Reactions of hydroxylamido(-*O,N*)nitrosyl molybdenum complexes with EtAlCl$_2$; olefin metathesis activity of these systems

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Abstract

The nitrosyl molybdenum complexes $[Mo(NO)(H_2NO)X_2L_2]^{n-}$ (L = X, $n = 2$; L_2 = phen, $n = 0$; X = Cl$^-$, NCS$^-$, N$_3$), $[Mo(NO)_2(HNO)_m(NCS)_2L_2]^{n-}$ ($m = 0$, 1; L = NCS$^-$, $n = 2$; L = phen, $n = 0$) react with EtAlCl$_2$ to form the catalytically active systems for olefin metathesis. The carbene dinitrosyl molybdenum complexes are the real catalysts in these systems. The mechanism by which these complexes are formed was determined from their IR spectra recorded in PhCl in the range 1600–2300 cm^{-1} i.e. in the ν(NO), ν(CN), and ν(NN) regions.

The synthesis and characterization of the novel complexes $[Mo(NO)(H_2NO)L_2$-(phen)] (L = Cl$^-$ and N$_3^-$) are described.

Introduction

Carbene complexes play a crucial role in many important organic processes – olefin metathesis, cyclopropanation, polymerization, isomerization and Fischer–Tropsch syntheses [1–4]. Many of these well studied complexes have proved to be good catalysts of olefin metathesis [1b,5]. However, Ziegler–Natta catalysts are usually applied. The most active catalysts of this type are the nitrosyl molybdenum complex–aluminum alkyl systems [6]. However, details of the formation and the nature of the real catalysts in such different complexes are limited.

Quite recently the interactions of the molybdenum dinitrosyl complexes $\{Mo(NO)_2(OR)_2\}_n$, $\{Mo(NO_2)(OR)_2L\}_n$ and $Mo(NO)_2(O_2CMe)_2$ with EtAlCl$_2$ were investigated and the outcome permitted the subsequent formation stages of the formation of the catalytically essential carbene-molybdenum complexes to be determined [6g,6h]. Then, the first example of a nonheteroatom-stabilized carbene dinitrosyl molybdenum complex was synthesized [5f].

The results of the study of the reaction of the nitrosyl molybdenum complexes, containing *O,N*-coordinated hydroxylamido (1 −) or (2 −) ligands, with EtAlCl$_2$ are reported in this paper, as is the activity of the various complex–EtAlCl$_2$ systems.

Table 1

Analytical and selected IR data for the complexes

Complex	Analysis (Found (calcd.) (%))							IR data (cm^{-1}) [a]		
	Mo	Cs	N	C	H	Cl	P	ν(NO)	ν_{as}(NN)	ν(MoCl)
2	9.05 (9.55)		18.82 (19.52)	57.89 (57.37)	4.78 (4.13)		6.70 (6.17)	1615(vs)	2070(vs) 2045(vs)	
3	16.66 (16.96)	46.58 (46.99)	4.28 (4.95)		0.56 (0.36)	25.29 (25.07)		1569(vs)		318 (m) 303(m) 288(m)
4	50.20 (49.97)		14.11 (14.59)		2.33 (2.10)			1607(vs)		
10	23.08 (23.45)		13.10 (13.70)	35.90 (35.23)	2.98 (2.46)	17.88 (17.33)		1643(vs)		302(s)
11	22.51 (22.72)		32.62 (33.18)	34.92 (34.13)	2.55 (2.39)			1627(vs)	2053(vs) 2026(s)	

[a] In Nujol mulls.

Experimental

Starting materials

The reactions of catalyst precursors with $EtAlCl_2$ and the study of their catalytic activity were carried out under dry argon, with reagents and solvents purified and dried by standard procedures. The complexes $[PPh_4]_2[Mo(NO)(H_2NO)(NCS)_4]$ (1), $[PPh_4]_2[Mo(NO)(H_2NO)(N_3)_4]$ (2), $Cs_2[Mo(NO)(H_2NO)Cl_4]$ (3), $\{Mo(NO)(H_2-NO)(OH)_2\}_n$ (4), $[Mo(NO)(H_2NO)(NCS)_2(phen)]$ (5), $[PPh_4]_2[Mo(NO)_2-(HNO)(NCS)_4]$ (6), $[Mo(NO)_2(HNO)(NCS)_2(phen)]$ (7), $[PPh_4]_2[Mo(NO)_2-(NCS)_4]$ (8) and $[Mo(NO)_2(NCS)_2(phen)]$ (9) were prepared by a published procedure [7]. Their purity was determined analytically and by IR spectroscopy. Anhydrous 2 and 3 were obtained from their monoaqueous precipitates, by desiccation at $100°C$ in dynamic vacuo. Complex 4 was obtained from the compound called the "polymeric material" [7b] under the same conditions as those used for 2 and 3. The results of elemental analysis and the selected IR spectra frequencies are listed in Table 1.

[Mo(NO)(H₂NO)Cl₂(phen)] (10). To a hot solution of 1,10-phenanthroline (phen) (5 mmol in 50 cm^3 H_2O) was added 3 (3,5 mmol) in small portions with stirring. Then the mixture was left in a refrigerator for 24 h. The yellow-brown precipitate that had formed was collected by filtration, washed with hot water, ethanol, and ether, and dried in vacuo.

