Dalton Transactions

Cite this: Dalton Trans., 2011, 40, 4315

PAPER

Transition metal complexes of the novel hexadentate ligand 1,4-bis(di(*N*-methylimidazol-2-yl)methyl)phthalazine[†]

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Received 17th October 2010, Accepted 18th February 2011 DOI: 10.1039/c0dt01406k

The novel polydentate ligand 1,4-bis(di(N-methylimidazol-2-yl)methyl)phthalazine, bimptz, has been synthesized and its coordination chemistry was investigated. Bimptz is neutral and contains a central phthalazine unit, to which two di-(N-methylimidazol-2-yl)methyl groups are attached in the 1,4-positions. This ligand therefore provides up to 6 donor sites for coordination to metal ions. A series of metal complexes of **bimptz** was prepared and their molecular structures were determined by X-ray diffraction. Upon reaction of bimptz with two equivalents of MnCl₂·4H₂O, CoCl₂·6H₂O and $[Ru(dmso)_4Cl_2]$, the dinuclear complexes $[Mn_2(bimptz)(\mu-Cl)_2Cl_2]$ (1), $[Co_2(bimptz)(CH_3OH)_2(\mu-Cl)_2Cl_2]$ (1), $[Co_2(bimptz)(CH_3OH)_2Cl_2]$ (1), $[Co_2(bimptz)(CH_3$ $Cl_{2}(PF_{6})_{2}$ (3) and $[Ru_{2}(bimptz)(dmso)_{2}(\mu-Cl)_{2}(PF_{6})_{2}$ (4), respectively, were isolated. The latter were found to have similar solid state structures with octahedrally coordinated metal centers bridged by the phthalazine unit and two chloro ligands. The cobalt and ruthenium complexes 3 and 4 were isolated as PF_6^- salts and contain neutral methanol and dmso ligands, respectively, at the terminal coordination sites of the metal centres. The mononuclear ruthenium complex $[Ru(Hbimptz)_2](PF_6)_4$ (6) was obtained from the reaction of two equivalents bimptz with [Ru(dmso)₄Cl₂]. In complex 6, three donor sites per ligand molecule are used for coordination of the Ru(II) center. In each bimptz ligand, one of the remaining, dangling N-methylimidazole rings is protonated and forms a hydrogen bond with the unprotonated N-methylimidazole ring of the other bimptz ligand.

Introduction

Di- and polynuclear metal complexes play an important role in many areas of chemistry, and for this reason investigations of ligand systems tailored for the complexation of more than one metal centre continues to be an active area of research.¹ Since many enzymes possess two or more metal centres at their active sites, the bioinorganic community has significantly advanced this area of research, in search of synthetic models and biomimetic complexes. Attractive targets include artificial mimics for methane monooxygenase and [FeFe]-hydrogenase, which catalyze the oxidation of methane to methanol, and the reduction of H⁺ to H₂, respectively. In both cases the catalytic site contains a diiron centre that has been the focus of considerable research efforts, given the desire to develop efficient synthetic catalysts for these reactions.^{2–5} Another important enzyme-based reaction in biology is the oxidation of water to oxygen, which occurs in the oxygen-evolving complex (OEC) of photosystem II. It is believed that the catalytic site in the OEC consists of a cubane-like Mn_4Ca oxocluster, but the detailed mechanism of this four-electron oxidation process is still under intense discussion.⁶ A growing interest in electrocatalytic water splitting, which results from the motivation to establish viable strategies for conversion of solar energy to chemical fuels, has led to the synthesis of dinuclear manganese and ruthenium complexes which have been reported to catalyze the oxidation of water in the presence of an oxidant such as Ce(IV).^{7,8} More generally, the interest in dinuclear metal complexes stems from possible cooperative effects that may be of use in the design of more efficient catalytic transformations.⁹

For exploration of cooperative effects in dinuclear complexes, it is important to utilize ligands that possess the desired property of rigidly binding two metals such that they are in close proximity. Thus, there has been considerable interest in binucleating ligands which place the metal fragments at a desired distance and with a predetermined orientation. This should allow tuning of the steric and electronic properties of the dinuclear core.

Previous studies have shown that the phthalazine group is a versatile building block for the synthesis of dinuclear complexes, and dinucleating ligands based on this moiety have been used to obtain metal-metal separations ranging from 2.550 Å to 4.045 Å.^{10,11} Here we present the results of investigations on the synthesis and coordination chemistry of the ligand 1,4-bis(di(*N*-methylimidazol-2-yl)methyl)phthalazine, **bimptz**, which is based

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numbers 765494–765497. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01406k

on a central phthalazine unit, to which two di-*N*-methylimidazol-2-ylmethyl groups are attached in the 1- and 4-positions (Scheme 1). The **bimptz** ligand provides up to six N-donor functions for binding metal ions and possesses four imidazolyl groups, which in principle have the potential to mimic biologically relevant histidine residues.



Scheme 1 Synthesis of the ligand bimptz.

Results and discussion

The bimptz ligand was obtained in high yield by reaction of 2 equivalents of lithiated bis-(N-methylimidazol-2-yl)methane and 1,4-dichlorophthalazine in THF at -70 °C (Scheme 1). The monosubstituted 1-chloro-4-(bis-(N-methylimidazolyl)methane)phthalazine and unreacted Im'CH₂Im' were identified as side products by ¹H NMR spectroscopy after workup. This suggests that the intermediate mono-substitution product, ClptzCH(Im'₂), may react with Li(CHIm'₂) via a competing proton-transfer process. Further support for this was observed in the use of benzylpotassium for the deprotonation of Im'CH₂Im' (to generate K(CHIm'₂) as the nucleophilic agent in the reaction mixture), which gave only mono-substituted ClptzCH(Im'₂) and Im'CH₂Im', in equimolar amounts, as isolated compounds after work up. In the latter case, nucleophilic substitution of the second chlorine atom of the pthalazine unit appears to be significantly slower than protonation of K(CIm'₂) by Clptz(CHIm'₂).

To investigate the properties of **bimptz** as a binucleating ligand, the latter was allowed to react with various metal salts. Addition of a solution of **bimptz** in ethanol to 2 equivalents of manganese(II)chloride hydrate in ethanol resulted in precipitation of a light yellow solid. Crystallization of this solid from MeOH/Et₂O provided X-ray quality crystals of the compound, identified by an X-ray diffraction analysis as the dinuclear manganese complex [Mn₂(**bimptz**)(μ -Cl)₂Cl₂] (1; Scheme 2), and the molecular structure is shown in Fig. 1.



Scheme 2 Synthesis of the dimanganese complex $[Mn_2(\textit{bimptz})(\mu\text{-}Cl)_2Cl_2]$ (1).



