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BINUCLEAR METAL CARBONYL DAB COMPLEXES

VII *. A ^{13}C NMR INVESTIGATION OF MM'(CO)$_6$(DAB) COMPLEXES (M = M' = Fe, Ru; M = Mn, Re AND M' = Co; DAB = 1,4-DIAZABUTADIENE). DYNAMIC BEHAVIOUR OF σ^2-N, σ^2-N', η^2-C=N COORDINATED DAB IN MnCo(CO)$_6$(DAB) AND LOCAL SCRAMBLING OF THE CARBONYL GROUPS

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Summary

The ^{13}C NMR spectra of MM'(CO)$_6$(DAB) complexes (M = M' = Fe, Ru; M = Mn, Re and M' = Co; DAB = 1,4-diazabutadiene) show very characteristic features which are directly related with the bonding mode of the DAB ligand to the binuclear metal carbonyl fragment. In these complexes the DAB ligand is σ^2-N, μ^2-N', η^2-C=N or σ^2-N, σ^2-N', η^2-C=N coordinated. Chemical shifts of about 175 ppm are observed for the σ-coordinated imine fragments and about 60 or 80 ppm for the η^2-C=N coordinated imine fragments.

In MnCo(CO)$_6$[diacetylbis(cyclopropylimine)] the DAB ligand is fluxional, and the changes in the spectra when recorded at various temperatures can be interpreted in terms of an exchange between the σ- and π-coordinated part of the DAB ligand.

The homodinuclear M$_2$(CO)$_6$(DAB) complexes (M = Fe or Ru) contain M(CO)$_3$ fragments on which the carbonyl groups are involved in a local scrambling process with very different activation parameters (T_c = —50°C and +85°C).

MCo(CO)$_6$(DAB) complexes (M = Mn, Re), which contain a semi-bridging carbonyl group according to the crystal structure, show rapid interchange of this carbonyl group with the terminal carbonyl groups on cobalt. The electronic balance is kept in equilibrium by an internal compensation within the DAB ligand.

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Introduction

Recently, a series of homo- and heterodinuclear metal carbonyl 1,4-diazabutadiene (DAB) complexes has been prepared which have in common the six electron donor mode of the DAB ligand. The DAB ligand is coordinated via the two lone-pairs on nitrogen and via one pair of π-electrons, resulting in σ^2-N, σ^2-N$'$, η^2-C=N$'$ or σ^2-N, μ^2-N$'$, η^2-C=N$'$ coordination. Examples of these complexes are: $Fe_2(CO)_6(DAB)$ [1], $Ru_2(CO)_6(DAB)$ [2,3], $FeRu(CO)_5(DAB)$ [2], $Os_2(CO)_6(DAB)$ [4], $MnCo(CO)_6(DAB)$, $ReCo(CO)_6(DAB)$ [5] and $Ru_2(CO)_4(DAB)_2$ [3].

The structure of the complexes given in Figure 1 show the structural features of the 1,4-diazabutadiene ligand as established by X-ray structural studies of $Fe_2(CO)_6$[glyoxalbis(cyclohexylimine)] [1], $MnCo(CO)_6$[glyoxalbis(tert-butylimine)] [5] and $Ru_2(CO)_4$[glyoxalbis(isopropylimine)]$_2$ [3].

In general, 1,4-diazabutadienes coordinate via the lone pairs on nitrogen, forming five membered chelate rings. Involvement of the π-electron system in

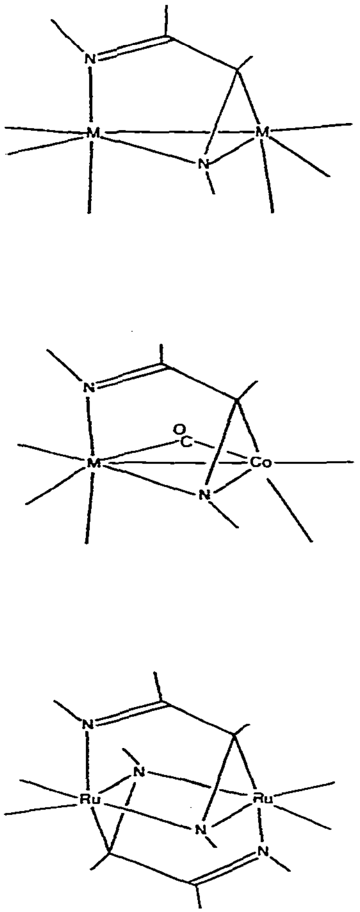

Fig. 1. Structures of $M_2(CO)_6(DAB)$ (M = Fe, Ru, Os) (top) $MCo(\mu$-$CO)_6(DAB)$ (M = Mn, Re) (middle) and $Ru_2(CO)_4(DAB)_2$ (bottom) which have in common the σ-N, μ^2-N$'$, η^2-C=N coordinated mode.

the coordination of the DAB ligands is at present encountered only in the class of compounds mentioned above.

