

ELECTROCHEMICAL BEHAVIOUR OF MOLYBDENUM-NITROSYL COMPLEXES OF THE TYPE $\text{Mo}(\text{NO})_2\text{Cl}_2\text{L}_2$ AND $\text{Mo}(\text{NO})\text{Cl}_3\text{L}_2$

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Electrochemical behaviour of 22 molybdenum-nitrosyl complexes of the title types serving as catalyst precursors of olefin metathesis reactions was investigated and the odd-electron localization in the 1-electron reduction products was determined by ESR spectroscopy. It was found that the mononitrosyl complexes containing the fragment $\{\text{Mo}(\text{NO})\}^4$ are reduced in a potential region more positive and distinctly separated from that of the dinitrosyl complexes containing the fragment $\{\text{Mo}(\text{NO})_2\}^6$. In the reduction of the former complexes the electrons are accepted into a MO having prevalingly metal *d*-character while with the latter class of complexes the electrons accepted in the reduction are accommodated in a π^* -NO based MO. The comparison of the electrochemical results with the catalytic activity of the corresponding systems shows that the ability of the precursor complexes to form the catalytically active species depends on their substitution lability rather than on their redox properties.

In recent years considerable attention has been paid to complexes of the $\text{Mo}(\text{NO})_2\text{Cl}_2\text{L}_2$ and $\text{Mo}(\text{NO})\text{Cl}_3\text{L}_2$ (where L_2 are two monodentate or one bidentate neutral ligand), mainly owing to their demonstrated activity as catalyst precursors for homogeneous olefin metathesis¹⁻³. With both types of these complexes the presence of organylating co-catalysts, such as $\text{C}_2\text{H}_5\text{AlCl}_2$, has been proved to be essential to develop their catalytic activity and in this combination the mononitrosyl complexes have been found to be considerably more catalytically active than the dinitrosyl ones³. On basis of mechanistic studies the catalytically active complex has been assumed to contain the $\text{Mo}^0(\text{NO})\text{Cl}$ fragment stabilized by the co-catalyst component⁴. Hence it follows that the reaction route from the precursor to the active species should involve a two-electron reduction in case of $\text{Mo}(\text{NO})\text{Cl}_3\text{L}_2$ and the elimination of the NO ligand from the singly reduced or of NOCl from the non-reduced $\text{Mo}(\text{NO})_2\text{Cl}_2\text{L}_2$, respectively. In this connection a knowledge of the redox properties of both types of precursor complexes appears to be of interest.

We report here results concerning the electrochemical behaviour of 22 molybdenum mono- and dinitrosyl complexes of the above mentioned and related types, accomplished in some cases by the ESR data on the paramagnetic electrode reaction products to determine the localization of the odd electron density after the 1-electron electrode reaction.*

* Note added upon submission of the paper: after finishing the manuscript we found that redox behaviour of a similar type of dinitrosyl complexes was recently investigated. However, as far as it can be seen from the available abstract¹⁷ the subject of this work differs from that of the present paper both as regards the individual substances, medium and kind of processes under investigation.

