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THE SYNTHESES AND COORDINATION PROPERTIES OF $M(CO)_3X(DAB)$ (M = Mn, Re; X = Cl, Br, I; DAB = 1,4-DIAZABUTADIENE)

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Summary

$M(CO)_5X$ (M = Mn, Re; X = Cl, Br, I) reacts with DAB (1,4-diazabutadiene = $R_1N{=}C(R_2)C(R_2)'{=}NR_1'$) to give $M(CO)_3X(DAB)$. The ^1H, ^{13}C NMR and IR spectra indicate that the facial isomer is formed exclusively. A comparison of the ^{13}C NMR spectra of $M(CO)_3X(DAB)$ (M = Mn, Re; X = Cl, Br, I; DAB = glyoxalbis-t-butylimine, glyoxyalbisisopropylimine) and the related $M(CO)_4DAB$ complexes (M = Cr, Mo, W) with $Fe(CO)_3DAB$ complexes shows that the charge density on the ligands is comparable in both types of d^6 metal complexes but is slightly different in the Fe-d^8 complexes. The effect of the DAB substituents on the carbonyl stretching frequencies is in agreement with the $A'(cis) > A''(cis) > A'(trans)$ band ordering.

$Mn(CO)_3Cl$(t-Bu—N=CH—CH=N—t-Bu) reacts with $AgBF_4$ under a CO atmosphere yielding $[Mn(CO)_4$(t-Bu—N=CH—CH=N-t-Bu)$]BF_4$. The cationic complex is isoelectronic with $M(CO)_4$(t-Bu—N=CH—CH=N—t-Bu) (M = Cr, Mo, W).

Introduction

DAB 1,4-diazabutadiene (= $R_1N{=}C(R_2)C(R_2')'{=}NR_1'$) metal carbonyl complexes of Cr,Mo,W [1—7], Fe [8,9] and Ni [10] have been investigated in the last few years, and interesting variations in bonding behaviour have become apparent. In $Fe(CO)_3DAB$ for example, the σ,π-coordination mode has been found for DAB ligands with bulky aliphatic substituents on the nitrogen atoms while for other DAB ligands the σ,σ-coordination mode was found.

The DAB ligands are closely related to 1,10-phenanthroline, 2,2'-bipyridine, and pyridinecarbaldehyde derivatives which are shown in Fig. 1, but σ,π-coor-

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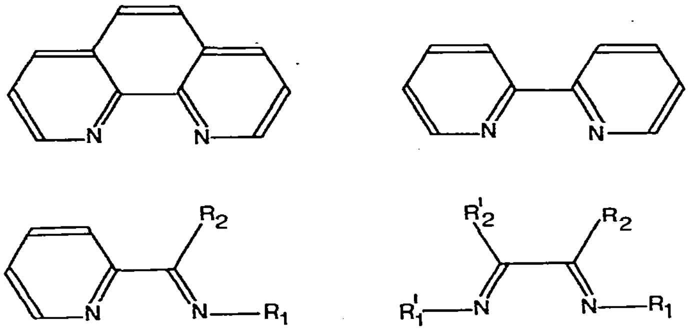

Fig. 1. DAB and related ligands: 1,10-phenanthroline (top left), 2,2′-bipyridine (top right), pyridinealdimine (or pyridineketimine) (bottom left), DAB (bottom right).

dination has not yet been observed, for these latter ligands, which are well known four electron σ,σ-donors. This coordination mode is also commonly found for the DAB ligands.

Besides the unusual bonding behaviour found in Fe(CO)$_3$DAB complexes, a further variation in bonding of DAB ligands with aliphatic and aromatic substituents has been observed. The σ-monodentate coordination mode is observed in Cr(CO)$_5$DAB at low temperature [1] for aromatic substituted DAB ligands, which contrasts with the formation of 1,2-dialkylimino-*N*,*N*′-1,2-μ,μ'-dialkylaminoethane in binuclear molybdenum carbonyl complexes for DAB ligands with bulky aliphatic substituents [11]. In order to obtain more information about the factors determining the type of coordination exhibited by these ligands in the corresponding complexes, a systematic study of the electronic and coordination properties of DAB in metal carbonyl complexes has been undertaken. As part of these investigations we report the syntheses and spectroscopic properties of M(CO)$_3$X(DAB) (M = Mn, Re; X = Cl, Br, I). Recently the preliminary results of X-ray diffraction studies on Mn(CO)$_3$Br(glyoxalbiscyclohexyldiimine) and Re(CO)$_3$Cl(glyoxalbisisopropyldiimine) were published [12,13] but no details of syntheses or spectroscopic properties were given.

Experimental

Complexes M(CO)$_5$X (M = Mn, Re; X = Cl, Br, I) were prepared according to literature methods [14,15]. Syntheses of the DAB ligands were previously described by tom Dieck and Renk [16].

