Simultaneous Cation/Anion Coordination by Bifunctional 1,2-Diimine/1,2-Diamine Type Ligands: Synthesis, Structures, and Properties of Tight Ion Pair Complexes of Ruthenium and Iron

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The reaction between $[(\eta^6-p-cymene)RuCl_2]_2$ and tetra-p-tolyloxalic amidine (oxam1) results in a coupled cation/anion coordination forming the ion-paired complex $[(\eta^6-p-cy$ mene)RuCl(oxam1)Cl] (1a). According to an X-ray single crystal diffraction analysis the Ru moiety is coordinated at the 1,2-diimine part yielding a five-membered chelate ring. Furthermore, the 1,2-diamine group on the opposite side binds to a chloride anion via two N-H groups. Exchange of the chloride anion by trifluoractetate yields $[(\eta^6-p-cy$ mene)RuCl(oxam1)CF₃CO₂] (1c) in which the C=O group is bonded to the diamine part. Similarly, bis(mesityl)bis(pyridylmethyl)oxalic amidine (oxam2) reacts with FeX₂ to yield the ion-paired complexes 3a (X: Cl), and 3b (X: Br). X-ray diffraction studies of both compounds reveal that the oxalic amidine ligand acts as a four-dentate chelating ligand. One halide is fixed in the same way as in 1a. The complex 1a

Introduction

Oxalic amidines containing the structural element A are not only variable building blocks for bi- and oligonuclear complexes^[1-8] but can also be considered as bifunctional ligands which should be capable of coupled cation/anion coordination forming tight contact ion-paired complexes according to Scheme 1.



Scheme 1. Formation of ion-paired complexes by coupled cation/ anion coordination

reacts with Pd(acac)₂ (acac: acetylacetonate) to give the tetranuclear heterobimetallic complex [(η⁶-*p*-cymene)RuCl-(oxam1)PdCl]₂ (2). The related complexes [(tbbpy)₂Ru- $(bbimH_2)(OOC-CF_3)](PF_6)$ (4), $[(tbbpy)_2Ru(bbimH_2)(OOC-CF_3)](PF_6)$ $(CF_2)_7CF_3$)][OOC(CF_2)_7CF_3] (5), [{(tbbpy)_2Ru(bbimH_2)}_2- $(OOC-C_6F_4-COO)](PF_6)_2$ [{(tbbpy)₂Ru-(6), and $(bbimH_2)_2(OOC-C_6F_4-COO)$] (7), $(bbimH_2: bibenzimida$ zole; tbbpy: 4,4'-di-tert-butyl-2,2'-bipyridine) also form ionpaired compounds. According to the X-ray diffraction analyses of **4–6** both oxygen atoms of the carboxylate ions are coordinated to the two N-H functions via strong N-H···O bonds. Although 5 contains a dication, the compound is soluble in solvents of low polarity, even in supercritical carbon dioxide.

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Structure **B**, the tautomer of **A** can be stabilized by formation of a 1,2-diimine metal compound provided a suitable metal complex fragment is used. Additionally, anion bonding via hydrogen bonds on the opposite 1,2-diamine side of the oxalic amidine system may stabilize the mononuclear complex preventing undesired coordination polymerization.

The general principle behind this process is strongly reminiscent of anion recognition events in supramolecular chemistry between cationic diamine-based hosts and anionic guests.^[9] The stability of the resulting aggregates is commonly influenced by steric and electronic tuning of the host molecule with regard to the guest. The application of these construction principles in metallorganic and coordination chemistry is still relatively underdeveloped even so multinuclear supramolecular aggregates are promising candidates for multistep catalytic processes or biomimetic analogues, such as light harvesting complexes.

Simultaneous cation/anion coordination could therefore result in the generation of "supramolecularly" protected metalloligands, useful as starting products for the construction of heterobi- or oligometallic complexes, but also for the formation of ion-paired metal complexes with untypical high solubilities in solvents of low polarity. In addition, in-

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teraction of dicarboxylates as dianions with appropriately designed 1,2-diamine containing complexes should result in the formation of hydrogen-bonded stable dimers. Furthermore, this type of reaction may be used to force ligands bearing additional donor groups in R^1 into untypical coordination modes. Additionally, the generation of 1,2-diimine metal species containing cationic electrophilic parts may be of special interest because of their well-known catalytic potential.^[10,11]

We describe here the first examples for simultaneous cation/anion bonding using oxalic amidines as ligands and investigate the structures and properties of the new compounds. Furthermore, we report on ion-paired complexes consisting of the photoactive fragment (tbbpy)₂Ru(bbimH₂)²⁺ and carboxylates that are hydrogen bonded to the related bibenzimidazole ligand. Although in these complexes a dication is part of the tight ion-paired compound, these compounds show surprisingly high solubilities in nonpolar solvents if long chained perfluoro-substituted carboxylates are coordinated to the N–H groups.

Results and Discussion

Reaction between $[(\eta^6-p-cymene)RuCl_2]_2$ and tetra-p-tolyloxalic amidine (oxam1) in refluxing toluene resulted in the formation of $[(\eta^6-p-cymene)RuCl(oxam1)Cl]$, 1a, which was isolated as an orange-red crystalline compound at room temperature. Elemental analysis and a mass spectrum confirmed its composition. In the ESI-mass spectrum the complex ion $[1a - Cl]^+$ (m/z = 716) was detected. The ¹H NMR spectrum of 1a, recorded in [D₈]THF at room temperature supports the assumption of a C_s symmetrical complex. It showed one doublet belonging to the methyl protons of the isopropyl group at $\delta = 1.14$ and 1.17 ppm and a singlet for the methyl group of coordinated cymene at $\delta = 2.27$ ppm. Two singlets for the methyl groups of the coordinated *oxam1* were detected at $\delta = 2.09$ and 2.18 ppm. The relative intensities of these resonances are, as expected, (1:1):(1:2):2. The multiplet corresponding to the CH proton of the isopropyl group was detected at $\delta = 2.50$ ppm. The aromatic protons of the *p*-cymene ligand ($\delta = 4.59$ ppm), and the protons of the aromatic substituents ($\delta = 6.66$ and 7.60 ppm) were detected with the expected intensities. Furthermore, the ¹H NMR spectrum shows one sharp singlet for both NH groups at $\delta = 12.83$ ppm, which is in agreement with a strong chloride binding to the N-H functions according to Figure 1. The ¹³C NMR spectrum for 1a in [D₈]THF also showed the expected simple pattern corresponding to a symmetrical complex.

The molecular structure of compound **1a** has been confirmed by X-ray crystallography (Figure 1). The compound consists of a cationic portion in which the metal center is surrounded by the *p*-cymene, the diimine part of the oxalic amidine ligand and one chloride to form a typical "piano stool" complex in which the arene acts as the "bench" and the other ligands form "the legs" of the stool. The ruthenium coordination environment is best described as a dis-



