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Carbon–Carbon Bond Formation between Two α-Diimines with the Simultaneous Formation of a Metal–Metal Bond. X-ray Structure of Hexacarbonylbis[μ-(1-(isopropylamino)-2-(isopropylimino)ethane-*N*,*N*′)]-dimolybdenum

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Reduction and subsequent oxidation of $Mo(CO)_4(DAB)$ (DAB = 1,4-diazabutadiene = α-diimine) yield complexes with the formula $Mo_2(CO)_6(IAE)$ (IAE = μ-(1-(isopropylamino)-2-(isopropylimino)ethane-*N*,*N*′)). Several methods were developed for the preparation of $Mo_2(CO)_6(IAE)$ of which one involves a cyclic process with respect to $Mn_2(CO)_{10}$ and one a pseudocatalytic process with Hg^{2+} as catalyst. All methods have in common the oxidative elimination of CO from $(Mo(CO)_4(DAB))^-$, resulting in the generation of the coordinative unsaturated $Mo(CO)_3(DAB)$ intermediate for which a structure containing a σ,π-coordinated DAB ligand has been proposed. Dimerization of these 16-electron species yield the $Mo_2(CO)_6(IAE)$ complexes. The X-ray crystal structure for the isopropyl derivative showed the formation of a carbon–carbon bond between two DAB ligands (1.61 (2) Å) and the formation of a short Mo–Mo single bond (2.813 (3) Å). The crystal was orthorhombic with space group $P22_12_1$ and cell constants $a = 8.190$ (1) Å, $b = 10.099$ (2) Å, $c = 16.844$ (2) Å, and $Z = 2$.

Introduction

During the last few years the coordination properties of conjugated heterodiene systems have been investigated extensively. Among these systems 1,4-diazabutadienes or α-diimines (abbreviated throughout this paper as DAB) have been shown to be excellent four-electron donors with ambident bonding behavior. The ligands possess two free electron pairs on nitrogen which are available for σ coordination and four delocalized π electrons on the diimine skeleton which are available for π coordination.

The variety of coordination modes is illustrated by Figure 1.

In Figure 1a the σ,σ-bidentate coordination mode is shown. This is the most common and has been found in many metal carbonyl complexes and in complexes with low-valent metals: Cr^0, Mo^0, W^0;[1-4] Mn^+, Re^+;[5-7] Fe^0,[8,9] Ni^0.[10]

Recently the σ-monodentate coordination mode, shown in Figure 1b, has been observed for Cr^0[4] while the σ,σ-bridging mode has been found for Rh^+[11] (see Figure 1c).

Examples of complexes in which DAB uses its π electrons for coordination are relatively scarce. The σ,π-coordination mode shown in Figure 1d has been found in $Fe(CO)_3(DAB)$[8,9] while π,π coordination (see Figure 1e) is only found for cyclic α-diimine systems coordinated to $Fe(CO)_3$ or $Ni(CO)_2$ fragments.[12,13]

In contrast to the large variety of complexes in which DAB acts as a four-electron donor, only one example is known in which DAB donates more than four electrons. In the binuclear iron carbonyl complexes $Fe_2(CO)_6(DAB)$, the DAB ligand donates six electrons to the $Fe_2(CO)_6$ moiety via two lone pairs on nitrogen and one pair of π electrons[14] (see Figure 1f).

As a part of our investigations on the coordination properties of DAB in bi- and polynuclear metal carbonyls and the possible involvement of the π electrons in the coordination to the metals, we wish to report now full details on the formation of $Mo_2(CO)_6(IAE)$ (IAE is used as an abbreviation for μ-(1-(isopropylamino)-2-(isopropylimino)ethane-*N*,*N*′)). In our preliminary paper on this subject[15] we proposed two possible structures for these complexes both involving σ,π coordination, which agreed with all spectroscopic properties. However, the actual structure as derived from a single-crystal X-ray determination showed the formation of a molybdenum–molybdenum single bond and a carbon–carbon bond between two α-diimines, thereby creating a ten-electron donor system coordinated to a $Mo_2(CO)_6$ moiety.

Experimental Section

NMR spectra were recorded on a Varian T60 and a Varian XL100 apparatus, IR spectra were obtained with a Beckman IR 4250, and UV–visible spectra were obtained with a Cary 14 spectrophotometer.

All preparations involving the reduced $Mo(CO)_4(DAB)$ complexes were carried out in an atmosphere of deoxygenated dry nitrogen. The solvents used for the reduction reactions were carefully dried and distilled before use.

The preparation of sodium–potassium alloy and a safe and quick method for the destruction of residues after reaction have been described by Ellis and Flom.[16,17]

The preparations of the ligands and the $Mo(CO)_4(DAB)$ complexes were carried out according to the methods described by tom Dieck et al.[2] except for methylglyoxal bis(isopropylimine) which was prepared by a method similar to the preparation of diacetyl-*n*-butylimine.[18]

Molybdenum hexacarbonyl and dimanganese decacarbonyl have been obtained from Strem Chemicals and were used without further purification. Manganese pentacarbonyl halides have been prepared as described by Brimm et al.[19] and by Abel and Wilkinson.[20]

Preparations of $Mn(CO)_3Br(DAB)$ (DAB = Glyoxal Bis(*tert*-butylimine), Glyoxal Bis(isopropylimine)). $Mn(CO)_5Br$ (0.825 g) and DAB (3 mmol) were refluxed in 50 mL of ether for 0.5 h. The product precipitated immediately and was filtered and washed twice with 50 mL of ether to yield 90% of orange microcrystals.

Preparations of $Mo_2(CO)_6(IAE)$. Method i. $Mn(CO)_3Br(DAB)$ as Oxidizing Agent. $Mo(CO)_4(DAB)$ (2 mmol) was stirred in 100 mL of ether or ether/THF 50:50 with 0.5 mL of $NaK_{2.8}$ until the color of the solution was changed from red-violet into orange which took about 1 h. The reaction mixture was filtered to remove excess $NaK_{2.8}$ and 2 mmol of $Mn(CO)_3Br(DAB)$ was added. The $Mo_2(CO)_6(IAE)$ complexes were formed instantaneously and precipitated in ether or precipitated after addition of 100 mL of pentane in ether/THF 50:50. The crude product was filtered off and washed with ether until the ether remained colorless. The green residue was extracted with dichloromethane (50 mL) and afterward 25 mL of pentane was added. Recrystallization at −20 °C yielded 25–60% green crystals depending on the temperature of the solution at the moment that $Mn(CO)_3Br(DAB)$ was added. The yields increased at decreasing temperature.

