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# Binuclear Metal Carbonyl DAB Complexes. 6. Syntheses and Spectroscopic Properties of $MCo(CO)_5(\mu^2\text{-}CO)(DAB)$ (M = Mn, Re; DAB = 1,4-Diazabutadiene). X-ray Structure of [$\sigma^2$-N,$\sigma^2$-N′,$\eta^2$-C=N-[Glyoxal bis(*tert*-butylimine)]]hexacarbonylcobaltmanganese

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The reaction between $Mn(CO)_3Br(DAB)$ (DAB = 1,4-diazabutadiene) and $[Co(CO)_4]^-$ yields complexes of the composition $MnCo(CO)_6(DAB)$. The analogous rhenium complexes could also be prepared. The single-crystal structure determination of [glyoxal bis(*tert*-butylimine)]hexacarbonylcobaltmanganese has been carried out on monoclinic crystals of space group $P2_1/c$. Cell constants are $a = 9.024$ (5) Å, $b = 12.793$ (3) Å, $c = 17.324$ (6) Å, $\beta = 105.1$ (1)°, $Z = 4$, $d$(calcd) = 1.540 g cm$^{-3}$, and $d$(measd) = 1.55 g cm$^{-3}$. A total of 1305 reflections have been used in the refinement, resulting in a final $R$ value of 0.066, for 234 parameters varied. The DAB ligand acts as a six-electron donor system, donating two lone pairs on nitrogen and one pair of $\pi$ electrons via a N=C unit. The Co–Mn distance of 2.639 (3) Å points to a Co–Mn single bond. The DAB ligand is $\eta^2$-C=N coordinated to cobalt with Co–N(1) equal to 1.89 (1) Å and Co–C(3) equal to 2.07 (1) Å. The metal carbonyl skeleton of the complex contains a semibridging carbonyl group with Mn–C(63) equal to 2.33 (1) Å and Co–C(63) equal to 1.80 (1) Å and bond angles Mn–C(63)–O(63) of 127 (1)° and Co–C(63)–O(63) of 154 (1)°. $MnCo(CO)_7(DAB)$ complexes were observed as unstable intermediates in the reaction sequence, containing the DAB ligands in the $\sigma,\sigma$-N,N′ coordination mode. This indicates that the complexes are formed in a nucleophilic mechanism. All complexes have been characterized by $^1H$ NMR, IR, and mass spectrometry. For $MnCo(CO)_6$[biacetyl bis(cyclopropylimine)] an exchange between the $\sigma^2$-N and the $\sigma^2$-N′,$\eta^2$-C=N′ coordinated parts of the DAB ligand was observed with a coalescence temperature of −15 °C. A mechanism for the exchange process has been proposed. It is shown that $(CH_3)C{=}N$ fragments have poor $\pi$-bonding abilitites as compared with $(H)C{=}N$ fragments. A DAB ligand containing both fragments is found with the $(CH_3)C{=}N$ fragment on the $\sigma$-coordinated part of the molecule exclusively. A comparison is made with the reaction of $[Mn(CO)_5]^-$ and $Mn(CO)_3Br(DAB)$, giving information about the role of the metal carbonyl fragment on the coordination of the DAB ligand.

## Introduction

1,4-Diazabutadienes can be envisaged as four-center $\pi$-electron systems with nitrogen atoms at the 1,4 positions. The coordination properties of the 1,3-butadiene analogues are mainly determined by the good donor capacity of the lone pairs on nitrogen and by the two LUMO's of the $\pi$ system which can overlap with filled d orbitals on the metal, giving a strong stabilizing effect of the chelate ring, especially in low-valent metal carbonyl complexes.[1] For this reason the predominant coordination mode of DAB ligands (1,4-diazabutadiene = $R_1{-}N{=}C(R_2){-}(R_2)C{=}N{-}R_1$) is $\sigma,\sigma$-N,N′ coordination.

Still there has been some discussion about the possible involvement of the $\pi$ electrons in the coordination of DAB ligands to metal carbonyl fragments. It was shown that cyclic ligands containing the N=C—C=N moiety coordinate to $Fe(CO)_3$ and $Ni(CO)_2$ fragments via the $\pi$ electrons.[2] Obviously the $\pi$-donor properties of the diimine skeleton allow coordination via C=N double bonds, when chelate ring formation is not possible.

MO calculations,[3] UV–visible spectroscopy,[4] ESR experiments,[5,6] resonance raman excitation profiles,[7,8] and electrochemical experiments[5,9,10] have shown that the LUMO's of the diimine skeleton are very good $\pi$ acceptors. $^{13}C$ NMR data of $\sigma,\sigma$-N,N′ coordinated DAB metal carbonyl complexes demonstrated an increase of charge density on the metallocyclic ring in the order $d^6 < d^7 < d^8$ metals,[11] which is caused by an increase of the $d_\pi$–$\pi^*$ interaction. These results indicate that involvement of the $\pi$ orbitals of the N=C—C=N skeleton in coordination toward metal carbonyls might be possible.

The first example of involvement of one pair of $\pi$ electrons in the coordination of DAB ligands has recently been reported for $Fe_2(CO)_6(DAB)$ complexes[12] in which the DAB ligands act as a six-electron donor ($\sigma^2$-N,$\mu^2$-N′,$\eta^2$-C=N coordination). The structure of the complexes has been elucidated by X-ray analyses.

We have assumed in earlier work that $\pi$ coordination of the DAB ligands could be an important factor for the activation of the C=N moiety toward C—C bond formation. After subsequent reduction of $Mo(CO)_4(DAB)$ to $[Mo(CO)_4DAB]^-$ and oxidation of the complex anion, $Mo_2(CO)_6(IAE)$ is formed (IAE = bis[(alkylimino)(alkylamino)ethane]) containing a C–C bond between two DAB ligands.[13] Recently this assumption has been confirmed. We were able to isolate $Ru_2(CO)_6(DAB)$ as intermediates in the syntheses of $Ru_2(CO)_5(IAE)$.[14] $Ru_2(CO)_6(DAB)$ complexes are isostructural to $Fe_2(CO)_6(DAB)$, thus containing a $\eta^2$-C=N-coordinated imine fragment. Furthermore, at the end of a complicated reaction sequence, $Ru_2(CO)_4(DAB)_2$ complexes were formed, which are the third example of $\sigma^2$-N,$\mu^2$-N′,$\eta^2$-C=N-coordinated DAB ligands.[14]

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**Table I.** Analytical Data of $MCo(CO)_6(DAB)$ (M = Mn, Re) and $MCo(CO)_7$[biacetyl bis(cyclopropylimine)]

| compd | mol wt$^a$ | | IR $\nu$(CO)$^b$ |
|---|---|---|---|
| | found | calcd | |
| $CoMn(CO)_6$[glyoxal bis(isopropylimine)] | 422 | 422 | 2050 (s), 2009 (vs), 1989 (s), 1943 (s), 1937 (s), 1898 (w) |
| $CoMn(CO)_6$[glyoxal bis(*tert*-butylimine)] | 450 | 450 | 2047 (s), 2006 (vs), 1986 (s), 1935 (s, br), 1894 (w) |
| $CoMn(CO)_6$[glyoxal bis(cyclohexylimine)] | 502 | 502 | 2052 (s), 2002 (vs), 1983 (s), 1940 (s), 1935 (sh), 1895 (w) |
| $CoMn(CO)_6$[glyoxal bis(cyclopropylimine)] | 418 | 418 | 2049 (s), 2011 (vs), 1988 (s), 1950 (s), 1942 (sh), 1895 (w) |
| $CoMn(CO)_6$[methylglyoxal bis(isopropylimine)] | 436 | 436 | 2045 (s), 2006 (vs), 1982 (s), 1941 (s), 1932 (s), 1896 (w) |
| $CoRe(CO)_6$[glyoxal bis(*tert*-butylimine)] | 580, 582 | 581$^c$ | 2049 (s), 2013 (vs), 1989 (s), 1937 (s), 1932 (s), 1876 (w) |
| $CoRe(CO)_6$[glyoxal bis(cyclohexylimine)] | 632, 634 | 633$^c$ | 2051 (s), 2014 (vs), 1987 (s), 1938 (s), 1931 (s), 1877 (w) |
| $CoMn(CO)_7$[biacetyl bis(cyclopropylimine)] | 446 | 474$^d$ | 2044 (s), 2005 (vs), 1979 (s), 1945 (s), 1924 (s), 1909 (w, sh) |
| $CoRe(CO)_7$[biacetyl bis(cyclopropylimine)] | 604, 606 | 605$^c$ | 2046 (s), 2011 (s), 1982 (s), (1940) (s), 1921 (s), 1896 (w), 1873 (w) |

$^a$ Molecular weights taken from the molecular ions in the field desorption mass spectra. $^b$ Obtained in hexane solutions. $^c$ Two isotopes of rhenium $^{185}Re$ and $^{187}Re$ while atomic weight is 186.21. $^d$ Molecular ion not observed due to thermal instability. Highest peak in the FD mass spectrum is due to the $[M - CO]^+$ ion.

