Organometallics 1991, *10*, 251–255

Reactions of the Linear Tetranuclear Complex $Ru_4(CO)_{10}(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)_2$ with Oxidizing Reagents. Syntheses of Halide-Bridged $[Ru(CO)_2X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2$ and *fac*-$Ru(CO)_3X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)$[1]

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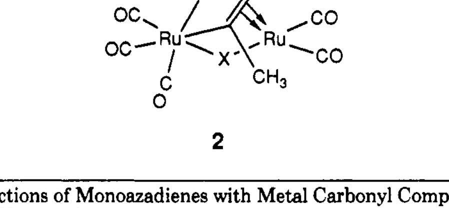
Received May 17, 1990

The linear tetranuclear complex $Ru_4(CO)_{10}(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)_2$ (**1**), containing two η^5-azaruthenacyclopentadienyl systems, reacts with oxidizing reagents (I_2, Br_2, NBS, CCl_4) at elevated temperatures (40–90 °C) in heptane or benzene to give the new dimeric halide-bridged organoruthenium(II) complexes $[Ru(CO)_2X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2$ (X = I (**3a**), X = Br (**3b**), Cl (**3c**); yield 30–80%) together with $[Ru(CO)_3X_2]_2$. The reactions of **1** with CX_4 (X = I, Br, Cl) are accelerated by CO, probably because $Ru_4(CO)_{12}(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)_2$ (**5**), which contains two unbridged metal–metal bonds, is formed prior to oxidation. The halide-bridged dimers **3a–c** are obtained as mixtures of four isomers, the configurations of which are discussed. Splitting of the halide bridges takes place when a solution of **3a–c** is saturated with CO, whereby mononuclear *fac*-$Ru(CO)_3X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)$ (**4a–c**) is obtained. This process is reversible; i.e., passing a stream of nitrogen through a solution of **4a–c** or removal of the solvent under vacuum causes the reverse reaction with reformation of **3a–c**. Compounds **3a–c** and **4a–c** have been characterized by IR (**3**, **4**), FD mass (**3**), ^1H (**3**, **4**), and $^{13}C\{^1H\}$ NMR (**4**) spectroscopy and satisfactory elemental analyses have been obtained for **3a–c**. Compounds **3** and **4** are suitable percursors for the preparation of new homo- and heteronuclear transition-metal complexes.

Introduction

In the course of our study focused on the formation and reactivity of metalated monoazadiene (MAD)[2] ligands in ruthenium carbonyl complexes, we recently reported a series of linear tetranuclear clusters, $Ru_4(CO)_{10}(R^1C{=}C(H)C(H){=}NR^2)_2$, which have been obtained in good yield from thermal reactions of $Ru_3(CO)_{12}$ with $R^1C(H){=}C(H)C(H){=}NR^2$.[3,4] Since a monoazadien-4-yl (MAD-yl)[2] ligand coordinated to a dinuclear metal carbonyl fragment causes that fragment to be chiral, these linear tetranuclear complexes, which contain two such fragments, are formed as mixtures of two diastereomers. The fluxional behavior of both diastereomers of $Ru_4(CO)_{10}(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)_2$ (**1**) in solution[5] and their reactivity toward H_2[6] and CO[7] have been investigated. Both diastereomers are stable in solution at ambient temperature, but upon heating (>70 °C), interconversion takes place. Although the precise mechanism of this process is not known in detail, it has been shown to proceed *intermolecularly*, possibly via dinuclear radicals formed after fission of the central intermetallic bond.[5] This process occurs also at room temperature in the presence of CO. In that case, however, the diastereomer interconversion proceeds via an *intramolecular* pathway.[5]



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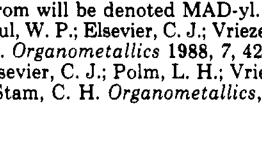

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Bearing in mind the isolobal relationship of **1** with $[CpRu(CO)_2]_2$[3] and the proposed formation of two dinuclear radicals $[Ru_2(CO)_5(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)^{\bullet}]$ upon thermolysis of **1**,[5] a complex with stoichiometry $Ru_2(CO)_5X[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ (**2**) might be formed upon oxidation of **1**. Since this dinuclear halide would be a useful precursor for the systematic buildup of new homo- and heteronuclear MAD-yl complexes, the reactivity of **1** toward oxidizing reagents was investigated. The results are presented in this paper.