Figure 1. Molecular structure of complex 1a, selected distances [Å] and bond angles [deg]: Ru-Cl1 2.398(1), Ru-XIA 1.692(4), Ru-N1 2.088(3), Ru-N2 2.079(3), C1-N1 1.301(4), C1-N3 1.436(4), C1-C2 1.497(4), C2-N2 1.298(4), C2-N4 1.350(5), Cl2-N3 3.077(2), Cl2-N4 3.088(2); X1A-Ru-Cl1 128.60(7), 83.9(2), X1A-Ru-N2 83.5(2), Cl1-Ru-N1 X1A-Ru-N1 83.54(8), N2-C2-N4 Cl1-Ru-N2 N1 - Ru - N283.93(9), 75.9(1), 13 127.2(3), C1-C2-N4 127.4(3), C1-C2-N2 N1-C1-N3 114.1(3), 118.2(3), C2-C1-N1 114.1(3), C2-C1-N3 118.6(3)

torted trigonal pyramidal geometry considering the aromatic ring as a unique coordination site, represented by the middle of the benzene unit, occupying one position of the polygon. The second chloride is bonded to the two N-H groups of the 1,2 diamine part of the oxalic amidine via two hydrogen bonds. Bond lengths and angles are listed in the figure caption and lie within typical ranges (see Figure 1 caption). The C1-N1 and C2-N2 bond lengths of 1.301(4), and 1.298(4) Å clearly indicate that the ligand coordinates with the 1,2-diimine part. Typically, due to the partial delocalization of the double bonds of the coordinated 1,2 diimine, the C1-C2 bond length 1.497(4) Å is shorter than that of a C-C single bond. The N3-Cl2 and N4-Cl2 distances of 3.077(2) and 3.088(2) A, respectively, are in the accepted range for these distances. Furthermore, the angles for the N3-H···Cl group, and the N4-H···Cl group (167 and 170°, respectively) show very little deviation from linearity. These findings clearly indicate a strong bonding between the N-H functions of the 1,2-diamine system and the chloride counterion. In the related compound tris(N,N'-diphenyloxalic amidine-N,N')cobalt(II) dichloride, the peripheral primary amine functions form tight hydrogen bonds to one chloride anion resulting in a polymeric three-dimensional network.^[12]

The complex **1a** has been proven to be a suitable "protected" ligand for the construction of oligonuclear complexes containing different metals. For example, reaction with $Pd(acac)_2$ resulted in the formation of the tetranuclear complex **2** containing palladium atoms in the inner part and two ruthenium centers on the peripheries (Scheme 2). Elemental analysis and a mass spectrum confirmed its composition. In the ESI-mass spectrum the complex cation [M

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- Cl]⁺ m/z = 1679 was detected and the obtained isotope pattern agrees well with the calculated molecular formula C₈₀H₈₄Cl₃N₈Pd₂Ru₂. Furthermore, the ¹H NMR and the ¹³C NMR spectra of **2** ([D₈]THF at room temperature) show the expected signals for a symmetrical complex and are similar to those of **1a**, except for the absence of the signals of the N–H protons. Red single crystals of compound **2** obtained from toluene were subjected to an X-ray diffraction analysis. Figure 2 displays the molecular structure of **2**.



Scheme 2. Formation of the tetranuclear heterobimetallic complex ${\bf 2}$

The Ru(oxam1)PdCl₂Pd(oxam1)Ru core of **2** is essentially planar and the peripheral ligands cymene and chloride are *trans* with respect towards each other. The coordination geometry around the ruthenium centers is the same as in **1a**.

Exchange of the hydrogen bonded chloride in 1a by BF₄⁻ or trifluoroacetate anions in THF resulted in the formation of the complexes $[(\eta^6-p-cymene)RuCl(oxam1)BF_4]$ (1b), and $[(\eta^6-p\text{-cymene})\text{RuCl}(oxam1)\text{OOCCF}_3]$ (1c). The ¹H NMR spectra of both compounds in [D₈]THF showed nearly identical signals for all of the CH groups; however the signals for the NH protons were very different. In 1b this signal appeared at $\delta = 9.05$ ppm as a sharp singlet. The magnitude of this upfield shift ($\delta = 3.8$ ppm) is indicative of a weaker hydrogen bond interaction compared with 1a. In contrast, the trifluoroacetate complex 1c showed very broad NH signals between $\delta = 11$ and $\delta = 12$ ppm, characteristic of a fast proton exchange or rotational effect. At lower temperature the signal became sharper at around $\delta = 11.6$ ppm. This low-field shift is indicative of a stronger hydrogen bond than that in 1b.

The solid-state structure of **1b** and **1c** could be determined by X-ray analyses. Both ruthenium cymene moieties



Figure 2. Molecular structure of complex **2**, selected distances [Å] and bond angles [deg]: Ru-Cl2 2.431(1), Ru-X1A 1.681(4), Ru-N4 2.104(3), Ru-N3 2.082(3), Pd-Cl1 2.333(1), Pd-Cl1A 2.341(1), Pd-N1 1.989(4), Pd-N2 2.011(3), C1-N1 1.342(5), C1-N3 1.312(5), C1-C2 1.495(5), C2-N2 1.332(5), C2-N4 1.318(5); X1A-Ru-Cl2 127.8(1), X1A-Ru-N3 86.5(2), X1A-Ru-N4 83.8(2), Cl2-Ru-N3 86.8(1), Cl2-Ru-N4 83.8(1), N3-Ru-N4 76.7(1), Cl1-Pd-Cl1A 82.99(4), Cl1-Pd-N1 179.4(1), Cl1-Pd-N2 97.7(1), N1-Pd-N2 81.7(1), N1-Pd-Cl1A 97.6(1), N2-Pd-Cl1A 179.3(1), N1-C1-N3 129.8(4), N2-C2-N4 130.9(4), C1-C2-N2 114.9(3), C1-C2-N4 114.2(3), C2-C1-N1 114.7(3), C2-C1-N3 115.5(3)

(1b not depicted) are identical to 1a within experimental errors. One fluoro substituent of the BF_4^- anion does form a hydrogen bond to both NH function [N3-F4 2.825(4) and N4-F4 3.034(4) Å]. The surprisingly short N3-F4 distance might be due to packing effects. Similar N-H···F hydrogen bond patterns have been observed in related copper azophenine complexes.^[13]

The trifluoroacetate anion in **1c** does form a hydrogen bond with both NH functions of the coordinated oxalic amidine (Figure 3). However, in contrast to the usual bonding mode of carboxylate anions in previously reported related metal complexes containing a diimine/diamine^[14–16] in **1c** only the oxygen of the C=O group [C41–O2 = 1.176(7) Å] is involved in the hydrogen bond network. The relatively short N–H···O distances of 2.771(3), and 2.761(3) Å, respectively suggest a very strong interaction.

The formation of the complexes **3a** and **3b** between bis-(mesityl)bis(pyridylmethyl)oxalic amidine (*oxam2*) and FeX₂ (X: Cl, Br) clearly demonstrates that coupled cation/ anion coordination can also be used for realizing untypical coordination modes (Scheme 3). Whereas in transition metal complexes containing additional coordinating anionic chelate ligands (such as acetylacetonate), *oxam2* typically acts as a three-dentate bridging ligand in dinuclear complexes^[18–20] whereas it forms mononuclear tetradentate complexes with iron halides.

The solid-state structure of **3a** determined by X-ray diffraction analysis shows the oxalic amidine ligand to be coordinated as tetradentate ligand in its prototropic form (Figure 4). The 1,2-diimine now residing on the picolyl based nitrogens is coordinated together with the pyridine donor sites to the five-coordinated Fe^{II} with the chloride ligand in the apical position resulting in a square-planar



Figure 3. Molecular structure of complex 1c, selected distances [Å] and bond angles [deg]: Ru-Cl 2.406(1), Ru-X1A 1.687(4), Ru-N1 2.079(3), Ru-N2 2.084(3), Cl-N1 1.304(5), Cl-N3 1.344(5), Cl-C2 1.513(6), C2-N2 1.308(5), C2-N4 1.347(5), O2-N3 2.761(3), O2-N4 2.771(3); X1A-Ru-Cl 128.3(1), X1A-Ru-N1 85.4(2), X1A-Ru-N2 84.4(2), Cl-Ru-N1 85.2(1), Cl-Ru-N2 84.4(1), N1-Ru-N2 75.8(1), N1-Cl-N3 129.0(4), N2-C2-N4 127.5(4), Cl-C2-N2 113.5(4), Cl-C2-N4 118.9(4), C2-Cl-N1 113.6(3), C2-Cl-N3 117.4(4)



Scheme 3. Structure of the free ligand bis(mesityl)bis(pyridylmethyl)-oxalic amidine, and coordination mode in the iron complexes 3a and 3b

pyramidal coordination environment. Similarly to complex 1a, one halide is coordinated to the two N-H groups on the opposite side of the oxalic amidine frame yielding a zwitterionic complex [Cl2-N5 = 3.051(1) Å, Cl2-N6 = 3.152(1) Å]. Other relevant bond lengths and angles fall in the range of typical values. The internal bond length and angles of the central oxalic amidine are similar to those in 1a. In contrast to 1a, the plane arranged by the four nitrogen donor atoms of the central oxalic amidine frame of 3a is slightly distorted. More significant are the differences between the bond angles Cl1-Fe-N2 [104.27(7)°] and Cl1-Fe-N4 [107.66(7)°] respectively to Cl1-Fe-N1 [109.27(7)°] and Cl1-Fe-N3 [114.36(7)°]. These differences result in a distorted square pyramidal coordination arrangement in 3a. In this arrangement the iron center is "out of plane" coordinated similar to well-known hem iron systems. According to X-ray structural analysis, 3b has the same ion-paired structure as 3a.