C–C bond formation is not restricted to DAB ligands. In $M_2(CO)_6(DAB)$ the imine carbon atom which is involved in the $\eta^2$-C=N coordination is very reactive toward any unsaturated molecule,[15] and these type of complexes promise to be good catalysts in the oligomerization of acetylenes and substituted (hetero) olefins.[15]

As part of the systematic investigation of the ability of $\pi$ coordination of DAB ligands, we investigated the redox reaction between $Mn(CO)_3Br(DAB)$ and $[Co(CO)_4]^-$. Complexes of the type $MnCo(CO)_6(DAB)$ were formed, containing a $\eta^2$-C=N-coordinated imine fragment as was shown by an X-ray structure determination. The syntheses of $MCo(CO)_6(DAB)$ (M = Mn, Re) give a better view on the mechanism by which $MM'(CO)_6(DAB)$ complexes are formed. The chemical properties and in particular the effect of $\pi$ coordination on the activation of the C=N double bonds will be discussed in a separate paper.

## Experimental Section

$^1H$ NMR spectra were recorded with a Varian T60 apparatus, IR spectra were obtained with a Perkin-Elmer 283 spectrophotometer, and mass spectra were recorded with a Varian MAT 711 mass spectrometer, by applying the field desorption technique.

$Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $Co_2(CO)_8$ have been purchased from Strem Chemicals; $Co_2(CO)_8$ was recrystallized before use, and other metal carbonyls were used without further purification.

$M(CO)_3Br(DAB)$ [M = Mn, Re; DAB = glyoxal bis(*tert*-butylimine), glyoxal bis(cyclohexylimine), glyoxal bis(isopropylimine), methylglyoxal bis(isopropylimine)] was prepared according to literature procedures.[16] $[Co(CO)_4]^-$ was prepared by stirring a solution of $Co_2(CO)_8$ in THF with an excess of sodium–potassium alloy ($NaK_{2.8}$). This method has been described by Ellis and Flom for the production of metal carbonyl anions.[17]

All solvents were carefully dried and distilled before use. Reactions were carried out with degassed solvents in an atmosphere of pure nitrogen.

**Preparation of Biacetyl Bis(cyclopropylimine).** Biacetyl (50 mmol) and cyclopropylimine (100 mmol) were stirred for 3 h in toluene at 80 °C. The solution was dried with $MgSO_4$ and filtered. The crude product precipitated at –60 °C. Recrystallization in ether at –30 °C gave a 50% yield of white crystals. The product must be kept at –20 °C to prevent thermal decomposition.

**Preparation of Glyoxal Bis(cyclopropylimine).** Glyoxal (50 mmol; 30% solution in water) and cyclopropylamine were stirred for 1 h at 0 °C in 100 mL of diethyl ether. The water was separated from the ether solution, which was dried with $MgSO_4$. The ether was evaporated from the crude product under vacuum, and a yellow oil was obtained. The pure product was obtained by sublimation, giving a 30% yield of colorless crystals. The product must be kept under nitrogen and stored at –20 °C to prevent thermal decomposition and polymerization.

**Preparation of $M(CO)_3Br(DAB)$ [M = Mn, Re; DAB = Glyoxal Bis(cyclopropylimine), Biacetyl Bis(cyclopropylimine)].** The general prescriptions for the syntheses of $M(CO)_3X(DAB)$ (M = Mn, Re; X = Cl, Br, I) complexes[16] were applied.

**Preparation of $MnCo(CO)_6(DAB)$ [DAB = Glyoxal Bis(*tert*-butylimine), Glyoxal Bis(cyclohexylimine), Glyoxal Bis(cyclopropylimine), Methylglyoxal Bis(isopropylimine), Biacetyl Bis(cyclopropylimine)].** $Mn(CO)_3Br(DAB)$ (2 mmol) was refluxed for 4 h in THF with a 10% molar excess of freshly prepared $[Co(CO)_4]^-$. The solvent was evaporated, and the residue was extracted with 100 mL of hexane. The crude product precipitated at –30 °C. Recrystallization of the product in hexane at –30 °C gave a 40–60% yield of red crystals (minimum yields).

**Preparation of $MnCo(CO)_6$[glyoxal bis(isopropylimine)].** The same procedure was followed as discussed above for the other derivatives. When the crude product was obtained, further purification on a silica gel column was required.

The silica gel (60 mesh) was dried and activated by heating it for 3 h at 180 °C under vacuum (0.1 mmHg). The separation was carried out with a column of 30 × 1.5 cm in a purified nitrogen atmosphere, by using diethyl ether as eluant. The red fraction was collected, and the solvent was evaporated. The pure product was obtained after a recrystallization from hexane at –30 °C, giving a 40% yield of red crystals.

**Preparation of $ReCo(CO)_6(DAB)$ [DAB = Glyoxal Bis(*tert*-butylimine), Glyoxal Bis(cyclohexylimine), Glyoxal Bis(isopropylimine)].** $Re(CO)_3Br(DAB)$ (1.0 mmol) was refluxed for 15 h in THF with a 100% molar excess of $[Co(CO)_4]^-$. Isolation and purification as with $MnCo(CO)_6(DAB)$ gave a 40% yield of orange-red crystals.

**Preparation of $ReCo(CO)_7$[biacetyl bis(cyclopropylimine)].** The same procedure was used as discussed for the $ReCo(CO)_6(DAB)$ complexes. The yields were in the same range as for the hexacarbonyl derivatives.

Elemental analyses were carried out by the Section Elemental Analyses of the Institute for Organic Chemistry, TNO, Utrecht, The Netherlands. Some of the complexes slowly released carbon monoxide at room temperature and accordingly failed to give fully satisfactory elemental analyses. However, glyoxal bis(*tert*-butylimine), glyoxalbis(cyclohexylimine), and biacetyl bis(cyclopropylimine) derivatives are relatively stable and give satisfactory elemental analyses. The composition of all the complexes was confirmed by field desorption mass spectrometry. The results are listed in Table I, including the $\nu$(CO) frequencies in the IR spectra by which the complexes can be characterized.

**Structure Determination of [Glyoxal bis(*tert*-butylimine)]hexacarbonylcobaltmanganese.** A crystal with the dimensions 0.04 × 0.006 × 0.016 $cm^{-3}$ was mounted on a Nonius CAD-4 diffractometer. Cell constants which were measured at room temperature are $a$ = 9.024 (5) Å, $b$ = 12.793 (3) Å, $c$ = 17.324 (6) Å, $\beta$ = 105.1 (1)°, $Z$ = 4, $d$(calcd) = 1.540 g $cm^{-3}$, and d(measd) = 1.55 g $cm^{-3}$ (by floatation). Intensities (1812) were measured with monochromated Mo K$\alpha$ radiation, by using a $\theta$–$2\theta$ scan, of which 1305 were significantly above the background intensity ($I > 3\sigma$); the maximum $\theta$ value was 20°.

From the extinctions it was deduced that the space group is $P2_1/c$. Absorption correction was carried out ($\mu$ = 16.1 $cm^{-1}$, maximum and minimum corrections are 1.49 and 1.10, respectively).

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(15) $Ru_2(CO)_5$([R—N=C(H)—C(H)-NR]—CH=CR) complexes are formed by insertion of substituted acetylene in the metal—carbon bond between the ruthenium atom and the $\eta^2$-C=N coordinated imine fragment: L. H. Staal, L. H. Polm, G. van Koten, and K. Vrieze, submitted for publication.