Fig. 1 Molecular structure of $[Mn_2(bimptz)(\mu-Cl)_2Cl_2]$ (1). All hydrogen atoms as well as one methanol solvent molecule of crystallization were omitted for clarity. See Table 1 and Table 2 for selected bond lengths and angles. For crystal parameters see Table 4.

 Table 1
 Selected bond lengths [Å] for the complexes 1, 3 and 4

N1=N2 N4 N1-N2 N5 N6					
	1 X3 C	3	4		
	$\overline{(M = Mn)}$	$\overline{(M = Co)}$	$\overline{(M = Ru)}$		
M1-N1 M2-N2 M1-N3 M1-N4 M2-N5 M2-N6 M1-C11 M2-C12 M1-C12 M2-C11 M1-X3	$\begin{array}{c} 2.432(5) \\ 2.514(5) \\ 2.205(5) \\ 2.287(5) \\ 2.268(5) \\ 2.179(5) \\ 2.484(2) \\ 2.493(2) \\ 2.595(2) \\ 2.595(2) \\ X3 = Cl3 \\ 2.432(2) \end{array}$	$\begin{array}{c} 2.190(3) \\ 2.192(3) \\ 2.073(3) \\ 2.077(3) \\ 2.103(3) \\ 2.107(3) \\ 2.449(2) \\ 2.449(2) \\ 2.469(2) \\ 2.437(2) \\ X3 = O1 \\ 2.9(2(2)) \end{array}$	$\begin{array}{c} 2.105(9)\\ 2.093(8)\\ 2.03(2)\\ 2.053(9)\\ 2.053(9)\\ 2.05(1)\\ 2.039(7)\\ 2.439(3)\\ 2.422(2)\\ 2.418(2)\\ 2.431(3)\\ X3 = S1\\ 2.221(4)\end{array}$		
M2–X4 M1–M2	2.433(2) X4 = Cl4 2.443(2) M = Mn 3.549(2)	2.069(3) X4 = O2 2.098(3) M = Co 3.255(2)	2.221(4) X4 = S2 2.229(7) M = Ru 3.273(2)		

Each manganese atom resides in a distorted octahedral coordination environment, in which the observed bond angles about the metal center deviate significantly from the ideal values (*e.g.* N5–Mn2–N6 82.9°) (Table 2). The Mn atoms are bridged by two chloride ligands and the phthalazine unit, resulting in a metal–metal distance of 3.549(2) Å. This distance is shorter than the analogous one found in [Mn₂(bdptz)(μ -OBz)₂(H₂O)₂](OTs)₂, (3.754(2) Å, bdptz = 1,4-bis(2,2'-dipyridylmethyl)phthalazine)), in which the μ -benzoate ligands induce a larger separation of the two



Table 2 Selected bond angles [°] for the complexes 1, 3 and 4

2+ N4 N3 N1 ⁻ N2 N5 N6 X3 C 1 X4					
	1	3	4		
	$\overline{(M = Mn)}$	(M = Co)	(M = Ru)		
Cl1-M1-Cl2 N1-M1-X3	84.85(5) X3 = Cl3	86.09(4) X3 = O1	84.35(9) X3 = S1 174.9(3)		
N1-M1-Cl1 Cl1-M2-Cl2 N5-M2-N6 Cl2-M2-N6 N2-M2-X4	86.6(2) 84.67(5) 82.9(2) 164.9(2) X4 = Cl4 172.1(2)	$ \begin{array}{l} 87.21(8) \\ 86.78(4) \\ 85.9(2) \\ 173.25(9) \\ X4 = O2 \\ 173.8(2) \end{array} $	$ \begin{array}{r} 174.9(3) \\ 87.9(2) \\ 84.44(9) \\ 88.2(3) \\ 172.1(2) \\ X4 = S2 \\ 173.8(2) \end{array} $		

metal ions.¹² The $Mn_2(\mu$ -Cl)₂ unit is unsymmetrical, and exhibits two comparatively short (Mn2–Cl2 2.493(2); Mn1–Cl1 2.484(2) Å) and two longer (Mn1–Cl2 2.595(2); Mn2–Cl1 2.595(2) Å) Mn–Cl bonds. This suggests a relatively weak bridging character for the μ -Cl ligands, since the terminal Mn–Cl bond distances (Mn1–Cl3 2.433(2); Mn2–Cl4 2.443(2) Å) are only slightly shorter than the shorter distances involving the bridging Cl atoms.

The reaction of **bimptz** with two equivalents of $CoCl_2 \cdot 6H_2O$ in ethanol led to a deep green-blue solution, which contained a very fine precipitate. After workup single crystals were grown by recrystallization from methanol/THF. Although the quality of the dataset obtained from an X-ray diffraction experiment was too poor to determine accurate geometrical parameters, the atom connectivity of the complex was clearly determined. Thus, this complex is the dinuclear cobalt species $[Co_2(bimptz)_2(CH_3OH)_2(\mu Cl_{2}$ [CoCl₄] (2), with a structure that is comparable to that of 1. However, in contrast to 1, 2 does not contain terminal chloride ligands. Instead, methanol (solvent) molecules are coordinated to the cobalt atoms, in positions *trans* to the phthalazine nitrogen atoms. The reaction also results in formation of tetrachlorocobaltate(II) as the counter anion. The reaction was repeated using three equivalents of CoCl₂.6H₂O and methanol as the solvent. A pink solution was obtained, from which pink crystals of $[Co_2(bimptz)_2(CH_3OH)_2(\mu-Cl)_2](PF_6)_2$ (3) precipitated after addition of NH_4PF_6 and cooling to -30 °C (Scheme 3). Single crystals suitable for X-ray diffraction were grown by ether diffusion into a solution of 3 in methanol at 4°C, and the molecular structure of **3** is shown in Fig. 2.

As expected, the coordination geometry of the cationic dicobalt complex of **3** is very similar to that of the dimanganese complex **1**. The two cobalt(II) ions are located at the centers of two slightly distorted, edge-sharing octahedrons. However, in **3** the bond angles about the metal centers are closer to ideal octahedral values. In contrast to the Mn₂Cl₂ unit of **1**, the Co₂(μ -Cl)₂ core is diamond-like, with no pronounced differences in the Co–Cl bond distances which range from 2.437 to 2.469 Å. The metal–metal distance in **3** (3.255(2) Å) is shorter than the corresponding value in **1** (3.549(2) Å).



Scheme 3 Synthesis of the dinuclear cobalt complexes 2 and 3.



Fig. 2 Molecular structure of $[Co_2(bimptz)(\mu-Cl)_2(CH_3OH)_2](PF_6)_2$ (3). Hydrogen atoms, except those for the methanol ligands, as well as the PF₆⁻ counter anions have been omitted for clarity. For selected bond lengths and angles see Table 1 and Table 2. For crystal parameters see Table 4.