(i) Preparation of Mn(CO)$_3$XDAB (X = Cl, Br, I; DAB = glyoxalbis-t-butyldiimine, glyoxalbisisopropyldiimine, glyoxalbiscyclohexyldiimine)

Mn(CO)$_5$X (2 mmol) and DAB (2 mmol) were refluxed in ether for 1/2 h. The product precipitated immediately as fine orange crystals. Complete precipitation was obtained by cooling the mother liquor to —80°C. After filtration the crystals were washed twice with 30 ml cooled diethyl ether and dried under vacuum. Yields were in the range 90—95%. The products were found to be slightly soluble in organic solvents, stable in air at room temperature but slightly sensitive towards light.

(ii) Preparation of $Mn(CO)_3Br(DAB)$ (DAB = glyoxalbisphenyldiimine)

$Mn(CO)_5Br$ (0.55 g), glyoxal (0.35 ml of a solution in water, 30%) and aniline (0.19 g) were refluxed for 3 h in toluene. The product precipitated at room temperature as dark purple micro crystals which were filtered off and washed twice with 30 ml of diethyl ether and dried under vacuum. Yield 80%. The product is almost insoluble in organic solvents, stable in air at room temperature and sensitive to light.

(iii) Preparation of $Mn(CO)_3X(DAB)$ (X = Cl, Br; DAB = glyoxalbis-p-tolyldiimine, glyoxalbis-p-anisidyldiimine, glyoxalbis-p-chlorophenyldimine)

$Mn(CO)_5X$ (2 mmol) and DAB (2 mmol) were stirred for 2 h in 25 ml of toluene and 25 ml heptane at 80°C. The products precipitated as dark brown-purple microcrystals at room temperature, and were filtered off, washed twice with 30 ml of toluene and twice with 30 ml of diethyl ether, and dried under vacuum. The complexes were obtained in almost quantitative yields. The products are almost insoluble in organic solvents, stable in air at room temperature, and very sensitive to light.

(iv) Preparation of $Re(CO)_3X(DAB)$ (X = Cl, Br; DAB = glyoxalbis-t-butyldiimine, glyoxalbisisopropyldiimine, glyoxalbis-p-tolyldiimine)

$Re(CO)_5X$ (X = Cl, Br) (1 mmol) and DAB (1 mmol) were stirred in a mixture of 20 ml toluene and 30 ml heptane at 80°C for 3 h. Upon cooling to room temperature the products precipitated as orange red microcrystals, in the case of aliphatic substituted DAB complexes, or as brown small cubic crystals in the case of the glyoxalbis-*p*-tolyldiimine complex. The products were filtered off, washed twice with 30 ml of toluene and twice with 50 ml of pentane and finally dried under vacuum. Yields were nearly quantitative.

The t-butyl and isopropyl derivatives were found to be only slightly soluble and the *p*-tolyl compound almost insoluble in organic solvents. All three complexes were found to be stable in air at room temperature and slightly sensitive to light.

(v) Preparation of $Mn(CO)_3BrL$ (L = bipyridine, phenanthroline)

The analogous $Mn(CO)_3XL$ complexes were reported by Abel and Wilkinson [15]. An excess of ligand was used but this is not necessary for the isolation of the pure products. In this work the same conditions were used as described in method (*i*) for the preparations of the DAB complexes. The products precipitated as yellow microcrystals in almost quantitative yields.

(vi) Preparation of $[Mn(CO)_4(t\text{-}Bu{-}N{=}CH{-}CH{=}N{-}t\text{-}Bu)]BF_4$

$Mn(CO)_3Cl(t\text{-}Bu{-}N{=}CH{-}CH{=}N{-}t\text{-}Bu)$ (1 mmol) and $AgBF_4$ (1 mmol) were stirred for 3 h in 30 ml of THF in an atmosphere of CO (pressure 1.5 atm), AgCl precipitated and was filtered off, 30 ml of pentane was added to the mother liquor and at −60°C the crude product precipitated. The product was filtered off and washed twice with 50 ml of pentane and finally dried under vacuum. Yield 80%.

