

Binuclear Metal Carbonyl DAB Complexes. V. The Syntheses, Structural and Chemical Properties of $\text{Co}_2(\text{CO})_6(\text{DAB})$ (DAB = 1,4-diazabutadiene)

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Complexes of the composition $\text{Co}_2(\text{CO})_6(\text{DAB})$ (DAB = $\text{R}-\text{N}=\text{C}(\text{R}')-\text{C}(\text{R}'')=\text{N}-\text{R}$; R = isopropyl, 2,6-xylyl, 2,4,6-mesityl, p-methoxyphenyl; $\text{R}' = \text{H}$, $\text{R}'' = \text{H}$, CH_3) have been obtained by a substitution reaction involving $\text{Co}_2(\text{CO})_8$ and DAB. Refluxing of $\text{Co}_2(\text{CO})_6(\text{DAB})$ in n-hexane yields $\text{Co}_4(\text{CO})_8(\text{DAB})_2$, while reactions with DAB lead to the formation of $\text{Co}_2(\text{CO})_4(\text{DAB})_2$.

The complexes have been characterized by means of mass spectrometry, IR, UV, Raman and NMR spectroscopy. It is shown that $\text{Co}_2(\text{CO})_6(\text{DAB})$ contains a σ, σ -coordinated 1,4-diazabutadiene, linked to one of the Co-atoms and four terminal and two bridging carbonyl groups.

Both ^1H and ^{13}C NMR show high field chemical shifts for the imine H and imine C atoms respectively, indicating strong π -backbonding to the diimine ligand. Indeed it was found that in a series of zerovalent d^6 , d^7 , d^8 , d^9 metal carbonyl DAB complexes, in which the DAB ligand acts a σ -N, σ -N'-donor, the chemical shifts of the imine hydrogen atoms depend on the number of d-electrons, i.e. there is an increasing π -backbonding in the order $d^6 < d^7 < d^8 < d^9$. Finally, it is argued that for binuclear complexes the relative stability of the $4e$ - σ, σ -donor mode versus the $6e$ - σ -N, μ^2 -N', η^2 -C=N' coordination mode, in which the diimine bridges two metals (e.g. in $\text{Ru}_2(\text{CO})_6(\text{DAB})$), is strongly dependent on a number of factors.

Introduction

Part of the work at our laboratory is focused on the coordinating behaviour of 1,4-diazabutadienes (DAB). In metal DAB complexes of the late transition metals the DAB ligand has demonstrated a versatility in bonding behaviour in which only the lone pairs on the imine nitrogens participated; i.e. σ -monodentate, σ, σ -bridging and σ, σ -bidentate coordination [1–3]. The coordination of DAB ligands in

complexes of the main group elements resulted in the selective reduction of one or two C=N double bonds, leading to amino-imino compounds or to di-amino ligands [4].

Our work is concerned with the reactivity and coordinating behaviour of DAB ligands in metal carbonyl complexes. A systematic study of metal carbonyl DAB complexes was undertaken in order to determine the role of the central metal in the bonding behaviour of the DAB ligands. Coordination *via* the lone pairs on nitrogen could be achieved with all metal carbonyls (Fig. 1a), forming a five membered chelate ring, although with some metals special precautions were necessary. In the case of the relatively electron rich binuclear metal carbonyl complexes of the iron triad: $\text{Fe}_2(\text{CO})_6(\text{DAB})$ [5], $\text{Ru}_2(\text{CO})_6(\text{DAB})$ [6, 7], $\text{FeRu}(\text{CO})_6(\text{DAB})$ [6], $\text{Os}_2(\text{CO})_6(\text{DAB})$ [8] and for the heterobinuclear complexes $\text{MnCo}(\text{CO})_6(\text{DAB})$ and $\text{ReCo}(\text{CO})_6(\text{DAB})$ [9] the ligands were found to behave as six electron donor systems, coordinating formally *via* the two lone pairs on nitrogen and *via* one pair of π -electrons of the N=C-C=N skeleton (see Fig. 1b).

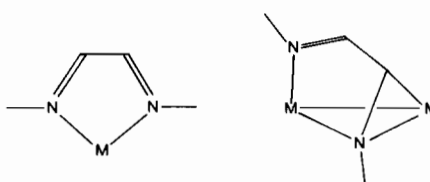


Fig. 1. The two relevant coordination modes of the DAB ligand.

Coordination *via* the π -electron system is very common for butadienes, but examples of 1,4-dihetero butadienes coordinated *via* the C=X bonds (X = hetero atom) are scarce. All examples of DAB complexes containing η^2 -C=N coordination are mentioned above. An earlier proposed example in the literature of η^2 -C=N coordination in $\text{Fe}(\text{CO})_3(\text{DAB})$ [10] is based on a misinterpretation of the experimental results as has been shown independently by us [11] and by Frühauf *et al.* [5].

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In this paper we present our results for cobalt carbonyl DAB examples, which may be regarded as the missing links in the series d^6 to d^{10} metal carbonyl DAB complexes. Furthermore, the synthesis of $\text{Co}_2(\text{CO})_6(\text{DAB})$ gives additional information about the factors determining the ambident bonding behaviour of DAB ligands. It will be shown that apart from the electron density on the central metal, the geometry of the coordination polyhedron is also an important factor determining the coordination mode of the DAB ligand in the complex.

Experimental

All solvents were carefully dried, deoxygenated and freshly distilled before use. $\text{Co}_2(\text{CO})_8$ obtained from Strem Chemicals was twice recrystallized from n-pentane. DAB-ligands were prepared from the corresponding primary amines and diketones by condensation according to standard procedures [12, 13]. The reactions between $\text{Co}_2(\text{CO})_8$ and DAB ligands were carried out in a purified nitrogen atmosphere and light was excluded to prevent photochemical decomposition.

Chromatographic separations were carried out with silica gel as stationary phase. The silica gel was dried, deoxygenated and activated before use by heating it for 5 h at 180°C under vacuum (10^{-2} torr). Extreme care was taken to keep the column under a nitrogen atmosphere.

