Synthesis and Reactivity of Ru-, Os-, Rh-, and Ir-Halide−Sulfoxide Complexes†

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Contents

† Dedicated to Professor Giovanni Mestroni on the occasion of his retirement.

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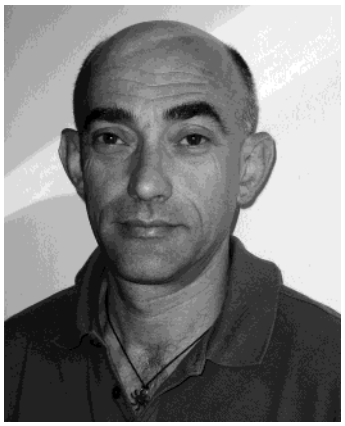

Enzo Alessio was born in 1958 and studied chemistry at the University of Trieste where he received his "Laurea" in 1982 and his Ph.D. degree in 1989. In 2000, he was appointed Associate Professor of Inorganic Chemistry at the same University. He spent one year as NATO–CNR fellow in the research group of Professor Luigi G. Marzilli at Emory University (Atlanta). In 1996, he was awarded the Nasini Prize to young researchers from the Italian Chemical Society. He is coauthor of ca. 120 publications and 9 patents in the fields of coordination chemistry, metal-based anticancer drugs, and metal-mediated self-assembly of supramolecular systems.

1. Introduction

Platinum-group metal halide−sulfoxide complexes, and dimethyl sulfoxide (dmso) complexes in particular, have a rich chemistry and are widely used as precursors in inorganic synthesis. Even though the coordination chemistry of dmso has been the subject of several reviews in the past,[1−5] most of them are not particularly recent, and, above all, none of them were specifically devoted to the synthetic inorganic chemist. The extensive and more recent reviews by Calligaris were focused mainly on structural and metrical aspects of coordinated sulfoxides.[4−6] Thus, this article has two main purposes: (1) to collect and review critically the available data concerning the preparation and the spectroscopic and structural characterization of ruthenium-, osmium-, rhodium-, and iridium-halide−dmso compounds. This effort is not superfluous as, surprisingly enough, also in recent papers there is still uncertainty about the geometry and dmso binding modes in a widely used precursor such as *cis*-$RuCl_2(dmso)_4$, almost 30 years after its unambiguous structural characterization.[7] (2) To give a comprehensive and detailed report on the use of such compounds as versatile precursors in inorganic synthesis. Most of the examples will concern *cis*-$RuCl_2(dmso)_4$, but also other complexes

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treated in point 1 above have a rich, even if not yet fully developed, chemistry.

According to the accepted binding model of Davies,[1] dmso coordination through O (dmso-O) induces a decrease in the S=O bond order, while the opposite occurs for the coordination through S (dmso-S). Thus, the average S−O bond distance for S-bonded (1.4738(7) Å) and that for O-bonded sulfoxides (1.528(1) Å) are markedly shorter and longer, respectively, than that of free sulfoxides (1.492(1) Å).[6] These differences in bond length are reflected in the frequency of the SO stretching mode: νSO for dmso-S is higher, and for dmso-O is lower, compared to that of free dmso at 1055 cm^{-1}. Thus, the typical frequency ranges for the SO stretching mode are 1080−1150 cm^{-1} for dmso-S, and 890−950 cm^{-1} for dmso-O.[6] Besides X-ray crystallography and infrared spectroscopy, ^{1}H NMR spectroscopy also is a powerful tool for determining the binding mode of dmso and the geometry of diamagnetic metal complexes. In the ^{1}H NMR spectra, coordination through oxygen induces small downfield shifts of dmso resonances compared to that of free dmso ($\Delta\delta_{max}$ = ca. 0.5), while coordination through sulfur induces larger downfield shifts ($\Delta\delta$ usually between 0.5 and 1.1); thus the ranges of chemical shifts for dmso-O (δ 2.6−3.0) and dmso-S (δ 3.1−3.6) are quite typical, even if a minor dependence on the nature of the solvent and of the metal center is found. Despite these many reliable investigation techniques available, the readers should become aware that there are several uncertain, or altogether inprecise, reports in the literature concerning both the precursors and their substitution products. Finally, the factors influencing the dmso bonding modes will be considered and discussed in detail, and several examples of linkage isomerism (S- vs O-coordination) will be reviewed.

The decision of limiting this review article to ruthenium(III/II), osmium(II), rhodium(III/I), and iridium(III/I)-halide−sulfoxide complexes was due to the author's first-hand experience. The other platinum-group metal sulfoxide complexes will not be treated here; information on such compounds can be found elsewhere.[1,2]

As the focus of this paper is on the preparation of inorganic compounds, other aspects will be mentioned only briefly. In particular, some of the precursors or their substituted derivatives have antitumor[8,9] and radiosensitizing properties,[10,11] and some have been also used as catalyst precursors in several processes, such as air oxidation of thioethers to sulfoxides[12−17] and of sulfoxides to sulfones,[18,19] oxidation of saturated hydrocarbons,[20,21] alkylaromatics,[22] alcohols,[23] amines,[24] and ethers[20,25,26] with a number of oxidants (e.g., persulfate, hypochlorite, *tert*-butylhydroperoxide), oxidation of cyclohexanone to adipic acid,[27] epoxidation of olefins with *tert*-butylhydroperoxide,[28] isomerization of allylic alcohols,[29] rearrangements of azobenzenes,[30] hydrogenolysis of O_2 to H_2O_2,[31] polymerization of olefins[32] and of cyclic olefins,[33] dimerization of acrylonitrile,[34] hydrogenation of 1-hexene in water/organic solvent biphasic systems,[35] asymmetric hydrogenation of prochiral olefinic substrates (using complexes with chelating chiral sulfoxide ligands),[36,37] and asymmetric transfer hydrogenation of prochiral ketones in the presence of chiral P,N,O Schiff base ligands.[38] However, these aspects will not be treated in detail here. The anticancer properties of Ru−dmso compounds have been reviewed very recently.[8,9]

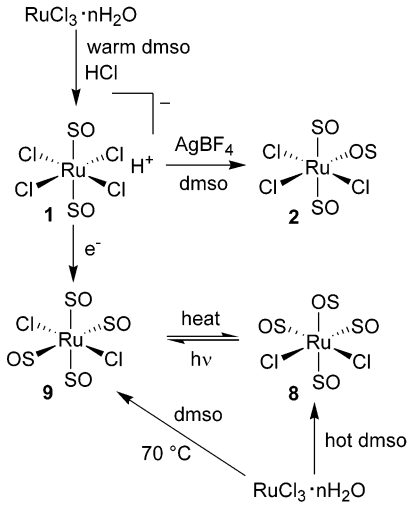
2. Ruthenium−Halide−Sulfoxide Complexes

The first report on Ru−halide−dmso compounds dates back to the pioneering work of James and co-workers in 1971, which described the synthesis of $RuCl_2(dmso)_4$ from hydrated $RuCl_3$;[39] the presence of both S-bonded and O-bonded dmso ligands was recognized from the IR and ^{1}H NMR spectra, and the geometry of the two chlorides was tentatively (but erroneously) assigned as trans. Another milestone in this field was set two years later, with the work by Evans and co-workers,[40] which reported an improved and simpler synthetic procedure for $RuCl_2(dmso)_4$ and thoroughly investigated its reactivity. The geometry of the complex, which was still uncertain in the report of Evans and co-workers, was unambiguously established as *cis,fac*-$RuCl_2(dmso\text{-}S)_3(dmso\text{-}O)$ in 1975 by Mercer and Trotter through single-crystal X-ray investigation.[7] Since then the field has expanded enormously, and now, despite some incorrect and misleading papers, there is a quite clear picture of the chemistry of halide−dmso compounds of ruthenium in both oxidation states +3 and +2.

2.1. Ru(III)−Halide−Sulfoxide Precursors

Treatment of hydrated $RuCl_3$ with warm dmso (80 °C) and HCl yields the Ru(III) complex $[(dmso)_2H][trans\text{-}RuCl_4(dmso\text{-}S)_2]$ (**1**), in which the two mutually trans sulfoxides are bound through sulfur (Scheme 1).[41,42] The cation in **1** can be easily exchanged (e.g.,

Scheme 1[a]



[a] SO = S-bonded dmso, OS = O-bonded dmso.

for Na^+, NH_4^+, $N(n\text{Bu})_4^+$), thus making the complex soluble in a wide range of solvents. Treatment of **1** with $AgBF_4$ in the presence of dmso led to the isolation of the neutral complex *mer,trans*-$RuCl_3(dmso\text{-}S)_2(dmso\text{-}O)$ (**2**) (Scheme 1), which is still soluble in water and also in chlorinated organic

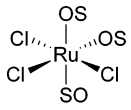
solvents.[42] In compound **2**, the new dmso binds through oxygen (νSO = 912 cm^{-1}). Both **1** and **2** were structurally characterized by X-ray investigations.[41,42] The S−O bond distance of the dmso-O in **2** (1.545(4) Å) is markedly longer than those of the dmso-S ligands (range from 1.461(3) to 1.484(4) Å), showing the expected considerable decrease of the double-bond character of the S−O bond upon O-coordination to the metal.

Ru(III) is paramagnetic, and thus NMR spectroscopy is less easily applied than on diamagnetic Ru(II) species, as the resonances of all ligands are broadened and shifted in hardly predictable ways. A careful comparison of the ^{1}H NMR spectra of the Ru(III) precursors **1** and **2** and of several neutral and anionic derivatives (see below) allowed us to establish that S-bonded dmso on Ru(III) gives a broad resonance at about $\delta = -14$, while O-bonded dmso gives a sharper resonance in the downfield region at about $\delta = 10$.

Ru(III)−chloride analogues of **1** and **2** bearing tetramethylenesulfoxide (tmso) instead of dmso, namely, [tmsoH][*trans*-RuCl$_4$(tmso-S)$_2$] (**3**) and *mer*,*trans*-RuCl$_3$(tmso-S)$_2$(tmso-O) (**4**), were also similarly prepared and characterized.[43] Noticeably, the cation in **3** is a single protonated sulfoxide, rather than a proton bridging two sulfoxides as in **1**.

The coordination chemistry of less common sulfoxides is not so straightforward as that of dmso and tmso, and for this reason there are very few well-characterized complexes with such sulfoxides. One example is the neutral Ru(III)−chloride derivative with diphenylsulfoxide (dpso), *mer*,*cis*-RuCl$_3$(dpso-O)$_2$(dpso-S) (**5**) (Chart 1), obtained from hydrated

Chart 1 [a]



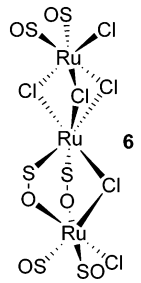
5

[a] SO = S-bonded dpso, OS = O-bonded dpso.

RuCl$_3$ under conditions very similar to those that, with dmso or tmso, led to the isolation of **1** and **3**, respectively.[44] Unlike the analogous neutral dmso and tmso complexes **2** and **4**, which have two trans S-bonded sulfoxides, **5** bears two cis sulfoxides bound through oxygen. This difference was attributed to steric reasons, because O-bonded sulfoxides have a lower steric demand than the S-bonded ones and dpso is bulkier than dmso and tmso.[44]

Under similar conditions, the reaction of hydrated RuCl$_3$ with methylphenylsulfoxide (mpso) led instead to the trinuclear Ru(II) complex [(mpso-S)$_2$ClRu(μ-Cl)$_3$Ru(μ-mpso-S,O)$_2$(μ-Cl)Ru(mpso-S)$_2$Cl] (**6**) that, according to a crystal structure determination, contains the rare S,O bridging sulfoxide ligands (Chart 2).[45] The S−O bond lengths of the bridging mpso's (1.518(5) and 1.507(5) Å) are intermediate between the average distances found for the S−O bond in S−(1.480(1) Å) and O-bonded (1.545(3) Å) sulfoxide complexes of Ru(II).[6] Similarly, also the SO stretching frequencies (1004 and 980 cm^{-1}) are intermediate between those typical for S- and O-bonded sulfoxides,

Chart 2 [a]



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[a] SO = S-bonded mpso, S−O = μ-mpso-S,O.

and lower than that of free sulfoxide (see Introduction).[45]

The chemistry of Ru(III)−bromide−sulfoxide complexes is much less developed. Treatment of hydrated RuBr$_3$ with dmso in the presence of moist HBr apparently yielded the Ru(III)−bromide complex corresponding to **1**, [(dmso)$_2$H][*trans*-RuBr$_4$(dmso-S)$_2$] (**7**).[46] In HBr solutions the coordinated dmso in **7** was rapidly deoxygenated, forming dimethyl sulfide (dms) complexes of Ru(III).[46] Indeed, a complex originally described as RuBr$_3$(dmso-O)$_3$[47] was later demonstrated to be the dms complex *mer*-RuBr$_3$(dms)$_3$.[41]

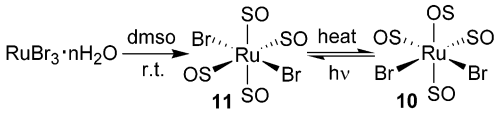
Early reports on synthetic routes to other scarcely characterized Ru(III)−halide−dmso compounds, such as [Ru(dmso)$_5$Cl]Cl$_2$ and [Ru(dmso)$_6$]Cl$_3$,[48,49] [Ru(dmso)$_6$]Br$_3$,[50] RuCl$_3$(dmso-O)$_3$,[51] *fac*-RuCl$_3$(dmso-S)$_3$ and Ru$_2$Cl$_6$(dmso-S)$_4$,[52] and RuCl$_3$·2dmso,[53] were later demonstrated to be unreproducible, thus contributing to the initial confusion in this field. When carefully repeated, such procedures were found to yield either **1** or Ru(II)−halide−dmso (see below) and Ru(III)−halide−dms species (*mer*-RuCl$_3$(dms)$_3$ and *mer*-RuBr$_3$(dms)$_3$)[41] or mixtures of these products.

2.2. Ru(II)–Halide–Sulfoxide Precursors

Treatment of hydrated RuCl$_3$ in hot dmso (120−150 °C) induces the reduction to Ru(II), with formation of *cis*,*fac*-RuCl$_2$(dmso-S)$_3$(dmso-O) (**8**) in high yield (Scheme 1);[40,54] the molecular structure of **8** was determined by Mercer and Trotter by X-ray crystallography in 1975.[7] Complex **8** is the thermodynamic most stable Ru(II)−Cl−dmso compound. Treatment of hydrated RuCl$_3$ in dmso at 70 °C,[41] or the electrochemical reduction of **1**,[42] yielded the kinetic isomer *trans*-RuCl$_2$(dmso-S)$_4$ (**9**), which was also conveniently obtained in high yield through a photochemical isomerization of **8** in dmso (Scheme 1).[54] Isomer **9** is considerably less soluble than **8** in dmso, while both isomers are well soluble in water and in chlorinated solvents. Analogous bromide compounds, *cis*,*fac*-RuBr$_2$(dmso-S)$_3$(dmso-O) (**10**) and *trans*-RuBr$_2$(dmso-S)$_4$ (**11**), were obtained from hydrated RuBr$_3$.[41,54,55] Hydrated RuBr$_3$ is reduced to Ru(II) species much more easily than hydrated RuCl$_3$. In fact, treatment of RuBr$_3$·nH$_2$O with dmso at room temperature (r. t.) was found to give the kinetic less soluble isomer **11**, which isomerizes to the thermodynamic product **10** in hot dmso (Scheme 2). As for the chloro compound, the reverse isomerization of **10** to **11** was found to be induced by light at room temperature.[54]

All chloride and bromide isomers **8**−**11** have been structurally characterized by X-ray crystallogra-

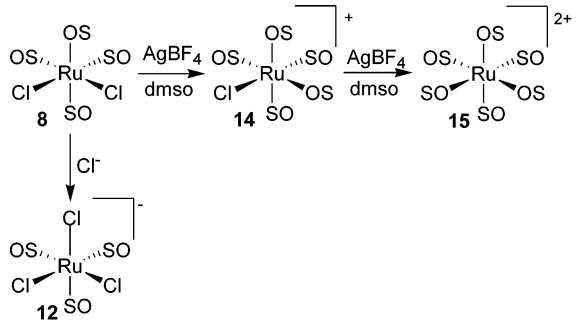
Scheme 2



phy.[7,41,54,55] Interestingly, in the trans isomers **9** and **11**, the Ru−S bond distances (2.352(2) Å in **9** and 2.360(1) Å in **11**)[54,55] are significantly longer than the average values found in the cis isomers **8** and **12** (for comparison, the average R(II)−S bond length for S-bonded sulfoxides not trans to S is 2.260(2) Å).[6] It seems likely that in the trans isomers the lengthening of the Ru−S bond is due both to the *trans*-influencing effect of dmso-S and to the greater π backbonding competition between the mutually trans dmso-S ligands. Accordingly, the S−O bond distances in **9** and **11** (1.491(5) and 1.484(3) Å, respectively) are longer than the average distance for dmso-S (1.480(1) Å), and the SO stretching frequency (1080 cm^{-1} in both complexes) is the lowest among those found for Ru−dmso-S complexes. In further accordance with the relatively low stability of the *trans*-$Ru^{II}(dmso\text{-}S)_2$ fragment (see below section 6), ^1H NMR spectroscopy established that upon dissolution of **9** in D_2O immediate hydrolysis of two dmso-S ligands occurs with formation of *trans*,*cis*,*cis*-$RuCl_2(dmso\text{-}S)_2(H_2O)_2$.[54]

Treatment of **8** with excess chloride led to selective replacement of the dmso-O ligand (Scheme 3); several

Scheme 3

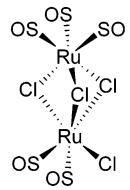


[Y][*fac*-$RuCl_3(dmso\text{-}S)_3$] complexes (**12**) have been prepared and some also structurally characterized ($Y^+ = NH_2Me_2^+$,[56] NEt_4^+,[42] $RR'NHOH^+$,[57] Na^+,[58] $N(nBu)_4^+$[58]). Similarly, treatment of *cis*,*fac*-$RuBr_2(dmso\text{-}S)_3(dmso\text{-}O)$ (**10**) with excess NR_4Br (R = *n*Bu, Et) led to the corresponding [NR_4][*fac*-$RuBr_3(dmso\text{-}S)_3$] complexes (**13**);[59,60] the tetraethyl ammonium derivative was also structurally characterized.[60] The rather improbable five-coordinate 16 electron complex $RuBr_2(dmso\text{-}S)_3$ proposed by Sarma and Poddar[47] was later demonstrated to be a mixture of Li[*fac*-$RuCl_nBr_{3-n}(dmso\text{-}S)_3$] compounds ($n = 0-3$).[60] Poddar and co-workers also described derivatives of this and other nonexisting, or incorrectly formulated, Ru−dmso complexes.[61]

Treatment of **8** with 1 or 2 equiv of a soluble silver salt AgX ($X^- = BF_4^-$, $CF_3SO_3^-$) in the presence of dmso led to the replacement of the chlorides with O-bonded dmso ligands, yielding the mono- and dicationic species [*fac*-$Ru(dmso\text{-}S)_3(dmso\text{-}O)_2Cl$][X] (**14**) and [*fac*-$Ru(dmso\text{-}S)_3(dmso\text{-}O)_3$][X]$_2$ (**15**), respectively (Scheme 3)[40,59,62] ([$Ru(dmso\text{-}S)_3(dmso\text{-}O)_3$][$BPh_4$]$_2$ was also obtained by treatment of [Ru(cod)$(dmso)_4$]-[BPh_4]$_2$ (cod = cyclooctadiene) in dmso at 80 °C).[63] The X-ray structure of **15** as BF_4^- salt was determined.[64]

Finally, the triply chloro-bridged diruthenium(II) complex [$(dmso\text{-}S)_3Ru(\mu\text{-}Cl)_3RuCl(dmso\text{-}S)_2$] (**16**) (Chart 3) was obtained in high yield by refluxing *cis*,*fac*-

Chart 3

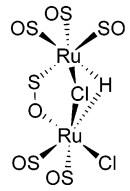


16

$RuCl_2(dmso\text{-}S)_3(dmso\text{-}O)$ (**8**) in wet toluene or ethanol.[65−67] Complex **16** has been thoroughly characterized spectroscopically,[66] and its structure was later confirmed by X-ray crystallography.[67]

Conversely, the diruthenium(II) complex [$(dmso\text{-}S)_3Ru(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-}dmso\text{-}S,O)RuCl_2(dmso\text{-}S)$], containing the first example of an S,O bridging dmso ligand (Chart 4), was unexpectedly obtained by

Chart 4 [a]



[a] S-O = μ-dmso-S,O.

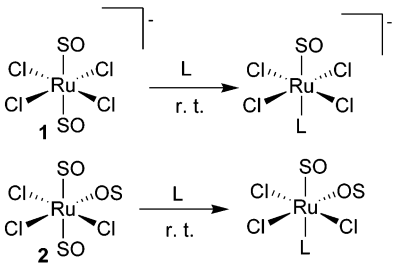
treatment of **8** with $Na_2(xdk)$ (H_2xdk = *m*-xylenediamine bis(Kemp's triacid imide)) in methanol.[68] The Ru−S bond distance of the bridging dmso (2.188(2) Å) is significantly shorter than those of the other terminal dmso-S ligands (2.223−2.313 Å), while the Ru−O (2.160(2) Å) and S−O (1.532(4) Å) bond distances are close to the typical values found for Ru(II)−dmso−O complexes. No IR and NMR attributions were reported.

The corresponding tmso derivatives of compounds **8**−**11** were obtained by tmso/dmso exchange[43] or by treatment of hydrated $RuCl_3$ with tmso.[69] Noticeably, with tmso, also in the thermodynamically most stable isomers *cis*-$RuCl_2(tmso\text{-}S)_4$ (**17**) and *cis*-$RuBr_2(tmso\text{-}S)_4$ (**18**), all four sulfoxides are bound through sulfur, as tmso-S is less sterically demanding than dmso-S (see section 6).[43,69] James and co-workers also reported that, by treatment of hydrated $RuCl_3$ with tmso in the presence of excess LiBr, the unusual diruthenium(II)−dilithium complex [$Br_6(tmso\text{-}S)_2Ru_2(\mu_2\text{-}tmso\text{-}S,O)_2(\mu_3\text{-}tmso\text{-}S,O)_2Li_2(tmso\text{-}O)_2$] was obtained, which contains four different bonding types of tmso ligands, including the rare μ_2-tmso-S,O (Ru−S−O−Li), and the unprecedented μ_3-tmso-S,O (Ru−S−$O(Li)_2$).[70] The same procedure using dmso yielded only *trans*-$RuBr_2(dmso\text{-}S)_4$ (**11**) in high yield.[71]

2.3. Reactions of Ru(III)–dmso Precursors with σ- and π-Donor Ligands

Owing to the remarkable *trans*-influencing effect of dmso-S, and to the relatively low stability of the *trans*-$Ru^{III}(dmso\text{-}S)_2$ fragment because of the competition of the two trans π-accepting ligands, in both [Y][*trans*-$RuCl_4(dmso\text{-}S)_2$] (**1**) and *mer*,*trans*-$RuCl_3(dmso\text{-}S)_2(dmso\text{-}O)$ (**2**) complexes one dmso-S was found to be easily and selectively replaced by heterocyclic N ligands L (or by ammonia) at ambient temperature.[72] Thus, compounds **1** and **2** became the precursors of two series of new complexes of formula [Y][*trans*-$RuCl_4(dmso\text{-}S)(L)$] (Y^+ = either LH^+ or as defined above for **1**) and *mer*-$RuCl_3(dmso\text{-}S)(dmso\text{-}O)(L)$ (L trans to dmso-S), respectively (Scheme 4).

Scheme 4[a]



[a] L = NH_3 or heterocyclic N ligand.

Replacement of one of the two trans S-bonded dmso ligands in **1** and **2** with a pure σ-donor (and eventually also π-donor) ligand leads to a strengthening of the remaining Ru−S bond. In fact, the Ru−S bond distances in Na[*trans*-$RuCl_4(dmso\text{-}S)(NH_3)$] (2.2797(7) Å), in Na[*trans*-$RuCl_4(dmso\text{-}S)(im)$] (2.2956(6) Å, im = imidazole), and in *mer*-$RuCl_3(dmso\text{-}S)(dmso\text{-}O)(NH_3)$ (2.2714(6) Å) are significantly shorter than the average value of 2.34(1) Å found in the precursors **1** and **2**. A reactivity similar to that of **1** and **2** toward N ligands (L) was found also with the corresponding tmso derivatives **3** and **4**.[43]

Several of these compounds were found to have remarkable antimetastatic activity against animal tumor models in vivo and one of them, [imH][*trans*-$RuCl_4(dmso\text{-}S)(im)$] (nicknamed NAMI-A), was the first ruthenium compound to be tested on humans in clinical phase I. The biological properties of NAMI-A and of other anticancer ruthenium−dmso compounds have been recently reviewed.[8,9]

The reactivity of **1** toward N ligands may change when they are capable of making strong hydrogen bonds, such as the bio-ligands 9-ethylguanine (9Etguo, Chart 5)[73] and acyclovir (acv = 9-(2-hydroxyethoxymethyl)guanine, Chart 5).[74] In such cases, coordination of L trans to dmso-S may be accompanied by hydrolysis of one chloride and the neutral species *mer*-$RuCl_3(dmso\text{-}S)(L)(H_2O)$, with a strong intramolecular hydrogen bond between L (the purine oxygen atom of 9Etguo and acv) and the *cis*-coordinated water molecule, were isolated also from nonaqueous solvents.[74] When the reaction of **1** with acv was performed in alcoholic solvents (ROH = MeOH or EtOH) the corresponding *mer*-$RuCl_3(dmso\text{-}S)(acv)(ROH)$ species were obtained.[74,75] When L = 5,7-dimethyl[1,2,4]triazolo[1,5-a]pyrimidine (dmtp,

Chart 5

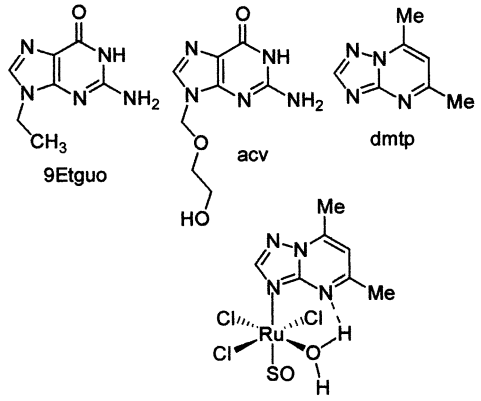
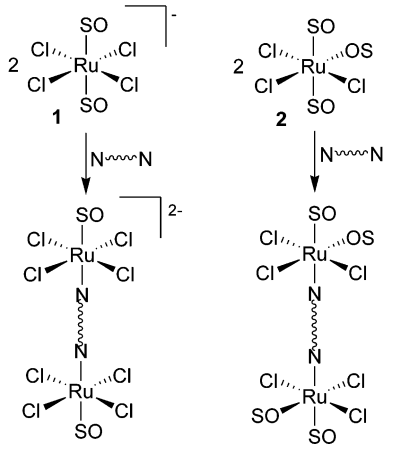


Chart 5), both the anionic [dmtpH][*trans*-$RuCl_4(dmso\text{-}S)(dmtp)$] and its neutral hydrolysis product, the aquo species *mer*-$RuCl_3(dmso\text{-}S)(dmtp)(H_2O)$, with strong intramolecular hydrogen bonds between the pyrimidinic N4 of dmtp and the coordinated water molecule, were isolated and structurally characterized.[76]

Reaction of **1** (sodium salt) and **2** with bridging heterocyclic N-donor ligands (N−N) such as pyrazine (pyz), pyrimidine (pym), 4,4′-bipyridine (4,4′-bpy), and derivatives thereof, afforded the dianionic and neutral dinuclear ruthenium(III) species $[Na]_2[\{trans\text{-}RuCl_4(dmso\text{-}S)\}_2(\mu\text{-}N{-}N)]$ and $[\{mer\text{-}RuCl_3(dmso\text{-}S)(dmso\text{-}O)\}_2(\mu\text{-}N{-}N)]$, respectively (Scheme 5).[77] Each

Scheme 5

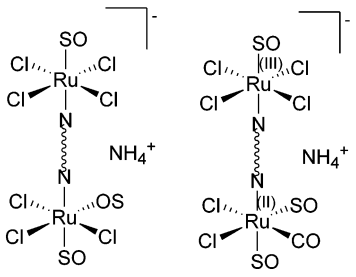


ruthenium center in these dinuclear species has a coordination environment similar to that of the anionic and neutral monomeric Ru(III) complexes described above (Scheme 4), respectively.

