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Monoazadienes ruthenium carbonyl chemistry

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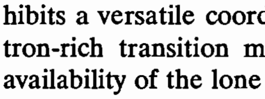
Abstract

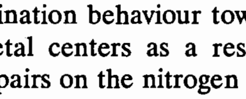
In this paper our recent research in the area of coordination and organometallic chemistry of monoazadienes (MAD) is reviewed. Emphasis is on the coordination of MAD to and activation by low-valent ruthenium carbonyl complexes and the reactivity and interconversions of the resulting oligonuclear azametallacycles.

Introduction

The organometallic chemistry of monoazadienes (MAD, **I**) has been studied in our laboratory since the early 1970s [1]. After some discontinuity in the research on this subject, it has recently gained considerable impetus as a result of a profound study concerning the reactivity of MAD towards triruthenium dodecacarbonyl [2–4].

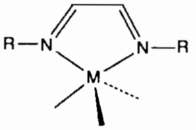


I



II

Our renewed interest in MAD systems stems from the ongoing development of the fascinating chemistry exhibited by transition metal complexes containing diazadienes (R-DAB, **II**) [5–7]. The R-DAB ligand exhibits a versatile coordination behaviour towards electron-rich transition metal centers as a result of the availability of the lone pairs on the nitrogen atoms and of the C=N double bonds for coordination. Apart from the chelating σ-N,σ-N′ (4 electron) mode, which occurs mainly in mononuclear systems, the σ-N,σ-N′,η^2-C=N (6e) and σ-N,σ-N′,η^2-C=N,η^2-C=N′ (8e) modes have been established in di- and oligonuclear systems. A number of these compounds of general structure **IIIa–c** were found to be sensitive towards, for example, C–C, C–N and C–H bond formation reactions [5–11].



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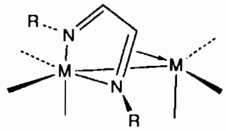

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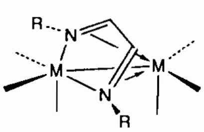

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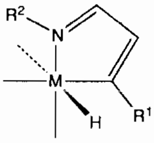

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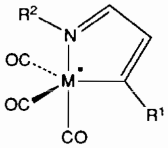

V

It was anticipated that, in analogy to 1,3-dienes, conjugated enones and diimines (R-DAB), the enimines (MAD) should be amenable to the formation of metallacyclic compounds. One could, for instance, imagine as shown in Scheme 1, cyclometallation of a low valent metal carbonyl fragment with MAD, leading to a hydrido-metallacycle **IV**. Such a compound may subsequently lose its hydrogen atom relatively easily, e.g. in a binuclear elimination reaction, thereby giving rise to dimeric species. In this way, new compounds containing one or more azametallacycles **V** should in principle be accessible.

Azametallacyclic compounds

Five-membered metallacyclic systems containing one nitrogen atom which is adjacent to the metal have been obtained by several methods, e.g. (see Scheme 2), cyclometalation by Ir(I) [1], condensation of an amine with a cycloplatinated enone [12], intramolecular coupling between a tantalum–η^2-acetimidoyl moiety and an alkyne [13] and hydrolysis of a molybdenum–σ-tricyanoethene complex [14]. Addition of a metal hydride to an ynimine or an α-iminoallene would be a potential method as well, but has hitherto not been reported.

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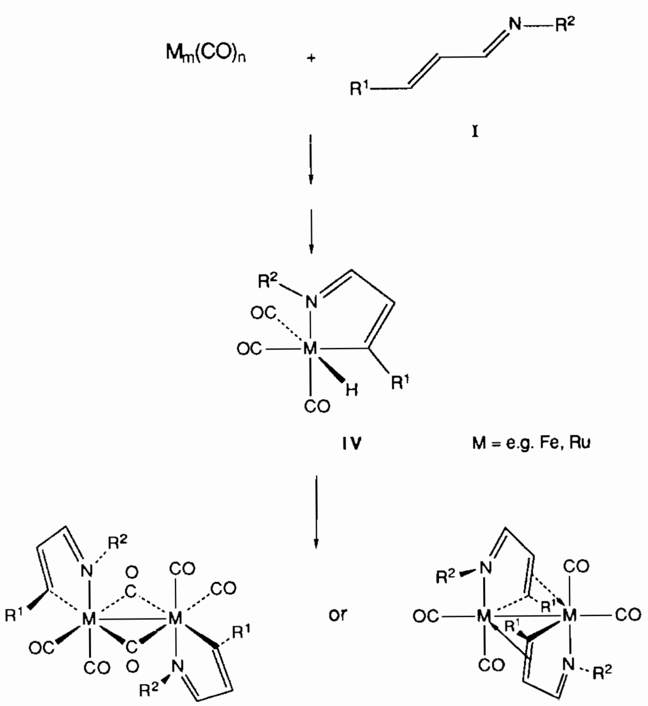
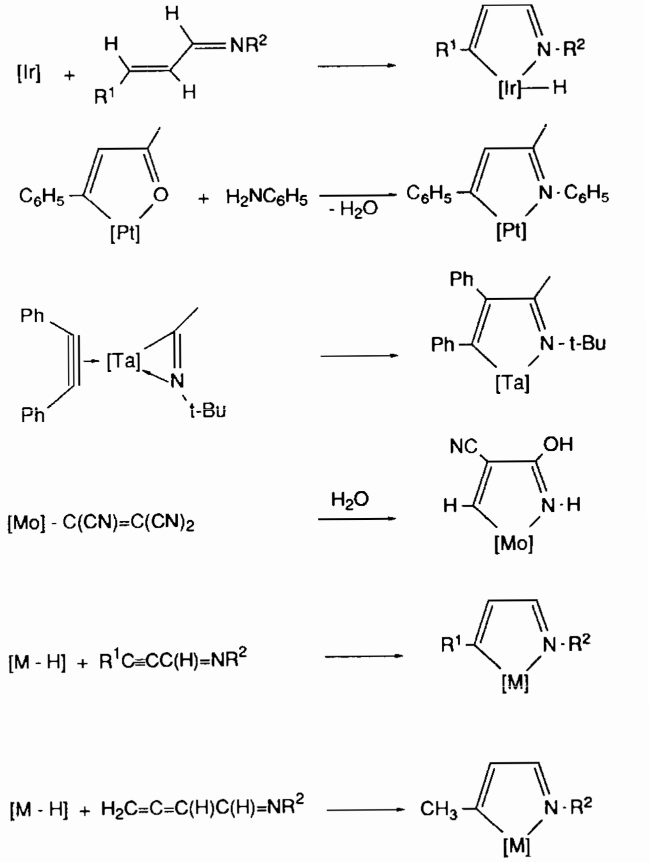


Scheme 1. Cyclometallation of MAD followed by binuclear elimination giving new dinuclear complexes.

The azametallacycle **V** and a number of analogues in Scheme 2 can be interpreted as pseudo-cyclopentadienyl systems by invoking isolobal relationships, e.g. $Ru(CO)_3 \leftarrow\!\!\sigma\!\!\rightarrow CH^+$ and $NR \leftarrow\!\!\sigma\!\!\rightarrow CH^-$, see Fig. 1. These heterametallacyclopentadienyl units **V** can in principle become coordinated to, say, a $Ru(CO)_2X$ unit, or two of these can be coordinated to a single Ru atom or to a $Ru_2(CO)_4$ core. In analogy, the pseudo-metallacyclopentadiene $HRu(CO)_3$(MAD-yl) (**IV**, see Scheme 1) could be coordinated to, for example, a $Ru(CO)_2$ fragment. By regarding the metallacyclic complexes arising from MAD in this way, a plethora of new organometallic compounds with interesting properties lay ahead.



Scheme 2. Selected synthetic methods leading to azametallacyclopentadienes.

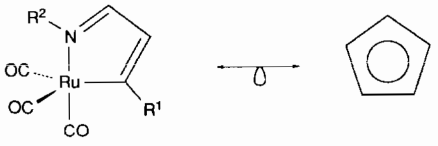


Fig. 1. $Ru(CO)_3$(MAD-yl) is isolobal with c-C_5H_5.

Coordination compounds of MAD

The coordination chemistry of monoazadienes has been documented [15]. The isolation and characterization of a number of different complexes over the last few decades has led to the definition of several types of coordination complexes involving MAD. A selection of the structural types, most of which have been authenticated by means of X-ray crystallography, is shown in Fig. 2.

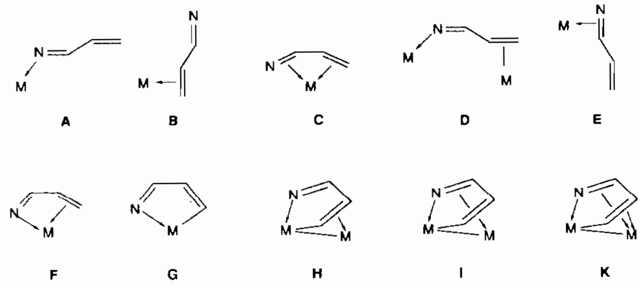
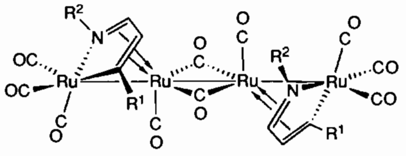


Fig. 2. Possible geometries of metal–MAD complexes.

