Synthesis and Structural and Spectroscopic Characterization of New Ru^{II}-dmso Precursors with Face-Capping Ligands for Use in Self-Assembly Reactions

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The aim of this work is the preparation of new, easy-to-make, octahedral Ru^{II} precursors with facial geometry to be used in self-assembly reactions. We chose dmso as a leaving group and 1,4,7-trithiacyclononane ([9]aneS$_3$), tris(pyrazolyl)methane [CH(pz)$_3$, pz = pyrazol-1-yl], or triphos [CH$_3$C(CH$_2$PPh$_2$)$_3$] as the face-capping ligand (fcl). We describe here the preparation and structural characterization of three new dicationic Ru^{II} complexes (as triflate salts) of the type *fac*-[Ru(fcl)(solv)$_3$]$^{2+}$, namely *fac*-[Ru([9]aneS$_3$)(dmso-O)(dmso-S)$_2$]$^{2+}$ (**3b**), which equilibrates in solution with the linkage isomer *fac*-[Ru([9]aneS$_3$)(dmso-O)$_2$(dmso-S)]$^{2+}$ (**3a**), *fac*-[Ru{CH(pz)$_3$}(dmso-O)(dmso-S)$_2$]$^{2+}$ (**7**), and *fac*-[Ru(triphos)(dmso-O)$_2$(H$_2$O)]$^{2+}$ (**9**). In all cases the preferred synthetic procedure involved coordination of the face-capping ligand to *cis*-[RuCl$_2$(dmso)$_4$] first, followed by replacement of the chlorides with dmso (or water) molecules assisted by addition of AgCF$_3$SO$_3$ (AgOTf). NMR investigations showed that hydrolysis of the dmso ligands occurs very easily for **3** in water and for **9** in chloroform, while for complex **7** only the O-bound dmso ligand is replaced in water. In the course of this work, the following complexes were also isolated and structurally characterized: *fac*-[Ru([9]aneS$_3$)Cl(dmso-S)$_2$][OTf] (**2**), *trans*,*cis*,*cis*-[RuCl$_2$(dmso-S)$_2${CH(pz)$_2$(pz)}] (**4**), *trans*,*cis*,*cis*-[RuCl$_2$(dmso-S)$_2$(pzH)$_2$] (**5**), *fac*-[Ru{CH(pz)$_3$}Cl$_2$(dmso-S)] (**6**), *fac*-[Ru([9]aneS$_3$)(py)$_3$][OTf]$_2$ (**11**), *fac*-[Ru([9]aneS$_3$)(py)$_2$(CH$_3$CN)][OTf]$_2$ (**13**), and *fac*-[Ru([9]aneS$_3$O)(dmso-O)$_2$(dmso-S)][OTf]$_2$ ([9]aneS$_3$O = 1,4,7-trithiacyclononane 1-oxide); in **4** the tripodal tris(pyrazolyl)methane acts as a bidentate ligand.

Introduction

Metal-mediated synthetic procedures involving the self-assembly of electron-donor building blocks (polytopic organic ligands) and electron-acceptor components (naked ions or coordination compounds with some labile ligands) are increasingly being exploited for the preparation of stable, shape-persistent supramolecular assemblies of nanoscopic dimensions.[1] Fascinating three-dimensional systems have been reported by several groups.[2,3] Compared to naked ions, in which the number of available coordination sites for self-assembly and their geometry is determined by the nature of the ion, the use of suitable coordination compounds allows, in principle, a better control of the number and geometry of such sites. In addition, useful properties can be introduced into the supramolecular systems by the nonparticipating ligands. Also, the solubility of the products can be largely influenced by the nature of the ancillary ligands at the metal centers.

However, a literature survey shows that, while a large number of polytopic organic ligands have been employed for the construction of metal-mediated supramolecular assemblies, the number of metal-containing components is relatively limited. Most frequently used are the square-planar complexes [Pd(en)(ONO$_2$)$_2$] (en = ethylenediamine),[3e–3g,3k,4] [Pd(bipy)(ONO$_2$)$_2$] (both soluble in water),[5] and [Pd(dppp)(OTf)$_2$] [soluble in chlorinated solvents, dppp = 1,2-bis(diphenylphosphanyl)propane, OTf = CF$_3$SO$_3$, triflate],[3d,6] which yield *cis* bifunctional dicationic metal fragments after dissociation of the two weakly coordinated anions. Square-planar complexes with labile neutral ligands, such as *cis*-[PtCl$_2$(PhCN)$_2$] and *trans*-[PdCl$_2$(PhCN)$_2$], which yield the bifunctional metal fragments *cis*-PtCl$_2$ and *trans*-PdCl$_2$, respectively, have also been employed in self-assembly reactions.[7] The use of octahedral coordination complexes is more rare and, in most cases, concerns complexes such as [ReX(CO)$_5$] (X = Cl, Br)[8] or *trans*-[RuCl$_2$(dmso)$_2$(L)$_2$] (L = CO, dmso)[9] that yield the *cis* bifunctional neutral fragments *fac*-ReX(CO)$_3$ and *trans*,*cis*-RuCl$_2$(L)$_2$, respectively.

Even though the two coordination sites available in these metal fragments define a linear or planar geometry, 3D adducts have been obtained; tridimensionality can be induced by flexible organic polytopic ligands or by a noncoplanar mutual orientation of planar rigid fragments. In general, in both cases, the shape of the 3D product is rarely predictable a priori.

We believe that the field of coordination-driven self-assembly would greatly benefit from the introduction of new,

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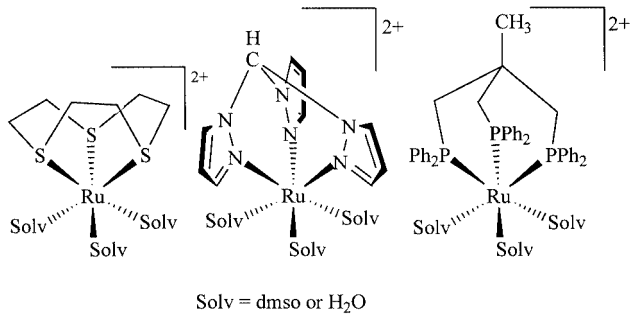
easy-to-make, coordination compounds having three (or more) readily available coordination sites for self-assembly. In particular, we are interested in the development of low-valent metal fragments with three sites in facial geometry occupied by good leaving groups, either weak neutral ligands (e.g. solvent molecules) or weakly coordinating anions. In such cases the tridimensionality of the adduct would be inherently determined by that of the metal fragment. The remaining three positions must be firmly held by nonparticipating ligands, so that neither dissociation nor isomerization occur during the substitution reaction with the bridging building blocks. Thus, the three permanent facial atoms may be conveniently embedded in a face-capping ligand (fcl), either a heterocycle,[10–12] a tripodal ligand,[13,14] or an organometallic fragment such as η^5-cyclopentadienyl or η^6-arene.[15]

Even though most of the low-valent, half-sandwich complexes described in the literature were not specifically developed for use in self-assembly reactions (for example, they have been widely investigated as homogeneous catalysts),[16] there are some remarkable exceptions.[3a,12,17] For example, Ru^{II}-, Rh^{III}-, and Ir^{III}-arene fragments have been exploited as building blocks for the construction of supramolecular cubes and metallamacrocyclic complexes.[3a,17] One striking example with a nonorganometallic fragment is that of the molecular cube $[\{Ru([9]aneS_3)\}_8(\mu\text{-}4,4'\text{-bipy})_{12}][OTf]_{16}$ ([9]aneS$_3$ = 1,4,7-trithiacyclononane), which is obtained by treatment of *fac*-[Ru([9]aneS$_3$)Cl$_2$(dmso-S)] with the linear ditopic ligand 4,4′-bipy in an 8:12 stoichiometry in noncoordinating solvents. The *fac*-Ru([9]aneS$_3$) and 4,4′-bipy fragments form the corners and edges of the cube, respectively.[12a] However, this synthetic procedure requires prolonged reaction times and heating (four weeks in nitromethane at refluxing temperature), and the addition of AgOTf to remove chlorides. In an ideal metal-mediated self-assembly process, two (or more) components are mixed in solution in the appropriate ratio and react spontaneously with each other to afford the desired product; external interventions, such as addition of silver salts to remove coordinated halides and filtration of precipitates (other than the product), should be avoided. Therefore, precursors with more-labile leaving ligands, such as those mentioned above, would be much preferred for self-assembly purposes.

In this work we report our results concerning the preparation of three new, easy-to-make [Ru(fcl)(solv)$_3$][OTf]$_2$ complexes {fcl = [9]aneS$_3$, tris(pyrazolyl)methane [CH-(pz)$_3$, pz = pyrazol-1-yl], or triphos [CH$_3$C(CH$_2$PPh$_2$)$_3$]; solv = dmso or H$_2$O} (Scheme 1); dmso was chosen as, in our experience with ruthenium precursors, it is normally a better leaving group than the widely used CH$_3$CN. The three face-capping ligands were chosen with the aim of investigating a range of electronic, steric, and solubility properties; in addition, they are either commercially available or very easily prepared and, unlike the organometallic fragments, their reactions do not require the use of Schlenk techniques. In the case of triphos, we partially revisited the work of Venanzi and co-workers on the Ru/dmso/triphos systems.[13]



Scheme 1. Schematic representations of the Ru^{II} complexes with face-capping ligands discussed in this work.

