Inorganica Chimica Acta, 149 (1988) 165–167

Synthesis and Properties of Dialkoxydinitrosylmolybdenum Compounds and their Derivatives

A. KELLER

Institute of Chemistry, University of Wrocław, Poland

(Received April 7, 1988)

The reactions of $[Mo(NO)_2(MeNO_2)_4](BF_4)_2$ with M^IOR (M^I = Li, Na; R = bulky groups) in suitable alcohols produce the dinitrosylmolybdenum compounds of the empirical formula $Mo(NO)_2(OR)_2$

$$[Mo(NO)_2(MeNO_2)_4](BF_4)_2 \xrightarrow[-M^IBF_4]{2M^IOR,\ ROH} Mo(NO)_2(OR)_2 \tag{1}$$

R = bulky groups

Such a reaction produced the $Mo(NO)_2(O\text{-}i\text{-}Pr)_2$ complex. When R is one of the less sterically demanding groups, e.g. R = Me or Et, compounds of the empirical formula $Mo(NO)_2(OR)_2S$ would arise (S = donor solvent—the reaction medium)

$$[Mo(NO)_2(MeNO_2)_4](BF_4)_2 \xrightarrow[-2M^IBF_4]{2M^IOR,\ S} Mo(NO)_2(OR)_2S \tag{2}$$

R = n-alkyl groups

The equivalent reaction is

$$[Mo(NO)_2S_4](BF_4)_2 \xrightarrow[-2M^IBF_4]{2M^IOR} Mo(NO)_2(OR)_2S \tag{3}$$

R = n-alkyl groups

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

Reactions (4) and (5) can be general reactions to obtain other dialkoxydinitrosyl derivatives of molybdenum, e.g. $Mo(NO)_2(OEt)_2(OPPh_3)$

$$[Mo(NO)_2(MeNO_2)_4](BF_4)_2 \xrightarrow[-2M^IBF_4]{L,\ M^IOR} Mo(NO)_2(OR)_2L \tag{4}$$

$$[Mo(NO)_2S_2L_2](BF_4)_2 \xrightarrow[-L,\ M^IBF_4]{2M^IOR} Mo(NO)_2(OR)_2L \tag{5}$$

The compounds obtained in reactions (2)–(5) are green ($Mo(NO)_2(OMe)_2(MeCN)$ is brown–green) and react very slowly with the air, moisture and oxygen. They are insoluble in alkanes and easily soluble in $C_nH_{2(n+1)-m}Cl_m$, C_6H_5Cl ($Mo(NO)_2(OMe)_2(MeCN)$ is less soluble in the chlorosubstituted solvents) and C_6H_6 except for $Mo(NO)_2(OEt)_2(OPPh_3)$ and $Mo(NO)_2(OMe)_2(MeCN)$ which are sparingly soluble in the latter solvent.

A cryoscopic molecular weight determination suggests the existence of tetrameric $\{Mo(NO)_2(O\text{-}i\text{-}Pr)_2\}_4$, octameric $\{Mo(NO)_2(OEt)_2(EtOH)\}_8$ and dimeric $\{Mo(NO)_2(OEt)_2(PPh_3)\}_2$ species. $Mo(NO)_2(OMe)_2(MeCN)_2$ is most likely the polymeric compound.

At 150 °C *in vacuo* (5×10^{-3} mm Hg) $\{Mo(NO)_2(OEt)_2(EtOH)\}_n$ loses EtOH to produce the brown compound formulated as $\{Mo(NO)_2(OEt)_2\}_n$. Undoubtedly, it is highly polymerized. It is insoluble in alkenes and benzene, very sparingly soluble in C_6H_5Cl and $C_nH_{2(n+1)-m}Cl_m$.

The IR spectra of all these complexes exhibit two strong bands in the ν(NO) region attributable to *cis*-nitrosyl ligands [1, 2]. The character of the spectra in the ν(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 (R = Et, O-i-Pr) is probably due to the terminal $\rightleftarrows$ bridge OR ligand exchange [4, 5]. For $\{Mo(NO)_2(OEt)_2(EtOH)\}_n$ no resonances of OH groups were identified.