An ESI-MS analysis of **3** in acetonitrile solution indicates that the methanol ligands are somewhat labile, as no signals were detected for species containing methanol, such as $[Co_2(bimptz)(CH_3OH)_2Cl_2]^{2+}$. Instead, only peaks for the methanol-free species { $[Co_2(bimptz)Cl_2](PF_6)$ } (m/z = 811.0) and $[Co_2(bimptz)Cl_2]^{2+}$ (m/z = 333.0), as well as for $[Co_2(bimptz)-Cl_2(CH_3CN)]^{2+}$ (m/z = 353.5), were observed.

Initial attempts to obtain a ruthenium complex of **bimptz** were based on a protocol which had been successfully employed by Thummel *et al.* and Åkermark *et al.* for the synthesis of dinuclear ruthenium complexes containing a bridging phthalazine unit.^{13,14} Accordingly, two equivalents of [Ru(dmso)₄Cl₂] were heated together with **bimptz**, LiCl and NEt₃ in an ethanol–water mixture for 48 h. However, the crude product that was isolated after addition of NH₄PF₆ was found to consist of an inseparable mixture of several products. Better results were obtained when a 2:1 mixture of $[Ru(dmso)_4Cl_2]$ and **bimptz** in ethylene glycol was heated in a microwave reactor for 15 min. After addition of excess NH_4PF_6 , the reaction mixture was subjected to column chromatography (silica gel). Initially, a deep red component was eluted, followed by a broad yellow band that contained the main product. NMR (¹H and ¹³C) and ESI-MS analyses identified the latter as the dinuclear complex [Ru₂(**bimptz**)(dmso)₂(μ -Cl)₂](PF₆)₂ (**4**), and an X-ray diffraction analysis confirmed this formulation (Fig. 3).



Fig. 3 Molecular structure of $[Ru_2(bimptz)(\mu-Cl)_2(dmso)_2](PF_6)_2$ (4). Hydrogen atoms, the PF₆⁻ counterions, and cocrystallized solvent molecules have been omitted for clarity. For selected bond lengths and angles see Table 1 and Table 2. For crystal parameters see Table 4.

As in the case of the manganese (1) and cobalt (2, 3) complexes, the two ruthenium ions are located at the centers of edgesharing octahedra. The $Ru_2(\mu$ -Cl)₂ core is symmetrical (Ru–Cl distances of 2.418(2)–2.439(3) Å and the metal-metal distance (3.273(2) Å) is very similar to that found for 3 (3.255(2) Å). As for 3, the neutral ligands (dmso) are positioned *trans* to the phthalazine nitrogen atoms. The dmso ligands are coordinated to the ruthenium centers via donation from sulfur, as is usually the case in ruthenium chemistry.¹⁵ An ESI-MS analysis for 4 in acetonitrile revealed a signal for the dication $[Ru_2(bimptz)(dmso)_2(\mu Cl_{2}^{2+}$ (m/z = 454.0053, calc. 454.0037) along with a peak corresponding to $\{[Ru_2(bimptz)(dmso)_2(\mu-Cl)_2](PF_6)\}^+$ (m/z =1052.9733, calc. 1052.9721). Heating 4 to reflux in CH₃CN induces the successive substitution of the dmso ligands by CH₃CN. After one day the solution contained 4, $[Ru_2(bimptz)(dmso)(CH_3CN)(\mu Cl_{2}^{2+}$ and $[Ru_{2}(bimptz)(CH_{3}CN)_{2}(\mu-Cl)_{2}^{2+}$ in a 1:4:2 ratio (as determined by ESI-MS), while after 2 days the formation of $[Ru_2(bimptz)(CH_3CN)_2(\mu-Cl)_2]^{2+}$ was nearly complete and only minor amounts (20%) of [Ru₂(bimptz)(dmso)(CH₃CN)(µ-Cl)₂]²⁺ could be detected (by ESI-MS and ¹H NMR spectroscopy).

The dark red solid isolated as a minor component during the chromatographic purification of 4 (vide supra) was analyzed by

¹H NMR spectroscopy and high resolution ESI-mass spectrometry. This information suggests that the complex is the dinuclear ruthenium complex $[Ru_2(bimptz)(\mu-Cl)_2(dmso)(dms)](PF_6)_2$ (5), which differs from 4 in that one of the dmso ligands has been replaced by dimethylsulfide (dms, Scheme 4). Accordingly, the mass spectrum showed two peaks corresponding to the mono- and dicationic species $\{[Ru_2(bimptz)(\mu Cl_{2}(dmso)(dms)](PF_{6})^{+}$ (m/z = 1036.9750, calc. 1036.9777) and $[Ru_2(bimptz)(\mu-Cl)_2(dmso)(dms)]^{2+}$ (m/z = 446.0057, calc.446.0068), respectively. In the ¹H NMR spectrum of 5 a new signal for the $(CH_3)_2S$ protons was detected, while in comparison to the spectrum of 4 the integration for the $(CH_3)_2$ SO protons was reduced by half. The relatively harsh reaction conditions employed for the preparation of **4** are possibly responsible for the partial deoxygenation of dimethylsulfoxide, which leads to the formation of 5 as a byproduct.



Scheme 4 Synthesis of the dinuclear ruthenium complexes 4 and 5.

Particularly interesting bimetallic complexes might incorporate two different metal atoms. Thus, it was of interest to investigate the 1 : 1 reaction of **bimptz** with [Ru(dmso)₄Cl₂], to see if only one Ru center could be selectively introduced onto the ligand. These compounds were allowed to react in refluxing ethylene glycol, and upon addition of excessive NH₄PF₆ to the reaction mixture, a microcrystalline, dark purple solid precipitated. Single crystals of this complex were grown by slow evaporation of a methanol– acetone solution. An X-ray diffraction analysis revealed a molecular structure that features one ruthenium atom coordinated by two **bimptz** ligands (Scheme 5). In addition, not two but four PF₆⁻ counterions were found to be contained in the structure. As an oxidation of the metal center from Ru(II) to Ru(IV) seemed



Scheme 5 Synthesis of $[Ru(Hbimptz)_2](PF_6)_4$ (6).

unreasonable, the structural data were examined for the presence of additional protons, and indeed it proved possible to locate two "new" hydrogen atoms (H7, H7') within the structure (Fig. 4). In each **bimptz** ligand, one of the dangling *N*-methylimidazole rings is protonated and these protons are hydrogen-bonded to an imidazole ring of the other **bimptz** ligand (*e.g.* N7–H7–N9', see Fig. 4). A comparison of the p K_a values for NH₄⁺ and *N*methylimidazolium (HIm') suggests that under normal conditions the ammonium cation would not be expected to be acidic enough to protonate *N*-methylimidazole (p K_a (NH₄⁺)=9.25; p K_a (HIm'⁺)= 6.6).¹⁶ Thus, formation of the hydrogen bond undoubtedly drives this proton-transfer reaction.