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**Table II.** Atomic Parameters of the Nonhydrogen Atoms of [Glyoxal bis(*tert*-butylimine)]hexacarbonylcobaltmanganese[a]

| atom | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co | 9109 (2) | 6380 (2) | 1561 (1) | 5.7 (1) | 2.4 (1) | 4.9 (1) | −0.43 (8) | 0.44 (8) | 0.22 (8) |
| Mn | 11647 (2) | 7120 (2) | 1277 (1) | 4.1 (1) | 3.5 (1) | 3.3 (2) | 0.33 (8) | 0.47 (8) | −0.37 (9) |
| O(51) | 14382 (10) | 5935 (9) | 1248 (6) | 6.2 (6) | 10.9 (9) | 7.8 (8) | 3.2 (6) | −0.3 (6) | −3.1 (7) |
| O(52) | 131265 (9) | 8931 (8) | 732 (6) | 7.2 (6) | 5.6 (7) | 9.0 (8) | −0.6 (5) | 2.7 (6) | 3.1 (6) |
| O(53) | 10601 (10) | 6353 (7) | −363 (7) | 8.2 (6) | 6.8 (7) | 4.9 (7) | 2.2 (5) | 0.8 (5) | −1.4 (6) |
| O(61) | 7036 (12) | 5566 (8) | 98 (7) | 10.3 (7) | 5.8 (7) | 8.3 (8) | −1.0 (6) | −2.3 (6) | −1.5 (7) |
| O(62) | 7536 (11) | 5529 (9) | 2656 (7) | 7.5 (6) | 9.5 (9) | 11.2 (9) | 0.1 (6) | 2.2 (7) | 4.2 (8) |
| O(63) | 11497 (10) | 4808 (8) | 1918 (6) | 8.1 (6) | 3.3 (6) | 7.1 (7) | 0.2 (5) | 1.1 (5) | 0.9 (5) |
| N(1) | 9620 (1) | 7770 (7) | 1360 (6) | 4.8 (6) | 2.5 (6) | 4.7 (8) | −1.5 (5) | 1.3 (5) | 1.4 (5) |
| N(2) | 12286 (10) | 7550 (7) | 2485 (5) | 4.5 (6) | 1.3 (6) | 3.3 (6) | −0.1 (4) | −0.4 (5) | 0.0 (5) |
| C(1) | 8497 (12) | 8571 (9) | 799 (7) | 4.1 (7) | 3.6 (8) | 4.5 (9) | 0.3 (5) | −0.9 (6) | 0.3 (6) |
| C(11) | 9223 (12) | 9662 (9) | 1018 (8) | 6.4 (8) | 1.4 (7) | 7.2 (10) | 1.2 (6) | 0.5 (7) | −0.3 (6) |
| C(12) | 6932 (11) | 8532 (9) | 981 (8) | 4.1 (7) | 4.6 (8) | 7.1 (10) | 0.2 (6) | 0.5 (6) | −0.3 (7) |
| C(13) | 8520 (13) | 8349 (9) | −77 (8) | 8.0 (9) | 2.5 (7) | 4.3 (9) | 1.6 (6) | −1.0 (7) | 1.8 (6) |
| C(2) | 13802 (13) | 7510 (9) | 3091 (7) | 5.1 (7) | 2.7 (7) | 3.9 (8) | −0.4 (6) | −1.0 (6) | 0.7 (6) |
| C(21) | 14214 (13) | 6363 (10) | 3275 (9) | 6.6 (7) | 5.6 (10) | 5.9 (10) | 1.0 (7) | −0.7 (7) | 1.3 (8) |
| C(22) | 13768 (14) | 8071 (11) | 3861 (8) | 7.1 (9) | 7.7 (10) | 4.3 (9) | −1.2 (8) | −0.3 (7) | −2.3 (8) |
| C(23) | 14992 (14) | 8032 (10) | 2741 (8) | 6.0 (8) | 3.9 (8) | 6.5 (10) | −1.4 (7) | −0.9 (7) | −0.9 (7) |
| C(3) | 9619 (13) | 7795 (9) | 2144 (7) | 6.7 (8) | 3.0 (7) | 2.6 (8) | −0.6 (5) | 1.5 (6) | −0.7 (6) |
| C(4) | 11077 (14) | 7759 (9) | 2688 (7) | 5.3 (8) | 3.3 (8) | 3.0 (8) | 0.7 (6) | 0.1 (7) | −1.0 (6) |
| C(51) | 13306 (15) | 6407 (11) | 1288 (8) | 5.1 (8) | 5.5 (9) | 3.9 (9) | −0.0 (7) | −0.3 (6) | −1.1 (7) |
| C(52) | 12522 (14) | 8289 (11) | 943 (8) | 5.4 (8) | 4.3 (8) | 4.4 (9) | 0.0 (7) | 1.1 (6) | 1.5 (7) |
| C(53) | 10970 (13) | 6667 (10) | 284 (8) | 6.5 (8) | 4.2 (8) | 2.5 (8) | 1.6 (7) | 0.6 (6) | −1.1 (7) |
| C(61) | 7839 (14) | 5913 (9) | 649 (9) | 5.9 (8) | 1.6 (7) | 7.7 (11) | −0.4 (6) | −0.7 (7) | −1.2 (7) |
| C(62) | 8179 (14) | 5855 (10) | 2192 (9) | 5.9 (8) | 4.1 (8) | 6.6 (10) | −0.6 (7) | 2.3 (7) | 0.1 (8) |
| C(63) | 10817 (14) | 5592 (11) | 1756 (8) | 6.9 (8) | 3.3 (9) | 4.6 (9) | −1.2 (8) | −0.5 (7) | 0.0 (8) |

[a] Positional parameters × $10^4$; thermal parameters × $10^2$.

**Table III.** Bond Lengths (Å) between Nonhydrogen Atoms of [Glyoxal bis(*tert*-butylimine)]hexacarbonylcobaltmanganese[a]

| | | | |
|---|---|---|---|
| Mn–Co | 2.639 (3) | N(2)–C(2) | 1.493 (13) |
| Co–N(1) | 1.891 (9) | C(3)–C(4) | 1.405 (15) |
| Co–C(3) | 2.065 (11) | C(1)–C(11) | 1.548 (15) |
| Co–C(61) | 1.795 (13) | C(1)–C(12) | 1.474 (17) |
| Co–C(62) | 1.683 (15) | C(1)–C(13) | 1.550 (18) |
| Co–C(63) | 1.798 (13) | C(2)–C(21) | 1.527 (17) |
| Mn–N(1) | 2.048 (9) | C(2)–C(22) | 1.522 (18) |
| Mn–N(2) | 2.094 (9) | C(2)–C(23) | 1.518 (19) |
| Mn–C(51) | 1.749 (14) | C(61)–O(61) | 1.129 (16) |
| Mn–C(52) | 1.853 (14) | C(62)–O(62) | 1.183 (20) |
| Mn–C(53) | 1.766 (13) | C(63)–O(63) | 1.172 (16) |
| Mn–C(63) | 2.332 (14) | C(51)–O(51) | 1.161 (17) |
| N(1)–C(1) | 1.584 (13) | C(52)–O(52) | 1.099 (17) |
| N(1)–C(3) | 1.358 (16) | C(53)–O(53) | 1.156 (16) |
| N(2)–C(4) | 1.260 (16) | | |

[a] Esd's are in parentheses.

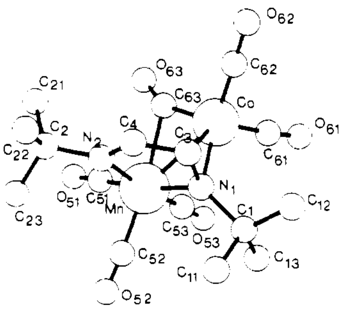

**Figure 1.** Molecular structure of [glyoxal bis(*tert*-butylimine)]hexacarbonylcobaltmanganese showing the numbering scheme of the atoms.

The structure was solved by use of a Patterson function to find the cobalt and manganese positions, and the remaining nonhydrogen atoms were positioned by the DIRDIF procedure.[18] A subsequent difference Fourier synthesis showed the positions of the nonhydrogen atoms. A total of 1305 reflections were used in the refinement by the full-matrix least-squares method, allowing anisotropic vibration for the nonhydrogen atoms. The weight for each reflection was calculated according to the formula $w = [\sigma^2(I) + 0.004F^2]^{-1}$ ($\sigma(I)$ based on counting statistics). The hydrogen atoms were placed at calculated positions. The conventional $R$ value was 0.066 for 1305 reflections and was based on 234 parameters varied.

