Organometallics 1988, *7*, 423–429 423

Reactions of Monoazadienes with Metal Carbonyl Complexes. 1. Reaction of *N*-Alkyl-(*E*)-crotonaldimine with $Ru_3(CO)_{12}$. The Molecular Structure (X-ray) of the Linear 66-Electron Tetraruthenium Cluster $Ru_4(CO)_{10}(CH_3C{=}CHCH{=}NC_3H_7\text{-}i)_2$, Which Is Isolobally Related to $[(\eta^5\text{-}C_5H_5)Ru(CO)(\mu\text{-}CO)]_2$

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Thermal reactions of monoazadienes (*E*)-$CH_3C(H){=}C(H)C(H){=}NR$ (R-MAD) with $Ru_3(CO)_{12}$ in heptane solution at reflux yield the linear tetraruthenium compounds bis[(σ-N,σ-C,η^2-N=C,η^2-C=C)-*N*-alkyl-(1*Z*,3*Z*)-crotonaldimin-4-yl]decacarbonyltetraruthenium, $Ru_4(CO)_{10}(CH_3C{=}C(H)C(H){=}NR)_2$. The molecular structure of the tetranuclear complex with R = *i*-Pr has been solved by means of X-ray diffraction. Crystals of $C_{24}H_{24}N_2O_{10}Ru_4$ are triclinic of space group $P\bar{1}$, $Z = 1$, and cell constants a = 8.5139 (4) Å, b = 12.9636 (6) Å, c = 8.0914 (7) Å, α = 106.43 (1)°, β = 114.78 (1)°, and γ = 67.62 (1)°. A total of 2045 reflections have been used in the refinement, which resulted in a final R value of 0.021 (R_w = 0.030). The molecule exhibits a centrosymmetric straight-chain geometry and has Ru–Ru distances of 2.7084 (4) Å (outer) and 2.7819 (5) Å (inner). The complex may be viewed as consisting of a central $\overline{Ru_2(CO)_2(\mu\text{-}CO)_2}$ core to which two mutually trans disposed η^5-ruthenaazacyclopentadienyl fragments, $(CO)_3\overline{RuC(CH_3){=}C(H)C(H){=}NR}$ (isolobal with C_5H_5), are coordinated; hence $Ru_4(CO)_{10}(CH_3C{=}C(H)C(H){=}NR)_2$ is an isolobally related analogue of (*E*)-$[(\eta^5\text{-}C_5H_5)Ru(CO)(\mu\text{-}CO)]_2$. The planar $\overline{Ru\text{-}C(CH_3){=}C(H)C(H){=}NR}$ heterocycle has been formed by metalation of the R-MAD ligand. The linear arrangement of the four ruthenium atoms in the 66e cluster is consistent with CVMO theory. The geometry of the cluster and its formation are discussed.

Introduction

Transition-metal carbonyl clusters possess interesting properties with respect to coordination and activation of organic molecules, which observation has led to the assumption that they might serve as (models for) catalysts for a range of chemical processes. The coordination chemistry and reactivity of 1,3-dienes on metal carbonyl fragments is well-documented.[1] More recently, the versatile coordination chemistry and chemical activation of 1,4-diaza-1,3-dienes[2] has received ample attention from the groups of, for example, tom Dieck,[3] Frühauf,[4,5] and Vrieze.[6,7] The last group has inter alia focused research on the ruthenium–carbonyl–diazadiene chemistry, with particular emphasis on C–C, C–N, and C–H bond formation and bond rupture reactions involving the coordinated α-diimine.[7-10] The combination of good σ-donor/π-acceptor characteristics, combined with the flexibility of the diazadiene skeleton, gives rise to several modes of activation of the coordinated diazadiene and hence a large range of stoichiometric as well as catalytic reactions.[3-10]

Relatively little is known about the behavior of monoazadienes (MAD),[2] containing a conjugated C=CC=N skeleton, toward metal carbonyl fragments. Several coordination modes of MAD ligands to metals, A–D in Figure 1, have been characterized. The 2e σ-N coordination (A) in the complexes $(MAD)Fe(CO)_4$[11] and $(MAD)_2CuCl$,[12] the 2e η^2-C=C coordination (B) in $(MAD)Ni(PPh_3)_2$[12,13] as well as the 4e η^2-N=C, η^2-C=C bonding mode (C) in $(MAD)Fe(CO)_3$[14,15] and $(MAD)Mo(CO)_2(PBu_3)_2$,[12] and the bridging 4e σ-N, η^2-C=C mode (D) in $[(MAD)Ni(PPh_3)]_2$[12,16] have all been established by X-ray structures. Other examples of 2e- and 4e-bonded MAD ligands were elucidated by spectroscopic means.[17,18] Thus far, no other possible coordination modes of monoazadienes, e.g. 7e (E), have been observed.

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[2] The 1,4-diaza-1,3-dienes, RN=CHCH=NR, will be abbreviated R-DAB.[6] The 1-aza-1,3-dienes of general formula $RN{=}C(R^1)C(R^2){=}CR^3R^4$ will be abbreviated MAD, which stands for the general class of *monoazadienes*. The monoazadienyl anion derived herefrom will be denoted MAD-yl. See also ref 22.

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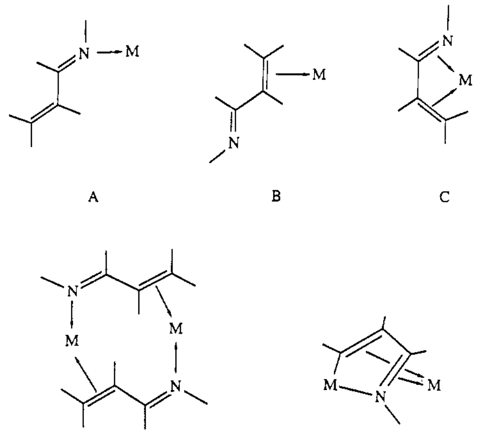
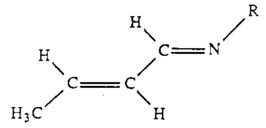


Figure 1. Some possible coordination geometries of metal–monoazadiene complexes.