Fig. 4 Molecular structure of 6. The four PF_6^- counterions and all hydrogen atoms except H7/H7' were omitted for clarity. The hydrogen atom H7 was found from a difference Fourier map and freely refined in the subsequent least square cycles. Selected bond distances [Å] and angles [°]: Ru–N1 2.035(2), Ru–N3 2.052(2), Ru–N5 2.054(2), N7–H7 0.89(4), N9'–H7 1.79(4); N5–Ru–N1' 177.10(9), N3–Ru–N3' 178.1(2), N1–Ru–N1' 93.4(2), N1–Ru–N3' 96.18(8), N7–H7–N9' 174(4).

Further evidence for the presence of two additional protons in **6** is provided by high-resolution ESI-MS analysis. For an acetonitrile solution of the complex, signals were observed for the complex cation $[\text{Ru}(\text{Hbimptz})_2]^{4+}$ (m/z = 265.0968; calc. 265.0965), and for its PF_6^- salt { $[\text{Ru}(\text{Hbimptz})_2](\text{PF}_6)_2$ }^{2+}. Peaks corresponding to the trication $[\text{Ru}(\text{Hbimptz})(\text{bimptz})]^{3+}$ (m/z = 353.1265; calc. 353.1263) and its PF_6^- adduct { $[\text{Ru}(\text{Hbimptz})(\text{bimptz})](\text{PF}_6)$ }^2+ provide evidence that deprotonation occurs to a certain degree in solution.

In **6** each of the two **bimptz** ligands contributes three Ndonor sites to the slightly distorted octahedral coordination of the Ru(II) center, leaving the other three nitrogen donors available for further reactivity. Complex **6** is C_2 -symmetric and contains a crystallographic axis of symmetry that passes through the ruthenium center and bisects the angle spanned by N1, Ru and N1'. As mentioned above, two of the dangling imidazolyl rings are protonated and are involved in hydrogen bonds to the nitrogen atoms of additional imidazolyl rings.

Table 3	CV^a	data	of	the	ruthenium	comp	lexes 4	and	6
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Complex	$E_{1/2}^{\text{ox}}(\Delta E)$
$[Ru_2(bimptz)(dmso)_2(\mu-Cl)_2](PF_6)_2 4 [Ru(Hbimptz)_2](PF_6)_4 6$	0.78 (68), 1.58(78) 0.79 (70)

^{*a*} Measured with a platinum electrode at 100 mV s⁻¹ in dry CH₃CN containing 0.1 M (*n*-Bu₄)PF₆ and reported in volts relative to SCE. $E_{1/2} = (E_{pa} + E_{pc})/2$ in V, $\Delta E = (E_{pa} - E_{pc})$ in mV.

The electrochemical properties of the ruthenium complexes 4 and 6 were studied by cyclic voltammetry (CV, Table 3). The CV of the dinuclear complex 4, recorded in anhydrous acetonitrile, exhibits two reversible one-electron waves at $E_{1/2}$ = 0.78 and 1.58 V vs. the saturated calomel electrode (SCE). These waves can be assigned to the stepwise one-electron oxidations Ru^{II}Ru^{II} to Ru^{II}Ru^{III} and Ru^{II}Ru^{III} to Ru^{III}Ru^{III}, respectively. The marked difference in the two oxidation potentials observed for 4 indicates a strong coupling of the two Ru centers. When negative potentials were applied, only irreversible, ligand reduction bands were observed. The oxidation potentials found for 4 are comparable to those reported by Thummel et al. for a series of pyridazine-bridged dinuclear ruthenium(II) complexes.13 These values are, however, much more positive than the oxidation potentials observed by Åkermark et al. for a diruthenium complex that contains a negatively charged pyridazine based ligand.¹⁴ For the mononuclear complex 6 a reversible one-electron oxidation wave was observed at $E_{1/2} = 0.79$ V, which is a potential very close to that found for oxidation of the first Ru(II) centre in 4.

Conclusions

Here we describe the synthesis and coordination properties of the neutral ligand **bimptz**, which is accessible in three steps starting from N-methylimidazole and diethoxycarbonate. Bimptz contains a bridging phthalazine unit with four tethered imidazolyl rings, and it is therefore able to provide up to 6 donor sites for the coordination of metal ions. The potential of **bimptz** for the synthesis of dinuclear metal complexes was demonstrated in reactions with MnCl₂·4H₂O, CoCl₂·6H₂O and [Ru(dmso)₄Cl₂], from which the corresponding dimetallic complexes 1, 3 and 4 could be obtained. The molecular structures of the latter are similar and contain two metal ions in a more or less distorted octahedral ligand environment. In all structures the two metal ions are bridged by the phthalazine moiety and two μ -chloro ligands. Diamond-like $M_2(\mu$ -Cl₂) units are found in the cobalt and ruthenium complexes 3 and 4, while the M-Cl bond lengths within the corresponding core of the manganese complex 1 reflect a significant bond alternation. The electrochemical properties of the two ruthenium complexes were investigated by means of cyclic voltammetry, which shows two reversible one electron oxidations for 4 and one reversible oxidation wave for 6. Further work will focus on the synthesis of chlorine free, dinuclear complexes of **bimptz** and on investigations of the ability of **6** to act as a precursor for the preparation of heteronuclear metal complexes.

General considerations

Bis(N-methylimidazol-2-yl)methane, Im'CH2Im', was synthesized following a procedure given by Rüther et al.¹⁷ and purified by sublimation (110 °C, 10⁻⁴ mbar). The C, H, N microanalyses were performed with a Leco CHNS-932 element analyzer. Chlorine was determined using Schöniger's method followed by titration with $Hg(ClO_4)_2$. NMR spectra were recorded on a Bruker AV 400 NMR spectrometer (1H: 400.13 MHz, 13C: 100.6 MHz) at 25 °C. Chemical shifts are reported relative to residual proton signals and natural abundance ¹³C resonances of the corresponding deuterated solvents. Chemical electronic absorption spectra were recorded with a Varian Cary 100 Scan UV-Vis spectrometer at room temperature using quarz cuvettes. IR spectra were measured between 400 and 4000 cm⁻¹ with a Shimadzu FTIR-8400S spectrometer using KBr pellets. The ESI-mass spectra were recorded using a Finnigan LTQ-FT spectrometer. Cyclic voltammograms were recorded on a Gamry Reference 600 Potentiostat using a platinum working electrode, a platinum counter electrode and a Ag/AgCl reference electrode. The half potentials were referenced against the Fc/Fc⁺ couple and the values conversed to SCE (saturated calomel electrode) by adding $+ 0.40 \text{ V}^{.18}$

