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Reactions of monoazadienes with metal carbonyl complexes

VII *. Preparation and spectroscopic characterization of a mononuclear ruthenium(II) complex containing two 3e-donating σ-*C*, σ-*N* coordinated 1-aza-1,3-dien-4-yl ligands

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Abstract

The pale yellow mononuclear ruthenium(II) complex $Ru(CO)_2[CH_3C{=}C(H)C(H){=}N^iPr]_2$ (**1a**) has been obtained (i) in ca. 25% yield by heating a solution of $Ru_3(CO)_{12}$ in $CH_3C(H){=}C(H)C(H){=}N^iPr$ at 110 °C for 8 h, and (ii) in ca. 80% yield from the reaction of $Ru_2(CO)_6[CH_2CCC(H)C(H){=}N^iPr]$ (**2a**) with $CH_3C(H){=}C(H)C(H){=}N^iPr$ in heptane for 16 h at 110 °C. Compound **1a** contains two *cis* positioned CO ligands and two inequivalent σ-*C*, σ-*N* coordinated 1-aza-1,3-dien-4-yl ligands. The formation of **1a** is discussed.

Introduction

Organometallic complexes containing a 3e-donating σ-*N*, σ-*C* coordinated 1-aza-1,3-dien-4-yl (R^1R^2-MAD-yl) ligand ** are not very common. So far only two such complexes, $Ir^{III}HCl[C_6H_5C{=}C(H)C(H){=}N^iPr][P(c\text{-}Hex)_3]_2$ [1] and $Pt^{II}Cl(L))[C_6H_5C{=}C(H)C(CH_3){=}NC_6H_5]$ (L = CO, PPh_3) [2] have been reported.

Recently we started a study of the reactivity of 1-aza-1,3-dienes (R^1R^2-MAD) towards ruthenium carbonyl complexes [3–9]. We found that metallation of either the α or the β olefin C–H bond takes place during thermal reactions of $Ru_3(CO)_{12}$

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* For part VI see ref. 8.

** MAD is used as acronym for 1-aza-1,3-dienes (monoazadienes) in general. In this paper we will use R^1R^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: $R^1C(H)_\beta{=}C(H)_\alpha C(H)_{im}{=}NR^2$. R^1R^2-MAD forms, when metallated at C_β, the formally monoanionic 1-aza-1,3-dien-4-yl ligand $R^1C{=}C(H)C(H){=}NR^2$(R^1R^2-MAD-yl).

with MAD, and that the abstracted H-atom is transferred to an sp^2-carbon atom of the ligand to give an isomerized MAD ligand ($R^1C{=}C(H)CH_2NR^2$ or $R^1CH_2CC(H)NR^2$) coordinated to a dinuclear hexacarbonyl moiety [5]. Further transformations take place, and the overall course of the reaction is strongly influenced by the R^1- and R^2-substituents, the reaction temperature, the reaction time, and the amount of MAD present [3–9].

In continuation of our studies, we report here the preparation and spectroscopic characterization of a mononuclear ruthenium(II) complex that contains two 3-electron donating σ-*N*, σ-*C* coordinated MAD-yl ligands.

Experimental

Materials and apparatus

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AC100 and WM250 spectrometers. IR spectra were recorded on a Nicolet 7199 B FT-IR spectrophotometer. The Field Ionization (FI) mass spectrum was obtained with a Varian MAT-711 double focusing mass spectrometer with a combined EI/FI/FD source.

Solvents were carefully dried and distilled under nitrogen prior to use. Reactions were performed under dry nitrogen. Silica gel for column chromatography (kieselgel 60, 70–230 mesh, E. Merck, Darmstadt) was dried before use. The monoazadienes $R^1C(H){=}C(H)C(H){=}NR^2$ (R^1, R^2 = CH_3, ^{i}Pr (**a**), CH_3, ^{t}Bu (**b**), C_6H_5, ^{i}Pr (**c**)) were prepared by standard procedures [10], and $Ru_2(CO)_6[CH_2CC(H)CH_2NR^2]$ (R^1, R^2 = CH_3, ^{i}Pr (**2a**); CH_3, ^{t}Bu (**2b**)) was synthesized and purified as described before [4].

