

Reductive nitrosylation of molybdate(VI) by hydroxylamine in alcoholic solutions. Preparation, spectroscopic characterization and electronic structure of mono- and dinitrosyl molybdenum complexes. Crystal structure of $[\text{Mo}(\text{NO})\text{Cl}(\text{OMe})_2(\text{phen})] \cdot \text{MeOH}$

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Abstract

The reaction of molybdenum(VI) with $\text{NH}_2\text{OH} \cdot \text{HCl}$ in ${}^i\text{PrOH}$ solution leads to the formation of dinitrosyl complexes, whereas that in MeOH leads fundamentally to the mononitrosyl complexes. In these reactions complexes of composition *cis*-dinitrosyl-*trans*-dichloro-*cis*- L_2 $\text{Mo}(\text{NO})_2\text{L}_2\text{Cl}_2$ ($\text{L} = {}^i\text{PrOH}$, py), $\{\text{Mo}(\text{NO})_2(\text{O}^i\text{Pr})_2\}_n$ and $\text{Mo}(\text{NO})_2\text{Cl}(\text{OMe})_2\text{L}_2$ ($\text{L} = \text{MeOH}$, py; $\text{L}_2 = \text{phen}$) were isolated. The complexes have been spectroscopically (IR, UV-Vis, ${}^1\text{H}$ NMR) characterized. The crystal structure of $[\text{Mo}(\text{NO})\text{Cl}(\text{OMe})_2(\text{phen})] \cdot \text{MeOH}$ was determined by the single-crystal X-ray diffraction method. The compound crystallized in the monoclinic space group $P2_1/m$ with $a = 8.364(3)$, $b = 11.674(4)$, $c = 9.125(3)$ Å, $\beta = 104.29(3)^\circ$ and $Z = 2$. The structure was solved by conventional methods, resulting in a final R factor of 0.028 for 1732 independent reflections. The electronic structure of these mono- and dinitrosyl complexes was recognized by semiquantitative Fenske–Hall LCAO MO calculations. Catalytic activity of these complexes in the olefin metathesis reaction was also examined.

Introduction

The nitrosyl molybdenum complexes are active catalysts or precatalysts to many organic reactions [1] – the olefin metathesis reactions first of all [2–8]. These mono- and dinitrosyl halogen derivatives can be obtained from carbonyl derivatives and nitrosyl halides by oxidative nitrosation or from MoX_5 ($\text{X} = \text{halide ion}$) and NO by reductive nitrosation [9–12].

$\text{Mo}(\text{CO})_6$ and its derivatives react with nitrosonium salts in MeCN or MeNO_2 to give $[\text{Mo}(\text{NO})_2(\text{solv})_4]^{2+}$ [12–14]. The reactions of the latter compounds with appropriate anionic donor ligands would produce non-halogen dinitrosyl derivatives [14–17]. Such complexes with the $[\text{Mo}(\text{NO})_2]^{2+}$ moiety were also prepared by the reductive nitrosylation of molybdate(VI) by hydroxylamine in DMF [18, 19]. Instead, in aqueous solutions, in the presence of excess hydroxylamine, mono- or dinitrosyl complexes containing O,N-coordinated hydroxylamido ligands are formed [20]. These complexes also make active catalytic systems for the olefin metathesis reaction [21].

We have studied the reaction between molybdate(VI) and hydroxylamine hydrochloride in alcoholic solutions.

The preparation, spectroscopic characteristics and the molecular and electronic structure of the mono- and dinitrosyl molybdenum complexes as well as their catalytic activity in the olefin metathesis reaction is reported.

Experimental

All reagents and solvents required for preparation of the compound were of an analytical grade. IR spectra were measured on Specord M 80 and Perkin-Elmer 180 spectrophotometers in Nujol and hexachlorobutadiene mulls and KBr discs. ${}^1\text{H}$ NMR spectra were recorded on a Tesla BS 567 spectrometer and referenced to Me_4Si . Electronic spectra were scanned on a Beckman UV 5240 spectrophotometer. GLC analysis was performed on a N-504 (Elpo) chromatograph.

Synthesis of $\text{Mo}(\text{NO})_2\text{Cl}_2({}^i\text{PrOH})_2$ (1)

Ammonium heptamolybdate (2 g) and hydroxylamine hydrochloride (3 g) were heated in 25 cm³ of ${}^i\text{PrOH}$ at 65–70 °C for about 3 h. The colourless solution turned light-green and then dark-green. It was cooled and filtered off. The crude product was precipitated with diethyl ether from the filtrate condensed *in vacuo*.

