Inorganica Chimica Acta, *133* (1987) 207–210

Pentanitrosyl Molybdenum Pentakis (Tetrafluoroborate)

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(Received November 26, 1986)

Abstract

Preparation and properties of pentanitrosyl molybdenum pentakis (tetrafluoroborate) are described. The structure was determined by IR and Raman spectroscopy methods. Assignments of fundamental modes were proposed. The applicability of the complex under study as the precatalyst of olefin metathesis reaction was investigated. The homogeneous system $Mo(NO)_5(BF_4)_5/EtAlCl_2$ proved to be a highly active catalyst for 2-pentene metathesis.

Introduction

The structure and properties of the nitrosyl complexes have been extensively studied for many years, because many of these compounds proved to catalyze the diene oligomerization [1, 2], polymerization [3] and metathesis of olefins [4–8]. Very active catalysts of the latter reaction are the mono- and polynitrosyl metal compounds of the Group VIB, mainly molybdenum compounds [8]. Quite a number of mono- and dinitrosyl chromium, molybdenum and tungsten compounds have been studied so far [9]. There are rather few polynitrosyl complexes with more than two coordinated NO groups which are known. They are $[W(NO)_3Br_2]_2$ [10], $W(NO)_3Cl_3$ [11], $W(NO)_4Cl_3$ [12] and $Cr(NO)_4$ [13, 14]. A new molybdenum complex of the unknown coordinated NO group number, formulated as $Mo(NO)_5(BF_4)_5$, has been synthesized. Its structure was determined from IR and Raman spectra. The applicability of this complex as the 2-pentene metathesis reaction precatalyst was examined.

Experimental

All reactions and subsequent manipulations were performed under a dry argon atmosphere. Solvents were distilled under argon from the appropriate drying agents.

Synthesis of $Mo(NO)_5(BF_4)_5$

To $Mo(CO)_6$ solution (2.64 g, 10 mmol) in 1,2-dichloroethane (100 cm^3), the solid $NOBF_4$ (5.02 g, 43 mmol) was added with vigorous stirring. The solution was heated to 60 °C and kept at that temperature for 8 h. Then the temperature was slowly (in 2 h) increased to 80 °C, and the reaction continued for one more hour. A green precipitate settled out and the solution turned light-green. The IR spectrum of the solution displayed two nitrosyl absorption bands at 1815 and 1680 cm^{-1}. Next, the solution was cooled to room temperature, the precipitate was filtered off, washed with 1,2-dichloroethane, repeatedly washed with small amounts of CH_2Cl_2 and dried *in vacuo* (5×10^{-3} mm) for 2 h. 5.35 g of compound was obtained (91.6% yield based on NO).

Anal. Calc. for $Mo(NO)_5(BF_4)_5$, Mo, 14.10; N, 10.29; C, 0.00; H, 0.00. Found: Mo, 14.01; N, 10.91; C, 0.10; H, 0.08%. IR (Nujol mull) ν(NO) 1816(s), 1685(vs).

Instrumentation

Raman spectra were measured on a Jeol IRS-S1 laser instrument on a powder sample in a capillary tube. IR spectra were recorded on Perkin-Elmer spectrophotometers type 181 and 621 in the range 60–400 cm^{-1} in Nujol mulls, and in the range 400–4000 cm^{-1} on the powder compound between KBr or CsJ plates.

Metathesis Reaction

The following procedure was used for the metathesis reaction. 0.047 mmol of $Mo(NO)_5(BF_4)_5$ and 5 cm^3 chlorobenzene were placed in the reaction vessel. A solution of ethylaluminium dichloride in chlorobenzene (0.47 mmol) was injected into the mixture. The catalyst formation reaction was allowed to proceed for 45 min at room temperature with magnetic stirring. Then, from the complex precipitate, insoluble in chlorobenzene, a light-green homogeneous solution was formed. Finally, 18.8 mmol of 2-pentene was injected into the catalyst solution. Samples taken after t_r = 2, 3 and 5 min were hydrolyzed to stop the reaction. Using a cyclohexane as

0020-1693/87/$3.50

the standard for GLPC, the following results were obtained for $t_r = 2$min: 2-pentene, 51 mol%; 3-hexene, 25 mol%; for $t_r = 3$ *min*: 2-pentene, 47 mol%; 3-hexene, 27 mol%; for $t_r = 5$ min: 2-pentene, 46 mol%, 3-hexene, 27 mol%.

