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Preliminary communication

DIAZABUTADIENES AS σ,π-BRIDGING LIGANDS IN BINUCLEAR MOLYBDENUM CARBONYL COMPLEXES CONTAINING MOLYBDENUM—MOLYBDENUM DOUBLE BONDS

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Summary

Reduction of $Mo(CO)_4DAB$ (DAB = diazabutadiene) followed by oxidation with $Mn(CO)_3BrDAB$ or HCl gives a small yield (15 to 25%) of complexes of the type $Mo_2(CO)_6(DAB)_2$, in which the two DAB ligands bridge a molybdenum—molybdenum double bond and act as σ,π-donors.

As part of our investigations on the coordination properties of diazabutadienes (DAB) ($R^1N{=}C(R^2)C(R^2){=}NR^1$ = α-diimine) and on the electronic properties of these ligands in complexes with metals in a low oxidation state [1], we have investigated the behaviour of $(Mo(CO)_4DAB)^-$ in oxidation reactions.

DAB is known to act as a σ-donor monodentate ligand [1,2], a σ, σ-donor bridging ligand, a σ,σ-donor chelating ligand [3—15] and a σ,π- and π,π-chelating ligand [16,17]. We now report the isolation and characterization of the first examples of metal—DAB complexes in which DAB acts as a σ,π-bridging ligand in binuclear molybdenum carbonyl complexes with metal—metal double bonds.

tom Dieck et al. have shown that $Mo(CO)_4DAB$ can be reduced by sodium and potassium using various ethers as solvents [18]. We reduced $Mo(CO)_4DAB$ with sodium—potassium alloy according to Ellis and Flom [19]. The proposed structure of the reduced $(Mo(CO)_4DAB)^-$ is shown in Fig. 1.

Subsequent oxidation of the reduced complexes with mild oxidizing agents gives, in addition to the starting material $Mo(CO)_4DAB$, a novel type of complex $Mo_2(CO)_6(DAB)_2$. When $Mn(CO)_3Br(t\text{-}BuN{=}CHCH{=}N\text{-}t\text{-}Bu)$ is used as oxidizing agent, yields are in the range of 15 to 25%. In addition to the com-

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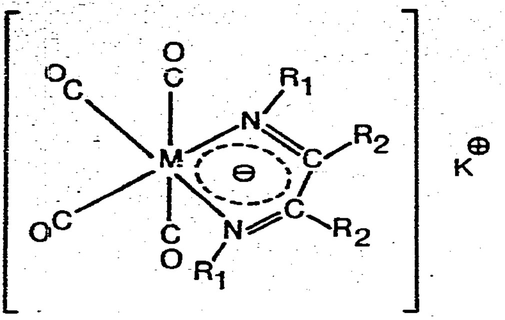

Fig. 1. The proposed structure of $(Mo(CO)_4 DAB)^{-}K^{+}$.

plexes $Mo_2(CO)_6(DAB)_2$, KBr and $Mn_2(CO)_{10}$ were formed and were isolated and identified. The molecular weights and elemental analyses are in accord with dimeric structures (see Table 1).

TABLE 1

ANALYTICAL DATA AND MOLECULAR WEIGHTS (calculated values in parentheses)

R	C	%H	%N	%O	Mol. wt.
t-Bu	44.82	5.74	8.04	13.79	704
	(44.24)	(5.72)	(8.03)	(13.88)	(696)
i-Pr	41.15	5.44	8.77	13.33	646
	(41.25)	(5.00)	(8.75)	(15.00)	(640)

The IR spectra of $Mo_2(CO)_6(DAB)_2$ show five to six bands between 2000 and 1800 cm^{-1} belonging to the CO vibrations of six terminal CO groups. At 1630 cm^{-1} there is a broad band, which is assigned to ν(C=N). The infrared frequencies of ν(CO) are listed in Table 2.

TABLE 2

IR DATA OF $Mo_2(CO)_6(DAB)_2$ IN CH_2Cl_2 SOLUTIONS (cm^{-1})

R					
t-Bu	1998	1944	1887[a]	1874	1850
i-Pr	1997	1942	1890	1875	1845

[a] Shoulder at high wavenumber side of the band.