Examples include the (2e) σ-N coordination mode (**A**) in $Fe(CO)_4$(MAD) [16] and $CuCl(MAD)_2$ [17], the (2e) η^2-C=C coordination (**B**) in $Ni(PPh_3)_2$(MAD) [17, 18] and the (4e) η^2-C=N,η^2-C=C bonding mode (**C**) in $Fe(CO)_3$(MAD) [19, 20], $Mo(CO)_2(PBu_3)_2$(MAD) [17] and $Ru(CO)_2(PPh_3)$(MAD) [21] as well as the (4e) σ-N,η^2-C=C bridging mode (**D**) in $[Ni(PPh_3)(MAD)]_2$ [17, 22]. More examples of 2e- and 4e-coordinated MAD and 3e MAD-yl (**G**) have been established by spectroscopic studies [1, 23–25], but other coordination modes, e.g. (2e) η^2-C=N (**E**), (4e) σ-N,η^2-C=C (**F**) or dinuclear complexes where MAD is (5e) σ-N,σ-C,η^2-C=C, (5e) σ-N,σ-C,η^2-C=N or (7e) σ-N,σ-C,η^2-C=N,η^2-C=C coordinated (**H**, **I**, **K**) were not known when we started our investigations.

It was reasoned that formation of complexes in which the MAD is present in such coordination modes should be feasible using coordinatively unsaturated, low-valent transition metal fragments like $Ru(CO)_4$, which can be easily obtained by thermal activation of $Ru_3(CO)_{12}$. These were expected to give rise to cyclometallation (see above) and, in view of the presence of reactive ruthenium fragments, metallacycles like **G** (see Fig. 2) can easily be formed. Indeed, the fortuitous and straightforward preparation of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-i-Pr}]_2$ (**1**) marked the entering of a new area in heterodiene chemistry, in which the very flexible adaptation of the MAD ligand in coordination complexes was going to be exploited. In the novel tetranuclear compound **1**, two monoazadienyl (MAD-yl) ligands are (7e) σ-N,σ-C,η^2-C=N,η^2-C=C coordinated to two ruthenium(I) centers each [2]. Much of the MAD chemistry we have been involved in over the last few years has originated from this linear tetranuclear 66e complex **1**. We will discuss several features of this eye-catching compound later on.



1

Synthesis and properties of MAD

Monoazadienes **I** can be readily prepared from an α,β-unsaturated aldehyde or ketone by condensation with an amine and in the case of unsaturated ketones in the presence of a catalyst such as zinc chloride or 4 Å molecular sieves [26–29]. Generally, these conjugated imines are moderately stable towards hydrolysis in water, but are rapidly hydrolyzed in acidic or basic media. Pure liquid monoazadienes should be kept at low temperatures, preferably −80 °C, in order to prevent polymerization.

Semi-empirical MNDO MO calculations have revealed that the *E-syn-trans-E* conformation of $CH_3C{=}C(H)C(H){=}NH$ is favoured over the *E-syn-cis-E* conformation by only 5 kJ mol^{-1} [30]. Therefore, interconversion between these two forms in σ-N coordination complexes, e.g. $Ru(CO)_4[R^1C{=}C(H)C(H){=}NR^2]$, will readily take place at ambient temperature in solution. One might, therefore, expect activation of both the H_α and H_β atoms in $R^1C(H_\beta){=}C(H_\alpha)C(H_{im}){=}NR^2$ to be feasible, see Fig. 3.

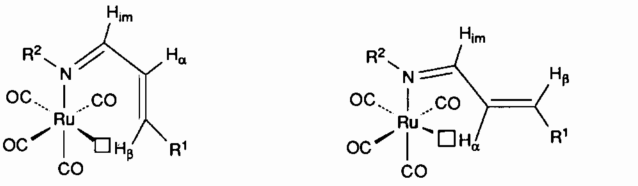


Fig. 3. Activation of the C–H_β or C–H_α bond of MAD by a coordinatively unsaturated Ru fragment.

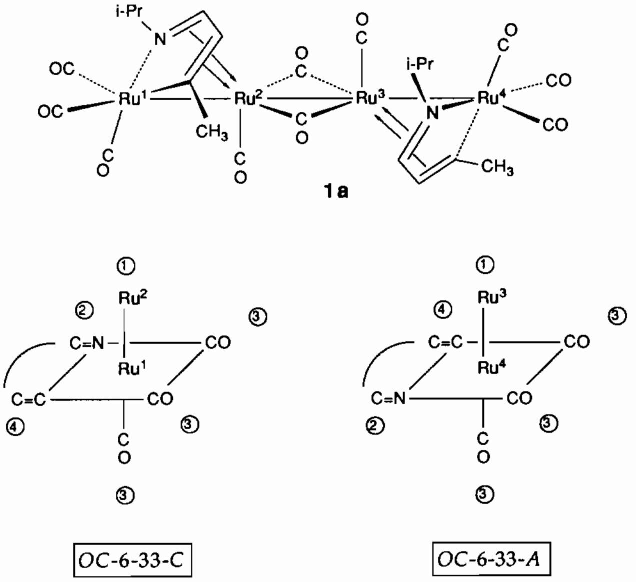


Fig. 4. The structure of *trans*-(CA)-$Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-i-Pr}]_2$ (**1a**) and chirality descriptors for Ru(1) and Ru(4).

Nomenclature and stereochemistry

The abbreviation MAD is used as an acronyme for monoazadienes in general and we will use R^1, R^2-MAD* when *N*-alkyl-(*E*)-crotonaldimines $CH_3C(H){=}C(H)C(H){=}NR^2$ or *N*-alkyl-(*E*)-cinnamaldimines $C_6H_5C(H){=}C(H)C(H){=}NR^2$ are meant. Suffixes to the atoms refer to $R^1C(H_\beta){=}C(H_\alpha)C(H_{im}){=}NR^2$. The metallated ligands are formally monoazadienyl anions $R^1C^-{=}C(H)C(H){=}NR^2$ or $R^1C(H){=}C^-C(H){=}NR^2$, which are abbreviated MAD-yl or R^1, R^2-MAD-yl.

The absolute configuration of chiral metal centers has been denoted by following the Brown–Cook–Sloan modification [4, 31, 32] of the CIP rules. In most cases, we deal with enantiomers and diastereomers of the OC-6-33 system; so OC-6-33-C, OC-6-33-A, and combinations thereof (see Fig. 4). In order to maintain a transparent way of describing the stereochemistry of the various systems, we only specify the chirality descriptors C and A. In many cases, the chirality of a given metal center is not independent of the chirality of another. For instance, in **1** the chirality of Ru(2)

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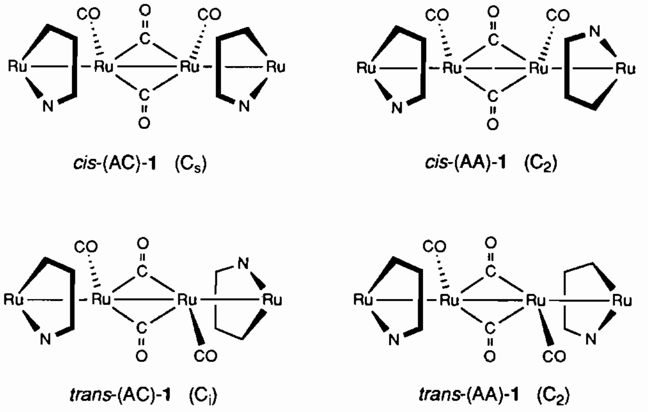
*In this paper, the following combinations of R^1, R^2 have been used: **a**: CH_3, i-Pr; **b**: CH_3, c-Hex; **c**: CH_3, t-Bu; **d**: C_6H_5, i-Pr, **e**: C_6H_5, t-Bu.



cis-(AC)-1 (C_s) *cis*-(AA)-1 (C_2)

trans-(AC)-1 (C_i) *trans*-(AA)-1 (C_2)

Fig. 5. Configurations of $Ru_4(CO)_{10}(MAD\text{-}yl)_2$ (1); symmetry in parentheses.

depends on that of Ru(1) and Ru(3), whereas that of Ru(3) depends on that of Ru(2) and Ru(4). As the chirality of Ru(2) and Ru(3) provides little insight into the overall geometry (at first sight), we prefer to denote the relative geometric stereochemistry involving Ru(2) and Ru(3) by using the *cis/trans* terminology, which can be readily evaluated from the mutual disposition of the terminal CO ligands on Ru(2) and Ru(3). Only the absolute configuration of Ru(1) and Ru(4) will be given, e.g. *cis*-(CC)-**1** for one of the stereoisomers with C_2 symmetry and *cis*-(CA)-**1** for one of C_s symmetry. As these are always accompanied by their enantiomeric counterpart, we write *cis*-(CC/AA)-**1** for the chiral and *cis*-(CA/AC)-**1** for the achiral $Ru_4(CO)_{10}[MAD\text{-}yl]_2$ molecules. As there are in total four diastereomeric pairs of enantiomers, also *trans*-(CC/AA)-**1** and *trans*-(CA/AC)-**1** exist (see Fig. 5).

NMR spectroscopy

It has been demonstrated that ^1H and ^{13}C NMR spectroscopy are valuable diagnostic tools to determine the coordination mode of MAD-yl ligands in metal carbonyl complexes. In general, the various coordination modes can clearly be distinguished. In Table 1 the NMR chemical shift ranges for MAD and for 3, 5 and 7e donating MAD-yl ligands, as found in $CDCl_3$ or CD_2Cl_2 solution, are given.

The $Ru_3(CO)_{12}$/MAD reaction sequence

It has been found that reactions of $Ru_3(CO)_{12}$ with R^1, R^2-MAD give rise to a complex reaction sequence and it took us several years before the various pieces of the MAD ruthenium carbonyl puzzle fell together and the overall Scheme 3 could be drawn. As we can see now, the sequence involves cyclometallation of MAD and the formation and intermediacy of a variety of ruthenium carbonyl complexes containing an isomerized or dehydrogenated MAD ligand. We have been able to influence the course of the reaction by selectively activating various C–H bonds of MAD, e.g. by adapting the reaction conditions or changing the R^1 and R^2 groups. Also the way individual compounds in the reaction sequence are activated (i.e. thermally or photochemically) has consequences for the course of the reaction. In retrospect, MAD could be transformed into a number of different nitrogen containing ligand types, all of which stabilize metal–metal bonds by adopting a bridging coordination mode.