Preparation of 1,4-Bis(di(*N*-methylimidazol-2yl)methyl)phthalazine (bimptz)

Im'CH₂Im' (4.02 g, 22.8 mmol) was dissolved in dry THF (200 mL) and cooled to -78 °C. It is possible that a part of the Im'CH₂Im' precipitates again at this temperature. n-BuLi (2.5 M in hexane, 9.31 mL, 23.3 mmol) was added during a period of 15 min and the resulting clear yellow solution was stirred for 2 h at -45 °C. After cooling the reaction mixture to -78 °C a solution of 1,4-dichlorophthalazine in dry THF (100 ml) was added dropwise through an addition funnel over a period of 35 min. A rubiginous suspension formed, which was stirred for 1 h at -78 °C before it was allowed to warm to room temperature. Stirring was continued for an additional 45 min, and subsequently water (8 mL) was added to the reaction mixture. The resulting cream-colored suspension was filtered and the sticky residue was washed with THF. Drying in vacuo yielded 5.66 g of a light brown crude product. In order to separate LiCl from crude bimptz, the latter was stirred in a mixture of 100 mL water and 300 mL CH₂Cl₂ until all solid had dissolved. The solution was transferred to a separatory funnel and the yellow organic layer was separated. The aqueous phase was repeatedly extracted with CH₂Cl₂ and the combined organic extracts were dried over Na₂SO₄. After filtration the solution was evaporated to dryness to give **bimptz** as a light yellow powder, which is pure according to ¹H NMR spectroscopy. Yield: 4.41 g (9.22 mmol, 81%). Further purification can be achieved by recrystallization from boiling acetonitrile. Anal. calc. for C₂₆H₂₈N₁₀O, [bimptz·H₂O]: C 62.89, H 5.68, N 28.21. Found: C 62.48, H 5.34, N 28.37%.

¹**H NMR** (CDCl₃): δ /ppm = 8.18 (m, 2H, *CH*_{*ptz*}), 7.72 (m, 2H, *CH*_{*ptz*}), 6.96 (d, 4H, ³*J*(H,H) = 1.2 Hz, *CH*_{*im*}), 6.85 (d, 4H, ³*J*(H,H) = 1.2 Hz, *CH*_{*im*}), 6.64 (s, 2H, *CH*Im₂), 3.45 (s, 12H, NC*H*₃). ¹³**C NMR** (CDCl₃): δ /ppm = 156.5, 143.9, 132.3, 127.5, 126.5, 125.6, 122.4, 44.8, 33.6. **IR**: *v*/cm⁻¹ = 3437 (br), 3149 (m), 3131 (s), 3115 (m), 3106 (m), 3092 (m), 2947 (m), 2881 (m), 1613

(m), 1579 (m), 1546 (m), 1523 (m), 1490 (vs), 1458 (m), 1412 (s), 1396 (s), 1361 (s), 1284 (s), 1271 (s), 1244 (m), 1177 (w), 1136 (s), 1082 (w), 1047 (w), 936 (w), 923 (w), 872 (m), 859 (s), 810 (m), 763 (s), 750 (vs), 717 (m), 695 (s), 678 (m), 662 (s), 650 (m), 586 (m), 550 (s), 525 (w), 490 (w), 441 (w). **UV-Vis** (CH₃CN): λ_{max} /nm, (log ε) = 269 (3.87), 218 (4.78). **MS** (EI): 478 (100%, M⁺⁺), 303 (90%, M⁺⁺ - CHIm'₂), 176 (60%, [Im'CH₂Im']⁺).

Preparation of [Mn₂(bimptz)Cl₄] (1)

A light yellow solid precipitated when a solution of **bimptz** (0.100 g, 0.21 mmol) in 10 mL absolute ethanol was added dropwise to a solution of MnCl₂·4H₂O (0.083 g, 0.42 mmol) in 5 mL of ethanol. The suspension was stirred for 30 min, and the precipitate was isolated by filtration and dried *in vacuo* to give analytically pure **1**. Yield: 0.117 g (0.16 mmol, 77%). Anal. calc. for $C_{26}H_{32}Cl_4Mn_2N_{10}O_3$, [Mn₂(**bimptz**)Cl₄]·3H₂O: C 39.82, H 4.11, N 17.86. Found: C 39.95, H 3.76, N 17.56%.

IR: $\nu/cm^{-1} = 3433$ (br), 3145 (w), 3119 (m), 3072 (m), 2960 (m), 1622 (br), 1567 (w), 1532 (m), 1509 (s), 1466 (w), 1405 (s), 1351 (m), 1284 (s), 1174 (m), 1161 (m), 1135 (m), 1089 (m), 1040 (m), 952 (m), 875 (m), 851 (s), 801 (w), 762 (s), 715 (m), 672 (w), 658 (m), 633 (m), 614 (m), 558 (m), 452 (m). **MS** (FAB⁺, m/z): 693 (5%, M⁺⁺ – Cl], 658 (5%, M⁺⁺ – 2Cl), 568 (3%, M⁺⁺ – Mn – 3Cl).

Preparation of [Co₂(bimptz)(CH₃OH)₂Cl₂][CoCl₄] (2)

A solution of **bimptz** (0.100 g, 0.21 mmol) in 8 mL of ethanol was added dropwise to a dark blue solution of $CoCl_2 \cdot 6H_2O$ (0.149 g, 0.63 mmol) in 8 mL of ethanol, which led to a color change to green-blue and the formation of a fine blue-green powder. After stirring the suspension for 3.5 h at room temperature, all volatile material was removed *in vacuo*, and the blue-green residue was washed with CH_2Cl_2 and recrystallized from methanol–ether. Anal. calc. for $C_{30}H_{40}Cl_6Co_3N_{10}O_3$, $[Co_2(bimptz)(CH_3OH)_2Cl_2][CoCl_4]\cdot EtOH$: C 36.83, H 4.12, N 14.32. Found: C 37.01, H 4.38, N 14.06%.