Method ii. $Mn(CO)_5Br$ as Oxidizing Agent. This method differs from (i) only in the addition of $Mn(CO)_5Br$ instead of $Mn(CO)_3Br(DAB)$ after the reduction of $Mo(CO)_4(DAB)$. The isolation procedures were essentially similar to those in method (i). After complete evaporation of the solvent, a residue was obtained which contained $Mn_2(CO)_{10}$. This could be recovered by extraction of the residue with pentane or by sublimation.

Method iii. Hg^{2+}/H^+ as Oxidizing Agent. After the reduction of 2 mmol of $Mo(CO)_4(DAB)$, the solution was filtered and 1 mmol of $HgCl_2$ was added. A purple complex precipitated in ether (in the

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Table I. Positional and Thermal Parameters of the Nonhydrogen Atoms[a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0110 (1)	0936 (1)	0618 (1)	300 (5)	449 (5)	413 (5)	31 (7)	25 (7)	2 (7)
C(1)	642 (2)	569 (2)	397 (1)	32 (8)	66 (13)	75 (12)	−5 (9)	0 (9)	20 (11)
C(2)	686 (2)	459 (2)	459 (1)	46 (9)	60 (11)	39 (9)	−20 (9)	−3 (8)	8 (8)
C(3)	723 (3)	750 (2)	313 (1)	78 (14)	64 (13)	60 (11)	−2 (11)	−21 (12)	33 (11)
C(4)	303 (5)	183 (3)	267 (1)	268 (43)	82 (18)	44 (13)	−9 (25)	−31 (21)	−17 (13)
C(5)	574 (3)	827 (2)	336 (2)	101 (19)	80 (17)	114 (21)	27 (15)	−9 (16)	47 (16)
C(6)	862 (3)	705 (2)	609 (1)	89 (15)	49 (11)	46 (10)	17 (12)	14 (11)	−17 (9)
C(7)	299 (4)	673 (2)	078 (1)	148 (23)	46 (12)	70 (15)	33 (14)	2 (16)	6 (11)
C(8)	801 (4)	332 (2)	306 (1)	174 (28)	73 (15)	48 (12)	5 (19)	−36 (17)	−12 (12)
C(9)	046 (3)	207 (2)	582 (1)	109 (20)	72 (14)	66 (13)	−1 (15)	−13 (13)	−10 (12)
C(10)	194 (2)	373 (2)	504 (1)	16 (6)	62 (13)	82 (12)	0 (8)	0 (9)	−7 (10)
C(11)	128 (2)	549 (2)	349 (1)	56 (11)	46 (11)	85 (14)	−5 (9)	22 (11)	14 (11)
N(1)	845 (1)	413 (1)	448 (1)	26 (5)	53 (8)	39 (7)	−10 (7)	−11 (6)	−1 (8)
N(2)	763 (2)	359 (1)	624 (1)	41 (8)	58 (9)	45 (8)	7 (7)	−7 (7)	6 (7)
O(1)	087 (3)	893 (1)	406 (1)	178 (20)	38 (8)	148 (16)	−39 (12)	1 (14)	20 (10)
O(2)	312 (2)	339 (2)	474 (1)	61 (9)	73 (10)	134 (16)	20 (8)	20 (10)	3 (10)
O(3)	217 (2)	484 (2)	702 (1)	121 (13)	82 (11)	84 (11)	−18 (11)	−53 (11)	5 (9)

[a] Multiplied by 10^4 and 10^2, respectively, for Mo and by 10^3 and 10, respectively, for all other atoms.

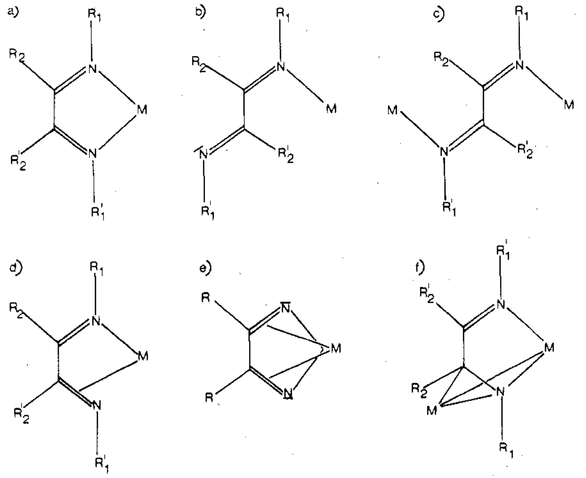


Figure 1. Coordination modes of DAB and related systems in metal carbonyl complexes.

case of the ether–THF mixture pentane had to be added) which was filtered off and washed twice with 50 mL of ether to yield 80% of $(DAB)(CO)_3Mo–Hg–Mo(CO)_3(DAB)$. For further reaction the $(DAB)(CO)_3Mo–Hg–Mo(CO)_3(DAB)$ complexes did not have to be isolated but could directly be reacted with 2 mmol of acetic acid or hydrochloric acid (in solution) which resulted in the formation of $Mo_2(CO)_6(IAE)$. Further isolation of the $Mo_2(CO)_6(IAE)$ complexes was described in method (i). Yields are in the range of 60–80%. Elemental analyses were carried out by the Section Elemental Analysis of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands, and gave satisfactory results.

Crystal Structure Determination of Hexacarbonylbis[μ-(1-(isopropylamino)-2-(isopropylimino)ethane-*N*,*N'*)]-dimolybdenum (2). Although it was difficult to obtain crystals, the molecular structure of complex **2** was determined by X-ray crystallography. The complex forms orthorhombic crystals (plates perpendicular to [100]) of poor quality. Nevertheless, a crystal with the dimensions 0.005 × 0.014 × 0.035 cm^3 was selected from which it was expected that satisfactory configurational and conformational data could be obtained.

Cell constants which were measured at room temperature on a Nonius CAD 4 diffractometer with graphite-monochromated Cu Kα radiation are a = 8.190 (1) Å, b = 10.099 (2) Å, and c = 16.844 (2) Å, Z = 2, d(calcd) = 1.545 g cm^{-3}, d(measd) = 1.53 g cm^{-3} (by flotation). Intensities (1571) were measured, by using a θ–2θ scan, of which 1403 were significantly above the background intensity; the maximum θ value was 65°. The crystal was oriented along the [021] axis. From the extinctions it was deduced that the space group was $P22_12_1$. As the molecular structure was the main interest of the investigation and as the quality of the crystals was taken into account, no attempt was made to correct for absorption (μ = 79 cm^{-1}, maximum and minimum values of μr are 2.8 and 0.4, respectively).

