

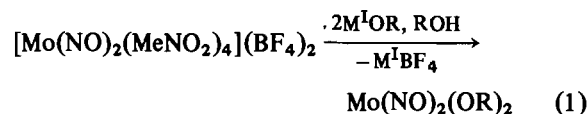
Synthesis and Properties of Dialkoxydinitrosyl-molybdenum Compounds and their Derivatives

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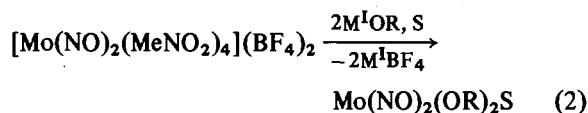
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The reactions of $[\text{Mo}(\text{NO})_2(\text{MeNO}_2)_4](\text{BF}_4)_2$ with M^IOR ($\text{M}^I = \text{Li}, \text{Na}$; $\text{R} =$ bulky groups) in suitable alcohols produce the dinitrosylmolybdenum compounds of the empirical formula $\text{Mo}(\text{NO})_2(\text{OR})_2$



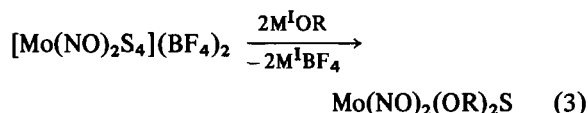
$\text{R} =$ bulky groups

Such a reaction produced the $\text{Mo}(\text{NO})_2(\text{O}-i\text{-Pr})_2$ complex. When R is one of the less sterically demanding groups, e.g. $\text{R} = \text{Me}$ or Et , compounds of the empirical formula $\text{Mo}(\text{NO})_2(\text{OR})_2\text{S}$ would arise ($\text{S} =$ donor solvent—the reaction medium)



$\text{R} = n$ -alkyl groups

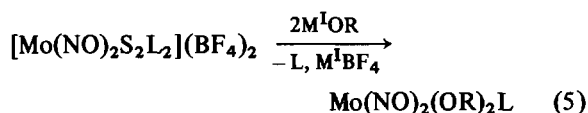
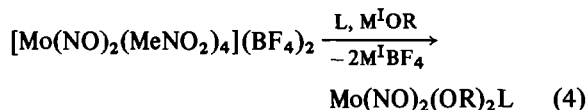
The equivalent reaction is



$\text{R} = n$ -alkyl groups

In reaction (2) and reaction (3) compounds of the empirical formula $\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{EtOH})$ and $\text{Mo}(\text{NO})_2(\text{OMe})_2(\text{MeCN})$ were obtained, respectively.

Reactions (4) and (5) can be general reactions to obtain other dialkoxydinitrosyl derivatives of molybdenum, e.g. $\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{OPPh}_3)$



The compounds obtained in reactions (2)–(5) are green ($\text{Mo}(\text{NO})_2(\text{OMe})_2(\text{MeCN})$ is brown–green) and react very slowly with the air, moisture and

oxygen. They are insoluble in alkanes and easily soluble in $\text{C}_n\text{H}_{2(n+1)-m}\text{Cl}_m$, $\text{C}_6\text{H}_5\text{Cl}$ ($\text{Mo}(\text{NO})_2(\text{OMe})_2(\text{MeCN})$ is less soluble in the chlorosubstituted solvents) and C_6H_6 except for $\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{OPPh}_3)$ and $\text{Mo}(\text{NO})_2(\text{OMe})_2(\text{MeCN})$ which are sparingly soluble in the latter solvent.

A cryoscopic molecular weight determination suggests the existence of tetrameric $\{\text{Mo}(\text{NO})_2(\text{O}-i\text{-Pr})_2\}_4$, octameric $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{EtOH})\}_8$ and dimeric $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{PPh}_3)\}_2$ species. $\text{Mo}(\text{NO})_2(\text{OMe})_2(\text{MeCN})_2$ is most likely the polymeric compound.

