rameters. For satisfactory convergence, we found it was necessary to model the halide sites such that the individual Cl multiplicities were constrained to be one minus the associated Br multiplicities. This assumption was supported by the spectroscopic properties of this batch of crystals, which provided convincing evidence for serious contamination by bromide. Specifically, the negative ion FABMS of the sample of (n-Bu_4N)[$OsCl_4$(CO)(EtOH)] showed clusters of peaks at $m/z = 450$ and $m/z = 494$ that are due to [$OsCl_3Br$(CO)(EtOH)]$^-$ and [$OsCl_2Br_2$(CO)(EtOH)]$^-$; these had intensities of 58% and 16%, respectively, relative tc the parent peak for [$OsCl_4$(CO)(EtOH)]$^-$ ($m/z = 406$, RI = 100%). In accord with these findings, we determined that some preparative batches of (n-$Bu_4N)_2Os_2Cl_8$ exhibited a weak band at 250 cm^{-1} in their low-frequency IR spectra that could be assigned[7] to the ν(Os-Br) mode of the bromide contaminant; the much more intense ν(Os-Cl) mode was located at 346 cm^{-1}. The source of the bromide is obviously the n-Bu_4NBr that is added during the synthesis of (n-$Bu_4N)_2Os_2Cl_8$ from the reaction of $Os_2(O_2CCH_3)_4Cl_2$ with ethanol/HCl(g) mixtures.[7,31] To avoid this occasional problem, n-Bu_4NPF_6 can be used in place of n-Bu_4NBr, as described in the modified procedure that is provided in the Experimental Section. This step gives a product that is free of a band at ca. 250 cm^{-1} in its IR spectrum.

Conclusions. As with the cleavage of the Os≡Os bond of (n-$Bu_4N)_2Os_2X_8$ (X = Cl, Br) by phosphine ligands,[1] we find that a similar reaction course ensures with isocyanide ligands and with carbon monoxide in ethanol. The mononuclear, paramagnetic, 17-electron osmium(III) complexes of the types (n-Bu_4N)[$OsX_4(CNR)_2$] and (n-Bu_4N)[OsX_4(CO)(EtOH)] are the major products and are obtained in very high yield. The ethanol ligand in the carbonyl complexes is readily displaced by other monodentate ligands, thereby providing an excellent general synthetic route to salts of the type (n-Bu_4N)[OsX_4(CO)L]. Crystal structure determinations on (n-Bu_4N)[$OsCl_4(CNxyl)_2$] and (n-Bu_4N)[$OsCl_{4-x}Br_x$(CO)(DMSO)] have shown the presence of trans octahedral geometries for the anions.

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Supplementary Material Available: Tables giving full details of the crystal data and data collection parameters (Tables S1 and S2), the positional parameters for all atoms (Tables S3 and S4), the thermal parameters (Tables S5 and S6), and complete bond distances (Tables S7 and S8) and bond angles (Tables S9 and S10) for (n-Bu_4N)[$OsCl_4(CNxyl)_2$] and (n-Bu_4N)[$OsCl_{2.68}Br_{1.32}$(CO)(DMSO)] (24 pages); tables of observed and calculated structure factors (56 pages). Ordering information is given on any current masthead page.

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[31] Note that we found no evidence for bromide contamination in the crystal of (n-Bu_4N)[$OsCl_4(CNxyl)_2$] that was also subjected to an X-ray structure determination. Also, the spectroscopic properties of the other isocyanide and carbonyl complexes gave only occasional evidence for minor contamination by bromide.

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Synthesis, Separation, and Structural Characterization (X-ray) of the Two Diastereomers of $Ru_3(CO)_6[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$, an Acyclic Trinuclear Complex That Is Isolobally Related to Cp_2Ru[1]

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Thermal reactions of $Ru_3(CO)_{12}$ (1 mmol) with the monoazadienes $R^1C(H){=}C(H)C(H){=}N\text{-}i\text{-}Pr$ (6 mmol; $R^1 = CH_3$ (**a**), C_6H_5 (**b**)) in refluxing heptane yield the trinuclear 50e complexes $Ru_3(CO)_6[R^1C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**5a,b**), containing two β-metalated monoazadien-4-yl ligands in a yield of 30% (**5a**) or 60% (**5b**). Compound **5** is formed via the intermediacy of the dinuclear complexes $Ru_2(CO)_6[R^1C{=}C(H)CH_2N\text{-}i\text{-}Pr]$ (**1**) and $(\mu\text{-}H)Ru_2(CO)_5[R^1C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ (**2**). Alternatively, compound **5a** has been obtained in low yield by pyrolysis of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**3a**). Compounds **5a,b** are both formed as a mixture of two diastereomers (*CC/AA*)- and (*CA/AC*)-**5a** have been separated by preparative HPLC on a reversed-phase column. Both diastereomers of **5a** have been characterized by X-ray crystal structures. Crystals of (*CA/AC*)-**5a** are monoclinic, space group $P2_1/n$, with $a = 8.684$ (1) Å, $b = 16.743$ (2) Å, $c = 16.852$ (2) Å, $\beta = 91.66$ (1)°, $Z = 4$, and $R = 0.025$. Crystals of (*CC/AA*)-**5a** are monoclinic, space group $P2/a$, with $a = 17.716$ (8) Å, $b = 8.581$ (3) Å, $c = 18.189$ (5) Å, $\beta = 118.56$ (3)°, $Z = 4$, and $R = 0.026$. Both diastereomers of **5a** consist of two azaruthenacyclopentadienyl fragments (which are isolobal to Cp) η^5-coordinated to a central ruthenium atom. The dimetallametallocenes **5a,b** are isolobally related to ruthenocene. Compounds **5a,b** are the first 50e trinuclear complexes of the iron triad which contain an open-chain, bent metal framework that is not stabilized by one or more ligands bridging the outer two metal centers. NOESY spectra showed that the bent geometry of both diastereomers of **5a** is retained in solution.

Introduction

The isolobal principle as formulated by Hoffmann[2] suggests that electronically and structurally related species may result from the formal interchange of a metal fragment for an isolobal carbon counterpart (and vice versa) by virtue of similarities in symmetry, shape, occupancy, and energy of their frontier orbitals. $Ru(CO)_3$ and CH^+ are isolobal and their formal interchange in the linear tetranuclear cluster $Ru_4(CO)_{10}[R^1C{=}C(H)C(H){=}NR^2]_2$ (**3**), with concomitant substitution of the NR by isoelectronic CH^- fragments, leads to the isolobal relation of **3** with $Ru_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ (Figure 1).[3]

It has been shown that the similarities between **3** and $Ru_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ are not restricted to their structure. The formation path of **3**,[4] its dynamic behavior in solution,[5] and inter-

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0020-1669/91/1330-4152$02.50/0

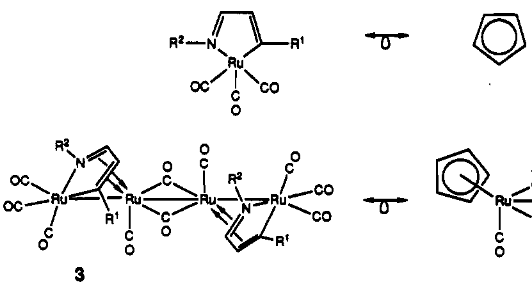

Figure 1. Some isolobal relations.

estingly also part of its chemical reactivity[5-7] appear to be comparable to that of $M_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ (M = Fe, Ru). The tetranuclear compound 3 has been obtained from thermal reactions of $Ru_3(CO)_{12}$ with $R^1C(H){=}C(H)C(H){=}NR^2$ (R^1,R^2-MAD)[8] as a mixture of two diastereomers.[4,5,9]

In this paper, we report on further investigations into the $Ru_3(CO)_{12}$/R^1,R^2-MAD system and describe the preparation, HPLC separation, and structural characterization of the two diastereomers of $Ru_3(CO)_6[R^1C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**5**), an acyclic trinuclear 50e complex, which is isolobally related to ruthenocene. Some aspects of this work have appeared as a communication,[10] whereas the results of a theoretical study on the electronic properties of one of the diastereomers of $Ru_3(CO)_6[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$, (*CC*/*AA*)-**5a**, performed by Casarin et al., have been published elsewhere.[11]

Experimental Section

Materials and Apparatus. ^1H and ^{13}C NMR spectra were obtained on Bruker AC100 and WM250 spectrometers. IR spectra were recorded with Perkin-Elmer 283 and Nicolet 7199 B FT-IR spectrophotometers using matched NaCl solution cells of 0.5-mm path length. Field desorption (FD) mass spectra[12] were obtained with a Varian MAT-711 double-focusing mass spectrometer with a combined EI/FI/FD source, fitted with a 10-μm tungsten-wire FD emitter containing carbon microneedles with an average length of 30 μm, using emitter currents of 0–15 mA. Elemental analysis were carried out by the Elemental Analysis Section of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands.

