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Ruthenium Carbonyl 1,4-Diaza-1,3-butadiene (R-DAB) Complexes.[1] Reactivity of $Ru_2(CO)_5$(R-DAB) toward Molecular Hydrogen. Molecular Structure of $H_2Ru_4(CO)_8$(R-DAB)$_2$, Containing an Unique Linear Chain of Four Ruthenium Atoms

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$Ru_2(CO)_5$(R-DAB) (R-DAB = 1,4-disubstituted 1,4-diaza-1,3-butadiene = RN=CHCH=NR;[2] R = *i*-Pr, c-Hx, c-HxCH$_2$) reacts smoothly at 90 °C with molecular hydrogen to yield the oxidative addition product $H_2Ru_2(CO)_5$(R-DAB). The same product can be obtained when $Ru_2(CO)_6$(R-DAB) (R = *i*-Pr, c-Hx, *t*-Bu) is used as starting material. In the products, which are characterized by FD-mass, IR, and ^{1}H NMR spectroscopy, the R-DAB ligand is in a 6e-bonding mode. The ^{1}H NMR spectra indicate that the two hydride atoms are bonded (presumably terminally) to the same Ru atom. $Ru_3(CO)_8$(neo-Pent-DAB) reacts with H_2 to yield both known $H_4Ru_4(CO)_{12}$ and novel $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$. The latter compound can also be obtained from the reaction of $Ru_2(CO)_5$(neo-Pent-DAB) with H_2. Possible reaction routes are discussed. An X-ray crystal structure determination established the molecular geometry of this tetranuclear Ru-α-diimine complex. Crystals of $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$ are monoclinic of space group $C2/c$ with cell constants a = 18.399 (7) Å, b = 8.725 (3) Å, c = 29.177 (8) Å, β = 110.43 (4)°, and Z = 4. A total of 1318 reflections have been used in the refinement resulting in a final R value of 0.038 (R_w = 0.064). The molecule possesses a pseudo-C_{2h} symmetry. Surprisingly, the four Ru atoms are located in a linear chain arrangement which is very unusual. The Ru(1)–Ru(2)–Ru(2)* angle is 176.48 (6)°. The Ru–Ru distances are in the range expected for single Ru–Ru bond lengths (Ru(1)–Ru(2) = 2.806 (2) Å, Ru(2)–Ru(2)* = 2.745 (2) Å). Ru(1) is coordinated by two terminal carbonyls and Ru(2) by one. The central Ru(2)–Ru(2)* bond is symmetrically bridged by two carbonyls. The neo-Pent-DAB ligand is σ-N,σ-N′-bonded to Ru(1) with equal Ru(1)–N bond lengths of 2.09 (1) Å and η^2-C=N,η^2-C′=N′ bonded to Ru(2) with an average Ru(2)–ligand atom distance of 2.30 (5) Å. Likewise, the C–N and C–C bond lengths within the α-diimine part are equal (1.36(3) Å) which is consistent with an 8e-bonding mode. The hydride ligands could not be located directly, however; the geometry around Ru(1) and the ^{1}H NMR data strongly indicate a terminal (on Ru(1)) bond position, which is quite unusual in a polynuclear metal carbonyl complex. Electronically, this species can be considered as electron precise, i.e., a 66e complex having three metal–metal bonds.

Introduction

Recently we have shown that during the reaction of $Ru_3(CO)_{12}$ with R-DAB (R-DAB = 1,4-disubstituted 1,4-diaza-1,3-butadiene = RN=CHCH=NR)[2], various reactive intermediates are formed.[3,4] Some of these intermediates, i.e., $Ru_2(CO)_n$(R-DAB) (n = 5, 6) and $Ru_3(CO)_8$(R-DAB) (see Figure 1), react rapidly with, e.g., CO, alkynes, olefins, and other 2e donors.[4] Interestingly, the reaction product of $Ru_2(CO)_6$(R-DAB) with monosubstituted alkynes is a precursor for a species that catalyzes the regiospecific trimerization of these alkynes.[5]

The use of transition-metal clusters as homogeneous catalysts is of great current interest.[6] Basic considerations are the following: (i) activation of the clusters may be achieved by the creation of electron-rich or -deficient metal centers through metal–metal (or metal–ligand) bond formation or bond cleavage;[7] (ii) small molecules may undergo facile transformations when multisite bonded.[8] An important difficulty, however, in the use of cluster complexes as homogeneous catalysts is their tendency to disintegrate, so that in fact mononuclear fragments may often be the real catalysts. To circumvent this latter problem, strongly bridging ligands are commonly employed to stabilize the polynuclear unit.[9]

The R-DAB ligand seems to have a great potential in cluster catalysis because of the following three reasons. (i) It can very easily adjust its number of donating electrons to the need of the cluster to which it is bonded;[10] in fact, $Ru_2(CO)_5$(R-DAB) reacts like an electron-deficient species because the ligand can change its coordination mode from 8e to 6e donating.[4] (ii) It is strongly activated when

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[1] Part 9; for earlier parts see, e.g., ref 3–5, 11, 13, 14, and 22.

[2] For a recent review, which also covers the nomenclature of the ligand R-DAB: van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151.

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[8] See, e.g.: Mott, N.; Carty, A. J. *Inorg. Chem.* **1983**, *22*, 2726 and references therein.

[9] (a) Adams, R. D.; Katahira, D. A. *Organometallics* **1982**, *1*, 53; (b) Braunstein, P.; Matt, D.; Bars, O.; Loeur, M.; Grandjean, D.; Fisher, J.; Mitschler, A. *J. Organomet. Chem.* **1981**, *213*, 79.

[10] During the thermal reaction of $CoMn(CO)_7$(R-DAB), yielding $CoMn(CO)_6$(R-DAB), R-DAB changes its coordination mode from 4e to 6e donating: Staal, L. H.; Keijsper, J.; van Koten, G.; Cras, J. A.; Bosman, W. P. *Inorg. Chem.* **1981**, *20*, 555. For other examples of R-DAB, adjusting its coordination mode: ref 4.

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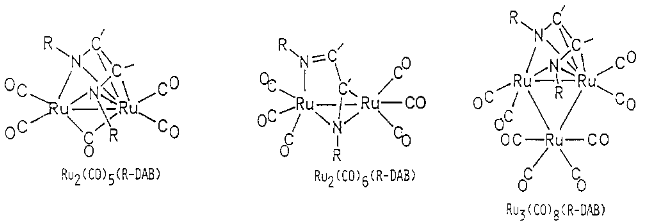

Figure 1. Schematic structures of some reactive Ru–R-DAB species.

multisite bonded, and it may couple then to various other ligands via new C–C[4,11] or N–C[12] bonds; in fact, the above-mentioned catalytic polymerization reaction of monosubstituted alkynes can only start after the formation of a R-DAB–alkyne coupled derivative.[5] (iii) R-DAB may form a rather strong bridge between two metal centers; e.g., the reaction of $Ru_3(CO)_8$(R-DAB) with CO yields electron-rich $Ru_3(CO)_9$(R-DAB) which probably gains its stability from the presence of a bridging, 8e-donating R-DAB ligand.[13]

To obtain a further insight into the (catalytic) reaction possibilities, we have undertaken a study dealing with the reactivity of the complexes, depicted in Figure 1, toward the formal 2e donor (vide infra) H_2. Furthermore, we present another example of R-DAB holding together a surprising cluster geometry.