At 150°C *in vacuo* (5×10^{-3} mm Hg) $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{EtOH})\}_n$ loses EtOH to produce the brown compound formulated as $\{\text{Mo}(\text{NO})_2(\text{OEt})_2\}_n$. Undoubtedly, it is highly polymerized. It is insoluble in alkenes and benzene, very sparingly soluble in $\text{C}_6\text{H}_5\text{Cl}$ and $\text{C}_n\text{H}_{2(n+1)-m}\text{Cl}_m$.

The IR spectra of all these complexes exhibit two strong bands in the $\nu(\text{NO})$ region attributable to *cis*-nitrosyl ligands [1, 2]. The character of the spectra in the $\nu(\text{OR})$ region corresponds to the polymeric structure [3].

All of the complexes are diamagnetic and give a very complex ^1H NMR spectra (at 25°C). The lack of well resolved resonances of terminal and bridging alkoxy groups ($\text{R} = \text{Et}, \text{O}-i\text{-Pr}$) is probably due to the terminal \rightleftharpoons bridge OR ligand exchange [4, 5]. For $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{EtOH})\}_n$ no resonances of OH groups were identified.

In the ^{13}C NMR spectra of $\{\text{Mo}(\text{NO})_2(\text{O}-i\text{-Pr})_2\}_4$ and $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{EtOH})\}_8$ (at 25°C) four methyne and nine methylene carbon signals were obtained, respectively. The ^{31}P NMR spectrum of $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{OPPh}_3)\}_2$ exhibits only one singlet. IR and NMR data are given in 'Experimental'.

Up to now obtained data do not allow us to propose the univocal structure of these complexes, because a number of structures may be ruled out by these observations.

These complexes form with EtAlCl_2 the catalytic systems active in the metathesis of pentene-2. The metathesis equilibrium [6] was established after a reaction time of 15 min for $\{\text{Mo}(\text{NO})_2(\text{O}-i\text{-Pr})_2\}_n$ and $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{EtOH})\}_n$, 5 min for $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{OPPh}_3)\}_2$ and only 1 min for $\{\text{Mo}(\text{NO})_2(\text{OMe})_2(\text{MeCN})\}_n$.

Experimental

All reactions were carried out under a dried and purified argon atmosphere. The $[\text{Mo}(\text{NO})_2(\text{MeNO}_2)_4](\text{BF}_4)_2$ and $[\text{Mo}(\text{NO})_2(\text{MeCN})_2(\text{OPPh}_3)_2](\text{BF}_4)_2$ complexes [7] and $[\text{Mo}(\text{NO})_2(\text{MeCN})_4](\text{BF}_4)_2$ [8] were prepared by published methods.

IR: Specord M80; ^1H NMR: Tesla BS576A; ^{13}C NMR: Jeol JNM-PS-100; Molecular weight: Perkin-Elmer 115; Magnetic susceptibility: Gouy methods; GLC: Chromatograph N-503, ELPO.

Synthesis of $\{\text{Mo}(\text{NO})_2(\text{O-i-Pr})_2\}_n$

To $[\text{Mo}(\text{NO})_2(\text{MeNO}_2)_4](\text{BF}_4)_2$ (5 mmol) dissolved at 0°C in *i*-PrOH (10 ml), the solution of $\text{M}^1\text{O-i-Pr}$ ($\text{M}^1 = \text{Li}$ or Na ; 10.1 mmol) in *i*-PrOH was slowly added at 0°C . At that temperature the reaction mixture was stirred for 15 min. The solution was filtered off and removed under vacuum. The complex was extracted from the remnant with a small amount of CH_2Cl_2 . The green complex was precipitated with hexane.

Synthesis of $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{EtOH})\}_n$

This complex was obtained in a similar manner to that described above, *i.e.* by treatment of $[\text{Mo}(\text{NO})_2(\text{MeNO}_2)_4](\text{BF}_4)_2$ with M^1OEt ($\text{M}^1 = \text{Li}$ or Na) in EtOH at 0°C .