 $\label{eq:rescaled_rescale} \begin{array}{l} {\rm I\!R\!:} v/cm^{-1} = 3412 \ ({\rm br},{\rm s}), 3146 \ ({\rm sh}), 3120 \ ({\rm s}), 2977 \ ({\rm m}), 2951 \ ({\rm sh}), 2897 \ ({\rm m}), 1624 \ ({\rm s}, {\rm br}), 1567 \ ({\rm m}), 1536 \ ({\rm s}), 1513 \ ({\rm s}), 1459 \ ({\rm m}), 1411 \ ({\rm s}), 1350 \ ({\rm m}), 1286 \ ({\rm m}), 1175 \ ({\rm m}), 1140 \ ({\rm m}), 1092 \ ({\rm m}), 1018 \ ({\rm m}), 961 \ ({\rm m}), 882 \ ({\rm m}), 852 \ ({\rm m}), 763 \ ({\rm s}), 717 \ ({\rm s}), 673 \ ({\rm m}), 660 \ ({\rm m}), 634 \ ({\rm m}), 599 \ ({\rm m}), 564 \ ({\rm m}), 529 \ ({\rm m}), 448 \ ({\rm m}). \end{array}$

Preparation of [Co₂(bimptz)(CH₃OH)₂Cl₂](PF₆)₂ (3)

A yellow solution of **bimptz** (0.200 g, 0.42 mmol) in 15 mL of methanol was added dropwise to a pink solution of $CoCl_2 \cdot 6 H_2O$ (0.298 g, 1.25 mmol) in 10 mL methanol. The reaction mixture initially darkened and then turned pink-red after 15 min at room temperature. Stirring was continued for 2 h, whereupon a solution of NH₄PF₆ (0.204 g, 1.25 mmol) in 5 mL of methanol was added quickly. After an additional 1.5 h the solution was concentrated *in vacuo* until a solid started to precipitate. The precipitate was redissolved by gentle heating and the resulting solution was then cooled to - 30 °C. After several days **3** was isolated as a pink-red solid by filtration, which was washed with cold methanol and dried on standing in air. Further amounts of **3** could be obtained by concentrating the mother liquor and cooling to - 30 °C. Yield:

 $\begin{array}{l} 0.248\,g\,(0.24\,mmol,\,58\%).\,Anal.\,calc.\,for\,C_{28}H_{38}Cl_2Co_2F_{12}N_{10}O_4P_2,\\ [Co_2(\textit{bimptz})(CH_3OH)_2Cl_2](PF_6)_2\cdot 2H_2O;\,C\,31.81,\,H\,3.62,\,N\,13.25,\\ Cl\,6.71.\,Found;\,C\,31.38,\,H\,3.57,\,N\,13.23,\,Cl\,6.72\%. \end{array}$

IR: $v/cm^{-1} = 3634$ (m), 3163 (m), 2966 (m), 1616 (m), 1569 (w), 1539 (m), 1516 (s), 1464 (m), 1414 (s), 1352 (m), 1288 (m), 1177 (m), 1169 (m), 1140 (m), 1090 (m), 1038 (w), 960 (m), 842 (vs), 760 (s), 740 (m), 719 (m), 675 (w), 660 (m), 635 (m), 557 (s), 447 (m). **MS** (ESI⁺(CH₃CN), m/z): 811.0 (100%, {[Co₂(**bimptz**)Cl₂](PF₆)}⁺, 353.5 (40%, [Co₂(**bimptz**)Cl₂(CH₃CN)]²⁺, 333.0 (45%, [Co₂(**bimptz**)Cl₂)]²⁺). **HRMS** (ESI⁺(CH₃CN), m/z): Calc. for C₂₆H₂₆N₁₀³⁵Cl₂⁵⁹Co₂F₆P₁ ({[Co₂(**bimptz**)Cl₂]{(PF₆)⁺): 811.0019. Found: 811.0007. Calc. for C₂₈H₂₉N₁₁³⁵Cl₂⁵⁹Co₂ ([Co₂(**bimptz**)Cl₂(CH₃CN)]²⁺): 707.0648. Found: 707.0630.

Preparation of [Ru₂(bimptz)(dmso)₂(µ-Cl)₂](PF₆)₂ (4)

Bimptz (0.100 g, 0.21 mmol) and [Ru(dmso)₄Cl₂] (202.5 mg, 0.41 mmol), each dissolved in 12 mL of ethylene glycol, were mixed to yield an orange-colored solution, which was degassed by evacuation and purging with argon three times. After refluxing the reaction mixture in a microwave reactor under argon for 15 min, a solution of NH_4PF_6 (1.36 g) in 10 mL of water was added to the still hot brown-red solution. Cooling to 0 °C and filtering yielded a brown crude product, which was washed with cold water and THF. The crude product was purified by column chromatography on silica and the column eluted with acetonitrileaqueous saturated KPF_6 (9:1). The first pale red fraction was rejected, the following narrow dark red and broad yellow bands were collected. 4 was contained in the third (yellow) fraction (along with KPF_6), which was evaporated to dryness using a rotovap. The residue was stirred in approximately 40 mL of water in order to dissolve the KPF₆ salt. After filtration a dark brown solid of crude 4 was obtained, which was washed with a minimum amount of cold water, followed by tetrahydrofuran and ether. 4 was dried in vacuo and recrystallized by slow diffusion of tetrahydrofuran into a solution of 4 in acetonitrile. Yield: 0.122 g (0.1 mmol, 48%). Anal. calc. for $C_{30}H_{38}Cl_2F_{12}N_{10}O_2P_2Ru_2S_2$, [Ru₂(bimptz)(dmso)₂Cl₂](PF₆)₂: C 30.08, H 3.20, N 11.69, Cl 5.92, S 5.35. Found: C 30.32, H 3.33, N 11.23, Cl 6.46, S 4.52%.

¹**H-NMR** (CD₃CN): δ /ppm = 9.10 (m, 2H, CH_{ptz}), 8.47 (m, 2H, CH_{ptz}), 7.08 (d, 4H, ${}^{3}J(H,H) = 1.6$ Hz, CH_{im}), 7.01 (d, 4H, ${}^{3}J(H,H) = 1.6$ Hz, CH_{im}), 6.95 (s, 2H, $(Ptz)(Im)_{2}CH$), 3.93 (s, 12H, NCH₃), 3.37 (s, 12H, H_{dmso}). ¹³C-NMR (CD₃CN): δ /ppm = 164.5, 140.4, 137.6, 132.5, 127.4, 125.9, 124.5, 47.2, 35.7, 35.5. **IR**: $v/cm^{-1} = 3144$ (m), 3021 (w), 2968 (m), 2923 (m), 2851 (w), 1628 (m, br), 1545 (m), 1521 (s), 1448 (m), 1424 (m), 1412 (m), 1350 (m), 1320 (w), 1287 (m), 1177 (m), 1150 (w), 1088 (s), 1018 (s), 982 (w), 965 (w), 910 (w), 839 (vs), 758 (m), 742 (m), 715 (m), 687 (w), 668 (w), 662 (w), 638 (w), 577 (m), 558 (s), 439 (m), 426 (m). UV-Vis (CH₃CN): λ_{max}/nm , (log ε) = 458 (sh, 3.61), 396 (3.93), 286 (4.05), 236 (4.79). MS (ESI+(CH₃CN), *m/z*): 1052.7 (15%, { $[Ru_2(bimptz)(dmso)_2Cl_2](PF_6)$ }⁺), 453.9 (100%, $[Ru_2(bimptz)(dmso)_2Cl_2]^{2+})$. HRMS (ESI+(CH₃CN), m/z): Calc. $C_{30}H_{38}O_2N_{10}{}^{35}Cl_2F_6P_1{}^{102}Ru_2{}^{32}S_2$ {([Ru₂(bimptz)(dmso)₂]for $Cl_2(PF_6)$ ⁺): 1052.9721. Found: 1052.9733. Calc. for $C_{30}H_{38}O_2N_{10}{}^{35}Cl_2{}^{102}Ru_2{}^{32}S_2$ ([Ru₂(bimptz)(dmso)₂Cl₂]²⁺): 454.0037. Found: 454.0053.

