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COMPLEX CATALYSIS

XX *. NITROSYLMOLYBDENUM COMPLEXES AS PRECATALYSTS FOR OLEFIN METATHESIS. THE FORMATION AND STABILITY OF A [$Mo^0Cl(NO)$]-CONTAINING INTERMEDIATE AND ITS SIGNIFICANCE FOR THE GENERATION OF THE CATALYTICALLY ACTIVE COMPLEX

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Summary

The reaction of the nitrosylmolybdenum complexes $Mo^{II}Cl_3(NO)(OPPh_3)_2$ and $Mo^0Cl_2(NO)_2(PPh_3)_2$ with $EtAlCl_2$ gives a [$Mo^0Cl(NO)$]-containing intermediate, the formation and further reaction of which were followed by IR-spectroscopy after trapping with CO/PPh_3 and $Et_2NC(S)S-S(S)CNEt_2$, respectively. The dependences on time and temperature of the formation and decomposition of the "[$Mo^0Cl(NO)$]" intermediate were also investigated. By comparison of metathesis activity and the decay of the "[$Mo^0Cl(NO)$]" intermediate, the latter was confirmed to be an essential catalyst precursor from which the actual metathesis catalyst, very probably a nitridomolybdenum complex, is formed.

Introduction

So far three different types of nitrosylmolybdenum complexes, namely $Mo^0Cl_2(NO)_2L_2$ [1,2], $Mo^{II}Cl_3(NO)L_2$ [3,4], and $Mo^0Cl(NO)(CO)_2L_2$ [5] (L = monodentate O-, N-, or P-ligand), have been described which form, on contact with $EtAlCl_2$, highly active, homogeneous catalyst systems for olefin metathesis. As proved by trapping experiments, the reaction of all these various nitrosyl complexes with $EtAlCl_2$ leads via different pathways to a common intermediate: a coordinatively labile, highly reactive "[$Mo^0Cl(NO)$]" complex [6–8]. The latter can be stabilized by carbon monoxide to give [$Mo^0(NO)(CO)_4Cl \cdot AlCl_3 \cdot Al(Et)Cl_2$] which is transformed into *trans*-$Mo^0Cl(NO)(CO)_2(PPh_3)_2$ after the subsequent addition of

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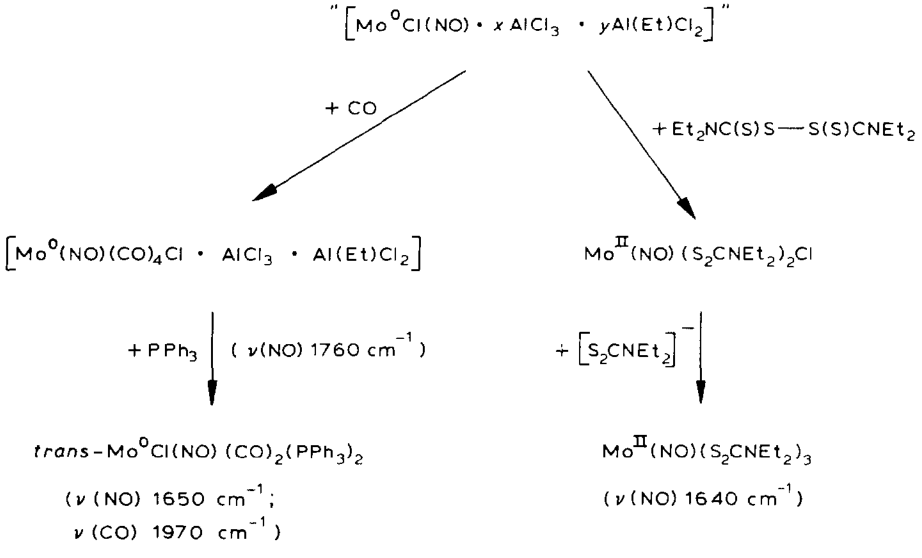
* For part XIX see ref. 20.

PPh_3. Trapping with $Ph_2PCH_2CH_2PPh_2$ yields $Mo^0Cl(NO)(diphos)_2$, whereas oxidation by $Et_2NC(S)S{-}S(S)CNEt_2$ in the presence of excess dithiocarbamate results in the formation of $Mo^{II}(NO)(S_2CNEt_2)_3$ [8]. By systematically varying the co-catalyst, we recently found that the occurrence of high metathesis activity is closely related to the generation of the $[Mo^0Cl(NO)]$-containing complex in the catalyst solution [9]. In this paper the time and temperature dependences of the formation and decomposition of the "$[Mo^0Cl(NO)]$" intermediate are investigated and compared with the catalytic activity in order to elucidate the role of this intermediate in the catalyst formation process.