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. All reactions were performed under an atmosphere of dry nitrogen by using Schlenk techniques. The complexes $Ru_2(CO)_6[R^1C{=}C(H)CH_2NR^2]$ (R^1, R^2 = CH_3, *i*-Pr (**1a**); R^1, R^2 = C_6H_5, *i*-Pr (**1b**)), $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**3a**) were synthesized and purified as described before.[3,4] The monoazadienes $R^1C(H){=}C(H)C(H){=}NR^2$ (R^1, R^2 = CH_3, *i*-Pr (**a**); R^1, R^2 = C_6H_5, *i*-Pr (**b**)) were prepared according to standard procedures.[13]

The HPLC separations were performed with a modular Gilson liquid chromatographic system consisting of two Model 303 elution pumps, a Model 811 mixing chamber, a Model 7125 Rheodyne injector equipped with a 20-μL (analytical) or a 2-mL (preparative) sample loop, a Model 802c manometric module, and a Model 111 B UV detector operated at 254 nm, all obtained from Meyvis. The system was controlled by an Apple Macintosh SE with Rainin software. The analytical column was a Hypersil ODS 5-μm (100 × 4.8 mm) reversed-phase (RP) column; the preparative column was a Dynamax-C18 8-μm (250 × 21.4 mm) RP column in combination with a Dynamax-C18 8-μm (50 × 21.4 mm) RP guard column. For the eluent, a helium-degassed solvent mixture of 92.5/7.5 (v/v) CH_3OH/H_2O was used isocratically. The aforementioned preparative RP column was purchased from Meyvis, and the analytical RP column, from Hewlett-Packard. Samples were filtered over a disposable PTFE syringe filter (25 mm membrane; pore size = 0.45 μm) from Core Palmer Instrument Co. before they were passed through an HPLC column.

Table I. Crystal Data for (*CC*/*AA*)-**5a** and (*CA*/*AC*)-**5a**

	(*CC*/*AA*)-**5a**	(*CA*/*AC*)-**5a**
chem formula	$C_{20}H_{24}N_2O_6Ru_3$	$C_{20}H_{24}N_2O_6Ru_3$
mol wt	691.63	691.63
Z	4	4
cryst syst	monoclinic	monoclinic
space group	*P*2/*a*	*P*2$_1$/*n*
a, Å	17.716 (8)	8.684 (1)
b, Å	8.581 (3)	16.743 (2)
c, Å	18.189 (5)	16.852 (2)
β, deg	118.56 (3)	91.66 (1)
V, Å^3	2428.6 (17)	2449.1 (5)
D_{calc}, g cm^{-3}	1.891	1.876
μ, cm^{-1}	18.4	18.3
F(000)	1352	1352

Synthesis of $Ru_3(CO)_6[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (5a). Method i. A mixture of $Ru_3(CO)_{12}$ (1 mmol) and $CH_3C(H){=}C(H)C(H){=}N\text{-}i\text{-}Pr$ (6 mmol) in 40 mL of heptane was heated at reflux for 16 h (the cold Schlenk tube was immersed directly into an oil bath at 130 °C). After this period the orange/red solution was cooled to 20 °C, and the orange/red precipitate of **3a** (0.25 mmol) was collected as described before.[3] The resulting heptane solution was purified by column chromatography. The yellow/orange hexane fraction containing $Ru_2(CO)_6[CH_2CC(H)C(H){=}N\text{-}i\text{-}Pr]$ (**4a**) and $Ru_3(CO)_6[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**5a**; mixture of diastereomers) was stored at −30 °C for 4 days. This afforded orange crystals in 15% yield of **5a** ((*CC*/*AA*) and (*CA*/*AC*) diastereomers in a 5:1 ratio). Recrystallization from hexane/diethyl ether (1:1) at −30 °C gave pure crystalline (*CC*/*AA*)-**5a**, suitable for X-ray diffraction. The (*CA*/*AC*) diastereomer decomposed slowly when passed through a silica column. Therefore, in order to obtain a diastereomeric mixture of **5a** from which the (*CA*/*AC*) diastereomer also can be isolated as a pure compound by HPLC (vide infra), the crude reaction mixture had to be passed rapidly through a short silica column using hexane/dichloromethane (9:1) as the eluent. Cooling of the mixture thus obtained in a minimal amount of hexane at −80 °C resulted in the precipitation of a nearly equimolar mixture of both diastereomers in a total yield of about 30%. Anal. data: Found (calcd) for $Ru_3C_{20}H_{24}N_2O_6$ (**5a**): C, 34.74 (34.73); H, 3.56 (3.50); N, 4.00 (4.05); FD-mass *m*/*e* = 691 (M = 691).[14]

Method ii. A solution of $Ru_2(CO)_6[CH_3C{=}C(H)CH_2N\text{-}i\text{-}Pr]$ (**1a**; 0.5 mmol) and $CH_3C(H){=}C(H)C(H){=}N\text{-}i\text{-}Pr$ (2 mmol) in 30 mL of heptane was stirred at reflux temperature for 3 h (the cold Schlenk tube was immersed directly into an oil bath at 130 °C). After this period the solvent was evaporated under vacuum and the reaction mixture worked up as described above, affording **5a** (mixture of diastereomers) in a yield of ca. 30%.

Method iii. A solution of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**3a**; 0.25 mmol) in 40 mL of heptane was stirred at reflux for 40 h. The reaction mixture was cooled to ambient temperature and $Ru_2(CO)_6[CH_2CC(H)C(H){=}N\text{-}i\text{-}Pr]$ (**4a**; 20%) and $Ru_3(CO)_6[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**5a**; 10%) were isolated by chromatography on silica as described above. Subsequent elution with hexane/CH_2Cl_2 (1:1) afforded unreacted starting material (**3a**; 40%) whereas a dark brown band remained on top of the column, indicating that some decomposition had taken place as well.

Preparative Separation of the (*CA*/*AC*) and (*CC*/*AA*) Diastereomers of 5a by HPLC. An approximately equimolar mixture of the (*CA*/*AC*) and (*CC*/*AA*) diastereomers of **5a** (ca. 60 mg), obtained as described above, was passed through a preparative RP-HPLC column (see above). Two fractions (355–385 mL and 405–460 mL) were collected. The first contained the (*CC*/*AA*) diastereomer, the second, the (*CA*/*AC*) diastereomer. Removal of the solvent afforded the two diastereomers as pure compounds.

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(8) MAD is used as 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. Metalated at C_β, these ligands form the formally monoanionic monoazadienyl (R^1,R^2-MAD-yl) ligand $R^1C{=}C(H)C(H){=}NR^2$. Suffixes to the atoms refer to $R^1C(H)_\beta{=}C(H)_\alpha C(H)_{im}{=}NR^2$.

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(14) Based on that peak of the isotopic pattern of the molecular ion that corresponded to ^{101}Ru, with the calculated value in parentheses.

Table II. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for (*CC*/*AA*)-**5a**

atom	*x*	*y*	*z*	*U*(eq), Å^2
		Molecule 1		
Ru(1)	0.32513 (2)	1.00125 (4)	0.11920 (2)	0.0547 (1)
Ru(2)	$^1/_4$	1.22232 (5)	0	0.0451 (2)
O(1)	0.4427 (3)	0.7847 (5)	0.0827 (3)	0.113 (2)
O(2)	0.2090 (3)	0.7296 (6)	0.1016 (3)	0.129 (3)
O(3)	0.4218 (3)	0.9899 (7)	0.3077 (2)	0.125 (2)
N(1)	0.3760 (2)	1.2102 (4)	0.1025 (2)	0.050 (1)
C(1)	0.1554 (3)	1.1273 (8)	0.1170 (3)	0.085 (2)
C(2)	0.2366 (3)	1.1641 (6)	0.1117 (3)	0.060 (2)
C(3)	0.2633 (4)	1.3177 (7)	0.1168 (3)	0.070 (2)
C(4)	0.3376 (3)	1.3440 (6)	0.1101 (3)	0.064 (2)
C(5)	0.4599 (3)	1.2221 (6)	0.1029 (3)	0.062 (2)
C(6)	0.4742 (4)	1.3713 (7)	0.0678 (4)	0.089 (2)
C(7)	0.5323 (3)	1.1932 (8)	0.1916 (3)	0.088 (2)
C(8)	0.3986 (3)	0.8649 (7)	0.0943 (3)	0.074 (2)
C(9)	0.2520 (4)	0.8310 (7)	0.1070 (4)	0.083 (2)
C(10)	0.3860 (3)	0.9888 (7)	0.2374 (3)	0.077 (2)
		Molecule 2		
Ru(3)	0.64194 (2)	−0.20675 (3)	0.50114 (2)	0.0353 (1)
Ru(4)	$^3/_4$	−0.42654 (4)	$^1/_2$	0.0313 (1)
O(4)	0.6311 (2)	0.0812 (4)	0.4002 (2)	0.072 (1)
O(5)	0.7366 (2)	−0.0096 (4)	0.6627 (2)	0.074 (1)
O(6)	0.4602 (2)	−0.1737 (4)	0.4718 (2)	0.070 (1)
N(2)	0.6735 (2)	−0.4213 (3)	0.5609 (2)	0.0379 (9)
C(11)	0.5860 (3)	−0.3159 (5)	0.3137 (3)	0.058 (2)
C(12)	0.6177 (2)	−0.3593 (5)	0.4048 (2)	0.042 (1)
C(13)	0.6185 (2)	−0.5171 (5)	0.4251 (3)	0.044 (1)
C(14)	0.6512 (2)	−0.5522 (5)	0.5100 (3)	0.044 (1)
C(15)	0.6981 (3)	−0.4453 (5)	0.6507 (2)	0.049 (1)
C(16)	0.7480 (3)	−0.5941 (6)	0.6884 (3)	0.073 (2)
C(17)	0.6168 (3)	−0.4402 (7)	0.6599 (3)	0.070 (2)
C(18)	0.6361 (3)	−0.0270 (5)	0.4378 (3)	0.047 (1)
C(19)	0.7021 (3)	−0.0836 (5)	0.6048 (3)	0.047 (1)
C(20)	0.5288 (3)	−0.1838 (4)	0.4840 (3)	0.049 (1)