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The solid was filtered off, washed with the diethyl ether and dried *in vacuo*. The crude product was treated with CH₂Cl₂ and the CH₂Cl₂-insoluble part was filtered off. The wanted green complex was precipitated from the filtrate with hexane, filtered off, washed with hexane and dried *in vacuo* at 80 °C. Yield 38%.

Anal. Calc. for C₆H₁₆N₂Cl₂MoO₄: C, 20.77; H, 4.65; Cl, 20.43; Mo, 27.64. Found: C, 21.30; H, 4.77; Cl, 20.12; Mo, 27.21%.

IR: $\nu(\text{OH})$ 3600–3300w, br, 3250–3060m, br; $\nu(\text{CH})$ 2930m, 2790m; $\nu(\text{NO})$ 1783s, 1654vs; $\nu(\text{MoCl})$ 304m; $\nu(\text{CO})$ 1085s, 1025sh.

Synthesis of Mo(NO)₂Cl₂py₂ (2)

Method A. To a ¹PrOH solution of 1 pyridine (py) was added in excess. The lemon-green precipitate thus formed was allowed to settle for an hour, filtered off, washed with water and diethyl ether and dried *in vacuo*. Yield 96%.

Method B. To a ¹PrOH solution of the crude product from the synthesis of 1 (1 g) pyridine (in excess) was added under stirring. The yellow-green precipitate thus formed was filtered off, washed with water, ethyl alcohol and diethyl ether and dried *in vacuo*. 2 was extracted from the precipitate with CHCl₃ (or CH₂Cl₂) and precipitated after condensation of the obtained solution, with hexane, then filtered off and dried *in vacuo*.

Anal. Calc. for C₁₀H₁₀N₄Cl₂MoO₂: C, 31.19; H, 2.62; N, 14.55; Cl, 18.41; Mo, 24.92. Found: C, 31.71; H, 2.73; N, 14.00; Cl, 18.09; Mo, 25.32%.

IR: $\nu(\text{CH})$ 3112m, 3075m; $\nu(\text{NO})$ 1772s, 1632vs; $\nu(\text{MoCl})$ 312s.

Synthesis of {Mo(NO)₂(OⁱPr)₂} (3)

To a ¹PrOH solution of the crude product from the synthesis of 1 (1 g) a solution of NaOⁱPr (1.0 g) in ¹PrOH was slowly added at 0 °C. Next, it was heated to 50 °C and stirred for an hour. The solution was filtered off and removed under vacuum. The complex was extracted from the remnant with a small amount of CH₂Cl₂. The green complex was precipitated with hexane. Yield 28%.

Anal. Calc. for C₆H₁₄N₂MoO₄: C, 26.29; H, 5.15; N, 10.22; Mo, 35.00. Found: C, 26.42; H, 5.49; N, 10.01; Mo, 34.77%.

IR: $\nu(\text{NO})$ 1772s, 1630vs.

Synthesis of [Mo(NO)Cl(OMe)₂(MeOH)₂]·2MeOH (4) and Mo(NO)Cl(OMe)₂(MeOH)₂ (4a)

A suspension of ammonium heptamolybdate (2 g) and NH₂OH·HCl (1.2 g) in MeOH (30 cm³) was stirred at the boiling point of this solvent for 30–40 min. The formed brown solution was cooled and diethyl ether (10 cm³) was added. The solution was filtered off and removed under vacuum. The product was purified by

repeated precipitation from MeOH solution with diethyl ether and next dried *in vacuo*. Yield 75%. Dessication of complex 4 *in vacuo* (about 5 × 10⁻³ mm Hg) at 100 °C results in the loss of two outer-sphere MeOH molecules.

Anal. Calc. for C₆H₂₂NCIMoO₇ (4): C, 20.49; H, 6.31; N, 3.98; Cl, 10.08; Mo, 27.28. Found: C, 20.91; H, 6.77; N, 3.70; Cl, 10.31; Mo, 26.89%. Calc. for C₄H₁₄NCIMoO₅ (4a): C, 16.71; H, 4.91; N, 4.87; Cl, 12.33; Mo, 33.36. Found: C, 17.02; H, 5.08; N, 4.70; Cl, 12.72; Mo, 33.09%.

IR (4): $\nu(\text{OH})$ 3430sh, 3170s; $\nu(\text{CH})$ 2915sh, 2840m; $\nu(\text{NO})$ 1610vs; $\nu(\text{MoN})$ 620m; $\delta(\text{MoNO})$ 563m; $\nu(\text{MoCl})$ 296m; $\nu(\text{CO})$ 1075sh, 1040w.