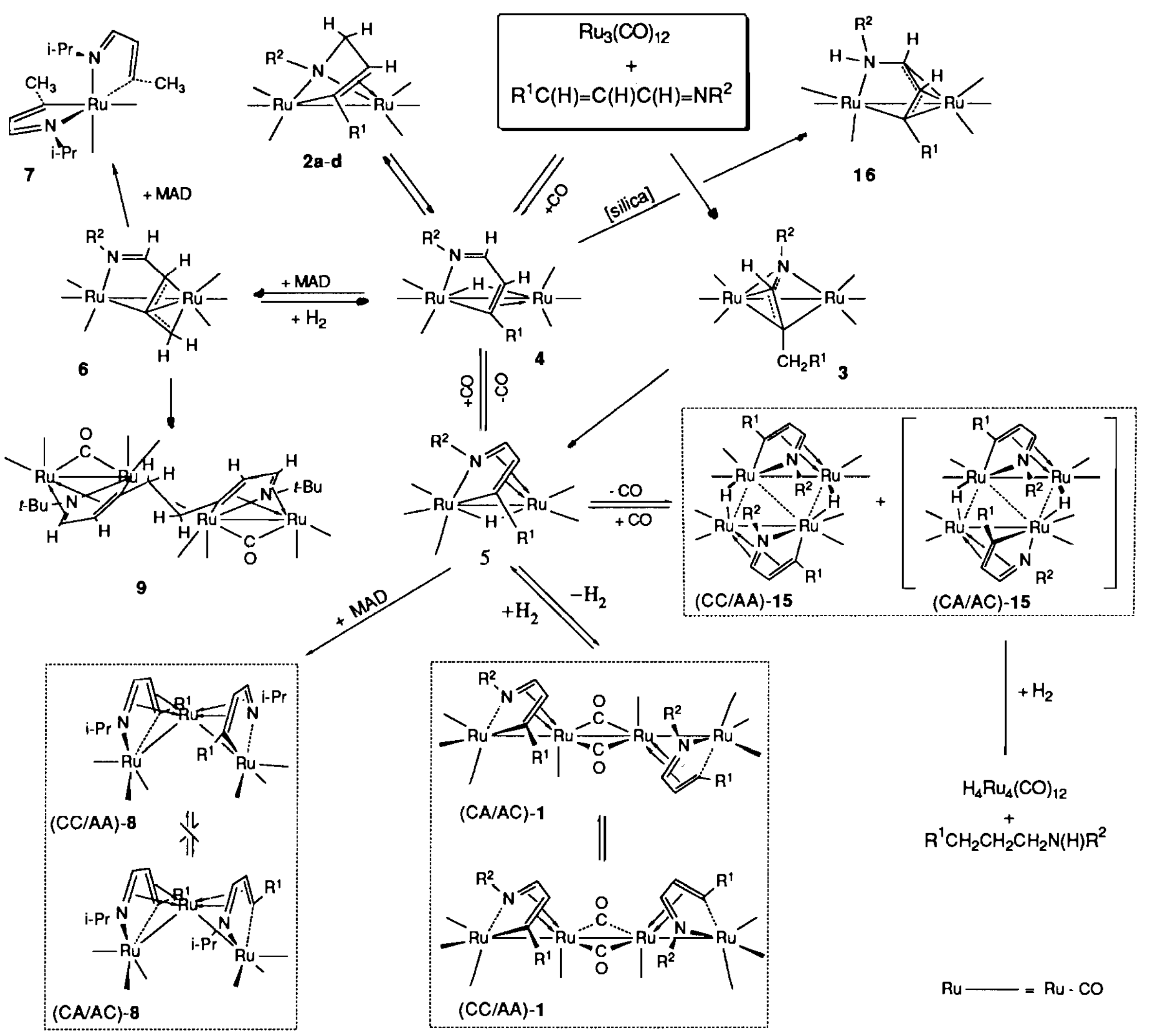
Historically, the first compound isolated was $Ru_4(CO)_{10}[R^1C{=}C(H)C(H){=}NR^2]_2$ (**1**), a fascinating linear 66-electron tetranuclear cluster that contains two β-metallated MAD-yl ligands, each present in the bridging 7e coordination mode. This cluster was obtained in good to excellent yields by refluxing $Ru_3(CO)_{12}$ and R^1, R^2-MAD in heptane solution for one day [2]. As compound **1** contains two azaruthenacyclopentadienyl rings, each of which is isolobally related to a cyclopentadienyl ligand (*vide supra*), that are η^5-coordinated to a central $Ru_2(CO)_4$ unit, it is an isolobal analogue of $[CpRu(CO)_2]_2$.

Besides **1** varying amounts of a number of mono-, di-, tri- and tetranuclear organometallic complexes were isolated after refluxing $Ru_3(CO)_{12}$ and MAD in heptane solution. In order to obtain a better insight into the factors controlling the formation of the various complexes and into the reaction sequences via which **1** and other complexes are formed, the course of the product

TABLE 1. Relevant ^1H and ^{13}C NMR chemical shifts for R^1, R^2-MAD and cyclometalated MAD-yl ligands in various coordination modes[a]

	H_{im}	H_α	H_β	H_γ[b]	C_{im}	C_α	C_β
MAD	7.6–8.1	5.9–6.9	5.9–6.9	1.6–1.8	*c.* 160	*c.* 140	130–137
3e MAD-yl	7.7–8.0	6.2–6.6		1.9–2.8	160–175	125–130	210–225
5e MAD-yl[c]	7.8–8.0	2.8–3.5		*c.* 3.2	170–180	45–70	150–200
7e MAD-yl	6.2–7.5	5.0–5.7		2.0–2.8	95–130	90–105	150–200

[a] δ Values in $CDCl_3$ or CD_2Cl_2 in ppm relative to $Si(CH_3)_4$. [b] For $R^1{=}CH_3$. [c] For σ-N,σ-C,η^2-C=C coordination (see Fig. 2, **H**).



Scheme 3. Selected reactions in the system $Ru_3(CO)_{12}/R^1$, R^2-MAD: R^1, $R^2 = CH_3$, i-Pr (**a**); CH_3, c-Hex (**b**); CH_3, t-Bu (**c**); C_6H_5, i-Pr (**d**); C_6H_5, t-Bu (**e**).

formation and the reactivity of several complexes was investigated.

The first two isolable complexes during reactions of $Ru_3(CO)_{12}$ with R^1,R^2-MAD are $Ru_2(CO)_6[R^1C{=}(H)CCH_2NR^2]$ (**2**) and $Ru_2(CO)_6[R^1CH_2CC(H)NR^2]$ (**3**) [33]. Both products contain an isomerized MAD ligand that is part of a five-membered (**2**) or four-membered (**3**) azaruthenacycle. Compound **2**, which is not formed for $R^2 = $ t-Bu, contains a β-metallated, formally dianionic enylamido ligand in which the initially abstracted H_β atom has been transferred to the C_{im} atom. Compound **3** contains an α-metallated, formally dianionic azaallyl ligand with the initially abstracted H_α atom being transferred to the C_β atom [3]. In solution both **2** and **3** are fluxional due to 'windshield wiper' motions of the asymmetrically bridging amido ligands. This process is more facile for **3** ($\Delta G \cong 35$ kJ mol^{-1}) than for **2** ($\Delta G \cong 62$ kJ mol^{-1}) [33].

Furthermore, as depicted in Scheme 3, formation of **2** takes place via the dinuclear hydride $HRu_2(CO)_6[R^1C{=}C(H)C(H){=}NR^2]$ (**4**), which contains a 5e donating σ-N,σ-C,η^2-C=C coordinated MAD-yl ligand. Although compound **4** is too reactive to be observed during thermal reactions of $Ru_3(CO)_{12}$ with MAD, it could be synthesized via an alternative reaction pathway (*vide infra*) and was found to isomerize thermally into **2**. In refluxing heptane compound **2** is smoothly converted into the linear tetraruthenium compound **1** in remarkably high yields (>80%). This conversion proceeds via the intermediacy of $HRu_2(CO)_5[R^1C{=}C(H)C(H){=}NR^2]$ (**5**), an air-sensitive and thermally labile compound, which could only be observed and isolated for $R^1 = C_6H_5$, $R^2 = $ i-Pr (**5d**). For other combinations of R groups this compound is too reactive to be observed during the thermally induced conversion of **2** into **1**. Compound **5** could be synthesized for other R groups as well via an alternative reaction path, i.e. by hydrogenation of **1** at 40 °C. The X-ray crystal structure of **5d** revealed the presence of an asymmetrically bridging hydride and confirmed the spectroscopically identified 7e coordination mode of the MAD-yl ligand [34].

Just as **1** is isolobally related to $[CpRu(CO)_2]_2$, compound **2** can be described as an isolobal analogue of $(\eta^4\text{-}C_4H_6)Ru(CO)_3$ and **5** is isolobally related to $CpRu(CO)_2H$. Clearly, all intermediates find an isolobal counterpart in the well-established formation pathway of $[CpRu(CO)_2]_2$ and hence the formation pathways of **1** and $[CpRu(CO)_2]_2$ are isolobally related (Scheme 4).