Experimental Section

Materials and Apparatus. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on Bruker AC100 and WM250 spectrometers. IR spectra were recorded on a Nicolet 7199 B FT-IR spectrophotometer using matched NaCl solution cells of 0.5-mm path length. Field desorption (FD) and field ionization (FI) mass spectra were obtained with a Varian MAT-711 double-focusing mass spectrometer with a combined EI/FI/FD source. Elemental analysis were carried out by the section of Elemental Analysis of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands.

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[1] Reactions of Monoazadienes with Metal Carbonyl Complexes. XII. For part XI see ref 7.

[2] The *monoazadiene* $CH_3C(H){=}C(H){-}C(H){=}N\text{-}i\text{-}Pr$ will be abbreviated MAD. The monoazadien-4-yl anion $[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]^-$ derived therefrom will be denoted MAD-yl. See also ref 12.

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

[4] Mul, W. P.; Elsevier, C. J.; Polm, L. H.; Vrieze, K.; Zoutberg, M. C.; Heijdenrijk, D.; Stam, C. H. *Organometallics*, to be submitted for publication.

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

[6] Mul, W. P.; Elsevier, C. J.; van Leijen, M.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics*, to be submitted for publication.

[7] Mul, W. P.; Elsevier, C. J.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics*, to be submitted for publication.

0276-7333/91/2310-0251$02.50/0

Solvents were carefully dried and distilled under nitrogen prior to use. Silica gel for column chromatography (Kieselgel 60, 70–230 mesh, E. Merck, Darmstadt, Germany) was dried before use. The reactions were performed under an atmosphere of dry nitrogen (unless stated otherwise) by using Schlenk techniques. The complex $Ru_4(CO)_{10}(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)_2$ (1) was synthesized and purified as described before.[3,4]

Synthesis of $[Ru(CO)_2I(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2$ (3a). A solution of $Ru_4(CO)_{10}(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)_2$ (1; 0.30 g, 0.33 mmol) and I_2 (0.25 g, 1.0 mmol) in 30 mL of heptane was stirred at 90 °C for 2 h. The solvent was removed under vacuum and the residue chromatographed on silica. Elution with hexane gave a small band of $Ru_2(CO)_6(CH_2CC(H)C(H){=}N\text{-}i\text{-}Pr)$.[8] Further elution with hexane/diethyl ether (9:1) afforded a second yellow band containing $[Ru(CO)_2I(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2$ (**3a**) in about 80% yield (based on recovered MAD-yl). Crystallization from a concentrated diethyl ether solution at −30 °C afforded pure microcrystalline **3a**. A third band, eluted with dichloromethane, contained an as yet uncharacterized organometallic product. Subsequent elution with tetrahydrofuran gave a yellow product that was identified as $[RuI_2(CO)_3]_2$ by IR and FD mass spectroscopy. IR ν(CO) in $CHCl_3$: 2124 (s), and 2069 (s) cm^{-1} (lit. α-form 2116 (m), 2059 (s), 2009 (m) cm^{-1}; β-form 2122 (s), 2064 (s), 2004 (vw) cm^{-1}).[9] FDMS: found *m/e* 882 (calcd $M^{\bullet+}$ 882).[10] Anal. Found (calcd for $Ru_2C_{18}H_{24}N_2O_4I_2$ (**3a**)): C, 27.52 (27.42); H, 3.12 (3.07); N, 3.37 (3.55); I, 31.58 (32.19). FDMS: found *m/e* 788 (calcd $M^{\bullet+}$ 788).[10]

Synthesis of $[Ru(CO)_2Br(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2$ (3b). Method i. A solution of $Ru_4(CO)_{10}(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)_2$ (1; 0.26 g, 0.3 mmol) and Br_2 (0.175 g, 1.1 mmol) in 40 mL of heptane was stirred at 80 °C for 2 h. After this period, the brown precipitate ($[RuBr_2(CO)_3]_2$), formed after cooling of the reaction mixture to room temperature, was removed by filtration and the solvent evaporated under vacuum. The residue was chromatographed on silica, first employing hexane and then hexane/diethyl ether (9:1) as the eluent. The latter gave $[Ru(CO)_2Br(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2$ (**3b**) in about 80% yield after removal of the eluent under vacuum. Subsequent elution with tetrahydrofuran gave a small yellow band of $[RuBr_2(CO)_3]_2$. IR ν(CO) in CH_2Cl_2: 2132 (s), 2071 (s) cm^{-1} (lit.[11] 2137 (s), 2078 (s) cm^{-1}).

