Dinitrosylmolybdenum Complexes with Anion Ligands Coordinating by Oxygen Atoms. Synthesis, Electronic Structure and Olefin Metathesis Activity of Carboxylato-Dinitrosyl-Molybdenum Complexes

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The new carboxylato-dinitrosyl-molybdenum complexes of the formula: $[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2] \cdot \text{MeOH}$, $\text{Na}_2[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_4]$ and $\text{Mo}(\text{NO})_2(\text{O}_2\text{CPh})_2$ have been synthesized. Their structure was resolved on the basis of spectroscopic investigations (^1H NMR, IR, UV–VIS). Catalytic activity of these complexes in olefin metathesis reaction was also examined.

The electronic structure of dinitrosyl-molybdenum complexes with ligands coordinating by oxygen atoms was calculated for the example of the di- and tetra-acetato-dinitrosyl-molybdenum complexes using the Fenske-Hall and INDO methods. To interpret the spectroscopic properties (UV–VIS) within the method of interaction configuration, the electronic structure of the excited states was calculated.

Introduction

Since many years transition metal nitrosyl complexes are the subject of intensive studies. Their crystal and molecular structures have been determined and their magnetic, spectroscopic and chemical properties investigated [1–4]. The interest in these compounds continues to grow because there now is a considerable number of complexes available, which could be catalysts or catalyst precursors of many organic reactions such as oligomerization [5–7], polymerization [7–8], chemical oxidation [9, 10], hydrogenation [11], isomerization [12, 13] and metathesis [14]. For the latter, the molybdenum complexes belong to the most active.

Basset *et al.* [15] have found that oxygen containing compounds (O_2 or alcohols) accelerate the metathesis reaction. It has also been proved, that oxygen and perhaps chlorine are essential for generation of active, table high-valent metathesis catalysts [16]. The results of an *ab initio* theoretical mechanistic study [17] were also used to suggest that oxygen-alkylidene complexes are the active chain-carrying metathesis catalysts for high-valent metal complexes, and that the oxygen ligand is in-

timately involved in the catalytic process. Moreover the synthesis of stable alkylidene complexes with oxygen ligands, very often active in olefin metathesis, points to the unusual role of ligands of that type as stabilizers and activators [18, 19]. The first synthesized stable and catalytically active alkylidene-dinitrosyl-molybdenum complexes also contain ligands with oxygen atoms [20, 21], and the $\{\text{Mo}(\text{NO})_2(\text{OMe})_2\text{L}\}_n$ -EtAlCl₂ and $\{\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2\}_n$ -EtAlCl₂ systems are some of the most powerful catalysts [22, 23].

Here the synthesis, spectroscopic characterization, electronic structure and metathesis activity of new carboxylato-dinitrosyl-molybdenum complexes are reported. The electronic structure of these complexes was calculated using Fenske-Hall and INDO methods. Their electronic spectra were interpreted in terms of the electronic structure of the excited states calculated by the interaction configuration method.

Experimental

All experiments were performed under argon atmosphere with standard Schlenk techniques and vacuum-line procedure. Solvents were purified and distilled under argon from appropriate agents. The complexes $[\text{Mo}(\text{NO})_2(\text{MeNO}_2)_4](\text{BF}_4)_2$ [24], $\{\text{Mo}(\text{NO})_2(\text{O}^i\text{Pr})_2\}_n$, $\{\text{Mo}(\text{NO})_2(\text{OR})_2\}_n$ (R = Me, S = MeCN; R = Et, S = EtOH) [25] and $\{\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2\}_n$ [23] were prepared by published procedure.

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The IR spectra were measured on a Specord M 80 spectrophotometer in hexachlorobutadiene and Nujol mulls. ^1H NMR spectra were recorded on a Tesla BS 567A spectrometer and were referenced to Me_4Si . Electronic spectra (absorption and reflectance) were measured on a Beckman UV 5240 spectrophotometer. Molecular weights were determined on a Perkin-Elmer 115 instrument. GLC analysis were performed on N-504 (Elpo) chromatograph.

