Ruthenium Carbonyl 1,4-Diaza-1,3-butadiene (R-DAB) Complexes.[1] Reactivity of Ru₃(CO)₈(R-DAB) toward Diazomethane. Addition of a Methylene Fragment to a Trinuclear Species with Concomitant Rupture of a Single Ru–Ru Bond. Molecular Structure of Octacarbonyl(1,4-dineopentyl-1,4-diaza-1,3-butadiene)-(μ-methylene)triruthenium: (μ-CH₂)Ru₃(CO)₈(neo-Pen-DAB)

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$Ru_3(CO)_8(R\text{-}DAB)$ (R = neo-Pen, i-Bu; R-DAB = 1,4-disubstituted 1,4-diaza-1,3-butadiene; RN=CHCH=NR)[2] reacts with ethereal diazomethane at room temperature to yield the novel addition product $(\mu\text{-}CH_2)Ru_3(CO)_8(R\text{-}DAB)$. During the reaction one single Ru–Ru bond is broken while the eight-electron-coordination mode of the diimine ligand is unaffected. This is shown by an X-ray crystal structure determination for the R = neo-Pen derivative. Crystals of $(\mu\text{-}CH_2)Ru_3(CO)_8(neo\text{-}Pen\text{-}DAB)$ are monoclinic of space group $P2_1/n$ with cell constants $a = 13.819$ (2) Å, $b = 21.339$ (2) Å, $c = 9.485$ (1) Å, $\beta = 108.22$ (1)°, and Z = 4. A total of 3159 reflections have been used in the refinement resulting in a final R value of 0.026 ($R_w = 0.040$). Electronically, this species can be considered as a 50-electron trinuclear complex accordingly having only two Ru–Ru bonds: Ru(1)–Ru(2) = 2.8690 (6) and Ru(1)–Ru(3) = 2.9079 (6) Å. The third Ru(2)···Ru(3) distance of 3.1021 (6) Å is considered as a nonbonding distance and is asymmetrically bridged by the methylene moiety: Ru(2)–C(17) = 2.048 (5) and Ru(3)–C(17) = 2.204 (6) Å, which is a rather unique feature. The $\overline{Ru(2)\text{-}Ru(1)\text{-}Ru(3)\text{-}C}C(17)$ moiety has a butterfly geometry with a dihedral angle of 143.1°. All carbonyls are terminally bonded: two to Ru(1) and Ru(2) each and four to Ru(3). The neo-Pen-DAB ligand is σ-N, σ-N' bonded to Ru(2) with equal Ru(2)-N bond lengths of 2.16 (1) Å. Besides, both imine bonds are η^2-coordinated to Ru(1) as evidenced by the observation that all four atoms of the N(1)=C(1)—C(2)=N(2) part are located at about equal distance (2.21 (2) Å) from Ru(1). Likewise, the three equal bond lengths within the diimine part (1.38 (1) Å) are consistent with an eight-electron σ-N, σ-N', η^2-C=N, η^2-C'=N' bonding mode. The complexes have been further characterized by IR, FD-mass, ¹H NMR, and ¹³C NMR spectroscopy. The carbene's chemical shifts are 3.7 (¹H NMR) and 32.5 ppm (¹³C NMR), which is in line with the absence of a direct Ru(2)–Ru(3) interaction. The two halves of the $\overline{R\text{-}DAB}$ ligand are magnetically equivalent, indicating that in solution the "flying" motion of the $\overline{Ru(2)\text{-}Ru}$-(1)-Ru(3)-C(17) butterfly is fast on the NMR time scale.

Introduction

Multisite bonded R-DAB ligands[2] (R-DAB = RN=CHCH=NR = 1,4-disubstituted 1,4-diaza-1,3-butadiene) can exhibit strong activation, resulting in C—C,[3] C–H,[4] N-C,[5] or N-H[6] bond formation. The synthesis of polynuclear R-DAB complexes, in which such multisite bonding may occur because of possible involvement of the π-electrons in the coordination,[7] therefore is of great interest. One of the possibilities to obtain polynuclear R-DAB species is the reaction of polynuclear metal carbonyls with R-DAB. During the last 5 years we have gained much insight in the $Ru_3(CO)_{12}$/R-DAB reaction sequence and several reactive intermediates have been isolated. Attention is now especially focused on the study of the reactivity of these intermediates. It has been found that, e.g., $Ru_2(CO)_n(R\text{-}DAB)$ (n = 5,6) reacts with several ligands L (L = R-DAB, sulfine, carbodiimide, acetylene, and ketene) to yield R-DAB-L coupled products.[3] Another promising intermediate, i.e., $Ru_3(CO)_8(R\text{-}DAB)$, reacts quickly and reversibly with CO to yield the 50-electron trinuclear compound $Ru_3(CO)_9(R\text{-}DAB)$ (see Figure 1).[8a]

(1) Part 8; for earlier parts see ref 3a–c and 8.

(2) For a recent review on R-DAB chemistry: van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* 1982, 21, 151. In this review the nomenclature for the ligands is also explained.

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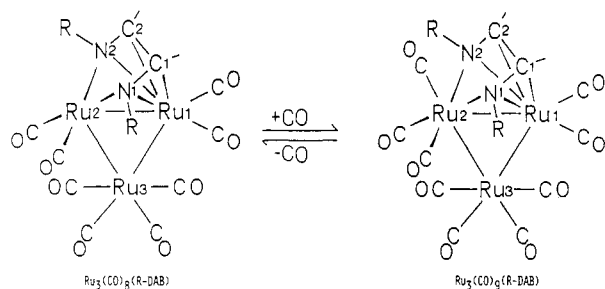
Figure 1. The reversible reaction of CO with $Ru_3(CO)_8$(R-DAB) showing the schematic structures of the Ru_3 species and the empty coordination site on Ru(2).