The σ^2-N, μ^2-N', η^2-C=N' coordination mode of the DAB ligands is of special interest for synthetic purposes, since the η^2-C=N coordinated part of the ligand appeared to be highly activated for further reaction. In the series $M_2(CO)_6$-(DAB) (M = Fe, Ru, Os) the iron and ruthenium complexes (no studies were made with $Os_2(CO)_6(DAB)$) are very reactive towards hetero-acetylenes and hetero-olefins (DAB included). An example of this behaviour is the dimerisation of DAB ligands on the binuclear Ru complexes to give $Ru_2(CO)_5(IAE)$ (IAE = bis{(alkylimino)-(alkylamino)ethane}) [2,3]. In these complexes two DAB ligands are coupled via two imine carbon atoms. In the iron-ruthenium-osmium triad, IAE complexes have only been isolated for ruthenium, but small amounts of $Os_2(CO)_4(IAE)$ were detected by means of mass spectrometry [25]. IAE formation has not yet been observed with $MCo(CO)_6(DAB)$ complexes (M = Mn, Re) [5].

Although in each of these complexes the DAB is similarly bonded, the extent of activation is obviously not the same or there are additional, unknown factors determining the reactivity of the η^2-C=N coordinated imine fragment.

^{13}C NMR data give information about the electronic rearrangements within the DAB ligand after σ^2-N, μ^2 (or σ^2)-N', η^2-C=N' coordination. In this paper we compare the ^{13}C NMR spectra of the $MM'(CO)_6(DAB)$ (M = M' = Fe, Ru; M = Mn, Re and M' = Co) and of the $Ru_2(CO)_4(DAB)_2$ complexes in order to find out whether there is a correlation between the chemical shifts of the imine carbon atoms in the η^2-coordinated C=N fragments and their tendency to react with unsaturated organic systems to give C—C bond formation (of which IAE formation is one example).

Experimental

The complexes were prepared according to literature procedures [1—5]. The ^{13}C NMR spectra were recorded with a Bruker WP 80 spectrometer, using $CDCl_3$, CD_2Cl_2, $C_2D_2Cl_4$ and $CD_3C_6D_5$ as solvents and TMS as an internal standard. Variable temperature measurements were carried out using the Bruker variable temperature accessories to the Bruker WP 80 spectrometer. The reported temperatures are accurate within ±1°C.

Results and discussion

The DAB ligands

The chemical shifts of the imine carbon atoms of coordinated DAB ligands appear to be indicative for the coordination mode of the ligand. The σ,σ-coordinated DAB ligands in metal carbonyl- and metal carbonyl halide 1,4-diazabutadiene complexes give chemical shifts for the imine carbon atoms between 140 and 175 ppm, depending on the metal in the chelate ring [7]. These values are in the range of 20 ppm upfield to 20 ppm downfield compared with the values for the free ligands.

Due to the asymmetric coordination of the DAB ligands in $MM'(CO)_6(DAB)$ (M = M' = Fe, Ru; M = Mn, Re and M' = Co) and in $Ru_2(CO)_4(DAB)_2$, both