Experimental Section

Materials and Apparatus. ^{1}H NMR spectra were obtained on a Varian T60 and a Bruker WM 250 spectrometer. IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer; mass spectra (field desorption; FD) were obtained on a Varian MAT 711 double-focusing mass spectrometer with combined EI/FI/FD ion source and coupled to a spectro system MAT 100 data acquisition unit. The 10-μm tungsten wire FD emitters containing carbon microneedles with an average lengths of 30 μm were used. The samples were dissolved in toluene and then loaded onto the emitters with the dipping technique. An emitter current of 0–10 mA was used to desorb the samples. The ion source temperature was generally 70 °C. Elemental analyses were carried out by the section Elemental Analysis of the Institute for Applied Chemistry, TNO, Utrecht, The Netherlands.

All 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.

$Ru_2(CO)_5$(R-DAB) (R = *i*-Pr, c-Hx, neo-Pent), $Ru_2(CO)_6$(R-DAB) (R = *i*-Pr, c-Hx, *t*-Bu), and $Ru_3(CO)_8$(neo-Pent-DAB) have been prepared in situ according to literature procedures.[3,4] The new ligand c-HxCH$_2$-DAB and its derivative $Ru_2(CO)_5$(c-HxCH$_2$-DAB) have been prepared analogously to the methods followed for neo-Pent-DAB and $Ru_2(CO)_5$(neo-Pent-DAB).[4]

Synthesis of $H_2Ru_2(CO)_5$(R-DAB) (R = *i*-Pr, c-Hx, *t*-Bu, c-HxCH$_2$). H_2 gas was bubbled through a toluene solution (30 mL) of $Ru_2(CO)_5$(R-DAB) (R = *i*-Pr, c-Hx, c-HxCH$_2$) (0.5 mmol) at 90 °C for about 30 min. When $Ru_2(CO)_6$(R-DAB) was used as starting material and the reaction was carried out in heptane, the reaction time was about 3 h. IR spectroscopy indicated that the ν(CO) pattern of the starting complexes (see ref 3 and 4) was replaced by that of $H_2Ru_2(CO)_5$(R-DAB) (see Table I). The solvent was evaporated in vacuo, leaving a yellowish residue that was purified by column chromatography. A yellow fraction (eluent hexane and hexane/diethyl ether = 1/1) was obtained, and crystallization from diethyl ether/hexane (1/2) yielded about 30% of microcrystalline $H_2Ru_2(CO)_5$(R-DAB). Several attempts to prepare crystals, suitable for an X-ray measurement, failed. The compounds were identified by elemental analyses and IR, FD-mass, and ^{1}H NMR spectroscopy.

Table I. IR and FD-Mass Data

compd	*M* found (calcd)[a]	IR ν(CO),[b] cm^{-1}
$H_2Ru_2(CO)_5$-(R-DAB)		
R = *i*-Pr	484 (484.4)	2073 (s), 2023 (vs), 1999 (s), 1961 (s)
R = *t*-Bu	*c* (512.5)	2073 (s), 2023 (vs), 1998 (s), 1960 (s)
R = c-Hx	564 (564.6)	2073 (s), 2023 (vs), 1998 (s), 1960 (s)
R = c-HxCH$_2$	593 (592.6)	2073 (m), 2024 (vs), 2000 (s), 1964 (s)
R = neo-Pent[d]	*c* (540.5)	2073 (s), 2026 (vs), 2000 (vs), 1965 (s)
$H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$	1024 (1023.1)	2018 (s), 1951 (s), 1764 (m)[e]

[a] The observed *M* values account for the highest peak of the isotope pattern; the calculated *M* values are based on ^{101}Ru. [b] In hexane, unless otherwise stated. [c] Not measured. [d] Only observed in solution. [e] In dichloromethane.

Synthesis of $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$. Method 1. H_2 gas was bubbled through a toluene solution (30 mL) of 0.5 mmol of $Ru_3(CO)_8$(neo-Pent-DAB), prepared in situ, at 80 °C for about 1 h. A mixture of two complexes was obtained which appeared to be very difficult to separate by column chromatography. Successful separation, however, could be achieved by using their different solubilities in warm hexane. A yellow complex that was fairly soluble in warm hexane was identified as $H_4Ru_4(CO)_{12}$ by IR (ν(CO) in hexane 2077 (s), 2063 (vs), 2021 (s) cm^{-1}; cf. ref 15), ^{1}H NMR (δ(hydride) in toluene-d_8 −17.66), and FD-mass (highest peak among the Ru$_4$ isotope pattern 746, calculated mass 744.6) spectroscopy. A red complex that was hardly soluble in warm hexane was identified as $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$ by elemental analyses, IR, ^{1}H NMR, and FD-mass spectroscopy, and an X-ray crystal structure determination (see below).

Method 2. H_2 gas was bubbled through a toluene solution (30 mL) of 0.5 mmol of $Ru_2(CO)_5$(neo-Pent-DAB) prepared in situ, at 80 °C. After the formation of unstable $H_2Ru_2(CO)_5$(neo-Pent-DAB) that was identified by IR spectroscopy, the tetranuclear product was formed. After 2 h, nitrogen was bubbled through the solution for about 0.5 h, after which the solvent was evaporated in vacuo. The mixture was purified by column chromatography using dichloromethane as eluent. Recrystallization from dichloromethane/diethyl ether (1/1) yielded red crystals of $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$ in about 40% yield.

Crystal Structure Determination of $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$, Dihydridooctacarbonylbis[1,4-dineopentyl-1,4-diaza-1,3-butadiene]tetraruthenium ($C_{32}H_{50}N_4O_8Ru_4$). Crystals of the title compound were of rather poor quality, but nevertheless one of sufficient quality was selected for the X-ray determination. The crystals were monoclinic with cell constants a = 18.399 (7) Å, b = 8.725 (3) Å, c = 29.177 (8) Å, and β = 110.43 (4)° which were determined by a least-squares procedure from 24 reflections in the range $18 < \theta < 20°$ (Mo Kα radiation; V = 4389 (6) Å^3, Z = 4). Two space groups, Cc and $C2/c$, were compatible with the systematic extinctions, and the structure was satisfactorily solved in $C2/c$. From a total number of 6400 independent accessible reflections, only 1318 had intensities above the 2.5σ(I) level. These reflections with $\theta < 30°$ were measured on a Nonius CAD 4 diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å).

The structure was solved by means of a Patterson minimum function based on the positions of the four Ru atoms in the unit cell. It became soon apparent that additional electron density

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[11] Reactions of $Ru_2(CO)_6$(R-DAB) with heteroallenes L (L = sulfine, carbodiimide) lead to R-DAB–L coupled products: Keijsper, J.; Polm, L. H.; van Koten, G.; Vrieze, K.; Schagen, J. D. Stam, C. H. *Inorg. Chim. Acta*, submitted for publication.