[Mo(NO)(H₂NO)(N₃)₂(phen)] (11). A suspension of 4 (10.4 mmol) in an aqueous solution of NaN_3 (42 mmol in 100 cm^3 H_2O) was heated to $60°C$ with stirring until a yellow solution had formed. Then a hot aqueous solution of phen (15 mmol in 100 cm^3 H_2O) was slowly added. The mixture was cooled to room temperature, and the yellow-orange oily product was separated by decantation, and stirred in ethanol for about 4 h to give the product as a precipitate which was filtered off, washed with H_2O, ethanol, and ether, and dried in vacuo.

Metathesis reactions

The following general procedure was used. The precatalyst and PhCl were placed in the reaction vessel and cooled to below $0°C$. To this mixture was added the $EtAlCl_2$ in PhCl. The solution was separated from the PhCl-insoluble precipitate and then heated to room temperature. After t_a min pent-2-ene was added to the solution for the sample taken after t_r min (reaction time) the reaction was quenched and the metathesis products were subjected to GLC. Reaction conditions are listed in Table 2.

Reaction of the precatalysts with EtAlCl₂

The following procedure was used. To a solution of the precatalyst in PhCl cooled to below $0°C$, was added a solution of $EtAlCl_2$ in PhCl with vigorous stirring. The solution was separated from PhCl-insoluble precipitate and cooled to about $-40°C$. Their IR spectra were recorded, at regular intervals (t_a), in CaF_2 cuvettes, in the range $1600-2300$ cm^{-1} at room temperature ($[Mo] = 2.5 \times 10^{-4}$ mol in 5 cm^3 PhCl).

Instrumentation

The IR spectra were recorded with a Specord M80 spectrophotometer in the range $1600-2300$ cm^{-1} in PhCl solution and on a Perkin–Elmer 180 spectropho-

tometer in the range 60–4000 cm^{-1} in Nujol mulls. GLC analyses were performed with a N-503 chromatograph (ELPO).
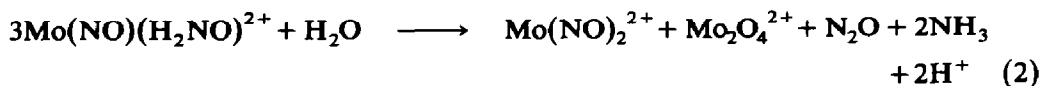
Results and discussion

Precatalyst preparation and characterization

Several procedures to synthetize transition metal nitrosyl have been described [8]. One involves the reductive nitrosylation of tetraoxometallates by hydroxylamine in acidic, neutral or alkaline media. This method permits the synthesis of the mono- and di-nitrosyl molybdenum complexes, as well as that of the complexes containing O,N-coordination hydroxylamido $(1 -)$ or $(2 -)$ ligands [7,9]. The complexes examined here are: $[PPh_4]_2[Mo(NO)(H_2NO)(NCS)_4]$ (1), $[PPh_4]_2[Mo(NO)(H_2NO)(N_3)_4]$ (2), $Cs_2[Mo(NO)(H_2NO)Cl_4]$ (3), $\{Mo(NO)(H_2NO)(OH)_2\}_n$ (4), $[Mo(NO)(H_2NO)(NCS)_2(phen)]$ (5a,b,c), $[PPh_4]_2[Mo(NO)_2(HNO)(NCS)_4]$ (6), $[Mo(NO)_2(HNO)(NCS)_2(phen)]$ (7), $[PPh_4]_2[Mo(NO)_2(NCS)_4]$ (8) and $[Mo(NO)_2(NCS)_2(phen)]$ (9).

In addition, the novel complexes $[Mo(NO)(H_2NO)Cl_2(phen)]$ (10) and $[Mo(NO)(H_2NO)(N_3)_2(phen)]$ (11) were synthetized. The following mechanism of formation of these complexes was assumed [9b]:
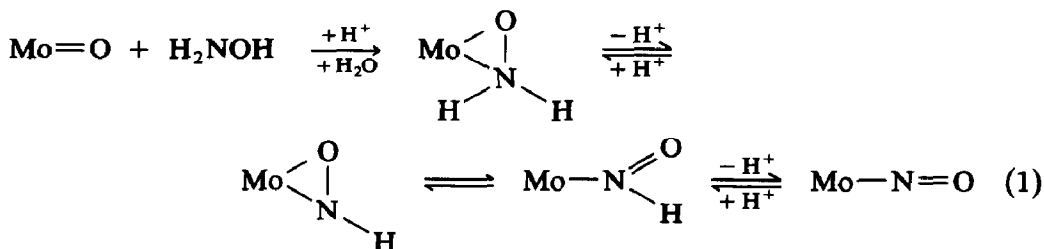
$$3Mo(NO)(H_2NO)^{2+} + H_2O \longrightarrow Mo(NO)_2^{2+} + Mo_2O_4^{2+} + N_2O + 2NH_3 + 2H^+ \quad (2)$$

The complexes containing H_2NO^- (1–5, 10 and 11, with $\{MoNO\}^4$ electronic structure) are heptacoordinated. The O,N-bonds of H_2NO^- ligand are always cis to the NO group [7a,b; 9b,e]. The $[Mo(NO)(H_2NO)X_2(phen)]$ complexes (5, 10 and 11) can exist as three distinct isomers: I, in which the X ligands are $trans$ to each other; II, in which the X ligands are in cis positions and the phen is coordinated in the plane of the $Mo\overset{O}{\underset{NH_2}{\diagdown|}}$ bonds; III, in which the cis X ligands lie in the plane of the $Mo\overset{O}{\underset{NH_2}{\diagdown|}}$ bonds. Only 5 can exist in all three isomeric forms (5a, 5b and 5c are isomers I, II and III, respectively) [7a]. However 10 and 11 exist as only one of these three isomeric forms. The single ν(MoCl) band in the IR spectrum of 10 (Table 1) shows it to be isomer I. Two ν_{as}(NN) frequencies observed in the IR spectrum of 11 (Table 1) indicate that the N_3^- ligands are probably cis to each other, but it is impossible to determine whether it is isomer II or III. The complexes with the

