

SPECTRA, FORMATION CONSTANTS, REACTIONS AND CATALYTIC ACTIVITIES OF NITROGEN-BONDED UNSATURATED NITRILE COMPLEXES OF RHODIUM(I)

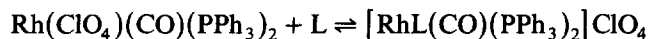
MYOUNG KIE LEE, IN BUM KIM and CHONG SHIK CHIN *

Department of Chemistry, Sogang University, IPO Box 1142, 121 Seoul (Korea)

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Summary

Cationic rhodium(I) complexes, $[\text{RhL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ ($\text{L} = \text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$, *cis*- $\text{CH}_3\text{CH}=\text{CHCN}$, *trans*- $\text{CH}_3\text{CH}=\text{CHCN}$, $\text{CH}_2=\text{CHCH}_2\text{CN}$; $\text{PPh}_3 = \text{P}(\text{C}_6\text{H}_5)_3$) have been prepared by the reactions of $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ with L. Spectral data suggest that L is coordinated to rhodium through the nitrogen atom. Formation constants for the reaction:



have been measured to be $2.93 \times 10^5 \text{ M}^{-1}$ ($\text{L} = \text{cis-CH}_3\text{CH}=\text{CHCN}$), $2.12 \times 10^5 \text{ M}^{-1}$ ($\text{L} = \text{CH}_2=\text{CHCH}_2\text{CN}$), $1.97 \times 10^5 \text{ M}^{-1}$ ($\text{L} = \text{trans-CH}_3\text{CH}=\text{CHCN}$), $5.61 \times 10^4 \text{ M}^{-1}$ ($\text{L} = \text{CH}_2=\text{CHCN}$) and $4.77 \times 10^4 \text{ M}^{-1}$ ($\text{L} = \text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$) at 25°C in monochlorobenzene. Both complexes with $\text{L} = \text{CH}_3\text{CH}=\text{CHCN}$ (*cis* and *trans*) show catalytic activities for the hydrogenation of $\text{CH}_3\text{CH}=\text{CHCN}$ to $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$ at 30°C while complexes with $\text{L} = \text{CH}_2=\text{CHCH}_2\text{CN}$ and $\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$ do not catalyze the hydrogenation of L at 30°C . It was found that the hydrogenation of $\text{CH}_3\text{CH}=\text{CHCN}$ with complexes ($\text{L} = \text{CH}_3\text{CH}=\text{CHCN}$) is faster than that of $\text{CH}_2=\text{CHCN}$ with the complex ($\text{L} = \text{CH}_2=\text{CHCN}$) while the oligomerization of $\text{CH}_3\text{CH}=\text{CHCN}$ is slower than that of $\text{CH}_2=\text{CHCN}$.

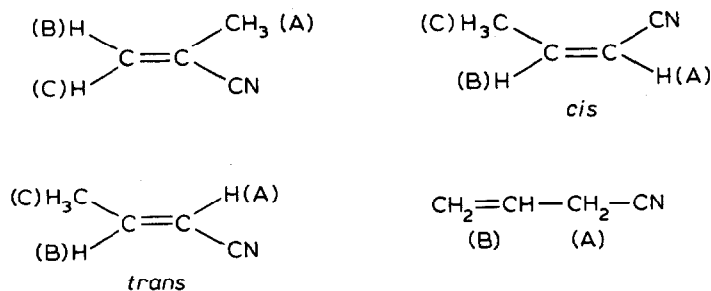
Introduction

Cationic iridium(I) complexes, $[\text{IrL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ ($\text{L} = \text{CH}_2=\text{CHCN}$ [1], $\text{CH}_3\text{CH}=\text{CHCN}$ [2], $\text{CH}_2=\text{CHCH}_2\text{CN}$ [2]) show catalytic activities for the hydrogenation of the corresponding unsaturated nitriles to the saturated nitriles and for the oligomerization of the corresponding unsaturated nitriles. It has been briefly reported that the reaction of $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (1) with $\text{CH}_2=\text{CHCN}$ gives $[\text{Rh}(\text{CH}_2=\text{CHCN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (2) which is catalytically active for the hydrogenation and oligomerization of $\text{CH}_2=\text{CHCN}$ [3]. It would be interesting to investi-

gate the effects of substituents and the position of the double bond of an unsaturated nitrile on the physical properties and catalytic activities of $[\text{ML}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (L = unsaturated nitrile). We now report the detailed spectral data, formation constants, reactions and catalytic activities of new cationic rhodium(I) complexes, $[\text{RhL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**3**: $\text{L} = \text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$; **4**: $\text{L} = \text{cis-CH}_3\text{CH}=\text{CHCN}$; **5**: $\text{L} = \text{trans-CH}_3\text{CH}=\text{CHCN}$; **6**: $\text{L} = \text{CH}_2=\text{CHCH}_2\text{CN}$).

