Reactivity of the Linear Tetranuclear Ruthenium Cluster $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}NC(H)(CH_3)_2]_2$ toward CO. Regioselective Aliphatic C–H Activation Processes and the X-ray Crystal Structure of $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_3)_2]$[1]

Wilhelmus P. Mul, Cornelis J. Elsevier,* and Kees Vrieze

Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, J.H. van 't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Wilberth J. J. Smeets and Anthony L. Spek

Vakgroep Kristal- en Structuurchemie, Universiteit te Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received October 9, 1991

The linear tetranuclear cluster $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**3a**) reacts with CO at ambient temperature under exclusion of light to give ultimately $Ru_4(CO)_{14}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**11a**). During this conversion the coordination of the two MAD-yl ligands is changed from the bridging $\sigma(N)\text{-}\sigma(C)\text{-}\eta^2\text{-}(C{=}N){:}\eta^2(C{=}C)$ (7e) to the chelating σ(N)-σ(CO (3e) mode. The compounds $Ru_4(CO)_{12}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**9a**), containing one 7e- and one 3e-donating MAD-yl ligand, and $Ru_4(CO)_{13}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**10a**), containing one 5e-donating $(\sigma(N)\text{-}\sigma(C)\text{-}\eta^2(C{=}C)$ and one 3e-donating MAD-yl ligand, were shown to be intermediates during the formation of **11a**. Complete conversion of **3a** into **9a** takes about 12 h, into **10a** about 3 days, and into **11a** about 2 weeks. These conversions are reversible; i.e., heating or irradiating a solution of **11a** results in the re-formation of **3a**. Compound **11a**, which has been characterized by IR and ^1H and ^{13}C NMR spectroscopy and elemental analysis, is proposed to contain a linear tetraruthenium cluster core in which the metal centers are connected via metal–metal bonds only. Thermolysis of **3a** under CO (1 atm, 80 °C, heptane) results in the breakdown of the tetranuclear cluster core with formation of two dinuclear compounds, $Ru_2(CO)_6[CH_3C{=}C(H)CH_2N\text{-}i\text{-}Pr]$ (**1a**; 40%) and $Ru_2(CO)_6[CH_2CC(H)C(H){=}N\text{-}i\text{-}Pr]$ (**4a**; 40%). Thermolysis of **3a** under 11 atm of CO results in the formation of **4a**, $Ru_3(CO)_{12}$, and $CH_3C(H){=}C(H)C(H){=}N\text{-}i\text{-}Pr$. Photolysis of **3a** under CO also results in the breakdown of the cluster core, but in this case $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_3)_2]$ (**12a**), $Ru_3(CO)_{12}$, and $CH_3C(H){=}C(H)C(H){=}N\text{-}i\text{-}Pr$ are formed. The X-ray crystal structure of **12a** has been determined. Crystals of $C_{13}H_{11}NO_6Ru_2$ are triclinic, space group $P\bar{1}$, $a = 6.799$ (2) Å, $b = 10.098$ (2) Å, $c = 12.676$ (3) Å, $\alpha = 84.70$ (2)°, $\beta = 82.91$ (2)°, $\gamma = 74.36$ (2)°, $Z = 2$, $R = 0.035$, and $R_w = 0.050$. Possible mechanisms for the regioselective C–H activation processes, which are based on the hemilability of the MAD-yl ligand and which are dependent on the way **3a** is activated, as well as the subsequent intramolecular H migrations and H additions, are discussed.

Introduction

One of the more fascinating properties of transition-metal clusters is their ability to activate aliphatic C–H bonds in positions α or β to donor nuclei.[2] Several interesting examples of such processes have appeared in the literature, and factors influencing the reaction routes are now well understood. However, the controlled regioselective activation of different aliphatic C–H bonds of one ligand by manipulation of reaction conditions leading to specific products is still an unexplored area. Such regioselective C–H activations are of particular interest since regioselective functionalization of specific aliphatic groups is a very important goal.[3]

During a study of the reactivity of $Ru_3(CO)_{12}$ toward monoazadienes ($R^1C(H){=}C(H)C(H){=}NR^2$, abbreviated as R^1,R^2-MAD),[4] it was found that thermal activation of either the α or β olefinic C–H bond takes place. Subsequent transfer of the abstracted H atom to an unsaturated part of the ligand and breakdown of the trinuclear cluster core resulted in the formation of two dinuclear compounds, $Ru_2(CO)_6[R^1C{=}C(H)CH_2NR^2]$ (**1**) and $Ru_2(CO)_6[R^1CH_2CC(H)NR^2]$, both containing an isomerized R^1,R^2-MAD ligand, as the first isolable products (see Scheme II of the preceding paper).[5,9] Upon continued

---

[1] Reactions of Monoazadienes with Metal Carbonyl Complexes. 11. Part 10: Reference 9.

[2] (a) Adams, R. D.; Golembeski, N. M. *Inorg. Chem.* **1978**, *17*, 1969. (b) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2727. (c) Yin, C. C.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1975**, 2091. (d) Yin, C. C.; Deeming, A. J. *J. Organomet. Chem.* **1977**, *133*, 123. (e) Zoet, R.; van Koten, G.; Vrieze, K.; Duisenberg, A. J. M.; Spek, A. L. *Inorg. Chim. Acta* **1988**, *148*, 71. (f) Zoet, R.; von Koten, G.; Vrieze, K.; Jansen, J.; Goubitz, K.; Stam, C. H. *Organometallics* **1988**, *8*, 1565. (g) Deeming, A. J. *J. Organomet. Chem.* **1977**, *128*, 63. (h) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 407. (i) Colbran, S. B.; Irele, P. T.; Johnson, B. F. G.; Lahoz, F. J.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1989**, 2023. (j) Adams, R. D.; Selegue, J. P. *Inorg. Chem.* **1980**, *19*, 1795. (k) Foulds, G. A.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1985**, *295*, 123.

[3] (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (b) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41. (c) Sakahura, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1987**, 758. (d) Alkane Activation and Functionalization. *New J. Chem.* **1989**, *13* (10/11), and references cited therein.

[4] MAD is used as an acronym for monoazadienes in general. In this paper we will use R^1,R^2-MAD when *N*-alkyl-(*E*)-crotonaldimines ($CH_3C(H){=}C(H)C(H){=}NR^2$) or *N*-alkyl-(*E*)-cinnamaldimines ($C_6H_5C(H){=}C(H)C(H){=}NR^2$) are meant. These ligands may be metalated at the C=C moiety, thus forming a formal monoanionic monoazadienyl (R^1,R^2-MAD-yl)[5] ligand, $R^1C(H){=}C^-C(H){=}NR^2$ or $R^1C^-{=}C(H)C(H){=}NR^2$. Subscripts of the atoms of the MAD and MAD-yl ligands refer to the general $N{=}C_{im}C_\alpha{=}C_\beta C_\gamma$ moiety.

[5] Mul, W. P.; Elsevier, C. J.; Polm, L. H.; Vrieze, K.; Zoutberg, M. C.; Heijdenrijk, D.; Stam, C. H. *Organometallics* **1991**, *10*, 2247.

0276-7333/92/2311-1891$03.00/0

heating complex **1** is converted into the linear tetranuclear cluster $Ru_4(CO)_{10}[R^1C{=}C(H)C(H){=}NR^2]_2$ (**3**), via the intermediacy of the dinuclear hydride $(\mu\text{-}H)Ru_2(CO)_5[R^1C{=}C(H)C(H){=}NR^2]$ (**2**).[5-8] In the presence of MAD or crotonaldehyde, complex **1** ($R^1 = CH_3$) gave, upon thermolysis, $Ru_2(CO)_6[CH_2CC(H)C(H){=}NR^2]$ (**4**), which contains a dehydrogenated MAD ligand. During this conversion the organic substrate acts as a hydrogen acceptor.[5]

As H migration and H abstraction are facile processes in these ruthenium carbonyl complexes, it was anticipated that the reaction pathways by which **1**–**4** are formed might be reversed whereby a better insight into specific conversions might be obtained. In the preceding article the reactivity of **3** toward H_2 and mixtures of H_2 and CO has been described.[9] It was shown that both diastereomers of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**3a**) react with H_2 to give $(\mu\text{-}H)_2Ru_4(CO)_8[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**5a**), via the intermediacy of **2a**, and that conversion of (*CA*/*AC*)-**3a** was more facile compared to that of (*CC*/*AA*)-**3a**. At elevated temperatures clusters **3** and **5** react under an atmosphere of H_2/CO (9:1) or CO to give **1**, via **2** and **6**, respectively. By this route the crucial intermediate $(\mu\text{-}H)Ru_2(CO)_6[R^1C{=}C(H)C(H){=}NR^2]$ (**6**) could be isolated, and its spectroscopic properties and reactivity could be investigated. Thermolysis of **4** under an atmosphere of H_2 yielded **2** (R^1, R^2 = CH_3, *i*-Pr) or **3** (R^1, R^2 = CH_3, *t*-Bu), most likely via the intermediacy of **6**.

Here we extend these studies and report on the various reactions of **3a** with CO. It will be shown that the course of the reaction depends dramatically on whether **3a** is activated or not and whether it is activated thermally or photochemically.

Experimental Section

Materials and Apparatus. For apparatus and general techniques, see the preceding paper in this issue and refs 10 and 11. Synthetic manipulations were carried out under an atmosphere of dry nitrogen or, when stated, carbon monoxide by using Schlenk techniques. Silica gel for column chromatography (Kieselgel 60, 70–230 mesh, E. Merck, Darmstadt, Germany) was dried before use. For the photolysis experiments an Oriel mercury arc source equipped with an Osram 200-W mercury lamp was used in combination with a Pyrex cutoff filter ($\lambda \geq 300$ nm). The compounds $Ru_2(CO)_6[R^1C{=}C(H)CH_2NR^2]$ (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**)), $HRu_2(CO)_5[C_6H_5C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ (**2d**), $Ru_4(CO)_{10}[R^1C{=}C(H)C(H){=}NR^2]_2$ (R^1, R^2 = CH_3, *i*-Pr (**3a**), CH_3, c-Hex (**3b**), CH_3, *t*-Bu (**3c**), C_6H_5, *i*-Pr (**3d**)), and $Ru_2(CO)_6[CH_2CC(H)C(H){=}NR^2]$ (R^2 = *i*-Pr (**4a**), *t*-Bu (**4c**)) were synthesized as described before.[5,6,12]

Synthesis of $Ru_4(CO)_{12}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (9a). A solution of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**3a**; 0.5 mmol) in 50 mL of tetrahydrofuran was stirred under 1.2 atm of CO at ambient temperature with exclusion of light. After 2 h the reaction was stopped by removal of CO and the solvent under vacuum. The orange residue was chromatographed on silica. Elution with hexane/dichloromethane (9:1) afforded a bright yellow-orange band which contained $Ru_4(CO)_{12}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**9a**; ca. 30%) together with a small amount of $Ru_4(CO)_{13}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**10a**; ca. 2%). Subsequent elution with hexane/dichloromethane (1:1) gave unreacted **3a**. Removal of the solvent of the first fraction gave a thick orange oil. All efforts to obtain **9a** as a pure solid material failed. Complex **9a** was characterized on the basis of its IR and ^1H and ^{13}C NMR spectroscopic properties. When it stood, the oily material converted very slowly into the parent compound **3a**. This process was accelerated under reduced pressure.