Table II. Bond Lengths in Å Involving All Nonhydrogen Atoms[a]

Mo–Mo′	2.813 (3)	N(2)–C(3)	1.57 (3)
Mo–N(1)	2.18 (1)	C(1)–C(2′)	1.56 (3)
Mo–N(1′)	2.25 (1)	C(2)–C(2′)	1.61 (2)
Mo–N(2)	2.18 (1)	C(3)–C(4)	1.52 (3)
Mo–C(9)	2.09 (2)	C(3)–C(5)	1.49 (3)
Mo–C(10)	1.97 (2)	C(6)–C(7)	1.53 (3)
Mo–C(11)	1.94 (2)	C(6)–C(8)	1.55 (3)
N(1)–C(2)	1.39 (2)	C(9)–O(1)	1.09 (3)
N(1)–C(6)	1.53 (2)	C(10)–O(2)	1.14 (2)
N(2)–C(1)	1.28 (2)	C(11)–O(3)	1.17 (3)

[a] Esd's are given in parentheses.

Table III. Bond Angles in Deg Involving All Nonhydrogen Atoms[a]

Mo′–Mo–N(1)	51.7 (3)	Mo–N(1)–C(2)	103 (1)
Mo′–Mo–N(1′)	49.5 (4)	Mo–N(1)–C(6)	123 (1)
Mo′–Mo–N(2)	120.1 (4)	Mo′–N(1)–C(2)	113 (1)
Mo′–Mo–C(9)	140.2 (6)	Mo′–N(1)–C(6)	118 (1)
Mo′–Mo–C(10)	75.4 (6)	C(2)–N(1)–C(6)	115 (1)
Mo′–Mo–C(11)	114.7 (6)	C(1)–N(2)–C(3)	115 (1)
N(1)–Mo–N(1′)	68.1 (5)	C(1)–N(2)–Mo	114 (1)
N(1)–Mo–N(2)	88.1 (5)	C(3)–N(2)–Mo	131 (1)
N(1)–Mo–C(9)	106.6 (7)	N(2)–C(1)–C(2′)	114 (1)
N(1)–Mo–C(10)	91.6 (7)	N(1)–C(2)–C(1′)	112 (1)
N(1)–Mo–C(11)	164.0 (7)	N(1)–C(2)–C(2′)	107 (1)
N(1′)–Mo–N(2)	76.1 (5)	C(1′)–C(2)–C(2′)	102 (1)
N(1′)–Mo–C(9)	159.7 (7)	N(2)–C(3)–C(4)	108 (2)
N(1′)–Mo–C(10)	124.5 (6)	N(2)–C(3)–C(5)	111 (2)
N(1′)–Mo–C(11)	100.5 (6)	C(4)–C(3)–C(5)	110 (2)
N(2)–Mo–C(9)	84.2 (8)	N(1)–C(6)–C(7)	112 (2)
N(2)–Mo–C(10)	157.3 (7)	N(1)–C(6)–C(8)	111 (2)
N(2)–Mo–C(11)	100.4 (7)	C(7)–C(6)–C(8)	110 (2)
C(9)–Mo–C(10)	74.1 (8)	Mo–C(9)–O(1)	175 (2)
C(9)–Mo–C(11)	88.0 (8)	Mo–C(10)–O(2)	172 (2)
C(10)–Mo–C(11)	85.8 (8)	Mo–C(11)–O(3)	176 (2)
Mo–N(1)–Mo′	78.8 (4)		

[a] Esd's are given in parentheses.

The structure was solved by use of a Patterson function to find the molybdenum positions and a difference Fourier map to locate the carbon, nitrogen, and oxygen atoms. The refinement was carried out with a block-diagonal least-squares procedure, using a Cruickshanks weighting scheme, resulting in a final R value of 6.7%. In the subsequent difference Fourier synthesis two peaks of 3.0 e/$Å^3$ appeared at positions +0.9 and −0.9 Å away from the molybdenum positions. Since the difference in positions is in the x direction only, this is in agreement with the fact that no absorption correction was applied. Furthermore, most hydrogen atoms were present with peak heights between 0.20 and 0.40 e/$Å^3$. The hydrogens were not used for further refinement. Refinement of the inverted coordinates resulted in R = 6.8%.

The molecular structure (with the numbering of the atoms) is shown in Figure 2 and a stereopair in Figure 3. Tables I, II, and III contain

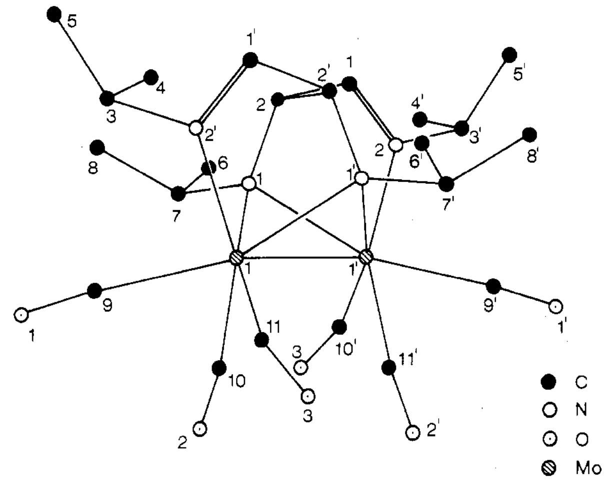


Figure 2. Molecular structure of hexacarbonylbis[μ-(1-(isopropylamino)-2-(isopropylimino)ethane-*N,N'*)]-dimolybdenum with the numbering of the atoms.

the atomic parameters, the bond lengths, and the bond angles, respectively.