$[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2] \cdot \text{MeOH}$

Method A. The mixture of $\text{Mo}(\text{CO})_6$ (4 mmol), $\text{Na}(\text{O}_2\text{CMe})$ (8 mmol) and NOBF_4 (8.2 mmol) in 15 ml MeNO_2 were stirred for 2 h at room temperature and next 6 ml MeOH was added. The white precipitate of NaBF_4 was filtered off and the solvent was removed from the filtrate *in vacuo*. The complex was extracted from the residue with CH_2Cl_2 . The light-green complex was precipitated with hexane. Yield 35%.

Method B. To $[\text{Mo}(\text{NO})_2(\text{MeNO}_2)_4](\text{BF}_4)_2$ (4 mmol) dissolved in 15 ml MeNO_2 and 6 ml MeOH $\text{Na}(\text{O}_2\text{CMe})$ (8 mmol) was added. The white precipitate of NaBF_4 was filtered off. Subsequent procedure was as above.

$[\text{C}_5\text{H}_{10}\text{N}_2\text{Mo}]$

Calcd C 19.62 H 3.29 N 9.15 Mo 31.34%,
Found C 19.21 H 3.52 N 8.90 Mo 31.25%.

IR: $\nu(\text{OH})$ 3400 br, $\nu(\text{CH})$ 2950 sh, 2917 w, $\nu_s(\text{NO})$ 1770 vs, $\nu_{as}(\text{NO})$ 1650 vs, $\nu_{as}(\text{CO}_2)$ 1520 s, $\nu_s(\text{CO}_2) + \delta(\text{CH}_3)$ 1437 s, 1410 s, also: 1300 w, 1150 w, 1030 m, 950 sh, 835 br, 688 w, 672 w, 651 w, 618 vw, 565 m, 509 m, 477 w, 425 sh.

$\text{Na}_2[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_4]$

To the solution of $[\text{Mo}(\text{NO})_2(\text{MeNO}_2)_4](\text{BF}_4)_2$ (4 mmol) in 10 ml $\text{MeNO}_2\text{Na}(\text{O}_2\text{CMe})$ (16.2 mmol) in 12 MeOH was added. The white NaBF_4 precipitate was filtered off. From the filtrate the very fine-crystalline light-green precipitate settled down, which after filtration was washed repeatedly with small amounts of MeOH and dried *in vacuo*. Yield 70%.

$[\text{C}_8\text{H}_{12}\text{N}_2\text{MoNa}_2]$

Calcd C 21.93 H 2.76 N 6.39 Mo 21.90 Na 10.49%,
Found C 21.55 H 2.91 N 6.09 Mo 21.78 Na 10.60%.

IR: $\nu(\text{CH})$ 2935 vw, $\nu_s(\text{NO})$ 1788 s, $\nu_{as}(\text{NO})$ 1652 vs, br, $\nu_{as}(\text{CO}_2)$ 1596 vs, $\delta(\text{CH}_3)$ 1440 w, 1423 w, 1396 m, 1376 m, 1335 w, $\nu_s(\text{CO}_2)$ 1300 vs, $\rho_r(\text{CH}_3)$ 1040 m, 1018 m, $\nu(\text{CC})$ 940 w, 930 w, also: 578 m,

587 m, 570 sh, 550 vw, 532 vw, 529 vw, 485 m, 475 sh, 438 m, 420 sh.

$\text{Mo}(\text{NO})_2(\text{O}_2\text{CPh})_2$

To $[\text{Mo}(\text{NO})_2(\text{MeNO}_2)](\text{BF}_4)_2$ (4 mmol) in 10 ml MeNO_2 or MeOH the solution of $\text{Li}(\text{O}_2\text{CPh})$ (8 mmol) in MeOH (6 ml) was added. The resulting solution was stirred for about 1 h at room temperature and the solvent removed under vacuum. The complex was extracted from the residue with a small amount of CH_2Cl_2 . The green complex was precipitated with hexane, filtered off and dried *in vacuo*. Yield 90%.

$[\text{C}_{14}\text{H}_{10}\text{N}_2\text{Mo}]$

Calcd C 42.23 H 2.53 N 7.04 Mo 24.09%,
Found C 41.90 H 2.80 N 6.74 Mo 24.20%.

