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BINUCLEAR METAL CARBONYL DAB COMPLEXES

II *. THE SYNTHESIS AND COORDINATION PROPERTIES OF $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3\text{DAB}$ ($\text{M}' = \text{Mn, Re}$; DAB = 1,4-DIAZABUTADIENE)

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Summary

$\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3\text{DAB}$ complexes ($\text{M}' = \text{Mn, Re}$; DAB = $\text{R}_1\text{N}=\text{C}(\text{R}_2)-\text{C}(\text{R}'_2)=\text{NR}_1$) can be easily obtained from the reaction between $\text{Mn}(\text{CO})_5^-$ and $\text{M}'(\text{CO})_3\text{X}(\text{DAB})$ ($\text{M}' = \text{Mn, Re}$; X = Cl, Br, I). The complexes are formed by a nucleophilic mechanism, while a redistribution is responsible for the formation of a small amount of $\text{Mn}_2(\text{CO})_{10}$.

A diastereotopic effect can be observed in the ^1H and ^{13}C NMR spectra of complexes having isopropyl groups attached to the DAB ligand skeleton. A comparison is made with mononuclear complexes of the same symmetry, and the chemical shift differences for the methyl groups strongly depend on the substituent on the central metal responsible for the asymmetry.

The low temperature enhancement of the $\sigma \rightarrow \sigma^*$ transition localised on the metal–metal bond, which is normally observed for this type of compounds, was not observed for the $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3(\text{DAB})$ complexes. The metal–metal bond can be activated by irradiating at the wave lengths associated with the CT transitions between the metal and the DAB ligand. Metal–metal bond cleavage occurs and $\text{Mn}_2(\text{CO})_{10}$ is formed.

Introduction

During a systematic study on the bonding behaviour of 1,4-diazabutadiene (DAB) in metal carbonyl complexes we investigated the coordination properties of DAB ligands in $\text{M}(\text{CO})_4\text{DAB}$ ($\text{M} = \text{Cr, Mo, W}$) [1–3] and $\text{M}(\text{CO})_3\text{X}$ -

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(DAB) ($M = \text{Mn, Re; X = Cl, Br, I}$) [4], in which DAB acts as a four electron σ -donor ligand.

The four electron σ -donor coordination mode has been found in many other metal carbonyl and higher substituted complexes such as: $\text{Mo}(\text{CO})_{3-n}(\text{PR}_3)_n(\text{DAB})$ [5-7], $\text{Mo}(\text{CO})_2\text{X}(\pi\text{-allyl})(\text{DAB})$ ($\text{X} = \text{Cl, Br, I}$) [8,9], $\text{Fe}(\text{CO})_3\text{DAB}$ [10,11], $\text{Fe}(\text{CO})(\text{diene})(\text{DAB})$ [12], $\text{Co}_2(\text{CO})_6(\text{DAB})$ [13], $\text{Ni}(\text{CO})_2(\text{DAB})$ [14, 15] and $\text{Ni}(\text{DAB})_2$ [16]. These samples show the variety of complexes in which DAB occurs as a four electron donating ligand.

Besides the four electron σ -donor coordination mode, which must be considered as the most important for the DAB ligands, the two electron σ -donor mode [1,17,18] and the six electron σ, σ, π coordination mode [19] have recently been established in binuclear iron complexes. The coordination modes in which the π -electron are involved are particularly interesting from the point of view of activation of the double bonds of the diimine skeleton in reactions of the coordinated ligands [3]. For a complete understanding of the reactivity of the coordinated ligands knowledge of the factors determining the coordination modes is necessary.

In this paper we present results of a study of the coordination chemistry of DAB ligands in formally zero valent dinuclear d^7 metal carbonyl complexes.

Experimental

$\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ were obtained from Strem Chemicals and used without purification. The mononuclear complexes $\text{M}(\text{CO})_3\text{X}(\text{DAB})$ ($\text{X} = \text{Cl, Br, I}$), which have been reported earlier [4,20,21] were used as starting materials for the synthesis of the $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3(\text{DAB})$ complexes ($\text{M}' = \text{Mn, Re}$). The $\text{Mn}(\text{CO})_5^-$ anion used in the redox reactions was prepared by the reduction of $\text{Mn}_2(\text{CO})_{10}$ with sodium/potassium alloy $\text{NaK}_{2.8}$, as described by Ellis and Flom for the reduction of metal carbonyl complexes [22].

Solvents were carefully dried, and all preparations were carried out under purified nitrogen using standard Schlenk techniques.

General method for the preparation of $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3(\text{DAB})$ ($\text{M}' = \text{Mn, Re}$; DAB = glyoxaldiisopropyldiimine, glyoxaldi-p-tolyldiimine, glyoxaldi-p-anisyl-diimine, methylglyoxaldiisopropyldiimine).

$\text{M}(\text{CO})_3\text{X}(\text{DAB})$ ($\text{M} = \text{Mn, Re; X} = \text{Cl, Br, I}$) (1 mmol) and $\text{Mn}(\text{CO})_5^-$ (1 mmol) were stirred for $\frac{1}{2}$ h in 40 ml ether. Because of the high sensitivity towards photochemical decomposition light was excluded. During the reaction the colour changed from pale orange to intense blue or violet. The solution was filtered and the filtrate evaporated to dryness. $\text{Mn}_2(\text{CO})_{10}$ was removed from the solid residue by vacuum sublimation at 40°C , and the residue was extracted with 20 ml of pentane. The pentane solution was kept at -70°C overnight, and the products separated as dark red violet crystals in about 80% yield. The purity of the complexes was confirmed by micro analyses and IR spectroscopy. The results are listed in Table 1.

In solution the complexes are extremely sensitive to photochemical decomposition. Solutions are air stable at room temperature for several hours but above 50°C thermal decomposition occurs. $\text{Mn}_2(\text{CO})_{10}$ is one of the main decomposition products.

