

# Synthesis and catalytic activity of dinitosylchromium complexes of the type $[\text{Cr}(\text{NO})_2(\text{CO})_2\text{L}_2]^{2+}$ , $\{\text{Cr}(\text{NO})_2(\text{OR})_2\}_n$ ( $\text{R} = \text{Et}, i\text{-Pr}$ ) and $\text{Cr}(\text{NO})_2(\text{O}_2\text{CPh})_2$

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Received 18 September 1998; accepted 9 December 1998

## Abstract

New *trans*-dinitosylchromium complexes of the type  $[\text{Cr}(\text{NO})_2(\text{CO})_2\text{L}_2](\text{BF}_4)_2$  ( $\text{L} = \text{MeNO}_2, \text{MeCN}, \text{MeOH}$ ;  $\text{L}_2 = \text{bipy}$ ),  $[\text{Cr}(\text{NO})_2\text{L}_4](\text{BF}_4)_2$  ( $\text{L} = \text{MeNO}_2, \text{MeOH}$ ,  $\text{L}_2 = \text{bipy}$ ),  $\{\text{Cr}(\text{NO})_2(\text{OR})_2\}_n$  ( $\text{R} = \text{Et}, i\text{-Pr}$ ) and  $\text{Cr}(\text{NO})_2(\text{O}_2\text{CR})_2$  ( $\text{R} = \text{Ph}$ ) were obtained. Interactions of these complexes with Lewis acids ( $\text{TiCl}_4$ ,  $\text{SnCl}_4$  and  $\text{EtAlCl}_2$ ) were investigated. The effect of those interactions is *trans*–*cis* isomerization of nitrosyl ligands and formation of respective adducts, while the adducts with  $\text{EtAlCl}_2$ , by further transformations, form *cis*-dinitosylchromium ethylidene complexes. Catalytic activities of the systems complexes—Lewis acids were tested in the reactions with olefins (pent-1-ene, pent-2-ene, cyclopentene) and phenylacetylene. The adduct  $[\text{Cr}(\text{NO})_2(\text{OEt})_2(\text{EtAlCl}_2)_2]$  and the first dinitosylalkylidenechromium complex  $\{\text{Cr}(\text{NO})_2(\text{CHMe})_2(\text{OEt})_2(\text{AlCl}_2)_2\}_n$  were synthesized and characterized spectroscopically. Their catalytic activities were studied, too. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Chromium; Nitrosyl complexes; Ethylidene complexes; Metathesis; Oligomerization; Polymerization

## 1. Introduction

The nitrosyl complexes of transition metals have been studied for over 100 years [1]. The unique physical and chemical properties imparted to the compounds by the presence of strongly electron-withdrawing nitrosyl ligands, as well as possibility of their application in, among others, organic synthesis [2] are the reason of this interest. They are the catalysts or precursors of catalysts of many organic reactions, as oxidation [3–8], hydrogenation [9–11], oligomerization and polymerization [12–15], isomerization [16–20] and metathesis [16,21,22].

One of the most active catalysts of the reaction of olefin metathesis are nitrosyl complexes of molybdenum [2,16,23–25] and, a bit less, tungsten [16,21,26]. They also are catalysts of the oligomerization and polymerization reactions of alkenes and alkynes [15,27,28].

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The first examples of alkylidene complexes with low oxidation state and having nucleophilic  $=\text{CHR}$  ligands were obtained by reactions of dinitrosylmolybdenum complexes containing O-ligands (alkoxy and carboxylic ligands) with  $\text{EtAlCl}_2$  [27,29,30].

There are not many data on the catalytic activity of nitrosyl chromium complexes in reactions with alkenes and alkynes. These complexes, especially the dinitrosyl ones, are the less known among compounds of this type of the VI B group metals, possibly with the exception of the compounds with cyclopentadienyl ligands [31–37]. The dicationic complex *trans*- $[\text{Cr}(\text{NO})_2(\text{MeCN})_4](\text{PF}_6)_2$  is the only one known which cannot be predicted by theory [38], the six-coordinate dinitrosyl complex with  $\{\text{M}(\text{NO})_2\}^6$  electronic structure with *trans* position of nitrosyl ligands to each other [39].

(i) Synthesis of new dicationic *trans*-dinitrosylchromium complexes, especially of the dicarbonyl-dinitrosyl complexes and neutral *trans*-dinitrosylchromium complexes with alkoxy and carboxylic ligands, (ii) investigation of the interaction of these complexes with Lewis acids ( $\text{MCl}_4$ ,  $\text{M} = \text{Ti}$ ,  $\text{Sn}$  and  $\text{EtAlCl}_2$ ), (iii) synthesis and spectroscopy characterization of the first example of dinitrosylalkylidenechromium complex, and (iv) the study of catalytic properties of these complexes in metathesis and polymerization reactions of olefins and monosubstituted acetylene are described in this paper.

## 2. Experimental

All experiments were carried out under argon atmosphere using Schlenk techniques either in vacuum-line systems. Reagents were purified by standard methods. Solvents were distilled using appropriate drying agents under argon.

The IR spectra were recorded on a Nicolet Impact 400 spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured using a Bruker 300 spectrometer. Tetramethylsilane was used as an internal standard. Metathesis, oligomerization and polymerization reactions of olefins and acetylenes were monitored by gas chromatography, and the product were identified by GC-MS analysis (HP-5890II + 5971A).

The weight-average molecular weight ( $\overline{M}_w$ ) and number-average molecular weight ( $\overline{M}_n$ ) of the obtained polymers were determined by gel permeation chromatography (GPC) using polystyrene calibration (HPLC-HP109011 with DAD-UV/VIS and RJ detector HP1047A).

### 2.1. Synthesis of $[\text{Cr}(\text{NO})_2(\text{MeCN})_4](\text{BF}_4)_2$

Two equivalents of  $\text{NOBF}_4$  in MeCN were added to a stirred suspension of  $\text{Cr}(\text{CO})_6$  (2 g, 9 mmol) in MeCN (25 ml). When the carbonyl substrate was consumed (controlled by IR spectra), the green solution was filtered off, and dark green hygroscopic solid was isolated by precipitation using diethyl ether. The solid was washed with diethyl ether and dried in vacuo (90% yield).

IR (nujol mulls):  $\nu(\text{NO})$  1793 vs,  $\nu(\text{CN})$  2334 s, 2306 m,  $\nu(\text{BF}_4)$  1035 vs.  $^1\text{H}$  NMR (in  $\text{CD}_3\text{NO}_2$  at  $20^\circ\text{C}$ ):  $\delta$  2.01 (s, 12H,  $\text{CH}_3\text{CN}$ ). Anal. Calc. for  $\text{C}_8\text{H}_{12}\text{N}_6\text{B}_2\text{F}_8\text{O}_2\text{Cr}$ : C, 21.36; H, 2.69; N, 18.68%. Found: C, 21.49; H, 2.77; N, 18.40%.