TABLE 1

^{13}C NMR DATA OF MM′$(CO)_6$(DAB) AND $Ru_2(CO)_4$(DAB) COMPLEXES (δ, ppm RELATIVE TO TMS) AT 20°C

Complex	Substituents	Imine-C		CO
$Fe_2(CO)_6$(t-Bu—N=CH—CH=N—t-Bu)	30.8; 32.9; 60.1; 64.4	60.1	175.1	205.5; 210.6; 214.3; 218.9
$Fe_2(CO)_6$(i-Pr—N=CH—CH=N—i-Pr)	22.0/22.8 [a]; 26.8; 63.5; 66.8	58.9	173.3	213.9
$Fe_2(CO)_6$(c-hex—N=CH—CH=N—c-hex)	25.1; 25.4; 26.0; 26.2; 27.0; 29.4; 32.8; 33.5; 38.6; 39.0; 67.4; 74.9	63.7	173.6	214.0; 207.5
$Fe_2(CO)_6$(i-Pr—N=C(CH_3)—CH=N—i-Pr)	15.5(CH_3); 20.9/23.1 [a]; 26.5/26.9 [a]; 66.7; 68.1	54.4	184.9	205.0; 210.7; 214.2; 218.5
$Ru_2(CO)_6$(t-Bu—N=CH—CH=N—t-Bu)	30.2; 32.8; 59.4; 61.3	56.3	173.5	216.1; 199.0
$Ru_2(CO)_6$(c-hex—N=CH—CH=N—c-hex)	25.1; 25.7; 25.9; 26.0; 32.8; 33.14; 38.7; 40.1; 68.2; 73.6	61.5	173.6	
$Ru_2(CO)_4$(i-Pr—N=CH—CH=N—i-Pr$)_2$	21.9/23.7 [a]; 23.9/25.4; 61.5; 63.7	63.8	172.1	200.5; 203.6
$CoMn(CO)_6$(t-Bu—N=CH—CH=N—t-Bu)	30.5; 33.1; 62.3; 63.0	74.4	171.3	
$CoMn(CO)_6$(i=Pr=CH—CH=N—i-Pr)	22.7/23.4 [a]; 25.4/27.6 [a]; 61.8; 65.1	75.8	170.5	209.3; 218.5; 222.2; 223.3
$CoMn(CO)_6$(i-Pr—N=CH_3—CH=N—i-Pr)	16.4(CH_3); 21.2/23.7 [a]; 25.6/27.6 [a]; 54.6; 65.1	80.8	180.2	
$CoMn(CO)_6$(c-hex—N=CH—CH=N—c-hex)	25.18; 25.4; 26.0; 26.2; 33.4; 34.0; 37.6; 39.3; 69.8; 73.6	76.6	170.7	
$CoMn(CO)_6$(c-Pr—N=CH—CH=N—c-Pr)	9.5/7.5 [a]; 11.9/9.8 [a]; 49.1/43.5 [a]	79.6	172.1	210.0; 220.4; 223.1; 225.2
$CoMn(CO)_6$(c-Pr—N=C(CH_3)—C(CH_3)=N—c-Pr)	8.8/9.0 [a]; 10.6/13.0 [a]; 18.8; 19.5(CH_3); 38.2; 43.6	96.7	186.5	208.2; 218.8; 221.8; 224.5
$CoRe(CO)_6$(t-Bu—N=CH—CH=N—t-Bu)	30.5; 33.1; 63.1	75.5	172.4	
$CoRe(CO)_6$(c-hex—N=CH—CH=N—c-hex)	23.8; 24.8; 32.8; 33.6; 36.8; 38.1; 70.7; 71.8	78.6	173.6	

[a] Values corresponding with diastereotopic pairs.

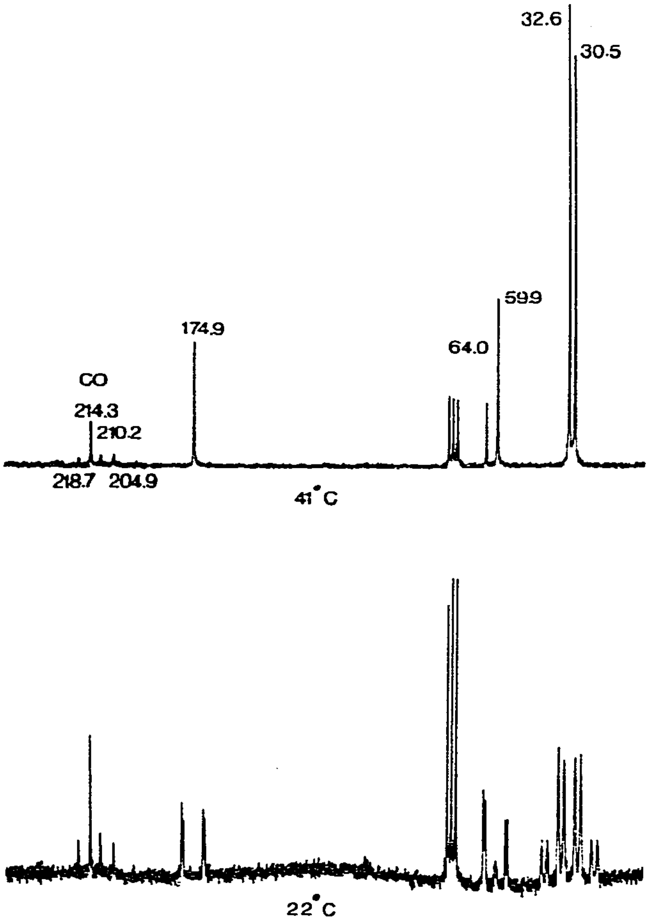

Fig. 2. ^{13}C NMR spectra of $Fe_2(CO)_6$[t-Bu—N=CH—CH=N—t-Bu]; ^{1}H decoupled (top) and without decoupling (bottom).

