7 Å²). Individual weights were given as $w = 1/\sigma^2(F_o)$, where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (pI)^2]^{1/2}/L_p$, and p, the "ignorance factor", is equal to 0.04 for **1a** and to 0.05 for **2a**. Scattering factors and anomalous dispersion corrections were taken from ref 31. Although some of the thermal amplitudes of terminal carbonyls of compound **1a** even after the DIFABS correction show high anisotropy and a certain amount of along-bond motion (see Figure 2), it was decided to rely on the final fractional coordinates obtained in the anisotropic refinement, as suggested by Braga et al.[32] The small decrease of R_w (0.0469 vs 0.0437) on passing from isotropic to anisotropic carbonyls was however significant on the basis of Hamilton's test[33] at the 0.5% level, for 371 and 521 parameters, respectively. The two refinements showed slight differences in the Ir–C and C–O distances, with a systematic shortening of about 0.02 Å for the Ir–C ones in the isotropic case, due to a possible misplacement of the carbon atoms. A similar effect has been reported.[32b] Three peaks, refined with high (11–17 Å²) isotropic thermal parameters around a crystallographic inversion center in the unit cell of compound **1a** were interpreted as a cyclohexane molecule; an ordered THF molecule was located and refined in the unit cell of compound **2a**. All computations were performed on a PDP 11/73 computer using the SDP package[28] and the physical constants tabulated therein. The positional parameters for compounds **1a** and **2a** are listed in Tables VII and VIII, respectively.

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Registry No. 1, 134152-26-4; $1{\cdot}0.5C_6H_{12}$, 134208-29-0; **2**, 134131-36-5; $2{\cdot}C_4H_8O$, 134152-24-2; $[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$, 87525-25-5; $[NMe_3(CH_2Ph)]_2[Ir_6(CO)_{15}]$, 76540-42-6; $HgCl_2$, 7487-94-7; $Au(PPh_3)Cl$, 14243-64-2.

Supplementary Material Available: Tables A and E, listing anisotropic thermal parameters for **1a** and **2a**, Tables B and F, giving calculated fractional coordinates of the cation hydrogen atoms for **1a** and **2a**, and Tables D and H, listing distances and angles for **1a** and **2a** (26 pages); Tables C and G, listing structure factors for **1a** and **2a** (72 pages). Ordering information is given on any current masthead page.

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Cyclometalation of 1-Aza 1,3-Dienes in Reactions with $Ru_3(CO)_{12}$ with Formation of Four- and Five-Membered Azaruthenacycles[1]

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The dinuclear compounds $Ru_2(CO)_6[R^1CH_2CC(H)NR^2]$ (**2a–e**) and $Ru_2(CO)_6[R^1C{=}C(H)CH_2NR^2]$ (**3a,b,d**) are the first isolable products during thermal reactions of $Ru_3(CO)_{12}$ with 1-aza 1,3-dienes $R^1C(H){=}C(H)C(H){=}NR^2$ (R^1,R^2-MAD; R^1, R^2 = CH_3, *i*-Pr (**1a**), CH_3, c-Hex (**1b**), CH_3, *t*-Bu (**1c**), C_6H_5, *i*-Pr (**1d**), C_6H_5, *t*-Bu (**1e**)). Both primary products **2** and **3** contain an isomerized MAD ligand that is part of a four- (**2**) or five-membered (**3**) azaruthenacycle. The molecular structure of **3a** has been solved by X-ray crystallography: space group $P\bar{1}$, with a = 22.511 (4) Å, b = 13.740 (3) Å, c = 12.443 (2) Å, α = 103.21 (1)°, β = 113.00 (1)°, γ = 77.71 (1)°, V = 851.3 Å, Z = 2, and R = 0.027 (R_w = 0.042), for 2540 observed reflections. Compound **3a** contains a formally 6-electron donating enyl–amido ligand and is μ-N,σ-C_β,η^2-C=C-coordinated to a "sawhorse" $Ru_2(CO)_6$ core. In solution both **2** and **3** are stereochemically nonrigid, due to "windshield wiper" motions of the asymmetrically bridged amido ligands. This process is more facile for **2** ($\Delta G^* \approx 35$ kJ mol^{-1}) than for **3** ($\Delta G^* \approx 62$ kJ mol^{-1}), and the ΔG^* value for **3** was shown to be independent of the R^1 and R^2 substituents. In refluxing heptane **2** and **3** are converted into the linear 66-electron cluster $Ru_4(CO)_{10}[R^1C{=}C(H)C(H){=}NR^2]_2$ (**5a–e**), albeit conversion of **2** into **5** proceeded very slowly and incompletely. Conversion of **3** into **5** proceeds via the intermediacy of $(\mu\text{-H})Ru_2(CO)_5[R^1C{=}C(H)C(H){=}NR^2]$ (**4**), which air-sensitive compound could be observed and isolated for R^1, R^2 = C_6H_5, *i*-Pr (**4d**). Reaction of **3a,b** with CH_3,R^2-MAD or crotonaldehyde in heptane at 90 °C results in the formation of $Ru_2(CO)_6[CH_2CC(H)C(H){=}NR^2]$ (**6a,b**). During this conversion the coordinated ligand is dehydrogenated whereas the added substrate acts as a hydrogen acceptor. For crotonaldehyde it was shown that the olefin moiety was hydrogenated chemoselectively. The formation of **2** and **3** out of $Ru_3(CO)_{12}$ and R^1,R^2-MAD and their conversion into **4–6** are discussed.

Introduction

Transition-metal complexes containing a (hetero)-metallacyclopentadiene moiety (A–D) (Figure 1) have attracted attention throughout the years. Interest arises from (i) the versatile coordination behavior of metallacycles in di- and polynuclear compounds,[2] (ii) the electronic

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[1] Reactions of Monoazadienes with Metal Carbonyl Complexes. 4. Part 3: See ref 7.

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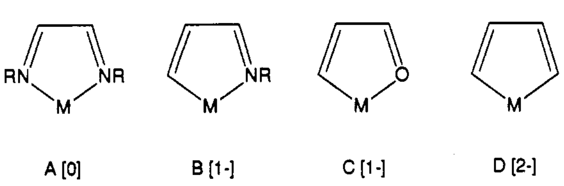

Figure 1. (Hetero)metallacyclopentadiene systems. The formal charge of the ligands is given between brackets.

properties within the metallacycle,[3] and (iii) the possibility of functionalizing the activated (hetero)diene.[4]

Compared to the other metallacycles shown in Figure 1, the azametallacyclopentadiene B has received relatively little attention. This is probably due to the lack of suitable synthetic pathways leading to such azametallacycles, the chemical potential of which is obvious. In the course of our study involving the coordination behavior of R-DAB (RN=C(H)C(H)=NR) in metal carbonyl complexes[2a] and the activation of this ligand toward C–C and C–N coupling reactions in the diazametallacycle A,[4h-k] we became interested in isoelectronic systems like the azaruthenacycle B. This prompted us to investigate the reactivity of conjugated 1-aza 1,3-dienes R^{1}C(H)=C(H)C(H)=NR^2 (R^1,R^2-MAD)[5] toward electron-rich transition metals, aiming at activation of the C$_\beta$–H bond of the MAD ligand and formation of the desired five-membered azametallacycle B.

Since coordinatively unsaturated zerovalent ruthenium centers are fairly reactive toward both inter- and intramolecular C–H activation,[6] we started our investigations with thermal reactions between Ru$_3$(CO)$_{12}$ and N-substituted crotonaldimines (CH$_3$,R^2-MAD). New di-,[7] tri-,[8] and tetranuclear[9,10] organometallic complexes containing one or two azaruthenacycles arising from metalation and isomerization or hydrogen abstraction of the parent CH$_3$,R^2-MAD have been isolated and characterized. It was found that the R^2 substituent on N has a large influence on the product distribution.[7,9] After the refluxing of Ru$_3$(CO)$_{12}$ and CH$_3$,R^2-MAD for 16 h in heptane, Ru$_4$(CO)$_{10}$[CH$_3$C=C(H)C(H)=NR^2]$_2$ (**5**) and Ru$_2$(CO)$_6$[CH$_2$CC(H)C(H)=NR^2] (**6**) were found to be the major products for R^2 = *i*-Pr and c-Hex.[7,9] For R^2 = *t*-Bu, however, only small amounts of **5** could be detected, whereas a considerable amount of the azaallyl compound Ru$_2$(CO)$_6$[CH$_3$CH$_2$CC(H)N-*t*-Bu] (**2c**) was formed.[7]

The tetranuclear complex Ru$_4$(CO)$_{10}$[CH$_3$C=C(H)C(H)=NR^2]$_2$ (**5**), containing two 7e-donating μ^2-η^4-CH$_3$C$^-$=C(H)C(H)=NR^2 ligands, represents a rare example of a cluster consisting of a linear array of four transition-metal atoms.[9] Each of these ligands is part of an η^5-coordinated azaruthenacyclopentadienyl ring, which is isolobally related to an η^5-coordinated cyclopentadienyl ring. The coordination of two such heterocycles to a central [Ru(CO)(μ-CO)]$_2$ unit led us to the conclusion that **5** is an isolobal analogue of [CpRu(CO)(μ-CO)]$_2$.[9]

Here we report on the complexes initially formed during thermal reactions of Ru$_3$(CO)$_{12}$ with R^{1}C(H)=C(H)C(H)=NR^2 (R^1,R^2-MAD; R^1, R^2 = CH$_3$, *i*-Pr (**1a**), CH$_3$, c-Hex (**1b**), CH$_3$, *t*-Bu (**1c**), C$_6$H$_5$, *i*-Pr (**1d**), C$_6$H$_5$, *t*-Bu (**1e**)) and on their conversions into **5** and **6**. The isolation and characterization of Ru$_2$(CO)$_6$[R^{1}C=C(H)CH$_2$NR^2] (**3**), which complex appears to be the main precursor of **5**, as well as its isolobal relation to (η^4-C$_5$H$_6$)M(CO)$_3$ and its fluxional behavior in solution, will be considered in detail. We will also show that the reaction steps involved in the formation of **5** resemble those of the formation of [CpRu(CO)(μ-CO)]$_2$.[11]

Experimental Section

Materials and Apparatus. Solvents were carefully dried and distilled prior to use. All preparations were carried out under an atmosphere of dry nitrogen by using Schlenk techniques. Silica gel for column chromatography (kieselgel 60, 70–230 mesh, E. Merck, Darmstadt, Germany) was dried before use. Ru$_3$(CO)$_{12}$ was used as purchased from Strem Chemicals, Inc. (^{13}C)Carbon monoxide (99.7 atom % ^{13}C) was obtained from MSD Isotopes and used as received. The monoazadienes R^1,R^2-MAD (R^1, R^2 = CH$_3$, *i*-Pr (**1a**), CH$_3$, c-Hex (**1b**), CH$_3$, *t*-Bu (**1c**), C$_6$H$_5$, *i*-Pr (**1d**), C$_6$H$_5$, *t*-Bu (**1e**)) have been prepared according to standard procedures.[12]

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[5] MAD is used as acronym for monoaza dienes in general. In this paper we will use R^1,R^2-MAD when *N*-alkyl-(*E*)-crotonaldimines CH$_3$C(H)=C(H)C(H)=NR^2 or *N*-alkyl-(*E*)-cinnamaldimines C$_6$C$_5$C(H)=C(H)C(H)=NR^2 are meant.[22] These ligands may be metalated at the vinyl moiety, thus forming a formal monoanionic aza dienyl (R^1,R^2-MAD-yl) ligand R^{1}C(H)=C$^-$C(H)=NR^2 or R^{1}C$^-$=C(H)C(H)=NR^2, the latter giving the azametallacyclopentadiene B when chelating a metal center.

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^{1}H and ^{13}C{^{1}H} NMR spectra were obtained on Bruker AC100 and WM250 spectrometers. IR spectra were recorded with Perkin-Elmer 283 and Nicolet 7199 B FT-IR spectrophotometers using a matched NaCl solution cell of 0.5-mm path length. Field desorption (FD) and field ionization (FI) mass spectra[13] were obtained with a Varian MAT-711 double-focusing mass spectrometer with a combined EI/FI/FD source, fitted with a 10-μm tungsten wire FD-emitter containing carbon microneedles with an average length of 30 μm, using emitter currents of 0–15 mA. The ion source temperature was generally 50–130 °C. Elemental analyses were carried out by the Elemental Analysis Section of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands. HPLC separations were carried out on a Nicolet 100082 B chromatographic system equipped with a 10-μL sample loop and an analytical Hypersil ODS 5-μm column (100 × 4.8 mm), which was purchased from Hewlett-Packard. Detection of the products was performed with an UV detector operating at 254 nm. Small samples (ca. 0.5 mL) taken from reactions between $Ru_3(CO)_{12}$ and R^1,R^2-MAD (**1a**,**c**) were evaporated to dryness and dissolved in 0.1 mL of dichloromethane whereafter 2 mL of MeOH was added. These samples were subsequently filtered over a disposable PTFE syringe filter (25-mm membranes; pore size 0.45 μm) before they were passed through the HPLC column using isocratic $MeOH/H_2O$ (**1a**, 90/10; **1c**, 87/13) as the mobile phase (2 mL/min).