IR: $\nu(\text{CH})$ 2960 m, 2923 w, 2895 sh, $\nu_s(\text{NO})$ 1790 s, $\nu_{as}(\text{NO})$ 1682 vs, $\nu_{as}(\text{CO}_2)$ 1548 s, $\nu_s(\text{CO}_2)$ 1420 vs, also: 2035 w, 1955 w, 1598 m, 1508 m, 1492 m, 1450 s, 1310 w, 1250 sh, 1178 m, 1150 sh, 1126 m, 1092 w, 1070 m, 1040 w, 1025 m, 955 sh, 873 w, 840 m, 750 sh, 675 m, 650 w, 617 m, 572 w, 472 m, 425 sh.

$[\text{Mo}(\text{NO})_2(\text{O}_2\text{CPh})_2] \cdot 2\text{PhCO}_2\text{H}$

The complex was obtained in a manner similar to that described above, *i.e.* by treatment of $[\text{Mo}(\text{NO})_2(\text{MeNO}_2)_4](\text{BF}_4)_2$ with $\text{Li}(\text{O}_2\text{CPh})$ in MeOH at room temperature in molecular ratio $\leq 1:4$.

$[\text{C}_{28}\text{H}_{22}\text{N}_2\text{Mo}]$

Calcd C 52.35 H 3.45 N 4.36 Mo 14.93%,
Found C 52.09 H 3.60 N 4.00 Mo 14.81%.

IR: $\nu(\text{OH})$ 3100 br, $\nu(\text{CH})$ 2960 sh, 2925 sh, $\nu_s(\text{NO})$ 1790 s, $\nu_{as}(\text{NO}) + \nu_{as}(\text{CO}_2)$ 1680 vs, br, $\nu_{as}(\text{CO}_2)$ 1555 s, $\nu_s(\text{CO}_2)$ 1420 vs, also: 2077 w, 2025 vw, 1960 vw, 1910 w, 1598 s, 1580 sh, 1490 m, 1323 s, 1280 s, 1178 m, 1155 w, 1125 m, 1019 w, 1070 m, 1040 w, 1025 m, 998 vw, 965 s, 927 m, 875 sh, 830 vw, 800 w, 775 w, 680 m, 665 m, 640 sh, 615 vw, 575 sh, 545 w, 475 w, br, 420 sh.

Metathesis reaction

The following general procedure was used. The precatalyst ($2.5 \cdot 10^{-4}$ mol) and PhCl (5 ml) were placed in the reaction vessel, and cooled to below 0°C ; next EtAlCl_2 in PhCl was added ($\text{Mo}:\text{Al} = 1:6$). The resulting homogeneous reaction mixture was heated to room temperature and aged for 15 min (t_a). After ageing pent-2-ene as test olefin ($\text{Mo}:\text{olefin} = 1:400$) was added to the solution. For the sample taken after reaction time (t_r) the

reaction was quenched and the metathesis products were subjected to GLC.

Results and Discussion

Preparation and properties of carboxylato-dinitrosyl-molybdenum complexes

A few examples of dinitrosyl-molybdenum complexes with anion ligands containing oxygen atom have been described in the literature, *i.e.* $\text{Mo}(\text{NO})_2(\text{acac})_2$ [26], $\{\text{Mo}(\text{NO})_2(\text{OR})_2\}_n$ ($\text{R} = \text{Et}$, $i\text{Pr}$) and $\{\text{Mo}(\text{NO})_2(\text{OR})_2\text{L}\}_n$ ($\text{R} = \text{Me}$, Et ; $\text{L} = \text{EtOH}$) [25, 27], $(\text{Et}_4\text{N})_2[\text{Mo}(\text{NO})_2(\text{ox})_2]$ [28] and $\text{Mo}(\text{NO})_2(\text{HSO}_4)_n$ ($n = 3, 4$) [29].

Almost all these complexes could be obtained by substitution of the coordinated solvent in $[\text{Mo}(\text{NO})_2(\text{sol})_4]^{2+}$ type complexes by the appropriate oxygen anion ligands.