(R')C=N—R halves of the DAB ligand are anisochronous, which is reflected in the ^{13}C NMR pattern of the ligand. This is shown in Figure 2.

At 175 ppm a signal appears which is near the value for the imine carbon atoms in free ligands and for σ,σ-coordinated DAB ligands [6—10]. This signal is therefore assigned to the imine carbon atom of the σ^2-N coordinated C=N fragment of the ligand. The chemical shifts for the imine carbon atoms of the η^2-C=N coordinated imine fragments are found between 50 and 80 ppm which is approximately 100 ppm upfield compared with the free ligand positions. This olefinic shielding is as expected for imine ligands which are coordinated via the π-electron system. In Table 1 the ^{13}C NMR data are listed of MM'$(CO)_6$-(DAB) and $Ru_2(CO)_4(DAB)_2$ complexes.

Figure 2a gives the ^{13}C NMR spectrum of $Fe_2(CO)_6$[glyoxalbis(tert-butylimine)] and shows the non proton decoupled spectrum which confirms the assignment of the signals at 175.1 and 60.1 ppm to the imine carbon atoms.

Table 1 shows that on the basis of the chemical shifts for the imine carbon atoms in the η^2-coordinated C=N moiety, the complexes can be divided into two classes. Class I contains the $M_2(CO)_6(DAB)$ (M = Fe, Ru) and $Ru_2(CO)_4(DAB)_2$ complexes for which the imine C signals are observed near 60 ppm. Class II consists of $MCo(CO)_6(DAB)$ (M = Mn, Re) complexes for which the imine-C chemical shifts are near 80 ppm.

In class I the chemical shift differences are small, which points to a similar electron density at the carbon centre in the η^2-coordinated imine fragments. Consequently, the different chemical behaviour between $Fe_2(CO)_6(DAB)$ and $Ru_2(CO)_6(DAB)$ complexes seems not to be the result of different degrees of activation of the η^2-C=N system in the complexes. Other factors, probably associated with the metals, seem to predominate. The small downfield shifts for the class II complexes compared with class I compounds show that the bond order of the η^2-coordinated imine fragments in these complexes is still more than 1. This is in accordance with the ^1H NMR and crystallographic data.

Analogous conclusions were put forward for the π,π-coordinated mono-azadiene ligand in $Fe(CO)_3$(Ph—N=C(H)—C(H)=C(H)—Ph) [12]. The chemical shifts of the imine carbon atoms in $Fe(CO)_3$(aza-diene) (azadiene = t-Bu-N=C(H)—C(H)=C(H)—CH_3, Ph—N=C(H)—C(H)—Ph) are 110.2 and 104.4, respectively [11], which is in agreement with the conclusion based upon the X-ray structure determination [12] that the C=N bond order in the coordinated ligand is much greater than 1.

Interestingly, the chemical shift of 96.7 ppm of the imine carbon atom of the η^2-C=N coordinated fragment in $MnCo(CO)_6$[c-Pr—N=C(CH_3)—C(CH_3)=N—c-Pr] is 20 ppm downfield as compared with the chemical shifts for $MCo(CO)_6$[glyoxalbis(alkylimine)] derivatives (M = Mn, Re). The chemical shifts for the σ^2-N coordinated -(CH_3)C=N- fragments in $MnCo(CO)_6$[c-Pr—N=C(CH_3)—(CH_3)C=N—c-Pr] and in Mn(Co(CO)$_6$[i-Pr—N=C(H)—(CH_3)C=N—i-Pr] are 186.5 ppm and 180.2 ppm, respectively, which is 10 to 15 ppm downfield from the values for glyoxalbis(alkylimine) derivatives. These data point to the conclusion that -(H)C=NR moieties are better π-acceptors than -(CH_3)C=NR moieties and consequently will also give stronger η^2-C=N bonds. This is in agreement with earlier conclusions [5].

Dynamic behaviour of the DAB ligand in $MnCo(CO)_6$[c-Pr—N=C(CH_3)—(CH_3)-C=N—c-Pr]

The variable temperature spectra of $MnCo(CO)_6$[c-Pr—N=C(CH_3)—(CH_3)-C=N—c-Pr] which are given in Figure 3, show at —20°C the resonance pattern which can be expected for the σ^2-N, σ^2-N′, η^2-C=N′ coordinated diacetylbis(cyclopropylimine). At 50°C the signals of the methyl groups and the cyclopropyl ring appear as a single set of lines and the signals due to the imine carbon atoms have disappeared. This can be explained by a fast exchange between the σ^2-N and the σ^2-N′, η^2-C=N′ coordinated parts of ligands on the NMR time scale.