Synthesis of $Ru_2(CO)_6[CH_3CH_2CC(H)NR^2]$ (R^2 = *i*-Pr (2a), c-Hex (2b)) and $Ru_2(CO)_6[CH_3C{=}C(H)CH_2NR^2]$ (R^2 = *i*-Pr (3a), c-Hex (3b)). A solution of $Ru_3(CO)_{12}$ (0.64 g, 1.0 mmol) and CH_3,R^2-MAD (**1a**,**b**; 2.0 mmol) in 50 mL of heptane was stirred at reflux during 1 h (or at 100 °C during 5 h). The reaction was monitored by IR spectroscopy and stopped when the ν(CO) pattern of $Ru_3(CO)_{12}$ had disappeared. The solvent was removed under vacuum and the orange residue purified by chromatography on silica. Elution with hexane gave two bands. The first pale yellow band afforded $Ru_2(CO)_6[CH_3C{=}C(H)CH_2NR^2]$ (**3a**,**b**; ca. 50%) as oils after removal of the eluent under vacuum. The second less mobile yellow band produced small amounts of $Ru_2(CO)_6[CH_2CC(H)C(H){=}NR^2]$ (**6a**,**b**), as was indicated by IR and ^{1}H NMR spectroscopy. Subsequent elution with hexane/dichloromethane (9:1) gave yellow/green (*i*-Pr) or yellow (c-Hex) $Ru_2(CO)_6[CH_3CH_2CC(H)NR^2]$ (**2a**,**b**; ca. 25%) as oils after removal of the eluent. For **2a** crystallization was achieved by cooling a concentrated ethanol solution at −80 °C. For **2b** all attempts to crystallize the oily material failed, and therefore, although spectroscopically pure, a satisfactory microanalysis of **2b** could not be obtained. Product **3a** was recrystallized from ethanol at −30 °C, yielding pale yellow crystals suitable for X-ray analysis. Anal. Found (calcd) for $C_{13}H_{13}NO_6Ru_2$ (**2a**): C, 32.35 (32.44); H, 2.75 (2.72); N, 2.92 (2.91). FD mass for **2a**: m/e = 481 (M, 481) and less intense m/e = 452 (M − CO, 453).[14] FD mass for $C_{16}H_{17}NO_6Ru_2$ (**2b**): m/e = 521 (M, 521). Found (calcd) for $C_{13}H_{13}NO_6Ru_2$ (**3a**): C, 32.24 (32.44); H, 2.72 (2.72); N, 2.91 (2.91). FD mass for **3a**: m/e = 481 (M, 481).[14] Found (calcd) for $C_{16}H_{17}NO_6Ru_2$ (**3b**): C, 36.80 (36.85); H, 3.13 (3.29); N, 2.64 (2.69). FD mass for **3b**: m/e = 521 (M, 521).[14]

Synthesis of $Ru_2(CO)_6[CH_3CH_2CC(H){=}N\text{-}t\text{-}Bu]$ (2c) and $Ru_2(CO)_6[CH_2CC(H)C(H)N\text{-}t\text{-}Bu]$ (6c) at Various Temperatures. A solution of $Ru_3(CO)_{12}$ (0.32 g, 0.5 mmol) and CH_3,*t*-Bu-MAD (**1c**, 1.5 mmol) in 40 mL of heptanes was immersed into a hot oil bath of 125 °C and stirred at reflux during 8 h. The reaction mixture was then cooled to ambient temperature and filtered over silica. After removal of the solvent under vacuum the yellow residue was examined by ^{1}H NMR spectroscopy ($CDCl_3$), showing the presence of two components, **2c** and **6c**, in a relative ratio of about 2:1.

When the reaction was performed at 95 °C during 72 h and worked up similarly, the ratio **2c**:**6c** amounted to 1:2. These yellow products could be separated and isolated as described before,[7] yielding **2c** (50%) and **6c** (30%) from the high-temperature reaction and **2c** (25%) and **6c** (55%) from the low-temperature reaction.

Synthesis of $Ru_2(CO)_6[C_6H_5CH_2CC(H)N\text{-}i\text{-}Pr]$ (2d) and $Ru_2(CO)_6[C_6H_5C{=}C(H)CH_2N\text{-}i\text{-}Pr]$ (3d). A solution of $Ru_3(CO)_{12}$ (0.64 g, 1.0 mmol) and C_6H_5,*i*-Pr-MAD (**1d**; 0.29 g, 1.7 mmol) in 50 mL of heptanes was stirred at 100 °C for 5 h. The solution was cooled to ambient temperature, and a small amount of a red precipitate (**5d**) was removed by filtration. The solution was evaporated to dryness, and the components present in the residue were separated by chromatography on silica. Elution with hexane afforded a yellow fraction, from which crystalline **3d** was obtained in 70% yield after evaporation of the solvent. Subsequent elution with hexane/dichloromethane (9:1) gave a red/brown fraction containing a mixture of yellow **2d** and a small amount of an as yet unidentified purple product. After reduction of the volume of the eluent to 5 mL, cooling at −80 °C resulted in the precipitation of **2d** (20%). Further elution with dichloromethane gave a small red band, which contained a small amount of **5d**. Anal. Found (calcd) for $Ru_2C_{18}H_{15}NO_6$ (**2d**): C, 39.48 (39.78); H, 2.63 (2.78); N, 2.68 (2.58). FD mass for **2d**: m/e = 543 (M, 543).[14] Found (calcd) for $Ru_2C_{18}H_{15}NO_6$ (**3d**): C, 39.76 (39.78); H, 2.79 (2.78); N, 2.61 (2.58). FD mass for **3d**: m/e = 543 (M, 543).[14]

Synthesis of $Ru_2(CO)_6[C_6H_5CH_2CC(H)N\text{-}t\text{-}Bu]$ (2e) and $Ru_4(CO)_{10}[C_6H_5C{=}C(H)C(H){=}N\text{-}t\text{-}Bu]_2$ (5e). A solution of $Ru_3(CO)_{12}$ (0.64 g, 1.0 mmol) and C_6H_5,*t*-Bu-MAD (**1e**; 0.21 g, 1.7 mmol) in 50 mL of heptanes was stirred at reflux. After 20 h, the red solution was cooled at ambient temperature and the yellow precipitate of $Ru_4(CO)_{10}[C_6H_5C{=}C(H)C(H){=}N\text{-}t\text{-}Bu]_2$ (**5e**; 60%)[15] was isolated by filtration. The remaining solution was chromatographed on silica. Elution with hexane afforded a yellow band of $Ru_2(CO)_6[C_6H_5CH_2CC(H)N\text{-}t\text{-}Bu]$ (**2e**; 20%). Subsequent elution with hexane/dichloromethane (9:1) gave a small amount (5–10%) of $Ru_2(CO)_6[C_6H_5CC(H)C(H)N(H)t\text{-}Bu]$. Further elution with dichloromethane produced a red band containing products that have not been characterized. Anal. Found (calcd) for $Ru_2C_{19}H_{17}NO_6$ (**2e**): C, 40.56 (40.93); H, 2.93 (3.08); N, 2.68 (2.51). FI mass for **2e**: m/e = 557 (M, 557).[14] Found (calcd) for $Ru_4C_{36}H_{32}N_2O_{10}$ (**5e**): C, 40.69 (40.91); H, 3.37 (3.05); N, 2.42 (2.65).

Synthesis of (μ-H)$Ru_2(CO)_5[C_6H_5C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ (4d). A solution of $Ru_2(CO)_6[C_6H_5C{=}C(H)CH_2N\text{-}i\text{-}Pr]$ (**3d**; 0.41 g, 0.75 mmol) in 50 mL of heptanes was stirred at reflux during 0.5 h. The residue remaining after removal of the solvent under vacuum was chromatographed on silica. Elution with hexane gave unreacted starting material **3d** (0.28 g, 0.52 mmol). Subsequent elution with hexane/dichloromethane (4:1) gave a mixture of $HRu_2(CO)_5[C_6H_5C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ (**4d**) and $Ru_2(CO)_6[C_6H_5CC(H)C(H)N(H)i\text{-}Pr]$. The solvent of this fraction was removed under vacuum, the residue was dissolved in 5 mL of hexane, and the solution was cooled at −30 °C. After 3 days the small crystals of **4d** (0.07 g, 0.14 mmol; 60% (based on converted **3d**)) formed were isolated and recrystallized from hexane to afford regular-shaped orange crystals of **4d**, one of which was selected for an X-ray crystal structure determination.[16] Anal. Found (calcd) for $Ru_2C_{17}H_{14}NO_5$ (**4d**): C, 39.30 (39.69), H, 2.57 (2.75), N, 2.79 (2.72). FD mass for **4d**: m/e = 515 (M, 515).[14]

Synthesis of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}t\text{-}Bu]_2$ (5c). Satisfactory yields of this cluster could not be obtained by using the method described for the *i*-Pr and c-Hex analogues.[9] Therefore, another method has been developed to prepare **5c**.

A solution of $CH_3C(H){=}C(H)C(H){=}N\text{-}t\text{-}Bu$ (**1c**; 0.17 g, 1.36 mmol) in 10 mL of heptane was slowly added (over a period of 2 h) to a stirred solution of $Ru_3(CO)_{12}$ (0.5 g, 0.78 mmol) in 50 mL of refluxing heptane. After this solution was refluxed for another 4 h, the reaction mixture was cooled to ambient temperature and chromatographed on silica, first employing hexane and then hexane/dichloromethane (1:1) as the eluent. The yellow hexane fraction contained both $Ru_2(CO)_6[CH_3CH_2CC(H)N\text{-}t\text{-}Bu]$ (**2c**) and $Ru_2(CO)_6[CH_2CC(H)C(H){=}N\text{-}t\text{-}Bu]$ (**6c**), which could be separated as described before.[7] The orange-red hexane/dichloromethane fraction was concentrated to 20 mL and then

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[13] Barany, H. C.; Braude, E. A.; Pianka, M. *J. Chem. Soc.* **1949**, 1898.

[14] Based on that peak of the isotopic pattern of the molecular ion that corresponded to ^{101}Ru; calculated value in parentheses.

[15] ^{1}H NMR spectroscopy indicated that this yellow precipitate of **5e** consisted of one diastereomer, whereas this product may be formed as a mixture of two diastereomers, (CC/AA)-**5e** and (CA/AC)-**5e**.[24]

[16] Spek, A. L.; Duisenberg, A. J. M.; Mul, W. P.; Beers, O. C. P.; Elsevier, C. J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, in press.

cooled at −80 °C. This afforded pure $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}t\text{-}Bu]_2$ (**5c**) (two diastereomers) in about 30% yield. Anal. Found (calcd) for $C_{26}H_{28}N_2O_{10}Ru_4$ (**5c**): C, 33.27 (33.48); H, 3.03 (3.03); N, 3.01 (3.00). FD mass for **5c**: m/e = 932 (M, 933).[14]

Synthesis of $Ru_4(CO)_{10}[C_6H_5C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (5d). A solution of $Ru_3(CO)_{12}$ (0.64 g, 1.0 mmol) and C_6H_5,i-Pr-MAD (**1d**; 1.75 mmol) in 50 mL of heptanes was stirred at reflux. After 20 h, the red solution was cooled at ambient temperature and the red precipitate collected. This solid was washed with dichloromethane (3 portions of 20 mL), affording the red isomer[17] of **5d** in a yield of ca. 70%. The solution and the combined washings were chromatographed on silica. Elution with hexane gave a yellow fraction containing $H_4Ru_4(CO)_{12}$ as the main component. Subsequent elution with dichloromethane afforded an orange-red fraction from which **5d** (10%; mainly the orange isomer)[17] precipitated upon cooling at −30 °C. Anal. Found (calcd) for $Ru_4C_{34}H_{28}N_2O_{10}$ (**5d**): C, 38.65 (39.69); H, 2.69 (2.75); N, 2.39 (2.72). FD mass for **5d**: m/e = 1020–1035 (M, 1028).[14]

Thermolysis of $Ru_2(CO)_6[R^1C{=}C(H)CH_2NR^2]$ (3a–d). i. Open System. A heptane solution (30 mL) of **3a–d** (0.2–0.3 mmol) was refluxed for about 4 h (**3a**), 24 h (**3b**), 2 h (**3c**), or 8 h (**3d**), times necessary to replace the ν(CO) patterns of **3a–d** by those of $Ru_4(CO)_{10}[R^1C{=}C(H)C(H){=}NR^2]_2$ (**5a–d**), respectively. Cooling at −80 °C resulted in the precipitation of **5a–d** (two diastereomers) in almost quantitative yields (80–90%).

ii. Closed System. Thermolysis of **3a** in heptane, as described above, was also performed in a sealed Schlenk tube. ^1H NMR spectra of the concentrated reaction mixture in $CDCl_3$ revealed not only the presence of **5a** but also that of **6a** and $H_2Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ in relative amounts of 3:1:1, respectively.

iii. Under CO. When the reaction was performed under an atmosphere of carbon monoxide, only a very slow decomposition was observed, with formation of products that have not further been identified. No formation of **5a–d** was observed.