Table 2

Metathesis activity of hydroxylamido(-O,N)nitrosyl molybdenum complex–EtAlCl$_2$ systems [a]

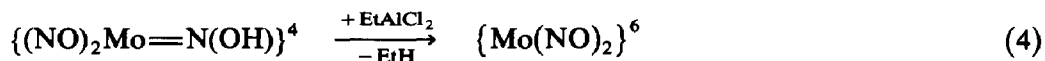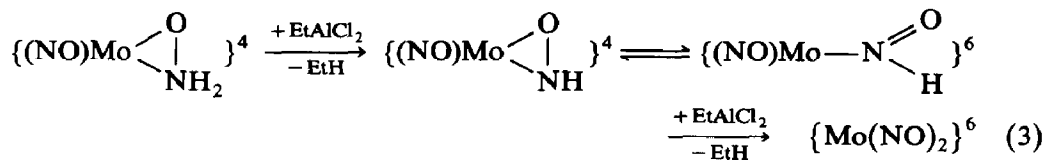| Precatalyst	t_a (min)	t_r (min)	Conversion (mol%)
1	1		39
	5		40
	60	30	40
	180		37
2	5	30	47
3	5	2	54
4	5	10	51
5a	5		3
	15	60	11
	30		17
5b	5	60	50
5c	5	60	49
6	5	30	41
7	5	60	3
	30		17
8	5	30	43
9	5	60	53
	60		54
10	5	60	4
	30		16
11	5		50
	60	50	51
	240		46

[a] Reaction conditions: solvent, chlorobenzene (5 cm^3); cocatalyst, EtAlCl$_2$; test olefin, pent-2-ene; [Mo] = 2.5×10^{-4} mol; [Mo]/[Al]/[pent-2-ene] = 1/10/400; conversion of pent-2-ene into but-2-ene and hex-3-ene.

coordinated HNO^{2-} ligand (6 and 7) contain primarily the $\{Mo(NO)_2\}^4$ cores; thus the coordination number of seven would conform to the 18-electron rule. The hydroxylamido(2 −) ligand is probably unidentate – coordinating as the hydroxyl-imido =N(OH)$^{2-}$ [7a]. It is probable that 7 contains trans NCS$^-$ groups. 8 and 9 are the six-coordinate complexes of $\{Mo(NO)_2\}^6$ electronic structure [7a]. 9 exists as only one of the two possible isomeric forms, viz. that in which the NCS$^-$ groups are *cis* to each other.

Interaction of [Mo(NO)(H$_2$NO)X$_2$L$_2$]$^{n-}$ (L = X, n = 2; L$_2$ = phen, n = 0; X = Cl$^-$, NCS$^-$ and N$_3^-$), [Mo(NO)$_2$(HNO)$_m$(NCS)$_2$L$_2$]$^{n-}$ (m = 0, 1; L = NCS$^-$, n = 2; L$_2$ = phen, n = 0) with EtAlCl$_2$

The studies were carried out in PhCl solution. The IR spectra of the precatalyst–EtAlCl$_2$ systems were recorded in the range 1600–2300 cm^{-1} (i.e. in the ν(NO), ν(CN) and ν(NN) regions) and their changes with time were noted. The catalytic systems are denoted in the same way as the precatalysts from which they were obtained. The IR spectra are shown in Figs. 1–5. The IR spectrum of 1 and the changes in time of the spectra of systems 1, 6, and 8 are shown in Fig. 1. The spectra

of the latter show no bands at 1636 and 1750 cm^{-1} assigned to the ν_{as}(NO) and ν_s(NO) of the dinitrosyl complexes deriving from1 (reaction 3) and 6 (reaction 4).

$$\{(NO)Mo\underset{NH_2}{\overset{O}{<}} \}^4 \xrightarrow[-EtH]{+EtAlCl_2} \{(NO)Mo\underset{NH}{\overset{O}{<}} \}^4 \rightleftharpoons \{(NO)Mo-N\underset{H}{\overset{O}{<}} \}^6$$

$$\xrightarrow[-EtH]{+EtAlCl_2} \quad \{Mo(NO)_2\}^6 \quad (3)$$

$$\{(NO)_2Mo=N(OH)\}^4 \quad \xrightarrow[-EtH]{+EtAlCl_2} \quad \{Mo(NO)_2\}^6 \qquad (4)$$

The above dinitrosyl complexes and 8 react with EtAlCl$_2$ initially to form the intermediate complexes, most probably the adducts with EtAlCl$_2$ (ν(NO), 1730; ν_s(NO), 1856 cm^{-1}; Fig. 1). The reaction then proceeds via a double alkylation of molybdenum to an α-elimination to give the carbene complexes containing the $\{Mo(NO)_2\}^6$ unit (ν_{as}(NO) 1740; ν_s(NO) 1844 cm^{-1}; Fig. 1).

All the systems 1–11, were found to liberate EtH.