TABLE 2

PROTON NMR SPECTRAL DATA FOR $[\text{RhL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (3: $\text{L} = \text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$; 4: $\text{L} = \text{cis-CH}_3\text{CH=CHCN}$; 5: $\text{L} = \text{trans-CH}_3\text{CH=CHCN}$; 6: $\text{L} = \text{CH}_2=\text{CHCH}_2\text{CN}$) IN CDCl_3 AT 25°C AT 60 MHz ^a



Compound	Chemical shift, ppm ^b		
	H(A)	H(B)	H(C)
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$	1.94(dd)	5.88(dq)	5.91(dq)
3	1.22(dd,3H)	4.98(dq,1H)	5.67(dq,1H)
$\text{cis-CH}_3\text{CH=CHCN}$	5.18(dq)	6.35(m)	1.90(dd)
4	4.74(dq,1H)	6.48(m,1H)	1.02(dd,3H)
$\text{trans-CH}_3\text{CH=CHCN}$	5.25(dq)	6.60(m)	1.81(dd)
5	4.68(dq,1H)	5.72(m,1H)	1.63(dd,3H)
$\text{CH}_2=\text{CHCH}_2\text{CN}$	2.92(m)	5.20(m)	—
6	2.95(m,2H)	4.90(m,3H)	—

^a Complexes 3–6 show a multiplet due to the phenyl protons of PPh_3 at ca. 7.5 ppm. ^b Relative to TMS.

although one could expect that the σ -basicity of the nitrogen atoms of methacrylonitrile, crotonitrile and allyl cyanide would be stronger than that of acrylonitrile. No infrared spectral data have been reported for nitrogen-bonded allyl cyanide complexes thus far, while some data have been reported for nitrogen-bonded methacrylonitrile [5], acrylonitrile [6] and crotonitrile [7] complexes.

Electronic absorption spectral data for 2–6 (Table 1) also support that 2–6 are four-coordinated rhodium(I) complexes and the unsaturated nitriles in 2–6 are coordinated through the nitrogen atom. It is well known that the four-coordinated rhodium(I) complexes, $\text{RhA}(\text{CO})(\text{PPh}_3)_2$ (A = monodentate ligand) show an absorption band in the region of 350–400 nm (ϵ , 2600–4300) which shifts with respect to the ligating atom A [9]. $\text{RhA}(\text{CO})(\text{PPh}_3)_2$ shows an absorption band at 365–374 nm (ϵ , 4200–4300) in benzene when A is the ligand that coordinates through the nitrogen atom such as N_3 , NCO , NO_2 , NCS and $\text{N}(\text{CN})_2$ [9].

Detailed ^1H NMR data for $\text{CH}_2=\text{CHCN}$ in 2 were reported [10], and the data for $\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$ in 3, $\text{CH}_3\text{CH=CHCN}$ in 4 and 5, and $\text{CH}_2=\text{CHCH}_2\text{CN}$ in 6 are summarized in Table 2. The changes in coupling constants and in chemical shifts of the protons in $\text{CH}_2=\text{CHCN}$ upon coordination to $\text{Rh}(\text{CO})(\text{PPh}_3)_2^+$ converts the complex 13-line ABC pattern spectrum of free $\text{CH}_2=\text{CHCN}$ into a simple 8-line spectrum of $\text{CH}_2=\text{CHCN}$ in 2 at 60 MHz [10]. Significant changes in the coupling constants and chemical shifts were also observed for the protons of $\text{CH}_2=\text{CHCN}$ and $\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$ upon their coordination to $\text{Ru}(\text{NH}_3)_5^{2+}$ and $\text{Rh}(\text{NH}_3)_5^{3+}$.

The reactions of 2–6 with unsaturated aldehydes do not yield $[\text{Rh}(\text{RCH}=\text{CHCHO})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ ($\text{R} = \text{H}, \text{CH}_3$) which are readily formed by the reactions of 1 with $\text{RCH}=\text{CHCHO}$ [14].

