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Binuclear Metal Carbonyl DAB Complexes. III. Activation of a C=N Double Bond in $Ru_2(CO)_6(DAB)$ Complexes (DAB = 1,4-diazabutadiene). C–C Bond Formation between Two DAB Ligands

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Recently a variety of mono- and dinuclear metal carbonyl DAB complexes (DAB = 1,4-diazabutadiene = α-diimine) have been prepared and the electronic and spectroscopic properties investigated [1–6]. In almost all complexes the DAB ligand is σ, σ-coordinated to the metal carbonyl fragment via the two lone pairs on nitrogen. Only one example has been reported where the π-electrons were involved in the metal-to-ligand bonding [7], while for some reactions of coordinated DAB ligands π-coordinated intermediates were assumed [8].

In this preliminary paper on ruthenium carbonyl DAB complexes, the earlier assumption that π-coordination is very important for the activation of the C=N double bond will be shown to be correct.

Ruthenium carbonyl reacts with DAB ligands according to equation (1).

$$2/3Ru_3(CO)_{12} + DAB \rightarrow Ru_2(CO)_6DAB + 2CO \quad (1)$$

The spectroscopic properties of $Ru_2(CO)_6(DAB)$ show that these complexes are isostructural to $Fe_2(CO)_6(DAB)$ of which a crystal structure is known [7]. In these complexes the DAB ligand is a six electron donor including one pair of π-electrons. Apart from the crystal structure of $Fe_2(CO)_6$(c-hex–N=CH–CH=N–c-hex) the σ, π-coordination can be deduced from the NMR data. As a result of the asymmetric coordination a double set of resonances has been observed in the NMR spectra and the two imine protons appear as an AX-pattern in ^1H NMR spectra at about 7.5 and 3.5 ppm with a coupling constant of 1.9 Hz (in $CDCl_3$). The large upfield shift for one of the imine protons is indicative for π-coordination (see Table I). The structure of $Ru_2(CO)_6(DAB)$, which is shown in Fig. 1 (I), is also confirmed by the ν(CO) pattern in the IR spectra which is similar to that of $Fe_2(CO)_6(DAB)$.

Spectroscopic evidence was found for the existence of a mixed Ru–Fe complex, prepared from $Fe(CO)_3(DAB)$ (R_1 = tbu, R_2 = H) and $Ru_3(CO)_{12}$ according to equation (2).

$$Fe(CO)_3(DAB) + 1/3Ru_3(CO)_{12} \rightarrow FeRu(CO)_6(DAB) + CO \quad (2)$$

The ^1H NMR and IR data of $FeRu(CO)_6(DAB)$ show that these complexes are isostructural to the homonuclear $Fe_2(CO)_6(DAB)$ and $Ru_2(CO)_6(DAB)$ complexes, of which the structure is shown in Fig. 1 (I).

The mixed complexes exist as two isomers, one with Fe on the π-coordinated part of the DAB ligand and one with Ru in this position. Both isomers can be formed during the reaction; the ratio in which they are formed depends on the reaction temperature and the reaction time. In Table I the spectroscopic properties of $M'M(CO)_6$(tbu–N=CH–CH=N-tbu) are listed.

$Ru_2(CO)_6(DAB)$ reacts with one equivalent of DAB to form $Ru_2(CO)_5(IAE)$ (IAE = bis[dialkylimino-μ-dialkylamino]ethaneN,N') according to equation (3).

$$Ru_2(CO)_6(DAB) + DAB \rightarrow Ru_2(CO)_5(IAE) + CO \quad (3)$$

To obtain an 18 electron configuration in the complexes which formally have the formula $Ru_2(CO)_5(DAB)_2$, the two DAB ligands should each donate five electrons to the ruthenium carbonyl fragment. The only coordination mode in which DAB donates five electrons known at present is in the case of the IAE ligand [8]. In this ligand the two DAB groups are linked to each other via the imine carbon atoms so that a ten electron donating system is formed.

TABLE I. Spectroscopic Properties of $MM'(CO)_6(DAB)$ (M = Fe, Ru, M' = Fe, Ru, DAB = tbu–N=CH–CH=N–tbu).

M	M'	IR:ν(CO) (cm^{-1})					^1H NMR Data (δ ppm in $CDCl_3$)
Fe	Fe	2053	2004	1981	1968	1945	δ(tbu) = 1.20, 1.53; $\delta(H)^{im}$ = 3.33; 7.63^a
Ru	Ru	2069	2030	1994	1983	1961	δ(tbu) = 1.13, 1.47; $\delta(H)^{im}$ = 3.28, 7.85^b

^{a}J = 1.9 Hz. ^{b}J = 2.2 Hz.

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The ^1H NMR pattern of $Ru_2(CO)_5(IAE)$ is identical to the ^1H NMR pattern of $Mo_2(CO)_6(IAE)$ for which a crystal structure is known [8]. The proposed structure of $Ru_2(CO)_5IAE$ is shown in Fig. 1 (II).

The C=N double bond in $Ru_2(CO)_6DAB$ is activated by π-coordination and in the reaction with DAB the Ru–C bond is broken in favour of the formation of a C–C bond.