Analyses

Elemental analyses were carried out by the Section Elemental Analysis of the

TABLE 1

ELEMENTAL ANALYSES

Elemental values in parentheses

Complex	C (%)	H (%)	N (%)
Mn(CO)$_3$Cl(t-Bu—N=CH—CH=N—t-Bu)	44.40(45.54)	5.81(5.83)	8.14(8.17)
Mn(CO)$_3$Br(t-Bu—N=CH—CH=N—t-Bu)	40.79(40.34)	5.29(5.17)	7.08(7.24)
Mn(CO)$_3$Br(i-Pr—N=CH—CH=N—i-Pr)	37.92(37.84)	4.70(4.59)	8.26(8.03)
Mn(CO)$_3$Br(Phen—N=CH—CH=N—Phen)	47.80(47.81)	2.94(2.81)	6.59(6.56)
Mn(CO)$_3$Br(*p*-tol—N=CH—CH=N—*p*-tol)	49.64(50.11)	3.56(3.52)	6.43(6.15)
Mn(CO)$_3$Br(*p*-anis—N=CH—CH=N—*p*-anis)	46.16(46.82)	3.19(3.29)	5.14(5.75)
Mn(CO)$_3$Br(*p*-Clphen—N=CH—CH=N—*p*-Clphen)	40.12(40.14)	1.99(2.02)	5.50(5.65)
Mn(CO)$_3$Br(1,10-phenanthroline)	45.22(45.15)	2.14(2.00)	7.00(7.02)
Mn(CO)$_3$Br(2,2′-bipyridyl)	41.50(41.64)	2.11(2.13)	7.46(7.47)
Mn(CO)$_3$I(t-Bu—N=CH—CH=N—t-Bu)	34.68(35.94)	4.48(4.61)	6.48(6.46)
Re(CO)$_3$Cl(t-Bu—N=CH—CH=N—t-Bu)	33.13(32.95)	4.36(4.23)	5.91(5.91)
Re(CO)$_3$Cl(i-Pr—N=CH—CH=N—i-Pr)	28.93(29.60)	3.46(3.59)	6.28(6.19)
Re(CO)$_3$Cl(p-tol—N=CH—CH=N—p-tol)	42.07(42.07)	2.95(2.95)	5.28(5.17)
Re(CO)$_3$Br(t-Bu—N=CH—CH=N—t-Bu)	30.50(30.12)	3.95(3.86)	5.37(5.40)

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Spectroscopy

^{1}H NMR spectra were recorded on a Varian T60 NMR spectrometer, ^{13}C NMR spectra on a Varian CFT 20 spectrometer, IR spectra were obtained with a Perkin—Elmer 283 spectrometer and UV-visible spectra using a Cary 14 spectrometer.

Results and discussion

The complexes are formed according to eq. 1, in which two moles of CO are replaced by the DAB ligand

$$M(CO)_5X + DAB \rightarrow M(CO)_3X(DAB) + 2\,CO \qquad (1)$$

The details of the synthesis given in the experimental section show the difference in the ease of formation of aliphatic and aromatic substituted DAB complexes. The aliphatic ligands form complexes readily in ether even at 30°C, whereas the aromatic ligands require prolonged heating in toluene/heptane mixtures. Re(CO)$_5$X (X = Cl, Br) are less reactive towards DAB ligands than the Mn complexes.

A similar difference in reactivity of aromatic and aliphatic ligands has been observed in the formation of Mn(CO)$_3$Br(sulphurdiimine), for which only the di-t-butylsulphurdiimine complex could be prepared. The other sulphurdiimine ligands did not react with Mn(CO)$_5$Br [17].

The Mn(CO)$_3$X(BAD) complexes could also be prepared from the [Mn(CO)$_4$X]$_2$ dimers, according to eq. 2.

$$[Mn(CO)_4X]_2 + 2\,DAB \rightarrow 2\,Mn(CO)_3X(DAB) + 2\,CO \qquad (2)$$

In this reaction two halogen bridges are broken. Attempts to obtain products which still contain bridging halogen atoms failed. The DAB ligands and the dimers only reacted in the ratio 2/1.

The $Mn(CO)_3I$(t-Bu—N=CH—CH=N—t-Bu) complex could be obtained by direct substitution of CO groups in $Mn(CO)_5I$ by the DAB ligand. An alternative method is halogen exchange in $Mn(CO)_3Cl$(t-Bu—N=CH—CH=N—t-Bu). Stirring of an excess of KI with the chlorine complex in THF at 40°C yielded the iodine complex. Other X groups could be coordinated to the complexes by stirring equimolar amounts of $Mn(CO)_3X$(DAB) (X = Cl, Br, I; M = Mn, Re) and AgX′ (X′ = cyanide, acetate, isobutyrate) in THF.

The use of $AgBF_4$ in an atmosphere of carbon monoxide (1.5 atm) resulted in the formation of $[Mn(CO)_4DAB]^+BF_4^-$, which is isoelectronic with $Cr(CO)_4$-DAB. A comparison of the carbonyl stretching frequencies in the case where tbu—N=CH—CH=N-tbu is the coordinated ligand is discussed in the IR section of this paper.