Method ii. A solution of 1 (0.27 g, 0.3 mmol) and NBS (0.32 g, 1.8 mmol) in 30 mL of benzene was stirred at 80 °C for 3 h. After this period, the brown precipitate containing $[RuBr_2(CO)_3]_2$ was removed by filtration and the filtrate worked up as described above, affording $[Ru(CO)_2Br(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2$ (**3b**) in a yield of 30%. Anal. Found (calcd for $Ru_2C_{18}H_{24}N_2O_4Br_2$ (**3b**)): C, 31.35 (31.14); H, 3.61 (3.49); N, 3.81 (4.03); Br, 22.60 (23.02). FDMS: found *m/e* 694 (calcd $M^{\bullet+}$ 694).[10]

Synthesis of $[Ru(CO)_2Cl(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2$ (3c). A solution of $Ru_4(CO)_{10}(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)_2$ (1; 0.45 g, 0.5 mmol) and CCl_4 (0.46 g, 3 mmol) in 40 mL of heptane was stirred at 80 °C for 2 h. After this period, the solution was cooled to ambient temperature, and the orange precipitate formed, $[RuCl_2(CO)_3]_2$ (IR ν(CO) in $CHCl_3$: 2140 (s), 2075(s) cm^{-1} (lit.[11] 2143 (s), 2083 (s) cm^{-1})), was removed by filtration. The solution was then evaporated to dryness and the residue chromatographed on silica. Elution with hexane/diethyl ether (9:1) afforded a yellow fraction of $[Ru(CO)_2Cl(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2$ (**3c**) in a yield of about 60%. Anal. Found (calcd for $Ru_2C_{18}H_{24}N_2O_4Cl_2$ (**3c**)): C, 35.93 (35.71), H, 4.14 (4.00), N, 4.50 (4.63), Cl, 11.46 (11.71). FIMS: found *m/e* 302 (calcd $M^{\bullet+}$ 604).[10]

Alternative Synthesis of 3a–c. A solution of $Ru_4(CO)_{10}(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)_2$ (1; 0.18 g, 0.2 mmol) and CX_4 (X = Cl, Br, I; 5.0 mmol) in 10 mL of benzene in a 100-mL Schlenk tube was stirred under an atmosphere of CO. The reaction was monitored by IR and stopped when the absorption band belonging to the bridging CO ligands of 1 (~1775 cm^{-1}) had disappeared. After this period (of about 24 h), the solvent was removed under vacuum and the residue chromatographed on silica. With hexane/dichloromethane (9:1) as the eluent, a yellow band was obtained containing an as yet unidentified organometallic product. Subsequent elution with hexane/diethyl ether (9:1) gave $[Ru(CO)_2X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2$ (X = I (**3a**), Br (**3b**), Cl (**3c**)) in 40–60% yield. Further elution with tetrahydrofuran gave yellow $[RuX_2(CO)_3]_2$.

Table I. IR Data of $[Ru(CO)_2X(CH_3{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2$ (X = I (3a), Br (3b), Cl (3c)) and *fac*-$Ru(CO)_3X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)$ (X = I (4a), Br (4b), Cl (4c))[a]

	ν(CO), cm^{-1}				
3a	2052 (m)	2044 (w)	2037 (s)	1986 (m)	1977 (vs)
3b	2048 (m)	2032 (s)	1982 (w)	1972 (vs)	
3c	2044 (w)	2029 (s)	2022 (m)	1968 (vs)	1957 (m)
4a	2097 (s)	2041 (s)	2015 (s)		
4b	2103 (s)	2047 (s)	2015 (s)		
4c	2109 (s)	2051 (s)	2020 (s)		

[a] Measured in hexane solution.

Reversible Reaction of 3a–c with CO to 4a–c. A solution of $[Ru(CO)_2X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2$ (**3a–c**) in benzene, hexane, or chloroform was stirred for 1 min (X = Cl), 10 min (X = Br), or 2 h (X = I) under an atmosphere of CO. After this period, the characteristic ν(CO) pattern of **3a–c** was replaced by that of $Ru(CO)_3X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)$ (X = I (**4a**), Br (**4b**), Cl (**4c**)). Removal of the solvent under vacuum or passing a stream of nitrogen through the solution caused the reverse of this conversion, yielding the parent compounds **3a–c** in quantitative yield. This procedure could be repeated several times without noticeable decomposition.

