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Preliminary communication

THE EIGHT ELECTRON DONOR MODE OF 1,4-DIAZABUTADIENE LIGANDS AS REVEALED BY THE CRYSTAL STRUCTURES OF $Ru_2(CO)_4(\mu^2$-ACETYLENE)[$\sigma,\sigma,\eta^2,\eta^2$-GLYOXALBIS(ISOPROPYLIMINE)] AND $Ru_4(CO)_8[\sigma,\sigma,\eta^2,\eta^2$-GLYOXALBIS(ISOPROPYLIMINE)]

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Summary

The crystal structures of $Ru_2(CO)_4(\mu^2$-acetylene){glyoxalbis(isopropylimine)} and $Ru_4(CO)_8${glyoxalbis(isopropylimine)}$_2$ have been determined, and provide the first examples of the σ-*N*, σ-*N'*, η^2-C=N, η^2C=N'-coordination mode of the DAB ligands. The chemical shift values of the imine hydrogen atoms are 6.17 and 6.56 ppm, respectively, and confirm the bonding mode of the 1,4-diazabutadiene (DAB).

It has been shown recently that 1,4-diazabutadiene (DAB) can react as six electron donor ligands in a variety of binuclear metal carbonyl complexes [1—5]. In these complexes the DAB ligand is coordinated via the two lone pairs on nitrogen and via one pair of π-electrons thus being σ-N, σ^2-N', η^2-C=N'- or σ-N, σ-N', η^2-C=N' coordinated. However in addition to the two lone pairs, the DAB ligands have two pairs of π-electrons, and consequently the maximum number of electrons available for coordination is eight. The eight electron donor mode of DAB ligands, i.e. σ-N, σ-N', η^2-C=N, η^2C=N'-coordination, has not previously been reported.

As part of our study on the coordination behaviour of 1,4-diazabutadienes we have prepared $Ru_2(CO)_4${glyoxalbis(isopropylimine)}(μ^2-acetylene) (I) and $Ru_4(CO)_8${glyoxalbis(isopropylimine)}$_2$ (II). Compound I was formed by treating $Ru_2(CO)_6$glyoxalbis(isopropylimine) [2, 3] with HC≡CH in n-heptane solutions at 90°C. Compound II was formed by dimerisation of $Ru_2(CO)_6${glyoxalbis(isopropylimine)} in refluxing n-heptane under an inert atmosphere as is indicated by equation 1.

$$Ru_2(CO)_6(DAB) \xrightarrow[\text{n-heptane}]{\Delta T,\ HC\equiv CH} \underset{(I)}{Ru_2(CO)_4(\mu^2HC\equiv CH)(DAB)} + 2\ CO \qquad (1a)$$

$$Ru_2(CO)_6(DAB) \xrightarrow[\text{n-heptane}]{\Delta T,\ N_2} \underset{(II)}{Ru_4(CO)_8(DAB)_2} + 4\ CO \qquad (1b)$$

For both compounds a crystal structure determination was carried out. The crystallographic data are summarized in Table 1.

TABLE 1

CRYSTALLOGRAPHIC DATA OF COMPOUNDS I AND II

	Compound I	Compound II
Formula	$C_{14}H_{18}N_2O_4Ru_2$	$C_{24}H_{32}N_4O_8Ru_4$
Crystal system	orthorombic	monoclinic
Space group	$P_{2_12_12_1}$	P_n
a	9.543(1) Å	9.506(1) Å
b	13.404(1) Å	9.952(3) Å
c	13.054(1) Å	16.625(1) Å
α	90°	90°
β	90°	94.975°
γ	90°	90°
$d_{calc.}$	1.911 g cm^{-3}	1.926 g cm^{-3}
Z	4	2
Radiation	Cu-K_α[a]	Mo-K_α
Reflections	1600	3251
R	3.4	4.9

[a] An absorption correction was applied.

The molecular structure of compound I is shown in Fig. 1. The binuclear complex contains a Ru(1)–Ru(2) single bond with a length of 2.936(1) Å. The most striking feature of the structure is the bridging of the metal—metal bond by a DAB ligand which is bonded via N(1) and N(2) to Ru(2) and via N(1), N(2), C(7) and C(8) to Ru(1). According to the bond distances: Ru(2)—N(1) 2.117(6) Å, Ru(2)—N(2) 2.111(6) Å, Ru(1)—N(1) 2.226(7) Å, Ru(1)—C(7) 2.226(6) Å, Ru(1)—N(2) 2.225(7) Å, Ru(1)—C(8) 2.226 (7) Å, and according to the EAN rule the DAB ligand acts as a chelate with respect to Ru(2) and as a 4e-π donor with respect to Ru(1). Thus, the coordination mode is the eight electron donor σ-N, σ-N′, η^2-C=N, η^2-C=N′-mode.