Figure 4. Molecular structure of complex 3a, selected distances [Å] and bond angles [deg]: Fe-Cl1 2.663(9), Fe-N1 2.091(2), Fe-N2 104.27(7), 109.27(7), Cl1-Fe-N2 Cl1-Fe-N3 114.36(7). 76.98(9), Cl1-Fe-N4 107.66(7), N1-Fe-N2 N1-Fe-N3 N2-Fe-N3 75.64(9), N1-Fe-N4 140.04(9), 138.13(9). 75.70(9), N3-Fe-N4 N2-Fe-N4 108.03(9), N6-C1-N3 N1-C2-N5 128.5(3), C1-C2-N1 128.8(3),113.6(2),C1-C2-N5 117.9(2), C2-C1-N3 112.7(2), C2-C1-N6 118.5(2)

The cores of bibenzimidazole ($bbimH_2$) and biimidazole ($bimH_2$) are structurally related to the oxalic amidine ligand family. However, electronic differences exist which manifest themselves in different pK_a values of the coordinated ligands.^[3,17] Since ruthenium polypyridyl complexes of these ligands are photoactive it was our aim to use the coupled cation/anion coordination for the formation of tight ion-paired, photoactive complexes. The appropriate choice of anions should lead to stable assemblies of potentially higher nuclearity and in addition a tuning of their solubility in nonpolar solvents could be envisaged.

It is known that some biimidazole $(bimH_2)$ can form complexes in which one anion is linked to the imidazole based NH groups via hydrogen bonds;^[21–28] however, in most cases polymeric networks resulted.^[21,22–24] In contrast, well-defined mononuclear ion-paired bibenzimidazole complexes are rare. Ag^I and Cu^I complexes containing associated chloride or acetate anions have been characterized by de Souza Lemos.^[25,26] Iron(II) complexes with *bbimH*₂ exhibit complex hydrogen bonding patterns where cationic complexes are linked via hydrogen bonds to their respective anions.^[15] Recently, Beauchamp et al. have shown that some *bimH*₂ Re^{III} complexes form hydrogen bonds with halides or benzoate anions resulting in ion pairs that are stable in organic solvents.^[16,27,28]

In an initial work we have shown that N–H groups of $bbimH_2$ Ru complexes bind water molecules resulting in hydrogen bonded networks. The variation of the noncoordinating anion determined the supramolecular aggregation in these compounds.^[29]

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Based on these observations we choose to employ carboxylate anions in an attempt to obtain stable aggregates. trifluoroacetate complex [(tbbpy)₂Ru(bbimH₂)-The $(OOC-CF_3)$](PF₆) (4), could easily be prepared by deprotonation of [(tbbpy)₂Ru(bbimH₂)](PF₆)₂ followed by reaction of the deprotonated complex with the trifluoroacetic $[(tbbpy)_2Ru(bbimH_2){OOC(CF_2)_7CF_3})][OOC$ acid. $(CF_2)_7 CF_3$ (5) was prepared by deprotonation of $[(tbbpy)_2 -$ Ru(bbimH₂)](Cl)₂ followed by reaction of the fully deprotonated complex with the corresponding acid. The ¹H NMR spectra of both 4 and 5 show a new signal at $\delta =$ 16.4 ppm in deuterated acetone in addition to the other signals for the complex cation (see Exp. Sect.). Its broadness and extreme low-field shift suggests that it corresponds to the N-H protons. Since a signal for these protons in other ruthenium polypyridyl complexes with bbimH₂ as ligand has never been observed,^[29] we assume that strong ion paring may explain this effect. The ESI-mass spectroscopical investigation confirmed the nature of the complex cation.

The solid-state structure of 4 elucidated by an X-ray diffraction study showed the expected complex cation where the bibenzimidazole ligand coordinates via the 1,2-diimine part to the Ru^{II} atom that exhibits distorted-octahedral geometry. The peripheral NH functions form hydrogen bonds to the carboxylate anion resulting in an ion-paired structure (Figure 5). The distances between hydrogen atoms of the N-H functions and the oxygens of the carboxylate [N3-O1 = 2.703(3), N4-O1 = 2.659(3) Å] are in the range of strong hydrogen bonds.^[29] In contrast to the hydrogen bond association in 1c, both NH function interact with both carboxylate oxygens in 4. The complementary topology of the secondary amines of coordinated bibenzimidazole and the carboxylate anions allows a more efficient interaction between both parts leading to two strong N-H···O bonds (see also Figure 3).

In order to understand why the two strongly related complexes, 1c and 4, form different hydrogen bonding networks with trifluoroacetate the central cores of 1b and 4 were superimposed on each other (Figure 6). It is clearly evident from Figure 6 that the steric demand of the aryl substituents at the nitrogens in 1c determines the C1-N3-H angle in such a way that a favorable hydrogen bond interaction is only possible with one hydrogen bond acceptor. In contrast, the bibenzimidazole ligand in 4 is bent around the ruthenium center^[29] that results in the orientation of the two NH functions towards two hydrogen bond acceptors.

Although the diffraction data for complex **5**, containing perfluorooctylcarboxylate instead of trifluoroacetate, were insufficient for satisfactory refinement of all parameters, the data show without doubt that the perfluorooctylcarboxylate is anchored via the two imidazole NH to the complex cation, as is similar in **4** (O1–N4 = ca. 2.660 Å, O2–N3 = ca. 2.706 Å). The structural motif of **5** is displayed in Figure 7.

Complex 5 contains a twofold positively charged cation as part of the ion-paired unit but also a discrete anion. Surprisingly, 5 is even soluble in supercritical CO_2 , which is known to be an extremely poor solvent for ionic com-



Figure 5. Molecular structure of complex 4, selected distances [Å] and bond angles [deg]: Ru–N1 2.086(3), Ru–N2 2.109(3), Ru–N5 2.038(2), Ru–N6 2.037(3), Ru–N7 2.042(3), Ru–N8 2.074(3), Cl–N11.332(5), Cl–N3 1.336(6), Cl–C8 1.433(6), C8–N2 1.328(6), C8–N4 1.359(6), N4–O1 2.659(3), N3–O2 2.703(3), O1–C51 1.257(6), O2–C51 1.223(6), N1–Ru–N2 77.5(1); N1–Ru–N5 88.3(1), N1–Ru–N6 93.6(1), N1–Ru–N7 173.4(1), N1–Ru–N8 97.2(1), N1–Cl–N3 114.0(4), Cl–C8–N2 117.3(4), Cl–C8–N4 129.1(4), C8–C1–N1 115.9(4), C8–C1–N3 130.0(4), O1–C51–O2 131.2(5)



Figure 6. Least square fit of parts of complex 1c and 4, torsion angles N3-C1-C2-N4; for 1c -1.2° and for 4 -2.4° ; distance N3-N4: for 1c 2.784(4) Å and for 4 3.184(4) Å

pounds. This suggests that the tight ion-paired compound **5** is also stable in such nonpolar solvents. This could be explained by the interaction of the hydrophilic moieties, cationic 1,2-diamine and carboxylate with each other in such a way that only the lipophilic *tert*-butyl- and perfluorooctyl moieties interact with the solvent. In contrast, the ionic complex [(tbbpy)₃Ru][OOC(CF₂)₇CF₃]₂, which can be obtained by simple anion-exchange, is completely insoluble in *sc*CO₂. Due to the lack of N-H functions in this complex no hydrogen bonds can be formed, additionally confirming that the supramolecular association via hydrogen bonds is essential for this unexpected effect.