Results and discussion

Stability of the $[Mo^0Cl(NO)]$-containing intermediate in and metathesis activity of the systems $Mo^{II}Cl_3(NO)(OPPh_3)_2/6\ EtAlCl_2$ and $Mo^0Cl_2(NO)_2(PPh_3)_2/6\ EtAlCl_2$ as a function of catalyst aging time

In order to check if there is any correlation between metathesis activity and the concentration of the $[Mo^0Cl(NO)]$-containing complex in catalyst solutions derived from $Mo^{II}Cl_3(NO)(OPPh_3)_2$ and $Mo^0Cl_2(NO)_2(PPh_3)_2$, respectively, with $EtAlCl_2$ as co-catalyst, the formation and decomposition of the "$[Mo^0Cl(NO)]$" species were monitored by IR spectroscopy as a function of catalyst aging time, t_a, by trapping the intermediate with carbon monoxide and triphenylphosphine, or with thiuramdisulphide, respectively. Both methods have already been described in detail [7–9]. The reaction scheme and the IR frequencies are again outlined in Scheme 1. The concentration of "$[Mo^0Cl(NO)]$" in the catalyst solutions was estimated by recording the absorbance of the ν(CO)- and ν(NO)-stretching modes of the final trapping products $Mo^0Cl(NO)(CO)_2(PPh_3)_2$ and $Mo(NO)(dtc)_3$, respectively. $MoCl_3$-



SCHEME 1. Scheme of trapping reactions used for the quantitative determination of the $[Mo^0Cl(NO)]$-containing intermediate in catalyst solutions prepared from mono- and dinitrosylmolybdenum complexes, respectivley [7–9] (IR spectra in CH_2Cl_2).

(NO)$(OPPh_3)_2$ and $EtAlCl_2$ ([Mo]/[Al] = 1/6) in benzene react completely within a few minutes yielding a homogeneous, dark brown solution. From the plot indicating the concentration of the CO-containing trapping product *trans*-MoCl(NO)-$(CO)_2(PPh_3)_2$ (see Fig. 1a, plot 1), it may be concluded that right at the beginning of catalyst formation ca. 80% of the starting compound is converted into the "[Mo^0Cl(NO)]" intermediate. However, the latter is unstable, as can be inferred from the drop of the MoCl(NO)$(CO)_2(PPh_3)_2$ curve with increasing catalyst aging time, t_a, under argon. After 3 days, the Mo^0Cl(NO) species is no longer detectable by IR spectroscopy. These results are in good agreement with trapping experiments based on thiuramdisulphide (see Fig. 2). The somewhat lower Mo(NO)$(S_2CNEt_2)_3$ content found throughout all these measurements is certainly due to a side reaction between the organic disulphide and $EtAlCl_2$ (see also [8]).

All trapping reactions which make use of CO are accompanied with the formation of small amounts of $Mo(CO)_6$ (see also [8,9]). By contrast to the time-dependent yield of the main trapping product MoCl(NO)$(CO)_2(PPh_3)_2$, the content of $Mo(CO)_6$ determined by IR spectroscopy after treating the system $MoCl_3$(NO)$(PPh_3)_2$/6 $EtAlCl_2$/benzene with CO was found to be nearly constant between 5 and 10 mol% in a time period of 5 days of catalyst aging (see Fig. 1a, plot 4).