Crystallization of (*CA*/*AC*)-5a. Pure (*CA*/*AC*)-**5a** was dissolved in a minimum amount of ethanol (ca. 10 mL) and cooled at −30 °C. After 5 days, orange crystals of the title compound, suitable for X-ray analysis, were isolated by removal of the solvent and two washings with 10 mL of cold (0 °C) hexane.

Synthesis of $Ru_3(CO)_6[C_6H_5C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (5b). Method i. A solution of $Ru_3(CO)_{12}$ (1 mmol) and $C_6H_5C(H){=}C(H)C(H){=}N\text{-}i\text{-}Pr$ (6 mmol) in 40 mL of heptane was heated at 100 °C for 16 h. The solution was cooled to 20 °C and chromatographed on silica. Rapid elution with hexane/dichloromethane (9:1) afforded an orange band containing both (*CA*/*AC*)- and (*CC*/*AA*)-$Ru_3(CO)_6[C_6H_5C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**5b**). Recrystallization from hexane/diethyl ether (1:1) at −30 °C gave pure **5b** (60%). When the crude product was slowly chromatographed on silica, the (*CA*/*AC*) diastereomer decomposed selectively, affording pure orange (*CC*/*AA*)-**5b** after recrystallization. Anal. Found (calcd) for $Ru_3C_{30}H_{28}N_2O_6$ (**5b**): C, 44.01 (44.17); H, 3.56 (3.46); N, 3.44 (3.43); FD-mass: *m*/*e* = 811–825 (M = 815).[14]

Method ii. A solution of $Ru_2(CO)_6[C_6H_5C{=}C(H)CH_2N\text{-}i\text{-}Pr]$ (**1b**; 0.5 mmol) and $C_6H_5C(H){=}C(H)C(H){=}N\text{-}i\text{-}Pr$ (2 mmol) in 30 mL of heptane was stirred at 100 °C for 16 h. After this period the solvent was evaporated under vacuum, and $Ru_3(CO)_6[C_6H_5C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**5b**) was isolated as described above in a yield of about 90%.

Crystal Structure Determinations of (*CC*/*AA*)-5a and (*CA*/*AC*)-5a. X-ray data were collected on an Enraf-Nonius CAD4F diffractometer (Mo Kα, Zr filtered, λ = 0.71073 Å). Crystal data are collected in Table I. Both structures were solved with Patterson and Fourier techniques (SHELXS-86)[15] and refined on *F* by full-matrix least-squares techniques (SHELX-76).[16] Scattering factors were taken from ref 17 and corrected for anomalous dispersion.[18] All calculations, including the derived geometrical data and preparation of the thermal motion ellipsoid plots (PLATON),[19] were carried out on a microVAX-II cluster. Positional parameters are listed in Tables II and III.

Table III. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for (*CA*/*AC*)-**5a**

atom	*x*	*y*	*z*	*U*(eq), Å^2
Ru(1)	0.22238 (3)	0.14574 (1)	0.43983 (2)	0.0433 (1)
Ru(2)	0.43698 (3)	0.26224 (1)	0.43736 (1)	0.0370 (1)
Ru(3)	0.23852 (3)	0.38186 (1)	0.39981 (1)	0.0438 (1)
O(1)	0.0520 (3)	0.1242 (2)	0.2774 (2)	0.092 (1)
O(2)	−0.0736 (3)	0.2140 (2)	0.5017 (2)	0.080 (1)
O(3)	0.1727 (3)	−0.0173 (2)	0.5113 (2)	0.115 (2)
O(4)	−0.0357 (3)	0.3189 (2)	0.2979 (2)	0.098 (1)
O(5)	−0.0049 (4)	0.4016 (2)	0.5231 (2)	0.118 (2)
O(6)	0.2242 (3)	0.5556 (1)	0.3511 (2)	0.076 (1)
N(1)	0.4474 (3)	0.1378 (1)	0.4001 (2)	0.0471 (8)
N(2)	0.4343 (3)	0.3445 (1)	0.3390 (1)	0.0461 (8)
C(1)	0.2899 (5)	0.2167 (2)	0.6139 (2)	0.069 (2)
C(2)	0.3504 (4)	0.1893 (2)	0.5350 (2)	0.049 (1)
C(3)	0.5104 (4)	0.1781 (2)	0.5291 (2)	0.054 (1)
C(4)	0.5621 (4)	0.1521 (2)	0.4560 (2)	0.053 (1)
C(5)	0.4922 (4)	0.1000 (2)	0.3244 (2)	0.062 (1)
C(6)	0.6457 (5)	0.1279 (3)	0.2932 (3)	0.091 (2)
C(7)	0.4882 (5)	0.0101 (2)	0.3337 (3)	0.089 (2)
C(8)	0.1191 (4)	0.1315 (2)	0.3352 (2)	0.061 (1)
C(9)	0.0379 (4)	0.1886 (2)	0.4783 (2)	0.054 (1)
C(10)	0.1892 (4)	0.0432 (2)	0.4824 (3)	0.069 (1)
C(11)	0.3901 (5)	0.4079 (2)	0.5732 (2)	0.079 (2)
C(12)	0.4085 (4)	0.3839 (2)	0.4877 (2)	0.053 (1)
C(13)	0.5580 (4)	0.3740 (2)	0.4607 (2)	0.059 (1)
C(14)	0.5726 (4)	0.3521 (2)	0.3819 (2)	0.056 (1)
C(15)	0.4510 (5)	0.3316 (2)	0.2524 (2)	0.066 (1)
C(16)	0.4721 (6)	0.4127 (3)	0.2131 (3)	0.101 (2)
C(17)	0.3231 (6)	0.2841 (3)	0.2154 (2)	0.092 (2)
C(18)	0.0726 (4)	0.3402 (2)	0.3294 (2)	0.066 (1)
C(19)	0.0859 (5)	0.3938 (2)	0.4759 (2)	0.071 (2)
C(20)	0.2283 (4)	0.4904 (2)	0.3687 (2)	0.055 (1)

(*CA*/*AC*)-5a. Data were collected ($\omega/2\theta$ scan; $\Delta\omega = 0.60 + 0.35 \tan \theta°$; θ_{max} = 25°; *h*, −21 to 21; *k*, 0 to 10; *l*, −21 to 21) for a red crystal (0.12 × 0.22 × 0.50 mm) glued on top of a glass fiber. Unit cell parameters were calculated from the setting angles of 25 reflections. The intensities of 9140 reflections were corrected for *Lp* but not for absorption and merged (R_{av} = 0.017) into a unique set of 3531 reflections with $I > 2.5\sigma(I)$. Hydrogen atoms were introduced at their calculated positions (except for H(31), H(41), H(131), and H(141) that were located from a difference Fourier map and their positions refined) and refined riding on their carrier atoms with two common isotropic thermal parameters. The refinement converged at *R* = 0.026 (R_w = 0.033; $w^{-1} = \sigma^2(F) + 0.0004F^2$; *S* = 1.30; 313 parameters; −0.48, $\Delta\rho < 0.83$ e Å^{-3}; $\langle\Delta/\sigma\rangle$ = 0.02).

(*CC*/*AA*)-5a. Data were collected ($\omega/2\theta$ scan; $\Delta\omega = 0.50 + 0.35 \tan \theta°$; θ_{max} = 27.5°; *h*, 0 to 11; *k*, −21 to 21; *l*, −21 to 21) for a red crystal (0.15 × 0.15 × 0.75 mm) glued on top of a glass fiber. Unit cell parameters were calculated from the setting angles of 25 SET4 reflections. The intensities of 11 964 reflections were corrected for *Lp*, a small decay of 4%, and absorption (DIFABS;[20] correction 0.83:1.08) averaged (R_{av} = 0.015) into a unique set of 4495 reflections with $I > 2.5\sigma(I)$. Hydrogen atoms were located and refined similar to the (*CC*/*AA*)-**5a** structure. Refinement converged at *R* = 0.025 (R_w = 0.025; $w^{-1} = \sigma^2(F)$; *S* = 1.13; 312 parameters; −0.3, $\Delta\rho < 0.3$ e Å^{-3}; $\langle\Delta/\sigma\rangle$ = 0.01).

