Acknowledgment. Support received under NSF Grant CHE77-01372 is gratefully acknowledged.

Registry No. MoO_2L_2 (R = OC_2H_5, R′ = CH_3), 76514-85-7; MoO_2L_2 (R = H, R′ = CH_3), 76581-99-2; MoO_2L_2 (R = Cl, R′ = CH_3), 76514-86-8; MoO_2L_2 (R = $OC(O)C_6H_5$, R′ = CH_3), 76514-87-9; MoO_2L_2 (R = H, R′ = C_6H_5), 76582-00-8; phenacetin, 62-44-2; acetanilide, 103-84-4; *p*-chloroacetanilide, 539-03-7; *p*-(benzoyloxy)acetanilide, 537-52-0; benzanilide, 93-98-1; MoO_3HMPT, 25377-12-2; BSA, 10416-58-7.

Supplementary Material Available: Tables of least-squares planes and observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Binuclear Metal Carbonyl DAB Complexes. 9. Syntheses and X-ray Structure of (μ-Acetylene)-[σ-N,σ-N′,η^2-C=N,η^2-C=N′-glyoxal bis(isopropylimine)]tetracarbonyldiruthenium. First Example of the 8e-Donating DAB Ligand (DAB = 1,4-Diazabutadiene)

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The reactions between $Ru_2(CO)_6$[glyoxal bis(isopropylimine)] or $Ru_2(CO)_6$[glyoxal bis(cyclohexylimine)] and acetylene (HC≡CH) yield complexes of the composition $Ru_2(CO)_4$(DAB)(HC≡CH). A crystal structure determination has been carried out for (μ-acetylene)[$\sigma,\sigma,\eta^2,\eta^2$-glyoxal bis(isopropylimine)]tetracarbonyldiruthenium. The crystals are orthorhombic, of space groups $P2_12_12_1$, with four molecules in a unit cell of dimensions a = 9.541 (1), b = 13.054 (1), and c = 13.404 (1) Å. The structure was solved by means of the heavy-atom method and refined to R = 0.034 for 1600 reflections. The binuclear metal carbonyl fragment contains a two-electron Ru–Ru bond of length 2.936 (1) Å. The metal–metal bond is bridged by a DAB molecule which is coordinated to one of the ruthenium atoms via the lone pairs of the N atoms and to the other ruthenium atom via the π electrons of the two C–N double bonds. This is the first example of a σ-N,σ-N′,η^2-C=N,η^2-C=N′-coordinated 1,4-diazabutadiene ligand. The Ru–Ru bond is furthermore bridged by an acetylene forming in Ru–C σ bonds of lengths 2.09 and 2.06 Å. The coordinated acetylene is parallel to the Ru–Ru bond. The ^{1}H NMR chemical shifts for the imine hydrogen atoms are observed near 6.2 ppm, which is in agreement with the proposed bonding mode for the DAB ligand.

Introduction

Studies of the coordination behavior of 1,4-diazabutadienes (DAB = R_1N=$C(R_2)(R_2)C$=NR_1) revealed an interesting variety of bonding modes for this heterobutadiene molecule. In principle a maximum of eight electrons are available for coordination: two lone pairs on the imine nitrogen atoms and two pairs of π electrons on the N=C—C=N skeleton.

The predominant cooridnation mode is chelate ring formation via the two lone pairs on nitrogen,[1-8] but recently the σ-N monodentate and σ-N,σ-N′ bridging modes have also been established.[9,10]

Involvement of the π electrons of the N=C—C=N skeleton in the coordination toward methyl carbonyl complexes has been the subject of extensive investigations. A series of binuclear metal carbonyl complexes of the general formula $MM'(CO)_6$(DAB) has been synthesized (M = M′ = Fe,[11] Ru,[12,13] Os;[14] M = Co and M′ = Mn, Re.[15] In all these complexes the DAB ligand is coordinated via the two lone pairs on nitrogen and via one pair of π electrons, thus being a six-electron donating system. Only one example is known at present of a complex containing two DAB ligands coordinated in the 6e donor mode: $Ru_2(CO)_4(DAB)_2$.[13]

Although the N=C—C=N system might be regarded as a formal analogue of butadiene, the π,π-bonding mode which is commonly found for the butadienes has so far not been observed for 1,4-diazabutadienes. We now report the first example of the σ-N,σ-N′,η^2-C=N,η^2-C=N′ coordination mode of 1,4-diazabutadienes. In addition to the two lone pairs on nitrogen, the ligand uses both pairs of π electrons of the N=C—C=N skeleton for the coordination toward a binuclear ruthenium fragment.

Experimental Section

^{1}H NMR spectra were recorded with a Varian T 60 and a Varian XL 100 apparatus, IR spectra were obtained with a Perkin-Elmer 283 spectrophotometer, and mass spectra have been recorded with a Varian MAT 711 mass spectrometer, using a field desorption device. The elemental analyses were carried out by the Section Elemental Analysis of the Institute for Organic Chemistry, TNO, Utrecht, The Netherlands.