### 2.2. Synthesis of $[\text{Cr}(\text{NO})_2(\text{CO})_2(\text{MeNO}_2)_2](\text{BF}_4)_2$

Solid  $\text{NOBF}_4$  (2.1 g, 9 mmol) was added to a stirred suspension of  $\text{Cr}(\text{CO})_6$  (2 g, 9 mmol) in  $\text{MeNO}_2$  (25 ml), and the reaction mixture was stirred for 3 h at  $60^\circ\text{C}$ . After this time the solution was filtered and concentrated to half of its original volume in vacuo before being treated dropwise with  $\text{CH}_2\text{Cl}_2$  to induce precipitation of an orange–brown solid. The solid was collected by filtration, washed with  $\text{CH}_2\text{Cl}_2$  and dried in vacuo (90% yield).

IR (nujol mulls):  $\nu(\text{NO})$  1791 vs,  $\nu(\text{CO})$  1928 s, 1911 s,  $\nu(\text{NO}_2)$  1575 m,  $\nu(\text{BF}_4)$  1035 vs.  $^1\text{H}$  NMR (in  $\text{CD}_3\text{CN}$  at  $20^\circ\text{C}$ ):  $\delta$  4.37 (s, 6H,  $\text{CH}_3\text{NO}_2$ ). Anal. Calc. for  $\text{C}_4\text{H}_6\text{N}_4\text{B}_2\text{F}_8\text{O}_8\text{Cr}$ : C, 10.35, H, 1.30; N, 12.07%. Found: C, 10.83; H, 1.62; N, 11.90%.

### 2.3. Synthesis of $[\text{Cr}(\text{NO})_2(\text{MeNO}_2)_4](\text{BF}_4)_2$

Solution of  $[\text{Cr}(\text{NO})_2(\text{CO})_2(\text{MeNO}_2)_2](\text{BF}_4)_2$  in  $\text{MeNO}_2$  was refluxed for about 3 h, until the bands  $\nu(\text{CO})$  in the IR spectrum of the solution of the starting complex disappeared. The complex was precipitated with diethyl ether, washed with  $\text{CH}_2\text{Cl}_2$  and hexane and dried in vacuo (98% yield).

IR (nujol mulls):  $\nu(\text{NO})$  1798 vs,  $\nu(\text{NO}_2)$  1570 s,  $\nu(\text{BF}_4)$  1035 vs.  $^1\text{H}$  NMR (in  $\text{CD}_3\text{CN}$  at  $20^\circ\text{C}$ ):  $\delta$  4.75 (s, 12H,  $\text{CH}_3\text{NO}_2$ ). Anal. Calc. for  $\text{C}_4\text{H}_{12}\text{N}_6\text{B}_2\text{F}_8\text{O}_{10}\text{Cr}$ : C, 9.07; H, 2.28; N, 15.86%. Found: C, 9.48; H, 2.34; N, 15.66%.

### 2.4. Synthesis of $[\text{Cr}(\text{NO})_2(\text{CO})_2(\text{bipy})](\text{BF}_4)_2$

Equimolar amount of 2,2'-bipyridyl (bipy) in  $\text{MeNO}_2$  was added to a solution of  $[\text{Cr}(\text{NO})_2(\text{CO})_2(\text{MeNO}_2)_2](\text{BF}_4)_2$  (2 g, 4.3 mmol) in  $\text{MeNO}_2$  (25 ml). The solution was stirred for 15 min, and the compound was precipitated with diethyl ether, washed with  $\text{CH}_2\text{Cl}_2$  and hexane and dried in vacuo.

IR (nujol mulls):  $\nu(\text{NO})$  1761 vs,  $\nu(\text{CO})$  1891 s, 1860 s,  $\nu(\text{C}=\text{C})$  1608 m,  $\nu(\text{BF}_4)$  1035 vs.  $^1\text{H}$  NMR (in  $\text{CD}_3\text{CN}$  at  $20^\circ\text{C}$ ):  $\delta$  7.49–9.28 (m, 8H, bipy). Anal. Calc. for  $\text{C}_{12}\text{H}_8\text{N}_4\text{B}_2\text{F}_8\text{O}_4\text{Cr}$ : C, 28.95; H, 1.62; N, 11.25%. Found: C, 28.81; H, 1.71; N, 11.09%.

### 2.5. Synthesis of $[\text{Cr}(\text{NO})_2(\text{CO})_2(\text{MeCN})_2](\text{BF}_4)_2$ , $[\text{Cr}(\text{NO})_2(\text{CO})_2(\text{MeOH})_2](\text{BF}_4)_2$ and $[\text{Cr}(\text{NO})_2(\text{bipy})_2](\text{BF}_4)_2$

These complexes were obtained in a similar manner to that described above, i.e., by treatment of  $[\text{Cr}(\text{NO})_2(\text{CO})_2(\text{MeNO}_2)_2](\text{BF}_4)_2$  in  $\text{MeNO}_2$  with 2 M equivalents of MeCN, MeOH and 2,2'-bipyridyl, respectively.

#### 2.5.1. $[\text{Cr}(\text{NO})_2(\text{CO})_2(\text{MeCN})_2](\text{BF}_4)_2$

IR (nujol mulls):  $\nu(\text{NO})$  1797 vs,  $\nu(\text{CO})$  1920 s, 1870 s,  $\nu(\text{CN})$  2334 vs, 2290 vs,  $\nu(\text{BF}_4)$  1035 vs.  $^1\text{H}$  NMR (in  $\text{CD}_3\text{NO}_2$  at  $20^\circ\text{C}$ ):  $\delta$  2.01 (s, 6H,  $\text{CH}_3\text{CN}$ ). Anal. Calc. for  $\text{C}_6\text{H}_6\text{N}_4\text{B}_2\text{F}_8\text{O}_4\text{Cr}$ : C, 17.01; H, 1.43; N, 13.22%. Found: C, 17.12; H, 1.52; N, 13.01%.

#### 2.5.2. $[\text{Cr}(\text{NO})_2(\text{CO})_2(\text{MeOH})_2](\text{BF}_4)_2$

IR (nujol mulls):  $\nu(\text{NO})$  1767 vs,  $\nu(\text{CO})$  1910 s, 1893 s,  $\nu(\text{OH})$  3411 vs,  $\nu(\text{BF}_4)$  1035 vs.  $^1\text{H}$  NMR (in  $\text{CD}_3\text{CN}$  at  $20^\circ\text{C}$ ):  $\delta$  3.47 (s, 6H,  $\text{CH}_3\text{OH}$ ), 4.06 (s, br, 2H,  $\text{CH}_3\text{OH}$ ). Anal. Calc. for  $\text{C}_4\text{H}_8\text{N}_2\text{B}_2\text{F}_8\text{O}_2\text{Cr}$ : C, 11.84; H, 1.99; N, 6.90%. Found: C, 11.91; H, 2.08; N, 6.78%.