Using a stepwise synthetic approach, new unsymmetrical monoanionic Ru(III) and mixed-valence Ru(III)/Ru(II) dinuclear compounds of formula $[NH_4][\{trans\text{-}RuCl_4(dmso\text{-}S)\}(\mu\text{-}N{-}N)\{mer\text{-}RuCl_3(dmso\text{-}S)(dmso\text{-}O)\}]$ and $[NH_4][\{trans\text{-}RuCl_4(dmso\text{-}S)\}(\mu\text{-}N{-}N)\{cis,cis,cis\text{-}RuCl_2(dmso\text{-}S)_2(CO)\}]$ (N−N = pyz or pym), respectively, were also prepared (Chart 6).[78] Most of these new species were structurally characterized in the solid state by X-ray crystallography.[77,78]

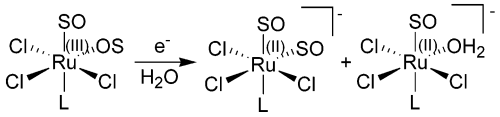
We found that, in aqueous solution at physiological pH, both mononuclear ([Y][*trans*-$RuCl_4(dmso\text{-}S)(L)$] and *mer*-$RuCl_3(dmso\text{-}S)(dmso\text{-}O)(L)$) and dinuclear ($[Na]_2[\{trans\text{-}RuCl_4(dmso\text{-}S)\}_2(\mu\text{-}N{-}N)]$ and [{*mer*-

Chart 6



$RuCl_3$(dmso-S)(dmso-O)$\}_2(\mu$-N−N)]) complexes are rapidly and completely reduced to the corresponding Ru(II) species by addition of one equivalent amount of a biological reductant (e.g., cysteine or ascorbic acid) per Ru atom.[77,79] Interestingly, for the neutral species *mer*-$RuCl_3$(dmso-S)(dmso-O)(L) reduction induced the O/S linkage isomerization of the equatorial dmso-O (accompanied by partial hydrolysis) (Scheme 6);[77] the same behavior was observed for the corresponding dinuclear species.[77]

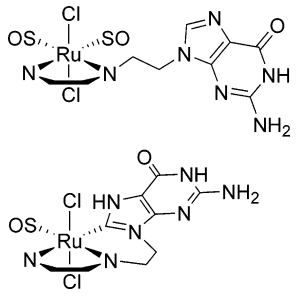
Scheme 6[a]



[a] L = N-donor ligand.

Houlton and co-workers investigated the reactivity of **1** with a particular biomimetic ligand (L) formed by an ethylenediamine unit linked, through an ethyl group, to a purine nucleobase (adenine[80] or guanine[73]). Reaction of [$(dmso)_2$H][*trans*-$RuCl_4$$(dmso-S)_2$] with L·HCl in refluxing methanol yielded, after column chromatography, two main products, both containing Ru(II): *trans,cis*-$RuCl_2$$(dmso-S)_2$(LH), in which the nucleobase-ligand conjugate L is bound through the ethylenediamine group leaving the protonated nucleobase moiety pendent, and the cyclometalated species *trans*-$RuCl_2$(dmso-S)(L), in which L binds to ruthenium in a meridional tridentate manner through the ethylenediammine group and the C^8 atom of the nucleobase moiety (Chart 7, guanine).[73,80]

Chart 7



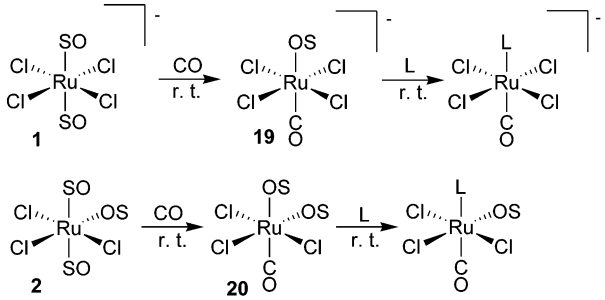
Finally, treatment of **2** with 2 equiv of 1-methylimidazole (1Me-im) in refluxing chloroform, that is under more forcing conditions than those leading to *mer*-$RuCl_3$(dmso-S)(dmso-O)(1Me-im), afforded the cis disubstituted product *mer,cis*-$RuCl_3$$(1Me-im)_2$-(dmso-S), in which also the O-bonded dmso is replaced by the N-donor ligand. Interestingly, when the reaction was performed with imidazole, reduction to Ru(II) occurred and the complex *trans,cis,cis*-$RuCl_2$-$(im)_2$$(dmso-S)_2$ was isolated in good yield.[81]

2.4. Reactions of Ru(III)–dmso Precursors with π-Acceptor Ligands (CO and NO)

The structural and spectroscopic evidence collected on Ru−dmso complexes led us to believe that the ruthenium−sulfur bond has a relevant component of metal-to-ligand π backdonation not only in Ru(II) but also in Ru(III) compounds (see below Section 6). Thus, with the aim of assessing the effect of π backbonding competition on the Ru(III)−dmso-S bond, we investigated the reactivity of **1** and **2** toward strong π-acceptor ligands such as CO and NO.

Both **1** and **2** were found to react readily with carbon monoxide at room temperature and atmospheric pressure by replacing one of the two trans S-bonded dmso ligands and give [Y][*trans*-$RuCl_4$-(dmso-O)(CO)] (**19**) and *mer,cis*-$RuCl_3$$(dmso-O)_2$(CO) (**20**), respectively (Scheme 7).[82]

Scheme 7[a]



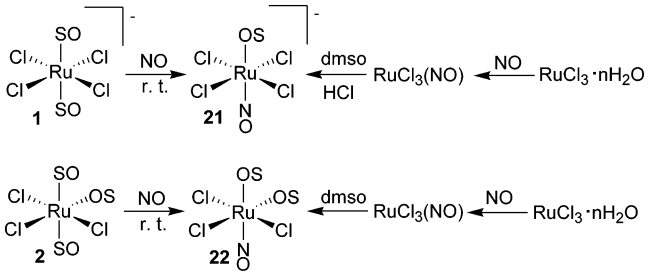
[a] L = NH_3 or heterocyclic N-ligand.

Noticeably, even though this reactivity is similar to that found with N-donor ligands, coordination of CO induces the S- to O-linkage isomerization of the *trans*-coordinated dmso to avoid competition for π-backbonding. The corresponding tmso complexes were recently prepared using similar procedures.[83]

Owing to the large trans influence of carbonyl, the dmso-O trans to CO in **19** and **20** is weakly bonded to ruthenium. This feature results clearly from the Ru−O bond distances: 2.130(3) Å in **19** and 2.124(3) Å in **20** (trans to CO), to be compared to 2.070(2) Å in **2** and 2.054(6) Å in **20** (both trans to Cl).[82] In accordance with the binding model for dmso,[1] the weakening of the Ru−O σ bonds leads to a strengthening of the corresponding S−O bond, which is reflected in a shortening of the S−O bond distances (e.g., 1.514 Å in **19** vs 1.545(4) Å in **2**) and in SO stretching frequencies (957 cm^{-1} for **19** and 932 cm^{-1} for **20**) that fall in the upper section of the typical range for dmso-O. Thus, compounds **19** and **20** became precursors for new derivatives as the dmso-O trans to CO was easily and selectively replaced by a stronger σ-donor ligand L, such as ammonia or pyridine (py), to give compounds [Y][*trans*-$RuCl_4$(L)(CO)] and *mer*-$RuCl_3$(dmso-O)(L)(CO) (CO trans to L), respectively (Scheme 7).[82]

The reactivity of **1** and **2** toward NO is similar to that with CO. Treatment of **1** and **2** with gaseous NO at room temperature yielded [Y][*trans*-$RuCl_4$(dmso-

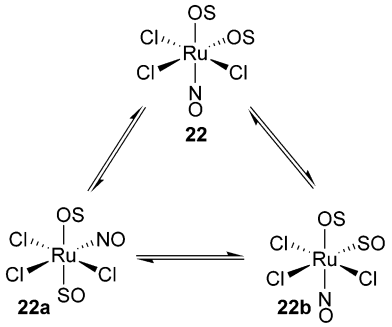
Scheme 8



O)(NO)] (**21**) and *mer*,*cis*-$RuCl_3$(dmso-O)$_2$(NO) (**22**), respectively (Scheme 8).[84] As with CO (see above), coordination of the strong π-acceptor NO induces the S- to O-linkage isomerization of the dmso trans to it to avoid competition for π electrons. In conclusion, it was impossible to prepare compounds with a dmso-S coordinated trans to a strong π-acceptor ligand such as CO or NO. Compound **22** and its bromo analogue were also obtained by us,[84] and by others,[85−87] by treatment of the "$RuCl_3$(NO)" or "$RuBr_3$(NO)" intermediates, respectively, with dmso (Scheme 8). Similarly, treatment of $RuCl_3$(NO) with dmso and HCl yielded compound **21** (Scheme 8).[84,86]

We also found that in light-protected nitromethane solutions, complex **22** equilibrates slowly with the two isomers *mer*,*trans*-$RuCl_3$(dmso-O)(dmso-S)(NO) (**22a**), with NO trans to Cl, and *mer*,*cis*-$RuCl_3$(dmso-O)(dmso-S)(NO) (**22b**), with NO trans to dmso-O (Scheme 9); the equilibrium mixture (after 1 week

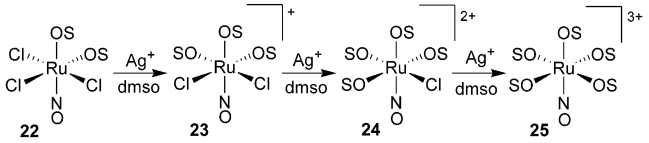
Scheme 9



at 30 °C) consists of ca. 64% **22**, 3% **22a**, and 33% **22b**. Complex **22a** was also isolated as a byproduct in the preparation of **21** performed in water, while **22b** was identified only in solution through NMR spectroscopy.[84]

In addition, we found that treatment of **22** with 1−3 equiv of a soluble silver salt AgX (such as $AgBF_4$ or AgOTf) in the presence of dmso led to the stepwise replacement of chlorides with dmso and to the isolation of the cationic species [*cis*,*fac*-$RuCl_2$(dmso-O)$_3$(NO)][X] (**23**),[88] [RuCl(dmso-O)$_4$(NO)][X]$_2$ (**24**), and [Ru(dmso-O)$_5$(NO)][X]$_3$ (**25**),[89] respectively (Scheme 10).

Scheme 10

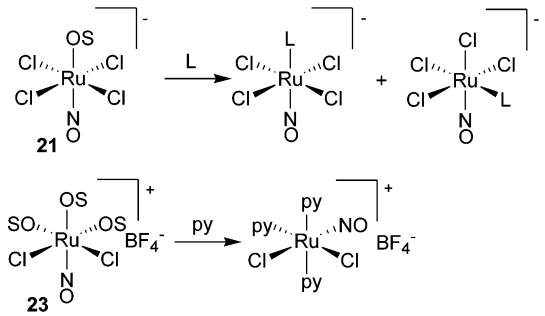


Thus, we have prepared and structurally characterized the whole series of [Ru(dmso-O)$_x$Cl$_{5-x}$(NO)]$^{(x-2)}$ complexes (x = 1−5), in which all dmso ligands are bound through oxygen. Indeed, compounds **24** and **25** are the first Ru complexes having more than three O-bonded dmso ligands and contain also the first examples of the *trans*-Ru(dmso-O)$_2$ fragment.[89] In **24**, the Ru−O bond lengths of the two mutually trans dmso-O's (2.025(3) and 2.056(3) Å) differ by 10σ, probably because of intramolecular steric interactions (the lower structural accuracy of **23**, due to disorder in the orientations of some dmso-O's, prevented comparison).

The spectroscopic features for each of the above nitrosyl complexes (e.g., NO stretching frequencies in the range 1864−1903 cm^{-1}, typical for linear nitrosyls) are consistent with the {Ru(NO)}^{6} formulation,[90] i.e., a diamagnetic Ru(II) nucleus bound to NO^+. Thus, coordination of NO to the Ru(III) precursors involved the formal reduction to Ru(II) by intramolecular transfer of one electron. X-ray analysis showed that compounds **21**−**25** all share a linear nitrosyl group, with short Ru−NO bond distances (from 1.712(5) Å in **21** to 1.733(7) Å in **25**) consistent with a strong $d_\pi \rightarrow \pi^*$ NO backbonding.[84,88,89] Interestingly, the Ru−O-dmso bond distances trans to NO (e.g., 2.029(3) Å in **21** and 2.035(3) Å in **22**) were found to be significantly shorter, by about 0.1 Å, than those observed in compounds of the same charge when the trans ligand is CO (i.e., in **19** and **20**, see above). The short Ru−O distances trans to NO in **21**−**25** are a further manifestation of the well-documented *trans*-shortening effect exerted by the strongly π-accepting nitrosyl ligand trans to a good σ-donor ligand.[84, 90b]

The above Ru(II)−dmso nitrosyl complexes proved also to be suitable precursors for the preparation of new derivatives upon replacement of the dmso-O ligands with N-heterocycles (L); this substitution process may be accompanied by a geometrical isomerization (Scheme 11). For example, treatment of

Scheme 11[a]



[a] L = heterocyclic N-ligand.

[imH][*trans*-$RuCl_4$(dmso-O)(NO)] with an excess of imidazole in refluxing acetone yielded selectively [(im)$_2$H][*trans*-$RuCl_4$(im)(NO)],[84] while the reaction of [N(*n*Bu)$_4$][*trans*-$RuCl_4$(dmso-O)(NO)] with an excess of pyrazine yielded a mixture of the two isomers [N(*n*Bu)$_4$][*trans*-$RuCl_4$(pyz)(NO)] and [N(*n*Bu)$_4$][*cis*-$RuCl_4$(pyz)(NO)] that were separated and structurally characterized.[91] Treatment of [N(*n*Bu)$_4$][*trans*-$RuCl_4$(dmso-O)(NO)] with 0.5 equiv of pyrazine

afforded a mixture of the three possible dinuclear ruthenium nitrosyls with bridging pyrazine, $[N(nBu)_4]_2[\{trans/cis\text{-}RuCl_4(NO)\}_2(\mu\text{-pyz})]$ (*trans,trans*; *cis,cis*; *trans,cis*).[91] In general, in agreement with the shorter Ru−O bond length (see above), we found that replacement of dmso-O trans to NO in **21** required more forcing conditions compared to replacement of dmso-O trans to CO in **19**.[84,91] Finally, the complex $[cis,mer\text{-}RuCl_2(py)_3(NO)][BF_4]$ was prepared by reaction of $[cis,fac\text{-}RuCl_2(dmso\text{-}O)_3(NO)][BF_4]$ (**23**) with excess pyridine (Scheme 11).[88]

2.5. Reactions of Ru(II)–dmso Precursors with σ- and π-Donor Ligands

The potentialities of $cis,fac\text{-}RuCl_2(dmso\text{-}S)_3(dmso\text{-}O)$ (**8**) as a versatile precursor were recognized since the early work by Evans and co-workers,[40] which established that either the dmso's or the chlorides, or both, can be replaced by neutral or anionic ligands under appropriate reaction conditions. Since then, **8** has been increasingly used as precursor in the synthesis of ruthenium compounds, as illustrated in Figure 1. The success of this precursor has to be

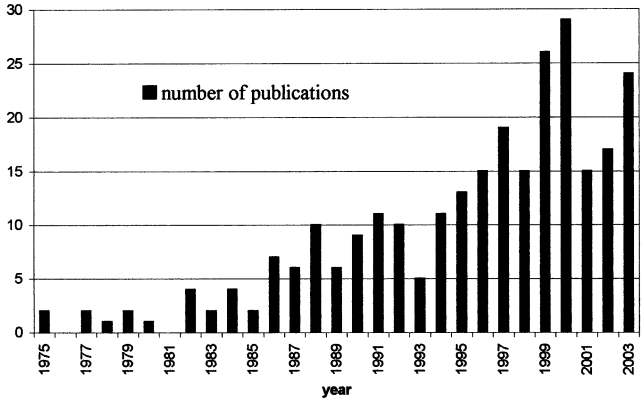


Figure 1. Number of publications per year (1975−2003) that reported **8** as precursor in inorganic synthesis.

ascribed, in addition to its versatile reactivity, also to the ease of its preparation (high yield and purity) and handling, and to its good solubility in a wide range of solvents.

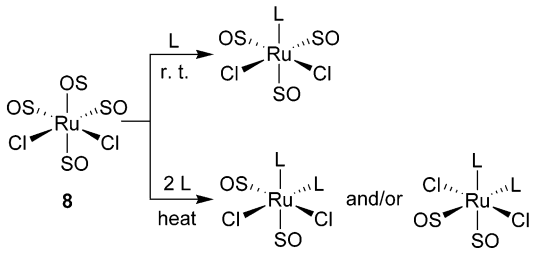
As a rule (with some exceptions), it can be stated that neutral ligands replace preferentially from one to four sulfoxides in **8**, depending on their nature and the reaction conditions (ligand-to-ruthenium ratio, solvent, temperature). Substitution of the dmso ligands can be accompanied by a rearrangement of the $RuCl_2$ fragment from cis to trans. The corresponding dibromo compounds are usually obtained from **11** under the same reaction conditions. Neutral chelating ligands may, in some cases, replace also the halides of **8** and **11**. On the other hand, treatment of **8** or **11** with anionic ligands or weak organic acids (usually in the presence of a suitable base such as NEt_3) normally leads to the replacement of both dmso and halide ligands, depending on reaction conditions.

In the following sections, a large number of examples will be described; the ligands have been divided according to the nature of the donor atoms and to their number; neutral ligands will be treated first, followed by anionic ligands.

2.5.1. Monodentate N Ligands

The O-bonded dmso is the most labile ligand in **8**, and it is selectively replaced by stronger σ- and/or π-donors under mild conditions. We described the synthesis of $cis,fac\text{-}RuCl_2(dmso\text{-}S)_3(L)$ complexes by treatment of **8** with the N-donor ligand L (e.g., L = NH_3, im, py, Me_3Bzm = 1,5,6-trimethylbenzimidazole) in methanol at ambient temperature (Scheme 12);[92,93] the pyrazole (pzH) derivative was obtained

Scheme 12[a]



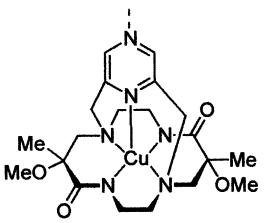
[a] L = NH_3 or heterocyclic N-ligand.

from **8** under similarly mild conditions.[94] Dissolution of **8** in acetonitrile solution yielded crystals of $cis,fac\text{-}RuCl_2(dmso\text{-}S)_3(CH_3CN)$.[58] Interestingly, Farrell and co-workers reported that treatment of **8** with the mono Boc-protected diamine $NH_2(CH_2)_4NHCO_2C(CH_3)_3$, followed by deprotection of the "dangling" moiety and reaction with $K[PtCl_3(NH_3)]$, afforded the heterodinuclear complex $[\{cis,fac\text{-}RuCl_2(dmso\text{-}S)_3\}(\mu\text{-}NH_2(CH_2)_4NH_2)\{cis\text{-}PtCl_2(NH_3)\}]$.[95]

Two dmso ligands in **8** can be also replaced quite easily: treatment of **8** with excess L in refluxing ethanol or toluene yielded the disubstituted species $cis,cis,cis\text{-}RuCl_2(dmso\text{-}S)_2(L)_2$ (e.g., L: Me_3Bzm, 1,2-Me_2im = 1,2-dimethylimidazole,[93,96,97] 4-NO_2im = 4-nitroimidazole[10,11]), often as a mixture with the thermodynamically less stable $trans,cis,cis\text{-}RuCl_2(dmso\text{-}S)_2(L)_2$ isomer (Scheme 12). The two isomers are easily distinguished by ^1H NMR spectroscopy: four singlets in the region of S-bonded dmso for the *cis,cis,cis* isomer (one for each diastereotopic methyl) vs one singlet for the more symmetrical *trans,cis,cis* isomer. Apparently, treatment of **8** with excess pyrazole in refuxing acetonitrile led to the isolation of $trans,cis,cis\text{-}RuCl_2(dmso\text{-}S)_2(pzH)_2$ exclusively.[94,98] It has to be noted that in early works $trans,cis,cis\text{-}RuCl_2(dmso\text{-}S)_2(L)_2$ complexes with L = 2,6-dimethylpyrazine or 4-*tert*-butylpyridine had been erroneously assigned the *cis,cis,trans* geometry.[99,100]

There are also examples in which L is a complexed bridging ligand: treatment of **8** with 2 equiv of a pyrazine-capped cyclam copper complex (Chart 8) led to the replacement of two dmso ligands by the remote nitrogen atoms of pyrazine and produced a trimetallic

Chart 8

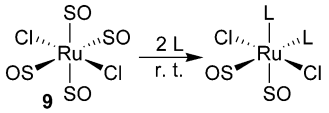


Cu−Ru−Cu complex, in which the geometry of the central $RuCl_2(dmso)_2$ unit and the dmso binding mode were not determined.[101]

Stepwise substitution of two sulfoxides in **8** with two different L ligands (L1 and L2), the first performed at ambient temperature and the second in refluxing ethanol, afforded compounds of the type *cis,cis,cis*-$RuCl_2$(dmso-S)$_2$(L1)(L2).[93,102] Interestingly, in *cis,cis,cis*-$RuCl_2$(dmso-S)$_2$(L1)(L2) complexes (either with L1 = L2 or L1 ≠ L2) the two N ligands experience restricted rotation on the NMR time scale already at room temperature. This phenomenon has been extensively investigated by NMR spectroscopy and the role of the ligand size and of the electrostatic interactions between the L ligands and the two cis halides evidenced.[103] It is worth noting that in such complexes the singlet resonance of one or two of the methyl groups of the two inequivalent dmso-S ligands can be remarkably upfield shifted compared to the usual region for dmso-S (δ = 3.1−3.6) so as to fall in the region typical for dmso-O (δ = 2.6−3.0); this upfield shift very likely results from the ring current shielding of a proximal heterocyclic ligand.[93,96,102]

While substitution of two dmso ligands in **8** can be accompanied by isomerization, treatment of *trans*-$RuCl_2$(dmso-S)$_4$ (**9**) with excess L at ambient temperature (e.g., in chloroform) invariably yielded pure *trans,cis,cis*-$RuCl_2$(dmso-S)$_2$(L)$_2$ complexes (Scheme 13). In other words, compound **9** (and **11** too) under

Scheme 13[a]



[a] L = NH_3 or heterocyclic N-ligand.

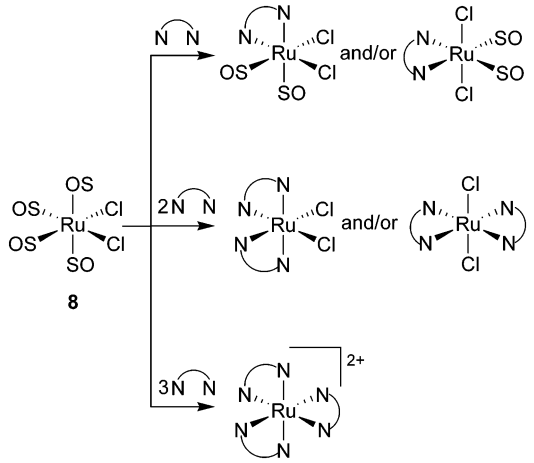
mild reaction conditions *selectively* replaces two cis dmso-S ligands.[92,97] Conversely, when the above reactions are performed at higher temperature, complex **9** behaves like **8** and yields preferentially the thermodynamically more stable *cis,cis,cis* isomer.

Evans and co-workers reported that refluxing **8** in pyridine yielded $RuCl_2(py)_4$ upon replacement of all four sulfoxide ligands;[40] however, the geometry of this product was not established until later, when it was found to be *trans*-$RuCl_2(py)_4$.[104] The corresponding bromo-derivative *trans*-$RuBr_2(py)_4$ was similarly obtained from *trans*-$RuBr_2$(dmso-S)$_4$ (**11**).[14] Similar isostructural *trans*-$RuCl_2(L)_4$ complexes were obtained with L = 4-formylpyridine,[105] pyrazine,[106] and mono-pyridylporphyrin.[107] Finally, refluxing **8** in acetonitrile yielded $RuCl_2(CH_3CN)_4$ of undisclosed (but probably trans) geometry,[108−110] which was then used as Ru precursor.

2.5.2. Polydentate N Ligands

Bidentate N_2 Ligands. There are many examples concerning the reactivity of *cis,fac*-$RuCl_2$(dmso-S)$_3$(dmso-O) (**8**) toward N−N chelating ligands. Early publications reported that treatment of **8** with N−N chelators such as 2-aminopyridine, 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or 8-aminoquinoline in refluxing organic solvents (e.g., chloroform, ethanol, toluene) yielded $RuCl_2$(dmso)$_2$(N−N) complexes.[40,65] The geometry of the complexes and the binding modes of the sulfoxides were not determined. In the case of 8-aminoquinoline, however, the presence of both S-bonded and O-bonded sulfoxides was apparently deduced from the IR spectrum.[65] In the following years, several examples indicated that treatment of **8** with an equimolar amount of a chelating N−N ligand, either diimine or diamine, yielded preferentially *cis,cis*-$RuCl_2$(dmso-S)$_2$(N−N) complexes (Scheme 14) (N−N = phen,[29] 2,2′-bipyr-

Scheme 14

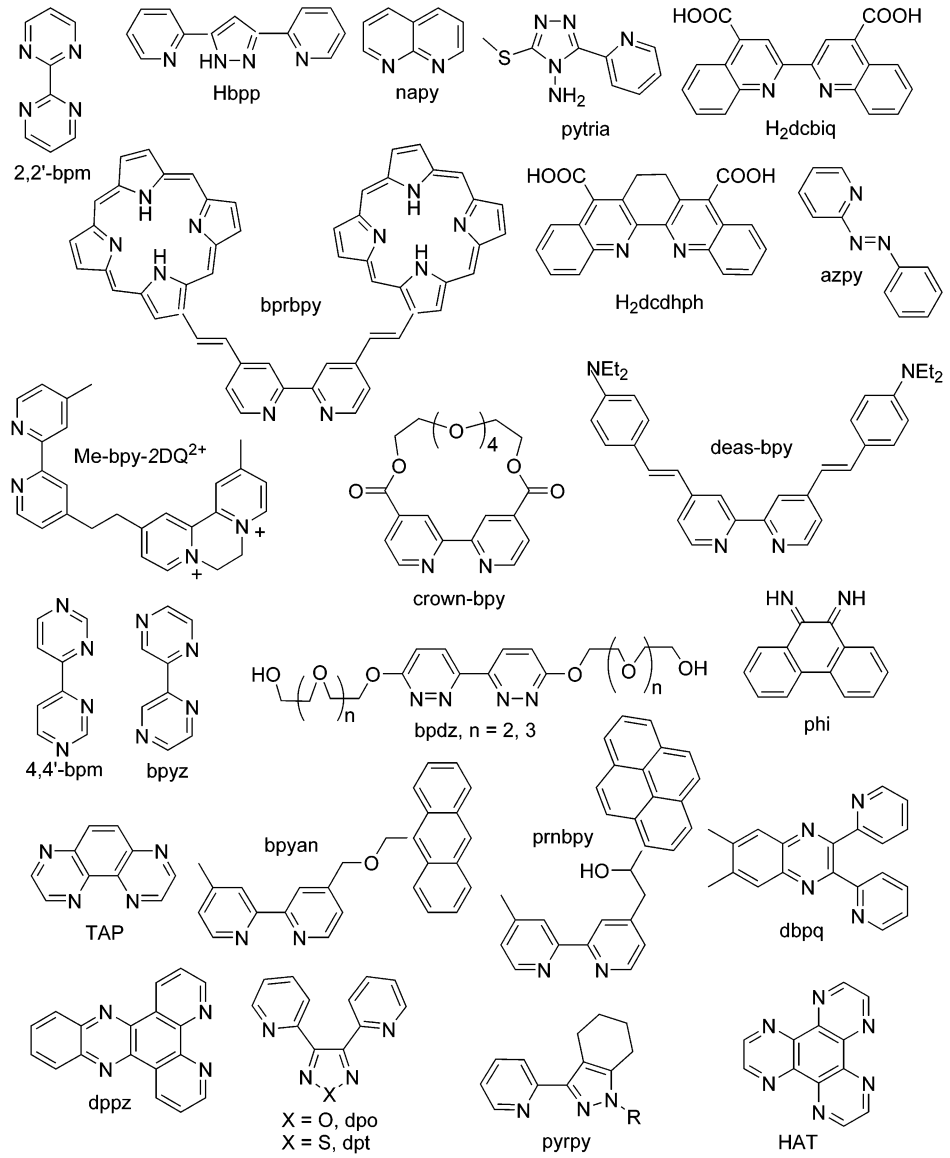


imidine (2,2′-bpm, Chart 9) and related ligands,[111] *N,N,N′,N′*-tetramethylethylenediamine,[112] bpy,[113] 4,4′-dimethyl-2,2′-bipyridine (dmbpy),[114] 4,4′-di-*tert*-butyl-2,2′-bipyridine (dbbpy)[115]).

