

## BINUCLEAR METAL CARBONYL DAB COMPLEXES

### VIII \*. THE SYNTHESSES OF $\text{Os}_2(\text{CO})_6(\text{DAB})$ COMPLEXES (DAB = 1,4-DIAZABUTADIENE). SPECTROSCOPIC CHARACTERIZATION AND COMPARISON WITH ANALOGOUS IRON AND RUTHENIUM COMPLEXES

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#### Summary

The reaction of  $\text{Os}_3(\text{CO})_{12}$  with glyoxalbis(alkylimine) (alkyl = i-Pr, t-Bu) yielded  $\text{Os}_2(\text{CO})_6(\text{DAB})$  complexes. The complexes have been characterized by field desorption mass spectrometry,  $^1\text{H}$  NMR and IR spectroscopy. They are isostructural with  $\text{Fe}_2(\text{CO})_6(\text{DAB})$  and  $\text{Ru}_2(\text{CO})_6(\text{DAB})$ . In these complexes the DAB ligand is a six-electron donor system coordinated via two lone pairs and one pair of  $\pi$  electrons. The complex  $\text{Os}_3(\text{CO})_9(\text{i-PrN}=\text{CH}-\text{CH}=\text{N-iPr})$  was also isolated. This is the first example of a trinuclear metal carbonyl DAB complex, in which the DAB ligand is  $\sigma\text{-N}, \sigma\text{-N}', \eta^2\text{-C}=\text{N}$  coordinated. The reactions of the metal carbonyl complexes of the iron triad with DAB ligands are compared, and the ruthenium system shown to be the most versatile.

#### Introduction

In the course of our systematic study of the coordination properties of 1,4-diazabutadienes (DAB =  $\text{R}^1\text{N}=\text{C}(\text{R}^2)-\text{C}(\text{R}^{2'})=\text{NR}^1$ ) \*\*\* we investigated the reactions between DAB ligands and metal carbonyl complexes. It appeared that involvement of the  $\pi$ -electron system of the  $\text{N}=\text{C}-\text{C}=\text{N}$  skeleton in the coordination towards binuclear metal carbonyl units causes a strong activation of the

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\*\*\* 1,4-Diazabutadienes are prepared by condensation of primary amines and glyoxal or diacetyl. The name commonly used for the  $\alpha$ -diimine is derived from the diketone, as in glyoxalbis(t-butylimine). In this case, the systematic name should be 2,2,6,6-tetramethyl-3,6-diaza-1,5-octadiene. However, the ligand skeleton contains a 1,4-diazabutadiene fragment (abbreviated as DAB) and therefore the incorrect name bis(alkyl)-1,4-diazabutadiene is sometimes used in the literature.

$\eta^2$ -coordinated C=N bond. This activation was used to form carbon—carbon bonds between the coordinated DAB ligand and unsaturated small molecules [2].

The first example of this C—C bond formation was found in  $\text{Mo}_2(\text{CO})_6(\text{IAE})$  (IAE = bis $\{\mu(1\text{-}(\text{alkylamino})\text{-}2\text{-}(\text{alkylimino})\text{ethane-}N,N')\}$ ). In these complexes two DAB ligands are linked via two imine carbon atoms [3]. More recently  $\text{Ru}_2(\text{CO})_6(\text{DAB})$  complexes were observed as stable intermediates in the syntheses of  $\text{Ru}_2(\text{CO})_5(\text{IAE})$  [4,5], which are analogous to  $\text{Mo}_2(\text{CO})_6(\text{IAE})$ . The  $\text{Ru}_2(\text{CO})_6(\text{DAB})$  complexes contain a  $\sigma\text{-N}, \mu^2\text{-N}', \eta^2\text{-C=N}$  coordinated 1,4-diazabutadiene which is activated towards reaction with uncoordinated DAB ligands. It has now been found that  $\sigma\text{-N}, \mu^2\text{-N}', \eta^2\text{-C=N}'$  coordinated DAB ligands in  $\text{M}_2(\text{CO})_6(\text{DAB})$  ( $\text{M} = \text{Fe}, \text{Ru}$ ) react with  $\text{R}_2\text{C=CR}'$ ,  $\text{H}_2\text{C=C=CH}_2$ ,  $\text{RC}\equiv\text{CR}'$ ,  $\text{RC=N}$ ,  $\text{RN=C}$ ,  $(\text{CH}_3)_2\text{S=O}$ ,  $\text{S=C=S}$ , etc. showing that C—C bond formation between two DAB ligands is a special case of a general type of reaction [6].