**Table IV.** Bond Angles (Deg) between Nonhydrogen Atoms of [Glyoxal bis(*tert*-butylimine)]hexacarbonylcobaltmanganese[a]

| | | | |
|---|---|---|---|
| Mn–Co–N(1) | 50.5 (3) | C(53)–Mn–C(63) | 90.8 (5) |
| Mn–Co–C(3) | 71.5 (4) | Co–N(1)–Mn | 84.1 (3) |
| Mn–Co–C(61) | 110.0 (5) | Co–N(1)–C(1) | 125.0 (6) |
| Mn–Co–C(62) | 150.3 (4) | Co–N(1)–C(3) | 77.0 (6) |
| Mn–Co–C(63) | 59.6 (4) | Mn–N(1)–C(1) | 131.3 (8) |
| N(1)–Co–C(3) | 39.8 (5) | Mn–N(1)–C(3) | 108.2 (7) |
| N(1)–Co–C(61) | 106.4 (5) | C(1)–N(1)–C(3) | 115.6 (9) |
| N(1)–Co–C(62) | 132.9 (6) | Mn–N(2)–C(2) | 113.1 (7) |
| N(1)–Co–C(63) | 108.9 (5) | Mn–N(2)–C(4) | 107.6 (6) |
| C(3)–Co–C(61) | 137.0 (5) | C2–N(2)–C(4) | 120.8 (9) |
| C(3)–Co–C(62) | 96.7 (6) | Co–C(3)–N(1) | 63.1 (6) |
| C(3)–Co–C(63) | 109.2 (5) | Co–C(3)–C(4) | 110.5 (8) |
| C(61)–Co–C(62) | 97.3 (6) | N(1)–C(3)–C(4) | 115.2 (11) |
| C(61)–Co–C(63) | 107.4 (6) | N(2)–C(4)–C(3) | 123.1 (10) |
| C(62)–Co–C(63) | 101.7 (6) | N(1)–C(1)–C(11) | 105.7 (7) |
| Co–Mn–N(1) | 45.4 (3) | N(1)–C(1)–C(12) | 112.3 (10) |
| Co–Mn–N(2) | 86.2 (3) | N(1)–C(1)–C(13) | 108.3 (10) |
| Co–Mn–C(51) | 126.3 (4) | C(11)–C(1)–C(12) | 110.9 (10) |
| Co–Mn–C(52) | 143.9 (4) | C(11)–C(1)–C(13) | 107.0 (10) |
| Co–Mn–C(53) | 88.1 (4) | C(12)–C(1)–C(13) | 112.2 (9) |
| Co–Mn–C(63) | 42.0 (3) | N(2)–C(2)–C(21) | 107.9 (8) |
| N(1)–Mn–N(2) | 80.9 (4) | N(2)–C(2)–C(22) | 112.1 (9) |
| N(1)–Mn–C(51) | 171.3 (5) | N(2)–C(2)–C(23) | 108.6 (9) |
| N(1)–Mn–C(52) | 99.0 (5) | C(21)–C(2)–C(22) | 109.3 (10) |
| N(1)–Mn–C(53) | 96.5 (5) | C(21)–C(2)–C(23) | 110.2 (10) |
| N(1)–Mn–C(63) | 83.6 (4) | C(22)–C(2)–C(23) | 108.7 (9) |
| N(2)–Mn–C(51) | 96.5 (4) | Mn–C(51)–C(51) | 176.0 (10) |
| N(2)–Mn–C(52) | 94.1 (5) | Mn–C(52)–O(52) | 174.3 (12) |
| N(2)–Mn–C(53) | 174.0 (4) | Mn–C(53)–O(53) | 176.5 (11) |
| N(2)–Mn–C(63) | 83.6 (4) | Mn–C(63)–O(63) | 127.0 (10) |
| C(51)–Mn–C(52) | 89.5 (6) | Mn–C(63)–Co | 78.0 (5) |
| C(51)–Mn–C(53) | 85.3 (5) | Co–C(61)–O(61) | 176.2 (12) |
| C(51)–Mn–C(63) | 85.1 (5) | Co–C(62)–O(62) | 177.4 (14) |
| C(52)–Mn–C(53) | 91.6 (6) | Co–C(63)–O(63) | 154.4 (11) |
| C(52)–Mn–C(63) | 173.8 (5) | | |

[a] Esd's are in parentheses.

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Table V. Bond Distances (Å) and Angles (Deg) in Binuclear Metal Carbonyl Complexes and Related Compounds

| | *t*-Bu–N=CH–CH=N–*t*-Bu[a] | $MnCo(CO)_6$-(DAB)[b] | $Fe_2(CO)_6$-(DAB)[c] | $Ru_2(CO)_4$-$(DAB)_2$[d] | $Mo_2(CO)_6$-(IAE)[e] | $Fe_2(CO)_6$-(iminoacetate)[f] |
|---|---|---|---|---|---|---|
| C(1)-C(3) | 1.283 (6) | 1.358 (16) | 1.397 (4) | 1.432 (9) | 1.39 (2) | 1.417 (7) |
| C(3)-C(4) | 1.496 (20) | 1.405 (15) | 1.435 (5) | 1.451 (9) | 1.56 (3) | 1.435 (10) |
| C(2)-C(4) | 1.283 (6) | 1.260 (16) | 1.280 (5) | 1.289 (9) | 1.28 (2) | 1.258 (7)[g] |
| C(4)-C(3)-N(1) | 117.3 (4) | 115 (2) | nr[h] | 115.9 (6) | 112 (1) | nr |
| $\theta$ | 65 | 11 | 12 | 5 | 33 | nr |
| C(1)-M(1) | | 1.891 (9) | 1.972 (3) | 2.110 (6) | 2.18 (1) | 1.927 (5) |
| C(1)-M(2) | | 2.048 (9) | 1.930 (3) | 2.155 (6) | 2.25 (1) | 1.960 (4) |
| C(2)-M(1) | | 2.094 (9) | 1.991 (3) | 2.139 (6) | 2.09 (2) | 2.011 (4)[g] |
| C(3)-M(1) | | 2.065 (11) | 2.069 (3) | 2.140 (7) | | 2.055 (6) |
| C(1)-M(2) | | 2.640 (3) | 2.597 (1) | 3.308 (1) | 2.813 (3) | 2.551 (1) |

[a] Electron diffraction study in the gas phase.[24] [b] DAB = glyoxal bis(*tert*-butylimine). [c] DAB = glyoxal bis(cyclohexylimine).[12] [d] DAB = glyoxal bis(isopropylimine).[14] [e] IAE = bis[$\mu$-(1-(isopropylamino)-2-(isopropylimino)ethane-*N*,*N'*)].[13] [f] Iminoacetate = ethyl *N*-($\alpha$-methylbenzyl)iminoacetate.[31] [g] In this ligand N(2) is replaced by O. [h] nr = not reported.

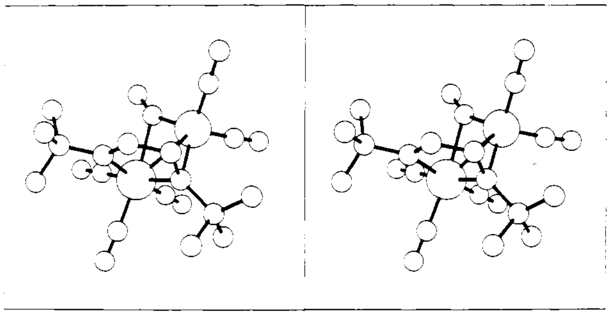

Figure 2. Stereoview of the molecule.

The relative high *R* value is the result of a rotation disorder in the *tert*-butyl group with central carbon atom C(1) (see Figure 1). No attempts have been made to solve the disorder problem, since the conformation of the backbone of the molecule was our main interest.

The molecular structure with the numbering of the atoms is shown in Figure 1, and Tables II–IV contain the atomic parameters, the bond lengths, and bond angles, respectively.

## Results

**Molecular Structure of [Glyoxal bis(*tert*-butylimine)]hexacarbonylcobaltmanganese.** A two-electron metal–metal bond is required to obtain an 18-electron configuration on both manganese and cobalt. The observed manganese–cobalt distance is 2.639 (3) Å, which is in agreement with a single metal–metal bond.

The Mn–Co bond is shorter than the single Mn–Mn bond in $Mn_2(CO)_{10}$ but longer than the single Co–Co bond in $Co_2(CO)_8$, which are 2.923[19] and 2.54 Å,[20] respectively.