It was recently found that treatment of **8** with an equimolar amount of the unsymmetric N−N′ ligand 3,5-bis(2-pyridyl)pyrazole (Hbpp, Chart 9) in refluxing methanol for 45 min yielded *trans,cis*-$RuCl_2$(dmso-S)$_2$(Hbpp), while prolonged reflux yielded the thermodynamically more stable geometrical isomer *cis,cis*-$RuCl_2$(dmso-S)$_2$(Hbpp); both compounds were structurally characterized by X-ray.[116] Similarly, treatment of **8** with an equimolar amount of 1,8-naphthyridine (napy, Chart 9) in EtOH/MeOH mixtures at 60 °C afforded *trans,cis*-$RuCl_2$(dmso-S)$_2$(napy) selectively.[117] Conversely, the reaction of **8** with a slight excess of bpy in refluxing chloroform was found to yield a mixture of (not better defined) geometrical isomers of $RuCl_2$(dmso)$_2$(bpy).[118] It was also reported that 4-amino-5-methylthio-3-(2-pyridyl)-1,2,4-triazole (pytria, Chart 9) behaves as a N−N chelating ligand (through the triazole N2 and the pyridyl N atoms) upon reaction with **8**, yielding a mixture of the two isomers *cis,cis*-$RuCl_2$(dmso-S)$_2$(pytria) and *trans,cis*-$RuCl_2$(dmso-S)$_2$(pytria), which were structurally characterized by X-ray investigations.[119]

Finally, it is well established that treatment of **8** with a chelating N−N ligand in the presence of HCl leads to oxidation of Ru(II) to Ru(III) and isolation of *mer*-$RuCl_3$(N−N)(dmso-S) complexes (N−N = phen,[29] *N,N,N′,N′*-tetramethylethylenediamine[120]). The nature of the oxidizing agent in these reactions was not investigated. However, in a similar case with the N−S chelate ligands 4-amino-3-methyl-1,2,4-Δ^2-tri-

Chart 9. Selection of Bidentate N_2 Ligands (with labels) Mentioned in Section 2.5.2.1

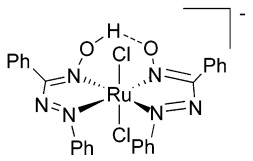


azoline-5-thione and 4-amino-3-ethyl-1,2,4-Δ^2-triazoline-5-thione (see below in section 2.5.3 and Chart 15), the oxidizing agent was found to be dmso, which was reduced to dimethysulfide in acidic conditions.[119]

Several reports indicated that treatment of **8** with 2 equiv of a chelating N−N ligand leads usually to the replacement of all four dmso ligands, which may be accompanied by geometrical isomerization of the two chlorides (Scheme 14). Constable and co-workers found that the reaction of **8** with 2 equiv of 6-phenyl-2,2′-bipyridine (HL) in refluxing ethanol yielded selectively *cis*-$RuCl_2(HL)_2$ as a pair of enantiomers that were characterized by X-ray crystallography.[121] Similar *cis*-$RuCl_2(N{-}N)_2$ complexes were prepared by the reaction of **8** with 2 equiv of N−N chelating ligands in refluxing organic solvents ranging from chloroform to ethylene glycol (N−N = dmbpy,[122] 4,4′-bisporphyrin-2,2′-bipyridine (bprbpy, Chart 9),[123] 3,3′-dicarboxy-2,2′-bipyridine,[124] 2,2′-bipyridine-4,4′-bisphosphonic acid,[125] 2,2′-bipyridine-5,5′-bisphosphonic acid,[125] 4,4′-dicarboxy-2,2′-biquinoline (H_2dcbiq, Chart 9), or 5,8-dicarboxy-6,7-dihydro-dibenzo[1,10]-phenanthroline (H_2dcdhph, Chart 9)[126]). The bis-heteroleptic polypyridyl complex *cis*-$RuCl_2$(dmbpy)(dcbpy) (dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) was obtained from **8** by stepwise assembly;[114] substitution of the first pair of dmso ligands required refluxing chloroform (see above), while substitution of the second pair required refluxing DMF.

Conversely, treatment of **8** with 2 equiv of the bidentate ligand 2-(phenylazo)pyridine (azpy, Chart 9) (or substituted azpy) in refluxing acetone or methanol yielded *trans*-$RuCl_2(azpy)_2$.[127,128] According to Chakravorty and co-workers, the reaction of **8** with 2 equiv of a glyoxal diimine in warm ethanol afforded the *trans*-$RuCl_2(N{-}N)_2$ complex, while the more stable *cis*-$RuCl_2(N{-}N)_2$ isomer was obtained performing the reaction in refluxing ethanol.[129] The same group later reported that reaction of **8** with 2 equiv of (phenylazo)benzaldoxime (HL) in refluxing ethanol afforded the [*trans*-$RuCl_2(HL)(L)]^-$ complex, with a strong hydrogen bond between the cis oximate (L) and the oxime (HL) ligand (Chart 10).[130] On the other hand, Taqui Khan and co-workers reported that treatment of **8** with 2 mol of dimethylglyoxime (dmg-H_2) in refluxing methanol−dichloromethane mixtures

Chart 10



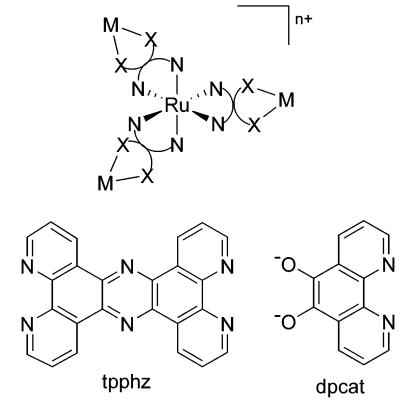
yielded a mixture of the two complexes *cis*,*cis*-$RuCl_2(dmso\text{-}S)_2(dmg\text{-}H_2)$ (confirmed by X-ray structural analysis) and [*cis*-$RuCl(dmso\text{-}S)(dmg\text{-}H_2)_2$]Cl, which were separated by column chromatography.[131] When the same reaction was performed at 100 °C in DMF a complex with two partially deprotonated dmg-H_2 ligands, *trans*-$Ru(dmso\text{-}S)_2(dmg\text{-}H)_2$, was apparently obtained.[131]

Trischelate Ru(II) diimine complexes of the type $[Ru(N{-}N)_3]^{2+}$ have been widely investigated in recent years both as efficient photosensitizers in model systems for the study of photoinduced electron transfer and artificial photosynthesis,[132] and as DNA probes and cleaving agents.[133] In particular, the famous complex $Ru(bpy)_3^{2+}$ has been extensively used as photoredox reagent. Many examples can be found in the literature in which **8** was used as ruthenium source in the synthesis of such complexes. Treatment of **8** with excess N−N ligand under relatively harsh conditions (usually in refluxing ethylene glycol or benzene/ethanol or water/ethanol mixtures) normally yielded the corresponding homoleptic $[Ru(N{-}N)_3]^{2+}$ complex (Scheme 14) (N−N = bpy;[134] 4,4′-dimethyl- and 4,4′-diaryl-2,2′-bipyridine;[122] 4,4′-bis(diethylamino)-2,2′-bipyridine;[135] 6,6′-diamino-2,2′-bipyridine;[136] 5,5′-bis(trimethylsilyl)- and 5,5′-bis(pentamethyldisilanyl)-2,2′-bipyridine;[137] 2,2′-bipyridines substituted in 5,5′-positions with fully conjugated ligands terminated with thiol groups,[138] 2,2′-bipyridines substituted in the 5,5′-positions with electron-withdrawing groups,[139] covalently linked 2,2′-bipyridine-diquat ligands (Me-bpy-*2*DQ^{2+}, Chart 9),[140] 2,2′-bipyridine ligands functionalized with dialkoxybenzene[141] or trimethoxysilyl[142] units at 4,4′ positions, crown ethers incorporating 2,2′-bipyridine (crown-bpy, Chart 9),[143] 4,4′-bis(diethylaminostyryl)-2,2′-bipyridine (deas-bpy, Chart 9),[144] 4-methyl-4′-(2-hydroxyethylpyrenyl)-2,2′-bipyridine (prnbpy, Chart 9),[145] 4,4′-bipyrimidine (4,4′-bpm, Chart 9),[146] 2,2′-bipyrazine (bpyz, Chart 9),[147] 6,6′-oligoethyleneglycol-3,3′-bipyridazine (bpdz, Chart 9),[148] phenanthrenequinone diimine (phi, Chart 9),[149] 2-pyridino-pyrazole and 2-pyridino-pyrazoline ligands,[150] 1,4,5,8-tetraazaphenanthrene (TAP, Chart 9),[151,152] 4-[(9-anthrylmethoxy)methyl]-4′-methyl-2,2′-bipyridine (bpyan, Chart 9),[153] 6,7-dimethyl-2,3-bis-(2′-pyridyl)-quinoxaline (dbpq, Chart 9),[154] 1,4,5,8,9,12-hexaazatriphenylene (HAT, Chart 9),[155] dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz, Chart 9);[156] 3,4-di(2-pyridyl)-1,2,5-oxadiazole (dpo, Chart 9) and 3,4-di(2-pyridyl)-1,2,5-thiadiazole (dpt, Chart 9)[157]).

In some cases, the three bpy or phen units were connected together to form hexadentate, podand-type, polypyridyl ligands L that, upon reaction with 1 equiv of **8**, produced the corresponding $[RuL]^{2+}$ complexes.[158,159] Ruthenium(II) clathrochelate complexes were obtained through a template reaction between **8**, a dioxime ligand (e.g., dmg-H_2) and various boron capping agents (boronic acid, borate esters, and boron halides).[160] The reaction, that involved the prolonged reflux of **8** with the oxime in methanol or THF, produced first (presumably) the intermediate $Ru(dmg\text{-}H_2)_3^{2+}$, that was then fully deprotonated and capped at both ends by the boron agent.

Homo- and heterometallic tetranuclear systems have been prepared by treatment of **8** with 3 equiv of chelating diimine ligands that bear an appended metal center (Chart 11); examples are the prepara-

Chart 11[a]

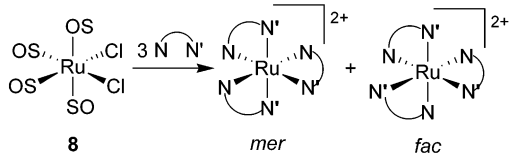


[a] M = Ru or Pt, X = N or O.

tion of $\{Ru[(\mu\text{-tpphz})Ru(bpy)_2]_3\}^{8+}$ (tpphz = tetrapyrido[3,2-a:2′,3′−c:3“,2”-h:2‴,3‴−j]phenazine), obtained by reaction of $[Ru(bpy)_2(tpphz)]^{2+}$ with **8**,[161] and the preparation of $\{Ru[(\mu\text{-dpcat})Pt(dbbpy)]_3\}^{2+}$ (dpcat = 1,10-phenanthroline-5,6-dithiolate), obtained by reaction of [Pt(dpcat)(dbbpy)] with **8**.[115]

By treatment of **8** with unsymmetrical N−N′ chelating ligands (N−N′ = pyrazole linked through nitrogen to another heterocycle which possesses an adjacent nitrogen, such as pyridine, pyrazine, pyrimidine, etc.), the statistically expected 3:1 mixture of *mer*- and *fac*-$[Ru(N{-}N')_3]^{2+}$ isomers was obtained (Scheme 15).[162]

Scheme 15

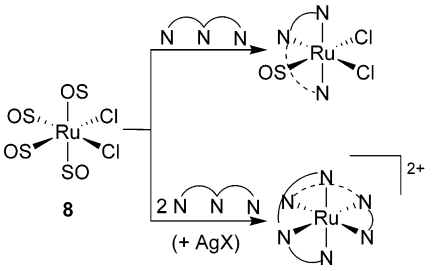


However, the reaction of **8** with 3 equiv of substituted pyrazolylpyridines (pyrpy, 1-substituted-3-(2-pyridinyl)-4,5,6,7-tetrahydroindazoles, Chart 9) was reported to give the meridional isomers exclusively.[163] More recently, the selective synthesis of [*fac*-Ru(5-carboxy-2,2′-$bpy)_3]^{2+}$, using complex **8** as Ru precursor, has been described.[164]

Bis-heteroleptic $[Ru(N{-}N)_2(N'{-}N')]^{2+}$ and tris-heteroleptic $[Ru(N{-}N)(N'{-}N')(N''{-}N'')]^{2+}$ compounds were also obtained from **8** using either a stepwise,[140] or a statistical synthetic approach (one-pot reaction) followed by chromatographic purification of the desired product.[134,163,165,166] One of the chelating ligands might also bear an appended metal center.[167]

Tridentate N_3 Ligands. There are several reports concerning the reactivity of *cis*,*fac*-$RuCl_2(dmso\text{-}S)_3$-

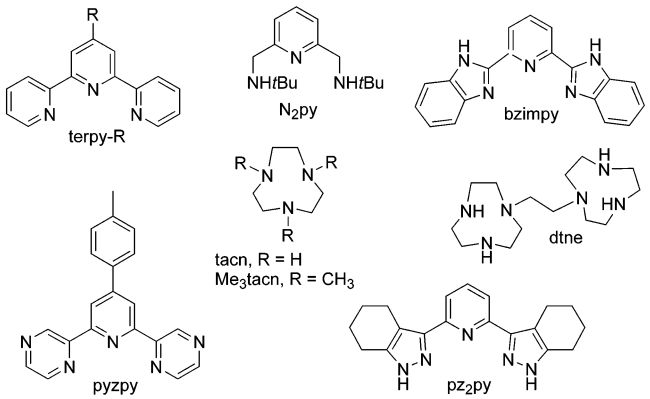
Scheme 16



(dmso-O) (**8**) toward tridentate N ligands (Scheme 16). The reaction of **8** with 1 equiv of 2,2′:6′,2"-terpyridine (terpy), or of a 4′-substituted terpy analogue, in refluxing ethanol afforded *cis,mer*-$RuCl_2$(terpy)(dmso-S) complexes, which were further used for the preparation of heteroleptic bis-trischelate compounds $[Ru(terpy)(L)]^{2+}$ upon replacement of the dmso and Cl ligands with a further tridentate ligand L.[168,169]

Treatment of **8** with 2 equiv of terpy, or modified terpy ligands (terpy-R, Chart 12), sometimes in conjunction with the addition of 2 equiv of a soluble Ag salt, produced a series of homoleptic $[Ru(terpy\text{-}R)_2]^{2+}$ complexes (substitution in 4′ position: R = H,[170] 4-anilino,[171] hydroquinones,[172] 4-pyridyl,[173] ferrocenyl groups,[169,173,174] metal complexes with pendant terpy moieties;[175] substitution in 5 position: R = thiourea[176]). Heteroleptic complexes bearing two different modified terpy ligands were prepared from **8** either through a stepwise synthetic procedure involving $RuCl_2$(terpy-R)(dmso-S) intermediates (see above) or through one-pot reactions followed by chromatographic purification of the product.[177]

Chart 12. Selection of Tridentate N_3 Ligands (with labels) Mentioned in Section 2.5.2.2



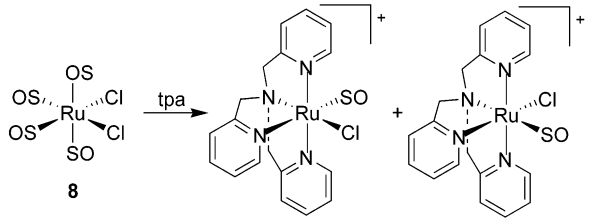
There are examples in which **8** was treated with bridging ligands made by two terpy fragments linked through a connecting unit; the reactions led to dimeric[178] or polymeric complexes (molecular wires) containing $[Ru(terpy)_2]^{2+}$ repeating units,[179] depending on the reaction conditions and on the presence of stopper ligands. Elegant examples of the use of **8** in the construction of elaborate supramolecular assemblies were given by the group of Sauvage.[180,181] Treatment of **8** with a multidentate ligand containing two terpy units strapped through one dpp fragment (dpp = 2,9-diphenyl-1,10-phenanthroline) under high-dilution conditions gave in good yield a 29-membered macrocycle in which both terpy units clipped to the Ru center replacing all ligands. This synthetic strategy was further developed, exploiting the coordination of the dpp fragments to a Cu(I) template ion, to afford the construction of catenanes and rotaxanes containing $Ru(terpy)_2^{2+}$ units within the rings.

Several examples can be found in the literature with tridentate N ligands structurally similar to terpy. The group of Caulton reported that treatment of **8** with the "pincer ligand" 2,6-bis-(*t*BuNHCH$_2$)$_2$-NC_5H_3 (N_2py, Chart 12) in refluxing benzene gave isomerically pure *cis,mer*-$RuCl_2(N_2py)$(dmso-S); the meridional geometry of the coordinated N_2py ligand was confirmed by the solid-state structure determination.[182] Conversely, treatment of **8** with 2,6-bis-(benzimidazol-2-yl)pyridine (bzimpy, Chart 12) in refluxing methanol yielded $[Ru(bzimpy)_2]Cl_2$.[183] Similarly, treatment of **8** with 2 equiv of the rigid tridentate bis(pyrazolyl)pyridine ligand 2,6-di(1*H*-4,5,6,7-tetrahydrobenzopyrazol-3-yl)pyridine (pz_2py, Chart 12) in refluxing ethanol afforded $[Ru(pz_2py)_2]Cl_2$;[184] reactions with N-substituted pz_2py ligands gave similar products but required more forcing conditions (refluxing ethylene glycol).[185,186] Also the reaction of **8** with 2 equiv of the tridentate 4-*p*-tolyl-2,6-di(2-pyrazinyl)-pyridine ligand (pyzpy, Chart 12) in refluxing 1,2-ethanediol produced the corresponding $[Ru(pyzpy)_2]^{2+}$ complex in high yield.[187]

The reaction of **8** with the cyclic tridentate amines 1,4,7-triazacyclononane (tacn, Chart 12) or 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn, Chart 12) in refluxing toluene or ethanol afforded complexes formulated as $[RuCl(tacn)(dmso)_2]Cl$[188] and $Ru(Me_3tacn)(dmso)_xCl_2$ ($x = 1-2$),[189,190] respectively. Similarly, reaction of **8** with the strapped analogue 1,2-bis(1,4,7-triazacyclononan-1-yl)ethane (dtne, Chart 12) afforded the dinuclear species $[Ru_2(dtne)(dmso)_4Cl_2]Cl_2$ in nearly quantitative yield.[188] Unfortunately, these compounds were not fully characterized but further reacted with concentrated HCl in the presence of O_2 to produce the Ru(III) species $Ru(tacn)Cl_3$, $Ru(Me_3tacn)Cl_3$, and $Ru_2(dtne)_2Cl_6$, respectively.[188-190]

Tetradentate N_4 Ligands. The reactivity of **8** toward the potentially tetradentate ligand tris(2-pyridylmethyl)amine (tpa) has been extensively investigated.[191-194] According to Bjernemose and coworkers, treatment of **8** with tpa in refluxing ethanol followed by precipitation as the PF_6^- salt yielded exclusively the $[RuCl(tpa)(dmso\text{-}S)][PF_6]$ complex (characterized by X-ray crystallography), in which tpa acts as a tripodal tetradentate ligand and Cl is trans to the tertiary amino group of tpa (Scheme 17).[193] The same geometry of cation had been previously reported

Scheme 17[a]

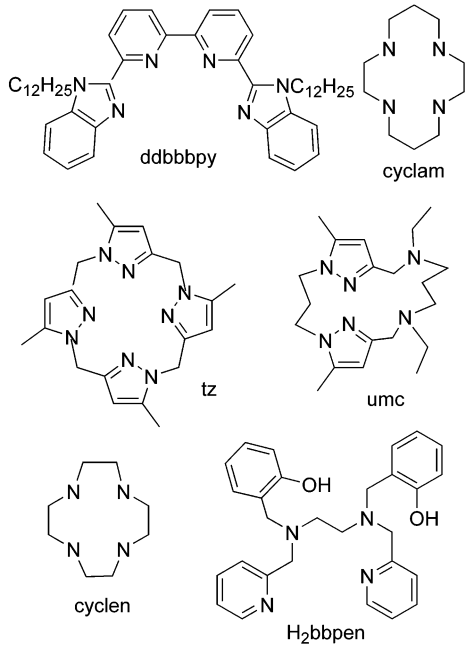


[a] tpa = tris(2-pyridylmethyl)amine.

by Kojima and co-workers for the 5-methyl substituted analogue of tpa.[192] Conversely, Yamaguchi and co-workers obtained (under unreported reaction conditions) a mixture of the above complex and of the geometrical isomer in which dmso-S, rather than Cl, is trans to the sp^3 N atom (Scheme 17);[191] the two isomers were separated by fractional crystallization and the X-ray structure of the cis(Cl, N_{amino}) complex determined.

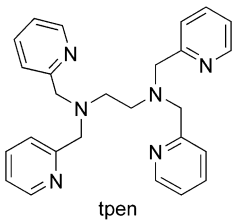
The reaction of **8** with the tetradentate ligand 6,6-bis(*N*-dodecylbenzimidazol-2-yl)-2,2′-bipyridine (ddbbbpy, Chart 13) in either refluxing toluene or dichloromethane afforded *trans*-$RuCl_2$(ddbbbpy).[195] Marzin, Tarrago, and co-workers investigated the reactivity of **8** toward polyaza- and, in particular, tetrapyrazolic macrocycles, such as 2,7,12,17-tetramethyl-1,6,11,16-tetraazaporphyrinogen (tz, Chart 13); treatment of **8** with tz in refluxing water/ethanol mixtures yielded compounds formulated first as [*trans*-Ru(tz)(dmso-S)Cl]Cl or [*trans*-Ru(tz)(dmso)$_2$]-Cl_2,[196,197] and later as [*trans*-Ru(tz)(dmso-S)(H_2O)]-Cl_2.[198] The treatment of **8** with unsymmetrical macrocycles containing two pyrazole and two amine units (umc, one example in Chart 13) led to the isolation of $RuCl_2$(umc)(dmso-S)$_2$ complexes (of undetermined geometry) in which only the two sp^3 nitrogen atoms of umc are coordinated to the metal.[199,200] Sakai and co-workers reported an improved method for the preparation of the Ru(III) complex [*cis*-$RuCl_2$(cyclam)]-Cl (cyclam = 1,4,8,11-tetraazacyclotetradecane, Chart 13) that involved treatment of **8** with cyclam in refluxing ethanol, followed by addition of concentrated HCl.[201] Reaction of **8** with the similar tetradentate ligand tren (tris(2-aminoethyl)amine) under various conditions yielded no products.[201] The corresponding [*cis*-$RuCl_2$(cyclen)]Cl (cyclen = 1,4,7,10-tetraazacyclododecane, Chart 13) was recently prepared under very similar conditions.[202] The reaction of **8** with *N*,*N*′-bis(2-hydroxybenzyl)-*N*,*N*′-bis(2-methylpyridyl)ethylenediamine (H_2bbpen, Chart 13) in refluxing ethanol afforded a poorly characterized complex, formulated as [Ru(H_2bbpen)(dmso)$_2$]Cl_2, in which apparently H_2bbpen acts as a tetradentate N_4 neutral ligand with two uncoordinated phenol groups.[203] Recently, Sauvage and co-workers reported that treatment of **8** in high dilution conditions (80 °C, 1,2-dichloroethane) with an acyclic tetradentate ligand (N_4) containing two 1,10-phenanthroline moieties afforded *cis*-$RuCl_2$(N_4); this complex was then used as starting material for the synthesis of a [2]catenane.[204]

Chart 13. Selection of Tetradentate N_4 Ligands (with labels) Mentioned in Section 2.5.2.3



Hexadentate N_6 Ligands. Examples of hexadentate N ligands made by three strapped bipy or phen units,[158,159] or made by two linked terpy units,[179,180] that were found to react with **8** by replacing all the dmso and Cl ligands, were mentioned above. It has been also reported that reaction of **8** with *N*,*N*,*N*′*N*′-tetrakis(2-pyridylmethyl)ethylenediamine (tpen, Chart 14) in refluxing acetonitrile gave smoothly the $[Ru(tpen)]^{2+}$ complex, with fully coordinated hexadentate tpen.[205]

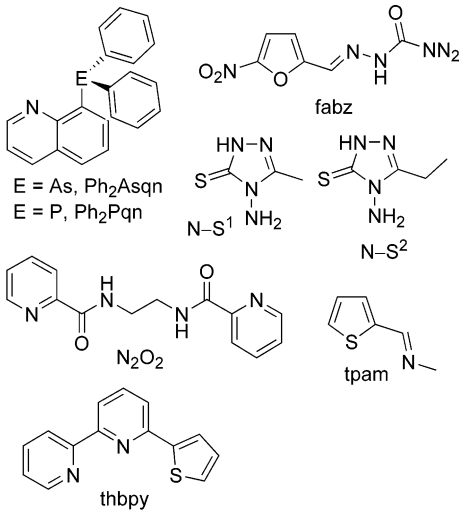
Chart 14



2.5.3 Polydentate N,X Ligands (X = As, O, S)

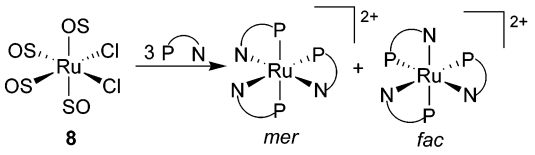
The N−As chelate ligand 8-(diphenylarsino)quinoline (Ph_2Asqn, Chart 15) was found to react with **8** in refluxing toluene to yield $RuCl_2$(Ph_2Asqn)(dmso)$_2$ (as for the corresponding complex with 8-aminoquinoline, the presence of both dmso-S and dmso-O was deduced from the IR spectrum).[65] Conversely, under similar conditions, the corresponding N−P chelate ligand 8-(diphenylphosphino)quinoline (Ph_2-Pqn, Chart 15) did not react with **8** and only the dinuclear Ru-dmso compound **16** (Chart 3) was isolated.[65] The different behavior of **8** toward the two

Chart 15



similar N−As and N−P chelate ligands was attributed to the competition between dimerization and substitution reactions: dmso substitution appears to be faster than dimerization in the case of Ph_2Asqn, while the opposite occurs with Ph_2Pqn. It should be noted however that replacement of all ligands of **8** was found to occur when the ruthenium precursor was treated with a 3-fold excess of 8-(dimethylphosphino)quinoline (Me_2Pqn) in refluxing ethylene glycol; by tuning the reaction conditions, the two geometrical isomers [*mer*-$Ru(Me_2Pqn)_3]^{2+}$ and [*fac*-$Ru(Me_2Pqn)_3]^{2+}$ were selectively synthesized, isolated in pure, form and structurally characterized (Scheme 18).[118]

Scheme 18[a]



[a] P,N ligand = Me_2Pqn.