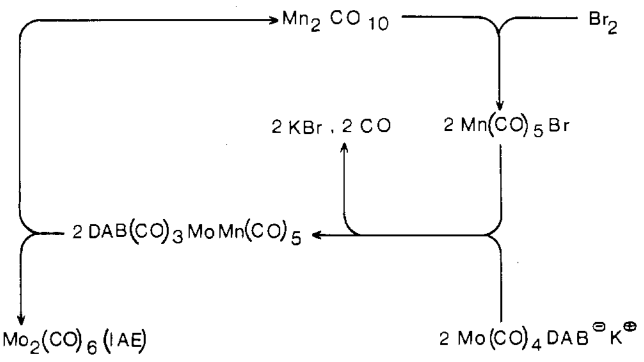
Results and Discussion

Preparative Routes. $Mo(CO)_4(DAB)$ is the starting material for all reactions. The first step in the reaction sequence is the reduction of $Mo(CO)_4(DAB)$ in ether or a 1:1 mixture of ether and THF with sodium–potassium alloy of the approximate composition $NaK_{2.8}$. The use of this alloy for the production of metal carbonyl monoanions has many advantages over other methods as described by Ellis and Flom[16] and is for example a much cleaner and quicker method to obtain $[Mo(CO)_4(DAB)]^-$ than the reduction with pure potassium as described by tom Dieck.[3,21]

After the reduction of $Mo(CO)_4(DAB)$, the reduced complexes are oxidized and it will be shown that the subsequent reduction and oxidation reactions are irreversible when suitable oxidizing agents are selected. In addition to the starting material new complexes are formed which at first instance seemed to be $Mo_2(CO)_6(DAB)_2$ but which were actually $Mo_2(CO)_6(IAE)$. The different methods to oxidize $[Mo(CO)_4(DAB)]^-$ will be subsequently discussed. For reasons mentioned below we will report exclusively on the syntheses of the molybdenum complexes at this stage of our research. The spectroscopic properties of an analogous chromium complex are included in the listings of the spectroscopic data.

(i) Oxidation by $Mn(CO)_3Br(DAB)$ (DAB = Glyoxal Bis(*tert*-butylimine), Glyoxal Bis(isopropylimine)). Although the crystal structure of $Mn(CO)_3Br$(glyoxal bis(cyclohexylimine)) is known, no details have been reported in the literature concerning the preparative and spectroscopic aspects of $Mn(CO)_3X(DAB)$ complexes (M = Mn, Re; X = Cl, Br, I).[22]

Scheme I. Reaction Sequence for the Formation of $Mo_2(CO)_6(IAE)$ with $Mn(CO)_5Br$ as Oxidizing Agent



The complexes are formed by substitution of CO in $Mn(CO)_5X$ by DAB ligands.

$$Mn(CO)_5Br + DAB \xrightarrow[\Delta T]{\text{ether}} Mn(CO)_3Br(DAB) + 2CO \qquad (1)$$

The oxidation of $(Mo(CO)_4(DAB))^-K^+$ with $Mn(CO)_3Br(DAB)$ proceeds according to eq 2.

$$2Mn(CO)_3Br(DAB) + (Mo(CO)_4(DAB))^-K^+ \rightarrow Mo_2(CO)_6(IAE) + 2KBr + Mn_2(CO)_{10} + \text{decomposition products} \qquad (2)$$

In this reaction a heterobinuclear metal carbonyl intermediate is expected in which two DAB ligands are coordinated to the metals. After cleavage of the molybdenum–manganese bond in this intermediate, dimerization of the molybdenum fragments will result in the formation of $Mo_2(CO)_6(IAE)$ complexes, while dimerization of the manganese fragments yields a binuclear manganese carbonyl complex containing two DAB ligands. However, only $Mn_2(CO)_{10}$ was formed as dimeric manganese complex and no manganese DAB products could be isolated.

The DAB ligand from the manganese carbonyl halide complex was not transferred to the molybdenum carbonyl which was shown conclusively by the use of various combinations of different DAB ligands on the respective manganese and molybdenum complexes.

(ii) Oxidation by $Mn(CO)_5Br$. Instead of $Mn(CO)_3Br(DAB)$, $Mn(CO)_5Br$ can be used as oxidizing agent; this shows that the DAB ligand in the manganese complex is not essential for the formation of $Mo_2(CO)_6(IAE)$. The reaction sequence is shown in Scheme I.

This cyclic reaction sequence starts with the oxidation of $Mn_2(CO)_{10}$ with Br_2 (or Cl_2) according to literature methods.[20] The formed $Mn(CO)_5Br$ (or $Mn(CO)_5Cl$) reacts with $[Mo(CO)_4(DAB)]^-$ to produce the intermediate $Mn(CO)_5Mo(CO)_3(DAB)$ which can be isolated at low temperature but which decomposes readily at room temperature

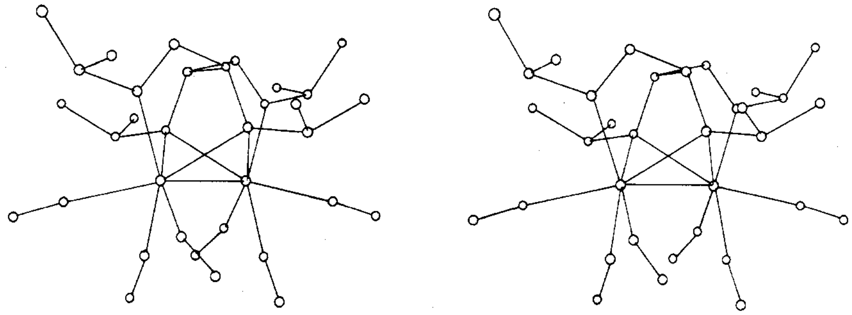


Figure 3. A stereoview of the molecule hexacarbonylbis[μ-(1-(isopropylamino)-2-(isopropylimino)ethane-*N,N'*)]-dimolybdenum.