#### 2.5.3. $[\text{Cr}(\text{NO})_2(\text{bipy})_2](\text{BF}_4)_2$

IR (nujol mulls):  $\nu(\text{NO})$  1702 vs,  $\nu(\text{C}=\text{C})$  1606 s,  $\nu(\text{BF}_4)$  1035 vs.  $^1\text{H}$  NMR (in  $\text{CD}_3\text{NO}_2$  at  $20^\circ\text{C}$ ):  $\delta$  7.49–9.28 (m, 16H, bipy). Anal. Calc. for  $\text{C}_{20}\text{H}_{16}\text{N}_6\text{B}_2\text{F}_8\text{O}_2\text{Cr}$ : C, 42.29; H, 2.84; N, 12.33%. Found: C, 42.33; H 2.95; N, 12.15%.

## 2.6. Synthesis of $\{Cr(NO)_2(OR)_2\}_n$ ( $R = Et, i-Pr$ )

$[Cr(NO)_2(CO)_2(MeNO_2)_2](BF_4)_2$  (2 g, 4.3 mmol) was dissolved in appropriate alcohol (EtOH, *i*-PrOH; 10 ml) at about 0°C. The solution was heated to the room temperature and cooled again to below 0°C. NaOR ( $R = Et, i-Pr$ ) in appropriate alcohol was added at this temperature to the solution. After 15 min, the solutions were filtered and removed under vacuum. The complexes were extracted from the remainder with a small amount of  $CH_2Cl_2$  and precipitated with hexane (60% yield).

### 2.6.1. $\{Cr(NO)_2(OEt)_2\}_n$

IR (nujol mulls):  $\nu(NO)$  1720 vs,  $\nu(OR)$  1080 m, 1025 s, 980 sh.  $^1H$  NMR (in MeCN at 20°C):  $\delta$  3.65 (s, br, 4H,  $CH_2CH_3$ ), 1.25 (s, br, 6H,  $CH_2CH_3$ ). Anal. Calc. for  $C_4H_{10}N_2O_4Cr$ : C, 23.77; H, 4.99; N, 13.86%. Found: C, 24.08; H, 4.88; N, 13.08%.

### 2.6.2. $\{Cr(NO)_2(O-i-Pr)_2\}_n$

IR (nujol mulls):  $\nu(NO)$  1718 vs,  $\nu(OR)$  1093 m, 1029 s, 969 sh.  $^1H$  NMR (in MeCN):  $\delta$  3.81 (s, br, 2H,  $CH(CH_3)_2$ ), 1.06 (s, br, 12H,  $CH(CH_3)_2$ ). Anal. Calc. for  $C_6H_{14}N_2O_4Cr$ : C, 31.31; H, 6.13; N, 12.07%. Found: C, 31.24; H, 6.25; N, 11.95%.

## 2.7. Synthesis of $Cr(NO)_2(O_2CPh)_2$

$NaO_2CPh$  (1.24 g, 8.6 mmol) in 2 ml MeOH was added to  $[Cr(NO)_2(CO)_2(MeNO_2)_2](BF_4)_2$  (2 g, 4.3 mmol) in  $MeNO_2$  (20 ml) at room temperature. The reaction mixture was stirred for 15 min. Subsequent procedure as above.

IR (nujol mulls):  $\nu(NO)$  1700 vs,  $\nu_{as}(CO_2)$  1596 s.  $^1H$  NMR (in  $CD_2Cl_2$  at 20°C):  $\delta$  7.53 (s, 4H,  $H_\alpha$ -Ph), 8.21 (s, 6H,  $H_\beta, H_\gamma$ -Ph). Anal. Calc. for  $C_{14}H_{10}N_2O_6Cr$ : C, 47.47; H, 2.85; N, 7.91%. Found: C, 47.62; H, 2.91; N, 7.78%.

## 2.8. Synthesis of $[Cr(NO)_2(OR)_2(MCl_4)_2]$ and $[Cr(NO)_2(O_2CPh)_2(MCl_4)_2]$ ( $M = Ti$ or $Sn$ )

$MCl_4$  ( $M = Ti$  or  $Sn$ ) in  $CH_2Cl_2$  was added to a stirred solution of appropriate  $\{Cr(NO)_2L_2\}_n$  complex ( $L = OEt, O-i-Pr, O_2CPh$ ) in  $CH_2Cl_2$  in 1/2 molar ratio. The yellow–brown precipitates of the adducts were filtered off, washed with  $CH_2Cl_2$  and dried in vacuo.

### 2.8.1. $[Cr(NO)_2(OEt)_2(TiCl_4)_2]$

IR (nujol mulls):  $\nu_s(NO)$  1882 vs,  $\nu_{as}(NO)$  1767 vs,  $\nu(OR)$  1088 m, 1019 s, 993 sh.  $^1H$  NMR (in  $CD_3CN$  at 20°C):  $\delta$  4.76 (s, br, 2H,  $CH_2CH_3$ ), 3.68 (s, br, 2H,  $CH_2CH_3$ ), 1.26 (s, br, 3H,  $CH_2CH_3$ ), 0.87 (s, br, 3H,  $CH_2CH_3$ ). Anal. Calc. for  $C_4H_{10}N_2Cl_8O_4CrTi_2$ : C, 8.31; H, 1.74; N, 4.85; Cl, 48.43%. Found: C, 8.52; H, 1.80; N, 4.60; Cl, 48.60%.

### 2.8.2. $[Cr(NO)_2(O-i-Pr)_2(SnCl_4)_2]$

IR (nujol mulls):  $\nu_s(NO)$  1885 s,  $\nu_{as}(NO)$  1753 vs,  $\nu(OR)$  1087 vs, 1025 s, 913 m.  $^1H$  NMR (in  $CD_3CN$  at 20°C):  $\delta$  4.15 (s, br,  $^1H$ ,  $CH(CH_3)_2$ ), 3.92 (s, br, 1H,  $CH(CH_3)_2$ ), 1.35 (s, 6H,  $CH(CH_3)_2$ ), 1.09 (s, 6H,  $CH(CH_3)_2$ ). Anal. Calc. for  $C_6H_{14}N_2Cl_8O_4CrSn_2$ : C, 9.61; H, 1.88; N, 3.74; Cl, 37.32%. Found: C, 9.82; H, 1.92; N, 3.48; Cl, 37.60%.