The fast exchange limit could not be reached for the two imine carbon atoms because of the large chemical shift difference for these two carbon atoms and the extensive decomposition of the complex which started above 50°C. This exchange process was also studied by ^1H NMR spectroscopy and similar conclusions were reached [5].

On the basis of the ^1H NMR results two mechanisms have been proposed for

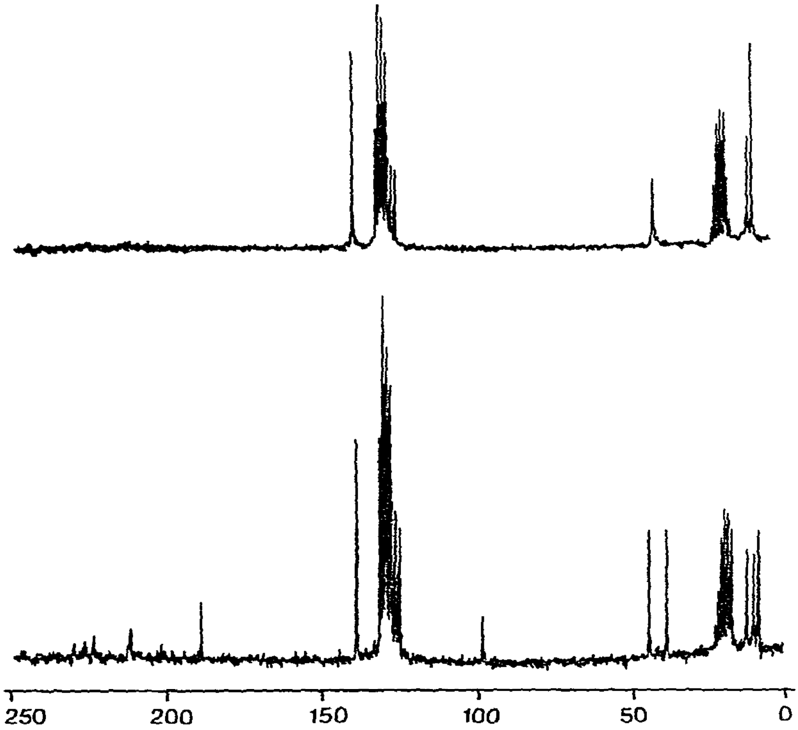

Fig. 3. ^{13}C NMR spectra of $MnCo(CO)_6[c\text{-}Pr\text{—}N{=}C(CH_3)\text{—}(CH_3)C{=}N\text{—}c\text{-}Pr]$ at 50°C (top) and −20°C (bottom).

the exchange process [5]. It has been pointed out before that $\text{-}(CH_3)C{=}N\text{-}$ fragments have weaker π-interactions with cobalt then $\text{-}(H)C{=}N$ fragments. Therefore the mechanism involving the cleavage of the η^2-C=N bond between cobalt and the DAB ligand is preferred, since this also accounts for the fact that glyoxalbis(alkylimine) and methylglyoxalbis(alkylimine) derivatives of $MCo(CO)_6(DAB)$ (M = Mn, Re) are rigid with respect to the coordinated DAB.

The proposed mechanism shown in Figure 4 produces an intermediate structure with three terminal carbonyl groups on cobalt, whereas the complex itself contains a semi-bridging carbonyl group, according to an X-ray structure determination for $MnCo(CO)_6$[glyoxalbis(tert-butylimine)]. This mechanism would therefore also account for the bridge—terminal interchange which has been found for class II compounds. However, an independent mechanism is proposed which also applies to the scrambling of carbonyl groups in the methylglyoxal(alkylimine) and glyoxalbis(alkylimine) derivatives (see the next section).

The metal carbonyl skeleton

a) Class I complexes. Because of the asymmetric coordination of the DAB ligands, the six terminal carbonyl groups in $M_2(CO)_6(DAB)$ complexes (M = Fe, Ru) are inequivalent. In a rigid metal carbonyl skeleton this should result in six independent resonances at low field for the carbonyl groups.