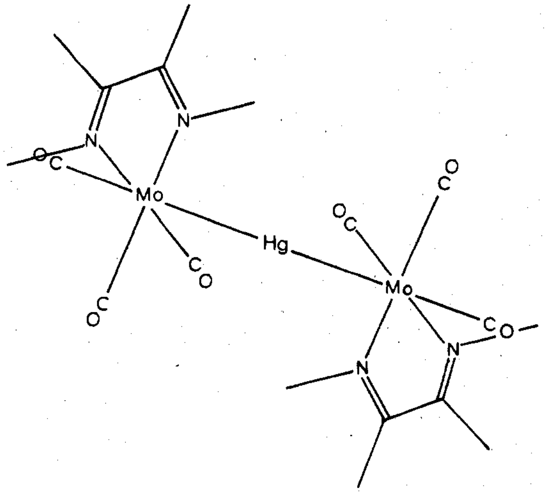
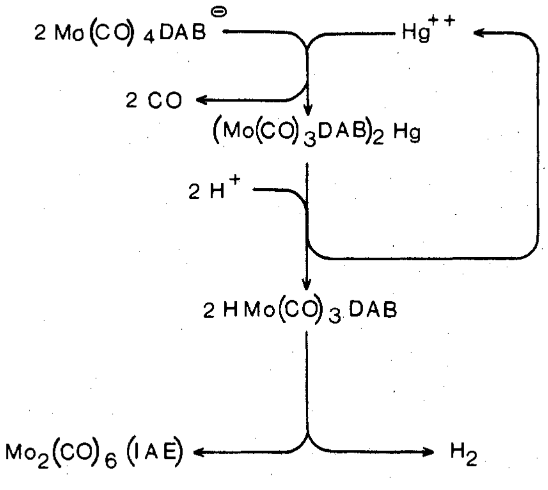


Figure 4. Proposed structure of $(Mo(CO)_4(DAB))_2Hg$.

Scheme II. Reaction Sequence of the Formation of $Mo_2(CO)_6(IAE)$ with Hg^{2+}/H^+ as Oxidizing Agent



into $Mo_2(CO)_6(IAE)$ and $Mn_2(CO)_{10}$, even in the solid state. In this final stage $Mn_2(CO)_{10}$ is regained and the reaction cycle is closed. The yields strongly depend on the temperature at which the oxidation of $[Mo(CO)_4(DAB)]^-$ is carried out. For example at room temperature $Mo_2(CO)_6(IAE)$ is formed in 25% yield while at −30 °C as much as 60% yield is obtained.

(iii) Oxidation by Hg^{2+}/H^+. Many examples of polynuclear complexes are known in which metal–metal carbonyl fragments are bonded to mercury. It was expected that the cleavage of the metal–metal bonds in $((DAB)(CO)_3Mo)_2Hg$, if this complex existed, must also yield the desired type of complexes. The molybdenum–mercury cluster was obtained according to the reaction equation

$$2K^+[Mo(CO)_4(DAB)]^- + HgCl_2 \rightarrow 2KCl + 2CO + (Mo(CO)_3(DAB))_2Hg \quad (3)$$

the structure of these complexes is assumed to be as given in Figure 4. The ^1H NMR spectra indicated the equivalence of the substituents on nitrogen which is in accordance with the proposed structure. The metal–metal bonds in the molybdenum–mercury cluster were broken with hydrochloric acid or acetic acid and an instable molybdenum carbonyl DAB hydride intermediate will be formed. Subsequently, this intermediate decomposes into $Mo_2(CO)_6(IAE)$ and hydrogen. The reaction sequence is given in Scheme II. Although the $Mo_2(CO)_6(IAE)$ complexes are formed in a cyclic reaction with respect to Hg^{2+}, the reaction is not catalytic for reasons mentioned in the next section.

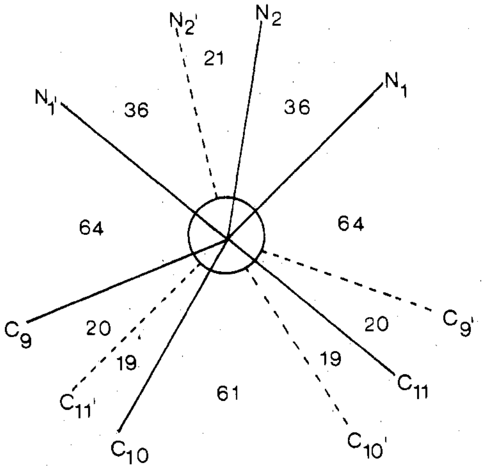


Figure 5. Newman projection of hexacarbonylbis[μ-(1-(isopropylamino)-2-(isopropylimino)ethane-*N*,*N*′)]-dimolybdenum along the Mo–Mo bond.

The advantage of the method is the relatively easy formation of $((DAB)Mo(CO)_3)_2Hg$ which appears to be a good starting material for the preparation of $Mo_2(CO)_6(IAE)$ complexes. Furthermore, the cleavage of the molybdenum–mercury bonds with acid can be carried out at lower temperatures than the thermal cleavage of the manganese–molybdenum bonds as a result of which the side reaction responsible for the formation of $Mo(CO)_4(DAB)$ again is suppressed. This side reaction together with the reaction mechanism will be discussed below. With the Hg^{2+}/H^+ method yields of $Mo_2(CO)_6(IAE)$ are in the range of 80%.

(iv) Oxidation by H^+. The direct oxidation of the reduced molybdenum complexes with hydrochloric acid or acetic acid is also a possible method to obtain $Mo_2(CO)_6(IAE)$ complexes of which, however, yields are less than 1%. Insoluble reaction residues and the starting compound $Mo(CO)_4(DAB)$ are the main products. For this reason the Hg^{2+}/H^+ method cannot be carried out with catalytic amounts of $HgCl_2$, thus excluding the possibility to transform method (iii) into a catalytic process.

(v) Molecular Structure of 2. The asymmetric unit of the unit cell contains only half a molecule; thus the twofold axis of the molecule coincides with one of the twofold axes of the space group symmetry. This axis runs through the middle of the bonds C(2)–C(2′) and Mo–Mo′, respectively.

The most unexpected feature of the structure was C(2)–C(2′) = 1.61 (2) Å, linking two DAB ligands. A possible mechanism for the reaction leading to this bond will be given in the next paragraph. Another result of the reaction is that the nitrogen N(1) bridges the metal–metal bond with bond lengths N(1)–Mo and N(1)–Mo′ of 2.18 (1) and 2.25 (1) Å, respectively. The nitrogen atom N(2) forms part of the double bond C(1)–N(2) and is connected to molybdenum by a bond of 2.18 (1) Å.

The Mo–Mo distance of 2.813 (3) Å is rather short for complexes containing the $Mo_2(CO)_6$ unit, in which the formal metal–metal bond order is 1. In similar complexes Mo–Mo lengths are observed varying from 3.19 to 3.27 Å[23–28] while in single-bonded binuclear molybdenum carbonyl complexes in which bridging ligands are bonded to both metals by the same atom metal–metal distances are observed between 2.95 and 3.27 Å.[29–33] Much shorter Mo–Mo single bonds varying between 2.54 and 2.89 Å[35] are observed for noncarbonyl complexes. The observed Mo–Mo distance in $Mo_2(CO)_6(IAE)$ is between the metal–metal distances found for both classes of compounds and is one of the shortest distances observed for single-bonded binuclear molybdenum carbonyl complexes.