### 2.8.3. $[Cr(NO)_2(O_2CPh)_2(TiCl_4)_2]$

IR (nujol mulls):  $\nu_s(NO)$  1881 s,  $\nu_{as}(NO)$  1755 vs,  $\nu(CO)$  1595 vs.  $^1H$  NMR (in  $CD_3CN$  at 20°C):  $\delta$  8.01 (s, 4H,  $H_\alpha$ -Ph), 7.63 (s, 2H,  $H_\beta$ -Ph), 7.50 (s, 4H,  $H_\gamma$ -Ph). Anal. Calc. for

$C_{14}H_{10}N_2Cl_8O_6CrTi_2$ : C, 23.03; H, 1.38; N, 3.84; Cl, 38.34%. Found: C, 23.38; H, 1.41; N, 3.60; Cl, 38.72%.

## 2.9. Synthesis of $[Cr(NO)_2(OEt)_2(EtAlCl_2)_2]$

A vigorously stirred solution of  $\{Cr(NO)_2(OEt)_2\}_n$  (0.1 g, 0.49 mmol) in PhCl (5 ml) was cooled down to  $-40^\circ C$ . A solution of  $EtAlCl_2$  in hexane (2.94 mmol) was added dropwise. Next, about 20 ml of hexane was added at this temperature. The brown precipitate of an adduct was filtered off, repeatedly washed with hexane and dried in vacuo.

IR (nujol mulls):  $\nu_s(NO)$  1884 s,  $\nu_{as}(NO)$  1756 vs,  $\nu(OR)$  1091 m, 1052 s, 997 m.  $^1H$  NMR (in  $CD_3CN$  at  $20^\circ C$ ):  $\delta$  3.80 and 3.52 (s, br, 4H,  $OCH_2CH_3$ ), 0.97 (s, br, 6H,  $OCH_2CH_3$ ), 1.26 (s, 6H,  $CH_3H_2AlCl_2$ ),  $-0.068$  (s, 4H,  $CH_3H_2AlCl_2$ ). Anal. Calc. for  $C_8H_{20}N_2Cl_4O_4CrAl$ : C, 21.07; H, 4.42; N, 6.14%. Found: C, 21.21; H, 4.50; N, 5.92%.

## 2.10. Synthesis of $\{Cr(NO)_2(CHMe)(OEt)_2(AlCl_2)_2\}_n$

$EtAlCl_2$  in hexane (2.94 mmol) was added dropwise to a vigorously stirred solution of  $\{Cr(NO)_2(OEt)_2\}_n$  (0.1 g, 0.49 mmol) in PhCl (5 ml), at about  $-10^\circ C$ . The solution was heated to room temperature and after 15 min the product was precipitated with hexane, filtered off, repeatedly washed with hexane and dried in vacuo.

IR (nujol mulls):  $\nu_s(NO)$  1895 s,  $\nu_{as}(NO)$  1770 vs,  $\nu(OR)$  1091 m, 1030s, 995 m.  $^1H$  NMR (in  $CD_3CN$ , at  $-300^\circ C$ ):  $\delta$  7.66 (s, br, 1H,  $CHCH_3$ ), 4.71 and 4.35 (s, br; 4H,  $CH_2CH_3$ ), 0.91 (s, br; 9H,  $CH_2CH_3$ ). Anal. Calc. for  $C_6H_{14}N_2Cl_4O_4CrAl_2$ : C, 16.92; H, 3.31; N, 6.58%. Found: C, 17.08; H, 3.38; N, 6.17%.

# 3. Results and discussion

## 3.1. Synthesis of dinitrosylchromium complexes

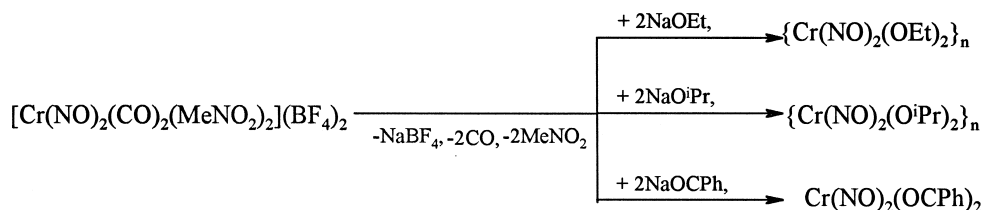
All the six-coordinated dinitrosyl complexes of the VIB group metals have the  $\{M(NO)_2\}^6$  electronic structure with nitrosyl ligands in *cis* position to each other [38,40]. The only exception among these complexes is *trans*- $[Cr(NO)_2(MeCN)_4](PF_6)_2$  [39]. This unique, as far, dinitrosylchromium complex with *trans* position of nitrosyl groups was found in the reaction of  $Cr(CO)_3(PhMe)$  with  $NOPF_6$  in MeCN. The same complex is formed when  $Cr(CO)_6$  is treated with two equivalents of  $NOBF_4$  in a MeCN solution. Its IR spectrum exhibits only one strong  $\nu(NO)$  band ((nujol mull)  $1793\text{ cm}^{-1}$ ; (in MeCN)  $1789\text{ cm}^{-1}$ ) and two  $\nu(CN)$  frequencies of coordinated MeCN ligands ((nujol mull)  $2306$ ,  $2334\text{ cm}^{-1}$ ). Its  $^1H$  NMR spectrum in  $CD_3NO_2$  consists of one singlet ( $\delta$ , 2.01 ppm) of the methyl groups of MeCN ligands.

Reaction of  $Cr(CO)_6$  with  $NOBF_4$  in  $MeNO_2$  ( $60^\circ C$ ,  $t_r \geq 3\text{ h}$ ) leads to the formation of a new type *trans*-dinitrosylchromium complex,  $[Cr(NO)_2(CO)_2(MeNO_2)_2](BF_4)_2$ . This brown diamagnetic complex is moisture and oxygen sensitive and soluble in polar solvents; its solution decompose slowly in air. The IR spectra ((nujol mull)  $\nu(CO)$  1911, 1828,  $\nu(NO)$  1791,  $\nu(NO_2)$   $1575\text{ cm}^{-1}$ ; (in  $MeNO_2$ )  $\nu(CO)$  1926 and 1910,  $\nu(NO)$   $1790\text{ cm}^{-1}$ ) and  $^1H$  NMR spectrum ((acetone- $d_6$ )  $\delta$  4.37 (s,  $CH_3$ ) ppm) are consistent with the stereochemistry *trans-cis-cis*- $[Cr(NO)_2(CO)_2(MeNO_2)_2](BF_4)_2$ .