A similar mechanism of carbene dinitrosyl complex formation (i.e. via an adduct with EtAlCl$_2$) has been discovered in the systems: $\{Mo(NO)(OR)_2\}_n$ and/or Mo(NO)$_2$(O$_2$CR)$_2$–EtAlCl$_2$ [6g,h,i]. The adduct and the carbene complex were isolated from the $\{Mo(NO)_2(O-i-Pr)_2\}_n$–EtAlCl$_2$ system [5f].

In the carbene complexes the ν(NO) do not depend on the oxygen-containing coordinating ligands OR$^-$ or O$_2$CR$^-$ (ν_{as}(NO) 1744 and ν_s(NO) 1848 cm^{-1}). The carbene complexes formed in the systems described show very close or even identical ν(NO) frequencies.

For the carbene dinitrosyl complex formed in system 3 (Fig. 2) ν_{as}(NO) is 1750 cm^{-1} and ν_s(NO) is 1850 cm^{-1} (in the adduct 1730 and 1860 cm^{-1}), whereas for the carbene formed in system 4, ν(NO) is 1744 and 1848 cm^{-1}.

The reactions of 5b, 5c, and 9 with EtAlCl$_2$ yield a product having identical electronic and molecular structures. Hence their IR spectra are also identical. The spectrum of system 9 shows no bands at 1636 and 1750 cm^{-1} (Fig. 3), which (like that of system 1) are the ν_{as}(NO) and ν_s(NO) frequencies fo the dinitrosyl inter-mediate complexes formed from 5b and 5c (Reaction 3). The bands at 1720, 1860 and 1740, 1844 cm^{-1} (Fig. 3) were assigned to the ν(NO) of the adduct and carbene, respectively.

In the IR spectra of 1, 5b, 5c, 6, 8, and 9, the addition of EtAlCl$_2$ caused a shift of the ν(CN) bands of NCS$^-$ ligands to 2168 cm^{-1} (Figs. 1 and 3). Such an unusually high frequency could originate in the bridge coordination of the NCS$^-$ groups [11]. The spectra of the systems containing the complexes with NCS$^-$ ligands also display the bands at 1880 cm^{-1} (Figs. 1 and 3), but when these disappear, the intensity of the band at 2168 cm^{-1} increases.

Identical changes in ν(CN) frequencies are observed in the spectra of the systems 5a and 7 (precatalysts with trans NCS$^-$). Thus these spectra indicate that these complexes also formed adducts with EtAlCl$_2$ (ν_{as}(NO) 1720; ν_s(NO) 1852 cm^{-1}) via dinitrosyl intermediate complexes (ν(NO) 1636, 1732 cm^{-1}) and even the carbene complexes (ν(NO) 1740(w), 1844(w) cm^{-1}). The formation of these carbene
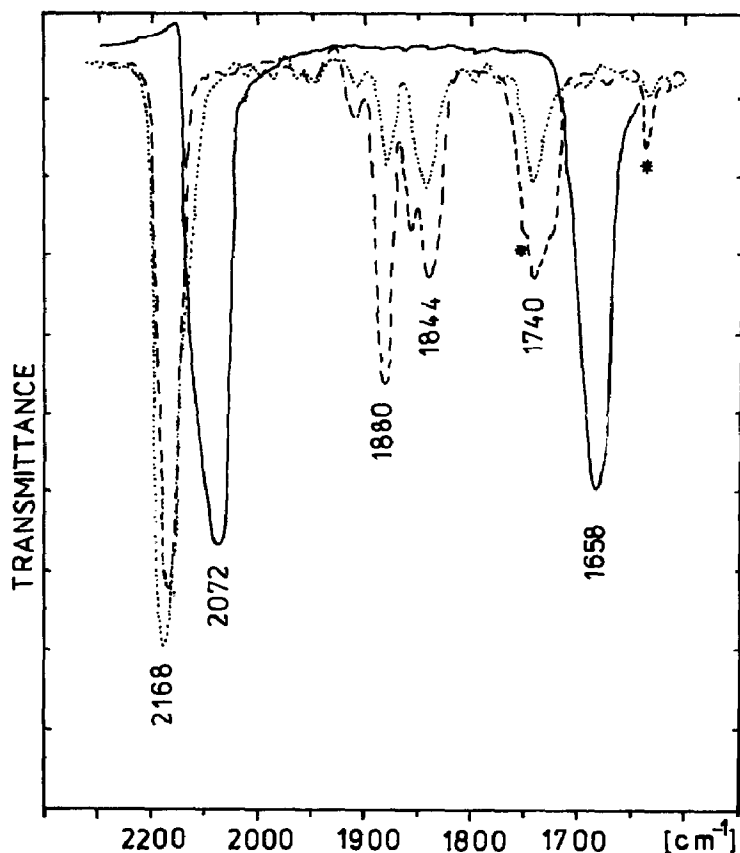
Fig. 1. IR spectra of 1 in Nujol mull ———— and systems 1, 6, and 8 (without marked * bands) in PhCl after $t_a \approx 2$ min ------ and 30 min ·······. Concentration of complexes [Mo] = 2.5×10^{-4} mol in 5 cm³ PhCl; [Mo]/[Al] = 1/4.

complexes requires the isomerization of the starting complexes, or of some of the intermediates, to give the forms with *cis* NCS⁻.

The behaviour of **10** (with *trans* Cl⁻ ligands) is similar to that of **5a** and **7** in the system with EtAlCl₂. The ν(NO) of the adduct appears at 1725 and 1855 cm⁻¹, whereas that of the carbene appears at 1745 and 1844 cm⁻¹. The bands at 1632 and 1736 cm⁻¹ are the ν(NO) originating from the dinitrosyl intermediate formed in reaction 3.