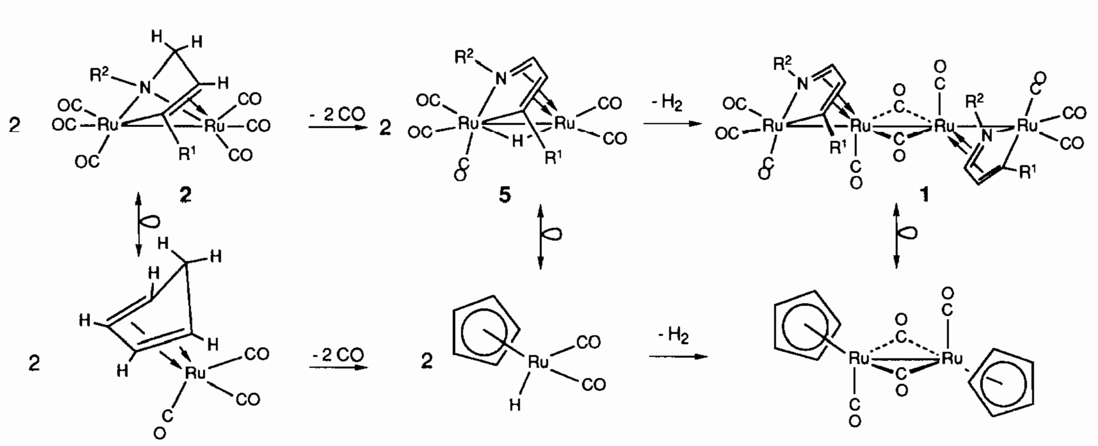
If MAD or crotonaldehyde is present during thermolysis of **2** ($R^1 = CH_3$), another reaction becomes kinetically favored whereby $Ru_2(CO)_6[CH_2CC(H)C(H)=NR^2]$ (**6**) is formed instead of **1** [33]. During this conversion the coordinated enylamido ligand in **2** is dehydrogenated, whereas the added substrate acts as a hydrogen acceptor. For crotonaldehyde it was shown that the alkene moiety is hydrogenated chemoselectively. The X-ray crystal structure of **6c** ($R^2 = \text{t-Bu}$) showed the presence of a 6e donating $\sigma\text{-N},\mu^2\text{-}\eta^3$-coordinated allylimine ligand which contains a distorted η^3-allyl fragment bridging the two $Ru(CO)_3$ units [3].

In the presence of an excess of MAD compound **6a** reacts further to give ultimately the pale yellow compound $Ru(CO)_2[CH_3C=C(H)C(H)=N\text{-i-Pr}]_2$ (**7**), which structure has been determined on the basis of its IR, FD-mass, ^1H and ^{13}C NMR spectroscopic data [35]. This compound could be isolated only for R^1, $R^2 = CH_3$, i-Pr. For R^1, $R^2 = CH_3$, t-Bu and C_6H_5, i-Pr such a compound could not be obtained, which has been ascribed to steric restrictions (R^1, $R^2 = CH_3$, t-Bu) and the lack of H_γ protons (R^1, $R^2 = C_6H_5$, i-Pr), precluding the formation of its precursor, a compound like **6**.

In the case where R^1, $R^2 = C_6H_5$, i-Pr thermolysis of **2** at 90 °C in the presence of an excess of MAD gave the 50e trinuclear cluster $Ru_3(CO)_6[C_6H_5C=C(H)\text{-}C(H)=N\text{-i-Pr}]_2$ (**8**), as the main product [36, 37]. IR spectroscopy revealed the intermediacy of dinuclear **5** during formation of **8**. For R^1, $R^2 = CH_3$, i-Pr compound **8** could only be obtained at a high reaction temperature of 120 °C in moderate yield due to the competitive reaction to **6**. This compound could not be obtained for $R^2 = \text{t-Bu}$, probably because the hypothetical compounds **8c** and **8e** would suffer from severe internal interligand interactions as a result of the presence of the bulky t-Bu substituents. Compound **8** contains two 7e donating MAD-yl ligands and is isolobally related to Cp_2Ru. It is obtained as a mixture of two diastereomers, (CC/AA)-**8** and (CA/AC)-**8**, which are formed in approximately equal amounts. The two diastereomers of **8** have been separated for R^1, $R^2 = CH_3$, i-Pr (**8a**) by preparative HPLC on a reversed phase column and the X-ray crystal structures of both diastereomers have been determined (see Fig. 6).

Both diastereomers of compound **8a** consist of two $Ru(CO)_3$(MAD-yl) units, which are η^5-coordinated to a central ruthenium atom. The difference between the two diastereomers can readily be inferred from the different mutual dispositions of the two N-i-Pr groups, at the same side of the metal chain in (CA/AC)-**8a** and at opposite sides in (CC/AA)-**8a**. Both electron precise 50e diastereomers contain two single Ru–Ru bonds of about 2.70 Å, while there is no bonding interaction between the two outer ruthenium centers; Ru(1)–Ru(1′) amounts to 3.8539(18) Å in (CC/AA)-**8a** and the distance between Ru(1) and Ru(3) in (CA/AC)-**8a** is 4.0136(5) Å.

The N-i-Pr moieties in both diastereomers are twisted somewhat in order to minimize intramolecular interligand interactions. A NOESY experiment revealed that the mutual orientation of the azaruthenacyclopentadienyl rings in the solid state is maintained in solution, i.e. if any, only little rotation of one metallacycle with respect to the other takes place in solution.



Scheme 4. Some isolobal relations.

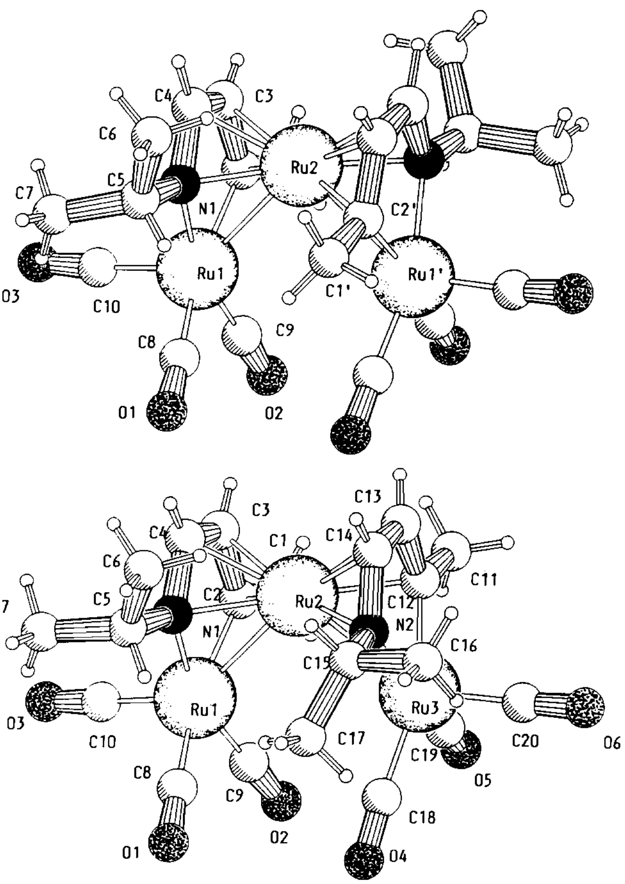


Fig. 6. X-ray molecular structures of (AA)-**8a** (top) and (AC)-**8a** (bottom).

Compound **8** represents the first 50e acyclic cluster which contains a bent geometry that is not stabilized by one or more ligands bridging the outer two metal centers. The unique cluster geometry of **8** is possible due to the lack of steric interactions between the ligand spheres on the outer ruthenium centers, which usually preclude a bent geometry. Apparently, the bent conformation of the metal core in **8** is electronically favored over the linear one. This conjecture could be corroborated by DV-X_α calculations for (CC/AA)-**8a** which revealed that the bent geometry of the cluster core is slightly favored over the linear one [38].

So far, we have dealt with a number of metal mediated transformations of MAD into a variety of isomerized or dehydrogenated ligands. In one case we encountered a very selective C–C coupling of two ligands taking place on the metal core. Thermolysis of dinuclear $Ru_2(CO)_6[CH_2CC(H)C(H)=N\text{-t-Bu}]$ (**6c**), which contains a 6e donating σ-N,σ-C,η^3-bonded allylimine ligand, in refluxing n-octane yielded the new acyclic tetranuclear cluster $Ru_4(CO)_{10}[(CH_2C=C(H)C(H)=N\text{-t-Bu})_2]$ (**9**; see Fig. 7) [39]. This electron precise 66e cluster contains a 1,10-di-tert-butyl-1,10-diazadeca-1,3,7,9-tetraene ligand, which is formed by completely regio- and diastereoselective coupling of the two η^3-allylimine fragments. The diastereospecific formation of only one of the two possible diastereomers of **9** is the result of chiral recognition between two homochiral molecules of $Ru_2(CO)_n[CH_2CC(H)C(H)=N\text{-t-Bu}]$ ($n=5,6$) during cluster assemblage.

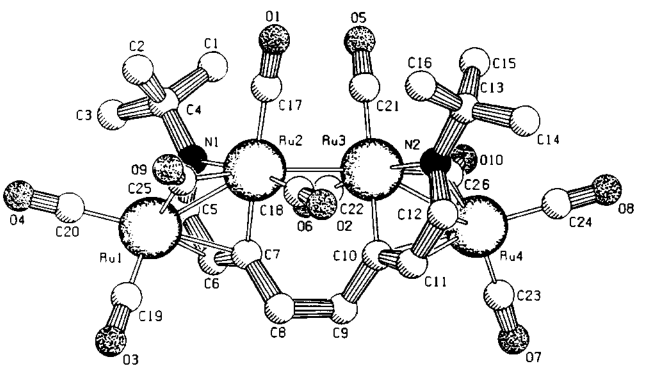


Fig. 7. X-ray molecular structure of $Ru_4(CO)_{10}[(CH_2C=C(H)C(H)=N\text{-t-Bu})_2]$ (**9**).