This reaction is accompanied with a green to red color change and may occur because of the gap in the coordination sphere of Ru(2), trans to the Ru(3)(CO)$_4$ unit (see Figure 1). Surprisingly, no metal–metal nor a metal–ligand bond is broken during the CO addition but instead the Ru(2)–Ru(n) (n = 1, 3) and Ru(2)–C(O) bonds are weakened.[8a] It has been argued that this may happen because the extra electron density is moved to an antibonding orbital, mainly localized on Ru(2). The availability of the empty coordination site on Ru(2) to which other ligands L can be bonded, in combination with the proximity of the multisite bonded R-DAB ligand may lead to novel types of interaction between R-DAB and L. We therefore are extensively studying the chemistry of $Ru_3(CO)_8$(R-DAB), and it is has already been found that $Ru_3(CO)_8$(R-DAB) reacts with acetylenes, allenes, phosphines, and molecular hydrogen.[9]

Recently, the formal two-electron-donating carbene ligand has drawn much attention because it may play an important intermediate role in FT synthesis and alkyne polymerization.[10] Analogous C–C coupling to that occurring during FT synthesis[11] as well as C–C coupling between a CH_2 fragment and CO or alkyne[12] has been observed. Recently, Herrmann has extensively reviewed the novel structural and chemical features of methylene-bridged complexes.[13]

We were interested to find out (i) if a methylene unit could add to $Ru_3(CO)_8$(R-DAB) and (ii) if so, whether it may react further with the activated R-DAB ligand. Therefore, we have carried out the reaction of $Ru_3(CO)_8$-(R-DAB) with diazomethane, which method is generally the most direct way to obtain a methylene complex,[13] and the results of this reaction are described in this paper.

Experimental Section

Materials and Apparatus. NMR spectra were obtained on a Bruker WM250 (^{1}H) and a Bruker WP80 (^{13}C) apparatus. IR spectra were recorded with a Perkin Elmer 283 spectrophotometer. mass spectra were obtained with a Varian MAT 711 mass spectrometer, applying field desorption technique. Elemental analyses were obtained from the elemental analysis section of the Institute for Applied Chemistry, TNO, Utrecht, The Netherlands. All

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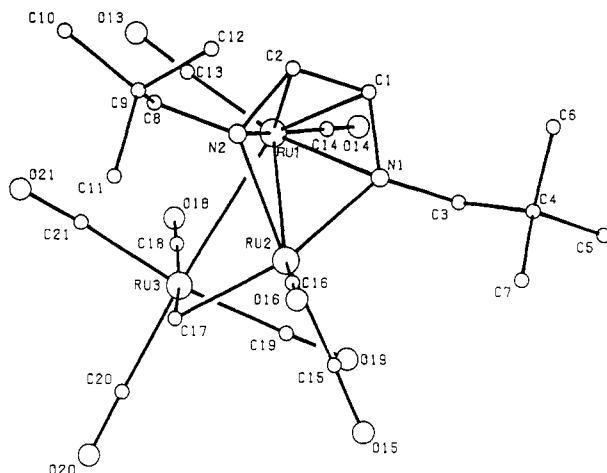(13) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

Figure 2. The molecular geometry of $(\mu\text{-}CH_2)Ru_3(CO)_8$(neo-Pen-DAB).

preparations were carried out in an atmosphere of purified nitrogen, using carefully dried solvents. Silica gel for column chromatography (60 mesh) was dried and activated before use. $Ru_3(CO)_8$(R-DAB)[3c] and an diethyl ether solution of diazomethane[14] (from KOH and N-methyl-N-nitrosoureum) have been prepared according to literature procedures.

Synthesis of $(\mu\text{-}CH_2)Ru_3(CO)_8$(R-DAB) (R = *i*-Bu, neo-Pen). $Ru_3(CO)_8$(R-DAB) (0.33 mmol; prepared in situ[3c]) was stirred in 30 mL of toluene at room temperature. Diazomethane (dissolved in diethyl ether) was slowly added until all the ν(CO) IR peaks due to the starting complex had been replaced by those of the product. During the reaction, the color of the solution changed from green to yellow/green. After additional stirring for 0.5 h, the solvent was evaporated in vacuo at 60 °C and the residue purified by column chromatography (silica, eluent hexane). A yellow fraction was obtained which at –80 °C yielded 80% of yellow crystals. These were identified as $(\mu\text{-}CH_2)Ru_3(CO)_8$(R-DAB) by elemental analysis, by IR, FD-mass, ^{1}H NMR, and ^{13}C NMR spectroscopy (Table III), and by an X-ray crystal structure determination for the R = neo-Pen derivative.