Results

Synthesis of $Ru_3(CO)_6[R^1C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$. The open-chain trinuclear clusters $Ru_3(CO)_6[R^1C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ ($R^1 = CH_3$ (**5a**), C_6H_5 (**5b**)) may be obtained from thermal reactions of $Ru_3(CO)_{12}$ (1 mmol) with R^1,*i*-Pr-MAD (6 mmol) in heptane. The reaction temperature to be used in order to obtain optimum yields of **5** depends on the R^1 substituent. For $R^1 = C_6H_5$ the best yield of **5b** (ca. 60%) is obtained when the reaction is performed at about 100 °C for 16 h. At this temperature the reaction of $Ru_3(CO)_{12}$ with CH_3,*i*-Pr-MAD only results in a disappointing yield of **5a**. Better yields (ca. 30%) of **5a** are obtained when the reaction is carried out in heptane at vigorous reflux (oil bath temperature 130 °C). Furthermore, the reaction has to be started by immersing the reaction Schlenk tube into a hot oil bath; otherwise, lower yields are obtained. This adapted

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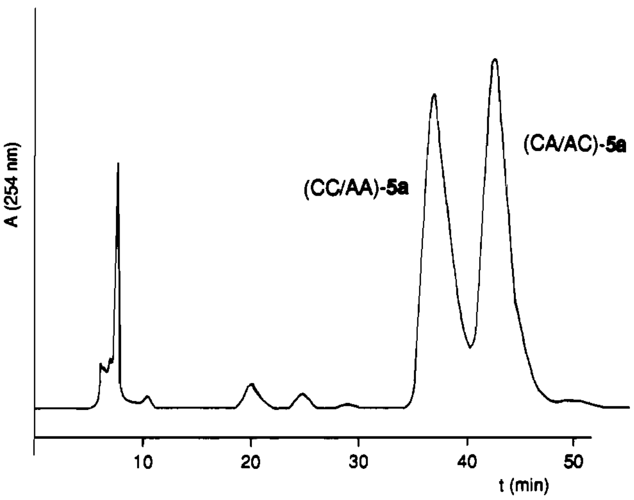

Figure 2. HPLC elution profile of a mixture of diastereomers of $Ru_3(CO)_6[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**5a**).

procedure is necessary since at lower temperatures an alternative reaction path, leading to $Ru_2(CO)_6[CH_2CC(H)C(H){=}N\text{-}i\text{-}Pr]$ (**4a**), is favored.[4]

Attempts to obtain **5** where R^2 = *t*-Bu by similar synthetic procedures were unsuccessful, which failure is probably due to geometric constraints within the hypothetical complex **5c**. Modeling studies have shown that substitution of the *i*-Pr by *t*-Bu substituents in either of the molecular structures of **5a** would give rise to severe interligand overlap of the van der Waals radii of the R substituents.

The trinuclear compounds **5a,b** could also be obtained from the reaction of $Ru_2(CO)_6[R^1C{=}C(H)CH_2N\text{-}i\text{-}Pr]$ (**1**), one of the products initially formed during thermal reactions of $Ru_3(CO)_{12}$ with R^1,*i*-Pr-MAD,[4] with 4 equiv of $R^1C(H){=}C(H)C(H){=}N$-*i*-Pr. When performed at 100 °C, the reaction for R^1 = C_6H_5 resulted in the nearly quantative production of **5b**. Furthermore, the intermediacy of $HRu_2(CO)_5[C_6H_5C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ (**2b**) was observed by IR spectroscopy.[21] Alternatively, cluster **5a** can also, albeit in low yield, be prepared by pyrolysis of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**3a**). In refluxing heptane, **3a** slowly disproportionates whereby small amounts of **4a** and **5a** are formed along with other, uncharacterized decomposition products. The orange trinuclear complexes **5a,b** are air stable in the solid state and decompose only slowly when stored in solution at ambient conditions. So far, we have been unable to find conditions to interconvert the diastereomers of **5a,b**.

The reaction paths by which complexes **5** are formed out of parent ruthenium carbonyl complexes are outlined in Scheme I.

Due to their substitution pattern, the outer ruthenium atoms in **5a,b** are chiral, and hence four stereoisomers are possible: the racemic (*CC*/*AA*) enantiomeric pair and the meso (*CA*/*AC*) enantiomeric pair.[22] The trinuclear complexes **5a,b** are formed as 1:1 mixtures of two diastereomers, as evidenced by ^1H NMR spectroscopy of crude reaction mixtures. Taking advantage of the selective destruction of (*CA*/*AC*)-**5a,b** on silica and the better solubility of (*CA*/*AC*)-**5a,b**, the (*CC*/*AA*) diastereomers of **5a,b** may be obtained as pure compounds suitable for X-ray crystallography by HPLC techniques (see Experimental Section and Figure 2).

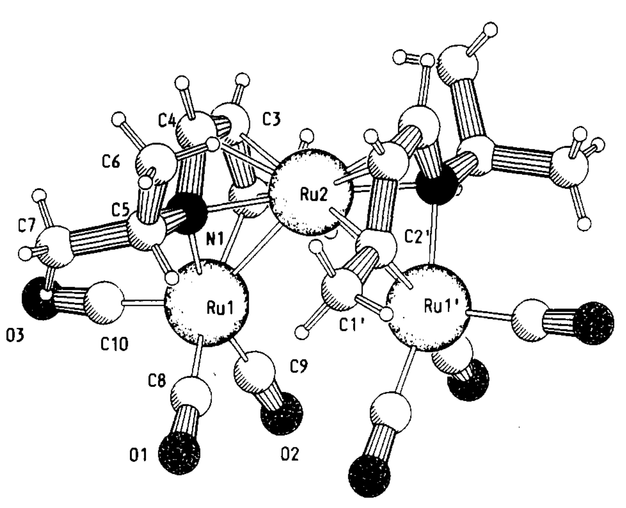

Figure 3. Molecular structure of (*CC*/*AA*)-**5a** (*AA* enantiomer).

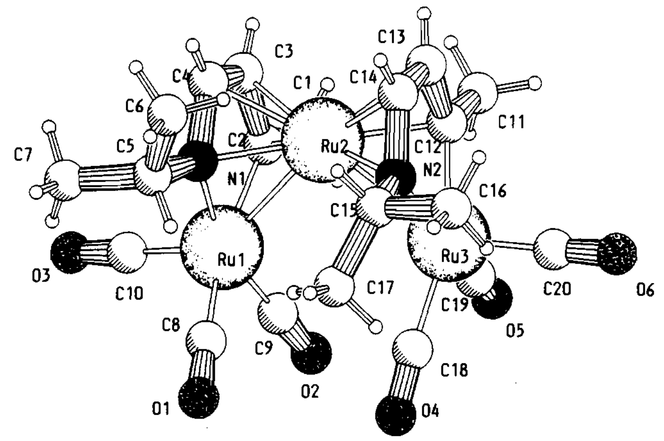

Figure 4. Molecular structure of (*CA*/*AC*)-**5a** (*AC* enantiomer).

Molecular Structures of (*CA*/*AC*) and (*CC*/*AA*)-$Ru_3(CO)_6[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (5a). Perspective views of the molecular structures of the two diastereomers of $Ru_3(CO)_6[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (**5a**), in the (*AC*) and (*AA*) configurations, respectively, along with the adopted numbering schemes are presented in Figures 3–5. Positional parameters, selected bond lengths, and bond angles are listed in Tables II–IV Only one of the two independent (nearly identical) molecules of (*AA*) configuration present in the unit cell of (*CC*/*AA*)-**5a** is shown, and only the data pertaining to this molecule (molecule 1) will be discussed. The presence of a center of symmetry in space group *P*2/*a* requires that the corresponding (*CC*) enantiomers are present in the unit cell of (*CC*/*AA*)-**5a** as well. A crystallographically imposed 2-fold rotation axis is present for both independent half-molecules.