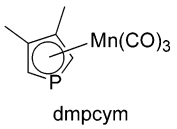
Complexes of general formula *trans,cis*-$RuCl_2$(dmso-S)$_2$(N−O), in which N−O is an anti-trypanosomal active semicarbazone such as 5-nitro-2-furaldehyde semicarbazone (fabz, Chart 15) and similar, were obtained in good yields by reaction of **8** with fabz in refluxing ethanol or toluene.[206] Spectroscopic and X-ray data indicate that in such products the semicarbazone acts as a bidentate ligand through its carbonylic oxygen and azomethynic nitrogen atoms, forming a five-membered ring with Ru. Treatment of **8** with 0.5 equiv of a series of binucleating N_2O_2 amide ligands (obtained by condensation of pyridine-2-carboxylic acid with aromatic and aliphatic diamines, one example shown in Chart 15) produced dinuclear Ru(II) complexes of formula [{*trans,cis*-$RuCl_2$(dmso-S)$_2$}$_2$(μ-N_2O_2)].[207]

Reaction of **8** with N−S ligands (N−S^1 = 4-amino-3-methyl-1,2,4-Δ^2-triazoline-5-thione, N−S^2 = 4-amino-3-ethyl-1,2,4-Δ^2-triazoline-5-thione, Chart 15) in the presence of aqueous HCl was found to lead to *mer*-$RuCl_3$(N−S)(dmso-S) complexes (dmso, the oxidizing agent, was found to be reduced to dms in acidic conditions).[119] Treatment of **8** with the *N*-methyl-2-thiophenealdimine N−S ligand (tpam, Chart 15) yielded the poorly characterized complex $RuCl_2$(dmso-S)$_2$(tpam) of undetermined geometry.[112] Finally, a tridentate N_2S coordination to ruthenium was found with the ligand 6-(2-thienyl)-2,2′-bipyridine (thbpy, Chart 15): treatment of **8** with thbpy in refluxing ethanol yielded a complex formulated as *trans,mer*-$RuCl_2$(thbpy)(dmso-S).[208]

2.5.4. Monodentate P, As, and Sb Ligands

Riley and co-workers reported that treatment of *trans*-$RuBr_2$(dmso-S)$_4$ (**11**) with an equimolar amount of a phosphine (P, e.g., triphenyl- or tributylphosphine) in refluxing toluene yielded $RuBr_2$(dmso-S)$_3$(P) complexes of undisclosed geometry.[14] They also found that $RuX_2(dmso)_n$(E) complexes, where X = Cl, Br, *n* = 2 or 3, and E = trialkyl- or triarylphosphine or arsine, are excellent catalysts for the selective molecular oxygen oxidation of thioethers to sulfoxides.[14,15] This reactivity of **11** with phosphines is in contrast to that reported by Evans et al. for **8**, which apparently led to five-coordinate $RuCl_2(dmso)_2$(P) compounds.[40] The complex *cis,fac*-$RuCl_2$(dmso-S)$_3$-$(PPh)_3$ was prepared by treatment of $RuCl_2(PPh_3)_3$ with dmso;[15] when this product was heated in refluxing methanol the triply chloro-bridged dimeric complex [(dmso-S)$_2$(PPh_3)Ru(μ-Cl)$_3$RuCl(dmso-S)-(PPh_3)] was obtained, which can be thought of as deriving formally from the dinuclear species **16** (similarly obtained from **8**, see above Chart 3) upon replacement of one dmso-S molecule on each Ru atom by a PPh_3 ligand.[15] The group of Dixneuf reported that the reaction of **8** with 1 equiv of the bulky tricyclohexylphosphine (Pcy_3) in dichloromethane at ambient temperature gives the five-coordinate complex $RuCl_2$(dmso-S)$_2$(Pcy_3), while a six-coordinate $RuCl_2$(dmso-S)$_2$(Pcy_3)$_2$ complex of undetermined geometry was isolated when 2 equiv of Pcy_3 were used;[209] these species were exploited as precursors for the preparation of a variety of ruthenium−allenylidene compounds. Apparently the reaction of **8** with 4 equiv of the bulky aminophosphine $Ph_2PN(H)C_6H_{11}$ at ambient temperature yielded a low-coordination Ru(II) complex formulated either as an anionic tetrahedron, [RuCl{$Ph_2PN(H)C_6H_{11}$}$_3$]Cl, or as a neutral trigonal bipyramid, [$RuCl_2$\{$Ph_2PN(H)$-C_6H_{11}\}$_3$].[210] The reaction of **8** with 4 equiv of 3,4-dimethylphosphacymantrene (dmpcym, phosphacymantrene = η^5-phosphacyclopentadienyl-manganese-tricarbonyl, Chart 16) in THF at 40 °C produced *cis*-

Chart 16



dmpcym

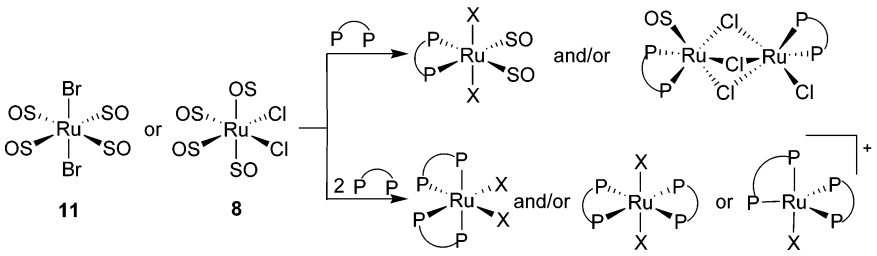
$RuCl_2(dmpcym)_4$.[211] Treatment of **8** with methoxydiphenylphosphine (Ph_2POMe) in refluxing methanol yielded the five-coordinate phosphinite complex $RuCl_2(Ph_2POMe)_3$, which in the solid state has a triply chloro-bridged dimeric structure, [{$Ru(Ph_2$-$POMe)_3$}$_2$(μ-Cl)$_3$]Cl.[212,213] The reaction of **8** with 3 equiv of triphenylphosphine monosulfonate (tppms) in refluxing toluene apparently afforded the water-soluble *cis*-$RuCl_2$(dmso-S)(tppms)$_3$ complex.[214]

Taqui Kahn and co-workers reported that treatment of **8** with a number of monodentate arsines and stibines in refluxing ethanol/hydrochloric acid mixtures led to replacement of either two or three dmso ligands, yielding a series of scarcely characterized six-coordinate complexes, formulated as *cis,cis,cis*-$RuCl_2$(dmso-S)$_2$($AsPh_3$)$_2$, *cis,cis,trans*-$RuCl_2$(dmso-S)$_2$($AsPh_3$)$_2$, and *trans*-$RuCl_2$(dmso-S)(L)$_3$ (L = $AsMePh_2$, $AsMe_2Ph$, $SbPh_3$).[215]

2.5.5. Polydentate P and As Ligands

Bidentate P_2 and As_2 Ligands. The reactivity of **8** and **11** with bidentate phosphine ligands has been investigated by a number of authors. Riley reported that the reaction of **11** with the chelating 1,2-bis-(diphenylphosphino)ethane ligand (dppe) in refluxing

Scheme 19[a]

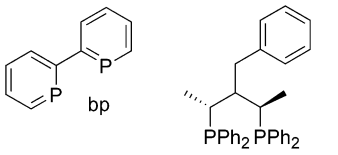


[a] X = Cl or Br.

toluene yielded the disubstituted complex *trans,cis*-$RuBr_2$(dmso-S)$_2$(dppe) (Scheme 19).[14]

A complex with the same stoichiometry but different geometry, *cis,trans*-$RuCl_2$(dmso-S)$_2$(bp) was prepared by treatment of **8** with a 2,2′-biphosphinine (bp, a phosphorus analogue of bpy, Chart 17) in THF at ambient temperature;[216] the bisphosphinine is a rather good π-acceptor ligand, and, interestingly, the above complex has the same uncommon geometry, with trans S-bonded dmso ligands, as found in the bis-carbonyl complex *cis,trans,cis*-$RuCl_2$(dmso-S)$_2$(CO)$_2$ (see below section 2.6). In addition, treatment of **8** with excess bp in refluxing chloroform led to the isolation of the tetra-substituted species *cis*-$RuCl_2$(bp)$_2$.[216]

Chart 17



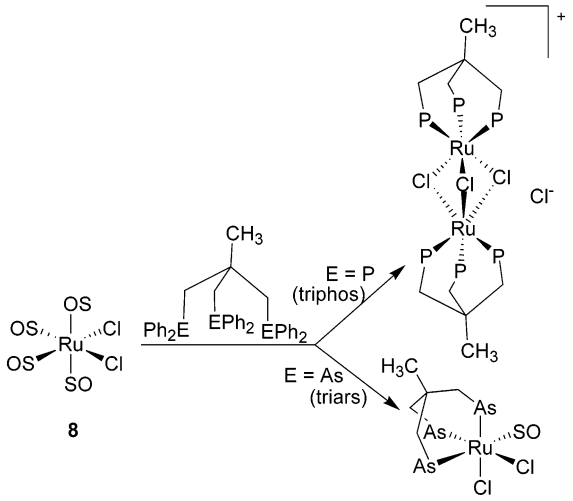
(*R*)-(*R*)-BDPBzP

Indeed, replacement of all four dmso molecules upon treatment of **8** or **11** with excess chelating diphosphines or diarsines seems to be a common feature (Scheme 19). Taqui Kahn and co-workers reported that the reaction of **8** with the bidentate ligands 1,2-bis(diphenylarsino)methane (dpam), 1,2-bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylarsino)ethane (dpae), and 1,2-bis(diphenylphosphino)ethane (dppe) in refluxing ethanol gave the complexes *cis*-$RuCl_2$(dpam)$_2$, *cis*-$RuCl_2$(dppm)$_2$ (which is apparently five-coordinate with one monodentate dppm unit), *trans*-$RuCl_2$(dpae)$_2$, and *trans*-$RuCl_2$(dppe)$_2$, respectively.[215] The preparation of *cis*-$RuCl_2$(dppm)$_2$ (apparently six-coordinate) and of *trans*-$RuCl_2$(dppe)$_2$ from **8** was later described also by other authors.[217−219] Bautista and co-workers reported that treatment of **8** with 2 equiv of dppe affords a ca. 3:1 mixture of *cis*- and *trans*-$RuCl_2$(dppe)$_2$ (Scheme 19); similar results were obtained also with 1,2-bis(diethylphosphino)ethane (depe).[220] More recently, the *cis*-$RuCl_2$(depe)$_2$ isomer was obtained in excellent yield and high isomeric purity by the reaction of **8** with 2 equiv of depe in refluxing acetone.[221] Conversely, Mezzetti et al. found that treatment of either **8** or **11** with 2 equiv of the bulky diphosphine ligand 1,2-bis(dicyclohexylphosphino)ethane (dcpe) led to five- or six-coordinate complexes, depending on the reaction medium: coordinatively unsaturated [RuX(dcpe)$_2$][BPh_4] species were obtained from refluxing ethanol (in the presence of excess $NaBPh_4$), while *trans*-RuX_2(dcpe)$_2$ complexes were isolated from boiling benzene (X = Cl, Br).[222] Later, Winter and Hornung found that the reaction between **8**, dcpe, and $NaBPh_4$, performed under conditions very similar to those described above, afforded two different hydrido (rather than halide) ruthenium products, their relative amounts depending on the reaction conditions: the five-coordinate, 16 valence electron, cation complexes [RuH(dcpe)$_2$][BPh_4], and the neutral zwitterionic, 18 valence electron, complex {(η^6-C_6H_5)-BPh_3}RuH(dcpe) (both characterized through X-ray crystal structure).[223] The same authors found that when the reaction was performed with the smaller chelate 1,1-bis(dicyclohexylphosphino)methane (dcpm) different products were isolated, either *trans*-RuHCl(dcpm)$_2$ or *trans*-$RuCl_2$(dcpm)$_2$, depending on conditions.[223] The reaction of **8** with 2 equiv of bis(phosphino)amines of the type $Ph_2PN(R)PPh_2$ (R = H, Me) at ambient temperature yielded exclusively *cis*-$RuCl_2$($Ph_2PN(R)PPh_2$)$_2$;[224] however, similar reactions with the bulkier bis(phosphino)amines with R = Et, *n*Pr, *i*Pr, *n*Bu led to the isolation of only the geometrical isomers *trans*-$RuCl_2$($Ph_2PN(R)PPh_2$)$_2$.[224]

Besides mononuclear complexes, also chloro-bridged dinuclear species were obtained from the reaction of **8** with chelating diphosphines (Scheme 19). James and co-workers reported that treatment of **8** with 1 equiv of 1,4-bis(diphenylphosphino)butane (dppb) in a dichloromethane/acetone mixture at reflux yielded the triply chloro-bridged dinuclear complex [(dmso-S)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] (together with a small amount of the coordinatively unsaturated Ru_2Cl_4(dppb) dimer);[225] the complex was structurally characterized also by X-ray crystallography. An analogous dinuclear complex, [(dmso-S)(BDPBzP)Ru(μ-Cl)$_3$RuCl(BDPBzP)], was obtained by Bianchini and co-workers under similar conditions with the C_1-symmetric diphosphine ligand (*R*)−(*R*)-3-benzyl-2,4-bis(diphenylphosphino)pentane (BDPBzP, Chart 17).[226]

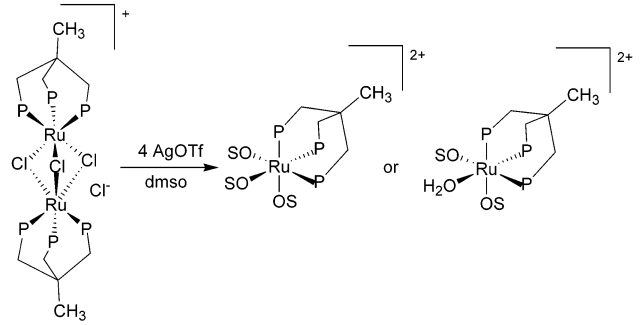
Tridentate P_3 and As_3 Ligands. As detailed below, the reactivity of *cis,fac*-$RuCl_2$(dmso-S)$_3$(dmso-O) (**8**) toward tridentate phosphines and arsines has been investigated by several authors. Venanzi and co-workers found that treatment of **8** with the facially coordinating tripodal ligand $MeC(CH_2PPh_2)_3$ (triphos) in refluxing toluene gives the triply chloro-bridged dinuclear species [(triphos)Ru(μ-Cl)$_3$Ru(triphos)]Cl in high yield (Scheme 20), whose X-ray structure was determined as BPh_4 salt.[227] This complex had been erroneously formulated before as $RuCl_2$(triphos).[228]

Scheme 20. Phenyl Groups of Triphos and Triars Omitted in the Products



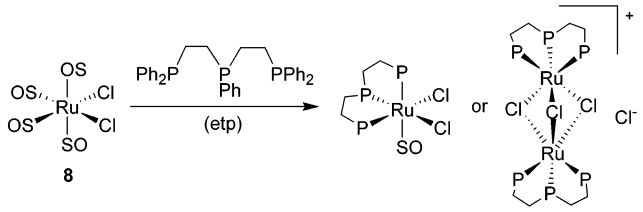
Interestingly, when the corresponding As tripod ligand $MeC(CH_2AsPh_2)_3$ (triars) was reacted with **8** under the same conditions, the mononuclear species *fac*-Ru(triars)Cl_2(dmso-S) was isolated in very high yield (Scheme 20).[227] Treatment of [(triphos)Ru(μ-Cl)$_3$Ru(triphos)]Cl with an excess of AgOTf in warm dmso led to the abstraction of all chloride ligands and to the isolation of [*fac*-Ru(triphos)(dmso-O)$_3$](OTf)$_2$ or of [*fac*-Ru(triphos)(dmso-O)$_2$(H_2O)](OTf)$_2$ (depending on reaction conditions). Both complexes, according to IR and NMR data, bear exclusively O-bonded dmso ligands (Scheme 21).[227]

Scheme 21. Phenyl Groups of Triphos Omitted



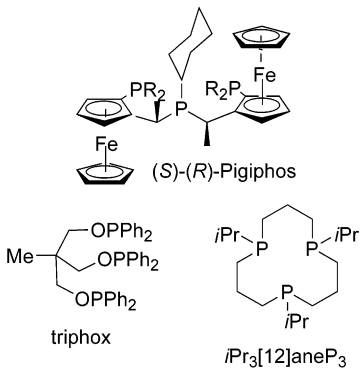
Similarly, the reaction of **8** with an equivalent amount of the water-soluble tripodal ligand $NaO_3S(C_6H_4)CH_2C(CH_2PPh_2)_3$ in toluene at 90 °C yielded the triply chloro-bridged dimer Na[{$O_3S(C_6H_4)CH_2C(CH_2PPh_2)_3Ru$}$_2$($\mu$-Cl)$_3$].[229] Dinuclear species similar to [(triphos)Ru(μ-Cl)$_3$Ru(triphos)]Cl, namely, [(etp)Ru(μ-Cl)$_3$Ru(etp)]Cl (whose nature was confirmed by the X-ray structure of the triflate salt) and [(etpR)Ru(μ-Cl)$_3$Ru(etpR)]Cl, were obtained by the group of Venanzi when **8** was prolongately refluxed in dry toluene with the chainlike tridentate phosphines $PhP(CH_2CH_2PPh_2)_2$ (etp) and $PhP\{CH_2CH_2P(p\text{-}R\text{-}C_6H_4)_2\}_2$ (etpR, R = F, Me, OMe), respectively (Scheme 22).[230,231] However, other authors later reported that the same reaction, performed for a much shorter time (3 vs 68 h), yielded instead the mononuclear species *fac*-Ru(etp)Cl_2(dmso-S) (similar to the triars complex obtained by Venanzi[227]) (Scheme 22), whose X-ray structure was also determined[232] (a poorly characterized complex tentatively formulated as *cis*,*trans*-$RuCl_2$(dmso-S)$_2$(etp), in which one terminal P atom of etp is uncoordinated, had been previously reported by Taqui Khan and co-workers[233]).

Scheme 22. Phenyl Groups of etp Omitted in Products



Finally, the reaction of **8** with $PhP(CH_2CH_2CH_2PPh_2)_2$ (ttp) gave the mononuclear five-coordinate complex *fac*-$RuCl_2$(ttp), with a geometry (determined by X-ray analysis) intermediate between square pyramidal and trigonal bipyramidal.[230] The mononuclear nature of *fac*-$RuCl_2$(ttp), as opposed to the triply chloro-bridged bimetallic structure of [(etp)Ru(μ-Cl)$_3$Ru(etp)]Cl, was attributed to purely steric reasons, as the Ru(ttp) unit occupies a larger volume than Ru(etp).[230] Similar five-coordinate mononuclear complexes of formula $RuCl_2(P_3)$ were obtained from **8** with chiral bis(ferrocenyl)-triphosphine ligands such as (*S*)−(*R*)-Pigiphos (bis{(*S*)-1-(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl}cyclohexylphosphine, Chart 18),[234] with the chiral ligand (*R*)-$Ph_2PCH_2CH(PPh_2)CH_2CH_2PPh_2$ (etp*),[235] with $PhP(CH_2CH_2CH_2P(C_6H_{11})_2)_2$ (Cyttp),[236] and with the tridentate phosphinite ligand $MeC(CH_2OPPh_2)_3$ (triphox, Chart 18);[212] interestingly, this latter complex showed a triply chloro-bridged dimeric structure in the solid state, while in chloroform solution a significant part of the complex existed as the monomeric form.

Chart 18

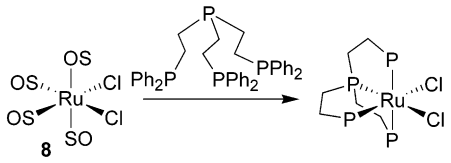


The complex *cis*,*fac*-$RuCl_2$(*i*Pr_3[12]aneP_3)(dmso) was obtained by treatment of **8** with the macrocyclic P-ligand 1,5,9-tris(2-propyl)-1,5,9-triphosphacyclododecane (*i*Pr_3[12]aneP_3, Chart 18) in dichloromethane at room temperature;[237] the coordination mode of the dmso ligand was not clearly determined.

Tetradentate P_4 Ligands. There are also a few examples in which complex **8** was reacted with potentially tetradentate phosphine ligands. According to Taqui Khan and co-workers, the reaction of **8** with the chainlike $Ph_2PCH_2CH_2(PPh)CH_2CH_2(PPh)CH_2CH_2PPh_2$ ligand (tetraphos-1) or with the tripodal $P(CH_2CH_2PPh_2)_3$ ligand (tetraphos-2) in refluxing

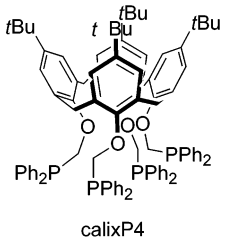
benzene−methanol mixtures afforded poorly characterized complexes, formulated as [*trans*-RuCl(dmso-S)(tetraphos-1)]Cl and [*cis*-RuCl(dmso-S)(tetraphos-2)]Cl, respectively.[233] Conversely, according to later works, treatment of **8** with an equivalent amount of the tripodal tetradentate PP_3 ligands $P(CH_2CH_2CH_2PMe_2)_3$[238] or $P(CH_2CH_2PPh_2)_3$[239] in refluxing toluene afforded in good yield the corresponding six-coordinate *cis*-$RuCl_2(PP_3)$ complexes (Scheme 23 for $P(CH_2CH_2PPh_2)_3$).

Scheme 23. P Substitutents Omitted in Product



Finally, the reaction of **8** with a *p-tert*-butylcalyx[4]arene functionalized at the lower rim with four pendent CH_2PPh_2 units (calixP4 = cone-5,11,17,23-tetra-*t*Bu-25,26,27,28-tetrakis(diphenylphosphinomethoxy)calyx[4]arene, Chart 19) in dichloromethane

Chart 19

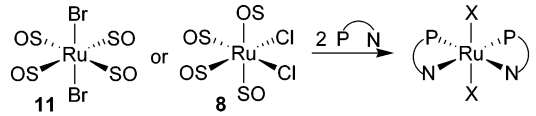


at room temperature led to the selective formation of a *fac*-$RuCl_2$(calixP4) species in which the calixarene behaved as a *fac*-bonded tridentate ligand with one phosphine remaining free.[240]

2.5.6. Polydentate P,N, P,As, and P,N,O Ligands

According to an early report by Taqui Khan and co-workers, a poorly characterized five-coordinate complex of formula $[RuCl(Ph_2PCH_2CH_2NHCH_2Ph-P,N)_2]Cl$ apparently formed upon reaction of **8** with 2 equiv of 2-(diphenylphosphino)ethyl-benzylamine.[241] Later, Rigo and co-workers reported that treatment of either *cis*,*fac*-$RuCl_2$(dmso-S)$_3$(dmso-O) (**8**) or *trans*-$RuBr_2$(dmso-S)$_4$ (**11**) with 2 equiv of 1-(diphenylphosphino)-2-(2-pyridyl)ethane (ppye, Chart 20) in boiling toluene led to the substitution of all four dmso ligands and yielded *trans*,*cis*,*cis*-RuX_2(ppye-*P*,*N*)$_2$ complexes (X = Cl, Br) (Scheme 24).[242]

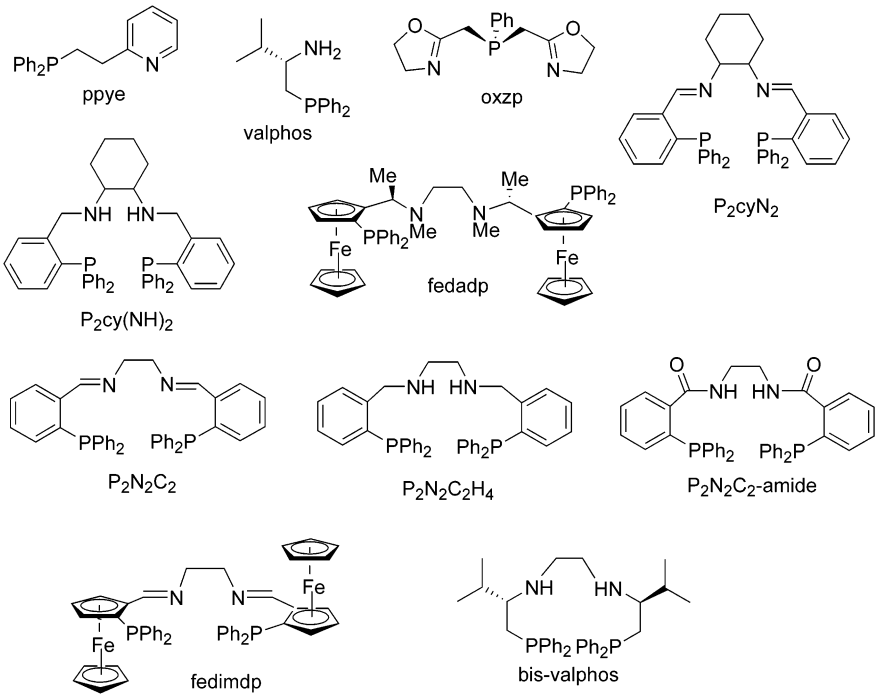
Scheme 24[a]



[a] X = Cl, Br.

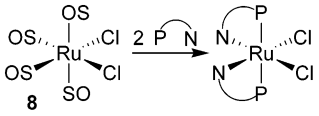
Similarly, according to Sadler and co-workers, precursor **8** reacted with 2 equiv of $Ph_2PCH_2CH_2NMe_2$ in dichloromethane at room temperature to give *trans*,*cis*,*cis*-$RuCl_2(Ph_2PCH_2CH_2NMe_2-P,N)_2$, whose geometry was confirmed by X-ray crystallography.[243] Treatment of **8** with 2 equiv of the chelating iminophosphine ligand 2-$Ph_2PC_6H_4CH$=N*i*Pr in refluxing THF led to the isolation of *trans*,*cis*,*cis*-$RuCl_2$(2-$Ph_2PC_6H_4CH$=N*i*Pr-*P*,*N*)$_2$ in almost quantitative yield.[244] The same authors had previously reported that the reaction of **8** with 1 equiv of the similar iminophosphine ligand 2-$Ph_2PC_6H_4CH$=N*t*Bu yielded the *trans*,*cis*-$RuCl_2$(dmso-S)$_2$(2-$Ph_2PC_6H_4CH$=N*t*Bu-*P*,*N*) complex after the replacement of only two dmso ligands.[245] A similar reaction with the bulkier aminophosphine 2-$Ph_2PC_6H_4CH_2NHtBu$ ligand led instead to the formation of the five-

Chart 20. Selection of Polydentate P,N Ligands (with labels) Mentioned in Section 2.5.6



coordinate complex *trans*-$RuCl_2$(2-$Ph_2PC_6H_4CH_2$-NH*t*Bu-*P,N*)(dmso-S).[245] Conversely, Börner and coworkers reported that the reaction of **8** with 2 equiv of the chiral aminophosphine valphos ligand (valphos = (*S*)-1-(diphenylphosphinomethyl)-2-methyl-propylamine, derived from the L-valine frame, Chart 20) in refluxing toluene afforded *cis,cis*-$RuCl_2$(valphos)$_2$ (with mutually trans P atoms, Scheme 25).[246]

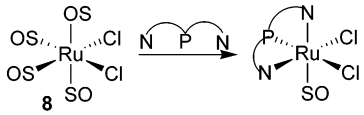
Scheme 25[a]



[a] P,N ligand = valphos.

Treatment of **8** with 2 equiv of the NP_2 tridentate ligand $PhCH_2N(CH_2CH_2PPh_2)_2$ (dpba) in refluxing acetone yielded the poorly characterized cationic complex [RuCl(dmso-S)$_2$(dpba)]Cl; under the same reaction conditions, the corresponding NAs_2 ligand (daba) apparently produced instead the neutral complex $RuCl_2$(dmso-S)(daba).[247] The reaction of **8** in refluxing ethanol with 0.5 equiv the bis-tridentate bridging ligand $(Ph_2PCH_2CH_2)_2NCH_2C_6H_4CH_2N(Ph_2PCH_2CH_2)_2$, in which the two NP_2 moieties are separated by a *p*-xylyl bridge, afforded a complex tentatively formulated as the dinuclear cation [RuCl(dmso-S)$_2$(μ-P_2N-NP_2)RuCl(dmso-S)$_2$]$^{2+}$.[248] Treament of **8** with 1 equiv of the tridentate N,P,N ligand bis(2-oxazolin-2-ylmethyl)phenylphosphine (oxzp, Chart 20) in refluxing toluene afforded the well characterized *fac*-$RuCl_2$(dmso-S)(oxzp) complex, with the phosphorus atom cis to one chloride and to the dmso ligand (Scheme 26).[249]

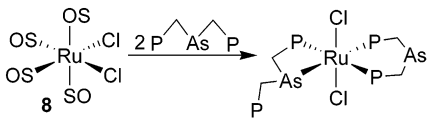
Scheme 26[a]



[a] N,P,N ligand = oxzp.

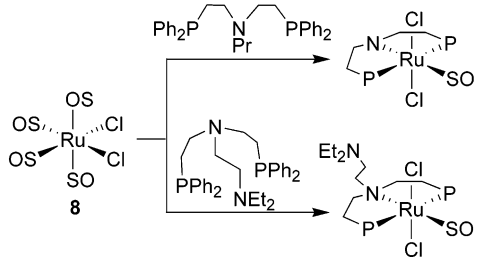
Treatment of **8** with 2 equiv of the potentially tridentate P_2As ligand $(Ph_2PCH_2)_2AsPh$ (dpma) in dichloromethane at room temperature afforded trans-$RuCl_2$(dpma)$_2$; the X-ray structure determination showed that in the complex one dpma ligand binds to Ru through the two P atoms, forming a six-membered chelate ring, with the internal As atom uncoordinated, while the other dpma ligand is bound through the As and a P atoms, forming a four-membered chelate ring, with the remaining P atom uncoordinated (Scheme 27).[250]

Scheme 27. Substituents on P and As Atoms of dpma Omitted



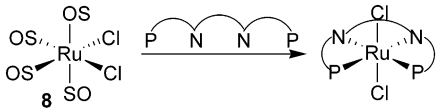
The reaction of **8** with 2 equiv of the chiral tridentate P,N,O Schiff base ligand (*S*)-$Ph_2PC_6H_4C$=NCHPhCH$_2$OH in refluxing ethanol yielded the fully substituted [*mer*-Ru(P,N,O)$_2$]Cl_2 complex.[251] The potentially tri- and tetradentate aminophosphine ligands $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$ (PNP) and $Et_2NCH_2CH_2N(CH_2CH_2PPh_2)_2$ (N_2P_2) were found to react with **8** in refluxing toluene to give in excellent yields complexes *trans,mer*-$RuCl_2$(PNP)(dmso-S) and *trans,mer*-$RuCl_2$(N_2P_2)(dmso-S), respectively, in which both PNP and N_2P_2 act as tridentate meridional ligands (Scheme 28).[252]

Scheme 28. Substituents on Coordinated P and N Atoms of PNP and N_2P_2 Omitted



Similarly, treatment of **8** with the potentially tetradentate NP_3 ligand $N(CH_2CH_2PPh_2)_3$ (tpea) in refluxing acetone afforded a scarcely characterized complex, formulated as $RuCl_2$(dmso-S)(tpea), as a mixture of two isomers in which tpea acts as a tridentate ligand, either through the NP_2 or the P_3 moieties.[253] On the other hand, it has been reported that treatment of **8** with an equimolar amount of the structurally similar chiral tetradentate ligands *N,N′*-bis[*o*-(diphenylphosphino)benzylidene]cyclohexane-1,2-diamine (P_2cyN_2, Chart 20) and *N,N′*-bis[*o*-(diphenylphosphino)benzyl]cyclohexane-1,2-diamine ($P_2cy(NH)_2$, Chart 20) in refluxing toluene yielded *trans*-$RuCl_2$(P_2cyN_2) and *trans*-$RuCl_2$($P_2cy(NH)_2$) complexes, respectively, that were structurally characterized by X-ray crystallography (Scheme 29).[254,255] A similar

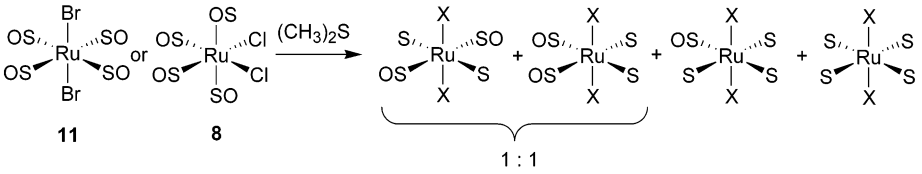
Scheme 29



complex, *trans*-$RuCl_2$(fedadp), was obtained by the reaction of **8** with another chiral P,N,N,P ligand, the C_2-symmetrical bisferrocenyl diamine *N*1,*N*2-bis{(*R*)-1-[(*S*)-2-(diphenylphosphino)]ferrocenylethyl}-*N*1,*N*2-dimethyl-1,2-ethanediamine (fedadp, Chart 20).[256]

The potentially tetradentate P_2N_2 diamino-, diimino-, or diamido-diphosphine ligands *N,N′*-bis[*o*-(diphenylphosphino)benzylidene]ethylenediamine ($P_2N_2C_2$, Chart 20), *N,N′*-bis[*o*-(diphenylphosphino)-benzyl]ethylenediamine ($P_2N_2C_2H_4$, Chart 20), and *N,N′*-bis[*o*-(diphenylphosphino)benzamido]ethane ($P_2N_2C_2$-amide, Chart 20) were found to react with 1 equiv of **8** in refluxing toluene yielding the complexes *trans*-$RuCl_2$($P_2N_2C_2$), *trans*-$RuCl_2$($P_2N_2C_2H_4$), and *trans*-$RuCl_2$($P_2N_2C_2$-amide), respectively, after replacement of all dmso ligands in the precursor (Scheme 29).[257] Similarly, *trans*-$RuCl_2$(P_2N_2) complexes were obtained by reaction of **8** with 1 equiv of the chiral diimino-diphosphine ligand based on a bis(diphenylphosphinoferrocenyl) moiety (fedimdp, Chart

Scheme 30[a]



[a] S = dms; X = Cl or Br.

