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Homogeneous catalytic dimerization of propylene with bis(imino)pyridine vanadium(III) complexes

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Dedicated to Professor Uwe Rosenthal on the occasion of his 60th birthday.

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ABSTRACT

A series of new bis(imino)pyridine vanadium(III) complexes was synthesized. They were tested for the homogeneous catalytic dimerization of propylene after activation with MAO. The activity and selectivity depend on the ligand structure of the corresponding organic coordination compound. The influence of PPh_3 as an additive was investigated and high dependency could be observed.

1. Introduction

Unsaturated short chained hydrocarbons are low priced educts for polymerization, oligomerization and metathesis application, produced by unselective thermal cracking processes [1]. Especially the dimerization of propylene plays an important role for the formation of gasoline with a high octane number. As a result branched hexenes can be obtained and used as gasoline blending compounds. The Research Octane Number (RON) rises with the number of branching [2–6], from RON = 96–99 for methylpentenes to 101 for dimethylbutene [2,7,8]. Linear hexenes are in the range from 73 to 94 and play no role as additives for gasoline improvement. With the ban of lead-alkyl compounds and methyl-*tert*-butyl as anti-knocking agent ether from gasoline, branched hydrocarbons represent a very important class of compounds for gasoline reformulation [9].

The invention of highly active iron- and cobalt-based olefin polymerization catalysts in the late 1990s has led to much interest in the chemistry of transition metal complexes bearing tridentate bis(imino)pyridine ligands [10–21]. These types of complexes were applied by Gibson and Brookhart in 1998 and great progress has been achieved since then. It is well established that bis(imino)pyridine iron(III) complexes show high activities and selectivities for the oligo- and polymerization of ethylene after activation with methyl aluminoxane (MAO). Several complexes with various metal centers and different ligand structures were published and many studies have reported the effects of ligand substitution patterns on activity and selectivity [19–23]. Bis(imino)pyridine vanadium(III) complexes were found to be selective for the oligomerization of ethylene to give linear olefins [13,24–26]. These facts underline the importance of such catalysts.

Here we report the application of bis(imino)pyridine vanadium(III) complexes combined with MAO as cocatalyst in the selective dimerization of propylene. The influence of phosphorous containing additives is another aspect in this work.

2. Results and discussion

2.1. Synthesis of the bis(imino)pyridine compounds *1a–d*

The bis(imino)pyridine ligand precursors were synthesized via a condensation reaction (Scheme 1) of 2,6-diacetylpyridine with the respective aniline according to the literature [27].

The yields of the compounds **1a–d** are generally high (up to 94%).

2.2. Synthesis of the complexes *2–5*

The complexes were synthesized via an addition reaction (Scheme 2) of the vanadium(III)trichloride THF adduct and the

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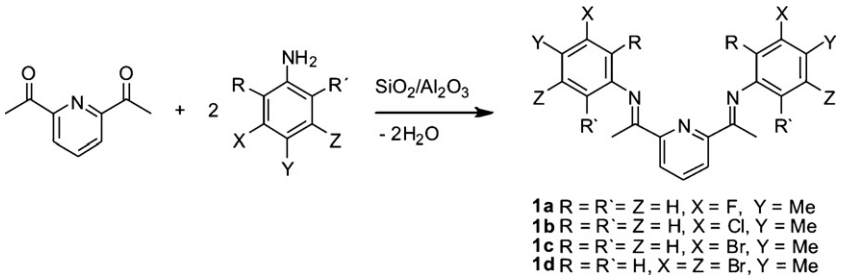
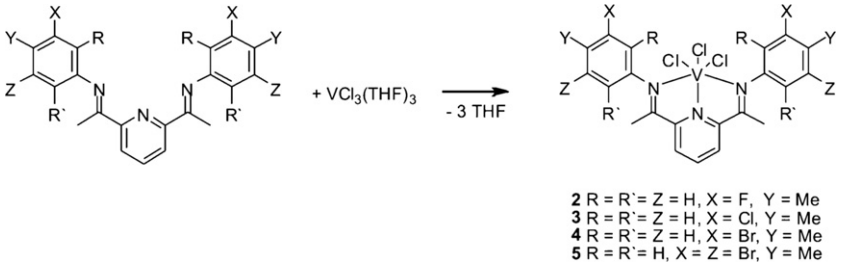


Scheme 1. Synthesis of the bis(imino)pyridine compounds **1a–d**.