The reactions were performed at the Mo/Al concentration ratios of 1/2, 1/3, 1/4, 1/6 and 1/10. The various ratios caused changes only in the reaction rate. At Mo/Al < 1/6 after a t_a of 2 min the IR spectra show only the bands corresponding to the ν(NO) of the carbene complexes. At Mo/Al ratios of 1/2 and 1/3 only some of the precatalyst was found to react with EtAlCl₂, hence the real Mo/Al ratio was different, viz. < 1/3. Complexes **2** and **11** in the presence of EtAlCl₂ undergo similar transformations, like those of the complexes mentioned (Figs. 4 and 5), i.e. via dinitrosyl intermediates (ν(NO) 1670, 1775 cm⁻¹ for **2** and 1634, 1750 cm⁻¹ for **11**), adducts with EtAlCl₂ (ν(NO) 1724, 1824 cm⁻¹ for **2** and 1738, 1836 cm⁻¹ for **11**), into the carbene complexes (ν(NO)1746, 1850 cm⁻¹ for **2** and 1740, 1844 cm⁻¹ for **11**). A decrease in the EtAlCl₂ concentration retards these transformations. In system **2** the change of Mo/Al from 1/6 to 1/4 revealed the presence of an
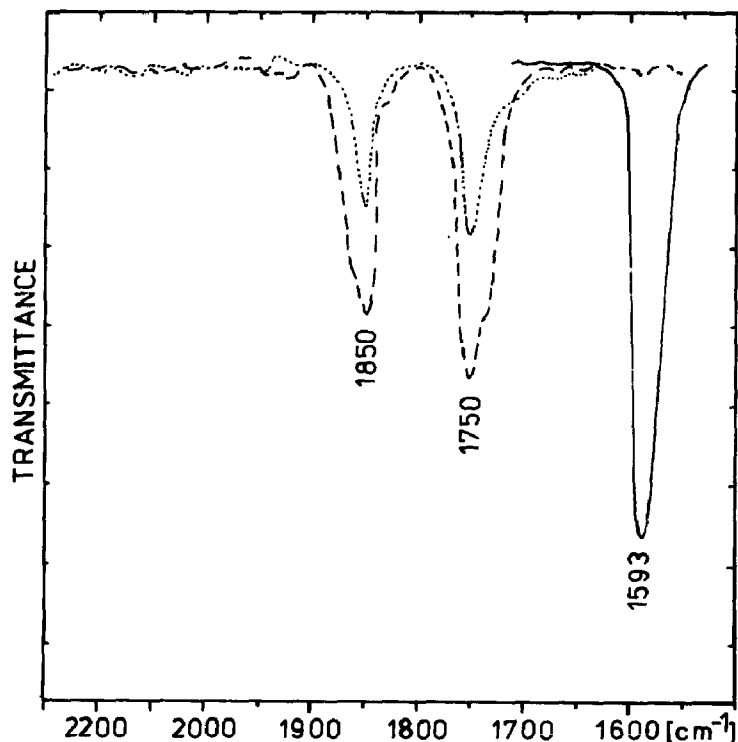
Fig. 2. IR spectra of 3 in Nujol mull ——— and system 3 in PhCl after t_a = 2 min - - - - - - and 20 min
· · · · · ·. Concentration of reagents see legend of Fig. 1.

additional intermediate (ν(NO) 1700 and 1860 cm^{-1}; Fig. 4b). The IR spectra of
the systems 2 and 11 (Figs. 4 and 5) are indicative of the simultaneous transforma-
tions of the coordinated N_3^- ligands. The bands at 2026–2070 cm^{-1} characteristic
for the $\nu_{as}(N_3^-)$ vibrations [11,12] are replaced by the intense bands at 2105, 2140,
2164, 2168 and 2176 cm^{-1}. After t_a > 30 min or at Mo/Al ≤ 1/6 (t_a ≥ 2 min) only
the band at 2176 cm^{-1} remained. The bands of such a high frequencies cannot be
assigned to the vibrations of the bridging of the terminally coordinated N_3^- [11,12].
Their position and character point to a possible transformation of the N_3^- into N_2
ligands. The conversions of the azido complexes into dinitrogen complexes have
been reported [13]. Terminal dinitrogen complexes have $\nu(N_2)$ in the region 1930–
2230 cm^{-1} and $\nu(N_2$, terminal) > $\nu(N_2$, bridging) [13b,14].

The above transformation should lead to terminal dinitrogen complexes. In such
complexes, however, molybdenum should be in a high oxidation state [13b,14a],
because they probably do not contain the powerful π-electron acceptors, the NO
ligands. The IR spectra of the systems 2 and 11, show no ν(NO) bands after t_a > 24
h and only the bands at 2176 cm^{-1} at a reduced intensity are present. (Fig. 5).