Quite recently a new complex of that type was synthesized in the same manner:

This compound is also formed in the direct reaction among $\text{Me}(\text{CO})_6$, $\text{Na}(\text{O}_2\text{CMe})$ and NOBF_4 :

The mechanism of its formation is the same in both reactions.

Both reactions were carried out in MeCN at room temperature. The brown product is unsoluble in alkanes, benzene, PhCl, CH_2Cl_2 and H_2O , sparingly soluble in MeCN, and readily soluble in alcohols and DMSO. Its structure is most likely polymeric $\{\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2\}_n$.

The complex of the identical composition in the coordination sphere but of different physical properties is formed in the reaction of $[\text{Mo}(\text{NO})_2(\text{MeNO}_2)_4](\text{BF}_4)_2$ with $\text{Na}(\text{O}_2\text{CMe})$ (1:2) in MeNO_2 –MeOH solution (reaction (3)), a light-green compound of the formula

$[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2] \cdot \text{MeOH}$, insoluble in alkanes and H_2O , soluble in CH_2Cl_2 , benzene and PhCl. It is a monomer, as indicated by its molecular weight (found 310.10; calcd for $[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2]$: 274.04).

The change of the ratio of reagents $[\text{Mo}(\text{NO})_2(\text{MeNO}_2)_4](\text{BF}_4)_2$ and $\text{Na}(\text{O}_2\text{CMe})$ from 1:2 to 1:4 in MeNO_2 –MeOH solution allows the coordination of two additional acetate groups (reaction (3)).

$\text{Na}_2[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_4]$ is a very fine-crystalline green compound, sparingly soluble in MeOH and MeCN.

Reaction between $[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_4](\text{BF}_4)_2$ and $\text{Li}(\text{O}_2\text{CPh})$ in MeNO_2 –MeOH or MeOH solution gives rise to the formation of the complex $\text{Mo}(\text{NO})_2(\text{O}_2\text{CPh})_2$, readily soluble in CH_2Cl_2 , CHCl_3 , benzene, PhCl, alcohols and MeCN. A cryoscopic molecular weight determination suggests the existence of monomeric species (found: 389.40; calcd for $\text{Mo}(\text{NO})_2(\text{O}_2\text{CPh})_2$: 398.18).

Excess of $\text{Li}(\text{O}_2\text{CPh})$ causes no changes in the coordination sphere of the complex. In the reaction system where

$[\text{Mo}(\text{NO})_2(\text{MeNO}_2)_2](\text{BF}_4)_2 : \text{Li}(\text{O}_2\text{CPh}) \leq 1:4$ the complex of the formula

$[\text{Mo}(\text{NO})_2(\text{O}_2\text{CPh})_2] \cdot 2\text{PhCO}_2\text{H}$ is formed. Two molecules of benzoic acid could be removed *in vacuo* (10^{-3} mm Hg) at 100°C .

IR spectra

The IR spectra of the carboxylato-dinitrosyl-molybdenum complexes (see Experimental Section and Fig. 1) showed two $\nu(\text{NO})$ bands typical for *cis*-dinitrosyl-molybdenum complexes [30] and bands characteristic for coordinated carboxylate ligands.

The $\nu(\text{NO})$ and $\nu(\text{CO}_2)$ frequencies in the IR spectrum of $[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2] \cdot \text{MeOH}$ are somewhat different from those observed for $\{\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2\}_n$ [23] but the $\Delta\nu(\text{CO}_2) = \nu_{\text{as}} - \nu_{\text{s}}$ values are in both cases almost identical (97 and 95 cm^{-1} , respectively).

Fig. 1. IR spectra (in KBr pellet) of
a) $[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2] \cdot \text{MeOH}$;
b) $\text{Na}_2[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_4]$; c) $\text{Mo}(\text{NO})_2(\text{O}_2\text{CPh})_2$.

Very low $\Delta\nu(\text{CO}_2)$ values ($< 105 \text{ cm}^{-1}$) generally indicate chelation (such as in $[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2] \cdot \text{MeOH}$) or a combination of chelation and bridging (most likely in $\{\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2\}_n$ [23]) if short metal-metal bonds are not present [31].