TABLE I

ANALYTICAL DATA FOR $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3(\text{R}_1\text{N}=\text{CR}_2^1=\text{NR}_1)$ ($\text{M}' = \text{Mn, Re}$)Calculated analytical data are given in parenthesis. IR $\nu(\text{CO})$ data were obtained in pentane solutions.

Compound($\text{R}_1, \text{R}_2, \text{R}_2^1$) (formula)	C (%)	H (%)	N (%)	IR $\nu(\text{CO})$ (cm^{-1})
$\text{Mn}(\text{CO})_5\text{Mn}(\text{CO})_3(\text{i-pr, H, H})$ $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_8\text{Mn}_2$	(40.51) 40.35	(3.38) 3.47	(5.91) 5.91	2064s, 2047m, 2010w, 1983m, 1948m, 1970m
$\text{Mn}(\text{CO})_5\text{Mn}(\text{CO})_3(\text{i-pr, H, CH}_3)$ $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_8\text{Mn}_2$	(41.80) 41.82	(3.69) 3.58	(5.74) 5.82	2061s, 2021m, 1999w, 1981ss, 1972ss, 1949m, 1911m
$\text{Mn}(\text{CO})_5\text{Mn}(\text{CO})_3(\text{p-tol, H, H})$ $\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}_8\text{Mn}_2$	(50.53) 50.41	(2.81) 2.95	(4.91) 5.13	2068s, 2041m, 2009w, 1985s, 1984s, 1960m, 1885m
$\text{Mn}(\text{CO})_5\text{Mn}(\text{CO})_3(\text{p-methoxy, H, H})$ $\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}_{10}\text{Mn}_2$	(47.84) 47.75	(2.66) 2.71	(4.65) 4.64	2071s, 2046m, 1989s, 1979m, 1921m, 1911m
$\text{Mn}(\text{CO})_5\text{Re}(\text{CO})_3(\text{i-pr, H, H})$ $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_8\text{MnRe}$	(31.74) 31.20	(2.65) 2.93	(4.63) 4.66	2057s, 2045m, 1999s, 1974m, 1907m
$\text{Mn}(\text{CO})_5\text{Re}(\text{CO})_3(\text{p-tol, H, H})$ $\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}_8\text{MnRe}$	(41.08) 41.01	(2.28) 2.37	(3.99) 4.02	2065s, 2042m, 1999s, 1968m, 1920m, 1910m

The solid compounds are easily sublimed under vacuum even at room temperature, but decompose above 100°C (thermobalance).

Analyses

Elemental analyses were carried out by the Section Elemental Analyses of the Institute for Organic Chemistry, TNO, Utrecht, The Netherlands.

Spectroscopy

The IR spectra were recorded on a Beckman IR 4250 spectrometer and the UV-visible spectra on a Cary 14 spectrophotometer, the ^1H NMR spectra were recorded on a Varian T 60 and the ^{13}C NMR spectra on a Varian CFT 20 spectrometer.

The organic glass EPA (ethanol/2,2-dimethylpropane/diethyl ether, 2/5/5), used for low temperature UV-visible spectroscopy was prepared from Uvasol grade solvents obtained from Merck.

Results and discussion

Reaction mechanism

For the syntheses of substituted dimanganese decacarbonyl complexes and related compounds a few alternative reaction routes were considered. One method which is normally used to produce photochemically stable complexes is the photochemical substitution of carbon monoxide [23], a second is nucleophilic attack by $\text{Mn}(\text{CO})_5^-$ on a monomeric species [24,25] while a more

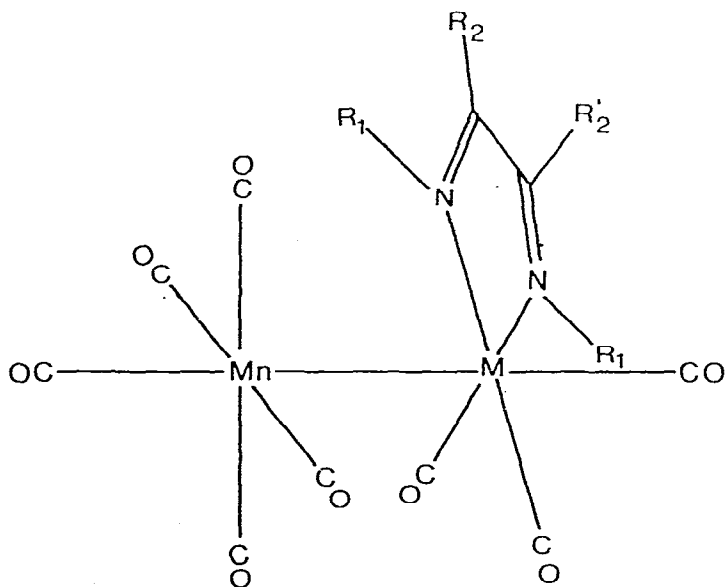
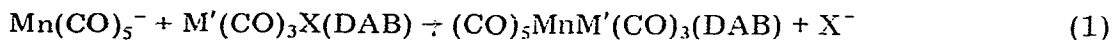


Fig. 1. The proposed structure of $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3(\text{DAB})$ ($\text{M}' = \text{Mn, Re}$).

recently developed method is the aminoxide-induced ligand substitution [26, 27]. Because of the expected photochemical instability [1–4] and the relative ease of preparation of $\text{M}(\text{CO})_3\text{X}(\text{DAB})$ ($\text{M} = \text{Mn, Re}$; $\text{X} = \text{Cl, Br, I}$) [4] the second method was chosen.

The binuclear $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3(\text{DAB})$ ($\text{M}' = \text{Mn, Re}$) complexes are formed according to eq. 1 in which the halide in the monomeric species is replaced by $\text{Mn}(\text{CO})_5^-$.