The π-systems of the 7e donating MAD-yl subunits in **9** are bonded to the outer ruthenium centers, whereas in **1** the π-systems of the MAD-yl ligands are bonded to the inner ruthenium centers. Despite the presence of a bridging CO ligand over the MAD-yl bridged Ru–Ru bond in **9**, the Ru–Ru bond lengths in **1** and **9** differ only little; the Ru(1)–Ru(2) in **1** amounts to 2.71 Å (mean) and in **9** to 2.69 Å (mean). The intermetallic angles in **9** deviate considerably from linearity, i.e. the Ru(1)–Ru(2)–Ru(3) and Ru(2)–Ru(3)–Ru(4) angles amount to 137.38(2) and 138.68(2)°, respectively. This is probably caused by the reduced conformational freedom of the tetraruthenium moiety due to coupling of the carbon fragments at C(8)–C(9) in the ligand. In contrast to the hemilable 7e MAD-yl ligands in **1** (*vide infra*) the π-systems of the MAD-yl subunits in **9** are not readily substituted by CO. This is probably the result of the rigidity of the octadentate ligand, caused by its snake-like winding around the metal frame. Interestingly, the color of compound **9** changes upon solidification. In solution **9** is deep purple, whereas shining hazel brown crystals are obtained in the solid state. Thus far, we have no straightforward explanation for this intriguing phenomenon, but we note that the ^1H and $^{13}C\{^1H\}$ NMR data for **9** in $CDCl_3$ solution are consistent with the molecular structure in the solid state.

Properties and reactivity of the linear tetranuclear cluster $Ru_4(CO)_{10}[CH_3C=C(H)C(H)=N\text{-i-Pr}]_2$ (1a)

Structural aspects and dynamic behaviour

The linear tetranuclear 66e clusters $Ru_4(CO)_{10}[R^1C=C(H)C(H)=NR^2]_2$ (**1**) are formed as mixtures of two diastereomers, (CA/AC)-**1** and (CC/AA)-**1**, due to the presence of two chiral azaruthenacycles in these complexes (*vide supra*). Approximately equal amounts of both diastereomers were obtained for R^1, $R^2=CH_3$, i-Pr; CH_3, c-Hex; CH_3, t-Bu. For R^1, $R^2=C_6H_5$, i-Pr, however, the ratio of (CA/AC) and (CC/AA) diastereomers was 3, whereas only one diastereomer has been isolated for R^1, $R^2=C_6H_5$, t-Bu [33]. The formation of unequal amounts of diastereomers for R^1, $R^2=C_6H_5$, i-Pr and C_6H_5, t-Bu has been rationalized on the basis of thermally induced interconversions between diastereomers of **1** and differences in solubility.

The two diastereomers of $Ru_4(CO)_{10}[CH_3C{=}C(H)\text{-}C(H){=}N\text{-i-Pr}]_2$ (**1a**) have been separated by preparative HPLC on a silica column (Fig. 8), thus enabling us to study their individual properties [40]. Just as their isolobal analogues $[CpM(CO)_2]_2$ (M = Fe, Ru), both diastereomers of **1a** can exist in a *cis* and a *trans* form (Fig. 5). For each of the two diastereomers both forms have been observed in the solid state (IR) and in solution (IR, NMR). As expected, in analogy with $[CpM(CO)_2]_2$, the *cis* isomers are favored in more polar solvents [40].

Both diastereomers of **1a** undergo facile *cis*/*trans* isomerization in solution at 20 °C, which can be brought about by concerted pairwise opening of the CO bridges giving a non-bridged intermediate, rotation about the central metal–metal bond and reclosing of the CO bridges (see Scheme 5).

At low temperature (−90 °C) in CD_2Cl_2 solution, these processes are slow on the NMR time scale and the presence of both the *cis* and *trans* form could be established for each of the diastereomers of **1a**. The value for the free enthalpy of activation, $\Delta G^{\neq}$, of the *cis*/*trans* isomerization for the two diastereomers of **1a** differ slightly, $\Delta G^{\neq}$ (CA/AC)-**1a** = 38 kJ mol^{-1} and $\Delta G^{\neq}$ (CC/AA)-**1a** = 42 kJ mol^{-1}. Interestingly, the CO ligands in the central unit of *trans*-(CA/AC)-**1a** are in the intermediate exchange at −90 °C (125.8 MHz), whereas those in the other forms of **1a** are in the slow exchange. The difference in kinetic barriers for bridge/terminal CO exchange in the two *trans* forms has been rationalized by invoking their diastereomeric relationship [40].

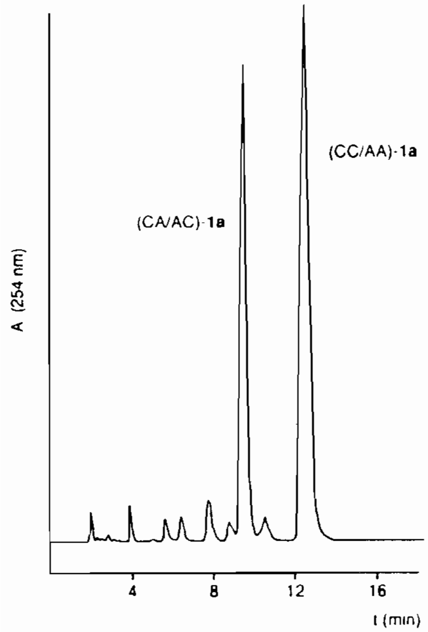


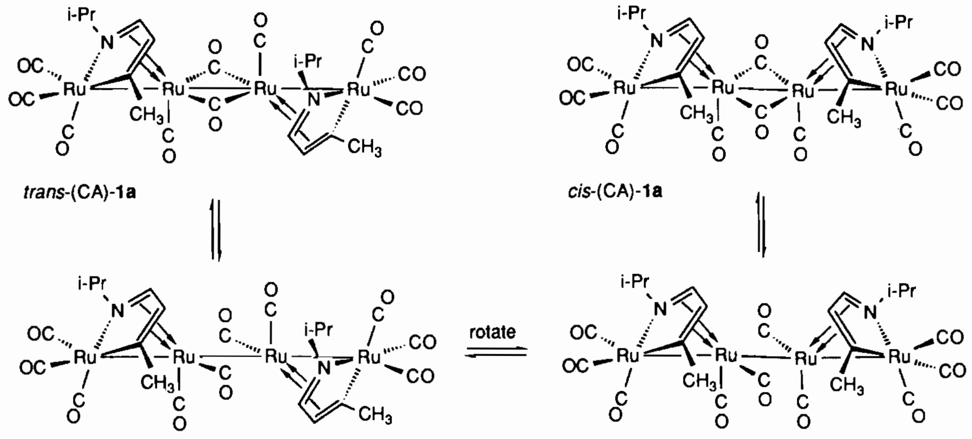
Fig. 8. HPLC elution profile of a mixture of (CA/AC)-**1a** and (CC/AA)-**1a**.

The X-ray structures of *trans*-(CA/AC)-**1a** and *cis*-(CC/AA)-**1a** have been determined, and are depicted in Fig. 9. [2, 40]. Both molecules contain three single metal–metal bonds, with the inner intermetallic distances of about 2.77 Å being somewhat longer compared to the outer intermetallic distances which are about 2.71 Å. The MAD-yl ligands are bonded in the bridging 7e mode. Both molecules contain a compensating set of bridging CO ligands, which keep the two central ruthenium atoms electronically equivalent. The asymmetry of the CO bridges has been explained by considering the difference in π-accepting properties of η^2-C=C and η^2-C=N units. A noticeable difference between the crystal structures of both molecules are the dihedral angles between the two planes defined by the inner Ru atoms and the two bridging C atoms of the CO ligands. In *trans*-(CA/AC)-**1a** this angle amounts to 180°, whereas in *cis*-(CC/AA)-**1a** this angle is 166°. A similar difference has been observed for *trans*- and *cis*-$[CpFe(CO)_2]_2$ [41, 42].

Two different modes for diastereomer interconversion have been assessed. The thermally induced interconversion occurs in solution at temperatures exceeding 70 °C, whereas CO induces rapid interconversion at room temperature [40]. Labelling experiments showed that both processes occur via different mechanisms. The thermally induced diastereomer interconversion takes place intermolecularly, presumably via the intermediacy of dinuclear radicals, whereas the CO-induced interconversion proceeds intramolecularly, probably via formation of the intermediate CO adduct $Ru_4(CO)_{11}[CH_3C{=}C(H)C(H){=}N\text{-i-Pr}]_2$ (**10a**), followed by a Ray and Dutt twist involving the η^3-coordinated MAD-yl ligand in this intermediate.

Reactions with CO

Part of the reactivity of **1** emerges from the hemilability of its 7e donating MAD-yl ligands. Particularly illustrative in this respect are the different reactions of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-i-Pr}]_2$ (**1**) with CO under various conditions. Compound **1a** stepwise and reversibly adds four equivalents of CO to give ultimately



Scheme 5. Interconversion of diastereomers of **1a** by bridge-opening and rotation about the central Ru–Ru bond.