The molecule contains five terminal carbonyl groups. Remarkable is the presence of a semibridging carbonyl group in the metal carbonyl skeleton. For this carbonyl group a Co–C(63) bond length of 1.80 (1) Å and a Mn–C(63) bond length of 2.33 (1) Å are found. The Co–C(63)–O(63) angle is 154 (1) which deviates only 22° from the Co–C(61)–O(61) and Co–C(62)–O(62) angles which are 176 (1) and 177 (1)°, respectively. The Mn–C(63)–O(63) angle is 127 (1)° and the Mn–C(63)–Co angle is 78 (1)°, and consequently the semibridging carbonyl group is coplanar with Mn and Co. Recently criteria have been put forward by Colton and McCormick[21] for the classification of bridging carbonyl groups. When the difference between the M–C distances is more than 0.3 Å and the difference in the M–C–O bond angles is more than 20°, the carbonyl group is classified as semibridging. The semibridging carbonyl group in $MnCo(CO)_6$[glyoxal bis(*tert*-butylimine)] satisfies these conditions.

The semibridging coordination mode is of special interest in the terminal bridging exchange processes of carbonyl groups. This coordination mode is considered as an intermediate stage between bridging and terminal coordination in exchange processes, and the solid-state structures containing semibridging carbonyl groups have been called "stop-action" views of the bridge–terminal interchange.[22,23]

The DAB ligand is coordinated to manganese via N(1) and N(2) with bond lengths of 2.05 (1) and 2.09 (1) Å, respectively. Furthermore the DAB ligand is coordinated to cobalt via N(1) and C(3) with Co–N(1) and Co–C(3) bond lengths of 1.89 (1) and 2.07 (1) Å, respectively. The two imine fragments have different C–N bond lengths: C(4)–N(2) is 1.26 (1) Å and C(3)–N(1) is 1.36 (1) Å, which shows the asymmetric coordination of the DAB ligand. Apparently, the DAB ligand acts as a six-electron donor, donating the two lone pairs on nitrogen and one pair of $\pi$ electrons. However, the exact electronic structure of the MnCo(DAB) fragment is not evident from these data.

Formally it is possible to distinguish between $\sigma^2$-N, $\sigma^2$-N',$\eta^2$-C=N' coordination and $\sigma^2$-N,$\mu^2$-N',$\sigma^2$-C=N' coordination. In the first case the two lone pairs on nitrogen are coordinated to manganese and the $\pi$ electrons to cobalt, which would be the case if the semi-bridging carbonyl was not taken into account. In the latter case, one lone pair is donated to manganese, the second lone pair is shared between manganese and cobalt, and the $\pi$ electrons are donated to cobalt. This type of coordination is found in the homodinuclear complexes $M_2(CO)_6$(DAB) (M = Fe, Ru),[12,14] and this would also be the coordination mode of the DAB ligand in $MCo(CO)_6$(DAB) (M = Mn, Re) if the carbonyl group between manganese and cobalt was a symmetrical carbonyl bridge. Since the bridging carbonyl group is of the semibridging type, the actual electronic structure is in between $\sigma^2$-N,$\sigma^2$-N',$\eta^2$-C=N' and $\sigma^2$-N,$\mu^2$-N',$\eta^2$-C=N' (i.e., a resonance structure), with the largest contribution of the former type of bonding.

In Table V a comparison is made between related bond lengths in binuclear complexes containing $\sigma^2$-N,$\mu^2$-N',$\eta^2$-C=N' (or $\sigma^2$-O,$\mu^2$-N,$\eta^2$-C=N) coordinated diimines (or iminoacetate), including values for the related $Mo_2(CO)_6$(IAE) (IAE = bis[$\mu$-(1-(isopropylamino)-2-(isopropylimino)ethane-*N*,*N'*)]) and the free ligand *t*-Bu—N=CH—CH=N—*t*-Bu.

The values for the free ligand are from an electron diffraction (gas phase) study, and a few remarks should be made before comparing these with the solid-state structures. The 1,4-diazabutadienes are, as free ligands, in the anti conformation with respect to the central C–C bond (C(3)–C(4))

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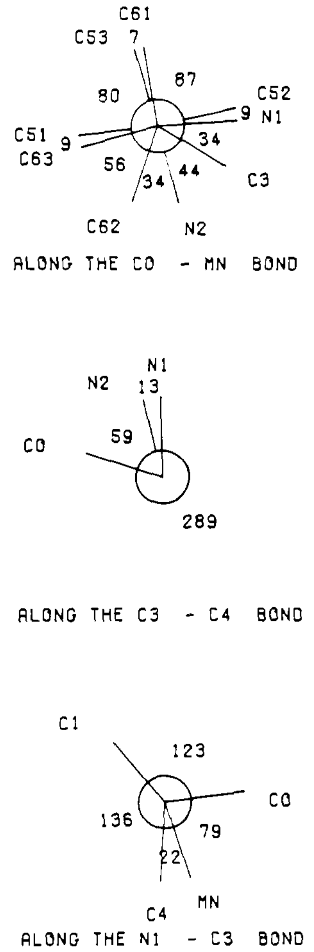

**Figure 3.** Newman projections along the Mn–Co, C(3)–C(4), and N(1)–C(3) bond axes.

while the coordinated ligands are in the syn conformation. The free ligands are nonplanar, with a torsion angle $\theta$ of 65° around the central C–C bond for glyoxal bis(*tert*-butylimine).[24] The nonplanarity has been confirmed for the structure in solution by dipole moment measurements.[25] DAB ligands which are coordinated via the lone pairs on nitrogen ($\sigma,\sigma$ coordination) are planar,[26–29] in both the chelating and the bridging forms. Consequently, the $\pi$-electron system in the free ligand is localized on the C=N bonds because of the gauche conformation, while in $\sigma,\sigma$-coordinated DAB ligands it can delocalize through the five-membered chelate ring, resulting in a contraction of the C(3)–C(4) bond. Evidence for the pseudoaromatic character of five-membered chelate rings in complexes containing DAB ligands has been found by $^1$H NMR spectroscopy.[30] The extent of the delocalization depends on the metal in the ring system.

When the values in Table V are compared, it can be seen that $\sigma^2$-N coordination of the N(2)=C(4) imine fragment does not influence the N(2)—C(4) bond length very much, while the $\eta^2$-C=N coordination of the N(1)—C(3) imine fragment causes an increase of the N(1)—C(3) bond length which corresponds with a decrease of the bond orders to almost 1.

The planarity of the coordinated ligand is not drastically influenced by the $\eta^2$-C=N bond formation, as is shown by the Newman projections along C(3)—C(4) and N(1)—C(3) which are given in Figure 3. That the preservation of the planarity of the ligands is a general trend in these type of complexes is obvious from Table V; the torsion angle $\theta$ varies between 5 and 13°. In $Mo_2(CO)_6$(IAE) $\theta$ is 33°, but N(1)–C(3) is a real single bond[13] in these complexes, although resulting from a DAB ligand. In the $\sigma^2$-N,$\mu^2$-N′($\sigma^2$-N′),$\eta^2$-C=N′-coordinated 1,4-diazabutadienes, the angle C(4)–C(3)–N(1) is comparable with the angle in the free ligand. Furthermore, the C(2)–C(4) bond lengths remain relatively short. All these data confirm that the coordinated DAB ligand should be regarded more as a diimine rather than as a amino–imino ligand. To describe the interaction between the C(3)—N(1) double bond and cobalt as $\eta^2$-C=N coordination is better than to regard the N(1)—C(3)—Co fragment as a cyclic metallazapropane.

Characteristic for the homodinuclear complexes ($Mo_2(CO)_6$(IAE) excluded) is that M(1)–N(1) and M(2)–N(1) have comparable bond lengths. In the heterodinuclear complex $MnCo(CO)_6$[glyoxal bis(*tert*-butylimine)] the Co–N(1) distance is 0.16 Å shorter than the Mn–N(1) distance. Whether this is caused by the fact that the bridged metals are different (a heteronuclear effect) or that it is the result of the slightly different electronic structure within the diimine ($\sigma^2,\sigma^2,\eta^2$ vs. $\sigma^2,\mu^2,\eta^2$) is not clear.

**$^1$H NMR Spectroscopy.** 1,4-Diazabutadienes which are only coordinated via the lone pairs on nitrogen give $^1$H NMR signals for the imine hydrogen atoms in the range of 7–9 ppm.[11,32] These values do not differ very much from the values obtained for the free ligands, and the shifts relative to the free-ligand positions depend on the metal in the chelate ring.[1,11,16]

When a C=N bond is also involved in the coordination of the DAB ligand, one might expect drastic upfield shifts for the imine hydrogen atom attached to the $\eta^2$-C=N-coordinated imine fragment.