Crystal Structure Determination of $(\mu\text{-}CH_2)Ru_3(CO)_8$-(neo-Pen-DAB) [$C_{21}H_{26}N_2O_8Ru_3$; Octaconyl(1,4-dineopentyl-1,4-diaza-1,3-butadiene)(μ-methylene)triruthenium]. Crystals of the title compound are monoclinic of space group $P2_1/n$. The unit cel has the following dimensions: a = 13.819 (2) Å, b = 21.339 (2) Å, c = 9.485 (1) Å, β = 108.22 (1)°; Z = 4, V = 2656 (3) Å^3, d_{calcd} = 1.84 g cm^{-3}. A total of 4502 reflections ($2.5 \le \theta \le 65°$; $-16 \le h \le 15, 0 \le k \le 24, 0 \le l \le 10$) were measured on a NONIUS CAD 4 diffractometer using graphite-monochromated Cu Kα radiation. a total of 1343 reflections of the 4502 reflections were below the $2.5\sigma(I)$ level and treated as unobserved. Crystal dimensions: $0.08 \times 0.08 \times 0.16$ mm; μ = 143.8 cm^{-1}. The Ru positions were found from an E Fourier obtained by means of the symbolic addition program set SIMPEL.[15a] The remaining non-hydrogen atoms were derived from subsequent ΔF syntheses. After isotropic block-diagonal least-squares refinement (R = 0.083) the empirical absorption correction DIFABS[15b] was applied. Subsequent anisotropic refinement converged to R = 0.026 (R_w = 0.040) for the 3159 reflections observed. During the final cycles the H atoms, which were located in a ΔF synthesis, were included in the refinement with isotropic temperature parameters. A weighting scheme of $w = 1/(2.7 + F_o + 0.026F_o^2)$ was employed, and an extinction correction was applied. The anomalous scat-

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Table I. The Final Atomic Coordinates (Esd) of (μ-CH₂)Ru₃(CO)₈(neo-Pen-DAB)

atoms	x	y	z	atoms	x	y	z
Ru(1)	0.27583 (3)	0.15987 (2)	0.23603 (5)	C(18)	0.1719 (5)	0.1375 (3)	-0.1254 (6)
Ru(2)	0.10654 (3)	0.12365 (2)	0.33202 (4)	C(19)	0.1128 (4)	0.0540 (2)	-0.0461 (6)
Ru(3)	0.08474 (3)	0.14212 (2)	-0.00088 (4)	C(20)	-0.0470 (5)	0.1277 (2)	-0.1450 (6)
O(13)	0.3230 (4)	0.2663 (2)	0.0617 (6)	C(21)	0.0766 (4)	0.2323 (3)	-0.0250 (7)
O(14)	0.4031 (4)	0.0772 (2)	0.1051 (6)	H(11)	0.398 (4)	0.129 (2)	0.516 (6)
O(15)	-0.0079 (3)	0.0017 (2)	0.2783 (5)	H(21)	0.336 (4)	0.234 (2)	0.485 (6)
O(16)	-0.0003 (4)	0.1384 (2)	0.5567 (6)	H(31)	0.255 (4)	0.005 (3)	0.352 (6)
O(18)	0.2225 (4)	0.1365 (2)	-0.2009 (5)	H(32)	0.370 (4)	0.032 (3)	0.400 (6)
O(19)	0.1327 (3)	0.0026 (2)	0.0597 (5)	H(51)	0.312 (4)	-0.094 (3)	0.478 (6)
O(20)	-0.1258 (3)	0.1192 (-)	-0.2260 (5)	H(52)	0.417 (4)	-0.065 (3)	0.515 (6)
O(21)	0.0679 (4)	0.2852 (2)	-0.0416 (6)	H(53)	0.374 (4)	-0.095 (3)	0.638 (6)
N(1)	0.2638 (3)	0.0938 (2)	0.4144 (5)	H(61)	0.464 (4)	0.029 (3)	0.684 (6)
N(2)	0.1970 (3)	0.2083 (2)	0.3750 (5)	H(62)	0.366 (4)	0.069 (2)	0.707 (6)
C(1)	0.3346 (4)	0.1399 (2)	0.4734 (6)	H(63)	0.404 (4)	0.005 (3)	0.805 (6)
C(2)	0.2989 (4)	0.2004 (2)	0.4570 (6)	H(71)	0.222 (4)	-0.036 (3)	0.710 (6)
C(3)	0.3044 (4)	0.0289 (2)	0.4252 (6)	H(72)	0.188 (4)	0.031 (3)	0.618 (6)
C(4)	0.3170 (4)	-0.0070 (3)	0.5684 (7)	H(73)	0.174 (4)	-0.036 (3)	0.517 (6)
C(5)	0.3595 (6)	-0.0711 (3)	0.5484 (8)	H(81)	0.114 (4)	0.277 (3)	0.246 (6)
C(6)	0.3931 (5)	0.0260 (3)	0.7017 (7)	H(82)	0.234 (4)	0.300 (3)	0.352 (6)
C(7)	0.2165 (5)	-0.0149 (3)	0.5994 (8)	H(101)	0.101 (4)	0.388 (3)	0.339 (6)
C(8)	0.1672 (4)	0.2754 (2)	0.3467 (7)	H(102)	0.216 (4)	0.391 (3)	0.464 (6)
C(9)	0.1302 (5)	0.3099 (3)	0.4629 (8)	H(103)	0.122 (4)	0.403 (3)	0.508 (6)
C(10)	0.1423 (7)	0.3795 (3)	0.4392 (11)	H(111)	-0.034 (4)	0.316 (3)	0.340 (6)
C(11)	0.0207 (7)	0.299 (4)	0.4417 (13)	H(112)	-0.001 (4)	0.251 (3)	0.457 (6)
C(12)	0.1955 (7)	0.2947 (4)	0.6183 (9)	H(113)	-0.007 (4)	0.319 (3)	0.505 (6)
C(13)	0.3026 (4)	0.2268 (3)	0.1266 (7)	H(121)	0.148 (4)	0.304 (3)	0.676 (6)
C(14)	0.3546 (4)	0.1090 (3)	0.1550 (6)	H(122)	0.264 (4)	0.310 (3)	0.675 (6)
C(15)	0.0385 (4)	0.0476 (2)	0.2965 (6)	H(123)	0.198 (4)	0.245 (3)	0.624 (6)
C(16)	0.0426 (4)	0.1334 (3)	0.4711 (6)	H(171)	-0.054 (4)	0.140 (3)	0.114 (6)
C(17)	-0.0044 (4)	0.1588 (2)	0.1519 (6)	H(172)	-0.022 (4)	0.198 (3)	0.155 (6)

tering of Ru was taken into account. The programs were taken from the XRAY 76 system,[15] unless otherwise stated. The scattering factors, dispersion correction, absorption coefficients[15d] and the program for plotting[15e] were taken from the literature.