In the ^{13}C NMR spectra of $\{Mo(NO)_2(O\text{-}i\text{-}Pr)_2\}_4$ and $\{Mo(NO)_2(OEt)_2(EtOH)\}_8$ (at 25 °C) four methyne and nine methylene carbon signals were obtained, respectively. The ^{31}P NMR spectrum of $\{Mo(NO)_2(OEt)_2(OPPh_3)\}_2$ 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 $\{Mo(NO)_2(O\text{-}i\text{-}Pr)_2\}_n$ and $\{Mo(NO)_2(OEt)_2(EtOH)\}_n$, 5 min for $\{Mo(NO)_2(OEt)_2(OPPh_3)\}_2$ and only 1 min for $\{Mo(NO)_2(OMe)_2(MeCN)\}_n$.

Experimental

All reactions were carried out under a dried and purified argon atmosphere. The $[Mo(NO)_2(MeNO_2)_4](BF_4)_2$ and $[Mo(NO)_2(MeCN)_2(OPPh_3)_2](BF_4)_2$ complexes [7] and $[Mo(NO)_2(MeCN)_4](BF_4)_2$ [8] were prepared by published methods.

0020-1693/88/$3.50

IR: Specord M80; ^{1}H 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 $\{Mo(NO)_2(O\text{-}i\text{-}Pr)_2\}_n$

To $[Mo(NO)_2(MeNO_2)_4](BF_4)_2$ (5 mmol) dissolved at 0 °C in i-PrOH (10 ml), the solution of M^{I}O-i-Pr (M^{I} = 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 $\{Mo(NO)_2(OEt)_2(EtOH)\}_n$

This complex was obtained in a similar manner to that described above, *i.e.* by treatment of $[Mo(NO)_2(MeNO_2)_4](BF_4)_2$ with M^{I}OEt (M^{I} = Li or Na) in EtOH at 0 °C.

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

To $[Mo(NO)_2(MeCN)_4](BF_4)_2$ (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 $\{Mo(NO)_2(OEt)_2(OPPh_3)\}_2$

Procedure A. $[Mo(NO)_2(MeNO_2)_4](BF_4)_2$ (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^{I}OEt (M^{I} = 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 $[Mo(NO)_2(MeCN)_2(OPPh_3)_2](BF_4)_2$ (2.5 mmol) in EtOH (10 ml), the solution of M^{I}OEt (M^{I} = Li or Na; 5.10 mmol) in EtOH was slowly added. Procedure A was then followed.

Analytical Data

Calc. for $Mo(NO)_2(O\text{-}i\text{-}Pr)_2$: 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 $Mo(NO)_2(OEt)_2(EtOH)$: 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 $Mo(NO)_2(OMe)_2(MeCN)$: 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 $Mo(NO)_2(OEt)_2(OPPh_3)$: 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 $Mo(NO)_2(OEt)_2$: 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. $\{Mo(NO)_2(O\text{-}i\text{-}Pr)\}_n$: $2 \times \nu_s$(NO), 3540vw; $\nu_s + \nu_{as}$(NO), 3405w; ν(NO), 1772s, 1630vs, br; ν(O-i-Pr), 1110s, 1030m, 944s; also: 1265vw, 1234w, 1170sh, 1164m, 830m, 770w, 650m, 610sh, 586m, 500sh, 460m, br. $\{Mo(NO)_2(OEt)_2(EtOH)\}_n$: $2 \times \nu_s$(NO), 3480vw; $\nu_s + \nu_{as}$(NO), 3352w; ν(OH), 3250br; ν(NO), 1740vs, 1616vs, br; ν(O–Et), 1083s, 1050sh, 1027vs; also: 1149m, 970sh, 872s, 750sh, 644m, 610sh, 565s, br, 530sh, 475m. $\{Mo(NO)_2(OEt)_2\}_n$: $2 \times \nu_s$(NO), 3495vw; $\nu_s + \nu_{as}$(NO), 3365w; ν(NO), 1745s, 1620vs, br; ν(O–Et), 1080s, 1030vs; also: 1152m, 970sh, 880m, 760sh, 630m, 610sh, 580s, br, 520sh, 460m, 425sh. $\{Mo(NO)_2(OMe)_2(MeCN)\}_n$: $2 \times \nu_s$(NO), 3510vw; $\nu_s + \nu_{as}$(NO), 3360vw; ν(CN), 2280vw; ν(NO), 1753s, 1605vs; ν(O–Me), 1065s, 1020vs; also: 1223m, 1163m, 966sh, 840m, 765w, 650w, 590m, 490s, br. $\{Mo(NO)_2(OEt)_2(OPPh_3)\}_2$: ν(NO), 1750s, 1610vs, br; ν(P–O), 1120s, 1045sh; ν(O–Et), 1080s, 1025s; also: 2150w, 1980vw, 1310w, 1274w, 1140w, 985m, 970m, 880m, 850sh, 740m, 685m, 615w, 580sh, 520s, br, 450m.