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Table II. ^{1}H NMR Data

compd	R group[b]	imine H	hydride H
$H_2Ru_2(CO)_5$(R-DAB)			
R = *i*-Pr	3.18 (sept, 6 Hz, 1 H), 2.44 (sept, 6 Hz, 1 H), 1.10 (d, 6 Hz, 3 H)/1.07 (d, 6 Hz, 3 H), 1.51 (d, 6 Hz, 3 H)/1.43 (d, 6 Hz, 3 H)	7.22 (d, 2 Hz, 1 H), 3.01 (d, 2 Hz, 1 H)	−7.76 (d, 6 Hz, 1 H), −11.82 (d, 6 Hz, 1 H)
R = *t*-Bu	1.36 (s, 9 H), 1.17 (s, 9 H)	7.32 (d, 2 Hz, 1 H), 3.17 (d, 2 Hz, 1 H)	−6.87 (d, 8 Hz, 1 H), −11.72 (d, 8 Hz, 1 H)
R = c-Hx	2.94 (m, 1 H), 2.2–1.0 (m, 21 H)	7.35 (d, 2 Hz, 1 H), 3.15 (d, 2 Hz, 1 H)	−7.63 (d, 6 Hz, 1 H), −11.73 (d, 6 Hz, 1 H)
R = c-HxCH_2	400 (d[c] of d,[d] 1 H)/2.99 (d of d, 1 H), 2.65 (m, 2 H), 2–0.8 (m, 22 H)	7.08 (d, 2 Hz, 1 H), 3.16 (d, 2 Hz, 1 H)	−7.75 (d, 6 Hz, 1 H), −11.59 (d, 6 Hz, 1 H)
$H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$	3.63 (d, 13 Hz, 2 H)/3.27 (d, 13 Hz, 2 H), 1.07 (s, 18 H)	5.90 (s, 2 H)	−10.07 (s, 1 H)

[a] The values (multiplicity, *J*, integral) are in ppm relatively to Me_4Si and have been obtained in toluene-d_8 solution. [b] Vertical bars separate diastereotopic pairs; s = singlet, d = doublet, and sept = septet. [c] *J* = 13 Hz. [d] *J* = 4 Hz.

Table III. Atomic Coordinates (Esd) of $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$

	x	*y*	*z*
Ru(1)	0.39448 (7)	0.53588 (15)	0.60857 (5)
Ru(2)	0.29834 (7)	0.33879 (14)	0.53693 (5)
N(1)	0.3314 (7)	0.3510 (15)	0.6221 (5)
N(2)	0.4318 (7)	0.3447 (14)	0.5801 (4)
C(1)	0.3477 (8)	0.2098 (16)	0.6075 (5)
C(2)	0.4033 (8)	0.2078 (17)	0.5853 (6)
C(3)	0.4896 (9)	0.3441 (19)	0.5536 (6)
C(4)	0.5745 (9)	0.3147 (21)	0.5876 (7)
C(5)	0.5826 (12)	0.1737 (31)	0.6171 (11)
C(6)	0.6065 (11)	0.4559 (32)	0.6219 (8)
C(7)	0.6227 (10)	0.3011 (35)	0.5560 (7)
C(8)	0.2706 (10)	0.3561 (20)	0.6453 (7)
C(9)	0.3027 (10)	0.3370 (21)	0.7017 (6)
C(10)	0.3427 (16)	0.1806 (28)	0.7151 (9)
C(11)	0.3552 (16)	0.4648 (33)	0.7284 (8)
C(12)	0.2313 (15)	0.3386 (30)	0.7179 (8)
C(13)	0.3458 (10)	0.6996 (20)	0.6289 (6)
C(14)	0.4447 (10)	0.6907 (22)	0.5846 (8)
C(15)	0.3086 (9)	0.2462 (21)	0.4757 (6)
C(16)	0.2512 (11)	0.5127 (18)	0.5025 (8)
O(13)	0.3183 (8)	0.7949 (17)	0.6424 (6)
O(14)	0.4748 (9)	0.7837 (18)	0.5741 (6)
O(15)	0.3553 (6)	0.2490 (18)	0.4567 (5)
O(16)	0.2167 (8)	0.6129 (15)	0.4786 (6)

Scheme I

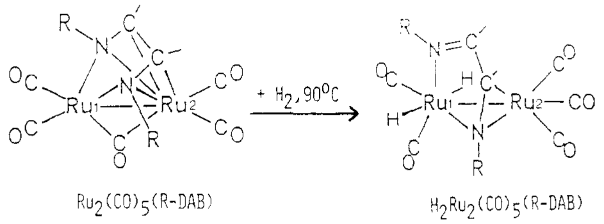

Table IV. Selected Geometric Parameters of $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$

Bond Lengths (Esd) in Å	
Metal Carbonyl Part	
Ru(1)–Ru(2) 2.806 (2)	Ru(2)*–C(15) 2.01 (2)
Ru(2)–Ru(2)* 2.745 (2)	C(13)–O(13) 1.11 (2)
Ru(1)–C(13) 1.89 (2)	C(14)–O(14) 1.08 (3)
Ru(1)–C(14) 1.90 (2)	C(15)–O(15) 1.17 (2)
Ru(2)–C(16) 1.86 (2)	C(16)–O(16) 1.16 (2)
Ru(2)–C(15) 2.03 (2)	
Metal Ligand Part	
Ru(1)–N(1) 2.10 (1)	Ru(2)–N(2) 2.34 (1)
Ru(1)–N(2) 2.08 (1)	Ru(2)–C(1) 2.24 (1)
Ru(2)–N(1) 2.35 (1)	Ru(2)–C(2) 2.26 (1)
Ligand Part	
N(1)–C(1) 1.37 (2)	N(2)–C(3) 1.52 (2)
N(2)–C(2) 1.33 (2)	C(3)–C(4) 1.55 (2)
C(1)–C(2) 1.39 (2)	C(8)–C(9) 1.55 (2)
N(1)–C(8) 1.50 (3)	C–C(*t*-Bu) 1.52 (3) (mean)[a]
Bond Angles (Esd) in deg	
Metal Carbonyl Part	
Ru(1)–Ru(2)–Ru(2)* 176.48 (6)	Ru(2)*–C(15)–O(15) 138.7 (12)
Ru(1)–C(13)–O(13) 177.6 (14)	Ru(2)–C(16)–O(16) 174.1 (14)
Ru(1)–C(14)–O(14) 174.8 (19)	Ru–C–O(terminal) 175.5 (16) (mean)[a]
Ru(2)–C(15)–O(15) 135.7 (12)	
Ligand Part	
Ru(1)–N(1)–Ru(2) 78.0 (5)	C(2)–N(2)–C(3) 115.3 (13)
Ru(1)–N(1)–C(1) 115.9 (11)	N(1)–C(1)–C(2) 115.6 (13)
Ru(1)–N(1)–C(8) 127.6 (10)	N(2)–C(2)–C(1) 115.1 (14)
C(1)–N(1)–C(8) 116.5 (13)	N(2)–C(3)–C(4) 113.7 (13)
Ru(1)–N(2)–Ru(2) 78.6 (4)	N(1)–C(8)–C(9) 114.1 (13)
Ru(1)–N(2)–C(2) 118.3 (11)	C–C–C(neo-Pent) 109.4 (24) (mean)[a]
Ru(1)–N(2)–C(3) 126.4 (10)	
Around Ru(1)	
Ru(2)–Ru(1)–N(1) 54.8 (3)	N(1)–Ru(1)–C(13) 99.7 (7)
Ru(2)–Ru(1)–N(2) 54.7 (3)	N(1)–Ru(1)–C(14) 169.7 (7)
Ru(2)–Ru(1)–C(13) 116.9 (4)	N(2)–Ru(1)–C(13) 171.6 (5)
Ru(2)–Ru(1)–C(14) 114.9 (6)	N(2)–Ru(1)–C(14) 98.7 (8)
N(1)–Ru(1)–N(2) 75.0 (5)	C(13)–Ru(1)–C(14) 85.6 (9)
Around Ru(2)	
Ru(1)–Ru(2)–C(15)* 133.1 (5)	Ru(2)*–Ru(2)–C(15) 47.0 (4)
Ru(1)–Ru(2)–C(15) 132.2 (5)	C(15)*–Ru(2)–C(15)* 94.5 (6)
Ru(1)–Ru(2)–C(16) 87.5 (5)	Ru(2)*–Ru(2)–C(16) 89.1 (5)
N(1)–Ru(2)–N(2) 66.0 (5)	C(15)*–Ru(2)–C(16) 87.7 (7)
C(15)–Ru(2)–C(16) 91.0 (8)	Ru(2)*–Ru(2)–C(15)* 47.5 (5)