The molecular geometry of (μ-CH₂)Ru₃(CO)₈(neo-Pen-DAB) with the numbering of the atoms is shown in Figure 2, which is a PLUTO[15e] drawing of the molecule. Atomic parameters, bond lengths, and selected bond angles are given in Tables I and II. All bond angles, anisotropic thermal parameters, and a list of observed and calculated structure factors are included with the supplementary material.

Results

Formation of (μ-CH₂)Ru₃(CO)₈(R-DAB). Ru₃(CO)₈(R-DAB) (R = neo-Pe, i-Bu) reacts with diazomethane according to eq 1. The addition of the methylene

$$\text{Ru}_3(\text{CO})_8(\text{R-DAB}) \xrightarrow[-\text{N}_2,\ \text{RT}]{+\text{CH}_2\text{N}_2} (\mu\text{-CH}_2)\text{Ru}_3(\text{CO})_8(\text{R-DAB}) \quad (1)$$
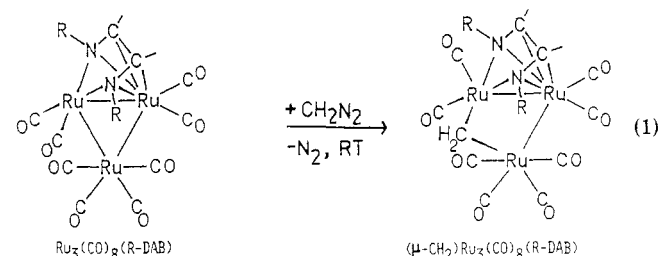
unit occurs smoothly and produces the methylenetriruthenium complex in high yield at room temperature, i.e., without any noticeable decomposition of the trinuclear metal carbonyl. Reaction of Ru₃(CO)₈ (R-DAB) with the much less reactive diphenyldiazomethane[16] did not lead to a carbene complex, and instead only slow decomposition was observed.

The methylene complex is soluble in hexane and relatively stable as compared to the starting complex.

Molecular Geometry of (μ-CH₂)Ru₃(CO)₈(neo-Pen-DAB). The molecular geometry of (μ-CH₂)Ru₃(CO)₈-

(neo-Pen-DAB) is depicted in Figure 2. In Tables I and II the atomic coordinates and selected bond distances and angles are given.

The addition of the two-electron-donating methylene group to the 48-electron Ru₃(CO)₈(neo-Pen-DAB) complex results in a rupture of one single Ru–Ru bond: Ru(2)···Ru(3) amounts to 3.1012 (6) Å, which can be considered as a nonbonding distance. In the starting complex[9] the analogous Ru–Ru bond distance is 2.768 (1) Å while in Ru complexes in which the methylene bridge is supported by a Ru–Ru bond, this bonding distance is ca. 2.67 Å.[13] We know of only one other Ru complex that contains a methylene group bridging a nonbonding Ru···Ru distance; in fact, in [(η⁵-C₅H₅)Ru(CO)₂]₂(μ-CH₂), having a Ru···Ru separation of 3.8 Å, it is the CH₂ group that holds together the two Ru centers.[17] The other two Ru–Ru bond lengths in (μ-CH₂)Ru₃(CO)₈(neo-Pen-DAB) can be envisaged as normal single bond lengths (Ru(1)–Ru(2) = 2.8690 (6) Å, Ru(1)–Ru(3) = 2.9079 (6) Å) which are comparable with the single bond lengths found in Ru₃(CO)₁₂ (2.854 (3) Å (mean)).[18] With the exception of a few examples,[8a] such a rupture of a bond (in the present case a metal–metal bond) can be expected when a two-electron donor is added to a 48-electron trinuclear species.[19]

All eight carbonyls in (μ-CH₂)Ru₃(CO)₈(neo-Pen-DAB) are terminally bonded: two to Ru(1) and Ru(2) each and four to Ru(3), all with normal Ru–C and C–O bond lengths and Ru–C–O bond angles. Ru(3) is approximately octahedrally surrounded by C(17), C(18), C(19), C(20), C(21), and Ru(2) (see Table II).

The Ru(1)–Ru(2) bond is bridged by the neo-Pen-DAB ligand, which is bonded to Ru(2) via N(1) and N(2) with equal bond lengths of 2.162 (4) Å (mean). The four central

(16) See, e.g., ref 13, p 180.