20),[258] and with chiral diamino- and diamido-diphosphine ligands based on the L-valine frame such as bis-valphos (Chart 20).[246]

Taqui Khan and co-workers described a series of mono- and dinuclear ruthenium complexes obtained by treatment of **8** with the hexadentate P_4N_2 ligands $((Ph_2PCH_2CH_2)_2NCH_2)_2$ (bdpe) and $((Ph_2PCH_2CH_2)_2NCH_2)_2(o\text{-}C_6H_4)$ (bdpx) and tentatively formulated as $[RuCl(dmso\text{-}S)(bdpe)]Cl$ (two uncoordinated P atoms), *cis,trans*-$RuCl_2(dmso\text{-}S)_2(bdpx)$ (bdpx bound only through two P atoms), $[Ru_2Cl_2(dmso\text{-}S)_4(bdpe)]Cl_2$, $[Ru_2Cl_4(dmso\text{-}S)_2(bdpe)]$, $[Ru_2Cl_2(dmso\text{-}S)_4(bdpx)]Cl_2$, and $[Ru_2Cl_4(dmso\text{-}S)_2(bdpe)]$; similar structures were proposed for the As_4N_2 ligand $((Ph_2AsCH_2CH_2)_2NCH_2)_2$ (bdae).[259]

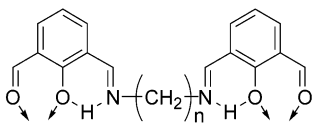
2.5.7. Polydentate P,O and P,S Ligands

Treatment of **8** with aromatic phosphines bearing ortho-methoxy groups yielded products containing either bidentate P,O (ether-O) or tridentate P,O,O′ (phenoxide-O) coordination. An example is *trans, cis,cis*-$RuCl_2(mdmpp\text{-}P,O)_2$ (mdmpp = (2,6-dimethoxyphenyl)diphenylphosphine), in which all four sulfoxides of **8** were replaced.[260] The reaction between **8** and the phosphine-thioether ligands $Ph_2PCH_2CH_2SR$ (PSR; R = Me, Et, *cyclo*-C_6H_{11}) afforded the six-coordinate compounds $RuCl_2(PSR\text{-}P,S)_2$ upon replacement of all four dmso ligands;[261] three of the five possible isomers, namely *cis,cis,cis-*, *cis,cis,trans-*, and *trans,cis,cis*-$RuCl_2(PSR\text{-}P,S)_2$ were obtained in pure form (those with mutually trans P atoms were not observed).

2.5.8. O Ligands

There is apparently only one example of reaction between **8** and a neutral polydentate O-ligand. The condensation of two molecules of 2,6-diformyl-4-methylphenol with one molecule of an aliphatic diamine $NH_2(CH_2)_nNH_2$ ($n = 2-4$) yields a bridging Schiff-base L ligand (Chart 21); when this reaction

Chart 21



was performed in the presence of **8**, it produced the acyclic dinuclear six-coordinate Ru(II) complexes [*trans,cis*-$RuCl_2(dmso\text{-}S)_2](\mu\text{-L})$, in which L acts as a tetradentate O_4 donor and coordinates to each Ru(II) nucleus through an aldehydic and a phenolyc oxygen.[262]

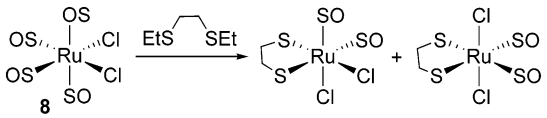
A poorly characterized complex of formula $RuCl_2(dmso)_2(PhNO)_2$ was apparently synthesized by reaction of **8** with 2 equiv of nitrosobenzene in dichloromethane at room temperature;[263] it was however unclear whether the end-on coordination of PhNO occurred through the nitrogen or oxygen atom.

2.5.9 S and SO Ligands

There are several examples concerning the use of *cis,fac*-$RuCl_2(dmso\text{-}S)_3(dmso\text{-}O)$ (**8**) and *trans*-$RuBr_2(dmso\text{-}S)_4$ (**11**) as precursors in the synthesis of Ru compounds with thioether ligands, both mono- and polydentate. An extensive investigation was performed by Riley and co-workers,[264−266] with the aim of determining the nature of the active species generated in the oxygen oxidation of thioethers catalyzed by the $RuX_2(dmso)_4$ complexes **8** and **11**.[12−14] The nature of the products isolated was found to depend on the steric bulk of the thioether donor ligand.[264] Reaction of both **8** and **11** with excess dimethyl sulfide (dms) produced three major products, in similar ratios. They were separated by column chromatography and identified by elemental analysis and IR and NMR spectroscopies as *trans*-$RuX_2(dms)_2(dmso\text{-}S)_2$ (as a 1:1 mixture of the *all-trans* and *trans,cis,cis* isomers), *trans*-$RuX_2(dms)_3(dmso\text{-}S)$, and *trans*-$RuX_2(dms)_4$ (Scheme 30). Treatment of **8** or **11** with excess tetrahydrothiophene (tht) in refluxing ethanol yielded a single major species, *trans*-$RuX_2(tht)_4$, in both cases. Conversely, only the monosubstituted complex $RuBr_2(tBu_2S)(dmso\text{-}S)_3$, presumably with a trans geometry of the two bromides, was obtained by treatment of **11** with the bulky di-*tert*-butylsulfide (tBu_2S) ligand.[264]

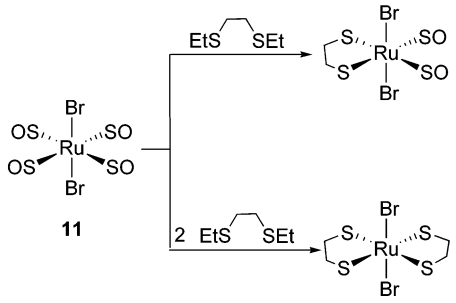
Reaction of **8** with 1 equiv of the potentially bidentate 3,6-dithiaoctane ligand ($EtSCH_2CH_2SEt$) in refluxing chloroform yielded a mixture of the two isomers *cis,cis*-$RuCl_2(dmso\text{-}S)_2(EtSCH_2CH_2SEt)$ and *trans,cis*-$RuCl_2(dmso\text{-}S)_2(EtSCH_2CH_2SEt)$, that were separated by column chromatography (Scheme 31).[264]

Scheme 31. Ethyl Substituents on Coordinated S Atoms Omitted



Interestingly, reaction of **11** with the same bidentate ligand (1:1 ratio) in refluxing 2-methoxyethanol produced the *trans,cis*-$RuBr_2(dmso\text{-}S)_2(EtSCH_2CH_2SEt)$ isomer selectively (Scheme 32). When 2 equiv of chelating ligand were used, the bischelated complex *trans*-$RuBr_2(EtSCH_2CH_2SEt)_2$ was obtained (Scheme 32).[264] The same authors also found that treatment of **11** with the sulfide/sulfoxide bidentate ligand $PhS(CH_2)_2SOPh$ (1-phenylsulfinyl-2-phenyl-

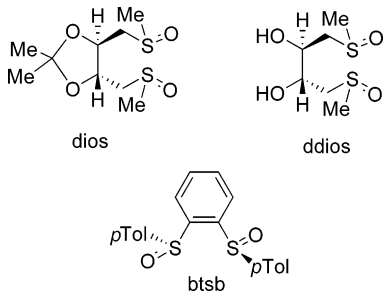
Scheme 32. Ethyl Substituents on Coordinated S Atoms Omitted



thioethane) in ethanol at ambient temperature yielded *cis,trans*-$RuBr_2(dmso\text{-}S)_2(PhS(CH_2)_2SOPh\text{-}S)$.[266]

James and co-workers reported that **8** is a useful precursor for the preparation of neutral Ru(II) complexes with the chelating chiral sulfoxide ligands (2*R*,3*R*)-2,3-dihydroxy-1,4-bis(methylsulfinyl)butane (ddios, Chart 22), and (2*R*,3*R*)−(−)-2,3-*O*-iso-

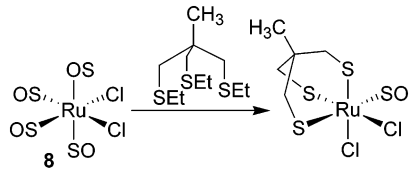
Chart 22



propylidene-2,3-dihydroxy-1,4-bis(methylsulfinyl)-butane (dios, Chart 22); the complexes $RuCl_2(ddios)_2$ and $RuCl_2(ddios)(dios)$ were obtained from **8** by sulfoxide exchange in refluxing methanol or chloroform.[37] The reaction of **8** with 2 equiv of the chiral bis-sulfoxide chelating ligand (*S,S*)-1,2-bis(p-tolylsulfinyl)benzene (btsb) in refluxing chloroform afforded *trans*-$RuCl_2(btsb)_2$, in which the sulfoxide moieties are coordinated through the S atoms.[267] Chiral sulfoxides, including their coordination chemistry, were recently reviewed.[268]

Tridentate S-ligands were also investigated.[264] The reaction of **8** with the tripodal ligand 1,1,1-tris-((ethylthio)methyl)ethane, $CH_3C(CH_2SEt)_3$, in refluxing 2-methoxyethanol afforded selectively the complex *fac*-$Ru(CH_3C(CH_2SEt)_3)Cl_2(dmso\text{-}S)$ (Scheme 33). The facial coordination of the tridentate thioether ligand was confirmed by X-ray analysis.

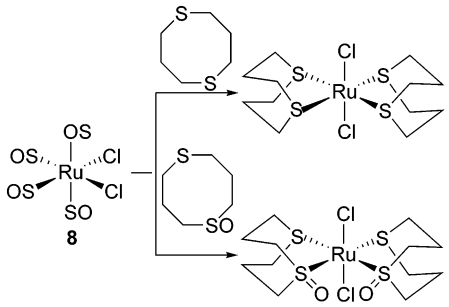
Scheme 33. Ethyl Groups Omitted in Product



Treatment of **11**, under the above reaction conditions, with the linear tridentate ligand bis(2-(ethylthio)ethyl)sulfide, $EtSCH_2CH_2SCH_2CH_2SEt$, produced only one complex with a presumably facial geometry, *cis,fac*-$RuBr_2(EtSCH_2CH_2SCH_2CH_2SEt)$-(dmso-S). Finally, it was found that treatment of either **8** or **11** with the sulfide/sulfoxide tridentate ligand 3-(ethylthio)-1-((3-(ethylthio)propyl)sulfinyl)-propane, $EtS(CH_2)_3SO(CH_2)_3SEt$, produced only one geometric isomer, *cis,mer*-$RuX_2(EtS(CH_2)_3SO(CH_2)_3\text{-}SEt)(dmso\text{-}S)$, in which the tridentate chelate ligand is meridionally coordinated to Ru(II).[265]

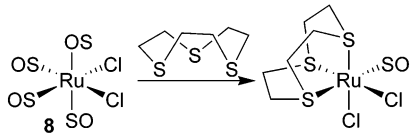
The reactivity of **8** toward macrocyclic polydentate thioether ligands (crown thioethers) has been extensively investigated by several groups. Reaction of **8** with the cyclic bidentate ligand 1,5-dithiacyclooctane (1,5-dtco) yielded *trans*-$RuCl_2(1,5\text{-}dtco)_2$, while the reaction with the corresponding mixed sulfide/sulfoxide ligand 1,5-dithiacyclooctane 1-oxide (1,5-dtco-O) afforded *trans*-$RuCl_2(1,5\text{-}dtco\text{-}O)_2$ (with a cis arrangement of the two S-bound sulfoxide moieties) (Scheme 34).[269]

Scheme 34



The face-capping macrocyclic ligand 1,4,7-trithiacyclononane ([9]aneS_3) was found to displace easily three molecules of dmso from **8** (in refluxing chloroform) to give *fac*-$Ru([9]aneS_3)Cl_2(dmso\text{-}S)$ in high yield (Scheme 35);[270] this compound was then used

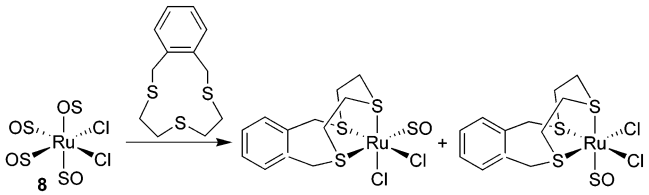
Scheme 35



as precursor for the synthesis of mixed-ligand sandwich complexes,[270] for $[RuCl([9]aneS_3)(N{-}N)]^+$ (N−N = phen, bpy) derivatives,[271] and for a supramolecular cube made by eight *fac*-$Ru([9]aneS_3)^{2+}$ corners and 12 bridging 4,4′-bpy ligands as edges.[272]

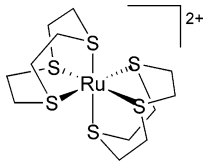
The complex *fac*-$Ru(tt[9]oc)Cl_2(dmso\text{-}S)$ was obtained by treatment of **8** with the thiacyclophane ligand 2,5,8-trithia[9]-*o*-cyclophane (tt[9]oc);[273] the compound formed as a mixture of two isomers that differ from the position of the dmso-S ligand: either trans to the benzylic S-atoms or trans to the central S donor atom of the thiacyclophane (Scheme 36).

Scheme 36



The reaction of $[Ru(dmso)_6][BF_4]_2$ (**15**) with 2 equiv of tridentate thioether ligands S_3 in refluxing methanol (S_3 = 2,5,8-trithianonane, 1,4,7-trithiacyclononane, and 1,5,9-trithiacyclododecane) afforded the corresponding very robust $[Ru(S_3)_2]^{2+}$ complexes (Chart 23), in which the central Ru(II) ion coordinates to an

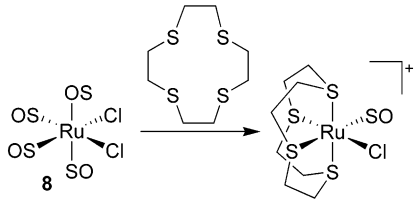
Chart 23. Schematic Representation of $[Ru([9]aneS_3)_2]^{2+}$



octahedral array of six thioether S atoms.[274] Similarly, treatment of **8** with 2 equiv of the 10- or 11-membered ring crown trithioethers 1,4,7-trithiacyclodecane ([10]aneS$_3$) or 1,4,7-trithiacycloundecane ([11]aneS$_3$) in refluxing methanol afforded the fully substituted $[Ru([10]aneS_3)_2]^{2+}$ or $[Ru([11]aneS_3)_2]^{2+}$ complexes, respectively.[275,276]

The reaction between **8** and the larger tetradentate macrocycle 1,4,7,10-tetrathiacyclododecane ([12]aneS$_4$) in refluxing ethanol gave [RuCl([12]aneS$_4$)(dmso-S)]-Cl (Cl cis to dmso-S) in high yield (Scheme 37);[277] the

Scheme 37

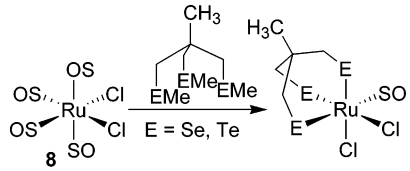


product (previously formulated erroneously by the same authors as $[RuCl_2([12]aneS_4)]$[278]) was structurally characterized by X-ray crystallography as PF_6^- salt, and proved to be a useful starting material for a series of complexes upon replacement of the two monodentate ligands.[277,279]

2.5.10. Se and Te Ligands

The examples concerning the reactivity of Ru(II)−dmso precursors toward Se- and Te-donor ligands are relatively scarce and concern *cis*,*fac*-$RuCl_2$(dmso-S)$_3$-(dmso-O) (**8**) exclusively. Treatment of **8** with the ditelluroether bis(4-methoxyphenyltelluro)methane, $(4\text{-}MeOC_6H_4Te)_2CH_2$, in chloroform at ambient temperature yielded the disubstituted complex *cis*,*cis*-$RuCl_2$(dmso-S)$_2$$(4\text{-}MeOC_6H_4Te)_2CH_2$, which was structurally characterized by X-ray crystallography.[280] The reaction of **8** with 2 equiv of $MeTe(CH_2)_3TeMe$ in refluxing methanol afforded *trans*-$RuCl_2(MeTe(CH_2)_3TeMe)_2$.[281] Finally, similar to that found by Riley and co-workers with tripodal S-ligands (see above),[264] the reaction of **8** with 1 equiv of the tripodal Group 16 donor ligands $MeC(CH_2EMe)_3$ (E = Se or Te) in toluene at 100 °C afforded the corresponding *fac*-$Ru(MeC(CH_2EMe)_3)Cl_2$(dmso-S) complexes. X-ray crystallographic investigation on $Ru(MeC(CH_2SeMe)_3)$-Cl_2(dmso-S) confirmed the facial coordination of the selenoether to ruthenium (Scheme 38).[282]

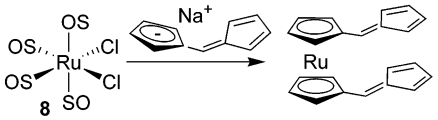
Scheme 38. Methyl Groups Omitted in Product



2.5.11. Organometallic Derivatives

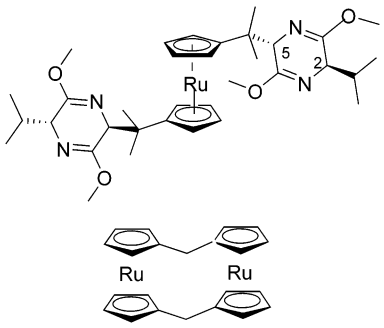
There are quite a few examples in which **8** has been used as precursor for the preparation of organometallic compounds. Ruthenocene was prepared in excellent yield by reaction of **8** with a 3-fold excess of sodium cyclopentadiene in refluxing dry 1,2-dimethoxyethane.[283] The reaction of **8** with the fulvenyl cyclopentadienide anion afforded 1,1′-bis(6-fulvenyl)ruthenocene in good yield (Scheme 39).[284]

Scheme 39



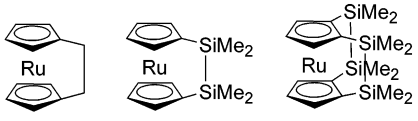
Similarly, the reaction of **8** with enantiomerically pure lithium cyclopentadienyl-valine (either $R_{C2}S_{C5}$ or $S_{C2}R_{C5}$) yielded the corresponding diastereomeric ruthenocene $[Ru\{C_5H_4-CMe_2-[C_4H_2N_2(OMe)_2iPr]\}_2]$ (Chart 24).[285] Reduction of 1,1′-bis(6-fulvenyl)ruthenocene to the corresponding dianion, followed by reaction with **8**, yielded a novel [1,1]ruthenocenophane (Chart 24).[284]

Chart 24



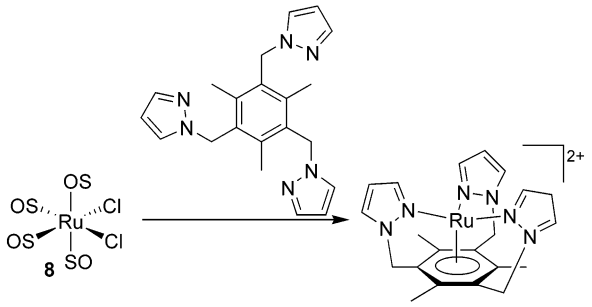
Treatment of **8** with $Li_2(C_5H_4CH_2)_2$ produced the first example of a [2]ruthenocenophane, $Ru(\eta^5\text{-}C_5H_4CH_2)_2$, after replacement of the chloride and dmso ligands (Chart 25);[286] similarly, disilane-bridged [2]ruthenocenophane $Ru(\eta^5\text{-}C_5H_4SiMe_2)_2$ and bis-(silane)-bridged [2][2]ruthenocenophane, $Ru\{(\eta^5\text{-}C_5H_3\text{-}(SiMe_2)_2\}_2$, were prepared from **8** and the corresponding dilithium salts (Chart 25).[287] All these products were characterized by X-ray crystallography.

Chart 25



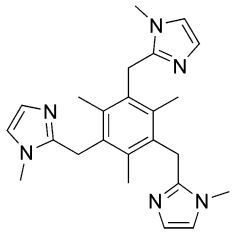
Treatment of **8** with 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-trimethylbenzene in refluxing ethanol/water

Scheme 40



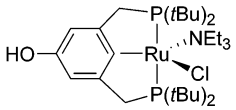
yielded a dicationic complex (structurally characterized by X-ray analysis) in which the ligand encapsulates the ruthenium atom with joint chelation by the three pyrazole nitrogens and η^6 π-coordination by the benzene ring (Scheme 40).[288,289] A similar encapsulated complex was obtained from the reaction of **8** with 1,3,5-tris(1-methylimidazol-2-ylmethyl)-2,4,6-trimethylbenzene (Chart 26).[290]

Chart 26



The reaction of **8** with 3,5-bis-(di-*tert*-butylphosphinomethylene)phenol in the presence of 2 equiv of NEt_3 afforded the first example of a stable metallaquinone, i.e., a complex in which one of the oxygen atoms of the p-quinone system is replaced by ruthenium (Chart 27).[291]

Chart 27



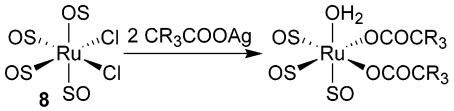
Finally, a double-cluster Ru(II) complex containing two tricarbollide ligands (that is, 11-vertex nidotricarbaboranes) was obtained by treatment of **8** with 7-(tBuNH$_2$)-7,8,9-$C_3B_8H_{10}$ and excess NaH in refluxing diglyme.[292]

2.5.12. Anionic or Easily Deprotonated Ligands

A complex formulated as Na[*fac*-Ru(dmso-S)$_3$(O$_2$CCH$_3$)$_2$Cl] (based on elemental analysis and IR spectrum), with monodentate acetate ions, was apparently isolated upon treatment of *cis*,*fac*-RuCl$_2$(dmso-S)$_3$(dmso-O) (**8**) with sodium acetate in methanol solution.[293] Reaction of **8** with silver acetate (or trifluoroacetate) in dichloromethane at room temperature afforded *fac*,*cis*-Ru(dmso-S)$_3$(O$_2$CCH$_3$)$_2$(H$_2$O) (or *fac*,*cis*-Ru(dmso-S)$_3$(O$_2$CCF$_3$)$_2$(H$_2$O)) (Scheme 41).[294]

The X-ray structures showed that the two cis monodentate carboxylate anions are strongly hydrogen bonded to the H$_2$O ligand via their noncoordinated oxygen atoms. Indeed, as found in *fac*,*cis*-Ru(dmso-S)$_3$(O$_2$CCH$_3$)$_2$(H$_2$O),[294] the replacement of

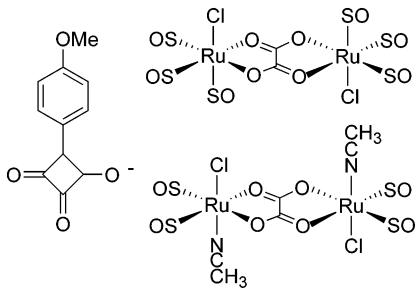
Scheme 41[a]



[a] R = H, F.

the Cl$^-$ ligands in **8** by anionic ligand(s) is often accompanied by replacement of the dmso-O by a water molecule when it can form hydrogen bonding with the new ligand(s). Other examples are the species *fac*-Ru(dmso-S)$_3$Cl(sq)(H$_2$O), obtained by treatment of **8** with monosubstituted squarates (sq, in Chart 28 anisolesquarate); X-ray structures showed

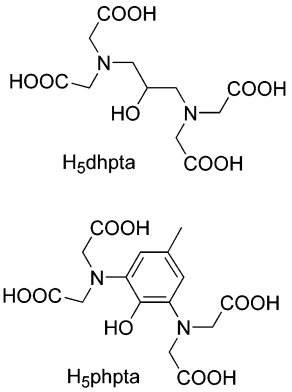
Chart 28



that in these compounds the coordinated water molecule, in addition to forming a strong intramolecular hydrogen bond with a chetonic oxygen of the squarate moiety, can form also a weaker hydrogen bond with the oxygen atom of an adjacent dmso-S ligand.[295,296] The same authors reported that the dinuclear species with a bridging oxalate ligand [{*fac*-RuCl(dmso-S)$_3$}$_2$(μ-C$_2$O$_4$)] and [{RuCl(dmso-S)$_2$(CH$_3$CN)}$_2$(μ-C$_2$O$_4$)] (Chart 28) were serendipitously obtained in low yield by treatment of **8** with substituted squarates that underwent decomposition.[58]

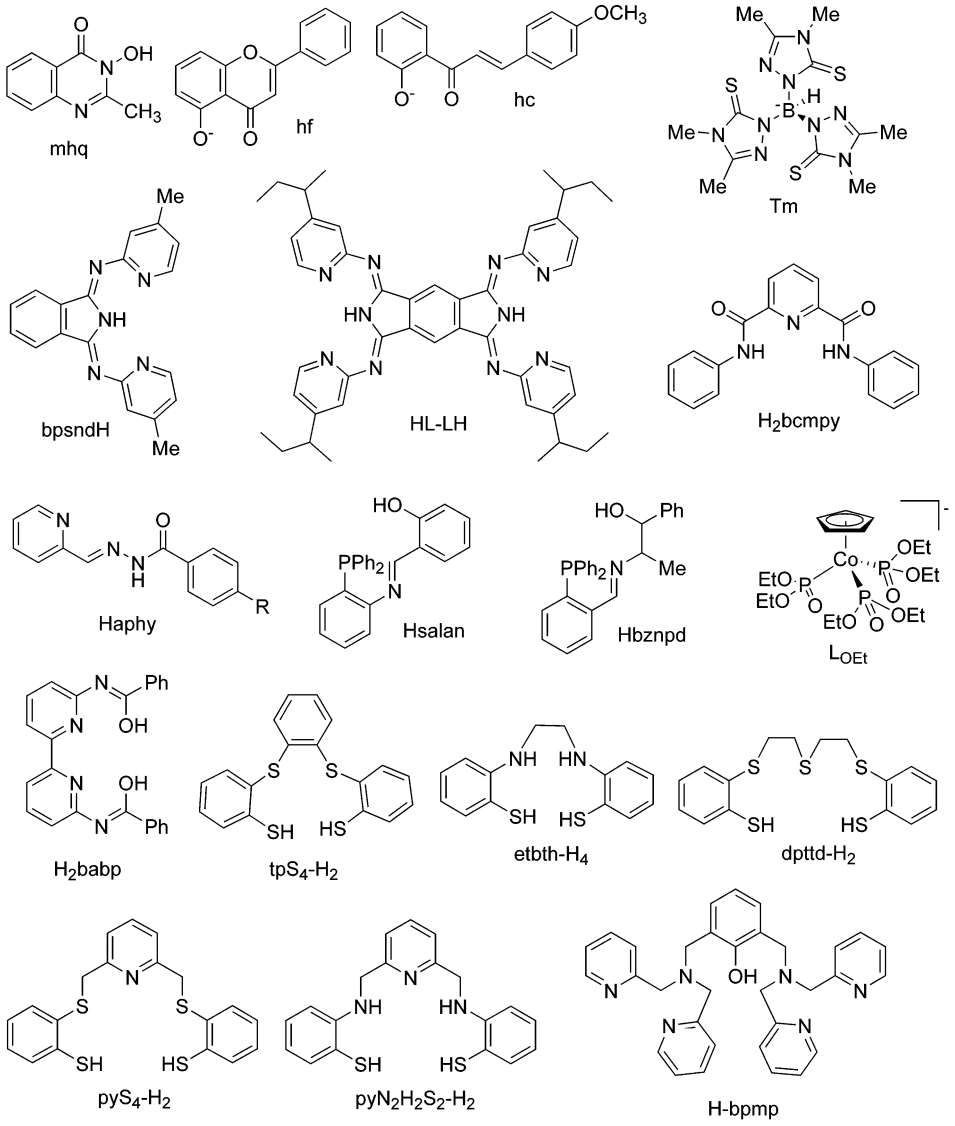
Tanase and co-workers described a series of (μ-alkoxo)bis(μ-carboxylato)diruthenium(III) complexes, [Ru$_2$(μ-dhpta)(μ-O$_2$CR)$_2$]$^-$ (H$_5$dhpta = 2-hydroxytrimethylenedinitrilotetraacetic acid, Chart 29),[297,298]

Chart 29



and of (μ-aryloxo)bis(μ-carboxylato)diruthenium(III) complexes, [Ru$_2$(μ-phpta)(μ-O$_2$CR)$_2$]$^-$ (H$_5$phpta = 2-hydroxy-5-methyl-*m*-phenylenedimethylenedinitrilotetraacetic acid, Chart 29),[299] prepared by the reaction of **8** with either H$_5$dhpta or H$_5$phpta and RCO$_2$H in a slightly acidic solution.