Both diastereomers of compound **5a** consist of two $Ru(CO)_3[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ units, which are η^5-coordinated to a central Ru atom with like faces or unlike faces, respectively. The difference between the two diastereomers of **5a** can readily be inferred from the different mutual dispositions of the two N-*i*-Pr groups: at the same side of the metal chain in (*CA*/*AC*)-**5a** and at opposite sides in (*CC*/*AA*)-**5a**.[22]

The trinuclear metal framework of both diastereomers is bent. The Ru(1)–Ru(2)–Ru(1′) angle in (*CC*/*AA*)-**5a** amounts to 90.90 (3)° whereas the Ru(1)–Ru(2)–Ru(3) angle in (*CA*/*AC*)-**5a** of 95.92 (2)° is somewhat larger. This difference is best ascribed to steric repulsion of the N-*i*-Pr groups in (*CA*/*AC*)-**5a**, resulting in a widening of the bent cluster framework. This steric interaction

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(21) The intermediate **2b** showed four IR bands at 2087 (m), 2021 (m), 2007 (s) and 1947 (m) cm^{-1}, of which the 2007-cm^{-1} band overlapped with one of the IR bands of **1b**.[4]

(22) The configurations of the two outer ruthenium atoms of **5** have been determined according to the Brown–Cook–Sloan modification of the Cahn–Ingold–Prelog rules,[22a–c] which have recently been recommended by IUPAC.[22d] Throughout this paper the official stereochemical descriptors, i.e. *OC*-6-33-*C* and *OC*-6-33-*A* will be abbreviated *C* and *A*, respectively. It should be noted, however, that the inner ruthenium atom of **5**, Ru(2), is chiral too, but, since its chirality is related to the chirality of the outer ruthenium atoms, the chirality of Ru(2) will be omitted in order to avoid the use of redundant chirality descriptors; i.e. (*CA*) stands for $[C_{Ru(1)},A_{Ru(3)}]$ and (*CC*) for $[C_{Ru(1)}, C_{Ru(1')}]$. (a) Brown, M. F.; Cook, B. R.; Sloan, T. E. *Inorg. Chem.* **1975**, *14*, 1273. (b) Brown, M. F.; Cook, B. R.; Sloan, T. E. *Inorg. Chem.* **1978**, *17*, 1563. (c) Sloan, T. E. In *Topics in Inorganic and Organometallic Stereochemistry*; Geoffroy, G. L., Ed., Wiley-Interscience: New York, 1981; Vol. 12, p 1. (d) *IUPAC Nomenclature of Inorganic Chemistry, Recommendations 1990*; Blackwell Scientific Publications: Oxford, England, 1990.

Scheme I. $Ru_3(CO)_{12}/R^1,R^2$-MAD Reaction Sequence

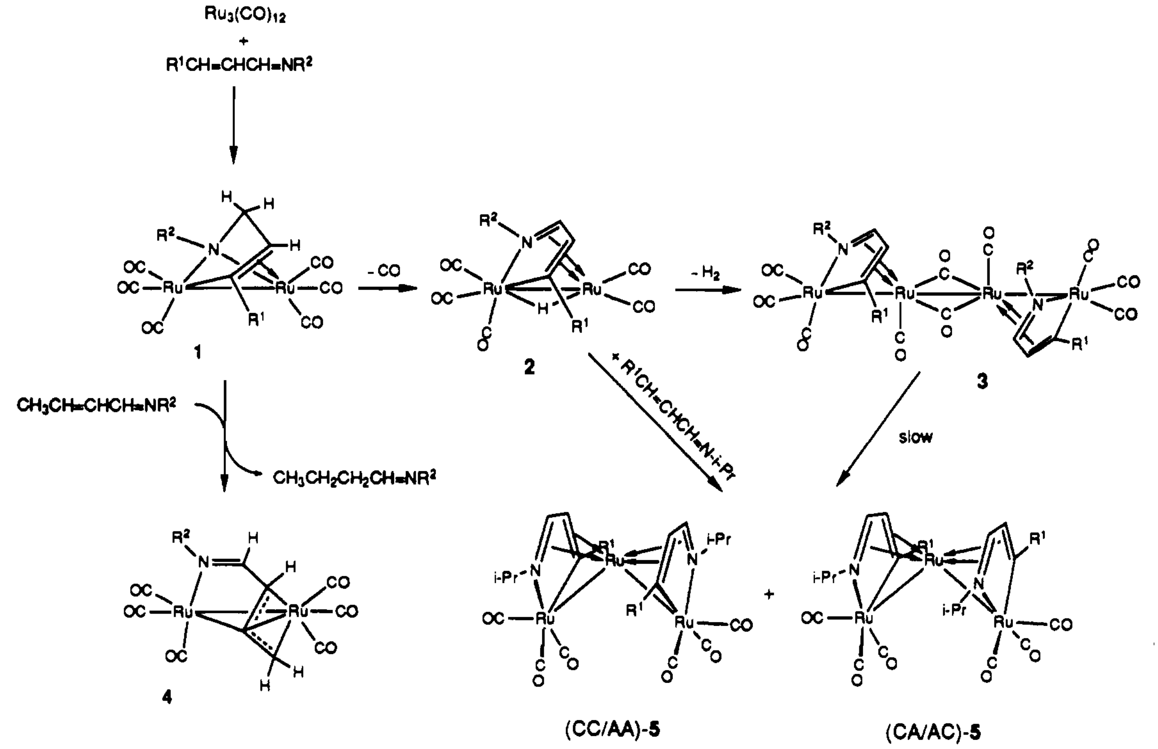

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) of (*CC*/*AA*)-**5a** and (*CA*/*AC*)-**5a** (Esd's in Parentheses)

(*CC*/*AA*)-**5a**

	mol 1	mol 2		mol 1	mol 2		mol 1	mol 2
Ru(1)–Ru(2)	2.704 (1)	2.694 (1)	Ru(1)–C(9)	1.894 (7)	1.898 (5)	Ru(2)–N(1)	2.119 (4)	2.122 (4)
Ru(1)···Ru(1′)	3.8539 (18)	3.8488 (18)	Ru(1)–C(10)	1.892 (5)	1.886 (6)	C(2)–C(3)	1.388 (8)	1.402 (6)
Ru(1)–C(2)	2.056 (6)	2.061 (1)	Ru(2)–C(2)	2.212 (5)	2.224 (4)	C(3)–C(4)	1.40 (1)	1.398 (7)
Ru(1)–N(1)	2.093 (4)	2.074 (3)	Ru(2)–C(3)	2.182 (5)	2.203 (5)	C(4)–N(1)	1.375 (7)	1.388 (5)
Ru(1)–C(8)	1.958 (6)	1.971 (5)	Ru(2)–C(4)	2.130 (5)	2.136 (4)			

(*CA*/*AC*)-**5a**

Ru(1)–Ru(2)	2.6988 (4)	Ru(2)–Ru(3)	2.7053 (4)	Ru(2)–C(2)	2.199 (3)	Ru(2)–C(12)	2.222 (3)
Ru(1)···Ru(1′)	4.0136 (5)			Ru(2)–C(3)	2.173 (3)	Ru(2)–C(13)	2.176 (3)
Ru(1)–C(2)	2.059 (3)	Ru(3)–C(12)	2.060 (3)	Ru(2)–C(4)	2.158 (3)	Ru(2)–C(14)	2.142 (3)
Ru(1)–N(1)	2.088 (3)	Ru(3)–N(2)	2.105 (3)	Ru(2)–N(1)	2.179 (2)	Ru(2)–N(2)	2.154 (2)
Ru(1)–C(8)	1.970 (3)	Ru(3)–C(18)	1.968 (3)	C(2)–C(3)	1.408 (5)	C(12)–C(13)	1.398 (5)
Ru(1)–C(9)	1.887 (3)	Ru(3)–C(19)	1.881 (4)	C(3)–C(4)	1.395 (5)	C(13)–C(14)	1.387 (5)
Ru(1)–C(10)	1.886 (4)	Ru(3)–C(20)	1.893 (3)	C(4)–N(1)	1.371 (4)	C(14)–N(2)	1.389 (4)

(*CC*/*AA*)-**5a**

	mol 1	mol 2		mol 1	mol 2
Ru(1)–Ru(2)–Ru(1′)	90.90 (3)	91.15 (3)	C(2)–Ru(1)–N(1)	77.0 (2)	77.1 (1)
C(2)–Ru(1)–C(8)	164.0 (2)	162.0 (2)	Ru(1)–C(2)–C(3)	114.6 (5)	114.7 (3)
N(1)–Ru(1)–C(9)	164.1 (2)	164.2 (2)	C(2)–C(3)–C(4)	116.9 (6)	116.5 (4)
Ru(2)–Ru(1)–C(2)	53.3 (1)	53.8 (1)	C(3)–C(4)–N(1)	113.9 (5)	113.5 (4)
Ru(2)–Ru(1)–C(8)	111.1 (2)	108.7 (2)	Ru(1)–C(8)–O(1)	177.7 (5)	178.0 (4)
Ru(2)–Ru(1)–C(9)	113.6 (2)	113.4 (2)	Ru(1)–C(9)–O(2)	178.5 (6)	178.5 (5)
Ru(2)–Ru(1)–C(10)	138.2 (2)	140.8 (1)	Ru(1)–C(10)–O(3)	176.3 (6)	177.8 (4)
Ru(2)–Ru(1)–N(1)	50.5 (1)	50.8 (1)	C(8)–Ru(1)–C(9)	90.3 (3)	89.6 (2)