Thermolysis of $Ru_2(CO)_6[CH_3CH_2CC(H)NR^2]$ (2a–c). i. Open System. A heptane solution of **2a–c** (0.3 mmol) was refluxed for about 48 h. ^1H NMR spectroscopy of the concentrated reaction mixture in $CDCl_3$ revealed the presence of two isomeric forms of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}NR^2]_2$ (**5a–c**) (together about 50%) together with unreacted **2a–c** (about 25%) and small amounts of $Ru_2(CO)_6[CH_2CC(H)C(H){=}NR^2]$ (**6a–c**; <5%), $H_2Ru_4(CO)_8[CH_3C{=}C(H)C(H){=}NR^2]_2$ (R^2 = i-Pr, c-Hex; <5%), and $Ru_3(CO)_6[CH_3C{=}C(H)C(H){=}NR^2]_2$ (R^2 = i-Pr, c-Hex; <5%).

ii. Under CO. When the same reaction was carried out under an atmosphere of carbon monoxide a slow decomposition reaction was observed leading to products that have not further been identified. No formation of **5a–c** was observed.

Reaction of $Ru_2(CO)_6[CH_3C{=}C(H)CH_2NR^2]$ (3a,b) with $CH_3C(H){=}C(H)C(H){=}NR^2$ (1a,b). A solution of **3a** or **3b** (0.4 mmol) and CH_3,i-Pr-MAD (**1a**, 1 mmol) or CH_3,c-Hex-MAD (**1b**, 1 mmol), respectively, in 20 mL of heptanes was stirred at 90 °C for about 16 h. The solvent was evaporated, the residue was dissolved in diethyl ether, and the mixture was filtered over silica (to remove excess and decomposition produts of **1a,b**). ^1H NMR spectra of the concentrated eluent in $CDCl_3$ showed the presence of $Ru_2(CO)_6[CH_2CC(H)C(H){=}NR^2]$ (**6a,b**) as the main product, together with small amounts of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}NR^2]_2$ (**5a,b**) and uncharacterized products. Pure **6a,b** could be isolated as described before in about 75% yield.[7]

Reaction of $Ru_2(CO)_6[CH_3C{=}C(H)CH_2N\text{-}i\text{-}Pr]$ (3a) with (*E*)-Crotonaldehyde. A solution of **3a** (0.31 mmol) and (*E*)-crotonaldehyde (0.27 mmol) in 2.5 mL of toluene-d_8 was stirred at 90 °C for 16 h. The reaction mixture was cooled at room temperature, and the volatile components were isolated by slow evaporation into a cold (−80 °C) Schlenk tube under reduced pressure. ^1H NMR spectra showed n-butyraldehyde to be the main organic product (>90%). ^1H NMR (δ in ppm relative to Me_4Si, toluene-d_8, 293 K, 250 MHz): 9.22 (tr, ^3J = 2.0 Hz, 1 H), 1.69 (d tr, ^3J = 2.0 Hz, ^3J = 9.0 Hz, 2 H), 1.24 (tr q, ^3J = 9.0 Hz, ^3J = 9.0 Hz, 2 H), 0.63 (tr, ^3J = 9.0 Hz, 3 H). This spectrum matched an ^1H NMR spectrum of pure n-butyraldehyde in toluene-d_8. Workup of the nonvolatile residue by chromatography on silica[7] gave **6a** in a yield of 70%.

Reaction of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (5a) with 1a. A solution of **5a** (0.2 mmol) and CH_3,i-Pr-MAD (**1a**; 1.0 mmol) in 20 mL of heptanes was stirred at 90 °C for 16 h. The reaction mixture was evaporated to dryness, the residue dissolved in diethyl ether, and the mixture was filtered over silica (to remove excess and decomposition products of **1a**). ^1H NMR spectroscopy in $CDCl_3$ showed the presence of a plethora of organometallic derivatives including small amounts of **6a** and starting material **5a**. This implies that the conversion of **3a** into **6a** in a reaction with monoazadiene **1a** does not proceed via the intermediacy of **5a**.

Enrichment of $Ru_2(CO)_6[CH_3C{=}C(H)CH_2N\text{-}i\text{-}Pr]$ (3a) with ^{13}CO. A hexane solution (20 mL) of **3a** (197 mg, 0.41 mmol) was stirred at 55 °C for 40 h in a sealed tube (200 mL) under an atmosphere of nitrogen containing carbon (^{13}C)carbon monoxide (25 mL, 1.1 mmol). The enrichment was estimated to be about 10%, on the basis of the relative intensities of the CO signals in ^{13}C spectra (263 K) of the ^{13}CO-enriched compound and the compound containing CO of natural abundance.

X-ray Structure Analysis of $Ru_2(CO)_6[CH_3C{=}C(H)CH_2N\text{-}i\text{-}Pr]$ (3a). Crystals of the title compound are triclinic, space group $P\bar{1}$, with 2 formula units $C_{13}H_{13}Ru_2NO_6$ in a unit cell of dimensions a = 22.511 (4), b = 13.740 (3), and c = 12.443 (2) Å and α = 103.21 (1), β = 113.00 (1), and γ = 77.71 (1)°. V = 851.3 Å^3, D_{calc} = 1.88 g·cm^{-3}, and μ(Cu Kα) = 149.7 cm^{-1}. Of the 5782 intensities ($2.5 \leq \theta \leq 55°$; $-9 \leq h \leq 10$, $-13 \leq k \leq 13$, $-10 \leq l \leq 0$) measured at −20 °C on an Enraf-Nonius CAD4F diffractometer employing graphite-monochromated Cu Kα radiation, 3242 intensities were below the $2.5\sigma(I)$ level and were treated as unobserved. The dimensions of the crystal were 0.20 × 0.20 × 0.15 mm. The structure was solved by using the symbolic addition program system SIMPEL,[18] which yielded the positions of both Ru atoms and part of the rest of the structure, which was completed by means of subsequent difference Fourier syntheses. Refinement proceeded through block-diagonal least-squares calculations, anisotropic for Ru, C, N, and O and isotropic for H. The H atoms were located in a ΔF synthesis. A weighting scheme $w = 1/(9.5 + F_o + 0.0097F_o^2)$ was employed, while an empirical absorption correction (DIFABS)[19] and an extinction correction were applied. The anomalous dispersion of Ru was taken into account. The final R value was 0.027 for 2540 observed reflections (R_w = 0.042). The programs used, apart from SIMPEL, were from XRAY76.[20] The scattering factors were taken from ref 21.

Spectroscopic Data. The IR (ν(CO) region), ^1H NMR, and ^{13}C NMR data for all new complexes are listed in Tables I–III.

Results

Formation of the Complexes. The formation of products resulting from reactions between $Ru_3(CO)_{12}$ and $R^1C(H){=}C(H)C(H){=}NR^2$ (R^1,R^2-MAD; R^1, R^2 = CH_3, i-Pr (**1a**), CH_3, c-Hex (**1b**), CH_3, t-Bu (**1c**), C_6H_5, i-Pr (**1d**), C_6H_5, t-Bu (**1e**)) depends on the reaction temperature, the reaction time, the ratio $Ru_3(CO)_{12}$:R^1,R^2-MAD, and the R^1 and R^2-substituents.

Reactions of $Ru_3(CO)_{12}$ (1 mmol) with **1a**, **1b**, or **1d** (2 mmol) in refluxing heptane proceed readily to give two isomeric dinuclear compounds $Ru_2(CO)_6[R^1CH_2CC(H)$-

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[17] As shown for **5a**,[25] it is possible to discriminate between the four stereoisomeric configurations on the basis of their different IR patterns in the ν(CO) region (in solid state; KBr). An IR spectrum (in KBr) of the red diastereomer of **5d** showed five absorptions of approximately equal intensity: 2063, 2016, 1982, 1945, and 1770 cm^{-1}. This clearly indicates that the red diastereomer of **5d** has the *trans*-(CA/AC) configuration in the solid state. Hence, the orange diastereomer is (CC/AA)-**5d**. For a detailed discussion about the geometric and spectroscopic properties of the four diastereomers of **5a**, see ref 25.

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[20] Stewart, J. M. The XRAY76 system. Technical Report TR466; Computer Science Center, University of Maryland: College Park, MD, 1976.

[21] *International Tables for X-ray Crystallography*; Kynoch Press: Brimingham, England, 1974; Vol. IV.

Table I. IR Data[a] for $Ru_2(CO)_6[R^1CH_2CC(H)NR^2]$ (2a,b,d,e), $Ru_2(CO)_6[R^1C{=}C(H)CH_2NR^2]$ (3a,b,d), $HRu_2(CO)_5[R^1C{=}C(H)C(H){=}NR^2]$ (4d), and $Ru_4(CO)_{10}[R^1C{=}C(H)C(H){=}NR^2]_2$ (5c–e) (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))

compd	ν(CO), cm^{-1}					
2a	2076 (m)	2043 (vs)	2003 (s)	1991 (s)	1980 (m)	
2b	2075 (m)	2042 (vs)	2002 (s)	1990 (s)	1979 (m)	
2d	2076 (m)	2044 (s)	2008 (s)	1993 (s)	1984 (vw)	1979 (w)
2e	2075 (m)	2044 (vs)	2003 (s)	1992 (s)	1984 (vw)	1978 (w)
3a	2075 (m)	2046 (vs)	2000 (s)	1996 (s)	1986 (w)	1979 (m)
3b	2076 (m)	2046 (vs)	1999 (s)	1995 (s)	1985 (w)	1978 (m)
3d	2077 (m)	2049 (vs)	2001 (s)	1998 (s)	1990 (m)	1980 (w)
4d	2085 (m)	2018 (m)	2007 (vs)	1946 (m)		
5c	2064 (vs)	2002 (m)	1991 (vs)	1951 (w)	1768 (m)	
5d[b]	2071 (vs)	2005 (sh)	1997 (vs)	1943 (vw)	1770 (m)	
5e[c]	2067 (vs)	2003 (sh)	1993 (vs)	1770 (m)		

[a] Measured in hexane; for IR data for compounds **2c**, **5a**,**b**, and **6a–c** see refs 7, 9, and 26a. [b] In dichloromethane. [c] In tetrahydrofuran.

Table II. **^1H *NMR Data[a] for* $R^1C(H){=}C(H)C(H){=}NR^2$ (1c–e), $Ru_2(CO)_6[R^1CH_2CC(H)NR^2]$ (2a,b,d,e), $Ru_2(CO)_6[R^1C{=}C(H)CH_2NR^2]$ (3a,b,d), $HRu_2(CO)_5[R^1C{=}C(H)C(H){=}NR^2]$ (4d), and $Ru_4(CO)_{10}[R^1C{=}C(H)C(H){=}NR^2]_2$ (5c–e) (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))**

compd	$H_{im/am}$	H_α	H_β	R^1	R^2
1c	7.74 (d, 7.0)	6.17 (m)	6.10 (m)	1.78 (d, 5.0)	1.11 (s)
1d	8.05 (dd, 5.0; 3.5)	6.90 (m)	6.90 (m)	7.49–7.26 (m)	3.41 (sept, 6.5), 1.23 (d, 6.5)
1e	8.01 (dd, 5.0, 3.5)	6.90 (m)	6.90 (m)	7.41–7.28 (m)	1.24 (s)
2a	6.90 (s)		2.40 (q, 7.5)	1.07 (t, 7.5)	2.39 (sept, 6.0), 0.89 (d, 6.0)
2b	6.92 (s)		2.41 (q, 7.5)	1.08 (t, 7.5)	2.0–0.8 (br m)
2d	6.76 (s)		3.87 (s)	7.25–7.15 (m)	2.61 (sept, 6.5), 1.05 (d, 6.5)
2e	6.78 (s)		3.62 (s)	7.27–7.23 (m)	0.91 (s)
3a[b]	3.77 (br s)	4.96 (br s)		2.51 (d, 0.6)	2.55 (sept, 6.5), 1.02 (d, 6.5)
3a[c]	3.76 (dd, 9.0; 2.5), 3.68 (d, 9.0)	4.93 (br s)		2.48 (d, 0.6)	2.50 (sept, 6.5), 1.05/0.94 (d, 6.5)
3b	3.75 (br s)	4.91 (br s)		2.48 (d, 0.6)	2.0–0.8 (br m)
3d[d]	3.87 (br s)	5.28 (tr, 1.6)		7.25–7.15 (m)	2.61 (sept, 6.5); 1.05 (d, 6.5)
3d[e]	3.94 (dd, 9.1; 2.5), 3.72 (d, 9.1)	5.27 (d, 2.5)		7.25–7.15 (m)	2.56 (sept, 6.5), 1.10/0.97 (d, 6.5)
4d[f]	6.08 (d, 2.0)	5.84 (d, 2.0)		7.10–6.90 (m)	2.20 (sept, 6.5), 0.61/0.56 (d, 6.5), –9.66 (s, hydride)
5c[g]	7.10 (br s)	5.10 (br s)		2.61 (s)	1.38 (s)
5c[g]	7.25 (br s)	5.05 (br s)		2.51 (s)	1.38 (s)
5d[h]	6.92 (d, 2.0)	5.54 (d)		7.26 (s)	3.55 (sept, 6.5), 1.31/1.23 (d, 6.5)
5d[i]	6.61 (d, 2.0)	5.62 (d, 2.0)		7.30–7.20 (m)	3.40 (sept, 6.5), 1.26/0.92 (d, 6.5)
5e[k]	7.45 (br s)	5.47 (br s)		7.30–6.90	1.48 (s)