At present the  $\sigma\text{-N}, \mu^2\text{-N}', \eta^2\text{-C=N}'$  and (the indistinguishable)  $\sigma\text{-N}, \sigma\text{-N}', \eta^2\text{-C=N}'$  coordination mode has been found for  $\text{M}_2(\text{CO})_6(\text{DAB})$  ( $\text{M} = \text{Fe}, \text{Ru}$ ) [4,5,7] and  $\text{MCo}(\text{CO})_6(\text{DAB})$  ( $\text{M} = \text{Mn}, \text{Re}$ ) [8]. Although in all these complexes the DAB ligand is highly reactive, IAE formation seems to be restricted to the ruthenium complexes. With excess DAB ligand,  $\text{Fe}_2(\text{CO})_6(\text{DAB})$  is converted into the mononuclear species  $\text{Fe}(\text{CO})_5(\text{DAB})$  (vide infra). Since the chemistry of  $\text{Ru}_2(\text{CO})_6(\text{DAB})$  and, in general, that of  $\text{Ru}_3(\text{CO})_{12}$  is markedly different from that of  $\text{Fe}_2(\text{CO})_6(\text{DAB})$  with DAB, we investigated the reaction of  $\text{Os}_3(\text{CO})_{12}$  with 1,4-diazabutadienes in order to obtain more information about the factors determining the reactivity of these ligands especially towards metal carbonyl complexes of the iron triad.

## Experimental

$^1\text{H}$  NMR spectra were recorded with a Varian T60 spectrometer,  $^{13}\text{C}$  NMR spectra with a Bruker WP 80 spectrometer and IR spectra with Perkin—Elmer 283 spectrophotometer. Mass spectra were recorded with a Varian MAT 711 spectrometer using field desorption techniques.

$\text{Os}_3(\text{CO})_{12}$  was obtained from commercial sources and was used without purification. DAB ligands were prepared according to standard procedures [9] and were freshly sublimed prior to use. Solvents were carefully dried and distilled. Silica was dried, activated and deoxygenated before use under vacuum for 3 h at  $180^\circ\text{C}$ .

### *Preparation of $\text{Os}_2(\text{CO})_6[t\text{-BuN=CH—CH=N-t-Bu}]$*

$\text{Os}_3(\text{CO})_{12}$  (300 mg) and glyoxalbis(*t*-butylimine) (200 mg) were refluxed for 72 h in 20 ml of *n*-octane under pure nitrogen. The reaction was stopped and the solution allowed to cool after which 150 mg of unreacted  $\text{Os}_3(\text{CO})_{12}$  was removed by filtration. The filtrate was evaporated to dryness under vacuum. A mixture of products was obtained, and was separated on a silica column of  $1 \times 20$  cm. The column was treated with 100 ml of *n*-hexane after which the product was eluted with diethyl ether. The ether fraction was evaporated to dryness and the product was recrystallized from *n*-pentane at  $-70^\circ\text{C}$ , yielding 135 mg of pale yellow crystals of  $\text{Os}_2(\text{CO})_6[t\text{-BuN=CH—CH=N-t-Bu}]$ . Traces of other

products were extracted from the column using dichloromethane and THF as eluents. However, according to the mass spectra the complexes were clusters containing fragments of the DAB ligand and were not studied in detail.

$\text{Os}_2(\text{CO})_6[\text{t-BuN}=\text{CH}-\text{CH}=\text{N-t-Bu}]$  was identified by its spectroscopic properties (vide infra) and by its field desorption (FD) mass spectrum  $[M]^+ = 720$  (based upon  $^{192}\text{Os}$ ) and  $M_{\text{calc}} = 716.4$  (based upon the atomic weight of Os: 190.2).

*Preparation of  $\text{Os}_2(\text{CO})_6[\text{i-PrN}=\text{CH}-\text{CH}=\text{N-i-Pr}]$*

The reaction was carried out with 200 mg of  $\text{i-PrN}=\text{CH}-\text{CH}=\text{N-i-Pr}$  as described above. The product however was isolated by use of high pressure liquid chromatography (HPLC), using a device as described elsewhere [10]. n-Hexane/dichloromethane was used as an eluent and seven products could be detected (see Fig. 1). The first fraction contained four complexes with similar retention behaviour, having a total yield of 10 mg. In three subsequent fractions the other products could be isolated. The last fraction contained  $\text{Os}_2(\text{CO})_6[\text{i-PrN}=\text{CH}-\text{CH}=\text{N-i-Pr}]$ . Recrystallization yielded 30 mg of pale yellow crystals.