Intramolecular interactions of sp^2 C-H fragments have been observed in d^8 metal–diazadiene complexes, e.g. Pd(II)[19] and Rh(I),[12] and also in (MAD)$_2$Rh(CO)Cl,[12] but no metalation occurred in these instances. Interestingly, insertion of Ir(I) in the γ-C-H bond of (*E*)-PhC(H)=C(H)C(H)=NC$_3$H$_7$-*i* occurs readily in a reaction of this ligand with Ir(PPh$_3$)$_2$(CO)Cl.[20] Such behavior has not been observed in d^8 complexes like (MAD)Fe(CO)$_3$, but β-C-H activation occurs in reactions of MAD's with H$_2$Os$_3$(CO)$_{10}$.[21] Possibly, the propensity of Ru to form octahedral d^6 complexes might favor metalation of the N=CC=C skeleton. If this would be the case, then a formally monoanionic monoazadienyl (MAD-yl)[2] ligand RN=C(H)C(H)=C$^-$R or RN=C(H)C$^-$=C(H)R would arise, the former being isoelectronic with α-diimine ligands RN=C(H)C(H)=NR. Hence, complexes like HRu$_2$(CO)$_5$(MAD-yl)[2] that are structurally related to Ru$_2$(CO)$_5$(R-DAB)[2] may be expected to emerge from reactions of ruthenium carbonyls and **1**.

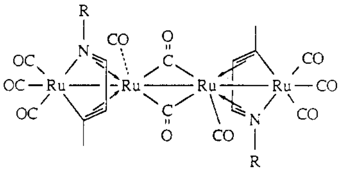


1a; R = i-Pr
1b; R = c-Hex

It was anticipated that monoazadienes like N-substituted crotonaldimines **1** (R-CAI)[22] derived from (*E*)-crotonaldehyde might be likely candidates to stabilize several di- and polynuclear Ru clusters. Therefore, and in order to see whether descending the triad from Fe to Ru may lead to insertion of Ru into one or more C–H bonds of the monoazadiene, we started our investigations with thermal reactions between Ru$_3$(CO)$_{12}$ and R-CAI's **1a** and **1b**.

Experimental Section

Materials and Apparatus. NMR spectra were obtained on a Bruker WM 250 spectrometer at 250.13 MHz (^{1}H) and on a Bruker WP 80 apparatus at 20.1 MHz (^{13}C). IR spectra were recorded by using a Perkin-Elmer 283 spectrophotometer. Mass spectra (field desorption, FD) were obtained on a Varian MAT 711 double-focusing mass spectrometer with a combined EI/FD/FI ion source as described elsewhere.[23] Elemental analysis were carried out by the section Elemental Analyses of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands.



2a; R = i-Pr
2b; R = c-Hex

All preparations were carried out in an atmosphere of purified nitrogen, using carefully dried solvents. Silica gel for column chromatography (Merck, 60 Mesh) was dried and activated before use. Ru$_3$(CO)$_{12}$ was obtained from Strem Chemicals, Ltd. The monoazadienes *N*-isopropyl-(*E*)-crotonaldimine (**1a**) and *N*-cyclohexyl-(*E*)-crotonaldimine (**1b**) were prepared from (*E*)-crotonaldehyde and the relevant primary amine according to standard procedures.[24] The compounds were distilled at 0.2 mmHg and were stored at −80 °C. NMR data are collected in Tables IV and V.

Synthesis of Ru$_4$(CO)$_{10}$(CH$_3$C=C(H)C(H)=NC$_3$H$_7$-*i*)$_2$ (2a). Ru$_3$(CO)$_{12}$ (0.64 g, 1.0 mmol) and monoazadiene **1a** (0.17 g, 1.5 mmol) were stirred under reflux in 50 mL of heptanes (bp 98.5 °C, bath temperature ca. 125 °C). After 20 h, the orange solution was cooled to 20 °C and the orange/red precipitate was collected. This solid was then chromatographed on a silica gel column, employing first hexane and then dichloromethane as the eluent. The hexane fraction contained as yet unidentified products. The orange-red dichloromethane fraction was concentrated, and hexane was allowed to evaporate slowly into the solution. This afforded orange-red crystals in 32% (0.22 g, 0.24 mmol) yield of **2a**. Anal. Found (Calcd for C$_{24}$H$_{24}$N$_2$O$_{10}$Ru$_4$): C, 31.39 (31.79); H, 2.93 (2.89); N, 3.07 (3.09); O, 16.87 (17.65). FD-mass: *m/z* 906 (904).[25] IR (ν(CO)/cm^{-1}): 2059 (s), 1999 (s), 1994 (br, s), 1946 (m), 1750 (s) in KBr disk; 2067 (s), 2005 (m), 1993 (s), 1951 (w), 1775 (m) in hexane; 2065 (vs), 2000 (s, sh), 1992 (vs), 1943 (w), 1762 (m) in CH$_2$Cl$_2$. NMR data: see Tables IV and V.

Synthesis of Ru$_4$(CO)$_{10}$(CH$_3$C=C(H)C(H)=NC$_6$H$_{11}$-c)$_2$ (2b). The same procedure as for the synthesis of **2a** was followed, using 0.23 g (1.5 mmol) of **1b**. The yield of **2b** amounted to ca. 30% (0.21 g, 0.22 mmol). Anal. Found (Calcd for C$_{30}$H$_{32}$N$_2$O$_{10}$Ru$_4$): C, 36.51 (36.58); H, 3.31 (3.27); N, 2.78 (2.84); O, 16.10 (16.21). FD-mass: *m/z* 946 (944). IR (ν(CO)/cm^{-1}): 2066 (s), 2003 (m), 1992 (s), 1950 (w), 1772 (m) in hexane. NMR data: see Tables IV and V.

Crystal Structure Determination of Bis[(σ-N,σ-C,η^2-N=C,η^2-C=C)-*N*-isopropyl-(1*Z*,3*Z*)-crotonaldimin-4-yl]decacarbonyltetraruthenium, Ru$_4$(CO)$_{10}$(H$_3$CC=C(H)C(H)=NC$_3$H$_7$-*i*)$_2$ (C$_{24}$H$_{24}$N$_2$O$_{10}$Ru$_4$, 2a). Crystals of the title compound are triclinic of space group $P\bar{1}$, $Z = 1$, and cell constants $a = 8.5139$ (4) Å, $b = 12.9636$ (6) Å, $c = 8.0914$ (7) Å, $\alpha = 106.43$ (1)°, $\beta = 114.78$ (1)°, $\gamma = 67.62$ (1)°, $V = 741.6$ (1) Å^3, $d_{\text{calcd}} = 2.03$ g cm^{-3}, and μ(Cu Kα) = 170.9 cm^{-1}. The crystal dimensions are 0.07 × 0.08 × 0.15 mm. A total of 2520 intensities ($2 < \theta < 65°$) were measured on a Nonius CAD4 diffractometer using graphite-monochromated Cu Kα radiation, of which 475 were below the 2.5$\sigma(I)$ level and were treated as unobserved. The intensities were corrected for Lorentz and polarization factors. Absorption correction was deemed unnecessary in view of the small and relatively even dimensions of the crystals. The structure was solved by means of the heavy-atom method. Refinement proceeded by means of block-diagonal least-squares calculations, anisotropic

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[22] MAD is used as acronym for monoazadienes in general. In this paper we will use R-CAI when *N-alkyl-(E)-crotonaldimines* CH$_3$C(H)=C(H)C(H)=NR are meant. R-CAI-yl stands for the corresponding azadienyl anion [CH$_3$C=C(H)C(H)=NR]$^-$.