Synthesis of $Ru_4(CO)_{14}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (11a). A solution of **3a** (0.5 mmol) in 25 mL of benzene or tetrahydrofuran was stirred at ambient temperature with the exclusion of light under 1.2 atm of CO for 2 weeks. During this period the initial orange-red color changed to yellow-orange. Removal of the solvent under vacuum afforded pure $Ru_4(CO)_{14}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**11a**) in quantitative yield. The new complex **11a** was characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy and elemental analysis. Anal. Found (calcd) for $C_{28}H_{24}N_2O_{14}Ru_4$ (**11a**): C, 33.08 (33.22); H, 2.38 (2.60); N, 2.76 (2.77). Attempts to obtain crystals of **11a** suitable for X-ray diffraction failed due to the formation of crystals of limited size only.

Thermolysis of $Ru_4(CO)_{14}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (11a). A solution of **11a** (0.1 mmol) in 25 mL of heptane was stirred at 80 °C for 1.5 h. The solvent was removed under vacuum and the residue dissolved in a minimum amount of $CDCl_3$. A ^1H NMR spectrum recorded for this solution showed the presence of two components: $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**3a**; ca. 95%) and $Ru_2(CO)_6[CH_2CC(H)C(H){=}N\text{-}i\text{-}Pr]$ (**4a**; ca. 5%). The products could be separated and isolated as described before.[6,12]

Photolysis of $Ru_4(CO)_{14}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (11a). A solution of **11a** (0.1 mmol) in 25 mL of heptane was irradiated at ambient temperature for 0.5 h. The solvent was removed under vacuum and the residue dissolved in hexane and brought up on top of a column of silica. Elution with hexane afforded a yellow fraction containing a small amount of $Ru_2(CO)_6[CH_2CC(H)C(H){=}N\text{-}i\text{-}Pr]$ (**4a**; <5%). Subsequent elution with hexane/diethyl ether (19:1) gave a second yellow fraction containing $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_3)_2]$ (**12a**; ca. 15%), and further elution with diethyl ether produced an orange-red fraction of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**3a**; 80%).

Thermolysis of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (3a) under a CO Atmosphere. A solution of **3a** (0.5 mmol) in 25 mL of heptane was stirred at 90 °C under a CO atmosphere for 4 h. During this period the initial red color slowly changed to yellow. The solvent was reduced under vacuum to 5 mL. When this solution was cooled to −80 °C, small amounts of $Ru_3(CO)_{12}$ and starting material **3a** precipitated. The organometallic components remaining in solution were separated by column chromatography on silica. Two yellow bands were obtained by using hexane as the eluent. The first contained $Ru_2(CO)_6[CH_3C{=}C(H)CH_2N\text{-}i\text{-}Pr]$ (**1a**; 0.4 mmol, 40%), and the second contained $Ru_2(CO)_6[CH_2CC(H)C(H){=}N\text{-}i\text{-}Pr]$ (**4a**; 0.4 mmol, 40%). Further elution with hexane/diethyl ether (19:1) produced a small amount of $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_3)_2]$ (**12a**; 0.02 mmol, 2%).

Without CO being present, compound **3a** is rather stable in solution at 90 °C. In refluxing heptane under an atmosphere of dry nitrogen slow conversion of **3a** into **4a**, $Ru_3(CO)_6[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$, and decomposition products takes place.[13]

Thermolysis of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}t\text{-}Bu]_2$ (3c) under a CO Atmosphere. An orange solution of **3c** (0.2 mmol) in 25 mL of heptane was stirred at 80 °C under an atmosphere of CO for 2 h. After this period the color of the solution had become yellow and the IR band attributable to the bridging carbonyl ligands of **3c** (~1770 cm^{-1})[5] had disappeared. When the reaction was stopped at this stage ^1H NMR spectroscopy in $CDCl_3$ revealed the presence of three components, $Ru_2(CO)_6[CH_3C{=}C(H)CH_2N\text{-}t\text{-}Bu]$ (**1c**), $Ru_2(CO)_6[CH_2CC(H)C(H){=}N\text{-}t\text{-}Bu]$ (**4c**), and $HRu_2(CO)_6[CH_3C{=}C(H)C(H){=}N\text{-}t\text{-}Bu]$ (**6c**), in a ratio of about 1:2:1. When the reaction was continued and stopped after about 6 h, complex **7c** had converted completely into **1c**. The complexes **1c** and **4c** could be isolated, each in about 0.18 mmol yield (45%), from the reaction mixture by chroma-

---

[6] Polm, L. H.; Mul, W. P.; Elsevier, C. J.; Vrieze, K.; Christophersen, M. J. N.; Stam, C. H. *Organometallics* **1988**, *7*, 423.

[7] Spek, A. L.; Duisenberg, A. J. M.; Mul, W. P.; Beers, O. C. P.; Elsevier, C. J. *Acta Crystallogr.* **1991**, *C47*, 297.

[8] 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. *J. Am. Chem. Soc.*, submitted for publication.

[9] Mul, W. P.; Elsevier, C. J.; van Leijen, M.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics*, preceding article in this issue.

[10] Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388.

[11] Schulten, H. R. *Int. J. Mass Spectrosc. Ion Phys.* **1979**, *32*, 97.

[12] Polm, L. H.; Elsevier, C. J.; Mul, W. P.; Vrieze, K.; Christophersen, M. J. N.; Muller, F.; Stam, C. H. *Polyhedron* **1988**, *7*, 2521.

[13] (a) Mul, W. P.; Elsevier, C. J.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 297. (b) Mul, W. P.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1991**, *30*, 4152.

Table I. Crystal Data for 12a

chem formula	$C_{13}H_{11}NO_6Ru_2$	α	84.70 (2)°
mol wt	479.37	β	82.91 (2)°
space group	$P\bar{1}$	γ	74.36 (2)°
Z	2	V	830.1 (4) Å^3
a	6.799 (2) Å	D_{calc}	1.918 g cm^{-3}
b	10.098 (2) Å	$F(000)$	464
c	12.676 (3) Å	μ(Mo Kα)	18.1

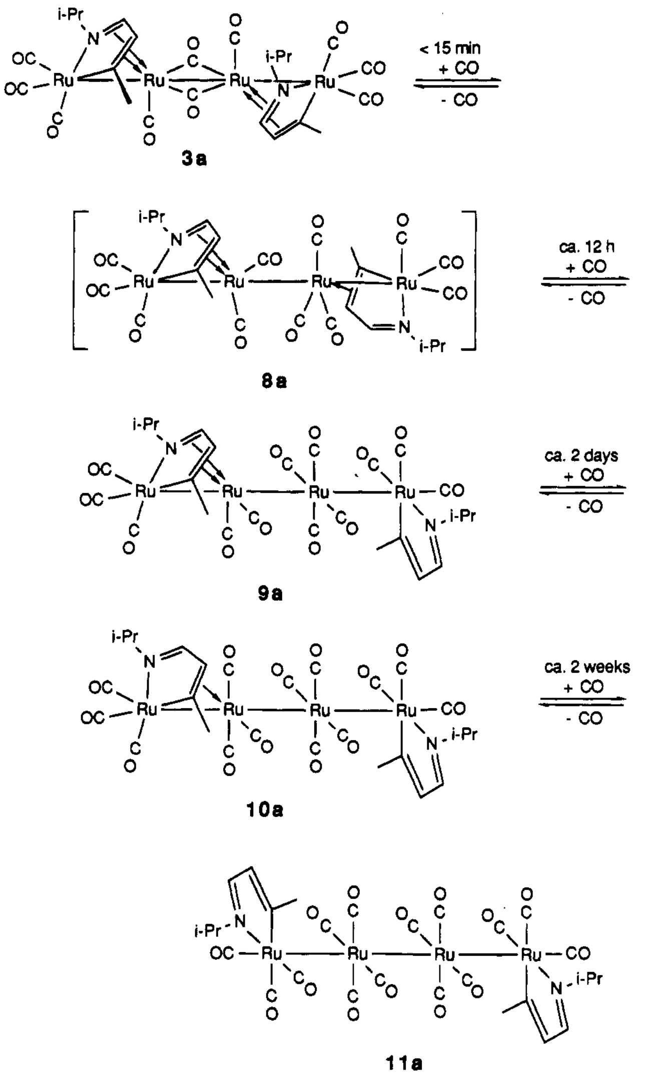
tography on silica as described before.[5]

Photolysis of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (3a) under a CO Atmosphere. Synthesis of $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_3)_2]$ (12a). A solution of **3a** (0.5 mmol) in 25 mL of benzene was irradiated with a 200-W Hg lamp at ambient temperature under 1 atm of CO for about 2 h. After this period a thin red-purple coating, identified as polymeric $[Ru(CO)_4]_n$,[14] covered the glass wall. The solution was concentrated to 5 mL, and $Ru_3(CO)_{12}$ precipitated from this solution upon cooling at −80 °C overnight. The organometallic products remaining dissolved were separated by column chromatography. With hexane as the eluent a small amount of **4a** (0.03 mmol; 3%) was obtained. Elution with hexane/diethyl ether (19:1) gave $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_3)_2]$ (**12a**; 0.4 mmol, 40%) as the main product. Further elution with hexane/diethyl ether (1:1) produced a very small amount of unreacted starting material **3a**. Anal. Found (calcd) for $Ru_2C_{13}H_{11}NO_6$ (**12a**): C, 32.57 (32.57); H, 2.38 (2.31); N, 2.96 (2.92). FD-MS: found, *m/e* 480; calcd, M_r 480).[15] Under an atmosphere of dry nitrogen **3a** is slowly photochemically converted into a mixture of products, including **12a** and a small amount of $H_2Ru_4(CO)_8[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**5a**). These products were isolated, from a reaction mixture obtained after 24 h of irradiation of **3a** in toluene, by chromatography on silica as a brown band with hexane/diethyl ether (20:1) as the eluent.