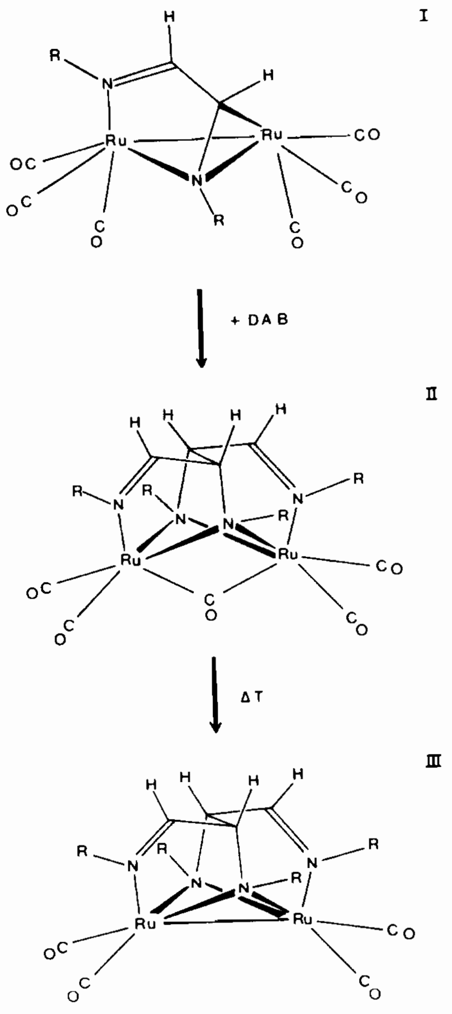

Fig. 1. Reaction sequence for the reaction of DAB and $Ru_3(CO)_{12}$.

The spectroscopic properties of $Ru_2(CO)_5IAE$ are listed in Table II. As a result of the C–C bond formation one of the ^1H NMR signals of the imine protons shifts from 8 ppm in the free ligand to 3.7 ppm in the IAE complex. The imine protons on the remaining HC=N–R moieties of the IAE system appear at 8 ppm in the ^1H NMR spectra (see Table II).

In the IR spectra one band near 1700 cm^{-1} and three bands between 2100 and 1900 cm^{-1} can be observed which is in agreement with the proposed structure shown in Fig. 1 (II).

$Ru_2(CO)_5IAE$ reacts further to form $Ru_2(CO)_4$-IAE.

$$Ru_2(CO)_5(IAE) \rightarrow Ru_2(CO)_4(IAE) + CO \qquad (4)$$

Whether $Ru_2(CO)_5(IAE)$ or $Ru_2(CO)_4(IAE)$ is the stable end product strongly depends on the substituents attached to the nitrogen atoms. In case of R = tert-butyl, $Ru_2(CO)_5(IAE)$ is the stable end product while in case of R = i-propyl $Ru_2(CO)_4(IAE)$ is formed.

In these complexes the bridging carbonyl group is lost and a metal–metal bond is formed, as evidenced by the disappearance of the band at 1700 cm^{-1} in the IR spectra (see Fig. 1 (III)). The spectroscopic properties of the IAE complexes are listed in Table II.

The activation of the C=N bond and subsequent C–C bond formation does not occur in $Fe_2(CO)_6$-DAB. Whether or not $RuFe(CO)_6(DAB)$ can form IAE complexes is still uncertain. Under the conditions at which $Ru_2(CO)_6(DAB)$ rapidly reacts to form $Ru_2(CO)_5(IAE)$ or $Ru_2(CO)_4(IAE)$ very long reaction times are necessary to have a reaction at all. The reactivity of each of the isomers is still subject of further investigations.

Experimental

^1H NMR spectra have been recorded on a Varian T-60 NMR apparatus or on a Varian XL-100 apparatus using FT-technique, ^{13}C NMR spectra have been obtained with a Varian CFT-20 spectrometer and IR spectra have been recorded on a Perkin Elmer 283 spectrophotometer. The microanalyses gave satis-

TABLE II. Spectroscopic Data of $Ru_2(CO)_n(IAE)$ ($n = 4, 5, R_1$ = tbu; ipr; R_2 = H).

Complex	IR ν(CO)				^1H NMR Data (δ ppm in $CDCl_3$)
$Ru_2(CO)_5(IAE)(tbu, H)$	2014	1994	1937	1703	$\delta(CH_3)^{tbu} = 1.13, 1.47; \delta(H) = 3.87, 8.41$
$Ru_2(CO)_5(IAE)(ipr, H)$	2025	1997	1943	1692	$\delta(CH_3)^{ipr} = 1.01/1.14, 1.26/1.29^a$ $\delta(CH)^{ipr} = 3.30, 3.43; \delta(H)^{im} = 3.77, 8.08$
$Ru_2(CO)_4(IAE)(ipr, H)$	1991	1947	1899		$\delta(CH_3)^{ipr} = 0.99/1.04^a, 1.30$ $\delta(CH)^{ipr} = 3.64, 3.68; \delta(H)^{im} = 3.77, 8.40$

[a] The isopropyl signals split since the two methyl groups are diastereotopic.

factory results and mass spectroscopic data were in agreement with the calculated masses.

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