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Bis(imino)cyclodiphosph(V)azane complexes of late transition metals: Efficient catalyst precursors for ethene and propene oligomerization and dimerization

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Abstract

New bis(imino)cyclodiphosph(V)azanes and their Fe, Co, and Ni complexes were synthesized and characterized. The MAO actived Ni and Co complexes exhibited high catalytic activity in ethene dimerization and oligomerization [up to 4000 kg of olefins/(mol$_{cat}$ h)], as well as in propene dimerization, whereas Fe derivatives yielded negligible activity. The dependence of catalytic behavior on oligomerization conditions was studied. The Ni catalysts revealed high selectivity in ethene (butene content up to 94%) and especially in propene dimerization (hexene content up to 100%). The Ni complexes catalyzed also codimerization of ethene and propene, with the yield of the resulting pentenes depending on the initial ethene/propene ratio. The main propagation route in the propene dimerization with Co catalysts was a 1,2 insertion of propene into the M–H bond followed by a 2,1 insertion and β-H elimination, whereas with Ni catalysts, the reaction proceeded with equal probabilities via 1,2–1,2 and 1,2–2,1 propene insertions.

Keywords: Homogeneous catalysis; Oligomerization; Dimerization; Late transition metal complexes; Cyclodiphosph(V)azanes

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1. Introduction

Over the last three decades, catalytic oligomerization of ethene has attracted considerable attention as a large-scale source of linear higher olefins [1]. Oligomers of various sizes are important intermediates; uses include the production of detergents (C_6–C_{16}) and as comonomers in the production of linear low-density polyethylene (LLDPE, C_6, and C_8) [2]. Since the development of the Shell higher olefins process (SHOP), which is catalyzed by Ni P∩O-chelate complexes [3–5], late transition metal complexes have played an essential role in catalytic oligomerization reactions [6]. To date, an impressive number of late transition metal complexes based on salen-type [7], cyclopentadienyl [8,9], bidentate diimine [10], bis(imino)pyridyl [11–13], phosphinopyridine [14,15], and chelate P∩O ligands [16] have been introduced as catalysts for olefin oligomerization.

Over the last decade, ligands based on the cyclodiphosph(III or V)azane framework have been extensively studied because of their ability to coordinate with main group [17] and transition metals [18]. In particular, bis(amido)cyclodiphosph(III)-azane complexes of group 4 metals have been a focus of research because they exhibit substantial catalytic activity in homogeneous ethene polymerization after methylalumoxane (MAO) activation [19–21]. In these complexes, the central metal atom is coordinated to a ligand by two amido nitrogen atoms, and the coordination sphere of complex is often accomplished by an additional interaction with one of the endocyclic nitrogen atoms (Fig. 1a). Soft oxidation of the bis(amino)cyclodiphosph(III)azans with oxygen, chalcogens, or organic azides leads to corresponding cyclodiphosph(V)-azane compounds, which are attractive tetradentate ligands for the synthesis of late transition metal complexes (Fig. 1b) [22–24].

Phosphor(V)-imino complexes of late transition metals based on bis(aryliminophosphoranyl)methane or bis(arylphosph(V)imino)pyridine ligands also exhibit considerable cata-

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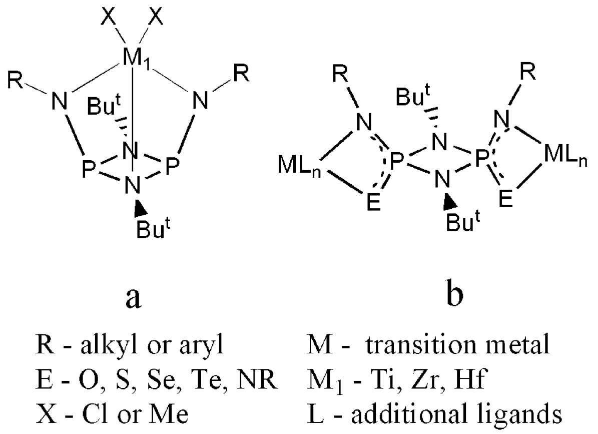


Fig. 1. Cyclodiphosph(III and V)azane complexes previously described in literature.

lytic activity in ethene polymerization [25,26]. Augmenting our previous studies with bis(amino)cyclodiphosph(III)azane complexes, and inspired by earlier observations, herein we report the preparation of cyclodihosph(V)azanes bearing bulky phosph(V)imino groups and the synthesis of the corresponding Fe, Co, and Ni complexes. Reactivity of the complexes after MAO activation toward ethene and propene oligomerization was investigated.