Scheme 2. Synthesis of the bis(imino)pyridine vanadium(III) complexes **2–5**.

respective bis(imino)pyridine compound in diethyl ether. The resulting complexes were obtained in good yields (65–87%).

The listed complexes **2–28** were all tested for their catalytic activities in dimerization reactions (Table 1).

2.3. Catalytic dimerization reactions of propylene

Various bis(imino)pyridine vanadium(III) compounds were tested for the dimerization of propylene after activation with MAO (V:Al = 1:500) to give hexene isomers. The catalytic activities and selectivities of the corresponding catalysts are important aspects.

Table 1
Synthesized complexes **2–28**. Complexes **6–28** were already reported in the literature [25]. Compounds **2–5** are new.

V(III) complex no.	R	X	Y	Z	R′
2	H	F	Methyl	H	H
3	H	Cl	Methyl	H	H
4	H	Br	Methyl	H	H
5	H	Br	Methyl	Br	H
6	H	H	Cl	H	H
7	H	H	I	H	H
8	H	H	NO_2	H	H
9	Methyl	H	I	H	H
10	Methyl	H	Methyl	H	Methyl
11	Methyl	H	H	H	H
12	Ethyl	H	H	H	H
13	*iso*-Propyl	H	H	H	H
14	*tert*-Butyl	H	H	H	H
15	Propyl	H	H	H	H
16	Benzyl	H	H	H	H
17	*iso*-Propyl	H	H	H	Methyl
18	*iso*-Propyl	H	H	H	*iso*-Propyl
19	Methyl	H	Methyl	H	H
20	H	H	Butyl	H	H
21	Methyl	Methyl	H	H	H
22	Methyl	H	H	H	Cl
23	Methyl	H	H	Methyl	H
24	H	H	Br	H	H
25	Methyl	H	Cl	H	H
26	Methyl	H	H	H	Methyl
27	H	H	F	H	H
28	Methyl	Cl	H	H	H

The activity was determined by the weight increase of the reaction vessel after removing the propylene. While high activities for the oligo- and polymerization of ethylene were achieved with this type of catalyst [25,28], the results with propylene varied in the range of 95–215 kg/mol h (TOF = 1130–2560 h^{-1}). For our application, it is more important to have a look at the selectivities and product distributions.

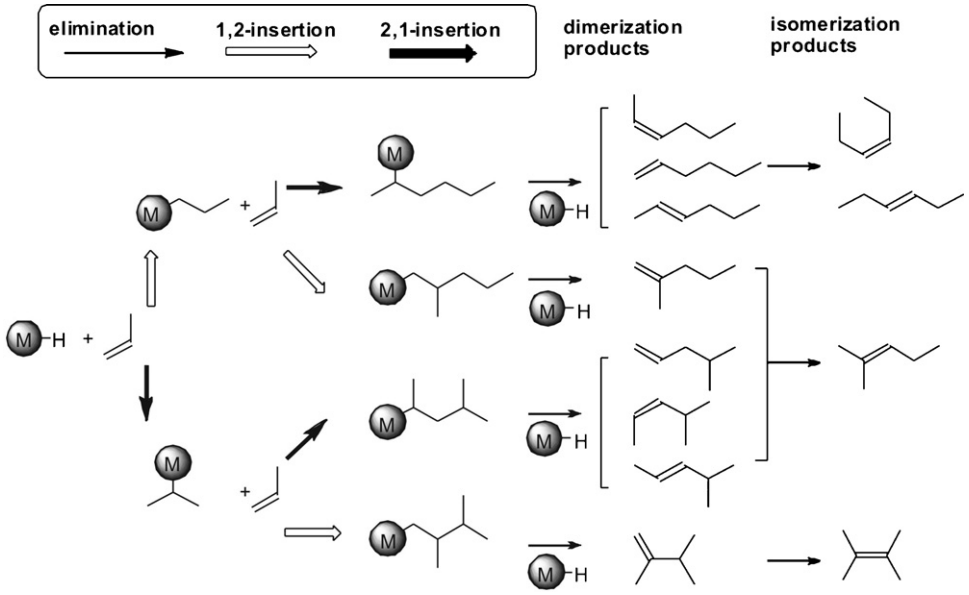
The dimerization of propylene can lead to 12 hexene isomers via coordination, double insertion and elimination reactions (Scheme 3). The names and abbreviations of all isomers are listed in Table 2.