$\text{Os}_2(\text{CO})_6[\text{i-PrN}=\text{CH}-\text{CH}=\text{N-i-Pr}]$  was characterized by its spectroscopic data (vide infra) and by the FD mass spectra  $[M]^+ = 692$  (based on  $^{192}\text{Os}$ ) and  $M_{\text{calc}} = 688.4$  (based on the averaged atomic weight of Os: 190.2). According to the mass spectra the other fraction contained clusters with fragments of the DAB ligand. Fraction II however, consisted of a deep orange-red complex which was characterized as  $\text{Os}_3(\text{CO})_9[\text{i-PrN}=\text{CH}-\text{CH}=\text{N-i-Pr}]$  by means of FD mass spectrometry:  $[M]^+ = 968$  (based on  $^{192}\text{Os}$ ) and  $M_{\text{calc}} = 962.6$  (based on the averaged atomic weight of Os: 190.2); IR absorptions ( $\nu(\text{CO})$ ) were observed at 2088m, 2059s, 2026s, 2020(sh), 1987s and 1970w  $\text{cm}^{-1}$  in n-pentane solution.

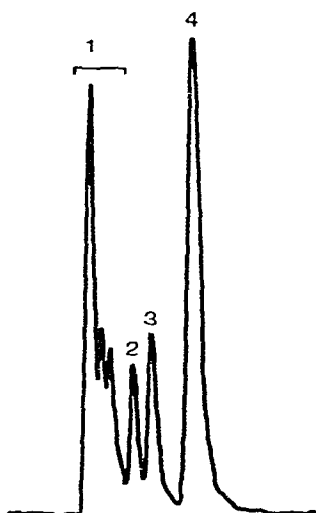


Fig. 1. HPLC diagram of the product mixture from  $\text{Os}_3(\text{CO})_{12}$  and  $\text{i-PrN}=\text{CH}-\text{CH}=\text{N-i-Pr}$ .

## Results

### IR spectroscopy

The  $\text{Os}_2(\text{CO})_6(\text{DAB})$  complexes have a  $\nu(\text{CO})$  pattern which is identical to that of  $\text{M}_2(\text{CO})_6(\text{DAB})$  complexes ( $\text{M} = \text{Fe}, \text{Ru}$ ). This strongly suggests that these complexes are isostructural and this is indeed confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR results (vide infra). The general structure of the  $\text{M}_2(\text{CO})_6(\text{DAB})$  complexes is shown in Fig. 2 and has been confirmed by a single crystal X-ray structure determination for  $\text{Fe}_2(\text{CO})_6[\text{chex-N}=\text{CH}-\text{CH}=\text{N-chex}]$  (chex = cyclohexyl) [7]. The six terminal carbonyl groups give rise to five strong IR absorptions, between  $2100$  and  $1900\text{ cm}^{-1}$ , which are listed in Table 1. The values for analogous iron and ruthenium complexes are included. Although the overall pattern is the same for the  $\text{M}_2(\text{CO})_6(\text{DAB})$  complexes ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ), as is shown in Fig. 3, small shifts can be observed which seem to depend on the metal.

### $^1\text{H}$ NMR data

The DAB ligand in  $\text{M}_2(\text{CO})_6(\text{DAB})$  complexes ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) acts as a six electron donor system, donating three electrons to each metal centre. The two lone pairs on the nitrogen atoms and one pair of  $\pi$ -electrons are involved in the coordination, causing an asymmetry within the electronic system of the  $\text{N}=\text{C}-\text{C}=\text{N}$  skeleton. This asymmetry is reflected in the  $^1\text{H}$  NMR spectrum by the appearance of two separate signals for the alkyl groups attached to nitrogen and also by the AX pattern for the two imine hydrogen atoms. The AX pattern consists of two doublets at ca. 8 and ca. 4 ppm respectively ( $J_{\text{AX}} 2\text{ Hz}$ ). The 8 ppm value agrees well with the shift data found for the free ligands and for  $\sigma, \sigma$ -coordinated DAB ligands [11] and is therefore assigned to the imine hydrogen atom on the  $\sigma$ -coordinated  $(\text{H})\text{C}=\text{N}$  moiety. An upfield shift may be expected after  $\eta^2\text{-C}=\text{N}$  coordination as the result of a strong olefinic shielding and consequently the doublet near 4 ppm is assigned to the  $\eta^2$ -coordinated  $(\text{H})\text{C}=\text{N}$  fragment.