The ^{13}C NMR spectra of all the $M_2(CO)_6(DAB)$ complexes demonstrate a

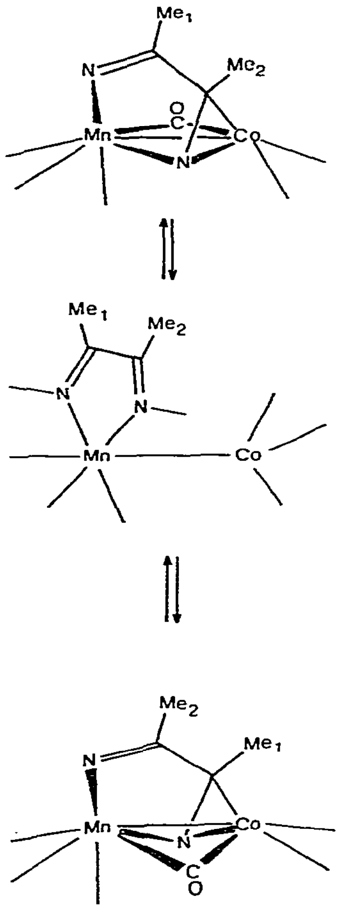

Fig. 4. Proposed mechanism for the exchange process of the DAB ligand on $MnCo(CO)_6$[c-Pr—N=C-(CH_3)—(CH_3)C=N—c-Pr].

local scrambling of the carbonyl groups on each metal which have strongly different activation parameters. This exchange process has been studied in detail for $Fe_2(CO)_6$ glyoxalbis(tert-butylimine) in the temperature range —90° C to 105° C. The spectra are shown in Figure 5.

At —90° C the six carbonyl groups of the $Fe_2(CO)_6$ unit give six signals at 223.3, 219.1, 212.2, 210.5 (deg.) and 205.0 ppm (solvent CD_2Cl_2), of which two are accidently degenerate. At —50° C the signals at 223.3, 212.2 and one of the degenerate pair at 210.5 ppm coalesce, to give one sharp signal at 214.4 ppm at still higher temperatures (calculated 215.3 ppm). At room temperature the carbonyl groups on the second $Fe(CO)_3$ fragment are involved in a fast local scrambling process.

At 85° C the signals at 219.1, 210.5 and 205.0 ppm have disappeared and at 105° C a small broad signal appears at 211 ppm. Unfortunately at this temperature (in $C_2D_2Cl_4$) the complex decomposes violently.

A fast local scrambling on both $M(CO)_3$ fragments (M = Fe, Ru) was observed at 41° C for $Fe_2(CO)_6$[glyoxalbis(cyclohexylimine)] with signals at 214.0