It is obvious that complexes **14–17** with bulky ligands like alkyl/aryl substituents on positions 2 or 6 (ortho position) of the imine fragment (Scheme 4), achieve high selectivities up to 95% (**16**). Bulky substituents on both sides have a negative effect. The selectivity falls from 90% to 81% with the replacement of methyl (**17**) to *iso*-propyl (**18**). Moreover, steric hindrance in ortho position has an influence on the product distribution. While complexes **11–13** produce 4-methyl-1-pentene as main product, bulky substituents shift it to 2-methyl-1-pentene. These bulky groups favor 1,2-insertion as an initial step.

A substitution with halides on the para position has a great influence on the formation of hexenes. Compared to complex **11** (main product 4-methyl-1-pentene with a selectivity of 62%), a halide substitution gives 4-methyl-1-pentene with selectivities between 74% (**25**) and 82% (**9**).

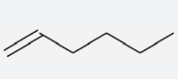
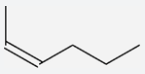
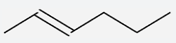
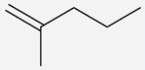
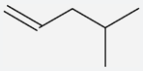
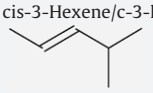
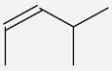
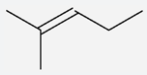
The selectivity of the formation of hexene isomers decreases in the following manner F (93%) (**2**) > Cl (87%) (**3**) > Br (83%) (**4**) on the meta position (Scheme 4). The β-hydrogen elimination is favored by electron withdrawing groups compared to the heavier homologue halides. The distribution of the dimeric products is nearly the same for all three halide substituted complexes with 4-methyl-1-pentene as main product and selectivities up to 90% are observed (Table 3). With the high dimer and product selectivity of **2**, 4-methyl-1-pentene is produced with a total amount of 83%.

Electron withdrawing or pushing groups on position 4 of the imine fragment have no influence on the dimer selectivity (**6–8**, **20**, **24** and **27**). The difference is obvious in product distribution. Complex **20** with a withdrawing group produces 2-methyl-1-pentene



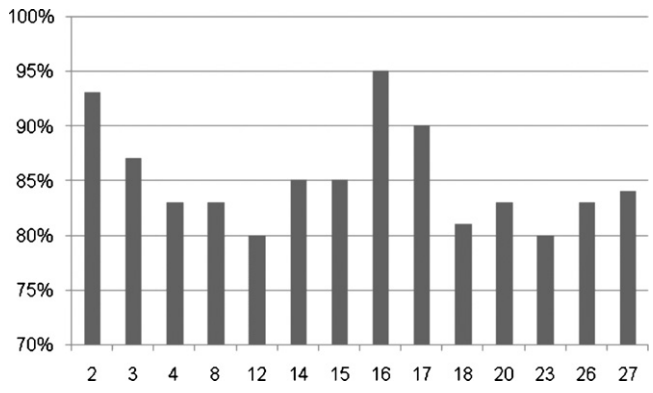
Scheme 3. Dimerization products of propylene and catalytic cycles.

Table 2
All hexene isomers with full names and abbreviations.

Isomer				
Name/abbreviation	1-Hexene/1-hex	cis-2-Hexene/c-2-hex	trans-2-Hexene/t-2-hex	cis-3-Hexene/c-3-hex
Isomer				
Name/abbreviation	trans-3-Hexene/t-3-hex	2-Methyl-1-pentene/2-MP-2	4-Methyl-1-pentene/4-MP-1	trans-4-Methyl-2-pentene/t-4-MP-2
Isomer				
Name/abbreviation	cis-4-Methyl-pentene/c-4-MP-2	2-Methyl-2-pentene/2-MP-2	2,3-Dimethyl-1-butene/DMB-1	2,3-Dimethyl-2-butene/DMB-2

with 47%. On the other side, electron pushing groups generate 4-methyl-1-pentene with an amount of up to 75%.

The kind of substitution at the meta position of the bis(imino)pyridine complex has no influence on the selectivity of the dimers, but it effects the distribution of the dimers immensely. Complexes **6**–**9**, **24**, **25** and **27** with a –J-effect at the meta position of the phenyl group give a maximum selectivity of 2-methyl-1-pentene of 13%. A ligand with a +J-effect at the same position gives



Scheme 4. Catalysts **2**–**4**, **8**, **12**, **14**–**18**, **20**, **23**, **26** and **27** with the highest selectivity towards dimerization products of propylene.

complex **20** which shows a selectivity for 2-methyl-1-pentene of 47%. The formation of 4-methyl-1-pentene shows its highest selectivity (90%) (**2**) in contrast to the formation of 2-methyl-1-pentene by the reaction of complexes with a –J-effect at the ligand precursor like Cl, Br or I.