Comparison of the chemical shifts of a series of analogous  $\text{M}_2(\text{CO})_6(\text{DAB})$  complexes ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) as given in Table 2, shows some unexpected features. The chemical shift values of the imine hydrogen atoms (which are very sensitive to small electronic disturbances of the  $\text{N}=\text{C}-\text{C}=\text{N}$  skeleton) are comparable for the iron and ruthenium complexes. However, a significant down-

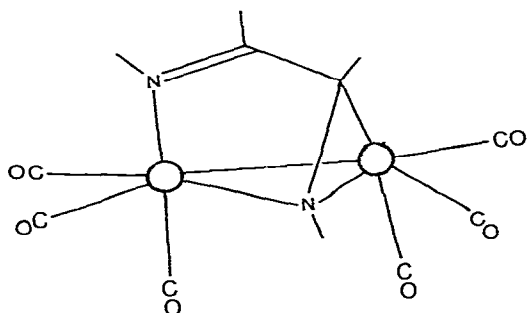


Fig. 2. Structure of  $\text{M}_2(\text{CO})_6(\text{DAB})$  complexes ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ).

TABLE 1

$\nu(\text{CO})$  FREQUENCIES OF  $\text{M}_2(\text{CO})_6(\text{DAB})$  COMPLEXES ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) IN *n*-PENTANE SOLUTIONS

Complex	$\nu(\text{CO})$ ( $\text{cm}^{-1}$ )
$\text{Fe}_2(\text{CO})_6[\text{glyoxalbis}(\text{t-butylimine})]$	2053, 2003, 1981, 1969, 1945
$\text{Ru}_2(\text{CO})_6[\text{glyoxalbis}(\text{t-butylimine})]$	2069, 2030, 1994, 1983, 1961
$\text{Os}_2(\text{CO})_6[\text{glyoxalbis}(\text{t-butylimine})]$	2067, 2026, 1987, 1971, 1953
$\text{Fe}_2(\text{CO})_6[\text{glyoxalbis}(\text{isopropylimine})]$	2057, 2005, 1987, 1975, 1945
$\text{Ru}_2(\text{CO})_6[\text{glyoxalbis}(\text{isopropylimine})]$	2067, 2025, 1999, 1988, 1961
$\text{Os}_2(\text{CO})_6[\text{glyoxalbis}(\text{isopropylimine})]$	2069, 2028, 1990, 1974, 1955

field shift is observed for the osmium complexes, especially for the imine hydrogen atom on the  $\eta^2$ -coordinated imine moiety. If these results for the osmium complexes are interpreted in terms of direct DAB ligand-metal interactions, this would point to a deshielding effect caused by either stronger  $\sigma$ -interactions or weaker  $\pi$ -interactions, although the opposite would be expected.

### $^{13}\text{C}$ NMR data

The  $^{13}\text{C}$  NMR data of  $\text{M}_2(\text{CO})_6(\text{DAB})$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) are given in Table 3. A signal at 175 ppm can be assigned to the carbon atom in the  $\sigma$ -coordinated part of the DAB ligand. This value is about 20 ppm downfield from that for the

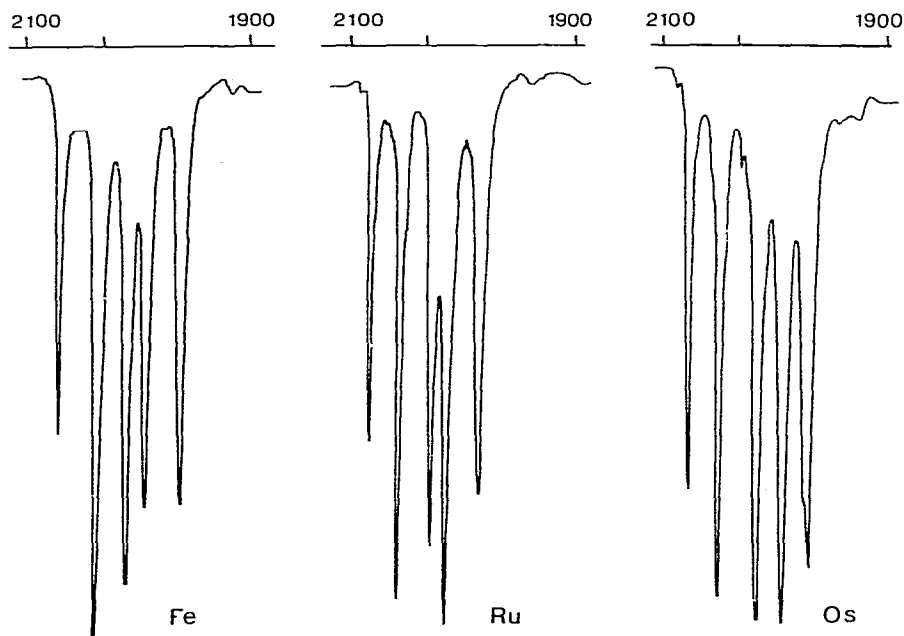


Fig. 3. The IR spectra of  $\text{M}_2(\text{CO})_6[\text{t-BuN}=\text{CH}-\text{CH}=\text{N-t-Bu}]$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) between 2100 and 1900  $\text{cm}^{-1}$ .