EXPERIMENTAL

The nitrosyl-molybdenum complexes (abbreviations of the ligands see Table I) $\text{Mo}(\text{NO})_2\text{Cl}_2\text{L}_2$ ($\text{L} = \text{py}$, HMPT , OPPh_3 , DMSO , DMF ; $\text{L}_2 = \text{en}$, dipy) as well as the ionic complexes $[\text{Mo}(\text{NO})_2\text{Cl}_4][\text{NEt}_4]_2$ and $[\text{Mo}(\text{NO})\text{Cl}_5][\text{NEt}_4]_2$ were prepared by nitrosylating reduction of MoCl_5 to $\text{Mo}(\text{NO})_2\text{Cl}_2$ and $\text{Mo}(\text{NO})\text{Cl}_3$, respectively, followed by ligand addition^{5,6}. $\text{Mo}(\text{NO})(\text{salen})\text{Cl}$ (ref.⁶), $\text{Mo}(\text{NO})_2(\text{acac})_2$ (ref.⁷), $\text{Mo}(\text{NO})_2(\text{dtc})_2$ and $\text{Mo}(\text{NO})(\text{dtc})_3$ (ref.⁸) were obtained by similar methods. The yellow crystallized complexes $\text{Mo}(\text{NO})\text{Cl}_3(\text{diphos})$ and $\text{Mo}(\text{NO})(\text{dtc})_2\text{Cl}$ are formed in the reaction of $\text{Mo}(\text{NO})\text{Cl}_3$ with diphos in acetonitrile and with two equivalents of $\text{Nadtc} \cdot 3 \text{H}_2\text{O}$ in methanol, respectively⁹. The airstable, yellow crystallized $\text{Mo}(\text{NO})(\text{diphos})_2\text{Cl}$ can be isolated after reduction of $\text{Mo}(\text{NO})\text{Cl}_3$ with $\text{C}_2\text{H}_5\text{AlCl}_2$ in benzene or with Mg/MgI_2 in THF in the presence of an excess of diphos⁹. $\text{Mo}(\text{NO})(\text{CO})_2(\text{PPh}_3)_2\text{Cl}$ was prepared from $\text{Mo}(\text{NO})\text{Cl}_3$ and related complexes by carbonylation under reducing conditions as described earlier¹⁰.

Both solvents (THF-Merck pure and CH_2Cl_2 -Merck Uvasol) and supporting electrolytes (Bu_4NClO_4 and Bu_4NPF_6) serving as electrochemical media were dried and de-aerated prior to use by standard methods. Experiments were performed under argon purified by passing over the BTS-catalyst (BASF) and P_2O_5 .

For d.c. polarography and cyclic voltammetry the polarograph GWP 673 (GDR) was used, voltammetric curves were recorded with the storage oscilloscope Tektronix 5103 N. The three-electrode system consisted of the mercury dropping electrode, Pt-sheet counter electrode and aqueous calomel electrode separated from the investigated solution by a salt bridge filled with the corresponding supporting electrolyte, as a reference electrode. The potential values were measured against the half-wave potential of the reversible reduction wave of the bis-biphenylchromium iodide (BBCr) used as pilot substance which is assumed to have the same value in all solvents amounting to -0.78 V vs. saturated aqueous Ag/AgCl electrode¹¹. ESR spectra were recorded at room temperature using a Varian E-4 spectrometer working in the X-band with 100 kHz modulation frequency. Electrolyses for ESR measurements were performed on a mercury pool electrode directly within the ESR cavity using a special cell.

RESULTS

Electrochemistry

The electrochemical behaviour of any particular substance was studied by d.c. polarography and cyclic voltammetry. Reversibility of the electrode processes was tested by the log analysis of d.c. wave and by the cyclic voltammetry. Cases in which the log analysis indicated a reversible process and the cyclic voltammetry showed no or small counter peak increasing with sweep-rate were denoted as reversible with inactivation of the product. Most of the complexes were investigated in two solvents (CH_2Cl_2 and THF) containing tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as supporting electrolyte, in one case Bu_4NClO_4 was used for comparison. A survey of the results is listed in Table I in which the complexes are divided into 3 groups:

i) Complexes containing the fragment* $\{\text{Mo}(\text{NO}_2)\}^6$. Most of the dinitrosyl complexes yield 2 reduction steps (the absence of the second reduction wave in CH_2Cl_2 is due to the final increase of current which in this solvent appears at potentials of about $-1.0\text{ V vs } E_{\frac{1}{2}\text{BBCr}}$ and obscures more negative depolarization effects). The half-wave potentials of the first wave range with this class of complexes within the limits from $+0.08$ to $-0.43\text{ V vs } E_{\frac{1}{2}\text{BBCr}}$. The corresponding electrode processes are polarographically reversible in cases where the coordination sphere contains a chelate ligand (en, acac, dipy, etc.) or pyridine. With exception of the dipy complex there is a slight voltammetric indication of the inactivation of the electrode reaction product. With monodentate ligands the processes of the first wave are semireversible but in all cases the first wave corresponds to the uptake of 1 electron (the only exception of $1.2e$ in case of the HMPT complex No 9 is presumably due to the superposition of a second process at the same potential). The electrode processes in the second wave are in most cases irreversible, the wave height corresponds to the uptake of less than 1 electron, and the wave has a semikinetic character. Only with the dipy complex (No 5 and 6) the second wave is reversible with inactivation of the product and attains the height of 1 electron. In most cases the limiting current of the first wave has an irregularly increasing shape indicating that the uptake of the first electron is followed by a partial decomposition of the product yielding small amounts of electroactive substances.

ii) Complexes containing the fragment $\{\text{Mo}(\text{NO})\}^4$. The mononitrosyl complexes show essentially also two reduction waves but in contrast to the dinitrosyl complexes the mononitrosyl compounds are less stable in the solution and the first wave attains the 1-electron height only with complexes containing as ligands salen, dipy, $(\text{OPPh}_3)_2$ and $(\text{dtc})_3$. In other cases the first wave is smaller indicating a different degree of decomposition of the original complex in solution. In most cases also time changes of the polarographic pattern are observed. Reversibility of the processes in the first wave is observed only for complexes containing chelate ligands salen, dipy, diphos, $(\text{dtc})_3$. The most significant difference between the two classes of complexes is in the potential range of the first wave which in case of the mononitrosyl complexes is shifted to more positive values to such an extent ($+0.8$ to $+0.2\text{ V vs } E_{\frac{1}{2}\text{BBCr}}$) that it does not overlap with that of the dinitrosyl complexes. There are only two exceptions and in both cases (the salen complex No 17 and 18 and the $(\text{dtc})_3$ complex No 34) the bulky chelate ligands occupy most of the coordination sphere (4 and 6 places, respectively) shielding thus the central atom from the electron attack. The height of the second wave corresponds to the uptake of 1 electron only in case of the salen and dipy complex, in other cases the second wave is smaller

* A formalism introduced by Enemark and Feltham¹² is adopted treating the nitrosyl complexes as derivatives of molecular fragments $\{\text{M}(\text{NO})_x\}^n$ where n is the total number of electrons residing in metal d -orbitals and π^* -(NO) orbitals.

TABLE I

Electrochemical behaviour of molybdenum-nitrosyl complexes of the type $\text{Mo}(\text{NO})_2\text{L}_2\text{Cl}_2$ and $\text{Mo}(\text{NO})\text{L}_2\text{Cl}_3^a$