Synthesis of $Ru(CO)_2[CH_3C{=}C(H)C(H){=}N^iPr]_2$ *(1a)*

Method i. A suspension of $Ru_3(CO)_{12}$ (0.64 g, 1.0 mmol) in 5 mL of $CH_3C(H){=}C(H)C(H){=}N^iPr$ was stirred at 110 °C. When the Schlenk tube was immersed in the hot oil bath a vigorous reaction took place with liberation of gaseous products. After 8 h the Schlenk tube was cooled to room temperature, and 20 mL of hexane was added, to give a brown precipitate, which was removed by filtration. The solution was concentrated to 5 mL and then chromatographed on silica with hexane as eluent. A yellow band was obtained which yielded $Ru(CO)_2[CH_3C{=}C(H)C(H){=}N^iPr]_2$ (**1a**, ca. 25%) as a waxy solid after removal of the solvent under vacuum. So far, all attempts to crystallize **1a** have been unsuccessful. FI-mass (based on the ^{101}Ru isotope): Found: $m/e = 377$ ($RuC_{16}H_{24}N_2O_2$ (**1a**) calcd.: $M = 377$).

Method ii. A solution of $Ru_2(CO)_6[CH_2CC(H)C(H){=}N^iPr]$ (**2a**, 0.5 mmol) in a mixture of 5 mL of heptane and 2 mL of $CH_3C(H){=}C(H)C(H){=}N^iPr$ was refluxed for about 16 h until the characteristic ν(CO) pattern of **2a** had disappeared and been replaced by the ν(CO) pattern of **1a** (Table 1). Work-up as described above gave **1a** in about 80% yield.

Attempted synthesis of $Ru(CO)_2[CH_3C{=}C(H)C(H){=}N^tBu]_2$ *(1b)*

A solution of $Ru_2(CO)_6[CH_2CC(H)C(H){=}N^tBu]$ (**2b**, 0.5 mmol) and 2 mL of $CH_3C(H){=}C(H)C(H){=}N^tBu$ in 15 mL of heptane was stirred at 110 °C. Complex **2b** was slowly converted into new organometallic products, as indicated by the appearance of several new absorption bands in the ν(CO) region of IR spectra of small samples taken from the reaction mixture. After 16 h the brown reaction mixture was cooled to ambient temperature and a green precipitate was removed by filtration. The mixture was chromatographed on silica with diethyl ether as eluent. After removal of the eluent under vacuum, ^{1}H NMR showed the presence of several new products, which have not yet been characterized. No resonances were observed that could be ascribed to $Ru(CO)_2[CH_3C{=}C(H)C(H){=}N^tBu]_2$ (**1b**).

Attempted synthesis of $Ru(CO)_2[C_6H_5C{=}C(H)C(H){=}N^iPr]_2$ *(1c)*

A solution of $Ru_3(CO)_{12}$ (0.64 g, 1 mmol) in 7 mL of $C_6H_5C(H){=}C(H)C(H){=}N^iPr$ was stirred overnight at 110 °C. The mixture was cooled to ambient temperature and 20 mL of hexane was added. After filtration, $Ru_3(CO)_6[C_6H_5C{=}C(H)C(H){=}N^iPr]_2$ (**7c**, ca. 55%) was isolated by the work-up procedure described before [8]. No formation of $Ru(CO)_2[C_6H_5C{=}C(H)C(H){=}N^iPr]_2$ (**1c**) had taken place, as indicated by IR and ^{1}H NMR spectra of the filtrate.

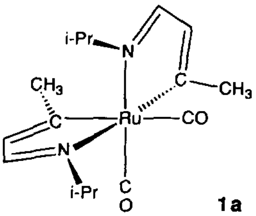
Reaction of $Ru_2(CO)_6[CH_2CC(H)C(H){=}N^tBu]$ *(2b) with* $CH_3C(H){=}C(H)C(H){=}N^iPr$

A solution of $Ru_2(CO)_6[CH_2CC(H)C(H){=}N^tBu]$ (**2b**, 0.1 g, 0.2 mmol) and $CH_3C(H){=}C(H)C(H){=}N^iPr$ (0.22 g, 2.0 mmol) in 40 mL of heptane was stirred at 90 °C for 70 h. The solvent was removed under vacuum and the residue dissolved in diethyl ether and filtered through silica (to remove residual and decomposed $CH_3C(H){=}C(H)C(H){=}N^iPr$). The ^{1}H NMR spectrum of the concentrated reaction mixture showed the presence of four organometallic components **1a**, **2a**, **2b** and an unknown product, in an approximate 3 : 1 : 2 : 2 ratio.