TABLE 2

$^1\text{H}$  NMR DATA FOR  $\text{M}_2(\text{CO})_6(\text{DAB})$  COMPLEXES ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) OBTAINED IN  $\text{CDCl}_3$  SOLUTIONS ( $\delta$ , ppm RELATIVE TO TMS)

Complex	$\delta$ (ppm)	Imine hydrogens
$\text{Fe}_2(\text{CO})_6(\text{i-Pr}, \text{H})$	1.02/1.15 1.58/1.68	3.30 7.52
$\text{Ru}_2(\text{CO})_6(\text{i-Pr}, \text{H})$	1.02/1.09 1.37/1.43 3.18	3.24 7.70
$\text{Os}_2(\text{CO})_6(\text{i-Pr}, \text{H})$	1.05/1.13 1.29/1.49	3.98 8.17
$\text{Fe}_2(\text{CO})_6(\text{t-Bu}, \text{H})$	1.20 1.53	3.33 7.63
$\text{Ru}_2(\text{CO})_6(\text{t-Bu}, \text{H})$	1.20 1.40	3.41 7.79
$\text{Os}_2(\text{CO})_6(\text{t-Bu}, \text{H})$	1.20 1.38	4.06 8.12

TABLE 3

$^{13}\text{C}$  NMR DATA FOR  $\text{M}_2(\text{CO})_6[\text{t-BuN}=\text{CH}-\text{CH}=\text{N-tBu}]$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) OBTAINED IN  $\text{CDCl}_3$  SOLUTIONS AT ROOM TEMPERATURE ( $\delta$ , ppm RELATIVE TO TMS)

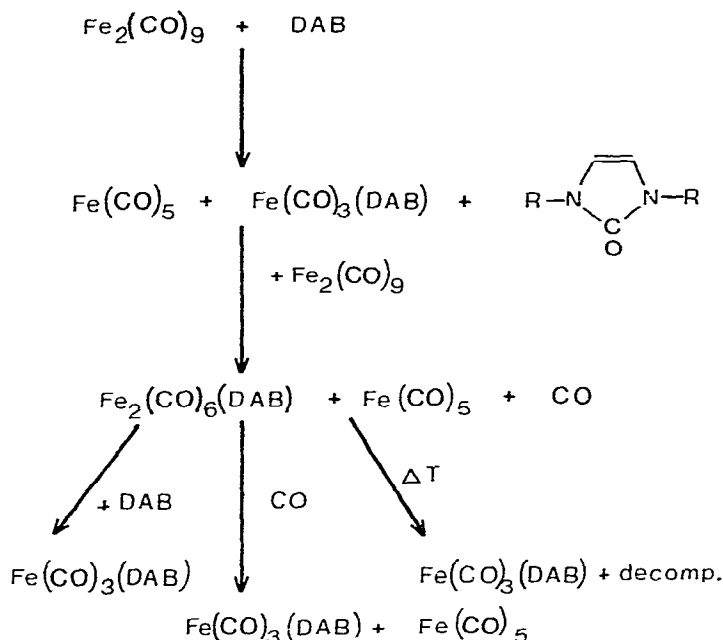
Complex	t-Bu signals	Imine carbons
$\text{Fe}_2(\text{CO})_6(\text{DAB})$	30.8, 32.9 60.1 64.4	60.1 175.1
$\text{Ru}_2(\text{CO})_6(\text{DAB})$	30.2 32.8 59.4 61.3	56.3 173.5
$\text{Os}_2(\text{CO})_6(\text{DAB})$	30.3 32.0 61.2 62.2	49.3 176.1

free ligand [11–13]. At 50 ppm a signal is found which is assigned to the imine carbon atom on the  $\eta^2$ -coordinated fragment of the ligand and this assignment is confirmed by off resonance experiments. These data confirm the interpretation of the electronic structure of the DAB ligand in the  $\text{M}_2(\text{CO})_6(\text{DAB})$  complexes ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) based on the  $^1\text{H}$  NMR results.