No	Complex (solvent ^b)	$E_{1/2}^1$ ^c (char. ^d)	n^e	$E_{1/2}^2$ ^c (char. ^d)	n^e	Note
Dinitrosyls $\{\text{Mo}(\text{NO})_2\}^6$						
1	$\text{Mo}(\text{NO})_2\text{en Cl}_2$ (CH_2Cl_2)	0.00 red, r	1	—	—	
2	$\text{Mo}(\text{NO})_2\text{en Cl}_2$ (THF)	-0.21 red, r	1	-1.29 red, ir	0.7	
3	$\text{Mo}(\text{NO})_2\text{acac}_2$ (CH_2Cl_2)	-0.19 red, r	1	—	—	
4	$\text{Mo}(\text{NO})_2\text{acac}_2$ (THF)	-0.33 red, r	1	-1.41 red, ir	0.3	ill-defined wave -1.83 V, red, ir $n = 1.6$
5	$\text{Mo}(\text{NO})_2\text{dipy Cl}_2$ (CH_2Cl_2)	+0.08 red, r	1	-0.86 red, ri	1	
6	$\text{Mo}(\text{NO})_2\text{dipy Cl}_2$ (THF)	-0.03 red, r	1	-0.95 red, ri	1	2 waves -1.63 V -2.08 V (free dipy)
7	$\text{Mo}(\text{NO})_2(\text{dtc})_2$ (CH_2Cl_2)	-0.19 red, r	1	—	—	
8	$\text{Mo}(\text{NO})_2\text{py}_2\text{Cl}_2$ (CH_2Cl_2)	+0.05 red, r	1	-0.23 red, ir	0.2	
9	$\text{Mo}(\text{NO})_2\text{py}_2\text{Cl}_2$ (THF)	-0.07 red, r	1	-0.34 red, ir	0.2	
10	$\text{Mo}(\text{NO})_2(\text{HMPT})_2\text{Cl}_2$ (CH_2Cl_2)	-0.27 red, ri	1.2	—	—	apparently composed of processes which in THF are separated
11	$\text{Mo}(\text{NO})_2(\text{HMPT})_2\text{Cl}_2$ (THF)	-0.35 red, ri	1	-0.78 red, ir	0.2	
12	$\text{Mo}(\text{NO})_2(\text{OPPh}_3)_2\text{Cl}_2$ (CH_2Cl_2)	-0.19 red, ri	1	—	—	
13	$\text{Mo}(\text{NO})_2(\text{OPPh}_3)_2\text{Cl}_2$ (THF)	-0.27 red, sr	1	-0.76 red, ir	0.2	
14	$\text{Mo}(\text{NO})_2(\text{DMSO})_2\text{Cl}_2$ (CH_2Cl_2)	+0.01 red, sr	1	—	—	
15	$\text{Mo}(\text{NO})_2(\text{DMF})_2\text{Cl}_2$ (CH_2Cl_2)	0.00 red, sr	1	—	—	
16	$\text{Mo}(\text{NO})_2\text{Cl}_4\text{Et}_4\text{N}_2$ (CH_2Cl_2)	-0.43 red, sr	1	—	—	

TABLE I
(Continued)

No	Complex (solvent ^b)	$E_{1/2}^{1c}$ (char. ^d)	n^e	$E_{1/2}^{2c}$ (char. ^d)	n^e	Note
Mononitrosyls {Mo(NO)} ⁴						
17	Mo(NO)(salen)Cl (CH ₂ Cl ₂)	+0.03 red, r	1	—	—	
18	Mo(NO)(salen)Cl (THF)	-0.09 red, r	1	-1.23 red, ir -1.59 red, r	1 1	free salen -1.3 V red, ir, $n = 1$
19	Mo(NO)dipy Cl ₃ (CH ₂ Cl ₂)	+0.80 red, r	1	-0.56 red, r -0.90 red, ri	1 1	close to 2nd wave of the (NO ₂)-complex
20	Mo(NO)dipy Cl ₃ (THF)	+0.60 red, r	1	-0.67 red, r	1	
21	Mo(NO)(dtc) ₂ Cl (CH ₂ Cl ₂)	+0.20 red, sr kinetic	0.2	-0.58 red, ir	0.8	
22	Mo(NO)(dtc) ₃ (CH ₂ Cl ₂)	-0.78 red, sr	1	—	—	
23	Mo(NO)py ₂ Cl ₃ (CH ₂ Cl ₂)	+0.34 red, ir	0.3	-0.81 red, ir	0.4	decomposition
24	Mo(NO)(diphos)Cl ₃ (CH ₂ Cl ₂)	+0.81 red, r	0.3	+0.48 red, ir -0.56 red, ir	0.25 2.7	time changes, decomposition
25	Mo(NO)(diphos)Cl ₃ (THF)	+0.68 red, r	0.5	+0.3 red, ir -0.60 red, ir	0.3 0.8	time changes, decomposition
26	Mo(NO)(HMPT) ₂ Cl ₃ (CH ₂ Cl ₂)	+0.44 red, ir	0.8	2 ill- defined waves +0.03, -0.2, red, ir	0.7	

TABLE I
 (Continued)