The structure of the $Mo_2(CO)_6$ unit deviates from the sawhorse shape usually found for $M_2(CO)_6$ fragments,[36] which

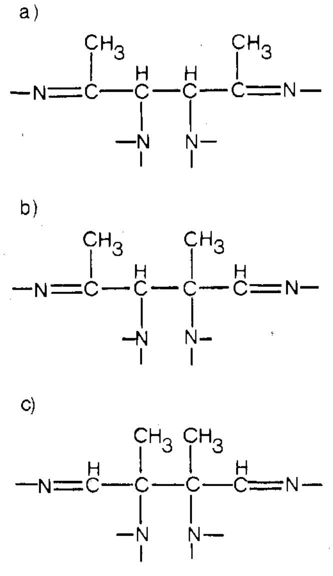


Figure 6. Three possible isomers of the IAE ligand formed out of methylglyoxal bis(isopropylimine). Only (a) was found in the $Mo_2(CO)_6$(IAE) complex.

is shown in the Newman projection along the Mo–Mo bond in Figure 5; C(10) and C(11) are 19° rotated around the Mo–Mo bond with respect to C10′) and C(11′).

(vi) Reaction Mechanism. The reaction starts with the reduction of $Mo(CO)_4$(DAB). The geometry of the reduced species has not much changed as compared with the unreduced complexes. ESR experiments have shown the strong delocalization of the unpaired electron through the metallocyclic ring of $(Mo(CO)_4(DAB))^-$.[3,21]

The reduced complexes are sensitive to oxidative elimination of CO and the different preparative methods have in common the generation of the 16-electron intermediate $Mo(CO)_3$(DAB). After the generation of this coordinative unsaturated species, the following two possible reactions might be involved as the decisive steps in the formation of $Mo_2(CO)_6$(IAE).

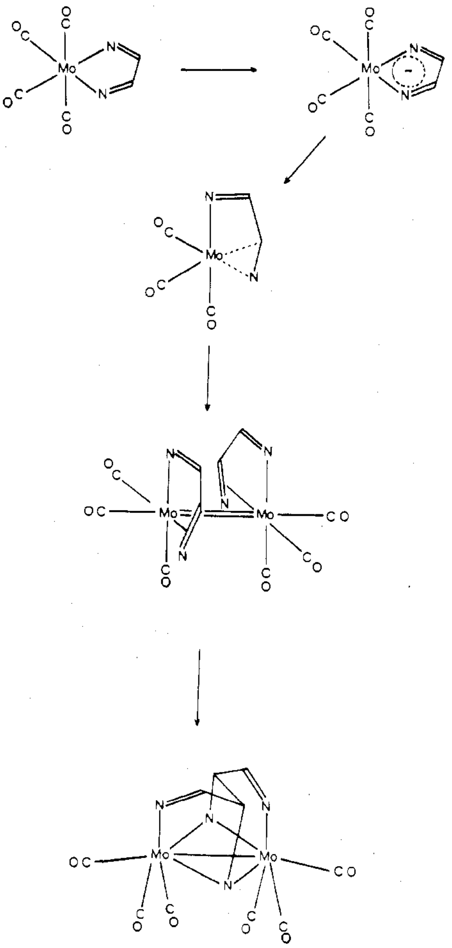
$$2Mo(CO)_3(DAB) \rightarrow Mo(CO)_4(DAB) + \text{decomposition products} \quad (4)$$

$$2Mo(CO)_3(DAB) \rightarrow Mo_2(CO)_6(IAE) \quad (5)$$

Reaction 4 is responsible for formation of the $Mo(CO)_4$(DAB) complexes which were used as starting complexes and is slow at low temperature while reaction 5 is almost temperature independent which explains the higher yields at low temperature. A possible explanation for the very low yields of analogous chromium and tungsten complexes (less than 1%) may be that in these cases reaction 4 is much faster, even at low temperature.

More details about the structure of the $Mo(CO)_3$(DAB) species can be obtained when the different substituents on nitrogen are taken into consideration. Only DAB ligands with bulky aliphatic substituents on nitrogen form $Mo_2(CO)_6$(IAE) complexes. The conditions are similar to those required for σ,π coordination in $Fe(CO)_3$(DAB) complexes (see Figure 1) and assume that the $Mo(CO)_3$(DAB) intermediate is isostructural to these complexes but only for those DAB ligands which form IAE. A second condition for the formation of IAE is that at least one of the substituents on the imine carbon atoms is a hydrogen atom. Diacetyl derivatives which have methyl groups on both positions do not form IAE complexes but only give the reverse reaction (4) to $Mo(CO)_4$(DAB) after the oxidation of the reduced complexes. Diacetyl derivatives only occur as σ,σ donors and not as σ,π donors in $Fe(CO)_3$(DAB) which seems consistent with the assumption about the structure of $Mo(CO)_3$(DAB) intermediates which are reactive with respect to the formation of $Mo_2(CO)_6$(IAE).

Scheme III. Proposed Reaction Mechanism for the Formation of $Mo_2(CO)_6$(IAE)



A methylglyoxal derivative of $Mo_2(CO)_6$(IAE), which could be prepared in a good yield, in principle exists in three isomeric forms shown in Figure 6. Only the isomer with both methyl groups on the remaining imine positions shown in Figure 6a was formed. This was indicated by the NMR spectrum which will be discussed in detail in the spectroscopic paragraph of this paper.

After the generation of $Mo(CO)_3$(DAB) with σ,π-coordinated α-diimine, the next step in the reaction mechanism will most likely be the formation of a metal–metal bond between two of these coordinative unsaturated 16-electron particles. For an 18-electron configuration to be around the metals the metal–metal bond has to be formally a double bond.

After the formation of the metal–metal bond, an intramolecular redox reaction causes the oxidation of the molybdenum atoms and the reduction of the DAB ligands which results in the linkage of two DAB ligands by carbon–carbon bond formation and a decrease of the metal–metal bond order from formally 2 to 1. The proposed reaction mechanism is shown in Scheme III. The reaction mechanism may be compared with the reaction mechanism proposed for the acetylene linkage in binuclear chromium and molybdenum complexes.[37] In this case a metal–metal triple bond existed before the coordination of acetylene while during the formation of the carbon–carbon bond the metal–metal bond order is decreased. This mechanism is analogous to the final steps proposed for the formation of $Mo_2(CO)_6$(IAE).