Interestingly, the chemical shift values of the imine carbon atom on the  $\eta^2\text{-C}=\text{N}$  coordinated fragment decrease in the order  $\text{Fe} > \text{Ru} > \text{Os}$ . Such an order would be expected as the result of an increasing  $\pi$ -interaction between the metal and the  $\text{N}=\text{C}-\text{C}=\text{N}$  skeleton. However, the trend is opposite to that as observed by the  $^1\text{H}$  NMR spectroscopy, showing that care has to be taken in interpreting these results in terms of an over-simplified MO model.

## Discussion

Comparison of the reactions of  $\text{Fe}_2(\text{CO})_9$  ( $\text{Fe}_3(\text{CO})_{12}$ ),  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Os}_3(\text{CO})_{12}$  with DAB ligands reveals some significant differences. The main product from the reactions between glyoxalbis(alkylimine) and  $\text{Os}_3(\text{CO})_{12}$  is the binuclear complex  $\text{Os}_2(\text{CO})_6(\text{DAB})$ . However, the overall yield is low due to the many side-reactions which occur under the drastic conditions required for a satisfactory conversion of  $\text{Os}_3(\text{CO})_{12}$ , a problem which appears to be general for four electron donating ligands [14]. The side-products contain DAB fragments due to either pyrolysis of the free ligand to generate highly reactive species, or decomposition of the final osmium carbonyl DAB complexes. However, the main product,  $\text{Os}_2(\text{CO})_6(\text{DAB})$  is a species of general formula  $\text{M}_2(\text{CO})_6(\text{DAB})$  which can be isolated for all the three elements of the iron triad. Therefore these isostructural complexes form a link in the comparison of the products obtained by reaction of DAB ligands with metal carbonyl clusters of the iron triad.



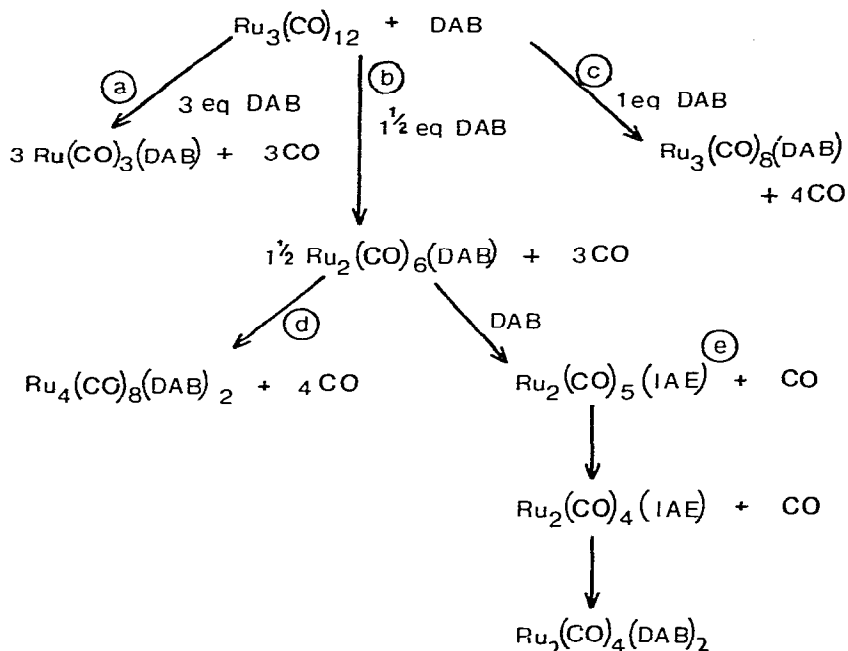
Scheme 1. Reactions of the system  $\text{Fe}_2(\text{CO})_9/\text{DAB}$ .

The reactions of DAB and  $\text{Fe}_2(\text{CO})_9$  are summarized in Scheme 1; some of them have already been discussed in the Introduction. The binuclear complex  $\text{Fe}_2(\text{CO})_6(\text{DAB})$  which is analogous to the  $\text{Os}_2(\text{CO})_6(\text{DAB})$  complex can be prepared for a variety of DAB ligands. However, the yields are low (generally less than 10%) and the complexes are rapidly converted into the mononuclear  $\text{Fe}(\text{CO})_3(\text{DAB})$  complexes, either by thermal decomposition, reaction with further DAB ligand or reaction with carbon monoxide [7]. Under oxygen-free conditions,  $\text{Fe}(\text{CO})_3(\text{DAB})$  is the thermodynamically favoured product.