Photolysis of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}c\text{-}Hex]_2$ (3b) under a CO Atmosphere. Synthesis of $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_2CH_2)_2CH_2]$ (12b). A solution of **3b** (0.2 mmol) in 25 mL of benzene was irradiated with a 200-W Hg lamp at ambient temperature under 1 atm of CO for about 6 h. ^1H NMR spectroscopy of the concentrated reaction mixture in $CDCl_3$ showed the presence of a complex mixture of components, including unreacted **3b 4b**, **9b**, **10b**, and $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_2CH_2)_2CH_2]$ (**12b**). The first purification was performed by column chromatography. A yellow fraction which was obtained using hexane as the eluent was not further investigated. Subsequent elution with hexane/diethyl ether (99:1) produced an orange fraction and contained a mixture of **3b**, **9b**, and **10b**, and **12b** as evidenced by ^1H NMR spectroscopy. This mixture proved to be inseparable by chromatography on silica. Therefore, this mixture was dissolved in 20 mL of heptane and heated for 1 h at 90 °C. During this period the complexes **9b** and **10b** converted into the parent compound **3b**. This reaction mixture was then purified by column chromatography. With hexane as the eluent a light yellow fraction was obtained which contained a very small amount of **4b**. Further elution with hexane/diethyl ether (99:1) produced a second yellow fraction, containing merely the new product **12b** (ca. 5%). Compound **12b** was identified by IR, ^1H NMR, and FD-MS methods. Finally, elution with hexane/diethyl ether (5:1) produced **3b**. FD-MS for **12b**: found, *m/e* 520; calcd, M_r 520.[15]

Crystal Structure Determination of $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_3)_2]$ (12a). A suitable crystal (0.4 × 0.75 × 1.00 mm) was glued to a glass fiber and transferred to an Enraf-Nonius CAD4F diffractometer for data collection (Mo Kα, Zr filtered; λ = 0.71073 Å; θ_{max} = 30°; $\omega/2\theta$ scan, $\Delta\omega$ = 0.65 + 0.35 tan θ°). Crystal data are given in Table I. Unit cell parameters and their estimated standard deviations were derived from the SET4 setting angles of 25 reflections (14 < θ < 18°). A total of 5240 reflections were scanned (h, 0–9; k, −13 to +14; l, −17 to +17). The intensities were corrected for Lp, for a linear intensity increase of 9%, as indicated by two reference reflections, and for absorption (DIFABS;[16] corrections 0.81–1.29). The structure was solved with Patterson techniques (SHELXS86)[17] and refined on F with anisotropic weighted least squares (SHELX76)[18] to a final R = 0.035 (R_w = 0.050); $w^{-1} = \sigma^2(F)$; S = 0.64, 217 parameters) with 4134 reflections with $I > 2.5\sigma(I)$. Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms (C–H = 0.98 Å) with one common isotropic thermal parameter. A final difference Fourier map did not show residual densities outside −1.04 and 0.73 e Å^{-3}. Scattering factors were taken from ref 19 and corrected for anomalous dispersion.[20] Calculations were done on a microVax-II cluster with SHELX76[18] and PLATON.[21]

Scheme I. Stepwise Reaction of 3a with CO To Give 11a



Results

Reaction of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (3a) with CO at Ambient Temperature. The linear tetranuclear complex $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**3a**) adds 4 equiv of CO stepwise in THF or benzene solution at ambient temperature with exclusion of light to give ultimately $Ru_4(CO)_{14}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**11a**) in quantitative yield. The reaction is schematically depicted in Scheme I, which also shows likely geometries

---

(14) Hastings, W. R.; Baird, M. C. *Inorg. Chem.* **1986**, *25*, 2913.

(15) Based on that peak of the isotopic pattern of the molecular ion that corresponded to ^{101}Ru.

(16) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(17) Sheldrick, G. M. SHELXS86: Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, 1986.

(18) Sheldrick, G. M. SHELX76: Crystal Structure Analysis Package; University of Cambridge: Cambridge, England, 1976.

(19) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

(20) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(21) Spek, A. L. The Euclid Package. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, England, 1982; p 528.

Table II. Spectroscopic Data for $Ru_4(CO)_{12}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (9a), $Ru_4(CO)_{13}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (10a), and $Ru_4(CO)_{14}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (11a)

IR Spectra[a]

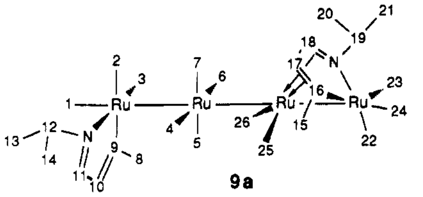
9a	2091 (w)	2061 (vs)	2045 (m)	1997 (s)	1985 (sh)
11a[b]	2102 (w)	2059 (s)	2047 (w)	2035 (w)	2007 (vs)

^{1}H NMR Spectra[c]

	d	H_{im}	H_α	H_γ	*i*-Pr
9a	[3e]	7.89 (m)	6.54 (dd, 2.0, 1.0)	2.80 (d, 1.0)	4.05 (m), $1.37^4/1.36^9$; 1.32 (d)[e]
	[7e]	7.35 (d, 2.0)	5.29 (dd, 2.0, 1.0)	2.56 (d, 1.0)	$3.89^6/3.88^7$ (sept),[e] 1.12; $1.01^1/1.00^2$ (d)[e]
10a	[3e]	7.90 (br s)	6.55 (br s)	2.81 (d, 1.0)	4.12 (sept),[e] 1.37; 1.32 (d)[e]
	[5e]	7.78 (br s)	3.45 (br s)	3.22 (s)	3.52 (sept),[e] 1.15; 1.11 (d)[e]
11a	[3e]	7.90 (d, 2.0)	6.56 (dd, 2.0, 1.0)	2.82 (d, 1.0)	4.11 (sept),[e] 1.39; 1.33 (d)[e]

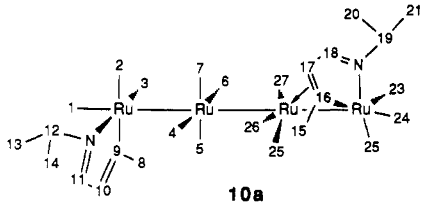
^{13}C NMR Spectra

9a[f] $221.9^1/221.8^7$ (C_9), 212.9 (br, 4 *C*O, C_{4-7}), 207.5 (br, C_{25}), 204.8 (br, C_{26}), 202.9, 200.0 ($C_{2,3}$), 198.7, 194.0, 191.4 (C_{22-24}), 187.4 (C_1), 181.5 (C_{16}), 163.0/162.9 (C_{11}), 128.5 (C_{10}, C_{18}), 93.9 (C_{17}), 61.2, 60.4/60.3 (C_{12}, C_{19}), 33.2 (C_8, C_{15}), 28.0, 27.4, $25.3^4/25.3^0$, $21.8^0/21.7^5$ (C_{13}, C_{14}, C_{20}, C_{21})



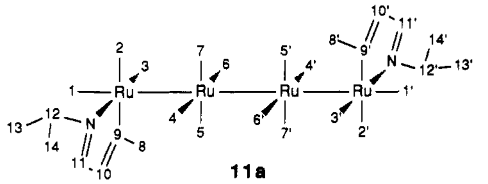
9a

10a[f] 222.0 (C_9), 212.9, 209.1 (C_{26}, C_{27}), 210.5 (4 *C*O, C_{4-7}), 203.2, 202.7, 200.0, 199.8, 199.6, 195.5, 193.7 (C_2, C_3, C_{16}, C_{22-25}), 187.2 (C_1), 173.5 (C_{18}), 163.0 (C_{11}), 128.6 (C_{10}), 67.3 (C_{17}), 60.3, 58.5 (C_{12}, C_{19}), 37.3 (C_{15}), 33.2 (C_8), 26.3, 23.4, 22.3, 21.8 (C_{13}, C_{14}, C_{20}, C_{21})



10a

11a[g] 221.7 (C_9), 209.9 (4 *C*O, C_{4-7}), 203.1, 199.9 (C_2, C_3), 187.9 (C_1), 164.1 (C_{11}), 129.6 (C_{10}), 61.1 (C_{12}), 34.0 (C_8), 26.1, 22.4 (C_{13}, C_{14})



11a

[a] ν(CO) in cm^{-1}, in hexane solution. [b] ν(C=N) = 1574 cm^{-1} (KBr pellet). [c] δ values in ppm (*J* values in Hz), relative to TMS; $CDCl_3$, 250.1 MHz, 297 K. Resonances due to diastereomeric H atoms are separated by slants and resonances due to diastereotopic H atoms separated by semicolons. H atom notation refers to $C(H_\gamma)_3C{=}C(H_\alpha)C(H_{im}){=}N\text{-}i\text{-}Pr$. [d] Number of electrons donated to the cluster core by the CH_3,*i*-Pr-MAD-yl ligand. [e] ^3J = 6.5 Hz. [f] δ values in ppm, relative to TMS; $CDCl_3$, 62.9 MHz, 263 K. Resonances due to diastereomeric C atoms are separated by slants. [g] δ values in ppm, relative to TMS; $CDCl_3$, 25.0 MHz, 263 K.

for **11a**, the proposed intermediate **8a**, and the observed intermediates **9a** and **10a**. Complete conversion of **3a** into **9a** takes about 12 h, into **10a** about 2 days, and into **11a** about 2 weeks. Overall, the reaction constitutes substitution of the π-coordinating systems of the two MAD-yl[4] ligands in **3a** by CO ligands; i.e., the coordination of both MAD-yl ligands is changed from the bridging σ(N)-σ(C)-η^2(C=N):η^2(C=C) (7e) in **3a** to the chelating σ(N)-σ(C) (3e) bonding mode in **11a**.

The conversions are reversible; heating or irradiating a solution of **9a**, **10a**, or **11a** (or mixtures thereof) results in the re-formation of the parent compound **3a**, together with small amounts of dinuclear products. The thermal and photochemical reactions of **3a** in the presence of CO will be discussed in detail further below. Unfortunately, all attempts to prepare crystals suitable for X-ray diffraction of the novel linear tetranuclear complex **11a**, in which the metal centers are connected via metal–metal bonds only, have failed thus far.

The structure of the tetradecacarbonyl compound **11a** has been assigned on the basis of its IR and NMR (^{1}H, ^{13}C) spectroscopic characteristics, which are included in Table II, and an elemental analysis. Unfortunately, FD-mass spectroscopic analysis of **11a** only showed fragments resulting from cluster breakdown, indicating that the unbridged metal–metal bonds in **11a** are rather fragile.

In hexane solution complex **11a** shows two intense IR bands at 2059 and 2007 cm^{-1}, which are assigned to the eight terminal CO ligands of the central $Ru_2(CO)_8$ unit. Furthermore, three weak bands at 2102, 2047, and 2035 cm^{-1} are present corresponding to the two equivalent terminal $Ru(CO)_3$ units, each containing three CO ligands in a *facial* arrangement. The positions of the IR bands of these $Ru(CO)_3$ units differ only slightly from those observed for the mononuclear complexes $Ru(CO)_3X$-$[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ (X = Cl, Br, I), which contain a similar *fac*-$Ru(CO)_3$ unit chelated by a MAD-yl ligand.[22] The ν(C=N) band of the two equivalent MAD-yl ligands is observed at 1574 cm^{-1} (in a KBr pellet) and points to σ(N) coordination of the imine moieties in **11a**. For $Fe(CO)_3[CH_3C{=}C(H)C(H){=}N\text{-}t\text{-}Bu]$, containing a π,π-coordinated MAD ligand, the ν(C=N) band has been found at 1475 cm^{-1}, which is considerably lower compared to

---

[22] Mul, W. P.; Elsevier, C. J.; van Leijen, M.; Spaans, J. *Organometallics* **1991**, *10*, 251.