Figure 7. Structural motif of complex 5

Deprotonation of $[(tbbpy)_2Ru(bbimH_2)](PF_6)_2$ and subsequent reaction with tetetrafluoroterephthalic acid in a molar ratio 2:1 in acetone/water resulted in the formation of complex **6**. Upon recrystallization of **6** from acetonitrile/ water the deep red complex **7** was obtained. Both complexes could be isolated as single crystals.

Figure 8 shows the molecular structure for compound **6** and lists relevant bond lengths and angles in the figure captions.



Figure 8. Molecular structure of complex **6**, selected distances [Å] and bond angles [deg]: O1–N3 2.673(5), O2–N4 2.652(5), O1–C54 1.240(5), O2–C54 1.232(5); O1–C54–O2 128.5(4)

In the solid state two ruthenium bibenzimidazole units are connected via a deprotonated tetrafluoroterephthalic acid dianion. Two PF₆ anions remain isolated. Both imidazole based NH functions interact with both oxygen atoms of one carboxylate function, resulting in N···O distances of 2.673(5) and 2.652(5) Å, respectively. The interaction between the ruthenium complex units and the carboxylate moiety is very similar to that observed in **4**. Both ruthenium complexes are twisted out of the plane defined by the two coplanar carboxylate moieties by 152.8°. The Ru···Ru distance defined by this supramolecular arrangement is 1.957 nm. Although the combination of two inherently chiral ruthenium complexes may lead to a mixture of diastereomers^[3] the crystals of **6** only contained the MESO isomer.

According to the X-ray analysis of single crystals, 7 contains two monodeprotonated ruthenium units, also connected by the terephthalate bridge (Figure 9 and Scheme 4). However, only the protonated imidazole nitrogen forms a hydrogen bond to one oxygen of the carboxylate group [N3-O2 = 2.693(5) Å] whereas the deprotonated imidazole nitrogen acts as a hydrogen bond acceptor for an additional water molecule [N4-O3 = 2.871(5) Å].



Figure 9. Molecular structures of complex 7, selected distances [Å] and bond angles [deg]: O3-N4 2.871(5), O2-N3 2.693(4), O2-O3 2.926 (5), O1-C54 1.230(5), O2-C54 1.248(5); O1-C54-O2 127.9(4)

The ruthenium complexes are consequently twisted out of the plane defined by the two carboxylate moieties by 65.0° . This is a difference of 87.8° compared with the value obtained for **6**. As expected, the Ru···Ru distance in **7** (2.025 nm) is longer than in **6** (1.957 nm). The isolated compound **7** contains, as in **6**, only the MESO isomer.

The dimeric arrangement is therefore stable even if the essential ruthenium based NH functions are monodeprotonated.

Conclusion

Tight ion-paired complexes with different anions can be synthesized using diimine/diamine type bridging ligands, which are able to split M-X bonds under formation of a coupled cation/anion coordination. The resulting ionpaired complexes can be considered as "protected metalloligands" useful for the construction of oligonuclear organometallic complexes, as demonstrated by the reaction of 1a with Pd(acac)₂ resulting in the formation of the tetranuclear mixed metal complex 2. The hydrogen bonded anion in 1 can be varied in a wide range. The novel hydrogen bonding pattern displayed in 1a-c between the cationic oxalic amidine fragment and one specific spatially well defined point opens the possibility of designing supramolecular compounds using new, "single point" bridging components such as the redox active 1,4-benzoquinone and similar systems.

The connection of chromophores such as ruthenium polypyridyl complexes employing supramolecular construction principles is strongly reminiscent of the building principles of the naturally occurring Light Harvesting Complexes (LHA). Additionally, the simple building blocks em-



Scheme 4. Structural formula of complexes 6 and 7

ployed here, as in 6, would allow a wide variation of the structures obtained, for example simply by switching the coordination mode by altering the pH values. Furthermore, the enhanced solubility of 5 offers the interesting possibility of investigating reactions of the photoactive complex 5 and related complexes in supercritical CO_2 . Further studies along these lines are now in progress.

Experimental Section

General: *p*-Tolyl oxalic amidine ligand (*oxam1*);^[30] the ligand *N*,*N*'bis(2-pyridylmethyl)-1,2-bis(2,4,6-trimethylphenylimino)ethane-1,2-diamine (*oxam2*),^[20,31] and [(tbbpy)₂Ru]Cl₂ and [(tbbpy)₂Ru-(bbimH₂)](X)₂ (X = Cl, PF₆)^[3,29] were prepared according to described methods. The complexes (η^6 -*p*-cymene)RuCl₂, PdCl₂(CH₃CN)₂, and trifluoroacetic acid (Aldrich) and perfluorooctylcarboxylic acid (ABCR) were used without additional purification. All manipulations were carried out under Argon using standard Schlenk techniques and the solvents used were dried and distilled.

¹H NMR and ¹³C NMR spectra were recorded at ambient temperature unless otherwise stated on a Bruker AC 200 MHz spectrometer. All spectra were referenced to TMS or deuterated solvent as an internal standard. FAB-mass spectra were obtained on a Finnigan MAT SSQ 710 system (2,4-dimethoxybenzyl alcohol as matrix), ESI-mass spectra were recorded on a Finnigan MAT, MAT 95 XL. IR measurements were carried out on a Perkin–Elmer System 2000 FT-IR.

Complex 1a: A solution of *oxam1* (1.30 g, 2.92 mmol) in toluene (30 mL) was added to a suspension of $[(\eta^6-p\text{-cymene})\text{RuCl}_2]_2$ (0.89 g, 1.46 mmol) in toluene (30 mL) and the mixture was refluxed for 2 hours. After cooling to room temperature, the orange-red microcrystalline solid was filtered, washed with diethyl ether (20 mL) and dried in vacuo. Single crystals of **1** were obtained by recrystallization from hot toluene. Yield: 1.75 g (79%).