Chart 30. Selection of Anionic or Easily Deprotonated Ligands (with Labels) Mentioned in Section 2.5.12

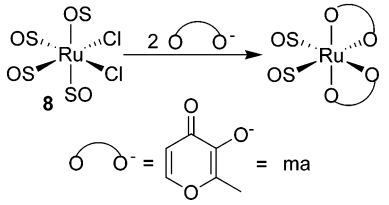


As originally reported by Evans and co-workers, the reaction of **8** with *N*,*N*-diethyldithiocarbamate (Et_2NCS_2) afforded, after displacement of two dmso groups and of the two chlorides, the complex Ru(Et_2-NCS_2)$_2$(dmso)$_2$, in which the two dithiocarbamates act as S−S$^-$ chelates.[40] The complex Ru(Et_2NCS_2)$_2$-(dmso)$_2$ was later used as precursor for the preparation of Ru(II) dithiocarbamate complexes of the type Ru(Et_2NCS_2)$_2$(L)$_2$ (L = neutral ligand) and was found to have presumably a *trans*-Ru(Et_2NCS_2)$_2$(dmso-S)$_2$ geometry.[300]

Following the initial report by Evans and co-workers,[40] the reaction of **8** with other bidentate anionic (X−Y$^-$) or easily deprotonated (X-YH) ligands has been later widely employed as a general route to Ru(II) bis-chelate complexes of the type Ru(X−Y)$_2$-(dmso)$_2$. In an early report, a series of bidentate X-YH ligands containing a carboxylic function (YH) and an amide group (X; e.g., X-YH = 2-(acetylamino)benzoic acid) were reacted with *cis*,*fac*-$RuCl_2$(dmso-S)$_3$(dmso-O) (**8**) (4:1 ratio) in refluxing toluene/methanol mixtures to give poorly characterized neutral Ru(X−Y)$_2$(dmso-S)$_2$ complexes of undetermined geometry.[301] The same group later reported similar Ru(O−O)$_2$-(dmso-S)$_2$ complexes of undisclosed geometry obtained by treatment of **8** with negative bidentate O,O-donor ligands derived from 2-methyl-quinazolin-4-one substituted on N3 with an -OH (mhq, Chart 30) or a -CH_2COOH (mcmq) group.[302] The reaction of **8** with diphenylphosphinoacetic acid (PPh_2CH_2COOH) in refluxing ethanol afforded an anionic complex (of undisclosed geometry) formulated as H[RuCl(PPh_2-CH_2COO)$_2$(dmso-S)] when the ligand/Ru ratio was 2:1, while gave H[*fac*-Ru(PPh_2CH_2COO)$_3$] when the ligand/Ru ratio was 3:1.[303]

Treatment of **8** with potassium maltolate (Kma) in hot toluene led to the isolation of *cis*-Ru(ma)$_2$(dmso-S)$_2$ in which the maltolato ligands act as bidentate O−O$^-$ chelates (Scheme 42).[304] The isomer with O trans to O$^-$ was structurally characterized by X-ray crystallography, while all the three possible cis isomers were found in solution by NMR spectroscopy.[304] The corresponding complex with tmso, *cis*-Ru(ma)$_2$(tmso-S)$_2$, has been recently described by the group of James.[305] The same group also prepared the analogous acetylacetonato complex, *cis*-Ru(acac)$_2$-(dmso-S)$_2$, by treatment of **8** with a slight excess of H(acac) in refluxing ethanol in the presence of

Scheme 42



$NaHCO_3$.[306] Structurally similar complexes with the chelating disulfoxide ligand $EtS(O)(CH_2)_2S(O)Et$ (BESE), *cis*-Ru(ma)$_2$(BESE), and Ru(acac)$_2$(BESE), were obtained upon treatment of $[RuCl(H_2O)(BESE)]_2$-(μ-Cl)$_2$ with Kma or H(acac), respectively, under conditions similar to those described above for the dmso and tmso compounds.[305,306] The molecular structure of *cis*-Ru(ma)$_2$(*S*,*R*-BESE) was determined by X-ray crystallography; both sulfoxide groups of BESE were found to be S-bonded.[305]

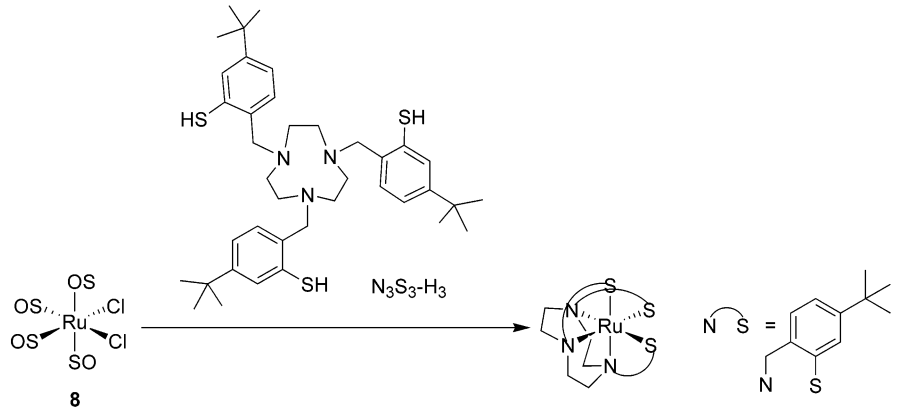
The reaction of **8** with 2 equiv of the sodium salt of 5-hydroxyflavone (Nahf, Chart 30), or of substituted derivatives, afforded neutral bis-flavonato complexes formulated as *cis*-Ru(hf)$_2$(dmso-S)(dmso-O).[307] The same authors later reported that treatment of **8** with the potassium salts of 2′-hydroxychalcones, such as 2′-hydroxy-4-methoxychalcone (Khc, Chart 30), led to neutral bis-chalconate complexes *cis*-Ru(hc)$_2$(dmso-S)$_2$, each as a mixture of three isomers that were separated by thin-layer chromatography.[308] On the basis of extensive NMR spectroscopic investigations the stereochemistry of the three isomers was found to be determined by the orientation of the unsymmetrical chelating O−O$^-$ ligands hc$^-$: both phenolic O$^-$ trans to S in one isomer, both chetonic O trans to S in the second, and one O$^-$ and one O trans to S in the third. Treatment of **8** in refluxing DMF with 1,3-diaryltriazenes, ArNNNHAr, in the presence of triethylamine afforded *cis*-Ru(ArNNNAr)$_2$(dmso-S)$_2$ in good yield.[309] Conversely, the same authors found that the reaction of **8** with *N*,*N*′-diphenylformamidine, PhNC(H)NHPh, under the same conditions, took an unexpected course involving fragmentation of the ligand and gave in modest yield the aniline complex *cis*-RuCl(NH$_2$Ph)(PhNC(H)NPh)(dmso-S)$_2$ that was characterized by X-ray diffraction.[309] The reaction of **8** with 2 equiv of KN(SPPh$_2$)$_2$ (HN(SPPh$_2$)$_2$ = bis(diphenylthiophosphoryl)amide) in refluxing THF afforded *cis*-Ru(N(SPPh$_2$)$_2$)$_2$(dmso-S)$_2$.[310] Treatment of **8** with the potentially bidentate ligand potassium dihydrobis(1-pyrazolyl)borate, K[H$_2$B(pz)$_2$], in refluxing acetonitrile led to cleavage of the B−N bond followed by formation of [Ru(pz)$_2$(pzH)$_3$(dmso-S)] (pzH = pyrazole), which was structurally characterized by X-ray analysis.[98] Instead, the reaction of **8** with 1 equiv of the tripodal ligand sodium tris(methimazolyl)hydroborate (NaTm, Chart 30) at ambient temperature afforded *fac*-Ru(Tm)Cl(dmso-S)$_2$ in low yield, in which Tm is coordinated through the three sulfur atoms.[311]

The reaction of **8** with 1 equiv of the N_2O chelate 6-carboxy-2,2′-bipyridine (6-carboxy-bpy) in refluxing aqueous methanol yielded, after deprotonation, [RuCl(dmso)$_2$(6-carboxylato-bpy)], while the reaction with 2 equiv of the ligand in the presence of NEt_3 afforded the homoleptic complex [Ru(6-carboxylato-bpy)$_2$], in which each anionic chelate has a meridional coordination geometry.[168] Treatment of **8** with 2 equiv of the N_3 tridentate chelating isoindoline ligand 1,3-bis(2-(4-methylpyridyl)imino)isoindoline (bpsndH, Chart 30) in a basic alcoholic solution afforded the bis(isoindolinato) complex Ru(bpsnd)$_2$, which bears two deprotonated tridentate ligands.[312] Similarly, the reaction of **8** with an excess of the bridging bis-tridentate chelating ligand 1,3,5,7-tetrakis(2-(4-*sec*-butylpyridyl)imino)benzopyrrole (HL-LH, Chart 30) in basic dioxane yielded the (HL-L)Ru(L-LH) complex, further exploited for the construction of a trinuclear Ru(II) species.[311] Conversely, the reaction of **8** with 2 equiv of the N_3 tridentate bis-amide ligand 2,6-bis-(*N*-phenylcarbamoyl)pyridine (H_2bcmpy, Chart 30) in its deprotonated form afforded the Ru(III) complex [*mer*-Ru(bcmpy)$_2$]$^-$;[313] X-ray structural analysis of [NEt$_4$][*mer*-Ru(bcmpy)$_2$] confirmed that the two pyridine-N atoms are mutually trans and the four deprotonated amide-N atoms define the equatorial plane.[313] A series of mononuclear ruthenium(II) complexes of general formula [*mer*-Ru(aphy)$_2$] were prepared by the reaction of **8** in refluxing methanol in the presence of NaOH with 2 equiv of tridentate *N*-(aroyl)-*N*′-(picolinylidene)hydrazine ligands (Haphy, Chart 30), having the pyridine-N, imine-N and amide-O set of donor atoms.[314] The reaction of **8** with a stoichiometric amount of tridentate ligands with P,N,O donor sets (e.g., Hsalan, Chart 30, derived by the condensation of 2-(diphenylphosphino)aniline with salicylaldehyde) in refluxing THF led to the formation of the neutral octahedral complex *cis*,*mer*-RuCl(dmso-S)$_2$(P,N,O), with a coordinated aryloxide moiety.[315] Formation of [Ru(P,N,O)′$_2$] occurred only when **8** was treated with 2 equiv of the similar tridentate ligand Hbznpd (Chart 30), derived by the condensation of 2-(diphenylphosphino)benzaldehyde with 1*S*,2*R*-norephedrine, which has an alkoxide rather than an aryloxide moiety.[315] Reaction of **8** in refluxing THF with the anionic Co(III)-based tripodal ligand Na[CpCo{P(O)(OEt$_2$)}$_3$] (NaL$_{OEt}$, Chart 30), having an O,O,O donor set, afforded the *fac*-Ru(L$_{OEt}$)-Cl(dmso-S)$_2$ complex, which was characterized also through X-ray crystallography.[316]

The reaction of **8** with the square-planar tetradentate N_2O_2 ligand 6,6′-bis(benzoylamino)-2,2′-bipyridine (H_2babp, Chart 30) in the presence of NaH gave *trans*-Ru(babp)(dmso)$_2$;[317] one of the two dmso ligands, whose coordination mode was not addressed, was easily replaced by heterocyclic N-donors (L) to yield *trans*-Ru(babp)(dmso)(L) complexes. The X-ray structure of *trans*-Ru(babp)(dmso-S)(4Mepy) (4Mepy = 4-methylpyridine) was reported.[317]

Sellmann and co-workers have extensively investigated the reactivity of several ruthenium precursors, including **8**, toward tetra- and pentadentate thioether-thiolate ligands and also toward S,N^{n-} polydentate ligands. Treatment of **8** with the tetradentate thioether-thiolate ligand 1,2-bis(2-mercaptophenylthio)phenylene (tpS_4-H_2, Chart 30) in refluxing methanol in the presence of NaOMe and excess PEt_3 produced *cis*-Ru(tpS_4)(PEt$_3$)$_2$ in which, as shown by the X-ray structure, the thiolate groups of

Scheme 43



the tpS_4^{2-} ligand occupy trans positions;[318] in the absence of PEt_3 the reaction between **8** and tpS_4^{2-} afforded *cis*-Ru(tpS_4)(dmso-S)$_2$.[319] Treatment of **8** with the tetradentate $S_2N_2^{4-}$ ligand 1,2-ethanediamide-*N*,*N*′-bis(2-benzenethiolate)(4-) (etbth, Chart 30) in refluxing methanol in the presence of tricyclohexylphosphine (Pcy_3) afforded the five-coordinate Ru(IV) complex Ru(Pcy_3)(S_2N_2), whose X-ray structure was determined.[320] The reaction of **8** with the pentadentate ligand $dpttd^{2-}$ ($dpttd^{2-}$ = 2,3,11,12-dibenzo-1,4,7,10,13-pentathiatridecane(−2), Chart 30) in refluxing methanol afforded Ru(dpttd)(dmso).[321] Similarly, treatment of **8** with the pentadentate NS_4^{2-} ligand 2,6-bis(2-mercaptophenylthio)dimethylpyridine-(2-) (pyS_4^{2-}, Chart 30) in methanol at room temperature gave the Ru(II) complex Ru(pyS_4)(dmso-S), whose X-ray structure was also determined.[322] Finally, the reaction of **8** with the pentadentate N_3S_2 ligand 2,6-bis(2-mercaptophenylamino)dimethylpyridine ($pyN_2H_2S_2-H_2$, Chart 30) yielded Ru($pyN_2H_2S_2$)-(dmso-S), after deprotonation of the two sulfide groups.[323]

The group of Wieghardt reported that the reaction of **8** with the deprotonated trianionic form of the N_3S_3 hexadentate pendent arm macrocycle 1,4,7-tris-(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane ($N_3S_3-H_3$, Chart 30) in refluxing methanol in the presence of air afforded the mononuclear Ru(III) complex [Ru(N_3S_3)] (Scheme 43).[324,325]

Further treatment of [Ru(N_3S_3)] with 1 equiv of **8** in refluxing methanol under argon produced the trinuclear species $[(N_3S_3)RuRuRu(N_3S_3)]^{2+}$ in low yield; the X-ray crystal structure showed that the linear trinuclear dication consists of three face-sharing thiolato-bridged octahedra with a central RuS_6 and two terminal *fac*-RuN_3S_3 ruthenium fragments.[325] Similarly, the corresponding linear heterotrinuclear complex $[(N_3S_3)FeRuFe(N_3S_3)]^{2+}$ was obtained by reaction of the mononuclear Fe(III) species [Fe(N_3S_3)] with **8**.[326]

The mixed-valence dinuclear Ru(II)/Ru(III) complex $[Ru_2(\mu\text{-bpmp})(\mu\text{-OAc})_2]^{2+}$, where bpmp is the phenolate anion of the binucleating eptadentate ligand 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol (H-bpmp, Chart 30), was obtained by treatment of **8** with 0.5 equiv of H-bpmp and NaOAc in refluxing methanol.[327]

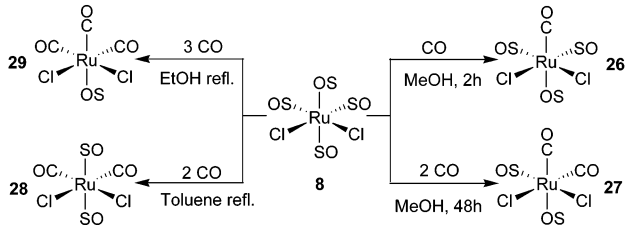
Complex **8** has been used also as a source for the preparation of ruthenium-substituted polyoxometalates, a field pioneered by Neumann and co-workers. This group described several Ru(III)- and Ru(II)-substituted polyoxometalates, such as the "sandwich"-type compound $[WZnRu_2^{III}(OH)(H_2O)(ZnW_9O_{34})_2]$,[11−] the Keggin-type polyoxomolybdate $[PRu^{III}(H_2O)Mo_{11}O_{39}]$,[4−] and the quasi-Wells−Dawson-type polyfluorometalate $[Ru^{II}(H_2O)H_2F_6NaW_{17}O_{55}]$,[9−] in which the precursor **8** has lost all its original ligands.[328−331] More recently, the same group described the ruthenium-substituted heptamolybdate polyoxometalate structure [*fac*-Ru(dmso-S)$_3$(Mo_7O_{24})],[4−] synthesized by reaction between $(NH_4)_6Mo_7O_{24}$ and **8**, in which part of the original coordination sphere of **8** was preserved; the X-ray structural analysis revealed that the heptamolybdate fragment is facially bound to ruthenium through three oxygen atoms.[332] Other groups reported that treatment of **8** with the monolacunary Dawson polyoxotungstate $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ in ice-cooled, HCl-acidic aqueous solution, afforded a water-soluble diamagnetic Ru(II) complex with formula $K_{18}[Ru(dmso\text{-}S)_2(P_2W_{17}O_{61})_2]$.[333] Similarly, the diamagnetic, air-stable, Ru(II) complex $[PW_{11}O_{39}Ru(dmso\text{-}S)]^{5-}$ was obtained by treatment of **8** with the lacunary tungstate ligand $[PW_{11}O_{39}]^{7-}$ under microwave irradiation in aqueous solution.[334]

Finally, Teixidor and co-workers reported that the reaction of **8** in refluxing ethanol with 7,8-dicarba-*nido*-undecaborane derivatives containing sulfur atoms connected to the cluster carbon atoms (NEt_4L) yielded RuCl(dmso-S)$_2$(L) complexes.[335]

2.6 Reactions of Ru(II)–dmso Precursors with π-Acceptor Ligands (CO and NO)

The first example of a Ru(II)−dmso carbonyl complex of formula $RuCl_2(dmso)_2(CO)_2$ was obtained by Evans and co-workers upon carbonylation of *cis*,*fac*-RuCl$_2$(dmso-S)$_3$(dmso-O) (**8**) in refluxing toluene.[40] No details on its geometry and on the binding mode of the two sulfoxides were reported. More recently, the reactivity of both isomers **8** and **9** toward CO has been thoroughly investigated.[336] Depending on the choice of the solvent and reaction conditions **8** was found to react with CO at ambient pressure replacing one, two, or three dmso ligands, while the chlorides maintained the cis geometry (Scheme 44). The following compounds were isolated and characterized: *cis*,*cis*,*trans*-RuCl$_2$(dmso-S)$_2$(dmso-O)(CO) (**26**), *cis*,*cis*,*cis*-RuCl$_2$(dmso-S)(dmso-O)(CO)$_2$

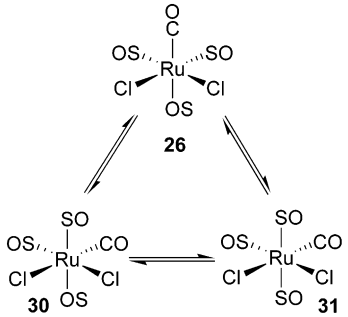
Scheme 44



(**27**), *cis,trans,cis*-$RuCl_2(dmso\text{-}S)_2(CO)_2$ (**28**), and *cis, fac*-$RuCl_2(CO)_3(dmso\text{-}O)$ (**29**). Complex **28** corresponds to that previously reported by Evans and coworkers,[40] and turned out to be the thermodynamically most stable $RuCl_2(dmso)_2(CO)_2$ species among those prepared.

Similarly to that found with the neutral mononitrosyl complex *mer,cis*-$RuCl_3(dmso\text{-}O)_2(NO)$ (**22**) (see above Scheme 9),[84] the monocarbonyl complex **26** was found to equilibrate slowly (48 h) in light-protected chloroform solution with two new geometrical isomers in which CO is trans to a Cl, of formula *cis,cis,cis*-$RuCl_2(dmso\text{-}S)_2(dmso\text{-}O)(CO)$ (**30**) and *cis,mer*-$RuCl_2(dmso\text{-}S)_3(CO)$ (**31**), which are linkage isomers of each other (Scheme 45).[337] The three

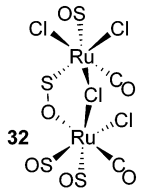
Scheme 45



isomers have similar stabilities in solution. Complex **30** was isolated and structurally characterized, while isomer **31**, which is the first example of a Ru(II)−dmso complex featuring three S-bonded dmso ligands with a *mer* geometry, was identified only in solution through NMR spectroscopy.

In addition, complex **26** was found to dimerize in refluxing acetone, yielding the biscarbonyl Ru(II) complex [(dmso-S)Cl_2(CO)Ru(μ-Cl)(μ-dmso-S,O)RuCl-(dmso-S)$_2$(CO)] (**32**) that contains the rare S,O bridging dmso ligand (Chart 31).[338] Similar to that found

Chart 31[a]

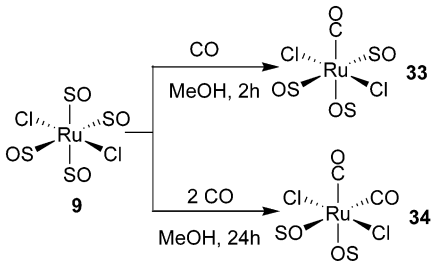


[a] S−O = μ-dmso-S,O.

in the trinuclear Ru(II) complex **6** containing two bridging mpso ligands (see Chart 2),[45] the S−O bond length of the bridging dmso (1.508(5) Å) in **32** is intermediate between the average values found for the S−O bond in S- (1.480(1) Å) and O-bonded (1.545(3) Å) Ru(II)−dmso compounds, and not too far from that in free sulfoxides (average 1.492(1) Å).[6] Accordingly, the SO stretching mode falls at 1010 cm^{-1}, i.e., at slightly lower frequencies compared to free dmso (1055 cm^{-1}). In the ^1H NMR spectrum ($CDCl_3$) the methyl groups of the bridging dmso have unprecedented downfield shifted singlets, at $\delta = 3.89$ and 3.92.[338] Interestingly, in the ^1H NMR spectrum ($CDCl_3$) of **6** the methyl resonances of the bridging ligands occurred in the region for O-bonded sulfoxides ($\delta = 2.70$ and 2.81). As the metrical features of the bridging mpso's in **6** were similar to those found for the bridging dmso in **32** (Ru−S distances slightly shorter than those of the terminal S-bonded sulfoxides in the same compound, longer than average S−O distances as discussed above), the unexpected shift to higher field of the two methyl resonances of the μ-mpso-S,O ligands was attributed to a strong localized shielding effect of the phenyl groups.[45]

Treatment of *trans*-$RuCl_2(dmso\text{-}S)_4$ (**9**) with CO at ambient temperature and pressure led, depending on the reaction time, to the selective replacement of either one or two cis dmso ligands while the chlorides maintained the trans geometry yielding *trans,trans, trans*-$RuCl_2(dmso\text{-}S)_2(dmso\text{-}O)(CO)$ (**33**) and *trans, cis,cis*-$RuCl_2(dmso\text{-}O)_2(CO)_2$ (**34**) (Scheme 46).[336]

Scheme 46



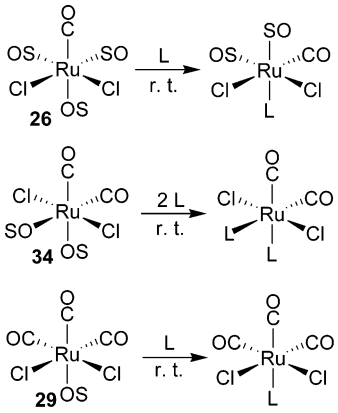
In all the above compounds, coordination of CO induces the selective isomerization of the dmso trans to it from S- to O-bonding. In this way, the moderate π-acceptor dmso-S avoids competition for π backbonding with the trans coordinated and much stronger π-acceptor CO. The binding mode of the other sulfoxides was unaffected by coordination of CO. Comparison of the three dicarbonyl complexes *cis,cis,cis*-$RuCl_2(dmso\text{-}S)(dmso\text{-}O)(CO)_2$ (**27**), *cis,trans, cis*-$RuCl_2(dmso\text{-}S)_2(CO)_2$ (**28**), and *trans,cis,cis*-$RuCl_2$-$(dmso\text{-}O)_2(CO)_2$ (**34**) suggests that the competition with CO for π-electrons does not seem to prevent coordination of dmso through sulfur, unless when it is trans to CO.

In the mononuclear $RuCl_2(dmso)_{4-x}(CO)_x$ ($x = 1-3$) compounds **26**−**30**, **33**, and **34** the CO stretching frequencies fall in the range from 1980 to 2130 cm^{-1} (1995, 2001, and 1980 cm^{-1} for the monocarbonyls **26**, **30**, and **33**, respectively). For comparison, and in agreement with the lower π-backbonding ability of Ru(III) compared to Ru(II), the Ru(III) monocarbonyls **19** and **20** described above have higher CO stretching frequencies (in the range 2025−2047 cm^{-1}).[82]

The carbonyl−dmso compounds were found to be versatile precursors for the preparation of derivatives upon replacement of the sulfoxides with stronger σ-

and/or π-donor ligands. For example, for each complex selective replacement of all the dmso-O ligands with N-donor ligands L such as pyridine was achieved under mild conditions, yielding complexes such as *cis*,*cis*,*cis*-$RuCl_2(dmso\text{-}S)_2(L)(CO)$, *trans*,*cis*,*cis*-$RuCl_2(L)_2(CO)_2$, and *cis*,*fac*-$RuCl_2(CO)_3(L)$ (Scheme 47).[97,335]

Scheme 47[a]

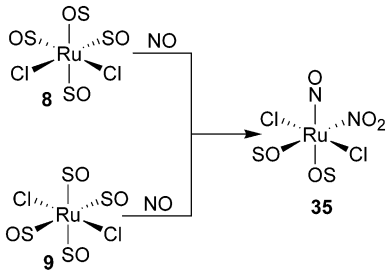


[a] L = N-donor ligand.

In particular, **34** was found to be a very useful building block in the construction of several supramolecular adducts with pyridylporphyrins, including molecular squares.[339−346] It should be noted that the substitution reactions of the Ru(II)-dmso carbonyls can be sometimes accompanied by geometrical isomerization, as in the case of **26**, which, upon replacement of the dmso-O trans to CO with L, yields selectively *cis*,*cis*,*cis*-$RuCl_2(dmso\text{-}S)_2(L)(CO)$ complexes in which CO (previously trans to dmso) is trans to a Cl (Scheme 47).

Finally, treatment of either Ru(II)−dmso precursors **8** or **9** with gaseous NO in CH_2Cl_2 solution yielded the nitrosyl-nitro Ru(II) derivative *trans*,*cis*,*cis*-$RuCl_2(dmso\text{-}O)_2(NO)(NO_2)$ (**35**) (Scheme 48), which can be thought of as deriving formally from *mer*,*cis*-$RuCl_3(dmso\text{-}O)_2(NO)$ (**22**) upon replacement of the chloride trans to dmso-O with a nitro group.[84]

Scheme 48



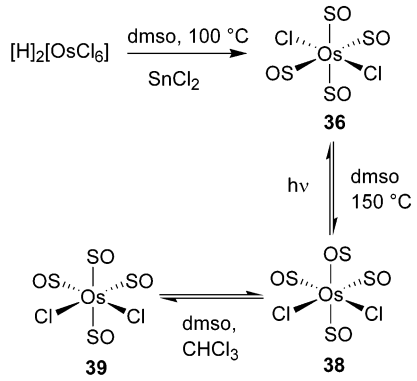
2.7. Interactions of Ru–dmso Complexes with Bioligands

By virtue of their well documented anticancer activity, the interactions of *cis*- and *trans*-$RuCl_2(dmso)_4$ and of some Ru(III)−dmso complexes, in particular NAMI-A, with a number of biologically relevant molecules, including nucleobases, nucleotides and nucleosides,[75,347−354] acyclovir,[74,75,355] oligonucleotides,[356,357] DNA,[358−362] and plasma proteins,[363−366] have been investigated. As normally these investigations did not lead to the isolation of new compounds (with some exceptions mentioned above), they will not be reviewed here in detail.