Results and Discussion

Preparation and Properties of $Mo(NO)_5(BF_4)_5$

Addition of solid $NOBF_4$ to $Mo(CO)_6$ dissolved in 1,2-dichloroethane produced a green precipitate compound, defined, after chemical analysis, as $Mo(NO)_5(BF_4)_5$ (eqn. (1)).

$$Mo(CO)_6 + 5NOBF_4 \xrightarrow[60-80\,°C]{(ClCH_2)_2} Mo(NO)_5(BF_4)_5 + 6CO \qquad (1)$$

The nitrosyl complex precipitates from solution in high yields. It is favourable to carry out reaction (1) with some excess of $Mo(CO)_6$ so that $NOBF_4$, insoluble in 1,2-dichloroethane, can react completely. The identical product was obtained even at $Mo(CO)_6$: $NOBF_4$ = 1:2 ratio.

Formation of the pentanitrosyl complex proceeds via intermediates (eqn. (2)):

$$Mo(CO)_6 + xNOBF_4 \xrightarrow[20\,°C]{(ClCH_2)_2} [Mo(NO)_x(CO)_{6-x}](BF_4)_x + xCO \qquad (2)$$

This became evident after the reaction had been carried out between 2 and 12 h, at room temperature, at $Mo(CO)_6$:$NOBF_4 \approx 1:2$. Afterwards, the light-green precipitate was filtered off, washed with 1,2-dichloroethane and CH_2Cl_2 and dried *in vacuo*. The IR spectrum of the product presents, besides the bands deriving from the non-reacted $NOBF_4$, the nitrosyl and carbonyl absorption bands (in Nujol) at 1700(sh), 1735(m), 1780(s,br), 1815(sh), 1850(w), 1880(s) and 2165(s) cm^{-1}. It was not possible, however, to determine univocally the precipitate composition. It is most likely a mixture of the intermediates and the final form. In the IR spectrum of the products of eqn. (2) an especially high frequency of $\nu(CO) = 2165$ cm^{-1} (*cf.* ν(free CO) = 2143 cm^{-1}) is amazing. It is most likely the result of a considerable delocalization of the electron density towards the coordinated NO groups, due to the fact that NO groups are more powerful π-acceptors when compared with CO groups in this system.

Legzdins and Oxley [15], who have carried out the reaction between $Mo(CO)_6$ and $NOPF_6$ in CH_2Cl_2 in a 1:1 ratio at room temperature for 40 h, have obtained the product defined as $[Mo(NO)_2(PF_6)_2]_n$, in which the $[Mo(NO)_2]^{2+}$ units are bridged by weakly ligated PF_6^- anions and the NO groups are in a mutual *cis* position. $Mo(NO)_2(PF_6)_2$ is a very air-sensitive, involatile, hygroscopic, green solid.

$Mo(NO)_5(BF_4)_5$ is also highly hygroscopic, but under dry air it could be stored for several hours. Humidity traces initiate its fast decomposition. $Mo(NO)_5(BF_4)_5$ is insoluble in non-donor solvents such as alkanes, benzene, CCl_4, CH_2Cl_2, $C_2H_4Cl_2$, CH_3Cl, but soluble in many coordinating solvents, e.g. CH_3CN, THF etc. The following reactions occur simultaneously [16]:

$$Mo(NO)_5(BF_4)_5 + (n+1)\,\text{solvent} \longrightarrow [Mo(NO)_{5-n}(\text{solvent})_{n+1}](BF_4)_n + nNOBF_4 \qquad (3)$$

$Mo(NO)_5(BF_4)_5$ is insoluble in CH_3NO_2.