(*CA*/*AC*)-**5a**

Ru(1)–Ru(2)–Ru(3)	95.92 (1)	C(12)–Ru(3)–C(18)	159.4 (1)	C(2)–Ru(1)–N(1)	77.5 (1)	Ru(3)–C(12)–C(13)	114.7 (2)
C(2)–Ru(1)–C(8)	164.2 (1)	N(2)–Ru(3)–C(19)	163.3 (1)	Ru(1)–C(2)–C(3)	114.2 (2)	C(12)–C(13)–C(14)	117.0 (3)
N(1)–Ru(1)–C(9)	161.1 (1)	Ru(2)–Ru(3)–C(12)	53.53 (9)	C(2)–C(3)–C(4)	116.6 (3)	C(13)–C(14)–N(2)	114.9 (3)
Ru(2)–Ru(1)–C(2)	53.02 (9)	Ru(2)–Ru(3)–C(18)	109.2 (1)	C(3)–C(4)–N(1)	114.5 (3)	Ru(3)–C(18)–O(4)	170.1 (3)
Ru(2)–Ru(1)–C(8)	111.8 (1)	Ru(2)–Ru(3)–C(19)	112.1 (1)	Ru(1)–C(8)–O(1)	176.0 (3)	Ru(1)–C(19)–O(5)	178.8 (4)
Ru(2)–Ru(1)–C(9)	108.9 (1)	Ru(2)–Ru(3)–C(20)	143.1 (1)	Ru(1)–C(9)–O(2)	179.6 (3)	Ru(1)–C(20)–O(6)	178.7 (3)
Ru(2)–Ru(1)–C(10)	141.0 (1)	Ru(2)–Ru(3)–N(2)	51.37 (7)	Ru(1)–C(10)–O(3)	176.7 (4)	C(18)–Ru(3)–C(19)	86.0 (2)
Ru(2)–Ru(1)–N(1)	52.26 (7)	C(12)–Ru(3)–N(2)	77.4 (1)	C(8)–Ru(1)–C(9)	89.1 (1)		

is further expressed by somewhat longer bonds between the central Ru atom and the N atoms in the (*CA*/*AC*) isomer compared to those in the (*CC*/*AA*) isomer; i.e. Ru(2)–N(1) = 2.119 (4) Å in (*CC*/*AA*)-**5a**, and Ru(2)–N(1) = 2.179 (2) Å and Ru(1)–N(2) = 2.154 (2) Å in (*CA*/*AC*)-**5a**. The other bonds in the two diastereomers connecting the central Ru centers to the η^5-bonded azaruthenacyclopentadienyl systems are, within crystallographic error, of equal length. The Ru(2)–η^4-(C=C—C=N) distances in (*CA*/*AC*)-**5a** and (*CC*/*AA*)-**5a** are the shortest encountered thus far in 7e donating MAD-yl-containing ruthenium carbonyl

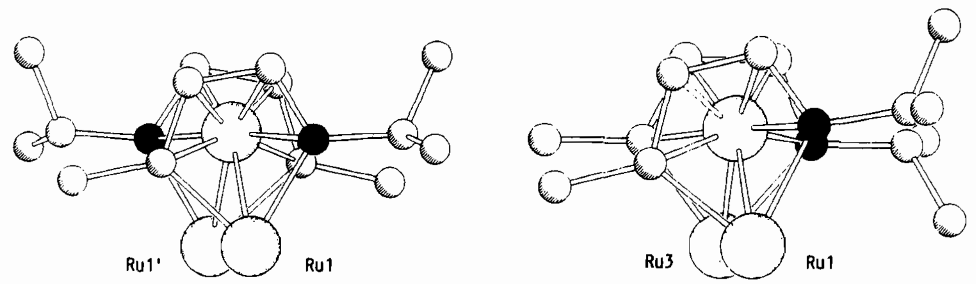

Figure 5. Perspective views of the molecular structures of (*CC*/*AA*)-**5a** (left) and (*CA*/*AC*)-**5a** (right), showing the mutual dispositions of the two azaruthenacyclopentadienyl rings (CO ligands have been omitted for clarity).

Table V. IR Data for $Ru_3(CO)_6[R^1C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ (R^1 = CH_3 (**5a**), C_6H_5 (**5b**))[a]

compd	ν(CO), cm^{-1}					
(*CC*/*AA*)-**5a**	2064 (vs)	2041 (vs)	1995 (vs)	1979 (m)	1965 (vs)	
(*CA*/*AC*)-**5a**	2063 (m)	2042 (vs)	1991 (w)	1978 (m)	1972 (s)	1965 (s)
(*CC*/*AA*)-**5b**	2064 (vs)	2045 (vs)	1990 (s)	1986 (m)	1973 (s)	

[a] Measured in hexane solution.

complexes.[3,5,6,23] This is most probably a result of a higher electron density of the central Ru center in **5a** compared to the relevant Ru centers in **2b**,[23] (*CA*/*AC*)-**3a**,[3] (*CC*/*AA*)-**3a**,[4] and $H_2Ru_4(CO)_8[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$,[6] which results in a stronger π-back-bonding to the π* orbitals of the C=C—C=N skeleton of the MAD-yl ligand in **5a**. Interestingly, the intermetallic bonds in (*CA*/*AC*)-**3a**, (*CC*/*AA*)-**3a**, and both diastereomers of **5a** are of similar length (about 2.70 Å), indicating that the basicity of the central ruthenium centers has little influence on the intermetallic distances to the outer ruthenium centers. The intermetallic distances between the outer Ru atoms of 3.8539 (18) Å in (*CC*/*AA*)-**5a** and 4.0136 (5) Å in (*CA*/*AC*)-**5a**, respectively, clearly indicate that there are no bonding interactions between these metal centers. The occurrence of two metal–metal bonds in **5** is in agreement with CVMO theory for a trinuclear cluster that contains 50 closed valence electrons.

The clusters contain six terminally bonded CO ligands, three on each of the outer ruthenium atoms. The Ru–C distances in these $Ru(CO)_3$ units are comparable to those found in (*CA*/*AC*)-**3a** and (*CC*/*AA*)-**3a**.[3,5] Due to the strong trans influence exerted by the σ-bonded metalated C_β atoms the Ru–C(O) bonds trans to C_β are significantly longer than the other two Ru–C(O) bonds. Except for Ru(3)–C(18)–O(4) in (*CA*/*AC*)-**5a** all Ru—C≡O angles are virtually linear; i.e., all exceed 176°. The Ru(3)–C(18)–O(4) angle of 170.1 (3)° in (*CA*/*AC*)-**5a** deviates significantly from linearity, which may be due to the steric interaction that the C(18)O(4) moiety suffers from the C(17) methyl of the N(2)-*i*-Pr group. These geometrical constraints are also reflected in a somewhat smaller C(18)–Ru(3)–C(19) angle of 86.0 (2)° compared to the C(18)–Ru(1)–C(9) angles in (*CA*/*AC*)-**5a** of 89.1 (1)° and in (*CC*/*AA*)-**5a** of 90.3 (3)°, respectively.

The N-*i*-Pr moieties in both diastereomers are twisted somewhat in order to minimize steric *intra*molecular *inter*ligand interactions of the N(1)-*i*-Pr group of one MAD-yl ligand and the CH_3 or the N(2)-*i*-Pr moiety of the other MAD-yl ligand.

Spectroscopic Properties of 5. The results of IR, FD-mass, and ^1H and ^{13}C NMR spectroscopic studies performed on **5a,b** have been collected in Tables V–VII and in the experimental section (FD-mass).

In contrast to the IR spectra of the two diastereomers of **3a**,[5] the IR spectra of the (*CC*/*AA*) and (*CA*/*AC*) diastereomers of **5a** in hexane solution are fairly different. The (*CC*/*AA*) enantiomeric pair shows one weak and four strong absorptions whereas the (*CA*/*AC*) enantiomeric pair shows six absorptions of varying intensities in the ν(CO) region. Only one of the two diastereomers of **5b** has been obtained as a pure compound; on the basis of the IR data, this is (*CC*/*AA*)-**5b**.

Table VI. ^1H NMR Data for $Ru_3(CO)_6[R^1C{=}C(H_\alpha)C(H_{im}){=}N\text{-}i\text{-}Pr]_2$ (R^1 = CH_3 (**5a**), C_6H_5 (**5b**))[a]

compd	δ, ppm			
	H_{im}	H_α	R^1	*i*-Pr
(*CC*/*AA*)-**5a**	6.29 (d)[b]	5.03 (d)[b]	1.79 (s)	2.54 (sept);[c] 1.22/0.84 (d)[c]
(*CA*/*AC*)-**5a**	6.38 (d)[b]	5.05 (d)[b]	2.06 (s)	2.86 (sept);[c] 1.16/1.14 (d)[c]
(*CC*/*AA*)-**5b**	6.28 (d)[b]	5.56 (d)[b]	7.15 (m)	2.61 (sept);[c] 1.13/−0.03 (d)[c]
(*CA*/*AC*)-**5b**	6.68 (d)[b]	5.88 (d)[b]	7.12 (m)	2.90 (sept);[c] 1.14/1.03 (d)[c]

[a] Measured in $CDCl_3$ at 297 K, 100.1 MHz; chemical shifts relative to $SiMe_4$; diastereotopic resonances separated by [/]. [b] ^3J = 1.5 Hz. [c] ^3J = 6.5 Hz.