2. Experimental

2.1. General remarks

All manipulations were performed under an inert argon atmosphere using standard Schlenk techniques. The hydrocarbon and ether solvents were refluxed over sodium and benzophenone, distilled, and stored under an inert atmosphere with sodium flakes. CH_2Cl_2 was refluxed with $LiAlH_4$, distilled, and stored over dry molecular sieves. $CDCl_3$ was dried over dry molecular sieves, and CD_2Cl_2 was refluxed with P_4O_{10}, distilled, and stored over dry molecular sieves in a glovebox. C_6D_6 was refluxed with sodium, distilled, and stored over dry sieves in a glovebox. Mass spectra were measured using a JEOL SX102 spectrometer, and ^1H and ^{13}C NMR spectra were recorded using a Varian Gemini 200-MHz spectrometer. The ^1H and ^{13}C NMR spectra were referenced relative to $CHDCl_2$ (5.28 and 53.73 ppm, respectively), $CHCl_3$ (7.24 and 77.0 ppm, respectively), and C_6D_5H (7.24 and 128.0 ppm, respectively). ^{31}P NMR and some of the ^1H NMR spectra were collected with a Bruker AMX 400 spectrometer. Phosphorus signals were referenced relative to an external 85% H_3PO_4 solution. Elemental analyses were performed at the Laboratory of Pharmaceutical Chemistry, Department of Pharmacy, University of Helsinki. Gas chromatography–mass spectroscopy (GC–MS) of polymerization products was performed with an Agilent Technologies 6890N Network GC System.

tert-Butylamine and phosphorus trichloride were purchased from Merck and purified by distillation under argon ($^t BuNH_2$ over sodium hydroxide). 2,6-di-*i*-Propylaniline was received from Aldrich and distilled in vacuo over sodium hydroxide before use. Trimethylsilylazide (Fluka) and 1-azidoadamantane, AdN_3 (Aldrich), were used as received. A 1.6 M solution of MeLi in Et_2O was received from Aldrich. Anhydrous $FeCl_2$, $NiBr_2$, and $CoCl_2$ were received from Aldrich and stored in Schlenk flasks under argon. Methylalumoxane (MAO, 30 wt% solution in toluene) was received from Borealis Polymers Oy. 2,6-di-*i*-Propylphenylazide [25] and *cis*-($^t BuNPCl)_2$ [27] (**1**) were prepared according to modified literature procedures.

2.2. Synthesis of ligands

2.2.1. *cis*-($^t BuNPMe)_2$ (**2**)

The solution of MeLi (1.6 M, 89 ml, 142.4 mmol) was added slowly over 40 min to the cooled (−50 °C) solution of ($^t BuNPCl)_2$ (**1**) (18.2 g, 66.2 mmol) in Et_2O (30 ml). The reaction mixture was allowed to warm and stirred overnight. After separation of LiCl precipitation by filtration through a glass filter, the volume of the filtrate was diminished to ca. 30 ml by careful evaporation under low argon pressure (100 mm Hg). The orange viscous residue was transferred via syringe to a vacuum distillation system with a short deflegmator. Because the product is thermally sensitive, it must be distilled quickly. Distillation yielded a yellowish viscosous liquid (6.2 g, 37.5%). Bp. = 57–64 °C/2 mm_{Hg} (31–32 °C/0.5 mm_{Hg} [28]). This compound was dissolved in toluene and used as a toluene solution. ^1H NMR (400 MHz, C_6D_6, 29 °C): $\delta_H = 1.22$ (t, 18H, ^{t}Bu, P_2N_2 cycle), 1.62 (m, 6H, MeP). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 31 °C): $\delta_P = 173.00$ (s) (171.4) (see also supplementary material). The data resemble those obtained for *cis*-($^t BuNPMe)_2$ in previous work [28], in which the exact values of coupling constants are given. MS(EI): m/z (%) 236 (80, M^+), 220 (80, M^+–Me).

2.2.2. *cis*-[(Me_3SiN)($^t BuNPMe$)]$_2$ (**3**)

Me_3SiN_3 (3.64 g, 4.2 ml, 31.6 mmol) was added slowly via syringe to the stirred solution of *cis*-($^t BuNPMe)_2$ (3.15 g, 13.45 mmol) in toluene (20 ml). The reaction mixture was warmed to 90 °C and maintained at this temperature overnight. All volatiles were removed in vacuo, and the residue was treated with hexane. After filtration, hexane was removed from the filtrate to give a colorless solid product (4.89 g, 95.7%). ^1H NMR (200 MHz, C_6D_6, 29 °C): $\delta_H = 0.37$ (s, 18H, Me_3Si), 1.37 (s, 18H, ^{t}Bu, P_2N_2 cycle), 1.72 (m, 6H, MeP). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 29 °C): $\delta_C = 3.71$ (t, $J_{PC} = 1.5$ Hz, CH_3 of Me_3Si), 24.10 (d, $J_1 = 5.7$ Hz, CH_3 of MeP), 26.24 (d, $J_1 = 5.7$ Hz, CH_3 of MeP), 30.91 (t, $J_{PC} = 4.2$ Hz, CH_3, ^{t}Bu), 53.56 (*C*, ^{t}Bu). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 31 °C): $\delta_P = -12.7$ (s). MS(EI): m/z (%) 408 (60, M^+), 337 (80, M^+–Me_3Si), 235 (70, M^+–$2Me_3Si$). These characteristics (see also supplementary material) are in accordance with those reported for compound **3** earlier [28].