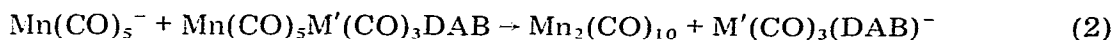


Reduction of the substituted metal carbonyl fragment and oxidation of $\text{Mn}(\text{CO})_5^-$ leads to the formation of a complex containing a single metal–metal bond, the proposed structure of which is shown in Fig. 1.

The mechanism of formation of metal–metal bonds from nucleophiles and metal halide complexes has been the subject of an extensive electrochemical study [28–31]. In their paper on the formation of the complexes $\text{M}_2(\text{CO})_8\text{L}$ ($\text{M} = \text{Mn, Re}$; $\text{L} = 1,10\text{-phenanthroline, biquinoline}$), which complexes are related to the $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3\text{DAB}$ complexes ($\text{M}' = \text{Mn, Re}$), Morse and Wrighton proposed an electron transfer mechanism, on the basis of the extensive electrochemical study of Dessy et al. [28–31]. The evidence for this mechanism was the isolation of $\text{M}_2(\text{CO})_6\text{L}_2$ and $\text{M}_2(\text{CO})_{10}$ ($\text{M} = \text{Mn, Re}$), which show that radicals were involved in the metal–metal bond formation. Unfortunately these authors did not indicate the yields of these side products. In an electron transfer mechanism the product ratio of $\text{M}_2(\text{CO})_8\text{L}$, $\text{M}_2(\text{CO})_6\text{L}_2$ and $\text{M}_2(\text{CO})_{10}$ should be approximately 1 : 1 : 1.

The yields of $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3(\text{DAB})$ ($\text{M}' = \text{Mn, Re}$) in the present study are 80–90%, and so there must be another mechanism responsible for the formation of the dimeric DAB complexes. We assume that the binuclear complexes

are formed in a nucleophilic mechanism which could theoretically give 100% yields of the $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3\text{DAB}$ complexes ($\text{M}' = \text{Mn}, \text{Re}$). The formation of $\text{Mn}_2(\text{CO})_{10}$ can be explained by a redistribution reaction [31] between $\text{Mn}(\text{CO})_5^-$ and $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3(\text{DAB})$ ($\text{M}' = \text{Mn}, \text{Re}$) according to eq. 2.



The $\text{M}'(\text{CO})_3(\text{DAB})^-$ anion must then react with $\text{M}'(\text{CO})_3\text{X}(\text{DAB})$ to form $\text{M}'_2(\text{CO})_6(\text{DAB})_2$ but these complexes are unstable and decompose to give $\text{Mn}_2(\text{CO})_{10}$. This reaction mechanism is also in agreement with the formation of the side products as described by Morse and Wrighton [24,25]. The lack of reaction of $\text{Re}(\text{CO})_3\text{X}(1,10\text{-phenanthroline})$ and $\text{Re}(\text{CO})_3\text{X}(\text{pyridine})_2$, which was also reported by these authors, seems not to fit in the model of nucleophilic substitution by redistribution. However, the extent of ionic character of the $\text{M}-\text{X}$ bond depends on the ligands around the metal and on the metal itself [32], which means that the properties of X as a leaving group are determined by these two factors.

Ligand influences on the stability of the complexes

Some of the formed $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3(\text{DAB})$ complexes are unstable. For example, when *t*-butyl groups were attached to the DAB ligand the colour change during the reaction indicated that the binuclear complexes were formed, but in solution the colour changed to yellow after a few hours, even at low temperature. A large amount of $\text{Mn}_2(\text{CO})_{10}$ and the free ligand was isolated.

The instability of complexes $\text{Mn}_2(\text{CO})_6(\text{DAB})_2$ and the stability of the related 1,10-phenanthroline, 2,2'-bipyridine and biquinoline complexes again illustrates the difference between these ligands although they all contain the α -diimine moiety. This is shown in Fig. 2. In a paper on the reduction potentials of $\text{Mo}(\text{CO})_4\text{L}$ complexes ($\text{L} = \text{DAB}; 1,10\text{-phenanthroline}; 2,2\text{-bipyridine}$), tom Dieck et al. showed that 1,10-phenanthroline and 2,2'-bipyridine are poor π -acceptors compared with the DAB ligands [33]. This difference in electronic

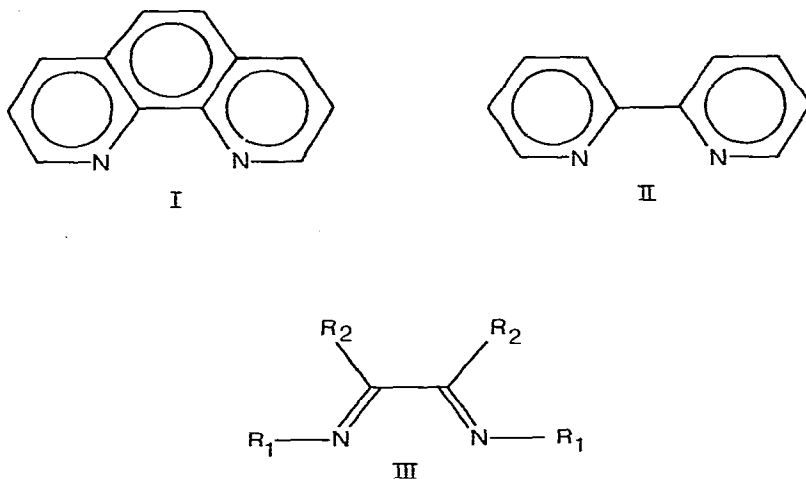


Fig. 2. (I) 1,10-phenanthroline, (II) 2,2'-bipyridine, (III) 1,4-diazabutadiene.

structure between these ligands may be responsible for the different behaviour in redox reactions.