Preparation of $\text{Co}_2(\text{CO})_6(\text{DAB})$ [DAB = glyoxalbis(isopropylimine), glyoxalbis(p-tolylimine), glyoxalbis(2,6-xylylimine), glyoxalbis(2,4,6-mesitylimine) and diacetylbis(p-tolylimine)]

$\text{Co}_2(\text{CO})_8$ (3.0 mmol) and DAB (3.0 mmol) were stirred overnight in 50 ml of diethyl ether. An intense purple solution was formed which was evaporated to dryness. The solid residue was purified by column chromatography. Unreacted $\text{Co}_2(\text{CO})_8$ was extracted

from the column with n-pentane as eluent. The crude product was eluted with diethyl ether. The ether fraction was concentrated to 20 ml and the product $\text{Co}_2(\text{CO})_6(\text{DAB})$ crystallized at -70°C . Recrystallization from ether/n-pentane at -70°C yielded 40%–60% of black metallic glittering crystals.

$\text{Co}_2(\text{CO})_4(\text{DAB})_2$ [DAB = glyoxalbis(p-tolylimine)]

i) $\text{Co}_2(\text{CO})_8$ (3.0 mmol) and DAB (6.0 mmol) were stirred overnight in 100 ml of diethyl ether. An intense dark purple solution was formed which was filtered. The filtrate was concentrated and the crude product was obtained by precipitation at -20°C . After two crystallizations from diethyl ether 40% of black glittering crystals were obtained.

ii) Same procedure as in *i)*, but starting from $\text{Co}_2(\text{CO})_6(\text{DAB})$ (1 mmol) and DAB.

$\text{Co}_4(\text{CO})_8(\text{DAB})_2$ [DAB = glyoxalbis(p-tolylimine)]

$\text{Co}_2(\text{CO})_6$ [glyoxalbis(p-tolylimine)] (1.0 mmol) was refluxed for 2 h in n-hexane (50 ml). The dark purple solution was filtered hot and was allowed to cool. The crude product was recrystallized from diethyl ether to give 60% of black purple crystals.

Elemental analyses were carried out by the section of Elemental Analyses of The Institute of Organic Chemistry, TNO, Utrecht, The Netherlands. The results are listed in Table I.

IR spectra have been recorded using a Perkin Elmer 283 spectrophotometer, ^{13}C NMR spectra with a Varian CFT 20 and a Bruker WP 80 and ^1H NMR spectra using a Varian T 60 apparatus. UV-visible spectra were recorded with a Cary 14 spectrophotometer and mass spectra were obtained with a Varian MS 902 spectrometer. Raman spectra were recorded with a Coderg PH 1 spectrophotometer, using an argon CR model 53 ion laser with a CR 490 tunable dye laser operating with sodium fluoresceine and rhodamine 6G in ethylene glycol as dyes. A spinning cell according to Kiefer was used [14] operating at -10°C to suppress decomposition. $\text{Co}_2(\text{CO})_6$

TABLE I. Elemental Analysis of $\text{Co}_2(\text{CO})_6(\text{DAB})$ Complexes. Calculated Values in Parentheses.

Compound	%C	%H	%N
$\text{Co}_2(\text{CO})_6$ [glyoxalbis(isopropylimine)]	(39.44)	(3.78)	(6.98)
$\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_6\text{Co}_2$	38.16	4.04	6.55
$\text{Co}_2(\text{CO})_6$ [glyoxalbis(p-tolylimine)]	(50.58)	(3.09)	(5.36)
$\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_6\text{Co}_2$	50.26	3.35	5.61
$\text{Co}_2(\text{CO})_6$ [glyoxalbis(2,6-xylylimine)]	(50.19)	(3.80)	(5.32)
$\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_6\text{Co}_2$	50.71	3.75	4.81
$\text{Co}_2(\text{CO})_6$ [glyoxalbis(2,4,6-mesitylimine)]	(53.98)	(4.15)	(4.84)
$\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_6\text{Co}_2$	53.02	4.39	4.90
$\text{Co}_2(\text{CO})_6$ [diacetylbis(p-tolylimine)]	(52.37)	(3.66)	(5.09)
$\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_6\text{Co}_2$	51.59	4.37	5.02

[glyoxalbis(isopropylimine)] was studied in dichloromethane solutions (10^{-3} – 10^{-4} M) and the intensities of solvent bands were used to check on decomposition. Due to photochemical instability the spectrum had to be recorded in steps of 500 cm^{-1} using a fresh solution for all separate steps.

Results and Discussion

Mass Spectrometry

Only $\text{Co}_2(\text{CO})_6$ [glyoxalbis(isopropylimine)] was stable in the gas phase and showed a characteristic fragmentation pattern. The parent ion peak was observed at 426 mass units which is in agreement with the expected molecular weight of the binuclear complex. The subsequent loss of six carbonyl groups was observed, resulting in the bimetallic $[\text{Co}_2(\text{DAB})]^+$ fragment. Loss of a cobalt atom resulted in the formation of the mononuclear $[\text{Co}(\text{DAB})]^+$ fragment and loss of a second cobalt atom gave the cation of the free ligand. In the Table II the most characteristic fragments observed in the mass spectrum of $\text{Co}_2(\text{CO})_6$ [glyoxalbis(isopropylimine)] are listed.

It was not possible to obtain mass spectra of the $\text{Co}_2(\text{CO})_6(\text{DAB})$ complexes with aromatic substituents at room temperature. At elevated temperatures these complexes decomposed and $\text{Co}_4(\text{CO})_{12}$ was detected.

^1H NMR Spectroscopy

The coordination mode of the DAB ligands in the complexes can be determined with NMR spectroscopy. In the case of σ, σ -coordination, *i.e.* coordination *via* the two lone pairs on nitrogen, only minor changes will be observed in the ^1H NMR patterns as compared with the pattern of the free ligands. In particular the chemical shifts of the imine hydrogen

TABLE II. Fragmentation Observed in the Mass Spectrum of $\text{Co}_2(\text{CO})_6$ [glyoxalbis(isopropylimine)].