 $\begin{array}{l} {\rm C}_{40}{\rm H}_{44}{\rm Cl}_2{\rm N}_4{\rm Ru}\ (752.8):\ {\rm calcd.:}\ {\rm C}\ 63.82,\ {\rm H}\ 5.89,\ {\rm N}\ 7.44,\ {\rm Cl}\ 9.42;\\ {\rm found}\ {\rm C}\ 63.52,\ {\rm H}\ 6.23,\ {\rm N}\ 7.05,\ {\rm Cl}\ 9.24.\ ^1{\rm H}\ {\rm NMR}\ ([{\rm D}_8]{\rm THF}):\ \delta=\\ 1.14,\ 1.17\ [{\rm d},\ ^3J_{H-H}=6.9\ {\rm Hz},\ 6\ {\rm H},\ -{\rm CH}({\rm C}H_3)_2\ {\rm cymene}],\ 2.09,\ 2.18\\ (2\ {\rm s},\ 6\ {\rm H}\ {\rm each},\ -{\rm CH}_3\ {\rm tolyl}),\ 2.27\ ({\rm s},\ 3\ {\rm H},\ -{\rm CH}_3\ {\rm cymene}],\ 2.09,\ 2.18\\ (2\ {\rm s},\ 6\ {\rm H}\ {\rm each},\ -{\rm CH}_3\ {\rm tolyl}),\ 2.27\ ({\rm s},\ 3\ {\rm H},\ -{\rm CH}_3\ {\rm cymene}],\ 4.55,\ 4.58,\ 4.60,\\ 4.64\ (2\ {\rm d},\ ^3J_{H-H}=6.2\ {\rm Hz},\ 2\ {\rm H}\ {\rm each},\ {\rm H}^{2.3,5,6}\ {\rm cymene}],\ 4.55,\ 4.58,\ 4.60,\\ 4.64\ (2\ {\rm d},\ ^3J_{H-H}=6.2\ {\rm Hz},\ 2\ {\rm H}\ {\rm each},\ {\rm H}^{2.3,5,6}\ {\rm cymene}],\ 6.62,\ 6.66,\\ 6.74,\ 6.78\ [2\ {\rm d}_{{\rm AA'BB'}},\ ^3J_{H-H}=8.3\ {\rm Hz},\ 6\ {\rm H}\ {\rm each},\ -{\rm CH}\ {\rm tolyl}),\ 7.02,\\ 7.60\ (2\ {\rm s}_{{\rm broad}},\ 2\ {\rm H}\ {\rm each},\ -{\rm CH}\ {\rm tolyl}),\ 12.83\ ({\rm s},\ 2\ {\rm H},\ -{\rm NH})\ {\rm ppm}.\\ {\rm ^{13}C}\ {\rm NMR}\ ([{\rm D}_8]{\rm THF}):\ \delta=15.5\ (-{\rm CH}_3\ {\rm cymene}),\ 20.9\ (-{\rm CH}_3\ {\rm tolyl}),\ 22.6\ (-{\rm CH}({\rm CH}_3)_2\ {\rm cymene}),\ 31.0\ [-{\rm CH}({\rm CH}_3)_2\ {\rm cymene}],\ 123.9,\\ 126.2,\ 128.6,\ 129.3\ ({\rm CH}\ {\rm tolyl}),\ 124.7,\ 126.3\ ({\rm C}-{\rm CH}_3\ {\rm tolyl}),\ 138.3\ ({\rm NH-C}\ {\rm tolyl}),\ 148.8\ (={\rm N-C}\ {\rm tolyl}),\ 155.6\ ({\rm C}_{{\rm bridge}})\ {\rm ppm}.\ {\rm MS}\ ({\rm ESI}\ {\rm in\ THF}):\ m/z\ (\%)=716\ (100)\ [{\rm M}-{\rm Cl}]^+,\ 680\ (20)\ [{\rm M}-2\ {\rm Cl}]^+. \end{array}$

The red-orange complex **1b** was prepared by reaction of **1a** in THF with equimolar amounts of NaBF₄. yield: 80% C₄₀H₄₄BClF₄N₄Ru (804.2) calcd.: C 59.74, H 5.52, N 6.97; found C 58.63, H 5.43, N 6.53. ¹H NMR ([D₈]THF): $\delta = 1.13$, 1.17 [d, ³J_{H,H} = 6.9 Hz, 6 H, -CH(CH₃)₂ cymene], 2.10 (s, 12 H, -CH₃ tolyl), 2.19 (s, 3 H, -CH₃ cymene), 2.63 [m, ³J_{H,H} = 6.8 Hz, 1 H, -CH(CH₃)₂ cymene], 4.63 (s, 4 H, H^{2,3,5,6} cymene), 6.69, 6.84, 6.96, 7.17, 7.50 (four broad signals, one s, 16 H overall, -CH tolyl), 9.05 (s_{broad}, 2 H, -NH) ppm. ¹³C NMR ([D₈]THF): $\delta = 15.9$ (-CH₃ cymene), 20.7 (-CH₃ tolyl), 22.5 [-CH(CH₃)₂ cymene], 31.7 [-CH(CH₃)₂ cymene], 84.7, 87.3 (C^{2,3,5,6} cymene), 102.0, 104.3 (C^{1,4} cymene), 123.7, 128.8 (CH tolyl), 134.2 (C-CH₃ tolyl), 136.5 (NH-C tolyl), 149.7 (=N-C tolyl), 156.7 (C_{bridge}).

Analogously, **1c** was synthesized by reaction of **1a** in THF with an equimolar quantity of Ag(OOCCF₃). yield: nearly quantitative $C_{42}H_{44}ClF_3N_4O_2Ru$ (830.4) calcd.: C 60.75 H 5.33 N 6.75 Cl 4.27 found C 60.01 H 5.13 N 6.44. ¹H NMR ([D₈]THF): $\delta = 1.14$, 1.18 [d, ³J_{H,H} = 6.9 Hz, 6 H, -CH(CH₃)₂ cymene], 2.10 (s, 12 H, -CH₃ tolyl), 2.18 (s, 3 H, -CH₃ cymene), 2.51 [m, 1 H, -CH(CH₃)₂ cymene], 4.57, 4.60, 4.62, 4.65 (s, 1 H each, ³J_{H,H} = 4.3 Hz, H^{2,3,5,6} cymene), 6.67, 6.87, 7.56 (m, 16 H, -CH tolyl), 11–12 (s_{very broad}, 2 H, -NH).

Single crystals of these complexes, suitable for an X-ray diffraction analysis, were obtained from THF or toluene.

Complex 2: Complex 1 (0.38 g, 0.5 mmol) and Pd(acac)₂ (0.154 g, 0.5 mmol) were suspended in toluene (20 mL) and refluxed for 4 h or until a clear, dark red solution resulted. The solution was concentrated to 5 mL and pentane (20 mL) was added. The red microcrystalline solid was filtered, washed with pentane (20 mL) and dried in vacuo. Single crystals of 2 were obtained by recrystallization from diethyl ether or toluene. Yield: 0.28 g (65%). C₈₀H₈₄Cl₄N₈Pd₂Ru₂ (1714.35) calcd.: C 56.04, H 4.94, N 6.53, Cl 8.27; found C 55.63, H 5.49, N 5.90, Cl 8.25. ¹H NMR (400 MHz, $[D_8]$ THF): $\delta = 1.11$, 1.13 [d, ${}^{3}J_{H-H} = 6.9$ Hz, 6 H, $-CH(CH_3)_2$ cymene], 2.00 (s, 24 H, -CH3 tolyl), 2.09 (s, 6 H, -CH3 cymene), 2.43 [m, ${}^{3}J_{H-H} = 7.0$ Hz, 2 H, $-CH(CH_{3})_{2}$ cymene], 4.07, 4.09, 4.21, 4.23 (2 d, ${}^{3}J_{H-H} = 5.9$ Hz, 4 H each, H^{2,3,5,6} cymene), 6.45, 6.47, 6.49, 6.51 (2 d_{AA'BB'}, ${}^{3}J_{H-H} = 8.0$ Hz, 8 H each, -CH tolyl), 6.65, 6.68, 7.22, 7.24 (2 d_{AA'BB'}, ${}^{3}J_{H-H} = 8.0$ Hz, 8 H each, -CH tolyl) ppm. ¹³C NMR (100.6 MHz, $[D_8]$ THF): $\delta = 19.0 (-CH_3)$ cymene), 20.8, 21.0 (2 s, -CH₃ tolyl), 22.7 [-CH(CH₃)₂ cymene], 31.5 $[-CH(CH_3)_2 \text{ cymene}]$, 82.7, 85.5 $(C^{2,3,5,6} \text{ cymene})$, 100.2, 101.6 (C1,4 cymene), 125.9, 127.5, 127.7, 128.6 (CH tolyl), 132.9, 133.3 (C-CH₃ tolyl), 144.7, 151.1 (-N-C tolyl), 167.8 (C_{bridge}) ppm. MS (ESI in toluene + methanol): m/z (%) = 1679 (46) [M - $Cl]^+$ (isotope pattern found), 854 (100) $[M - C_{40}H_{42}N_4Cl_2RuPd]^+$, $680 \ [M - C_{40}H_{42}N_4Cl_4Pd_2Ru]^+.$

Complex 3a: This compound was prepared as a crystalline bright orange solid analogously to **3b** from FeCl₂ (66 mg, 0.52 mmol) using *N*,*N'*-bis(2-pyridylmethyl)-1,2-bis(2,4,6-trimethylphenylimino)-ethane-1,2-diamine (*oxam2*) (262 mg, 0.52 mmol). Single crystals suitable for X-ray determination were obtained from THF. Yield: 286 mg (87%). $C_{36}H_{44}Cl_2FeN_6O$ (703.6) calcd.: C 61.46, H 6.30, N 11.95; found C 61.91, H 6.55, N 12.15. MS (FAB in NBA): *m/z* (%) = 630 (1) [M]⁺, 595 (58) [M - Cl]⁺, 560 (33) [M - 2 Cl]⁺, 559 (83) [M - 2 Cl]⁺.