Catalytic activities

It was reported that complex 2 catalyzes the hydrogenation and oligomerization of $\text{CH}_2=\text{CHCN}$ at room temperature [3]. In this study, it has been found that complexes 4 and 5 catalyze the hydrogenation and oligomerization of *cis*- and *trans*- $\text{CH}_3\text{CH}=\text{CHCN}$, respectively, at room temperature while complexes 3 and 6 do not show catalytic activities for the hydrogenation and oligomerization of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$ and $\text{CH}_2=\text{CHCH}_2\text{CN}$, respectively. Hydrogenation with 2, 4 and 5 always occurs at the olefinic group to produce saturated nitriles (see Table 4) while neither amines nor imines have been obtained. To explain the catalytic activities of 2, 4 and 5, it is possible that an equilibrium between the nitrogen-bonded unsaturated nitrile complex and the olefinic π -bonded unsaturated nitrile complex is established. Then the π -complex would undergo the well-established catalytic routes for hydrogenation and oligomerization of olefins. A similar reaction mechanism (conversion of a nitrogen-bonded complex to a π -complex) was previously suggested for dimerization of $\text{CH}_2=\text{CHCN}$ to dicyanobutene with a nitrogen-bonded $\text{CH}_2=\text{CHCN}$ ruthenium(II) complex [15]. However, no evidence was obtained for the presence of the olefinic π -bonded complexes in solutions of 2, 4 and 5. No differences have been observed between the rates of the catalytic reactions of *cis*- and *trans*- $\text{CH}_3\text{CH}=\text{CHCN}$. Hydrogenation of $\text{CH}_2=\text{CHCN}$ is slower than that of $\text{CH}_3\text{CH}=\text{CHCN}$ while the oligomerization is faster (see Table 4). The slower reaction rate for the oligomerization of crotononitrile can be understood in terms of steric effects: the insertion of $\text{CH}_3\text{CH}=\text{CHCN}$ into the $\text{Rh}-\text{C}$ bond to increase the oligomers chainlength may be more difficult than that of $\text{CH}_2=\text{CHCN}$. It is interesting to notice that there is a striking difference between the catalytic activities of 2 and 3, and between those of 4 (or 5) and 6 although no significant differences have been observed between the physical properties (in spectral data and formation

TABLE 4

HYDROGENATION AND OLIGOMERIZATION OF UNSATURATED NITRILES (L) WITH $[\text{RhL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (2: $\text{L} = \text{CH}_2=\text{CHCN}$; 3: $\text{L} = \text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$; 4: $\text{L} = \text{cis}-\text{CH}_3\text{CH}=\text{CHCN}$; 5: $\text{L} = \text{trans}-\text{CH}_3\text{CH}=\text{CHCN}$; 6: $\text{L} = \text{CH}_2=\text{CHCH}_2\text{CN}$) AT 30°C UNDER HYDROGEN ($P(\text{H}_2) + \text{VAPOR PRESSURE OF L} = 1 \text{ atm}$) FOR 48 h

Catalyst ^a	L (mmol)	Products (mmol)
2	$\text{CH}_2=\text{CHCN}$ (150)	$\text{CH}_3\text{CH}_2\text{CN}$ (4.4) oligomers (14.3) ^b
3	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$ (150)	none
4	<i>cis</i> - $\text{CH}_3\text{CH}=\text{CHCN}$ (150)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$ (63.4) oligomers (3.1) ^b
5	<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHCN}$ (150)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$ (61.6) oligomers (3.2) ^b
6	$\text{CH}_2=\text{CHCH}_2\text{CN}$ (150)	none

^a 0.3 mmol of catalyst was used in all experiments. ^b Non-volatile and soluble in chloroform, acetonitrile and benzene. The numbers in parentheses (mmol) were obtained by dividing the weight of oligomers with molecular weight of the corresponding monomer.

constants) of the nitrogen-bonded complexes **2** and **3**, and between those of **4** (or **5**) and **6**. These observations may indicate that the nitrogen-bonded unsaturated nitrile complexes do not play an important role in the catalytic cycles, but the olefinic π -bonded complexes do. Then the catalytic activities of **2–6** can be understood in terms of ability of the unsaturated nitriles to form the olefinic π -bonded complexes. Lately it has been reported that the formation of the π -complexes through the π -system of the olefinic group of the unsaturated nitriles is favored by conjugation of the double bond with the nitrile group [16]. It could now be said that the poor catalytic activities of **6** may be due to the non-conjugation of $\text{CH}_2=\text{CHCH}_2\text{CN}$ while those of **3** may be due to the steric effects of the methyl group of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$.