[a] Measured in $CDCl_3$, 100 MHz, 298 K (unless stated otherwise); δ values in ppm relative to Me_4Si. Diastereotopic pairs separated by a solidus (/). Suffixes to the atoms refer to $R^1C(H_\beta)_nC(H_\alpha)_nC(H_{im/am})_nNR^2$ (n = 0, 1, 2). In parentheses: multiplicity, J(H,H) (Hz). For ^1H data for the compounds **1a**,**b**, **2c**, **5a**,**b** and **6a–c** see refs 7, 9, and 26a. [b] 250.1 MHz, 323 K. [c] 250.1 MHz, 263 K. [d] 250.1 MHz, 313 K. [e] 250.1 MHz, 243 K. [f] In C_6D_6. [g] One of the diastereomers. [h] Red diastereomer (less soluble).[17] [i] Orange diastereomer.[17] [k] In CD_2Cl_2; only one diastereomer observed.[15]

Table III. ^{13}C NMR Data[a] for $R^1C(H){=}C(H)C(H){=}NR^2$ (1c–e), $Ru_2(CO)_6[R^1CH_2CC(H)NR^2]$ (2a,b,d,e), $Ru_2(CO)_6[R^1C{=}C(H)CH_2NR^2]$ (3a,b,d), $HRu_2(CO)_5[R^1C{=}C(H)C(H){=}NR^2]$ (4d), and $Ru_4(CO)_{10}[R^1C{=}C(H)C(H){=}NR^2]_2$ (5c–e) (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))

compd	$C_{im/am}$	C_α	C_β	R^1	R^2	CO's
1c[b]	157.4	139.8	133.1	18.4	56.7, 29.8	
1d[b]	160.1	141.3	136.1	129.2, 129.0, 128.7, 127.3	61.4, 24.4	
1e[b]	157.4	141.1	136.2	129.6, 129.1, 129.0, 127.3	57.3, 29.9	
2a	108.1	142.2	31.1	17.1	56.2, 26.0	197.4
2b	108.3	141.6	31.1	17.1	37.6, 25.5, 25.3	197.5
2d	109.5	140.8	44.0	135.2, 128.9, 126.8, 124.5	56.2, 26.1	197.2
2e	108.0	140.9	44.0	134.8, 128.9, 126.8, 124.5	55.5, 30.5	197.2
3a	63.4	77.9	186.3	34.5	63.6, 24.7/22.4	200.5, 199.2, 197.8, 196.2, 194.2, 194.0
3b	65.6	78.2	186.4	34.8	72.3, 36.7/34.5, 26.4/26.1, 26.1	200.8, 199.4, 198.1, 196.5, 194.6, 194.4
3d	64.9	76.1	188.8	149.2, 129.4, 128.0, 127.7	63.9, 25.0/22.7	200.0, 199.9, 197.6, 196.8, 194.8, 194.4
4d[c]	112.1	105.1	155.4	150.5, 128.4, 128.3, 126.6	63.3; 28.1/24.6	204.9, 204.1, 195.8, 191.4, 191.2
5c[d]	128.9	102.6	196.5	32.5	63.2, 33.8	*e*
	128.4	102.2	196.5	32.3	63.1, 33.7	

[a] Measured in $CDCl_3$, 25.0 MHz, 263 K (unless stated otherwise); chemical shift values in ppm relative to Me_4Si. Suffixes to atoms refer to $R^1C_\beta(H)_nC_\alpha(H)_nC_{im/am}(H)_nNR^2$ (n = 0, 1, 2). Diastereotopic pairs separated by a solidus (/). For ^{13}C data for the compounds **1a**,**b**, **2c**, **5a**,**b**, and **6a–c** see refs 7, 9, and 26a. [b] In $CDCl_3$, 298 K. [c] In CD_2Cl_2, 62.9 MHz. [d] In CD_2Cl_2, 283 K, 2 diastereomers. [e] Not observed.

$NR^2]$ (**2a**,**b**,**d**) and $Ru_2(CO)_6[R^1C{=}C(H)CH_2NR^2]$ (**3a**,**b**,**d**), as the first isolable products. The ratio **2**:**3** formed (1:2 for **a**, **b** and 1:3.5 for **d**) was independent of the reaction temperature over the range 90–120 °C, although their formation at 90 °C (24 h) proceeded considerable slower than at 120 °C (<1 h).

Both **2** and **3** contain a 6e-donating isomerized R^1,R^2-MAD ligand formed after metalation of one of the vinylic C atoms (C_α or C_β)[22] and migration of the abstracted H atom via a formal 1,2-hydrogen shift from C_α to C_β (**2**) or 1,3-hydrogen shift from C_β to C_{im} (**3**) on the R^1,R^2-MAD skeleton. In complex **2**, the structure of which is based on an X-ray analysis of **2c**,[7] a four-membered azaruthenacycle

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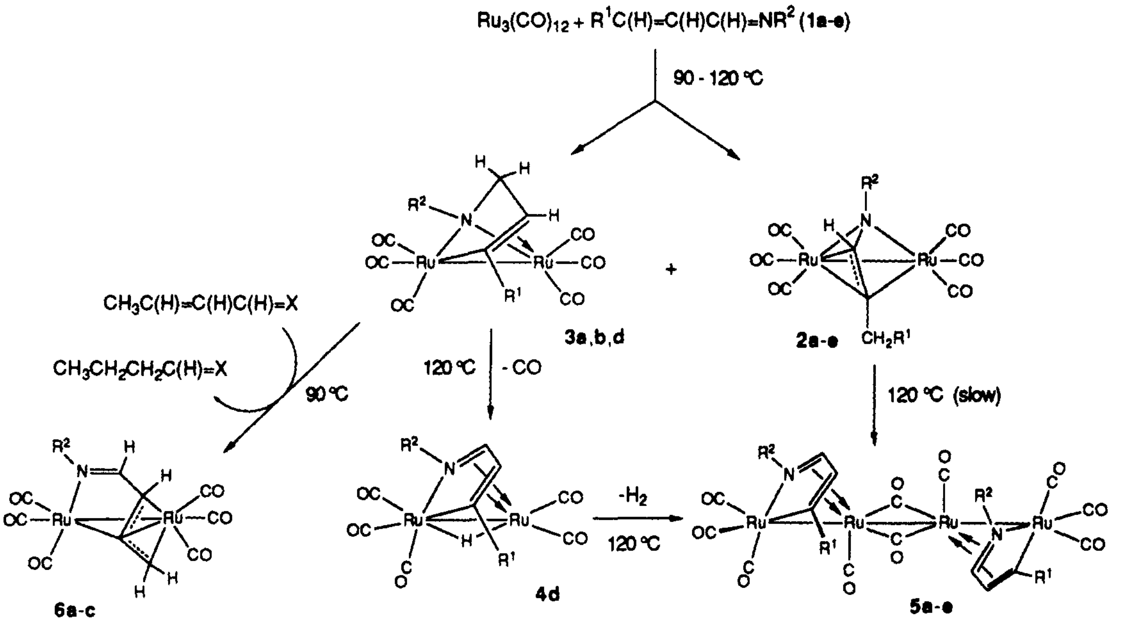
[22] Suffixes to the atoms refer to $R^2N{=}C(H)_{im}C(H)_\alpha{=}C(H)_\beta R^1$.

Scheme I. Known Products and Intermediates from the Reaction of $Ru_3(CO)_{12}$ and $R^1C(H){=}C(H)C(H){=}NR^2$ (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))



can be discerned with bonding interactions of all four atoms to a second ruthenium atom. Complex 3 contains a five-membered azaruthenacyclopentenyl system, of which four atoms are bonded to a ruthenium tricarbonyl unit. The molecular structure of **3a** will be described in detail further below.

In refluxing heptane the initially formed dinuclear complexes **2a–c** and **3a,b,d** are converted into the linear tetranuclear complex $Ru_4(CO)_{10}[R^1C{=}C(H)C(H){=}NR^2]_2$ (**5a–d**), although conversion of **2a–c** proceeds very slowly (48 h) and incompletely with concomitant formation of several byproducts. The conversion of **3** to **5**, which takes 2–8 h, proceeds via the intermediate $(\mu\text{-H})Ru_2(CO)_5[R^1C{=}C(H)C(H){=}NR^2]$ (**4**), which air-sensitive complex has been observed in the case of R^1, R^2 = C_6H_5, *i*-Pr (**4d**)[23] and could be isolated from the reaction mixture (by column chromatography on silica) obtained after refluxing **3d** in heptane for 0.5 h.[18] Details of the X-ray structure of **4d**, which revealed the presence of an asymmetrically bridging hydride as depicted in Scheme I, will be published elsewhere.[16]

The linear tetranuclear clusters **5a–d** are formed in two diastereomeric conformations,[24a] which solid-state structures and fluxional behavior in solution have been elucidated for **5a**.[25] Overall, **5** is formed by reductive dimerization of two molecules **2** or **3** whereby a CO ligand and a H atom have been abstracted from each of the parent dinuclear complexes. It should be noted that, during the conversion of **2** to **5**, the originally four-membered azaruthenacycle is expanded by one carbon atom. When the thermolysis of **3a** is performed in a sealed reaction vessel, considerable amounts of $Ru_2(CO)_6[CH_2CC(H)C(H){=}N\text{-}i\text{-}Pr]$ (**6a**) and $(\mu\text{-H})_2Ru_4(CO)_8[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ are formed besides **5a** (ratio 1:1:3). This is in line with

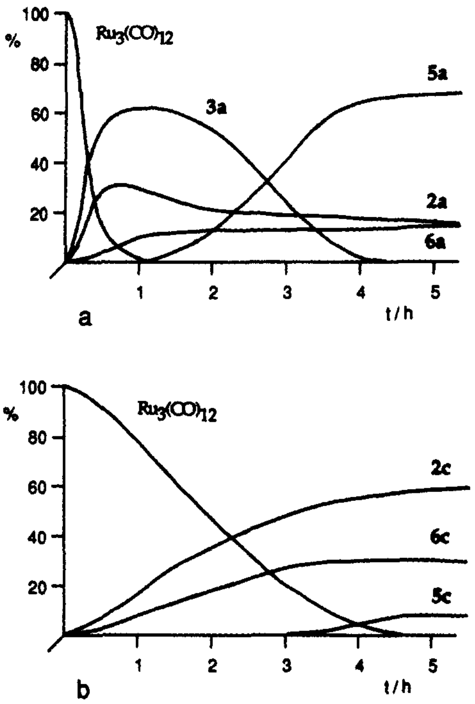


Figure 2. Time vs composition diagrams for the conversion of $Ru_3(CO)_{12}$ and (a) CH_3, *i*-Pr-MAD and (b) CH_3, *t*-Bu-MAD obtained by HPLC analysis of aliquots of the reaction mixtures taken at regular intervals.

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[23] The hydrides **4a** and **4c**, which could however be prepared via an alternative route,[26a] are too reactive to be observed under the applied reaction conditions.

[24] (a) Although diastereoselective dimerization of 4 can not a priori be excluded, dimerization of 4 is expected give about equal quantities of the (CA/AC) and (CC/AA)[61] diastereomers of 5. In the case of **5d** and **5e**, however, the ratio in which the two diastereomeric forms are isolated markedly differs from 1:1. Since it has been shown that isomerization of the two diastereomers is induced thermally,[25] this process can be held responsible for the deviating ratios isolated. As the red diastereomer of **5d**[17] and the isolated diastereomer of **5e**[15] are only poorly soluble in refluxing heptane, these diastereomers precipitate selectively during synthesis, resulting in unequal amounts of diastereomers in solution and the isolation of the less soluble diastereomer in a higher quantity than the better soluble diastereomer. (b) The absolute configuration of the chiral metal centers has been assigned according to the Baird–Cook–Sloan modification of the CIP rules: *IUPAC Nomenclature of Inorganic Chemistry, Recommendations 1990*; Blackwell Scientific Publications: Oxford, England, 1990; p 171. As the chirality of the four Ru centers is pairwise related, only the outer two Ru atoms were labeled as OC-6-33-A or OC-6-33-C, which is abbreviated to AA, CC, AC, and CA for diastereomers of **5a–d**.