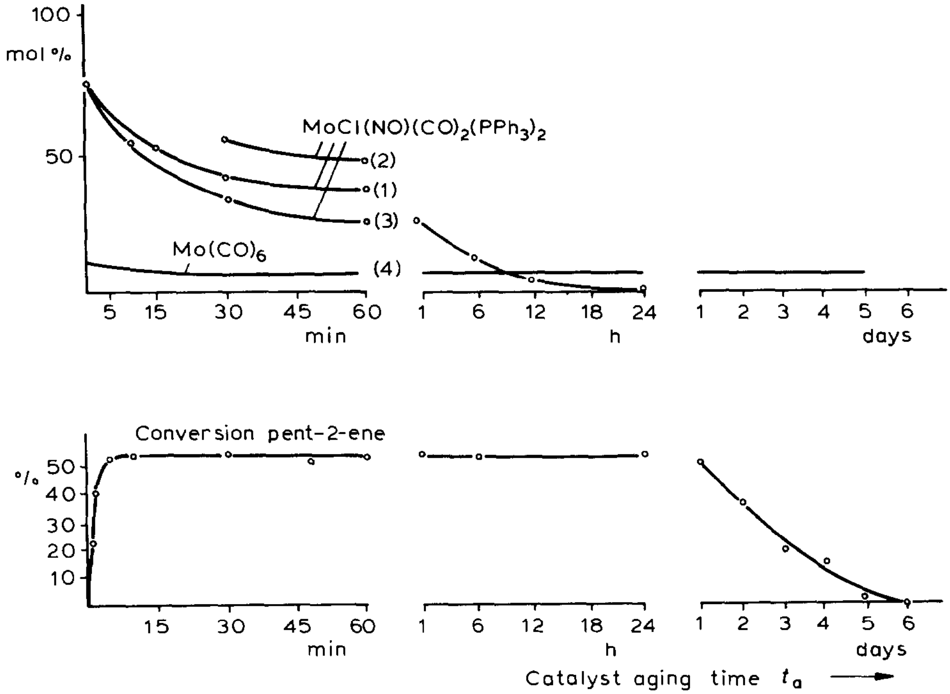


Fig. 1. Formation and decomposition of the [Mo^0Cl(NO)]-containing intermediate and metathesis activity in the system $MoCl_3$(NO)$(OPPh_3)_2$/6 $EtAlCl_2$. [Mo] = 10^{-2} mol l^{-1}. (a) Trapping of the "Mo^0Cl(NO)]" intermediate with CO/PPh_3 as *trans*-MoCl(NO)$(CO)_2(PPh_3)_2$ using different solvents and catalyst aging times, t_a: Plot 1, in benzene; plot 2, in benzene + 50 vol% pent-2-ene; plot 3, in chlorobenzene; plot 4, percentage of $Mo(CO)_6$ formed on trapping with CO in benzene. (b) Conversion of pent-2-ene into but-2-ene and hex-3-ene in chlorobenzene as a function of catalyst aging time, t_a. [Mo]/[Al]/[pent-2-ene] = 1/6/1000; reaction time with the olefin, t_r = 1 min.

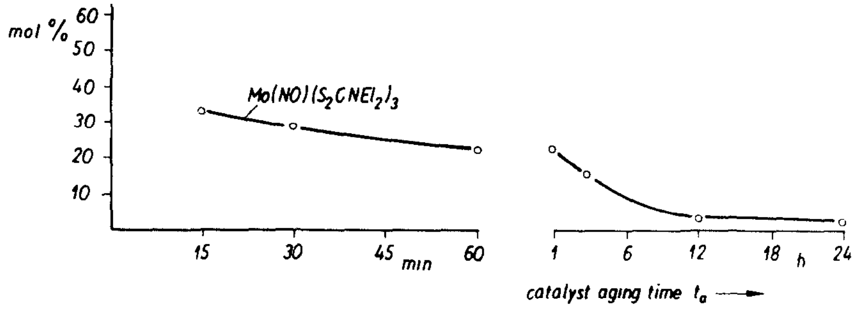


Fig. 2. Formation and decomposition of the $[Mo^0Cl(NO)]$-containing intermediate in the system $MoCl_3(NO)(OPPh_3)_2/6\ EtAlCl_2$ in benzene at different catalyst aging times, t_a. $[Mo] = 10^{-2}$ mol l^{-1}. Trapping by oxidation with thiuramdisulphide and IR spectroscopic detection as $Mo(NO)(S_2CNEt_2)_3$.

The stability of the "$[Mo^0Cl(NO)]$" intermediate in the catalyst solution depends greatly on the kind of solvent employed. Thus, the rate of its decay is significantly decreased by adding pent-2-ene (see Fig. 1a, plot 2). This might suggest direct interaction between the coordinatively labile "$[Mo^0Cl(NO)]$" complex and the olefin. On the other hand, substitution of the solvent benzene by chlorobenzene, which is supposed to have a lower tendency for π-complex formation, enhances the decomposition rate of the intermediate considerably. The decay is already completed after 1 day of catalyst aging (see Fig. 2a, plot 3).

The metathesis activity of the system $MoCl_3(NO)(OPPh_3)_2/6\ EtAlCl_2$ in chlorobenzene was measured using pent-2-ene as a test olefin (see also [4,9]). The reaction results in a thermodynamic equilibrium of 46 mol% pent-2-ene and 27 mol% each of but-2-ene and hex-3-ene [10].

$$2\ Me{-}CH{=}CH{-}Et \rightleftarrows Me{-}CH{=}CH{-}Me + Et{-}CH{=}CH{-}Et \qquad (1)$$

In Fig. 2b, the conversion of pent-2-ene is plotted versus the catalyst aging time, t_a, with a metathesis time, t_r, of 1 min. Even after a few minutes of catalyst aging and parallel to the high concentration of the "$[Mo^0Cl(NO)]$" intermediate, a high metathesis activity, i.e. equilibrium conversion of pent-2-ene after only 1 min of reaction, is achieved. When, after 24 h, the content of $[Mo^0Cl(NO)]$ drops below the analytical limit of detection, a simultaneous decrease in metathesis activity can be observed. However, it still takes some 6 days of catalyst aging before the catalytic activity of the solution is completely exhausted.

Dinitrosylmolybdenum(0) complexes were found to react much more slowly with $EtAlCl_2$ than the corresponding mononitrosyl derivatives [4,9,11]. With $Mo^0Cl_2(NO)_2(PPh_3)_2$ and 6 equivalents of $EtAlCl_2$ in chlorobenzene 2 h are required to degrade 50% of the starting compound (see Table 1). Surprisingly, it then takes 2 days for all the nitrosyl complex to react. The formation of a $[Mo^0Cl(NO)]$-containing complex in this catalyst solution was also followed quantitatively by trapping with CO/PPh_3 and monitoring by IR spectroscopy. Although a relatively rapid increase in the amount of trapping product $MoCl(NO)(CO)_2(PPh_3)_2$ was observed during the initial period of catalyst aging, namely 6 mol% after 0.5 h and 14 mol% after 2 h, the maximum value of 29 mol% could only be recorded after 2 days when all the dinitrosyl complex had been completely converted. The "$[Mo^0Cl(NO)]$" intermediate generated in this way is obviously much more stable