Complex 3b: FeBr₂·2THF (181 mg, 0.50 mmol) and *N*,*N*′-bis(2-pyr-idylmethyl)-1,2-bis(2,4,6-trimethylphenylimino)ethane-1,2-diamine (*oxam2*) (261 mg, 0.52 mmol) were dissolved in THF (40 mL) and stirred overnight, at room temperature. After concentrating the solution to 10 mL, the precipitate was filtered off, washed with THF (3 × 10 mL) and dried by oil pump vacuum (9 h) at room temperature. A light orange solid was obtained. Yield: 317 mg (88%). Single crystals suitable for X-ray-determination were obtained from THF. C₃₂H₃₆Br₂FeN₆ (720.33): calcd. C 53.36; H 5.04; N 11.67; found C 52.44; H 5.22; N 11.07. IR (Nujol): $\tilde{v} = 3127$ (m, NH), 1605, 1622, 1554 cm⁻¹. MS (FAB in NBA): *m*/*z* (%) = 639 (17) [M – Br]⁺, 560 (14)[M – 2 Br]⁺, 559 (83)[M – 2 Br–H]⁺.

Complex 4: [(tbbpy)₂Ru(bbimH₂)](PF₆)₂ (500 mg, 0.43 mmol) was dissolved in predistilled THF. Freshly prepared NaOMe (0.43 mmol) in MeOH was then added, resulting in a bathochromic shift of the absorption. The solution was stirred for 20 min. CF₃COOH (49 mg, 0.43 mmol,) was added to this solution, which resulted in a hypsochromic shift of absorption, the solution was stirred for 20 min, the solvent removed and the precipitate recrystallized from acetone/water resulting in single crystals. ¹H NMR spectra were recorded in deuterated acetone. Yield: 410 mg (84.4%). C₅₅H₆₄F₉N₈O₃PRu (1188.21): calcd. C 55.59, H 5.43, N 9.43; found C 55.87, H 5.13, N 8.84. ¹H NMR ([D₆]acetone): $\delta = 16.4$ (s, 1 H, NH), 8.85 (s, 2 H, 3a-H), 8.75 (s, 2 H, 3b-H), 8.04 (m, 2 H, 6a-H), 8.04 (m, 2 H, 6b-H), 7.76 (d, 2 H, 6-H), 7.61 (d, 2 H, 5a-H), 7.45 (d, 2 H 5b-H), 7.37 (t, 2 H, 5-H) 7.01 (t, 2 H, 4-H), 5.72 (d, 2 H, 3-H), 1.47 (s, 18 H, C₄H₉), 1.35 (s, 18 H, C₄H₉) ppm.

MS (ESI in methanol): m/z (%) = 871 (100) [M - H - PF₆ - CF₃COO]⁺ (isotope pattern found) IR (Nujol): \tilde{v} = 3060 (m, NH), 1776 (s, C=O), 1614 (s, C=N) cm⁻¹.

Complex 5: [(tbbpy)₂Ru(bbimH₂)](Cl)₂ (405 mg, 0.43 mmol) was dissolved in predistilled THF. Freshly prepared NaOMe (0.87 mmol) in MeOH was then added, resulting in a bathochromic shift of the absorption. The solution was stirred for 30 min. C₇F₁₅COOH (358 mg, 0.87 mmol) was added to this solution, which resulted in a hypsochromic shift of the absorption, the solution was stirred for 20 min, the solvent removed and the precipitate recrystallized from acetone/water. ¹H NMR spectra were recorded in deuterated acetone. Yield 705 mg, 92%, ¹H NMR ([D₆]acetone): $\delta = 16.4$ (s, 1 H, NH), 8.85 (s, 2 H, 3a-H), 8.75 (s, 2 H, 3b-H), 8.04 (m, 2 H, 6a-H), 8.04 (m, 2 H, 6b-H), 7.76 (d, 2 H, 6-H), 7.61 (d, 2 H, 5a-H), 7.45 (d, 2 H, 5b-H), 7.37 (t, 2 H, 5-H) 7.01 (t, 2 H, 4-H), 5.72 (d, 2 H, 3-H), 1.47 (s, 18 H, C₄H₉), 1.35 (s, 18 H, C₄H₉) ppm. MS (ESI in methanol): m/z (%) = 871 (100) [M - H - $2 C_7 F_{15} COO]^+$ (isotope pattern found) IR (Nujol): $\tilde{v} = 3060$ (m, NH), 1730 (s, C=O), 1612 (s, C=N) cm^{-1} .

Complex 6: [(tbbpy)₂Ru(bbimH₂)](PF₆)₂ (500 mg, 0.43 mmol) was dissolved in THF. Freshly prepared NaOMe (0.43 mmol) in MeOH was then added, resulting in a bathochromic shift of the color. After stirring for 20 min COOHC₆F₄COOH (0.43 mmol, 103 mg) was added to this solution resulting in a hypsochromic shift of the color. The solution was then stirred for 20 min, the solvent removed and the precipitate recrystallized from acetone/water. Yield 404 mg, 75%, ¹H NMR ([D₆]acetone): $\delta = 8.85$ (s, 2 H, 3a-H), 8.75 (s, 2 H, 3b-H), 8.04 (m, 2 H, 6a-H), 8.04 (m, 2 H, 6b-H), 7.76 (d, 2 H, 6-H), 7.61 (d, 2 H, 5a-H), 7.45 (d, 2 H, 5b-H), 7.37 (t, 2 H, 5-H) 7.01 (t, 2 H, 4-H), 5.72 (d, 2 H, 3-H), 1.47 (s, 18 H, C₄H₉), 1.35 (s, 18 H, C₄H₉) ppm. MS (ESI in methanol): *mlz* (%) = 871 (100) [M – (tbbpy)₂Ru(bbimH₂) – H – 2 PF₆ – COOC₆F₄COO]⁺ (isotope pattern found) IR (Nujol): $\tilde{v} = 3410$ (w, OH), 3177 (m, NH), 1704 (m, C=O), 1613 (s, C=N) cm⁻¹.

Complex 7: Compound **6** (200 mg) was dissolved in acetonitrile/ water (80:20). The color of the solution changed from bright orange to red. The solvent was allowed to evaporate slowly and the small crystals that appeared were collected by filtration. X-ray suitable crystals were obtained by recrystallization from acetonitrile/ water. Yield 110 mg 55%, ¹H NMR ([D₆]acetonitrile): $\delta = 8.51$ (s, 2 H, 3a-H), 8.42 (s, 2 H, 3b-H), 7.87 (d, 2 H, 6a-H), 7.76 (m, 4 H, 6b/6-H), 7.48 (d, 2 H, 5a-H), 7.43 (t, 2 H, 5-H) 7.35 (d, 2 H, 5b-H), 7.06 (t, 2 H, 4-H), 5.68 (d, 2 H, 3-H), 1.47 (s, 18 H, C₄H₉), 1.35 (s, 18 H, C₄H₉) ppm. MS (ESI in methanol): m/z (%) = 871 (100) [M - (tbbpy)₂Ru(bbimH₂) - H - COOC₆F₄COO]⁺ (isotope pattern found) IR (Nujol): $\tilde{v} = 3460$ (m, OH), 3177 (m, NH), 1674 (m, C=O), 1607 (s, C=N) cm⁻¹.