The ^1H NMR data of (*CC*/*AA*)-**5a** in $CDCl_3$ solution are consistent with the molecular structure in the solid state. Only one set of resonances is observed for the two 7e-donating MAD-yl ligands due to the C_2 symmetry of the complex. The imine and olefin protons H_{im} and H_α are found as doublets (^3J = 1.5 Hz) at 6.29 and 5.03 ppm, respectively. These δ values are within the regions of 6.2–7.5 ppm for H_{im} and 5.0–5.7 ppm for H_α, usually observed for MAD-yl ligands in the 7e coordination mode.[3-7] The R^1 methyl protons of (*CC*/*AA*)-**5a** are observed as a singlet resonance at 1.79 ppm, whereas in other complexes containing 7e-bonded crotonaldimin-4-yl ligands this resonance is usually observed in the region of 2.4–2.9 ppm.[3-7]

The diastereotopic *i*-Pr CH_3 groups appear as two doublets at 1.22 and 0.84 ppm and the septet of the corresponding *i*-Pr CH protons is found at 2.54 ppm. The ^1H NMR signals of the two *i*-Pr CH_3 groups of (*CC*/*AA*)-**5a** could be assigned individually by a NOE experiment; saturation of the imine proton at 6.29 ppm caused an increase in intensity of the doublet resonance at 0.84 ppm, whereas the doublet resonance at 1.22 ppm was unaffected. Consequently, in solution the imine proton must be adjacent to the CH_3 group resonating at 0.84 ppm, and hence this doublet will correspond to $C(6)H_3$. This NOE experiment shows (i) that the twist of the *i*-Pr group, as found in the solid state (vide supra), is retained in solution and (ii) that rotation of the *i*-Pr group with respect to the C=C—C=N backbone is restricted.

A NOESY experiment (Figure 6) revealed through-space interactions of the $C(1)H_3$ protons with the *i*-Pr C(5)H and $C(6)H_3$ protons, and also with the *i*-Pr $C(7)H_3$ protons. Hence, in solution the $C(1)H_3$ group of each MAD-yl ligand is situated in the neighborhood of the *i*-Pr substituent of the other MAD-yl ligand. This corresponds to the solid-state situation of (*CC*/*AA*)-**5a** in the crystal structure (vide supra). The result of the NOE experiment discussed above was confirmed by this NOESY experiment: interaction of the imine proton (6.29 ppm) with only one of the *i*-Pr methyl protons (0.84 ppm) is observed.

The ^1H NMR spectrum of the other diastereomer (*CA*/*AC*)-**5a** shows, in contrast to the crystal structure, equivalent MAD-yl ligands. The proposed fluxional process by which the two CH_3-*i*-Pr-MAD-yl ligands become equivalent is depicted in Figure 7 and constitutes a rotation of one of the azaruthenacyclo-

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(23) Spek, A. L.; Duisenberg, A. J. M.; Mul, W. P.; Beers, O. C. P.; Elsevier, C. J. *Acta Crystallogr.* **1991**, *C47*, 297.

Table VII. ^{13}C NMR Data for $Ru_3(CO)_6[R^1C_\beta{=}C_\alpha(H)C_{im}(H){=}N\text{-}i\text{-}Pr]_2$ (R^1 = CH_3 (**5a**), C_6H_5 (**5b**))[a]

	δ, ppm					
compd	C_{im}	C_α	C_β	R^1	*i*-Pr	CO
(*CC*/*AA*)-**5a**	94.2	89.9	153.7	32.0	59.9; 29.2/22.1	204.4, 197.8, 193.0
(*CA*/*AC*)-**5a**[b]	98.8	88.0	155.5	31.8	62.0; 28.2/24.4	204.0, 198.4, 192.4[c]
(*CC*/*AA*)-**5b**	93.8	85.7	155.6	150.5, 128.4 127.4, 126.0	60.2; 29.1/20.2	203.5, 199.2, 192.4

[a] Measured in $CDCl_3$ at 263 K, 25.0 MHz; chemical shifts relative to $SiMe_4$; diastereotopic resonances separated by [/]. [b] 62.9 MHz. [c] Broad signals.

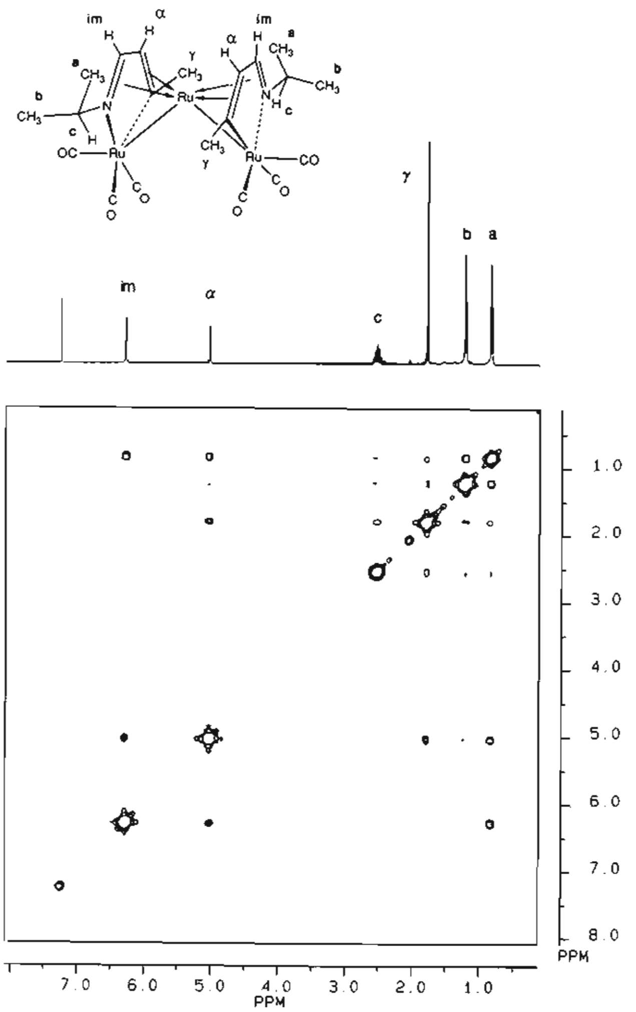

Figure 6. NOESY spectrum of (*CC*/*AA*)-**5a** ($CDCl_3$, 297 K) showing both intra- and interligand through-space interactions.

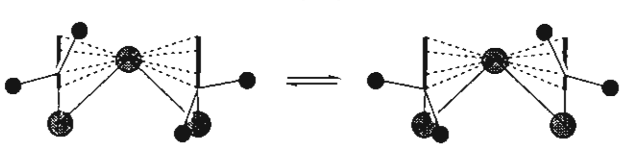

Figure 7. Proposed dynamic process for (*CA*/*AC*)-**5a**.

pentadienyl rings by about 30° with respect to the other and a simultaneous rotation of the *i*-Pr groups around the C–N bond by about 120°. The motion that the two azaruthenacycles make relative to each other can be referred to as a type of "Bailar twist".[24]

The ^1H NMR resonances of the MAD-yl ligands in (*CA*/*AC*)-**5a** are observed at δ values somewhat different from those of (*CC*/*AA*)-**5a**, in agreement with their diastereomeric relation. A NOESY experiment showed no *inter*ligand through-space interactions between the two MAD-yl ligands; hence also for the (*CA*/*AC*) diastereomer, the bent cluster geometry as found in the solid state is retained in solution.

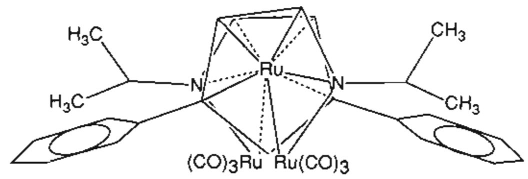

Figure 8. Structure of (*CC*/*AA*)-**5b**.

One of the diastereotopic *i*-Pr CH_3 groups of (*CC*/*AA*)-**5b** resonates at a very low δ value: –0.03 ppm. Most likely this strong shielding is caused by the magnetic anisotropy of the phenyl ring of the other C_6H_5,*i*-Pr-MAD-yl ligand. This implies that, in agreement with the proposed geometry (Figure 8), one of the methyl groups of each of the *i*-Pr substituents in (*CC*/*AA*)-**5b** is adjacent to the phenyl ring of the other ligand.

A NOE experiment for **5b** showed that the *i*-Pr CH_3 group resonating at –0.03 ppm is closer to the imine proton than the one at 1.13 ppm, which is reminiscent of the situation in (*CC*/*AA*)-**5a** and consistent with the geometry of (*CC*/*AA*)-**5b** as shown in Figure 8.