Synthesis of [Mo(NO)Cl(OMe)₂(phen)]·MeOH (5), Mo(NO)Cl(OMe)₂(phen) (5a), [Mo(NO)Cl(OMe)₂py₂]·MeOH (6) and Mo(NO)Cl(OMe)₂py₂ (6a)

To an MeOH solution of 4, 1,10-phenanthroline (phen) in MeOH or pyridine in excess, respectively, were added. The solutions were filtered off and stored at 0 °C for a few days. Afterwards crystalline brown-orange products were separated from the solutions via filtration. Yield *c.* 70%.

At 100 °C *in vacuo* (about 5 × 10⁻³ mmHg) 5 and 6 lose MeOH molecules.

Anal. Calc. for C₁₅H₁₈N₃ClMoO₄ (5): C, 41.35; H, 4.16; N, 9.64; Cl, 8.14; Mo, 22.04. Found: C, 41.71; H, 4.30; N, 9.31; Cl, 8.22; Mo, 21.88%. Calc. for C₁₄H₁₄N₃ClMoO₃ (5a): C, 41.66; H, 3.50; N, 10.41; Cl, 8.78; Mo, 23.77. Found: C, 41.49; H, 3.72; N, 10.12; Cl, 8.90; Mo, 24.00%.

IR (5): $\nu(\text{OH})$ 3440sh, 3170s; $\nu(\text{CH})$ 3058s, 2920s, 2812s; $\nu(\text{NO})$ 1626vs; $\nu(\text{MoN})$ 612m; $\delta(\text{MoNO})$ 570m; $\nu(\text{MoCl})$ 315m; $\nu(\text{CO})$ 1060sh, 1032vs.

Anal. Calc. for C₁₃H₂₀N₃ClMoO₄ (6): C, 37.74; H, 4.87; N, 10.16; Cl, 8.57; Mo, 23.19. Found: C, 40.01; H, 4.95; N, 9.98; Cl, 8.71; Mo, 23.33%. Calc. for C₁₁H₁₆N₃ClMoO₃ (6a): C, 37.76; H, 4.23; N, 11.01; Cl, 9.29; Mo, 25.14. Found: C, 37.58; H, 4.40; N, 10.89; Cl, 9.43; Mo, 25.37%.

IR (6): 3400sh, 3200m; $\nu(\text{CH})$ 3060m, 3038sh, 2930m; $\nu(\text{NO})$ 1625vs; $\nu(\text{MoN})$ 614m; $\delta(\text{MoNO})$ 572w; $\nu(\text{MoCl})$ 315m; $\nu(\text{CO})$ 1070m, 1048m.

Metathesis reaction

The metathesis reactions of pent-2-ene were carried out as described in ref. 22 under the same reaction conditions.

X-ray structural determination of 5

The space group and approximate unit-cell dimensions were determined from the rotation and Weissenberg photographs. The diffraction data were collected with Cu K α radiation on a KM4 κ (KUMA

Diffraction) four-circle diffractometer with a graphite monochromator. The crystallographic data and the refinement procedure details are given in Table 1. The intensities were corrected for Lorentz and polarization effects, but not for extinction or absorption.

The structure was solved by direct methods using the program SHELXS-86 [23] and refined by full-matrix least-squares using the SYNTX/XTL/XTLE structure determination system. The positions of all hydrogen atoms were determined from the difference Fourier synthesis.

Several cycles of refinement of the non-hydrogen coordinates with anisotropic thermal parameters (parameters of the H atoms were fixed) reduced the R and R_w values to 0.028 and 0.033, respectively. Neutral atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography [24].

TABLE 1. Crystal data, data collection details and refinement

Formula	$C_{15}H_{18}N_3O_4ClMo$
M_r	435.72
a (Å)	8.364(3)
b (Å)	11.674(4)
c (Å)	9.125(3)
β (°)	104.29(3)
V (Å ³)	863.4(5)
Space group	$P2_1/m$
Z	2
$F(000)$	400
T (K)	296
λ (Å) (Cu $K\alpha$)	1.54178
Monochromator	graphite
Crystal size (mm)	0.08 × 0.10 × 0.2
25 ref. to determine cell constants, range (2θ)	21.0–33.0
D_m (Mg m ⁻³) (flotation $CHCl_3/C_2H_4Br_2$)	1.67(1)
D_c (Mg m ⁻³)	1.676
Linear absorption coefficient (cm ⁻¹)	81.50
Data collection method	θ - 2θ scan
2θ limit (°)	164
h range	-14 to 14
k range	-10 to 40
l range	-14 to 14
No. standard reflections	3/100
Variation in standard reflections (%)	2
Reflections measured	3675
Independent reflections	1732
R_{int} (for 1629 double reflections)	0.014
Observed data with $I \geq 3.5\sigma(I)$	1529
Variable parameters	118
Final R $\sum F_o - F_c /\sum F_o $	0.028
Final R_w $[\sum w(F_o - F_c) ^2/\sum w F_o ^2]^{1/2}$	0.033
Final S $[\sum w(F_o - F_c) ^2/(n - \rho)]^{1/2}$	3.621
Function minimized ($w = 1/\sigma^2(F_o)$)	$\sum w(F_o - F_c)^2$
Final (Δ/σ)	0.01
Final ($\Delta\rho$)	0.40