TABLE 1

FORMATION AND TRAPPING OF THE [Mo^{0}Cl(NO)]-CONTAINING INTERMEDIATE IN THE SYSTEM $MoCl_2(NO)_2(PPh_3)_2$/6 $EtAlCl_2$ IN BENZENE AT DIFFERENT CATALYST AGING TIMES, t_a ([Mo] = 10^{-2} mol l^{-1}, trapping reagent CO/PPh_3)

t_a (h)	$MoCl_2(NO)_2(PPh_3)_2$ (mol%)	$MoCl(NO)(CO)_2(PPh_3)_2$ [a] (mol%)
0.5	81	6
1	67	10
2	53	14
3	47	14
4	46	14
6	41	15
48 (2 d)	0	29
96 (4 d)	0	28
168 (7 d)	0	12

[a] In the case of catalyst aging periods t_a = 0.5 to 6 h, the system was not preformed in argon but directly in CO in order to trap the overall amount of the "[MoCl(NO)]"-intermediate generated during the initial stage of reaction.

than that obtained from $MoCl_3(NO)(OPPh_3)_2$/6 $EtAlCl_2$ in the same solvent. A significant drop in the concentration of $MoCl(NO)(CO)_2(PPh_3)_2$ could not be measured before 7 days of catalyst aging (see Table 1).

As can be seen from Table 2, the metathesis activity of the system $MoCl_2(NO)_2(PPh_3)_2$/6 $EtAlCl_2$/chlorobenzene with respect to pent-2-ene increases slightly within the first 90 min of catalyst aging. After this initial period, the time needed to adjust the metathesis equilibrium amounts to 15 min. Although there

TABLE 2

METATHESIS ACTIVITY OF THE CATALYST SYSTEM $MoCl_2(NO)_2(PPh_3)_2$/6 $EtAlCl_2$ WITH RESPECT TO PENT-2-ENE AS A FUNCTION OF CATALYST AGING TIME (solvent chlorobenzene; [Mo] = 10^{-2} mol l^{-1}; [Mo]/[Al]/[pent-2-ene] = 1/6/1000; t_a = catalyst aging time in argon; t_r = reaction time with pent-2-ene; conversion into but-2-ene and hex-3-ene)

t_a	t_r (min)	Conversion pent-2-ene (mol%)
2 min	1	2
10	1	3
30	1	4
60	1	7
90	1	12
90	5	21
90	15	52
1 day	15	46
2	15	52
3	15	31
4	15	20
5	15	37
6	15	18
7	15	42

are some minor changes in the butene/hexene yield at longer catalyst aging intervals, the solution keeps its average metathesis activity for at least 1 week.

The results presented above for the catalyst systems $MoCl_3(NO)(OPPh_3)_2/6$ $EtAlCl_2$ and $MoCl_2(NO)_2(PPh_3)_2/6$ $EtAlCl_2$ can be taken as proof for an at least semi-quantitative relationship between the occurrence of a $[Mo^0Cl(NO)]$-containing intermediate and the metathesis activity of the catalyst solutions.

Influence of temperature on the formation and stability of the "$[Mo^0Cl(NO)]$" intermediate and the metathesis activity

The rapid thermal decomposition of the $[Mo^0Cl(NO)]$-containing complex in the catalyst system $MoCl_3(NO)(OPPh_3)_2/6$ $EtAlCl_2$/chlorobenzene which is finished after 24 h at room temperature can be completely suppressed by lowering the temperature to below −20°C (see Table 3). Thus, when a catalyst solution preformed for 10 min at ambient temperature was cooled and kept for 5 days at −30°C, no change in the $[Mo^0Cl(NO)]$ concentration could be detected. Simultaneously, the deactivation of the catalyst system, i.e. the decay of the catalytically active complex, was suppressed (see Table 4).

Albeit the same temperature dependence of the stability of the "$[Mo^0Cl(NO)]$" intermediate and the catalyst complex again suggests a close relationship between these two, they are not identical. The $[Mo^0Cl(NO)]$-containing complex can, however, be shown to represent an essential catalyst precursor. One observation which justifies such an interpretation is the fact that even when the decomposition of the "$[Mo^0Cl(NO)]$" intermediate in the system $MoCl_3(NO)(OPPh_3)_2/6$ $EtAlCl_2$/chlorobenzene is complete after 24 h, the solution still remains catalytically active for several days (see Fig. 2).