The ^{13}C NMR spectra of (*CA*/*AC*)-**5a** and (*CC*/*AA*)-**5a** each show, in keeping with their ^1H NMR properties, one set of resonances corresponding to the presence of equivalent $Ru(CO)_3$-$[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ units in each diastereomer. The six CO ligands in each diastereomer give rise to three signals near 200 ppm. The metalated C_β atoms are found at about 155 ppm, which are considerably lower δ values compared to those found for the C_β atoms in (*CA*/*AC*)-**3a**, (*CC*/*AA*)-**3a**, and H_2Ru_4-$(CO)_8[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$ at about 195 ppm, but comparable to the δ value of 155.4 ppm observed for HRu_2-$(CO)_5[C_6H_5C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ (**2d**).[3-6] The C_{im} and C_α carbon signals are found at 94.2 and 89.9 ppm, respectively, for (*CC*/*AA*)-**5a** and at 98.8 and 88.0 ppm, respectively, for (*CA*/*AC*)-**5a**. The higher chemical shift of C_{im} in (*CA*/*AC*)-**5a** indicates a somewhat poorer π-overlap between filled d orbitals of the central Ru atom and the π*-C=N orbitals of the MAD-yl ligands in this diastereomer compared to (*CC*/*AA*)-**5a**. This observation is in keeping with the molecular structures, in which it was found that the Ru(2)-N distances in (*CC*/*AA*)-**5a** are somewhat shorter than those in (*CA*/*AC*)-**5a**.

Discussion

Formation of $Ru_3(CO)_6[R^1C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$. There are several methods by which a new metal–metal bond can be made: (i) aggregation of metal centers of which at least one is coordinatively unsaturated, (ii) binuclear reductive elimination of metal hydrides with concomitant loss of H_2, (iii) substitution of a metal-bonded halide by an anionic metal fragment, (iv) dimerization of metal radicals, and (v) bond formation between cationic and anionic metal fragments.

It has been shown that formation of **5** from $Ru_3(CO)_{12}$ and R^1,*i*-Pr-MAD proceeds via initial breakdown of the trinuclear cluster unit to dinuclear species and subsequent rebuilding of the trinuclear unit (Scheme I). The last observable intermediate is $HRu_2(CO)_5[R^1C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ (**2**). Hence, trinuclear **5** is probably formed by aggregation of the dinuclear hydride **2** (a crystal structure has appeared for R^1 = Ph)[23] and a mononuclear hydride with stoichiometry $HRu(CO)_3[R^1C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ as visualized in Scheme II.

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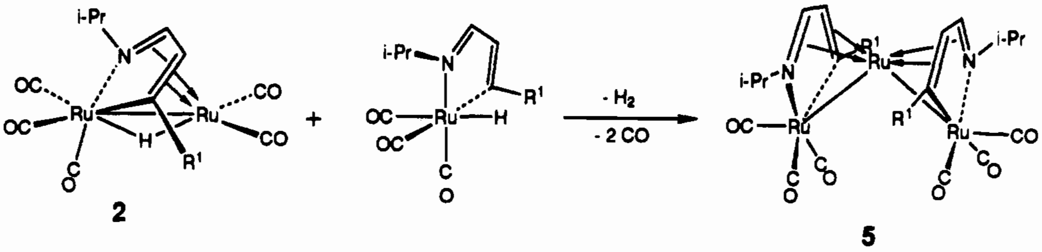
[24] Holm, R. H. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L., Cotton, F. A., Ed., Academic Press: New York, 1975; p 340 ff.

Scheme II. Proposed Reaction Pathway for the Formation of Trinuclear 5



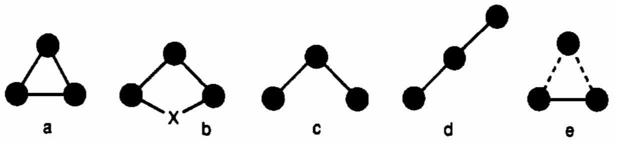


Figure 9. Possible geometries for trinuclear clusters: (a) closed triangle (48e); (b) acyclic bent, stabilized by bridging ligand(s) X (50e); (c) acyclic bent (50e); (d) acyclic linear (50e); (e) closed triangle with two elongated M–M bonds (50e).

Complex **2** obeys the 18e rule, but it has been shown to react as if it is an unsaturated complex. For example, it readily adds CO at ambient temperature to form $HRu_2(CO)_6[R^1C{=}C(H)C(H){=}NR^2]$, which contains a 5e σ-N, σ-C_β η^2-C=C coordinated MAD-yl ligand.[6] Reaction of **2** with MAD, which has to be present for the formation of **5**, then produces two mononuclear molecules, $HRu(CO)_3[R^1C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$ and $HRu(CO)_2[R^1C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]$. Subsequent reaction of either of these mononuclear species with another molecule of the parent complex **2** and concomitant loss of H_2 and of one or two CO ligands then results in the formation of **5**. In the absence of MAD, reductive dimerization of **2** takes place upon heating in solution, to give tetranuclear **3** (Scheme I).[4]

Alternatively, **5** can be formed by pyrolysis of the linear tetranuclear cluster **3**. The observed thermal (homolytic) fission of the central Ru–Ru bond[5] and the hemilability of the MAD-yl ligand in **3**, i.e., the ready substitution of the π-coordinated C=CC=N systems by CO ligands,[7] provide the basis for a likely mechanism for the formation of **5** out of **3**. Upon vigorous reflux of **3**, mononuclear radicals with the stoichiometry $\{Ru(CO)_3[R^1C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]^\bullet\}$ will be formed. These then react with dinuclear radicals $\{Ru_2(CO)_5[R^1C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]^\bullet\}$, which are present under the applied conditions as well,[5] resulting in the formation of **5** with release of two CO ligands. A similar reaction has been observed for an isolobal counterpart of **3**; in an attempt to sublime $Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2$, ferrocene was obtained.[25]

Geometry of M_3 Clusters. The present cluster contains 50 closed valence electrons (CVE)[26] and two single metal–metal bonds, which implies that it is electron precise, i.e., all Ru-atoms have an 18e configuration.

The normal geometry for an electron-precise trinuclear cluster having 48e is a closed triangle (Figure 9a).[27] Addition of two electrons to such a cluster results in a complex with 50 CVE, which usually has two metal–metal bonds and a bent (Figure 9b,c) or linear (Figure 9d) geometry. Several trinuclear 50e iron, ruthenium, and osmium complexes have been reported that contain a bent cluster core.[28] Invariably, this bent geometry is a result of one or more ligand(s) X bridging the outer two metal centers (Figure 9b). Without such a bridging ligand, a linear geometry is generally preferred in acyclic 50e clusters. In contrast to these characteristics, the present Ru_3 cluster exhibits a bent geometry in which the outer metal centers are not bridged by any ligand (Figure 9c). Hence, it represents an unique member of this class of clusters. Rotation of one of the azaruthenacyclopentadienyl rings in **5** by about 180° with respect to the other, resulting in a linear arrangement of the metal core, is easy to conceive and, on the basis of computer-simulated molecular models, not restricted by geometrical constraints.

The "anomalous" bent structure of **5** may be rationalized by considering the geometries of the "normal" linear 50e trinuclear clusters. In acyclic trinuclear clusters, the outer metal atoms bear, apart from another metal, five ligands in their coordination spheres. In case a bent geometry would be adopted in these systems, this usually induces severe steric interaction of the ligand spheres of the outer two metal centers. Hence, the linear geometry is, for steric reasons, normally preferred in these systems. In the case of **5**, however, two of the five ligands (the imine and olefin parts of the MAD-yl ligands) that are σ-coordinated to the outer ruthenium centers are π-coordinated to the central ruthenium center as well. As a consequence the fixed ligand arrangements around the outer ruthenium centers are not perpendicular to the M–M bonds. The CO ligands coordinating at positions trans to the MAD-yl ligand are bent away from the center of the cluster, and no severe steric interactions between the ligand spheres of the outer ruthenium atoms are induced in a bent cluster geometry. Therefore, a bent geometry is adopted in **5** and even retained in solution (vide supra). As there is no steric factor that can be held responsible, the relative stability of the bent geometry most likely has an electronic cause. DV–Xα quantum mechanical calculations have revealed that the central Ru d_{z^2} atomic orbital in (*CC*/*AA*)-**5a** interacts with suitable combinations of the outer Ru d levels to give rise to strong bonding intermetallic interactions.[11] Apparently, an optimum for this interaction is obtained for the bent geometry of the sandwichlike dimetallametallocene **5**.

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Supplementary Material Available: Tables of all bond lengths and angles, anisotropic thermal parameters of the non-H atoms, and the calculated fractional coordinates and the isotropic thermal parameters of the H atoms and ORTEP drawings of (*CC*/*AA*)-**5a** and (*CA*/*AC*)-**5a** (10 pages); listings of the structure factor amplitudes (54 pages). Ordering information is given on any current masthead page.

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(25) Piper, T. S.; Cotton, F. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *1*, 165.

(26) Lauher, J. W. *J. Organomet. Chem.* **1981**, *213*, 25.

(27) See, e.g.: Johnson, B. F. G.; Lewis, J. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 225.

(28) (a) Albers, M. O.; Robinson, D. J.; Coville, N. J. *Coord. Chem. Rev.* **1986**, *69*, 127 and references cited therein. (b) Robinson, S. D. *Annual Reports on the Progress of Chemistry, Section A: Inorganic Chemistry*; Royal Society of Chemistry: London, England: 1986, p 301; 1987, p 227; 1988, p 209 and references cited therein.