The bulkiness of the ligands is also very different. The 1,10-phenanthroline, 2,2'-bipyridine and biquinoline ligands are bulky but planar, while the DAB ligands are also bulky perpendicular to the diimine plane because of the substituents R_1 . This steric factor will be more important for the instability of the $M_2(CO)_6DAB$ complexes ($M = Mn, Re$) than the electronic factors. The planar 1,10-phenanthroline and 2,2'-bipyridine form stable complexes of this type [24,25]. The importance of the steric factors is confirmed by the instability of $Mn(CO)_5M'(CO)_3(t-BuN=CHCH=Nt-Bu)$ ($M' = Mn, Re$), which contrasts with the stability of the analogous isopropyl derivatives.

NMR Spectroscopy

The actual coordination mode of the DAB ligand can be determined with the help of 1H and ^{13}C NMR spectroscopy. The chemical shifts of the imine protons are near 7.8 ppm in the free ligand and they are found between 7 and 9 ppm in the σ,σ -coordination modes [34]. In the case of π -coordination large upfield shifts have been observed, which are the result of the shielding by the metal atom [19]. Similar behaviour has been observed for the imine carbon atom shifts in the ^{13}C NMR spectra; in the case of σ -coordination, shifts of between 140 and 145 ppm have been observed [34,35], while in the case of π -coordination shifts of about 60 ppm were found [36].

The 1H NMR data, listed in Table 2, show that both halves of the ligand are equivalent; and all the lines appear as a single set. This indicates that the ligand must be *cis* to the metal-metal bond as is shown in Fig. 1.

In Table 3 the ^{13}C NMR chemical shifts are listed for the complexes containing isopropyl groups, which were measured at $-30^\circ C$ to prevent thermal decomposition. The ^{13}C data of analogous d^6 and d^8 complexes are included in Table 3 and an interesting variation can be observed in the shifts for the imine carbon atoms. The chemical shifts decrease from a d^6 to d^8 metal, indicating that the strength of the π -interaction between the metal and the DAB ligand decreases in the sequence $d^8 > d^7 > d^6$.

For complexes with isopropyl groups attached to the diimine ligands a

TABLE 2

1H -NMR CHEMICAL SHIFTS FOR $Mn(CO)_5M'(CO)_3(R_1N=CR_2CR_2^1=NR_1)$ ($M' = Mn, Re$) IN $CDCl_3$ SOLUTIONS δ (ppm) RELATIVE TO TMS

Compound (R_1, R_2, R_2^1)	δ (ppm)
$Mn(CO)_5Mn(CO)_3(i\text{-}pr, H, H)$	$\delta(CH_3)^{i\text{-}pr} = 1.36^{a,b}, 1.51^{a,b}; \delta(CH)^{i\text{-}pr} = 4.46^a;$ $\delta(H)^{imine} = 8.18$
$Mn(CO)_5Mn(CO)_3(i\text{-}pr, H, CH_3)$	$\delta(CH_3)^{i\text{-}pr} = 1.36^a; \delta(CH_3) = 1.39^a; \delta(CH)^{i\text{-}pr} = 4.50^a;$ $\delta(CH)^{i\text{-}pr} = 4.52^a; \delta(CH_3) = 4.52; \delta(H)^{imine} = 7.84$
$Mn(CO)_5Mn(CO)_3(p\text{-}tol, H, H)$	$\delta(CH_3)^{p\text{-}tol} = 2.40; \delta(H)^{arom} = 4.21; \delta(H)^{imine} = 8.15$
$Mn(CO)_5Mn(CO)_3(p\text{-}methoxy, H, H)$	$\delta(CH_3)^{methoxy} = 3.84; \delta(H)^{arom} = 7.03^c; \delta(H)^{imine} = 8.17$
$Mn(CO)_5Re(CO)_3(i\text{-}pr, H, H)$	$\delta(CH_3)^{i\text{-}pr} = 1.35^{a,b}; \delta(CH)^{i\text{-}pr} = 4.56^a; \delta(H)^{imine} = 8.57$
$Mn(CO)_5Re(CO)_3(p\text{-}tol, H, H)$	$\delta(CH_3)^{p\text{-}tol} = 2.42; \delta(H)^{arom} = 7.23; \delta(H)^{imine} = 8.65$

$^a J = 7$ Hz. b Splitting of lines caused by chirality. $^c J = 9$ Hz.

TABLE 3

 ^{13}C CHEMICAL SHIFTS OF $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3(\text{i-prN}=\text{CHC}(\text{R})=\text{Ni-pr})$ CDCl_3 solutions (δ (ppm) relative to TMS). Some data of analogous compounds are included.

Compound	δ (ppm)	Ref.
$\text{Mn}(\text{CO})_5\text{Mn}(\text{CO})_3(\text{i-prN}=\text{CHCH}=\text{Ni-pr})$	$\delta(\text{CH}_3)^{\text{i-pr}} = 22.03, 27.02$; $\delta(\text{CH})^{\text{i-pr}} = 61.63$; $\delta(\text{CH})^{\text{imine}} = 149.46$	
$\text{Mn}(\text{CO})_5\text{Mn}(\text{CO})_3(\text{i-prN}=\text{CHCCH}_3=\text{Ni-pr})$	$\delta(\text{CH}_3)^{\text{i-pr}} = 20.68, 26.96$; $\delta(\text{CH}_3)^{\text{i-pr}} = 21.97, 22.19$; $\delta(\text{CH})^{\text{i-pr}} = 61.09$; $\delta(\text{CH}_3) = 61.34$; $\delta(\text{CH})^{\text{imine}} = 154.96$	
$\text{Mn}(\text{CO})_5\text{Re}(\text{CO})_3(\text{i-prN}=\text{CHCH}=\text{Ni-pr})$	$\delta(\text{CH}_3)^{\text{i-pr}} = 21.49, 27.01$; $\delta(\text{CH})^{\text{i-pr}} = 63.41$; $\delta(\text{C})^{\text{imine}} = 150.48$	
$\text{Fe}(\text{CO})_3(\text{i-prN}=\text{CHCH}=\text{Ni-pr})$	$\delta(\text{CH}_3)^{\text{i-pr}} = 15.9$; $\delta(\text{CH})^{\text{i-pr}} = 63.6$; $\delta(\text{C})^{\text{imine}} = 141.6$	35
$\text{Mo}(\text{CO})_4(\text{i-prN}=\text{CHCH}=\text{Ni-pr})$	$\delta(\text{CH}_3)^{\text{i-pr}} = 34.2$; $\delta(\text{CH})^{\text{i-pr}} = 66.1$; $\delta(\text{C})^{\text{imine}} = 155.8$	7