Fragment	m/e
$[\text{Co}_2(\text{CO})_6(\text{C}_3\text{H}_7\text{-N}=\text{CH}-\text{CH}=\text{N}-\text{C}_3\text{H}_7)]^+$	426
$[\text{Co}_2(\text{CO})_5(\text{C}_3\text{H}_7\text{-N}=\text{CH}-\text{CH}=\text{N}-\text{C}_3\text{H}_7)]^+$	398
$[\text{Co}_2(\text{CO})_4(\text{C}_3\text{H}_7\text{-N}=\text{CH}-\text{CH}=\text{N}-\text{C}_3\text{H}_7)]^+$	370
$[\text{Co}_2(\text{CO})_3(\text{C}_3\text{H}_7\text{-N}=\text{CH}-\text{CH}=\text{N}-\text{C}_3\text{H}_7)]^+$	342
$[\text{Co}_2(\text{CO})_2(\text{C}_3\text{H}_7\text{-N}=\text{CH}-\text{CH}=\text{N}-\text{C}_3\text{H}_7)]^+$	314
$[\text{Co}_2(\text{CO})(\text{C}_3\text{H}_7\text{-N}=\text{CH}-\text{CH}=\text{N}-\text{C}_3\text{H}_7)]^+$	286
$[\text{Co}(\text{C}_3\text{H}_7\text{-N}=\text{CH}-\text{CH}=\text{N}-\text{C}_3\text{H}_7)]^+$	258
$[\text{Co}(\text{C}_3\text{H}_7\text{-N}=\text{CH}-\text{CH}=\text{N}-\text{C}_3\text{H}_7)]^+$	199
$[\text{C}_3\text{H}_7\text{-N}=\text{CH}-\text{CH}=\text{N}-\text{C}_3\text{H}_7]^+$	140

atoms are indicative. Generally, values between 7 and 9 ppm are observed for these atoms in DAB ligands coordinated to low valent metals [15].

The ^1H NMR data listed in Table III are evidence that the DAB ligands in $\text{Co}_2(\text{CO})_6(\text{DAB})$ complexes are σ -coordinated, forming a five membered chelate ring with one of the cobalt atoms. The DAB ligand is symmetrically coordinated since a single set of resonances is observed for the two identical $\text{R}-\text{N}=\text{CH}$ -moieties of the ligands.

The symmetrical five membered chelate ring may be regarded as the symmetry forced coordination mode of the DAB system [15] and is therefore the common type of bonding for these ligands. Furthermore a stabilizing effect of chelate ring formation has been deduced by ascribing aromatic or pseudo aromatic character to the five membered ring [16], especially in cases with zero valent metals [17].

In Table IV the ^1H NMR chemical shifts are listed for the imine hydrogen atoms of d^6 to d^9 metal carbonyl DAB complexes derived from glyoxalbis(isopropylimine), glyoxalbis(*tert.*-butylimine) and glyoxalbis(*p*-tolylimine). The chemical shift values of

TABLE III. ^1H NMR Data of $\text{Co}_2(\text{CO})_6(\text{DAB})$ Complexes Obtained in CDCl_3 Solutions (δ ppm relative to TMS).

Complex	δ (ppm)		Imine-H
$^i\text{Pr}-\text{N}=\text{CH}-\text{CH}=\text{N}-^i\text{Pr}$	1.23 ^{<i>i</i>Pr^a}	3.46 ^{<i>i</i>Pr^b}	7.88
$\text{Co}_2(\text{CO})_6(\text{DAB})$	1.52	4.97	7.84
<i>p</i> -tol-N = CH-CH = N- <i>p</i> -tol	2.35 ^{CH₃}	7.20 ^{arom}	8.34
$\text{Co}_2(\text{CO})_6(\text{DAB})$	2.45 ^{CH₃}	7.35	7.83
<i>p</i> -methoxyphen-N = CH-CH = N- <i>p</i> -methoxyphen.	3.80 ^{OCH₃}	7.07 ^{arom^c}	8.32
$\text{Co}_2(\text{CO})_6(\text{DAB})$	3.85	7.20	7.80
2,6-xyl-N = CH-CH = N-2,6-xyl.	2.14	6.90	7.98
$\text{Co}_2(\text{CO})_6(\text{DAB})$	2.23	7.19	7.74
2,4,6-mesityl-N = CH-CH = N-2,4,6-mesityl	2.15 ^{ortho-CH₃}	2.26 ^{<i>p</i>-CH₃}	6.84 ^{arom}
$\text{Co}_2(\text{CO})_6(\text{DAB})$	2.25	2.37	7.00
<i>p</i> -tol-N = C(CH ₃)-C(CH ₃) = N- <i>p</i> -tol	2.11 ^{CH₃}	2.24 ^{CH₃}	6.92 ^{arom^c}
$\text{Co}_2(\text{CO})_6(\text{DAB})$ (<i>d</i>)	1.4 ^{CH₃}	2.2 ^{CH₃}	7.1 ^{arom}
$\text{Co}_4(\text{CO})_8$ (<i>p</i> -tol, H) ₂	2.30 ^{CH₃}	7.28 ^{arom}	8.50
$\text{Co}_2(\text{CO})_4$ (<i>p</i> -tol, H) ₂	2.40 ^{CH₃}	7.35 ^{arom}	7.10

^aDoublet $J = 8$ Hz. ^bSeptet. ^cAB-pattern. ^dExternal reference TMS, solvent toluene- d^8 .

TABLE IV. ^1H NMR Shifts of the Imine Hydrogen Atoms in Metal Carbonyl DAB Complexes.

Ligand	$\text{Cr}(\text{CO})_4(\text{DAB})$	$\text{Mn}_2(\text{CO})_8(\text{DAB})$	$\text{Fe}(\text{CO})_3(\text{DAB})$	$\text{Co}_2(\text{CO})_6(\text{DAB})$
$^i\text{Pr}-\text{N}=\text{CH}-\text{CH}=\text{N}-^i\text{Pr}$	8.22	8.18	7.62	7.84
$^t\text{Bu}-\text{N}=\text{CH}-\text{CH}=\text{N}-^t\text{Bu}$	8.30	^a	8.01	7.88
$p\text{-tol}-\text{N}=\text{CH}-\text{CH}=\text{N}-p\text{-tol}$	8.39	8.18	^a	7.83

^aNot reported.TABLE V. ^{13}C NMR Data of $\text{Co}_2(\text{CO})_6(\text{DAB})$ ($\text{R}_1 = \text{xylyl}$, mesityl; $\text{R}_2 = \text{H}$) and the Corresponding Free Ligands (δ ppm relative to TMS).