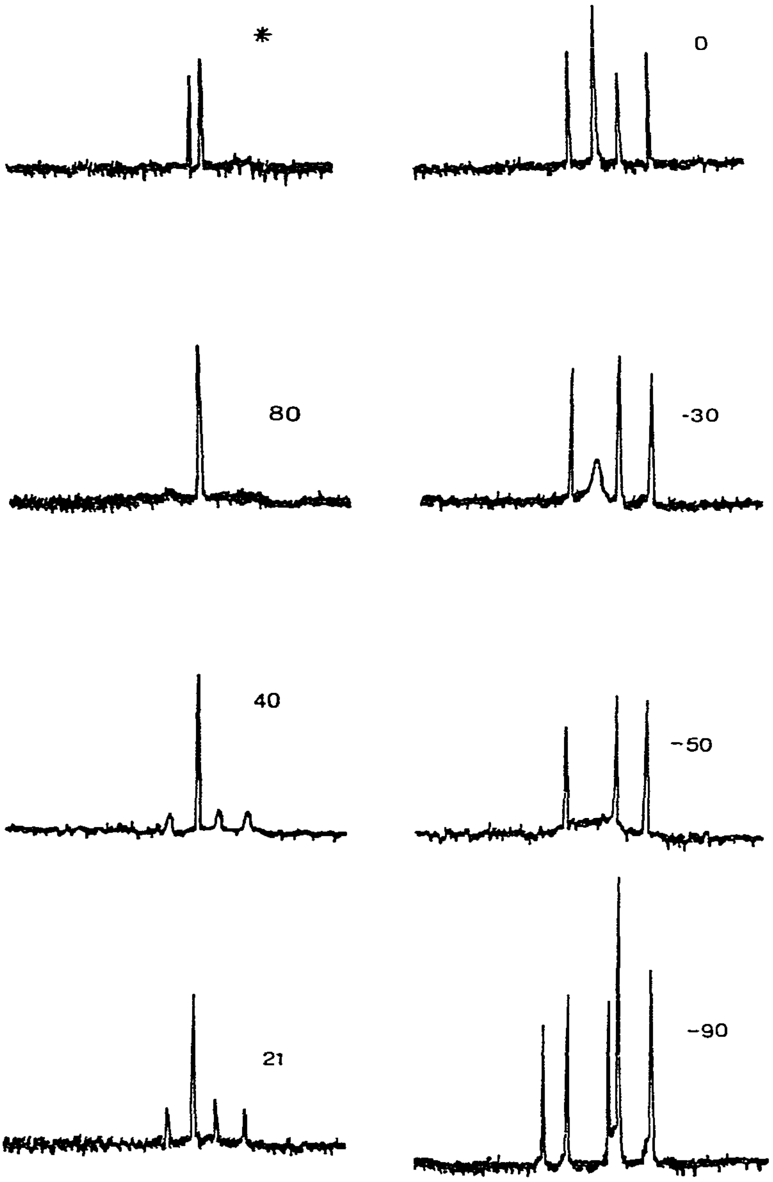

Fig. 5. ^{13}C NMR spectra of $Fe_2(CO)_6$[t-Bu—N=CH—CH=N—t-Bu] in the carbonyl region at temperatures between —90°C and 80°C. The spectrum marked with an asterix is the spectrum of $Fe_2(CO)_6$[c-hex—N=CH—CH=N—c-hex] at 41°C, showing the limit of the fast exchange for both $Fe(CO)_3$ fragments. This could not be reached for $Fe_2(CO)_6$[t-Bu—N=CH—CH=N—t-Bu] due to rapid decomposition at elevated temperatures.

and 207.5 ppm and for $Ru_2(CO)_6$[glyoxalbis(tert-butylimine)] with signals at 216.1 and 199.0 ppm. For $Fe_2(CO)_6$[glyoxalbis(isopropylimine)] and $Fe_2(CO)_6$[methylglyoxalbis(isopropylimine)] only one signal was observed at 41°C at 213.9 and 205.0 ppm, respectively. For the latter compound three additional weak bands appeared at 218.3, 210.7 and 205.0 ppm at 20°C. These results demonstrate that the activation parameters for the two independent scrambling processes on the $M_2(CO)_6$ unit depend strongly upon the substituents attached to the DAB ligand. Local scrambling is a general phenomenon in complexes containing $M_2(CO)_6$ units and cyclic unsaturated hydrocarbon systems [13—14] and can become rather complicated when exchange processes on the cyclic ligand interfere with the local scrambling of the carbonyl groups [18—20].

The carbonyl resonances of the $M_2(CO)_6(DAB)$ complexes can tentatively be assigned to the corresponding $M(CO)_3$ fragment (M = Fe, Ru), considering the following facts. $Fe(CO)_3(DAB)$ complexes give one signal at 215 ppm for the three carbonyl groups [11]. $Fe(CO)_3$(diene) and $Fe(CO)_3$(azadiene) complexes give signals at slightly higher field [11,21,22]. When these trends hold for the binuclear $Fe_2(CO)_6$ complexes the signals at 223.3, 212.2 and 210.5 ppm of $Fe_2(CO)_6$[glyoxalbis(tert-butylimine)] correspond with the $Fe(CO)_3$ fragment to which the DAB ligand is coordinated via the two nitrogen atoms and the signals at 219.1, 210.5 and 205.0 ppm correspond with the $Fe(CO)_3$ fragment to which DAB is μ^2-N′, η^2-C=N coordinated. Analogous assignments can be made for the other complexes.

b) Class II complexes. $MnCo(CO)_6(DAB)$ and $ReCo(CO)_6(DAB)$ complexes contain a semi-bridging carbonyl group [5]. The X-ray structure determination of $MnCo(CO)_6$[glyoxalbis(tert-butylimine)] showed that this carbonyl group is 2.33 Å from manganese and 1.80 Å from cobalt. IR spectra obtained in n-hexane and in a KBr disk (or Nujol mull) gave similar absorption patterns in the ν(CO) stretching region which evidences that the structures in solution and in the solid state are the same [5]. Accordingly, the metal carbonyl skeleton of the $MCo(CO)_6(DAB)$ complexes in solution (M = Mn, Re) consists of

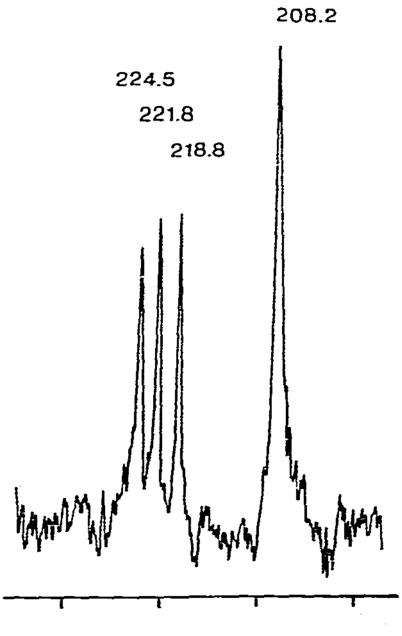

Fig. 6. ^{13}C NMR spectrum of $MnCo(CO)_6(DAB)$ in the carbonyl region.

three terminal carbonyl groups on manganese (or rhenium), two terminal carbonyl groups on cobalt and one semi-bridging carbonyl group (see Figure 1).