One competing reaction is the formation of the five-membered ring imidazolone, which was formed in a semi-catalytic reaction [15]. This reaction is restricted to the iron carbonyl complexes and has not been observed for ruthenium and osmium; the reasons for which will be discussed later in this section.

The reactions of  $\text{Ru}_3(\text{CO})_{12}$  and DAB ligands are listed in Scheme 2. Three reaction pathways can be observed: formation of  $\text{Ru}_2(\text{CO})_6(\text{DAB})$  (the precursor for the IAE complexes which have already been discussed in the Introduction), mononuclear  $\text{Ru}(\text{CO})_3(\text{DAB})$  complexes and  $\text{Ru}_3(\text{CO})_8(\text{DAB})$  complexes. The actual complex formed strongly depends upon the nitrogen substituents and mononuclear  $\text{Ru}(\text{CO})_3(\text{DAB})$  complexes have only been formed with extremely bulky groupings. After prolonged heating  $\text{Ru}_2(\text{CO})_6(\text{DAB})$  dimerizes to give the tetranuclear species  $\text{Ru}_4(\text{CO})_8(\text{DAB})_2$ , which according to the crystal structure contain two  $\sigma, \sigma, \pi, \pi$ -coordinated DAB ligands [16].

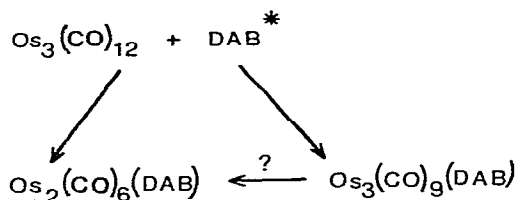
The metal-metal bond cleavage of  $\text{Fe}_2(\text{CO})_6(\text{DAB})$  and the dimerization of  $\text{Ru}_2(\text{CO})_6(\text{DAB})$  under comparable conditions illustrate the importance of the metal-metal bond strength in addition to the tendency to eliminate carbon monoxide at higher temperatures. The balance between these two factors deter-



Scheme 2. Reactions of the system  $\text{Ru}_3(\text{CO})_{12}/\text{DAB}$ . (a) When DAB = 2,4-dimethylpentyl-N=CH-CH=N-2,4-dimethylpentyl, 2,4,6-mesityl-N=CH-CH=N-2,4,6-mesityl, 2,6-xylyl-N=CH-CH=N-2,6-xylyl. (b) When DAB = t-Bu-N=CH-CH=N-t-Bu, i-Pr-N=CH-CH=N-i-Pr, chex-N=CH-CH=N-chex, i-PrN=CH-C(CH<sub>3</sub>)<sub>3</sub>-N-i-Pr, ptol-N=CH-CH=N-ptol. (c) When DAB = neop-N=CH-CH=N-neop, i-BuN=CH-CH=N-i-Bu. (d) When DAB = i-BuN=CH-CH=N-i-Bu, neop-N=CH-CH=N-neop, i-PrN=CH-CH=N-i-Pr, chex-N=CH-CH=N-chex. (e) IAE = bis[ $\mu$ -(2-{alkylimino}-1-{alkylimono}ethane)].

mines the stability of the end product.

A striking difference can be observed between the reaction pathways through which  $\text{Fe}_2(\text{CO})_6(\text{DAB})$  and  $\text{Ru}_2(\text{CO})_6(\text{DAB})$  are obtained. In the reaction of  $\text{Fe}_2(\text{CO})_9$  with DAB the metal carbonyl dimer will split into the relatively unreactive  $\text{Fe}(\text{CO})_5$  and the highly reactive intermediate  $\text{Fe}(\text{CO})_4$ . Consequently,  $\text{Fe}(\text{CO})_3(\text{DAB})$  is formed, and reacts with further  $\text{Fe}(\text{CO})_4$  to form  $\text{Fe}_2(\text{CO})_6(\text{DAB})$ . The ruthenium complex is formed by displacement of CO groups from  $\text{Ru}_3(\text{CO})_{12}$  and the trinuclear complex  $\text{Ru}_3(\text{CO})_{10}(\text{DAB})$  has been proposed as an intermediate which reacts either forming  $\text{Ru}_2(\text{CO})_6(\text{DAB})$  or  $\text{Ru}_3(\text{CO})_8(\text{DAB})$ , depending on the substituents on the 1,4-diazabutadiene. This



\* excess

Scheme 3. Reactions of the system  $\text{Os}_3(\text{CO})_{12}/\text{DAB}$  (omitting non relevant side reactions).