The clearly higher $\nu_{\text{as}}(\text{CO}_2)$ value in the IR spectrum of $\text{Na}_2[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_4]$ (1596 cm^{-1} ; Fig. 1) as compared to diacetato-dinitrosyl-molybdenum complexes (about 1520 cm^{-1}) and the very high $\Delta\nu(\text{CO}_2)$ value (296 cm^{-1}) are typical for unidentate acetate groups [31].

The $\Delta\nu(\text{CO}_2)$ value for the chelate ligands in $\text{Mo}(\text{NO})_2(\text{O}_2\text{CPh})_2$ (128 cm^{-1}) exceeds that for the acetate ligands coordinating in a similar way. The IR spectrum of $[\text{Mo}(\text{NO})_2(\text{O}_2\text{CPh})_2] \cdot 2\text{PhCO}_2\text{H}$ displayed ν_{as} and $\nu_{\text{s}}(\text{CO}_2)$ frequencies characteristic for chelating PhCO_2^- ligands and non-coordinated benzoic acid molecules.

^1H NMR spectra

The ^1H NMR spectrum of $[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2] \cdot \text{MeOH}$ (in CD_2Cl_2 , at 25°C) exhibits one methyl proton signal of the acetate group ($\delta = 2.00 \text{ ppm}$, s, $2 \cdot 3 \text{ H}$) and proton resonances of methyl alcohol ($\delta(\text{CH}_3) = 3.38 \text{ ppm}$, s, 3 H ; $\delta(\text{OH}) = 4.20 \text{ ppm}$, s, 1 H).

The ^1H NMR spectrum (in d_6 -DMSO at 25°C) of the polymeric complex $\{\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2\}_n$, most likely with chelating and bridging acetates, exhibits also only one methyl proton resonance ($\delta = 1.95 \text{ ppm}$) [23]. This may be caused by dynamic exchange process between chelating and bridging acetates, or, even more likely, by destruction of the polymeric structure of the compound with possible coordination of the solvent molecules. Since the recorded in MeOH spectrum in the range -90°C to $+60^\circ\text{C}$ the latter suggestion is preferred.

The ^1H NMR spectrum of $\text{Na}_2[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_4]$ in CD_3OD exhibits two singlets of equal intensity reflecting the nonequivalence of the ligands coordinated in the *trans* and *cis* positions ($\delta(\text{CH}_3) = 1.97$ and 2.07 ppm).

The ^1H NMR spectrum of $\text{Mo}(\text{NO})_2(\text{O}_2\text{CPh})_2$ in CD_2Cl_2 exhibits a multiplet at 7.55 ppm of an intensity corresponding to three protons (2 H *meta* and 1 H *para*) and a doublet at 8.07 ppm corresponding to two *ortho* protons. In the ^1H NMR spectrum of $[\text{Mo}(\text{NO})_2(\text{O}_2\text{CPh})_2] \cdot 2\text{PhCO}_2\text{H}$ the signals of the phenyl protons of the attached benzoic acid (7.45 ppm , m, 3 H ; 7.96 ppm , d, 2 H) and the signal of the carboxyl proton ($\delta(\text{PhCO}_2\text{H}) = 10.45 \text{ ppm}$, s, 1 H) are observed additionally.

Electronic structure

The bonding in dinitrosyl-molybdenum complexes and their electronic structure has been discussed quantitatively by Enemark and Feldham [1] as dominated by the $\{\text{Mo}(\text{NO})_2\}^6$ unit, in which six electrons are associated with the molybdenum $4d$ and $\pi^*(\text{NO})$ orbitals.

In this paragraph the results of theoretical studies on the electronic structure of dinitrosyl molybdenum complexes with oxygen anion ligands, exemplified on the di- and tetraacetato-dinitrosyl molybdenum complexes, are reported.

The calculations were performed by the parameter-free Fenske-Hall [32] and the semiempirical INDO methods [33].