Results and Discussion

The mixed valence (I,0,0,I) tetranuclear organoruthenium complex $Ru_4(CO)_{10}(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)_2$ (1) reacts with appropriate oxidizing reagents (I_2, Br_2, NBS, CCl_4) at elevated temperatures (40–90 °C) in benzene or heptane to give the new yellow halide-bridged dimeric organoruthenium(II) complexes $[Ru(CO)_2X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2$ (X = I (**3a**), Br (**3b**), Cl (**3c**); yield: 30–80%) together with $[Ru(CO)_3X_2]_2$ (eq 1; method i). The dinuclear halide-bridged products **3a–c**, which

$$\underset{\mathbf{1}}{Ru_4(CO)_{10}(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)_2} + 3\text{ox} \rightarrow$$
$$\underset{\mathbf{3a\text{–}c}}{[Ru(CO)_2X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2} + [Ru(CO)_3X_2]_2 \quad (1)$$

(i) ox = I_2, Br_2, 2 NBS, 2 CCl_4; T = 80–90 °C
(ii) ox = 2 CX_4 (X = I, Br, Cl); T = 20 °C; catalyst CO

contain two MAD-yl[2] ligands, have been characterized by elemental analysis and FD/FI mass (Experimental Section), IR, and ^1H NMR spectroscopy (Tables I and II). On the basis of the elemental analyses in combination with the mass spectra, complexes **3a–c** are dinuclear species consisting of two 16e $[Ru(CO)_2X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]$ units. Because the ^1H NMR spectra of **3a–c** show chelating σ-N, σ-C coordinated (3e) MAD-yl ligands and in the IR spectra no bridging CO ligands are observed, the halides must be bridging between the metal centers in order to render the metals coordinatively saturated.

The use of an excess of oxidant (>6 equiv) should be avoided because this results in the formation of considerable quantities of other products. Although these products have not been characterized, electrophilic substitution of H_α of the MAD-yl ligand[12] in **3a–c** is feasible since such reactions have been observed for related

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

[9] Johnson, B. F. G.; Johnson, R. D.; Lewis, J. *J. Chem. Soc. A* **1969**, 792.

[10] Based on that peak of the isotopic pattern of the molecular ion that corresponds to ^{101}Ru.

[11] Benedetti, E.; Braca, G.; Sbrana, G.; Salvetti, F.; Grassi, B. *J. Organomet. Chem.* **1972**, *37*, 361.

[12] Suffixes to the atoms refer to $C(H_\gamma)_3C(H_\beta){=}C(H_\alpha)C(H_{im}){=}N\text{-}i\text{-}Pr$.

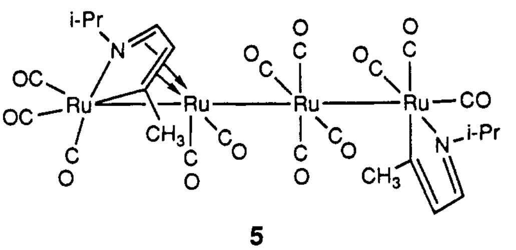
Table II. ^{1}H NMR Data of $[Ru(CO)_2X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2$ (X = I (3a), Br (3b), Cl (3c)) and *fac*-$Ru(CO)_3X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)$ (X = I (4a), Br (4b), Cl (4c))[a]

	H_{im}	H_α	H_γ	*i*-Pr (H)	*i*-Pr (CH_3)
3a[b]	7.86 (br s)	6.33 (m)	2.67 (d, 1.4)	4.94 (sept, 6.5)[c]	1.26–1.61
	7.74 (br s)	6.28 (m)	2.66 (d, 1.4)	5.07 (sept, 6.5)[d]	
	7.95 (br s)	6.33 (m)	2.59 (d, 1.4)	5.27 (sept, 6.5)[e]	
	7.95 (br s)	6.38 (m)	2.51 (d, 1.4)	5.37 (sept, 6.5)[e]	
3b	8.00 (br s)	6.28 (br s)	2.60 (br s)	4.40–5.40	1.22–1.60
	7.90 (br s)		2.54 (br s)		
			2.45 (br s)		
3c	8.00 (br s)	6.25 (br s)	2.57 (br s)	5.01 (sept, 6.5)	1.14–1.53
	7.89 (br s)		2.55 (br s)	4.87 (sept, 6.5)	
			2.43 (br s)	4.50 (sept, 6.5)	
				4.36 (sept, 6.5)	
4a	7.80 (d, 1.5)	6.41 (dd, 1.5, 1.5)	2.78 (d, 1.5)	3.94 (sept, 6.5)	1.42, 1.36 (d, 6.5)
4b[f]	7.84 (d, 2.0)	6.45 (dd, 2.0, 1.5)	2.74 (d, 1.5)	3.90 (sept, 6.5)	1.39, 1.35 (d, 6.5)
4c	7.89 (dd, 2.0, 1.0)	6.50 (dd, 2.0, 1.5)	2.73 (d, 1.5)	3.91 (dsept, 1.0, 6.5)	1.39, 1.37 (d, 6.5)