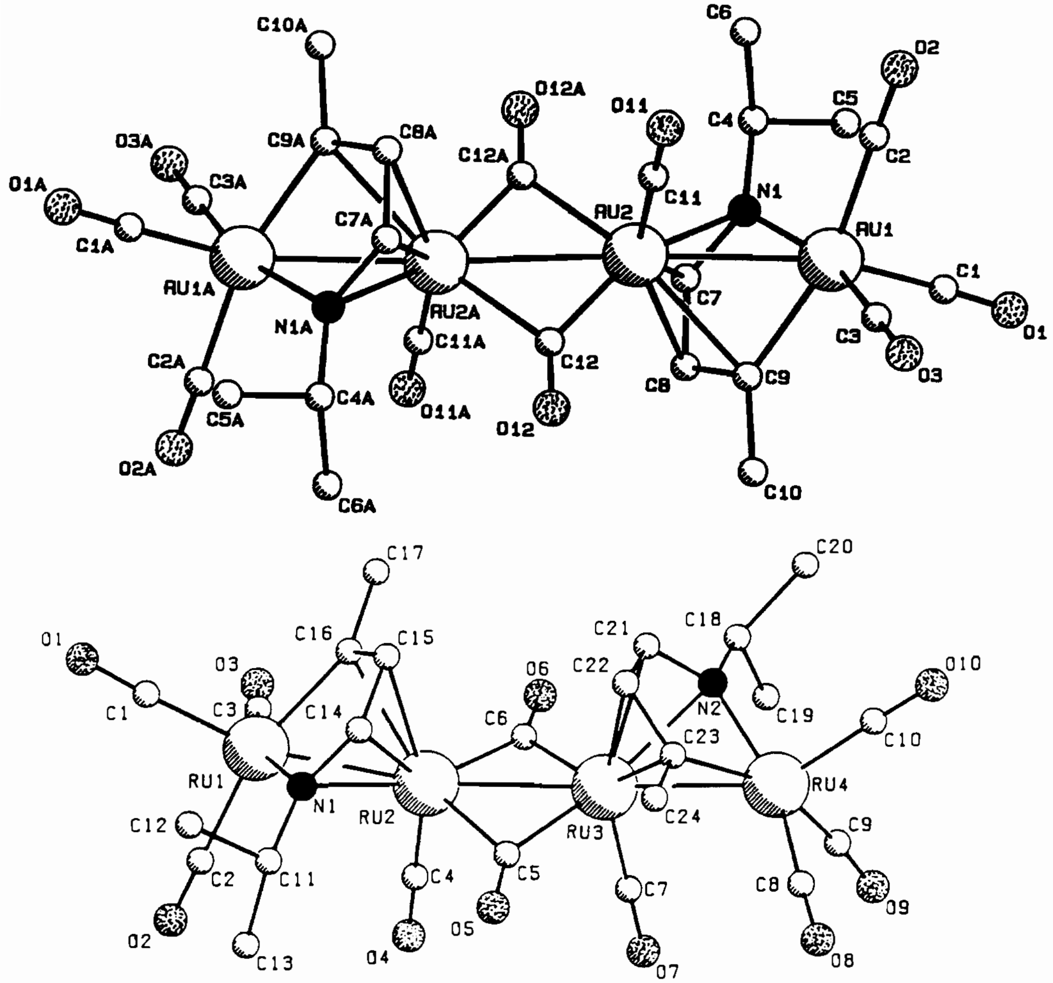
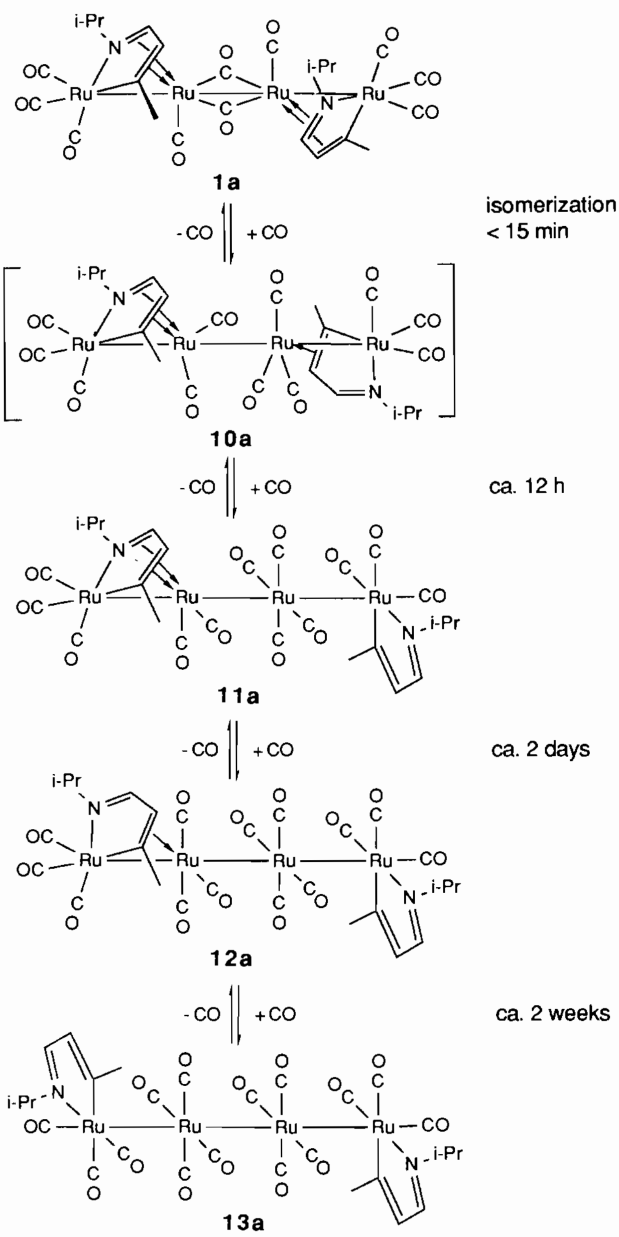


Fig. 9. X-ray molecular structures of *trans*-(AC)-**1a** (top) and of *cis*-(AA)-**1a** (bottom).

$Ru_4(CO)_{14}[CH_3C{=}C(H)C(H){=}N\text{-i-Pr}]_2$ (**13**) in quantitative yield [43]. The reaction is presented in Scheme 6, which also shows likely geometries for **13**, the proposed intermediate **10**, and the observed intermediates **11** and **12**. The compounds **11–13** have been characterized on the basis of the distinct ^1H and ^{13}C NMR spectroscopic features exhibited by 3, 5 and 7e donating MAD-yl ligands (*vide supra*). Overall, the reaction involves the consecutive substitution of the π-coordinating systems of the two MAD-yl ligands by CO ligands. Interestingly,



Scheme 6. Stepwise reaction of **1a** with CO to give **13a**.

first complete substitution of both the π-systems of one MAD-yl ligand takes place prior to those of the other MAD-yl moiety. During substitution of the second MAD-yl ligand, first the η^2-C=N moiety is displaced and then the η^2-C=C moiety, indicating that the η^2-bond of the C=C moiety to the cluster core is stronger than the η^2-bond of the C=N moiety. The reversible reactions of CO express the hemilable character of the MAD-yl ligand, i.e. the number of electrons donated by this ligand (3, 5 or 7e) can be flexibly adjusted to the need of a transition metal complex.

Thermolysis of **1a** under an atmosphere of CO results in breakdown of the tetranuclear cluster core and formation of two known dinuclear compounds, $Ru_2(CO)_6[CH_2CC(H)C(H){=}N\text{-i-Pr}]$ (**6a**) and $HRu_2(CO)_6[CH_3C{=}C(H)C(H){=}N\text{-i-Pr}]$ (**4a**) [43]. The latter quickly isomerizes under the applied reaction conditions into $Ru_2(CO)_6[CH_3C{=}C(H)CH_2N\text{-i-Pr}]$ (**2a**; Scheme 7). During this reaction an H atom of the $C_\gamma H_3$ group of one of the MAD-yl ligands of **1a** is selectively and, presumably intramolecularly, transferred to the imine carbon atom of the other MAD-yl ligand.