Another argument confirming the necessity of the "$[Mo^0Cl(NO)]$"-decay for the formation of the catalyst complex was obtained from a closer look at the temperature behaviour of the catalyst solutions. First of all, the formation of the "$[MoCl(NO)]$" intermediate was found to be almost temperature-independent in the

TABLE 3

STABILITY OF THE $[Mo^0Cl(NO)]$-CONTAINING INTERMEDIATE IN THE SYSTEM $MoCl_3(NO)(OPPh_3)_2/6$ $EtAlCl_2$ AT DIFFERENT CATALYST AGING TEMPERATURES, T_a (solvent chlorobenzene; $[Mo] = 10^{-2}$ mol l^{-1}; trapping reaction with CO/PPh_3 carried out at 25°C; t_a = aging time)

t_a	T_a [a] (°C)	$MoCl(NO)(CO)_2(PPh_3)_2$ (mol%)
10 min	25	52
1 h	25	29
6 h	25	14
24 h	25	0
1 day	0	8
11	−10	26
1	−20	51
1	−30	52
2	−30	51
5	−30	47

[a] All catalyst solutions were prepared at 25°C and were stirred for 10 min prior to cooling at T_a.

TABLE 4

METATHESIS ACTIVITY OF THE CATALYST SYSTEM $MoCl_3(NO)(OPPh_3)_2/6\ EtAlCl_2$ WITH RESPECT TO PENT-2-ENE AT DIFFERENT CATALYST AGING TEMPERATURES, T_a, AND AGING TIMES, t_a (solvent chlorobenzene; [Mo] = 10^{-2} mol l^{-1}; [Mo]/[Al]/[pent-2-ene] = 1/6/1000; conversion into but-2-ene and hex-3-ene)

t_a (days)	Conversion pent-2-ene (mol%)	
	T_a 25°C	T_a −30°C [a]
1	37	55
2	16	54
5	1	48
7	0	53
9	0	55

[a] These catalyst solutions were preformed for 10 min at 25°C before cooling to −30°C.

range 25 to −40°C as proved by trapping with CO/PPh_3: 82 mol% $MoCl(NO)(CO)_2(PPh_3)_2$ at 25°C, 57 mol% at −40°C with $t_a = 0$ (see Table 5). The initially light brown solution keeps its colour at temperatures below −20°C but slowly turns dark brown on warming to room temperature, the colour change indicating that "$[Mo^0Cl(NO)]$"-decay is occurring. Moreover, it is important to know that the metathesis activity of the above system is almost invariable to any temperature change in the same interval (see Table 6, experiments 1 to 6). Provided that the catalyst solution was generated at room temperature with $t_a = 1$ h, the metathesis equilibrium was adjusted after a reaction time $t_r = 1$ min likewise at reaction temperatures, T_r, of 25 and −30°C, respectively. This result is thermodynamically reasonable because the metathesis of acyclic olefins is a thermoneutral process [10] with the equilibrium composition being largely temperature-independent. Furthermore, it demonstrates the extremely high activity of the catalyst system examined. The situation changed if the two catalyst components were mixed and aged ($t_a = 1$ h) at $T = -30$°C followed by the addition of the olefin at the same temperature (T_r −30°C). No, or only traces of, metathesis products could be detected (see Table 6, experiments 7 to 12). Therefore, the "$[Mo^0Cl(NO)]$" intermediate which is evidently present under these conditions cannot be the catalyst

TABLE 5

TEMPERATURE DEPENDENCE OF THE FORMATION OF THE "$[Mo^0Cl(NO)]$" INTERMEDIATE IN THE CATALYST SYSTEM $MoCl_3(NO)(OPPh_3)_2/6\ EtAlCl_2$ (solvent chlorobenzene; [Mo] = 10^{-2} mol l^{-1}; t_a = aging time; T_a = aging temperature; both catalyst formation and trapping with CO/PPh_3 were carried out at the T_a's given in the table)

t_a (h)	T_a (°C)	$MoCl(NO)(CO)_2(PPh_3)_2$ (mol%)
0	25	82
0	−30	60
0	−40	57
1	−30	64
1	−40	58

TABLE 6

METATHESIS ACTIVITY OF THE CATALYST SYSTEM $MoCl_3(NO)(OPPh_3)_2/6\ EtAlCl_2$ WITH RESPECT TO PENT-2-ENE UNDER VARIOUS CATALYST FORMATION AND METATHESIS CONDITIONS (solvent chlorobenzene; $[Mo] = 10^{-2}$ mol l^{-1}; [Mo]/[Al]/[pent-2-ene] = 1/6/1000; conversion into but-2-ene and hex-3-ene; t_a = catalyst aging time; T_a = aging temperature; t_r = reaction time with pent-2-ene; T_r = reaction temperature)

No.	t_a (h)	T_a (°C)	t_r (min)	T_r (°C)	Conversion pent-2-ene (mol%)
1	1	25	1	25	55
2	1	25	1	0	53
3	1	25	1	−10	55
4	1	25	1	−20	54
5	1	25	1	−30	52
6	1	25	1	−40	37
7	1	0	1	−30	49
8	1	−10	1	−30	28
9	1	−20	1	−30	5
10	1	−30	1	−30	0
11	1	−30	5	−30	1
12	1	−30	15	−30	14
13	1	0[a]	1	25	55
14	1	−10[a]	1	25	55
15	1	−20[a]	1	25	54
16	1	−30[a]	1	25	54

[a] Before adding the olefin, the preformed catalyst solution was warmed up to 25°C for 10 min.

complex itself. However, after warming this inactive mixture, preformed at −30°C, up to room temperature, which means allowing the "$[Mo^0Cl(NO)]$" species to decompose and then adding the olefin, the expectedly high metathesis activity with the metathesis equilibrium being adjusted within 1 min is again retained (see Table 6, experiments 13 to 16).