$Ru_3(CO)_{12}$ and acetylene were obtained from commercial sources

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Table I. Positional Parameters of the Atoms in Fractional Coordinates[a]

Atoms	x (σ)	y (σ)	z (σ)	Atoms	x (σ)	y (σ)	z (σ)
Ru (1)	-0.07349 (5)	-0.23411 (4)	-0.15634 (4)	C (4)	-0.0536 (10)	-0.1197 (7)	-0.4645 (6)
Ru (2)	0.02196 (5)	-0.13000 (4)	-0.33823 (4)	C (5)	-0.0136 (9)	-0.3336 (6)	-0.2710 (6)
O (1)	0.0718 (9)	-0.3643 (6)	-0.0055 (5)	C (6)	0.0307 (9)	-0.2869 (7)	-0.3545 (7)
O (2)	-0.3349 (7)	-0.3536 (6)	-0.1143 (5)	C (7)	-0.0082 (9)	-0.0745 (5)	-0.1209 (6)
O (3)	0.2982 (7)	-0.1083 (8)	-0.4444 (5)	C (8)	-0.1475 (8)	-0.0724 (6)	-0.1528 (6)
O (4)	-0.0986 (8)	-0.1131 (7)	-0.5453 (5)	C (9)	0.2347 (7)	-0.1214 (6)	-0.1482 (6)
N (1)	0.0895 (7)	-0.1128 (5)	-0.1887 (4)	C (10)	0.3148 (10)	-0.2147 (7)	-0.1871 (7)
N (2)	-0.1630 (6)	-0.1097 (5)	-0.2542 (4)	C (11)	0.3106 (10)	-0.0192 (8)	-0.1643 (8)
C (1)	0.0169 (10)	-0.3152 (6)	-0.0611 (6)	C (12)	-0.3128 (7)	-0.1086 (7)	-0.2863 (6)
C (2)	-0.2348 (8)	-0.3098 (6)	-0.1297 (6)	C (13)	-0.3458 (11)	-0.0068 (8)	-0.3292 (9)
C (3)	0.1934 (9)	-0.1188 (7)	-0.4037 (6)	C (14)	-0.3428 (9)	-0.2004 (8)	-0.3557 (7)

[a] Esd's are given in parentheses.

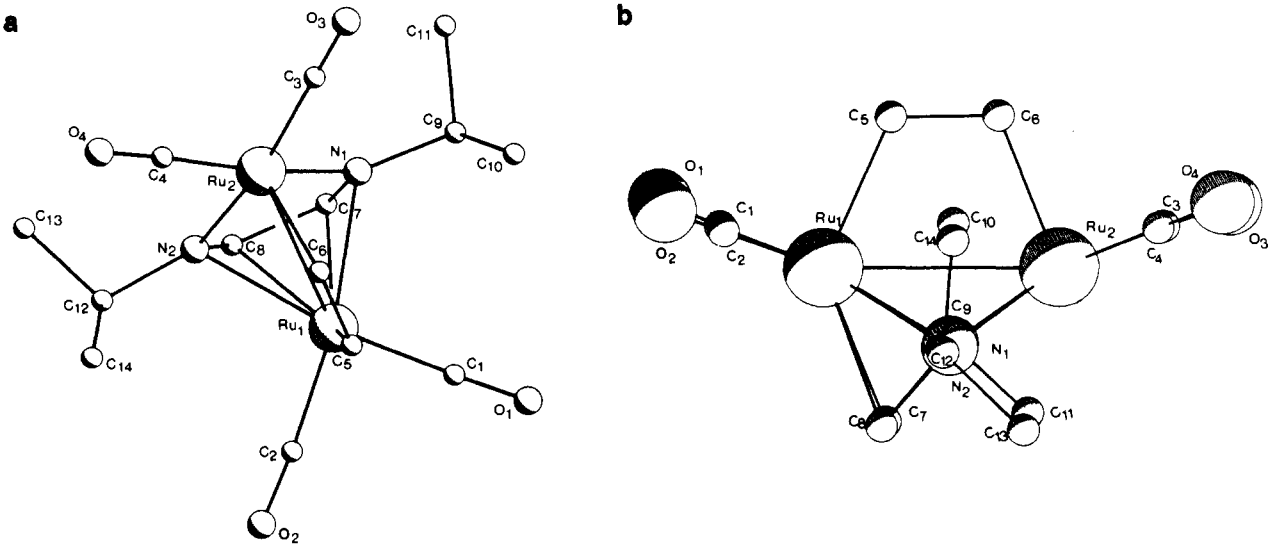

Figure 1. Two projections of the molecular structure of (μ-acetylene)-[σ-N,σ-N′,η²-C=N,η²-C=N′-glyoxal bis(isopropylimine)]tetracarbonyldiruthenium.

and were used without purification. Glyoxal bis(isopropylimine) and glyoxal bis(cyclohexylimine) were prepared according to standard procedures.[8] All solvents were carefully dried and distilled prior to use.

Silica (Merck 60) was dried, deoxygenated, and activated under vacuum for 3 h at 180 °C and stored under nitrogen.