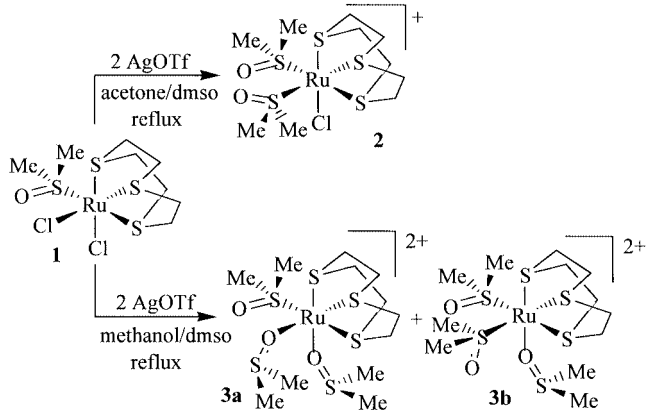
Results

The main ruthenium precursor used in this work is the well known complex *cis*-[RuCl$_2$(dmso)$_4$]. Several examples in the literature indicate that the reaction of *cis*-[RuCl$_2$(dmso)$_4$] with one equivalent of a neutral, face-capping ligand usually leads to *fac*-[Ru(fcl)Cl$_2$(dmso-S)] complexes after replacement of three facial sulfoxides (one O-bonded and two S-bonded).[18] Treatment of *fac*-[Ru(fcl)-Cl$_2$(dmso-S)] with two equivalents of a soluble silver salt, such as AgOTf, in a weakly coordinating solvent (solv) is expected to yield the desired *fac*-[Ru(fcl)(solv)$_3$][OTf]$_2$ complexes.[11a,13,18] For example, the reaction of *fac*-[Ru([9]-aneS$_3$)Cl$_2$(dmso-S)] (**1**) with AgOTf in refluxing acetonitrile produces *fac*-[Ru([9]aneS$_3$)(CH$_3$CN)$_3$][OTf]$_2$ in excellent yield.[11a]

As an alternative, in some cases we also employed the dicationic precursor *fac*-[Ru(dmso-S)$_3$(dmso-O)$_3$][OTf]$_2$. In this synthetic approach removal of the chlorides from *cis*-[RuCl$_2$(dmso)$_4$] occurred first and was followed by coordination of the face-capping ligand (see also Scheme 5).

Compounds with 1,4,7-Trithiacyclononane ([9]aneS$_3$)

The complex *fac*-[Ru([9]aneS$_3$)Cl$_2$(dmso-S)] (**1**), despite being an excellent precursor for inorganic synthesis,[11,12] is not suitable *as such* for facial self-assembly reactions with neutral, monodentate bridging ligands, as chloride replace-



Scheme 2.

ment needs the assistance of Ag^+.[12d–12f] For example, *fac*-[Ru([9]aneS$_3$)(L)$_3$][PF$_6$]$_2$ complexes (L = py or 4,4′-bipy) can be obtained by treatment of **1** with $AgPF_6$ and a large excess of ligand (L/Ru = in the range from 14 to 25) in refluxing ethanol/water mixtures.[12b,12c]

With the aim of preparing *fac*-[Ru([9]aneS$_3$)(dmso)$_3$][OTf]$_2$, we found that the reaction of **1** with two equivalents of AgOTf in refluxing acetone in the presence of dmso afforded a crystalline product (**2**) that, according to spectroscopic investigations and X-ray diffraction analysis, was established to be the monocationic complex *fac*-[Ru([9]aneS$_3$)Cl(dmso-S)$_2$][OTf] (**2**) (Scheme 2, Figure 1).[19] The same product was also obtained when the above reaction was performed in pure dmso at 100 °C.

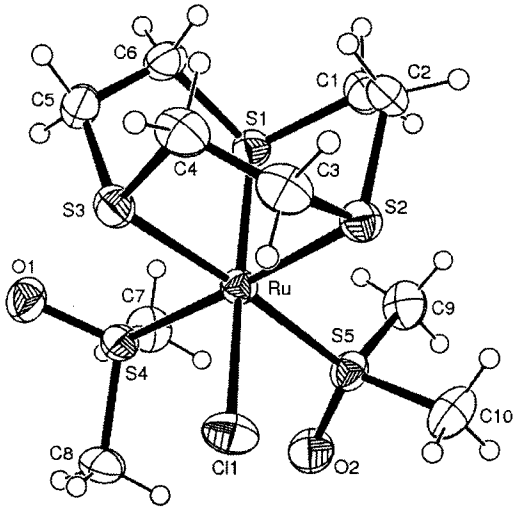


Figure 1. Molecular structure of the cation of *fac*-[Ru([9]aneS$_3$)Cl(dmso-S)$_2$][OTf] (**2**) with thermal ellipsoids at the 40% probability level. Selected bond lengths [Å] and angles [°]: Ru–S(1) 2.313(1), Ru–S(2) 2.346(1), Ru–S(3) 2.351(1), Ru–S(4) 2.325(1), Ru–S(5) 2.339(1), Ru–Cl(1) 2.420(1); S(2)–Ru–S(4) 174.69(3), S(3)–Ru–S(5) 175.21(3), S(1)–Ru–Cl(1) 173.03(3).

Replacement of both chlorides of **1** with dmso molecules was accomplished by performing the reaction with a slight excess of AgOTf in refluxing methanol in the presence of dmso (Scheme 2).

The IR spectrum of the product, which analyzed correctly for [Ru([9]aneS$_3$)(dmso)$_3$][OTf]$_2$ (**3**), showed the presence of both S-bonded (S=O stretching at $\tilde{\nu}$ = 1088 cm^{-1}) and O-bonded (S=O stretching at $\tilde{\nu}$ = 933 and 914 cm^{-1}) dmso molecules. The ^{1}H NMR spectrum of **3** in noncoordinating solvents (e.g. CD_3NO_2 or [D$_6$]acetone), besides many, low-intensity multiplets for the [9]aneS$_3$ protons between δ = 2.8 and 3.4 ppm, contains two sets of signals in an approximate 2.5 to 1 ratio in the region of dmso resonances; the most abundant has two singlets for dmso-O and one for dmso-S ligands, while the less abundant one has one singlet for dmso-O and two for dmso-S ligands (Figure 2). These two sets were attributed to the linkage isomers *fac*-[Ru([9]aneS$_3$)(dmso-O)$_2$(dmso-S)]$^{2+}$ (**3a**) and *fac*-[Ru([9]aneS$_3$)(dmso-O)(dmso-S)$_2$]$^{2+}$ (**3b**), respectively. In each isomer there are two equivalent dmso ligands with diastereotopic methyl groups; accordingly, their NMR resonances are slightly broader than that of the other dmso because of the long-range coupling ($^4J_{H,H} \approx 0.5$ Hz).[20]

X-ray structural determinations performed on crystals selected both from the raw material and from a sample recrystallized from acetone (at room temperature, upon addition of diethyl ether) gave the same results: in both cases the solid-state structure corresponded to *fac*-[Ru([9]aneS$_3$)(dmso-O)(dmso-S)$_2$][OTf]$_2$ (**3b**), i.e. the less-abundant isomer in solution (Figure 3).[21] It is noteworthy that the Ru–S distance in **3b***trans* to dmso-O [2.298(1) Å] is shorter than the values observed for the other S atoms of [9]aneS$_3$ [mean value 2.352(1) Å].

Dissolution of the crystals in CD_3NO_2 or [D$_6$]acetone afforded the usual NMR spectrum, with the same ratio between **3a** and **3b**, thus suggesting that an equilibrium between the two linkage isomers occurs in solution. However, saturation of the dmso resonances of one isomer did not result in any appreciable transfer of saturation to those of the other one, thus indicating that the equilibrium must be quite slow on the NMR timescale. As progressive hydrolysis

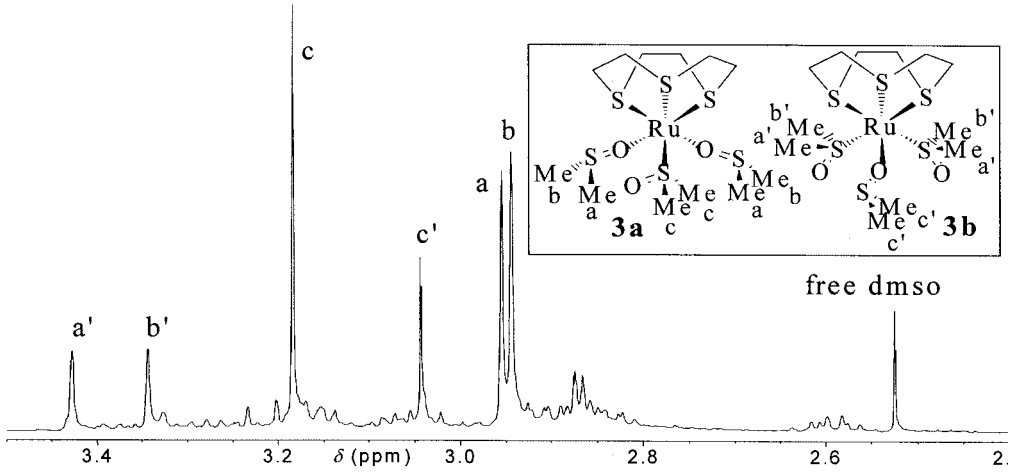


Figure 2. ^{1}H NMR spectrum (CD_3NO_2) of the mixture of the two linkage isomers **3a** and **3b**; dmso singlets are labeled (see insert for labeling scheme). The other small resonances belong to [9]aneS$_3$ protons.

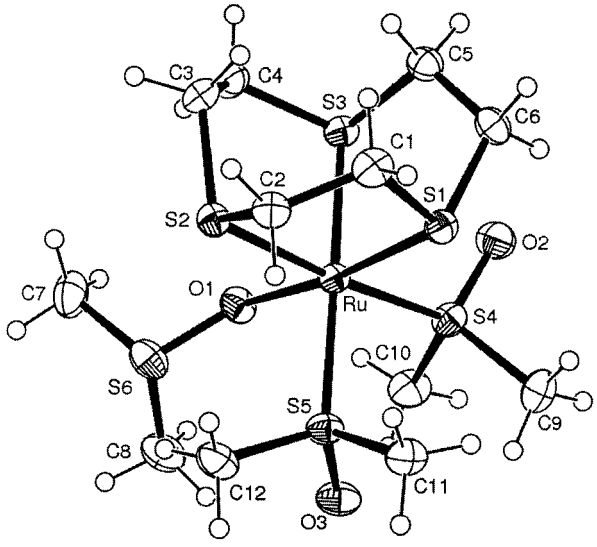


Figure 3. Molecular structure of the cation of *fac*-[Ru([9]aneS$_3$)(dmso-O)(dmso-S)$_2$][OTf]$_2$ (**3b**) with thermal ellipsoids at the 40% probability level. Selected bond lengths [Å] and angles [°]: Ru–O(1) 2.169(3), Ru–S(1) 2.298(1), Ru–S(2) 2.350(1), Ru–S(3) 2.355(1), Ru–S(4) 2.326(1), Ru–S(5) 2.307(1); O(1)–Ru–S(1) 171.49(10), S(2)–Ru–S(4) 174.15(5), S(3)–Ru–S(5) 176.64(5).

of coordinated dmso was observed (minutes), it was not possible to perform a saturation-transfer experiment (and/or line-shape analysis) above room temperature.