strong diastereotopic effect was observed in the NMR spectra. The asymmetry in the complexes causes a splitting of lines for the methyl groups of the isopropyl substituent in the ^1H NMR as well as in the ^{13}C NMR spectra. This effect has also been observed in the mononuclear $\text{Mn}(\text{CO})_3\text{X}(\text{isopropyl-N}=\text{CH}-\text{CH}=\text{N-isopropyl})$ complexes [4], but is much more pronounced in the binuclear complexes. In Fig. 3 the asymmetry in the isopropyl derivatives of both types of complexes, which is responsible for the line splitting in the NMR spectra, is shown.

It is possible to distinguish three cases: (a) the chemical shift difference is

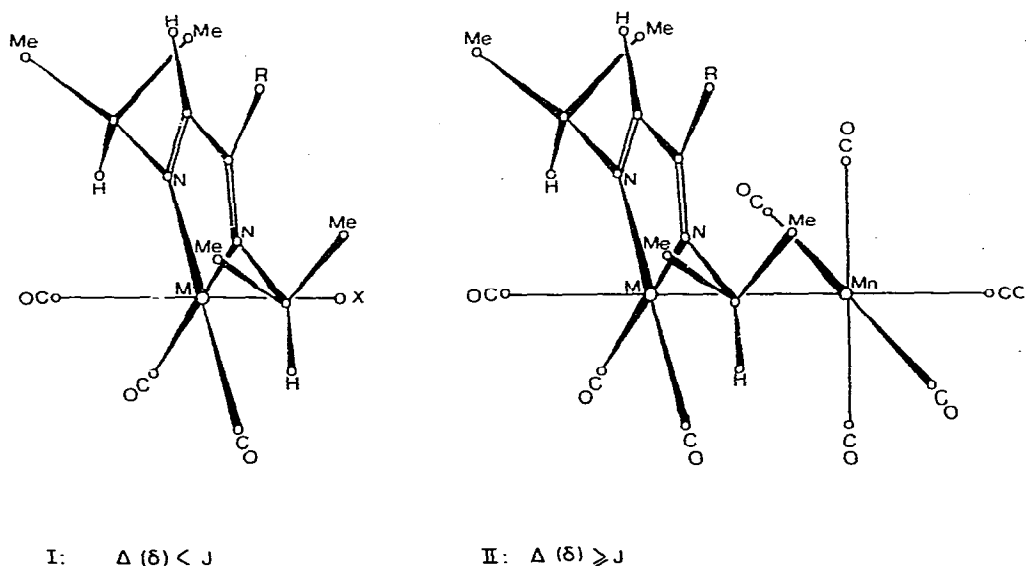


Fig. 3. Structures of $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3(\text{i-pr-N}=\text{CHCH}=\text{N-i-pr})$ and $\text{M}'(\text{CO})_3\text{X}(\text{i-pr-N}=\text{CHCH}=\text{N-i-pr})$ ($\text{M}' = \text{Mn, Re}$) showing the nature of the asymmetry in the isopropyl group.

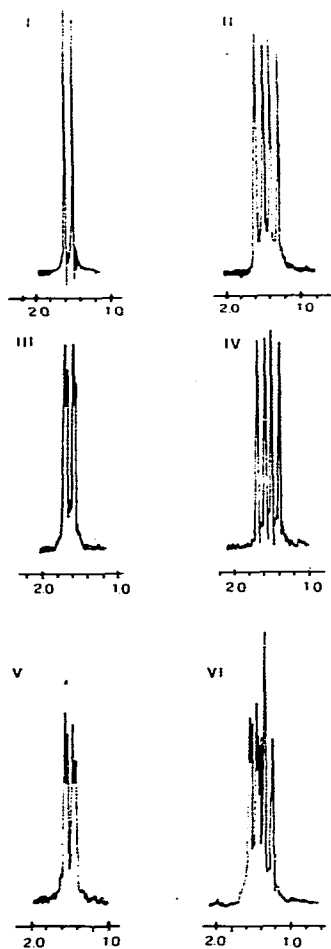


Fig. 4. The ^1H NMR pattern for the isopropyl groups of: (I) $\text{Re}(\text{CO})_3\text{Cl}(\text{i-pr-N}=\text{CHCH}=\text{N-i-pr})$; (II) $\text{Mn}(\text{CO})_5\text{Re}(\text{CO})_3(\text{i-pr-N}=\text{CHCH}=\text{N-i-pr})$; (III) $\text{Mn}(\text{CO})_3\text{Br}(\text{i-pr-N}=\text{CHCH}=\text{N-i-pr})$; (IV) $\text{Mn}(\text{CO})_5\text{Mn}(\text{CO})_3(\text{i-pr-N}=\text{CHCH}=\text{N-i-pr})$; (V) $\text{Mn}(\text{CO})_3\text{Br}(\text{i-pr-N}=\text{CHC}(\text{CH}_3)=\text{N-i-pr})$; and (VI) $\text{Mn}(\text{CO})_5\text{Mn}(\text{CO})_3(\text{i-pr-N}=\text{CHC}(\text{CH}_3)=\text{N-i-pr})$.

less than the coupling in the isopropyl group ($\Delta\delta < J$), (b) the chemical shift difference is approximately equal to the coupling ($\Delta\delta \approx J$), and (c) the chemical shift difference is larger than the coupling ($\Delta\delta > J$). In Fig. 4 the ^1H NMR pattern for the isopropyl groups of some mono- and binuclear complexes is given, showing the three possible situations. The mononuclear complexes are shown alongside the corresponding binuclear complexes. For the mononuclear complexes shown in Fig. 4 (I, III, and V) only in the case of complex III was a small chemical shift difference observed ($\Delta\delta \approx J$). For the other complexes no diastereotopic effect was found. The splitting of the lines in V is the result of the inequivalence of the isopropyl groups, due to the different substituents on the ligand imine carbon atoms ($\text{R}_2 = \text{H}, \text{CH}_3$).