Synthesis of $\{\text{Mo}(\text{NO})_2(\text{OMe})_2(\text{MeCN})\}_n$

To $[\text{Mo}(\text{NO})_2(\text{MeCN})_4](\text{BF}_4)_2$ (2.50 mmol) in MeCN (5 ml), cooled down to 0°C , was added dropwise NaOMe (5.06 mmol) in MeOH. The resulting yellow-green solution was stirred for 15 min at 0°C . Subsequent procedure as above.

Synthesis of $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{OPPh}_3)_2\}_n$

Procedure A. $[\text{Mo}(\text{NO})_2(\text{MeNO}_2)_4](\text{BF}_4)_2$ (2.44 mmol) dissolved in MeNO_2 (20 ml) was treated with Ph_3PO (4.9 mmol). The solution was stirred for 30 min, next cooled to 0°C and treated with M^1OEt ($\text{M}^1 = \text{Li}$ or Na ; 5.0 mmol) in EtOH. After 15 min the solution was filtered off and removed under vacuum. The solids were treated with CH_2Cl_2 (10 ml) and the CH_2Cl_2 -insoluble part was filtered off. The green complex was precipitated with hexane from the filtrate. The product was purified by repeated precipitation from CH_2Cl_2 solutions with hexane.

Procedure B. To the cooled (0°C) solution of $[\text{Mo}(\text{NO})_2(\text{MeCN})_2(\text{OPPh}_3)_2](\text{BF}_4)_2$ (2.5 mmol) in EtOH (10 ml), the solution of M^1OEt ($\text{M}^1 = \text{Li}$ or Na ; 5.10 mmol) in EtOH was slowly added. Procedure A was then followed.

Analytical Data

Calc. for $\text{Mo}(\text{NO})_2(\text{O-i-Pr})_2$: Mo, 35.00; N, 10.22; C, 26.29; H, 5.15. Found: Mo, 34.89; N, 10.01; C, 26.39; H, 5.30%. Calc. for $\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{EtOH})$: Mo, 32.84; N, 9.59; C, 24.67; H, 5.52. Found: Mo, 32.76; N, 9.30; C, 24.41; H, 5.70%. Calc. for $\text{Mo}(\text{NO})_2(\text{OMe})_2(\text{MeCN})$: Mo, 37.03; N, 16.22; C, 18.54; H, 3.50. Found: Mo, 36.89; N, 16.01; C, 18.70; H, 3.89%. Calc. for $\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{OPPh}_3)$: Mo, 18.30; N, 5.34; C, 50.39; H, 4.81;

P, 5.91. Found: Mo, 18.22; N, 5.01; C, 50.63; H, 5.02; P, 6.02%. Calc. for $\text{Mo}(\text{NO})_2(\text{OEt})_2$: Mo, 38.99; N, 11.38; C, 19.52; H, 4.10. Found: Mo, 38.91; N, 11.15; C, 19.40; H, 4.41%.