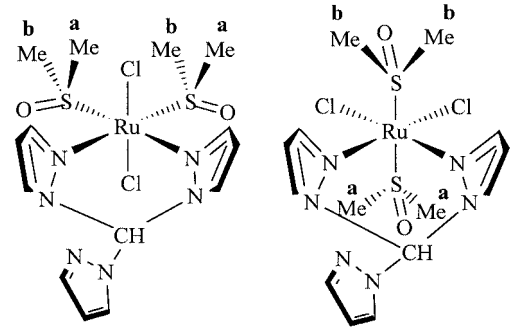
We also found that the reaction of *fac*-[Ru(dmso-S)$_3$(dmso-O)$_3$][OTf]$_2$ with *one* equivalent of [9]aneS$_3$ in a number of refluxing solvents (nitromethane, methanol, chloroform, and chloroform/acetone mixtures) yielded only mixtures of the unreacted precursor and of the fully substituted product [Ru([9]aneS$_3$)$_2$][OTf]$_2$, identified by elemental analysis and by comparison with the NMR spectrum reported in the literature.[22]

The ^{1}H NMR spectrum of *fac*-[Ru([9]aneS$_3$)(dmso)$_3$]$^{2+}$ (mixture of the two isomers) in D$_2$O showed that hydrolysis of the dmso ligands occurs within minutes after dissolution (the resonance of a species with one coordinated dmso-S, δ = 3.31 ppm, that integrates for 1/3 of the free dmso appears and remains unchanged for longer observation times, up to 2 days). Under the same conditions only very slow hydrolysis of acetonitrile from *fac*-[Ru([9]aneS$_3$)(CH$_3$CN)$_3$]$^{2+}$ was observed (ca. 30% after one week at ambient temperature).

Compounds with Tris(pyrazolyl)methane [CH(pz)$_3$]

The reaction of *cis*-[RuCl$_2$(dmso)$_4$] with tris(pyrazolyl)methane, CH(pz)$_3$, has not been described so far. We found that treatment of *cis*-[RuCl$_2$(dmso)$_4$] with one equivalent of CH(pz)$_3$ in refluxing methanol yielded a yellow precipitate and large, deep-orange crystals. The mixture was found to contain three products, **4**–**6**, in approximately equimolar amounts (NMR ratio measured in [D$_6$]DMSO, in which the mixture is well soluble), which were separated and obtained in pure form (see Experimental Section).

The elemental analysis of compound **4** was consistent with the formula [RuCl$_2$(dmso)$_2$CH(pz)$_3$], and the solid-state IR spectrum indicated the presence of S-bonded dmso exclusively. The ^{1}H NMR spectrum of **4** in CDCl$_3$ shows two singlets for dmso-S, integrating for six protons each, which is consistent with two geometries, each featuring a bidentate coordination for the tris(pyrazolyl)methane, CH(pz)$_2$(pz): either *trans,cis,cis*-[RuCl$_2$(dmso-S)$_2${CH(pz)$_2$(pz)}] or *cis,trans,cis*-[RuCl$_2$(dmso-S)$_2${CH(pz)$_2$(pz)}] (Scheme 3).[23] In the first hypothesis the two dmso-S ligands are equivalent but have diastereotopic methyls, while in the second hypothesis the two *trans* dmso-S ligands have enantiotopic methyl groups but are not equivalent as the N$_2$Cl$_2$ plane is not a plane of symmetry for the complex.



Scheme 3. The two possible geometries of compound **4** that are compatible with the observed ^{1}H NMR spectrum.

A *cis,cis,cis* geometry can be excluded since four methyl resonances for the two sulfoxides would be expected. The *trans,cis,cis*-[RuCl$_2$(dmso-S)$_2${CH(pz)$_2$(pz)}] geometry was eventually confirmed by an X-ray structural investigation (Figure 4), which showed that the tris(pyrazolyl)methane in **4** indeed acts as a bidentate ligand, with a chelating angle of 81.61(13)°.

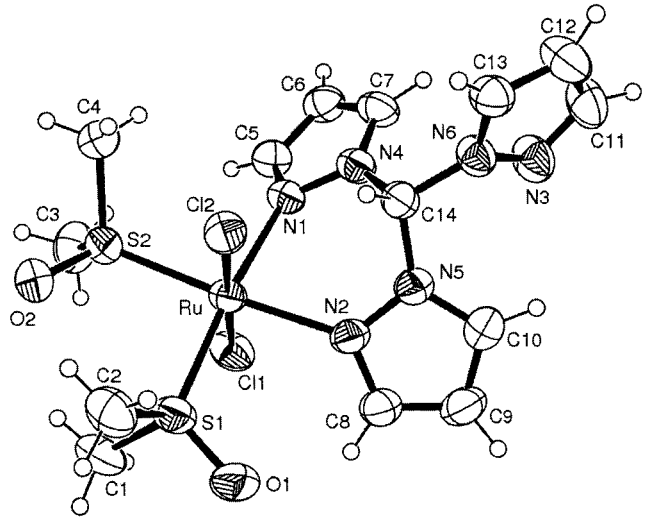


Figure 4. Molecular structure of *trans,cis,cis*-[RuCl$_2$(dmso-S)$_2${CH(pz)$_2$(pz)}] (**4**) with thermal ellipsoids at the 40% probability level. Selected bond lengths [Å] and angles [°]: Ru–N(1) 2.119(3), Ru–N(2) 2.148(4), Ru–S(1) 2.278(1), Ru–S(2) 2.262(1), Ru–Cl(1) 2.402(1), Ru–Cl(2) 2.416(1); N(1)–Ru–N(2) 81.61(13), N(1)–Ru–S(1) 173.84(10), N(2)–Ru–S(2) 176.01(9), Cl(1)–Ru–Cl(2) 179.04(5).

Complex **4** was also selectively prepared in good yield by reaction of *trans*-[$RuCl_2$(dmso-S)$_4$] with one equivalent of $CH(pz)_3$ in chloroform at ambient temperature. It is in fact well known that *trans*-[$RuCl_2$(dmso-S)$_4$] replaces two *cis* dmso-S ligands to affording the *trans,cis*-$RuCl_2$(dmso-S)$_2$ fragment selectively.[24]

The ^{1}H NMR spectrum of **5** in $CDCl_3$ is very simple (see Experimental Section), suggesting that the complex must be highly symmetrical and that, most likely, simple pyrazole ligands (pzH), derived from the decomposition of tris(pyrazolyl)methane, are bound to ruthenium. X-ray analysis confirmed this hypothesis, indicating that the molecular structure of **5** is *trans,cis,cis*-[$RuCl_2$(dmso-S)$_2$(pzH)$_2$] (see Supporting Information). Complex **5**, which had been already prepared by Taqui Khan and co-workers by treatment of *cis*-[$RuCl_2$(dmso)$_4$] with two equivalents of pyrazole in acetonitrile at 60 °C,[25] is structurally similar to **4**, as it contains two *cis* pyrazole ligands instead of the two *cis* pyrazole units belonging to $CH(pz)_3$ found in **4**.

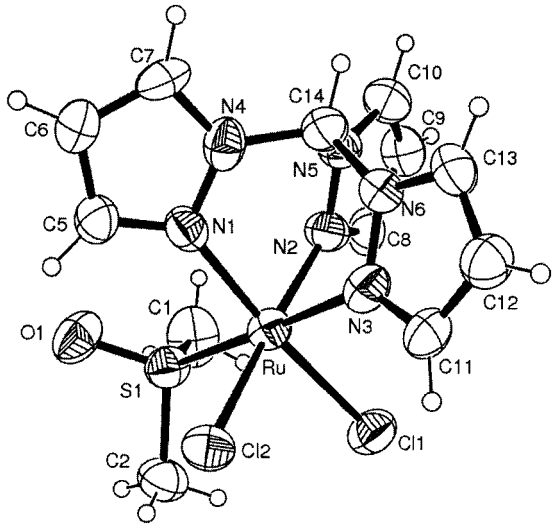
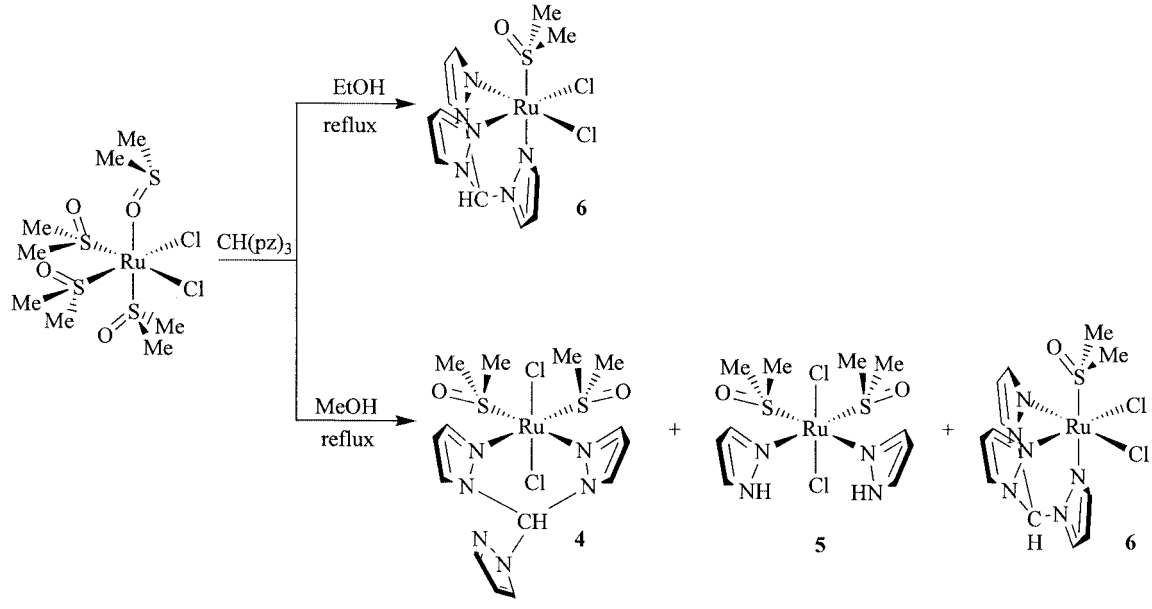


Figure 5. Molecular structure of *fac*-[Ru{CH(pz)$_3$}Cl$_2$(dmso-S)] (**6**) with thermal ellipsoids at the 40% probability level. Selected bond lengths [Å] and angles [°]: Ru–N(1) 2.052(9), Ru–N(2) 2.049(11), Ru–N(3) 2.078(10), Ru–S(1) 2.251(4), Ru–Cl(1) 2.419(3), Ru–Cl(2) 2.406(3); N(1)–Ru–N(2) 87.8(4), N(1)–Ru–N(3) 84.4(4), N(2)–Ru–N(3) 83.3(4), N(1)–Ru–Cl(1) 174.8(4), N(2)–Ru–Cl(2) 172.4(3), N(3)–Ru–S(1) 177.1(3).