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[25] Based on the highest peak of the isotope pattern of the molecular ion, calculated value in parentheses based on ^{101}Ru.

Table I. Atomic Coordinates of 2a[a]

	x	*y*	*z*
Ru(1)	0.46434 (4)	0.18241 (2)	0.25809 (4)
Ru(2)	0.47648 (3)	0.39462 (2)	0.41680 (3)
C(1)	0.4239 (6)	0.0506 (4)	0.2688 (6)
C(2)	0.3251 (6)	0.1910 (4)	−0.0072 (6)
C(3)	0.6753 (6)	0.1001 (3)	0.1984 (6)
C(4)	0.0669 (6)	0.3410 (3)	0.2784 (6)
C(5)	−0.0012 (8)	0.2435 (5)	0.2558 (10)
C(6)	−0.0010 (6)	0.3872 (3)	0.1010 (5)
C(7)	0.3364 (6)	0.3388 (3)	0.5504 (6)
C(8)	0.5246 (6)	0.2953 (4)	0.6386 (5)
C(9)	0.6226 (6)	0.2188 (3)	0.5259 (5)
C(10)	0.8214 (7)	0.1661 (4)	0.6170 (7)
C(11)	0.4706 (6)	0.4060 (4)	0.1907 (6)
C(12)	0.6997 (6)	0.4421 (3)	0.5493 (6)
N	0.2683 (4)	0.3653 (2)	0.3664 (4)
O(1)	0.4026 (6)	−0.0281 (3)	0.2809 (6)
O(2)	0.2618 (5)	0.1930 (3)	−0.1597 (5)
O(3)	0.8031 (5)	0.0495 (3)	0.1652 (5)
O(11)	0.4647 (6)	0.4127 (3)	0.0498 (5)
O(12)	0.8590 (4)	0.4066 (3)	0.5975 (5)
H(4)	0.019 (7)	0.402 (4)	0.357 (6)
H(51)	0.053 (9)	0.211 (5)	0.383 (9)
H(52)	0.045 (6)	0.182 (4)	0.179 (6)
H(53)	−0.118 (9)	0.262 (6)	0.207 (9)
H(61)	0.022 (8)	0.331 (5)	0.013 (8)
H(62)	−0.135 (8)	0.419 (5)	0.053 (7)
H(63)	0.060 (7)	0.443 (4)	0.123 (7)
H(7)	0.242 (6)	0.396 (4)	0.594 (6)
H(8)	0.591 (8)	0.314 (5)	0.777 (8)
H(101)	0.847 (8)	0.089 (4)	0.629 (8)
H(102)	0.888 (7)	0.161 (5)	0.550 (7)
H(103)	0.863 (8)	0.203 (5)	0.736 (7)

[a] Esd's in parentheses.

Table II. Selected Bond Lengths (Å) of 2a[a]

	The Metal Carbonyl Part		
Ru(1)-Ru(2)	2.7084 (4)	Ru(2)*-C(12)	2.098 (3)
Ru(2)-Ru(2)*	2.7819 (5)	C(1)-O(1)	1.138 (4)
Ru(1)-C(1)	1.899 (3)	C(2)-O(2)	1.124 (4)
Ru(1)-C(2)	1.981 (3)	C(3)-O(3)	1.135 (4)
Ru(1)-C(3)	1.890 (3)	C(11)-O(11)	1.147 (4)
Ru(2)-C(11)	1.855 (3)	C(12)-O(12)	1.177 (4)
Ru(2)-C(12)	1.987 (3)		
	The Metal Ligand Part		
Ru(1)-N	2.123 (2)	Ru(2)-C(7)	2.300 (4)
Ru(2)-N	2.311 (3)	Ru(2)-C(8)	2.311 (3)
Ru(1)-C(9)	2.048 (3)	Ru(2)-C(9)	2.362 (3)
	The Ligand Part		
N-C(7)	1.358 (3)	N-C(4)	1.490 (4)
C(7)-C(8)	1.405 (5)	C(4)-C(5)	1.518 (6)
C(8)-C(9)	1.417 (4)	C(4)-C(6)	1.510 (4)
C(9)-C(10)	1.495 (5)		

[a] Esd's in parentheses.

for Ru, C, N, and O and isotropic for H. The H-atom positions were derived from a ΔF synthesis. A weighting scheme $w = 1/(2.2 + F_o + 0.0073F_o^2)$ was used, and the anomalous scattering of Ru was taken into account. The final R value was 0.021 ($R_w = 0.030$). A final difference synthesis revealed no excursions above +0.5 and −0.9 e/Å^3. The calculations were performed with XRAY-76. The scattering factors and the dispersion corrections were taken from the literature.[26]

Results and Discussion

Molecular Structure of 2a. The molecular geometry of **2a** with the adopted numbering scheme is shown in the PLUTO drawing (Figure 2), also provides an ORTEP view. Atomic parameters and selected bond lengths and angles are given in Tables I, II, and III, respectively. The molecule exhibits an essentially centrosymmetric straight-chain geometry with the inversion center halfway between Ru(2) and Ru(2)*. There are three single metal–metal bonds. Each of the outermost Ru atoms bears three terminal CO molecules, while the inner two Ru atoms have each one terminal CO (in mutual trans position) and share two asymmetrically bridging CO's. The monoazadienyl ligand is σ-N, σ-C(9) bonded to Ru(1) and η^2-N=C(7), η^2-C(8)=C(9) bonded to Ru(2). The overall geometry closely resembles that of $H_2Ru_4(CO)_8(R\text{-}DAB)_2$ (**3**).[27] However, in **2a** no pseudo mirror plane can be defined because of the intrinsic asymmetry of the N=CC=C