Results

When a solution of $Ru_3(CO)_{12}$ in $CH_3C(H){=}C(H)C(H){=}N^iPr$ was stirred at 110 °C for 8 h $Ru^{II}(CO)_2[CH_3C{=}C(H)C(H){=}N^iPr]_2$ (**1a**) was formed in about 25% yield. This pale yellow mononuclear compound was isolated by chromatography on silica with hexane as eluent. Complex **1a** (see Fig. 1) was also made from $Ru_2(CO)_6[CH_2CC(H)C(H){=}N^iPr]$ (**2a**) [4] by thermal reaction with $CH_3C(H){=}C(H)C(H){=}N^iPr$ (yield: about 80%). The reactions of $Ru_3(CO)_{12}$ with $R^1C(H){=}C(H)C(H) = NR^2$, including those described above, are outlined in Scheme 1 (vide infra).

Attempts to prepare similar mononuclear complexes with R^1, R^2 = CH_3, ^tBu (**1b**) or C_6H_5, ^iPr (**1c**) by similar procedures were unsuccessful. Exchange of ligands may take place during these reactions, as was found for the reaction of $Ru_2(CO)_6$-$[CH_2CC(H)C(H){=}N^tBu]$ (**2b**) with $CH_3C(H){=}C(H)C(H){=}N^iPr$. In addition to un-



1a

Fig. 1. Structure of $Ru(CO)_2[CH_3C{=}C(H)C(H){=}N^iPr]_2$ (**1a**).

changed starting material and an unknown product, both $Ru(CO)_2[CH_3C{=}C(H)C(H){=}N^iPr]_2$ (**1a**) and $Ru_2(CO)_6[CH_2CC(H)C(H){=}N^iPr]$ (**2a**) were found to be present in the reaction mixture obtained after 70 h in heptane at 90 °C.

Spectroscopic characterization of $Ru(CO)_2[CH_3C{=}C(H)C(H){=}N^iPr]_2$ (1a)

Although the new mononuclear compound **1a** has so far been isolated only as a waxy solid, it has been unambiguously characterized by means of combined IR, ^1H, $^{13}C\{^1H\}$ NMR (Table 1), and FI-mass spectroscopy (see Experimental section). The molecular structure of **1a** is shown in Fig. 1 and is akin to those of a series of complexes with formula $Ru(CO)_2[C \sim N]_2$, in which $[C \sim N]$ is an *ortho*-metallated Schiff base ($[C \sim N]$: benzylideneaniline (bza) [11], benzylidenemethylamine (bzm) [11], or benzoquinoline (bq) [12]).

The IR spectrum of **1a** in hexane shows two absorption bands of approximately equal intensity at 2016 and 1953 cm^{-1}, characteristic of a *cis*-$M(CO)_2$ unit (Table 1). These values are comparable to those for the related $Ru(CO)_2[C \sim N]_2$ compounds [11,12]. The FI-mass spectrum of **1a** showed the expected isotopic pattern around $m/e = 377$.

Both the ^1H and $^{13}C\{^1H\}$ NMR spectra (Table 1) of **1a** show the presence of two inequivalent metallated 3-electron donating σ-N, σ-C_β coordinated isopropylcrotonaldimin-4-yl (MAD-yl) ligands. The H_{im} and H_α protons of both ligands are found near 8.0 and at 6.43 ppm, respectively, with a mutual ^3J coupling of 1.5 Hz. The two R^I methyl groups resonate at 1.94 and 2.74 ppm, and both show ^4J coupling with the H_α protons of 1.2 Hz. This coupling is somewhat larger than those usually found for 7-electron donating crotonaldimin-4-yl ligands in di-, tri-, and tetra-nuclear complexes, in which in addition to σ-N, σ-C coordination to one metal center, the C=C and C=N units of the MAD-yl ligand are π-coordinated to a second metal center [3,5,8]. The two ^iPr substituents give rise to four doublets near 1 ppm and two septets near 3.5 ppm. The diastereotopicity of the methyl groups of these substituents indicates that both N atoms are coordinated to the metal center.