These two products are generated by different first insertion steps (Scheme 3), and are caused by the electronic influence of both substituents. Complex **5** is the only complex that produces 2,3-dimethylbutene in satisfying yields (25%) with medium selectivity towards dimerization products (Table 3).

2.4. Influence of PPh_3 as an additive

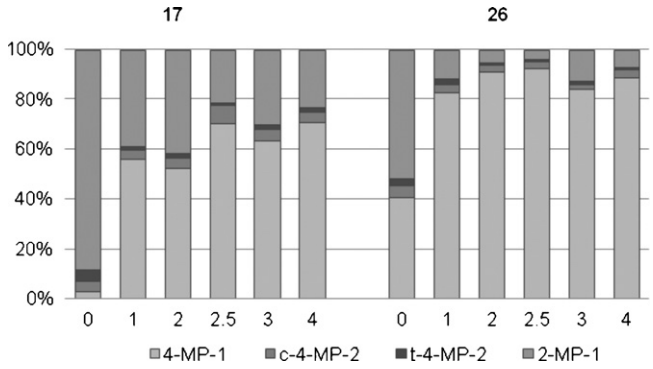
In the late 60s Wilke recognized the influence of additives in catalytic reactions [29]. Phosphanes are widely used additives and a positive influence on selectivity and activity was observed during dimerization of propylene [30].

The relevant complexes were dissolved in toluene, PPh_3 was added in a ratio of metal:additive = 1:1 (2, 2.5, 3 and 4). The solutions were stirred for 30 min and activated with MAO.

The addition of the additive had a positive influence on the dimer selectivity (90%) with the use of 2 equiv. PPh_3 for **17**. The selectivity could be improved up to 95%. For all other amounts no improvement could be observed. In contrast, the use of additive had a great influence on the product distribution (Scheme 5). With

Table 3
Selectivity of dimerization products and product distribution within hexene isomers for the vanadium(III) complexes **2**–**28**.

V(III) complex no.	Selectivity to dimers (%)	Products within the dimers (%)							
		4-MP-1	2,3-DMB-1	c-4-MP-2	t-4-MP-2	2-MP-1	t-2-hex	2-MP-2	c-2-hex
2	93	90	1	4	–	5	–	–	–
3	87	85	2	6	3	4	–	–	–
4	83	89	1	7	1	2	–	–	–
5	60	24	25	45	0	6	–	–	–
6	70	68	5	14	3	9	–	1	–
7	72	71	2	13	2	8	–	4	–
8	83	73	5	3	3	13	–	3	–
9	75	82	–	9	3	6	–	–	–
10	55	73	–	7	–	20	–	–	–
11	55	62	2	18	4	14	–	–	–
12	80	68	2	14	5	10	1	–	–
13	60	55	–	13	3	26	3	–	1
14	85	5	–	8	11	75	1	–	–
15	85	36	–	10	6	46	1	1	–
16	95	7	–	7	6	80	–	–	–
17	90	3	–	4	5	88	–	–	–
18	81	11	–	5	7	77	–	–	–
19	75	8	–	7	9	76	–	–	–
20	83	19	5	15	7	47	1	6	1
21	76	34	1	10	8	45	1	1	1
22	70	32	2	10	4	52	–	–	–
23	80	25	–	7	5	63	–	–	–
24	77	70	–	17	2	6	–	5	–
25	40	74	1	13	4	8	–	–	–
26	83	41	–	5	3	51	–	–	–
27	84	75	3	9	3	6	–	4	–
28	77	72	2	14	6	6	–	–	–



Scheme 5. Product distribution of the reaction of the complexes **17** and **26** and propylene with a various ratio of the additive PPh_3.

the addition of 2.5 equiv. a maximum of 70% for the formation of 4-methyl-1-pentene (**17**) could be achieved. The absence of PPh_3 effects the formation of 2-methyl-1-pentene with a selectivity of 88%. Insertion mechanisms are influenced by the use of phosphine containing additives, which results in a 1,2-insertion instead of 2,1-insertion. The results of the corresponding reactions of complex **26** (Scheme 5) confirm the additive dependency as discussed before. A selectivity of 90% was detected for 4-methyl-1-pentene by the addition of 2–2.5 mol PPh_3 in contrast to 51% without an additive.