Preparation of [Ru₂(bimptz)(dmso)(dms)(µ-Cl)₂][PF₆]₂ (5)

The evaporated dark red second fraction obtained from the purification of **4** was worked up analogously as described for **4** yielding **5** as dark red crystalline solid. Yield: 0.053 g (45 μ mol, 21%).

¹**H-NMR** (CD₃CN): δ /ppm = 9.03 (m, 2H, CH_{ptz}), 8.38 (m, 2H, CH_{ptz}), 7.09 (d, 2H, ${}^{3}J(H,H) = 1.4$ Hz, CH_{im}), 7.03 (d, 2H, ${}^{3}J(H,H) = 1.4$ Hz, CH_{in}), 7.00 (d, 2H, ${}^{3}J(H,H) =$ 1.4 Hz, CH_{im}), 6.98 (d, 2H, ${}^{3}J(H,H) = 1.4$ Hz, CH_{im}) 6.93 (s, 1H, (Ptz)(Im)₂CH), 6.89 (s, 1H, (Ptz)(Im)₂CH), 3.93 (s, 12H, NCH₃), 3.38 (s, 6H, H_{dmso}), 2.37 (s, 6H, H_{dms}). IR: $v/cm^{-1} =$ 3147 (w), 2959 (m), 2920 (m), 2851 (m), 1624 (br), 1541 (m), 1519 (m), 1464 (w), 1427 (m), 1348 (w), 1286 (m), 1261 (w), 1236 (w), 1176 (w), 1088 (m), 1060 (w), 1018 (m), 982 (m), 912 (w), 840 (vs), 756 (m), 715 (w), 688 (w), 661 (w), 578 (w), 557 (s), 427 (w). UV-Vis (CH₃CN): λ_{max}/nm , (log ε) = 503 (sh), 416 (3.71), 292 (3.85), 234 (4.67), 209 (4.53). HRMS (ESI⁺(CH₃CN), m/z): Calc. for $C_{30}H_{38}O_1N_{10}{}^{35}Cl_2F_6P_1{}^{102}Ru_2{}^{32}S_2$ $({[Ru_2(bimptz)(dmso)(dms)Cl_2](PF_6)}^+): 1036.9777.$ Found: 1036.9750. Calc. for $C_{30}H_{38}O_1N_{10}{}^{35}Cl_2{}^{102}Ru_2{}^{32}S_2$ ([Ru₂(bimptz)-(dmso)(dms)Cl₂]²⁺): 446.0068. Found: 446.0057.

Preparation of [Ru(Hbimptz)₂](PF₆)₄ (6)

Bimptz (0.200 g, 0.42 mmol) and [Ru(dmso)₄Cl₂] (0.101 g, 0.21 mmol), each dissolved in 25 mL ethylene glycol were mixed and heated to 100 °C in an oil bath under argon. After 10 min at this temperature the red solution was refluxed for an additional 5 h. Solid NH₄PF₆ (1.36 g) was then added to the still hot reaction mixture. After cooling to room temperature **6** was isolated as a fine microcrystalline dark purple solid, which was washed subsequently with cold water and ether and dried *in vacuo*. Yield: 0.155 g (0.11 mmol, 55%). Anal. calc. for C₅₂H₅₄N₂₀F₂₄P₄Ru, [Ru(H**bimptz**)₂](PF₆)₄: C 38.08, H 3.32, N 17.08. Found C 37.68, H 3.52, N 16.58%.

¹**H-NMR** (CD₃CN): δ /ppm = 8.96 (d, 1H, ³*J*(H,H) = 8.6 Hz, CH_{ptz}), 8.24 (m, 1H, CH_{ptz}), 7.93 (m, 1H, CH_{ptz}), 7.36 (d, 1H, ${}^{3}J(H,H) = 8.3 \text{ Hz}, CH_{ptz}), 7.17 (d, 1H, {}^{3}J(H,H) = 1.2 \text{ Hz}, CH_{im}),$ 7.08 (d, 1H, ${}^{3}J(H,H) = 1.4$ Hz, CH_{im}), 7.03 (d, 1H, ${}^{3}J(H,H) =$ 1.4 Hz, CH_{im}), 6.88 (s, 1H, (Ptz)(Im)₂CH), 6.66 (d, 1H, ${}^{3}J$ (H,H) = 1.9 Hz, CH_{im}), 6.64 (s, 1H, (Ptz)(Im)₂CH), 6.36 (d, 1H, ${}^{3}J$ (H,H) = 1.4 Hz, CH_{im}), 6.27 (d, 1H, ${}^{3}J(H,H) = 1.3$ Hz, CH_{im}), 6.07 (d, 1H, ${}^{3}J(H,H) = 1.4$ Hz, CH_{im}), 5.30 (d, 1H, ${}^{3}J(H,H) = 1.9$ Hz, CH_{im}), 4.15 (s, 3H, NCH₃), 4.03 (s, 3H, NCH₃), 3.65 (s, 3H, NCH₃), 3.47 (s, 3H, NCH₃). ¹³C-NMR (CD₃CN): δ /ppm = 159.5, 155.3, 142.1, 141.5, 140.1, 140.0, 136.1, 134.0, 130.7, 129.8, 128.1, 126.9, 126.6, 125.0, 124.7, 124.3, 124.1, 123.8, 123.7, 119.4, 39.0, 35.9, 35.2, 35.1, 34.9, 34.4. **IR**: $v/cm^{-1} = 3163$ (m), 2956 (m), 2927 (m), 2869 (w), 2854 (w), 1610 (m), 1576 (w), 1543 (s), 1521 (s), 1500 (m), 1460 (m), 1441 (w), 1427 (m), 1358 (w), 1323 (w), 1288 (s), 1238 (w), 1170 (m), 1148 (m), 1092 (m), 1051 (w), 1041 (w), 1016 (w), 957 (w), 834 (vs), 756 (s), 715 (m), 704 (w), 694 (w), 669 (w), 663(w), 640 (w), 621 (w), 601 (w), 557 (s), 538 (w). UV-Vis (CH₃CN): $\lambda_{\text{max}}/\text{nm}$, (log ε) = 515 (4.21), 421 (4.00), 293 (4.15), 224 (5.02). MS $(\text{ESI}^+(\text{CH}_3\text{CN}), m/z)$: 674.9 (10%, $\{[\text{Ru}(\text{Hbimptz})_2](\text{PF}_6)_2\}^{2+}$), 601.9 (15%, { $[Ru_2(Hbimptz)(bimptz)](PF_6)$ }²⁺), 353.3 (100%, $[Ru_2(Hbimptz)(bimptz)]^{3+})$, 265.2 (85%, $[Ru_2(Hbimptz)_2]^{4+})$. HRMS (ESI⁺(CH₃CN), m/z): Calc. for $C_{52}H_{54}F_{12}N_{20}P_2^{-102}Ru$