This characteristic behaviour is not a feature of a particular catalyst system but

TABLE 7

METATHESIS ACTIVITY OF CATALYST SYSTEMS BASED ON NITROSYLMOLYBDENUM COMPLEXES WITH RESPECT TO PENT-2-ENE UNDER VARIOUS CATALYST FORMATION AND METATHESIS CONDITIONS (solvent chloro-benzene; $[Mo] = 10^{-2}$ mol l^{-1}; [Mo]/[Al]/[pent-2-ene] = 1/6/1000; conversion into but-2-ene and hex-3-ene; catalyst aging time $t_a = 1$ h; T_a = aging temperature; t_r = reaction time with pent-2-ene; T_r = reaction temperature)

T_a (°C)	T_r (°C)	Conversion pent-2-ene (mol%)		
		$MoCl_3(NO)(OPPh_3)_2$ /6EtAlC$_2$ $t_r = 1$ min	$MoCl(NO)(CO)_2(PPh_3)_2$ /6 $EtAlCl_2$ $t_r = 1$ min	$MoCl_2(NO)_2(PPh_3)_2$ /6 $EtAlCl_2$ $t_r = 15$ min
25	25	55	51	43
25	−30[a]	52	39	12
−30	25[b]	54	44	21
−30	−30	0	1	3

[a] Before adding the olefin, the preformed catalyst solution was cooled down to −30°C for 10 min

[b] Before adding the olefin, the preformed catalyst solution was warmed up to 25°C for 10 min.

was likewise found for the combinations $MoCl_2(NO)_2(PPh_3)_2$/6 $EtAlCl_2$ and $MoCl(NO)(CO)_2(PPh_3)_2$/6 $EtAlCl_2$, (see Table 7).

Conclusions concerning the significance of a [$Mo^0Cl(NO)$]-containing intermediate for the formation of the metathesis-active complex in catalyst systems based on nitrosylmolybdenum compounds

As confirmed by the results of various preparative, spectroscopic, and catalytic investigations with the three classes of nitrosylmolybdenum complexes, which in this paper are represented by $Mo^{II}Cl_3(NO)(OPPh_3)_2$, $Mo^0Cl_2(NO)_2(PPh_3)_2$, and $Mo^0Cl(NO)(CO)_2(PPh_3)_2$, there are at least two essential prerequisites for the generation of the actual catalytically active complex:

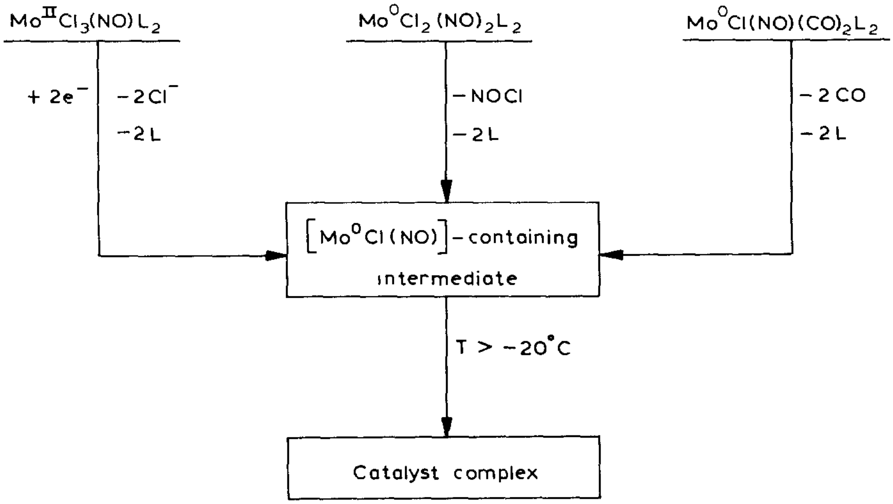
(1) The formation of a [$Mo^0Cl(NO)$]-containing intermediate from the three different starting compounds.

(2) The subsequent conversion of the thermally unstable "[$Mo^0Cl(NO)$]" intermediate into the actual catalyst complex.

These initial steps of catalyst formation are explicitly outlined in Scheme 2.

The emergence of the [$Mo^0Cl(NO)$] intermediate in the catalyst solutions has been unambiguously proved by various trapping experiments with carbon monoxide and tetraphenylethylene diphosphine, as well as by oxidation with thiuramdisulphide to give the corresponding dithiocarbamatonitrosylmolybdenum(II) complex [8]. Its relevance for the formation of highly active metathesis catalysts is additionally corroborated by the following experimental results:

(1) The generation of very active systems from $Mo^{II}Cl_3(NO)L_2$, $Mo^0Cl_2(NO)_2L_2$, and $Mo^0Cl(NO)(CO)_2L_2$ complexes, respectively, can only be accomplished by means of co-catalysts exhibiting a certain level of both Lewis-acidity and organylating/reducing power, namely $RAlCl_2$ (R = Me, Et, Ph) and $R_3Al_2Cl_3$ (R = Me, Et). It is exclusively these co-catalysts which in addition to inducing excellent activity also bring about the formation of a [$Mo^0Cl(NO)$]-containing intermediate in the catalyst solutions [8,9].