(vii) Chemical Properties. The stability of $Mo_2(CO)_6$(IAE) is demonstrated by the following reactions. The complexes are inert to carbon monoxide. After stirring of a CH_2Cl_2 solution of $Mo_2(CO)_6$(IAE) (R_1 = *t*-Bu, R_2 = H; **1**) for 24

Table IV. ^{1}H NMR Data of $M_2(CO)_6$(IAE) in Acetone-d_6

	M	R$_1$	R$_2$	δ
1	Mo	tbu	H	$\delta(C_4H_9) = 1.01, 1.38$; $\delta(H)^{\mathrm{amino}} = 4.09$;[a] $\delta(H)^{\mathrm{imino}} = 8.86$[a]
2	Mo	ipr	H	$\delta(C(CH_3)_2) = 1.03$,[b] 1.37;[b] $\delta(CH)^{\mathrm{ipr}} = 3.20$,[b] 4.02;[b] $\delta(H)^{\mathrm{am}} = 4.02$; $\delta(H)^{\mathrm{imino}} = 8.68$
3	Mo	chex	H	$\delta(H)^{\mathrm{chex}}$ = broad multiplet near 1.5 ppm; $\delta(N\text{-}CH)^{\mathrm{chex}} = 3.6$; $\delta(H)^{\mathrm{amino}} = 3.69$; $\delta(H)^{\mathrm{imino}} = 8.35$
4	Mo	ipr	H/CH$_3$	$\delta(C(CH_3)_2) = 1.01, 1.31$;[b] $\delta(CH)^{\mathrm{ipr}} = 3.08, 4.20$;[b] $\delta(CH_3) = 2.46$; $\delta(H)^{\mathrm{am}} = 3.86$
5	Cr	ipr	H	$\delta(C(CH_3)_2) = 0.96$,[b] 1.22;[b] $\delta(H\text{–}C)^{\mathrm{ipr}} = 3.09$,[b] 3.8;[b] $\delta(H)^{\mathrm{am}} = 3.66$; $\delta(H)^{\mathrm{im}} = 8.38$

[a] $J = 1.7$ Hz. [b] $J = 7$ Hz.

h, no reaction could be observed.

Refluxing of a solution of the same compound with triphenylphosphine in toluene resulted in the substitution of a CO group trans to the metal–metal bond. This is in agreement with the results of Cotton et al., who substituted a CO group in $Mo_2(CO)_6$(guaiazulene) with triethylphosphine.[25] The IR data on which this conclusion is based are given in Table V. An interesting feature is the slow polymerization in solution of hexacarbonylbis[μ-(1-cyclohexylamino)-2-(cyclohexylimino)ethane-*N,N'*)]-dimolybdenum. At room temperature the molecular weight increased from 800 to 4000 (based on VPO measurements in dichloromethane and acetone) and the color changed from green to red. The ^{1}H NMR spectrum of the polymer in hexadeuterioacetone indicated that the IAE ligand remained unchanged after the polymerization. At this moment the structure of the polymer is not clear and attempts to obtain crystals failed.

Spectroscopic Properties. (i) ^{1}H NMR. The $Mo_2(CO)_6$(IAE) complexes contain two different types of alkyl groups, the alkyl groups attached to the imine nitrogen atoms and the alkyl groups attached to the amine nitrogen atom. The proton resonances of the alkyl substituents on the imine moiety have been found downfield relative to the resonances found for the alkyl groups substituted to the amine moiety.

The chemical shifts of the azomethine protons are drastically changed after the formation of the carbon–carbon bond in IAE with respect to the chemical shifts in the free ligand and mononuclear complexes.

In the free ligand the azomethine proton resonances have been observed at 7.8 ppm and in σ-coordinated complexes between 7.8 and 8.3 ppm.[4,38] Chemical shift values for the azomethine protons of π-coordinated imine fragments are 6.3 ppm in $Fe(CO)_3$(DAB)[8,9] and 3 ppm in $Fe_2(CO)_6$(DAB).[14]

In the $Mo_2(CO)_6$(IAE) complexes formed out of glyoxal derivatives, one doublet at 4.1 ppm and one doublet at 8.8 ppm were observed (see Table IV) with a coupling constant of 1.7 Hz. The doublet at high field is assigned to the hydrogen atoms on the ethane carbon atoms and the downfield doublet is assigned to the imine protons. The σ coordination of the imino groups is confirmed by the chemical shifts observed for these protons. In Table IV the chemical shifts of the $Mo_2(CO)_6$(IAE) complexes are listed and the values for one chromium complex are included. In compounds **2**, **4**, and **5** the methyl groups of the isopropyl substituents are inequivalent as a result of the chirality of the ethane carbon atoms C(2) and C(2'). In **2** and **5** the lines in the ^{1}H NMR spectra assigned to the hydrogen atoms of the isopropyl groups substituted to the amine fragments are split while in **4** this effect is more pronounced for the isopropyl groups on the imine fragments. The ^{1}H NMR spectra of **2** and **4** showing the inequivalency of the isopropyl methyl groups are shown in Figure 7.

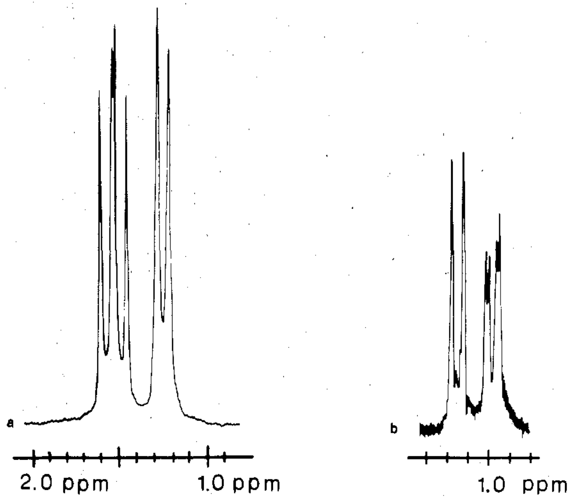


Figure 7. The ^{1}H NMR spectra for the isopropyl groups of **4** (a) and compound **2** (b). Spectrum (a) is a Varian XL-100 spectrum and spectrum (b) a Varian T-60 spectrum. The calibration in (b) is in steps of 0.2 ppm.