[25] Mul, W. P.; Elsevier, C. J.; Ernsting, J.-M.; de Lange, W. G. J.; van Straalen, M. D. M.; Vrieze, K.; de Wit, M.; Stam, C. H. To be submitted for publication in *J. Am. Chem. Soc.*

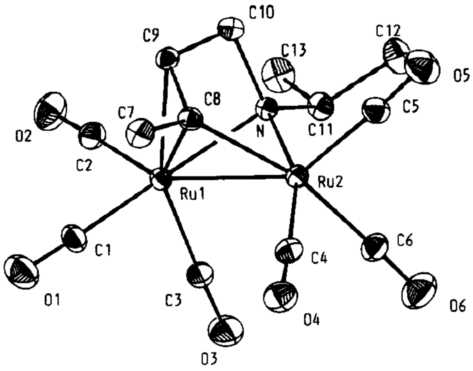

Figure 3. Molecular structure of $Ru_2(CO)_6[CH_3C{=}C(H)CH_2N$-*i*-Pr] (**3a**).

the stepwise liberation of CO and H_2, as depicted in Scheme I, since the complexes **6a** and (μ-H)$_2Ru_4(CO)_8$-[$CH_3C{=}C(H)C(H){=}N$-*i*-Pr]$_2$ are known to be the result of reactions of **5a** with CO and H_2, respectively, which will be described in detail elsewhere.[26]

In the presence of CH_3,R^2-MAD (**1a**) or (*E*)-crotonaldehyde, compound **3a** was converted into the known complex **6a**.[7] During this reaction, which gives best yields at 90 °C, the coordinated ligand is dehydrogenated whereas the added unsaturated substrate acts as a hydrogen acceptor. In the case of the reaction of **3a** with (*E*)-crotonaldehyde it was found that the C=C moiety of (*E*)-crotonaldehyde was hydrogenated chemoselectively; ^{1}H NMR spectra of the volatile organic products showed the almost exclusive (>90%) formation of *n*-butyraldehyde. When $R^1 = C_6H_5$, compounds like **6** cannot be formed, due to the absence of hydrogen atoms at the *ipso* carbon of the R^1 substituent.[27]

An illustrative time vs composition diagram for the conversion of $Ru_3(CO)_{12}$ and **1a** into the products described above, obtained by HPLC analysis of aliquots of the reaction mixture taken at regular intervals, is provided in Figure 2a.

Thermal reactions of $Ru_3(CO)_{12}$ with R^1,*t*-Bu-MAD (R^1 = CH_3 (**1c**), C_6H_5 (**1e**)) proceed more slowly as compared to **1a**, **1b**, or **1d** and give other product distributions. Whereas $Ru_3(CO)_{12}$ was converted within 1 h in refluxing heptane into **2** and **3** during reactions with **1a**, **1b**, or **1d**, complete conversion of $Ru_3(CO)_{12}$ in a reaction with **1c** under the same conditions took about 4 h. Furthermore, **3c** and **3e** could not be isolated nor be observed in solution by IR or HPLC measurements performed on samples taken from the reaction mixtures at intervals of 0.5–1 h (For a time vs composition diagram for the reaction of $Ru_3(CO)_{12}$ with **1c**, see Figure 2b).[28] In the case of R^1, R^2 = C_6H_5, *t*-Bu (**1e**), the main product was **5e** (yield 60%; one diastereomer),[15] a yellow product that was hardly soluble in any organic solvent, and furthermore, some **2e** (about 20%) was formed. For R^1, R^2 = CH_3, *t*-Bu (**1c**), **2c** and **6c** are the main products formed together with a small amount of **5c** (less then 10%). The ratio in which **2c** and **6c** could be isolated after the reaction was complete depended on the reaction temperature. When the reaction was performed at 95 °C, this ratio amounted to 1:2, whereas carried out at vigorous reflux (the Schlenk tube was immersed directly into a hot oil bath at 125 °C) this ratio was about 2:1.

Table IV. Fractional Coordinates of the Non-Hydrogen Atoms and Equivalent Isotropic Thermal Parameters of 3a

atom	*x*	*y*	*z*	U_{eq}, Å^2
Ru(1)	0.71540 (4)	0.21611 (3)	0.95034 (4)	0.0332 (2)
Ru(2)	0.84879 (4)	0.22729 (3)	0.74110 (4)	0.0347 (2)
C(1)	0.8686 (7)	0.1637 (5)	1.1452 (6)	0.050 (3)
C(2)	0.5417 (7)	0.2611 (5)	1.0323 (7)	0.050 (3)
C(3)	0.6845 (7)	0.0547 (5)	0.8482 (6)	0.050 (3)
C(4)	1.0660 (6)	0.1543 (4)	0.8083 (7)	0.046 (3)
C(5)	0.8764 (7)	0.3280 (5)	0.6182 (7)	0.049 (3)
C(6)	0.7863 (7)	0.0945 (5)	0.5646 (7)	0.052 (3)
C(7)	1.0446 (6)	0.3541 (5)	1.0983 (7)	0.052 (3)
C(8)	0.8865 (6)	0.3400 (4)	0.9604 (6)	0.038 (2)
C(9)	0.7472 (6)	0.4095 (4)	0.9735 (6)	0.036 (2)
C(10)	0.6057 (6)	0.4204 (4)	0.8192 (6)	0.041 (3)
C(11)	0.4668 (6)	0.2615 (5)	0.5947 (6)	0.043 (3)
C(12)	0.4447 (8)	0.3249 (7)	0.4580 (7)	0.068 (4)
C(13)	0.3136 (7)	0.2867 (7)	0.6326 (8)	0.068 (4)
N	0.6101 (4)	0.2934 (3)	0.7381 (4)	0.032 (2)
O(1)	0.9626 (7)	0.1379 (5)	1.2639 (6)	0.085 (3)
O(2)	0.4413 (6)	0.2847 (5)	1.0834 (6)	0.081 (3)
O(3)	0.6601 (7)	−0.0393 (4)	0.7830 (6)	0.082 (3)
O(4)	1.1985 (5)	0.1095 (4)	0.8553 (6)	0.066 (3)
O(5)	0.8910 (7)	0.3911 (5)	0.5471 (7)	0.085 (4)
O(6)	0.7510 (7)	0.0146 (5)	0.4638 (6)	0.093 (4)

Table V. Selected Bond Distances Involving Non-Hydrogen Atoms of 3a (Å) (Esd's in Parentheses)

Ru(1)–Ru(2)	2.666 (2)	Ru(2)–C(5)	1.948 (4)
Ru(1)–C(1)	1.912 (4)	Ru(2)–C(6)	1.892 (4)
Ru(1)–C(2)	1.929 (5)	Ru(2)–C(8)	2.066 (4)
Ru(1)–C(3)	1.913 (4)	Ru(2)–N	2.136 (3)
Ru(1)–C(8)	2.296 (4)	C(8)–C(9)	1.382 (6)
Ru(1)–C(9)	2.269 (4)	C(9)–C(10)	1.499 (5)
Ru(1)–N	2.104 (3)	C(10)–N	1.486 (5)
Ru(2)–C(4)	1.892 (4)		

Table VI. Selected Bond Angles Involving Non-Hydrogen Atoms of 3a (deg) (Esd's in Parentheses)

Ru(2)–Ru(1)–C(1)	113.1 (2)	C(4)–Ru(2)–N	160.9 (2)
Ru(2)–Ru(1)–C(2)	151.3 (1)	C(6)–Ru(2)–C(8)	162.4 (2)
Ru(2)–Ru(1)–C(3)	88.4 (2)	Ru(1)–C(8)–Ru(2)	75.1 (2)
Ru(2)–Ru(1)–C(8)	48.5 (1)	Ru(1)–C(8)–C(9)	71.3 (4)
Ru(2)–Ru(1)–C(9)	71.6 (1)	Ru(2)–C(8)–C(9)	113.3 (3)
Ru(2)–Ru(1)–N	51.6 (1)	C(7)–C(8)–C(9)	119.4 (4)
C(1)–Ru(1)–N	162.1 (2)	Ru(1)–C(9)–C(8)	73.4 (3)
C(8)–Ru(1)–N	72.6 (2)	Ru(1)–C(9)–C(10)	89.7 (3)
C(9)–Ru(1)–N	63.1 (2)	C(8)–C(9)–C(10)	116.7 (4)
Ru(1)–Ru(2)–C(4)	110.4 (2)	C(9)–C(10)–N	100.4 (4)
Ru(1)–Ru(2)–C(5)	145.0 (2)	Ru(1)–N–Ru(2)	77.9 (2)
Ru(1)–Ru(2)–C(6)	106.5 (2)	Ru(1)–N–C(10)	96.7 (3)
Ru(1)–Ru(2)–C(8)	56.3 (1)	Ru(2)–N–C(10)	108.6 (3)
Ru(1)–Ru(2)–N	50.5 (1)	C(10)–N–C(11)	117.1 (3)

In order to obtain a larger amount of **5c**, another synthetic method was applied. In order to maintain a low concentration of **1c** in the reaction mixture throughout the experiment (to prevent formation of **6c**), 1.36 mmol of **1c** was dissolved in 10 mL of heptane and slowly added over a period of 2 h to a refluxing solution of $Ru_3(CO)_{12}$ (0.78 mmol) in heptane, which was then refluxed for another 4 h. In this way **5c** could be obtained in a yield of about 30%.

The complex $Ru_2(CO)_6[R^1C{=}C(H)CH_2NR^2]$ (**3a,b,d**) is one of the main products initially formed during reactions of $Ru_3(CO)_{12}$ with R^1,R^2-MAD. Before its fluxional behavior in solution, its formation path, and its reactivity are considered in more detail, the molecular structure of **3a** will be discussed.

Molecular Structure of $Ru_2(CO)_6[CH_3C{=}C(H)$-CH_2N-*i*-Pr]. The molecular geometry of **3a** along with

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(26) (a) Mul, W. P.; Elsevier, C. J.; van Leijen, M.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. To be submitted for publication in *Organometallics*. (b) Mul, W. P.; Elsevier, C. J.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. To be submitted for publication in *Organometallics*.

(27) Compound **3d** reacts with C_6H_5,*i*-Pr-MAD to give $Ru_2(CO)_6$-[$C_6H_5C{=}C(H)C(H){=}N$-*i*-Pr]$_2$. This will be published elsewhere.[8b]

(28) Via an alternative reaction pathway we have been able to isolate **3c** as well,[26a] indicating that the fact that **3c** is not being formed during thermal reactions of $Ru_3(CO)_{12}$ with **1c** is of kinetic rather than of thermodynamic origin.

the adopted numbering scheme is shown in Figure 3. Positional parameters, bond lengths, and selected bond angles are given in Tables IV–VI.

From the internuclear distances and the hybridization of the atoms within the 6e-donating ligand in **3** and its coordination to the metal carbonyl framework, the H shift that has taken place over the MAD skeleton becomes immediately evident. The C(8)–C(9), C(9)–C(10), and C(10)–N distances are 1.382 (6), 1.499 (5), and 1.486 (5) Å, respectively, indicating a rather long double bond between C(8) and C(9) and two single bonds for C(9)–C(10) and C(10)–N. The double-bond character of C(8)–C(9) is confirmed by the C(7)–C(8)–C(9) and C(8)–C(9)–C(10) bond angles of 119.4 (4) and 116.7 (4)°, respectively, in agreement with sp^2 hybridization of C(8) and C(9). The C(9)–C(10)–N angle of 100.4 (4)° is slightly smaller than might be expected for a sp^3-hybridized C(10). This can be ascribed to the fixed coordination of the enyl–amido ligand to the two metal centers. The hydrogen atoms of **3a** were located and refined. From these observations the conclusion can be drawn that a formally dianionic enyl–amido ligand with formula $CH_3C{=}C^-(H)CH_2N^-C_3H_7$-*i* has been formed and that a formal 1,3-hydrogen shift has taken place.

The metal carbonyl part has the normal "*saw-horse*" structure with a $(CO)_3RuRu(CO)_3$ unit deviating only slightly from an eclipsed configuration. (Dihedral angles: Ru(1)–C(1)/Ru(2)–C(4) = 10°; Ru(1)–C(2)/Ru(2)–C(5) = 36°; Ru(1)–C(3)/Ru(2)–C(6) = 17°). The Ru–C and C–O bonds of the $Ru_2(CO)_6$ core exhibit normal lengths with the exception of the Ru(2)–C(6) distance of 1.948 (4) Å, which is slightly elongated as a consequence of the large trans influence exerted by C(8).