[a] Measured in $CDCl_3$, at 100 MHz and 298 K (unless stated otherwise), chemical shift values in ppm relative to (external) Me_4Si. Suffixes refer to $C(H_\gamma)_3C{=}C(H_\alpha)C(H_{im}){=}N\text{-}i\text{-}Pr$. In parentheses: multiplicity (d = doublet, sept = septet, m = multiplet, dd = doublet of a doublet, dsept = doublet of a septet, br = broad, br s = broad singlet), *J*(H,H). [b] 250.1 MHz. [c] Relative abundance: 84; corresponds to Figure 1C. [d] Relative abundance: 34; corresponds to Figure 1D. [e] Relative abundance: 100 or 98; corresponds to Figure 1A or 1B. [f] At 263 K.

azairidacyclopentadienyl[13] and oxamanganacyclopentadienyl species.[14]

The reactions of 1 with CX_4 (X = I, Br, Cl) are accelerated by CO. At room temperature, no reaction was observed between 1 and CX_4, whereas when performed under an atmosphere of CO complete conversion of the starting material took place within 1 day. Workup yielded $[Ru(CO)_2X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2$ (**3a–c**) and $[Ru(CO)_3X_2]_2$ as the main products (eq 1; method ii), in combination with an as yet uncharacterized organometallic complex, which was not formed during the thermal oxidation of 1, as described above. Most likely, $Ru_4(CO)_{12}(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)_2$ (**5**) is formed prior to oxidation during the CO-catalyzed reaction. This compound, which contains one 3e-donating MAD-yl ligand and one 7e-donating MAD-yl ligand and merely terminal CO ligands, is the first observable product during reactions of 1 with CO at ambient temperature.[15] Apparently, the presence of unbridged metal–metal bonds in **5** renders the linear tetranuclear metal core more prone to oxidative addition reactions than in **1**.



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Complexes **3a–c** are obtained as mixtures of isomers, as indicated by IR and ^{1}H NMR spectroscopy. The relative concentration of these isomers varied from reaction to reaction and also depended on the work-up procedure. Reproducible isomeric ratios, however, could be obtained by applying a CO assisted bridge-splitting/bridge-reformation cycle according to eq 2 (vide infra). Spectroscopic data of the thus obtained mixtures of isomers of **3a–c** are included in Tables I and II.

A high-resolution 250-MHz ^{1}H NMR spectrum of **3a** in $CDCl_3$ showed the presence of four doublet resonances at 2.67, 2.66, 2.59, and 2.51 ppm for the methyl protons in a relative abundance of 84:34:98:100, respectively (Table II). This ^{1}H NMR spectrum indicates that **3a** is formed either as a mixture of four isomers, of which each isomer possesses an element of symmetry by which the two MAD-yl ligands become chemically equivalent, or as a mixture of three isomers in which two (abundance 84 and 34) possess an element of symmetry and one does not. In the latter case, the asymmetric isomer would give rise to four strong IR absorptions in the ν(CO) region. Since only two strong IR bands are observed, it can be concluded that the halide-bridged dimers **3a–c** are formed as mixtures of four isomers, all containing a symmetry element (either C_i, C_2, or C_s). The 100-MHz ^{1}H NMR spectra of **3b** and **3c** also showed the presence of at least three isomers.

IR spectra of **3a–c** in hexane solution are less informative with respect to the relative isomer concentrations, but the presence of two main bands at about 2030 and 1970 cm^{-1} and a few weak ones clearly indicates (i) a cis orientation of the two carbonyls present in each $Ru(CO)_2$ fragment, (ii) the presence of an element of symmetry in each isomer, and (iii) the geometries of the $[Ru(CO)_2X(\text{MAD-yl})]$ units in all isomers are similar. The fact that each ruthenium atom in the dinuclear complexes contains two CO ligands in cis position implies that one of the CO ligands is located in cis position with respect to the two bridging halides and in the trans position to either the metalated C_β atom or the N atom. Given the fact that the N atom of the MAD-yl ligand is a harder donor compared to the C_β atom (which has good π-acceptor properties in view of its carbene-like character in the CO adducts **4a–c** (vide infra))[16] and the fact that the π-acceptor properties of a terminal CO ligand are notably better than those of a (bridging) halide (which is actually a π-donor), the N atoms will preferentially occupy trans positions relative to CO ligands; hence, the four configurations (A–D) as shown in Figure 1 are most likely to occur. Considering the steric interaction between the two MAD-yl ligands, the major isomers as observed by ^{1}H NMR (vide supra) most probably correspond to the C_i and C_2 forms A and B. The least abundant isomer will correspond to D.