No	Complex (solvent ^b)	$E_{1/2}^1$ ^c (char. ^d)	n^e	$E_{1/2}^2$ (char. ^d)	n^e	Note
27	Mo(NO)(HMPT) ₂ Cl ₃ (THF)	+0.39 red, ir	1	2 ill- defined waves -0.31, -0.84, red, ir	0.55	oxid. wave +0.65 V, ir, $n = 1$
28	Mo(NO)(OPPh ₃) ₂ Cl ₃ (CH ₂ Cl ₂)	+0.45 red, sr	1	-0.05 red, ir	0.2	time changes, decomposition
29	Mo(NO)(OPPh ₃) ₂ Cl ₃ (CH ₂ Cl ₂ -Bu ₄ NClO ₄)	+0.50 red, ir	1	+0.12 red, ir	0.8	time changes, decomposition
30	Mo(NO)OPPh ₃) ₂ Cl ₃ (THF)	+0.40 red, ir	0.3	+0.07 red, ir	0.8	time changes, decomposition
31	Mo(NO)(DMSO) ₂ Cl ₃ (CH ₂ Cl ₂)	+0.63 red, ir	0.5	+0.04 red, ir	0.5	
32	Mo(NO)(DMF) ₂ Cl ₃ (CH ₂ Cl ₂)	+0.68 red, ir	0.6	+0.05 red, ir	0.6	
33	Mo(NO)Cl ₅ Et ₄ N ₂ (CH ₂ Cl ₂)	+0.40 red, sr	0.8	-0.21 red, ir	0.2	
34	Mo(NO)Cl ₅ Et ₄ N ₂ (THF)	+0.26 red, sr	0.2	ill- defined wave at -0.4	0.2	poor solubility, decomposition
Mononitrosyls {Mo(NO)} ⁶						
35	Mo(NO)(diphos) ₂ Cl (CH ₂ Cl ₂)	+0.73 ox, r	1	—	—	
36	Mo(NO)(diphos) ₂ Cl (THF)	+0.75 ox, r	1	—	—	
37	Mo(NO)(CO) ₂ (PPh ₃) ₂ Cl (CH ₂ Cl ₂)	—	—	—	—	

^a Abbreviations of the ligands: en = ethylenediamine, acac⁻ = acetylacetonate, dipy = α, α' -dipyridyl, py = pyridine, HMPT = hexamethylphosphortriamide, OPPh₃ = triphenylphosphine oxide, DMSO = dimethyl sulphoxide, DMF = dimethylformamide, dtc⁻ = diethyldithiocarbamate, diphos = P,P',P',P'-tetraphenylethylenediphosphine. salen²⁻ = N,N'-bis(salicylaldehyde)-ethylene-diiimine-dianion; ^b unless otherwise stated Bu₄NPF₆ was used as supporting electrolyte; ^c values of the half-wave potentials are indicated in volts and related to that of bis-biphenyl-

which is due to the decomposition processes either of the starting materials or the products of the first reduction. The dipy complex shows a third wave which cannot be ascribed to the ligand reduction and which is located at the same potential as the second wave of the dinitrosyl complex.

Both with mono- and dinitrosyl complexes the half-wave potential values measured against the $E_{\frac{1}{2}\text{BBCr}}$ in the same medium are more negative in THF than in CH_2Cl_2 . On the other hand in THF are the complexes less stable than in CH_2Cl_2 . The influence of the supporting electrolyte was tested only in one case (No 26 and 27) and a difference of 50 mV in $E_{\frac{1}{2}}$ was found between Bu_4NClO_4 and Bu_4NPF_6 . Similar effects of the supporting electrolyte were found in other cases, too¹³.

iii) Complexes containing the fragment $\{\text{Mo}(\text{NO})\}$ ⁶. Only two complexes of this class were examined (No 35–37). The diphos complex No 35, 36 exhibits a reversible, 1-electron oxidation wave, whereas the complex No 37 containing in the coordination sphere stronger π -acceptors CO and PPh_3 is neither reduced nor oxidized in the potential range available in CH_2Cl_2 .