Elemental analysis of the third product, **6**, suggested an [$RuCl_2$(dmso)CH(pz)$_3$] stoichiometry. The pattern of the downfield region of the ^{1}H NMR spectrum of **6** in noncoordinating solvents (CD_3NO_2) is similar to that of complex **4**, as it shows two sets of pyrazole resonances with a 2:1 intensity ratio and a singlet at δ = 8.87 ppm for the CH proton of tris(pyrazolyl)methane. The region of the dmso resonances contains one singlet for dmso-S (δ = 3.41 ppm), integrating for six protons. The NMR spectrum of **6** is thus consistent with a *fac*-[Ru{CH(pz)$_3$}Cl$_2$(dmso-S)] geometry in which the two pz units *trans* to the chlorides are equivalent and the methyl groups of dmso-S are enantiotopic. This geometry was confirmed by an X-ray investigation (Figure 5).

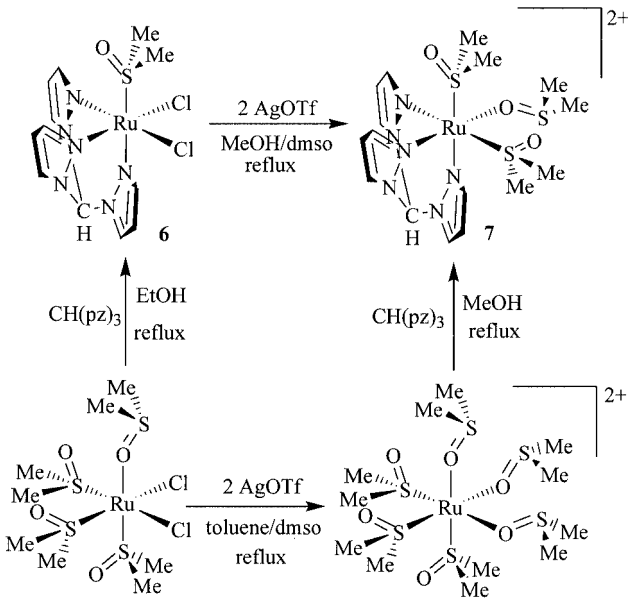
As anticipated in the Introduction, complex **6** is the product expected from the reaction of *cis*-[$RuCl_2$(dmso)$_4$] with one equivalent of a face-capping ligand. We found that compound **6** can also be obtained in almost pure form and in good yield by performing the reaction between *cis*-[$RuCl_2$(dmso)$_4$] and $CH(pz)_3$ at slightly higher temperature (in refluxing ethanol rather than methanol), as the product precipitates spontaneously from the reaction mixture. The reactivity of *cis*-[$RuCl_2$(dmso)$_4$] towards $CH(pz)_3$ is summarized in Scheme 4.

Treatment of **6** with two equivalents of AgOTf in refluxing methanol in the presence of dmso afforded *fac*-[Ru{CH(pz)$_3$}(dmso-O)(dmso-S)$_2$][OTf]$_2$ (**7**; Scheme 5). The IR spectrum of **7** clearly indicates the presence of both



Scheme 4.

S-bonded (S–O stretching at $\tilde{\nu}$ = 1155 cm^{-1}) and O-bonded (S–O stretching at $\tilde{\nu}$ = 938 cm^{-1}) dmso ligands. Its ^1H NMR spectrum in noncoordinating solvents ([D_6]acetone or CD_3NO_2) shows three singlets for the dmso ligands, integrating for six protons each, one O-bonded and two S-bonded; the resonances for coordinated $CH(pz)_3$ consist of two sets of pyrazole protons with a 2:1 intensity ratio and a singlet for the CH proton. X-ray diffraction studies confirmed the molecular structure of complex **7** (Figure 6); the two equivalent dmso-S ligands have diastereotopic methyl groups, which are responsible for the two NMR resonances in the dmso-S region.



Scheme 5.

When **7** was dissolved in D_2O the O-bonded dmso was rapidly and completely hydrolyzed as, in this solvent, the dmso-O resonance was replaced by the signal of free dmso at δ = 2.72 ppm; hydrolysis of the dmso-S ligands was not observed. In addition, in D_2O the resonance of the CH proton of coordinated $CH(pz)_3$ decreased rather rapidly (minutes) because of exchange with the deuterated solvent. This result suggests that, as might be expected, the acidity of this proton in **7** is greater than in the neutral precursor **6**, for which this phenomenon was not observed.

As an alternative, complex **7** was also obtained by reaction of *fac*-[Ru(dmso-S)$_3$(dmso-O)$_3$][OTf]$_2$ with one equivalent of $CH(pz)_3$ in refluxing methanol (Scheme 5). In this case, unlike with [9]aneS_3 (see above), we found no evidence of the formation of the homoleptic sandwich adduct *fac*-[Ru{$CH(pz)_3$}$_2$][OTf]$_2$.

The structural characterizations indicated that the metal in complexes **4**–**7** displays a distorted octahedral geometry with coordination bond lengths falling in a range already observed for similar ruthenium species.[26] Interestingly, the mean Ru–N bond length found in *fac*-[Ru{$CH(pz)_3$}Cl_2(dmso-S)] (**6**) is shorter (by about 0.1 Å) than those found in the other structures, but similar to that *trans* to the dmso-O in *fac*-[Ru{$CH(pz)_3$}(dmso-O)(dmso-S)$_2$][OTf]$_2$ (**7**).

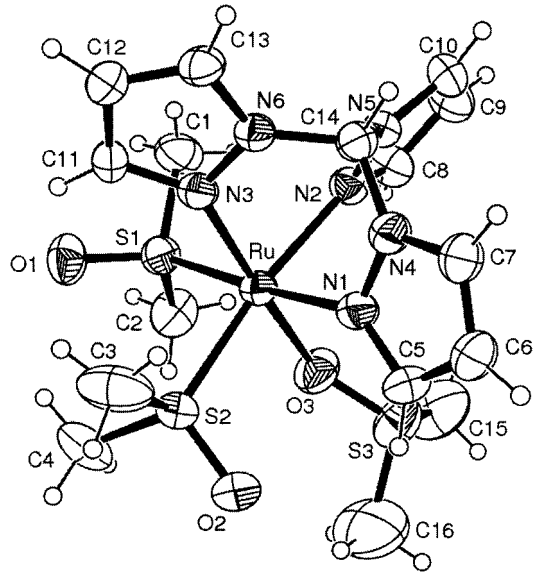
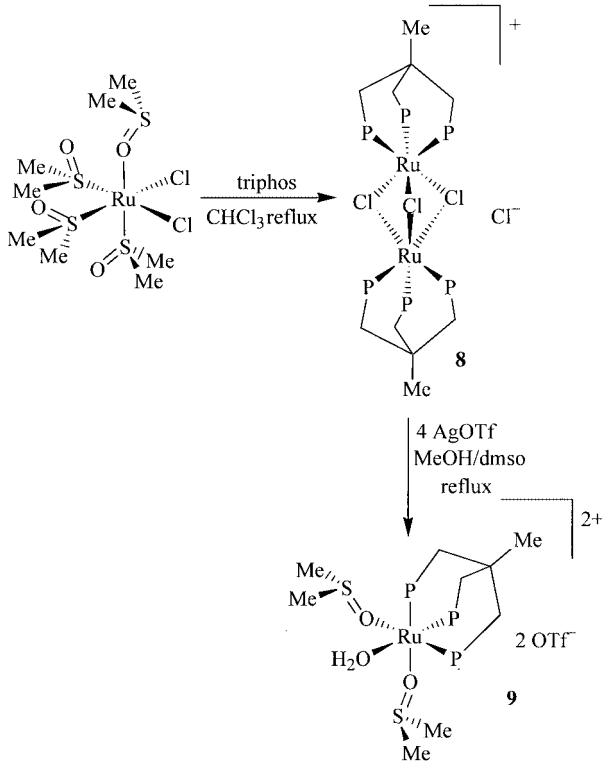


Figure 6. Molecular structure of the cation of *fac*-[Ru{$CH(pz)_3$}(dmso-O)(dmso-S)$_2$][OTf]$_2$ (**7**) with thermal ellipsoids at the 40% probability level. Selected bond lengths [Å] and angles [°]: Ru–N(1) 2.130(5), Ru–N(2) 2.123(4), Ru–N(3) 2.051(4), Ru–S(1) 2.272(2), Ru–S(2) 2.283(2), Ru–O(3) 2.110(4); N(1)–Ru–N(2) 81.89(17), N(1)–Ru–N(3) 86.70(18), N(2)–Ru–N(3) 85.42(17), N(3)–Ru–O(3) 174.32(18), N(1)–Ru–S(1) 175.61(12), N(2)–Ru–S(2) 169.52(13).

The different binding mode of $CH(pz)_3$ in **4** (bidentate) compared to **6** and **7** (tripodal) is reflected in the values of the Ru–N–N and Ru–N–C bond angles. Those found in **4** (131.0° and 123.6°, respectively) are quite different from those found in **6** and **7** (mean values of 136.6° and 118.0°, respectively).

Compounds with $CH_3C(CH_2PPh_2)_3$ (triphos)

We reinvestigated the reaction between *cis*-[$RuCl_2$-(dmso)$_4$] and $CH_3C(CH_2PPh_2)_3$ with the aim of obtaining a more detailed characterization of the *fac*-[Ru(triphos)(dmso)$_3$]$^{2+}$ and *fac*-[Ru(triphos)(dmso)$_2$(H_2O)]$^{2+}$ complexes described by Venanzi and co-workers.[13] Initially, we found that the reaction of *cis*-[$RuCl_2$(dmso)$_4$] with one equivalent of triphos, even when performed under milder conditions than those reported in the literature (4 h in refluxing chloroform vs. 24 h in refluxing toluene),[13] led to the isolation of the dinuclear species [(triphos)Ru(μ-Cl)$_3$Ru(triphos)]Cl (**8**) exclusively (Scheme 6). Formation of the mononuclear complex *fac*-[$RuCl_2$(triphos)(dmso-S)] was not observed. Then, we found that treatment of **8** with four equivalents of AgOTf in refluxing methanol in the presence of dmso led exclusively to the isolation of crystalline *fac*-[Ru(triphos)(dmso-O)$_2$(H_2O)][OTf]$_2$ (**9**) in good yield (Scheme 6).