3. Osmium–Halide–dmso Complexes

The chemistry of osmium−dmso complexes has not been investigated so extensively as that of ruthenium and, to our knowledge, concerns mainly Os(II) (reports on the preparation of the Os(III) and Os(IV) complexes $OsCl_3(dmso)_3$ and $[(dmso)_2H][OsCl_5(dmso)]$, respectively, by treatment of H_2OsCl_6 with dmso can be found in the Russian literature[367,368]). According to an early report,[369] the reactivity of Os precursors toward dmso was substantially similar to that of hydrated $RuCl_3$. Treatment of $H_2[OsCl_6]$ with $SnCl_2$ in dmso at 100 °C yielded *trans*-$OsCl_2(dmso\text{-}S)_4$ (**36**), which spontaneously precipitated from the hot reaction mixture (Scheme 49). Compound **36** was spec-

Scheme 49



troscopically and structurally characterized,[370] and the X-ray structure of the corresponding dibromo complex, *trans*-$OsBr_2(dmso\text{-}S)_4$ (**37**), was also determined.[371] When the above reaction was performed at higher temperature (150 °C), complete dissolution of the trans isomer **36** occurred and a white precipitate of *cis*,*fac*-$OsCl_2(dmso\text{-}S)_3(dmso\text{-}O)$ (**38**) formed from the dmso solution after cooling to room temperature and addition of acetone (Scheme 49).[369] Thus, as for the corresponding Ru compounds, in hot dmso the thermal isomerization from **36** to **38** occurred, while the reverse isomerization was found to be induced by light at ambient temperature.[372] Crystallization of **36** at room temperature from chloroform/diethyl ether mixtures yielded crystals that were found by X-ray crystallography to correspond to the unprecedented all-S-bonded isomer *cis*-$OsCl_2(dmso\text{-}S)_4$ (**39**), which is unknown for Ru(II).[370] NMR spectroscopy established that both in chloroform and in dmso solution the slow equilibration between **38** and **39** occurs, and **38** is thermodynamically slightly less stable than **39** (Scheme 49).[372] However, while crystals of **38** were obtained from dmso solutions,[372] crystals of **39** were recovered from chloroform solutions.[370] This difference of behavior between Os(II) and Ru(II) can be attributed to the greater preference of Os(II) for S-bonding, compared to Ru(II), as shown by the trend of the metal-sulfur bond distances (Os−S distances are, on average, ca. 0.008 Å shorter than the corresponding Ru−S distances) and the calcu-

lated metal−dmso binding energies (Os−S is from 30 to 40 kJ mol^{-1} larger than Ru−S, depending on the nature of the trans ligand).[372]

There are relatively few examples in which the Os(II)−dmso complexes were used as precursors in inorganic synthesis. Treatment of **36** with $RTe(CH_2)_3TeR$ (R = Ph, CH_3) or *o*-$C_6H_4(TeMe)_2$ (Te−Te) in refluxing ethanol produced *trans*-$OsCl_2$(Te−Te)$_2$ complexes, in which the ditelluroethers act as chelating ligands;[373] similarly, reaction of **36** with the distibine ligand $Ph_2Sb(CH_2)_3SbPh_2$ afforded *trans*-$OsCl_2(Ph_2Sb(CH_2)_3SbPh_2)_2$.[373] Conversely, treatment of **36** or **37** in refluxing ethanol with 4 equiv of bis(diphenylstibino)methane (dpsm, $Ph_2SbCH_2SbPh_2$) yielded *trans*-$OsCl_2(\eta^1\text{-dpsm})_4$ and $OsBr_2(\eta^1\text{-dpsm})_2(\eta^2\text{-dpsm})$, respectively, in which the distibinomethane can act both as a monodentate and as a chelating ligand.[374] McDonagh and co-workers reported that treatment of the two isomers **36** and **38** with (*S,S*)-1,2-phenylenebis(methylphenylphosphine) in refluxing methanol yielded selectively the corresponding *trans*- and *cis*-$OsCl_2${(*R,R*)-1,2-phenylenebis(methylphenylphosphine)}$_2$ compounds.[375] Thus, the appropriate choice of the cis or trans isomer of the precursor complex allowed selective preparation of either cis or trans isomers of the chiral bidentate phosphine complex. Similar to that observed with the corresponding Ru complex **8**,[332] treatment of **38** with $(NH_4)_6Mo_7O_{24}$ yielded the heptamolybdate polyoxometalate $(NH_4)_4$[Os(dmso-S)$_3$$Mo_7O_{24}$].[332]

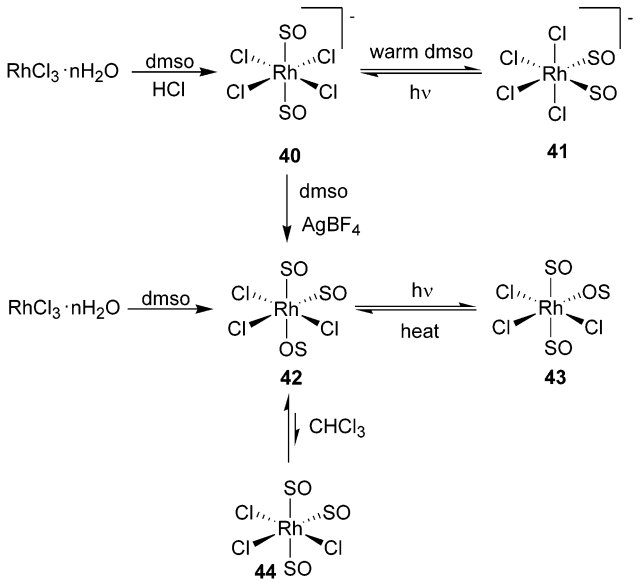
The Os(III) carbonyls [N(*n*Bu_4)][*trans*-OsX_4(dmso-O)(CO)] (X = Cl, Br), structurally similar to the Ru(III) complex **19**, were obtained by stepwise treatment of the triply bonded di-osmium(III) complexes [N(*n*Bu_4)]$_2$$Os_2X_8$ with carbon monoxide and dmso.[376] The nitrosyl Os(II) complex [(dmso)$_2$H][*trans*-$OsCl_4$(dmso-O)(NO)], analogue of the Ru complex **21**, was obtained by treatment of $H_2[OsCl_5(NO)]$ with warm dmso.[377]

4. Rhodium–Halide–dmso Complexes

Rhodium(III)−chloride−dmso complexes of general formula $[RhCl_x(dmso)_{6-x}]^{3-x}$ (x = 1−4) have been investigated since the late sixties.[18,378−381] Dimethyl sulfoxide can bind to Rh(III) either through the sulfur or through the oxygen atom; in general, the number of O-bonded sulfoxides increases upon increasing the positive charge of the complex and dmso-O prefers to be trans either to dmso-S or to Cl. Accurate NMR studies showed that, in solution of noncoordinating solvents, almost every derivative of the $[RhCl_x(dmso)_{6-x}]^{3-x}$ (x = 1−4) series exists as more than one isomer.[382] The isomers may differ from one another both in the geometry and in the binding modes of the dmso ligands (linkage isomers).

Despite early reports on the preparation of Na[$RhCl_4$(dmso-S)$_2$] and $RhCl_3$(dmso)$_3$ from Na_3RhCl_6,[379,380] the most recent and detailed preparations of Rh(III)−chloride−dmso complexes used hydrated $RhCl_3$ as precursor. Treatment of hydrated $RhCl_3$ with concentrated warm HCl (70 °C) followed by addition of dmso at room temperature yielded [(dmso)$_2$H][*trans*-$RhCl_4$(dmso-S)$_2$] (**40**) (Scheme 50), which is isostructural to the Ru(III) complex **1**.[18,19]

Scheme 50



The corresponding methylphenylsulfoxide (mpso) derivative was similarly prepared.[383] As for the corresponding Ru(III) complex, the cation of **40** can be easily exchanged and several X-ray structures of [Y][*trans*-$RhCl_4$(dmso-S)$_2$] compounds have been determined (Y^+ = Na^+,[384] $(dmso)_2H^+$,[385] PSH^+ (PS = "proton sponge"),[386] and $NEt_2H_2^+$ [387]).

Nevertheless, complex **40** was found to be only the kinetic product of the reaction between hydrated $RhCl_3$, HCl, and dmso; in fact, when the reaction was repeated at higher temperature (100 °C), the thermodynamically more stable cis isomer, [(dmso)$_2$H][*cis*-$RhCl_4$(dmso-S)$_2$] (**41**), was obtained in good yield.[388] Also recrystallization of **40** from warm dmso produced the cis isomer **41** (Scheme 50). In both procedures, the product cocrystallized with variable amounts of **40** (5−15%). The reverse isomerization process, from the cis (**41**) to the trans (**40**) isomer, was found to be promoted by visible light at ambient temperature. The X-ray structure of **41** was determined for the tetraethylammonium salt, [NEt_4][*cis*-$RhCl_4$(dmso-S)$_2$].[388] The average Rh−S bond distance in the cis isomer (2.279(8) Å) is considerably shorter than that of 2.323(3) Å for mutually trans Rh−S bonds.[6,388]

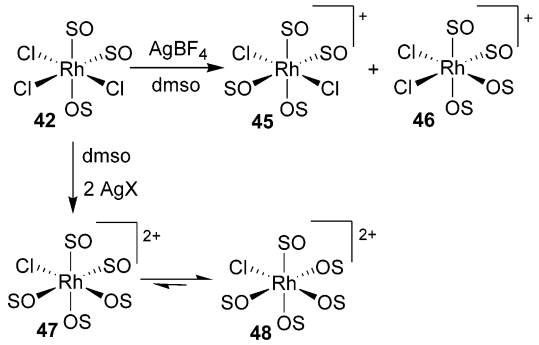
Treatment of hydrated $RhCl_3$ with dmso or,[378,383] alternatively, treatment of **40** with 1 equiv of $AgBF_4$ in refluxing dmso/acetone mixtures,[389] yielded the neutral complex *mer,cis*-$RhCl_3$(dmso-S)$_2$(dmso-O) (**42**) (Scheme 50). Compound **42** was investigated spectroscopically,[390] and its solid-state structure was also determined.[391] The corresponding derivatives with tmso and mpso were similarly prepared.[383,392] Interestingly, while the anionic Rh(III) complex **40** is isostructural to the corresponding Ru(III) analogue, the neutral complex **42** is formally an isomer of the Ru(III) counterpart **2**: in fact, the two dmso-S ligands are cis in **42**, while they are trans in **2**. The thermodynamically less stable linkage isomer of **42**, *mer, trans*-$RhCl_3$(dmso-S)$_2$(dmso-O) (**43**) (isostructural to **2**), was obtained upon irradiation of an acetone solution of **42** with visible light (Scheme 50) and its X-ray structure was also determined.[389] In addition,

NMR spectroscopy established that in $CDCl_3$ solution complex **42** equilibrates with an all S-bonded minor isomer formulated as *mer*-$RhCl_3$(dmso-S)$_3$ (**44**), which was never isolated (Scheme 50).[382,383,389] As found for the anionic isomers **40** and **41**, a significant increase of the Rh−S bond length was observed in the neutral trans isomer **43** (average 2.311(6) Å), compared to the cis isomer **42** (average 2.243(16) Å).

Thus, unlike for the corresponding Ru(III) complexes **1** and **2**, both for the anionic and the neutral Rh(III)-dmso compounds the isomers with two cis S-bonded sulfoxides (i.e., **41** and **42**) were found to be thermodynamically more stable compared to those with the trans dmso-S ligands (i.e. **40** and **43**).

Treatment of **42** with 1 equiv of $AgBF_4$ in refluxing dmso/acetone mixtures yielded the cationic species [*trans,cis,cis*-$RhCl_2$(dmso-S)$_2$(dmso-O)$_2$][BF_4] (**45**) (Scheme 51), whose X-ray structure was also deter-

Scheme 51

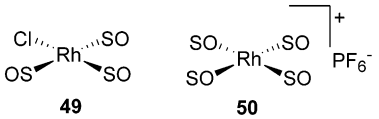


mined.[393] When the preparation was performed at ambient temperature a mixture of **45** and of another isomer, identified as [*cis,cis,cis*-$RhCl_2$(dmso-S)$_2$(dmso-O)$_2$][BF_4] (**46**) on the basis of its NMR spectrum, was isolated instead (Scheme 51).[382]

Treatment of **42** with 2 (or more) equiv of a soluble silver salt AgX yielded [*fac*-RhCl(dmso-S)$_2$(dmso-O)$_3$][X]$_2$ (**47**) (Scheme 51),[382] thus confirming an early report by Kukushkin and co-workers that provided no detail on the geometry of this product.[381] Complex **47** was found to isomerize slowly in nitromethane solution to the more stable isomer with four O-bonded dmso ligands [RhCl(dmso-S)(dmso-O)$_4$][X]$_2$ (**48**, dmso-S trans to dmso-O) (Scheme 51).[382] Finally, the preparation of [Rh(dmso)$_6$][BF_4]$_3$, originally described by Sen and Singh,[394] could not be reproduced later.[382] Therefore, the existence of this complex, described as having two dmso-S and four dmso-O ligands,[394] is highly uncertain.

Very recently the synthesis of unprecedented neutral and cationic Rh(I) complexes having dmso as the only dative ligand has been reported by the group of Milstein.[395,396] The square-planar monomeric complex RhCl(dmso-S)$_3$ (**49**) (Chart 32) was prepared by treatment of a toluene slurry of [Rh_2Cl_2(coe)$_6$] (coe = cyclooctene) with excess dmso (a dinuclear Rh(I)-

Chart 32



dmso compound, formulated as [RhCl(dmso)$_2$] on the basis of its IR spectrum, had been described by James and co-workers[383]). Treatment of a dilute solution of [Rh_2Cl_2(coe)$_6$] with 2−4 equiv of dmso yielded instead the doubly bridged dinuclear compound [(coe)(dmso-S)Rh(μ-Cl)(μ-dmso-S,O)RhCl(dmso-S)], which represents the most recent example of the rare S,O bridging mode of dmso.[395,396] Substitution of the dmso ligands in **49** was investigated: treatment of **49** with excess pyridine gave [*cis*-RhCl(py)(dmso-S)$_2$] by replacement of one dmso, while treatment with 1 equiv of the chelating ligand 4,4′-dimethyl-2,2′-bipyridine (dmbpy) gave [RhCl(dmbpy)(dmso-S)] with concomitant loss of 2 equiv of dmso.[396]

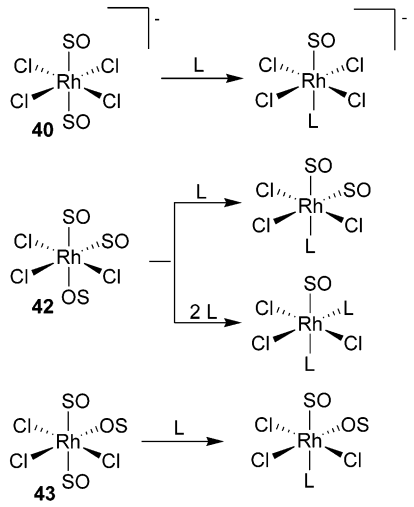
The reaction of a toluene slurry of [Rh(coe)$_2$(acetone)$_2$][PF_6] with excess dmso afforded the first cationic, all dmso-stabilized Rh(I) complex, [*cis*-Rh(dmso-S)$_2$(dmso-O)$_2$][PF_6] (**50**) (Chart 32).[395,396] Conversely, treatment of [Rh(cod)$_2$][BF_4] (cod = cyclooctadiene) with dmso yielded [Rh(cod)(dmso-O)$_2$][BF_4].[396] The above species have been also structurally characterized in the solid state by X-ray crystallography; as expected, the O-bonding mode is preferred with the harder, cationic metal center **50**, while in the neutral complex **49** all the dmso ligands are S-bonded. The reaction of [*cis*-Rh(dmso-S)$_2$(dmso-O)$_2$][PF_6] with 1 equiv of dmbpy in dmso at room temperature afforded [*cis*-Rh(dmso-S)$_2$(dmbpy)][PF_6] by displacement of the two O-bonded dmso ligands of **50**.[397]

4.1. Reactions of Rh(III)–dmso Precursors with σ- and π-Donor Ligands

The reactions of [Y][*trans*-$RhCl_4$(dmso-S)$_2$] (**40**) and *mer,cis*-$RhCl_3$(dmso-S)$_2$(dmso-O) (**42**) toward σ- and π-donor ligands have been investigated extensively. Kukushkin and co-workers reported that treatment of [Na][*trans*-$RhCl_4$(dmso-S)$_2$] with N-donor ligands L yielded different products depending on the nature of L.[379] When L = NH_3 or CH_3NH_2, $RhCl_3$(dmso-S)$_2$(L) compounds were obtained, while when L = pyridine or 4-picoline, disubstituted products $RhCl_3$(dmso-S)-(L)$_2$ were isolated. However, these products were characterized only by elemental analysis and IR spectroscopy.[379] Later it was found that treatment of [Na][*trans*-$RhCl_4$(dmso-S)$_2$] with an excess of imidazole at ambient temperature gives in good yield [Na][*trans*-$RhCl_4$(dmso-S)(im)];[398] thus the reactivity of the Rh(III) precursor **40** was found to be similar to that of the isostructural Ru(III) precursor **1** (Scheme 52; see also Scheme 4).

The reactivity of *mer,cis*-$RhCl_3$(dmso-S)$_2$(dmso-O) (**42**) toward neutral σ- and π-donor ligands (L) was found to be quite straightforward and involved the selective replacement of the dmso-O under mild conditions to yield *mer,cis*-$RhCl_3$(dmso-S)$_2$(L) complexes (Scheme 52); examples are found in the literature for L = amides, amine oxides, phospine oxides,[383,399] ylides,[400] sulfides,[17] ammonia, and heterocyclic N ligands.[389,398,401] Treatment of **42** with an excess of L under more forcing conditions induced replacement also of the dmso-S trans to a Cl and yielded the disubstituted product *mer,cis*-$RhCl_3$(L)$_2$-(dmso-S) (Scheme 52).[17,389,398,402]

Scheme 52

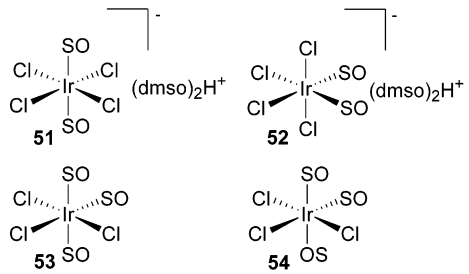


Even though isomer **43** in aprotic solvents is thermodynamically unstable with respect to **42**, the thermal isomerization at room temperature is slow and allowed its reaction with neutral ligands to be investigated. Thus, treatment of **43** with N-donor ligands (L) was found to involve the selective replacement of one of the two trans S-bonded dmso's yielding *mer*-$RhCl_3$(dmso-S)(dmso-O)(L) complexes (L trans to dmso-S), which are actually linkage isomers of the corresponding compounds obtained from **42** (Scheme 52).[389]

5. Iridium–Halide–dmso Complexes

The chemistry of Ir(III)−halide−dmso complexes has been less extensively investigated compared to that of the Rh(III) analogues. It concerns only anionic and neutral derivatives, and there is still uncertainty about the number of isomers and their geometry. Early works by Henbest and co-workers, dealing with the catalytic reduction of cyclohexanones to axial alcohols and hydrogenation of unsaturated ketones, reported that treatment of H_2IrCl_6 with 2-propanol at 55 °C, followed by addition of dmso at ambient temperature, yielded *orange-pink* crystals of an anionic complex formulated as [(dmso)$_2$H][*trans*-$IrCl_4$(dmso-S)$_2$] (**51**) (Chart 33).[403−405] According to the same authors, treatment of H_2IrCl_6 with aqueous dmso at 100 °C for 24 h yielded the cis isomer [(dmso)$_2$H][*cis*-$IrCl_4$(dmso-S)$_2$] (**52**) (Chart 33) as *yellow* needles.[405]

Chart 33



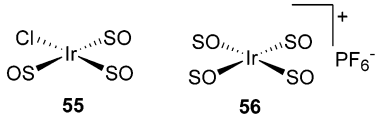
The geometry of the two isomers, which were reported to have different melting points, was assigned on the basis of ^{1}H NMR considerations, even if the difference between the singlets of the dmso-S ligands in the two isomers was indeed minimal: 0.4 ppm.[405] James and co-workers later described different synthetic routes to the yellow and pink-orange isomers, but they agreed on the previous structural assignments.[406] It should be noted that, when the NMR results of different authors are compared,[407] the dmso-S chemical shift for the same isomer is found to change from one reference to another, and it is even unclear which isomer should resonate at lowest field. The X-ray structure of [(dmso)$_2$H][*trans*-$IrCl_4$(dmso-S)$_2$] (**51**) (*orange* crystals obtained according to the original preparation by Henbest) was determined very recently and confirmed the trans geometry of the two sulfoxides;[408] thus, complex **51** is isostructural to the Ru(III) and Rh(III) compounds **1** and **40**, respectively. However, *yellow* crystals of [(dmso)$_2$H][$IrCl_4$(dmso-S)$_2$] obtained by a different synthetic route (from $IrCl_3$ at ambient temperature) were found to have the same trans geometry by X-ray analysis.[407] Interestingly, the *orange*[408] and the *yellow*[407] crystals have the same electronic absorption spectrum in water. This observation suggests that the color of the crystals should not be taken as a reliable parameter, but their spectrum in solution should always be considered and reported. In conclusion, to date there is no conclusive evidence about the existence of the cis isomer **52**.

An even larger uncertainty affects the neutral species $IrCl_3$(dmso)$_3$. Henbest and co-workers mentioned the isolation of a $IrCl_3$(dmso-S)$_2$(dmso-O) complex of undetermined geometry, obtained either as a byproduct in the synthesis of **52** or by treatment of $IrCl_4$ with warm dmso, as well as of a *mer*-$IrCl_3$(dmso-S)$_3$ complex, obtained by reaction of iridium(III)-hydrides (*cis,mer*- and *trans,mer*-$IrCl_2H$(dmso)$_3$) with HCl.[405] Later, James and co-workers reported that the decomposition of *trans*-$IrCl_2H$(dmso-S)$_3$ in chloroform led to a mixture of the two linkage isomers *mer*-$IrCl_3$(dmso-S)$_3$ (**53**) and *mer,cis*-$IrCl_3$(dmso-S)$_2$(dmso-O) (**54**) (Chart 33), while decomposition of the dihydride *cis,mer*-IrH_2Cl(dmso-S)$_3$ led to **53** exclusively.[406] It should be noted, though, that these neutral species were not isolated, but identified only in solution by NMR spectroscopy.[406]

A neutral Ir(III)-dmso species containing metalated benzylacetophenone, *cis,cis*-$IrCl_2$(dmso-S)$_2$(PhCO-(CH_2)CHPh), was isolated in small amounts during the hydrogenation of benzylideneacetophenone by propan-2-ol catalyzed by **51** and was structurally characterized by X-ray diffraction.[409]

The group of Milstein has recently reported the preparation of two novel Ir(I)−dmso complexes, IrCl-(dmso-S)$_3$ (**55**) and [*cis*-Ir(dmso-S)$_2$(dmso-O)$_2$][PF_6] (**56**) (Chart 34), analogues of the corresponding Rh(I) species (see above).[396,410] Dissolution of **55** in CH_2Cl_2 involved the immediate loss of one dmso ligand and

Chart 34



led to the isolation of the chloro-bridged dimer $[(dmso\text{-}S)_2Ir(\mu\text{-}Cl)_2Ir(dmso\text{-}S)_2]$ (**57**).[396] Similar to that found for the Rh(I) species, treatment of the neutral complex **55** with excess pyridine led to the substitution of only one of the dmso ligands (isolation of [*cis*-$IrCl(py)(dmso\text{-}S)_2$]), whereas the bidentate dmbpy ligand displaced two of them (isolation of [*cis*-IrCl(dmso-S)(dmbpy)]). Reaction of these two ligands with the cationic complex **56** led to the selective substitution of the two O-bonded ligands, affording [*cis*-$Ir(dmso\text{-}S)_2(py)_2][PF_6]$ and [*cis*-$Ir(dmso\text{-}S)_2(dmbpy)][PF_6]$, respectively.[396]

Oxidative addition of H_2 to **55** afforded *cis,fac*-$IrCl(H)_2(dmso\text{-}S)_3$ as kinetic product, which evolved to the thermodynamically more stable isomer *cis,mer*-$IrCl(H)_2(dmso\text{-}S)_3$.[396] Oxidative addition of H_2O to **55** yielded the triply bridged dimer $[(dmso\text{-}S)_2(H)Ir(\mu\text{-}OH)_2(\mu\text{-}Cl)Ir(H)(dmso\text{-}S)_2][cis\text{-}IrCl_2(dmso\text{-}S)_2]$, while addition of H_2O to **56** yielded the doubly bridged dimer $[(dmso\text{-}S)_2(dmso\text{-}O)(H)Ir(\mu\text{-}OH)_2Ir(dmso\text{-}S)_2(dmso\text{-}O)(H)][PF_6]_2$.[396,410] Both dimers were structurally characterized by X-ray crystallography. Interestingly, in the dicationic species the dmso ligands exhibit both coordination modes: each iridium atom is coordinated to two cis dmso-S molecules and to one dmso-O molecule located trans to the hydride.

5.1. Reactions of Ir(III)–dmso Precursors with σ- and π-Donor Ligands

Owing to the uncertainty that affects the Ir(III)–dmso compounds, there is only one clear-cut reaction that involves $[(dmso)_2H][trans\text{-}IrCl_4(dmso\text{-}S)_2]$ (**51**) as precursor: treatment of **51** with an excess of imidazole led to the selective replacement of one of the two trans dmso-S ligands yielding [imH][*trans*-$IrCl_4$(dmso-S)(im)], whose X-ray structure was also determined.[408] Thus, the reactivity of the Ir(III) precursor is similar to that of the corresponding Rh(III) and Ru(III) species (see Schemes 4 and 52), even though replacement of one dmso-S with imidazole in **51** required more forcing conditions, owing to the inertness of Ir(III).

6. General Factors Influencing the Binding Mode of dmso

The coordination mode of dmso to a metal center, either through the sulfur (dmso-S) or through the oxygen atom (dmso-O), depends both on steric and electronic features and can be distinguished, besides by X-ray crystallography, by IR[380,382,390,411] and NMR spectroscopy,[59,62,382,383] as thoroughly described above and in a number of papers. A density functional study of dmso linkage isomerism in Ru(III) and Rh(III) complexes has been performed recently.[412]

Coordination of dmso-S is sterically more demanding than that of dmso-O, and it is generally preferred on soft or borderline metal centers for electronic reasons. In fact, dmso-S is a moderate π-acceptor ligand that stabilizes metals in low oxidation states; nevertheless, coordination of two S-bonded dmso ligands trans to each other is relatively uncommon, often giving rise to unstable species which tend to isomerize to the cis derivatives. The main reason the trans geometry is unfavorable is the rather strong *trans*-influencing effect of dmso-S ligands. Among the examples reported above, this feature turned out clearly for the anionic and neutral Rh(III) derivatives (i.e., **41**, **42**), for which the *cis*-$Rh(dmso\text{-}S)_2$ fragment was found to be thermodynamically more stable compared to *trans*-$Rh(dmso\text{-}S)_2$ (i.e., **40**, **43**).[382,388,389] On the contrary, this was not the case for the Ru(III) complexes of the same charge, for which only the *trans*-$Ru(dmso\text{-}S)_2$ fragment has been observed to date. As the difference in the ionic size between Rh(III) and Ru(III) is almost negligible (0.015 Å), the reason for this preference of Ru(III) must be electronic rather than steric. According to spectroscopic and structural data, the Ru(III)–dmso-S bond involves also a π backbonding contribution, while the Rh(III)–dmso-S bond is essentially σ in character and excludes significant π backbonding.[388,389] The experimental observation that Rh(III) has a lower π backbonding ability than Ru(III) is in accordance with the expected trend in the energy of the metal orbitals due to the increase of the effective nuclear charge going from Ru(III) to Rh(III).