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Table II. Selected Geometric Parameters (Esd) of (μ-CH₂)Ru₃(CO)₈(neo-Pen-DAB)

Bond Lengths (Å)

Metal Carbonyl Part

Ru(1)-Ru(2)	2.8690 (6)	Ru(3)-C(21)	1.937 (6)
Ru(2)-Ru(3)[a]	3.1021 (6)	C(13)-O(13)	1.133 (8)
Ru(1-Bu(3)	2.9079 (6)	C(14)-O(14)	1.156 (9)
Ru(1)-C(13)	1.868 (6)	C(15)-O(15)	1.154 (7)
Ru(1)-C(14)	1.864 (6)	C(16)-O(16)	1.149 (9)
Ru(2)-C(15)	1.853 (5)	C(18)-O(18)	1.147 (9)
Ru(2)-C(16)	1.814 (7)	C(19)-O(19)	1.128 (6)
Ru(3)-C(18)	1.936 (7)	C(20)-O(20)	1.134 (7)
Ru(3)-C(19)	1.944 (5)	C(21)-O(21)	1.140 (7)
Ru(3)-C(20)	1.929 (5)		

Metal-neo-Pen-DAB Part

Ru(1)-N(1)	2.249 (4)	N(2)-C(8)	1.492 (6)
Ru(1)-N(2)	2.215 (5)	C(3)-C(4)	1.520 (8)
Ru(1)-C(1)	2.183 (5)	C(4)-C(5)	1.526 (9)
Ru(1)-C(2)	2.197 (6)	C(4)-C(6)	1.539 (8)
Ru(2)-N(1)	2.163 (4)	C(4)-C(7)	1.517 (10)
Ru(2)-N(2)	2.161 (4)	C(8)-C(9)	1.540 (10)
N(1)-C(1)	1.377 (6)	C(9)-C(10)	1.521 (9)
C(1)-C(2)	1.373 (7)	C(9)-C(11)	1.496 (12)
N(2)-C(2)	1.391 (6)	C(9)-C(12)	1.504 (10)
N(1)-C(3)	1.486 (7)		

Metal Carbene Part

Ru(2)-C(17)	2.048 (5)	Ru(3)-C(17)	2.204 (6)

Bond Angles (deg)

Metal Carbonyl Part

Ru(2)-Ru(1)-Ru(3)	64.95 (2)	Ru-C-O(mean)[b]	177.0 (20)

Metal Carbene Part

Ru(i)-C(17)-Ru(3)	93.6 (2)	H(171)-C(17)-H(172)	109.3 (55)

Around Ru(1)

Ru(2)-Ru(1)-N(1)	48.1 (1)	N(1)-Ru(1)-C(2)	63.4 (2)
Ru(2)-Ru(1)-N(2)	48.2 (1)	N(1)-Ru(1)-C(13)	166.2 (2)
Ru(2)-Ru(1)-C(1)	72.4 (1)	N(1)-Ru(1)-C(14)	97.8 (2)
Ru(2)-Ru(1)-C(2)	72.1 (1)	N(2)-Ru(1)-C(1)	64.5 (2)
Ru(2)-Ru(1)-C(13)	134.8 (2)	N(2)-Ru(1)-C(2)	36.8 (2)
Ru(2)-Ru(1)-C(14)	127.8 (2)	N(2)-Ru(1)-C(13)	101.2 (2)
Ru(3)-Ru(1)-N(1)	103.7 (1)	N(2)-Ru(1)-C(14)	167.8 (2)
Ru(3)-Ru(1)-N(2)	91.4 (1)	C(1)-Ru(1)-C(2)	36.5 (2)
Ru(3)-Ru(1)-C(1)	136.6 (1)	C(1)-Ru(1)-C(13)	130.4 (2)
Ru(3)-Ru(1)-C(2)	127.9 (1)	C(1)-Ru(1)-C(14)	103.6 (2)
Ru(3)-Ru(1)-C(13)	87.7 (2)	C(2)-Ru(1)-C(13)	103.5 (2)
Ru(3)-Ru(1)-C(14)	96.4 (1)	C(2)-Ru(1)-C(14)	133.9 (2)
N(1)-Ru(1)-N(2)	71.2 (2)	C(13)-Ru(1)-C(14)	88.5 (3)
N(1)-Ru(1)-C(1)	36.2 (2)		

Around Ru(2)

Ru(u)-Ru(2)-N(1)	50.8 (1)	N(1)-Ru(2)-C(17)	144.6 (2)
Ru(1)-Ru(2)-N(2)	49.8 (1)	N(2)-Ru(2)-C(15)	175.4 (2)
Ru(1)-Ru(2)-C(15)	126.6 (2)	N(2)-Ru(2)-C(16)	98.7 (2)
Ru(1)-Ru(2)-C(16)	146.1 (2)	N(2)-Ru(2)-C(17)	195.1 (2)
Ru(1)-Ru(2)-C(17)	96.2 (2)	C(15)-Ru(2)-C(16)	84.2 (3)
N(1)-Ru(2)-N(2)	73.8 (1)	C(15)-Ru(2)-C(17)	87.9 (2)
N(1)-Ru(2)-C(15)	101.7 (2)	C(16)-Ru(2)-C(17)	99.0 (2)
N(1)-Ru(2)-C(16)	115.7 (2)		

Around Ru(3)

Ru(1)-Ru(3)-C(17)	91.7 (1)	C(17)-Ru(3)-C(21)	83.9 (2)
Ru(1)-Ru(3)-C(18)	83.7 (2)	C(18)-Ru(3)-C(19)	88.5 (3)
Ru(1)-Ru(3)-C(19)	83.2 (1)	C(18)-Ru(3)-C(20)	100.9 (3)
Ru(1)-Ru(3)-C(20)	175.0 (2)	C(18)-Ru(3)-C(21)	90.1 (3)
Ru(1)-Ru(3)-C(21)	88.1 (1)	C(19)-Ru(3)-C(20)	94.9 (2)
C(17)-Ru(3)-C(18)	172.6 (2)	C(19)-Ru(3)-C(21)	171.3 (2)
C(17)-Ru(3)-C(19)	96.8 (2)	C(20)-Ru(3)-C(21)	93.9 (2)
C(17)-Ru(3)-C(20)	83.9 (2)		