In the $^1$H NMR spectra of $MCo(CO)_6$(DAB) (M = Mn, Re) the two imine hydrogen atoms appear as an AX pattern with signals near 8 and 5 ppm ($J_{ax}$ = 2 Hz). The signal at low field is in the range of $\sigma$-coordinated DAB ligands and is therefore assigned to the hydrogen atom attached to the $\sigma$-coordinated imine fragment. The signal at 5 ppm is assigned to the imine hydrogen atom on the $\eta^2$-coordinated C=N moiety. The asymmetry in the coordinated DAB ligands is furthermore confirmed by the anisochronous signals for the substituents attached to nitrogen.

In $MnCo(CO)_6$[methylglyoxal bis(isopropylimine)] one of the substituents on the imine carbon atoms is a methyl group. Consequently, there are two possible isomers, one with the methyl group attached to the $\sigma$-coordinated imine fragment and one with the methyl group on the $\eta^2$-C=N-coordinated imine fragment, respectively. The $^1$H NMR spectrum of the complex shows that the isomer with the hydrogen atom on the $\eta^2$-C=N fragment and the methyl group on the $\sigma$-coordinated part of the DAB ligand is formed exclusively. The imine hydrogen atom appears at 4.79 ppm in the $^1$H NMR spectrum.

In $MCo(CO)_7$[biacetyl bis(cyclopropylimine)] (M = Mn, Re) both positions on the imine carbon atoms are occupied by methyl groups. Only one signal is observed for the two methyl groups and a single set of signals for the cyclopropyl groups. Obviously the DAB ligand is coordinated via the lone pairs on nitrogen, thus forming a five-membered chelate ring. This is confirmed by $^{13}$C NMR spectroscopy.[33]

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**Table VI.** $^1$H NMR Data of MCo(CO)$_6$(DAB) and MCo(CO)$_7$(DAB) (M = Mn, Re) (Solvent CDCl$_3$, $\delta$ Relative to Me$_4$Si)

| complex | substituents | imine hydrogen[a] |
|---|---|---|
| MnCo(CO)$_6$[glyoxal bis(*tert*-butylimine)] | 1.34, 1.50 (*t*-Bu) | 4.76, 7.89 |
| MnCo(CO)$_6$[glyoxal bis(isopropylimine)] | 1.19/1.21, 1.39/1.60 (*i*-Pr),[b,c] 3.73 (*i*-Pr)[d] | 4.85, 7.79 |
| MnCo(CO)$_6$[glyoxal bis(cyclopropylimine)] | 1.0 (br), 2.9, 3.4 | 4.88, 7.65 |
| MnCo(CO)$_6$[glyoxal bis(cyclohexylimine)] | 1–2 (br, cHx), 2.8 (cHx), 3.3 (cHx) | 4.84, 7.80 |
| MnCo(CO)$_6$[methylglyoxal bis(isopropylimine)] | 1.16/1.31, 1.41/1.65 (*i*-Pr),[b,c] 4.62, 4.83 (*i*-Pr),[d] 1.96 (CH$_3$) | 4.75 |
| ReCo(CO)$_6$[glyoxal bis(*tert*-butylimine)] | 1.27, 1.34 (*t*-Bu) | 5.48, 8.06 |
| ReCo(CO)$_6$[glyoxal bis(cyclohexylimine)] | 1–2 (br, cHx), 3.0, 2.2 (cHx) | 5.54, 7.97 |
| MnCo(CO)$_7$[biacetyl bis(cyclopropylimine)] | 1–2 (br, cPr), 2.12 (CH$_3$), 2.55 (cPr) | |

[a] $J_{ax}$ = 2 Hz. [b] Values separated by vertical bars correspond to diastereotopic pairs. [c] Doublet $J$ = 7 Hz. [d] Septet $J$ = 7 Hz.

In MnCo(CO)$_6$[biacetyl bis(cyclopropylimine)] an exchange within the $\sigma^2$-N,$\sigma^2$-N′,$\eta^2$-C=N′-coordinated DAB ligand can be observed. The dynamic behavior of the coordinated ligand has been studied in the temperature range −40–+20 °C. At −20 °C the two methyl signals are inequivalent, giving resonances at 1.32 and 1.37 ppm while at −10 °C the two methyl groups give one single line at 1.45 ppm which sharpens at higher temperature. Obviously there is an interchange between the two (CH$_3$)C=N fragments which are $\sigma^2$-N and $\sigma^2$-N,$\eta^2$-C=N coordinated. This interchange has not been observed for glyoxal bis(alkylimine) derivatives (i.e., for (H)-C=N fragments). The cyclopropyl signals also coalesce, but since these signals are already broad multiplets, the effect is less pronounced as with the sharp signals of the methyl groups.

Two possible mechanisms can be put forward to explain this exchange process. The first mechanism involves a dissociation of the $\eta^2$-C=N bond, forming an intermediate with a vacant coordination site on cobalt and with the DAB ligand $\sigma,\sigma$ coordinated to manganese. The vacant site on cobalt can be filled by either of the two C=N double bonds, resulting in the complex again. This mechanism is shown in Figure 4.

In the second mechanism the Mn—Co bond is broken as a first step followed by coordination of the second C=N bond to cobalt, creating a $\sigma^2$-N,$\sigma^2$-N′,$\eta^2$-C=N′,$\eta^2$-C=N′ type of coordination of DAB. The initial situation can be restored by dissociation of one of the $\eta^2$-C=N bonds as is shown in Figure 5. Recently we prepared Ru$_2$(CO)$_4$(DAB)(HC≡CH) which contains a $\sigma^2$-N,$\sigma^2$-N′,$\eta^2$-C=N,$\eta^2$-C=N′-coordinated DAB ligand.[15] This complex could be a precedent for the proposed transition state in the second mechanism.

When we assume that (H)C=N fragments have stronger $\eta^2$-C=N interactions with cobalt than (CH$_3$)C=N fragments, which is confirmed by the configuration of MnCo(CO)$_6$[*i*-Pr—N=C(H)—C(CH$_3$)=N—*i*-Pr] (vide infra) and by the absence of the dynamic behavior in ligands containing an N=C(H)—C(H)=N fragment, mechanism I (Figure 4) is more likely than mechanism II (Figure 5).

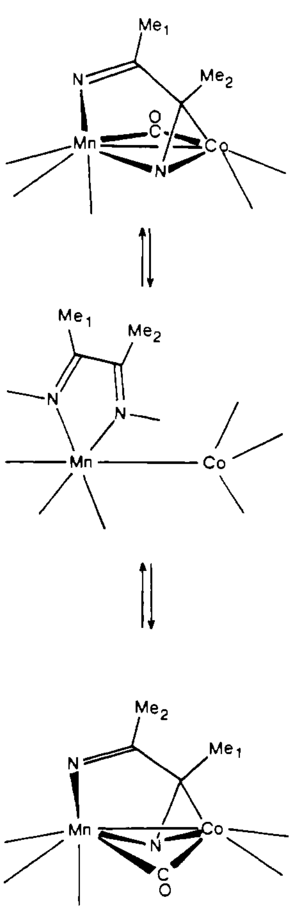

**Figure 4.** Proposed mechanism for the exchange process as observed in the $^1$H NMR spectrum of MnCo(CO)$_6$(cPr—N=C(CH$_3$)—(CH$_3$)C=N—cPr).