NMR spectroscopy

The positions of the azomethine proton resonances in the ^1H NMR spectra of DAB metal complexes is indicative of the coordination mode of the ligand. In the free ligands these signals have been observed at 7.8 ppm for the aliphatic DAB ligands and at 8.4 ppm for the aromatic ligands while in the σ,σ-coordinated DAB ligands values between 7.8 and 8.6 ppm have been observed [1,6,9,18]. The chemical shifts of these protons in $M(CO)_3X$(DAB) (M = Mn, Re; X = Cl, Br, I) indicate that the DAB ligands are in the σ,σ-bidentate coordination mode. Furthermore, in principle $M(CO)_3X$(DAB) can exist in two isomeric forms, the *cis*-meridional and the facial isomer. The equivalence of both ligand halves is indicated by the presence of a single set of line in the spectra which shows unambiguously that only the facial isomer was formed (Fig. 2). No *mer/fac* isomerisation could be observed on the NMR time scale between —90°C and +90°C.

In $Mn(CO)_3Br$(i-Pr—N=CH—CH=N—i-Pr) a small difference between the chemical shifts of the isopropyl methyl groups was observed, which is in accord with the methyl groups in the isopropyl groups being diastereotopic. The same effect is observed in the ^{13}C NMR spectrum of this complex. The nonequivalence of the two methyl groups is obvious from the two distinct lines at 22.6 and 22.8 ppm, respectively. In the ^1H NMR spectrum of $Re(CO)_3$(i-Pr—N=CH—CH=N—i-Pr) only one doublet is found for the methyl groups and only one line at 22.6 ppm for these methyl groups in the ^{13}C NMR spectrum of the complex.

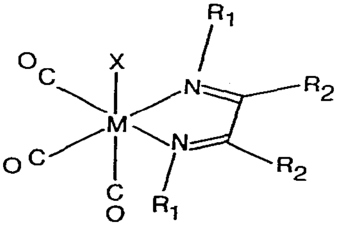

Fig. 2. Structure of $M(CO)_3X$(DAB) (M = Mn, Re; X = Cl, Br, I).

TABLE 2

^{1}H NMR DATA FOR M(CO)$_3$X(DAB) (M = Mn, Re; X = Cl, Br, I)

Chemical shifts in ppm relative to TMS; measurements were carried out in CDCl$_3$

Complex	δ (ppm)
Mn(CO)$_3$Cl(t-Bu—N=CH—CH=N—t-Bu)	δ(H, t-Bu) 1.64δ (H, im) 8.22
Mn(CO)$_3$Br(t-Bu—N=CH—CH=N—t-Bu)	δ(H, t-Bu) 1.70, δ(H, im) 8.25
Mn(CO)$_3$Br(i-Pr—N=CH—CH=N—i-Pr)	δ(H, i-Pr) 1.56 [a], δ(H, i-Pr) 4.5 [b], δ(H, im) 8.22
Mn(CO)$_3$Br(i-Pr—N=CH—CCH$_3$=N—i-Pr)	δ(H, i-Pr) 1.51/1.56 [a, c], δ(H, Me) 2.40, δ(H, i-Pr) 4.3/4.5 [b, c], δ(H, im) 8.07
Mn(CO)$_3$Br(phen—N=CH—CH=N—phen)	insoluble
Mn(CO)$_3$Br(*p*-tol—N=CH—CH=N—*p*-tol)	δ(H, *p*-tol) 2.39, δ(H, arom) 7.38, δ(H, im) 8.3(br)
Mn(CO)$_3$Br(*p*-Clphen—N=CH—CH=N—*p*-Clphen)	insoluble
Mn(CO)$_3$Br(*p*-anis—N=CH—CH=N—*p*-anis)	insoluble
Mn(CO)$_3$I(t-Bu—N=CH—CH=N—t-Bu)	δ(H, t-Bu) 1.76, δ(H, im) 8.34
Re(CO)$_3$Cl(t-Bu—N=CH—CH=N—t-Bu)	δ(H, t-Bu) 1.59, δ(H, im) 8.61
Re(CO)$_3$(i-Pr—N=CH—CH=N—i-Pr)	δ(H, i-Pr) 1.55 [a], δ(H, i-Pr) 4.22 [b], δ(H, im) 8.56
Re(CO)$_3$Cl(*p*-tol—N=CH—CH=N—*p*-tol)	δ(H, *p*-tol) 2.24, δ(H, arom) 7.36, δ(H, im) 8.60
Re(CO)$_3$Br(t-Bu—N=CH—CH=N—t-Bu)	δ(H, t-Bu) 1.61, δ(H, im) 8.60
[Mn(CO)$_4$(t-Bu—N=CH—CH=N—t-Bu)]BF$_4$	δ(H, t-Bu) 1.60, δ(H, im) 8.48

[a] Doublet J = 7 Hz. [b] Multiplet. [c] Inequivalent methyl groups. [d] Broad.

In Table 2 the ^{1}H NMR data are listed for those complexes for which the solubility was sufficient to give a spectrum.

More information about the electronic distribution in the metallocyclic ring was expected from a comparison between ^{13}C NMR spectra of the free ligands and the related metal carbonyl complexes. In Table 3 the ^{13}C NMR chemical shifts of the free ligands t-Bu—N=CH—CH=N—t-Bu and i-Pr—N=CH—CH=N—i-Pr and the respective metal carbonyl complexes of these ligands are listed.