Compounds	C^{methyl}		C^{arom}				C^{imine}	CO
	<i>para</i>	<i>ortho</i>						
$\text{meS}-\text{N}=\text{CH}-\text{CH}=\text{N}-\text{meS}$	18.0	20.5	126.8	128.8	133.8	147.3	163.15	
$\text{Co}_2(\text{CO})_6(\text{DAB})$	18.0	20.8		128.9 ^a	135.4	148.9	151.2	209.0
$\text{xylyl}-\text{N}=\text{CH}-\text{CH}=\text{N}-\text{xylyl}$		18.0	124.7	126.4	128.2	150.1		
$\text{Co}_2(\text{CO})_6(\text{DAB})$		17.6	125.9	126.9	128.9		150.6	208.7

^aDegenerate.

the imine hydrogen atoms depend on the number of d-electrons on the metal in the metallocyclic ring. An upfield shift is found with increasing number of d-electrons, which means that the $d_{\pi}-\pi^*$ interaction increases in the order $d^6 < d^7 < d^8 < d^9$. This confirms the bonding model for zero valent metal carbonyl DAB complexes [18–21]. The increasing shielding effect has also been observed for d^6 to d^8 metal carbonyl complexes of glyoxalbis(isopropylimine) with help of ^{13}C NMR spectroscopy [22] and the results are in agreement with the ^1H NMR shifts listed in Table IV. Analogous conclusions have been drawn for the ^{13}C NMR shifts of the carbonyl groups in unsubstituted metal carbonyl complexes [23].

^{13}C NMR Spectroscopy

^{13}C NMR data have been obtained for $\text{Co}_2(\text{CO})_6$ -[glyoxalbis(2,4,6-mesitylimine)] and $\text{Co}_2(\text{CO})_6$ -[glyoxalbis(xylylimine)]. Instability in solution did not allow measurements of other derivatives.

The ^{13}C NMR chemical shifts of the imine carbon atoms are generally observed between 175 and 140 ppm relative to TMS for DAB ligands which are coordinated via the lone pairs on nitrogen [22, 24]. The chemical shift values of the imine carbon atoms are 13 ppm upfield relative to the position in the free ligands which confirms the symmetrical σ, σ -coordination of the ligands in $\text{Co}_2(\text{CO})_6(\text{DAB})$. The shielding of the chelate ring resulting from a strong back donation is demonstrated by the upfield shift of the imine carbon resonances.

An interesting feature about the Co ^{13}C -resonances is the appearance of only one peak at room temperature. All carbonyl groups are equal because of a fast intramolecular process in which the carbonyl groups

on both metal centres are involved. The mechanism of this exchange process will be discussed separately in a latter section.

In Table V the ^{13}C NMR data are listed for the two $\text{Co}_2(\text{CO})_6(\text{DAB})$ complexes and for the corresponding free ligands.

IR Spectroscopy

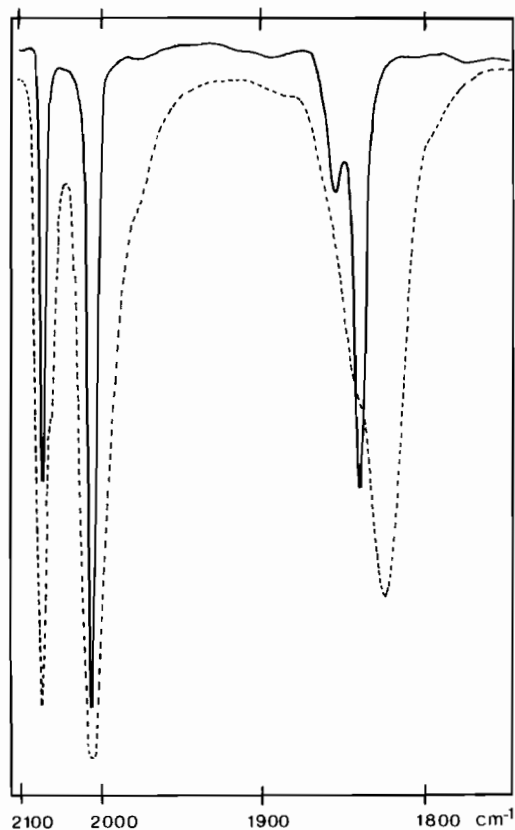
The CO stretching modes of $\text{Co}_2(\text{CO})_6(\text{DAB})$ are found in two distinct regions, one between 2000 and 2100 cm^{-1} in which vibrations due to terminal CO groups are found and one between 1800 and 1900 cm^{-1} in which modes of the bridging carbonyls are observed.

In the region of the terminal CO groups one very strong band (vs) at 2010 cm^{-1} is observed and one strong band (s) near 2070 cm^{-1} . In the region of the bridging carbonyl groups one medium (m) to strong band appears and one weak (w) band, at about 1840 and 1850 cm^{-1} respectively. As it is obvious from Table VI, the $\nu(\text{CO})$ frequencies belonging to the bridging carbonyl groups strongly depend on the substituents attached to the DAB skeleton, suggesting that these CO groups are trans to the DAB ligand.

As is shown in Fig. 2 for $\text{Co}_2(\text{CO})_6$ [glyoxalbis(2,4,6-mesitylimine)] the bands due to the bridging carbonyl groups are solvent dependent. In n-pentane solutions the bands appear at 1855 and 1842 cm^{-1} while in dichloromethane one band at 1822 cm^{-1} is found with a shoulder near 1840 cm^{-1} . This solvent effect was also found for the trans carbonyl groups in $\text{M}(\text{CO})_4(\text{DAB})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) [25] which confirms that the bridging carbonyl groups are trans to the DAB ligand.