Metathesis reactions

The metathesis reactions were carried out in the classical systems, i.e. precata-
lyst–alkylaluminum–olefin in PhCl solutions [6]; 1–11 were the precatalysts, $EtAlCl_2$
was the alkylaluminum and pent-2-ene was the test olefin. The reaction conditions
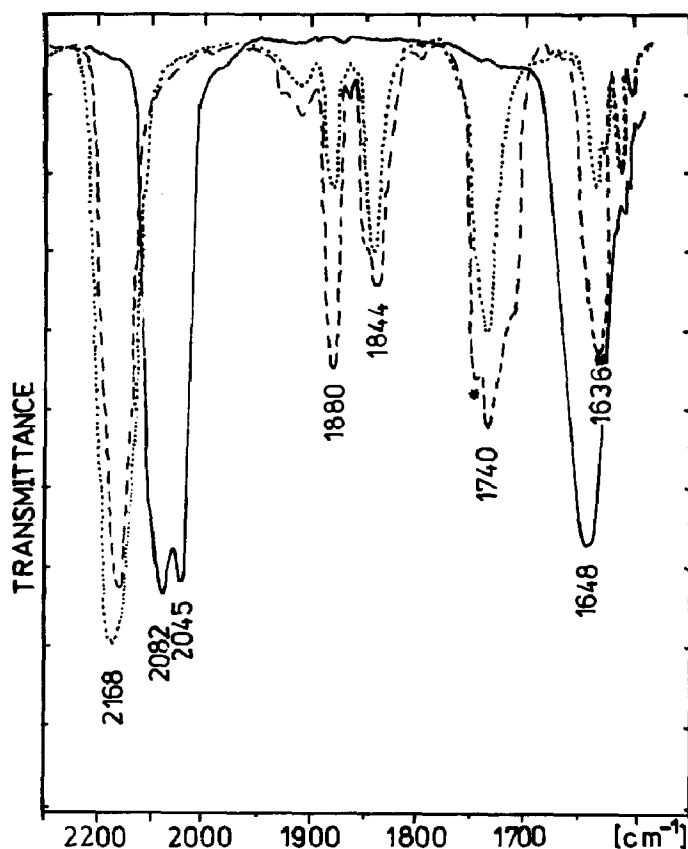and the results are listed in Table 2.

Fig. 3. IR spectra of 5c in Nujol mull ———— and systems 5b, 5c, and 9 (without marked ● bands) in PhCl after $t_a \approx 2$ min - - - - - and 20 min · · · · · · . Concentration of reagents see legend of Fig. 1.

Except for 5a, 7, and 10 in no system was a relation found between their catalytic activity and the time t_a in the first 60 min (t_a = the time required for the formation of the active catalyst). This is consistent with the results reported above. At a Mo/Al ratio of $\leq 1/6$ and after $t_a = 2$ min the corresponding carbene complexes were formed. The systems 5a, 7, and 10 (precatalysts with *trans* NCS⁻ and Cl⁻ ligands) require a prolonged t_a for the additional reactions that give the intermediates having the free coordination sites in the *cis* position to go to completion.

The spectroscopic data also revealed the instability of the systems under study. For that reason their activity declined after an appropriately long time. The activities of these systems do not depend on the electronic structure of the precatalyst, but on the number of coordinated NO groups and on the type of hydroxylamido ligand (1 − or 2 −) (see the systems 1, 6 and 8; 5b, 5c and 9; Table 2). In these particular groups of systems the carbene complexes of the activity-determining step have the same electronic and molecular structure.

The most active system is 3 then 4, less active are 2 then 1, 6, and 8 and the least actives 5b, 5c, 9, and 11 (except for 5a, 7 and 10). It follows from Table 2 that the activities of 5a, 7 and 10 are independent of ligand X (X = NCS⁻, N₃⁻).

From the postulated mechanism of formation of the carbene dinitrosylmolybdenum complexes, in the systems 5, 7, 9, 10 and 11 the carbenes
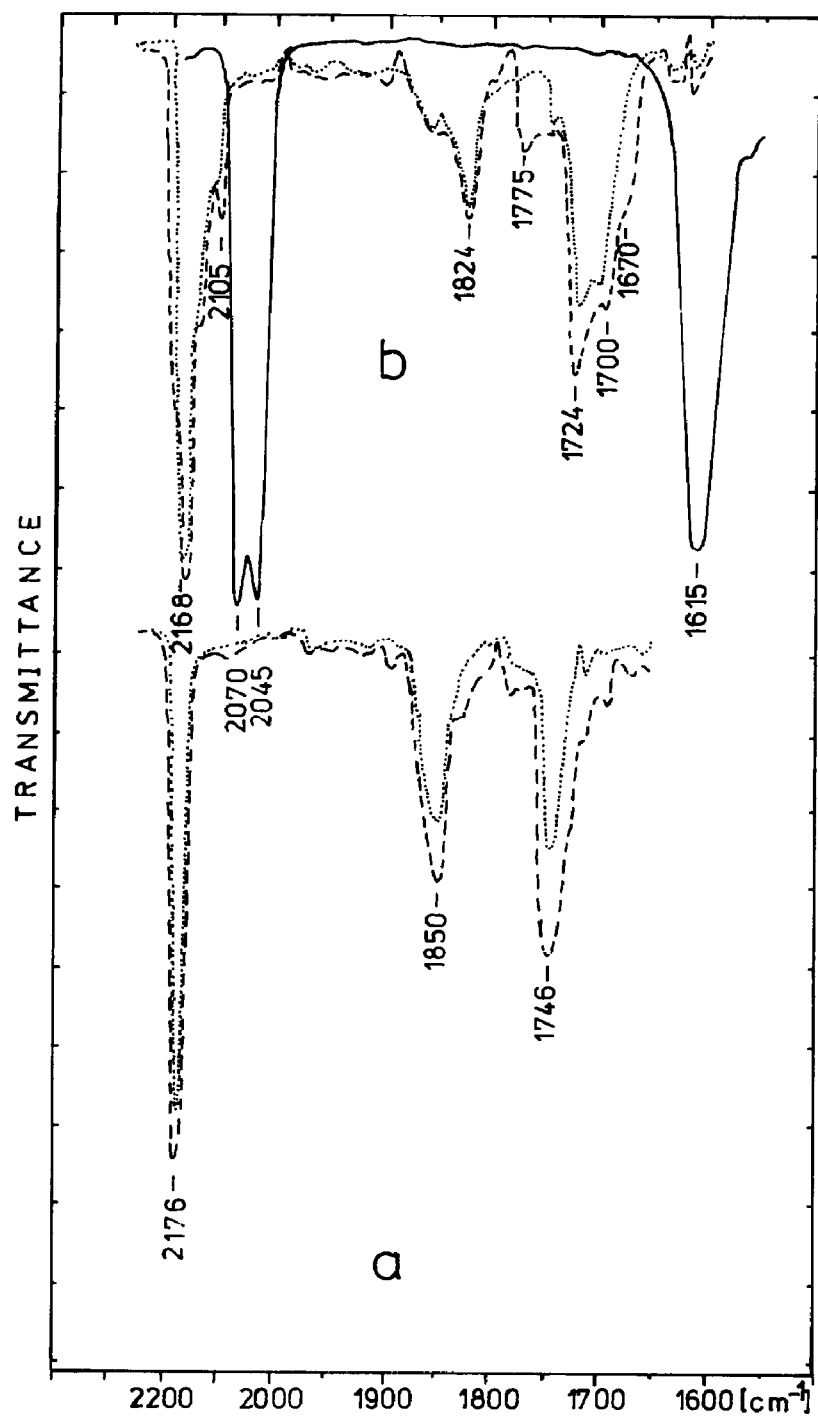
398