TABLE 3

^{13}C CHEMICAL SHIFTS FOR M(CO)$_3$X(t-Bu—N=CH—CH=N—t-Bu) (M = Mn, Re; X = Cl, Br, I), RELATED COMPLEXES AND THE FREE LIGAND

δ ppm relative to TMS

Compound	δ(C, CH$_3$)	δ(C) [a]	δ(C, imine)	Ref.
t-Bu—N=CH—CH=N—t-Bu	29.4	58.1	157.8	
Mn(CO)$_3$Cl(DAB)	32.2	67.6	163.1	
Mn(CO)$_3$Br(DAB)	30.5	66.7	158.9	
Mn(CO)$_3$I(DAB)	31.6	68.4	163.4	
Re(CO)$_3$Cl(DAB)	31.9	68.0	160.5	
Re(CO)$_3$Br(DAB)	30.2	67.6	161.3	
Cr(CO)$_4$DAB	30.7	65.5	155.1	1
Mo(CO)$_4$DAB	30.5	64.9	155.7	1
W(CO)$_4$DAB	31.2	66.3	158.9	1
Fe(CO)$_3$DAB [b]	33.7/28.2	64.0/54.6	142.9/106.5	14
i-Pr—N=CH—CH=N—i-Pr	21.9	59.2	157.7	
Mn(CO)$_3$Br(DAB)	22.9/23.6	64.7	158.6	
Re(CO)$_3$Cl(DAB)	22.6	66.2	161.3	

[a] In case of t-Bu, quaternary C-atom; in case of i-Pr, tertiary C atom. [b] In this complex the lines are split as a result of asymmetric coordination, but the highest values of each couple is representative for σ coordinated DAB ligands in these type of complexes.

The chemical shifts of the amine carbon atoms are indicative of the electronic distribution in the imine skeleton. The imine carbon resonances for the $M(CO)_3$-X(DAB) complexes (M = Mn, Re; X = Cl, Br, I) are found slightly downfield from the same resonances in the $M(CO)_4$DAB complexes (M = Cr, Mo, W), but the differences in chemical shifts do not indicate an important delocalisation of the positive charge through the metallocyclic ring of $M(CO)_3X$(DAB) complexes (M = Mn, Re; X = Cl, Br, I). This is in contrast to the situation in $[M(CO)_4DAB]^-$ (M = Cr, Mo, W) for which the ESR spectra showed a strong delocalisation of the negative charge through the metallocyclic ring, as would be expected [6,20—22].

The difference in chemical shifts for the $Fe(CO)_3$DAB complexes of nearly 18 ppm is more significant. In the electron rich iron complexes there is a high charge density on the diimine ligand caused by a strong back donation.

IR measurements

The NMR spectra conclusively showed that of the two possible isomers for the $M(CO)_3X$(DAB) complexes (M = Mn, Re; X = Cl, Br, I) only the *fac* isomer was formed. Supplementary arguments have been obtained from the intensity pattern of the carbonyl stretching bands in the IR spectra.

For *cis*-meridional isomers one weak band near 2050 cm^{-1} and two strong bands between 2000 cm^{-1} and 1900 cm^{-1} are expected, while for facial isomers all three bands are expected to be strong [23,24]. In the IR spectra of $M(CO)_3X$(DAB) (M = Mn, Re; X = Cl, Br, I) three strong bands between 2050 cm^{-1} and 1900 cm^{-1} have been observed, confirming the structure as derived from the NMR spectra. Furthermore, this conformation in solution is similar to the conformation in the solid state which was obtained from a crystal structure determination [12,13].

The CO stretch frequencies are listed in Table 4. The CO stretch frequencies of $Mn(CO)_3BrL$ (L = 2,2'-bipyridine, 1,10-phenanthroline) are also included in Table 4 and it is shown that they are quite similar to the values obtained for

TABLE 4

CARBONYL STRETCHING FREQUENCIES OBTAINED FROM CH_2Cl_2 SOLUTIONS (cm^{-1})