[a] The standard deviation of the mean value has been estimated by $\sigma = (\Sigma_i(\chi_i - \bar{\chi})^2/(N-1))^{1/2}$.

was present in the structure, the precise identity of which, however, could not be established. The extra electron density has been accounted for in an ad hoc manner by introducing a C and an O atom with variable population parameters. After isotropic block-diagonal least-squares refinement, an empirical correction was applied[16a] (crystal dimensions 0.13 × 0.13 × 0.13 mm; μ = 13.7 cm^{-1}). The refinement was continued anisotropically with the H atoms (except the hydrido ones) fixed at their calculated positions. This converged to $R = 0.038$ ($R_w = 0.064$). The anomalous scattering of Ru was taken into account, and a weighting scheme of $w = 1/(4.6 + F_o + 0.05F_o^2)$ was employed. A final difference synthesis revealed excursions within −0.3 and +0.5 e/Å.^{3} The programs used, except a local one for the Patterson minimum function, were from the XRAY-76 system.[16b] The atomic scattering factors were those of Cromer and Mann (1968).

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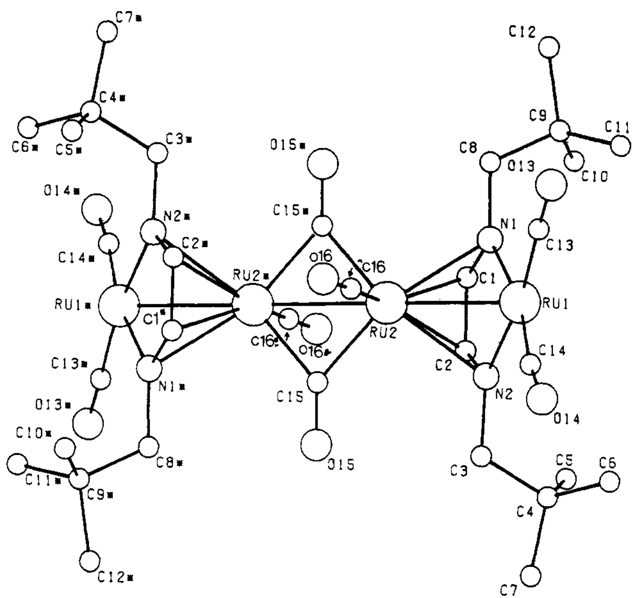


Figure 2. The molecular geometry of $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$.

The anomalous dispersion corrections were taken from ref 16c, d.

The molecular geometry of $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$ with the numbering of the atoms is depicted in Figure 2, which shows a PLUTO drawing of the molecule. Atomic parameters and selected bond lengths and angles are given in Tables III and IV, respectively. All bond lengths and angles, anisotropic thermal parameters, and structure factors are included with the supplementary material.

Results and Discussion

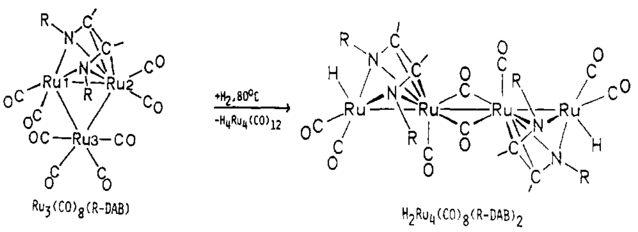
Formation of $H_2Ru_2(CO)_5$(R-DAB). $Ru_2(CO)_5$(R-DAB) (R = *i*-Pr, c-Hx, neo-Pent) reacts with H_2 at 90 °C to yield the oxidative addition product $H_2Ru_2(CO)_5$(R-DAB). The reaction is schematically presented in Scheme I that also shows a likely geometry for the dihydride product.

Overall, the reaction in Scheme I can be viewed as a 'ligand dissociation and oxidative addition of H_2'.[17]

When $Ru_2(CO)_6$(R-DAB) (R = *i*-Pr, c-Hx, *t*-Bu) is used as starting complex, the same dihydride product is formed. However, the reaction time is then much longer. Probably, the reaction then proceeds via a $Ru_2(CO)_5$(R-DAB) intermediate just as the reaction of $Ru_2(CO)_6$(R-DAB) with R-DAB, which has been proven to proceed via such an intermediate.[3,4] Moreover, it has been shown[4] that, at the reaction temperature used, $Ru_2(CO)_5$(R-DAB) is formed out of $Ru_2(CO)_6$(R-DAB).

It is likely that the two hydride ligands are terminally bonded to the same Ru atom in a cis fashion. This follows from the ^1H NMR results (see below) and from information obtained for mononuclear systems in which H_2 usually adds in a cis manner.[18]

Scheme II



In the literature there are three prerequisites mentioned for a reaction of a complex with H_2 to take place:[19a] (i) low formal oxidation state of the metal and (ii) site of unsaturation,[20,21] and (iii) high basicity of the complex. In the present case, prerequisites i and iii are obviously fulfilled while a site of unsaturation is probably created on Ru(1) (see Scheme I) during the reaction. A possible reaction route then implies an approach of H_2 to the Ru(1) atom trans with respect to the bridging carbonyl $Ru_2(CO)_5$(R-DAB). In that direction there is a gap in the coordination sphere of Ru(1) as evidenced by the crystal structure of $Ru_2(CO)_5$(*i*-Pr-DAB).[4] Because of the Ru(1)–H_2 interaction[19b] the bridging carbonyl becomes terminally bonded to Ru(2) and one η^2-C=N unit dissociates from Ru(2), leaving a 6e-bonded R-DAB ligand. The resulting dinuclear species is electron deficient on Ru(1) and H_2 can quickly add, yielding the final product.