Results and discussion

Reaction of molybdate(VI) with hydroxylamine hydrochloride in alcoholic solutions

The reaction of molybdate(VI) with hydroxylamine hydrochloride in aqueous solutions gives rise to the formation of mononitrosyl complexes with a $\{MoNO\}^4$ or $\{MoNO\}^6$ core (the superscript denotes the number of metal d-electrons) [25–29]. Nonetheless, in the presence of NCS^- , at the appropriate pH, the dinitrosyl complexes with the $\{Mo(NO)_2\}^4$ or $\{Mo(NO)_2\}^6$ core can also be obtained [20]. In non-aqueous solutions such as pyridine/glacial acetic acid or DMF the formation of the dinitrosyl $\{Mo(NO)_2\}^6$ type complexes can be expected [18, 19]. In alcoholic solutions the reaction products depend on the kind of alcohol.

In ¹PrOH solution only dinitrosyl complexes are formed, disregarding the reagents ratio. The stage of the mononitrosyl derivatives formation was not observable. Among the reaction products, the complex soluble in CH_2Cl_2 was identified as $Mo(NO)_2Cl_2 \cdot (^1PrOH)_2$ (**1**). The CH_2Cl_2 -insoluble residue most likely could be believed to be the complex with the $\{Mo(NO)_2(NHO)\}^4$ core. **1** is a green, hygroscopic complex, soluble also in PhCl, MeCN and in alcohols and insoluble in alkanes. The coordinated ¹PrOH ligands easily undergo substitution with pyridine, to produce a lemon-green complex of formula $Mo(NO)_2Cl_2py_2$ (**2**). $\{Mo(NO)_2(O^iPr)_2\}_n$ (**3**) was obtained by a similar method. Both complexes were previously synthesized by a different procedure [10, 16, 18].

In methyl alcohol, molybdate(VI) reacts with hydroxylamine hydroxychloride yielding the dimethoxy-nitrosyl complex $[Mo(NO)Cl(OMe)_2(MeOH)_2] \cdot 2MeOH$ (**4**). The side product of this reaction is still an unidentified dinitrosyl complex ($\nu(NO) = 1797, 1670$ cm⁻¹), particularly with $NH_2OH \cdot HCl$ in excess. It decomposes by itself after a prolonged reaction time, to the oxomolybdenum(V) compound and nitric oxide. **4** is a yellow-brown precipitate, moisture sensitive, soluble in the methyl and ethyl alcohols, DMF and DMSO. From MeOH solutions of **4** as well as of 1,10-phenanthroline and/or pyridine the brown-orange $[Mo(NO)Cl(OMe)_2(phen) \cdot MeOH]$ (**5**) and $[Mo(NO)Cl(OMe)_2py_2] \cdot MeOH$ (**6**) crystallize, respectively. Except for alcohols, they are soluble in the same solvents as **4**. Compounds **4**, **5** and **6** at 100 °C *in vacuo* lose their outer-sphere MeOH molecules and form **4a**, **5a** and **6a**.

Spectroscopic properties

IR spectra

The character of **1**, **2** and **3** in the $\nu(NO)$ region (see 'Experimental') is typical for dinitrosyl complexes with the *cis*- $\{Mo(NO)_2\}^6$ core.

The IR spectrum of **3** does not depend on the synthesis method [16]. This is indicative of an identical stereochemical arrangement of ligands around the *cis*-Mo(NO)₂ fragment. Such a stereochemical arrangement in the dichloro-dinitrosyl complexes seems to depend on the synthesis method. The method of Cotton and Johnson [10, 11] is suggested to give rise to the formation of the *cis*-dinitrosyl-*trans*-dichloro-*cis*-L₂ isomers [30, 31]; only at L = PPh₃ or RCN are the *cis*-dinitrosyl-*cis*-dichloro-*trans*-L₂ isomers formed [31]. Complexes obtained according to this method show two $\nu(\text{MoCl})$ frequencies in the far-IR spectra (*C*_{2v} is the molecular symmetry of these complexes) [31], whereas **1** and **2** prepared by our method show only one $\nu(\text{MoCl})$ band at 304 and 312 cm⁻¹, respectively (*D*_{∞h} is the local symmetry for the MoCl₂ fragment). **2**, prepared by reductive nitrosylation of molybdate(VI), but in pyridine/glacial acetic acid mixture shows identical $\nu(\text{MoCl})$ frequencies [18]. Both methods of synthesis of the Mo(NO)₂Cl₂L₂ type complexes seem to be stereospecific. The method of Cotton and Johnson (L₂ ≠ chelating ligand) gives the *cis*-dinitrosyl-*cis*-dichloro-*trans*-L₂ complexes and reductive nitrosylation of molybdate(VI)-*cis*-dinitrosyl-*trans*-dichloro-*cis*-L₂ isomers.