^1H NMR data (see Table 3) indicate that the ligand moieties (RN=CH—) are unsymmetrically bonded. In the free ligands the resonances of the imino protons (—N=CH—) are found at about 8.0 ppm, and for the σ,σ-bonded DAB, ligand, for example in $Mo(CO)_4DAB$, they are at 8.2 ppm. In the dinuclear molybdenum carbonyl complexes the resonances of the imino protons are found as doublets at 8.8 and 8.4 ppm, with a coupling of 1.6 Hz.

TABLE 3

^{1}H NMR DATA OF $Mo_2(CO)_6(DAB)_2$; SOLVENT ACETON-d_6

R	δ(ppm)
t-Bu	$\delta(C(CH_3)_3)$ 1.01, 1.38 $\delta(H^{imino})$ 4.09, 8.86^a
i-Pr	$\delta(C(CH_3)_2)$ 1.03, 1.37^b $\delta(H{-}C)^{i\text{-}Pr}$ 3.20, 4.02^b $\delta(H^{imino})$ 4.02, 8.68^c

^{a} J 1.6 Hz. ^{b} J 6.7 Hz. ^{c} J 1.6 Hz.

An upfield shift of the resonances of the imino protons indicate π-coordination. For example, $Fe(CO)_3$(t-BuN=CHCH=N-t-Bu), in which DAB acts as a σ,π-donor chelating ligand, there is an upfield shift of the imino proton of the π-bonded C=N group, which appears at 6.35 ppm [16]. In $Mo_2(CO)_6(DAB)_2$ the shielding of the imino protons of the π-bonded imino group is even larger.

On the basis of the NMR data the structures shown in Fig. 2a and 2b must be considered.

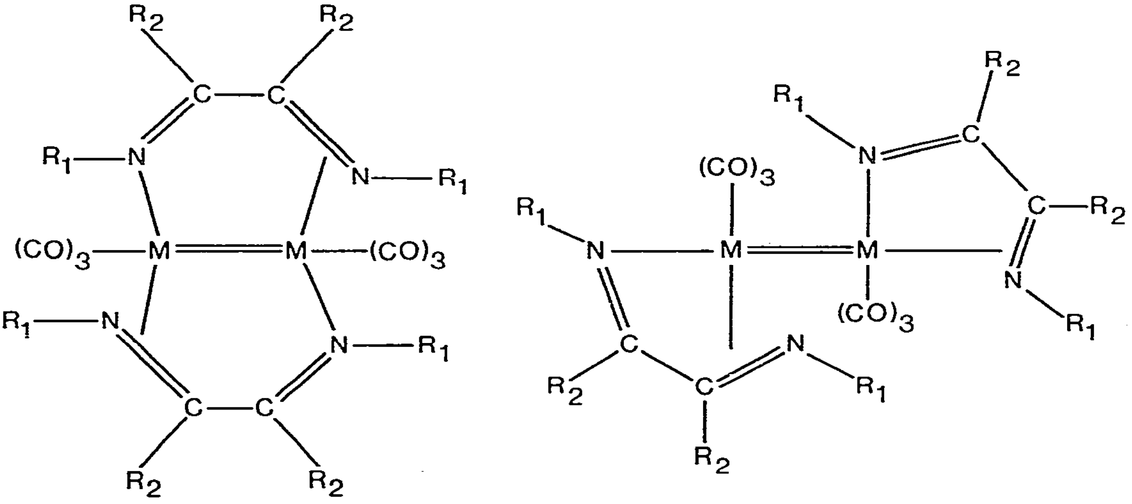

Fig. 2. Proposed structures of $Mo_2(CO)_6(DAB)_2$ as derived from NMR data.

The molybdenum—molybdenum bond must be formally a double bond, otherwise both metals would have a 17 electron configuration. Structure 2b is rather unlikely: metal—metal bonds are known to be stabilized by forming a five-membered ring with chelating ligands. The σ,π-bridging mode for the DAB ligand in $Mo_2(CO)_6(DAB)_2$ is supported by the observation of five to six CO vibrations, because σ,π-chelation which would give rise to a mirror plane through the molybdenum—molybdenum bond, would result in only three CO vibrations. Because of the arguments mentioned above the proposed structure of the complexes $Mo_2(CO)_6(DAB)_2$ can only be as shown in Fig. 2a. Complete details of these and related complexes will be described in a forthcoming paper.

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