TABLE VI. IR Absorption Data between 2100 and 1800 cm^{-1} of $\text{Co}_2(\text{CO})_6(\text{DAB})$ Obtained in *n*-Pentane Solutions.

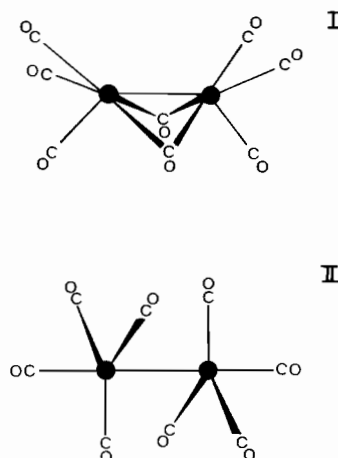
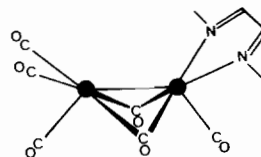
Complex	Terminal $\nu(\text{CO})$		Bridge $\nu(\text{CO})$	
$\text{Co}_2(\text{CO})_6[\text{glyoxalbis(isopropylimine)}]$	2065(s)	2006(s)	1835(w)	1825(s)
$\text{Co}_2(\text{CO})_6[\text{glyoxalbis}(p\text{-tolylimine)}]$	2068(s)	2004(s)	1850(w)	1836(m)
$\text{Co}_2(\text{CO})_6[\text{glyoxalbis(xylylimine)}]$	2069(s)	2013(s)	1855(w)	1839(s)
$\text{Co}_2(\text{CO})_6[\text{glyoxalbis(mesitylimine)}]$	2070(s)	2009(s)	1855(w)	1842(s)
$\text{Co}_2(\text{CO})_6[\text{diacetylbis}(p\text{-tolylimine)}]$	2054(s)	1998(s)	1842(w)	1838(m)

Fig. 2. Solvent effect on the CO-stretching modes of $\text{Co}_2(\text{CO})_6[\text{glyoxalbis(mesitylimine)}]$.

Structure and Formation of the Complexes

$\text{Co}_2(\text{CO})_8$ exists in solution in two different isomeric forms [26]. Form I (Fig. 3.I) contains two bridging and six terminal carbonyl groups, form II (Fig. 3.II) contains only terminal carbonyl groups, two in an axial position inline with the metal-metal bond and six CO groups in the equatorial positions of the two cobalt atoms. Recently a third isomer has been established with help of matrix isolation technique [27], in which all carbonyl groups were in a *cis* position to the metal-metal bond.

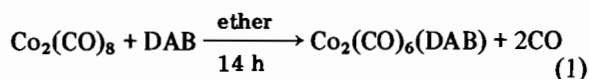
The IR-data evidence that $\text{Co}_2(\text{CO})_6(\text{DAB})$ complexes are exclusively formed as derivatives of $\text{Co}_2(\text{CO})_8$ in form I, which is the solid state form of $\text{Co}_2(\text{CO})_8$, as has been shown by an X-ray study [28].

Fig. 3. The two structures of $\text{Co}_2(\text{CO})_8$ which are found by IR spectroscopy.Fig. 4. The proposed structure of $\text{Co}_2(\text{CO})_6(\text{DAB})$ complexes.

The ^1H and ^{13}C NMR data demonstrate the presence of a symmetry plane in the complexes. The spectroscopic properties are in agreement with the proposed structure shown in Fig. 4. The two bridging carbonyl groups are *trans* to the DAB ligand which is in agreement with the solvent dependence of the $\nu(\text{CO})$ frequencies of these $\mu^2\text{-CO}$ groups.

There are several examples in the literature of $\text{Co}_2(\text{CO})_6(\text{L})$ complexes (in which L is a lone pair donor or a conjugated π -electron system) containing two bridging and four terminal carbonyl groups of which the structure has been confirmed by a single crystal structure determination. The results are included in a recent review concerning bridging carbonyl groups [29].

The complexes $\text{Co}_2(\text{CO})_6(\text{DAB})$ are formed in a simple substitution reaction as is indicated by eqn. 1.



Of interest is the question as to whether both isomers of $\text{Co}_2(\text{CO})_8$ in solution are reactive towards DAB ligands. The structure of $\text{Co}_2(\text{CO})_6(\text{DAB})$ suggests a straightforward substitution of carbonyl groups of form I (Fig. 3), but substitution followed by rearrangement starting from isomer II (Fig. 3) cannot be excluded. Especially since the rapid scrambling of carbonyl groups which is evidenced by ^{13}C NMR spectroscopy demonstrates the existence of a fast dynamic equilibrium between the bridged and the non bridged species (Fig. 5). The fact that the non bridged species do not occur in the IR spectra is evidence that k_{-1} is much larger than k_1 in eqn. 2 (Fig. 5). This exchange process is analogous to the exchange between form I and form II of $\text{Co}_2(\text{CO})_8$ and in general to the exchange of compensating bridging carbonyl pairs in binuclear metal carbonyl complexes [23].

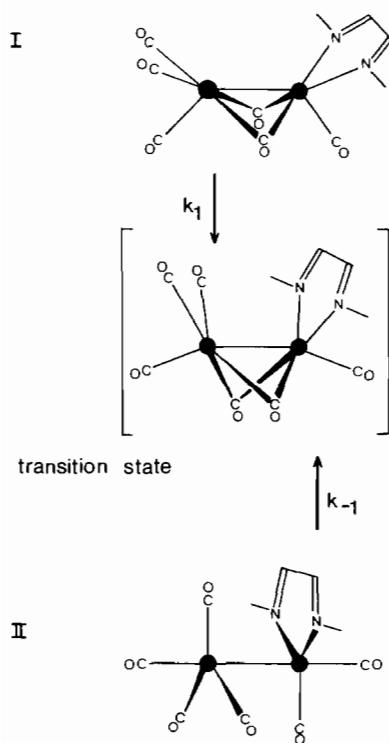


Fig. 5. Proposed mechanism for the bridge-terminal interchange of the carbonyl groups in $\text{Co}_2(\text{CO})_6(\text{DAB})$.