The IR spectra of mononitrosyl complexes **4**, **5** and **6** show characteristic frequencies for an MoNO fragment at 1610–1625 ($\nu(\text{NO})$) and 570–620 ($\nu(\text{MoN})$ and $\delta(\text{MoNO})$) cm⁻¹ and the frequencies characteristic for the OMe group and for the other coordinated ligands (see 'Experimental'). The bands at 296 cm⁻¹ for **4** and at 315 cm⁻¹ for **5** and **6** were assigned to the MoCl stretching vibrations.

¹H NMR spectra

The ¹H NMR spectrum of **1** exhibits in CD₃CN one doublet at 1.07 ppm (2 × 6H, *J*(HH) = 6.50 Hz), one quartet at 3.85 ppm (2 × 1H, *J*(HH) = 6.50 Hz) and one singlet at 2.70 ppm (2 × 1H), due to CH₃, CH and OH protons, respectively, showing the equivalence of the two ¹PrOH ligands. **2** (prepared as described herewith) displays a ¹H NMR spectrum in CD₂Cl₂ (or CDCl₃) with three multiplets at 7.37 (2 × 2H), 7.85 (2 × 1H) and 8.87 (2 × 2H) ppm due to β, γ and α protons, respectively. This complex, prepared by the method of Cotton and Johnson exhibits also three multiplets but their chemical shifts are downfield shifted: $\delta(\text{H}_\beta) = 7.53$, $\delta(\text{H}_\gamma) = 8.03$ and $\delta(\text{H}_\alpha) = 8.97$ ppm [31]. Such a direction of changes of their values is consistent with the calculated charge densities on the nitrogen atoms in the *cis* and *trans* positions towards NO (see paragraph 'Electronic structure'). The ¹H NMR spectrum of **3** in CDCl₃ (or CD₂Cl₂) ($\delta(\text{CH}_3) = 1.21$ ppm (2 × 6H), $\delta(\text{CH}) = 4.24$, 4.55 ppm (2 × 1H) proved to be independent of the synthesis method [16]. Its main feature is the lack of

well resolved resonances of the terminal and bridging iso-propoxy group, most probably due to the terminal ↔ bridge ligand exchange. This spectrum in the coordinating solvents, e.g. MeCN-d₃, exhibits the well resolved resonances of alkoxy groups within the temperature range -40 to +80 °C: $\delta(\text{CH}_3) = 1.07$ ppm (2 × 6H; *J*(HH) = 6.20 Hz), $\delta(\text{CH}) = 3.75$ ppm (2 × 1H; *J*(HH) = 6.20 Hz). It could thus be believed that in such a solvent both OⁱPr ligands are coordinated only terminally and the emptied coordination sites are occupied by the solvent molecules.

The ¹H NMR spectra of the Mo(NO)Cl(OMe)₂L₂ complexes were measured in DMSO-d₆ solvent. The spectrum of **4a** exhibits only two singlets at 3.20 (2 × 6H) and 3.55 (2 × 1H) ppm, due to the CH₃ and OH protons, respectively. The hydrogen bonds which allow proton exchange between the methyl alcohols and methoxy ligands are most likely responsible for such a character of this spectrum. The spectra of **5a** and **6a** exhibit one sharp signal at 3.25 and 3.23 ppm (2 × 3H), respectively, thus showing the equivalence of the two OMe groups in each complex. Moreover, these spectra display multiplets at 8.20–10.60 ppm due to 1,10-phenanthroline protons and three multiplets at 7.51 (2 × 2H_β), 7.81 (2 × 1H_γ) and 8.65 (2 × 2H_α) ppm due to the pyridine protons.

Crystal structure of **5**

Crystal data collection details and refinement, fractional atomic coordinates and selected bond distances and angles are listed in Tables 1, 2 and 3, respectively. Figure 1 shows an ORTEP diagram of the molecule with the atom numbering.

The crystal structure consists of discrete complex and MeOH molecules occupying general positions in the space group *P*2₁/*m*.