The four structures proposed for **3a–c** correspond to those considered for a series of isostructural chloride-bridged dimers, which also contain two σ-N, σ-C chelating ligands, $[Ru(CO)_2Cl(C{\sim}N)]_2$ ((C∼N) = metalated 1-

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[13] van Baar, J. F.; Klerks, J. M.; Overbosch, P.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1976**, *112*, 95.

[14] DeShong, P.; Sidler, D. R.; Rybczynski, P. J.; Slough, G. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 2575.

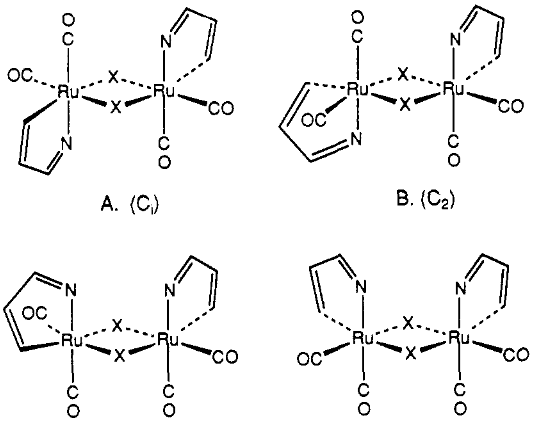
[15] Complete conversion of 1 into $Ru_4(CO)_{12}(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)_2$ (**5**) in solution under an atmosphere of CO at room temperature in the dark takes about 12 h.[7]

[16] Mul, W. P.; Elsevier, C. J.; Spaans, J. *J. Organomet. Chem.*, in press.

Table III. ^{13}C NMR Data of *fac*-$Ru(CO)_3X(CH_3C{=}C(H)C(H){=}N$-*i*-Pr) (X = I (4a), Br (4b), Cl (4c))[a]

	C_{im}	C_α	C_β	C_γ	*i*-Pr	CO's
4a[b]	171.0	130.2	210.2	34.0	63.0; 24.0; 22.8	191.7; 186.9; 185.6
4b[c]	172.0	130.9	211.1	34.0	63.5; 23.9; 23.4	192.4; 188.9; 186.1
4c[c]	171.9	130.8	211.2	33.8	63.3; 23.5; 23.3	192.3; 189.2; 186.1

[a] Measured in $CDCl_3$, at 263 K, chemical shift values in ppm relative to (external) Me_4Si. Suffixes refer to $C_\gamma(H)_3C_\beta{=}C_\alpha(H)C_{im}(H){=}N$-*i*-Pr. [b] At 62.9 MHz. [c] At 25.0 MHz.



A. (C_i) B. (C_2) C. (C_2) D. (C_s)

Figure 1. Proposed configurations of the halide-bridged dimers **3a–c** with their point group designation.

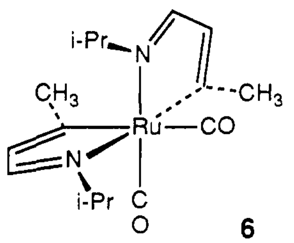
phenylpyrazole, 2-phenylpyridine, or benzoquinoline).[17] On the basis of (relatively uninformative) IR spectra in chloroform solution, however, only two of these configurations were proposed for these compounds. Considering that for the four isomers of **3a** clearly distinguishable by ^1H NMR, only two strong IR bands are observed, it may well be that (some of) the previously reported chloride-bridged complexes $[Ru(CO)_2Cl(C{\sim}N)]_2$ also exist as mixtures of four isomers instead of two.[17]

Facile splitting of the halide bridges takes place when a solution of **3a–c** is placed under an atmosphere of CO (eq 2). These reactions, whereby the mononuclear com-