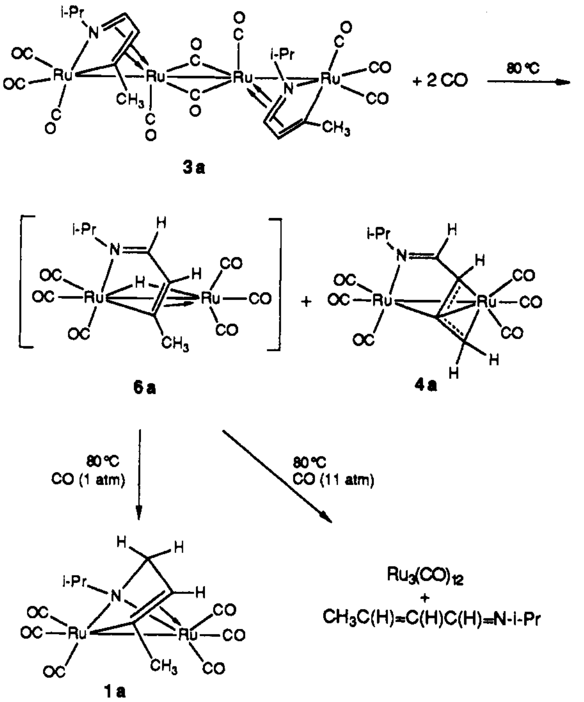
those of the MAD-yl ligands in **11a** or the free ligand value of 1657 cm^{-1}.[23]

The ^1H and ^{13}C NMR data of **11a** are indicative of merely $\sigma(N)$-$\sigma(C)$ coordination of the two equivalent MAD-yl ligands. The resonances of the imine and olefin protons H_{im} and H_α[4] are found at 7.90 and 6.56 ppm, respectively, and those of the corresponding carbon atoms C_{im} and C_α at 164.3 and 128.6 ppm, respectively. These chemical shifts are very similar to those found for $\sigma(N)$-$\sigma(C_\beta)$-coordinated (3e) MAD-yl ligands in other complexes (e.g. $Ru^{II}(CO)_3X[CH_3C{=}C(H)C(H){=}N$-*i*-Pr],[22] $Ru^{II}(CO)_2[CH_3C{=}C(H)C(H){=}N$-*i*-Pr$]_2$,[24] and $Ir^{III}HCl[C_6H_5C{=}C(H)C(H){=}N$-*i*-Pr][P(c-Hex$)_3$]).[25] The diastereotopicity of the two *i*-Pr methyl groups in the ^1H and ^{13}C NMR spectra of **11a** clearly reveals coordination of the N atoms to the cluster core. The ^{13}C NMR spectrum of **11a** ($CDCl_3$, 263 K) shows five resonances corresponding to sp or sp^2 carbon atoms which are directly coordinated to a ruthenium atom, i.e., with chemical shifts exceeding 185 ppm. Three of those, at 203.4, 199.9, and 187.4 ppm, can readily be assigned to the CO ligands of the two equivalent $Ru(CO)_3$ units. Assignment of the other two, at 222.1 and 210.8 ppm, which correspond to the metalated C_β atoms and the CO ligands of the symmetric $Ru(CO)_4$ units, was achieved by considering the fact that no bridging CO ligands are observed in the IR spectrum of **11a**. Since terminally coordinated CO ligands in ruthenium complexes are usually observed in the region of 185–215 ppm,[26] the 210.8 ppm resonance is assigned to the eight equivalent CO ligands of the inner $Ru(CO)_4$ units and, as a consequence, the 222.8 ppm signal is ascribed to the metalated C_β atoms. For other $\sigma(N)$-$\sigma(C)$ ruthenium-chelating MAD-yl ligands, the ^{13}C resonances for C_β have been observed in the region of 210–225 ppm.[22,24]

As shown in Scheme I, formation of **11a** proceeds via several intermediates. Of these, the undecacarbonyl compound **8a** has been neither isolated nor observed spectroscopically. Prior to the formation of the isolable CO adducts **9a**, **10a**, and **11a**, interconversion of the two diastereomers of **3a** takes place. From either of the pure diastereomers of **3a** an equimolar mixture of both diastereomers is formed in solution within 15 min after saturation with CO. As already discussed, this process takes place *intramolecularly* and is proposed to proceed via the intermediacy of **8a**.[8]

Compound **9a** could be isolated in an almost pure state by terminating the reaction of **3a** with CO after about 2 h and separation of the thus obtained mixture of **3a** and **9a** by column chromatography. The dodecacarbonyl compound **9a** could unfortunately only be obtained as an oil. When it stands, **9a** reverts slowly to the parent compound **3a**. The structure of **9a** has been assigned on the basis of its IR and NMR (^1H, ^{13}C) spectroscopic characteristics (Table II) and reactivity (with CO to afford **10a** and **11a**; upon heating to give **3a**). The IR spectrum of **9a** in hexane shows five IR bands in the terminal ν(CO) region. No bands are present in the bridging ν(CO) region (1650–1850 cm^{-1}), indicating that upon addition of two CO ligands to **3a** (giving **9a**) both CO bridges in **3a** open. The ^1H and ^{13}C NMR spectra of **9a** in $CDCl_3$ show the presence of two inequivalent coordinated MAD-yl ligands. One of the MAD-yl ligands adopts a chelating $\sigma(N)$-$\sigma(C)$ (3e) bonding mode, whereas the other donates seven electrons to the cluster core in a bridging $\sigma(N)$-$\sigma(C)$-$\eta^2(C{=}N)$:$\eta^2(C{=}C)$ bonding mode. Interestingly, doubling of some of the ^{13}C NMR resonances (e.g. the 221.9[1]/221.8[7] and 163.0/162.9 ppm signals assigned to C_9 and C_{11}, respectively), just as for parent **3a**,[5,8] indicates the existence of two diastereomers of **9a**. This proves that the distinguishable (^1H NMR) 3e- and 7e-donating MAD-yl ligands are coordinated to one and the same cluster core. Complete assignment of the ^1H and ^{13}C NMR data of **9a** is given in Table II.

Scheme II. Thermally Induced Transformation of 3a under CO



The tridecacarbonyl compound **10a** could not be isolated as a pure compound, but its intermediacy could be inferred from IR and ^1H and ^{13}C NMR spectra of mixtures containing **9a**, **10a**, and **11a**. Although IR spectra of **10a** recorded in hexane were not from pure samples, due to the inevitable presence of **9a** and/or **11a**, it was found that **10a** shows no ν(CO) bands attributable to bridging CO ligands, indicating that **10a**, just as **9a** and **11a**, contains merely terminal CO ligands. Both ^1H and ^{13}C NMR spectra of **10a** show the presence of two inequivalent MAD-yl ligands. One of these is chelating $\sigma(N)$-$\sigma(C)$ (3e) coordinated, whereas the other adopts a bridging $\sigma(N)$-$\sigma(C)$-$\eta^2(C{=}C)$ (5e) bonding mode. The latter coordination mode has also been found in $HRu_2(CO)_6[R^1C{=}C(H)C(H){=}NR^2]$ (R^1, R^2 = CH_3, *t*-Bu (**6c**), C_6H_5, *i*-Pr (**6d**))[9] and HFeRu(CO)6[$R^1C{=}C(H)C(H){=}NR^2$].[27] The NMR data for **10** are included in Table II.

Thermally Induced Reaction of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N$-*i*-Pr$]_2$ (3a) with CO. When a solution of **3a** in benzene or heptane is heated at 80 °C under 1 atm of CO for 2 h, conversion takes place, giving the known[5,12] dinuclear complexes $Ru_2(CO)_6[CH_3C{=}C(H)CH_2N$-*i*-Pr] (**1a**) and $Ru_2(CO)_6[CH_2CC(H)C(H){=}N$-*i*-Pr] (**4a**) as the main products, each in about 40% yield (Scheme II).

---

[23] Otsuka, S.; Yoshida, T.; Nakamura, A. *Inorg. Chem.* **1967**, *6*, 20.

[24] Mul, W. P.; Elsevier, C. J.; Spaans, J. *J. Organomet. Chem.* **1991**, *402*, 125.

[25] van Baar, J. F.; Vrieze, K.; Stufkens, D. *J. Organomet. Chem.* **1975**, *97*, 461.

[26] Brief inspection of the literature showed δ 216.7 ppm, found for $Ru(CO)(COD)_2$, to be the highest δ value thus far observed for a terminal CO ligand in a ruthenium complex. See: Cox, D. N.; Roulet, R. *Organometallics* **1986**, *5*, 1886.

[27] Beers, O. C. P.; Elsevier, C. J.; Mul, W. P.; Vrieze, K.; Häming, L. P.; Stam, C. H. *Inorg. Chim. Acta* **1990**, *171*, 129.

Furthermore, a small amount of a new organometallic compound, $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_3)_2]$ (**12a**, ca. 2%), was formed. During this conversion, the initial orange-red color gradually changes to yellow. Compound **3a** is rather thermally resistant in the absence of CO; i.e., a very slow decomposition takes place with formation of several products, including small amounts of **4a** and $Ru_3(CO)_6[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$.[13b]

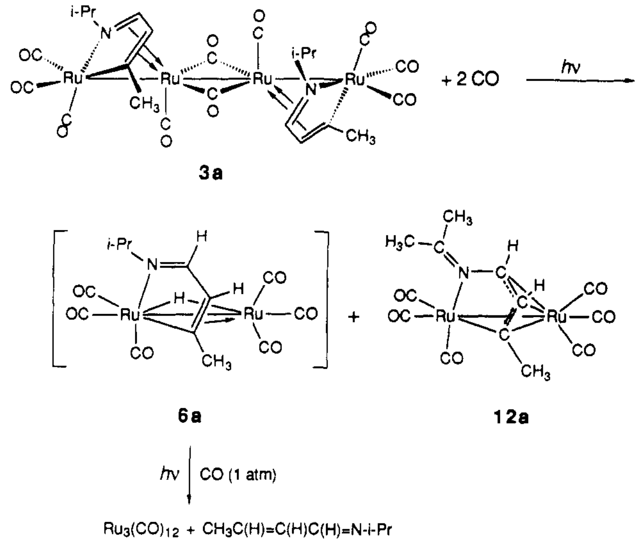
The formation of **1a** and **4a** in about equal quantities, the ligand of one of which (**1a**) contains an additional hydrogen atom compared to the parent MAD-yl ligand, whereas the ligand of the other (**4a**) has lost one, indicates that in the course of the reaction a H atom of the $C_\gamma H_3$ group[4] of one of the MAD-yl ligands of **3a** is selectively and presumably intramolecularly transferred to the imine carbon of the other MAD-yl ligand. Additional CO seems only to be required for cluster breakdown and to render the dinuclear products coordinatively saturated; two molecules of CO are consumed during this reaction.