TABLE 2. Fractional atomic coordinates and isotropic equivalent thermal parameters and their e.s.d.s for **5**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Mo	0.1562(5)	0.2500(0)	0.6189(5)	2.65(2)
Cl	-0.1105(17)	0.2500(0)	0.4168(17)	3.52(5)
O(1)	0.4934(46)	0.2500(0)	0.8112(47)	3.87(17)
O(2)	0.0716(32)	0.1196(21)	0.6979(31)	3.66(11)
O(3)	0.0107(82)	0.2500(0)	0.0990(76)	10.61(45)
N(1)	0.3562(52)	0.2500(0)	0.7419(48)	2.78(16)
N(2)	0.2489(34)	0.1370(23)	0.4596(33)	2.72(11)
C(1)	0.1453(58)	0.0505(37)	0.8224(53)	4.81(20)
C(2)	0.2395(46)	0.0229(30)	0.4566(44)	3.27(14)
C(3)	0.3063(51)	-0.0432(31)	0.3597(49)	3.82(16)
C(4)	0.3850(51)	0.0080(34)	0.2632(49)	3.95(16)
C(5)	0.3960(46)	0.1289(31)	0.2617(43)	3.22(14)
C(6)	0.3249(40)	0.1839(27)	0.3630(39)	2.80(14)
C(7)	0.4724(48)	0.1919(34)	0.1629(46)	4.05(18)
C(8)	-0.1223(105)	0.2500(0)	-0.0119(94)	6.98(44)

TABLE 3. Selected bond distances (Å) and angles with their e.s.d.s in parentheses

Mo–Cl	2.519(2)	C(2)–C(3)	1.391(6)
Mo–N(1)	1.770(4)	C(3)–C(4)	1.361(6)
O(1)–N(1)	1.166(6)	C(4)–C(5)	1.414(5)
Mo–O(2)	1.895(3)	C(5)–C(6)	1.406(5)
Mo–N(2)	2.238(3)	C(5)–C(7)	1.431(6)
O(2)–C(1)	1.406(5)	C(6)–C(6) ⁱ	1.417(4)
N(2)–C(2)	1.334(4)	C(7)–C(7) ⁱ	1.356(6)
Cl–Mo–O(2)	86.1(1)	O(2)–Mo–N(2) ⁱ	160.5(1)
Cl–Mo–N(1)	172.7(1)	N(1)–Mo–N(2)	89.3(1)
Cl–Mo–N(2)	84.9(1)	N(2)–Mo–N(2) ⁱ	72.2(1)
O(2)–Mo–O(2) ⁱ	106.9(1)	Mo–O(2)–C(1)	129.6(3)
O(2)–Mo–N(1)	98.2(1)	Mo–N(1)–O(1)	173.8(3)
O(2)–Mo–N(2)	89.8(1)		

Symmetry code: (i) $x, 0.5 - y, z$.

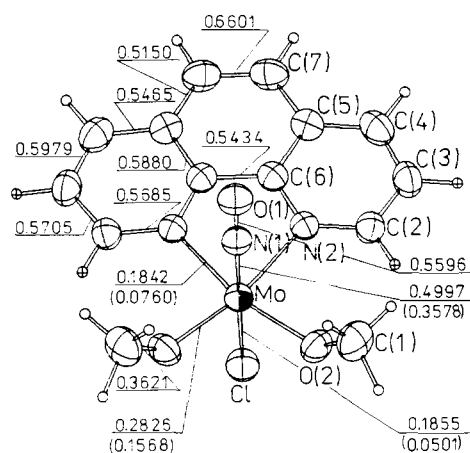


Fig. 1. ORTEP projection of **5** showing atom-numbering scheme (thermal ellipsoids are drawn at the 50% probability) and two-center overlap populations; $d(\text{Mo})$ orbitals taken into account only are given in brackets.

The molecular structure can be described as a square bipyramid with the NO and Cl ligands in the apical positions ($\text{Cl–Mo–N}(1) = 172.7^\circ$) and the OMe ligands and N,N-coordinated phenanthroline in the equatorial positions. The distortion of the octahedron is very small, since the angle between the mean equatorial plane ($\text{O}(2), \text{O}(2)^i, \text{N}(2), \text{N}(2)^i$) and the axial plane (Cl, Mo, N(1)) is near 90° .

The MoNO group is approximately linear and the range of Mo–N–O bond angles (173.8°) is typical for complexes with the $\{\text{Mo}(\text{NO})\}^4$ core [32]. The Mo–Cl bond lengths (2.519 Å) is one of the longest bonds in chloro-nitrosyl-molybdenum complexes.

The packing of the crystal is determined only by van der Waals' interaction and significant intermolecular interactions have not been observed.