ESR Spectra

The ESR spectra were studied with the products of 1-electron reduction of the following selected complexes: $\text{Mo}(\text{NO})\text{dipyCl}_3$, $\text{Mo}(\text{NO})(\text{salen})\text{Cl}$, $\text{Mo}(\text{NO})_2\text{enCl}_2$ and $\text{Mo}(\text{NO})_2\text{dipyCl}_2$. The spectra of the mononitrosyl complexes markedly differ from those of the dinitrosyl complexes both as regards the ESR parameters (Table II) and type of the hyperfine splitting.

The mononitrosyl complexes show spectra consisting of one intense line in the center and 6 less intense lines (Fig. 1). The position and relative intensities of the lines correspond to the interaction of the unpaired electron with the ⁹⁶Mo ($I = 0$; 75% abundance, intense line) and ^{95,97}Mo ($I = 5/2$; 15% and 10% abundance, less intense lines) nuclei, respectively. The splitting constants of the ligands are not detectable. The low value of the g -factors (Table II) indicate that the unpaired electron is localized in a MO composed prevalingly of the metal d -AO. A similarly low value of g -factor (1.95) is reported¹⁴ for the complex $\text{Cs}_2\text{Mo}(\text{NO})\text{Cl}_4(\text{H}_2\text{O})$.

On the other hand the spectra of the dinitrosyl complexes consist of 5 poorly resolved lines with the relative intensities 1 : 2 : 3 : 2 : 1 (Fig. 2). This result indicates the interaction of the unpaired electron with 2 equivalent ¹⁴N ($I = 1$) nuclei. The

chromium cation (BBCr) recorded in the same medium; ^d char. = character of the electrode process denoted in the following way: red = reduction, ox = oxidation, r = reversible, ir = irreversible, ri = reversible with rapid inactivation of the electrode reaction product, sr = semireversible (indicating processes with the slope S of the log analysis of the 1-electron polarographic wave in the range $60 \text{ mV} < S < 80 \text{ mV}$); ^e number of electrons derived from comparison with the 1-electron wave of BBCr in the same medium.

spectrum shows no indication of an electron interaction with the molybdenum nucleus. The conclusion that in this case the odd electron resides in a MO having prevalingly NO-ligand character is corroborated by the value of the g -factor which is close to that of the free electron.

TABLE II

ESR parameters of 1-electron reduction products of selected molybdenum-nitrosyl complexes

Original complex	ESR Parameters
Mo(NO)dipy Cl ₃	$g = 1.979$ $a_{\text{Mo}} = 4.9 \pm 0.02 \text{ mT}$
Mo(NO)(salen)Cl	$g = 1.967$ $a_{\text{Mo}} = 4.75 \pm 0.02 \text{ mT}$
Mo(NO) ₂ en Cl ₂	$g = 2.001$ $a_{\text{N}} = 0.79 \pm 0.01 \text{ mT}$
Mo(NO) ₂ dipy Cl ₂	$g = 2.009$ $a_{\text{N}} = 0.775 \pm 0.006 \text{ mT}$

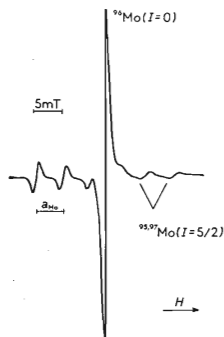


FIG. 1

ESR spectrum of the species generated by electrochemical 1-electron reduction of Mo(NO)(salen)Cl in CH_2Cl_2 - Bu_4NPF_6 at 298 K

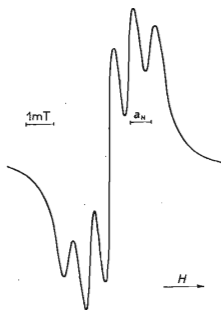


FIG. 2

ESR spectrum of the species generated by electrochemical 1-electron reduction of Mo(NO)₂(dipy)Cl₂ in CH_2Cl_2 - Bu_4NPF_6 at 298 K