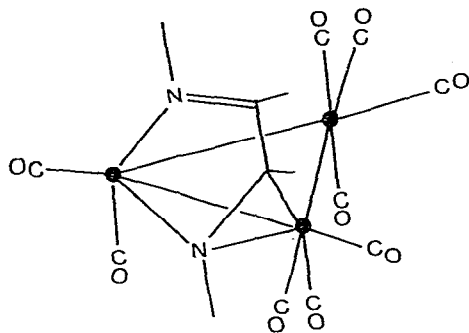


Fig. 4. The proposed structure of  $\text{Os}_3(\text{CO})_9(\text{DAB})$ .

reaction pathway has been confirmed recently by kinetic measurements using high pressure liquid chromatography to monitor the reaction [17].

Scheme 3 shows the reactions of  $\text{Os}_3(\text{CO})_{12}$  with DAB ligands and it is assumed that the reaction pathways are in the main similar to that of  $\text{Ru}_3(\text{CO})_{12}$ . However,  $\text{Os}_3(\text{CO})_{12}$  is less reactive than  $\text{Ru}_3(\text{CO})_{12}$ , which accounts for the fact that the reaction stops at the formation of  $\text{Os}_2(\text{CO})_6(\text{DAB})$ , even though the 1,4-diazabutadiene is present in an excess in the reaction mixture.  $\text{Os}_2(\text{CO})_6(\text{DAB})$  complexes are formed in refluxing n-octane. Neither  $\text{Fe}_2(\text{CO})_6(\text{DAB})$  nor  $\text{Ru}_2(\text{CO})_6(\text{DAB})$  is stable under these conditions, indicating that the order in stability is  $\text{Fe} < \text{Ru} < \text{Os}$ .

Interestingly,  $\text{Os}_3(\text{CO})_9(\text{DAB})$  could be isolated, and this is supporting evidence for the existence of  $\text{M}_3(\text{CO})_{10}(\text{DAB})$  ( $\text{M} = \text{Ru}, \text{Os}$ ) as an unstable intermediate in the production of both  $\text{Ru}_3(\text{CO})_8(\text{DAB})$  and  $\text{Os}_2(\text{CO})_6(\text{DAB})$ .  $\text{Os}_3(\text{CO})_9(\text{DAB})$  can also be envisaged as a stable analogue of “ $\text{Ru}_3(\text{CO})_9(\text{DAB})$ ” which might participate as intermediate in the formation of  $\text{Ru}_3(\text{CO})_8(\text{DAB})$ .

On the basis of electron counting, the DAB ligand in  $\text{Os}_3(\text{CO})_9[\text{i-PrN}=\text{CH}-\text{CH}=\text{N-i-Pr}]$  should be regarded as a six-electron donor system, analogous to the coordination mode of the 1,4-diazabutadiene in  $\text{Os}_2(\text{CO})_6(\text{DAB})$ . The proposed structure for  $\text{Os}_3(\text{CO})_9(\text{DAB})$  is shown in Fig. 4.

## Conclusion

It has been shown that  $\text{Fe}_2(\text{CO})_6(\text{DAB})$  is formed by a mechanism which is different from that for formation of  $\text{Ru}_2(\text{CO})_6(\text{DAB})$  and  $\text{Os}_2(\text{CO})_6(\text{DAB})$ . Consequently, imidazolone formation is restricted to the reaction of  $\text{Fe}_2(\text{CO})_6$  with DAB. A detailed discussion of the possible mechanism by which imidazolone is formed is given elsewhere [15]. The reactions of DAB with the metal carbonyl complexes of the iron triad have in common the formation of isostructural  $\text{M}_2(\text{CO})_6(\text{DAB})$  complexes, but markedly different stabilities were observed for the complexes. The greatest variety of products was obtained for ruthenium carbonyl derivatives due to a favourable balance between the metal-metal bond strength and the ability to eliminate or substitute carbonyl groups. With iron carbonyl derivatives there is a strong tendency to produce mononuclear species, a behaviour which has been ascribed to the fact that

iron—iron bonds are relatively weak (as compared with Ru—Ru or Os—Os bonds).  $\text{Os}_3(\text{CO})_{12}$  is very unreactive towards 1,4-diazabutadiene, and this prevents an extensive comparison. However, on the basis of the reactions with two DAB ligands it is shown that  $\text{Os}_3(\text{CO})_{12}$  is comparable with  $\text{Ru}_3(\text{CO})_{12}$ .

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