The present reaction proves again that R-DAB is a very flexible ligand that can easily adjust its number of donating electrons to the need of the cluster (see Introduction). It also indicates that $Ru_2(CO)_5$(R-DAB) indeed reacts like an unsaturated species, as has been demonstrated before in reactions with, e.g., CO.[4]

The $H_2Ru_2(CO)_5$(R-DAB) products are only moderately stable in solution whereas the neo-Pent-DAB derivative is unstable and its formation in situ could only be observed by IR spectroscopy. Further heating the latter complex in solution resulted in decomposition and the formation of tetranuclear $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$.

Formation of $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$. $Ru_3(CO)_8$(neo-Pent-DAB) reacts with H_2 to yield $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$ together with $H_4Ru_4(CO)_{12}$. The reaction is schematically presented in Scheme II. It is clear that the final product must be the result of a rather complex series of steps involving a breakdown of the starting cluster into smaller units and a buildup from these units. The starting cluster, i.e., $Ru_3(CO)_8$(neo-Pe-DAB), reacts just as $Ru_2(CO)_5$(R-DAB), like an unsaturated species because it has likewise a gap in the coordination sphere of Ru(1), trans to Ru(3). This is evidenced by its X-ray crystal structure.[13]

A likely route for the present reaction therefore starts with an interaction between H_2 and this Ru(1) atom.[19b] Next, the activated H_2 molecule adds across the Ru(1)–Ru(3) bond, thereby breaking this single bond. An analogous reaction is observed when $Ru_3(CO)_8$(neo-Pent-DAB) is reacted with CH_2N_2, yielding a Ru_3 species in which the methylene unit bridges a nonbonding Ru(1)–Ru(3) pair.[22a] The resulting dihydride species in the present case is not stable, and a homolytic cleavage of the Ru(2)–Ru(3) bond may give a $HRu_2(CO)_4$(neo-Pent-DAB) fragment and a $HRu(CO)_4$ unit. Upon dimerization the first fragment yields the final straight-chain tetranuclear product while the latter gives, upon tetramerization and

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[17] Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 146.

[18] See, e.g.; Heck, R. F. "Organotransition Metal Chemistry"; Maitlis, P. M., Stone, F. G. A., West, R., Eds.; Academic Press: New York and London, 1974. Cotton, F. A.; Wilkinson, G. "Advances Inorganic Chemistry"; Wiley: New York, 1980; p 1241.

[19] (a) Brothers, P. J. *Prog. Inorg. Chem.* **1981**, *28*, 1. (b) The assumed first step in the oxidative addition reaction of H_2 to an unsaturated metal complex, i.e., interaction between H_2 and the metal, has recently been "frozen out" as evidenced by the crystal structure of $H_2W(CO)_3(P\text{-}i\text{-}Pr_3)_2$, containing a side-on coordinated H_2 molecule. Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

[20] Deeming, A. J. In "Transition Metal Clusters", Johnson, B. F. G., Ed.; Wiley-Interscience: Chichester, 1980.

[21] Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169.

[22] (a) Keijsper, J.; Polm, L. H.; van Koten, G.; Vrieze, K.; Goubitz, K.; Stam, C. H. *Organometallics* **1985**, *4*, 1876. (b) The formation of $Ru_2(CO)_5$(R-DAB) has been observed in reactions of $Ru_3(CO)_8$(R-DAB) with fluorenone and diazo ligands at 100 °C; Keijsper, J.; van Koten, G.; Vrieze, K., unpublished results.

CO dissociation, the very stable $H_4Ru_4(CO)_{12}$ product.

Another possible route implies a disintegration of the starting $Ru_3(CO)_8$(neo-Pent-DAB) complex, yielding $Ru_2(CO)_5$(neo-Pent-DAB)[22b] and an, undefined Ru carbonyl fragment. The first complex will react with H_2 to yield $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$ (see above), and the second fragment then provides $H_4Ru_4(CO)_{12}$.

The observed change in geometry of the complex during the reaction is unprecedented. Trinuclear compounds such as $Ru_3(CO)_8(diphos)_2$, $HRu_3(CO)_9(C_2\text{-}t\text{-Bu})$, or $Ru_3(CO)_{11}(t\text{-BuNC})$ react with H_2 to give hydride complexes in which the triangular framework is retained often together with some $H_4Ru_4(CO)_{12}$,[23] while $Ru_3(CO)_{12}$ reacts with H_2 to give $H_4Ru_4(CO)_{12}$, having a tetrahedral geometry.

$H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$ can also be formed from $Ru_2(CO)_5$(R-DAB) and H_2. This reaction is likely to proceed via unstable $H_2Ru_2(CO)_5$(R-DAB) (see above). Final dimerization and CO and H_2 elimination them may yield the tetranuclear product.

IR ν(CO) Region. All $H_2Ru_2(CO)_5$(R-DAB) complexes and $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$ show characteristic absorption patterns in the ν(CO) region (see Table I). Spectra in solution and in the solid sate (KBr pellet) are comparable, indicating similar geometries in both phases.

The spectra of the $H_2Ru_2(CO)_5$(R-DAB) compounds are very much like those of [(alkyne)$Ru_2(CO)_5${RN=CHC(H)(NR)C(CO_2Me)C(CO_2Me)}][5] (R = *t*-Bu, *i*-Pr, c-Hx) and of [Ru(CO)$_5${N(*i*-Pr)$\overset{\dots}{-}$CH$\overset{\dots}{-}$CH-N(*i*-Pr)C(O)CH_2C(O)CH_2}],[12] indicating similar metal carbonyl skeletons. The latter compound has, as evidenced by its crystal structure, a $(CO)_3RuRu(CO)_2$ metal carbonyl skeleton, just as proposed for the former two types of complexes.

FD-Mass Spectroscopy. Also in the present study field-desorption (FD) mass spectroscopy has been a powerful tool for the characterization of the new polynuclear complexes. Since the molecular ion of the compounds had been observed exclusively even for the unexpected, tetranuclear complex, the overall formula had become immediately evident. The results are summarized in Table I.

^{1}H NMR Spectroscopy. The ^{1}H NMR data are listed in Table II.