(tbbpy)₃Ru(C₇F₁₅COO)₂: Triethylamine (45 mg, 0.44 mmol) was added to a solution of perfluorooctanoic acid (177 mg, 0.44 mmol) in CH₂Cl₂ while stirring. After 15 minutes this solution was poured into a suspension of [(tbbpy)₃Ru](PF₆)₂ (250 mg, 0.21 mmol in CH₂Cl₂/H₂O, 50:50). This mixture was stirred rapidly for 48 hours. The bright orange-red organic layer was separated and the solvent was removed. The remaining solid was recrystallized from acetone/water (10:1). The absence of the PF₆⁻ anion was established via ³¹P NMR spectroscopy. Yield 363 mg, quantitative C₇₀H₇₂F₃₀O₄N₆Ru (1732.4) calcd.: C 48.53, H 4.19, N 4.85 found C 46.33, H 3.93, N 4.42. ¹H NMR (298 K, 400 MHz, CD₂Cl₂): $\delta = 1.410$ (s, 9 H, CH₃), 7.436 (dd, 1 H, CH-arom.), 7.605 (d, 1 H, CH-arom.), 8.529 (s, 1 H, CH-arom.) ppm. IR (Nujol): $\tilde{v} = 1695$ (s, C=O), 1237, 1202 cm⁻¹ (s, CF). MS (ESI in methanol): *m/z* (%) = 1319 (100) [M - C₇F₁₅COO + 1]⁺, 905 (16) [M - 2 C₇F₁₅COO]⁺.

FULL PAPER

Crystal Structure Determination: The intensity data for the compounds were collected on a Nonius-Kappa CCD diffractometer, using graphite-monochromated Mo- K_a radiation. Data were corrected for Lorentz and polarization effects, but for absorption were only corrected for **3b**.^[32,33] The structures were solved by direct methods (SHELXS^[34]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97^[35]). The diffraction data obtained for compound **5** were insufficient for satisfactory refinement of the structure parameters. However, the data were sufficient to show the structural motif of the molecule (Figure 7), the hydrogenbridging system, and the crystallographic data. The data for compound **5** were not deposited in the Cambridge Crystallographic Data Centre.

For all compounds the hydrogen atoms of the diamine groups and the hydrogen atoms of the water molecule of 7 were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms (without the acetone and the disordered $[PF_6]^-$) were refined anisotropically.^[36] XP (SIE-MENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for 1a:^[36] C₄₀H₄₄Cl₂N₄Ru, $Mr = 752.76 \text{ g·mol}^{-1}$, orange prism, size $0.10 \times 0.10 \times 0.09 \text{ mm}$, monoclinic, space group $P2_1/n$, a = 12.0053(3), b = 18.2083(4), c = 17.2697(3) Å, $\beta = 95.763(2)^\circ$, V = 3756.01(14) Å³, T = -90 °C, Z = 4, $\rho_{calcd} = 1.331$ g·cm⁻³, μ (Mo- K_{α}) = 5.92 cm⁻¹, F(000) = 1560, 15215 reflections in h (-15/15), k (-23/21), l (-22/22), measured in the range 2.27° $\leq \Theta \leq 27.50^\circ$, completeness $\Theta_{max} = 98.8\%$, 8535 independent reflections, $R_{int} = 0.036$, 7120 reflections with $F_o > 4\sigma(F_o)$, 427 parameters, 0 restraints, $R1_{obs} = 0.0547$, $wR_{obs}^2 = 0.142$, $R1_{all} = 0.067$, $wR_{all}^2 = 0.152$, GOOF = 1.085, largest difference peak and hole: 1.219/-1.074 e·Å^{-3}.

Crystal Data for 1b:^[36] [C₄₀H₄₄ClN₄Ru(BF₄)], Mr = 804.12g·mol⁻¹, red-orange prism, size $0.10 \times 0.10 \times 0.03$ mm, orthorhombic, space group $P2_12_12_1$, a = 11.0377(2), b = 18.0910(3), c = 19.2852(4) Å, V = 3850.93(12) Å³, T = -90 °C, Z = 4, $\rho_{calcd.} = 1.387$ g·cm⁻³, μ (Mo- K_a) = 5.29 cm⁻¹, F(000) = 1656, 8625 reflections in h (-14/14), k (-23/23), l (-24/25), measured in the range 2.41° $\leq \Theta \leq 27.47^\circ$, completeness $\Theta_{max} = 98.7\%$, 8625 independent reflections, $R_{int} = 0.042$, 8018 reflections with $F_o > 4\sigma(F_o)$, 466 parameters, 0 restraints, $R1_{obs} = 0.032$, $wR_{obs}^2 = 0.079$, $R1_{all} = 0.037$, $wR_{all}^2 = 0.084$, GOOF = 1.036, Flack-parameter -0.04(2), largest difference peak and hole: 0.484/-0.501 e·Å⁻³.

Crystal Data for 1c:^[36] [C₄₀H₄₄ClN₄O₂Ru(CF₃COO)], Mr = 830.33 gmol⁻¹, red-orange prism, size 0.10 × 0.10 × 0.05 mm, triclinic, space group $P\bar{1}$, a = 10.9028(8), b = 13.4278(8), c = 13.5573(9) Å, a = 92.835(5), $\beta = 93.959(4)$, $\gamma = 93.280(4)^{\circ}$, V = 1974.0(2) Å³, T = -90 °C, Z = 2, $\rho_{calcd.} = 1.397$ g·cm⁻³, μ (Mo- K_a) = 5.19 cm⁻¹, F(000) = 856, 13866 reflections in h (-14/11), k (-15/17), l (-16/17), measured in the range $1.88^{\circ} \le \Theta \le 27.46^{\circ}$, completeness $\Theta_{max} = 98.7\%$, 8921 independent reflections, $R_{int} = 0.042$, 6350 reflections with $F_o > 4\sigma(F_o)$, 486 parameters, 0 restraints, $R1_{obs} = 0.059$, $wR_{obs}^{2} = 0.128$, $R1_{all} = 0.097$, $wR_{all}^{2} = 0.148$, GOOF = 1.037, largest difference peak and hole: 0.634/-0.701 e·Å⁻³.

Crystal Data for 2:^[36] C₈₀H₈₄Cl₄N₈Pd₂Ru₂·4C₇H₈, Mr = 2082.83 g·mol⁻¹, black-red prism, size 0.10 × 0.09 × 0.06 mm, monoclinic, space group $P2_1/c$, a = 13.6852(4), b = 18.2930(7), c = 19.9623(7) Å, $\beta = 101.706(2)^\circ$, V = 4893.5(3) Å³, T = -90 °C, Z = 2, $\rho_{calcd.} = 1.414$ g·cm⁻³, μ (Mo- K_{α}) = 8.25 cm⁻¹, F(000) = 2136, 14535 reflections in h (-15/17), k (-20/23), l (-25/25), measured in the range 3.74° $\leq \Theta \leq 27.46^\circ$, completeness $\Theta_{max} = 88.8\%$, 9942 inde-

pendent reflections, $R_{int} = 0.028$, 8442 reflections with $F_o > 4\sigma(F_o)$, 559 parameters, 0 restraints, $R1_{obs} = 0.048$, $wR_{obs}^2 = 0.120$, $R1_{all} = 0.062$, $wR_{all}^2 = 0.134$, GOOF = 1.099, largest difference peak and hole: 1.328/-0.865 e'Å⁻³.