$MeNO_2$  ligands are very easily replaced by a variety of other ligands. For example, the reaction of  $[Cr(NO)_2(CO)_2(MeNO_2)_2](BF_4)_2$  with 2,2'-dipyridyl (bipy) in eqimolar ratio and with MeCN, as well as MeOH in molar ratio of 1:2, leads to formation of  $[Cr(NO)_2(CO)_2L_2](BF_4)_2$  ( $L_2 = \text{bipy}$  or  $L = \text{MeCN}$  and  $\text{MeOH}$ ). All these complexes are brown and have the same stereochemistry core of

*trans-cis*-[Cr(NO)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>. Their IR spectra in nujol mulls and in MeNO<sub>2</sub> solutions exhibit one  $\nu(\text{NO})$  and two  $\nu(\text{CO})$  frequencies (see Section 2). These complexes display <sup>1</sup>H NMR spectra in CD<sub>3</sub>NO<sub>2</sub> with multiplets at 7.49–9.28 (8H, bipy) for [Cr(NO)<sub>2</sub>(CO)<sub>2</sub>(bipy)](BF<sub>4</sub>)<sub>2</sub>, one sharp signal at 2.01 (6H, CH<sub>3</sub>CN) for [Cr(NO)<sub>2</sub>(CO)<sub>2</sub>(MeCN)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, and two singlets at 3.47 (6H, CH<sub>3</sub>OH) and 4.06 (2H, CH<sub>3</sub>OH) for [Cr(NO)<sub>2</sub>(CO)<sub>2</sub>(MeOH)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>. Addition of donor ligands to [Cr(NO)<sub>2</sub>(CO)<sub>2</sub>(MeNO<sub>2</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> in excess gives *trans*-[Cr(NO)<sub>2</sub>L<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> type complexes. For example, reaction of [Cr(NO)<sub>2</sub>(CO)<sub>2</sub>(MeNO<sub>2</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> with two molar equivalents of 2,2'-dipyridyl in MeNO<sub>2</sub> yields [Cr(NO)<sub>2</sub>(bipy)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (IR (nujol mull)  $\nu(\text{NO})$  1720 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>CN)  $\delta$  7.49–9.28 (m, 16H) ppm). [Cr(NO)<sub>2</sub>(MeCN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> can also be obtained by dissolving [Cr(NO)<sub>2</sub>(CO)<sub>2</sub>(MeNO<sub>2</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> in MeCN. IR monitoring of the reaction of [Cr(NO)<sub>2</sub>(CO)<sub>2</sub>(MeNO<sub>2</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> an excess of solvents such as MeCN and MeOH shows that its transformation to [Cr(NO)<sub>2</sub>(MeCN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> and to [Cr(NO)<sub>2</sub>(MeOH)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>, proceeds via [Cr(NO)<sub>2</sub>(CO)<sub>2</sub>L<sub>2</sub>]<sup>2+</sup>, and [Cr(NO)<sub>2</sub>(CO)L<sub>3</sub>]<sup>2+</sup> intermediates (L = MeCN:  $\nu(\text{NO})$  1812,  $\nu(\text{CO})$  1928 cm<sup>-1</sup>, L = MeOH:  $\nu(\text{NO})$  1752,  $\nu(\text{CO})$  1890 cm<sup>-1</sup>).

Very convenient method for synthesis of different dinitrosyl complexes [11,41–45] is based on the reaction of complex containing [M(NO)<sub>2</sub>]<sup>2+</sup> moiety (M = Cr, Mo, W) with suitable ligands. Such a method was also applied by us for the synthesis of new neutral *trans*-dinitrosylchromium compounds:



The *trans*-dinitrosylchromium complexes, {Cr(NO)<sub>2</sub>(OR)<sub>2</sub>}<sub>n</sub> (R = Et, *i*-Pr) and Cr(NO)<sub>2</sub>(O<sub>2</sub>CR)<sub>2</sub> (R = Ph, Me) are brown–green, soluble in benzene, toluene and chlorosubstituted solvents. They are moisture and air sensitive. The alkoxy complexes are polymeric. The degree of polymerization depends mainly on the temperature during synthesis, and also changes in time. Their IR spectra (see Section 2) are also characterized by strong bands of  $\nu(\text{NO})$  at 1700–1720 cm<sup>-1</sup>, which are attributed to nitrosyl ligands *trans* coordinated in respect one to another. Characters of the spectra of {Cr(NO)<sub>2</sub>(OR)<sub>2</sub>}<sub>n</sub> in  $\nu(\text{OR})$  region correspond to the polymeric structure [46], like in dialkoxydinitrosylmolybdenum complexes [44]. Lack of well resolved resonances of alkoxy ligands in the <sup>1</sup>H NMR spectra of alkoxy complexes (see Section 2) is most probably caused by the terminal  $\rightleftharpoons$  bridge exchange of OR-ligands.

The <sup>1</sup>H NMR spectrum of Cr(NO)<sub>2</sub>(O<sub>2</sub>CPh)<sub>2</sub> exhibits two signals at 7.53 and 8.21 ppm due to  $\alpha$  and  $\beta + \gamma$  protons of phenyl groups, respectively.

Reaction of the complexes containing *trans*-[Cr(NO)<sub>2</sub>]<sup>2+</sup> core with sulfur chelating ligands leads to formation of respective *cis*-dinitrosylchromium complexes. For example, reaction of *trans*-[Cr(NO)<sub>2</sub>(MeCN)<sub>4</sub>]<sup>2+</sup> with S<sub>2</sub>CNEt<sub>2</sub><sup>-</sup> and/or S<sub>2</sub>C<sub>2</sub>(CN)<sub>2</sub><sup>2-</sup> leads to formation of *cis*-[Cr(NO)<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>] and *cis*-[Cr(NO)<sub>2</sub>(S<sub>2</sub>C<sub>2</sub>(CN)<sub>2</sub>)<sub>2</sub>]<sup>2-</sup> [39].

### 3.2. Reaction of dinitrosyl chromium complexes with Lewis acids

#### 3.2.1. Reaction with MCl<sub>4</sub> (M = Ti, Sn)

Interactions of {Cr(NO)<sub>2</sub>(OR)<sub>2</sub>}<sub>n</sub> (R = Et, *i*-Pr) and Cr(NO)<sub>2</sub>(O<sub>2</sub>CPh)<sub>2</sub> with TiCl<sub>4</sub> and SnCl<sub>4</sub> in PhCl and CH<sub>2</sub>Cl<sub>2</sub> solutions for molar ratios [Cr]/[MCl<sub>4</sub>] equal to 1/2 were investigated. The effect

of these interactions was *trans*–*cis* isomerization of these complexes. The reactions products are respective adducts  $[\text{Cr}(\text{NO})_2(\text{OR})_2(\text{MCl}_4)_2]$  and  $[\text{Cr}(\text{NO})_2(\text{O}_2\text{CPh})_2(\text{MCl}_4)_2]$  ( $\text{R} = \text{Et}$ , *i*-Pr;  $\text{M} = \text{Ti}$  or  $\text{Sn}$ ), where ligands NO are situated in mutual *cis* positions. Their IR spectra contain two characteristic frequencies  $\nu(\text{NO})$ :  $\nu_s$  at 1885–1875  $\text{cm}^{-1}$  and  $\nu_{\text{as}}$  at 1765–1753  $\text{cm}^{-1}$  (see Section 2). The attack of Lewis acids towards the oxygen atoms of alkoxy and carboxylic ligands causes, in the first stage, that free coordination sites appear at the central atom. This allows reaching lower energetic states of the complex molecules, i.e., formation of *cis*- $[\text{Cr}(\text{NO})_2]$  configuration [47]. The free coordination sites are successively occupied by chlorines of Lewis acids, forming bridges  $\text{Cr}-\text{Cl}-\text{M}$  ( $\text{M} = \text{Ti}$  and  $\text{Sn}$ ).