Complex	$A'(cis)$	$A''(cis)$	$A'(trans)$
$Mn(CO)_3Cl$(t-Bu—N=CH—CH=N—t-Bu)	2025	1936	1925
$Mn(CO)_3Br$(t-Bu—N=CH—CH=N—t-Bu)	2021	1936	1927
$Mn(CO)_3Br$(i-Pr—N=CH—CH=N—i-Pr)	2027	1946	1930
$Mn(CO)_3Br$(phen—N=CH—CH=N—phen)	2032	1966	1936
$Mn(CO)_3Br$(*p*-tol—N=CH—CH=N—*p*-tol)	2029	1958	1931
$Mn(CO)_3Br$(*p*-anis—N=CH—CH=N—*p*-anis)	2030	1956	1930
$Mn(CO)_3Br$(*p*-Clphen—N=CH—CH=N—*p*-Clphen)	2034	1962	1935
$Mn(CO)_3Br$(1,10phenanthroline)	2024	1938	1917
$Mn(CO)_3Br$(2,2'-bipyridine)	2025	1939	1925
$Mn(CO)_3I$(t-Bu—N=CH—CH=N—t-Bu)	2020	1933(sh)	1930
$Re(CO)_3Cl$(t-Bu—N=CH—CH=N—t-Bu)	2024	1928	1916
$Re(CO)_3Cl$(i-Pr—N=CH—CH=N—i-Pr)	2027	1931	1908
$Re(CO)_3Cl$(*p*-tol—N=CH—CH=N—p-tol)	2030	1940	1914
$Re(CO)_3Br$(t-Bu—N=CH—CH=N—t-Bu)	2025	1925	1910

the aliphatic DAB ligands, while the values for the aromatic substituted DAB ligands are higher.

There is some controversy in the literature concerning the assignment of the carbonyl bands in the IR spectra of $M(CO)_3X(LL)$ complexes. Wuyts and Van der Kelen investigated the IR spectra of an extensive series of $Mn(CO)_3X(LL)$ complexes (X = Cl, Br; L = phosphine, $AsPh_3$, $SnPh_3$) and they assigned the band above 2000 cm^{-1} to the symmetrical stretching mode (A') of the CO group *cis* to the halogen atom, the next band to the antisymmetrical mode (A'') of these carbonyl groups and the lowest band of the CO stretching mode of the carbonyl group *trans* to the halogen atom (A' mode). Recently Brisdom et al. prepared some $[M(CO)_3XL]^-$ complexes (M = Cr, Mo, W; X = Cl, Br, I; L = 1,10-phenanthroline, 2,2'-bipyridine) which are isoelectronic to the $M(CO)_3X$-(DAB) complexes (M = Mn, Re; X = Cl, Br, I) and for which the bidentate ligands are closely related to the DAB ligands [25]. They adopted the $A'(cis) > A'(trans) > A''(cis)$ ordering for the carbonyl bands in the IR spectra, which was based on a Cotton—Kraihanzel force field calculation as was the assignment of Wuyts and Van der Kelen.

The carbonyl stretching frequencies which were observed for the $M(CO)_3X$-(DAB) complexes (M = Mn, Re; X = Cl, Br, I) were assigned in agreement with the $A'(cis) > A''(cis) > A'(trans)$ ordering of the bands. It was expected that the carbonyl stretching mode *trans* to the halogen atom will be almost unaffected by substituents on the DAB ligand while a large effect was expected for the antisymmetrical stretching mode of the carbonyl groups *trans* to the DAB ligand. This behaviour has been observed as is obvious from Table 4 and confirms the assignments of the bands.

The C_{2v} symmetry of the $[Mn(CO)_4(t\text{-Bu—N=CH—CH=N—t-Bu})]^+$ cation is confirmed by the IR spectrum of the complex. The $A'(cis)$ mode has been observed at 2048 cm^{-1}, the $B_1(cis)$ vibration at 2013 cm^{-1}, the $A'(trans)$ at 1977 cm^{-1} and the $B_2(trans)$ mode at 1943 cm^{-1}. All bands are shifted 100 cm^{-1} to higher frequency except for the $A_1(cis)$ mode which is only shifted 20 cm^{-1} to higher frequency compared to the isoelectronic $M(CO)_4(t\text{-Bu—N=CH—CH=N—t-Bu})$ complexes (M = Cr, Mo, W) [1,4,5].

UV-visible spectroscopy

The complexes are all coloured as a result of the CT transitions between the metal and the DAB ligands. In Fig. 3 a tentative MO scheme is shown which is in agreement with the observed CT transitions in the UV-visible spectra. The most pronounced band has been assigned to the $a' \leftarrow a'$ transition while two $a' \leftarrow a''$ transitions were found as shoulders on the short wavelength side of the CT band. Transitions to the a'' level of the DAB ligand were not observed at room temperature. In principle there must exist six symmetry-allowed CT transitions to the DAB ligand. The maxima of the observed CT bands are listed in Table 5. In the literature the band near 380 nm in the UV spectra of d^6 metal carbonyl complexes is assigned to a LF transition [26—29] but in the case of $Mn(CO)_5X$ (X = Cl, Br, I) it has been shown that the halogen *p*-orbitals interact with the metal *d*-orbitals which results in some CT character for these transitions [30].