In the nearest environment of the central ion of the complexes there are two NO groups in mutual *cis* position and four carboxyl group oxygen atoms. Two coordination modes of the acetate ions were taken into account: as unidentate ligands in $[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2]^{2-}$ and as chelating ligands in $\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2$. For both complexes a linear coordination of the NO group was assumed, as most frequently observed in complexes of that type [1, 4].

The structure of $\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2$ was discussed in two geometries: 1) With one Mo–O bonding in each chelate ring shorter (2 Å) than the second one (2.2 Å), and an elongation of Mo–O bonds in the *cis* position 2) with the Mo–O bond lengths identical and equal 2 Å. In both cases the acetate group planes form a 90° angle. The assumed geometries and the systems of coordinates are depicted in Fig. 2. There were two reasons for the choice of such geometries:

- 1) The linearly coordinated NO ligands show little or no *trans* influence [4, 34].
- 2) Reactions of complexes of that type with *e.g.* EtAlCl_2 suggest, that a free coordination site can easily be reached in *trans* positions towards NO [22].
- 3) In $\text{M}_2(\text{NO})_2(\text{OR})_6\text{L}_2$ (M = Cr, Mo, W) complexes the M–O bonds in *trans* positions *vs.* NO are always much longer when compared to the other bonds of that type [35, 36].

The calculated two-center overlap population values and distribution of charges on metal and ligand atoms are listed in Tables I and II. The Wi-

Fig. 2. The geometry of studied complexes.

berg bond indexes [37] calculated by the INDO method are shown in Fig. 3. The molecular orbital schemes are plotted in Fig. 4. Qualitatively identical molecular orbital schemes were obtained for $\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2$, with the appropriate Mo–O bonds elongated. The results evidently confirm the predominant role of the $[\text{Mo}(\text{NO})_2]^{2+}$ unit, where 6 electrons occupy the delocalized 4d(Mo) and π^* (NO) orbitals. The highest occupied molecular orbitals are $a(d_{xy} \sim \pi^*\text{NO})$ and $b(d_{xz} \sim \pi^*\text{NO})$, and as it was noted previously the difference in their energies is very small [28, 38]. Both methods produced qualitatively identical sequences of molecular orbitals and similar MO splitting values, but it should be noted that the delocalization of the molecular orbitals in the INDO method is much greater.

	$\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2$	$[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_4]^{2-}$
d Mo–N	0.2750	0.2456
d Mo–O _{eq} (MeCO ₂ [–])	0.0792	0.0924
d Mo–O _{ax} (MeCO ₂ [–])	0.0832	0.0899

Table I. Two-center overlap populations for $\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2$ and $[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_4]^{2-}$ calculated by Fenske-Hall method.

Table II. Net charges on the molybdenum and ligand atoms.

Net charge	$[\text{Mo}(\text{NO})_2]^{2+}$		$\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2$		INDO ^c	$[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_4]^{2-}$
	F–H ^a	INDO ^b	F–H	INDO		F–H
qMo	+1.150	+0.688	+0.958	+0.945	+0.916	+1.048
qN	+0.183	+0.349	–0.017	–0.0168	+0.0078	–0.066
qO(NO)	+0.242	+0.307	–0.040	–0.0995	–0.0824	–0.150
qNO	+0.425	+0.656	–0.057	–0.116	–0.0746	–0.216
qO _{eq} (MeCO ₂ [–])			–0.527	–0.574	–0.591	–0.583
qO _{ax} (MeCO ₂ [–])			–0.527	–0.577	–0.571	–0.602
qMeCO ₂ [–]			–0.421	–0.358	–0.383	–0.668

^a By Fenske-Hall method; ^b by INDO method; ^c the complex with unequal Mo–O bonds.

Fig. 3. Wiberg bond indexes: a) for the complex with equivalent Mo–O bonds; b) for the complex with non-equivalent Mo–O bonds.

Fig. 4. Molecular orbital diagrams showing the highest filled and lowest unfilled orbitals for the investigated complexes: a, b, c – by Fenske-Hall method; d – by INDO method (for better understanding of the figure the HOMO energies were assigned with the same values).