As mentioned, both **1a** and **4a** are known products.[5,12] It has been shown that **1** may be formed by a thermally induced isomerization of $HRu_2(CO)_6[R^1C{=}C(H)C(H){=}NR^2]$ (**6**). This complex, however, has thus far only been isolated for R^1, R^2 = CH_3, *t*-Bu (**6c**) and C_6H_5, *i*-Pr (**6d**) and was shown to be thermally considerably more stable with R^2 = *t*-Bu.[9] It was anticipated that **6a** might be formed as an intermediate during the thermal reaction of **3a** with CO, whereafter it is converted into **1a**. The thermal reaction of **3b** with CO at 80 °C confirmed this hypothesis; besides formation of **4c**, dinuclear hydrido complex **6c** was observed as an intermediate (IR, ^{1}H NMR) which, upon continued heating under CO, isomerized quantitatively into **1c**.

In search for intermediates (i.e. **6a**), the reaction of **3a** with CO was followed by ^{1}H NMR spectroscopy in a pressurizable NMR tube.[10] An equimolar mixture of the *CA*/*AC* and *CC*/*AA* diastereomers of **3a** in toluene-d_8 was heated at 80 °C under 11 bar of CO. No buildup of a measurable steady-state concentration of the presumed intermediate **6a** was observed. The reaction path (Scheme II), however, had partly changed compared to the reaction carried out at 1 bar of CO pressure. Besides **4a**, formation of CH_3,*i*-Pr-MAD (ratio MAD:**4a** ~3:4)[28] instead of **1a** was observed. Furthermore, after the reaction was complete and the NMR tube was cooled to ambient temperature, one regularly shaped crystal was formed that was identified as $Ru_3(CO)_{12}$. Apparently, under high CO pressure (11 atm), the transient intermediate **6a** reductively eliminates CH_3,*i*-Pr-MAD, instead of isomerizing to **1a**.

Photochemically Induced Reaction of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (3a) with CO. When a solution of **3a** in an apolar solvent (hexane, benzene) is irradiated by a mercury arc source under an atmosphere of CO (1 atm), a new organometallic product, $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_3)_2]$ (**12a**), is obtained in about 40% yield. This product contains a ligand from which the methine hydrogen atom of the *i*-Pr substituent has been abstracted. Also, a small amount of **4a** (~3%) is isolated after chromatographic separation of the reaction products. Dinuclear **12a** is a constitutional isomer of **4a**, the dehydrogenated product obtained during the thermal reaction of **3a** with CO, as described above. In contrast to the thermal reaction, however, no organometallic complex was found that contained a ligand with an additional H atom with respect to the parent MAD-yl ligand. The fate of the photochemically abstracted CH hydrogen atom of the *i*-Pr group became clear by performing the photochemical reaction of **3a** with CO in a small amount of NMR solvent (C_6D_6) and running a ^{1}H NMR spectrum of the crude reaction mixture. After photolysis was completed, the reaction mixture was muddy and a red-purple deposit (polymeric $[Ru(CO)_4]_n$)[14] covered the glass wall. After filtration, ^{1}H NMR spectroscopy revealed, besides **12a** and a small amount of **4a**, the pressure of CH_3,*i*-Pr-MAD[27] as a major product in a quantity comparable to that of **12a**. We assume, just as during thermolysis of **3a** under CO, the intermediacy of the hydrido compound **6a**, which upon further irradiation under CO reductively eliminates CH_3,*i*-Pr-MAD with concomitant formation of $Ru_3(CO)_{12}$. The latter is subsequently photolyzed to $[Ru(CO)_4]_n$.[14] The photochemical reaction of **3a** with CO has been outlined in Scheme III.

Scheme III. Photochemically Induced Transformation of 3a under CO



The photochemical reaction of **3b** (R^1, R^2 = CH_3, c-Hex) with CO yielded a plethora of organometallic products, including a small amount of $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_2CH_2)_2CH_2]$ (**12b**; ca. 5%). Apparently, the photochemically induced abstraction of the tertiary hydrogen atom is less facile with R^2 = c-Hex than with R^2 = *i*-Pr.

Photochemically no isomerization of **4a** into **12a** could be induced, and thermally **12a** appeared to be rather stable; i.e., no isomerization into **4a** was observed. These experiments prove unambiguously that the different reaction products (i.e., **4a** and **12**), which contain a ligand from which one H atom has been abstracted, are formed during the primary reactions (C–H activation and H migration) on the cluster core.

Molecular Structure of $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_3)_2]$ (12a). The crystal structure of **12a** consists of two discrete molecules; two enantiomers of **12a** are present in the unit cell, space group $P\bar{1}$. A PLUTON drawing of the molecular geometry of **12a** and its atomic numbering scheme is shown in Figure 1. Positional parameters and bond lengths and selected bond angles are given in Tables III and IV, respectively.

The organometallic complex consists of a "sawhorse" type $Ru_2(CO)_6$ core, composed of two $Ru(CO)_3$ units held together by a 6e-donating bridging $\sigma(N)$-μ_2-η^3-2-methyl-3-azahepta-2,4-diene-6,6-diyl ligand and a Ru–Ru bond

---

[28] ^{1}H NMR for $CH_3C(H){=}C(H)C(H){=}N\text{-}i\text{-}Pr$ (C_6D_6, 298 K, 100 MHz; δ in ppm (*J* in Hz) relative to TMS): 7.60 (d, ^3J = 8.5, N=C*H*), 6.23 (ddq, ^3J = 8.5, ^3J = 16.0, ^4J = 1.0, N=CHC*H*), 5.72 (dq, ^3J = 16.0, ^3J = 6.5, CH=C*H*CH$_3$), 3.13 (sept, ^3J = 6.0, NC*H*(CH$_3$)$_2$), 1.50 (dd, ^3J = 6.5, ^4J = 1.0, CH=CHC*H*$_3$), 1.15 (d, ^3J = 6.5, NCH(C*H*$_3$)$_2$).

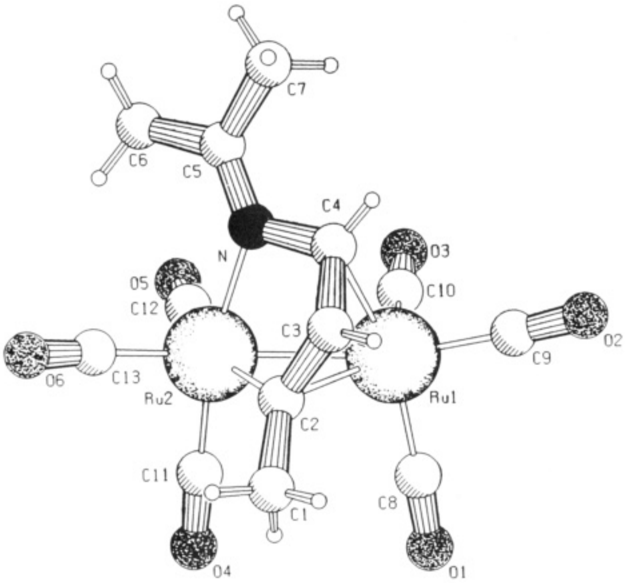


Figure 1. Molecular structure of $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_3)_2]$ (**12a**).

Table III. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for 12a

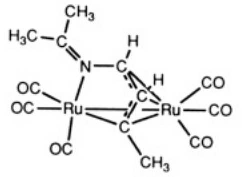
atom	*x*	*y*	*z*	*U*(eq),[a] Å^2
Ru(1)	0.03643 (4)	1.23047 (3)	0.11596 (2)	0.0488 (1)
Ru(2)	0.01917 (4)	1.26707 (2)	0.32827 (2)	0.0461 (1)
O(1)	0.3799 (7)	0.9639 (3)	0.1056 (3)	0.124 (2)
O(2)	−0.0667 (7)	1.2391 (4)	−0.1131 (3)	0.114 (2)
O(3)	0.2918 (5)	1.4371 (3)	0.0754 (2)	0.079 (1)
O(4)	0.3424 (6)	1.0080 (3)	0.3802 (3)	0.104 (1)
O(5)	0.3223 (5)	1.4392 (3)	0.3444 (3)	0.088 (1)
O(6)	−0.2114 (6)	1.2661 (3)	0.5486 (3)	0.101 (1)
N	−0.2047 (4)	1.4328 (2)	0.2589 (2)	0.0461 (7)
C(1)	−0.1517 (7)	1.0084 (4)	0.2897 (4)	0.078 (2)
C(2)	−0.1412 (5)	1.1545 (3)	0.2590 (3)	0.054 (1)
C(3)	−0.2725 (5)	1.2373 (3)	0.1907 (3)	0.056 (1)
C(4)	−0.2523 (5)	1.3753 (3)	0.1688 (3)	0.0511 (9)
C(5)	−0.2777 (6)	1.5603 (3)	0.2774 (3)	0.054 (1)
C(6)	−0.2228 (8)	1.6174 (4)	0.3698 (3)	0.073 (1)
C(7)	−0.4259 (7)	1.6601 (4)	0.2104 (3)	0.067 (1)
C(8)	0.2537 (7)	1.0631 (4)	0.1068 (4)	0.079 (2)
C(9)	−0.0263 (7)	1.2318 (4)	−0.0274 (3)	0.072 (1)
C(10)	0.1999 (5)	1.3585 (4)	0.0905 (3)	0.054 (1)
C(11)	0.2220 (7)	1.1062 (4)	0.3611 (4)	0.072 (1)
C(12)	0.2095 (6)	1.3786 (4)	0.3400 (3)	0.058 (1)
C(13)	−0.1252 (6)	1.2713 (4)	0.4687 (3)	0.063 (1)

[a] *U*(eq) is equal to one-third of the orthogonalized $\mathbf{U}_{ij}$ tensor.

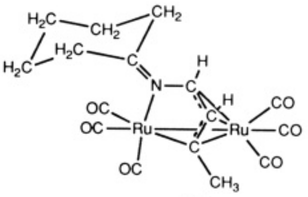
with a distance of 2.7341 (9) Å, which falls within the range of 2.70–2.90 Å for single Ru–Ru bonds.[29] The Ru–C bonds within the Ru(1)(CO)$_3$ unit are of similar length (1.903 (4)–1.924 (4) Å). In contrast, a rather long Ru(2)–C(12) bond of 1.957 (4) Å and a short Ru(2)–C(11) bond of 1.877 (5) Å are observed in the Ru(2)(CO)$_3$ moiety. These observations can readily be explained by invoking the large trans influence exerted by C(2), which tends to elongate the Ru(2)–C(12) bond, and the comparatively small trans influence of N on the Ru(2)–C(11) distance. The new dimethylimine fragment is σ(N)-coordinated to Ru(2) by a covalent bond of 2.139 (2) Å. The imine nature of this fragment is expressed by the N(1)–C(5) distance of 1.283 (4) Å and the trigonal bond angles around C(5).