In the $M(CO)_3X(DAB)$ complexes (M = Mn, Re; X = Cl, Br, I) this transition

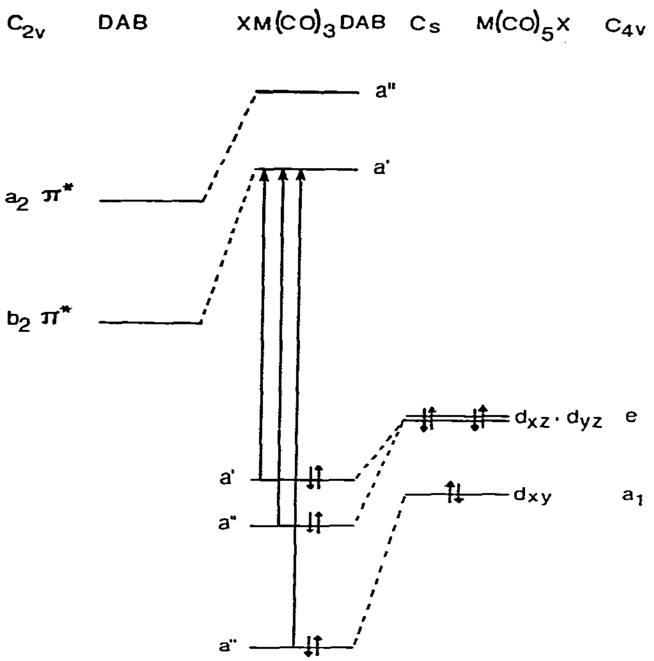

Fig. 3. Part of a tentative M.O. scheme showing the three observed CT transitions.

has been observed at 360 nm and the molar extinction shows that there must be some CT character in the LF transitions for these complexes as well. In complexes with atomatic substituents on the DAB ligand the LF transitions are obscured by interligand transitions (IL) on the aromatic ring 5. The LF and IL band maxima are also listed in Table 5. The solvent shift of the metal to DAB ligand CT transitions as was observed in M(CO)$_4$DAB (M = Cr, Mo, W) and related complexes [1,5,31,23] has also been found for M(CO)$_3$X(DAB) (M = Mn, Re; X = Cl, Br, I). The positive solvatochromism indicates that there is a

TABLE 5

POSITIONS OF THE BAND MAXIMA IN THE UV SPECTRA OF Mn(CO)$_3$XDAB (X = Cl, Br, I) IN CH$_2$Cl$_2$ SOLUTIONS

λ max in nm, ϵ_{mol} in mol^{-1} l cm^{-1} in parentheses

Complex	CT	LF	IL
Mn(CO)$_3$Cl(t-Bu—N=CH—CH=N—t-Bu)	467(2250)	357(1760)	—
Mn(CO)$_3$Br(t-Bu—N=CH—CH=N—t-Bu)	478(1510)	356(1190)	—
Mn(CO)$_3$Br(i-Pr—N=CH—CH=N—i-Pr)	484(643)	376(660)	—
Mn(CO)$_3$Br(phen—N=CH—CH=N—phen)	564(1760)	—	348(6400)
Mn(CO)$_3$Br(*p*-tol—N=CH—CH=N—*p*-tol)	556(1760)	—	367(11.400)
Mn(CO)$_3$Br(*p*-Clphen—N=CH—CH=N—*p*-Clphen)	581(2250)	—	359(11.500)
Mn(CO)$_3$Br(*p*-anis—N=CH—CH=N—*p*-anis)	546(1440)	—	378(10.700)
Mn(CO)$_3$I(t-Bu—N=CH—CH=N—t-Bu)	502(1320)	361(2770)	—
Re(CO)$_3$Cl(t-Bu—N=CH—CH=N—t-Bu)	434(3485)	—	—
Re(CO)$_3$Cl(i-Pr—N=CH—CH=N—i-Pr)	442	—	—
Re(CO)$_3$Cl(*p*-tol—N=CH—CH=N—*p*-tol)	501(12.500)	—	—
Re(CO)$_3$Br(t-Bu—N=CH—CH=N—t-Bu)	415	—	—