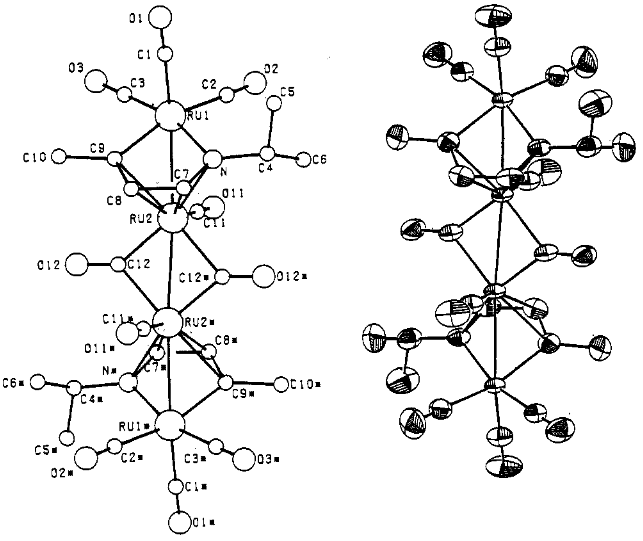

Figure 2. PLUTO and ORTEP drawings of the molecular geometry of $Ru_4(CO)_{10}(CH_3C{=}C(H)C(H){=}NC_3H_7\text{-}i)_2$ (**2a**) with the adopted numbering scheme.

Table III. Selected Bond Angles (deg) of 2a[a]

	The Metal Carbonyl Part		
Ru(1)-Ru(2)-Ru(2)*	174.550 (16)	Ru(2)-C(11)-O(11)	179.08 (23)
Ru(1)-C(1)-O(1)	177.92 (24)	Ru(2)-C(12)-O(12)	142.2 (3)
Ru(1)-C(2)-O(2)	173.28 (22)	Ru(2)*-C(12)-O(12)	132.00 (25)
Ru(1)-C(3)-O(3)	178.7 (3)	Ru-C-O(terminal)	177.25 (25)[b]
	The Ligand Part		
Ru(1)-N-Ru(2)	75.18 (14)	N-C(7)-C(8)	116.9 (3)
Ru(1)-N-C(7)	113.61 (24)	C(9)-C(8)-C(7)	116.2 (4)
Ru(1)-N-C(4)	128.74 (21)	N-C(4)-C(5)	108.8 (4)
C(7)-N-C(4)	116.4 (3)	N-C(4)-C(6)	113.6 (3)
Ru(1)-C(9)-Ru(2)	75.40 (14)	Ru(2)-C(8)-C(9)	74.4 (3)
Ru(1)-C(9)-C(8)	114.29 (24)	Ru(2)-C(9)-C(10)	127.64 (21)
Ru(1)-C(9)-C(10)	127.77 (23)	Ru(2)-C(7)-N	73.3 (3)
C(8)-C(9)-C(10)	117.6 (4)	Ru(2)-N-C(4)	130.50 (22)
	Around Ru(1)		
Ru(2)-Ru(1)-N	55.56 (7)	N-Ru(1)-C(3)	164.65 (13)
Ru(2)-Ru(1)-C(9)	57.57 (9)	C(9)-Ru(1)-C(1)	100.66 (17)
Ru(2)-Ru(1)-C(1)	147.11 (9)	C(9)-Ru(1)-C(2)	161.42 (14)
Ru(2)-Ru(1)-C(2)	105.70 (11)	C(9)-Ru(1)-C(3)	89.94 (19)
Ru(2)-Ru(1)-C(3)	109.55 (11)	C(1)-Ru(1)-C(2)	97.91 (18)
N-Ru(1)-C(9)	78.73 (15)	C(1)-Ru(1)-C(3)	93.34 (22)
N-Ru(1)-C(1)	98.87 (18)	C(2)-Ru(1)-C(3)	88.64 (19)
N-Ru(1)-C(2)	98.79 (16)		
	Around Ru(2)		
Ru(1)-Ru(2)-C(12)	125.88 (9)	Ru(2)*-Ru(2)-C(12)	48.79 (10)
Ru(1)-Ru(2)-C(12)*	139.87 (8)	C(12)*-Ru(2)-C(12)	94.22 (18)
Ru(1)-Ru(2)-C(11)	84.04 (12)	Ru(2)*-Ru(2)-C(11)	94.65 (14)
N-Ru(2)-C(9)	68.97 (14)	C(12)*-Ru(2)-C(11)	94.44 (17)
C(11)-Ru(2)-C(12)	91.82 (21)	Ru(2)*-Ru(2)-C(12)*	45.44 (8)

[a] Esd's in parentheses. [b] Mean value.

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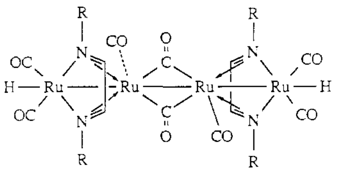
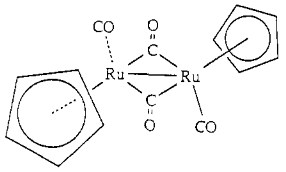
skeleton in **2a** compared to N=CC=N in **3**.

The 66-electron complex **2a** may be viewed as a symmetrical dimer, consisting of two linked 33-electron $Ru_2(CO)_5$(R-CAI-yl)[22] fragments, in which the R-CAI-yl ligands form 7e bridges between the $Ru(CO)_3$ and $Ru(CO)_2$ moieties. Alternatively, the molecule may be imagined as an isolobal analogue of (*E*)-$[(\eta^5\text{-}C_5H_5)Ru(CO)(\mu\text{-}CO)]_2$ (**4**), as will be elaborated below. In this view, **2a** consists basically of a central $Ru_2(CO)_2(\mu\text{-}CO)_2$ core, which is substituted with two mutually trans disposed ruthenaazacyclopentadienyl rings.



3



4

The most striking feature of the molecular structure is the linear arrangement of the four Ru atoms. The angle Ru(1)–Ru(2)–Ru(2)* amounts to 174.55 (2)°, which compares well with the value of 176.48 (6)° for the related angle in $H_2Ru_4(CO)_8(R\text{-}DAB)_2$[27] and of 177.0 (1)° and 165.2 (1)° (mean) in $[Rh_2Mn_2(\mu\text{-dimethyl-2,5-diisocyanohexane})_4(CO)_{10}]^{2+}$[28] and $Rh_2W_2(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_8$,[29] respectively.