Scheme 6.

The molecular structure of **9** was determined by X-ray analysis (Figure 7). The dimensions of the triphos ligand reflect a small degree of geometrical distortions, with Ru–P distances of 2.272(2), 2.296(2), 2.280(2) Å (the latter *trans* to the aqua ligand), and P–Ru–P bond angles that average 87.4°. Overall, the structural parameters of the tripodal ligand are very similar to those found in the dinuclear complex cation $[(triphos)Ru(\mu\text{-}Cl)_3Ru(triphos)]^+$.[13]

We found no evidence of the formation of *fac*-[Ru(triphos)(dmso-O)$_3$][OTf]$_2$ (**10**); compound **9** was the only product that we isolated, even under the conditions (dmso at 110 °C) that, according to the literature,[13] should afford **10**. Our synthetic procedure leading to **9** is simpler than that described by Venanzi and co-workers[13] in that it avoids the tedious removal of dmso. Several attempts to prepare either **9** or **10** by reaction of *fac*-[Ru(dmso-S)$_3$(dmso-O)$_3$][OTf]$_2$ with triphos in a number of refluxing solvents (e.g. acetone, methanol, toluene) were unsuccessful and led to the isolation of small amounts of unreacted precursor only.

Complex **9** was found to be insoluble in water but soluble in a range of organic solvents, including chloroform. The ^{1}H NMR spectrum of **9** in $CDCl_3$ shows, besides the resonances of coordinated triphos, only the singlet of free dmso at δ = 2.62 ppm, thus indicating that both dmso-O ligands are rapidly released and probably replaced by water molecules. The ^{31}P NMR spectrum shows a singlet at δ = 38.2 ppm, in agreement with the equivalence of the three P atoms in the hydrolyzed species.

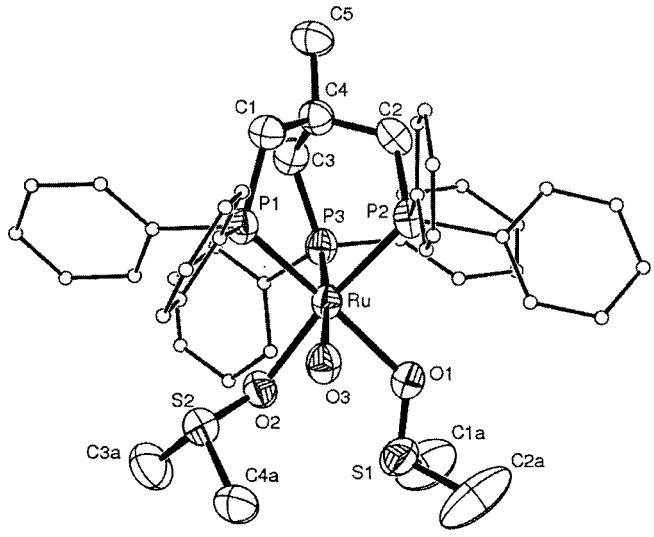
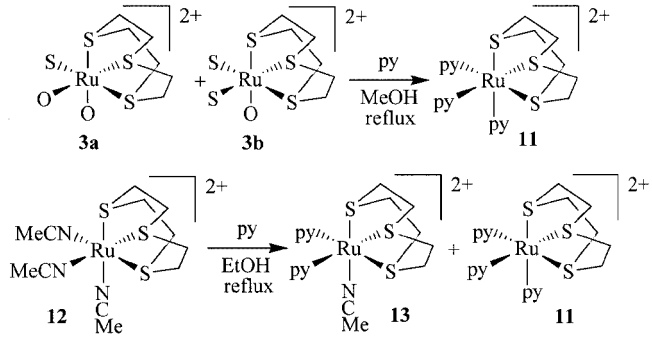


Figure 7. Molecular structure of the cation of *fac*-[Ru(triphos)(dmso-O)$_2$(H_2O)][OTf]$_2$ (**9**) with thermal ellipsoids the 40% probability level. For the sake of clarity the phenyl carbon atoms are indicated as spheres of fixed radius. Selected bond lengths [Å] and angles [°]: Ru–O(1) 2.215(4), Ru–O(2) 2.190(4), Ru–O(3) 2.197(4), Ru–P(1) 2.272(2), Ru–P(2) 2.296(2), Ru–P(3) 2.280(2); O(1)–Ru–P(1) 173.25(12), O(2)–Ru–P(2) 172.80(12), O(3)–Ru–P(3) 174.41(12).

Reactivity of the New Precursors

The reactivity of the new precursors with facial geometry, **3**, **7** and **9**, is currently being investigated in our laboratory and will be the subject of a subsequent paper. We report here only one example concerning the reactivity of the [9]aneS$_3$ complex **3** towards the model ligand pyridine.

The reaction between **3** and a slight excess of pyridine (py/Ru = 4) in refluxing methanol led selectively to the isolation of *fac*-[Ru([9]aneS$_3$)(py)$_3$][OTf]$_2$ (**11**) in excellent yield (Scheme 7). As expected from literature data,[12d–12f] reaction of **1** with pyridine under the same conditions did not yield complex **11**. By comparison, we found that the reaction between the known acetonitrile-containing precursor *fac*-[Ru([9]aneS$_3$)(CH_3CN)$_3$][OTf]$_2$ (**12**) and pyridine, despite being performed at higher temperature (refluxing ethanol) and with a larger excess of ligand (py/Ru = 8), always led to mixtures of **11** and of the disubstituted species *fac*-[Ru([9]aneS$_3$)(py)$_2$(CH_3CN)][OTf]$_2$ (**13**; Scheme 7); both



Scheme 7. For simplicity, in **3a** and **3b** O = dmso-O and S =dmso-S.

products were isolated in pure form and characterized spectroscopically and by X-ray diffraction analysis (see Supporting Information).[27]

Thus, owing to the greater lability of dmso than acetonitrile bound to the $Ru([9]aneS_3)^{2+}$ fragment (see above), complex **3** proved to be a better precursor than **12** in reactions involving the selective replacement of all three leaving groups with monodentate ligands.

Discussion and Conclusions

In summary, we have prepared and structurally characterized three new, easy-to-make, complexes of the type *fac*-$[Ru(fcl)(solv)_3][OTf]_2$, namely *fac*-$[Ru([9]aneS_3)(dmso\text{-}O)(dmso\text{-}S)_2][OTf]_2$ (**3b**), which equilibrates in solution of noncoordinating solvents with the linkage isomer *fac*-$[Ru([9]aneS_3)(dmso\text{-}O)_2(dmso\text{-}S)]^{2+}$ (**3a**), *fac*-$[Ru\{CH(pz)_3\}(dmso\text{-}O)(dmso\text{-}S)_2][OTf]_2$ (**7**), and *fac*-$[Ru(triphos)(dmso\text{-}O)_2(H_2O)][OTf]_2$ (**9**). In all cases the preferred synthetic procedure involves coordination of the face-capping ligand to *cis*-$[RuCl_2(dmso)_4]$ first, followed by replacement of chlorides with dmso (or water) molecules assisted by addition of AgOTf. The isolated yields of compounds **3** and **9** were satisfactory {ca. 80% for **3**, and ca. 50% for **9**, both calculated with respect to *cis*-$[RuCl_2(dmso)_4]$}, while that of **7** was quite low (18–24% depending on the synthetic route). In addition, unlike $[9]aneS_3$ and triphos, tris(pyrazolyl)methane is not commercially available and it is the only fcl, among the three tested, that undergoes decomposition rather easily and shows a tendency to coordinate in a bidentate rather than a tridentate manner.

It should be noted that while in the dications **3b** and **7** there are two S-bonded and one O-bonded dmso ligands, in **9** both dmso ligands are bonded through oxygen and, according to Venanzi and co-workers,[13] the third one also binds in the same manner when it replaces the water molecule to give **10**. The preferential O-bonding of dmso in **9** might be due to both steric and electronic reasons: the steric bulk of the phenyl groups of coordinated triphos might favor coordination of dmso through oxygen, as dmso-O is less sterically demanding than dmso-S. In addition, dmso might coordinate through oxygen to avoid competition for π-electrons with the *trans* phosphane, as is already well established for the coordination of dmso *trans* to other strong π-accepting ligands such as CO and NO.[18]

A comparison of the structural data of the dmso ligands in the three dicationic species *fac*-$[Ru([9]aneS_3)(dmso\text{-}S)_2(dmso\text{-}O)]^{2+}$ (**3b**), *fac*-$[Ru\{CH(pz)_3\}(dmso\text{-}O)(dmso\text{-}S)_2]^{2+}$ (**7**), and *fac*-$[Ru(triphos)(dmso\text{-}O)_2(H_2O)]^{2+}$ (**9**) shows the following trend for Ru–O(dmso) distances: *trans* to N [2.110(4) Å in **7**] < *trans* to S [2.169(3) Å in **3b**] < *trans* to P [2.202(4) Å, mean value in **9**]. In addition, the Ru–S(dmso) bonds *trans* to pyrazole N atoms in **7** are also significantly shorter (0.04 Å) than the corresponding bonds *trans* to the S atoms in **3b**. As both coordinated $CH(pz)_3$ and $[9]aneS_3$ have a small steric bulk in the region of space occupied by the dmso ligands, the reason for the longer Ru–dmso bond distances in **3b** compared to **7** might be found in the greater *trans* influence of trithiacyclononane than tris(pyrazolyl)methane. This consideration might also explain why the S/O linkage isomerization of one sulfoxide was observed for the trithiacyclononane complex **3**, but not in the case of the corresponding tris(pyrazolyl)methane complex **7**.

As the new complexes were prepared with the aim of being employed in self-assembly reactions, the lability of the coordinated dmso molecules is an important parameter to be assessed. NMR investigations showed that hydrolysis of the dmso ligands occurred very easily from **3** in waterand from **9** in chloroform. In the case of complex **7**, only the O-bound dmso ligand was found to be replaced in water. In general, the lability of the dmso ligands of the three dicationic precursors reflects the trend of Ru–dmso bond distances. In addition, NMR investigations of the two similar complexes *fac*-$[Ru([9]aneS_3)(dmso)_3]^{2+}$ (**3**) and *fac*-$[Ru([9]aneS_3)(CH_3CN)_3]^{2+}$ (**12**) in coordinating solvents such as water have shown that coordinated dmso is much more labile than acetonitrile. Accordingly, replacement of the three dmso ligands of **3** with pyridine occurs more easily than that of the acetonitrile ligands of **12**.