Table 1

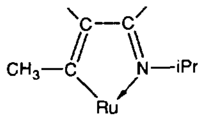
Spectroscopic data for **1a**

IR [a]	2016 (s)	1953 (s)				
	H_{im}	H_α	CH_3	^iPr		
^1H NMR [b]	7.94 (d,1.5)	6.43 (br.s)	1.94 (d,1.2)	3.83 (sept) [c]; 1.33, 1.33 (d,d) [c]		
	7.80 (d,1.5)	6.43 (br.s)	2.74 (d,1.2)	3.35 (sept) [c]; 1.08, 1.06 (d,d) [c]		
	C_{im}	C_α	C_β	CH_3	^iPr	CO's
^{13}C NMR [d]	166.6	128.6	223.1 [e]	34.8	62.0; 23.7; 23.5	200.5 [e]
	164.2	126.1	218.3 [f]	27.4	51.5; 23.3; 23.1	194.3 [g]

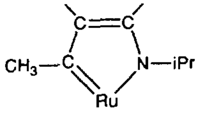
[a] (cm^{-1}), for solution in hexane. [b] $CDCl_3$, 100 MHz, 298 K; δ-values in ppm relative to Me_4Si; H_{im}, and H_α correspond to $CH_3C{=}C(H)_\alpha C(H)_{im}{=}N^iPr$. [c] $^3J = 6.5$ Hz. [d] Measured in $CDCl_3$, 62.9 MHz, 263 K, δ-values in ppm relative to Me_4Si. C_{im}, C_α, C_β and CH_3 correspond to $CH_3C_\beta{=}C_\alpha(H)C_{im}(H){=}N^iPr$. [e] *trans* to N(=C). [f] *trans* to (CO). [g] *trans* to C(=C).

The C_{im} and C_α resonances of the MAD-yl ligands are found near 165 and 127 ppm, respectively. These chemical shifts differ only slightly from those observed for the free ligand (C_{im}: 159.4 and C_α: 132.0 ppm) [3], and are comparable with those found for $Ir^{III}HCl[C_6H_5C(H)C(H){=}N^iPr][P(c\text{-}Hex)_3]_2$ [1] and $Ru^{II}(CO)_3 \times [CH_3\text{-}C{=}C(H)C(H){=}N^iPr$ [13]. Four resonances are observed in the ^{13}C NMR spectrum of **1a** in the 190–225 ppm region, and originate from the two metallated C_β atoms and the two carbon atoms of the CO ligands. Of these, the 200.5 and 194.3 ppm signals can be assigned to the carbon atoms of the two CO ligands, since terminal Ru–CO carbon atoms are usually observed between 185 and 215 ppm. Discrimination between the two CO signals was made by taking into account the difference in trans influences exerted by the N and C_β atoms (Table 1).

The most striking spectroscopic observations are the very high δ-values for the ^{13}C resonances of the C_β atoms at 218.3 and 223.1 ppm, corresponding to a high frequency shift of about 60 ppm relative to the non-metallated ligand [3]. This anomalous feature may be attributed to the presence of the ruthenium center at these C_β atoms. Owing to effective overlap between the π^*-orbitals located at the C_β atoms and relevant ruthenium *d*-orbitals, this results in a carbene-like character of the C_β atoms. Hence, the two azaruthenacycles in **1a** are best ascribed as a hybrid of the two extreme resonance forms **A** and **B**.