Preparation of $Ru_2(CO)_4$[glyoxal bis(isopropylimine)](HC≡CH). $Ru_3(CO)_{12}$ (320 mg) and glyoxal bis(isopropylimine) (105 mg) were refluxed under nitrogen in 30 mL of heptane. A bright yellow solution of $Ru_2(CO)_6$(*i*-Pr-N=CHCH=N-*i*-Pr) was obtained after cooling and filtration through a short column of finely divided silica.[16] The solution was then heated to 90 °C, and for 3 h acetylene was passed through, with use of a sintered glass tube as inlet. The brownish precipitate formed was filtered off the extracted with hot dichloromethane, resulting in a bright yellow solution. Recrystallization at −30 °C, produced yellow crystals of $Ru_2(CO)$(*i*-Pr-N=CHCH=N-*i*-Pr)(HC≡CH). Anal. Calcd: C, 34.43; H, 3.72; N, 572. Found: C, 34.98; H, 3.75; N, 583. M_r = 480 (calcd 480).

Although after 3 h not all the starting material was converted into $Ru_2(CO)_4$(DAB)(acetylene), the reaction was stopped to prevent a decrease of the yield due to thermal decomposition of the product. The solution of $Ru_2(CO)_6$(DAB) in heptane should be used shortly after its preparation since this starting material slowly decomposes.

Preparation of $Ru_2(CO)_4$[glyoxal bis(cyclohexylimine)](HC≡CH). The reaction was carried out as described for the isopropyl derivative. After the reaction with acetylene, the solution was evaporated to dryness, and the product was separated from the reaction mixture by column chromatography. The extraction of the column was started with diethyl ether–hexane (1:3, v/v) as eluant, yielding the unreacted starting material. The desired product was obtained with dichloromethane as eluant. The dichloromethane fraction was evaporated to dryness, and the residue was extracted with diethyl ether. The pure product was obtained as pale yellow crystals after crystallization at −70 °C in poor yields (generally less than 10%). M_r = 562 (calcd 562).

Structure Determination of (μ-Acetylene)-[σ-N,σ-N′,η²-C=N,η²-C=N′-glyoxal bis(isopropylimine)]tetracarbonyldiruthenium. The yellow crystals obtained from the dilute dichloromethane solution at −30 °C were orthorhombic with four molecules in a unit cell of dimensions a = 9.543 (1), b = 13.054 (1), c = 13.404 (1) Å (calculated density 1.91 g cm^{-3}). The space group is $P2_12_12_1$. A total of 1600 reflections with $\theta < 65°$ and intensities above the 2.5σ level were measured on a Nonius CAD4 diffractometer applying the θ–2θ scan technique and using graphite-monochromated Cu Kα radiation. An absorption correction was applied (crystal dimensions = 0.33 × 0.25 × 0.20 mm, μ = 155 cm^{-1}, minimum and maximum corrections = 5.53 and 42.90, respectively). An E^2-Patterson sythesis yielded the positions of the two Ru atoms in the asymmetric unit. From a subsequent difference Fourier synthesis based on the phases of the Ru contributions the remaining nonhydrogen atoms were obtained. Refinement was carried out by means of anisotropic block-diagonal least-squares calculations and converged to R = 0.034 for the 1600 observed reflections. The hydrogen atoms could not be located. A weighting scheme $w = (6 + F_o + 0.042F_o^2)^{-1}$ was used, and the anomalous dispersion of Ru was taken into account. The computer programs used were from the XRAY 76 system. The final coordinates are listed in Table I, and the temperature factors are available as supplementary material.

(16) Orange-yellow crystals of $Ru_2(CO)_6$[*i*-Pr-N=CH=CH=N-*i*-Pr] which decompose slowly at room temperature can be obtained at this stage by crystallization at −70 °C.[13]

Table II. Bond Lengths for Nonhydrogen Atoms[a] (Å)

Ru(1)-Ru(2)	2.936 (1)	Ru(2)-C(4)	1.844 (9)	C(9)-C(10)	1.530 (12)
Ru(1)-C(1)	1.869 (8)	Ru(2)-C(6)	2.062 (9)	C(9)-C(11)	1.533 (13)
Ru(1)-C(2)	1.864 (8)	Ru(2)-N(1)	2.117 (6)	C(12)-C(13)	1.482 (14)
Ru(1)-C(5)	2.092 (8)	Ru(2)-N(2)	2.111 (6)	C(12)-C(14)	1.543 (13)
Ru(1)-C(7)	2.226 (7)	N(1)-C(7)	1.395 (10)	C(1)-O(1)	1.114 (11)
Ru(1)-C(8)	2.226 (7)	N(1)-C(9)	1.493 (10)	C(2)-O(2)	1.133 (10)
Ru(1)-N(1)	2.226 (6)	N(2)-C(8)	1.451 (9)	C(3)-O(3)	1.148 (10)
Ru(1)-N(2)	2.225 (6)	N(2)-C(12)	1.493 (9)	C(4)-O(4)	1.168 (11)
Ru(2)-C(3)	1.862 (9)	C(7)-C(8)	1.396 (11)	C(5)-C(6)	1.342 (12)

[a] Esd's are given in parentheses.

Results

Molecular Structure of (μ-Acetylene)-[σ-N,σ-N′,η^2-C=N,η^2-C=N′-glyoxal bis(isopropylimine)]tetracarbonyldiruthenium. The molecular structure with the atomic numbering is shown in Figure 1. The bond lengths and bond angles are given in Tables II and III, respectively.

The Ru(1)–Ru(2) bond length is 2.936 (1) Å, which is in agreement with values recently reported for binuclear[17-21] and trinuclear[22-24] ruthenium carbonyl complexes.