Experimental

Methods

^1H NMR, infrared and electronic absorption spectra were obtained on Varian 60 MHz (EM-360A), Shimadzu IR-440 and Shimadzu UV-240 spectrophotometers. Conductance measurements were carried out with a Wiss-Tech. Werkstätten Weinheim/Obb. conductometer. Elemental analyses were carried out by Spang Micro-analytical Laboratory, Eagle Harbor, MI, U.S.A. A standard vacuum line and Schlenk type glassware were used in handling the metal complexes.

Materials

$\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**1**) and $[\text{Rh}(\text{CH}_2=\text{CHCN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**2**) were prepared according to literature methods [3,8]. All solvents were dried and distilled before use. *cis*- and *trans*-Crotononitrile ($\text{CH}_3\text{CH}=\text{CHCN}$) were separated from a mixture (*cis/trans* ca. 3.0. Eastman) by preparative GC using Carbowax 20M column. Acrylonitrile ($\text{CH}_2=\text{CHCN}$, Merck), allyl cyanide ($\text{CH}_2=\text{CHCH}_2\text{CN}$, Aldrich) and methacrylonitrile ($\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$, Fluka) were distilled before use.

Synthesis

$[\text{Rh}(\text{CH}_2=\text{C}(\text{CH}_3)\text{CN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**3**). Addition of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$ (two drops, ca. 0.6 mmol) into the benzene solution (10 ml) of **1** (0.15 g, 0.2 mmol) under nitrogen at 25°C immediately resulted in precipitation of yellow microcrystals which were collected by filtration, washed with benzene (10 ml) and dried in vacuum. The yield was 0.13 g or 80%. Anal. Found: C, 60.01; H, 4.09; N, 1.73; Cl, 4.30; P, 7.39. $\text{C}_{41}\text{H}_{35}\text{ClNO}_5\text{P}_2\text{Rh}$ calcd.: C, 59.91; H, 4.29; N, 1.70; Cl, 4.31; P, 7.54%. Molar conductance $110\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ ($[\text{Rh}] 5.0 \times 10^{-5}\text{ M}$ in $\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$).

$[\text{Rh}(\text{cis-CH}_3\text{CH}=\text{CHCN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**4**), $[\text{Rh}(\text{trans-CH}_3\text{CH}=\text{CHCN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**5**) and $[\text{Rh}(\text{CH}_2=\text{CHCH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**6**). These compounds were prepared in the same manner described for **3**. The yields, elemental analyses and molar conductance values of **4**, **5** and **6** were practically identical with those of **3**.

Formation constants measurements

Practically identical procedures were followed to determine the formation con-

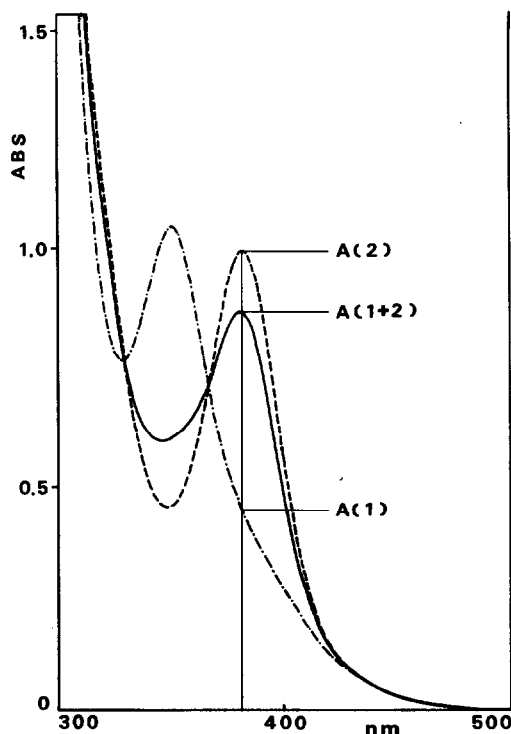


Fig. 1. Electronic absorption spectra of $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (---), $[\text{Rh}(\text{CH}_2=\text{CHCN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ in the absence of excess $\text{CH}_2=\text{CHCN}$ added (—) and $[\text{Rh}(\text{CH}_2=\text{CHCN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ in the presence of excess $\text{CH}_2=\text{CHCN}$ added ($[\text{CH}_2=\text{CHCN}]/[\text{Rh}] = 1000$) (- · - · -) in monochlorobenzene at 25°C under nitrogen. $[\text{Rh}] = 3.0 \times 10^{-4} \text{ M}$. Cell pathlength = 1.0 cm. See text for $A(1)$, $A(1+2)$ and $A(2)$.