The R-DAB Ligand. In free R-DAB the imine protons absorb near 8 ppm and the same chemical shift is observed when the ligand is coordinated via its N atoms only.[2] If, however, R-DAB uses its π-electrons for bonding, the imine protons are shifted upfield. Thus in symmetrical 8e, σ-N,σ-N′, η^2-C=N, η^2-C′=N′-bonded R-DAB derivatives, they give rise to one singlet at ca. 6 ppm.[2,4,13,14,22] In asymmetrical 6e, σ-N,σ-N′, η^2-C=N′-bonded R-DAB complexes, an AX pattern is observed.[2,3,11] The imine proton at the σ-N-coordinated part absorbs still near 8 ppm, but the proton of the η^2-C=N′-bonded part now appears near 4 ppm, with J_{AX} = 2 Hz.

Evidently, in the present $H_2Ru_2(CO)_5$(R-DAB) complexes, a 6e-bonding mode is present as evidenced by the observed AX pattern (J = 2 Hz) for the imine protons but also by the observation of two different chemical shift patterns pointing to two inequivalent R groupings.

The neo-Pent-DAB ligands $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$ are in solution 8e bonded, just as in the solid state. This is indicated by the observation of both the one singlet at 5.90 ppm for the imine protons and the one chemical shift pattern for the neo-Pent groupings. Moreover, these data indicate that the C_{2h} symmetry of the complex that is present in the solid sate is retained in solution.

Table V. Some Geometrical Data of Linear M_4 Complexes

compd	electron count (CVE)[31]	M(1)–M-(2)–M(2)*,[a] deg	idealized sym
$H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$	66	176.48 (6)	C_{2h}
$Ru_4(CO)_{10}${(*i*-Pr)-NCHCHCMe}$_2$	66	174.55 (2)	C_i[29]
$Fe_2Rh_2(\mu\text{-}PPh_2)_4(CO)_8$	62[b]	154.3 (1)	C_i[39a]
$Pt_2Mn_2(\mu\text{-}PPh_2)_4(CO)_8$	62[b]	146.11 (8)	C_i[9b]
[Rh_2Mn_2(μ-dimethyl-2,5-diisocyanohexane)$_4(CO)_{10}]^{2+}$		177.0 (1)	
[Rh_4(1,3-diisocyanopropane)-Cl]$^{5+}$	66	nm	nm[39c]

[a] The straight chain arrangements are numbered analogously as in the linear Ru_4 cluster of the present study; nm = not mentioned. [b] Pt and Rh adopt a 16e-configuration so these clusters accordingly have only 62 CVE.

The Hydride Ligands. The hydrido ligands in $H_2Ru_2(CO)_5$(R-DAB) appear as an AX pattern with $J_{AX} \approx 6$ Hz at ca. −7.5 and −11.7 ppm. The spectra recorded at 250- and 60-Mhz are similar with respect to both δ and J, indicating that the metal–hydride skeleton is rigid on the NMR time scale. Because of the relatively low-field chemical shift values, a terminal bonding position for at least the one H ligand at 7.5 ppm is strongly indicated. Bridging hydrides are usually observed upfield from −15 ppm.[21] The coupling constant ^2J(H,H) of about 6 Hz is in line with the two hydride ligands bonded to the same Ru atom in a "cis" geometry. It must be noted that in mononuclear Ru compounds having two hydrides bonded in a cis geometry, coupling constants between 6 and 9 Hz have been found.[24]

The η^2-C(H)=N-bonded proton resonates at about the same frequency as analogously bonded protons in zerovalent, 6e-bonded R-DAB complexes. Therefore, we suppose that the two hydride ligands are bonded to that Ru atom, to which R-DAB is σ-N,σ-N′-coordinated only, i.e., Ru(1) in Scheme I (see above).

The hydride ligands in $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$ give rise to one singlet only, while the chemical shift value of −10 ppm is within the region, given in the literature for terminally bonded hydrides.[21] The data are in accord with an identical position for the hydrides as derived indirectly from the X-ray data (vide infra).

Molecular Structure. Description. The molecular structure of $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$ is depicted in Figure 2, showing a PLUTO drawing of the molecule, together with the atomic numbering.

The molecule is strictly centrosymmetric with the inversion center halfway between Ru(2) and Ru(2)*. Moreover, there is a (pseudo) mirror plane through the four Ru atoms and the two C(16)O(16) carbonyl groups so that the overall geometry is pseudo-C_{2h}.

The linear arrangement of the four Ru atoms is the most exciting feature of the structure. The Ru–Ru distances are Ru(1)–Ru(2) = 2.806(2) Å and Ru(2)–Ru(2)* = 2.745 (2) Å, while the Ru(1)–Ru(2)–Ru(2)* angle is 176.48 (6)°. Corresponding geometric data of other straight-chain tetranuclear complexes, including another Ru_4 species, are listed in Table V. The Ru(1)–Ru(2) distance in the present complex is in line with values obtained earlier for single Ru–Ru bonds, bridged by a R-DAB ligand.[14,22,25]

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[23] (a) Lavigne, G.; Lugan, N.; Bonnet, J. J. *Organometallics* **1982**, *1*, 1040. (b) Bruce, M. I.; Wallis, R. C. *J. Organomet. Chem.* **1979**, *164*, C6. (c) Aime, S.; Gervasio, G.; Milone, L.; Sappa, E.; Franchini-Angela, M. *Inorg. Chim. Acta* **1978**, *26*, 223.

[24] Dewhirst, K. C.; Keim, W.; Reilly, C. A. *Inorg. Chem.* **1968**, *7*, 546. Knoth, W. H. *J. Am. Chem. Soc.* **1972**, *94*, 104.

[25] Polm, L. .; Keijsper, J.; van Koten, G.; Vrieze, K., to be submitted for publication.

The Ru(2)–Ru(2)* distance is normal for a CO-bridged single Ru–Ru bond length.[26] Two carbonyls are terminally bonded to Ru(1), and one is bonded to Ru(2). There are two symmetrically bridging carbonyls between Ru(2) and Ru(2)*, and they define a plane together with Ru(2) and Ru(2)* (maximum deviation from least-squares plane 0.015 Å) that is about perpendicular (87.6°) to the (pseudo) molecular mirror plane (vide infra).

The neo-Pent-DAB ligand is 4e, σ-N,σ-N′ bonded to Ru(1) via N(1) and N(2) with equal bond lengths of 2.09 (1) Å. The α-dimine ligand is further coordinated to Ru(2) via its two imine bonds. The Ru(2)–N and Ru(2)–C bond lengths of 2.35 (1) and 2.25 (1) Å, respectively, closely resemble those found in $\mathrm{Ru_3(CO)_8}$(neo-Pent-DAB) for which an 8e-bonding mode of the DAB ligand has been established.[25]

The bond lengths within the α-diimine part are likewise consistent with an 8e, σ-N,σ-N′, η^2-C=N, η^2-C′=N′ bond description. The two N–C bond length are about equal (1.35 (2) Å), while the central C(1)–C(2) bond length is not significantly different (1.39 (2) Å). The N–C–C bond angle is 115 (1)°. These geometries correspond very well with similar geometries observed in other 8e-bonded R-DAB complexes.[2,4,13,22,25] They also indicate that the LUMO of the ligand is extensively occupied, thereby lengthening the imine bonds and shortening the central C–C bond. In free c-Hex-DAB these bond lengths are 1.258 (3) and 1.457 (3) Å, respectively.[27]