TABLE 6

SOLVATOCHROMISM OF $Mn(CO)_3XDAB$ (X = Cl, Br, I). BAND MAXIMA OF THE CT TRANSITIONS FOR C_6H_6 AND CH_3OH SOLUTIONS

The differences in energy (ΔE) are given in cm^{-1}; λ_{max} in nm

Complex	C_6H_6	CH_3OH	ΔE
$Mn(CO)_3Cl$(t-Bu—N=CH—CH=N—t-Bu)	478	444	1600
$Mn(CO)_3Br$(t-Bu—N=CH—CH=N—t-Bu)	489	479	430
$Mn(CO)_3Br$(i-Pr—N=CH—CH=N—i-Pr)	505	470	480
$Mn(CO)_3Br$(phen—N=CH—CH=N—phen)	568	528	1480
$Mn(CO)_3Br$(*p*-tol—N=CH—CH=N—*p*-tol)	569	531	1360
$Mn(CO)_3Br$(*p*-Clphen—N=CH—CH=N—*p*-Clphen)	593	537	1760
$Mn(CO)_3Br$(*p*-anis—N=CH—CH=N—*p*-anis)	545(sh)	500	1650
$Mn(CO)_3I$(t-Bu—N=CH—CH=N—t-Bu)	518	445	2170
$Re(CO)_3Cl$(t-Bu—N=CH—CH=N—t-Bu)	437	432	260
$Re(CO)_3Cl$(i-Pr—N=CH—CH=N—i-Pr)	455	418	1040
$Re(CO)_3Cl$(*p*-tol—N=CH—CH=N—*p*-tol)	515	462	2230
$Re(CO)_3Br$(t-Bu—N=CH—CH=N—t-Bu)	453	415	2020
[$Mn(CO)_4$(t-Bu—N=CH—CH=N—t-Bu)]BF_4	680	423	2800

strong resultant dipole moment from the DAB ligand to the metal and that the electron transfer during the CT transition is antiparallel to it [32]. The solvatochromism is illustrated by the order of the CT bands in Table 6 in which the CT band maxima for C_6H_6 and CH_3OH solutions are listed. The solvent shifts are comparable to the solvent shifts of the $M(CO)_4DAB$ complexes (M = Cr, Mo, W) [5].

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References

1 L.H. Staal, D.J. Stufkens and A. Oskam, Inorg. Chim. Acta, 26 (1978) 255.
2 R.W. Balk, D.J. Stufkens and A. Oskam, Inorg. Chim. Acta, 28 (1978) 133.
3 D. Walther, Z. Prakt. Chem., 316 (1974) 604.
4 H. Bock and H. tom Dieck, Chem. Ber., 100 (1967) 228.
5 H. tom Dieck and I.W. Renk, Chem. Ber., 104 (1971) 110.
6 K.D. Franz, H. tom Dieck, U. Krynitz and I.W. Renk, J. Organometal. Chem., 64 (1974) 361.
7 W. Majunke, D. Liebfritz, Th. Mack and H. tom Dieck, Chem. Ber., 108 (1975) 3025.
8 S. Otsuka, T. Yoshida and A. Nakumara, Inorg. Chem., 6 (1967) 20.
9 H. tom Dieck and A. Orlopp, Angew. Chem., 14 (1975) 251.
10 D. Walther, Z. Chem., 15 (1975) 72.
11 L.H. Staal, A. Oskam and K. Vrieze, to be published.
12 A.J. Graham, D. Akrigg and B. Sheldrick, Cryst. Struct. Commun., 6 (1977) 571.
13 A.J. Graham, D. Akrigg and B. Sheldrick, Cryst. Struct. Commun., 6 (1977) 577.
14 E.O. Brimm, M.A. Lunch and W.J. Sasny, J. Amer. Chem. Soc., 76 (1954) 3831.
15 E.W. Abel and G. Wilkinson, J. Chem. Soc., (1959) 1501.
16 H. tom Dieck and I.W. Renk, Chem. Ber., 104 (1971) 92.
17 R. Meij, J.N. Louwen and K. Vrieze, unpublished results.
18 H. tom Dieck, I.W. Renk, and K.D. Franz, J. Organometal. Chem., 94 (1975) 417.
19 D. Liebfritz and H. tom Dieck, J. Organometal. Chem., 105 (1976) 255.
20 K.D. Franz, H. tom Dieck, K.A. Ostaja Storzewski and F. Hohmann, Tetrahedron, 31 (1975) 1465.
21 K.D. Franz, H. tom Dieck, U. Krynitz and I.W. Renk, J. Organometal. Chem., 64 (1974) 361.
22 H. tom Dieck, K.D. Franz and F. Hohmann, Chem. Ber., 108 (1975) 163.

23 L.F. Wuyts and G.P. van der Kelen, Inorg. Chim. Acta, 23 (1977) 19.
24 D.A. Edwards and J. Marshalsea, J. Organometal. Chem., 131 (1977) 73.
25 B.J. Brisdon, D.A. Edwards and J. White, J. Organometal. Chem., 156 (1978) 427.
26 M.S. Wrighton and D.L. Morse, J. Organometal. Chem., 97 (1975) 405.
27 M.S. Wrighton and D.L. Morse, J. Amer. Chem. Soc., 96 (1974) 998.
28 D.L. Morse and M.S. Wrighton, J. Amer. Chem. Soc., 98 (1976) 3931.
29 M.S. Wrighton, D.L. Morse, H.B. Gray and K.L. Ottesen, J. Amer. Chem. Soc., 98 (1976) 1111.
30 R.A.N. McLean, J. Chem. Soc. Dalton, (1974) 1568.
31 H. tom Dieck and I.W. Renk, Angew. Chem., 82 (1970) 805.
32 I.W. Renk and H. tom Dieck, Chem. Ber., 105 (1972) 1403.