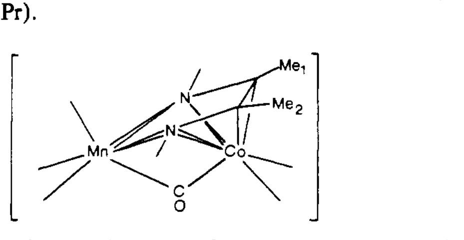

**Figure 5.** Alternative transition state for the exchange mechanism shown in Figure 4.

In Table VI are listed the $^1$H NMR data, including the chemical shifts of some related M$_2$(CO)$_6$(DAB) complexes (M = Fe, Ru). The $^1$H NMR shifts of the imine hydrogen atoms are compared in the series MM′(CO)$_6$(DAB) (M = M′ = Fe, Ru; M = Mn, Re and M′ = Co) and a striking difference is observed between the homodinuclear Fe and Ru complexes vs. the heterodinuclear Mn—Co and Re—Co complexes. The imine hydrogen atom attached to the $\eta^2$-C=N-coordinated part of the ligand is observed 2.5 ppm downfield in the heterodinuclear complexes as compared with the homodinuclear species M$_2$(CO)$_6$(DAB) (M = Fe, Ru).[14] In the latter complexes the $\eta^2$-C=N-coordinated fragment seems fully reduced, giving chemical shifts for the imine hydrogen atoms in the range of hydrogen on a sp$^3$ carbon atom, attached to nitrogen, although the corresponding imine carbon atom is essentially sp$^2$ hybridized (vide supra). In the MCo(CO)$_6$(DAB) complexes the bond order of the $\eta^2$-coordinated fragment is far greater than 1, resulting in chemical

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(33) Additional information on this subject was obtained by $^{13}$C NMR spectroscopy. For the free ligand the $^{13}$C NMR chemical shifts relative to Me$_4$Si are $\delta$(C-imine) = 166.3, $\delta$(CH$_3$) = 12.4, and $\delta$(cPr) = 34.0 and 9.2. For the starting material Mn(CO)$_3$Br[biacetyl bis(cyclopropylimine)], $\delta$(C-imine) = 176.5, $\delta$(CH$_3$) = 20.8, and $\delta$(C-propyl) = 11.7/11.42 (diastereotopic) and 40.0. Comparable values have been obtained for MnCo(CO)$_4$(cPr—N=C(CH$_3$)—(CH$_3$)C=N—cPr): $\delta$(C-imine) = 177.2, $\delta$(CH$_3$) = 20.3, $\delta$(cPr) = 11.4/11.6 (diastereotopic) and 40.9. These values are evidence that the DAB ligand is coordinated via the nitrogen lone pairs. The $^{13}$C NMR data of MCo(CO)$_6$(DAB) complexes (M = Mn, Re) are included in a paper concerning a $^{13}$C NMR study of MM′(CO)$_6$(DAB) complexes (M = M′ = Fe, Ru; M = Mn and Re, M′ = Co).[34]

(34) L. H. Staal, J. Keijsper, L. H. Polm, and K. Vrieze, submitted for publication.

shifts for the imine hydrogen atoms which are at lower field as compared with the values for $M_2(CO)_6(DAB)$ (M = Fe, Ru). This different electronic behavior of the 1,4-diazabutadienes in the various complexes might result from the slightly different coordinating behavior of the ligands ($\sigma^2,\sigma^2,\eta^2$ vs. $\sigma^2,\mu^2,\eta^2$ coordination).

A strong diastereotopic effect can be observed in the isopropyl groups of $MnCo(CO)_6$[glyoxal bis(isopropylimine)] and $MnCo(CO)_6$[methylglyoxal bis(isopropylimine)], reflecting the dissymmetry in the complexes. Each isopropyl group gives two doublets near 1.2 ppm. The influence of metal–metal bonds on this behavior has been studied before in detail.[11] Drastic changes between the $^1H$ NMR patterns of the isopropyl groups can be observed when either $CDCl_3$ or $C_6D_6$ solutions are used. The fact that the complexes are affected by the solvent is also evidenced by the drastic shifts for the imine hydrogen atoms in the complex, 4.85 and 7.79 ppm in $CDCl_3$ and 4.18 and 6.80 ppm in $C_6D_6$, respectively, for $MnCo(CO)_6$[glyoxal bis(isopropylimine)].

**IR Spectroscopy.** The metal carbonyl skeleton of $MCo(CO)_6(DAB)$ complexes (M = Mn, Re) consists of five terminal and one semibridging carbonyl groups. The terminal CO groups give rise to five strong bands between 2050 and 1900 $cm^{-1}$ in the $\nu$(CO) region of the IR spectra. The $\nu$(CO) frequencies are included in Table I.

The semibridging carbonyl group gives a weak and broad band near 1895 $cm^{-1}$ for the Mn–Co complexes and near 1875 $cm^{-1}$ for the Re–Co derivatives.

The spectra obtained in hexane solutions are similar to the spectra obtained in a KBr disk or in Nujol mull which is evidence that the solid-state structure and the structure in solution is the same for the $MCo(CO)_6(DAB)$ complexes (M = Mn, Re).

Recently, Cotton and Troup found a correlation between the degree of asymmetry and the $\nu$(CO) frequency for bridging carbonyl groups, in trinuclear iron complexes.[22] When their conclusion based on the iron complexes holds for $MCo(CO)_6(DAB)$ complexes (M = Mn, Re), the bridging carbonyl groups in rhenium–cobalt complexes should be regarded as asymmetrical bridging rather than as semibridging carbonyl groups. The low intensity is a common feature for many CO stretching frequencies belonging to bridging carbonyl groups, but the high frequency of the bridging carbonyl groups illustrates that this bonding mode is really a borderline case between bridging and terminal coordination of carbonyl groups.

Two fairly stable $MCo(CO)_7(DAB)$ complexes have been prepared of which the IR spectra in the CO-stretching region show only minor changes as compared with the spectra of $MCo(CO)_6(DAB)$. One additional weak band is found for the rhenium–cobalt complex at 1909 $cm^{-1}$ which can be assigned to a terminal $\nu$(CO) on cobalt. A precise description of the complexes is given in the next section.

## Discussion of Reaction Mechanism

One can only speculate about the exact route via which the $\sigma^2$-N,$\mu^2$-N′,$\eta^2$-C═N coordination occurs in the "one pot" syntheses of $Fe_2(CO)_6(DAB)^-$ [12] and $Ru_2(CO)_6(DAB)$.[14,35] However, the reaction between $[Co(CO)_4]^-$ and $Mn(CO)_3Br(DAB)$ is very illustrative with respect to the $\eta^2$-C═N bond formation.

In general five (competing) reaction pathways should be considered for a redox reaction between metal carbonyl anions and metal carbonyl halides: electron transfer, nucleophilic substitution with halide displacement, nucleophilic substitution with ligand displacement, charge–X interchange, and redistribution.[36–38] The reaction of $[Co(CO)_4]^-$ and $Mn(CO)_3Br(DAB)$ yields the heterodinuclear complexes exclusively (and the starting materials) which strongly suggests that the mechanism is a nucleophilic attack with bromide displacement. The reaction is remarkably clean. Analogous reactions of $Mn(CO)_3Br(DAB)$ with other metal carbonyl anions (e.g., $[Mo(CO)_4(DAB)]^-$,[13] $[Mn(CO)_5]^-$[11]) yielded side products due to competing side reactions.

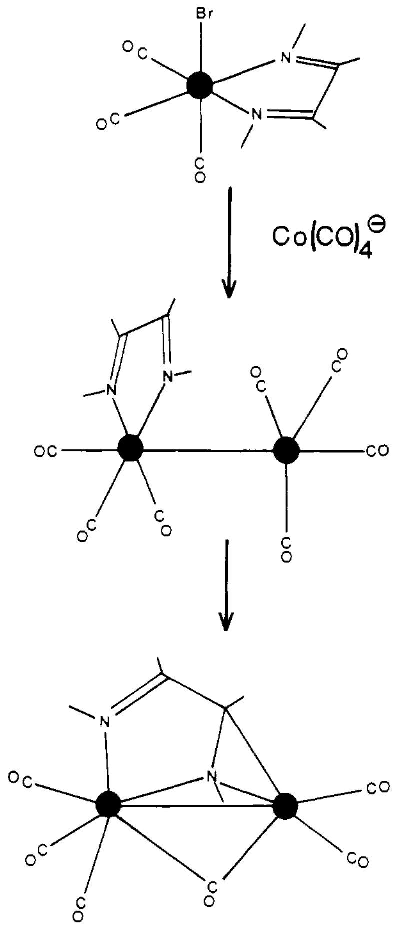

**Figure 6.** Reaction pathway of the formation of $MCo(CO)_6(DAB)$ complexes (M = Mn, Re).

The first step in the reaction sequence is proposed to be metal–metal bond formation between Mn and Co after which the DAB ligand is still on manganese. The proposed intermediates are $MnCo(CO)_7(DAB)$ which indeed have been found when biacetyl bis(cyclopropylimine) was used as a DAB ligand and which were identified by FD mass spectrometry and IR and $^1H$ and $^{13}C$ NMR spectroscopy.[33] When the reactions of other derivatives were monitored by IR spectroscopy in the $\nu$(CO) region, bands due to $MCo(CO)_7(DAB)$ complexes were observed which suggests that these complexes are indeed intermediates in the reaction sequence. This assumption is supported by the analogy with the reaction of $[Mn(CO)_5]^-$ with $Mn(CO)_3Br(DAB)$, yielding $Mn_2(CO)_8(DAB)$. The complexes contain $\sigma,\sigma$-bidentate DAB ligands and a single metal–metal bond.[11] The reaction sequence of the $MCo(CO)_6(DAB)$ formation is given in Figure 6, showing the structure of the $MCo(CO)_7(DAB)$ intermediates.