For the binuclear complexes shown in Fig. 4 (II, IV and VI) the chemical shift is larger than the coupling ($\Delta\delta > J$), and for one of the two inequivalent

isopropyl groups in compound VI situation (b) was observed (i.e., $\Delta\delta \approx J$).

The results show that the chemical shift differences of the methyl groups of the isopropyl derivatives strongly depend on the substituents causing the asymmetry in the complexes.

Additional information about the diastereotopic effect was obtained by ^{13}C NMR spectroscopy. The chemical shift differences for the methyl groups of the isopropyl substituents in the mononuclear halide complexes were less than 0.7 ppm, while in the binuclear species chemical shift differences up to 6 ppm were observed (see Table 3). The line splitting in the NMR pattern of the isopropyl groups has also been observed in other binuclear metal carbonyl DAB complexes [36] and in complexes containing ligands derived from DAB [3]. The effect seems to give useful structural information.

UV-visible spectroscopy

The $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3(\text{DAB})$ complexes ($\text{M}' = \text{Mn, Re}$) are all highly coloured in solution and have complex electronic absorption spectra in the visible and the near UV. Between 300 and 650 nm charge transfer (CT) transitions between the metal and the DAB ligand, intra-ligand (IL) transitions on the aromatic rings of substituents, and $\sigma \rightarrow \sigma^*$ transitions localised in the metal-metal bond have been observed, and will be discussed below.

In principle there exist six CT transitions from the three $d\pi$ orbitals to the two ligand π^* orbitals. All these transitions are symmetry allowed as is obvious from Fig. 5. Characteristic of the CT transitions between the metal $d\pi$ orbitals and the DAB ligand π^* orbitals in metal carbonyl complexes is the strong solvent dependence of the position of the absorption maxima [1,37-39]. For $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3(\text{DAB})$ complexes ($\text{M}' = \text{Mn, Re}$) a small shift to shorter wavelength is observed for the CT transitions to the $\pi^*(a')$ level with increasing polarity of the solvent (positive solvatochromism) while for the transitions to the $\pi^*(a'')$ level the shifts are uncertain because of overlap with other bands. The effects of charge on the wavelengths of the CT transitions are shown in Table 4.

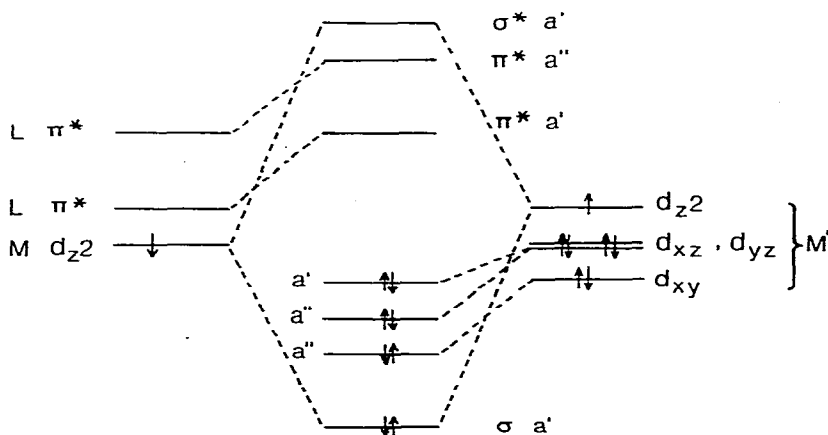


Fig. 5. Relevant part of a tentative MO-scheme which is in agreement with the observed UV-visible spec-

TABLE 4
SOLVATOCROMISM OF THE CT ABSORPTION BANDS OF SOME $M(\text{CO})_5M'(\text{CO})_3(\text{DAB})$ COMPLEXES (λ , nm)

Solvent	$\text{Mn}(\text{CO})_5\text{Re}(\text{CO})_3(\text{t-pr-N}=\text{CHCH}=\text{Ni-pr})$		$\text{Mn}(\text{CO})_5\text{Re}(\text{CO})_3(\text{p-to-I-N}=\text{CHCH}=\text{N-p-tal})$		$\text{Mn}(\text{CO})_5\text{Mn}(\text{CO})_3(\text{p-to-I-N}=\text{CHCH}=\text{N-p-tal})$	
	CT ₁ ^a	CT ₂ ^b	CT ₁	CT ₂	CT ₁	CT ₂
Pentane	542	380	596	430(sh)	604	n.o. ^c
Pentane/ether (1/1)	540	380	596	425(sh)	604	n.o.
Ether	534	378	590	430(sh)	604	n.o.
DMF	526	365	576	410(sh)	600	n.o.

^a CT transitions to σ' level. ^b CT transitions to σ'' level. ^c n.o. = not observed.