The carbon atom C(2) is σ-coordinated to Ru(2). The Ru(2)–C(2) bond of 2.084 (2) Å falls within the limits of 2.02–2.09 Å usually found for normal single Ru–C(sp^2) bonds.[30] The distances of the C(2)–C(3)–C(4) fragment to Ru(1) (Ru(1)–C(2) = 2.244 (4) Å, Ru(1)–C(3) = 2.181 (4) Å, Ru(1)–C(4) = 2.179 (3) Å) point to an η^3-allylic coordination. The interligand distances C(2)–C(3) = 1.378 (5) Å and C(3)–C(4) = 1.435 (4) Å, however, are notably different, which could not be expected in the case of a normal η^3-allylic coordination. Similar bridging three-carbon fragments have been found in $Fe_2(CO)_6[HCC(C(O)CH_3)C(OC(O)CH_3)S\text{-}t\text{-}Bu]$,[31] $Fe_2(CO)_5[C(H)C(H)C(O)][P(Ph)_2CH_2PPh_2]$,[32] $Ru_2(CO)_6[HCC(CH_3)C(H)C(H){=}N\text{-}i\text{-}Pr]$,[33] and $Ru_2(CO)_6[HCC(CH_3)C(H)CN(H)\text{-}t\text{-}Bu]$.[33] Invariably, inequivalent distances within the η^3-allyl fragments have been observed, the shorter one being the C–C bond between the central carbon atom and the carbon atom that is σ-coordinated to the second metal center. Possibly the attachment of Ru(2) to C(2) by a σ-bond in **12a** causes the asymmetry within the η^3-allyl fragment. The N–C(4) bond that connects the two unsaturated parts of the ligand in **12a** amounts to 1.436 (4) Å, which is shorter than a formally single N–C bond of 1.48 Å, and points to electron delocalization between the two π-systems. In $Ru_2(CO)_6[CH_2CCC(H)C(H){=}N\text{-}t\text{-}Bu]$ (**4c**) the formally single C–C bond connecting the imine and η^3-allyl moieties is also rather short (1.437 (5) Å), indicating a similar electron delocalization.[12]

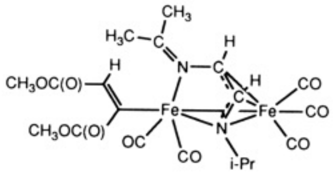
Compound **12a** represents the dehydrogenated analogue of $Ru_2(CO)_6[R^1CC(H)C(H)N(H)(i\text{-}Pr)]$ (**7**), which is formed after a silica-induced isomerization of $HRu_2(CO)_6[R^1C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ (**6**).[9]



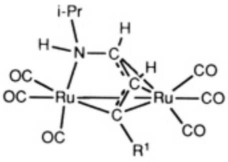
12a



12b



13



7

Finally, it is worth noting that the molecular geometry of **12a** is reminiscent of that of $Fe_2(CO)_5[(CH_3)_2C{=}NC(H)C(H)N(i\text{-}Pr)][\eta^1\text{-}CH_3OC(O)C{=}C(H)C(O)CH_3]$ (**13**), which is formed after a thermally induced isomerization of $Fe_2(CO)_5(i\text{-}Pr\text{-}DAB)[\mu_2\text{-}\eta^2\text{-}CH_3OC(O)C{\equiv}CC(O)CH_3]$.[34]

Spectroscopic Characteristics of 12a and 12b. The structures of the new organometallic compounds **12a** and **12b** could be assigned on the basis of their IR, FD-mass, and ^{1}H and ^{13}C NMR spectroscopic properties (see Table V), and an elemental analysis of **12a** (C, H, and N; see

---

[29] Bennett, M. A.; Bruce, M. I.; Matheson, T. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 4, p 691.

[30] A typical Ru–C(sp^2) bond length is about 2.07 Å. Tables of Ru–C bond lengths may be found in the following: (a) Wisner, J. M.; Bartczak, T. J.; Ibers, J. A. *Inorg. Chim. Acta* **1985**, *100*, 115. (b) Bruce, M. I. *Pure Appl. Chem.* **1986**, *58*, 553 and in ref 6.

[31] Seyferth, D.; Hoke, J. B.; Dewan, J. C. *Organometallics* **1987**, *6*, 895.

[32] Hogarth, G.; Knox, B. R.; Macperson, K. A.; Norton, D. A. V.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1988**, 360.

[33] Mul, W. P.; Elsevier, C. J.; Vuurman, M.; Smeets, W. J. J.; Spek, A. L., to be submitted for publication.

[34] Muller, F.; van Koten, G.; Vrieze, K.; Duineveld, K. A. A.; Heijdenrijk, D.; Mak, A. N. S.; Stam, C. H. *Organometallics* **1989**, *8*, 1324.

Table IV. Bond Distances (Å) and Selected Bond Angles (deg) for 12a (Esd's in Parentheses)

Ru(1)-Ru(2)	2.7341 (9)	Ru(2)-C(12)	1.957 (4)	C(5)-C(7)	1.503 (6)
Ru(1)-C(2)	2.244 (4)	Ru(2)-C(13)	1.922 (4)	O(1)-C(8)	1.130 (6)
Ru(1)-C(3)	2.181 (4)	Ru(2)-N(1)	2.139 (3)	O(2)-C(9)	1.144 (6)
Ru(1)-C(4)	2.179 (3)	C(1)-C(2)	1.509 (5)	O(3)-C(10)	1.126 (5)
Ru(1)-C(8)	1.924 (4)	C(2)-C(3)	1.378 (5)	O(4)-C(11)	1.131 (6)
Ru(1)-C(9)	1.915 (4)	C(3)-C(4)	1.435 (4)	O(5)-C(12)	1.112 (5)
Ru(1)-C(10)	1.903 (4)	N(1)-C(4)	1.436 (4)	O(6)-C(13)	1.110 (5)
Ru(2)-C(2)	2.084 (3)	N(1)-C(5)	1.283 (4)		
Ru(2)-C(11)	1.877 (5)	C(5)-C(6)	1.481 (6)		

Ru(2)-Ru(1)-C(2)	48.25 (9)	Ru(2)-N-C(4)	103.9 (2)
Ru(2)-Ru(1)-C(3)	70.9 (1)	Ru(2)-N-C(5)	133.7 (2)
Ru(2)-Ru(1)-C(4)	69.8 (1)	Ru(1)-C(8)-O(1)	177.3 (4)
Ru(2)-Ru(1)-C(8)	99.2 (2)	Ru(1)-C(9)-O(2)	176.8 (4)
Ru(2)-Ru(1)-C(9)	164.8 (1)	Ru(1)-C(10)-O(3)	178.1 (3)
Ru(2)-Ru(1)-C(10)	87.4 (1)	Ru(2)-C(11)-O(4)	178.8 (4)
N-Ru(2)-C(11)	167.9 (2)	Ru(2)-C(12)-O(5)	177.7 (4)
C(2)-Ru(2)-C(12)	159.4 (2)	Ru(2)-C(13)-O(6)	175.5 (4)
Ru(1)-Ru(2)-C(2)	53.5 (1)	C(1)-C(2)-C(3)	120.5 (3)
Ru(1)-Ru(2)-C(11)	96.8 (2)	C(2)-C(3)-C(4)	115.8 (3)
Ru(1)-Ru(2)-C(12)	105.9 (1)	N-C(5)-C(6)	120.9 (3)
Ru(1)-Ru(2)-C(13)	149.8 (1)	N-C(5)-C(7)	123.3 (3)
Ru(1)-Ru(2)-N	71.24 (7)	C(3)-C(4)-N	113.4 (3)
Ru(1)-C(2)-Ru(2)	78.3 (1)	C(4)-N-C(5)	122.1 (3)

Table V. Spectroscopic Data for $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_3)_2]$ (12a) and $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_2CH_2)_2CH_2]$ (12b)

IR Spectra						
12a[a,b]	2070 (s)	2034 (vs)	1999 (vs)	1985 (s)	1976 (m)	1970 (m)
12b[a]	2069 (m)	2033 (vs)	1998 (s)	1984 (m)	1975 (w)	

^1H NMR Spectra	
12a[c]	5.67 (br d, ^3J = 3.0, 1 H, $\mathrm{CH_3CC}\mathit{H}$), 4.98 (d, ^3J = 3.0, 1 H, $\mathrm{C}\mathit{H}\mathrm{N}$), 2.87 (s, 3 H, $\mathit{CH_3}\mathrm{CCH}$), 1.99, 1.98 (s, s, 3 H, 3 H, $\mathrm{N{=}C(C}\mathit{H_3}\mathrm{)_2}$)
12a[d]	5.24 (br d, ^3J = 2.5, 1 H, $\mathrm{CH_3CC}\mathit{H}$), 4.41 (d, ^3J = 2.5, 1 H, $\mathrm{C}\mathit{H}\mathrm{N}$), 2.78 (s, 3 H, $\mathit{CH_3}\mathrm{CCH}$), 1.24, 1.08 (s, s, 3 H, 3 H, $\mathrm{N{=}C(C}\mathit{H_3}\mathrm{)_2}$)
12b[c]	5.69 (br d, ^3J = 3.0, 1 H, $\mathrm{CH_3CC}\mathit{H}$), 5.18 (d, ^3J = 3.0, 1 H, $\mathrm{C}\mathit{H}\mathrm{N}$), 2.88 (s, 3 H, $\mathit{CH_3}\mathrm{CCH}$), 2.47, 2.28 (m, m, 2 H, 2 H, $\mathrm{N{=}C(C}\mathit{H_2}\mathrm{CH_2)_2CH_2}$), 1.60 (m, 4 H, $\mathrm{N{=}C(CH_2C}\mathit{H_2}\mathrm{)_2CH_2}$), 1.56 (m, 2 H, $\mathrm{N{=}C(CH_2CH_2)_2C}\mathit{H_2}$)
^{13}C NMR Spectra	
12a[e]	201.2, 200.5, 192.0 (3 $\mathit{C}\mathrm{O}$), 168.7, 165.0 ($\mathrm{CH_3}\mathit{C}\mathrm{CH}$, $\mathrm{N{=}}\mathit{C}\mathrm{(CH_3)_2}$), 88.3 ($\mathrm{C}\mathit{C}\mathrm{HCH}$), 64.8 ($\mathrm{CH}\mathit{C}\mathrm{HN}$), 21.0 ($\mathrm{C{=}C}\mathit{C}\mathrm{H_3}$), 33.0, 31.2 (2 $\mathrm{N{=}C(}\mathit{C}\mathrm{H_3)_2}$)
12b[e]	201.2, 200.5, 192.0 (3 $\mathit{C}\mathrm{O}$), 171.3, 168.6 ($\mathrm{CH_3}\mathit{C}\mathrm{CH}$, $\mathrm{N{=}}\mathit{C}\mathrm{(CH_2CH_2)_2}$), 88.4 ($\mathrm{C}\mathit{C}\mathrm{HCH}$), 63.8 ($\mathrm{CH}\mathit{C}\mathrm{HN}$), 33.1 ($\mathrm{C{=}C}\mathit{C}\mathrm{H_3}$), 41.3, 34.3, 30.6, 27.2, 26.8 ($\mathrm{N{=}C(}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2)_2}\mathit{C}\mathrm{H_2}$)

[a] ν(CO) in cm^{-1}; in hexane solution. [b] ν(C=N) = 1627 cm^{-1} (KBr pellet). [c] δ values in ppm (J values in Hz), relative to TMS; $CDCl_3$, 100 MHz, 297 K. [d] δ values in ppm (J values in Hz), relative to TMS; C_6D_6, 100 MHz, 297 K. [e] δ values in ppm, relative to TMS; $CDCl_3$, 25.0 MHz, 263 K.