The exchange between bridged and non bridged metal carbonyl complexes probably proceeds *via* asymmetrically bridged and semi-bridged complexes which is shown as the transition state in Fig. 5. There are some examples known in the literature in which the asymmetrical bridging or semi-bridging coordination of the carbonyl groups are stabilized in the solid state structures [29]. These bridging modes of bridging carbonyl groups has also been observed in $\text{Fe}_2(\text{CO})_7(\text{bipyridyl})$ [30] which complex is related to $\text{Co}_2(\text{CO})_6(\text{DAB})$.

UV-visible Measurements and the Electronic Structure of the Complexes

An interesting discrepancy can be observed in the literature between theory and experiments concerning the metal-metal bond in the bridged form of $\text{Co}_2(\text{CO})_8$. For many years it was believed that the binuclear complex owed its diamagnetic behaviour to the presence of a two electron metal-metal bond between the cobalt atoms. Recently SCF-X α calculations have been carried out on $\text{Co}_2(\text{CO})_8$ and $\text{Fe}_2(\text{CO})_9$, which showed that the d-orbital combination which form the σ and σ^* orbitals of the metal-metal interaction were both occupied [31]. This means that this interaction is nonbonding and that there is no stabilization by metal-metal bonding. In the same work similar conclusions were put forward for $\text{Fe}_2(\text{CO})_9$.

An alternative description has been suggested by Bernard. M.O.-calculations and electron density determinations for $[\text{CpFe}(\text{CO})_2]_2$ lead to the conclusion that there is no direct metal-metal bond in these complexes but, that the interaction between the bridging carbonyl groups and the metal atoms can best be described as a delocalized multicentre interaction [32]. However, experimental data have been obtained which confirm the presence of a metal-metal bond in $\text{Co}_2(\text{CO})_8$. In the UV-visible spectra of $\text{Co}_2(\text{CO})_8$ a $\sigma \rightarrow \sigma^*$ transition localized on the Co-Co bond was observed. Such a $\sigma \rightarrow \sigma^*$ transition will increase in intensity upon cooling [33]. This phenomenon has been observed for both isomeric forms of $\text{Co}_2(\text{CO})_8$ at 298 K and 50 K, which is in agreement with the assignment of the band [33]. Apparently the σ^* -orbital is unoccupied in the ground state of the molecule otherwise such a transition would be impossible. Heyser *et al.* suggested that a false assignment was the basis of the discrepancy between their calculation and the observed UV-visible data [31], but the general applicability of the low temperature criterium has been shown for many metal-metal bond containing complexes, including binuclear metal carbonyl DAB complexes [6, 22, 34].

The UV-visible spectra of $\text{Co}_2(\text{CO})_6(\text{DAB})$ complexes contain a very strong band near 360 nm which on the basis of position and intensity is assigned to a ligand field transition localized between the two metals. If it was assumed that a two electron metal-metal bond was present, this transition could unambiguously be assigned to the corresponding $\sigma \rightarrow \sigma^*$ transition, but as has been discussed above the nature of the interactions in a puckered ring system containing two metals and two bridging carbonyl groups is still uncertain. However, additional evidence for metal-metal interaction has been found in the Resonance Raman spectra of $\text{Co}_2(\text{CO})_6$ [glyoxalbis(isopropyl-imine)]. A strong band at 145 cm^{-1} has been observed which may tentatively be assigned to the

TABLE VII. UV-visible Data of $\text{Co}_2(\text{CO})_6(\text{DAB})$ (in CH_2Cl_2 , λ_{nm}).

Compound	CT		$\sigma \rightarrow \sigma^*$
$\text{Co}_2(\text{CO})_6(\text{}^i\text{Pr-N} = \text{CH-CH} = \text{N-}^i\text{Pr})$	610	490	355
$\text{Co}_2(\text{CO})_6(\text{}^p\text{-tol-N} = \text{CH-CH} = \text{N-}^p\text{-tol})$	654	sh	478
$\text{Co}_2(\text{CO})_6(\text{}^x\text{yl-N} = \text{CH-CH} = \text{N-}^x\text{yl})$	670	520	475 (sh)
$\text{Co}_2(\text{CO})_6(\text{Mes-N} = \text{CH-CH} = \text{N-Mes})$	691	525	485
$\text{Co}_2(\text{CO})_4(\text{}^p\text{-tol-N} = \text{CH-CH} = \text{N-}^p\text{-tol})_2$	675	590	488

$\nu(\text{Co-Co})$. On the basis of these results we propose a direct two electron metal-metal bond in $\text{Co}_2(\text{CO})_6(\text{DAB})$ complexes.

$\text{Co}_2(\text{CO})_6(\text{DAB})$ complexes are very intense purple of colour due to charge transfer (CT) transitions in the visible region. The four centre π -electron system of the DAB ligand contains two empty antibonding combinations which are available for electronic transitions from the metal d-orbitals to the ligand. In these complexes the separation between the π^* -orbitals is sufficient to obtain two distinct structured bands in the visible part of the spectrum. The CT bands of $\text{M}(\text{CO})_4(\text{DAB})$ ($\text{M} = \text{Cr, Mo, W}$) and related complexes have been studied with Resonance Raman spectroscopy and the maxima in the excitation profiles could be assigned, leading to analogous conclusions [18–21]. The structure in the CT bands of $\text{Co}_2(\text{CO})_6(\text{DAB})$ is comparable with the situation in d^6 -metal complexes and originates from transitions of different d-orbitals to the same π^* -orbitals. In Table VII the band maxima in the UV-visible spectra of $\text{Co}_2(\text{CO})_6(\text{DAB})$ are listed.

Solvatochromic shifts were not observed for $\text{Co}_2(\text{CO})_6(\text{DAB})$, this in contrast to the effects which were observed for d^6 and d^7 metal carbonyl DAB complexes [22, 35].