The intermetallic distances are 2.7084 (4) Å for Ru(1)–Ru(2) and 2.7819 (5) Å for Ru(2)–Ru(2)*. These values are indicative of a bond order of 1 between the metal centers. The Ru(2)–Ru(2)* single bond, which is part of the doubly CO-bridged central unit of **2a**, is about 0.04 Å longer than comparable Ru–Ru bonds in **3**[27] and **4**.[30] The different Ru(2)–C(12) and Ru(2)*–C(12) distances of 1.987 (3) and 2.098 (3) Å, respectively, reflect the asymmetry of the bridge caused by the asymmetric coordinated R-CAI-yl in **2a**. The Ru(1)–Ru(2) distance is significantly shorter than the 2.741 (1) Å in, for example, $Ru_2(CO)_5(DAB)$[31] or 2.806 (2) Å in $H_2Ru_4(CO)_8(R\text{-}DAB)_2$[27] and is a rather short Ru–Ru single-bond distance, cf. the Ru–Ru distances of 2.696 (1) Å in $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_3)]BF_4$[32] or 2.717 (1) Å in $Ru_2(CO)_5(\mu\text{-}CO)(C_4(CH_2CH_2OH)_2(C_2H_5)_2)$.[33] The short Ru(1)–Ru(2) distance in **2a** as compared to **3** may be due to effective charge relay from Ru(2) to Ru(1) to the π-system of the R-CAI-yl ligand back to Ru(2). Such a synergic effect shortens the Ru(1)–Ru(2) distance and may be brought about through π-overlap of, notably, Ru(1) with C(9) (vide infra). This effect will occur to a much smaller extent between the relevant Ru atom and the N atoms in, for example, diazabutadiene complexes like **3**.

Apart from the elongated Ru(1)–C(2) bond, compared to Ru(1)–C(1) and Ru(1)–C(3), the $Ru(1)(CO)_3$ moiety shows normal bond distances and angles. The longer Ru(1)–C(2) bond is due to the diminished back-donation from Ru(1) to this CO ligand compared to the other CO's, because of π-donation out of the relevant d orbital to C(9) (vide infra). Also, the angle C(2)–Ru(1)–C(3) is smaller than the C(1)–Ru(1)–C(2) and C(1)–Ru(1)–C(3) angles, due to this trans influence of C(9) (and N). The C(2)–Ru(1)–C(3) angle falls in the range that is generally observed for such an angle trans to σ-C and σ-N ligands.[14,33,34] An alternative explanation may be the steric interaction that the C(2)–O(2) moiety suffers from the *N*-isopropyl group, which also accounts for the Ru(1)–C(2)–O(2) angle of 173.3°, significantly deviating from linearity.

The C(12)–O(12) bond in the asymmetrically bridging CO is elongated, as expected, but also the bond order of the C(11)–O(11) bond is somewhat diminished. The Ru(2)–C(11) bond distance is shorter than the Ru(1)–CO bonds, indicating higher electron density on Ru(2) compared to Ru(1).

The Ru(1)–N distance amounts to 2.123 (2) Å, which is in magnitude close to comparable Ru–N distances in $H_2Ru_4(CO)_8(R\text{-}DAB)_2$ and other low-valent di- and trinuclear ruthenium–diazabutadiene complexes with 8e-donating R-DAB ligands.[6,31,34] The Ru–N bond of the pyridine $N(sp^2)$ atom to Ru in a dinuclear Ru(I)–Ru(I) complex amounts to 2.264 (11) Å (mean of two).[35a] Pyridine in trans position to CO in a low-valent Ru complex has a reported Ru–N bond length of 2.181 (2) Å.[35b] Clearly, the Ru–N distance in the present compound **2a** is shorter. Several still shorter Ru–N distances are known, e.g., 2.08–2.12 Å[36] or even as short as 2.02 Å in case of a cyclometalated azobenzene.[32] Probably, in such instances, some multiple-bond character due to charge delocalization in the metallacycle plays a role. Such effects may account for the observed Ru(1)–N distance in **2a**. The Ru(1)–C(3) bond (of CO trans to N) is not appreciably elongated, however, so the extent of the effect remains open to question. This contrasts with the effect on Ru(1)–C(2) trans to C(9), as discussed above.

The Ru(1)–C(9) distance amounts to 2.048 (3) Å and is approximately what one would expect for a Ru–C single bond. Although the precise nature of the single $Ru\text{–}C(sp^2)$ bond is subject to controversy (cf. ref 33, 37, 38), a reasonable assessment of this length as the sum of the covalent radii of Ru in $Ru_3(CO)_{12}$ (1.42 Å) and of $C(sp^2)$ in anthracene (0.71 Å) would be 2.13 Å. This estimation is in concert with observed $Ru\text{–}C(sp^2)$ distances of 2.128 (4)

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Å in a Ru–dimethylimidazolium complex[39] and of 2.160 (10) Å in a (σ-naphthyl)ruthenium compound.[40] The Ru(1)–C(9) distance of ca 2.05 Å in **2a** and reported Ru–C(sp^2) distances in comparable complexes, ranging from 2.02 (1) to 2.09 (1)Å,[33,37,38] are significantly shorter. It has been suggested[37] that a Ru–C distance of this magnitude represents some multiple-bond character and may be viewed as a elongated carbene-type bond.[37c,d] Therefore, and because of the elongated C(8)–C(9) double bond, it seems justified to describe the Ru–C(9) bond as a delocalized secondary carbene linkage.[41] The suggestion that electron density from Ru(1) is used for π-bonding with C(9) is corroborated by (i) the observed shortening of the Ru(1)–Ru(2) bond (cf. ref 33) and (ii) the lengthening of the Ru(1)–C(2) bond trans to C(9) (vide supra).