Metal-neo-Pen-DAB Part

Ru(1)-N(1)-Ru(2)	81.1 (1)	Ru(2)-N(2)-C(2)	115.5 (3)
Ru(1)-N(2)-Ru(2)	82.0 (1)	Ru(2)-N(1)-C(3)	128.0 (3)
Ru(2)-N(1)-C(1)	116.2 (3)	Ru(2)-N(2)-C(8)	131.1 (3)

The neo-Pen-DAB Part

N(1)-C(1)-C(2)	116.3 (4)	C(2)-N(2)-C(8)	113.0 (4)
N(2)-C(2)-C(1)	116.2 (4)	N(1)-C(3)-C(4)	117.8 (5)
C(1)-N(1)-C(3)	115.7 (4)	N(2)-C(8)-C(9)	117.7 (5)
C-C-C(t-Bu)	109.5 (20)		

(mean)[b]

[a] Nonbonding distance. [b] The standard deviation of the mean value is calculated by $\sigma = \{\sum_i (x_i - \bar{x})^2/(N-1)\}^{1/2}$.
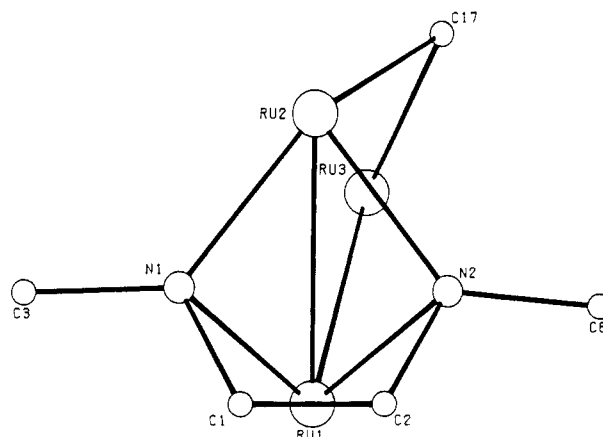

Figure 3. A view on the molecule showing its butterfly-like geometry and the two inequivalent halves of the α-diimine ligand.

atoms of the α-diimine ligand are located at about equal distance (2.21 (2) Å (mean)) from Ru(1). These geometries indicate that the neo-Pen-DAB ligand is σ-N, σ-N′ coordinated to Ru(2) and η²-C=N, η²-C′=N′ coordinated to Ru(1), thus donating its maximum of eight electrons to the metal carbonyl core,[3c,8] just as in the starting complex.[3c,9] The equal intraligand N(1)-C(1), N(2)-C(2), and C(1)-C(2) bond lengths of 1.38 (1) Å (mean) also point to an eight-electron-coordination. In free c-Hex-DAB the corresponding imine and central C-C bond lengths are 1.258 (3) and 1.457 (3) Å, respectively.[20] Obviously, π-backbonding from the metal carbonyl into the LUMO of the α-diimine extensively weakens the imine bonds in the present compound. The central C(1)-C(2) bond is strengthened because the LUMO has bonding character between these atoms.[20]

The dihedral angle between the flat N(1)C(1)C(2)N(2) skeleton (maximum deviation from the least-squares plane being 0.017 Å) and N(1)Ru(2)N(2) is 12.0°, which is a normal value for an eight-electron-bonded R-DAB complex.[3c,8] The α-diimine plane, which in the starting compound Ru₃(CO)₈(neo-Pen-DAB) is about perpendicular to the Ru₃ plane, makes in the present compound an angle of 82.0° with the Ru triangle obviously because of the presence of the μ-CH₂ unit (vide infra; see also Figure 3). The central C(1)-C(2) bond remains perpendicular (89.6°) to the Ru(1)-Ru(2) vector.

Surprisingly the methylene moiety C(17)H₂ asymmetrically bridges the nonbonding Ru(2)···Ru(3) distance: Ru(2)-C(17) = 2.048 (5) Å; Ru(3)-C(17) = 2.204 (6) Å. Such a large difference in bond lengths has, to our knowledge, never been observed before in homonuclear methylene complexes. Ru-Ru bond-assisted methylene bridges exhibit Ru-C bond lengths between 1.98 and 2.10 Å[13] while the Ru-C bond lengths in [(η⁵-C₅H₅)Ru-(CO)₂]₂(μ-CH₂) are 2.18 Å.[17]

The methylene carbon atom C(17) is not in one plane with the three Ru atoms. The dihedral angle between Ru(2)C(17)Ru(3) and the Ru₃ plane is 143.1° (see Figure 3). The "internal" angle Ru(2)-C(17)-Ru(3) of 93.6 (2)° is outside the range of 81 ± 7° given by Herrmann for M-CH₂-M systems, again pointing to the absence of a direct metal-metal bond. In other carbene complexes in which such a metal-metal bond is missing, M-C-M angles are found between 88.9 (4) and 123°. It has been noted that this angle corresponds with the M-M distance present.[13] The "external" angle H(171)C(17)H(172) of