Resonance Raman Spectroscopy

Dilute solutions of $\text{Co}_2(\text{CO})_6$ [glyoxalbis(isopropylimine)] have been studied with Resonance Raman spectroscopy ($\lambda = 640 \text{ nm}$, 550 nm ; $p = 150 \text{ mW}$). Since homolytic cleavage is a very efficient photochemical process in binuclear complexes a rapid decomposition was observed which prevented a meaningful quantitative interpretation of the results.

The most striking feature in the Resonance Raman spectra is that only bands belonging to the metal-carbonyl skeleton can be observed. Bands belonging to the DAB skeleton ($\nu(\text{C} = \text{N})$) which are very intense in the Resonance Raman spectra of $\text{M}(\text{CO})_4(\text{DAB})$ and related complexes ($\text{M} = \text{Cr, Mo, W}$) [18–21] have not been observed for $\text{Co}_2(\text{CO})_6(\text{DAB})$. Consequently, there is no net charge transfer on the ligand during excitation which means that $d\pi$ and π^* -orbitals which overlap to give π -backdonation are energetically approximately at the same level. This is in agreement with the fact that solvatochromic

shifts do not occur in the UV-visible spectra of $\text{Co}_2(\text{CO})_6(\text{DAB})$.

In Fig. 6 the Resonance Raman spectrum is shown of $\text{Co}_2(\text{CO})_6$ [glyoxalbis(isopropylimine)] between 100 and 600 cm^{-1} . At 150 cm^{-1} a band is found which can be assigned to the Co-Co stretching mode. The frequency of this mode is in agreement with values obtained for other binuclear metal carbonyl complexes [36]. For $\text{Co}_2(\text{CO})_6(\text{H-C}\equiv\text{C-H})$ and $\text{Co}_2(\text{CO})_6(\text{CF}_3\text{-C}\equiv\text{C-CF}_3)$ values of 210 and 190 cm^{-1} have been reported [34] which are slightly higher than the observed frequency of $\text{Co}_2(\text{CO})_6(\text{DAB})$. At 405 and 525 two intense bands have been observed which can be assigned to the $\nu(\text{Co-C})$ and $\delta(\text{Co-C-O})$ modes of the metal carbonyl skeleton. Both bands have weak shoulders at higher energy. The observed values are in agreement with the values found for $\text{Co}_2(\text{CO})_6(\text{R-C}\equiv\text{C-R})$ ($\text{R} = \text{H, CF}_3$) [34].

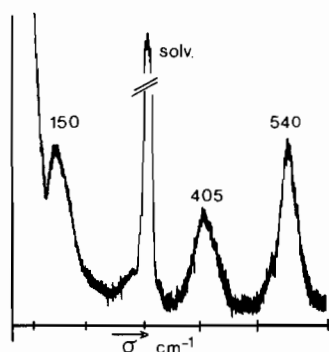


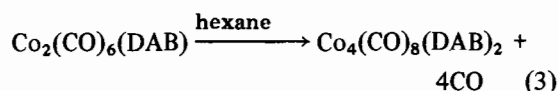
Fig. 6. The Resonance Raman spectrum of $\text{Co}_2(\text{CO})_6$ -[glyoxalbis(isopropylimine)] between $0\text{--}600 \text{ cm}^{-1}$, showing bands due to the $\nu(\text{Co-Co})$, $\nu(\text{Co-C})$ and $\delta(\text{Co-C-O})$.

Chemical Properties

The complexes decompose when they are exposed to air. Complexes with aromatic substituents attached to the DAB ligands are more stable than the aliphatic derivatives which are pyrophoric.

The complexes react when they are gently heated in hexane solutions. Molecular weight determinations suggested a dimerisation reaction. $\text{Co}_4(\text{CO})_8(\text{DAB})_2$ complexes were formed (eqn. 3) which are related to $\text{Rh}_4(\text{CO})_8(\text{DAB})_2$. The ^1H NMR chemical shifts are indicative of σ, σ -coordination of the DAB ligand.

The shifts of $\text{Co}_4(\text{CO})_8$ [glyoxalbis(*p*-tolylimine)] are included in Table III and will be discussed in more detail together with the results for the substitution products in the reaction of $\text{Rh}_4(\text{CO})_{12}$ with DAB [38].



When reacted with an extra mole of DAB ligand the $\text{Co}_2(\text{CO})_6(\text{DAB})$ complexes yield $\text{Co}_2(\text{CO})_4(\text{DAB})_2$. Unfortunately we have not been able to obtain pure samples of the bis-substituted products which are related to $\text{Co}_2(\text{CO})_4(\text{bipyridine})_2$ and $\text{Co}_2(\text{CO})_4(\text{phenanthroline})_2$ [39, 40]. However, these complexes have been characterized in solution by ^1H NMR. The ^1H NMR data of $\text{Co}_2(\text{CO})_4$ [glyoxalbis(*p*-tolylimine)]₂ are included in Table III.

Influences of the Geometry of the Coordination Polyhedron on the Coordination Mode of the DAB Ligands

It has recently been shown that in binuclear metal carbonyl DAB complexes an intramolecular attack on the π -electrons of a $\text{C}=\text{N}$ double bond is possible according to Fig. 7. This reaction has been studied in detail for $\text{MnCo}(\text{CO})_6(\text{DAB})$ complexes [9].

In Fig. 7a the plane defined by the five membered chelate ring is perpendicular to the metal-metal bond. The π -orbitals on the $\text{C}=\text{N}$ double bonds are forced in an interactive position relative to the coordination sphere around metal centre M_2 . When M_2 is

Fe, Ru, Os [9–11] or Co [9], elimination of a carbonyl group and subsequent attack on the π -system may occur, resulting in the six electron donor $\sigma\text{-N}$, $\mu^2\text{-N}$, $\eta^2\text{-C}=\text{N}$ coordination mode of the DAB ligand as is shown in Fig. 7b. In addition to the coordination *via* the lone pairs on nitrogen, the DAB ligand is coordinated *via* one pair of π -electrons. However, the structure shown in Fig. 7a can be stabilized by making use of DAB ligands with methyl groups on 2,3-positions (diacetyl derivatives) which have less tendency to π -coordination or by making use of metal carbonyl fragments which have less tendency to eliminate CO groups and consequently are more stable with respect to intramolecular π -attack. Examples are $\text{Mn}(\text{CO})_5\text{Mn}(\text{CO})_3(\text{DAB})$ and $\text{Mn}(\text{CO})_5\text{Re}(\text{CO})_3(\text{DAB})$ [22].