Vibrational Spectra

Two structures are possible for $Mo(NO)_5(BF_4)_5$, *i.e.* trigonal bipyramid (point group D_{3h}) or square pyramid (point group C_{4v}). The distribution of internal group vibrations of '$Mo(NO)_5$' on symmetry

TABLE I. Selection Rules for Pentanitrosylmolybdenum Complex

Point group	Total no. of modes and symmetry species[a]	ν(N–O)	ν(Mo–N)	δ(Mo–N–O)	δ(N–Mo–N)
D_{3h}	18; $4A'_1 + A'_2 + 4A''_2 + 6E' + 3E''$	$2A'_1 + A''_2 + E'$ IR IR R R $\nu_{1,2};\nu_3;\nu_{10}$	$2A'_1 + A''_2 + E'$ IR IR R R $\nu_{4,5};\nu_6;\nu_{11}$	$A'_2 + A''_2 + 2E' + 2E''$ n.a. IR IR R R $\nu_7;\nu_8;\nu_{12,13};\nu_{16,17}$	$A''_2 + 2E' + E''$ IR IR R R $\nu_9;\nu_{14,15};\nu_{18}$
C_{4v}	20; $6A_1 + A_2 + 4B_1 + 2B_2 + 7E$	$2A_1 + B_1 + E$ IR IR R R R $\nu_{1,2};\nu_8;\nu_{14}$	$2A_1 + B_1 + E$ IR IR R R R $\nu_{3,4};\nu_9;\nu_{15}$	$A_1 + A_2 + B_1 + B_2 + 3E$ IR n.a. IR R R R R $\nu_5;\nu_7;\nu_{10};\nu_{12};\nu_{16,17,18}$	$A_1 + B_1 + B_2 + 2E$ IR IR R R R R $\nu_6;\nu_{11};\nu_{13};\nu_{19,20}$

[a] All A_1 modes polarised in Raman, all others depolarized.

TABLE II. Vibrational Spectra of $Mo(NO)_5(BF_4)_5$

IR (cm^{-1})	Raman (cm^{-1})	Modes		Assignments
	1912(10)	$2A_1'$	$\nu_1;\nu_2$	ν(NO)
1816s		A_2''	ν_3	
1675s	1672(2½)	E'	ν_{10}	
665w		A_2''	$\nu_6;\nu_8$	ν(Mo–N), δ(Mo–N–O)
470sh		A_2''		
	633(8)	A_1'	ν_4	ν(Mo–N)
	380(6)	A_1'	ν_5	
560m(br)	560(3)	E'	$\nu_{11};\nu_{12};\nu_{13}$	ν(Mo–N), δ(Mo–N–O)
516m	512(4)	E'		
220sh	222	E'		
	320(3)	E''	ν_{16}	δ(Mo–N–O)
	186(1)	E''	ν_{17}	
150sh		A_2''	ν_9	δ(N–Mo–N)
120m	120(2)	E'	ν_{14}	
	104(4)	E''	ν_{18}	
95sh	94(5)	E'	ν_{15}	
1040vs,br	1064	F_2		ν(BF)
	737	A_1		ν(BF)
529m	528	F_2		δ(FBF)
	352	E		δ(FBF)

types is given in Table I. It can be seen that in the case of a square pyramid 13 vibrations ($6A_1 + 7E$) are active in the infrared and 19 vibrations in the Raman spectrum ($6A_1 + 4B_1 + 2B_2 + 7E$). For a trigonal pyramid 10 frequencies should be observed in the IR ($6E' + 4A_2''$) and 13 frequencies in the Raman spectrum ($4A_1 + 6E + 3E''$). The IR and Raman spectra of $Mo(NO)_5(BF_4)_5$ are given in Table II. These spectra univocally confirm the trigonal bipyramid structure of the complex; the IR spectrum displays two strong nitrosyl absorption bands at 1816 and 1675 cm^{-1} (ν_3 and ν_{10}), they are A_2'' and E' modes, respectively. The Raman spectrum also shows two bands in this range. To the first, of 1912 cm^{-1} frequency, were assigned two symmetrically stretching vibrations N–O (ν_1 and ν_2), both A_1' mode. The second, four times less intensive, located at 1672 cm^{-1} is the E' mode active also in IR (ν_{10}).

These relatively high ν(NO) values (*cf.* that of NO(g) at 1888 cm^{-1} [17], for mononitrosyl molybdenum complexes it is near 1600 cm^{-1}) reflect the lack of electron density available at Mo for π backbonding to the NO ligands.