Ru(II) is the metal center, among those treated, that provides the largest number of well-characterized dmso complexes. The wealth of structural and spectroscopic data collected on these species over the years indicated that dmso prefers to bind to Ru(II) through the sulfur atom for electronic reasons. In addition, it binds preferentially trans to pure σ- and/or π-donor ligands, but mild π-acceptor ligands (such as dmso-S itself) are also tolerated. When trans to a strong π-acceptor ligand, such as CO or NO, dmso prefers to bind through O rather than through S, to avoid competition for π backbonding. When two dmso ligands are bound to Ru(II), they are always in cis geometry. The only known exceptions are the dicarbonyl complex *cis,trans,cis*-$RuCl_2(dmso\text{-}S)_2(CO)_2$ (**28**)[336] and *cis,trans,cis*-$RuCl_2(dmso\text{-}S)_2(bp)$ (bp = 2,2′-biphosphinine),[216] both complexes containing strong π-acceptor ligands, either CO or bp. Very likely, this unusual geometry is due to the preference of the two chlorides to be trans to the strong π-acceptor ligands, that forces the two dmso-S ligands trans to each other. All the Ru(II) complexes with three dmso-S ligands reported so far have a *fac* geometry, the *mer* arrangement being probably less favored for both electronic and steric factors. The only exception to this rule is *cis,mer*-$RuCl_2(dmso\text{-}S)_3(CO)$ (**31**), which was characterized spectroscopically but not isolated.[337] Formal addition of a further dmso-S ligand to the *fac*-$Ru(dmso\text{-}S)_3$ fragment would cause a significant increase of the steric hindrance. In fact, in the well-known complex *cis,fac*-$RuCl_2(dmso\text{-}S)_3$(dmso-O) (**8**) the fourth dmso ligand binds through oxygen, and it is accepted that, besides to electronic reasons (two dmso-S ligands in trans geometry), this binding mode is due also to steric effects. There is no experimental evidence for an all S-bonded isomer *cis*-$RuCl_2(dmso\text{-}S)_4$, and DFT calculations have shown that the molecular energy of this hypothetical complex is 56 kJ mol^{-1} higher than that of **8**.[413] Coordination exclusively through S occurs only in the less sterically crowded (but thermodynamically unstable)

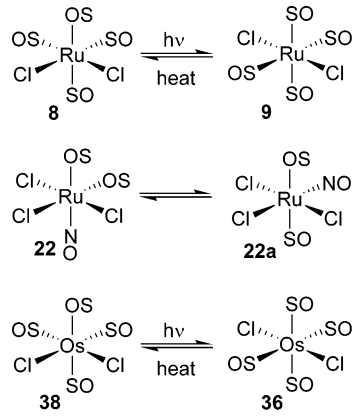
isomer *trans*-$RuCl_2$(dmso-S)$_4$ (**9**),[42,54] which is the only known ruthenium complex (together with **11**) with more than three S-bonded dmso ligands. For the less sterically demanding tmso, binding of the fourth sulfoxide occurs through sulfur also on the *cis*,*fac*-$RuCl_2$(tmso-S)$_3$ fragment (formally), as in *cis*-$RuCl_2$(tmso-S)$_4$ (**17**).[43,69] Os(II) is softer and slightly larger than Ru(II) and thus (formal) coordination of the fourth dmso on the *cis*,*fac*-$OsCl_2$(dmso-S)$_3$ fragment may occur either through S or through O. Both isomers *cis*,*fac*-$OsCl_2$(dmso-S)$_3$(dmso-O) (**38**) and *cis*-$OsCl_2$(dmso-S)$_4$ (**39**) have been isolated, depending on the solvent.[369,370,372]

In conclusion, the preferred binding mode of dmso on ruthenium is through S, unless the steric demand of the other ligands is significant. Besides that for steric reasons, dmso coordination through oxygen is also favored by a net positive charge of the complex. Until recently, before we described the Ru-nitrosyls [*cis*,*fac*-$RuCl_2$(dmso-O)$_3$(NO)]$^+$ (**23**), [RuCl(dmso-O)$_4$(NO)]$^{2+}$ (**24**), and [Ru(dmso-O)$_5$(NO)]$^{3+}$ (**25**) which contain up to five dmso-O ligands,[88,89] the only known Ru complex with three O-bonded dmso ligands was the dication [*fac*-Ru(dmso-O)$_3$(dmso-S)$_3$]$^{2+}$ (**15**)[40,59,64] (a [*fac*-Ru(triphos)(dmso-O)$_3$]$^{2+}$ complex was proposed by Venanzi and co-workers on the basis of elemental analysis and spectroscopic investigations but was not structurally characterized in the solid state).[227]

7. S/O Linkage Isomerization

As discussed above, coordination of sulfoxides either through S or through O depends on a combination of electronic and steric factors. Several cases of S/O linkage isomerization have been described and they can be distinguished in different categories. (1) The linkage isomerization can be induced by a change in the nature of the ancillary ligands. For example, an increase of the electron-withdrawing properties of the carboxylate ligands from $Rh_2(O_2CCH_3)_4$(dmso-S)$_2$ to $Rh_2(O_2CCF_3)_4$(dmso-O)$_2$ induced S- to O-isomerization.[414] Similarly, replacement of a dmso with a strong π-acceptor ligand, such as CO or NO, induced the selective S- to O-isomerization of the dmso-S trans to it (both on Ru(II) and on Ru(III) centers) to remove competition for π-electrons.[82,84,88,336] (2) The linkage isomerization can be induced by a change in the oxidation state of the metal center, such as in $[Ru^{II}(NH_3)_5$(dmso-S)$]^{2+}$ vs $[Ru^{III}(NH_3)_5$(dmso-O)$]^{3+}$,[415,416] in *mer*-$Ru^{III}Cl_3$(dmso-S)(dmso-O)(L) vs [*mer*-$Ru^{II}Cl_3$(dmso-S)$_2$(L)]$^-$ (L = N-donor ligand, see Scheme 6),[77] and in *trans*,*cis*-$Ru^{II}Cl_2$(dmso-S)$_2$(Hbpp) vs [*trans*,*cis*-$Ru^{III}Cl_2$(dmso-S)(dmso-O)(Hbpp)]$^+$ (Hbpp = 3,5-bis-(2-pyridyl)pyrazole, Chart 9).[116] As expected, dmso prefers to bind through S on Ru(II) and through O on Ru(III). 3) There are examples in which linkage isomerization is thermal (in some cases spontaneous at room temperature) and others in which isomerization in one direction is thermal, and it is induced by light in the reverse direction. In several cases, however, the linkage isomerization is accompanied by a rearrangement in the geometry of the complex (Scheme 53), such as in *cis*,*fac*-$RuCl_2$(dmso-S)$_3$(dmso-O) (**8**) vs *trans*-$RuCl_2$(dmso-S)$_4$ (**9**),[54] *mer*,*cis*-$RuCl_3$(dmso-O)$_2$(NO) (**22**) vs *mer*,*trans*-$RuCl_3$(dmso-O)-

Scheme 53. Examples of Thermal and Light-Induced S/O Linkage Isomerizations Accompanied by Geometrical Isomerization



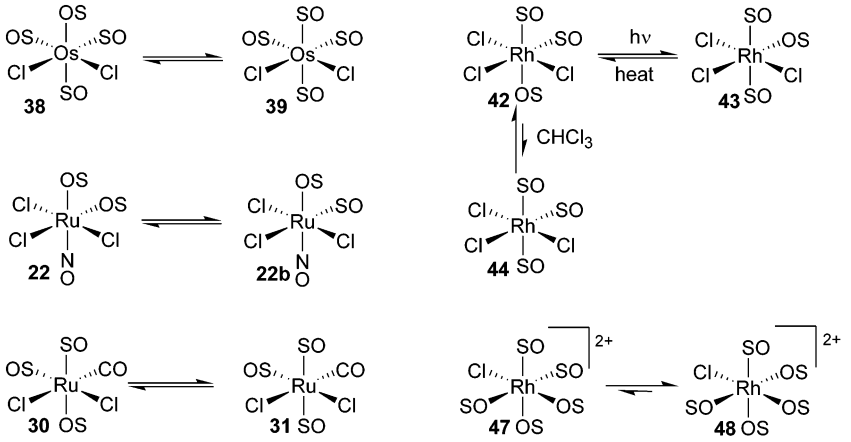
(dmso-S)(NO) (**22a**),[84] and *cis*,*fac*-$OsCl_2$(dmso-S)$_3$(dmso-O) (**38**) vs *trans*-$OsCl_2$(dmso-S)$_4$ (**36**).[369,370,372]

In some cases, the linkage/geometrical isomers are apparently not in equilibrium, and they derive either from different precursors or from the same precursor by different synthetic procedures: see for example *cis*,*cis*,*cis*-$RuCl_2$(dmso-S)(dmso-O)(CO)$_2$ (**27**), *cis*,*trans*,*cis*-$RuCl_2$(dmso-S)$_2$(CO)$_2$ (**28**), and *trans*,*cis*,*cis*-$RuCl_2$(dmso-O)$_2$(CO)$_2$ (**34**) (Schemes 44 and 46).[336]

There are instead relatively few examples concerning pure linkage isomers, in which the S/O isomerization leaves the rest of the complex unchanged. To the best of our knowledge, there is only one well-documented example, in which both isomers have been characterized both spectroscopically and structurally by X-ray: *cis*,*fac*-$OsCl_2$(dmso-S)$_3$(dmso-O) (**38**) vs *cis*-$OsCl_2$(dmso-S)$_4$ (**39**) (Scheme 54).[369,370,372] Other examples were documented in solution, but only one of the isomers (at best) could be isolated and structurally characterized in the solid state (Scheme 54): *mer*,*cis*-$RuCl_3$(dmso-O)$_2$(NO) (**22**) vs *mer*,*cis*-$RuCl_3$(dmso-O)(dmso-S)(NO) (**22b**),[84] *cis*,*cis*,*cis*-$RuCl_2$(dmso-S)$_2$(dmso-O)(CO) (**30**) vs *cis*,*mer*-$RuCl_2$(dmso-S)$_3$(CO) (**31**),[337] *mer*,*cis*-$RhCl_3$(dmso-S)$_2$(dmso-O) (**42**) and *mer*,*trans*-$RhCl_3$(dmso-S)$_2$(dmso-O) (**43**) vs *mer*-$RhCl_3$(dmso-S)$_3$ (**44**),[382,383,389] [*fac*-RhCl(dmso-S)$_2$(dmso-O)$_3$]$^{2+}$ (**47**) vs [RhCl(dmso-S)(dmso-O)$_4$]$^{2+}$ (**48**).[382]

Actually, the case of *mer*,*cis*-$RhCl_3$(dmso-S)$_2$(dmso-O) (**42**) vs *mer*,*trans*-$RhCl_3$(dmso-S)$_2$(dmso-O) (**43**) is particular, in the sense that it may be seen as involving either a double linkage isomerization or a geometrical isomerization. A similar case of double linkage isomerization induced by light is that of [*cis*-Ru(bpy)$_2$(dmso-S)$_2$]$^{2+}$ vs [*cis*-Ru(bpy)$_2$(dmso-O)$_2$]$^{2+}$.[417] Interestingly, intramolecular photoinduced S- to O-isomerization, accompanied by a net color change, was found also in the solid state (crystals and films) for [Ru(terpy)(bpy)(dmso-S)]$^{2+}$,[418,419] and for [*trans*-Ru(bpy)$_2$(dmso-O)(dmso-S)]$^{2+}$;[420] the same isomerization occurs also in solution upon Ru(II) to Ru(III) oxidation, while the reversal O- to S-isomerization occurs spontaneously in solution and in the solid state (within minutes at ambient temperature).[418,419] Recently, a full description of the ground and excited potential energy surfaces of [Ru(terpy)(bpy)(dmso)]$^{2+}$ using density functional theory (DFT) has been

Scheme 54



reported; the study focused mainly on the spectrochemical properties of the complex along the coordinate involved in the linkage isomerization of dmso, showing a good agreement between computed and experimental spectra for the S- and O-linked isomers.[421]

8. Concluding Remarks

This review summarizes the work of the last 40 years (the "oldest" reference, no. 203, dates back to 1964) in the field of the halide−dmso coordination complexes of Ru, Os, Rh, and Ir. These compounds have indeed a rich and interesting chemistry, characterized by the presence of several geometrical and/or linkage isomers, and by the possibility that either the dmso's or the chlorides, or both, are replaced by neutral or anionic ligands under appropriate reaction conditions. Section 6 discusses the preferred binding modes of dmso on these metal centers and the related geometry issues, while section 7 deals with the S/O linkage isomerization. It should be noted that the coordination chemistry of the other sulfoxides, with the exception of tmso, is less straightforward than that of dmso, and there are relatively few examples of well-characterized derivatives.

While the chemistry of Ru−dmso coordination compounds has been thoroughly investigated and is supported by a wealth of structural and spectroscopic data, that of the other metals is much less developed (perhaps with the exception of Rh(III) compounds). Several Ru−dmso precursors, in both oxidation states +3 and +2, have been widely exploited in inorganic synthesis. A few highlights are summarized below.

In the Ru(III) complex $[(dmso)_2H][trans\text{-}RuCl_4(dmso\text{-}S)_2]$ (**1**), one dmso-S is easily and selectively replaced by heterocyclic N ligands L (or by ammonia) at ambient temperature (section 2.3). Thus, compounds **1** became the precursor of a series of new complexes of formula $[LH][trans\text{-}RuCl_4(dmso\text{-}S)(L)]$ (the so-called NAMI-A-type compounds), many of which were found to have remarkable anticancer activity. One of the two trans dmso-S ligands of **1** is also easily and selectively replaced by strong π-acceptor ligands, such as CO and NO, leading, respectively, to $[trans\text{-}RuCl_4(dmso\text{-}O)(CO)]^-$ (**19**) and $[trans\text{-}RuCl_4(dmso\text{-}O)(NO)]^-$ (**21**) (section 2.4). These substitution reactions induce the linkage isomerization of the remaining dmso from S- to O-bonded to avoid competition for π backdonation. Actually, coordination of NO to Ru(III) involves the formal reduction to Ru(II) by intramolecular transfer of one electron. Thus, the ruthenium−dmso nitrosyl **21** is better described as a diamagnetic Ru(II) nucleus bound to NO^+. Both **19** and **21** became in turn precursors of new carbonyl and nitrosyl derivatives, respectively, upon replacement of the dmso-O and chlorides with σ- and π-donor ligands.

The most important Ru−dmso precursor is, by far, the Ru(II) complex $cis,fac\text{-}RuCl_2(dmso\text{-}S)_3(dmso\text{-}O)$ (**8**). A large part of this review has been devoted to the detailed analysis of its reactivity toward a number of neutral and anionic ligands, both mono- and polydentate (section 2.5). Monodentate neutral ligands L can replace either one or two or all four dmso's, depending on their nature and the reaction conditions (ligand-to-ruthenium ratio, solvent, temperature). The O-bonded dmso is the most labile ligand in **8**, and it is selectively replaced by stronger σ- and π-donors under mild conditions, leaving the geometry of the complex unchanged (i.e., formation of $cis,fac\text{-}RuCl_2(dmso\text{-}S)_3(L)$ complexes). Substitution of two dmso's of **8** usually requires more forcing conditions and can be accompanied by a rearrangement of the $RuCl_2$ fragment from cis to trans. Even though the $cis,cis,cis\text{-}RuCl_2(dmso\text{-}S)_2(L)_2$ isomer is thermodynamically more stable than the *trans,cis,cis* isomer (the *cis,trans,cis* isomer is very rare and found only when L is a very strong π-acceptor ligand), in same cases the kinetic product is isolated as it precipitates before being transformed into the more stable *cis,cis,cis*- isomer. However, it should be emphasyzed that the thermodynamically less stable geometrical isomer of **8**, $trans\text{-}RuCl_2(dmso\text{-}S)_4$ (**9**), under mild reaction conditions, *selectively* replaces two cis dmso-S ligands yielding pure $trans,cis,cis\text{-}RuCl_2(dmso\text{-}S)_2(L)_2$ complexes. Substitution of all four dmso's of **8** leads almost always to species with a trans geometry of the $RuCl_2$ fragment, either $trans\text{-}RuCl_2(L)_4$ or five-coordinate $trans\text{-}RuCl_2(L)_3$ for bulky L ligands. Treatment of **8** (or **9**) with neutral bischelating ligands L−L under mild reaction conditions yields $RuCl_2(dmso\text{-}S)_2(L{-}L)$ complexes, with *cis,cis* isomers normally more stable than *trans,cis* isomers. It should be noted that when these reactions are

performed in the presence of HCl, Ru oxidation by dmso was found to occur with formation of *mer*-$RuCl_3$(dmso-S)(L−L) species. Upon increasing the L−L to **8** ratio and the reaction temperature, both bischelate (*trans*-$RuCl_2(L-L)_2$ or *cis*-$RuCl_2(L-L)_2$, depending on the nature of L−L and reaction conditions) and trischelate $[Ru(L-L)_3]^{2+}$ complexes are selectively prepared. In some cases, replacement of the halides of **8** by the chelating ligands was assisted by the addition of 2 equiv of a soluble Ag salt. The reaction of **8** with bidentate anionic ($X-Y^-$) or easily deprotonated (X-YH) ligands (usually in the presence of a suitable base such as NEt_3) normally leads to the replacement of both dmso and halide ligands, depending on reaction conditions. For example, it is a general route to Ru(II) bis-chelate complexes of the type $Ru(X-Y)_2(dmso)_2$. The reactivity of compounds **8** and **9** toward CO has been also fully investigated (section 2.6) and several Ru−dmso carbonyls were prepared and characterized (up to three dmso's can be replaced). Also in this case, as for the Ru(III) precursor **1**, coordination of CO induces the selective isomerization of the dmso trans to it from S- to O-bonding. Interestingly, *cis,trans,cis*-$RuCl_2$(dmso-S)$_2(CO)_2$ (**28**), featuring the rare *trans*-Ru(dmso-S)$_2$ fragment, is the thermodynamically most stable geometrical isomer among the dicarbonyls. The carbonyl−dmso compounds were found to be good precursors for the preparation of derivatives upon replacement of the sulfoxides with stronger σ- and π-donor ligands. It might be concluded that the success of **8** as a precursor in inorganic synthesis has to be ascribed, besides to its versatile reactivity, to the ease of its preparation (high yield and purity) and handling, and to its good solubility in a wide range of solvents.

The chemistry of osmium−dmso complexes has not been investigated so extensively as that of ruthenium and, to my knowledge, concerns mainly Os(II) (section 3). The kinetic product of the reduction of $H_2[OsCl_6]$ with $SnCl_2$ in dmso is *trans*-$OsCl_2$(dmso-S)$_4$ (**36**), which isomerizes to the thermodynamically more stable isomer *cis,fac*-$OsCl_2$(dmso-S)$_3$(dmso-O) (**38**). However, in solution compound **38** was found to equilibrate with the unprecedented all-S-bonded isomer *cis*-$OsCl_2$(dmso-S)$_4$ (**39**), which is unknown for Ru(II). The case of compounds **38** and **39** represents the only well-documented example in which two pure linkage isomers (in which the S/O isomerization leaves the rest of the complex unchanged) have been fully characterized both spectroscopically and structurally by X-ray. The substitution chemistry of the Os(II)−dmso compounds seems to be similar to that of the corresponding Ru(II) species.

Several rhodium(III)−chloride−dmso complexes of general formula $[RhCl_x(dmso)_{6-x}]^{3-x}$ ($x = 1-4$) have been prepared and characterized (section 4). Accurate NMR studies showed that, in solution of noncoordinating solvents, almost every derivative of this series exists as more than one isomer. The isomers may differ from one another both in the geometry and in the binding modes of the dmso ligands (linkage isomers). In general, dmso can bind to Rh(III) either through the sulfur or through the oxygen atom and the number of O-bonded sulfoxides increases upon increasing the positive charge of the complex. When two dmso-S ligands are bound to Rh(III), the *cis*-Rh(dmso-S)$_2$ fragment was found to be thermodynamically more stable compared to *trans*-Rh(dmso-S)$_2$. On the contrary, this was not the case for the Ru(III) complexes of the same charge, for which only the *trans*-Ru(dmso-S)$_2$ fragment has been observed to date. The reason for this preference of Ru(III) must be electronic rather than steric: while the Ru(III)−dmso-S bond involves also a π backbonding contribution, the Rh(III)−dmso-S bond is essentially σ in character and excludes significant π backbonding.

Finally, the chemistry of Ir(III)−halide−dmso complexes has been less extensively investigated compared to that of the Rh(III) analogues (section 5). It concerns only anionic and neutral derivatives, and there is still uncertainty about the number of isomers and their geometry. To date, the only well-characterized Ir(III)−dmso derivative is [(dmso)$_2$H][*trans*-$IrCl_4$(dmso-S)$_2$] (**51**). Interestingly, several novel Rh(I) and Ir(I)−dmso compounds, such as RhCl(dmso-S)$_3$ (**49**) and [*cis*-Rh(dmso-S)$_2$(dmso-O)$_2$][PF_6] (**50**) (and the corresponding Ir(I) compounds **55** and **56**), have been described recently and their substitution and oxidative addition reactions investigated.

These recent results on Rh(I) and Ir(I), perhaps together with those concerning the Ru-dmso nitrosyls (e.g., first Ru complexes bearing more than three O-bonded dmso's, $[RuCl(dmso-O)_4(NO)]^{2+}$ (**24**), and $[Ru(dmso-O)_5(NO)]^{3+}$ (**25**), section 2.4), clearly show that, despite the huge amount of work done in the past, the chemistry of halo-sulfoxide complexes of Ru, Os, Rh, and Ir is still open to new exciting developments.

9. Abbreviations

H(acac)	acetylacetone
acv	acyclovir
[9]aneS_3	1,4,7-trithiacyclononane
[10]aneS_3	1,4,7-trithiacyclodecane
[11]aneS_3	1,4,7-trithiacycloundecane
[12]aneS_4	1,4,7,10-tetrathiacyclododecane
Haphy	*N*-(aroyl)-*N*′-(picolinylidene)hydrazines
azpy	2-(phenylazo)pyridine
H_2babp	6,6′-bis(benzoylamino)-2,2′-bipyridine
H_2bbpen	*N*,*N*′-bis(2-hydroxybenzyl)-*N*,*N*′-bis(2-methylpyridyl)ethylenediamine
H_2bcmpy	2,6-bis-(*N*-phenylcarbamoyl)pyridine
bdae	$((Ph_2AsCH_2CH_2)_2NCH_2)_2$
BDPBzP	(*R*)−(*R*)-3-benzyl-2,4-bis(diphenylphosphino)-pentane
bdpe	$((Ph_2PCH_2CH_2)_2NCH_2)_2$
bdpx	$((Ph_2PCH_2CH_2)_2NCH_2)_2(o\text{-}C_6H_4)$
BESE	$EtS(O)(CH_2)_2S(O)Et$
bp	2,2′-biphosphinine
bpdz	6,6′-oligoethyleneglycol-3,3′-bipyridazine
2,2′-bpm	2,2′-bipyrimidine
4,4′-bpm	4,4′-bipyrimidine
H-bpmp	2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol
Hbpp	3,5-bis(2-pyridyl)pyrazole
bprbpy	4,4′-bisporphyrin-2,2′-bipyridine
bpsndH	1,3-bis(2-(4-methylpyridyl)imino)isoindoline
bpy	2,2′-bipyridine

4,4′-bpy	4,4′-bipyridine
bpyan	4-[(9-anthrylmethoxy)methyl]-4′-methyl-2,2′-bipyridine
bpyz	2,2′-bipyrazine
btsb	(*S*,*S*)-1,2-bis(p-tolylsulfinyl)benzene
bzimpy	2,6-bis(benzimidazol-2-yl)pyridine
calixP4	cone-5,11,17,23-tetra-*t*Bu-25,26,27,28-tetrakis(diphenylphosphinomethoxy)-calyx[4]arene
6-carboxy-bpy	6-carboxy-2,2′-bipyridine
coe	cyclooctene
cod	cyclooctadiene
cyclam	1,4,8,11-tetraazacyclotetradecane
cyclen	1,4,7,10-tetraazacyclododecane
Cyttp	$PhP(CH_2CH_2CH_2P(C_6H_{11})_2)_2$
daba	$PhCH_2N(CH_2CH_2AsPh_2)_2$
dbbpy	di-*tert*-butylbipyridine
dbpq	6,7-dimethyl-2,3-bis-(2′-pyridyl)-quinoxaline
H_2dcbiq	4,4′-dicarboxy-2,2′-biquinoline
dcbpy	4,4′-dicarboxy-2,2′-bipyridine
H_2dcdhph	5,8-dicarboxy-6,7-dihydro-dibenzo[1,10]-phenanthroline
dcpe	1,2-bis(dicyclohexylphosphino)ethane
dcpm	1,1-bis(dicyclohexylphosphino)methane
ddbbbpy	6,6-bis(*N*-dodecylbenzimidazol-2-yl)-2,2′-bipyridine
ddios	(2*R*,3*R*)-2,3-dihydroxy-1,4-bis(methylsulfinyl)-butane
deas-bpy	4,4′-bis(diethylaminostyryl)-2,2′-bipyridine
depe	1,2-bis(diethylphosphino)ethane
H_5dhpta	2-hydroxytrimethylenedinitrilotetraacetic acid
dios	(2*R*,3*R*)−(−)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(methylsulfinyl)butane
diphos	1,2-bis(diphenylphosphino)ethane
dmbpy	4,4′-dimethyl-2,2′-bipyridine
dmg-H_2	dimethylglyoxime
dmpcym	3,4-dimethylphosphacymantrene
dms	dimethyl sulfide
dmso	dimethyl sulfoxide
dmtp	5,7-dimethyl[1,2,4]triazolo[1,5-a]pyrimidine
dpae	1,2-bis(diphenylarsino)ethane
dpam	1,2-bis(diphenylarsino)methane
dpba	$PhCH_2N(CH_2CH_2PPh_2)_2$
dpcat	1,10-phenanthroline-5,6-ditiolate
dpma	$(Ph_2PCH_2)_2AsPh$
dpo	3,4-di(2-pyridyl)-1,2,5-oxadiazole
dpp	2,9-diphenyl-1,10-phenanthroline
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	1,2-bis(diphenylphosphino)methane
dppz	dipyrido[3,2-*a*:2′,3′-*c*]phenazine
dpsm	bis(diphenylstibino)methane
dpso	diphenylsulfoxide
dpt	3,4-di(2-pyridyl)-1,2,5-thiadiazole
dpttd^{2-}	2,3,11,12-dibenzo-1,4,7,10,13-pentathiatridecane(−2)
1,5-dtco	1,5-dithiacyclooctane
1,5-dtco-O	1,5-dithiacyclooctane 1-oxide
dtne	1,2-bis(1,4,7-triazacyclononan-1-yl)ethane
etbth	1,2-ethanediamide-*N*,*N*′-bis(2-benzenethiolate)(4-)
etp	$PhP(CH_2CH_2PPh_2)_2$
etp*	(*R*)-$Ph_2PCH_2CH(PPh_2)CH_2CH_2PPh_2$
fabz	5-nitro-2-furaldehyde semicarbazone
fedadp	*N*1,*N*2-bis{(*R*)-1-[(*S*)-2-(diphenylphosphino)]-ferrocenylethyl}-*N*1,*N*2-dimethyl-1,2-ethanediamine
HAT	1,4,5,8,9,12-hexaazatriphenylene
Hhf	5-hydroxyflavones
Hhc	2′-hydroxychalcones
$[H_2B(pz)_2]^-$	dihydrobis(1-pyrazolyl)borate
im	imidazole
4-NO_2im	4-nitroimidazole
ma	maltolate
mdmpp	(2,6-dimethoxyphenyl)diphenylphosphine
Me_3Bzm	1,5,6-trimethylbenzimidazole
1Me-im	1-methylimidazole
1,2-Me_2im	1,2-dimethylimidazole
Me_2Pqn	8-(dimethylphosphino)quinoline
4Mepy	4-methylpyridine
Me_3tacn	1,4,7-trimethyl-1,4,7-triazacyclononane
mpso	methylphenylsulfoxide
N_2py	2,6-bis-(*t*-BuNHCH$_2$)$_2$NC$_5$H$_3$
napy	1,8-naphthyridine
OS	oxygen-bonded dmso in charts and schemes (unless otherwise stated in the caption)
OTf	triflate, CF_3SO_3
oxzp	bis(2-oxazolin-2-ylmethyl)phenylphosphine
Pcy_3	tricyclohexylphosphine
Ph_2Asqn	8-(diphenylarsino)quinoline
phen	1,10-phenanthroline
phi	phenanthrenequinone diimine
phospha-cymantrene	η^5-phosphacyclopentadienyl-manganese-tricarbonyl
Ph_2Pqn	8-(diphenylphosphino)quinoline
H_5phpta	2-hydroxy-5-methyl-*m*-phenylenedimethylenedinitrilotetraacetic acid
(*S*)−(*R*)-Pigiphos	(bis{(*S*)-1-(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl}cyclohexylphosphine
P_2cyN_2	*N*,*N*′-bis[*o*-(diphenylphosphino)benzylidene]-cyclohexane-1,2-diamine
$P_2cy(NH)_2$	*N*,*N*′-bis[*o*-(diphenylphosphino)benzyl]cyclohexane-1,2-diamine
$P_2N_2C_2$	*N*,*N*′-bis[*o*-(diphenylphosphino)benzylidene]-ethylenediamine
$P_2N_2C_2$-amide	*N*,*N*′-bis[*o*-(diphenylphosphino)benzamido]-ethane
$P_2N_2C_2H_4$	*N*,*N*′-bis[*o*-(diphenylphosphino)benzyl]ethylenediamine
ppye	1-(diphenylphosphino)-2-(2-pyridyl)-ethane
prnbpy	4-methyl-4′-(2-hydroxyethylpyrenyl)-2,2′-bipyridine
*i*Pr$_3$[12]aneP_3	1,5,9-tris(2-propyl)-1,5,9-triphosphacyclododecane
py	pyridine
pym	pyrimidine
$pyN_2H_2S_2-H_2$	2,6-bis(2-mercaptophenylamino)dimethylpyridine
pyrpy	pyrazolylpyridines
pyS_4^{2-}	2,6-bis(2-mercaptophenylthio)dimethylpyridine(2-)
pytria	4-amino-5-methylthio-3-(2-pyridyl)-1,2,4-triazole
pyz	pyrazine
pyzpy	4-*p*-tolyl-2,6-di(2-pyrazinyl)-pyridine
pzH	pyrazole
pz_2py	2,6-di(1*H*-4,5,6,7-tetrahydrobenzopyrazol-3-yl)pyridine
sq	monosubstituted squarates
SO	sulfur-bonded dmso in charts and schemes (unless otherwise stated in the caption)
tacn	1,4,7-triazacyclononane
TAP	1,4,5,8-tetraazaphenanthrene
terpy	2,2′:6′,2″-terpyridine
tetraphos-1	$Ph_2PCH_2CH_2(PPh)CH_2CH_2(PPh)CH_2CH_2PPh_2$

tetraphos-2	$P(CH_2CH_2PPh_2)_3$
thbpy	6-(2-thienyl)-2,2′-bipyridine
tht	tetrahydrothiophene
Tm	tris(methimazolyl)hydroborate
tmso	tetramethylenesulfoxide
tpa	tris(2-pyridylmethyl)amine
tpam	*N*-methyl-2-thiophenealdimine
tpea	$N(CH_2CH_2PPh_2)_3$
tpen	*N*,*N*,*N*′*N*′-tetrakis(2-pyridylmethyl)ethylenediamine
tpphz	tetrapyrido[3,2-a:2′,3′−c:3″,2″−h:2‴,3‴−j]-phenazine
tppms	triphenylphosphine monosulfonate
tpS_4-H_2	1,2-bis(2-mercaptophenylthio)phenylene
tren	tris(2-aminoethyl)amine
triars	$MeC(CH_2AsPh_2)_3$
triphos	$MeC(CH_2PPh_2)_3$
triphox	$MeC(CH_2OPPh_2)_3$
tt[9]oc	2,5,8-trithia[9]-*o*-cyclophane
ttp	$PhP(CH_2CH_2CH_2PPh_2)_2$
tz	2,7,12,17-tetramethyl-1,6,11,16-tetraazaporphyrinogen
valphos	(*S*)-1-(diphenylphosphinomethyl)-2-methylpropylamine
H_2xdk	*m*-xylenediamine bis(Kemp's triacid imide)

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