As is shown in Figure 1, the DAB ligand is coordinated to Ru(2) via N(1) and N(2) with bond lengths of 2.117 (6) and 2.111 (6) Å, respectively, and the DAB ligand can therefore be regarded as chelating with respect to Ru(2). Additionally, the 1,4-diazabutadiene is bonded to Ru(1) via N(1), N(2), C(7), and C(8), surprisingly with equal Ru–N and Ru–C bond lengths: Ru(1)–N(1) = 2.226 (6) Å, Ru(1)–N(2) = 2.225 (6) Å, Ru(1)–C(7) = 2.226 (7) Å, Ru(1)–C(8) = 2.226 (7) Å. The C(8)–N(2) and C(7)–N(1) bond distances of 1.395 (10) and 1.451 (9) Å are significantly longer than the C=N bond lengths in uncoordinated glyoxal bis(*tert*-butylimine)[25] (1.24 Å) and in σ,σ-coordinated DAB ligands[9,10] (between 1.24 and 1.28 Å) and are in range of η^2-C=N bond lengths[5,13,15] (approximately 1.4 Å). The central C(7)–C(8) bond of the diimine skeleton of 1.396 (11) Å is short as compared with the analogous bond of 1.52 Å of glyoxal bis(*tert*-butylimine).[25] From both the arrangement of the N=C—C=N skeleton with respect to Ru(1) and the changes in the bond lengths in the diimine moiety, we may conclude that the ligand is η^2-C=N,η^2-C=N′ coordinated to Ru(1). Accordingly, the 1,4-diazabutadiene acts as an 8e donor system, thus donating the maximum number of electrons which are available for coordination.

The planarity of the DAB ligand (including the N(1)–C(9) and N(2)–C(12) bonds) is not drastically influenced by the η^4 coordination. The N=C—C=N fragment is planar, and the N(1)–C(9) and N(2)–C(12) bonds are slightly bent out of the plane (4°). However, Ru(2) is not coplanar with N(1)–C(7)–C(8)–N(2) as is obvious from Figure 1b. The dihedral angle between the planes N(1)–Ru(2)–N(2) and N(1)–C(7)–C(8)–N(2) is 14°.

In addition to the bridging by the 1,4-diazabutadiene, the Ru(1)–Ru(2) bond is bridged by an acetylene molecule, coordinated with C(5) to Ru(1) and with C(6) to Ru(2). The ruthenium carbon bond lengths are 2.092 (8) and 2.062 (9) Å, respectively, and the C(5)–C(6) bond length is 1.342 (12) Å. In binuclear complexes two types of alkyne coordination have been observed. The carbon–carbon bond may be perpendicular to the metal–metal bond in which case the alkyne is a π-donor ligand. Alternatively the carbon–carbon bond can be parallel to the metal–metal bond which makes the alkyne a σ-bonded ligand. The π-bonded mode is predominantly observed for the first-row transition metals, while the

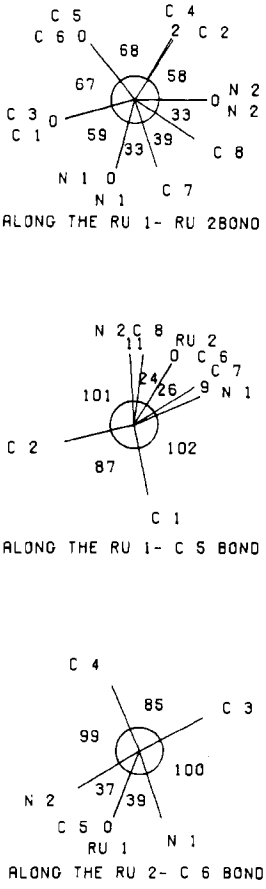

Figure 2. Newman projections along Ru(1)–Ru(2), Ru(1)–C(5), and Ru(2)–C(6).

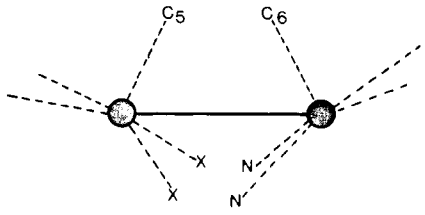

Figure 3. Schematic representation of the coordination polyhedron of (μ-acetylene)-[σ-N,σ-N′,η^2-C=N,η^2-C=N′-glyoxal bis(isopropylimine)]tetracarbonyldiruthenium.

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Table III. Bond Angles[a] (Deg)