The formally 6e-donating enyl–amido ligand bridges the rather short single Ru–Ru bond of 2.666 (2) Å, whereas usually distances of 2.70–2.90 Å are found.[29] Similarly, short M–M distances have been found in structurally analogous compounds like $Ru_2(CO)_6[C_6H_5C{=}C(C_6H_5)C(O)NC_6H_5]$ (2.677 (1) Å)[30] and $Fe_2(CO)_6[\mu\text{-}\eta^2\text{-}C_6H_4CH_2N(p\text{-Tol})]$ (2.43 Å).[31] Bridging N atoms have been found to shorten intermetallic distances (i.e. in **2c**),[7] whereas in $Ru_2(CO)_6[(i\text{-Pr})NCH_2CH_2N(i\text{-Pr})]$[32] and $(\mu\text{-H})FeMn(CO)_6[(p\text{-Tol})NCH_2CH_2N(p\text{-Tol})]$,[33] both containing a diamido ligand, even unusually short M–M bonds of 2.5745 (7) and 2.5393 (9) Å, respectively, have been observed. It has been put forward that the fixed metal–ligand geometry in these types of complexes, with M–N–M angles of about 75° (in **3a**, 77.9 (2)°), is responsible for the short intermetallic distances by inducing a bent bond between the metal centers.[34]

The metal–metal bond in **3a** is symmetrically bridged by the N atom [Ru(1)–N = 2.104 (3) Å; Ru(2)–N = 2.136 (3) Å] and asymmetrically bridged by C(8) [Ru(1)–C(8) = 2.296 (4) Å; Ru(2)–C(8) = 2.066 (4) Å]. The latter is a consequence of C(8) being connected to Ru(2) via a σ bond whereas coordination to Ru(1) is provided by the π bond present between C(8) and C(9).

Fluxional Behavior of 3 in Solution. The new dinuclear complex **3a** shows two-stage fluxional behavior in its ^1H NMR and ^{13}C NMR spectra (Tables II and III). At 263 K the ^1H and ^{13}C NMR spectra of **3a** in $CDCl_3$ (Figures 4 and 5) are in agreement with its solid-state structure.

Coordination of the enyl–amido ligand to both ruthenium atoms as shown by the crystal structure induces diastereotopicity of the *i*-Pr methyl groups, which appear as two separate doublets at 1.04 and 0.94 ppm (^3J = 65 Hz) in the ^1H NMR spectrum and as two singlets at 24.7 and 22.4 ppm in the proton-decoupled ^{13}C NMR spectrum. Also, the methylene hydrogen atoms H(101) and H(102)

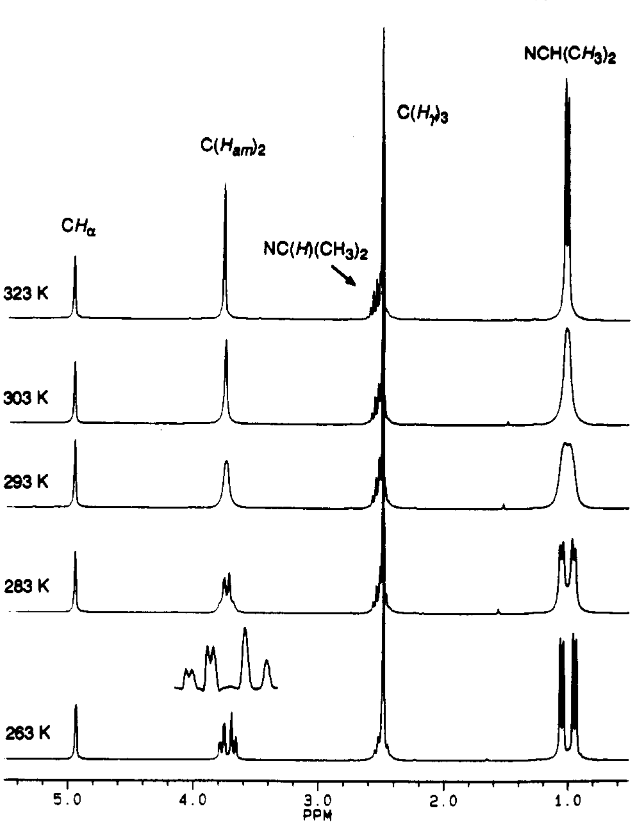

Figure 4. Temperature-dependent ^1H NMR spectra of **3a** in $CDCl_3$ at 250.1 MHz.

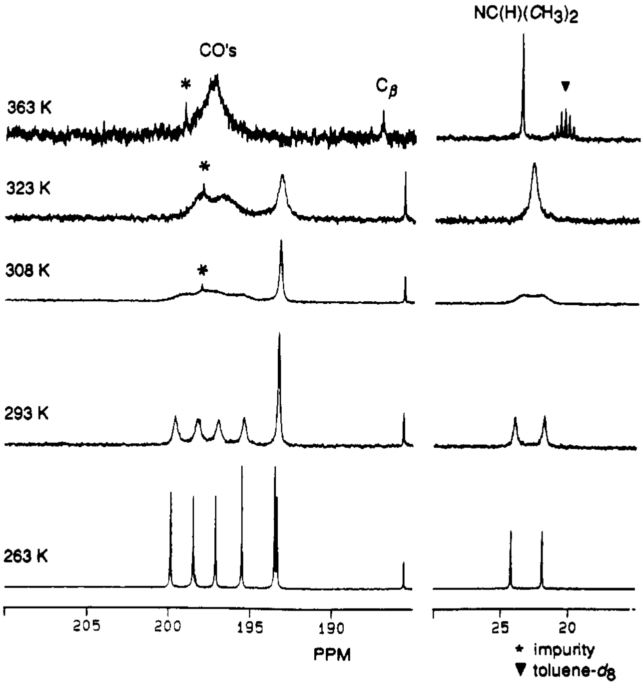

Figure 5. Temperature-dependent ^{13}C NMR spectra of **3a** in $CDCl_3$ (263–323 K) or toluene-d_8 (363 K) at 62.9 MHz.

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(29) Bennett, M. A.; Bruce, M. I.; Matheson, T. W. In *Comprehensive Organometallic Chemistry*, vol IV, Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; p 691.

(30) Han, S.-H.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1986**, *5*, 2561.

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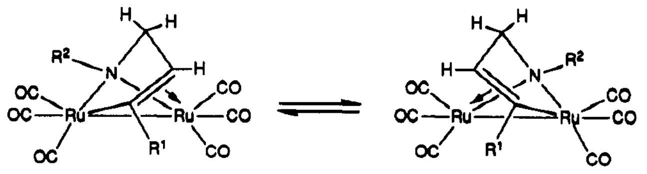
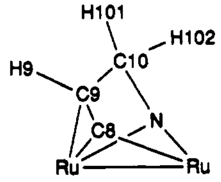


Figure 6. Fluxional behavior of 3 in solution.

give the expected AB part of an ABX pattern at 3.76 and 3.68 ppm with $^2J_{AB}$ = 9 Hz, $^3J_{AX}$ = 2.5 Hz, and $^3J_{BX}$ < 1.0 Hz. These couplings, in combination with the dihedral angles C(10)-H(101)/C(9)-H(9) and C(10)-H(102)/C(9)-H(9), derived from the crystal structure, of 115 and 105°, respectively, allow (Karplus-Conroy equation) the following assignment of the ^{1}H NMR signals (ppm): H(101), 3.76; H(102), 3.68.



3a

The vinylic H(9) proton is found as a broad singlet at 4.93 ppm due to coupling with both the methylene and the C(7) methyl hydrogen atoms. The C(7) methyl protons are found at 2.48 ppm as a doublet due to small coupling with H(9) (^4J = 0.6 Hz). The $\Delta\delta$ shift of approximately +1 ppm of the C(7) methyl protons, as compared to the free ligand value, can be attributed to the paramagnetic neighbor effect of C(8), which is σ-coordinated to one ruthenium atom and π-coordinated to a second one.[35]

The six CO ligands of the ^{13}CO-enriched sample of **3a** (enrichment about 10%) appear at 263 K as six separate resonances in the ^{13}C NMR spectrum between 194 and 201 ppm, whereas the seventh resonance found in this region at 186.3 ppm originates from C(8).

When the temperature of the sample is raised, the ^{1}H signals of the pair of *i*-Pr methyl groups coalesce at about 293 K and the pair of methylene protons at about 288 K (250.1 MHz). From these temperatures and the corresponding coalescence temperatures of the *i*-Pr methyl carbons and the CO carbon atoms (62.9 MHz), we have four independent estimates[36] for the barrier of this (low temperature) rearrangement yielding an average ΔG^* of 62 kJ mol^{-1}. On further warming the resonances sharpen, with the fast-exchange limit reached at 323 K. At this temperature the resonances of the *i*-Pr methyl and the methylene protons are observed as a sharp doublet and a singlet, respectively. The corresponding ^{13}C spectrum shows a singlet resonance for the *i*-Pr methyl groups and three signals for the CO ligands. The C(10) methylene carbon signal at approximately 63.0 ppm remains unaffected and sharp over the temperature range investigated. The spectra at 323 K reveal time-average C_s symmetry in the molecule, due to the presence of a time-average mirror plane perpendicular to the metal-metal bond in **3a**.

At higher temperatures the three CO carbon signals broaden and reappear at 363 K as a broad singlet at 197.4 ppm. This high-temperature spectrum has been obtained in toluene-d_8.

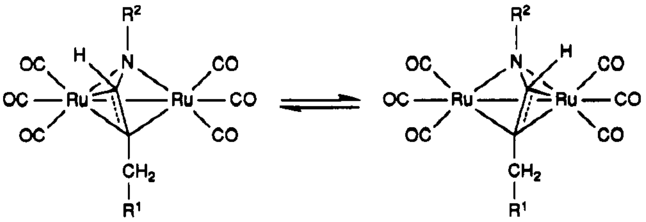
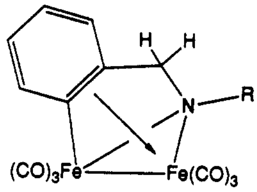


Figure 7. Fluxional behavior of 2 in solution.

The low-temperature fluxional process most likely involves the interchange of the σ-C and η^2-C=C bonds, as visualized in Figure 6. This so called "*windshield wiper*" type oscillation[37] has also been observed in a number of other enyl containing di-[38] and oligonuclear[39] complexes. There is virtually no influence of the R^1 and R^2 substituents of the enyl-amido ligand in 3 on the windshield wiper oscillation process, as ΔG^* values of 62, 60, and 61 kJ mol^{-1} were found for **3a**, **3c**,[28] and **3d**, respectively. The high-temperature process can be ascribed to local scrambling of the CO ligands.

Lack of diastereotopicity of the methylene and the R-group protons in $Fe_2(CO)_6[C_6H_5CH_2NR]$ (7), a structural analogue of 3, indicates that a fluxional process of the ligand also takes place in this complex,[40] similar to the one proceeding in 3.



7a: R = i-Pr
7b: R = p-Tol

Fluxional Behavior of 2 in Solution. The coordination of the azaallyl ligand in 2 can, in an alternative way,[7] be described as symmetrical bridging of the N atom to both Ru centers, σ coordination of C(8) to Ru(2) and η^2-coordination of C(7)=C(8) to Ru(1). In this view, the resemblance between the coordination modes of the ligands in compounds 2 and 3 is obvious. The only difference remaining between the spines of the two ligands is the methylene bridge connecting the amido and vinyl moieties in 3, whereas in 2 a σ bond exists between these two moieties. This alternative description of 2 is useful for comparison of the fluxional behavior of 2 and 3 in solution.

The ^{1}H and ^{13}C NMR spectra of **2a-c** show that these complexes are fluxional. For example in the ^{1}H NMR spectrum of **2a** in $CDCl_3$ at 297 K, the *i*-Pr methyl (0.89

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[35] Aime, S.; Milone, L.; Osella, D.; Valle, M.; Randell, E. W. *Inorg. Chim. Acta* **1976**, *20*, 217.

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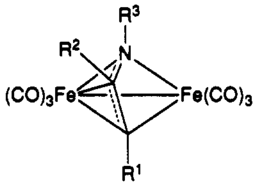
ppm, d) and the methylene protons (2.40 ppm, q) of **2a** lack diastereotopicity. Furthermore, the six CO ligands of **2a** give rise to only one signal at 197.4 ppm in the ^{13}C NMR spectrum ($CDCl_3$, 263 K). Upon cooling of a sample of **2a** dissolved in CD_2Cl_2, these NMR signals broaden. Unfortunately, it was not possible to obtain low-temperature-limiting spectra, due to precipitation of the complex below −80 °C. If the coalescence temperature of the *i*-Pr methyl groups of **2a** is estimated to be about −90 °C (^1H NMR; $\Delta\nu$ = 50 Hz at 2.35 T), a ΔG^* value of about 35 kJ mol^{-1} is obtained,[36] indicating that the fluxional process for **2a** requires less energy than that for **3a** ($\Delta G^* \approx 62$ kJ mol^{-1}). The fluxional process proposed for **2** is shown in Figure 7 and involves oscillation of C_{im} between the two ruthenium centers with concomitant local CO scrambling and closely resembles that of **3**.