SCHEME 2. Initial steps of the generation of the catalytically active complex in metathesis catalysts based on nitrosylmolybdenum compounds.

(2) The fact that $Mo^0Cl(NO)(CO)_2L_2$ complexes can be transformed into the "$[Mo^0Cl(NO)]$" intermediate by simply abstracting the ligands L and CO, a task which is expected to be fulfilled by the simple Lewis acids $AlCl_3$ and $AlBr_3$, might explain the moderate metathesis activity observed in these particular systems [8,9].
(3) In all other cases, pure Lewis acids ($AlCl_3$, $AlBr_3$) as well as strongly organylating/reducing compounds (Et_2AlCl, Et_3Al) initiate no, or only poor, metathesis activity and do not generate the "$[Mo^0Cl(NO)]$" intermediate mentioned above [8,9].
(4) As to the ligand L, a certain degree of lability, usually guaranteed by monodentate O-, N-, and P-donors, is obviously required in order to allow its partial or even complete removal from the coordination sphere in the course of formation of the apparently coordinatively unsaturated catalyst complex. Nitrosylmolybdenum complexes with strongly coordinating chelate ligands, such as $MoCl_2(NO)_2L_2$ (L_2 = en, dipy), $Mo(NO)_2(S_2CNEt_2)_2$, $MoCl_3(NO)(dipy)$, $MoCl(NO)(S_2CNEt_2)_2$, $Mo(NO)(S_2CNEt_2)_3$, MoCl(NO)(salene), etc., were found to be catalytically inactive [4,8].

Substantial evidence for the significant role played by the "$[Mo^0Cl(NO)]$" intermediate in the catalyst solution comes from the discovery that the formation and decomposition of this intermediate correlate with the initial and long-term metathesis activity as shown for the combinations $MoCl_3(NO)(OPPh_3)_2$/6 $EtAlCl_2$ and $MoCl_2(NO)_2(PPh_3)_2$/6 $EtAlCl_2$ (cf. Figs. 1 and 2, Tables 1 and 2). Interestingly, for the dinitrosyl system the lifetimes of both the "$[Mo^0Cl(NO)]$" intermediate and metathesis activity are considerably longer, but on the other hand, this system develops a distinctly lower catalytic activity than the $MoCl_3(NO)(OPPh_3)_2$-based catalyst mixture. These effects are due to subtle differences in the composition of these catalyst solutions and are not yet fully understood. By cooling the system $MoCl_3(NO)(OPPh_3)_2$/6 $EtAlCl_2$ down to or below −20°C, both the decay of the "$[Mo^0Cl(NO)]$" intermediate and the deactivation of the catalyst can be suppressed.

The conclusion that the $[Mo^0Cl(NO)]$-containing complex merely represents a thermally unstable intermediate, the further reaction of which evidently yields the actual catalyst complex, is basically substantiated by two observations:
(1) The decomposition of the "$[Mo^0Cl(NO)]$" intermediate in the system $MoCl_3(NO)(OPPh_3)_2$/6 $EtAlCl_2$/chlorobenzene is already complete after 24 h but the catalyst solution still remains active for several days.
(2) If the systems $MoCl_3(NO)(OPPh_3)_2$/6 $EtAlCl_2$, $MoCl_2(NO)_2(PPh_3)_2$/6 $EtAlCl_2$, and $MoCl(NO)(CO)_2(PPh_3)_2$/6 $EtAlCl_2$ are formed under conditions which allow the generation of the "$[Mo^0Cl(NO)]$" intermediate but strictly prohibit its further conversion, e.g. at −30°C, there is absolutely no metathesis activity to be detected.

Incidentally, the outstanding metathesis activity of the nitrosylmolybdenum complexes has to be attributed to the fact that they are useful starting compounds for the formation of the catalytically active complex on an exceptionally smooth pathway via a common "$[Mo^0Cl(NO)]$" intermediate. Although the course of its further reaction has not yet been fully elucidated, there are some indications suggesting an intramolecular redox isomerization into a nitridomolybdenum(VI) complex which could proceed according to eq. 2.

$$[Mo^0Cl(NO) \cdot x\,AlCl_3 \cdot y\,Al(Et)Cl_2] \rightarrow [NMo^{VI}Cl(O) \cdot x\,AlCl_3 \cdot x\,Al(Et)Cl_2] \quad (2)$$

The idea of a catalytically active nitridomolybdenum complex is substantially supported by our recent finding that the nitridomolybdenum(VI) complexes

$MoNCl_3L_2$ ($L = OPPh_3$, $L_2 = Bu_4NCl$) themselves constitute very efficient metathesis catalysts after activation with $EtAlCl_2$ [16]. Furthermore, we have proved by protolysis and subsequent Kjeldahl determination that the decomposition of the "$[Mo^0Cl(NO)]$" intermediate results in the formation of a nitrido-type complex in the catalyst solutions. The real catalyst should be a carbene complex [12–14].