The monoazadienyl fragment is coordinated to Ru(2) in a way similar to the π,π-coordination of PhC(H)=C(H)C(H)=NPh to Fe in the corresponding (MAD)Fe$(CO)_3$ complex.[14] The Ru(2)–N, Ru(2)–C(7), and Ru(2)–C(8) distances are equal within experimental error and amount to 2.311 (4) Å (mean). The Ru(2)–C(9) bond length of 2.362 (3) Å is significantly (0.05 Å) longer. This situation is comparable to that in (MAD)Fe$(CO)_3$, where the relevant Fe–C distance is 0.08 Å longer than the other Fe–C and Fe–N distances.[14] The C(7)–C(8) and C(8)–C(9) bond lengths of 1.405 (5) and 1.417 (4) Å, respectively, are comparable to those found in, for example, (η^4-C_8H_8)Fe$(CO)_3$,[42] and are longer than a C=C double bond (1.33 Å) but shorter than a C(sp^2)–C(sp^2) single bond (1.46 Å). The N–C(7) bond length of 1.358 (3) Å is of the same order of magnitude as the N–C bonds of 1.34 (1) Å in pyridine[43] and of 1.35 (2) Å (mean) in **3**. Furthermore, the bond lengths within the R-CAI-yl ligand are (within experimental error) equal to their congeners in (MAD)Fe$(CO)_3$.[14] The angles N–C(7)–C(8) and C(7)–C(8)–C(9) are equal and amount to 116.5 (5)°. The torsion angle between the N–C(7) and C(8)–C(9) bonds amounts to 1°. These facts point to effective delocalization of π-electrons in the N–C–C–C subsystem, which was also observed in the N–C–C–N moiety in, for example, (R-DAB)$M_2(CO)_4L$ (M = Ru, L = μ-CO, μ-Ru$(CO)_4$;[31,34] M = Fe, L = μ-HC≡CCOOMe[44]) and similar complexes like $Fe_2(CO)_6(C_6H_8O_2)$[45] and $Ru_2(CO)_6(C_4(CH_2OH)_4)$,[33] containing metalla(hetera)cyclopentadiene rings.

It has been shown above that the Ru(1)–C(9) and (to a lesser extent) Ru(1)–N bonds are shortened due to π-overlap with the metal; i.e., delocalization of electron density occurs within the Ru(1)–N–C(7)–C(8)–C(9) ring. The plane containing N, C(7), C(8), and C(9) also contains to a good approximation the Ru(1) atom, which is 0.12 Å out of this plane.[46] The largest deviation from the plane through Ru(1), N, C(7), C(8), and C(9) amounts to 0.034 Å (for N) which is equal to the root-mean-square deviation of 0.029 Å for this calculated plane. The sum of the enclosed angles amounts to 539.7°, which value is close to the theoretical 540° for a pentagon confined to one plane.

Table IV. ^1H NMR Data (ppm) of $CH_3{}^{10}C(H^9)=C(H^8)C(H^7)=NR$ (1a,b) and of $Ru_4(CO)_{10}(CH_3{}^{10}C=C(H^8)C(H^7)=NR)_2$ (2a,b)[a]

	R-CAI		complex	
atom	**1a** (R = *i*-Pr)	**1b** (R = c-Hex)	**2a** (R = *i*-Pr)	**2b** (R = c-Hex)
H(7)	7.57 (d, 8.0)	7.67 (d, 8.0)	6.81 (d, 2.0)	6.83 (br s)
H(8)	5.91 (m)	6.01 (m)	5.08 (d, 2.0)	5.07 (br s)
H(9)	5.91 (m)	6.01 (m)		
H(10)	1.59 (d, 5.0)	1.68 (d, 5.3)	2.55 (s)	2.54 (s)
NR	3.03 (sept, 6.3)	2.77 (m)	3.53 (sept, 6.5)	3.03 (m)
	0.90 (d, 6.3)	1.8–0.8 (m)	1.25 (d, 6.5)	1.8–1.0 (m)
			1.17 (d, 6.5)	

[a] At 250.1 MHz; solvent $CDCl_3$; T = 293 K; multiplicity (s, singlet; d, doublet; sept, septet; br, broad) and *J*(H,H) (±0.5 Hz) in parentheses.

On the basis of these considerations the ring constituted by Ru(1)–N–C(7)–C(8)–C(9) may be imagined as a diheteracyclopentadienyl fragment. In this sense, $Ru_4(CO)_{10}$(R-CAI-yl$)_2$ (**2**) has become an analogue of $[(\eta^5\text{-}C_5H_5)Ru(CO)(\mu\text{-}CO)]_2$ (**4**).

FD-Mass Spectrometry. The molecular formulas of **2a** and **2b** became immediately evident, using this powerful technique for the elucidation of the mass of nonvolatile organometallic compounds. The observed intensity patterns of the molecular ions (see Experimental Section) were successfully compared to computer-simulated patterns.

IR ν(CO) Region. The five IR ν(CO) frequencies of **2a** and **2b** (see Experimental Section) are characteristic for these complexes. The centrosymmetric geometry in solution is corroborated by the presence of only five bands for the 10 CO's. The ν(CO) frequencies in the Ru(1)$(CO)_3$ moiety can be directly compared to those in Ru$(CO)_3$(σ,σ-N,N′-R-DAB)[47,48] and Fe$(CO)_3$(η^4-MAD).[18] For Ru$(CO)_3$($Me_3C_6H_2$-DAB),[47] the Ru$(CO)_3$ unit has locally distorted C_{3v} symmetry, as evidenced by a sharp, intense band at 2053 cm^{-1} (A_1) and two bands at 1991 and 1978 cm^{-1} due to splitting of the E band. The bands of **2a** in hexane at 2067, 2005, and 1993 cm^{-1} correlate with these and can be ascribed to the A′ and A′ + A″ vibrations in the Ru(1)$(CO)_3$ group, in accordance with the local C_s symmetry of the entity. For **2b** a similar pattern is observed. These three bands in **2** have shifted toward higher frequencies compared to the Ru$(CO)_3$(R-DAB) complex, which indicates less π-back-donation from Ru(1) to these CO's in **2**. This observation is in qualitative agreement with the formal +1 oxidation state of Ru(1) and with the π-bonding of Ru(1) to C(9) as discussed under Molecular Structure of **2a**. The ν(CO) frequency of the terminal CO on Ru(2) is observed at lower frequency (1951 cm^{-1}) as might be expected for a CO with a lower bond order (see Table II). The 1775 cm^{-1} band is found in the stretching region of asymmetrically bridging CO's and is assigned to the antisymmetric stretching mode of the $M_2(\mu\text{-}CO)_2$ entity.

The spectra of **2a** and **2b** in CH_2Cl_2 solution are similar to that of **2a** in hexane. As the same pattern of ν(CO) bands pertains in KBr disk, it can be concluded that the geometry of **2a** and **2b** in solution is similar to that in the solid phase.

NMR Spectroscopy. ^1H NMR. The ^1H NMR data of the free R-CAI ligands (**1a,b**) and of the tetranuclear complexes **2a,b** are listed in Table IV. Due to the C_i symmetry of the complexes, only one set of resonances is observed for the two equivalent R-CAI-yl ligands. The resonances of H(7) and H(8) in **2a** and **2b** have shifted ca.