DISCUSSION

As follows from the above mentioned survey the decisive characteristic for the molybdenum nitrosyl complexes studied is the configuration of the fragment $\{\text{Mo}(\text{NO})_x\}^n$. Hence it is of interest to consider more closely the character of the corresponding redox orbitals. For mononitrosyl complexes with the fragment $\{\text{M}(\text{NO})\}^n$ where $n \leq 6$ the M-N-O bond should be linear¹² which is corroborated in the series of complexes under investigation by the value of ν_{NO} ranging around 1700 cm^{-1} (resp.⁶). Thus all mononitrosyl complexes studied in this paper may be considered to contain formally the coordinated NO^+ group. The generally accepted molecular orbital diagram for six-coordinate complexes containing a linear MNO group is depicted in Fig. 3. In our series of complexes containing the fragment $\{\text{Mo}(\text{NO})\}^4$ (No 17–34) the levels are fully occupied through $2e$ so that in the reduction process the additional electrons must enter the level $1b_2$ which has the character of metal d_{xy} orbital. This is in full agreement with our ESR findings according to which in the 1-electron reduction products of the mononitrosyl complexes the unpaired electron is localized on the central metal atom. There is reason to believe that the second electron enters the same $1b_2$ level so that the two-step reduction of the studied mononitrosyl complexes $\text{Mo}^{\text{II}}(\text{NO}^+)\text{L}_2\text{Cl}_3$ can be viewed formally as reduction of divalent

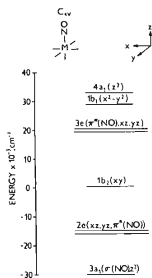


FIG. 3

The molecular orbital diagram for six-coordinate complexes with linear MNO groups. The energies of the molecular orbitals were estimated from the spectra of $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ (ref.¹²)

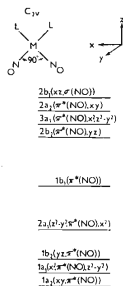


FIG. 4

The molecular orbital diagram for *cis*-square planar dinitrosyl complexes. The metal d orbitals were obtained from the conventional d orbitals by the transformation $x \rightarrow z$, $y \rightarrow y$, $z \rightarrow x$ (ref.¹²)

to zerovalent molybdenum species leaving the nitrosyl group formally in the NO^+ state. Compared with the dinitrosyl-molybdenum(O) complexes the d^4 -configuration of the molybdenum in the mononitrosyl complexes corresponding to the oxidation state +2 of the central atom explains the easier reducibility of these complexes. The energy scale in Fig. 3 serves just for indication of the relative separation of the energy levels and the position of the zero energy is quite arbitrary. However, from theoretical estimates made by Fenske and coworkers¹⁵ it may be extrapolated that for neutral molybdenum mononitrosyl complexes the $1b_2$ level is situated in the vicinity of the zero energy or slightly above unless it is stabilized by the presence of stabilizing ligands in the xy plane. Hence follows that the occupancy of this level will lower the stability of the complexes which is in agreement with the experimental findings of the decomposition of the reduction products except for complexes with chelate ligands, such as dipy , salen^{2-} and dtc^- .

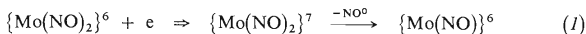
For the same reason the investigated $\{\text{Mo}(\text{NO})\}^6$ complexes No 35–37 are stable, containing ligands which stabilize the formally zero-valent molybdenum species. The $3e$ level is evidently too high in the neutral molybdenum complexes to be reached in a reduction process so that only a removal of electrons from the fully occupied $1b_2$ is possible. In accordance with this a reversible oxidation of the diphos complex (No 35 and 36) is observed. The coordination sphere of the other $\{\text{Mo}(\text{NO})\}^6$ complex, $\text{Mo}(\text{NO})(\text{CO})_2(\text{PPh}_3)_2\text{Cl}$, is composed of strong π -acceptors which lower the electron density in the $1b_2$ level to such an extent that the oxidation is impossible in the potential range available with the mercury electrode and thus no depolarization effects of this complex are observed.