The Ru(1)—Ru(2) bond is also bridged by an acetylene fragment, forming a planar dimetallocyclobutene with bond distances: Ru(1)—C(5) 2.092(8) Å, Ru(2)—C(6) 2.062(9) Å and C(5)—C(6) 1.342(12) Å.

The molecular structure of compound II is shown in Fig. 2. The tetranuclear cluster contains the ruthenium atoms in a butterfly arrangement with bond lengths Ru(1)–Ru(2) 2.846(2) Å, Ru(1)—Ru(3) 2.843(2) Å, Ru(2)—Ru(3) 2.991(2) Å, Ru(2)—Ru(4) 2.853(2) Å and Ru(3)—Ru(4) 2.846(2) Å. The clus-

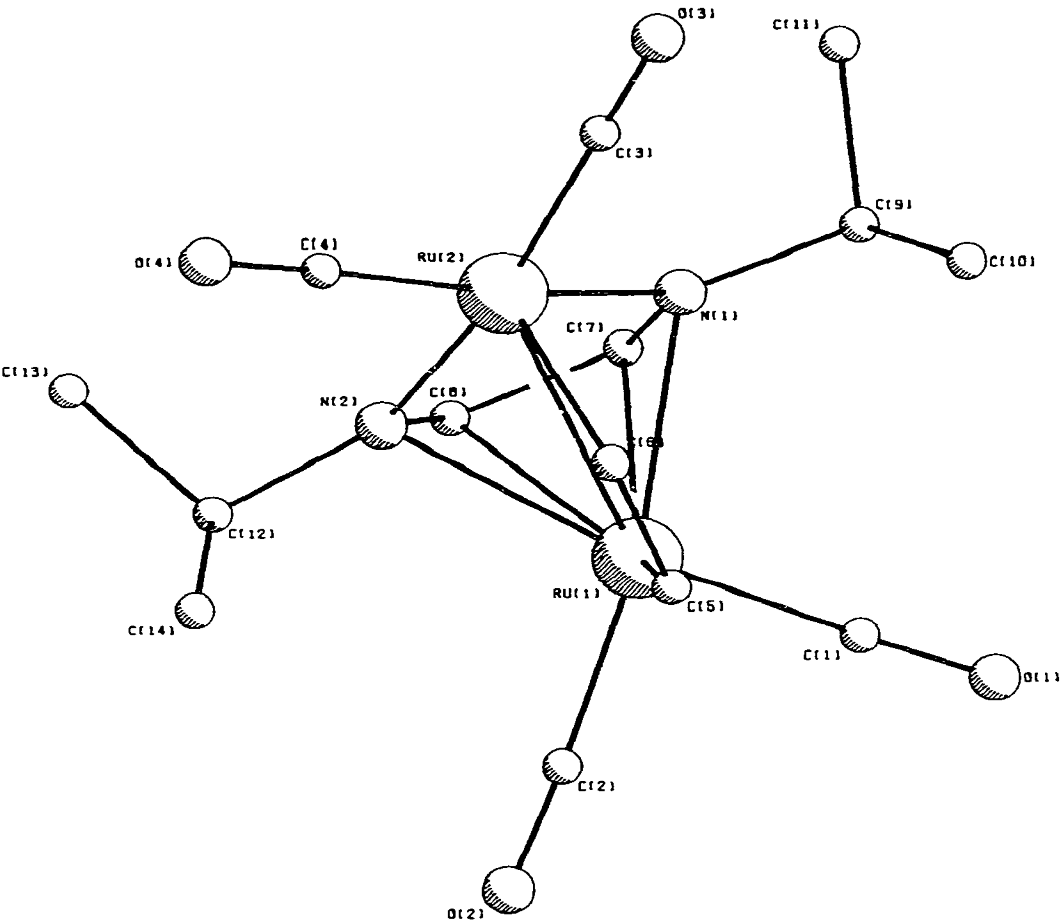

Fig. 1. The molecular structure of $Ru_2(CO)_4(\mu^2$-acetylene$)$ {glyoxalbis(isopropylimine)} (compound I).

ter contains two DAB ligands which form chelate rings with Ru(2) and Ru(3) and both ligands are coordinated to Ru(1) via the π-electron system. The 1,4-diazabutadienes are both σ-N, σ-N$'$, η^2-C=N, η^2-C=N$'$-coordinated analogously to the DAB ligands in compound I. The corresponding bond lengths are: Ru(1)—N(1) 2.20(1) Å, Ru(1)—C(9) 2.24(2) Å, Ru(1)—N(2) 2.24(2) Å, Ru(1)—C(10) 2.28(2) Å, Ru(2)—N(1) 2.07(1) Å, Ru(2)—N(2) 2.20(2) Å, Ru(1)—N(3) 2.26(2) N, Ru(1)—C(11) 2.25(2) Å, Ru(1)—N(4) 2.17(2) Å, Ru(1)—C(12) 2.23(2) Å, Ru(3)—N(3) 2.09(2) Å and Ru(3)—N(4) 2.09(2) Å.