To assign appropriate frequencies to ν(M–N) and δ(M–N–O) vibrations is not easy. The ν(M–N) and δ(M–N–O) modes are presumably strongly coupled and the corresponding bands ought to be considered as the absorption of mixed character. In the discussed case all of the nine vibrations ν(M–N) and δ(M–N–O) are in the range 665–186 cm^{-1}, because it could be supposed that the δ(N–M–N) deformation vibrations correspond to lower frequencies. In the case of $Cr(NO)_4$ this mode is near 100 cm^{-1} [13].

On the basis of intensities in Raman spectra the bands at 633 and 380 cm^{-1} are assigned to the ν_4 and ν_5 vibrations [ν(Mo–N)]; an intense band was assumed to correspond to the A_1' mode. This being so, the bands at 320 and 186 cm^{-1} in Raman spectra must be E'' mode arising from δ(Mo–N–O) modes (ν_{16} and ν_{17}). The bands remaining in the IR and Raman spectra in the range 665–180 cm^{-1} correspond to the Mo–N stretching and Mo–N–O deformation vibrations. Active only in the IR, ν(Mo–N) and δ(Mo–N–O) vibrations (at 665 and 470 cm^{-1} respectively), were A_2'' mode, and those active in both (IR, Raman) spectra are E' mode (in the IR at 560, 512 and 220 cm^{-1} and in the Raman at 560, 512 and 222 cm^{-1}). The assignment of the vibration frequencies for BF_4^- ion was based upon the literature data [18, 19] assuming its local symmetry T_d. For that point group, ν(BF) are F_2 and A_1 modes and δ(FBF) are F_2 and E modes. The A_1 and E modes are active only in the Raman spectrum at 737 and 352 cm^{-1}, respectively, while the F_2 modes are active in both spectra; ν(BF) is near 1050 cm^{-1} and δ(FBF) is near 530 cm^{-1}.

Metathesis Reaction

The metathesis reaction using $Mo(NO)_5(BF_4)_5$ as precatalyst was carried out in the routine system: complex–$RAlCl_2$–olefin. $EtAlCl_2$ was used as the cocatalyst and 2-pentene as the test olefin. The homogeneous system $Mo(NO)_5(BF_4)_5/EtAlCl_2$

proved to be very active in the 2-pentene metathesis reaction. Themodynamic metathesis equilibrium [5] according to eqn. (4) was established after a reaction time (t_r) of 2–3 min.

$$\underset{(46\ \mathrm{mol\%})}{2CH_3{-}CH{=}CH{-}C_2H_5} \rightleftharpoons$$

$$\underset{(27\ \mathrm{mol\%})}{CH_3{-}CH{=}CH{-}CH_3} + \underset{(27\ \mathrm{mol\%})}{C_2H_5CH{=}CH{-}C_2H_5} \qquad (4)$$

The reaction was carried out using a Mo/Al/2-pentene ratio of 1/10/400 in chlorobenzene at room temperature. The complex and cocatalyst had been stirred together for 45 min before the 2-pentene was added. The reaction of the molybdenum nitrosyl complex (insoluble in chlorobenzene) with organoaluminium halides produced the light-green homogeneous solution. The results of studies of the metathesis reaction using mono- and dinitrosyl complexes as precatalysts reveal two basic stages of the active catalyst formation. In the first stage, the adduct is formed, in which the Lewis acid ($RAlCl_2$) is coordinated to the halogen by acid–base complexation [20] and $RAlCl_2$:metal = 2:1 [21, 22]. This adduct, also defined as $[Mo^0Cl(NO)\cdot xAlCl_3\cdot yAl(Et)Cl_2]$ under intramolecular redox isomerization (eqn. (5)) should transform into the nitridomolybdenum(VI) complex,

$$[Mo^0Cl(NO)\cdot xAlCl_3\cdot yAl(Et)Cl_2] \longrightarrow$$

$$[NMo^{VI}(O)Cl\cdot xAlCl_3\cdot yAl(Et)Cl_2] \qquad (5)$$

and become the real precursor compound of the active catalyst [23]. In the second stage alkylation of the metal occurs, followed by the formation of the carbene catalyst, by means of α-elimination [24]. Using $Mo(NO)_5(BF_4)_5$ as the precatalyst, the formation of carbene necessary in the metathesis reaction should proceed via cocatalyst interaction with the coordinated NO groups, followed by alkylation of molybdenum. Detailed studies of this reaction may allow the determination of both the structure of the intermediates and of the active catalyst.

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