The DAB skeleton is flat (maximum deviation from least-squares plane 0.007 Å) and makes an angle of 2.1° with the N(1)Ru(1)N(2) plane, which is a normal value for 8e-bonded R-DAB derivatives.[4,13,14,22]

The Hydride. Interestingly, the position of the hydrido ligands, which could not be located directly, may be derived indirectly from the structural data. First, by electron counting, Ru(2) has an 18e configuration, while Ru(1) only has 17 valence electrons. Secondly, by the observation that the Ru–Ru bond lengths are normal single bond lengths, i.e., no bond lengthening, which can be expected if a bridging hydride is present, seems to occur.[28] Thirdly, by the recognition that there is a gap in the coordination sphere of Ru(1), N(1), N(2), C(13), and C(14) define a plane (maximum deviation from least-squares plane 0.007 Å) while Ru(1) is located at ca. 0.13 Å from this plane, in a direction opposite from Ru(2). Accordingly, Ru(1) and the four bonded ligand atoms define a square pyramid with Ru(1) on top, pointing away from the remaining part of the molecule.

These observations, in combination with the ^{1}H NMR data (vide supra), are in line with the presence of a terminally bonded hydride on Ru(1) positioned in such a way that the Ru(1)–H vector is perpendicular to the plane defined by N(1), N(2), C(13), and C(14); i.e., above the top of the square pyramid defined above. In $\mathrm{Ru_4(CO)_{10}}$\{(*i*-Pr)NCHCHCMe\}$_2$, which is isoelectronic with the present compound and has a similar linear metal framework,[29] a CO group is terminally bonded in the same position as derived indirectly for the hydrido ligand in the present case. Terminally bonded hydrides are rather uncommon in cluster chemistry,[30a] and only few examples are known.[30b] Almost always, hydrides occupy edge- or face-bridging positions.

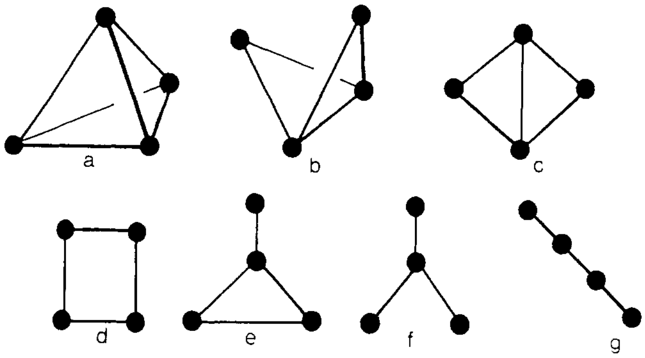

Figure 3. Possible geometries for tetranuclear clusters: a, tetrahedron (60 CVE); b, butterfly (62 CVE); c, planar butterfly (62 CVE); d, rectangle (64 CVE); e, spiked triangle (64 CVE); f, T configuration (66 CVE); g, linear chain (66 CVE).

The Geometry of M_4 Clusters. The present cluster contains 66 closed valence electrons (CVE)[31] and three single Ru–Ru bonds which implies that it is electron precise; i.e., all Ru-atoms have an 18e configuration. The normal geometry for an electron-precise tetranuclear cluster having 60 CVE is a tetrahedron (see Figure 3a). Addition of two electrons to such a cluster results in a complex with 62 CVE, having only five metal–metal bonds, and a butterfly structure or a planar, triangulated structure is observed (Figure 3b,c).[32] Electron-precise 64 CVE clusters should have four metal–metal bonds in a rectangular (Figure 3d) or spiked triangular (Figure 3e) arrangement,[33] but often a butterfly geometry is observed, with weakened metal–metal bonds.[34] Finally, tetranuclear clusters with 66 CVE should have only three metal–metal bonds and can accordingly adopt a chain configuration (Figure 3g) or a T geometry (Figure 3f).[35] For metal clusters containing exclusively transition metals, only the straight chain geometry (Figure 3g) has been observed.[36] Such a linear arrangement is present in a variety of trinuclear clusters, e.g., in M_3 species (M = Mn, Fe, Ru, Os)[37] but also in $\mathrm{Mn_2M}$ complexes (M = Pt, Fe, Hg).[38a,b]

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(26) See, e.g., ref 4 and 11 and references therein.

(27) Keijsper, J.; van der Poel, H.; Polm, L. H.; van Koten, G.; Vrieze, K.; Seignette, P. F. A. B.; Varenhorst, R.; Stam, C. H. *Polyhedron* **1983**, *2*, 1111.

(28) See, e.g.: Churchill, M. R.; Bueno, C.; Hsu, W. L.; Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 1958 and references therein. See also ref 23a.

(29) Polm, L. H.; Keijsper, J.; van Koten, G.; Vrieze, K., to be submitted for publication.

(30) (a) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1. (b) Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 6182.

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

(32) See, e.g., a $\mathrm{FeRu_3}$ species: Churchill, M. R.; Bueno, C.; Young, D. A. *J. Organomet. Chem.* **1981**, *213*, 139. A $\mathrm{Re_4}$ species: Churchill, M. R.; Bau, R. *Inorg. Chem.* **1968**, *7*, 2606. A $\mathrm{Os_3Re}$ species: Churchill, M. R.; Hollander, F. J. *Ibid.* **1977**, *16*, 2493. A $\mathrm{Ru_4}$ species: Carty, A. J.; MacLaughlin, S. A.; Wagner, J. V.; Taylor, N. J. *Organometallics* **1982**, *1*, 1013.

(33) A rectangular one is found, e.g., in a $\mathrm{Co_4}$ species: Ryan, R. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6904. A $\mathrm{Ru_4}$ species: Field, J. S.; Haines, R. J.; Smit, D. N. *J. Organomet. Chem.* **1982**, *224*, C49. A $\mathrm{Ir_4}$ species: Heveldt, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1978**, 340. Two $\mathrm{Fe_2Sn_2}$ species: Gilmore, C. J.; Woodwards, P. *J. Chem. Soc., Dalton Trans.* **1972**, 1387. Harrison, P. G.; King, T. J.; Richards, J. A. *Ibid.* **1975**, 2097. A spiked geometry is found, e.g., in a $\mathrm{Ru_4}$ species: Eisenstadt, A.; Frolow, F.; Efraty, A. *J. Chem. Soc., Chem. Commun.* **1982**, 642. A $\mathrm{Re_4}$ species: Albano, V. G.; Ciani, G.; Freni, M.; Romiti, P. *J. Organomet. Chem.* **1975**, *96*, 259.

(34) See, e.g.: Adams, R. D.; Young, L. W. *J. Am. Chem. Soc.* **1982**, *104*, 4115. See also the first example of ref 32.

(35) A T geometry is found in a $\mathrm{SbFe_3}$ species: Toan, T.; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *93*, 2654, while in $\mathrm{H_2Os_4Se_2(CO)_{12}}$ the six cluster atoms define a trigonal prism that contains only three Os–Os bonds: Johnson, B. F. G.; Lewis, J.; Lodge, P G.; Raithby, P. R.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1979**, 719.