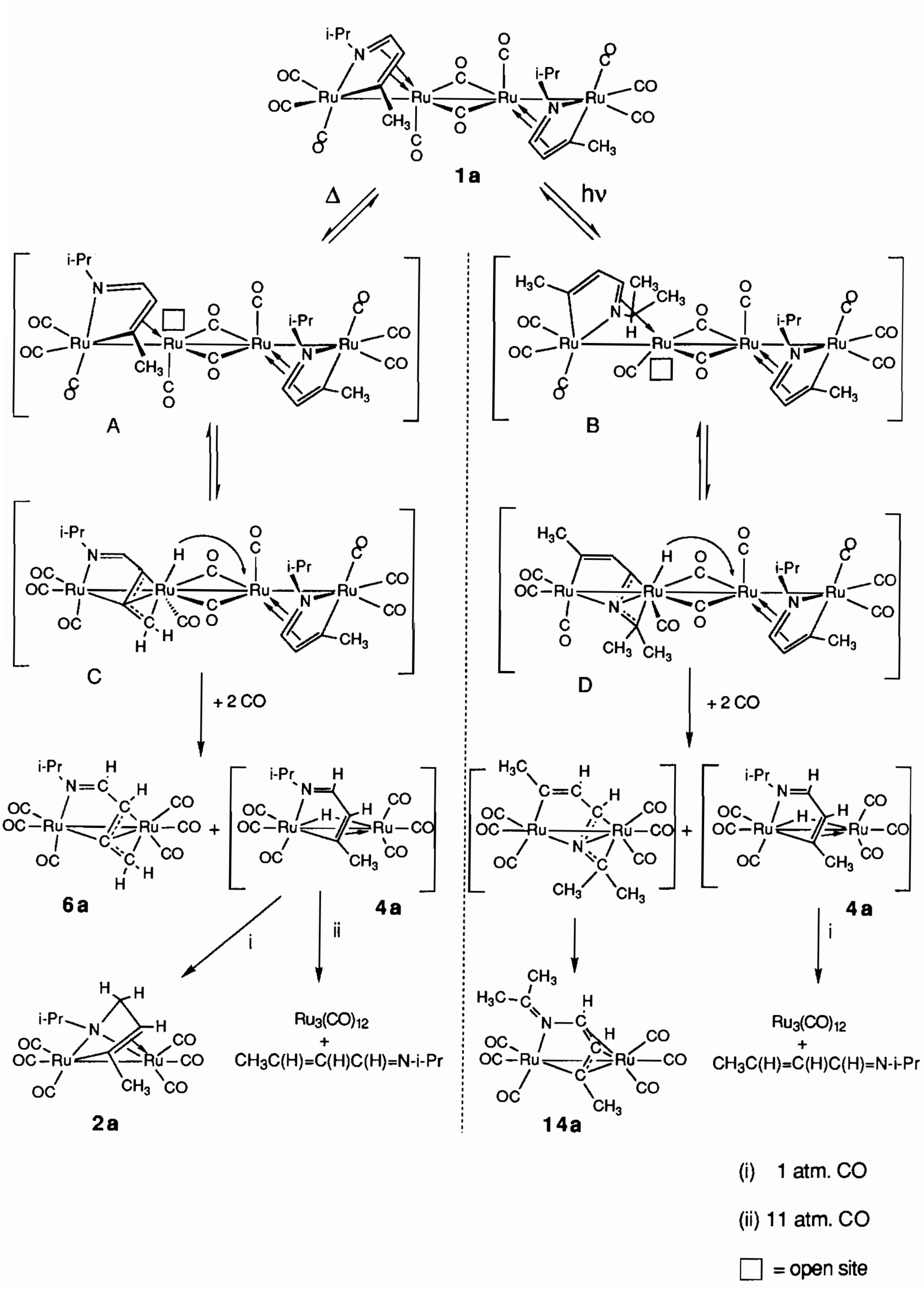
Photolysis of **1a** under CO also causes the break up of the tetranuclear cluster core but in this case the dinuclear compound $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_3)_2]$ (**14a**), $Ru_3(CO)_{12}$ and MAD are formed [43]. During this conversion the methine H atom of the i-Pr group of one of the MAD-yl ligands is abstracted and transferred to the C_β atom of the other MAD-yl ligand. As depicted in Scheme 7, we assume, just as during the thermally induced degradation of **1a** under CO, the intermediacy of $HRu_2(CO)_6[CH_3C{=}C(H)C(H){=}N\text{-i-Pr}]$ (**4a**), which, upon further irradiation under CO, reductively eliminates MAD with concomitant formation of $Ru_3(CO)_{12}$.

It is postulated that thermal activation of **1** first causes breaking of the π-bond between the η^2-C=N bond of one of the MAD-yl ligands and ruthenium, thus creating an open site on that ruthenium center (Scheme 7). The still coordinated η^2-C=C moiety forces its CH_3 substituent into proximity of the reactive 16e ruthenium center, whereafter insertion of that ruthenium center into the C_γ–H bond becomes feasible. Subsequent hydride transfer and CO-induced cluster break up, yields the diruthenium products. A similar mechanism rationalizes the photochemically induced activation of the methine C–H bond of one of the MAD-yl ligands in **1**. Instead of dissociation of the η^2-C=N moiety, photochemically induced dissociation of the η^2-C=C moiety seems a likely first step. Now, the still coordinated η^2-C=N moiety holds the i-Pr group into the proximity of the unsaturated ruthenium center, whereafter insertion of that ruthenium atom into the methine C–H bond becomes feasible. Subsequent H-transfer and cluster breakdown then results in the formation of the reaction products.

So, it is possible to induce selective dissociation of either the η^2-C=N or the η^2-C=C moiety of one of the 7e donating MAD-yl ligands in **1** by either thermal or photochemical activation.

Reactions with H_2

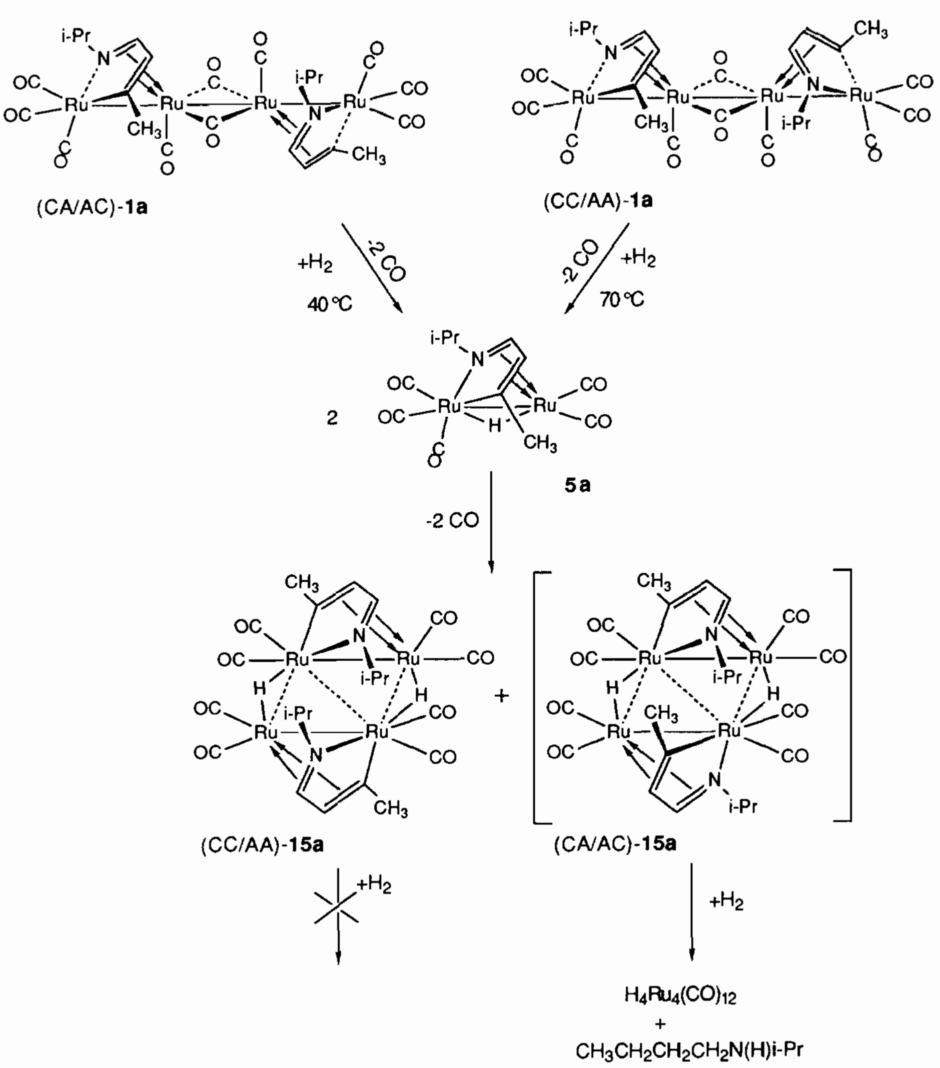
The 66e linear cluster **1** reacts with H_2 at 90 °C to give the 64e butterfly cluster $H_2Ru_4(CO)_8[R^1C{=}C(H)C(H){=}NR^2]_2$ (**15**), $H_4Ru_4(CO)_{12}$ and $R^1CH_2CH_2CH_2N(H)R^2$ as the main products [44]. The deep purple compound **15** was only obtained in one of its two



Scheme 7. Proposed mechanisms of the thermally and photochemically induced conversions of **1a** in the presence of CO.

possible geometric isomers, (CC/AA)-**15**. It is assumed that the other diastereomer, (CA/AC)-**15** is very reactive under the applied reaction conditions and decomposes into $H_4Ru_4(CO)_{12}$ and $R^1CH_2CH_2CH_2N(H)R^2$. Compound **15** could not be obtained for R^2 = t-Bu, which could be ascribed to the bulkiness of the R^2 substituents.

It has been found that the reactivity of the two diastereomers of **1a** towards H_2 differs. (CA/AC)-**1a** reacted at 40 °C, via the intermediacy of the dinuclear hydride $HRu_2(CO)_5[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ (**5a**), into the above mentioned products, whereas (CC/AA)-**1a** had to be brought at 70 °C before it reacted with



Scheme 8. Hydrogenation of (CC/AA)-**1a** and (CA/AC)-**1a**.

H_2. The stepwise conversion of **1a** during the reaction with H_2 is depicted in Scheme 8.

The X-ray crystal structure of one enantiomer of (CC/AA)-**15a** is depicted in Fig. 10. Compound (CC/AA)-**15a** possesses non-crystallographic C_2 symmetry and contains two 7e donating MAD-yl ligands and two bridging hydrides. The four ruthenium atoms occupy a butterfly arrangement ($\Phi = 137.05°$) and are mutually connected by two normal bonds; Ru(1)–Ru(3) = 2.8144(6) and Ru(2)–Ru(4) = 2.8262(6) Å and three long bonds; Ru(1)–Ru(2) = 3.1230, Ru(2)–Ru(3) = 3.1409(6) and Ru(3)–Ru(4) = 3.1243(6) Å. The two N-i-Pr groups of (CC/AA)-**15a** are both located in the cavity between the wing tips of the cluster.

Upon reaction of tetranuclear cluster **1** with H_2/CO (9:1) at 90 °C, it is converted into two molecules of **2** [44]. This conversion constitutes the reverse of the formation of **1** (see Scheme 3). The butterfly cluster **15** reacts at 90 °C with CO, which also yields **2**. These conversions take place via intermediacy of two dinuclear hydride compounds, **5** and **4**, sequentially. Compound **5** readily takes up one molecule of CO at room temperature to form $HRu_2(CO)_6[R^1C{=}C(H)C(H){=}NR^2]$ (**4**). During this conversion the coordination mode of the MAD-yl ligand changes from the 7e donating σ-N,σ-C,η^2-C=N,η^2-C=C mode into the 5e donating σ-N,σ-C,η^2-C=C mode. This addition reaction is reversible, the equilibrium being dependent on the temperature and the presence of CO.