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Table III. Spectroscopic Data of $(\mu$-CH$_2)$Ru$_3$(CO)$_8$(R-DAB)

compd	IR ν(CO) freq[a]	^{1}H NMR δ[b]	^{13}C NMR δ[b]	FD-mass[c]
R = neo-Pen	2085 (s), 2025 (s), 2013 (vs), 1997 (s), 1998 (s), 1942 (s), 1930 (s)	6.26 (ns, 1 H, imine H), 3.66 (s, 1 H, μ-CH$_2$), 2.67 (d,[e] 1 H, NCH$_2$)/1.70 (d,[e] 1 H, NCH$_2$), 0.97 (s, 9 H, CH$_3$)	102.9 (imine C), 71.0 (NCH$_2$), 47.9 (CMe$_3$), 33.4 (μ-CH$_2$), 28.7 (CH$_3$)	739 (727.7)
R = i-Bu	2085 (s), 2025 (m), 2010 (vs), 1997 (sh), 1989 (s), 1945 (s), 1930 (s)	6.16 ns, 1 H, imine H), 3.73 ns, 1 H, μ-CH$_2$), 2.70 (d[f] of d,[e] 1 H, NCH$_2$)/1.66 (m, 1 H, NCH$_2$), 1.87 (m, 1 H, CH), 0.90 (d,[f] 3 H, CH$_3$)/0.84 (d,[f] 3 H, CH$_3$)	101.8 (imine C), 67.5 (NCH$_2$), 48.7 (CH), 31.7 (μ-CH$_2$), 20.0 (CH$_3$)/19.6 (CH$_3$)	711 (709.6)

[a] Measured in hexane solution; in cm^{-1}. [b] Measured in CDCl$_3$ solution. The chemical shifts are given in ppm, relative to Me$_4$Si (multiplicity, integral, assignment). Vertical bars separate diastereotopic pairs. s = singlet; d = doublet; m = multiplet. [c] Observed (calculated). The highest peak of the isotope pattern of the molecular ion is given; calculated M values are based on ^{101}Ru. [e] J = 12 Hz. [f] J = 6 Hz.

109.3(55) in the present complex is within the range given by Herrmann.[13]

IR Spectroscopy. ν(CO) Region. The new $(\mu$-CH$_2)$-Ru$_3$(CO)$_8$(R-DAB) complexes have a characteristic ν(CO) absorption spectrum (see Table III). The spectra show seven intense peaks in the terminal region only, i.e., between 2085 and 1930 cm^{-1}.

FD-Mass Spectroscopy. The complexes have also been characterized by field-desorption (FD) mass spectroscopy (see Table III). The spectra show a typical Ru$_3$ isotopic pattern around the m/z value of the molecular ion. No peaks due to [M – CO]$^+$· species are observed.

^{1}H NMR Spectroscopy. The ^{1}H NMR data are listed in Table III and are similar over the whole temperature range studied (−20 to +40 °C). The asymmetry that is present in the solid-state structure (vide supra) is not apparent from these data. Both the R-DAB ligand and the methylene fragment give rise to one symmetrical pattern. Obviously, in solution a fast (on the NMR time scale) flying motion of the butterfly $\overline{\text{Ru}(2)\text{–C}(17)\text{–Ru}}$ $\overline{(3)\text{–Ru}(1)}$ is present, thereby creating a virtual mirror plane through these four atoms. In the tetranuclear cluster Ru$_4$(CO)$_8$(R-DAB)$_2$, in which the four metal atoms likewise define a butterfly, an identical flying motion has been proposed to account for the symmetrical chemical shift patterns observed.[3c,8c]

The two imine protons give rise to one singlet at about 6.2 ppm, indicating an eight-electron-coordination mode for the α-diimine ligand,[3c,8] just as found in the solid-state structure.

The methylene protons appear at 3.7 ppm, which agrees fairly well with the 1–3 ppm region, given by Herrmann for the ^{1}H NMR chemical shifts of μ-C(H)R moieties that are unsupported by a metal–metal bond.[13,21] In the latter type of compounds chemical shifts have recently been reported at 3.5 ppm for [Pt$_2$-μ-{o-C$_6$H$_4$P(Ph)-CH$_2$CH$_2$PPh$_2$}$_2(\mu$-CH$_2$)][22] and at 3.77 ppm for (η^5-C$_5$Me$_5)_2$Mo$_2$(CO)$_4(\mu$-CH$_2$)(CH$_2$N$_2$).[23] When an additional metal–metal bond is present, the μ-C(H)R proton appears in between 5 and 11 ppm.[13]

^{13}C NMR Spectroscopy. The ^{13}C NMR data are also listed in Table III. Again the two halves of the molecule are magnetically equivalent as a result of the "flying" motion of the $\overline{\text{Ru}(2)\text{–C}(17)\text{–Ru}(3)\text{–Ru}(1)}$ butterfly. The imine carbon atoms give rise to one signal near 100 ppm while the two neo-Pen groupings give rise to one single neo-Pen pattern at the expected chemical shift positions. The methylene carbon is observed at ca. 32 ppm, which is at a slightly lower field than the 0–10 ppm region, given

by Herrmann for bridging carbene atoms in species in which no supporting metal–metal bond is present.[13] However, this range may be too small because chemical shifts as low as 46 ppm ([Pt$_2$-μ-{o-C$_6$H$_4$P(Ph)-CH$_2$CH$_2$PPh$_2$}$_2(\mu$-CH$_2$)])[22] and 64 ppm ((η^5-C$_5$Me$_5)_2$Mo$_2$-(CO)$_4(\mu$-CH$_2$)(CH$_2$N$_2$))[23] have recently been reported. It must be noted that in case a supporting metal–metal bond is present, the μ-C atom resonates between 100 and 210 ppm.[13]