In conclusion, a number of experimental results (total yield, structural considerations in the solid state, the lability of the dmso ligands in solution, preliminary results on the reactivity towards model ligands) agree that *fac*-$[Ru([9]aneS_3)(dmso)_3][OTf]_2$ (**3**) and *fac*-$[Ru(triphos)(dmso\text{-}O)_2(H_2O)][OTf]_2$ (**9**) are the most promising complexes for further use in self-assembly reactions with polytopic ligands. Their solubility, a fundamental parameter to be considered in self-assembly reactions, is strongly influenced by the nature of the face-capping ligand. Taken together, they cover a broad range of solvents: while both complexes are soluble in nitromethane, acetone and methanol, **3** is also well soluble in water, while **9** is soluble in chloroform.

It may be argued that the steric demand of triphos in **9** might disfavor coordination of bulkier ligands in place of the dmso and water molecules; however, the steric bulk of dppp, which may be considered as the bidentate analog of triphos, has not prevented the use of $Pd(dppp)^{2+}$ and $Pt(dppp)^{2+}$ fragments in the construction of many 2D and 3D supramolecular adducts through self-assembly procedures.[3d,6]

Experimental Section

Infrared spectra (KBr) were obtained on a Perkin–Elmer 2000 NIR FT-Raman spectrometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were collected at room temperature at 400 and 161.9 MHz, respectively, on a Jeol Eclipse 400 FT spectrometer, with 2,2-dimethyl-2,2-silapentane-5-sulfonate (DSS) as an internal standard for D_2O solutions and the residual non-deuterated solvent signal as reference for spectra recorded from [D_6]acetone (δ = 2.04 ppm), CD_3NO_2 (δ = 4.33 ppm), and $CDCl_3$ (δ = 7.26 ppm) solutions. ^{31}P NMR spectra were referenced to external H_3PO_4 set at δ = 0 ppm. ES-MSdata were obtained on a Perkin–Elmer AP1 spectrometer. Samples were dissolved in acetonitrile; the spectra were recorded in the positive-ion mode at 5.6 kV accelerating potential. Elemental analyses were

performed at the Dipartimento di Scienze Chimiche, University of Trieste.

Trithiacyclononane, triphos, and deuterated solvents were purchased from Aldrich and used as received. Tris(pyrazolyl)methane,[28] *fac*-[Ru([9]aneS$_3$)(CH$_3$CN)$_3$][OTf]$_2$ (**12**),[11a] *fac*-[Ru([9]aneS$_3$)Cl$_2$(dmso-S)] (**1**),[11a] *cis*-[RuCl$_2$(dmso)$_4$],[29] and *trans*-[RuCl$_2$(dmso)$_4$][29] were prepared as described in the literature. *fac*-[Ru(dmso-O)$_3$(dmso-S)$_3$][OTf]$_2$ was prepared by an improved method compared to those reported in the literature for similar *fac*-[Ru(dmso-O)$_3$(dmso-S)$_3$][X]$_2$ (X = ClO$_4$, BF$_4$) compounds:[30,31] *cis*-[RuCl$_2$(dmso)$_4$] (0.48 g, 1 mmol) was treated with a slight excess of AgOTf in refluxing toluene in the presence of dmso (dmso/Ru = 4) for 30 min; the precipitate was extracted with methanol. Solvent removal afforded the product, which was recrystallized from acetone upon addition of diethyl ether. Yield: 0.6 g (70%).

***fac*-[Ru([9]aneS$_3$)Cl(dmso-S)$_2$][OTf] (2):** *fac*-[Ru([9]aneS$_3$)Cl$_2$(dmso-S)] (**1**; 0.18 g, 0.41 mmol) was dissolved in acetone (10 mL); dmso (75 μL, 1 mmol) and AgOTf (0.21 g, 0.82 mmol) were added and the light-protected mixture was heated to reflux for 1 h. After removal of AgCl by filtration through fine paper, the yellow solution was concentrated in vacuo to ca. 3 mL and stored at room temperature after dropwise addition of diethyl ether until saturation. A light-yellow precipitate formed within 24 h and was removed by filtration, washed with diethyl ether, and vacuum dried. Yield: 55 mg (20%). $C_{11}H_{24}ClF_3O_5RuS_6$ (622.19): calcd. C 21.2, H 3.88; found C 21.6, H 3.63. Selected IR (Nujol): $\tilde{\nu}$ = 1093 (s, νSO dmso-S), 428 cm^{-1} (w, νRu–S). ^{1}H NMR (400 MHz, D_2O, 25 °C): δ = 3.3–2.8 (m, 12 H, [9]aneS$_3$), 3.38 (s, 6 H, dmso-S), 3.46 (s, 6 H, dmso-S) ppm. ^{1}H NMR (400 MHz, CD_3NO_2, 25 °C): δ = 3.3–2.8 (m, 12 H, [9]aneS$_3$), 3.29 (s, 6 H, dmso-S), 3.38 (s, 6 H, dmso-S) ppm.

Crystals suitable for X-ray diffraction were obtained by diffusion of diethyl ether into an acetone solution of **2**.

***fac*-[Ru([9]aneS$_3$)(dmso)$_3$][OTf]$_2$ (3):** *fac*-[Ru([9]aneS$_3$)Cl$_2$(dmso-S)] (**1**; 0.43 g, 1 mmol) was partially dissolved in MeOH (10 mL); dmso (250 μL, 3.5 mmol) and AgOTf (0.60 g, 2.3 mmol) were added and the light-protected mixture was heated to reflux for 3 h. After removal of AgCl by filtration, the yellow solution was concentrated in vacuo to ca. 5 mL. A yellow crystalline precipitate was obtained within 24 h from the solution stored at room temperature after dropwise addition of diethyl ether until saturation. It was removed by filtration, washed with diethyl ether, and vacuum dried. Yield: 0.71 g (88%). $C_{14}H_{30}F_6O_9RuS_8$ (813.93): calcd. C 20.6, H 3.71; found C 20.7, H 3.77. Selected IR (Nujol): $\tilde{\nu}$ = 1088 (s, νSO dmso-S), 933 and 914 (s, νSO dmso-O), 517 (w, νRu–O), 418 cm^{-1} (w, νRu–S). ^{1}H NMR (400 MHz, CD_3NO_2, 25 °C): δ = 2.94 (s, 6 H, dmso-O **3a**), 2.96 (s, 6 H, dmso-O **3a**), 3.04 (s, 6 H, dmso-O **3b**), 3.18 (s, 6 H, dmso-S **3a**), 3.34 (s, 6 H, dmso-S **3b**), 3.43 (s, 6 H, dmso-S **3b**), 3.4–2.8 (m, 12 H, [9]aneS$_3$) ppm. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 3.03 (s, 6 H, dmso-O **3a**), 3.04 (s, 6 H, dmso-O **3a**), 3.13 (s, 6 H, dmso-O **3b**), 3.22 (s, 6 H, dmso-S **3a**), 3.42 (s, 6 H, dmso-S **3b**), 3.49 (s, 6 H, dmso-S **3b**), 3.5–2.7 (m, 12 H, [9]aneS$_3$) ppm. Recrystallization: the product was dissolved in acetone and then diethyl ether was added dropwise until saturation.

***trans*,*cis*,*cis*-[RuCl$_2$(dmso-S)$_2${CH(pz)$_2$(pz)}] (4) and *trans*,*cis*,*cis*-[RuCl$_2$(dmso-S)$_2$(pzH)$_2$] (5):** *cis*-[RuCl$_2$(dmso)$_4$] (0.20 g, 0.41 mmol) was partially dissolved in MeOH (15 mL); CH(pz)$_3$ (0.09 g, 0.41 mmol) was added and the mixture was heated to reflux for 2 h. The resulting orange solution was concentrated in vacuo to ca. 2 mL and stored at room temperature after dropwise addition of diethyl ether until saturation. A yellow microcrystalline precipitate containing big orange crystals formed within 12 h. It was removed by filtration, washed with diethyl ether, and vacuum dried (yield: 0.15 g). The mixture was found to contain approximately equimolar amounts of **4**, **5**, and **6** by NMR spectroscopy. The orange crystals of **4** were manually separated under a microscope, washed with cold methanol and diethyl ether, and vacuum dried. $C_{14}H_{22}N_6Cl_2O_2RuS_2$ (542.46): calcd. C 31.0, H 4.09, N 15.49; found C 31.4, H 4.01 N 15.23. Selected IR (Nujol): $\tilde{\nu}$ = 1086 (s, νSO dmso-S), 424 (w, νRu–S), 341 cm^{-1} (m, νRu–Cl). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.45 (s, 6 H, dmso-S), 3.47 (s, 6 H, dmso-S), 6.39 (m, 2 H, H4 bound pz), 6.60 (m, 1 H, H4 unbound pz), 7.79 (m, 2 H, H5 bound pz), 8.03 (m, 2 H, H3 + H5 unbound pz), 8.26 (m, 2 H, H3 bound pz), 10.97 (s, 1 H, C*H*) ppm.

The remaining yellow solid, according to ^{1}H NMR analysis, was a mixture of **5** and **6** (and some residual **4**). Treatment of the mixture with chloroform (twice 5 mL) afforded a small amount of almost pure **6** as an insoluble solid residue (see below). Diffusion of diethyl ether into the chloroform solution afforded yellow crystals of **5**. $C_{10}H_{20}N_4Cl_2O_2RuS_2$ (464.39): calcd. C 25.8, H 4.34, N 12.06; found C 25.3, H 4.18, N 12.02. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.21 (s, 12 H, dmso-S), 6.38 (m, 2 H, H4 pzH), 7.63 (m, 2 H, H5 pzH), 7.98 (m, 2 H, H3 pzH), 12.6 (br. s, 2 H, N*H* pzH) ppm.

***trans*,*cis*,*cis*-[RuCl$_2$(dmso-S)$_2${CH(pz)$_2$(pz)}] (4):** As an alternative, complex **4** was selectively prepared in good yield by the following route: *trans*-[RuCl$_2$(dmso-S)$_4$] (0.1 g, 0.2 mmol) was dissolved in $CHCl_3$ (20 mL) and CH(pz)$_3$ (45 mg, 0.21 mmol) was added. After standing 24 h at room temperature, the resulting orange solution was concentrated in vacuo to ca. 5 mL and stored at room temperature after dropwise addition of diethyl ether until saturation. Orange crystals formed within 24 h and were removed by filtration, washed with diethyl ether, and vacuum dried. Yield: 65 mg (60%). See above for elemental analysis and spectroscopic characterization.