In order to satisfy the effective atomic number rule the Ru(2)—Ru(3) interaction should not be regarded as a bond. The bond length of 2.99(2) Å is also rather long for a Ru—Ru single bond. However, some bonding interaction between Ru(2) and Ru(3) may occur as the result of delocalisation of electron density within the metal core.

In the ^{1}H NMR spectra the signals for the imine hydrogen atoms appear at 6.17 and 6.56 ppm for compounds I and II, respectively. This is approximately

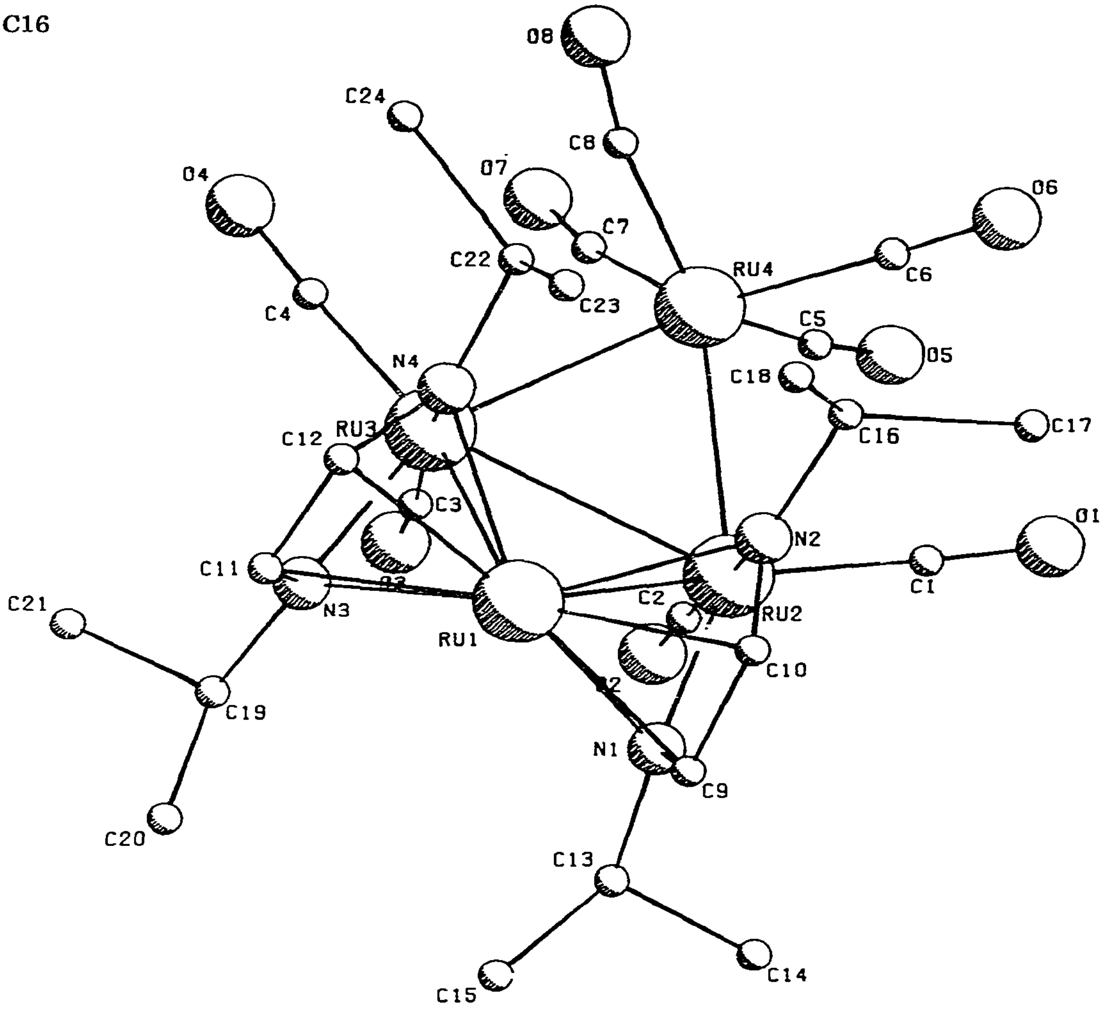

Fig. 2. The molecular structure of $Ru_4(CO)_8$$\{$glyoxalbis(isopropylimine)$\}_2$.

1.7 ppm upfield from the positions for the imine hydrogen atoms in the uncoordinated DAB ligand and confirms the σ^2-C=N,σ^2-C=N′ coordination of N=C—C=N skeleton in the complexes.

Detailed information about the structures, the formation of complexes, and the spectroscopic properties will be published in a forthcoming full paper.

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