TABLE 5

ELECTRONIC ABSORPTION MAXIMA OF $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3\text{DAB}$ ($\text{M}' = \text{Mn, Re}$) IN EPA SOLUTIONS (λ_{max} IN nm) AT ROOM TEMPERATURE

Compound(R_1, R_2, R_3)	CT(a')	CT(a'')	$\pi - \pi^*$ (IL)	$\sigma - \sigma^*$ (LF)
$\text{Mn}_2(\text{CO})_8(\text{i-pr. H, H})$	550, 475(sh) ^a	350(sh)	—	336
$\text{Mn}_2(\text{CO})_8(\text{i-pr. H, CH}_3)$	570	360(sh)	—	337
$\text{Mn}_2(\text{CO})_8(\text{p-tol. H, H})$	604	415(sh)	366	337
$\text{Mn}_2(\text{CO})_8(\text{p-CH}_3\text{O-phen. H, H})$	606, 560(sh)	440, 410	380	331
$\text{Mn}(\text{CO})_5\text{Re}(\text{CO})_3(\text{i-pr. H, H})$	530, 450(sh)	380(sh)	—	339
$\text{Mn}(\text{CO})_5\text{Me}(\text{CO})_3(\text{p-tol. H, H})$	592	420	376	n.o. ^b

^a sh = shoulder, most of which become more pronounced at 100 K. ^b n.o. = not observed.

At 370 nm an intra-ligand (IL) transition ($\pi \rightarrow \pi^*$) has been observed for complexes containing aromatic substituents on the DAB ligand.

The characteristic $\sigma \rightarrow \sigma^*$ transitions localised on the metal-metal bond appear at 330 nm, which is at almost the same position as that for $\text{Mn}_2(\text{CO})_{10}$. Only for complexes with substituents *trans* to the metal-metal bond is shift in the band position expected [24,25], and thus an absence of shift is in agreement with the proposed structure. In Table 5 the positions of the absorption maxima (or shoulders) are listed.

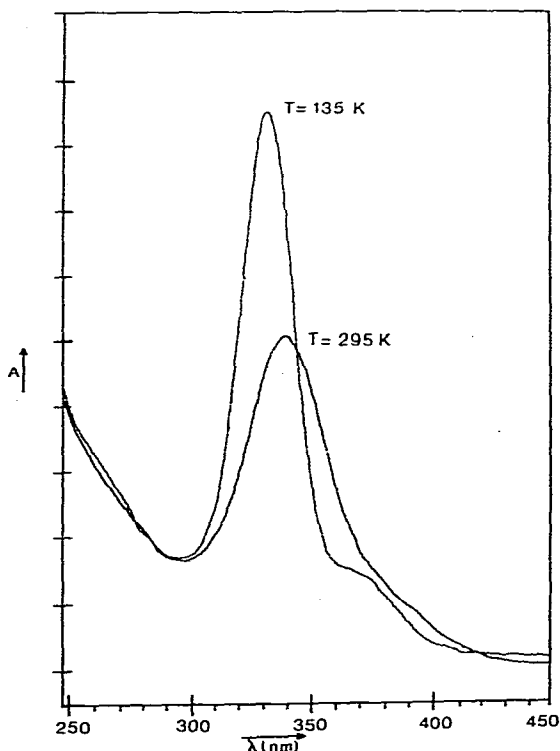


Fig. 6. Low temperature behaviour of the $\sigma \rightarrow \sigma^*$ transition of $\text{Mn}_2(\text{CO})_{10}$.

Low temperature measurements

For binuclear metal carbonyl complexes containing a two electron metal—metal bond an increase in the intensity of the $\sigma \rightarrow \sigma^*$ transition localised on the metal—metal bond has been observed in solutions of glassy solvents when the temperature is lowered [3,40–44]. The increase in intensity of the $\sigma \rightarrow \sigma^*$ transition which occurs at low temperatures for the unsubstituted $\text{Mn}_2(\text{CO})_{10}$, as is shown in Fig. 6, could not be observed for $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3(\text{DAB})$ solutions under the same conditions.

The low temperature spectra of $\text{Mn}(\text{CO})_5\text{Mn}(\text{CO})_3(\text{i-pr-N}=\text{CHCH}=\text{N-i-pr})$ and $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3(\text{p-anisidyl-N}=\text{CHCH}=\text{N-p-anisidyl})$, given in Figs. 7a and 7b do not show any enhancement of the $\sigma \rightarrow \sigma^*$ transition, nor do any other of the $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3\text{DAB}$ complexes. Why these complexes behave differently from other binuclear metal carbonyl complex with respect to the low temperature enhancement of the $\sigma \rightarrow \sigma^*$ band is not easy to explain.

Whether the low temperature intensity increase is universally applicable, so that we can decide that there is no metal—metal bond whenever the low temperature effects do not appear, or whether this rule may be used to determine the covalency of the metal—metal bond are questions which can only be answered when the effect itself is fully understood.

The solvatochromic shifts of the $\text{Mn}(\text{CO})_5\text{M}'(\text{CO})_3\text{DAB}$ complexes ($\text{M}' = \text{Mn}, \text{Re}$) already indicated that in polar glasses the complexes must be thermochromic [2]. In Figs. 7a and 7b the first CT transitions (I, II, III) to the $\pi^*(a')$ level of the DAB ligand are slightly shifted to shorter wavelengths at low temperature, while the shifts of the transitions to the second π^* level (a'') are less obvious. In the spectrum shown in Fig. 7b it is uncertain whether IV corresponds to IV' or to III'.

The assignment of the CT bands I, II and III to metal $d\pi$ to ligand π^* CT transitions is in contradiction with the proposals by Wrighton and Morse [24, 25]. They assigned these transitions in the spectra of the analogous $\text{M}_2(\text{CO})_8\text{L}$ complexes ($\text{M} = \text{Mn}, \text{Re}; \text{L} = 1,10\text{-phenanthroline}, \text{biquinoline}$) to a $d\sigma \rightarrow \pi^*$ CT transition, two of which can in principle exist. The similarity of the solvent and temperature dependence of the first band to those found for Fe^0 and Mo^0 complexes [1,2,11], and the fact that there are three electronic transitions underneath the absorption band are arguments which support our assignment.