Experimental Section) confirmed the relative abundance of the analyzed elements.

The molecular ions in the FD-mass spectra at *m/e* (**12a**) and 520 (**12b**) indicate a stoichiometry corresponding to a $Ru_2(CO)_6$ unit coordinated by a dehydrogenated (−2 H) CH_3,R^2-MAD (R^2 = *i*-Pr (**12a**), c-Hex (**12b**)) ligand. IR spectroscopy of **12a** and **12b** in hexane solution showed six (**12a**) or five (**12b**) bands in the 1970–2070-cm^{-1} region, consistent with the presence of six terminal CO ligands. The ν(CO) pattern of **12a** is almost identical with that of isostructural $Ru_2(CO)_6[CH_3CC(H)C(H)N(H)\text{-}i\text{-}Pr]$ (**7a**).[9] In the solid state (KBr pellet) **12a** shows a weak IR band at 1627 cm^{-1}, which can be attributed to the newly formed imine moiety, of which the π-bond is not involved in coordination to the metal core.

The NMR data for **12a** and **12b** in $CDCl_3$ are in accordance with their solid-state structures, as based on the crystal structure of **12a**. The former imine and olefin protons H(4) and H(3) of **12a** resonate at 4.98 and 5.67 ppm (**12b**, 5.18 and 5.69 ppm), respectively, which is in agreement with the present allylic character of the ligands. These protons are mutually coupled with ^3J = 3.0 Hz, whereas, due to a small long-range coupling ($^4J < 0.5$ Hz) with the methyl protons (H(1)), the H(3) resonance is somewhat broadened. The (asymmetric) allylic character of the ligands is also expressed by the ^{13}C resonances at about 169, 88, and 65 ppm for C(2), C(3), and C(4), respectively. The δ value of one of the outer allylic carbon atoms, C(2), has shifted about +100 ppm compared to the resonance for the other terminal allylic carbon atom, C(4). This high δ value for C(2) is attributable to its σ,π-allyl bridging coordination mode.[35] The resonance of the bridging terminal allyl carbon atom of isostructural **7** has been found at a similar δ value of 170 ppm,[9] and in $HRu_3(CO)_9(C_3R_3)$, the resonance of the relevant terminal allyl carbon atom of the μ_2-η^3-coordinated allyl fragment has been found at δ values between 160 and 200 ppm.[35]

As a consequence of the abstraction of the CH hydrogen atom of the *i*-Pr group, the CH_3 groups of the former *i*-Pr moiety of **12a** no longer appear as two doublets but as two sharp singlets between 1.0 and 2.0 ppm, their chemical shift difference being solvent dependent: in $CDCl_3$, $\Delta\delta$ = 0.01 ppm; in C_6D_6, $\Delta\delta$ = 0.16 ppm. The two inequivalent CH_2 groups of the rigid cyclic C_6H_{10} moiety in **12b** that are directly bonded to the imine carbon atom are found as broad multiplets at 2.47 and 2.28 ppm. The imine carbon atoms of **12a** and **12b** resonate at 165.0 and 171.3 ppm, respectively, and the aliphatic carbon atoms attached to these imine carbon atoms appear at 33.0 and 31.2 ppm (**12a**) or at 41.3 and 34.3 ppm (**12b**), which are somewhat higher δ values with respect to corresponding characteristic

---

(35) Aime, S.; Milone, L.; Osella, D.; Valle, M.; Randall, E. W. *Inorg. Chim. Acta* **1976**, *20*, 217.

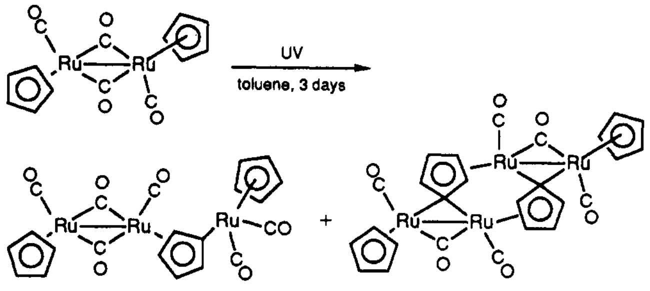
i-Pr methyl or c-Hex methylene resonances.

Discussion

Molecular Structure of 11a. The proposed linear tetranuclear compound **11a** is unique since it represents, to the best of our knowledge, the first homonuclear transition-metal chain complex that contains more than three metal centers in which no bridging or capping ligands or bridging metal units are present that stabilize the cluster core. Several linear trinuclear compounds have been reported which also lack the presence of bridging ligands.[36] Tetra- or oligonuclear acyclic transition-metal clusters reported thus far, however, invariably contain bridging ligands that stabilize their geometry.[36] Recently, however, the interesting heteropentametallic chain cluster [$Os_3(CO)_{12}Cl(SnCl_2)\{CpW(CO)_3\}$] has been reported, which also lacks bridging ligands.[37] In general, chain cluters, including the linear tetranuclear ruthenium clusters **3a**, **9a**, **10a**, and **11a** reported herein and the chain cluster $Ru_4(CO)_{10}[(CH_2C{=}C(H)C(H){=}N\text{-}t\text{-}Bu)_2]$, recently discovered by us,[38] may be useful as (models for) one-dimensional conductors or as precursors for metal polymers.[37]

Hemilability of the MAD-yl Ligand in 3a. During the course of the reaction of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**3a**) with CO, ultimately yielding **11a**, first the coordination geometry of one of the MAD-yl ligands is changed from the bridging 7e- (via 5e-) to the chelating 3e-donating mode, whereafter the second MAD-yl ligand undergoes the same selective stepwise decomplexation (see Scheme I). The complete conversion **3a** → **9a** takes about 12 h at ambient temperature. The next two CO additions to the cluster core are notably slower; **9a** → **10a** takes about 2 days, whereas **10a** → **11a** is completed after about 2 weeks. This indicates that the rate of substitution of the π-system of the 7e-donating MAD-yl ligand by CO ligands is considerably influenced by the coordination mode of the other MAD-yl ligand present on the linear tetranuclear cluster core. This influence is best explained by considering the coordination modes of the CO ligands of the central $Ru_2(CO)_n$ units in **3a**, **9a**, and **10a**. Each ruthenium atom of this unit in **3a** to which the π-system of a MAD-yl ligand is connected also bears one terminal and two bridging CO ligands.[39] It is apparent that there is a considerable effective π back-donation of d electrons from the inner ruthenium atoms into the π^* orbitals of these CO ligands. In **9a**, however, the 7e-donating MAD-yl ligand binds via its π-system to a ruthenium atom which contains two terminal CO ligands. The delocalization of d electrons from the inner ruthenium atoms into the π^* orbitals of the two terminal CO ligands will be less efficient compared to the situation in **3a**. As a consequence the basicity of these ruthenium atoms is higher and the back-bonding into the π^* orbitals of the 7e-donating MAD-yl ligand in **9a** will be enhanced compared to the case in **3a**, thereby stabilizing the 7e coordination mode of this π-system to the cluster in the former. Spectroscopic support may be gained from the ^{13}C NMR spectra of **3a** and **9a**. The chemical shifts of the C_{im} and C_α atoms for the 7e-donating MAD-yl ligands are found at lower frequencies in **9a** than in **3a** (**3a**, C_{im} 130 ppm, C_α 104.0 ppm (mean);[8] **9a**, C_{im} 128.5 ppm, C_α 93.9 ppm), indicating enhanced occupation of the π^* C=N and C=C orbitals. Thus, enhanced effective π-overlap between the relevant ruthenium d orbitals and the π-coordinated C=C—C=N moiety of the 7e-donating MAD-yl ligand in **9a** is assumed to stabilize the coordination of the π-system of this ligand with respect to substitution by CO ligands.

Scheme IV. Photochemically Induced Transformation of $[CpRu(CO)_2]_2$[37]



14 **15**

The reversible reactions of **3a** with CO express the hemilabile character of a MAD-yl ligand; i.e., the number of electrons (three, five, or seven) donated by this ligand can be flexibly adjusted to the need of a transition-metal complex. This flexible coordination behavior is reminescent of that of RN=C(H)C(H)=NR (R-DAB), a ligand that may donate four, six, or eight electrons via the N lone pairs and the C=N π-electrons to a metal fragment.[40] When the reactivity of **3a** is considered, the hemilability of the MAD-yl ligands should be borne in mind. Obviously, an open site is easily created on the cluster core of **3a**, which thus becomes prone to addition of, for example, CO, H_2, or other 2e-donating ligands. Furthermore, it is known that coordinatively unsaturated 16e or 14e d^8 centers (e.g. Fe(0), Ru(0), Rh(I), Ir(I), Pt(II)) readily undergo oxidative additions of C–H bonds, either *intra-* or *intermolecularly* (depending on factors discussed by Crabtree et al.).[41]

Mechanisms of the Thermally and Photochemically Induced C–H Activations in 3a. The mechanisms by which a C–H bond in either a positon α to the imine or in a position α to the olefin are regioselectively activated are of special interest. As described, different C–H activation processes take place after either thermal or photochemical activation of **3a**. Activation of C–H bonds in **3a** may take place on an in situ generated open site on the cluster core, i.e., a reactive 16e ruthenium center, or via a radical pathway. Both types of activations have several precedents in the literature.[42]

A radical pathway should be considered since the thermally induced isomerization of the two diastereomers of **3a** ((*CA*/*AC*)-**3a** ⇌ (*CC*/*AA*)-**3a**) takes place via dinuclear radicals, $\{Ru_2(CO)_5[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]^\bullet\}$, as reported elsewhere.[8] Such radicals may be photochemically formed out of **3a** as well. Furthermore, it should be

---

[36] Albers, M. O.; Robinson, D. J.; Coville, N. J. *Coord. Chem. Rev.* **1986**, *69*, 127.

[37] Dilshad, B. F.; Irving, A.; Moss, J. R. *J. Chem. Soc., Chem. Commun.* **1990**, 377.

[38] Mul, W. P.; Elsevier, C. J.; van Leijen, M.; Vrieze, K.; Spek, A. L. *Organometallics* **1991**, *10*, 533.