Pure  $[\text{Cr}(\text{NO})_2(\text{OR})_2(\text{MCl}_4)_2]$  ( $\text{R} = \text{Et}$ , *i*-Pr;  $\text{M} = \text{Ti}$  or  $\text{Sn}$ ) and  $[\text{Cr}(\text{NO})_2(\text{O}_2\text{CPh})_2(\text{TiCl}_4)_2]$  adducts were isolated from respective systems in  $\text{CH}_2\text{Cl}_2$ . These adducts are soluble only in donor solvents (alcohols, MeCN, etc.). The  $^1\text{H}$  NMR spectra of  $[\text{Cr}(\text{NO})_2(\text{OR})_2(\text{MCl}_4)_2]$  in  $\text{CD}_3\text{CN}$  contain signals of alkoxy ligands ( $\text{R} = \text{Et}$ ,  $\text{M} = \text{Ti}$ :  $\delta$  1.26, 0.87 ( $\text{CH}_3$ ), 4.76, 3.68 ( $\text{CH}_2$ ), ppm;  $\text{R} = \text{i-Pr}$ ,  $\text{M} = \text{Sn}$ :  $\delta$  4.15, 3.92 ( $\text{CH}$ ), 1.11 ( $\text{CH}_3$ )<sub>2</sub> ppm) and additional a signals at about 2.15 ppm ( $\delta$   $\text{CH}_3\text{CN}$ ), which proves interaction of the adducts with the solvent. Character of these spectra, as well as the existence, in the IR spectra of the adducts, of the bands corresponding to  $\nu(\text{CO})$  of bridge and terminal alkoxy ligands suggests that some alkoxy groups could be located only at the metals of Lewis acids, which are connected to chromium atoms by chlorine bridges.

The  $^1\text{H}$  NMR spectrum of  $[\text{Cr}(\text{NO})_2(\text{O}_2\text{CPh})_2(\text{TiCl}_4)_2]$  exhibits, at room temperature, three broad singlets at 8.01, 7.63 and 7.50 ppm, due to  $\alpha$ ,  $\beta$  and  $\gamma$ , respectively.

### 3.2.2. Reaction with $\text{EtAlCl}_2$

*Trans*–*cis* isomerization of nitrosyl ligands is also an effect of interactions of *trans*-dinitrosylchromium complexes with Lewis acids, leading to the formation of respective *cis*-adducts which, by further transformations into diethyl derivatives and their  $\alpha$ -hydrogen elimination leads to formation of *cis*-dinitrosylchromium ethylidene complexes, like it was observed in the case of the molybdenum analogs [27,29,30]. Theoretical calculation for the model alkylidenedinitrosylmolybdenum complex [24,48] revealed that coordination of the alkylidene ligand in the Mo–NO bonding plane, realized from the opposite side to the NO ligands, required the smallest amount of activation energy.

Interactions of *trans*-dinitrosylchromium complexes with  $\text{EtAlCl}_2$  were examined by IR method in the  $\nu(\text{NO})$  region in PhCl solutions for the complex/ $\text{EtAlCl}_2$  molar ratios 1/2, 1/4 and 1/6. The reagents were mixed at  $-40^\circ\text{C}$  and the IR spectra were recorded at ambient temperature, at fixed time intervals. The IR spectra of these solutions contain two  $\nu(\text{NO})$  frequencies ( $\nu_s = 1907 \text{ cm}^{-1}$  and  $\nu_{\text{as}} = 1793 \text{ cm}^{-1}$ ), the values independent on the type of ligand. It can be assumed that these frequencies characterize the ethylidenedinitrosylchromium complexes. Identical  $\nu(\text{NO})$  values of the complexes indicate that the kind of alkoxy and carboxylic ligands has no effect on electronic density of the central atom, similar to the case molybdenum analogs [24,30]. However, in contrary to the ethylidenedinitrosylmolybdenum complexes, the chromium ones undergo decomposition, seen in gradual disappearance of the  $\nu(\text{NO})$  frequency. Complete decomposition occurs after about 3 h.

Initially, in the IR spectra of these systems, two shoulders at 1880 and 1769  $\text{cm}^{-1}$  corresponding to the  $\nu_s$  i  $\nu_{\text{as}}(\text{NO})$  were observed, which quickly disappear (after about 5 min). These shoulders can be assumed to the  $\nu(\text{NO})$  vibrations of intermediate adducts formed.

The adduct  $[\text{Cr}(\text{NO})_2(\text{OEt})_2(\text{EtAlCl}_2)_2]$  and the ethylidene complexes  $\{\text{Cr}(\text{NO})_2(\text{CHMe})(\text{OEt})_2(\text{AlCl}_2)_2\}_n$  were synthesized and spectrally characterized. The adduct is a brown precipitate reacting with oxygen and moisture. It is insoluble in alkanes, PhCl and  $\text{CH}_2\text{Cl}_2$  and soluble in donor solvents, e.g., MeCN. Its IR spectrum (see Section 2) displays two  $\nu(\text{NO})$  bands typical of the

*cis*-[Cr(NO)<sub>2</sub>]<sub>6</sub> core. The character of this spectrum in the  $\nu(\text{OR})$  region indicates a bridge Cr–OR–Al coordination of ethoxy ligands ( $\nu(\text{CO}) < 1050 \text{ cm}^{-1}$  [46]), but also the existence of terminal alkoxy ligands [46], probably coordinated to aluminium of EtAlCl<sub>2</sub> molecules, bonded to the central atoms by Cr–Cl–Al bridges. Two proton resonances of CH<sub>2</sub> fragments of ethoxy ligands in the <sup>1</sup>H NMR spectrum of this adduct (in CD<sub>3</sub>CN, 20°C) at 3.80 and 3.52 ppm are consistent with the character of its IR spectrum in the region of  $\nu(\text{CO})$  alkoxy ligands. The <sup>1</sup>H NMR spectra exhibit also a broad singlet at 0.97 ppm due to methyl protons of ethoxy ligands, and triplet at 1.26 (6H, CH<sub>3</sub>CH<sub>2</sub>) and quartet at –0.068 (4H, CH<sub>3</sub>CH<sub>2</sub>) ppm due to protons of two EtAlCl<sub>2</sub> molecules.

The adduct exhibits no catalytic activity in reactions with alkenes and alkynes.