$MCo(CO)_6(DAB)$ complexes (M = Mn, Re) are formed in a subsequent elimination of a carbonyl group on cobalt in the $MCo(CO)_7(DAB)$ intermediates, creating a vacant co-

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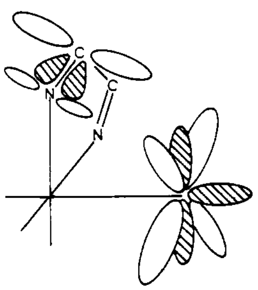

**Figure 7.** Molecular orbital picture for the interaction between the d orbitals on cobalt and the $\pi$ orbitals on the N=C—C=N skeleton.

ordination site on cobalt. The $\pi$-orbital system of the N=C—C=N skeleton is in a good position to give overlap with the d orbitals of cobalt and thus can give rise to $\eta^2$-C=N coordination. This is shown in Figure 7.

There is a remarkable difference in the $\pi$-coordinating behavior of (H)C=N and $(CH_3)$C=N fragments. This is reflected by the following phenomena: (a) when methylglyoxal bis(isopropylimine) is used as a DAB ligand, the isomer with the $(CH_3)$C=N fragment $\sigma$-coordinated is formed exclusively; (b) $MCo(CO)_7(DAB)$ complexes are stabilized by making use of biacetyl bis(cyclopropylimine); (c) there is an interchange between the $\sigma$- and the $\pi$-coordinated parts of the DAB ligand in $MnCo(CO)_6$[biacetyl bis(cyclopropylimine)] which does not occur in glyoxal bis(alkylimine) derivatives.

This behavior is not restricted to the heterobinuclear complexes. Methylglyoxal bis(isopropylimine) is found with the $(CH_3)$C=N fragment in the $\sigma$ coordination mode for all the $MM'(CO)_6(DAB)$ complexes (M = M′ = Fe, Ru; M = Mn and Re, M′ = Co). Therefore, the difference in coordinating behavior of $(CH_3)$C=N and (H)C=N fragments seems to be a property of the ligands and not of the metals.

Probably the methyl groups cause an increase of the already slightly polarized C=N bonds which results in a decrease of the $\pi$-acceptor properties of the imine fragments. This is confirmed by recent MO calculations which showed an increased LUMO energy after substitution on the 2,3 positions of the DAB skeleton with methyl groups.[3]

A comparison of the homodinuclear complexes $Mn_2(CO)_8(DAB)$[11] with the heterodinuclear complexes $MnCo(CO)_6(DAB)$ illustrates the role of the metal carbonyl fragments in the coordinating behavior of the N=C—C=N skeleton. In the $Mn_2(CO)_8(DAB)$ complexes the DAB ligand remains in the $\sigma,\sigma$-N,N′ coordination mode even after prolonged heating, while the heterobinuclear $MnCo(CO)_7(DAB)$ complexes rapidly convert into $MnCo(CO)_6(DAB)$. The stability of the metal carbonyl fragments with respect to elimination of carbon monoxide ($Mn(CO)_5$ vs. $Co(CO)_4$) and the tendency to have strong $d_\pi-\pi^*$ interactions seem to be predominant factors which determine the actual coordination mode of the DAB ligand. Recently, homodinuclear $Co_2(CO)_6(DAB)$ complexes have been prepared which contain $\sigma,\sigma$-N,N′-coordinated DAB ligands. The stability of these complexes toward $\eta^2$-C=N bond formation is determined by the geometry of the coordination polyhedron. The $\pi$-orbital system of the N=C—C=N skeleton is in a noninteractive position relative to the d orbitals on the cobalt atom which is not in the five-membered chelate ring.

## Conclusions

It is shown that under appropriate conditions DAB ligands can be forced to use their $\pi$-electron system for coordination. At present in all examples of $\eta^2$-C=N coordination of the DAB ligands, first the lone pairs are used to form a five-membered chelate ring, after which the $\pi$ orbitals become available for the coordination. Interestingly, the created situation is analogous to the coordination of cyclic ligands containing the N=C—C=N moiety, toward $Fe(CO)_3$ and $Ni(CO)_2$ fragments.[2]

With the syntheses of $MCo(CO)_6(DAB)$ complexes (M = Mn, Re), a first step is made for a more systematic approach of the $\eta^2$-C=N coordination mode of 1,4-diazabutadienes. This is of special interest for the metal carbonyl supported syntheses of organic chemicals and the (catalytic) oligomerization of unsaturated organic molecules by means of the highly activated imine carbon atoms in the $\sigma^2$-N,$\mu^2$-N′($\sigma^2$-N′),$\eta^2$-C=N′-$MM'(CO)_6(DAB)$ complexes.

The factors determining the $\pi$-coordinating ability of coordinated DAB ligands as discussed above give a better view of the dimerization of DAB ligands in $Mo_2(CO)_6(IAE)$[13] for which it was stated that oxidative elimination of CO from $[Mo(CO)_4(DAB)]^-$ followed by $\pi$ coordination of a C=N fragment was the driving force for the reaction. In fact dimerization of DAB ligands to form $Mo_2(CO)_6(IAE)$ (IAE = bis[(alkylimino)(alkylamino)ethane]) is the first example of activation of imine carbon atoms by $\eta^2$-C=N coordination.[13]

DAB ligands are very often compared with 2,2′-bipyridine and 1,10-phenanthroline. For many years it was believed that they had similar reactivity toward metal carbonyl fragments, but the ability to use the $\pi$ electrons in the coordination seems restricted to the 1,4-diazabutadienes.

An example of the different coordinating behavior can be found in the syntheses of binuclear iron carbonyl complexes. Bipyridine forms $Fe_2(CO)_7(bpy)$[39] while DAB ligands react to form $Fe_2(CO)_6(DAB)$ complexes.[12] In this respect it might be anticipated that $MnCo(CO)_7(bpy)$ is a stable molecule.

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**Registry No.** $CoMn(CO)_6$[glyoxal bis(isopropylimine)], 75548-65-1; $CoMn(CO)_6$[glyoxal bis(*tert*-butylimine)], 75548-66-2; $CoMn(CO)_6$[glyoxal bis(cyclohexylimine)], 75548-67-3; $CoMn(CO)_6$[glyoxal bis(cyclopropylimine)], 75548-68-4; $CoMn(CO)_6$[methylglyoxal bis(isopropylimine)], 75548-69-5; $CoRe(CO)_6$[glyoxal bis(*tert*-butylimine)], 75548-70-8; $CoRe(CO)_6$[glyoxal bis(cyclohexylimine)], 75548-71-9; $CoMn(CO)_7$[biacetyl bis(cyclopropylimine)], 75548-72-0; $CoRe(CO)_7$[biacetyl bis(cyclopropylimine)], 75548-73-1; $ReCo(CO)_6$[glyoxal bis(isopropylimine)], 75558-41-7; $MnCo(CO)_6$[biacetyl bis(cyclopropylimine)], 75548-74-2; $Mn(CO)_3Br$[glyoxal bis(*tert*-butylimine)], 70749-13-2; $Mn(CO)_3Br$[glyoxal bis(cyclohexylimine)], 64538-57-4; $Mn(CO)_3Br$[glyoxal bis(cyclopropylimine)], 75548-75-3; $Mn(CO)_3Br$[methylglyoxal bis(isopropylimine)], 75548-76-4; $Mn(CO)_3Br$[biacetyl bis(cyclopropylimine)], 75548-77-5; $Mn(CO)_3Br$[glyoxal bis(isopropylimine)], 70773-65-8; $Re(CO)_3Br$[glyoxal bis(*tert*-butylimine)], 70708-92-8; $Re(CO)_3Br$[glyoxal bis(cyclohexylimine)], 75548-78-6; $Re(CO)_3Br$[glyoxal bis(isopropylimine)], 75548-79-7; $Re(CO)_3Br$[biacetyl bis(cyclopropylimine)], 75548-80-0; $[Co(CO)_4]^-$, 14971-27-8; biacetyl bis(cyclopropylimine), 15677-40-4; glyoxal bis(cyclopropylimine), 57187-67-4; biacetyl, 431-03-8; cyclopropylamine, 765-30-0; glyoxal, 107-22-2.

**Supplementary Material Available:** A listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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