NMR Data

^{1}H NMR data were obtained in $CDCl_3$ at 25 °C relative to Me_4Si. $\{Mo(NO)_2(O\text{-}i\text{-}Pr)\}_n$: $\delta(CH_3)$ 1.21; δ(CH) 4.24, 4.55. $\{Mo(NO)_2(OEt)_2(EtOH)\}_n$: $\delta(CH_3)$ 1.22; $\delta(CH_2)$ 4.23. $\{Mo(NO)_2(OEt)_2\}_n$: $\delta(CH_3)$ 1.27; $\delta(CH_2)$ 4.17. $\{Mo(NO)_2(OMe)_2(MeCN)\}_n$: $\delta(CH_3CN)$ 1.96, 2.15; $\delta(OCH_3)$ 3.45, 3.65, 3.85, 4.00. $\{Mo(NO)_2(OEt)_2(OPPh_3)\}_2$: $\delta(CH_3)$ 1.19; $\delta(CH_2)$ 4.00, 4.20; $\delta(C_6H_5)$ 7.3–7.8.

^{13}C NMR data were obtained at 25 °C in benzene-d_6 relative to Me_4Si. $\{Mo(NO)_2(O\text{-}i\text{-}Pr)_2\}_n$: δ(C-methyl) 24.12, 24.42, 25.61, 25.91, 26.29; δ(C-methyne) 75.80(1), 81.94(1), 83.45(1), 84.25(1). $\{Mo(NO)_2(OEt)_2(EtOH)\}_n$: δ(C-methyl) 19.30, 21.85; δ(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 $\{Mo(NO)_2(OEt)_2(OPPh_3)\}_2$ was obtained at 25 °C in $CDCl_3$ relative to H_3PO_4. δ(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.

References

1 M. O. Visscher and K. G. Caulton, *J. Am. Chem. Soc., 94,* 5923 (1972).

2 D. Ballivet-Tkatchenko, C. Bremard, F. Abraham and G. Nowogrocki, *J. Chem. Soc., Dalton Trans.,* 1137 (1983).

3 D. C. Bradley, *Proc. Symp. Coord. Chem.,* 1964 (1965).

4 M. H. Chisholm, F. A. Cotton, M. W. Extine and R. L. Kelly, *J. Am. Chem. Soc., 100,* 3354 (1978).

5 D. C. Bradley, C. W. Newing, M. H. Chisholm, R. L. Kelly, D. A. Haitko, D. Little, F. A. Cotton and P. E. Fanwick, *Inorg. Chem., 19,* 3010 (1980).

6 W. B. Hughes, *J. Am. Chem. Soc., 92,* 532 (1970).

7 P. Legzdins and J. C. Oxley, *Inorg. Chem., 23,* 1053 (1984).

8 A. Sen and R. Thomas, *Organometallics, 1,* 1251 (1982).