Electronic structure

Bonding in metal mono- and dinitrosyl complexes has been qualitatively discussed by Enemark and Fel-

tham [33] utilizing the orbital correlation method. Up to now, we have calculated the electronic structure of the dinitrosyl-molybdenum complexes by parameter-free Fenske–Hall and semiempirical INDO methods [34]. The electronic structure of the excited states and oscillator strengths were also calculated for interpretation of spectroscopic (UV–Vis) properties. The bonding in these complexes is dominated by the $\{\text{Mo}(\text{NO})_2\}^6$ group, where six electrons occupy the delocalized orbitals of the $4d(\text{MO}) \sim \pi^*(\text{NO})$ character. The $d_{xz} \sim \pi^*(\text{NO})$ and $d_{xy} \sim \pi^*(\text{NO})$ are the highest occupied orbitals and their energy difference is low.

Table 4 shows the one-center densities and Mülliken gross atomic charges for both types of isomer of a model complex for **2** calculated as in ref. 35. The bond lengths of the model complex skeleton $\text{Mo}(\text{NO})_2\text{Cl}_2\text{N}_2$ were adapted from the crystal structure of $\text{Mo}(\text{NO})_2\text{Cl}_2(\text{bipy})$ [31], and the angles between Mo–ligand bonds in a *cis* position were approached to 90° .

Bonding in mononitrosyl complexes of the $\text{Mo}(\text{NO})\text{Cl}(\text{OMe})_2\text{L}_2$ type (**4**, **5** and **6**) was recognized on an example of **5**, by theoretical studies using the

TABLE 4. Mülliken gross atomic charges (I) and one-center densities (II) in *cis*-dinitrosyl-*trans*-dichloro-*cis*- NH_3 and *cis*-dinitrosyl-*cis*-dichloro-*trans*- NH_3 isomers of $\text{Mo}(\text{NO})_2\text{Cl}_2(\text{NH}_3)_2$

Atom	<i>cis</i> -NO- <i>trans</i> -Cl- <i>cis</i> - NH_3		<i>cis</i> -NO- <i>cis</i> -Cl- <i>trans</i> - NH_3	
	I	II	I	II
Mo	0.599	4.2282	0.624	4.2341
O(NO)	−0.022	4.7893	−0.035	4.8101
N(NO)	0.126	4.1967	0.074	4.2560
N(NH_3)	−0.179	4.2799	−0.160	4.2496
Cl	−0.616	7.3422	−0.587	7.2529

TABLE 5. Molecular orbitals calculation on **5**

(a) Characteristic of the frontier molecular orbitals

Mo	Percent character of molecular orbitals
ψ_1	38.2 $\pi^*\text{NO}$, 36.7 $d_{xy}\text{Mo}$, 16.1 πCl
ψ_2^a	42.6 $d_{xz}\text{Mo}$, 38.5 $\pi^*\text{NO}$
ψ_{-1}	π^* ring
ψ_{-2}	π^* ring
ψ_{-3}	51.4 $d_{z^2}\text{Mo}$
ψ_{-4}	π^* ring
ψ_{-5}	52.1 $\pi^*\text{NO}$, 40.1 d_{xz}
ψ_{-6}	45.3 $\pi^*\text{NO}$, 36.2 $d_{xy}\text{Mo}$

(b) Mülliken gross atomic charges

Mo	NO	Cl	CH_3O	phen
+1.057	−0.183	−0.598	−0.352	+0.440

^aHOMO.

Fenske–Hall molecular orbital model [35]. The resulting eigenvectors and eigenvalues were determined completely by the atomic basis sets and the geometry of **5**. All atomic positions were generated from the orthogonalized coordinates of **5** obtained from the structural determination.

The characteristics of the bonding are presented as the Mülliken two-center overlap populations that are given in Fig. 1. The correlation of these values is consistent with the bond lengths (Table 3). The population analyses of the frontier molecular orbitals and Mülliken gross atomic charges are summarized in Table 5. These molecular orbitals are presented also in the MO diagram (Fig. 2), depicting the orbital correlation for the complex formation: 'Mo(NO)Cl(OMe)₂' + phen → **5**. There is a large coupling of the 4d(Mo) and $\pi^*(\text{NO})$ orbitals of the {MoNO}⁴ group caused by the strong π -acceptor ability of the NO group. The $d_{xy} \sim \pi^*(\text{NO})$ and $d_{xz} \sim \pi^*(\text{NO})$ are the highest occupied molecular orbitals (HOMO), which are nearly degenerated. The $d_{z^2} \sim d_{x^2-y^2}$ is predicted to be the lowest unoccupied molecular orbital. Hence, the absorption bands at 22 900–24 000 cm⁻¹ (Table 6) can be assigned to a transition from $d_{xz} \sim \pi^*(\text{NO})$ to $d_{z^2} \sim d_{x^2-y^2}$ orbitals. For **4** with the central MoNClO₄ skeleton, the molecular orbital can be approximated to C_{4v} symmetry and its two absorption bands (Table 6) could be assigned as