(36) When main-group atoms are present as cluster elements, the T geometry is possible: see ref 35 and 39a.

(37) (a) Bau, R.; Kirtley, S. W.; Sorrell, T. N.; Winarko, S. *J. Am. Chem. Soc.* **1974**, *96*, 998. (b) Pannel, K. H.; Mayr, A. J.; Vanderveer, D. *Ibid.* **1983**, *105*, 6168. (c) Cook, N.; Smart, L. E.; Woodward, P.; Cotton, J. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1032. (d) Cook, N.; Smart, L. E.; Woodward, P. *Ibid.* **1977**, 1744. (e) Gochin, M.; Moss, J. R. *J. Organomet. Chem.* **1980**, *192*, 409.

However, so far only six examples of complexes having linear M_4 geometries[38c] have been reported, which are tabulated in Table V.

Interestingly, the central two metal atoms in all complexes are second- or third-row metals, while nearly all the complexes exhibit a centrosymmetric symmetry. Besides, the presence of strongly bridging ligands seems to be a prerequisite for the stability of these species. It indicates that the R-DAB ligand may form a strong bridge between two metal centers, thereby stabilizing unusual geometries (see Introduction).

Another point worth mentioning is that the present Ru_4 cluster is isoelectronic with $H_2Os_4(CO)_{16}$, a species that was claimed to have a linear structure with two terminally bonded H atoms.[40]

Conclusions

$Ru_2(CO)_5$(R-DAB) reacts readily with molecular hydrogen to yield the oxidative addition product $H_2Ru_2(CO)_5$(R-DAB) in which both H ligands are presumably terminally bonded. This reaction proves that $Ru_2(CO)_5$(R-DAB) indeed reacts like an unsaturated species as has already been indicated by the facile reaction with CO. Further interesting reactions therefore can be expected.

$Ru_3(CO)_8$(neo-Pent-DAB) reacts with molecular hydrogen to yield $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$. The observed change in geometry of the metal framework, i.e., from triangular to (unusual) linear, is unprecedented and can only be the result of a rather complex reaction mechanism. The hydrido ligands in the product are presumably terminally bonded which is very uncommon for such ligands bonded to a cluster. The geometry of the cluster indicates again that the R-DAB ligand is a strongly bridging ligand that may stabilize surprising cluster geometries.

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Registry No. $H_2Ru_2(CO)_5$(*i*-Pr-DAB), 97877-19-5; $H_2Ru_2(CO)_5$(c-Hx-DAB), 97877-20-8; $H_2Ru_2(CO)_5$(*t*-Bu-DAB), 97860-65-6; $H_2Ru_2(CO)_5$(c-HxCH$_2$-DAB), 97860-66-7; $Ru_2(CO)_5$(*i*-Pr-DAB), 90219-26-4; $Ru_2(CO)_5$(c-Hx-DAB), 90219-27-5; $Ru_2(CO)_5$(c-HxCH$_2$-DAB), 97877-21-9; $Ru_2(CO)_6$(*i*-Pr-DAB), 74552-69-5; $Ru_2(CO)_6$(c-Hx-DAB), 74552-70-8; $Ru_2(CO)_6$(*t*-Bu-DAB), 74552-68-4; $H_2Ru_4(CO)_8$(neo-Pent-DAB)$_2$, 97877-22-0; $Ru_3(CO)_8$(neo-Pent-DAB), 78199-28-7; $Ru_2(CO)_5$(neo-Pent-DAB), 90219-29-7; $H_4Ru_4(CO)_{12}$, 34438-91-0; neo-Pent-DAB, 78198-90-0; H_2, 1333-74-0; Ru, 7440-18-8.

Supplementary Material Available: Table VI, elemental analysis, Table VII, all bond lengths and angles, Table VIII, structure factors, Table IX, anisotropic thermal parameters, and Table X, positional parameters of hydrogen and solvate atoms (15 pages). Ordering information is given on any current masthead page.

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Reduction of SO_2 by $(C_5R_5)M(CO)_3H$ (M = Mo, W; R = H, Me). Chemistry and Structures of $(C_5H_5)Mo(CO)_3(SO_2H)$, the First Example of Insertion of SO_2 into a M–H Bond, and $[(C_5Me_5)Mo(CO)_3]_2(\mu\text{-}S_2O_4)$, an S-Bonded Dithionite Complex

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Addition of SO_2 to solutions of $(C_5R_5)M(CO)_3H$ (R = H, Me; M = Mo, W) has produced the new complexes $(C_5R_5)M(CO)_3(SO_2H)$ and $[(C_5R_5)M(CO)_3]_2(\mu\text{-}S_2O_4)$, depending on reaction conditions. Single-crystal X-ray studies of $CpMo(CO)_3(SO_2H)$ revealed coordination of an unprecedented $-SO_2H$ ligand with the proton being bound to oxygen [Mo–S = 2.521 (2) Å; S–O(1) = 1.637 (6) Å; S–O(2) = 1.515 (6) Å]. The solid is thermally unstable at 20 °C, decomposing to SO_2 reduction products (e.g., metal–sulfide complexes and H_2O), and dissociates in solution to $CpMo(CO)_3H$ and SO_2. The Cp* (= C_5Me_5) analogues are more stable but can be thermolyzed at 75 °C to several oxo/sulfido complexes, e.g., $[Cp^*MO(\mu\text{-}S)]_2$. Prolonged solution reactions of $(C_5R_5)M(CO)_3H$ and SO_2 yield similar products, including the new complexes $[CpW(CO)_3]_2(\mu\text{-}S)$ and $[Cp^*W(CO)_2(\mu\text{-}S\cdot SO_2)]_2$. X-ray studies of $[Cp^*Mo(CO)_3]_2(\mu\text{-}S_2O_4)$, a solution-unstable possible intermediate in the above reactions, revealed the first structurally characterized example of a sulfur-bound dithionite ion (C_{2h} symmetry). It exhibits a S–S bond distance of 2.266 (1) Å which is 0.12 Å shorter than that in $Na_2S_2O_4$. Crystallographic data for $CpMo(CO)_3(SO_2H)$: space group $P2_1/c$, a = 8.224 (2) Å, b = 9.902 (3) Å, c = 12.889 (6) Å, β = 100.61 (3)°; Z = 4, R = 0.049 for 1618 independent reflections with $I \geq 2\sigma(I)$ and $2\theta \leq 50°$. Crystallographic data for $[Cp^*Mo(CO)_3]_2(S_2O_4)$: space group *Pcab*, a = 12.513 (2) Å, b = 14.000 (3) Å, c = 16.763 (3) Å; Z = 4, R = 0.034 for 1641 independent reflections.

Introduction

Insertion of small molecules into metal–hydrogen bonds, while not uncommon, is limited to primarily carbon-containing species.[1] Prior to the work reported here, SO_2 insertion into metal–hydride bonds has not been observed despite the fact that insertion into M–R bonds[2] has been

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