Table 4Crystal and refinement data for 1, 3, 4, 6

	1·2MeOH ^a	3^b	4·thf·2(CH ₃ CN)	6
Empirical formula	$C_{28}H_{34}Cl_4Mn_2N_{10}O_2$	$C_{28}H_{34}Cl_2Co_2F_{12}N_{10}O_2P_2$	$C_{38}H_{52}Cl_2F_{12}N_{12}O_3P_2Ru_2S_2$	$C_{52}H_{54}F_{24}N_{20}P_4Ru$
Formula weight	794.33	1021.35	1352.02	1640.10
Temperature/K	100(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	P21/n	C2/c	Pna21	C2/c
Cell dimensions/Å	a = 13.1972(6)	a = 32.2485(7)	a = 33.468(2)	a = 22.7921(8)
	b = 16.7605(7)	b = 11.1423(2)	b = 13.7678(5)	b = 14.6642(4)
	c = 15.8055(8)	c = 27.0595(6)	c = 11.1687(7)	c = 21.0070(8)
	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$
	$\beta = 104.000(4)^{\circ}$	$\beta = 101.431(2)^{\circ}$	$\beta = 90^{\circ}$	$\beta = 114.484(3)^{\circ}$
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$
Cell volume/Å ³	3392.2(3)	9530.2(3)	5146.3(4)	6389.8(4)
Ζ	4	8	4	4
Calc. density/ Mg m ⁻³	1.555	1.424	1.745	1.705
Absorption coefficient/mm ⁻¹	1.103	0.958	0.928	0.472
F(000)	1624	4112	2720	3304
Crystal size/mm	$0.36 \times 0.24 \times 0.20$	$0.20 \times 0.12 \times 0.08$	$0.45 \times 0.2 \times 0.08$	$0.20 \times 0.12 \times 0.08$
Measured region/°	3.41-25.25	2.58-25.63	3.38-26.02	2.39-28.02
Index region	$-15 \le h \le 15$	$-39 \le h \le 38$	$-39 \le h \le 41$	$-30 \le h \le 29$
c	$0 \le k \le 20$	$0 \le k \le 13$	$-16 \le k \le 17$	$-19 \le k \le 18$
	$-18 \le l \le 18$	$0 \le l \le 32$	$-14 \le l \le 14$	$-27 \le l \le 27$
No of reflections	6116	8967	40 436	35726
No of independent reflections	$6116 [R_{int} = 0.1548]$	$8967 [R_{int} = 0.0000]$	9913 $[R_{int} = 0.0897]$	7643 $[R_{int} = 0.0640]$
Data/restrains/parameters	6116/15/396	8967/175/566	9913/11/630	7643/4/482
Goodness-of-fit on F^2	0.963	0.886	1.153	0.974
Final <i>R</i> values $[I > 2\sigma(I)]$	R1 = 0.0724	R1 = 0.0452	R1 = 0.0754	R1 = 0.0418
	wR2 = 0.0968	wR2 = 0.1121	wR2 = 0.1682	wR2 = 0.0734
R values (all data)	R1 = 0.1409	R1 = 0.0611	R1 = 0.0867	R1 = 0.0695
	wR2 = 0.1103	wR2 = 0.1157	wR2 = 0.1761	wR2 = 0.0792
Max/min electron density/eÅ ⁻³	0.477; -0.488	0.781; -0.652	0.878; -1.401	0.539, -0.583

" Including crystal solvent (methanol) removed by the programme SQUEEZE (Platon). " Data reflect unit cell content only.

 $(\{[Ru(Hbimptz)_2](PF_6)_2\}^{2+}): 675.1584. Found: 675.1589. Calc. for C_{52}H_{54}N_{20}^{-102}Ru ([Ru_2(Hbimptz)_2]^{4+}): 265.0965. Found: 265.0968.$

Crystal structure determinations[†]

All data were collected on a Stoe IPDS-2T diffractometer using MoK α radiation, $\lambda = 0.71073$ Å. In all cases, the structures were solved by direct methods (SHELXS-97)¹⁹ and refined versus F^2 (SHELXL-97)²⁰ with anisotropic temperature factors for all nonhydrogen atoms (Table 4). In 1 one of the two co-crystallized methanol molecules could not be modeled satisfactory and was excluded using the program SQUEEZE (Platon)²¹ In the crystal structure of 3 there is a region of disordered solvent molecules which could not be modeled successfully (trial modeling attempts indicated a mixture of methanol and diethyl ether). The program SQUEEZE (Platon)²¹ was used to remove the contribution of these diffusely scattering species from the structure factor calculations. The program calculated a solvent accessible region of 2404 Å³ per unit cell (25% of the total unit cell volume). The reported formula weight, F(000) and density reflect only the known unit cell contents. In 6 all hydrogen atoms except H7 were added geometrically and refined by using a riding model. Single crystals suitable for X-ray diffraction were obtained by the following procedures. 1: slow diffusion of degassed ether into a solution of 1 in degassed methanol at 4 °C. 2: slow diffusion of tetrahydrofuran into a solution of 2 in methanol at rt. 3: slow diffusion of ether into a diluted solution of 3 in methanol at 4 °C. 4: slow diffusion of tetrahydrofuran into a diluted solution of **4** in acetonitrile. **6**: slow evaporation of the solvent from an acetone–methanol solution of **6**. Crystallographic data for the structures **1**, **3**, **4** and **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 765497 (1), 765495 (3), 765496 (4), 765494 (**6**).†

Acknowledgements

This work was funded by the Deutsche Forschungsgemeinschaft as well as the Helios Solar Energy Research Center, which is supported by the Director, Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. S.R thanks the DAAD (German Academic Exchange Service) for a postdoctoral fellowship.

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