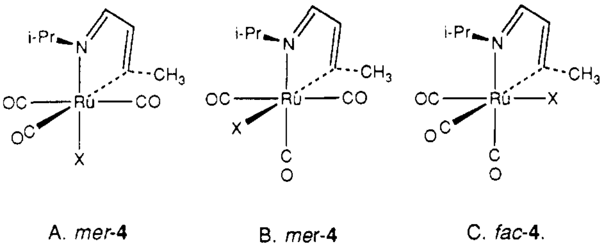
$$\underset{\mathbf{3a-c}}{[Ru(CO)_2X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)]_2} + 2CO \rightleftharpoons \underset{\mathbf{4a-c}}{2Ru(CO)_3X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)} \quad (2)$$

plexes $Ru(CO)_3X(CH_3C{=}C(H)C(H){=}N$-*i*-Pr) (X = I (**4a**), Br (**4b**), Cl (**4c**)) are formed, are reversible. Removal of the solvent or passing a stream of nitrogen through a solution of **4a–c** causes the reverse of eq 2. These conversions take place without a noticeable change of color; i.e., all complexes are yellow.

The mononuclear CO adducts **4a–c** have been characterized by IR, ^1H, and ^{13}C NMR spectroscopy (Tables I–III). The chelating σ-N, σ-C coordination mode of the MAD-yl ligand, which has also been observed in **3a–c**, $Ru_4(CO)_n(CH_3C{=}C(H)C(H){=}N$-*i*-$Pr)_2$ (*n* = 12 (**5**), 13, or 14),[7] $Ru^{II}(CO)_2(CH_3C{=}C(H)C(H){=}N$-*i*-$Pr)_2$ (**6**),[16] and



6



A. *mer*-4 B. *mer*-4 C. *fac*-4.

Figure 2. Possible structures for $Ru(CO)_3X(CH_3C{=}C(H)$-$C(H){=}N$-*i*-Pr) (X = I (**4a**), Br (**4b**), Cl (**4c**)).

$Ir^{III}HCl(C_6H_5C{=}C(H)C(H){=}N$-*i*-Pr)$[P(c\text{-}Hex)_3]_2$,[18] is clearly evident from its NMR characteristics. The H_{im} and H_α[12] resonances of **4a–c** (solvent: $CDCl_3$) are observed at 7.8–7.9 and 6.4–6.5 ppm, respectively, with mutual ^3J coupling of 1.5–2.0 Hz. Furthermore, ^4J coupling of 1.5 Hz of H_α with the γ-methyl protons is observed. The presence of two closely spaced doublets at about 1.4 ppm for the protons of the two *i*-Pr methyl groups reveals the diastereotopicity of these methyl groups. Similarly, the ^{13}C NMR spectra of complexes **4a–c** show diastereotopic *i*-Pr methyl resonances at about 23 ppm.

The C_{im} and C_α[12] resonances of **4a–c** are located at about 171 and 130 ppm, respectively. They compare very closely to the relevant chemical shifts observed for the two inequivalent MAD-yl ligands in mononuclear **6** (C_{im} 166.6 and 164.2 ppm; C_α 128.6 and 126.1 ppm)[16] and to the free ligand values of 168.25 and 127.81 ppm,[3] respectively. The ^{13}C resonances for the metalated C_β atoms of **4a–c** are observed at high δ values of about 211 ppm. In **6**, the metalated C_β atoms are observed at even higher δ values of 218.3 and 223.1 ppm. These relatively high-frequency chemical shifts can be explained by assuming a carbene-like character of these carbon atoms, cf. ref 16.

Three configurations, containing either facial or meridional CO ligands, are possible for the mononuclear complexes **4a–c**, as illustrated in Figure 2. Discrimination between the three possibilities is readily achieved by considering the ^1H NMR characteristics of **4a–c**. The CH_3 groups of the *i*-Pr substituent are diastereotopic, indicating that the Ru atoms are chiral, which implies a fac arrangement of the three CO ligands. This geometry is also apparent from the IR and ^{13}C NMR spectra of **4a–c**. In hexane solution, **4a–c** show three, approximately equally intense ν(CO) bands at about 2010, 2060, and 2020 cm^{-1}, and in the ^{13}C NMR spectra of **4a–c** recorded at −10 °C in $CDCl_3$, three resonances are observed in the terminal CO region (185–193 ppm), indicating the presence of three inequivalent CO ligands.

Stepwise breaking of the halide bridges of **3a–c** in the reaction with CO would result in the formation of both fac and mer isomers of **4a–c**. So the fac configuration must be thermodynamically favored, since only this configuration is observed in solution. Apparently, facile isomerization of the mer complex to the fac complex takes place. This can be rationalized considering the facile loss of CO

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[17] Hiraki, K.; Obayashi, Y.; Oki, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1372.