Ru(2)-Ru(1)-C(1)	133.3 (3)	C(8)-Ru(1)-N(1)	63.8 (3)	C(7)-C(8)-N(2)	112.1 (6)
Ru(2)-Ru(1)-C(2)	131.4 (2)	C(8)-Ru(1)-N(2)	37.8 (2)	C(10)-C(9)-C(11)	114.2 (7)
Ru(2)-Ru(1)-C(5)	65.9 (2)	N(1)-Ru(1)-N(2)	69.2 (2)	C(10)-C(9)-N(1)	113.6 (4)
Ru(2)-Ru(1)-C(7)	69.9 (2)	Ru(1)-Ru(2)-C(3)	134.4 (3)	C(11)-C(9)-N(1)	108.8 (4)
Ru(2)-Ru(1)-C(8)	41.2 (2)	Ru(1)-Ru(2)-C(4)	132.4 (3)	C(13)-C(12)-C(14)	115.0 (8)
Ru(2)-Ru(1)-N(1)	45.8 (1)	Ru(1)-Ru(2)-C(6)	68.9 (2)	C(13)-C(12)-N(2)	108.9 (7)
Ru(2)-Ru(1)-N(2)	45.7 (1)	Ru(1)-Ru(2)-N(1)	50.0 (2)	C(14)-C(12)-N(2)	110.1 (7)
C(1)-Ru(1)-C(2)	87.1 (4)	Ru(1)-Ru(2)-N(2)	49.9 (2)	Ru(1)-N(1)-Ru(2)	84.2 (2)
C(1)-Ru(1)-C(5)	91.4 (3)	C(3)-Ru(2)-C(4)	84.6 (4)	Ru(1)-N(1)-C(7)	70.5 (4)
C(1)-Ru(1)-C(7)	104.8 (3)	C(3)-Ru(2)-C(6)	89.6 (4)	Ru(1)-N(1)-C(9)	121.1 (5)
C(1)-Ru(1)-C(8)	132.0 (3)	C(3)-Ru(2)-N(1)	99.8 (3)	Ru(2)-N(1)-C(7)	116.8 (5)
C(1)-Ru(1)-N(1)	102.1 (3)	C(3)-Ru(2)-N(2)	167.5 (3)	Ru(2)-N(1)-C(9)	128.3 (5)
C(1)-Ru(1)-N(2)	168.4 (3)	C(4)-Ru(2)-C(6)	89.5 (4)	C(7)-N(1)-C(9)	114.3 (6)
C(2)-Ru(1)-C(5)	92.2 (3)	C(4)-Ru(2)-N(1)	168.5 (3)	Ru(1)-N(2)-Ru(2)	84.5 (2)
C(2)-Ru(1)-C(7)	133.3 (3)	C(4)-Ru(2)-N(2)	98.8 (3)	Ru(1)-N(2)-C(8)	70.0 (4)
C(2)-Ru(1)-C(8)	103.6 (3)	C(6)-Ru(2)-N(1)	101.2 (3)	Ru(1)-N(2)-C(12)	122.5 (5)
C(2)-Ru(1)-N(1)	167.4 (3)	C(6)-Ru(2)-N(2)	102.4 (3)	Ru(2)-N(2)-C(8)	117.2 (4)
C(2)-Ru(1)-N(2)	100.4 (3)	N(1)-Ru(2)-N(2)	74.7 (2)	Ru(2)-N(2)-C(12)	130.4 (5)
C(5)-Ru(1)-C(7)	131.4 (3)	Ru(1)-C(5)-C(6)	114.7 (6)	C(8)-N(2)-C(12)	111.3 (6)
C(5)-Ru(1)-C(8)	133.7 (3)	Ru(2)-C(6)-C(5)	110.5 (6)	Ru(1)-C(1)-O(1)	178.9 (8)
C(5)-Ru(1)-N(1)	96.1 (3)	Ru(1)-C(7)-C(8)	71.7 (4)	Ru(1)-C(2)-O(2)	178.2 (7)
C(5)-Ru(1)-N(2)	97.1 (3)	Ru(1)-C(7)-N(1)	73.3 (4)	Ru(2)-C(3)-O(3)	177.6 (9)
C(7)-Ru(1)-C(8)	36.6 (3)	C(8)-C(7)-N(1)	116.4 (7)	Ru(2)-C(4)-O(4)	178.6 (9)
C(7)-Ru(1)-N(1)	36.2 (3)	Ru(1)-C(8)-C(7)	71.7 (4)		
C(7)-Ru(1)-N(2)	63.6 (2)	Ru(1)-C(8)-N(2)	72.2 (4)		

[a] Esd's are given in parentheses.

σ bonding generally occurs for the second- and third-row elements.[26,27]

As is shown in the Newman projections along Ru(1)–Ru(2), given in Figure 2, the acetylene fragment is parallel to the metal–metal bond. The carbonyl groups C(2)–O(2) and C(4)–O(4) are coplanar with the Ru(1)–Ru(2) bond, and the same applies to C(1)–O(1) and C(3)–O(3). The angle between the planes is 135°, and the Ru–Ru bond is on the intersection.

Disregarding the metal–metal bond, the ligands are positioned on two square pyramids with the apices pointing toward each other. This is illustrated by the Newman projections along Ru(1)–C(5) and Ru(2)–C(6) depicted in Figure 2. The idealized representation of the coordination polyhedron of the binuclear complexes is shown in Figure 3. It can best be regarded as two bicapped square pyramids, taking into account the Ru–Ru bond. In this model the η^2 coordination is represented by two lines pointing to the middle of the C=N bond (indicated in Figure 3 by X).