Electronic spectra

Electronic spectra (absorption and reflectance) for carboxylato-dinitrosyl-molybdenum and di-

alkoxy-dinitrosyl-molybdenum complexes were recorded in the 200–800 nm region. Table III summarizes the absorption maxima ($\lambda_{\max}$) and the molar absorptivity values (ϵ), also for the other known dinitrosyl-molybdenum complexes with oxygen anion ligands.

In the case of $\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2$ we have tried to explain the spectroscopic properties of dinitrosyl-molybdenum complexes with four ligands coordinating to metal by oxygen atoms. The symmetry of this molecule was approximated to the C_{2v} point group. Equal Mo–O bond distances were assumed, since the theoretical calculations revealed no essential changes in the molecular orbitals caused by their differentiation.

The electronic structure of the excited states was calculated by the configuration interaction method [33]. Transition energies and oscillator strengths were determined considering the configurational interaction between the homogeneously excited states. The results of the calculations are confronted with the experimental data in the Table IV. Only the transitions of energies lower than 5.5 eV, *i.e.* those which could have been measured experimentally, were considered. The CT low intensity transitions adjacent to the high intensity ones and the d–d transitions located within the intensive CT transition were omitted. The character of transitions was estimated from their contributions to molecular orbitals between which a given transition proceeded.

For the dinitrosyl-molybdenum complexes with four oxygen atoms in the nearest central atom environment, the spectroscopically important molecular orbitals preserve the character of the delocalized orbitals of the $[\text{Mo}(\text{NO})_2]$ moiety. For that reason in the long wavelength region of their spectra (by 5 eV) one should expect the weak intensity d–d and $d\pi^*(\text{NO}) \rightarrow d\pi^*(\text{NO})$ transitions only within this unit (Table IV).

Olefin metathesis reaction

$\{\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2\}_n$ is known to form with EtAlCl_2 homogeneous, very active catalytic system for metathesis reaction of acyclic [23] and cyclic [27] olefins. $[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2] \cdot \text{MeOH}$ together with EtAlCl_2 displays similar activity. Less active is the system $\text{Na}_2[\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_4]/\text{EtAl}_2\text{Cl}_2$, a 50% conversion of pent-2-ene being achieved

Table III. Electronic absorption data of dinitrosyl-molybdenum complexes with ligands containing oxygen atoms.

Complex	Solvent	Solution			Solid	
		$\bar{\nu}_{\max}$ (cm^{-1})	$E_{\max}$ (eV)	ϵ^a	$\bar{\nu}_{\max}$ (cm^{-1})	$E_{\max}$ (eV)
[Mo(NO) ₂ (O ₂ CMe) ₂] · MeOH	CH ₂ Cl ₂	43470	5.392	6094	43500	5.393
		34720 sh	4.306	(1020)		
		28170	3.493	563	28570	3.542
		23420	2.904	1082	23400	2.901
{Mo(NO) ₂ (O ₂ CMe) ₂ } _n	MeOH				18350 sh	2.275 sh
		14030	1.740	37	14250	1.767
		42920	5.321	6108	43350	5.375
		28570	3.542	388	28600	3.546
Na ₂ [Mo(NO) ₂ (O ₂ CMe) ₄]	H ₂ O	23310	2.890	781	23500	2.914
					18190 sh	2.255
		13920	1.726	30	14560 sh	1.805
		43200	5.356	4550	43300	5.368
Mo(NO) ₂ (O ₂ CPh) ₂	CH ₂ Cl ₂	34600 sh	4.290	(609)		
		28650	3.552	395	28600	3.546
		23980	2.973	1806	23800	2.951
		14530	1.802	35	14500	1.796
{Mo(NO) ₂ (OMe) ₂ MeCN} _n	CH ₃ OH	39520 sh	4.900	(4126)	39520	4.900
		36360 sh	4.508	(741)		
		23420	2.904	1267	23450	2.907
		19050 sh	2.362	(154)	20000 sh	2.480
{Mo(NO) ₂ (OEt) ₂ EtOH} _n	CH ₂ Cl ₂	15380	1.907	80	15350 sh	1.903
		43550	5.400	3830		
		28010 sh	3.473	(318)		
		23260	2.884	1515		
{Mo(NO) ₂ (O'Pr) ₂ } _n	CH ₂ Cl ₂	13790	1.710	20		
		42950	5.325	3300		
		29070	3.604	415		
		23360	2.896	1108		
[Et ₄ N][Mo(NO) ₂ (ox) ₂] ^b	DMF	13610	1.687	34		
		43050	5.338	3770		
		29940 sh	3.712	(426)		
		23700	2.940	1065		
Mo(NO) ₂ (acac) ₂ ^b	DMF	14080	1.746	39		
		23260	2.884	1100		
		12990	1.611	50		
		22470	2.786	2100		
		13610	1.687	70		