Fig. 4. IR spectra of 2 in Nujol mull ——— and system 2 in PhCl (concentration of [Mo] = 2.5×10^{-4} mol in 5 cm³ PhCl): a) [Mo]/[Al] = 1/6, t_a = 2 min ------ and 20 min ······; b) [Mo]/[Al] = 1/4, t_a = 2 min ------ and 20 min ······.
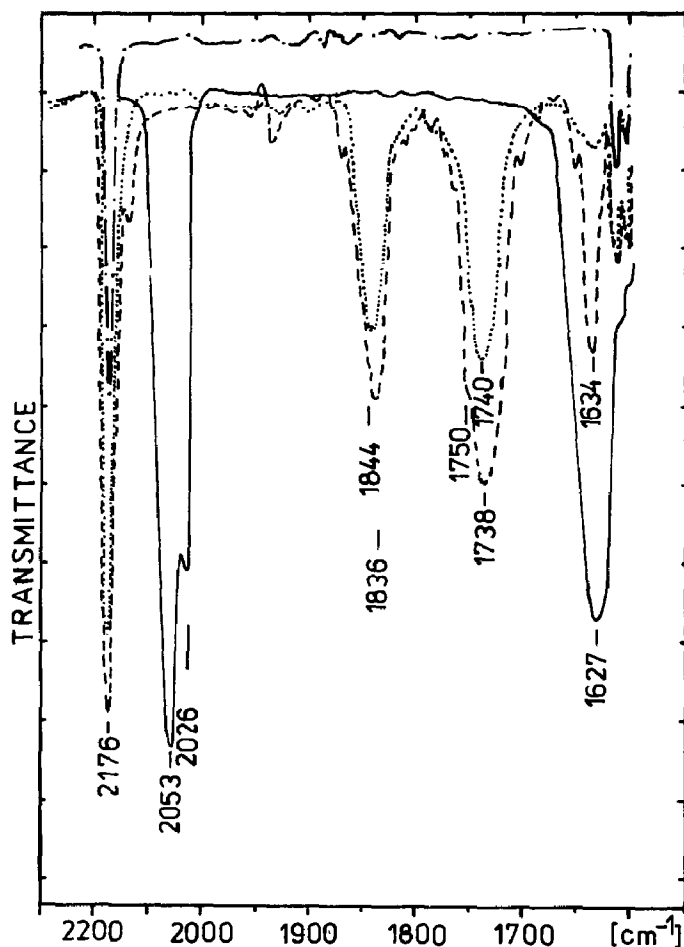
Fig. 5. IR spectra of 11 in Nujol mull ——— and system 11 in PhCl after $t_a = 2$ min · · · · · ·, 20 min · · · · · · and 24 h ·—·—·. Concentration of reagents see legend of Fig. 1.

[(phen)Mo(NO)$_2$(=CHMe)] (12) should be formed; other systems, except for 2, produce the carbenes [(AlCl$_2$)$_2$L$_2$Mo(NO)$_2$(=CHMe)] (L = Cl$^-$ (13), OH$^-$ (14) and NCS$^-$ (15)). System 2 is most likely to yield the N$_3^-$ ligand-free carbene complex (Fig. 4).