stands for 2–5 at various temperatures. The experimental details for 2 are described below. Electronic absorption spectra of 1* and 2 in the absence of excess $\text{CH}_2=\text{CHCN}$ and of 2 in the presence of excess $\text{CH}_2=\text{CHCN}$ were measured in monochlorobenzene to determine the absorbances, $A(1)$ (absorbance due to 1 at 381 nm where 2 shows the absorption maximum), $A(1+2)$ (absorbance due to 2 at 381 nm in the absence of excess $\text{CH}_2=\text{CHCN}$ added; $A(1+2)$ is actually the absorbance due to 2 and 1 which is produced by the reaction, $2 \rightarrow 1 + \text{CH}_2=\text{CHCN}$), and $A(2)$ (absorbance due to 2 at 381 nm in the presence of excess $\text{CH}_2=\text{CHCN}$ added) (see Fig. 1). The formation constant, $K = [\text{Rh}(\text{CH}_2=\text{CHCN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4 / ([\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2][\text{CH}_2=\text{CHCN}]^{**})$, is equal to $(A(2) - A(1))(A(1+2) - A(1)) / ((A(2) - A(1+2))^2[\text{Rh}])$ where $[\text{Rh}]$ is the total concentration of rhodium in solution.

* It has been found that the ClO_4 group does not dissociate from 1 in monochlorobenzene at $25\text{--}55^\circ\text{C}$, i.e., addition of AgClO_4 to the solution of 1 does not show any changes in the spectrum.

** Molar conductance of 2 in monochlorobenzene is practically zero indicating that the ionization, $2 \rightarrow [\text{Rh}(\text{CH}_2=\text{CHCN})(\text{CO})(\text{PPh}_3)_2]^+ + \text{ClO}_4^-$ is negligible while that of 2 in acrylonitrile is $110 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ suggesting that 2 undergoes complete ionization. Similar observation was previously reported for conductance measurements of 1 in monochlorobenzene and in methanol [8].

Reactions

Experimental details and yields were practically the same as for the reactions of 2–6 with various ligands. The reaction of 2 with PPh_3 is described below. Into the solution of 2 (0.16 g, 0.2 mmol) in chloroform (10 ml) PPh_3 (0.05 g, 0.4 mmol) was added, and the resulting reaction mixture was stirred under nitrogen for 30 min at 25°C. Addition of hexane (25 ml) into the reaction mixture resulted in precipitation of orange-yellow microcrystals which were collected by filtration, washed with benzene (10 ml) and dried in vacuum. The yield was 0.16 g or 80% based on $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ [13].

Catalyses

In all experiments, the same procedure was followed using 0.3 mmol of rhodium complex (2–6) and 150 mmol of the corresponding nitrile. Experimental details for the catalytic reaction with 2 are described below. Complex 2 (0.24 g, 0.3 mmol) in $\text{CH}_2=\text{CHCN}$ (10 ml, 150 mmol) was stirred under hydrogen ($P(\text{H}_2)$ + vapor pressure of the solution = 1 atm) at 30°C for 48 h. The volatile materials were separated from the reaction mixture by using a dry-ice trap and identified as $\text{CH}_2=\text{CHCN}$ and $\text{CH}_3\text{CH}_2\text{CN}$ (4.4 mmol) by ^1H NMR spectra. Non-volatile materials (ca. 1.75 g) in the reactor were identified as a carbonyl-rhodium complex (not fully characterized yet) and oligomers of acrylonitrile by ^1H NMR and infrared spectra. The carbonyl-rhodium complex is not soluble in benzene while the pale-yellow oily oligomers of $\text{CH}_2=\text{CHCN}$ are very soluble in benzene and chloroform. The ^1H NMR spectrum of the oligomers show multiplets at ca. 1.5, 2.0 and 2.8 ppm (relative to TMS in CDCl_3) but no signals at 5–7 ppm where $\text{CH}_2=\text{CHCN}$ shows signals. The infrared spectrum of the $\text{CH}_2=\text{CHCN}$ oligomers (neat) shows $\nu(\text{C}\equiv\text{N})$ at 2220 cm^{-1} .

The ^1H NMR spectra of the $\text{CH}_3\text{CH}=\text{CHCN}$ oligomers obtained in the catalyses with 4 and 5 show multiplets at ca. 1.1, 1.5 and 1.9 ppm (relative to TMS in CDCl_3) but no signals at 5–7 ppm where $\text{CH}_3\text{CH}=\text{CHCN}$ shows signals. Infrared spectrum of the $\text{CH}_3\text{CH}=\text{CHCN}$ oligomers (neat) shows $\nu(\text{C}\equiv\text{N})$ at 2200 cm^{-1} .

Molecular weights of the oligomers have not been determined yet.

Acknowledgements

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