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

from **4a–c** (eq 2), affording the coordinatively unsaturated 16e species $Ru(CO)_2X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)$, which, in the presence of CO, will rapidly react to give the thermodynamically favored fac adduct. In the fac arrangement, competition of the better π-acceptor CO ligands for the same electron density of the metal center is maximally avoided. Interestingly, a mer arrangement of the only CO and the two PPh_3 ligands has been observed for the PPh_3 adducts $Ru(CO)Cl(C{\sim}N)(PPh_3)_2$, derived from $[Ru(CO)_2Cl(C{\sim}N)]_2$.[17] In these complexes, the trans arrangement of the PPh_3 groups, observed by ^{31}P NMR spectroscopy, was ascribed to the bulkiness of the PPh_3 groups.

It is worth mentioning that, whereas cleavage of the halide bridge in $[Ru(CO)_3Br_2]_2$ affording mononuclear $Ru(CO)_4Br_2$ only proceeds quantitatively under 100 bar of CO at 70 °C, conversion of **3a–c** to **4a–c** requires much less vigorous conditions (vide supra).[11] The enhanced lability of the halide bridges in **3a–c** compared to $[Ru(CO)_3Br_2]_2$ can be ascribed to the weaker Lewis acidity of a $Ru(CO)_2X(C{\sim}N)$ unit relative to a $Ru(CO)_3Br_2$ unit and is a result of the less pronounced π-accepting properties of a metalated MAD-yl ligand compared to the π-accepting properties of the combination of a CO ligand and a halide.

Oxidation of **1** has been shown to give the dinuclear halide-bridged complexes **3a–c** and $[Ru(CO)_3X_2]_2$ instead of $Ru_2(CO)_5X(CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)$ (**2**), as was proposed in the Introduction. Possibly the latter is an intermediate during oxidation of **1** but reacts further under the applied reaction conditions. Considering the relatively low oxidation states of the individual ruthenium atoms of **2** (these are formally monovalent), oxidation of **2** can readily be brought about. These low oxidation states facilitate further oxidation reactions that result in the formation of the halide-bridged dimers **3a–c**, in which the ruthenium atoms possess the divalent oxidation state, and $[Ru(CO)_3X_2]_2$. This is in agreement with the observation that in ruthenium carbonyl chemistry generally divalent metal centers result from oxidations of zero-valent or monovalent metal centers.[19]

Although the products obtained from oxidation reactions of **1** are not the dinuclear complexes **2** but instead are the halide-bridged dimers **3a–c**, these Lewis acids may also successfully be used for synthetic purposes. Facile halide bridge splitting reactions may, apart from CO, take place with other 2-electron-donor ligands such as phosphines,[11,17,20,21] alkynes, alkenes, dihydrogen, and electronically saturated but coordinatively unsaturated $[M(CO)_x]$ fragments (e.g., $M(CO)_5$ (M = Fe, Ru, Os), $HCo(CO)_4$, $CpRh(CO)_2$, $CpIr(CO)_2$, $Ni(CO)_4$). Furthermore, the halide present in **3** or **4** might be substituted by various anionic metal carbonyl species like $[HM(CO)_4]^-$, $[M(CO)_4]^{2-}$, $[CpM(CO)_2]^-$ (M = Fe, Ru), or $[Co(CO)_4]^-$, thus affording a new entry into homo- and heteronuclear azaruthenacyclopentadienyl chemistry.[22] The first results already obtained via this synthetic methodology[20] are very promising and encourage us in our current efforts to explore MAD-yl ligands as stabilizing and controlling ligands in organometallic building blocks for the rational design and syntheses of di- and oligonuclear transition-metal complexes.

Acknowledgment. We express our gratitude to Prof. K. Vrieze and Dr. H.-W. Frühauf for their interest, O.C.P. Beers for performing some experiments, and G. U-A-Sai for recording the mass spectra. The research was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

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(22) For the first heteronuclear complex that is stabilized by a monoazadien-4-yl ligand, $HFeRu(CO)_6(R^1C{=}C(H)C(H){=}N\text{-}i\text{-}Pr)$, see: Beers, O. C. P.; Elsevier, C. J.; Mul, W. P.; Vrieze, K.; Häming, L. P.; Stam; C. H. *Inorg. Chim. Acta* **1990**, *171*, 129.