Crystal Data for 3a:^[36] C₃₂H₃₆Cl₂FeN₆·C₄H₈O, *Mr* = 703.52 g·mol⁻¹, orange prism, size 0.10 × 0.09 × 0.08 mm, monoclinic, space group *P*2₁/*c*, *a* = 9.7875(2), *b* = 13.6051(3), *c* = 27.9561(5) Å, β = 98.710(1)°, *V* = 3679.70(13) Å³, *T* = -90 °C, *Z* = 4, ρ_{caled.} = 1.270 g·cm⁻³, μ(Mo-*K*_a) = 5.91 cm⁻¹, *F*(000) = 1480, 27538 reflections in *h* (-12/12), *k* (-17/17), *l* (-36/35), measured in the range 2.10° ≤ Θ ≤ 27.46°, completeness Θ_{max} = 99.3%, 8375 independent reflections, *R*_{int} = 0.066, 6324 reflections with *F*_o > 4σ(*F*_o), 411 parameters, 10 restraints, *R*1_{obs} = 0.060, *wR*²_{obs} = 0.165, *R*1_{all} = 0.081, *wR*²_{all} = 0.184, GOOF = 1.020, largest difference peak and hole: 0.931/-0.577 e·Å⁻³.

Crystal Data for 3b:^[36] C₃₂H₃₆Br₂FeN₆·2.5C₄H₈O, Mr = 900.60 g·mol⁻¹, red-brown prism, size $0.08 \times 0.08 \times 0.06$ mm, triclinic, space group $P\bar{1}$, a = 15.9361(7), b = 18.4001(8), c = 18.5403(6) Å, a = 97.792(3), $\beta = 113.089(3)$, $\gamma = 108.091(2)^\circ$, V = 4543.2(3) Å³, T = -90 °C, Z = 4, $\rho_{calcd.} = 1.317$ g·cm⁻³, μ (Mo- K_a) = 21.31 cm⁻¹, semi-empirical, transmin: 0.5701, transmax: 0.6280, F(000) = 1864, 34660 reflections in h (-20/20), k (-22/23), l (-24/22), measured in the range 2.59° ≤ $\Theta \le 27.42^\circ$, completeness $\Theta_{max} = 91.2\%$, 18862 independent reflections, $R_{int} = 0.067$, 10654 reflections with $F_o > 4\sigma(F_o)$, 929 parameters, 0 restraints, $R1_{obs.} = 0.095$, $wR_{obs.}^2 = 0.232$, $R1_{all} = 0.169$, $wR_{all}^2 = 0.286$, GOOF = 1.034, largest difference peak and hole: 2.981/-1.214 e·Å⁻³.

Crystal Data for 4:^[36] [C₅₀H₅₈N₈Ru(C₂F₃O₂)][PF₆]·C₃H₆O, $Mr = 1188.18 \text{ g} \cdot \text{mol}^{-1}$, orange prism, size 0.12 × 0.10 × 0.10 mm, monoclinic, space group $P2_1/n$, a = 16.499(3), b = 18.947(4), c = 18.518(4) Å, $\beta = 99.09(3)^\circ$, V = 5716(2) Å³, T = -90 °C, Z = 4, $\rho_{\text{calcd.}} = 1.381 \text{ g} \cdot \text{cm}^{-3}$, μ (Mo- K_a) = 3.81 cm⁻¹, F(000) = 2456, 46833 reflections in h (-20/21), k (-23/24), l (-21/24), measured in the range 2.10° ≤ $\Theta \le 27.51^\circ$, completeness $\Theta_{\text{max}} = 98\%$, 12884 independent reflections, $R_{\text{int}} = 0.089$, 7991 reflections with $F_o > 4\sigma(F_o)$, 673 parameters, 36 restraints, $R1_{\text{obs.}} = 0.072$, $wR_{\text{obs.}}^2 = 0.205$, $R1_{\text{all}} = 0.114$, $wR_{\text{all}}^2 = 0.224$, GOOF = 1.336, largest difference peak and hole: 1.452/-1.101 e·Å^{-3}.

Crystal Data for 5: $[C_{50}H_{58}N_8Ru(C_7F_{15}COO)](C_7F_{15}COO)$, $Mr = 1578.17 \text{ g}\cdot\text{mol}^{-1}$, red-brown prism, size $0.20 \times 0.18 \times 0.12 \text{ mm}$, triclinic, space group $P\bar{1}$, a = 15.880(3), b = 21.334(4), c = 29.081(6) Å, a = 75.96(3), $\beta = 88.66(3)$, $\gamma = 86.98(3)^\circ$, V = 9544(3) Å³, T = -90 °C, Z = 4, $\rho_{calcd.} = 1.098 \text{ g}\cdot\text{cm}^{-3}$, $\mu(\text{Mo-}K_a) = 2.58 \text{ cm}^{-1}$, F(000) = 3184, 43889 reflections in h (-20/20), k (-27/22), l (-35/36), measured in the range $1.07^\circ \le \Theta \le 27.47^\circ$, completeness $\Theta_{\text{max}} = 78\%$, 34097 independent reflections.

Crystal Data for 6:^[36] [(C₅₀H₅₈N₈Ru)₂{C₄F₄(COO)₂}](PF₆)₂· 3(CH₃)₂CO, $Mr = 2462.50 \text{ g} \cdot \text{mol}^{-1}$, red-brown prism, size 0.10 × 0.09 × 0.08 mm, triclinic, space group $P\bar{1}$, a = 13.6330(4), b = 14.2867(5), c = 16.7479(5) Å, a = 98.356(2), $\beta = 94.201(2)$, $\gamma = 100.148(2)^{\circ}$, V = 3160.47(17) Å³, T = -90 °C, Z = 2, $\rho_{calcd.} = 1.294 \text{ g} \cdot \text{cm}^{-3}$, μ (Mo- K_{a}) = 3.46 cm⁻¹, F(000) = 1276, 20848 reflections in h (-17/17), k (-14/18), l (-21/21), measured in the range $3.07^{\circ} \le \Theta \le 27.47^{\circ}$, completeness $\Theta_{max} = 96.3\%$, 13947 independent reflections, $R_{int} = 0.028$, 11364 reflections with $F_o > 4\sigma(F_o)$, 731 parameters, 1 restraints, $R1_{obs} = 0.060$, $wR_{obs}^{\circ} = 0.159$, $R1_{all} = 0.078$, $wR_{all}^{2} = 0.1775$, GOOF = 1.055, largest difference peak and hole: 1.351/-0.589 e Å^{-3}.

Crystal Data for 7:^[36] $[(C_{50}H_{59}N_8Ru)_2\{C_4F_4(COO)_2\}][C_4F_4(COO)_2]\cdot H_2O\cdot 3CH_3CN, Mr = 2155.50 \text{ g·mol}^{-1}, \text{ red-brown prism},$

size $0.12 \times 0.10 \times 0.09$ mm, triclinic, space group $P\overline{1}$, a = 10.3448(2), b = 15.5248(4), c = 19.5865(5) Å, a = 88.110(1), $\beta = 78.075(1)$, $\gamma = 70.915(1)$ °, V = 2906.52(12) Å³, T = -90°C, Z = 1, $\rho_{calcd.} = 1.231$ g·cm⁻³, μ (Mo- K_a) = 3.26 cm⁻¹, F(000) = 1126, 20157 reflections in h (-12/13), k (-19/17), l (-22/25), measured in the range 7.07° $\leq \Theta \leq 27.45^{\circ}$, completeness $\Theta_{max} = 95.3\%$, 12680 independent reflections, $R_{int} = 0.033$, 10139 reflections with $F_o > 4\sigma(F_o)$, 668 parameters, 0 restraints, $R_{1obs.} = 0.060$, $wR_{obs}^2 = 0.150$, $R_{1all} = 0.083$, $wR_{all}^2 = 0.169$, GOOF = 1.053, largest difference peak and hole: 1.171/-0.567 e·Å⁻³.

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