***fac*-[Ru{CH(pz)$_3$}Cl$_2$(dmso-S)] (6):** *cis*-[RuCl$_2$(dmso)$_4$] (0.30 g, 0.62 mmol) was partially dissolved in absolute EtOH (20 mL); CH(pz)$_3$ (0.14 g, 0.62 mmol) was added and the mixture was heated to reflux for 2 h. A yellow precipitate formed from the hot orange solution. After cooling the mixture to room temperature, it was removed by filtration, washed with cold ethanol and diethyl ether, and vacuum dried. Yield: 0.13 g (45%). Concentration of the mother liquor and addition of diethyl ether afforded a further yellow precipitate that, according to ^{1}H NMR spectroscopy, was a mixture of **5** and **6**. Recrystallization: the product was dissolved in the minimum amount of dmso (e.g. 0.15 g of **6** in 0.5 mL dmso), the solution was diluted with acetone (5 mL) and diethyl ether was added dropwise until saturation. Crystals of **6** suitable for X-ray diffraction were obtained by diffusion of diethyl ether into the dmso/acetone solution. $C_{12}H_{16}N_6Cl_2ORuS$ (464.33): calcd. C 31.0, H 3.47, N 18.09; found C 30.9, H 3.37, N 17.85. Selected IR (Nujol): $\tilde{\nu}$ = 1078 (s, νSO dmso-S), 424 cm^{-1} (w, νRu–S). ^{1}H NMR (400 MHz, D_2O, 25 °C): δ = 3.49 (s, 6 H, dmso-S), 6.56 (m, 2 H, H4), 6.65 (m, 1 H, H4), 8.01 (m, 2 H, H5), 8.23 (m, 1 H, H5), 8.36 (m, 2 H, H3), 8.40 (m, 1 H, H3), 9.47 (s, 1 H, C*H*) ppm. ^{1}H NMR (400 MHz, CD_3NO_2, 25 °C): δ = 3.41 (s, 6 H, dmso-S), 6.49 (m, 2 H, H4), 6.60 (m, 1 H, H4), 8.07 (m, 2 H, H5), 8.23 (m, 1 H, H5), 8.28 (m, 2 H, H3), 8.31 (m, 1 H, H3), 8.87 (s, 1 H, C*H*) ppm.

***fac*-[Ru{CH(pz)$_3$}(dmso-O)(dmso-S)$_2$][OTf]$_2$ (7):** This complex was prepared by two different routes: a) by treatment of **6** with two equivalents of AgOTf in the presence of dmso; b) by reaction of *fac*-[Ru(dmso-S)$_3$(dmso-O)$_3$][OTf]$_2$ with CH(pz)$_3$. The yield of **7** with respect to the common precursor *cis*-[RuCl$_2$(dmso)$_4$] is similar in the two procedures: 18% via route a, and 24% via route b.

Route a: *fac*-[Ru{CH(pz)$_3$}Cl$_2$(dmso-S)] (**6**; 0.10 g, 0.21 mmol) was dissolved in MeOH (5 mL); dmso (46 μL, 0.65 mmol) and AgOTf (0.11 g, 0.43 mmol) were added and the light-protected mixture was heated to reflux for 3 h. After removal of AgCl by filtration, the yellow solution was concentrated in vacuo to ca. 2 mL and stored at room temperature after dropwise addition of diethyl ether until saturation. A pale-yellow microcrystalline precipitate formed within 24 h and was removed by filtration, washed with diethyl ether, and vacuum dried. Yield: 72 mg (40%). $C_{18}H_{28}N_6F_6O_9RuS_5$ (847.82): calcd. C 25.5, H 3.33, N 9.91; found C 25.0, H 3.12, N 9.76. Selected IR (Nujol): $\tilde{\nu}$ = 1092 (s, νSO dmso-S), 938 (s, νSO dmso-O), 518 (w, νRu–O), 428 cm^{-1} (w, νRu–S). ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 2.94 (s, 6 H, dmso-O), 3.27 (s, 6 H, dmso-S), 3.35 (s, 6 H, dmso-S), 6.75 (m, 1 H, H4 pz *trans* to dmso-O), 6.83 (m, 2 H, H4 pz *trans* to dmso-S), 8.22 (m, 1 H, H5 pz *trans* to dmso-O), 8.69 (m, 2 H, H5 pz *trans* to dmso-S), 8.75 (m, 3 H, H3), 10.19 (s, 1 H, C*H*) ppm. ^{1}H NMR (400 MHz, CD_3NO_2, 25 °C): δ = 2.83 (s, 6 H, dmso-O), 3.17 (s, 6 H, dmso-S), 3.22 (s, 6 H, dmso-S), 6.68 (m, 1 H, H4 pz *trans* to dmso-O), 6.75 (m, 2 H, H4 pz *trans* to dmso-S), 8.09 (m, 1 H, H5 pz *trans* to dmso-O), 8.46 (m, 2 H, H5 pz *trans* to dmso-S), 8.62 (m, 3 H, H3), 9.61 (s, 1 H, C*H*) ppm. ^{1}H NMR (400 MHz, D_2O, 25 °C): δ = 2.72 (s, 6 H, free dmso), 3.20 (s, 6 H, dmso-S), 3.29 (s, 6 H, dmso-S), 6.71 (m, 1 H, H4 pz *trans* to dmso-O), 6.75 (m, 2 H, H4 pz *trans* to dmso-S), 8.03 (m, 1 H, H5 pz *trans* to dmso-O), 8.42 (m, 2 H, H5 pz *trans* to dmso-S), 8.53 (m, 3 H, H3), 9.84 (s, 1 H, C*H*) ppm.
Route b: *fac*-[Ru(dmso-S)$_3$(dmso-O)$_3$][OTf]$_2$ (0.10 g, 0.11 mmol) was dissolved in MeOH (5 mL); CH(pz)$_3$ (25 mg, 0.11 mmol) was added and the mixture was heated to reflux for 30 min. During reflux the initially colorless solution turned yellow; it was then concentrated in vacuo to ca. 1.5 mL and stored at room temperature after dropwise addition of diethyl ether until saturation. A pale-yellow microcrystalline precipitate formed within a few days and was removed by filtration, washed with diethyl ether, and vacuum dried. Yield: 32 mg (35%). $C_{18}H_{28}N_6F_6O_9RuS_5$ (847.82): calcd. C 25.5, H 3.33, N 9.91; found C 26.0, H 3.23, N 10.06. Crystals suitable for X-ray diffraction were obtained by diffusion of diethyl ether into an acetone solution of **7** (15 mg in 2 mL).

[(triphos)Ru(μ-Cl)$_3$Ru(triphos)]Cl (8): *cis*-[RuCl$_2$(dmso)$_4$] (0.48 g, 1 mmol) was dissolved in CHCl$_3$ (20 mL); triphos (0.62 g, 1 mmol) was added and the mixture was heated to reflux for 4 h under a stream of Ar. A yellow precipitate formed from the hot orange solution. After cooling the mixture to room temperature, this precipitate was removed by filtration, washed with diethyl ether, and vacuum dried. Yield: 0.6 g (75%). $C_{82}H_{78}Cl_4P_6Ru_2$ (1593.29): calcd. C 61.8, H 4.93; found C 60.5, H 4.90. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.59 (br. s, 6 H, CH_3), 2.40 (br. s, 12 H, CH_2), 6.83 (m, 24 H, *m*-Ph), 7.18 (t, 12 H, *p*-Ph), 7.37 (t, 24 H, *o*-Ph) ppm.

***fac*-[Ru(triphos)(dmso-O)$_2$(H$_2$O)][OTf]$_2$ (9):** [(triphos)Ru(μ-Cl)$_3$Ru-(triphos)]Cl (**8**; 0.20 g, 0.12 mmol) was dissolved in MeOH (10 mL); dmso (60 μL, 0.84 mmol) and AgOTf (0.13 g, 0.52 mmol) were added and the light-protected mixture was heated to reflux for 2 h. AgCl was removed by filtration and thoroughly washed with MeOH. The pale-orange solution was concentrated in vacuo to ca. 2 mL and stored at room temperature after dropwise addition of diethyl ether until saturation. A pale-yellow microcrystalline precipitate formed within 24 h and was removed by filtration, washed with diethyl ether, and vacuum dried. Yield: 0.2 g (70%). $C_{47}H_{53}F_6O_9P_3RuS_4$ (1198.1): calcd. C 47.1, H 4.46; found C 46.4, H 4.56. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.63 (br. s, 3 H, CH_3), 2.40 (br. s, 6 H, CH_2), 2.61 (s, 12 H, free dmso), 7.13 (m, 12 H, *m*-Ph), 7.27 (m, 18 H, *o*+*p*-Ph) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 25 °C): δ = 38.2 ppm.

***fac*-[Ru([9]aneS$_3$)(py)$_3$][OTf]$_2$ (11) and *fac*-[Ru([9]aneS$_3$)(py)$_2$-(CH$_3$CN)][OTf]$_2$ (13):** *fac*-[Ru([9]aneS$_3$)(CH$_3$CN)$_3$][OTf]$_2$ (**12**; 0.1 g, 0.14 mmol) was partially dissolved in EtOH (20 mL); pyridine (92 μL, 1.13 mmol) was added and the mixture was heated to reflux for 4 h. The resulting yellow-green solution was filtered through fine paper to remove a small amount of a dark precipitate and then concentrated in vacuo to ca. 2 mL and stored at room temperature after dropwise addition of diethyl ether until saturation. A yellow crystalline precipitate containing two types of crystals (big prisms and small needles) formed within 24 h and was then removed by filtration, washed with chloroform and diethyl ether, and vacuum dried (yield 80 mg). The precipitate was shown to be an approximate 1:3 mixture of **11** and **13** by ^{1}H NMR spectroscopy. The large yellow prisms were manually separated from the mixture under a microscope and were found to be **13** (by X-ray diffraction and ^{1}H NMR spectroscopy). $C_{20}H_{25}N_3F_6O_6RuS_5$ (778.80): calcd. C 30.8, H 3.23, N 5.39; found C 31.0, H 3.17, N 5.41. ^{1}H NMR (400 MHz, D_2O, 25 °C): δ = 2.52 (s, 3 H, CH_3CN), 2.80 (m, 8 H, [9]aneS$_3$), 3.05 and 2.85 (m, 2 H each, [9]aneS$_3$), 7.45 (m, 4 H, *m*H py), 7.98 (t, 2 H, *p*H py), 8.61 (d, 4 H, *o*H py) ppm.