As stated before, compound **4** isomerizes into **2** upon heating in solution, by which the hydride is transferred to the imine carbon atom of the MAD-yl ligand. The rate of this conversion depends on the nature of the R^1,R^2 substituents. Whereas conversion is completed within 5 min at 68 °C for **4d**, isomerization of **4c** into **2** proceeds considerably slower and only takes place

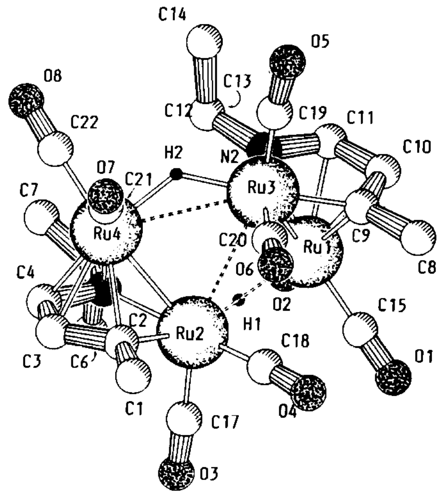


Fig. 10. X-ray molecular structure of $(\mu\text{-H})_2Ru_4(CO)_8[CH_3C{=}C(H)C(H){=}N\text{-i-Pr}]_2$ (**15a**).

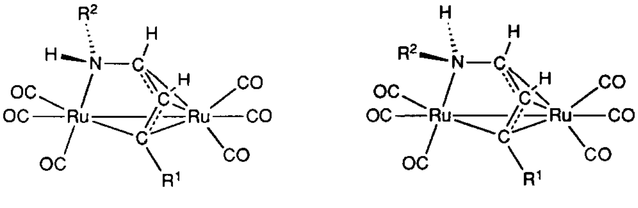
in 4 h at 80 °C under an atmosphere of CO. Otherwise **4** is converted into **1**. The different kinetic barriers for isomerization of **4** into **2** are proposed to be the result of a reversible change of the coordination mode of the 5e MAD-yl ligand from σ-N,σ-C,η^2-C=C into σ-N,σ-C,η^2-C=N, prior to hydride transfer to ligand. The presence of the bulky t-Bu group on nitrogen will destabilize the η^2-C=N bonding in the presumed intermediate and as a result hampers the hydride transfer. The enhanced thermal stability of **4** and its anomalous decomposition path with R^2 = t-Bu rationalizes the finding that **2** is not formed for R^2 = t-Bu during thermal reactions of $Ru_3(CO)_{12}$ with R^1, R^2-MAD (*vide infra*).

In the presence of MAD, compound **4c** is thermally converted into **6c**, suggesting the intermediacy of **4a–c** during the conversion of complexes **2a–c** in a reaction with MAD into **6a–c** as well. This reaction is reversible, at 100 °C compound **6** reacts with H_2 to give **2** (R^2 = i-Pr) or **1** (R^2 = t-Bu). This difference in reactivity points to the intermediacy of **4** during hydrogenation of **6** as well.

The dinuclear hydride compounds **4** have been found to isomerize into $Ru_2(CO)_6[R^1CC(H)C(H)N(H)R^2]$ (**16**) during column chromatography on silica. Although two diastereomers of **16** might be formed, only one is obtained during isomerization of **4** [44]. The two possible diastereomers of **16** are depicted in Fig. 11. Interestingly, small amounts of the other diastereomer were formed during the CO-catalyzed oxidation of **1** [45]. As no X-ray crystal structures have been determined of the two diastereomers of **16** it is as yet not clear which diastereomer is obtained via each pathway.

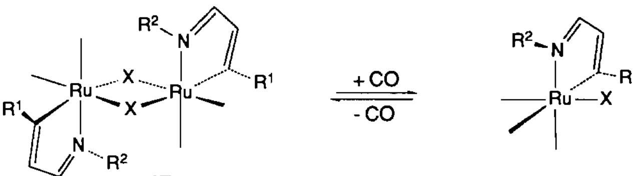
Reactions with oxidizing reagents

The tetranuclear cluster **1** reacts with oxidizing reagents like I_2, Br_2, NBS and CCl_4 at elevated temperatures to give the dimeric halide bridged organoruthenium(II) compounds $[Ru(CO)_2X[R^1C{=}C(H)\text{-}C(H){=}NR^2]_2$ (**17**; X = I, Br, Cl) together with $[Ru(CO)_3X_2]_2$ [45]. The compounds **17** are obtained as mixtures of diastereomers, the configurations of which have been established. The reactions of **1** with CX_4 are accelerated by CO, probably because $Ru_4(CO)_{12}[R^1C{=}C(H)C(H){=}NR^2]_2$ (**11**) is formed prior to oxidation. Facile splitting of the halogen bridges in **17** takes place during reactions with CO or PR_3 [45, 46]. Reaction with CO affords merely *fac*-$Ru(CO)_3X[R^1C{=}C(H)C(H){=}NR^2]$ (**18**), as shown in Scheme 9, whereas reaction with PR_3 gives mixtures of isomers of $Ru(CO)_2(PR_3)X[R^1C{=}C(H)C(H){=}NR^2]$, the relative amounts being dependent on the electronic and steric properties of the phosphine [46]. The reactions with CO are reversible, i.e. passing nitrogen through a solution of **18** or removal of the solvent under vacuum results in the reformation of the parent compound **17**. These mononuclear halide complexes have shown to be useful precursors for the systematic synthesis of a number of heteronuclear monoazadienyl compounds.



(R$_N$)-**16** (S$_N$)-**16**

Fig. 11. Drawings of two diastereomers of $Ru_2(CO)_6[R^1CC(H)C(H)N(H)R^2]$ (**16**).



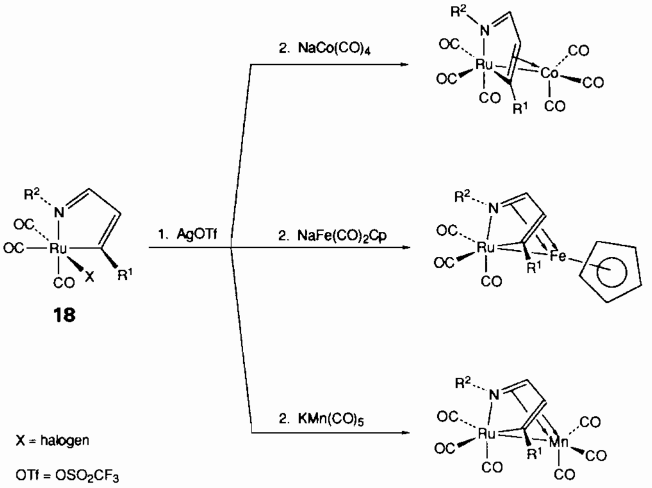
17 **18**

X = Cl, Br, I

Scheme 9. Reversible splitting of the halogen bridges of **17** by CO.

Heteronuclear MAD chemistry

Thus far, two different synthetic routes have shown to be useful in the preparation of heteronuclear monoazadienyl compounds. The first involves the exchange of the halide X in mononuclear $RuX(CO)_3[R^1C{=}C(H)\text{-}C(H){=}NR^2]$ (**18**) or $RuX(CO)_2PR_3[R^1C{=}C(H)C(H){=}NR^2]$ by a non-coordinating anion by treatment with, for example, AgOTf, followed by reaction with an anionic metal carbonyl fragment $M(CO)_n{}^-$ (see Scheme



18

X = halogen

OTf = OSO$_2$CF$_3$

Scheme 10. Synthesis of heterodinuclear monoazadienyl complexes from **18**.

10). By this approach we have successfully synthesized a number of heteronuclear monoazadienyl complexes containing a RuFe, RuCo or RuMn core [46].

Alternatively, the photochemically induced reaction of **1** with $Fe_2(CO)_9$, as a source of $Fe(CO)_4$, resulted in the formation of the heterodinuclear hydride compound $HFeRu(CO)_5[R^1C{=}C(H)C(H){=}NR^2]$ and small amounts of other compounds [47]. Meanwhile it has been shown that this compound is very useful for the further exploitation of heteronuclear iron–ruthenium carbonyl monoazadienyl chemistry, in which field we are currently active [46].

Conclusions

When we started this subject with the isolation of some di- and tetranuclear ruthenium carbonyl monoazadienyl complexes, obtained from the reaction of $Ru_3(CO)_{12}$ and MAD, their interconversions and mechanisms of formation were completely unknown. Meanwhile, much light has been shed upon these problems; many of the initially elusive intermediates, e.g. $HRu_2(CO)_n[R^1C{=}C(H)C(H){=}NR^2]$, have been isolated and/or characterized spectroscopically and it has been possible to study most of their individual reactions and interconversions. Among others, it has been shown that the $Ru_m(CO)_n$/MAD system has an aptitude for C–H activation and H-migration processes as well as a propensity for the formation of five-membered azaruthenacycles. Furthermore, there is the clear tendency to form di- and tetranuclear complexes. Due to the chirality of Ru in, for example, $RuX(CO)_3$(MAD-yl) and $Ru_2X(CO)_5$(MAD-yl) (X = substituent or open site), these fragments can be used as chiral building blocks in the synthesis of chiral systems of higher nuclearity. For instance, it has been shown that chiral recognition between homochiral units can be used for the diastereoselective coupling of two molecules of $Ru_2(CO)_6[CH_2CCH{-}CH{=}NR^2]$ to give a chiral C–C coupled tetraruthenium complex.

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