^{1}H NMR Data. The ^{1}H NMR shifts of the imine hydrogen atoms are indicative of the coordination mode of the DAB ligands. For σ,σ-coordinated 1,4-diazabutadienes (via the lone pairs on nitrogen), values between 7 and 9 ppm have been observed[2,28] which are in the same range as values observed for the imine hydrogen atoms in the free ligands. Recently binuclear metal carbonyl DAB complexes have been prepared containing one η^2-C=N-coordinated imine fragment in addition to the σ-N,σ-N′ coordination. The imine hydrogen atoms of these $M_2(CO)_6(DAB)$ complexes (M = Fe, Ru, Os) give an AX pattern with doublets near 8 and 3.5 ppm.[3,5,13,14] The signal at 8 ppm is assigned to the σ-coordinated imine fragment and the signal at about 3.5 ppm to the π-coordinated part of the N=CH—CH=N skeleton. In $MCo(CO)_6(DAB)$ complexes (M = Mn, Re) values near 5 ppm have been found for the chemical shift of the η^2-coordinated HC=N—R fragments.[15]

The $Ru_2(CO)_4(DAB)$(acetylene) complexes give only one single line in the ^{1}H NMR spectrum for the two imine hydrogen atoms. The positions are 6.16 and 6.22 ppm for the isopropyl and cyclohexyl derivatives, respectively. These values are approximately 1.6 ppm shifted to an upfield position due to the olefinic shielding. The chemical shifts for the imine hydrogen atoms confirm that in addition to σ-N,σ-N′ coordination both C=N fragments are involved in the coordination of the 1,4-diazabutadiene. It is not clear why the shielding effect caused by η^2 coordination is less pronounced in the σ-N,σ-N′,η^2-C=N,η^2-C=N′-coordination mode as compared with σ-N,μ-N′,η^2-C=N coordination.

The π,π-coordination mode of the monoazadiene ligand (R_2C=CH—CH=N—R′) has been established before.[29] The olefinic shielding on the imine hydrogen atom in $Fe(CO)_3$(monoazadiene)[29] is comparable with the effect in the $Ru_2(CO)_4(DAB)$(acetylene) complexes. The two alkyl groups attached to the imine nitrogen atoms of the 1,4-diazabutadiene give one set of resonances. The cyclohexyl groups in (μ-acetylene)-[glyoxal bis(cyclohexylimine)]tetracarbonyldiruthenium appear as a broad multiplet between 1 and 2 ppm in the ^{1}H NMR spectra. For the prochiral isopropyl group in (μ-acetylene)-[glyoxal bis(isopropylimine)]tetracarbonyldiruthenium two doublets are found at 0.63 and 1.19 ppm, respectively, and the septet of the isopropyl groups is observed at 2.23 ppm (all measurements were carried out in $CDCl_3$).

The acetylenic protons are observed at 7.50 and 8.22 ppm for the isopropyl derivative and at 7.49 and 8.28 ppm for the cyclohexyl derivative. The signals appeared as sharp singlets.

According to the ^{1}H NMR data, the complexes (in solution) contain a symmetry plane which is defined by the ruthenium atoms and the carbon atoms of the acetylene fragment. This plane is perpendicular to the diimine skeleton.

IR Absorption Data (ν(CO) Stretching Frequencies). The complexes have C_s symmetry and C_s the two pairs of equivalent carbonyl groups have two symmetrical and two antisymmetrical stretching modes which are all IR active.

In the IR spectra of the $Ru_2(CO)_4(DAB)$(acetylene) complexes four intense bands are found between 2100 and 1900 cm^{-1} which have a characteristic intensity pattern as is shown

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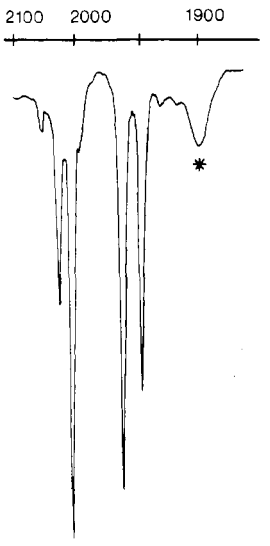


Figure 4. IR spectrum of (μ-acetylene)-[glyoxal bis(isopropylimine)]tetracarbonyldiruthenium (2100–1900 cm^{-1}; solvent pentane).

in Figure 4. For the isopropyl derivative bands at 2024, 2005, 1962, and 1944 cm^{-1} are found and for the cyclohexyl derivative at 2028, 2005, 1960, and 1944 cm^{-1}. For both complexes identical intensity patterns are observed.

Discussion

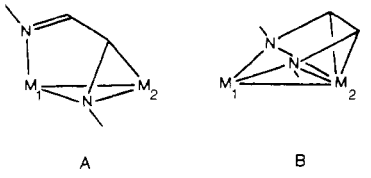
Although the overall reaction for the formation of $Ru_2(CO)_4(DAB)$(acetylene) is substitution of two carbonyl groups (eq 1), the reaction pathway is likely to be very complicated.

$$Ru_2(CO)_6(DAB) + HC{\equiv}CH \xrightarrow{\Delta T} Ru_2(CO)_4(DAB)(HC{\equiv}CH) + 2CO\uparrow \quad (1)$$

$Ru_2(CO)_6(DAB)$ complexes react with a variety of alkynes, forming complexes of the formula $Ru_2(CO)_5$(DAB-alkyne). The ^1H NMR spectra of these complexes indicate the existence of a carbon–carbon bond between the coordinated alkyne and the imine carbon atom which participated in the η^2-C=N bonding of the DAB molecule. [This has been confirmed by a crystal structure.]