Recrystallization of the remaining mixture from ethanol by diffusion of diethyl ether afforded yellow crystals of pure **11**. $C_{23}H_{27}N_3F_6O_6RuS_5$ (816.85): calcd. C 33.8, H 3.33, N 5.14; found C 33.9, H 3.27, N 5.27. ^{1}H NMR (400 MHz, D_2O, 25 °C): δ = 2.80 (s, 12 H, [9]aneS$_3$), 7.44 (m, 6 H, *m*H py), 7.98 (t, 3 H, *p*H py), 8.48 (d, 6 H, *o*H py) ppm.

As an alternative, *fac*-[Ru([9]aneS$_3$)(py)$_3$][OTf]$_2$ (**11**) was selectively prepared as follows: *fac*-[Ru([9]aneS$_3$)(dmso)$_3$][OTf]$_2$ (**3**; 0.1 g, 0.12 mmol) was dissolved in MeOH (5 mL); pyridine (41 μL, 0.5 mmol) was added and the mixture was heated to reflux for 2 h. The resulting yellow-green solution was concentrated in vacuo to ca. 2 mL and stored at room temperature after dropwise addition of diethyl ether until saturation. A yellow crystalline precipitate formed within 24 h and was then removed by filtration, washed with chloroform and diethyl ether, and vacuum dried. Yield: 68 mg (70%). $C_{23}H_{27}N_3F_6O_6RuS_5$ (816.85): calcd. C 33.8, H 3.33, N 5.14; found C 34.3, H 3.41, N 5.22. ^{1}H NMR (400 MHz, CD_3NO_2, 25 °C): δ = 2.89 (m, 12 H, [9]aneS$_3$), 7.52 (m, 6 H, *m*H py), 8.04 (t, 3 H, *p*H py), 8.50 (d, 6 H, *o*H py) ppm. ES-MS: *m*/*z* (calcd.) = 667.8 (667.8) [M – OTf]$^+$, 259.4 (259.2) [M – 2OTf]$^{2+}$.

X-ray Crystallography: All diffraction data, with the exception of **3b** [150(2) K] were collected at room temperature on a Nonius DIP-1030H system with graphite-monochromated Mo-K_α radiation. For each crystal, a total of 30 frames were collected (exposure time of 15–30 min, rotation angle of 6° about φ, with the detector at a distance of 80–90 mm from the crystal). Cell refinement, indexing, and scaling of the data sets were done using the programs Mosflm and Scala.[32] All the structures were solved by Patterson and Fourier analyses and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[33] The choice of the non-centrosymmetric space group $Pna2_1$ for **7** was confirmed by the successful final refinement; the Flack parameter of 0.49(10) indicates racemic twinning of the crystal. A difference Fourier map of **6** revealed a molecule of dmso and one of water. A residual in **3b** was assigned to a water oxygen (occupancy = 0.5, H atoms omitted). All the calculations were performed using the WinGX System, Ver. 1.64.05.[34]

Crystallographic Data for 2: $C_{11}H_{24}ClF_3O_5RuS_6$, M = 622.18, triclinic, space group $P\bar{1}$, a = 8.031(3), b = 9.501(3), c = 14.890(4) Å, α = 94.48(2)°, β = 104.01(3)°, γ = 89.12(2)°, V = 1099.0(6) Å^3, Z =

2, D_c = 1.880 g cm^{-3}, μ(Mo-K_α) = 1.450 mm^{-1}, F_{000} = 628, θ range = 2.65–29.01°. Final $R1$ = 0.0424, $wR2$ = 0.1130, S = 1.059 for 248 parameters and 8340 reflections, 5152 unique [R(int) = 0.0463], of which 4233 with $I > 2\sigma(I)$; max positive and negative peaks in ΔF map 0.678, –0.590 e Å^{-3}.

Crystallographic Data for 3b·0.5H$_2$O: $C_{14}H_{31}F_6O_{9.50}RuS_8$, M = 822.94, triclinic, space group $P\bar{1}$, a = 11.795(3), b = 12.115(3),c = 12.878(4) Å, α = 64.96(2)°, β = 66.88(3)°, γ = 71.14(2)°, V = 1505.8(7) Å^3, Z = 2, D_c = 1.815 g cm^{-3}, μ(Mo-K_α) = 1.155 mm^{-1}, F_{000} = 834, θ range = 1.83–27.48°. Final $R1$ = 0.0475, $wR2$ = 0.1234, S = 1.032 for 384 parameters and 10 769 reflections, 6407 unique [R(int) = 0.0626], of which 5004 with $I > 2\sigma(I)$; max positive and negative peaks in ΔF map 0.621, –1.267 e Å^{-3}.

Crystallographic Data for 4: $C_{14}H_{22}Cl_2N_6O_2RuS_2$, M = 542.47, orthorhombic, space group $Pbca$, a = 16.158(3), b = 13.456(3), c = 21.605(4) Å, V = 4697.4(16) Å^3, Z = 8, D_c = 1.534 g cm^{-3}, μ(Mo-K_α) = 1.093 mm^{-1}, F_{000} = 2192, θ range = 2.52–28.28°. Final $R1$ = 0.0494, $wR2$ = 0.1495, S = 1.079 for 249 parameters and 11 332 reflections, 5780 unique [R(int) = 0.0331], of which 4413 with $I > 2\sigma(I)$; max positive and negative peaks in ΔF map 1.164,–0.474 e Å^{-3}.

Crystallographic Data for 5: $C_{10}H_{20}Cl_2N_4O_2RuS_2$, M = 464.41, monoclinic, space group $P2_1/n$, a = 8.807(3), b = 16.668(4), c = 12.416(4) Å, β = 104.97(2)°, V = 1760.8(9) Å^3, Z = 4, D_c = 1.752 g cm^{-3}, μ(Mo-K_α) = 1.438 mm^{-1}, F_{000} = 936, θ range = 2.09–29.92°. Final $R1$ = 0.0363, $wR2$ = 0.0925, S = 1.055 for 194 parameters and 8455 reflections, 4950 unique [R(int) = 0.0335], of which 4326 with $I > 2\sigma(I)$; max positive and negative peaks in ΔF map 0.951, –0.604 e Å^{-3}.

Crystallographic Data for 6·dmso·H$_2$O: $C_{14}H_{24}Cl_2N_6O_3RuS_2$, M = 560.48, orthorhombic, space group $Pna2_1$, a = 18.614(4), b = 13.631(4), c = 8.585(3) Å, V = 2178.3(11) Å^3, Z = 4, D_c = 1.709 g cm^{-3}, μ(Mo-K_α) = 1.185 mm^{-1}, F_{000} = 1136, θ range = 2.65–26.37°. Final $R1$ = 0.0656, $wR2$ = 00.1486, S = 1.039 for 258 parameters and 4527 reflections, 4238 unique [R(int) = 0.0749], of which 2385 with $I > 2\sigma(I)$; max positive and negative peaks in ΔF map 0.733, –0.803 e Å^{-3}.

Crystallographic Data for 7: $C_{18}H_{28}F_6N_6O_9RuS_5$, M = 847.83, triclinic, space group $P\bar{1}$, a = 9.831(3), b = 13.378(4), c = 14.050(4) Å, α = 72.72(2)°, β = 69.29(3)°, γ = 72.05(3)°, V = 1607.3(8) Å^3, Z = 2, D_c = 1.752 g cm^{-3}, μ(Mo-K_α) = 0.901 mm^{-1}, F_{000} = 856, θ range = 2.37–26.37°. Final $R1$ = 0.0571, $wR2$ = 0.1509, S = 1.027 for 412 parameters and 10 399 reflections, 6148 unique [R(int) = 0.0494], of which 4620 with $I > 2\sigma(I)$; max positive and negative peaks in ΔF map 0.733, –0.792 e Å^{-3}.

Crystallographic Data for 9: $C_{47}H_{53}F_6O_9P_3RuS_4$, M = 1198.11, monoclinic, space group $P2_1/n$, a = 18.847(4), b = 15.173(4), c = 18.941(5) Å, β = 97.09(2)°, V = 5375(2) Å^3, Z = 4, D_c = 1.481 g cm^{-3}, μ(Mo-K_α) = 0.608 mm^{-1}, F_{000} = 2456, θ range = 1.73–27.48°. Final $R1$ = 0.0623, $wR2$ = 0.1703, S = 1.056 for 637 parameters and 22 951 reflections, 12 105 unique [R(int) = 0.0746], of which 6332 with $I > 2\sigma(I)$; max positive and negative peaks in ΔF map 0.477, –1.011 e Å^{-3}.

Crystallographic Data for 13: $C_{20}H_{25}F_6N_3O_6RuS_5$, M = 778.80, triclinic, space group $P\bar{1}$, a = 7.563(2), b = 10.777(3), c = 19.310(4) Å, α = 97.40(2)°, β = 86.63(3)°, γ = 104.66(3)°, V = 1509.4(7) Å^3, Z = 2, D_c = 1.714 g cm^{-3}, μ(Mo-K_α) = 0.942 mm^{-1}, F_{000} = 784, θ range = 2.34–27.10°. Final $R1$ = 0.0550, $wR2$ = 0.1558, S = 1.040 for 371 parameters and 8918 reflections, 5644 unique [R(int) = 0.0431], of which 4898 with $I > 2\sigma(I)$; max positive and negative peaks in ΔF map 1.446, –0.499 e·Å^{-3}.

CCDC-238841 (for **13**), -238842 ... -238847 (for **2**–**8**) and -238848 (for **9**) contain the supplementary crystallographic data forthis paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information: The molecular structures of *trans,cis,cis*-[$RuCl_2$(dmso-S)$_2$(pzH)$_2$] (**5**) and the cations of *fac*-[Ru([9]aneS_3)(py)$_3$][OTf]$_2$·CH_3OH (**11**), *fac*-[Ru([9]aneS_3)(py)$_2$(CH_3CN)][OTf]$_2$ (**13**), and of one of the two crystallographically independent cations of *fac*-[Ru([9]aneS_3O)(dmso-O)$_2$(dmso-S)][OTf]$_2$ are reported. Of these, only the data for compounds **5** and **13** have been deposited, as the other structures are of poor resolution mainly because of the disordered triflate anions. The preparation of *fac*-[Ru([9]aneS_3O)(dmso-O)$_2$(dmso-S)][OTf]$_2$ is also reported (see also footnote on the first page of this article).

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