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Table V. ^{13}C NMR Data (ppm) of $C^{10}H_3C^9(H)$=$C^8(H)C^7(H)$=NR (1a,b) and of $Ru_4(CO)_{10}(C^{10}H_3C^9$=$C^8(H)C^7(H)$=NR$)_2$ (2a,b)^a

	R-CAI		complex	
atom	1a (R = *i*-Pr)	1b (R = c-Hex)	2a (R = *i*-Pr)	2b (R = c-Hex)
C(7)	159.4	159.6	129.7	129.8
C(8)	138.8	138.8	102.6	102.4
C(9)	131.7	132.0	195.9	196.3
C(10)	17.5	17.6	32.1	32.1
NR	60.3	68.8	61.2	69.2
	23.5	33.9	26.0	38.9, 37.6
		25.1	29.8	25.7, 25.4
		24.3		25.0

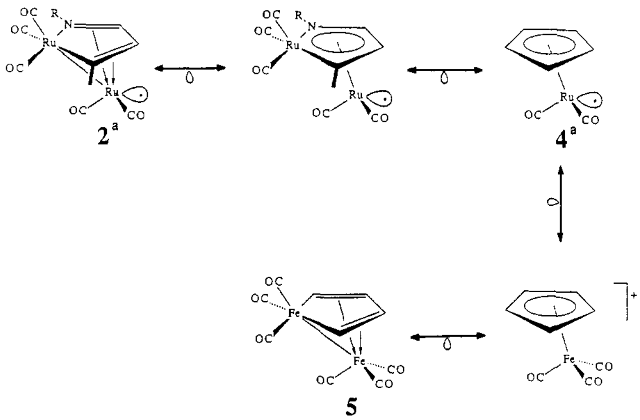
^{a}At 20.1 MHz; solvent $CDCl_3$; T = 263 K.

1 ppm upfield compared to those in the free ligands **1a** and **1b**. This is consistent with a decreased paramagnetic contribution (induced by the C=X (X = C, N) groups) to the chemical shift, due to η^2-coordination of both N=C(H) and (H)C=C moieties in **2a** and **2b**. The shift difference between free ligands and complexes is intermediate between that observed in $Ru_2(CO)_6$(butadiendiyl) of 0.1 ppm downfield[49] and in $Ru_2(CO)_5$(R-DAB) of 1.6–2.0 ppm upfield.[31] Protons H(7) and H(8) are weakly coupled, ^3J = 2 Hz, which is a smaller value than expected. In $M_2(CO)_6$(butadienediyl) (M = Fe, Ru, Os) in which the ligand $-C(H_A)$=$C(H_X)C(H_{X'})$=$C(H_{A'})-$ is σ,σ-C,C, η^2-C=C′, η^2-C=C′ bonded to the $M_2(CO)_6$ core, a coupling constant of $^3J(H_X,H_{X'}) \simeq$ 3.5 Hz has been observed.[49] The singlet of the $=C(CH_3)$ protons is found at 2.55 ppm in **2a** and **2b**. The downfield shift of ca. 1 ppm compared to those of **1a** and **1b** implies a more pronounced paramagnetic deshielding, probably due to the proximity of π-electron density between Ru(1) and C(9). The diastereotopicity of the *N-i*-Pr methyl groups is clearly demonstrated by the presence of two separate doublets in the ^{1}H NMR of **2a**.

^{13}C NMR. The ^{13}C NMR data of the free R-CAI ligands **1a,b** and of the complexes **2a,b** are listed in Table V. The signals (except C(9) in **2a,b**) have been assigned by $^{13}C\{^1H\}$ COSY. The upfield shifts of 30 and 36 ppm compared to those of the free ligand for C(7) and C(8), respectively, in **2a** as well as in **2b** are within the range of upfield shifts that have been observed in complexes $M_2(CO)_6$(butadienediyl).[49] Unfortunately, no ^{13}C NMR data are known for $M_2(CO)_5$(R-DAB) and $H_2Ru_4(CO)_8(\text{R-DAB})_2$.

The chemical shift of C(9) in **2a,b** (195 ppm) falls within the region of 160–200 ppm where resonances of carbon atoms are found, which are σ-coordinated to one Ru atom and π-coordinated to another.[50] This chemical shift is also in the neighborhood of values reminiscent of Ru and Os alkylcarbenes.[41b] Generally, δ values of such carbene carbon atoms are found slightly more downfield (200–240 ppm).[41] In the present case the carbene character of C(9) is less pronounced, in agreement with the X-ray data (vide supra). Anyhow, the large downfield shift relative to the free ligands of 64 ppm for C(9) must be due to an increased contribution to the paramagnetic chemical shift tensor, due to π-bonding of Ru(1) to C(9). The C(10) atoms of the R-CAI-yl ligands in complexes **2a,b** have shifted downfield by 15 ppm compared to the C(10) signals in free R-CAI, reflecting the proximity of Ru(1). The diastereotopicity of the carbon atoms of the substituents on nitrogen in **2a** and **2b**, respectively, is evidenced by the separate signals for all carbon atoms involved.

Scheme I. Isolobal Relationships^a



^{a}Half of the molecule of compounds 2 and 4 are drawn.

Cluster Geometry. Tetranuclear transition-metal clusters may exhibit several geometric configurations, depending on the number of valence electrons provided by the metal atoms and ligands, that are involved in bonding.[51] The present Ru_4 cluster contains three metal–metal bonds, in agreement with the presence of 66 closed valence electrons (CVE),[52] indicating that the molecule is electron-precise. In the electron count the σ-N, σ-C, η^2-N=C, η^2-C=C coordinated R-CAI-yl fragment contributes a total of seven valence electrons to the cluster and each Ru atom eight. In the complex, six CVE have been added to the basic tetrahedral M_4 configuration with 60 CVE, which contains six metal–metal bonds. The six added electrons occupy three high-lying antibonding cluster valence molecular orbitals, leaving a net bond order of 3 in **2a,b**. The linear tetranuclear configuration is favored with respect to the other possible geometry for M_4 clusters with 66 CVE, namely, a T or Y configuration, probably because **2a** is formed as a linear Ru_4 species (vide infra), which will not easily isomerize. For M_4 clusters containing only transition metals, the T or Y configuration has never been observed. Instead, the straight-chain M_4 geometry has been identified in seven cases, including the present one.[27–29,53–55] These complexes invariably contain strongly bridging ligands like Ph_2P^- and CO, indicating that the R-CAI-yl ligand in **2a** (like R-DAB in **3**) equally forms strong bridges between transition-metal centers and is thus able to stabilize unusual cluster geometries.