The diethoxydinitrosylethylidenechromium complex {Cr(NO)<sub>2</sub>(CHMe)(OEt)<sub>2</sub>(AlCl<sub>2</sub>)<sub>2</sub>}<sub>n</sub> is a brown precipitate, very sensitive on oxygen and moisture, insoluble in alkanes, aromatic solvents and CH<sub>2</sub>Cl<sub>2</sub>, undoubtedly because of its highly polymerized form. It is soluble in donor solvents, e.g., CH<sub>3</sub>CN. Its IR spectra (nujol mull) exhibit two  $\nu(\text{NO})$  frequencies (1895 and 1770 cm<sup>–1</sup>), the values a bit lower than the respective ones in solution. This effect was also observed for alkylidenedinitrosylmolybdenum complexes [27,30]. Character of IR spectra in  $\nu(\text{OEt})$  region is similar to that of the adduct (see Section 2), proving that some OEt groups are bonded to the AlCl<sub>2</sub> ones. The <sup>1</sup>H NMR spectrum in CD<sub>3</sub>CN at –30°C contains broad signals of CH<sub>2</sub> ( $\delta$  4.71 (s, br; 2H), and 4.35 (s, br; 2H) ppm) and CH<sub>3</sub> protons ( $\delta$  0.91 s, br; 9H) of ethoxy ligands and a singlet at 7.66 ppm due to H<sub>α</sub> of ethylidene ligand. The broad nature of this signal is an effect of dynamic exchange process, like in alkylidenedinitrosylmolybdenum complexes [27,30]. The high-field <sup>1</sup>H NMR resonance of  $\nu$ -hydrogen is a proof for nucleophilic character of alkylidene ligands [49–51].

Also the alkylidene complex in CD<sub>3</sub>CN undergoes destruction in time. It manifests in disappearance of the H<sub>α</sub> signal at 7.66 ppm, and appearance of a signal in the resonance region of olefin protons at 6.05 ppm.

Alkylidenedinitrosylmolybdenum complexes are stabilized by O-ligands (alkoxy and carboxylic) [27,30]. Such stabilizing effect of this kind of ligands was not observed in the case of chromium complexes under investigation. The reason could be lack of both alkoxy groups in the coordination sphere of chromium.

During the reaction of *trans*-dinitrosylchromium complexes of the type [Cr(NO)<sub>2</sub>(CO)<sub>2</sub>L<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (L = MeNO<sub>2</sub>, MeCN) with EtAlCl<sub>2</sub>, respective *cis*-dinitrosyl complexes are formed, too. IR spectra of these complexes (in PhCl) are characterized by two  $\nu(\text{NO})$  frequencies ( $\nu_s = 1895$  and  $\nu_{as} = 1775 \text{ cm}^{-1}$ ), the values identical to those described above for the ethylidenechromium complexes. The spectra do not contain the  $\nu(\text{CO})$  frequencies. After some time, these  $\nu(\text{NO})$  frequencies disappear, too.

### 3.3. Catalytic activity of dinitrosylchromium complexes

#### 3.3.1. Dicationic complexes

The [M(NO)<sub>2</sub>(MeCN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (M = Mo, W) compounds catalyze polymerization, oligomerization and rearrangement of olefins reactions [15]. A similar reactivity pattern has been observed for other weakly ligated transition-metal cations, e.g., [Pt(MeCN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> [52,53], [Rh(NO)(MeCN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> [54] and [Fe(NO)<sub>2</sub>(solv)<sub>n</sub>][X] [55]. All these reactions may well follow the same mechanistic pathway, where generation of incipient carbonium ions by interaction of olefins with electrophilic transition-metal complexes is a general phenomenon.

The dicationic dinitrosylchromium complexes, for example [Cr(NO)<sub>2</sub>(MeCN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> and [Cr(NO)<sub>2</sub>(CO)<sub>2</sub>(MeNO<sub>2</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, with NO groups mutually *trans* coordinated, also were found to



catalyze the polymerization of olefins. Their catalytic activity were tested in polymerization reaction of norbornene in MeNO<sub>2</sub> solution at the reagent concentration ratio [Cr]/[olefin] = 1/100. The yield of polynorbornene after 24 h was 30% for [Cr(NO)<sub>2</sub>(MeCN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> and 40% for [Cr(NO)<sub>2</sub>(CO)<sub>2</sub>(MeNO<sub>2</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>. The obtained polymers were insoluble in organic solvents.

### 3.3.2. {Cr(NO)<sub>2</sub>(OR)<sub>2</sub>}<sub>n</sub>-MCl<sub>4</sub> and Cr(NO)<sub>2</sub>(O<sub>2</sub>CPh)<sub>2</sub>-MCl<sub>2</sub> (M = Ti, Sn) systems

None of the adducts presented above exhibits any catalytic activity in the polymerization or oligomerization of phenylacetylene. However, after addition of a Lewis acid (TiCl<sub>4</sub> or SnCl<sub>4</sub>) to the solution of precursor complexes ((Cr(NO)<sub>2</sub>(O<sub>2</sub>CPh)<sub>2</sub> and/or {Cr(NO)<sub>2</sub>(OEt)<sub>2</sub>}<sub>n</sub>) and excess of phenylacetylene, the conversion was observed (Table 1).

No polymerization or oligomerization occurred in the similar system based on dialkoxydinitrosyl-molybdenum complex [56]. The steric effect, easier formation of a stable adduct caused a lack of catalytic activity in this system. The catalytic activity of the system with ethoxydinitrosylchromium complex is probably the effect of a lability of the ethoxy ligands, which manifests, among others, in their replacement from chromium atom to the Lewis acid metal.

The conversion of monomer and yield of methanol insoluble product (ca. 20%) hardly depend on the kind of Lewis acid. The products of these reactions are mainly triphenylbenzene derivatives, a small amount of linear oligomers, which weight-average molecular weights ( $\overline{M}_w$ ) are about 600, and 1-phenylnaphthalene. Low molecular weight of the obtained methanol insoluble products can be caused by kinetic effects, as well as by possible degradation induced by the catalysts. The degradation products can be also 1,3,5-triphenylbenzene and 1-phenylnaphthalene [57–60]. The structure of the methanol insoluble products is *trans*-cisoidal (by <sup>1</sup>H NMR and IR [61,62]).

Thus, the following mechanism of oligomerization and cyclotrimerization of phenylacetylene is proposed. Reaction of catalyst precursor complex with Lewis acids causes formation of free coordination sites at the metal. Consequently, rearrangement of NO ligands to *cis*-position occurs and, if phenylacetylene is present in the reaction system, it coordinates to the metal forming vinylidene complex [63,64]. Further polymerization (oligomerization) proceeds by metal carbene mechanism. If the catalysts are metal carbenes, the cyclic trimers are formed only through the *cis*-cisoidal-induced backbiting and/or intramolecular reactions [60]. When the free coordination sites are blocked by, for instance, chlorines of the Lewis acids, inactive adducts are formed and reaction is terminated. For the systems with metal chloride-based catalyst, Masuda and Higashimura [65] proposed a mechanism of polymerization and cyclotrimerization of phenylacetylene by metal carbene and by metallacyclopentadiene, respectively.