The ^{13}C NMR data of the present compounds are the first examples of such data for eight-electron-bonded R-DAB derivatives. Accordingly, it is now possible to derive the nature of the coordination mode present in new R-DAB complexes not only from the ^{1}H NMR chemical shifts of the imine protons[2,3,8] but also from the ^{13}C NMR pattern for the imine carbons. Thus these imine C atoms in free R-DAB resonate at ca. 160 ppm, and this position hardly changes when the ligand is four electron σ-N, σ-N' coordinated.[24] When R-DAB is six-electron σ-N, μ-N', η^2-C=N' bonded, the two imine halves are magnetically inequivalent and accordingly the two C atoms have different chemical shifts. The one of σ-N-coordinated part resonates at ca. 170 ppm, while the one which is η^2-C=N'-coordinated is drastically shifted upfield to about 70 ppm.[24] This upfield shift is the result of shielding caused by π-back-donation from the metal to the ligand. In symmetrically eight-electron σ-N, σ-N', η^2-C'=N' bonded R-DAB complexes, two imine C atoms are equivalent again and give rise to only one peak at about 100 ppm.[25]

Discussion

Formation of the Complexes. The present reaction can be viewed as an addition (or insertion) of a CH$_2$ moiety to (into) a single Ru–Ru bond. Carbene addition to multiple metal–metal bonds has been extensively studied by Herrmann et al.,[13] but addition to single bonds is less well documented. In the latter case this is because in the resulting species a supporting metal–metal bond, which generally stabilizes the M(μ-CH$_2$)M' interaction, is absent. The best known examples of products in which a methylene fragment has inserted into a single metal–metal bond are the so-called A-frame Pt dimers.[22,26] In these complexes the two Pt centers are held together by the bridging methylene group and by a bridging diphos ligand. Only one example is known in which the two metals are held together by the μ-CH$_2$ bridge only: i.e., [(η^5-C$_5$H$_5$)Ru-

(21) In [(η^5-C$_5$H$_5$)Ru(CO)$_2$]$_2(\mu$-CH$_2$) the methylene protons give chemical shifts at 2.3 ppm.[17]

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(25) In Mn$_2$(CO)$_6$(t-Bu-DAB), containing also an eight-electron-bonded α-diimine ligand, the ^{13}C NMR chemical shift of the imine carbon atoms is 103.4 ppm. Keijsper, J.; van Koten, G.; Vrieze, K., *Organometallics*, accepted for publication.

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$(CO)_2]_2(\mu\text{-}CH_2)$.[17] Also in the present complex the Ru-(2)$(\mu\text{-}CH_2)$Ru(3) unit is stabilized by the presence of a bridging group, i.e., the Ru(1) center, while the whole cluster itself gains additional stability from the bridging eight-electron-donating R-DAB.

Reaction Sequence. A prerequisite[27] for a reaction of a complex with diazoalkanes to occur seems to be the generation of a coordinatively unsaturated species. Electron-precise $Ru_3(CO)_8(R\text{-}DAB)$ indeed can react like an unsaturated species because of the presence of an empty coordination site on Ru(2). This has already been shown in the reaction with CO (see Introduction; Figure 1). The reaction of $Ru_3(CO)_8(R\text{-}DAB)$ with CH_2N_2 may start with metal-induced N_2 elimination from CH_2N_2 with concomitant addition of the CH_2 group to the Ru(2) atom. The resulting product is likely to be very unstable because of the presence of the terminal methylene group. A stable product is finally obtained, not through an intramolecular attack of the terminal CH_2 group on the α-diimine function, as we had anticipated, but via a small rearrangement reaction, yielding the bridging methylene derivative. Interestingly, the CH_2 bridge is a very asymmetric one which until now have never been observed in homonuclear complexes. This may have importance in view of the possible electron-balancing capability of the ligand which may be analogous to that of the carbonyl group.

Another possible, stepwise reaction route involves the intermediate formation of a diazomethane derivative, followed by N_2 elimination and formation of the product. Recently, several diazomethane complexes have been reported containing either a μ-N-bridging diazomethane group[23,28] or a $\overline{M\text{—}N\text{=}N}\text{-}CH_2\text{-}M'$ metallacycle.[29] In some instances these products react further to yield methylene derivatives. In the present case, however, this latter reaction sequence seems to be less likely because diphenyldiazomethane, which is indeed a much less reactive carbene precursor than diazomethane, does not react at

all with $Ru_3(CO)_8(R\text{-}DAB)$ although complexation seems to be possible.

Conclusions

Reaction of $Ru_3(CO)_8(R\text{-}DAB)$ with CH_2N_2 yields the addition product $(\mu\text{-}CH_2)Ru_3(CO)_8(R\text{-}DAB)$ that may gain its stability from the formation of the asymmetrical methylene bridge and from the presence of the strongly bridging, eight-electron-donating R-DAB ligand. No reaction between the CH_2 function and the α-diimine function has been observed.

There seems to be a wide range of possible two-electron-donor ligand addition reactions to $Ru_3(CO)_8(R\text{-}DAB)$ which establishes that through the empty coordination site on Ru(2) (see Figure 1) this 48-electron cluster reacts like an unsaturated species. This two-electron donation results in distinct bond breaking of a Ru–Ru bond (this report) or in overall bond weakening of Ru–Ru and Ru–C(OO) bonds.[8a]

In general the ^{13}C NMR chemical shift values of the imine C atoms of R-DAB appear to be a good assignment criterion for the bonding mode of the ligand: i, four-electron coordination, one peak at ca. 160 ppm ($\pm$20); ii, six-electron coordination, two peaks, one at ca. 175 ppm ($\pm$20) and one at ca. 70 ppm ($\pm$20); iii, eight-electron coordinati n, one peak at ca. 100 ppm.

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(29) See, e.g., ref 13 (p 176) and references therein.