The assignment by Morse and Wrighton [24] was based on the photochemical behaviour of $\text{M}_2(\text{CO})_8\text{L}$ complexes ($\text{L} = \text{bipy}, \text{phen}, \text{biquin}; \text{M} = \text{Mn}, \text{Re}$). When solutions of these complexes were irradiated with visible light the metal—metal bond was broken and $\text{M}_2(\text{CO})_6\text{L}$ complexes were formed together with the pure carbonyl $\text{Mn}_2(\text{CO})_{10}$. This photochemical behaviour indicates a loss of bonding character of the metal—metal bond as result of the first transition, which agrees very well with the assignment of the first band to a $d\sigma \rightarrow \pi^*$ transition. However, the number of transitions underneath the CT absorption band and the solvent dependence of the band positions are strong arguments against this assignment. The effect of weakening the metal—metal bond by irradiating a CT transition seems rather surprising, but this may be analogous to the photochemical release of CO in $\text{M}(\text{CO})_4\text{DAB}$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). In these complexes a *cis* CO group is activated by irradiating in the metal-to-DAB CT band [1,45]. In relation to these results, the activity of the metal—metal bond

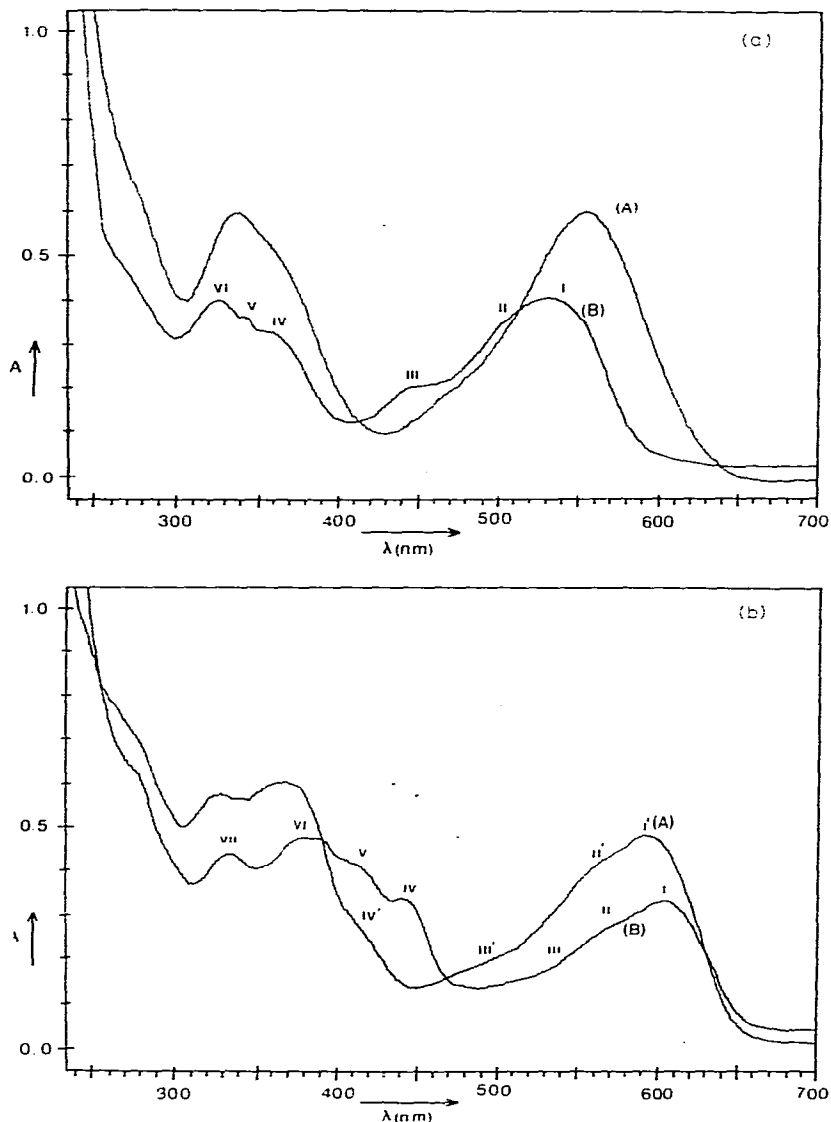


Fig.7. The UV-visible spectra of $Mn_2(CO)_8(DAB)$ ($DAB = i\text{-}pr\text{-}N=CHCH=N\text{-}i\text{-}pr$, $p\text{-}anisidyl\text{-}N=CHCH=N\text{-}p\text{-}anisidyl$) in EPA at room temperature (a) and 100 K (b).

will be studied with resonance Raman spectroscopy for $Mo_2(CO)_6IAE$ complexes [$IAE = bis(\mu\text{-}1\text{-}alkylamino\text{-}2\text{-}alkylimino)ethane\text{-}N,N'$] which are more photochemically stable.

Conclusion

It has been shown that although DAB ligands are closely related to bipyridine and 1,10-phenanthroline, they can behave differently in many types of reactions. Further evidence is found for the importance of the substituents on

the imine skeleton with respect to the reactivity of the ligands and the thermal stability of the complexes.

The manganese carbonyl DAB complexes were not previously known in the range of metal carbonyl DAB complexes. Now it has been shown that the π -interaction between the metal and the DAB ligand for these d^7 complexes falls between the π -interactions in d^6 and d^8 complexes.

The possible intramolecular reaction between the $\text{Mn}(\text{CO})_5$ fragment and the coordinated ligand does not occur. With respect to the attack on the C=N bond the $\text{M}(\text{CO})_5\text{M}'(\text{CO})_3(\text{DAB})$ complexes ($\text{M}' = \text{Mn}, \text{Re}$) differ from the binuclear d^8 $\text{Fe}_2(\text{CO})_6\text{DAB}$ complexes in which the DAB ligand is a six electron donor system.

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