A

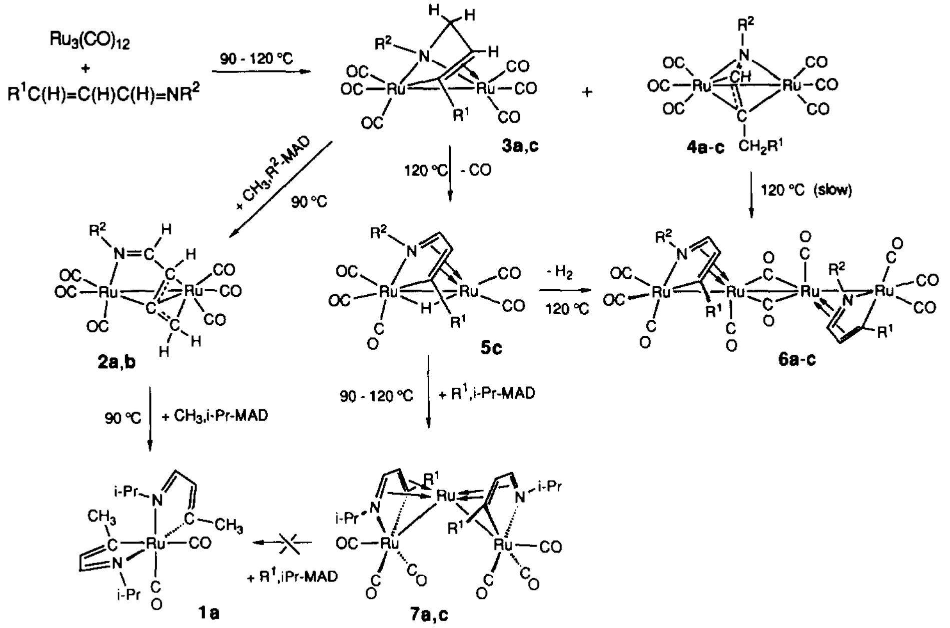


B

The difference in trans influence exerted by the N(=C) and CO groups allowed us to assign the two C_β atoms individually (see Table 1). Similar high frequency shifts have recently been reported by Pregosin and his colleagues [14] for the metallated C atoms of [C ~ N] systems chelated to a Rh^{III}-center, whereas in oxamanganacyclopentadienyl systems the metallated C_β-atom is also usually found above 200 ppm [15]. Recently a heterometallic RuRe dimer containing a bridging metallated α,β-unsaturated aldehyde σ-C_β bonded to the ruthenium center has been reported. The ^{13}C signal for this carbon nucleus was found at even higher frequency (251.3 ppm), which is in accordance with the very short Ru–C distance of 1.986(9) Å observed crystallographically, indicating partial double bond character [16].

Discussion

The new complex **1a** represents the first mononuclear carbonyl complex of the iron triad containing metallated MAD-yl ligands. For iron, the coordination complexes $Fe(CO)_4(MAD)$ [17,18] and $Fe(CO)_3(MAD)$, in which the MAD ligand is respectively σ-*N* and η^2-*C=C*, η^2-*C=N* coordinated, have been reported [19,20], but no mononuclear osmium complexes containing either coordinated or metallated MAD ligands are known. However, a number of closely related mononuclear complexes have been described. For example $CpRu^{II}(PPh_3)[CH_3OC(O)C{=}C(H)\text{-}(CH_3O)C{=}O]$ [21], $Ru^{II}Cl(CO)_3[C_2H_5OC(O)C{=}C(H)(C_2H_5O)C{=}O]$ [22] and $HRu^{II}(PPh_3)_2[C(H){=}C(CH_3)C(O)OR]$ [23] contain five membered oxaruthena-



Scheme 1. Overview of the products formed during thermal reactions between $Ru_3(CO)_{12}$ and R^1R^2-MAD (R^1R^2=CH_3, ^iPr (**a**), CH_3, ^tBu (**b**), C_6H_5, ^iPr (**c**)).

cyclopentadienyl rings, and in $HIr^{III}Cl(PPh_3)_2[C_6H_5C{=}C(H)C(H){=}N^iPr]$ [1] a five membered azairidacyclopentadienyl ring, similar to that in **1a**, is present.

In general, reactions of $Ru_3(CO)_{12}$ with organic substrates do not afford a single product. One reason for this is that the severe conditions usually employed result in further transformations of initially formed products. These latter reactions may result in the break-up of the trinuclear cluster unit, with formation of mono- or di-nuclear complexes or, more rarely, in condensation to clusters of higher nuclearity [24].