$Ru_2(CO)_5$(DAB-alkyne) complexes are active catalysts for the cyclotrimerization of alkynes. During the formation of $Ru_2(CO)_4(DAB)(HC{\equiv}CH)$ small amounts of benzene are formed, and it is therefore assumed that $Ru_2(CO)_5(DAB)(HC{\equiv}CH)$ complexes are instable intermediates in the reaction of $Ru_2(CO)_6(DAB)$ with acetylene. The formation of $Ru_2(DAB)(HC{\equiv}CH)$ seems to involve the formation and specific cleavage of carbon–carbon bonds between the DAB ligand and the acetylene. This subject will be included in a forthcoming paper concerning the syntheses and crystal structure of $Ru_2(CO)_5$(DAB-alkyne) complexes and the role of these species in the catalytic oligomerization of alkynes.

It has been pointed out in the Introduction that 1,4-diazabutadienes can occur in a variety of bonding modes. At present two coordination modes are found in which the π electrons of the N=C—C=N skeleton participate in the bonding of the ligand toward a metal carbonyl fragment. These two coordination modes which are schematically shown in structures A and B have in common that the two lone pairs are



donated to M_1, forming a five-membered chelate ring, while the π electrons are donated to the second metal M_2. It can be anticipated that chelate formation is a prerequisite prior to η^2-C=N bond formation in order to obviate the repulsive interaction between the lone pairs on nitrogen. In Figure 5 the four symmetrical conformations of the free ligand are shown. The trans–anti–trans conformation (top right) is the predominant one.[25] For η^2-C=N,η^2-C=N′ coordination rotation around the central C–C bond is required, resulting in the cis–syn–cis and trans–syn–trans conformation, respectively. The former one is sterically and the latter one electronically unfavorable. The required conformation is stabilized by chelate formation (bottom right). However, when the diimine is part of a cyclic ligand as is shown schematically in Figure 5 (bottom left), the trans–syn–trans conformation is fixed and η^2 coordination of these ring systems has indeed been observed toward $Ni(CO)_3$ and $Fe(CO)_3$ fragments.[30]

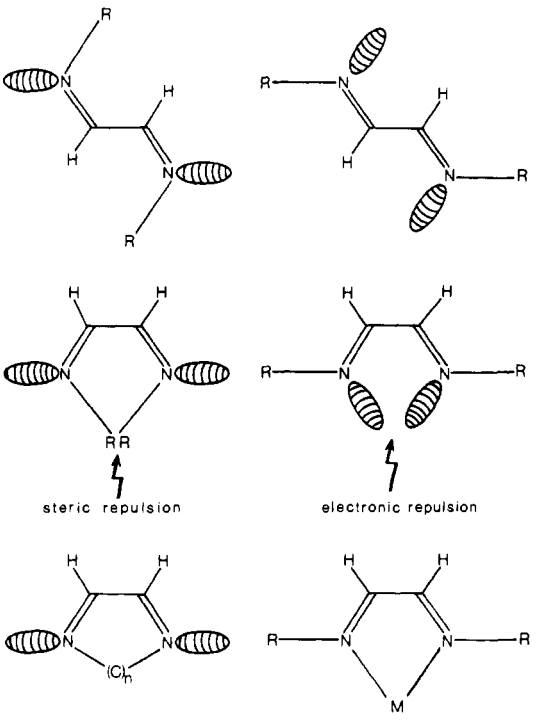


Figure 5. Conformations of 1,4-diazabutadienes and related species.

In η^2 coordination of α-diimines may have important implications in homogeneous catalysis. $Ru_2(CO)_6(DAB)$ complexes are efficient catalysts for the cyclooligomerization of alkynes. The η^2-C=N coordination of one of the imine fragments is of crucial importance for this process.[31] Analogous behavior might be expected for a complex with two activated sites.

Many electron deficient complexes containing DAB ligands are homogeneous catalysts for the cyclooligomerization and polymerization of olefins and diolefins.[32-34] It has been shown that the substituents attached to the DAB ligand strongly affect the product ratio, and it was assumed that the reactions are sterically controlled.[32] However, the use of biacetyl bis(isopropylimine), a ligand with very poor π-bonding capacity, resulted in the formation of polymers exclusively. These results indicate involvement of π-bonded intermediates in the reaction mechanism.

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Conclusions

It has been demonstrated that DAB ligands are capable of using the maximum number of eight electrons for the coordination of the N=C—C=N skeleton toward binuclear metal carbonyl units. The first example of the η^2-C=N,η^2C=N′ coordination of the 1,4-diazabutadienes as a stable electronic structure in $Ru_2(CO)_4(DAB)(HC{\equiv}CH)$ should be taken into account when inter- or intramolecular exchange processes of the ligand are studied.[15]

We have shown recently that σ^2-N,η^2-N′,η^2-C=N′ coordination of the DAB ligand in $Ru_2(CO)_6(DAB)$ complexes lead to a remarkable activation of the η^2-C=N bond. Reaction of these complexes with free DAB ligands yielded $Ru_2(CO)_5(IAE)$ complexes (IAE = bis[(alkylimino)(alkylamino)ethane]) in which the IAE ligand consists of two DAB ligands linked together via a C–C bond between two imine carbon atoms.[12,13] It might be expected that η^2 coordination of both C=N bonds leads to the activation of both imine carbon centers in the ligand, giving new opportunities to the metal carbonyl supported synthesis of 1,2-disubstituted 1,2-diaminoethanes and related derivatives.