<sup>1</sup>H NMR investigation of the Cr(NO)<sub>2</sub>(O<sub>2</sub>CPh)<sub>2</sub>-SnCl<sub>4</sub>-phenylacetylene (PA) system ([Cr]/[Sn]/[PA] = 1/2/1) did not allow to identify the vinylidene complex, because of its fast reaction with the molecules of phenylacetylene even in very low concentrations. Therefore, these spectra

Table 1

Polymerization of phenylacetylene by {Cr(NO)<sub>2</sub>(OR)<sub>2</sub>}<sub>n</sub>/MCl<sub>4</sub> i Cr(NO)<sub>2</sub>(O<sub>2</sub>CPh)<sub>2</sub>/MCl<sub>4</sub> catalysts<sup>a</sup>

System	Solvent	Conv. [%]	Linear oligomers [%]	Trimers [%]	Dimer [%]
{Cr(NO) <sub>2</sub> (OEt) <sub>2</sub> } <sub>n</sub> /SnCl <sub>4</sub>	PhCl	10	0.64	6.94	2.42
Cr(NO) <sub>2</sub> (O <sub>2</sub> CPh) <sub>2</sub> /TiCl <sub>4</sub>	PhCl	20		19.32	0.68
Cr(NO) <sub>2</sub> (O <sub>2</sub> CPh) <sub>2</sub> /SnCl <sub>4</sub>	PhCl	2	0.14	1.36	0.5
Cr(NO) <sub>2</sub> (O <sub>2</sub> CPh) <sub>2</sub> /SnCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	20	2.36	15.03	2.61
Cr(NO) <sub>2</sub> (O <sub>2</sub> CPh) <sub>2</sub> /TiCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	20	2.54	16.02	1.44

<sup>a</sup>Reaction conditions: concentration of catalyst [Cr] = 0.49 mmol; [Cr]/[MCl<sub>4</sub>] = 1/2; [Cr]/[PA] = 1:50; room temperature.

Table 2

Catalytic activity of diethoxydinitrosylethylidenechromium complex and  $\{\text{Cr}(\text{NO})_2(\text{OR})_2\}_n/\text{EtAlCl}_2$  ( $\text{R} = \text{Et}$ ,  $\text{O}-i\text{-Pr}$  and  $\text{Cr}(\text{NO})_2(\text{O}_2\text{CPh})/\text{EtAlCl}_2$  systems<sup>a</sup>

System	<i>t</i>	Pent-1-ene			Pent-2-ene		Cyclopentene		
		% Metathesis	% Isomerization	% Oligomerization	$\overline{M}_n$	% Metathesis	% Oligomerization	$\overline{M}_n$	% Polymerization
$\{\text{Cr}(\text{NO})_2(\text{OEt})_2\}_n/$ 6 $\text{EtAlCl}_2$	10 min 5 <sup>b</sup>		95 <sup>c</sup>		2 <sup>d</sup>				
	60 min		100	45			35		52 <sup>e</sup>
	24 h			100 <sup>f</sup>	660		100 <sup>f</sup>	570	100 <sup>e</sup>
$\{\text{Cr}(\text{NO})_2(\text{O}-i\text{-Pr})_2\}_n/$ 6 $\text{EtAlCl}_2$	60 min		100 <sup>c</sup>	30			25		
	24 h			45 <sup>f</sup>	630		40 <sup>f</sup>	530	30
$\{\text{Cr}(\text{NO})_2(\text{O}_2\text{CPh})_2\}_n/$ 6 $\text{EtAlCl}_2$	24 h		93 <sup>c</sup>	72 <sup>f</sup>	530		75 <sup>f</sup>	530	20
$\{\text{Cr}(\text{NO})_2(\text{CHMe})-(\text{OEt})_2(\text{AlCl}_2)_2\}_n$	24 h			20					$1.4 \times 10^4$

<sup>a</sup>Reaction conditions: solvent PhCl; concentrations of catalyst  $[\text{Cr}] = 0.49$  mmol;  $[\text{Cr}]/[\text{EtAlCl}_2] = 1/6$ ;  $[\text{Cr}]/[\text{olefine}] = 1/100$ ; room temperature.

<sup>b</sup>Metathesis to etene and okt-4-ene.

<sup>c</sup>Isomerisation to pent-2-ene.

<sup>d</sup>Metathesis to but-2-ene and hex-3-ene.

<sup>e</sup>Polymer insoluble in organic solvents.

<sup>f</sup>Oligomerisation of product of metathesis and isomerisation.

contain the proton resonances of polyphenylacetylene ( $\delta = 7.20\text{--}7.30$  ppm), and signals at 13.37 ppm most probably due to  $H_\alpha$  of the carbene ligand.

### 3.3.3. $\{\text{Cr}(\text{NO})_2(\text{OR})_2\}_n$ and/or $\text{Cr}(\text{NO})_2(\text{O}_2\text{CPh})_2\text{--EtAlCl}_2$ systems and $\{\text{Cr}(\text{NO})_2(\text{CHMe})-(\text{OEt})_2(\text{AlCl}_2)_2\}_n$

The catalytic activity of dinitrosylethylidenechromium complex  $\{\text{Cr}(\text{NO})_2(\text{CHMe})(\text{OEt})_2(\text{AlCl}_2)_2\}_n$  and the systems  $\{\text{Cr}(\text{NO})_2(\text{OEt})_2\}_n/\text{EtAlCl}_2$  and  $\text{Cr}(\text{NO})_2(\text{O}_2\text{CPh})_2/\text{EtAlCl}_2$  were tested in reaction with pent-1-ene, pent-2-ene and cyclopentene in PhCl solution at ambient temperature. The activities of the catalysts can be read from the data in Table 2.

The polymeric ethylidene complex forms heterogeneous system and catalyzes polymerization of pent-1-ene. No metathesis products were found. Similar catalytic properties were exhibited by the polymeric species of alkylidenedinitrosylmolybdenum complexes [27,30].

Two-component systems (complex/ $\text{EtAlCl}_2$ ) exhibit high activity in isomerization of pent-1-ene to pent-2-ene. Initially, after mixing the reagents, they catalyze also the metathesis reaction of pent-1-ene and pent-2-ene (Table 2). After some time, they cause only polymerization of the initial olefins and the products of their metathesis. Most probably, polymerization does not occur according to the carbene mechanism, and the catalysts of these reactions are the products of decomposition of ethylidene complexes formed in the system. The above suggestion could be supported by studies of the structure of polymers obtained in these systems from cyclopentene (Table 2). These polymers do not contain unsaturated fragments in their chains.

## Acknowledgements

We thank the State Committee for Scientific Research for supporting this work (grant no. 3T09A09410).

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