3. Summary and conclusion

Novel complexes of the type bis(imino)pyridine vanadium(III) (**2**–**5**) were synthesized. Because of the simple synthetic route, numerous substitution patterns can be performed. Bulky substituents on the ortho position have positive influence on the selectivity of the dimer products. Complex **16** with a benzyl substituent at the ortho position gave a selectivity of 95% for dimers. Substituents at the 2 and 6 positions of the phenyl group accrue the 1,2-propylene insertion. Different halide groups as substituents on the para position have no influence on the product distribution and selectivity. Effects can be obtained when electron withdrawing and donating groups are introduced. The first ones generate 4-methyl-1-pentene as main product. Electron pushing substituents give 2-methyl-1-pentene. The octane numbers of the main products are between 94% and 99%. It is obvious, that the structure of the precatalyst, in particular the substitution pattern of the organic compound has a great influence on the product distribution, but not on the selectivity. No dependence for dimer selectivity is obvious from the insertion pathway. In less cases the expected multiple branched hexenes could be obtained. Complex **5** produced 2,3-dimethylbutene in yields of 25% within the dimerization products. The use of additives had a positive influence on the product distribution and was very selective for complex **26**. Complex **26** and 2 equiv. of the additive PPh_3 produced 90% of 4-methyl-1-pentene within the dimers. In the case of complex **17** the use of an additive had an enormous effect on the initial insertion step. It changed from 90% of 1,2-insertion up to 78% for 2,1-insertion with the use of 2.5 equiv. of PPh_3.

4. Experimental

4.1. General considerations

Air- and moisture-sensitive reactions were carried out under an atmosphere of purified argon using conventional Schlenk or glove box techniques. The dimerization reactions were performed with pressure Schlenk tubes.

The products of the dimerization experiments were characterized by a gas chromatograph (Agilent 6890) and GC/MS (FOCUS DSQ™ Thermo Scientific). Mass spectra were recorded on a Varian MAT CH7 instrument (direct inlet system, electron impact ionization 70 eV). Elemental analyses were performed with a VarioEl III CHN instrument. Acetanilide was used as standard. NMR spectra were taken on a Varian Inova 400 instrument. The samples were

prepared under argon atmosphere and measured at room temperature. Chemical shifts (δ, ppm) were recorded relative to the residual solvent peak at $\delta = 7.24$ ppm for chloroform-*d*. The multiplicities were assigned as follows: s, singlet; m, multiplet; t, triplet. $^{13}C\{^1H\}$ NMR spectra were fully proton decoupled and the chemical shifts (δ, ppm) are relative to the solvent peak (77.0 ppm).

4.2. Materials

All solvents were purchased as technical grade and purified by distillation over Na/K alloy under an argon atmosphere. All other chemicals were purchased commercially from Aldrich or Acros or were synthesized according to literature procedures. The methyl aluminoxan solution (MAO, 30 wt.% in toluene) was obtained from Albemarle, USA.

4.3. General procedure for the synthesis of the preligands

10 g mol sieves (4 Å) and 0.5 g of catalytically active SiO_2/Al_2O_3 pellets were added to a solution of 0.49 g (3.0 mmol) diacetylpyridine in toluene. After addition of 7.0 mmol of the respective aniline, the solution was heated at 45 °C for 24 h. After filtration over Na_2SO_4 and evaporation to dryness, the products were precipitated as yellow solids from methanol over night at −20 °C (73–94%).

4.3.1. Spectroscopic data

1a: ^1H NMR (400 MHz, $CDCl_3$): 8.30 (d, 2H, Py–H_m), 7.85 (t, 1H, Py–H_p), 7.15 (t, 2H, Ph–H), 6.53 (m, 4H, Ph–H), 2.39 (s, 6H, N=C_{Me}), 2.26 (s, 6H, Ph–CH_3). 13C {1H} (100.5 MHz, $CDCl_3$): 167.9 (Cq), 163.1 (Cq), 159.9 (Cq), 155.3 (Cq), 150.4 (Cq), 136.9 (CH), 131.6 (CH), 122.4 (CH), 114.8 (CH), 106.6 (CH), 16.2 (CH_3), 14.1 (CH_3). MS data: 377 ($M^{\bullet+}$) (88), 362 (12), 150 (100).