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Registry No. $Ru_2(CO)_4$[glyoxal bis(isopropylimine)](HC≡CH), 75963-10-9; $Ru_2(CO)_4$[glyoxal bis(cyclohexylimine)](HC≡CH), 76822-76-9; $Ru_3(CO)_{12}$, 15243-33-1; $Ru_2(CO)_6$[glyoxal bis(isopropylimine)], 74552-69-5; $Ru_2(CO)_6$[glyoxal bis(cyclohexylimine)], 74552-70-8.

Supplementary Material Available: A list of temperature parameters and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of 7,9-Disubstituted 6-Oxopurine Metal Compounds. 3. Platinum(II) Coordination at N(1). Molecular and Crystal Structure of (Diethylenetriamine)(7,9-dimethylguanine)platinum(II) Hexafluorophosphate and (Diethylenetriamine)(7,9-dimethylhypoxanthine)platinum(II) Hexafluorophosphate Sesquihydrate[1]

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The preparation and molecular and crystal structure of the complexes (dien)(7,9-dimethylguanine)platinum(II) hexafluorophosphate, $Pt(C_4H_{13}N_3)(C_7H_9N_5O)(PF_6)_2$, and (dien)(7,9-dimethylhypoxanthine)platinum(II) hexafluorophosphate sesquihydrate, $Pt(C_4H_{13}N_3)(C_7H_8N_4O)(PF_6)_2(H_2O)_{1.5}$, are reported (dien = diethylenetriamine). The 7,9-dimethylguanine complex crystallizes in the triclinic system, of space group $P\bar{1}$, with a = 11.111 (3) Å, b = 11.940 (3) Å, c = 9.440 (3) Å, α = 103.54 (2)°, β = 102.39 (2)°, γ = 70.34 (2)°, V = 1133.8 Å^3, Z = 2, D_{measd} = 2.30 (4) g cm^{-3}, and D_{calcd} = 2.24 g cm^{-3}. The 7,9-dimethylhypoxanthine complex crystallizes in the monoclinic system, of space group $C2/c$, with a = 15.754 (5) Å, b = 19.162 (7) Å, c = 18.108 (4) Å, β = 119.02 (2)°, V = 4780.1 Å^3, Z = 8, D_{measd} = 2.137 (3) g cm^{-3}, and D_{calcd} = 2.166 g cm^{-3}. Intensities for 6632 (7,9-dimethylguanine complex) and 4889 (7,9-dimethylhypoxanthine complex) symmetry-averaged reflections were collected in the θ–2θ scan mode on an automated diffractometer employing graphite-monochromatized Mo Kα radiation. Both structures were solved by standard heavy-atom Patterson and Fourier methods. Full-matrix least-squares refinement has led to final R values of 0.049 and 0.057 for the 7,9-dimethylguanine and the 7,9-dimethylhypoxanthine structures, respectively. The primary coordination sphere about the platinum(II) center is approximately square planar in both complex cations, with the tridentate dien chelate, its terminal amino groups in trans positions, and N(1) of the 7,9-dimethylated purine base [Pt–N(1) = 2.044 (5) Å for the guanine base and Pt–N(1) = 2.051 (6) Å for the hypoxanthine base] occupying the four coordination sites. In both complexes, the exocyclic carbonyl oxygen atom O(6) participates in inter- and intracomplex hydrogen-bonding interactions with the amino protons of the dien chelate. For the 7,9-dimethylguanine system, this latter interaction is weak [N(dien)···O(6) = 3.039 (6) Å], but the observed Pt···O(6) intramolecular distance of 3.021 (6) Å suggests some O(6) participation in the metal binding scheme. In contrast, the interligand, intramolecular hydrogen bonding to O(6) in the 7,9-dimethylhypoxanthine complex is stronger [N(dien)···O(6) = 2.946 (6) Å] but there is little indication of O(6) participation [Pt···O(6) = 3.145 (5) Å] in the metal binding. The dihedral angle between the coordination plane and that of the purine base is a sensitive indicator of the relative degree of Pt···O(6) interaction and N(dien)···O(6) interligand hydrogen bonding, and the respective values for this angle for the guanine and hypoxanthine complexes are 62.4 (3) and 47.7 (3)°. The difference in the molecular geometry of the two complex cations can be ascribed to the additional intracomplex steric interactions in the 7,9-dimethylguanine system owing to the presence of the exocyclic amino group at position 2 of the purine ring. Qualitatively, the molecular properties of these N(1)-bound Pt–6-oxopurine complexes are similar to those displayed by N(3)-bound Pt–cytosine complexes. Both crystal structures are characterized by extensive intercomplex hydrogen bonding (direct in the 7,9-dimethylguanine complex and both direct and water mediated in the 7,9-dimethylhypoxanthine complex) and numerous interactions between the PF_6^- anions and the cationic coordination complexes.

Introduction

Since the original report by Rosenberg[2] on the antineoplastic activity of *cis*-$[Pt^{II}(NH_3)_2Cl_2]$, a large body of data have been acquired as to the mode of action of this and similar compounds.[3] Numerous studies have suggested that DNA is the

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