Infrared Data

IR data obtained in Nujol mulls. $\{\text{Mo}(\text{NO})_2(\text{O-i-Pr})_2\}_n$: $2 \times \nu_s(\text{NO})$, 3540vw; $\nu_s + \nu_{\text{as}}(\text{NO})$, 3405w; $\nu(\text{NO})$, 1772s, 1630vs, br; $\nu(\text{O-i-Pr})$, 1110s, 1030m, 944s; also: 1265vw, 1234w, 1170sh, 1164m, 830m, 770w, 650m, 610sh, 586m, 500sh, 460m, br. $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{EtOH})\}_n$: $2 \times \nu_s(\text{NO})$, 3480vw; $\nu_s + \nu_{\text{as}}(\text{NO})$, 3352w; $\nu(\text{OH})$, 3250br; $\nu(\text{NO})$, 1740vs, 1616vs, br; $\nu(\text{O-Et})$, 1083s, 1050sh, 1027vs; also: 1149m, 970sh, 872s, 750sh, 644m, 610sh, 565s, br, 530sh, 475m. $\{\text{Mo}(\text{NO})_2(\text{OEt})_2\}_n$: $2 \times \nu_s(\text{NO})$, 3495vw; $\nu_s + \nu_{\text{as}}(\text{NO})$, 3365w; $\nu(\text{NO})$, 1745s, 1620vs, br; $\nu(\text{O-Et})$, 1080s, 1030vs; also: 1152m, 970sh, 880m, 760sh, 630m, 610sh, 580s, br, 520sh, 460m, 425sh. $\{\text{Mo}(\text{NO})_2(\text{OMe})_2(\text{MeCN})\}_n$: $2 \times \nu_s(\text{NO})$, 3510vw; $\nu_s + \nu_{\text{as}}(\text{NO})$, 3360vw; $\nu(\text{CN})$, 2280vw; $\nu(\text{NO})$, 1753s, 1605vs; $\nu(\text{O-Me})$, 1065s, 1020vs; also: 1223m, 1163m, 966sh, 840m, 765w, 650w, 590m, 490s, br. $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{OPPh}_3)_2\}_n$: $\nu(\text{NO})$, 1750s, 1610vs, br; $\nu(\text{P-O})$, 1120s, 1045sh; $\nu(\text{O-Et})$, 1080s, 1025s; also: 2150w, 1980vw, 1310w, 1274w, 1140w, 985m, 970m, 880m, 850sh, 740m, 685m, 615w, 580sh, 520s, br, 450m.

NMR Data

^1H NMR data were obtained in CDCl_3 at 25°C relative to Me_4Si . $\{\text{Mo}(\text{NO})_2(\text{O-i-Pr})_2\}_n$: $\delta(\text{CH}_3)$ 1.21; $\delta(\text{CH})$ 4.24, 4.55. $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{EtOH})\}_n$: $\delta(\text{CH}_3)$ 1.22; $\delta(\text{CH}_2)$ 4.23. $\{\text{Mo}(\text{NO})_2(\text{OEt})_2\}_n$: $\delta(\text{CH}_3)$ 1.27; $\delta(\text{CH}_2)$ 4.17. $\{\text{Mo}(\text{NO})_2(\text{OMe})_2(\text{MeCN})\}_n$: $\delta(\text{CH}_3\text{CN})$ 1.96, 2.15; $\delta(\text{OCH}_3)$ 3.45, 3.65, 3.85, 4.00. $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{OPPh}_3)_2\}_n$: $\delta(\text{CH}_3)$ 1.19; $\delta(\text{CH}_2)$ 4.00, 4.20; $\delta(\text{C}_6\text{H}_5)$ 7.3–7.8.

^{13}C NMR data were obtained at 25°C in benzene- d_6 relative to Me_4Si . $\{\text{Mo}(\text{NO})_2(\text{O-i-Pr})_2\}_n$: $\delta(\text{C-methyl})$ 24.12, 24.42, 25.61, 25.91, 26.29; $\delta(\text{C-methylene})$ 75.80(1), 81.94(1), 83.45(1), 84.25(1). $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{EtOH})\}_n$: $\delta(\text{C-methyl})$ 19.30, 21.85; $\delta(\text{C-methylene})$ 58.82(1), 64.72(1), 68.38(1), 69.65(2), 70.18(2), 70.92(2), 75.70(1), 76.36(1), 77.10(1).

The ^{31}P NMR spectrum of $\{\text{Mo}(\text{NO})_2(\text{OEt})_2(\text{OPPh}_3)_2\}_n$ was obtained at 25°C in CDCl_3 relative to H_3PO_4 . $\delta(\text{P})$ 45.06(s).

Metathesis Reaction

EtAlCl_2 (1.50 mmol) in chlorobenzene was injected into the cooled down (0°C) solution of the complex (0.25 mmol) in chlorobenzene (5 ml). After 15 min (room temperature) pentene-2 (100 mmol) was added to the solution. Samples taken after t_r (reaction time) were hydrolyzed to stop the reaction and analyzed.

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