Although the structure of the dinitrosyl complexes studied in this paper is not known, in analogy with the known structure of the closely related complex $\text{Mo}(\text{NO})_2 \cdot (\text{PPh}_3)_2\text{Cl}_2$ (ref.¹⁶) it can be assumed that the NO groups are in *cis*-position. The energy level situation in these complexes is best approximated by the diagram shown in Fig. 4 which applies for *cis*-square planar complexes with C_{2v} symmetry¹². The addition of two ligands along the y -axis in the six-coordinate complex makes the $2a_1$ orbital strongly antibonding. In the present series of dinitrosyl complexes containing the fragment $\{\text{Mo}(\text{NO})_2\}^6$ the levels are fully occupied through $1b_2$ and the further electrons accepted in the reduction process are accommodated in the $2a_1$ level which has a significant $\pi^*(\text{NO})$ contribution or in the $1b_1$ orbital in case that the addition of two ligands along the y -axis brings about energetic interchange of the levels $2a_1$ and $1b_1$. Our ESR results indicate that the $\pi^*(\text{NO})$ contribution in the frontier orbital into which the electron enters must be very high since no interaction of the odd electron with the molybdenum nucleus was detected in the 1-electron reduction products. Thus it can be concluded that in our series of dinitrosyl complexes which can be formally viewed as $\text{Mo}^0(\text{NO})_2\text{L}_2\text{Cl}_2$ species the site of the reduction is localized on the coordinated NO^+ groups.

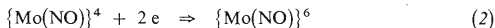
In the light of the above discussed results it is possible to rationalize the reaction path in which the catalytically active species are formed from the mono- and dinitrosyl complexes by the action of the co-catalyst. The electrochemical results show that the potential region in which the dinitrosyl complexes are reduced by the first electron nearly coincides with that in which the mononitrosyls are reduced by the second electron.

Assuming that the reduction power of the co-catalyst is strong enough to reach this region we can roughly formulate the reaction path for each of the series of complexes.

Dinitrosyls $\text{Mo}^0(\text{NO})_2\text{Cl}_2\text{L}_2$:



Mononitrosyls $\text{Mo}(\text{II})(\text{NO})\text{Cl}_3\text{L}_2$:



Both routes lead to the same $\{\text{Mo}(\text{NO})\}^6$ moiety which in presence of the co-catalyst is probably stabilized by a co-catalyst component. If the Lewis acidity of the co-catalyst is sufficiently high the dinitrosyl complexes can split off the NO ligand as NO^+ (e.g. in form of NOCl) without preceding reduction step. This reaction route leads to the same moiety $\{\text{Mo}(\text{NO})\}^6$, too.

When comparing the electrochemical redox behaviour of the molybdenum nitrosyl complexes with their catalytic activity in 2-pentene metathesis ($\text{C}_2\text{H}_5\text{AlCl}_2$ used as co-catalyst)⁶ it is seen that the electrochemically "well-behaved" complexes, i.e. those containing ligands stabilizing different oxidation states and thus affording well developed reversible 1-electron reduction waves are the worst catalysts. Thus e.g. with the dipy and salen complexes which yield the best polarographic pattern from all complexes studied the conversion after 5 min is 0 and 13 mol%, respectively, whereas with complexes containing poor ligands such as DMF, DMSO, HMPT etc. and showing polarographically pronounced decomposition of the reduction products the conversion amounts to the maximum available value round 50 mol%. The dinitrosyl complexes which in general yield better developed polarographic pattern than the mononitrosyl are in comparison with the latter ones much weaker catalysts. These results show that the decisive factor for the formation of the catalytically active species is over-all chemical lability of the complex, i.e. its ability to undergo decomposition except for the fragment $\text{Mo}(\text{NO})$ in the interaction with the co-catalyst. The redox properties of the complexes play only a secondary role even if the fundamental process by which the catalytically active species is formed is the reduction of the original complex.

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