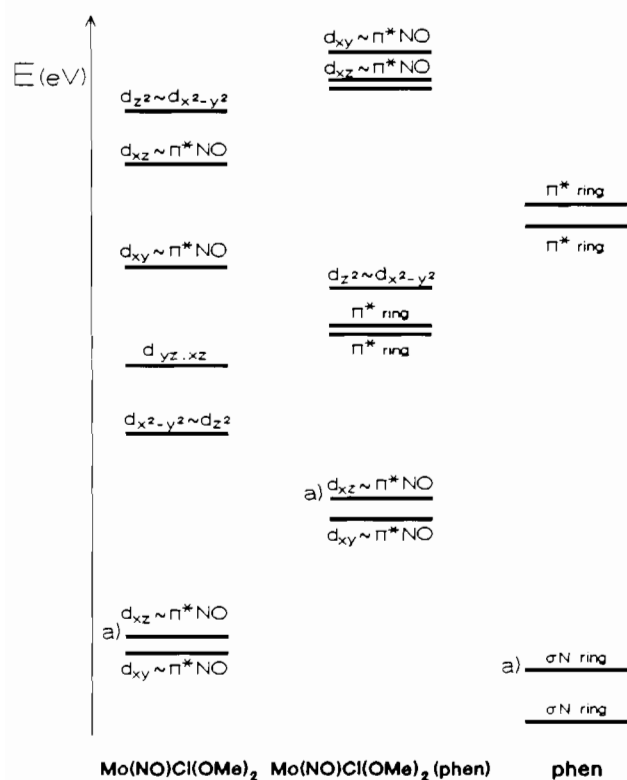


Fig. 2. Highest filled and lowest unfilled orbitals in molecular orbital diagrams.

TABLE 6. Electronic absorption spectra of **4**, **5** and **6**

4		5		6	
$\bar{\nu}_{\text{max}}$ (cm ⁻¹)	ϵ^a	$\bar{\nu}_{\text{max}}$ (cm ⁻¹)	ϵ^a	$\bar{\nu}_{\text{max}}$ (cm ⁻¹)	ϵ^a
24000	290	22900	580	2300	670
3560sh	(2290)	27200	1500	2700sh	2690
		28850	1890	30000sh	4170
		33950	11000		
		36300sh	(27200)		

^aValues of ϵ in dm³ mol⁻¹ cm⁻¹.

the $e \rightarrow b_2$ (24 000 cm⁻¹) and $e \rightarrow e$ (35 800 cm⁻¹) transitions.

Metathesis reaction

In 1968 Zeuch reported that dinitrosyl–molybdenum complexes with EtAlCl₂ acted as active catalysts of olefin metathesis reactions [36]. For such reactions **3** with EtAlCl₂ also forms a very active catalytic system [16, 22]. Spectroscopic investigations (IR in $\nu(\text{NO})$ region) of interactions between **3** and the other dialkoxy–dinitrosyl–molybdenum precatalysts with EtAlCl₂ allowed us to define the carbene catalyst formed in these systems as [(AlCl₂)₂(OR)₂Mo(NO)₂(CHMe)] [22]. These complexes were separated and characterized [37, 38]. In the carbene–dinitrosyl–molybdenum complexes the $\nu(\text{NO})$ frequencies do not depend on other coordinated ligands [17, 37–39]. The positions of $\nu(\text{NO})$ bands in the IR spectra of EtAlCl₂ with the *cis*-dichloro isomer (1750, 1850 cm⁻¹) [40] and/or with the *trans*-dichloro isomer of **2** (1744, 1848 cm⁻¹) as well as in that of **1** + EtAlCl₂ (1746, 1848 cm⁻¹) suggest the formation of appropriate alkylidene–dinitrosyl–molybdenum complexes. The IR investigations were carried out in the molar ratio of reagents Mo:Al = 1:6 in chlorobenzene at room temperature.

The *trans*-dichloro isomer of the 2–EtAlCl₂ system displays a similar activity to the system with the *cis*-dichloro derivative [41]. The metathesis equilibrium of pent-2-ene was achieved after 10 min. **1** together with EtAlCl₂ displays also similar activity.

The mononitrosyl complexes **4**, **5** and **6** with EtAlCl₂ also form homogeneous catalytic systems for olefin metathesis. The most active system is that with **4**, the least active that with **5**. The metathesis equilibria of pent-2-ene in these systems were achieved after 2 and 15 min, respectively. In the system 6–EtAlCl₂ the equilibrium was achieved after 5 min.

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