For $Fe_2(CO)_6[\mu_2\text{-}\eta^3\text{-}C(CO_2CH_3)C(CO_2CH_3)NC(C_6H_5){=}C(CH_3)_2]$ (**8a**),[41] a structural analogue of **2**, the authors noticed two independent dynamic processes, ascribed to *intranuclear* (at one of the iron atoms) and, less facile, *internuclear* scrambling of the CO ligands on the iron atoms. On the basis of the present results, however, it seems more likely that the less facile process in **8a** involves, as in **2**, oscillation of the azaallyl ligand in combination with local scrambling of the CO ligands on the individual iron atoms. Due to the lack of diastereotopic substituents at the azaallyl ligand in **8a**, fluxional behavior of this ligand cannot be observed directly. In the ^{13}C spectrum of **8b** at room temperature only one signal for all six CO ligands was observed,[42] pointing to the presence of a fluxional azaallyl ligand in this compound as well.



8a: $R^1 = C(O)OCH_3$; $R^2 = C(O)OCH_3$; $R^3 = C(C_6H_5){=}C(CH_3)_2$

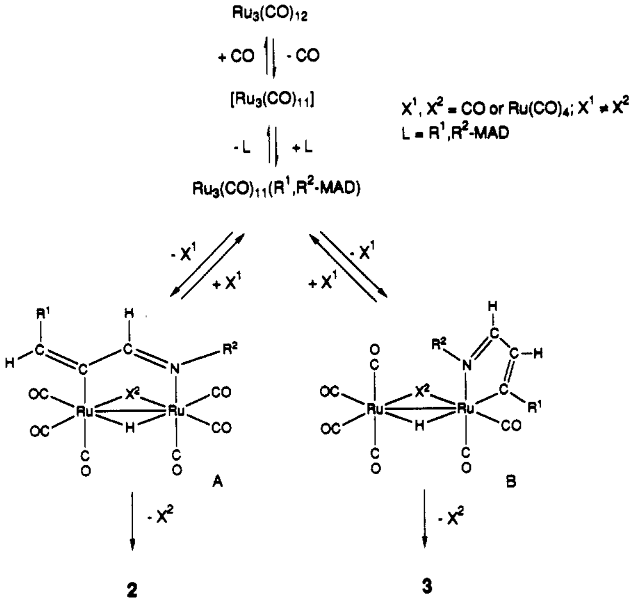
8b: $R^1 = H$; $R^2 = H$; $R^3 = t\text{-}Bu$

FD/FI Mass Spectroscopy. The isomeric nature of complexes **2** and **3** became immediately evident by comparing their FI mass spectra, which were almost identical (see Experimental Section). In the case of $Ru_2(CO)_6[CH_3C{=}C(H)CH_2N\text{-}i\text{-}Pr]$ (**3a**), however, a spectrum is obtained showing not only an isotopic pattern around *m*/*e* 481 but also a (less intense) isotopic pattern around *m*/*e* 453 corresponding to the $[M]^{\cdot+}$ and $[M\text{-}CO]^{\cdot+}$ ions, respectively. This observation is in line with the observed reactivity of this complex (vide supra).

Discussion

Formation of the Primary Products $Ru_2(CO)_6[R^1CH_2CC(H)NR^2]$ (2) and $Ru_2(CO)_6[R^1C{=}C(H)CH_2NR^2]$ (3). Thermal reactions of $Ru_3(CO)_{12}$ with nitrogen donor ligands (e.g. R-DAB,[2a] Schiff bases,[43] diazapines[44]) generally give rise to break up of the trinuclear cluster and formation of species of lower nuclearity. During the reactions of $Ru_3(CO)_{12}$ with R^1,R^2-MAD, the ruthenium triangle is not retained either. The first isolable products are the dinuclear compounds **2** and **3**, both containing an isomerized R^1,R^2-MAD ligand, formed after C–H activation of R^1,R^2-MAD at C_α or C_β[22] and transfer of the hydrogen atom to an unsaturated part of the ligand in a net 1,2- or 1,3-shift, respectively.

Scheme II. Proposed Pathways for the Formation of 2 and 3 from $Ru_3(CO)_{12}$ and R^1,R^2-MAD



Kinetic studies of reactions between $Ru_3(CO)_{12}$ and group 15 donor ligands (PR_3, AsR_3) showed the rate-determining step to be CO dissociation to give transient $[Ru_3(CO)_{11}]$.[45] Since η^2-C=N coordination of MAD ligands has thus far not been observed, it is likely that the R^1,R^2-MAD ligand is initially either η^2-C=C or σ-N coordinated to the $[Ru_3(CO)_{11}]$ cluster during the first reaction step. From the first species formed, $Ru_3(CO)_{11}(R^1,R^2\text{-MAD})$ cluster breakdown and ligand rearrangements will take place. It is difficult to discriminate between the two possible coordination modes in the initial stage, since both types have shown to facilitate C–H activation processes in organic substrates. It should be noted, however, that monodentate 2e σ-N coordination of MAD has been observed in $Fe(CO)_4(MAD)$,[46] and therefore, we assume σ-N coordination in transient $Ru_3(CO)_{11}(R^1,R^2\text{-MAD})$ to be more likely.

Irrespective of the initial bonding mode in $Ru_3(CO)_{11}(R^1,R^2\text{-MAD})$ two complexes A and B, both containing a five-membered-ring system, consisting of a metalated R^1,R^2-MAD ligand and one or two ruthenium atoms, are proposed to be intermediates from which **2** and **3** are formed (see Scheme II). For intermediates A and B analogues can be found in trinuclear osmium clusters derived from $H_2Os_3(CO)_{10}$ and α,β-unsaturated aldehydes[47] and in $HOs_2(CO)_6[CH_3CH_2C{=}C(H)C(CH_3){=}O]$[48] and

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[47] (a) Deeming, A. J.; Manning, P. J.; Rothwell, I. P.; Hursthouse, M. B.; Walker, N. P. C. *J. Chem. Soc., Dalton Trans.* **1984**, 2039. (b) Arce, A. J.; de Sanctis, Y.; Deeming, A. J. *J. Organomet. Chem.* **1985**, *295*, 365.

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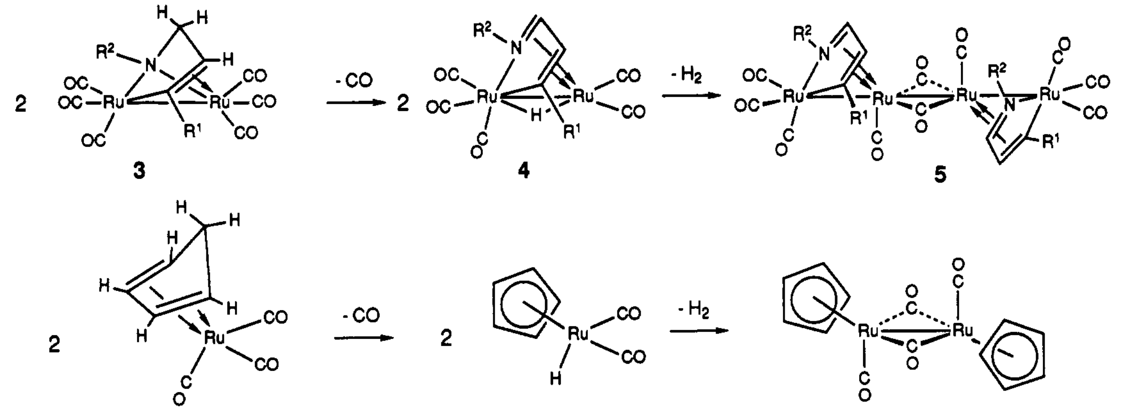
Scheme III. Comparison of the Formation Pathways of 5 and Its Isolobal Counterpart [CpRu(CO)(μ-CO)]₂



$HRu_2(CO)_6[C_6H_5C{=}C(H)C(CH_3){=}O]$.[49] Interestingly, reactions of $H_2Os_3(CO)_{10}$ with crotonaldehyde or cinnamaldehyde also gave considerable amounts of a C(aldehyde)-metalated product, $HOs_3(CO)_{10}[RC(H){=}C(H)C{=}O]$,[47] in contrast to the reaction of $Ru_3(CO)_{12}$ with **1a**–**e**, where no C(imine)-metalated products can be isolated. With another N donor ligand, pyridine, a C(imine)-metalated product was found in a reaction with $Ru_3(CO)_{12}$.[50] It should be noted that intermediate B, the precursor of **3**, is not necessarily a di- or trinuclear species but may also be a mononuclear complex, which later takes up a $Ru(CO)_n$ (n = 3, 4) fragment from the reaction mixture to form dinuclear **3**. Such a mononuclear species has precedents in e.g. $HIrCl(PPh_3)_2[C_6H_5C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$,[51] containing a β-metalated MAD-yl ligand and $HRu(PPh_3)_3[C(H){=}C(CH_3)C(O)OR]$, formed during the reaction of $H_2Ru(PPh_3)_4$ with alkyl methacrylate.[52]

After metalation and, eventually, cluster break down, the hydrides present in the transient species A and B are transferred to an unsaturated part of the ligand, resulting in a formal 1,2-H or 1,3-H shift over the skeleton of the MAD ligand. Concomitant or subsequent loss of X (X = CO or $Ru(CO)_4$) leads to the formation of the primary products **2** and **3**, respectively. A striking aspect is the observed selectivity of the H-migration processes taking place. No products containing ligands like $[CH_3C(H){=}CCH_2NR]$ or $[CH_3CCH_2C(H){=}NR]$ have been found.

Formation of the Secondary Products $Ru_4(CO)_{10}[R^1C{=}C(H)C(H){=}NR^2]_2$ (5) and $Ru_2(CO)_6[CH_2CC(H)C(H){=}NR^2]$ (6). Knowing the molecular geometries of dinuclear **3**, which is the main precursor of **5**, and of the hydrido intermediate **4**, we have obtained a clear picture of the reaction pathway leading to **5**. A remarkable feature is the selectivity of the conversion **3** → **5**, which occurs with a yield of about 90%. Such selectivity is rather uncommon for ruthenium carbonyl cluster chemistry.[28] The proposed sequence, as shown in Scheme I, involves two discrete steps. The first step involves elimination of a CO ligand from **3**, after which insertion of the coordinatively unsaturated ruthenium center into one of the methylene C–H bonds becomes conceivable. As **3** appeared to be rather stable when thermolysis of **3** was carried out under a CO atmosphere, this process must be reversible.

The second step involves dimerization of two of the transient hydrido species, $HRu_2(CO)_5[R^1C{=}C(H)C(H){=}NR^2]$ (**4**), with liberation of H_2 and formation of **5**. Dimerization of transition-metal hydrides with concomitant loss of H_2 is a well-known phenomenon. It constitutes a nice example of binuclear reductive elimination and accounts for the formation of two diastereomers of **5** from two molecules of **4**.[9]

The isolobal relation between **5** and $[\eta^5\text{-}C_5H_5Ru(CO)_2]_2$ has already been discussed.[9] Similarly **3** can be described as an isolobal analogue of $(\eta^4\text{-}C_5H_6)Ru(CO)_3$, by substitution of the $Ru^0(CO)_3$ and NR heterofragments in **3** by their corresponding isolobal carbon fragments CH^+ and CH^-, respectively. Since **4** may be envisaged to be an isolobal analogue of $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ (whereby we neglect the fact that a bridging hydride is present in **4** instead of a terminal one),[16] the formation pathways of **5** and $[\eta^5\text{-}C_5H_5Ru(CO)_2]_2$[11] become isolobally related (see Scheme III).

It should be noted, however, that formation of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ from $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ only proceeds efficiently in the presence of a hydrogen acceptor (O_2),[11] whereas in the presence case the presence of a hydrogen acceptor (i.e. MAD, crotonaldehyde) during thermolysis of **3** gives rise to other reactions whereby **6** (vide infra) or $Ru_3(CO)_6[R^1C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ are formed.[27]

Upon thermolysis, **2a**–**c** also give rise, albeit slowly and incompletely, to the formation of **5a**–**c**. Although we have not been able to obtain evidence, it seems likely that this dimerization also takes place via **4**. The driving force for this conversion might be ring strain in the four-membered azaruthenacycle of **2**. During formation of **5** this metallacycle is expanded by one carbon atom and converted into a more stable five-membered azaruthenacyclopentadienyl species. The preference for five-membered metallacycles, including those of ruthenium, is well-known.[28]

In the case where a hydrogen acceptor (e.g. R^1,R^2-MAD, (*E*)-crotonaldehyde) is present during thermolysis of $Ru_2(CO)_6[CH_3C{=}C(H)CH_2NR^2]$ (**3a**–**c**), an alternative reaction is kinetically favored, whereby $Ru_2(CO)_6[CH_2CC(H)C(H){=}NR^2]$ (**6a**–**c**) is formed instead of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}NR^2]_2$ (**5**). During this conversion the unsaturated organic substrate acts as a hydrogen acceptor, whereby the olefin moiety of this substrate is hydrogenated chemoselectively. During the transfer of the two H atoms from the enyl–amido ligand of **3** to the substrate, the coordinated enyl–amido moiety is transformed into an η^3-allylimine fragment. One H atom is abstracted from the methylene moiety and one from the methyl R^1 substituent of **3**. We propose the sequence depicted in Scheme IV to take place during this conversion.