An attractive alternative perception of **2a** is as a structural analogue of (*E*)-$[(\eta^5\text{-}C_5H_5)Ru(CO)(\mu\text{-}CO)]_2$ (**4**). In this view the Ru(1)–N–C(7)–C(8)–C(9) heterocycle is imagined as a diheteracyclopentadienyl fragment, which is η^5-coordinated to Ru(2). Credit for this proposal emerges from the formal, isolobal analogy between a $(CO)_3$RuN(R)=C(H)C(H)=CCH_3 fragment and $C_5H_5^-$ (Scheme I), since $Ru(CO)_3 \overset{}{\underset{\circ}{\leftrightarrow}} CH^+$ and RN $\underset{\circ}{\leftrightarrow}$ CH^-. One may also refer to the close relationship with the ferracyclopentadienyl ring in ferroles **5**, which is isolobal with $C_5H_5^+$.[56,57] It has been elaborated in the discussion of the X-ray structure that the metallaazacyclopentadienyl unit is almost planar, so

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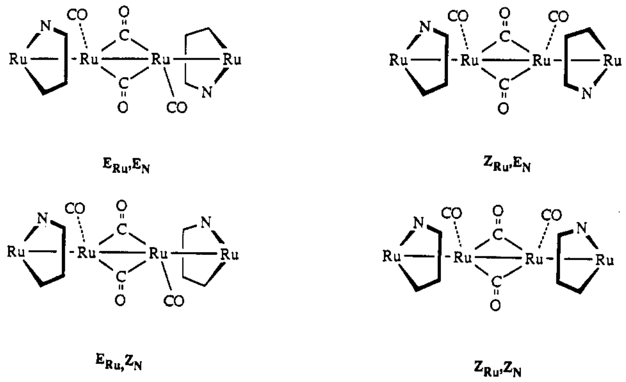


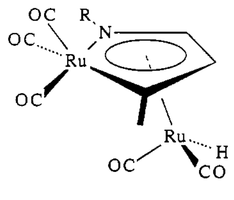
$E_{\mathrm{Ru}},E_{\mathrm{N}}$ $Z_{\mathrm{Ru}},E_{\mathrm{N}}$ $E_{\mathrm{Ru}},Z_{\mathrm{N}}$ $Z_{\mathrm{Ru}},Z_{\mathrm{N}}$

Figure 3. Geometric isomers of **2**.

the comparison of **2a** with **4** seems reasonable. Whether the chemical behavior resembles that of **4** remains open to question and will be the subject of future reports.

Formation of 2a,b. The thermal reaction of monoazadienes RN=C(H)C(H)=C(H)CH$_3$ with Ru$_3$(CO)$_{12}$ in refluxing heptane yields the tetranuclear complexes **2** in good yields for R = *i*-Pr or *c*-Hex. However, when R = *t*-Bu, little or no tetranuclear compound is formed. At present, this deviating reactivity is not understood. Molecular models reveal no large differences for different groups R, so thermodynamically formation of **2** with R = *t*-Bu should be possible. Apparently, another kinetic path is followed in this case, since different products are formed. These are presently under investigation.

About the mechanism of the reactions involved in the formation of **2a,b** from Ru$_3$(CO)$_{12}$ and **1a,b**, only speculative, though plausible, suggestions can be made. In analogy with the formation of **4**[58] one may envisage the intermediacy of hydride species like **6**. Related species, e.g. (CO)$_4$W(μ-PPh$_2$)$_2$RhH(CO)(PPh$_3$), have been identified as intermediates in the formation of [(CO)$_4$W(μ-PPh$_2$)$_2$Rh(CO)]$_2$ which is a 62 CVE linear tetranuclear complex,[29] exhibiting the basic features of our 66 CVE complex, **2a**. Hydrides **6** may be formed via activation of the γ-C-H bond of coordinated R-CAI on a ruthenium carbonyl fragment. It is well-known[58] that such metal hydrides dimerize easily.



6

There are four possible stereoisomers of **2** because of (i) *E,Z* isomerism with respect to the relative orientation of the diheteracyclopentadienyl rings (i.e. of the outer Ru atoms) designated $E_{\mathrm{Ru}},Z_{\mathrm{Ru}}$ and (ii) *E,Z* isomerism with respect to the relative positions of, say, the N atoms, at the same or different sides of the molecule, designated $E_{\mathrm{N}},Z_{\mathrm{N}}$ (see Figure 3). On thermodynamic grounds, dimerization of **6** will probably exclusively yield complexes (E_{Ru})-**2**. Neither the NMR nor IR spectra (solid and liquid phase) reveal indications of the presence of the Z_{Ru} isomer. This is in qualitative agreement with spectroscopic data for **3**, for which also only the E_{Ru} isomer has been identified.[27] Of the remaining two isomers, ($E_{\mathrm{Ru}},E_{\mathrm{N}}$)-**2** of C_i symmetry and ($E_{\mathrm{Ru}},Z_{\mathrm{N}}$)-**2** of C_2 symmetry, only the former has been isolated.[59] Upon dimerization of hydride **6** one might expect about equal amounts of the $E_{\mathrm{Ru}},E_{\mathrm{N}}$ and $E_{\mathrm{Ru}},Z_{\mathrm{N}}$ isomers of **2**, which should exhibit different spectral properties. As only (E_{Ru}, E_{N})-**2** is obtained, one may argue that this isomer is formed via a kinetically favored stereoselective pathway. More research will be necessary in order to obtain a satisfactory answer to this stereochemical problem.

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Registry No. **1a**, 32820-49-8; **1b**, 32820-47-6; 1 (R = *t*-Bu), 81569-07-5; **2a**, 111772-59-9; **2b**, 111772-60-2; Ru$_3$(CO)$_{12}$, 15243-33-1; Ru, 7440-18-8.

Supplementary Material Available: Table VI, all bond lengths and angles, and Table VIII, anisotropic thermal parameters (5 pages); Table VII, structure factors (11 pages). Ordering information is given on any current masthead page.

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[59] However, it cannot be excluded that ($E_{\mathrm{Ru}},E_{\mathrm{N}}$)-**2** is the ground state (X-ray) but that in solution very rapid rotation of the heteracyclopentadienyl rings (*E,E* $\rightleftharpoons$ *Z,Z*) and/or rotation around Ru(2)–Ru(2)* (via bridge opening) takes place (*E,E* $\rightleftharpoons$ *Z,Z*). Note, however, that *Z,E* and *E,Z* isomers can only arise during formation of **2**, but not out of (*E,E*)-**2** or (*Z,Z*)-**2**.