^a Values of ϵ in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$; ^b ref. [28].Table IV. Calculated and experimental electronic spectra of Mo(NO)₂(O₂CMe)₂.

Calculated		Experimental		Type of the transition	Excited state
E (eV)	f ^a	E (eV)	ϵ^b		
1.883	0.002894	1.740	37	$d_{z^2} \sim d_{xy} \rightarrow d_{z^2} \sim d_{x^2-y^2}$	¹ A
2.283	0.000878	2.275 sh ^c		$d_{z^2} \sim d_{xy} \rightarrow d_{z^2} \sim d_{xy} \sim d_{x^2-y^2}$	¹ A
2.338	0.000750			$d_{z^2} \sim d_{xy} \rightarrow d_{xy}$	¹ B
2.609	0.001408			$d \sim \pi^* \text{NO} \rightarrow d \sim \pi^* \text{NO}$	¹ A
2.733	0.045286			$d \sim \pi^* \text{NO} \rightarrow d \sim \pi^* \text{NO}$	¹ B
2.935	0.050450	2.905	1082	$d \sim \pi^* \text{NO} \rightarrow d \sim \pi^* \text{NO}$	¹ A
3.221	0.012095	3.493	563	$d \rightarrow d \sim \pi^* \text{NO}$	¹ B
4.221	0.001967	4.306 sh	(1020)	$d \sim \pi^* \text{NO} \rightarrow d \sim \pi^* \text{NO}$	¹ B
5.446	0.10887	5.392	6094	$p\text{O}_{\text{MeCO}_2^-} \rightarrow d \sim \pi^* \text{NO}$	¹ B
5.538	0.11116			$d \rightarrow d \sim \sigma\text{C}_{\text{MeCO}_2^-}$	¹ B

^a Oscillator strength; ^b values of ϵ in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$; ^c reflectance spectra data.

after 18 min. In all these systems, undoubtedly, the identical carbene catalysts are formed.

$\text{Mo}(\text{NO})_2(\text{O}_2\text{CPh})_2$ with EtAlCl_2 in chlorobenzene also forms an active catalytic system for olefin metathesis. The metathesis equilibrium of pent-2-ene was achieved after 15 min with the same reaction conditions as above.

Spectroscopic investigations [IR in $\nu(\text{NO})$ region] of the interactions of the catalyst precursors, *i.e.* of $\{\text{Mo}(\text{NO})_2(\text{O}_2\text{CMe})_2\}_n$ and of the other carboxylato complexes discussed here with EtAlCl_2 allowed to define the carbene catalyst as $[(\text{AlCl}_2)_2(\text{O}_2\text{CR})_2\text{Mo}(\text{NO})_2(\text{CHMe})]$ [23, 39].

The here reported results of the precatalyst electronic structure calculations for particularly char-

acteristic bonds (Wibergs bond indexes, Fig. 3), d-center overlapping population values (Table I), together with charge distribution on central atom and ligand atoms (Table II)) suggest the possibility of formation of such an active catalyst due to the favorable conditions for the electrophilic attack of Lewis acid molecules (EtAlCl_2) on carboxylic ligand oxygens in the equatorial plane. The weakest bonds and the highest negative charge concentrations, are associated with the elongated Mo–O bonds. In the same plane, *i.e.* in the Mo–NO bonding plane on the side opposite to the NO ligands, the coordination of a carbene ligand requires the smallest amount of activation energy [22].

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