hz].

Crystal data, X-Ray data collection, and structure determination

(a) $[\text{RuCl}(\text{PPh}_3)_2(\text{TPM})]\text{Cl} \cdot \text{PPh}_3 \cdot 2\text{CH}_3\text{CH}_2\text{OH}$ **3a**. The crystal data are summarised in Table 2. Cell constants were

Table 2 Crystallographic data for [RuCl(PPh₃)₂(TPM)]Cl·PPh₃·2CH₃CH₂OH **3a** and [(BPM)(Ph₃P)Ru(μ-Cl)₃Ru(PPh₃)(BPM)]⁺Cl[−] **6**

	3a	6
Empirical formula	C ₅₆ H ₅₄ Cl ₂ N ₆ O _{2.2} P _{2.33} Ru	C ₅₃ H ₄₆ Cl ₄ N ₈ O ₄ P ₂ Ru ₂
Formula weight	1090.43	1264.90
Crystal system	Rhombohedral	Monoclinic
Space group	<i>R</i> ³	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	6	4
<i>μ</i> /cm ^{−1}	(Mo-Kα) 4.30	(Cu-Kα) 38.9
<i>a</i> /Å	20.022(4)	16.089(3)
<i>b</i> /Å		10.260(2)
<i>c</i> /Å		33.837(7)
<i>α</i> /°	90.73(2)°	
<i>β</i> /°		96.80(1)
<i>V</i> /Å ³	8024.5(8)	5546(2)
<i>T</i> /K	293	294
No. of reflections measured	Total 10977, Unique 6318	Total 6449, Unique 6105
No. observations (<i>I</i> > 2.50σ(<i>I</i>))	5084	4865
No. variables	722	644
Residuals: <i>R</i> , <i>R</i> _w	0.048, 0.051	0.045, 0.049

determined by least-squares fit to the setting parameters of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4-F diffractometer with a graphite monochromator. Data were reduced and Lorentz, polarisation and absorption corrections applied using the Enraf-Nonius structure determination package (SDP).³⁷ The structure was solved by direct methods using SHELXS 86³⁸ and refined by blocked-matrix least-squares analysis with SHELX 76.³⁹ Hydrogen atoms were included at calculated sites (C–H, 0.97 Å) with individual isotropic thermal parameters. All other atoms except contributors to disordered groups (PPh₃, CH₃CH₂OH) were refined anisotropically. Scattering factors and anomalous dispersion corrections were taken from the values supplied in SHELX 76. Figures were drawn using ORTEP.²³

(b) [Ru(μ-Cl)₃Ru(PPh₃)(BPM)]⁺Cl[−] 6. The crystal was mounted on a glass fibre with cyanoacrylate resin. Lattice parameters at 21 °C were determined by least-squares fit to the setting parameters of 25 independent reflections, measured and refined on an AFC-7 four-circle diffractometer employing graphite monochromated Cu-Kα radiation. Data reduction and application of Lorentz, polarisation, absorption and decomposition corrections were carried out using the TEXSAN system.⁴⁰

The structure was solved by direct methods using SHELXS 86.³⁸ Hydrogen atoms were included at calculated sites with fixed isotropic thermal parameters. All other atoms were refined anisotropically. Full-matrix least-squares methods were used to refine an overall scale factor, positional and thermal parameters. Neutral atom scattering factors were taken from Cromer and Waber.⁴¹ Anomalous dispersion effects were included in *F*_c,⁴² the values for Δ*f*' and Δ*f*" were those of Creagh and McAuley.⁴³ The values for the mass attenuation coefficients are those of Creagh and Hubbell.⁴⁴ All calculations were performed using TEXSAN⁴⁰ and plots were drawn using ORTEP.²³

CCDC reference numbers 158383 and 158384.

See <http://www.rsc.org/suppdata/dt/b1/b103939n/> for crystallographic data in CIF or other electronic format.

Acknowledgements

We gratefully acknowledge financial support from the Australian Research Council and The University of Sydney for an H. B. and F. M. Gritton Scholarship (L. S.).

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