For MnCo(CO)$_6$[glyoxalbis(isopropylimine)] three signals are found at temperatures between −50° C and 50° C, and on the basis of the chemical shifts these can be assigned to the terminal carbonyl groups on manganese: 223.3, 222.2, 218.5 ppm, respectively. Furthermore, a more intense signal is found at 209.3 ppm, which is assigned to the semi-bridging carbonyl group and the two terminal carbonyl groups on cobalt. The four signals are all broadened and do not significantly sharpen in the temperature range −50° C to 50° C. Obviously the two terminal CO groups on cobalt and the semi-bridging carbonyl group are involved in a fast local scrambling process. The broadening of the signals is caused by the nuclear quadrupole moment of cobalt and manganese ($I = 7/2$ and 5/2, respectively). In Figure 6 the ^{13}C NMR pattern is shown of MnCo(CO)$_6$[glyoxalbis(isopropylimine)] in the carbonyl region (solvent toluene-d_8).

A detailed study of the exchange process of MCo(CO)$_6$(DAB) complexes is not possible because of insufficient solubility below −50° C and thermal instability above 50° C. However, in the temperature range −50° C to 50° C the Mn(CO)$_3$ fragment is rigid, and the bridge—terminal interchange involving the semi-bridging carbonyl group and the two terminal carbonyl groups on cobalt is at the limit of the fast exchange.

The bridge—terminal interchange as is shown in Figure 7, normally requires

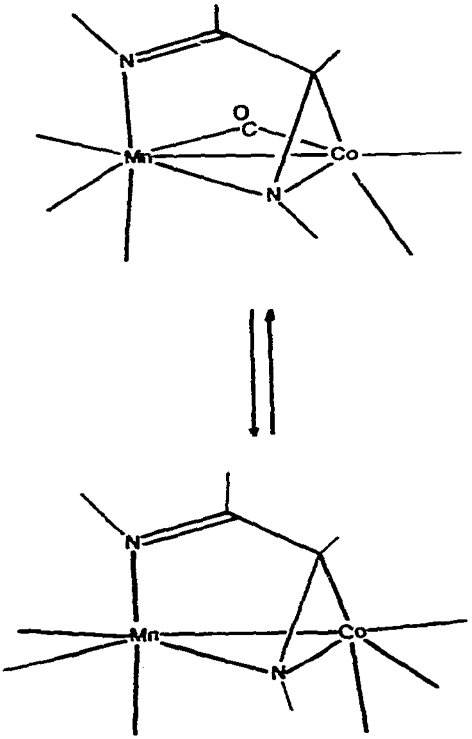

Fig. 7. Proposed mechanism for the terminal—bridging interchange in MCo(CO)$_6$(DAB) complexes.

two bridging carbonyl groups in the complex. Accordingly, these form compensating pairs which are able to retain 18 electron configurations on each metal centre [17,23,24]. The $MCo(CO)_6(DAB)$ complexes (M = Mn, Re) contain only one bridging carbonyl group which, however, is semi-bridging. In the formal electron counting the semi-bridging carbonyl group cannot be fully regarded as a two electron donor to cobalt, but to regard this carbonyl group as a one electron donor with respect to both metal centres is also unreal. The same problem arises with the lone pair on the nitrogen atom which bridges between cobalt and manganese. The coordination mode of the DAB ligand is in between σ^2-N, σ^2-N', η^2-C=N and σ^2-N, μ^2-N', η^2-C=N (i.e. a resonance structure) and the contribution of each of these bonding modes to the actual electronic structure is directly related to the electronic structure within the carbonyl bridge. It will be clear that the semi-bridging carbonyl group and the bridging imine fragment form a compensating pair in the bridge—terminal interchange of the carbonyl groups (σ^2-CO → μ^2-CO with σ^2-N, η^2-C=N → μ^2-N, η^2-C=N). The bridge—terminal interchange within the DAB ligand has no consequenses for the structure of the MCo(DAB) fragment, due to the η^2-C=N coordination of the DAB ligand.

Conclusion

The small chemical shift differences of glyoxalbis(alkylimine) derivatives within one class of compounds do not indicate different electronic structures for the coordinated DAB ligands. Accordingly, the difference in reactivity in the series $M_2(CO)_6(DAB)$ (M = Fe, Ru) towards excess of DAB ligands must have other reasons. Possible factors are the metal—metal bonds strengths, which are known to increase in the order Fe < Ru < Os, and the relative stability of the metal—CO interaction, which is known to increase in the same order.

Other techniques are needed if additional information on this subject is to be obtained.

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