In $\text{Co}_2(\text{CO})_6(\text{DAB})$ complexes a third stabilizing factor is found for the σ,σ -bidentate coordination mode in binuclear metal carbonyl complexes. The five membered chelate ring is no longer perpendicular to the metal-metal bond and the DAB ligand is bent away from the metal-centre M_2 (Fig. 7c). Consequently the π -electron system on the $\text{C}=\text{N}$ bonds is in a non interactive position, *i.e.* a geometrical barrier in the molecule prevents $\eta^2\text{-C}=\text{N}$ coordination of the DAB ligand. In principle the molecule is forced in this geometry by the puckered bridging carbonyl groups which are on the intersections of the dioctahedral structure [28, 41].

It has been shown by the ^{13}C NMR data of the metal carbonyl skeleton that $\text{Co}_2(\text{CO})_6(\text{DAB})$ exists mainly in the bridged form but that there is a fast

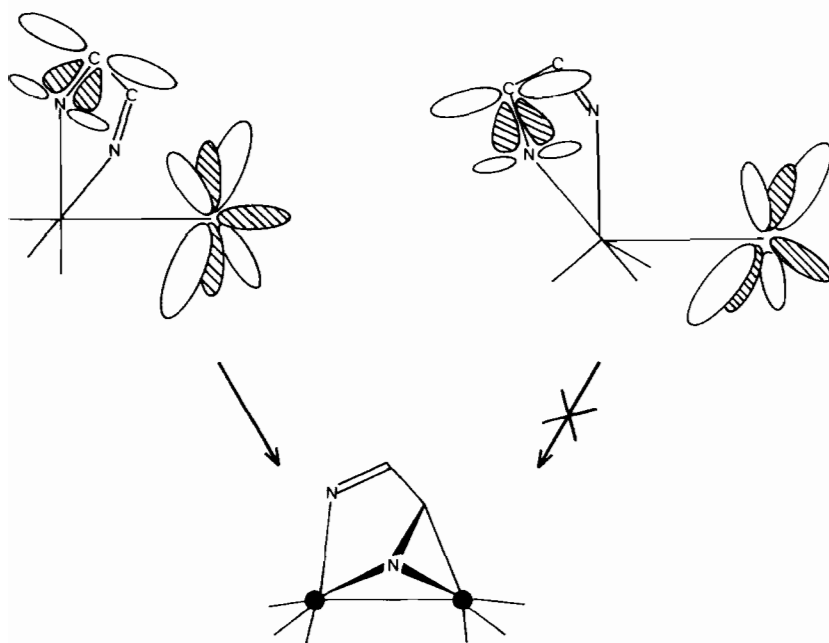


Fig. 7. The influence of the geometry of the coordination polyhedron on the possibility to give overlap between the ligand π -orbital system and the orbitals on the metal.

exchange process involving a short lived isomer with only terminal carbonyl groups. With regards to $\eta^2\text{-C}=\text{N}$ bond formation it will be obvious that this isomer satisfies the conditions which are shown in Fig. 7a, but the fact that the lifetime of the species with only terminal carbonyl groups is very short, makes the reaction very slow. Competing reactions like dimerisation, disproportionation giving $\text{Co}_4(\text{CO})_{12}$ and decomposition are favoured.

Conclusions

With the synthesis of $\text{Co}_2(\text{CO})_6(\text{DAB})$ complexes a gap has been filled in the array of monosubstituted metal carbonyl complexes of the first row transition elements. In all these cases the bonding picture, donation of the lone pairs and stabilization by a strong $d_\pi\text{-}\pi^*$ interaction, is fully confirmed by the spectroscopic properties of the complexes.

In one of our earlier papers concerning the coordination properties of DAB ligands we have stated that for a complete understanding of the reactivity of coordinated DAB ligands, knowledge about the factors determining the coordination modes is necessary [22]. The results for $\text{Co}_2(\text{CO})_6(\text{DAB})$ in comparison with the results for $\text{MnCo}(\text{CO})_6(\text{DAB})$ [9] demonstrate that the three most important factors are the electron density on the metal, substituents on the diimine skeleton influencing the electron withdrawing or electron repulsive behaviour of the $\text{N}=\text{C}-\text{C}=\text{N}$ skeleton and the geometry of the coordination polyhedron in binuclear complexes.

DAB ligands are very often compared with 2,2-bipyridine and 1,10-phenanthroline since they are related via the $\text{N}=\text{C}-\text{C}=\text{N}$ skeleton. The difference in donor-acceptor capacity between both type of ligands has been studied in detail [42, 43] and it has been shown that DAB ligands are much better π -acceptors than 2,2-bipyridine and 1,10-phenanthroline. This conclusion is in agreement with the different reactivity between the two types of ligands. Reactions between $\text{Co}_2(\text{CO})_8$ and bipyridine or phenanthroline yielded exclusively the ionic complexes $[\text{Co}(\text{phen})_3][\text{Co}(\text{CO})_4]_2$ while displacement of the diene in $\text{Co}_2(\text{CO})_4(\text{norbornadiene})_2$ yielded the ionic complexes and $\text{Co}_2(\text{CO})_4(\text{phen})_2$ in equimolar amount [40]. High yields of $\text{Co}_2(\text{CO})_4(\text{bipy})_2$ have been obtained by the reduction of $\text{CoCl}_3 \cdot 6\text{H}_2\text{O}$ in the presence of bipyridine and CO [39]. The tendency to form ionic complexes with cobalt carbonyl is determined by the poor π -acceptor qualities of bipyridine and phenanthroline. The higher π -acceptor capacity of DAB ligands stabilizes the zero valent binuclear cobalt carbonyl DAB complexes.

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