1b: ^1H NMR (400 MHz, $CDCl_3$): 8.30 (d, 2H, Py–H_m), 7.8t (t, 1H, Py–H_p), 7.21 (d, 2H, Ph–H), 6.87 (s, 2H, Ph–H), 6.64 (d, 2H, Ph–H), 2.40 (s, 6H, N=C_{Me}), 2.36 (s, 6H, Ph–CH_3). 13C {1H} (100.5 MHz, $CDCl_3$): 168.0 (Cq), 155.3 (Cq), 150.1 (Cq), 134.5 (Cq), 130.9 (Cq), 136.8 (CH), 131.2 (CH), 122.4 (CH), 119.8 (CH), 117.8 (CH), 19.4 (CH_3); 16.3 (CH_3). MS data: 409 ($M^{\bullet+}$) (52), 166 (100).

1c: ^1H NMR (400 MHz, $CDCl_3$): 8.30 (d, 2H, Py–H_m), 7.85 (t, 1H, Py–H_p), 7.21 (d, 2H, Ph–H), 7.06 (s, 2H, Ph–H), 6.70 (d, 2H, Ph–H), 2.40 (s, 6H, N=C_{Me}), 2.39 (s, 6H, Ph–CH_3). 13C {1H} (100.5 MHz, $CDCl_3$): 168.1 (Cq), 155.2 (Cq), 150.1 (Cq), 132.7 (Cq), 124.9 (Cq), 136.8 (CH), 131.0 (CH), 123.0 (CH), 122.4 (CH), 118.4 (CH), 22.2 (CH_3), 16.3 (CH_3). MS data: 499 ($M^{\bullet+}$) (52), 484 M–Me (8), 210 CH_3C=NAr (100).

1d: ^1H NMR (400 MHz, $CDCl_3$): 8.48 (d, 2H, Py–H_m), 8.07 (t, 1H, Py–H_p), 7.24–7.44 (m, 4H, Ph–H), 2.76 (s, 6H, Ph–CH_3), 2.62 (s, 6H, N=C_{Me}). 13C {1H} (100.5 MHz, $CDCl_3$): 169 (Cq), 155 (Cq), 151 (Cq), 132.0 (Cq), 125.2 (Cq), 137.0 (CH), 129 (CH), 122.7 (CH), 23.0 (CH_3), 16.5 (CH_3). MS data: 657 ($M^{\bullet+}$) (52), 577 M–Br (17), 290 M–CH_3C=N_{Ar} (100).

4.4. Synthesis of the bis(imino)pyridine vanadium(III) complexes

An amount of 0.22 mmol of the respective bis(imino)pyridine compound was dissolved in 20 ml diethylether and stirred. A stoichiometric amount of vanadium trichloride–tetrahydrofuran adduct was added at room temperature. Stirring was continued overnight. Pentane was added to precipitate the product, which was subsequently collected by filtration, washed with pentane and dried in vacuo. The resulting solids were obtained with an overall yield of 65–87%.

4.4.1. Spectroscopic data

2: MS data: 533 ($M^{\bullet+}$) (8), 497 M–Cl (100), 377 (30), 150 (62), 36 (100). $C_{23}H_{21}Cl_3F_2N_3V$ (533.02): calcd.: C, 51.66%; H, 3.96%; N, 7.86%. Found: C, 49.87%; H, 4.34%; N, 7.02%.

3: MS data: 565 ($M^{\bullet+}$) (13), 531 M–Cl (100), 406 (18), 396 (10). $C_{23}H_{21}Cl_5N_3V$ (564.96): calcd.: C, 48.67%; H, 3.73%; N, 7.40%. Found: C, 48.97%; H, 3.55%; N, 7.13%.

4: MS data: 653 ($M^{\bullet+}$) (7), 619 (37), 541 (10), 187 (63), 36 (100). $C_{23}H_{21}Cl_3Br_2N_3V$ (652.86): calcd.: C, 42.08%; H, 3.22%; N, 6.40%. Found: C, 42.61%; H, 3.33%; N, 6.42%.

5: MS data: 808 ($M^{\bullet+}$) (4), 772 (100). $C_{23}H_{19}Cl_3Br_4N_3V$ (808.68): calcd.: C, 33.92%; H, 2.35%; N, 5.16%. Found: C, 33.45%; H, 2.30%; N, 4.89%.

4.5. Homogeneous dimerization of propylene

The respective complex was dissolved in toluene and activated with MAO solution (V:Al = 1:500) and transferred into a 400 ml pressure Schlenk tube. The pressure Schlenk tube was filled with 50 ml liquid propylene and closed, warmed to room temperature with an external water bath and stirred. After the reaction time of 1 h, the Schlenk tube was opened and the solution was analyzed by GC.

Acknowledgement

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