With the generation of a catalytically active nitrido carbene complex in the three different nitrosylmolybdenum complex-based metathesis catalyst systems, the latter seem to fit nicely into the general concept of a structure-activity relationship for metathesis catalysts which has recently been presented [15,21].

Experimental

All reactions were carried out in pure argon and carbon monoxide, respectively. The solvents used were carefully dried and were free of oxygen. Methylene chloride was refluxed over P_4O_{10} for several hours and distilled in argon. In the same way, chlorobenzene was dried over CaH_2, and benzene over sodium benzophenone. The purification of pent-2-ene was carried out by successive fractional distillation over Et_3Al and $EtAlCl_2$. $EtAlCl_2$ needed as a co-catalyst was redistilled before use. Thiuramdisulphide $Et_2NC(S)S–S(S)CNEt_2$ [18] and $Et_2H_2N[S_2CNEt_2]$ [19] were synthesized by literature methods. The nitrosyl complexes $MoCl_3(NO)(OPPh_3)_2$ and $MoCl_2(NO)_2(PPh_3)_2$ were prepared from $MoCl_5$ by nitrosylating reduction to give $MoCl_3(NO)$ and $MoCl_2(NO)_2$ which were finally treated with the corresponding ligands $OPPh_3$ and PPh_3, respectively [4,17]. A convenient procedure for the preparation of *trans*-$MoCl(NO)(CO)_2(PPh_3)_2$ from $Mo(CO)_6$ and $NOAlCl_4$ was reported recently [5].

The IR spectra were recorded with a SPECORD IR 71 spectrometer made by VEB Carl Zeiss Jena, using a KBr cuvette ($d = 1$ mm) for liquid samples.

Trapping experiments with CO/PPh_3

0.1 mmol of the Mo complex was suspended in 5 ml of the aromatic solvent (benzene, benzene + 2.5 ml of pent-2-ene, chlorobenzene). Either directly in CO ($t_a = 0$) or first in argon (t_a = variable), the appropriate quantity of the $EtAlCl_2$ co-catalyst dissolved in 5 ml of the same solvent was added while stirring or shaking the mixture vigorously. In the case of those systems preformed in argon, the trapping reaction was carried out by pressing the aged solution into a 500 ml flask filled with CO and agitating for 1 h. After adding 0.7 mmol of PPh_3 dissolved in 5 ml of the aromatic solvent, the mixture was again stirred for 30 min followed by the complete removal of the solvent at 50°C in a vacuum. The dark brown, tarry residue was then redissolved in 40 ml (or less) of CH_2Cl_2 and the yield of the trapping product, *trans*-$MoCl(NO)(CO)_2(PPh_3)_2$, determined by IR spectroscopy by measuring the absorbance of the $\nu(NO)$ and $\nu(CO)$ absorptions at 1650 and 1970 cm^{-1}, respectively.

The unreacted dinitrosyl complex in the slowly reacting system $MoCl_2(NO)_2(PPh_3)_2/6\ EtAlCl_2$ was simultaneously estimated by evaluating the $\nu(NO)$ absorption of the starting compound $MoCl_2(NO)_2(PPh_3)_2$ at 1798 cm^{-1}.

The quantitative determination of $Mo(CO)_6$ formed was directly carried out with the reaction mixture prior to the addition of PPh_3 by estimating the absorbance of the $\nu(CO)$ band at 1990 cm^{-1}.

Trapping experiments with thiuramdisulphide

0.1 mmol of the Mo complex in 5 ml of benzene or chlorobenzene in argon was stirred and treated with the appropriate quantity of $EtAlCl_2$ dissolved in 5 ml of the same solvent. After a certain aging time t_a (the nitrosyl complex has to be completely degraded), 0.3 mmol of thiuramdisulphide dissolved in 3 ml of CH_2Cl_2 was added under cooling and stirring. The resulting mixture was then reacted with 0.6 mmol of $Et_2H_2N\,[S_2CNEt_2]$ in 3 ml of CH_2Cl_2 followed by completely removing the solvent in a vacuum. The brown, tarry residue was redissolved in 10 ml of benzene/CH_2Cl_2 (1/1) and the yield of the trapping product, $Mo(NO)(S_2CNEt_2)_3$, subsequently determined by IR spectroscopy by evaluating the $\nu(NO)$ absorption at 1640 cm^{-1}.

Procedure for metathesis experiments

0.03 mmol of the Mo complex was suspended in 1.5 ml of chlorobenzene under strict exclusion of air and moisture followed by the injection of an appropriate quantity of the $EtAlCl_2$ co-catalyst dissolved in 1.5 ml of the same solvent. After a certain time of catalyst formation (aging), t_a, 3 ml of pent-2-ene was added. In order to stop the metathesis reaction, 0.2 ml of isoamylalcohol was finally injected and the conversion determined by gas chromatography by estimating the amount of hex-3-ene formed.

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