In the course of our study on the formation and reactivity of metallated 1-aza-1,3-dienes in ruthenium carbonyl complexes a number of interesting di-, tri-, and tetra-nuclear complexes have been isolated [3–9]. It has been found that during the initial stages of reactions between $Ru_3(CO)_{12}$ and $R^1C(H){=}C(H)C(H){=}NR^2$ (R^1 = CH_3 or C_6H_5 and R^2 = ^iPr, ^cHex or ^tBu), metallation of either the C_α or the C_β atom takes place and that the abstracted H atom is subsequently transferred to a sp^2 carbon atom of the MAD-yl ligand, yielding $Ru_2(CO)_6[R^1C{=}C(H)CH_2NR^2]$ (**3**) and $Ru_2(CO)_6[R^1CH_2CC(H)NR^2]$ (**4**) as the first isolable products (see Scheme 1) [5]. Further reactions take place upon prolonged heating, the course of which depends on the R^1 and R^2 substituents and whether MAD is present or not. Thermolysis of **3** gave linear tetranuclear $Ru_4(CO)_{10}[R^1C{=}C(H)C(H){=}NR^2]_2$ (**6**; two diastereomers), via the intermediacy of $(\mu\text{-}H)Ru_2(CO)_5[R^1C{=}C(H)C(H){=}NR^2]$ (**5**) [5,6]. When MAD is present during thermolysis of **3** other reactions take place. For R^1 = CH_3, reaction of **3** with MAD (or crotonaldehyde) at 90 °C gives dinuclear $Ru_2(CO)_6[CH_2CC(H)C(H){=}NR^2]$ (**2**), which contains a dehydrogenated MAD ligand, as the main product. During this reaction the free MAD acts as a hydrogen acceptor, the olefin moiety of which is hydrogenated chemoselectively [5]. Due to the lack of H_γ atoms, a complex like **2** cannot be formed for $R^1 = C_6H_5$. In this case, reaction of **3c** with C_6H_5, ${}^iPr$-MAD at 90 °C affords the acyclic trinuclear cluster $Ru_3(CO)_6[C_6H_5C{=}C(H)C(H){=}N{}^iPr]_2$ (**7c**; two diastereomers) via **5c** [8]. This trinuclear cluster was also obtained for $R^1 = CH_3$, $R^2 = {}^iPr$ (**7a**), from the reaction of **3a** with CH_3, ${}^iPr$-MAD, but this reaction had to be performed at a high temperature (125 °C). Since three reaction pathways may be followed (giving either **2a**, **6a** or **7a**), trinuclear **7a** could only be obtained in moderate yield.

The reaction pathway resulting in the formation of mononuclear $Ru(CO)_2[CH_3C{=}C(H)C(H){=}N{}^iPr]_2$ (**1a**) proceeds via the dinuclear complexes **3a** and **2a** as shown in Scheme 1. During the last step, which involves conversion of **2a** into **1a** in a reaction with an excess of CH_3, ${}^iPr$-MAD, a number of C–H activation and formation processes must take place. One of these steps involves the transfer of a hydrogen atom from C_β of the originally free MAD ligand to the terminal CH_2 moiety of the allyl-imine ligand in **2a**. Since the overall conversion of **2a** into **1a** involves a complicated sequence of steps, in which exchange of coordinated and free MAD ligand may also occur, it is difficult to suggest a complete mechanism. It should be noted, however, that the first step, after which coordination and metallation of the free MAD ligand becomes feasible, probably involves $\eta^3 \to \eta^1$ slippage of the allyl function in **2a**, instead of CO dissociation. This assumption is based on the observations that (i) **2a** reacts smoothly with H_2 without CO loss [25], and (ii) CO loss from **2** (with formation of an acyclic tetranuclear compound) does take place, though only under rather severe conditions [9].

Mononuclear **1b** ($R^1 = CH_3$, $R^2 = {}^tBu$) has so far not been obtained. This product, however, would suffer from severe internal crowding due to the presence of two bulky ${}^tBu$ groups. Therefore **1b** is either not formed or is unstable, and other or subsequent reactions take place. Computer simulated models indicate that there are no steric restrictions for the existence of **1c** ($R^1 = C_6H_5$, $R^2 = {}^iPr$). Probably the lack of H_γ atoms, which precludes the formation of a complex like **2**, also precludes the formation of **1c**. When $Ru_3(CO)_{12}$ is treated at 110 °C with $C_6H_5C(H){=}C(H)$-$C(H){=}N{}^iPr$ as the solvent mainly **7c** is obtained [8]. This indicates that, in addition to the mononuclear **1**, this trinuclear cluster is one of the products ultimately formed in the reactions of $Ru_3(CO)_{12}$ with MAD ligands.

The isolation and characterization of mononuclear $Ru(CO)_2[CH_3C{=}C(H)$-$C(H){=}N{}^iPr]_2$ (**1a**) has provided a more detailed picture of the $Ru_3(CO)_{12}/R^1R^2$-MAD reaction sequence. The reactivity of the various ruthenium complexes so far isolated is being studied.

Acknowledgements

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