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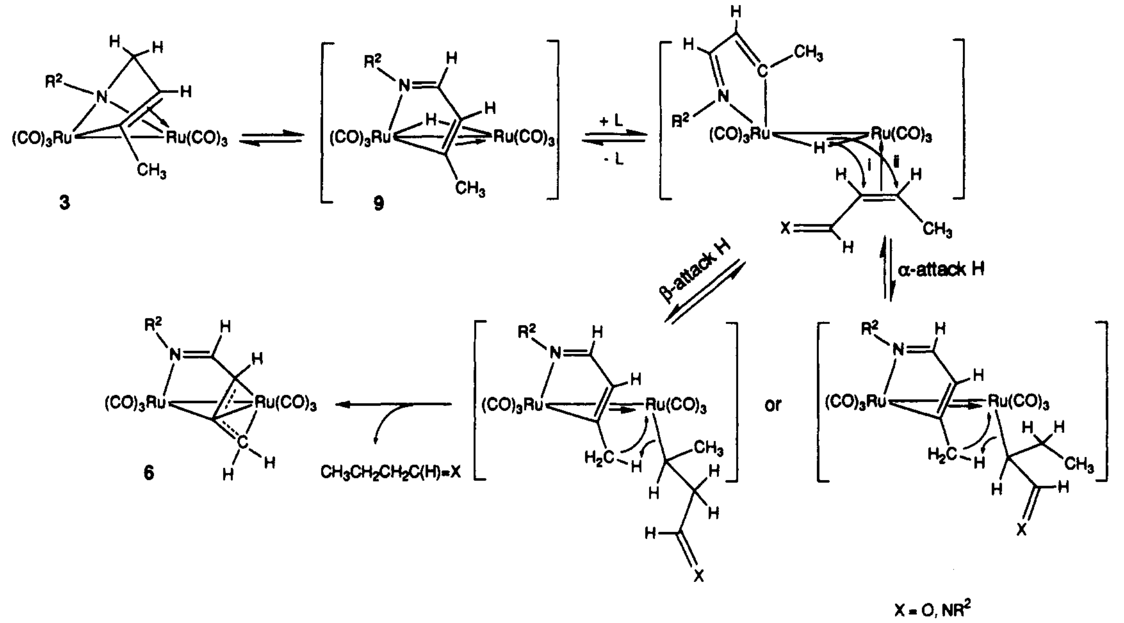
Scheme IV. Proposed Mechanism for the Formation of 6 from 3 and α,β-Unsaturated Imines and Aldehydes



The first step involves the reversible formation of a hydrido hexacarbonyl species (9).[53] In order to transfer the H atoms to the olefinic part of the unsaturated substrate, coordination of this moiety to the metal carbonyl core must take place. Substitution of the olefinic part of the enyl-amido ligand by the olefinic part of the organic substrate is therefore a likely next step. Insertion of the latter olefin into the Ru-H bond gives a σ-C-bonded $CH_3C(H)CH_2C(H){=}X$ or $CH_3CH_2C(H)C(H){=}X$ (X = NR, O) moiety. The last hydrogenation step then involves a direct H transfer from the CH_3 group to this σ-C atom via a 4-center transition state. The actual reaction is complicated by the partial exchange of free and coordinated MAD during conversion of 3 into 6.[54]

Uptake of H_2 from clusters by unsaturated substrates is a common feature. In most cases, however, reactions are accelerated due to a more facile loss of H_2 (usually present as two hydrides) from the cluster[55] contrary to the present case whereby another reaction is kinetically favored. An interesting aspect is that the two H atoms in 3, which are used to reduce the olefin, are both part of an organic moiety coordinated to a metal carbonyl frame. Usually, hydrogen atoms to be transferred to unsaturated ligands are present as hydrides. The overall reaction corresponds to known hydrogen-transfer reactions, catalyzed by several ruthenium complexes, whereby an alcohol or amine function is oxidized and the liberated hydrogen atoms are transferred to a hydrogen acceptor, usually an α,β-unsaturated aldehyde.[29] The complexes 3, 6, and 9 can be seen as models for the intermediates in the stepwise transfer of the two hydrogen atoms from an amine to a hydrogen acceptor.

Comparison with Related Iron-Triad Carbonyl Complexes. $Fe_2(CO)_9$ reacts with cinnamaldimine (C_6H_5,R^2-MAD) to give $[\eta^4\text{-}C_6H_5C(H){=}C(H)C(H){=}NR^2]Fe(CO)_3$, in which MAD donates 4e to the metal tricarbonyl unit by η^2-C=C,η^2-C=N coordination.[56] It has been found that $Fe(CO)_4$(MAD), in which the MAD ligand is σ-N coordinated, is an intermediate during the formation of the iron tricarbonyl complex.[46] Iron analogues of 2 and 3 are not formed during these reactions.[56] Via an alternative route, hydrodesulfurization of $Fe_2(CO)_6[2\text{-}(C_4H_2S)C{=}C(H)CH_2NC_6H_5]$ by treatment with Raney nickel, however, $Fe_2(CO)_6[CH_3CH_2C{=}C(H)CH_2NC_6H_5]$, an analogue of 3, was prepared.[57]

The product $M_2(CO)_6[C_6H_4CH_2NR]$ (7, M = Fe, Ru) formed during reactions between $Fe_2(CO)_9$ or $Ru_3(CO)_{12}$ and benzaldimine,[40] which organic substrate contains a C=CC=N moiety, the C=C function of which is part of an arene, is structurally comparable to complex 3.

During reactions of $Ru_3(CO)_{12}$ or $H_2Os_3(CO)_{10}$ with MAD ligands no formation of coordination complexes like $M_m(CO)_n(\eta^2\text{-MAD})$ or $M_m(CO)_n(\eta^4\text{-MAD})$ has been observed. Reactions of $Ru(CO)_5$ with MAD ligands at room temperature, however, give rise to the formation of $Ru(CO)_3(\eta^4\text{-MAD})$, as was indicated by IR spectroscopy.[58] All attempts to isolate this mononuclear complex, however, have failed thus far.[59] The reaction of $H_2Os_3(CO)_{10}$ with $(CH_3)_2C{=}C(H)C(CH_3){=}NC_6H_5$, reported by Adams et al., gives $(\mu\text{-}H)_2Os_3(CO)_9[(CH_3)_2C(H)CC(H){=}NC_6H_5]$, which

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[53] This hydride (9) has recently been prepared and indeed reacts as depicted in Scheme IV.[26a]

[54] When 3a (R = *i*-Pr) was reacted with 1c (R = *t*-Bu), both 6a and 6c were present after completion of the reaction in a ratio of about 70:30. Since breaking of C-N bonds and exchange of the R groups of the coordinated and the free ligand is very unlikely to occur, complete exchange of the coordinated and the free ligands via a complicated sequence of reaction steps seems to take place. It is difficult to obtain a clear picture of this ligand exchange, but it should involve several C-H oxidative addition/reductive elimination reactions.

[55] For example, dehydrogenation of $H_2Ru(PPh_3)_4$ by methyl methacrylate results in the formation of unsaturated $Ru(PPh_3)_4$, which then reacts with a second molecule of methyl methacrylate to give an oxidative-addition product.[51] Dehydrogenation of a coordinated ligand has also been found during the thermolysis of the μ_2-carbene imine ligand in $(\mu_2\text{-}H)(Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}(CH_3)_2C(H)CC(CH_3){=}NC_6H_5]$ to give $(\mu_2\text{-}H)(Os_3(CO)_9[CH_2C(CH_3)CC(CH_3){=}NC_6H_5]$, which conversion was found to proceed considerably faster in the presence of free MAD ligand $(CH_3)_2C{=}C(H)C(CH_3){=}NC_6H_5$.[60]

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[59] These mononuclear complexes decompose during column chromatography on silica and slowly disproportionate upon standing in hexane solution in the presence of excess MAD, and the η^4-coordinated MAD ligand is instantaneously displaced in a reaction with CO.

osmium cluster contains a ligand arising from activation of, like in **2**, the vinylic C_α–H bond of MAD.[60]

Conclusions

It has been shown that $Ru_3(CO)_{12}$ reacts thermally with R^1,R^2-MAD in a complicated reaction sequence, involving breakdown of the trinuclear cluster and formation of the dinuclear complexes $Ru_2(CO)_6[R^1CH_2CC(H)NR^2]$ (**2**) and $Ru_2(CO)_6[R^1C{=}C(H)CH_2NR^2]$ (**3**; $R^2 \neq$ *t*-Bu), containing a four- and five-membered azaruthenacycle, respectively. Subsequent conversion of these species into the linear tetranuclear cluster $Ru_4(CO)_{10}[R^1C{=}C(H)C(H){=}NR^2]_2$ (**5**) takes place via the air-sensitive intermediate $HRu_2(CO)_5[R^1C{=}C(H)C(H){=}NR^2]$ (**4**), which could be isolated for R^1, R^2 = C_6H_5, *i*-Pr. In the presence of a hydrogen acceptor (MAD, crotonaldehyde), however, thermolysis of **3** (R^1 = CH_3) results in dehydrogenation of the enyl–amido ligand and $Ru_2(CO)_6[CH_2CC(H)C(H){=}NR^2]$ (**6**) is obtained instead of **5**. For crotonaldehyde this conversion is accompanied by the chemoselective hydrogenation of its olefin moiety. The observed interconversions provide insights into isomerization, dimerization, and hydrogen-transfer reactions of unsaturated substrates taking place on (small) clusters and metal surfaces.

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Supplementary Material Available: Tables of complete crystal structure data, all bond lengths and angles, anisotropic thermal parameters of the non-H atoms, and calculated fractional coordinates and the isotropic thermal parameters of the H atoms (5 pages); a listing of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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New Azasilatranes: Thermal Conversion of Unusual Azasilatranium Pseudohalides to Neutral 1-(Pseudohalogeno)azasilatranes

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The azasilatranes $Z\text{–}\overline{Si(NHCH_2CH_2)_3N}$ (**5a**, Z = H; **5b**, Z = Me) react with the weakly electrophilic Me_3SiN_3 or Me_3SiNCS to give (among other products) salts, containing equatorially protonated cations of the type $[Z\text{-}\overline{Si(NH_2CH_2CH_2)(NRCH_2CH_2)_2N}]^+$ (**6**, Z = R = H; **10**, Z = H, R = $SiMe_3$; **11**, Z = Me, R = H). The constitution of the crystalline salts is apparently dependent on subtle differences in the crystal-packing forces among the cations, the counterions, and the parent neutral azasilatrane molecules. Thus, cocrystallization of **5a** with cation **6** occurs with N_3^- but not with SCN^- as the counterion, whereas the reverse is true for cocrystallization of **5b** with cation **11**. In the crystal structures of cations **6**[8] and **10**, the $Si\text{–}N_{eq}{}^+H_2$ bond is 10% longer than the other two $Si\text{–}N_{eq}H$ bonds. Furthermore, cation **10** (but not **6**) features a shorter $Si\text{–}N_{ax}$ bond than that in the parent azasilatrane **5a** present in **7**. Also in cation **10**, the $N_{ax}SiH$ fragment is bent significantly away from linearity. When they are heated, **6**(N_3) in **7** and **10**(NCS) easily undergo elimination of H_2 (along with disproportionation in the case of **10**), leading to the new azasilatranes $Z\text{–}\overline{Si(NHCH_2CH_2)_3N}$ (**8**, Z = N_3; **13** X = NCS–; **14**, X = –NCS). The IR and ^{13}C and ^{29}Si NMR spectra are consistent with the presence of five-coordinate silicon in these compounds. The ^{29}Si NMR chemical shift values of **8** and, in particular, of **13** appear to be anomalously low, relative to that of 1-chloroazasilatrane, indicating that the electronegativity of the axial substituent X alone cannot solely account for the observed trend in the $\delta(^{29}Si)$ values of these compounds. Compound **8** represents the firt example of a species in which a silicon atom is coordinated by five nitrogen ligands. Compound **10** belongs to the noncentric space group $P2_1$ with a = 9.804 (1) Å, b = 8.2600 (7) Å, c = 13.230 (2) Å, β = 99.379 (5)°, and Z = 2.

Introduction

In comparison with the substitution chemistry of silatranes of type **1a**,[1] that of the isoelectronic azasilatranes **1b** is of much wider scope, owing to the presence in the latter of three $N_{eq}H$ functional groups as well as the Z group. This has resulted in the synthesis of a variety of new azasilatranes,[2] including **2a–d**, in which the strength of the $Si\text{–}N_{ax}$ bond is varied systematically by fine tuning the steric repulsions among the substituents on the silicon and N_{eq} atoms.[3] The weakness of the $Si\text{–}N_{ax}$ bond in **2b** has been reported[3] to render the N_{ax} atom of this com-

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