The strong electron-withdrawing effect of the coordinated NO groups undoubtedly determines the electron density distribution in the carbene complex molecules. There is a close relation between the electron density distribution in the nitrosyl complex molecules and the ν(NO) [15]. In the molybdenum dinitrosyl carbene complexes with {Mo(NO)$_2$(=CHMe)}^{6} units reported up to now the ν(NO) frequencies scarcely depend on the other coordinated ligands (Figs. 1–5 and [6g,h,i]). The donor–acceptor properties of these complexes could however exercise some effect on the Mo–C$_{carbene}$ bonding character, and which in turn influences their catalytic activity, so that it declines in the order Cl$^-$ (13) > OH$^-$ (14) > NCS$^-$ (15) > phen (12). The lowering of the activity of the carbene 12 could be due to the spherical structure of the coordinated phen and its whole molecular structure is different from those of 13, 14, 15. In 12 the coordination of the carbene ligand in

the bonding plane $Mo(NO)_2$ is impossible because on the side opposite the NO, the ligands are in the most favourable positions for the formation of $Mo=CR_2$ bonds [6g].

References

1 (a) J.L. Herisson and Y. Chauvin, Makromol. Chem., 141 (1970) 161; (b) R.H. Grubbs, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 8 Pergamon Press Ltd., New York, 1982, p. 499.

2 (a) H. Nozaki, S. Moriuti, H. Takaya and R. Noyori, Tetrahedron Lett., (1966) 5239; (b) H. Nozaki, H. Takaya, S. Meriuti and R. Noyori, Tetrahedron, 24 (1968) 3655; (c) A. Nakamura, T. Yoshida, M. Cowie, S. Otsuka and J.A. Ibers, J. Am. Chem. Soc., 99 (1977) 2108.

3 (a) K.J. Ivin, I.I. Rooney, C.D. Stewart, M.L.H. Green and R. Mahtab, J. Chem. Soc., Chem. Commun., (1978) 604; (b) M.L.H. Green, Pure Appl. Chem., 50 (1978) 27.

4 (a) W.A. Herrmann, Angew. Chem., Int. Ed. Engl., 21 (1982) 117; (b) C. Masters, Adv. Organomet. Chem., 17 (1979) 61; (c) R.C. Brady III and R. Pettit, J. Am. Chem. Soc., 102 (1980) 6182; (d) R.C. Brady III and R. Pettit, ibid., 103 (1981) 1287.

5 (a) F.N. Tebbe, G.W. Parshall and D.W. Ovenall, J. Am. Chem. Soc., 101 (1979) 5074; (b) J.H. Wengrovius, R.R. Schrock, M.R. Churchill, J.R. Missert and W.J. Youngs, ibid., 102 (1980) 4515; (c) J. Kress and J.A. Osborn, ibid., 105 (1983) 6346; (d) J. Kress, A. Aguero and J.A. Osborn, J. Mol. Catal., 36 (1986) 1; (e) K. Weiss and P. Kindl, Angew. Chem. Int. Ed. Engl., 23 (1984) 629; (f) A. Keller, J. Organomet. Chem., 385 (1989) 285.

6 (a) E.A. Zuech, Chem. Commun., (1968) 1182; (b) W.B. Hughes, J. Am. Chem. Soc., 92 (1970) 532; (c) K. Seyferth and R. Taube, J. Mol. Catal., 28 (1985) 53 and refs. therein; (d) A. Keller, Inorg. Chim. Acta, 133 (1987) 207; (e) idem, ibid., 149 (1988) 165; (f) A. Keller, Transition Met. Chem., 12 (1987) 320; (g) A. Keller and L. Szterenberg, J. Mol. Catal., 57 (1989) 207; (h) A. Keller, ibid., 53 (1989) L9; (i) A. Keller, to be published.

7 (a) R. Bhattacharyya and G.P. Bhattacharjee, J. Chem. Soc., Dalton Trans., (1983) 1593; (b) K. Wieghardt, G.B. Dahmann, W. Swiridoff and J. Weiss, Inorg. Chem., 22 (1983) 1221; (c) A. Muller, N. Mohan, S. Sarka and W. Eltzner, Inorg. Chim. Acta, 55 (1981) L33.

8 K.G. Caulton, Coord. Chem. Rev., 14 (1975) 317.

9 (a) A. Muller, S. Sarkar, N. Mohan and R.G. Bhattacharyya, Inorg. Chim. Acta, 45 (1980) L245; (b) K. Wieghardt, W. Holzbach and J. Weiss, Z. Naturforsch, 37b (1982) 680; (c) S. Sarkar and P. Subramanian, Inorg. Chim. Acta, 35 (1979) L357; (d) K. Wieghardt, W. Holzbach, J. Weiss, B. Nuber and B. Prikner, Angew. Chem. Int. Ed. Engl., 18 (1979) 548; (e) K. Wieghardt, W. Holzbach, B. Nuber and J. Weiss, Chem. Ber., 113 (1980) 629.

10 J.H. Enemark and R.D. Feltham, Coord. Chem. Rev., 13 (1974) 339.

11 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1978.

12 Z. Dori and R.F. Ziolo, Chem. Rev., 73 (1973) 247.

13 (a) P.G. Douglas, R.D. Feltham and H.G. Metzger, J. Am. Chem. Soc., 93 (1971) 84; (b) J. Chatt, J.R. Dilworth and R.L. Richards Chem. Rev., 78 (1978) 589.

14 (a) D. Sellman, Angew. Chem. Int. Ed. Engl., 13 (1974) 639; (b) R.D. Sanner, J.M. Manriquez, R.E. Marsh and J.E. Bercaw, J. Am. Chem. Soc., 98 (1976) 8351; (c) F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry Wiley, New York, 1980, p. 86.

15 (a) A. Keller and B. Jeżowska-Trzebiatowska, Inorg. Chim. Acta, 51 (1981) 123; (b) A. Keller and B. Jeżowska-Trzebiatowska, Polyhedron, 4 (1985) 1847.