Table V. IR ν(CO) Values (cm^{-1}) Measured in CH_2Cl_2 Solutions

M	R$_1$	R$_2$	ν,[a] cm^{-1}
Mo	tbu	H	1998 s, 1944 s, 1887 w, sh, 1874 m, 1850 sh
Mo	ipr	H	1997 s, 1942 s, 1890 w, 1875 m, 1845 sh
Mo	chex	H	1999 s, 1941 s, 1906 w, 1867 m
Mo	ipr	H/CH$_3$	1992 s, 1938 s, 1890 w, 1868 m, 1850 sh
Cr	ipr	H	1999 s, 1944 s, 1907 w, 1870 m, 1841 sh
Mo[b]	tbu	H	1996 m, 1945 s, 1899 s, 1874 m

[a] Key: sh = shoulder, s = sharp, m = medium, w = weak. [b] Triphenylphosphine product.

(ii) IR Measurements. As was expected for a $M_2(CO)_6$ unit with bridging ligands, more than three bands have been observed for the CO stretch vibrations of $Mo_2(CO)_6$(IAE).[39,40]

As a result of the twofold axis perpendicular to the metal–metal bond, each CO vibration on one metal is coupled to a CO vibration on the other metal so no direct correlation is possible between the CO vibrational modes of $Mo(CO)_4$(DAB) and $Mo_2(CO)_6$(IAE). The frequencies of the modes of CO groups trans to the IAE ligand are comparable to the frequencies observed for the trans CO vibrational modes in $Mo(CO)_4$(DAB) which have been found between 1900 and 1850 cm^{-1}. However, a correlation between the cis vibrational modes is possible if the $Mo_2(CO)_6$ moiety is considered as a $Mo(CO)_4$ moiety with a $Mo(CO)_2$ fragment inserted in a cis Mo–CO bond. The symmetrical CO stretch vibration of the cis CO in $Mo(CO)_4$(DAB) which has been found at 2020 cm^{-1} is correlated to the symmetrical CO vibrational mode of the CO groups trans to the Mo–Mo bond in $Mo_2(CO)_6$(IAE) which is found at 1998 cm^{-1}. The antisymmetrical combinations of these modes have been observed at 1925 and 1945 cm^{-1}, respectively. The most important factors which influence the frequency shifts of these modes which are in general less sensitive to substituent effects than the trans vibrational modes are the inductive effect of the metal–metal bond and the changed oxidation state of molybdenum. Considering the shorter metal–metal bond and the distortion of the $Mo_2(CO)_6$ unit along the metal–metal bond, the CO stretch frequencies given in Table V are in good agreement with literature values for $Mo_2(CO)_6$ unit.[26]

(iii) UV–Visible Measurements. Crystals and solutions of $Mo_2(CO)_6$(IAE) are green as a result of the charge-transfer transitions between the metal and the IAE ligand. The maximum of the structured charge-transfer band has been

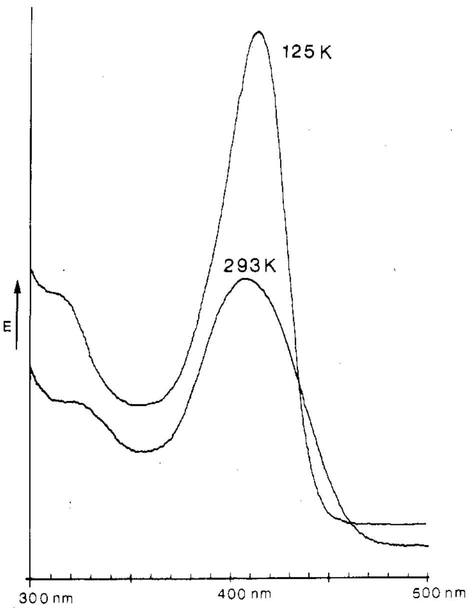


Figure 8. The temperature dependence of the LF band assigned to the $\sigma \rightarrow \sigma^*$ transition of $Mo_2(CO)_6(IAE)$ (R_1 = *t*-Bu, R_2 = H) in EPA solution (ethanol/2,2-dimethylpropane/diethyl ether, 2:5:5) at room temperature and 125 K.

Table VI. Electronic Transitions of $M_2(CO)_6(IAE)$ in CH_2Cl_2 Solutions (λ, nm)

M	R_1	R_2	CT	$\sigma \rightarrow \sigma^*$
Mo	tbu	H	559	408
Mo	cpr	H	568	404
Mo	chex	H	573	399
Mo	ipr	H/CH_3	562	407
Cr	ipr	H	605	412

found near 570 nm. Compared to the $Mo(CO)_4(DAB)$ complex, these transitions are very weak[3,4] and the remarkable solvatochromism has disappeared in the $Mo_2(CO)_6(IAE)$ complexes, as a result of the loss of conjugation in the IAE ligand.[3,4,41,42] At 400 nm, a very intense ligand field transition has been found which is assigned to the $\sigma \rightarrow \sigma^*$ transition localized on the metal–metal bond. At low temperature the intensity of this band increases most probably as a result of the increasing metal–metal interaction as shown in Figure 8. These phenomena have been found for other binuclear carbonyl complexes[43] and can be used as spectroscopic evidence for the existence of a metal–metal bond.

The maxima of the charge-transfer and ligand field bands of $Mo_2(CO)_6(IAE)$ are listed in Table VI. . The results for an analogous chromium compound have been included.

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Registry No. **1**, 69120-88-3; **2**, 69120-87-2; **3**, 69120-86-1; **4**, 69120-85-0; **5**, 69120-84-9; $Mo(CO)_4$(glyoxal bis(*tert*-butylimine)), 31027-20-0; $Mo(CO)_4$(glyoxal bis(isopropylimine)), 31027-19-7; $Mo(CO)_4$(glyoxal bis(cyclohexylimine)), 20500-64-5; $Mo(CO)_4$(methylglyoxal bis(isopropylimine)), 69120-83-8; $Mn(CO)_3Br$(glyoxal bis(*tert*-butylimine)), 69120-82-7; $Mn(CO)_3Br$(glyoxal bis(isopropylimine)), 69120-81-6; $Mn(CO)_5Br$, 14516-54-2; Hg^{2+}, 14302-87-5.

Supplementary Material Available: Elemental analyses and structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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