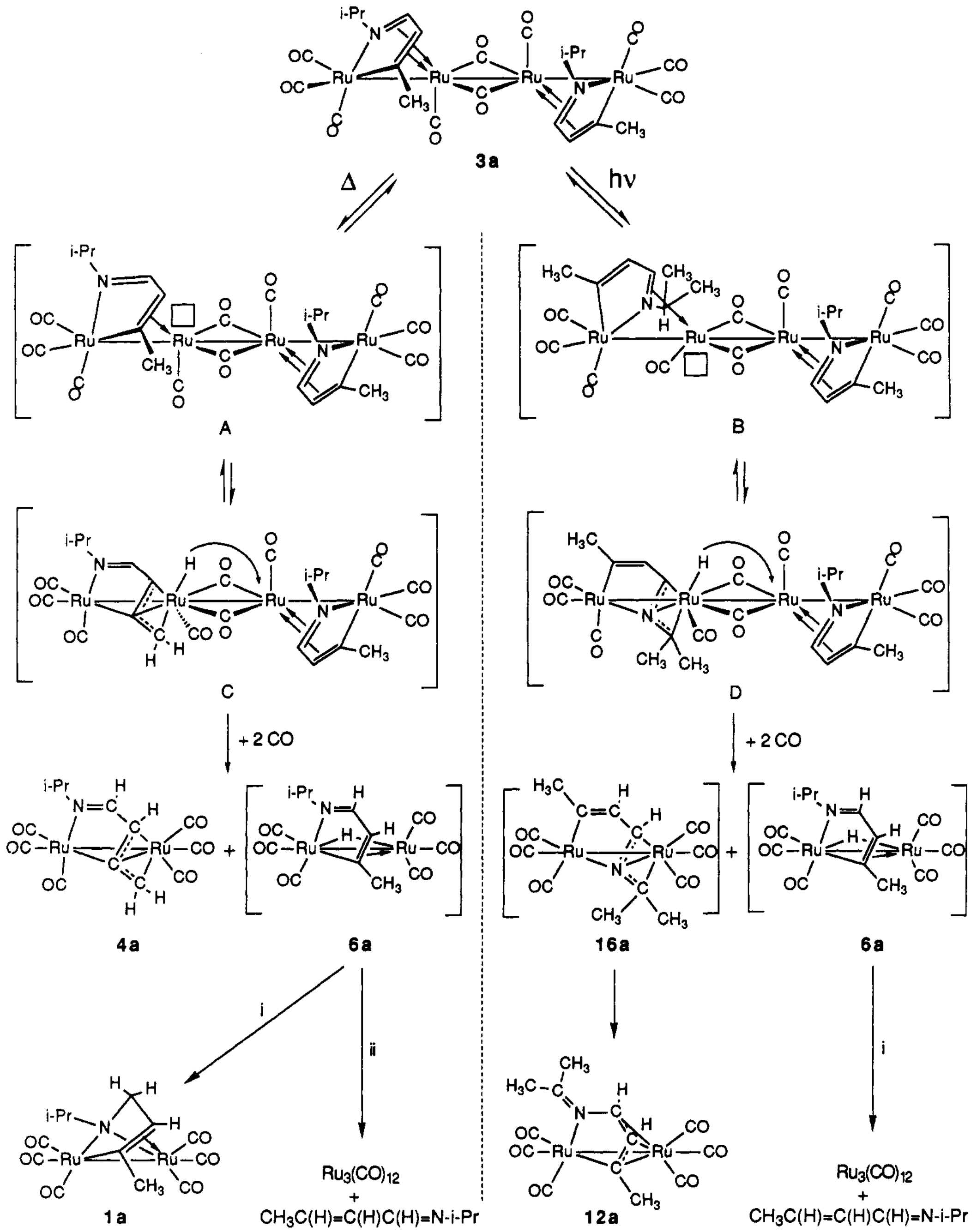
[39] This situation, however, in solution is not as fixed as in the crystal structures of the two diastereomers of **4a**. In solution rapid exchange of the terminal and bridging CO ligands takes place.[8]

[40] (a) van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151. (b) Vrieze, K.; van Koten, G. *Inorg. Chim. Acta* **1985**, *100*, 79. (c) Vrieze, K. *J. Organomet. Chem.* **1986**, *300*, 307.

[41] (a) Crabtree, R. H.; Lavin, M. E.; Holt, E. M. *Inorg. Chem.* **1985**, *24*, 1986. (b) Crabtree, R. H.; Lavin, M. E. *J. Chem. Soc., Chem. Commun.* **1985**, 794.

[42] (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (b) Green, M. L. H.; O'Hare, D. *Pure Appl. Chem.* **1985**, *57*, 897. (c) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41. (d) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113. (e) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147. (f) Muetterties, E. L. *J. Chem. Soc.* **1982**, *11*, 283. (g) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2007.

Scheme V. Proposed Mechanisms for the Thermally and Photochemically Induced Conversions of 3a in the Presence of CO[a]



[a] Legend: i, 1 atm of CO; ii, 11 atm of CO; □, open site.

noted that upon UV irradiation of $Ru_2(CO)_4(\eta^5\text{-}C_5H_5)_2$, the isolobal counterpart of **3**, the tri- and tetranuclear complexes **14** and **15** (Scheme IV) are formed presumably via radical pathways.[43]

A radical mechanism in our case, however, does not account for the observed difference in regioselectivity of the thermal and photochemical C–H activation processes. In general, C–H activation processes proceeding via a radical path show a preference for tertiary C–H > secondary C–H > primary C–H bonds.[41] In this way the photochemically induced abstraction of the *i*-Pr CH hydrogen might be rationalized, but not the selective thermally induced abstraction of a hydrogen atom from $C_\gamma H_3$.

The reactivity of aliphatic C–H bonds present in the coordination sphere of a cluster via a link with a donor ligand is usually the result of the facile loss (upon heating or irradiation) of other coordinating ligands such as CO or H_2, whereby an open site on the cluster core is created.[2] Since **3a** contains a number of CO ligands, formation of a reactive 16e ruthenium center may be achieved by CO elimination. However, the observed C–H bond activation processes only proceed readily in the presence of CO instead of being inhibited, which disfavors a mechanism in which CO dissociation is the first step. Furthermore, CO elimination, either thermally or photochemically, does not account for the different regioselective thermal and photochemical reaction paths.

Having excluded the above mentioned activation processes, only one likely possibility remains. Apparently, partial decoordination of a MAD-yl ligand takes place as

---

[43] Feasey, N. D.; Farrow, N. J.; Hogarth, G.; Knox, S. A. R.; MacPherson, K. A.; Morris, M. J.; Orpen, A. G. *J. Organomet. Chem.* 1984, *267*, C41.

the first reaction step. The observed hemilability of the MAD-yl ligands in **3a**, in which the π-systems of these ligands are stepwise substituted by CO ligands, clearly indicates by which way an open site on the cluster core may be created. Although the first observable substitution step includes decoordination of both the η^2(C=N) and η^2(C=C) moieties of one of the MAD-yl ligands, the stepwise substitution of the second MAD-yl ligand shows the η^2(C=N) fragment to be thermally more labile. Also, the reactivity of $HRu_2(CO)_5[R^1C{=}C(H)C(H){=}NR^2]$ (**2**) toward CO, whereby the η^2(C=N) moiety is selectively substituted by a CO ligand, giving $HRu_2(CO)_6[R^1C{=}C(H)C(H){=}NR^2]$ (**6**),[9] points to the presence of a more labile η^2(C=N) moiety compared to the η^2(C=C) entity in 7e-donating MAD-yl/ruthenium systems.

Thus, thermal activation of **3a** will most likely lead to intermediate A (Scheme V), containing an open site on one of the central ruthenium atoms, created after (reversible) breaking of a ruthenium η^2(C=N) π-bond. The still coordinated η^2(C=C) moiety forces its CH_3 substituent in the neighborhood of the reactive coordinatively unsaturated ruthenium center. Facile insertion of the 16e ruthenium center into one of the C_γ–H bonds leads to the formation of an η^3-allyl fragment and a hydride bonded to the same ruthenium center. Subsequent hydride transfer and cluster degadation into two inequivalent dinuclear complexes, $Ru_2(CO)_6[CH_2CC(H)C(H){=}N\text{-}i\text{-}Pr]$ (**4a**) and $HRu_2(CO)_6[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ (**6a**), only takes place in the presence of external CO, because two molecules of CO are necessary to render each of the two dinuclear products coordinatively saturated. The thermal decomposition of **6a** depends on the CO pressure, whereby the reaction paths as depicted in Scheme II are followed. We note that, on the basis of the proposed mechanistic aspects, no external CO is necessary for C–H activation in **3a**. Although **3a** is thermally rather stable, C–H activation may well take place reversibly in solutions of **3a** at elevated temperatures.

A similar mechanism rationalizes the photochemical activation of the *i*-Pr C–H bond of one of the MAD-yl ligands in **3a**. Instead of dissociation of the η^2(C=N) moiety, photochemically induced dissociation of the η^2-(C=C) moiety, giving intermediate B, seems a likely first step. Precedent for such behavior can be found in the breaking of the iron–olefin bond in $Fe(CO)_3(\eta^4\text{-MAD})$ upon photolysis in a CH_4 matrix at 10 K with formation of coordinatively unsaturated $Fe(CO)_3(\sigma\text{-MAD})$, containing a σ(N)-coordinated MAD ligand.[44] The still coordinating η^2(C=N) moiety in **3a** holds the *i*-Pr group into proximity of the created 16e ruthenium center, whereafter insertion of this ruthenium center into the *i*-Pr C–H bond becomes feasible. Subsequent H migration and CO-induced cluster breakdown then results in the formation of $Ru_2(CO)_6[CH_3C{=}C(H)C(H)NC(CH_3)_2]$ (**16a**) and $HRu_2(CO)_6[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ (**6a**). Both organometallic products are apparently not stable under the applied conditions. The former isomerizes to the observed product $Ru_2(CO)_6[CH_3CC(H)C(H)N{=}C(CH_3)_2]$ (**12a**), and the latter is assumed to reductively eliminate CH_3,*i*-Pr-MAD under the applied conditions. As far as we know, no examples of bridging μ-σ(*N*)-η^3-2-azaallyl ligand systems such as in **16a** have appeared in the literature. Since there is an excellent alternative coordination mode for the unsaturated ligand to the $Ru_2(CO)_6$ fragment, a combination of a common bridging σ(C)-η^3-allyl moiety and a σ(N)-bonded C=N fragment, the driving force for this isomerization is readily rationalized.

Acknowledgment. We wish to express our gratitude to Prof. G. van Koten and Dr. H.-W. Frühauf for helpful discussions, M. van Leijen and R. Schonk for performing part of the reactions, O. C. P. Beers for a sample of pure **11a**, J.-M. Ernsting for recording several ^{13}C NMR spectra, G. U-A-Sai and R. Fokkens for recording the mass spectra, and A. J. M. Duisenberg for X-ray data collection. This research was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Registry No. **1c**, 123083-56-7; **3a**, 111772-59-9; **3b**, 111772-60-2; **3c**, 134817-44-0; **4a**, 123083-57-8; **4c**, 123083-55-6; **5a**, 134817-46-2; **6c**, 140361-11-1; **9a**, 131078-67-6; **9b**, 140388-78-9; **10a**, 140409-87-6; **10b**, 140388-79-0; **11a**, 140361-09-7; **12a**, 140361-10-0; **12b**, 140361-12-2.

Supplementary Material Available: Tables of the anisotropic thermal parameters of the non-H atoms, calculated fractional coordinates and isotropic thermal parameters of the H atoms, and all bond distances and bond angles (2 pages); a listing of structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

OM910636M

---

[44] Kokkes, M. W.; Beentjes, P. C. J.; Stufkens, D. J.; Oskam, A. *J. Organomet. Chem.* **1986**, *306*, 77.