2.2.3. *cis*-[(2,6-$^i Pr_2C_6H_3N$)($^t BuNPMe$)]$_2$ (**4**)

A solution of raw 2,6-$^i Pr_2C_6H_3N_3$ (2.25 g, 11.1 mmol) in toluene (10 ml) was added slowly via syringe to the stirred solution of *cis*-($^t BuNPMe)_2$ (1.00 g, 4.3 mmol) in toluene (10 ml). The reaction mixture was warmed to 90 °C and maintained at this temperature overnight. All volatiles were removed in vacuo, and the red oil residue was dissolved in hexane. The volume of solution was diminished to ca. 5 ml, and this mixture was kept at −50 °C. After 2 days, the solid product was precipitated and isolated as a reddish solid (1.12 g, 44.6%). $C_{34}H_{58}N_4P_2$ calculated: C, 69.83; H, 10.00; N, 9.58; found: C, 70.07; H, 9.88; N, 9.31). ^{1}H NMR (200 MHz, C_6D_6, 29 °C): $\delta_H = 1.19$ (s, 18H, ^{t}Bu, P_2N_2 cycle), 1.37 (d, 24H, C*H*$_3$ of ^{i}Pr), 1.99 (m, 6H, MeP), 3.66 (m, 4H, C*H* of ^{i}Pr), 7.11 (m, 4H, Ar), 7.26 (d, 2H, Ar). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 29 °C): $\delta_C = 22.60$ (d, *C*H$_3$ of MeP), 24.44 (*C*H$_3$, ^{i}Pr), 25.30 (d, *C*H$_3$ of MeP), 28.78 (*C*H, ^{i}Pr), 30.68 (t, $J_{PC} = 4.2$ Hz, *C*H$_3$, ^{t}Bu), 53.37 (*C*, ^{t}Bu), 120.84 (Ar), 123.24 (Ar), 140.43 (t, $J = 1.9$ Hz, Ar), 141.46 (t, $J = 3.4$ Hz, Ar). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 31 °C): $\delta_P = -33.07$ (s). MS(EI): m/z (%) 584 (60, M^+), 409 (80, M^+–ArN), 235 (80, M^+–2ArN).

2.2.4. *cis-[(AdN)(^{t}BuNPMe)]$_2$ (**5**)*

A solution of AdN_3 (3.33 g, 18.8 mmol) in toluene (10 ml) was added slowly via syringe to the stirred solution of *cis*-(^{t}BuNPMe)$_2$ (2.00 g, 8.55 mmol) in toluene (20 ml). The yellow reaction mixture was warmed to 110 °C and maintained at this temperature overnight. The resulting mixture was filtrated, and all volatiles were removed from the filtrate in vacuo to yield a yellow sticky solid product (3.67 g, 80.7%). ($C_{30}H_{54}N_4P_2$ calculated: C, 67.64; H, 10.22; N, 10.52; found: C, 67.19; H, 10.37; N, 10.79). ^{1}H NMR (200 MHz, C_6D_6, 29 °C): $\delta_H = 1.38$ (s, 18H, ^{t}Bu, P_2N_2 cycle), 1.75 (m, 6H, MeP), 1.77 (br. m, 12H, C*H*$_2$ of Ad), 2.16 (br. m, 12H, C*H*$_2$ of Ad), 2.25 (br. m, 6H, C*H* of Ad). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 29 °C): $\delta_C = 21.50$ (d, *C*H$_3$ of MeP), 23.50 (d, *C*H$_3$ of MeP), 30.18 (*C*H, Ad), 31.68 (dd, $J_1 = 3.8$ Hz, $J_2 = 1.5$ Hz, *C*H$_3$, ^{t}Bu), 37.32 (*C*H$_2$, Ad), 42.88 (*C*H$_2$, Ad), 51.54 (d, $J_{PC} = 15.26$ Hz, *C*, ^{t}Bu), 52.71 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.1$ Hz, *C*N, Ad). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 31 °C): $\delta_P = 46.2$ (s). MS(EI): m/z (%) 532 (50, M^+), 383 (75, M^+–AdN), 235 (80, M^+–2AdN).

2.3. *Synthesis of complexes*

2.3.1. *[(Me$_3$SiN)(^{t}BuNPMe)]$_2$FeCl$_2$ (**6**)*

Solid $FeCl_2$ (0.65 g, 5.1 mmol) was added to the stirred solution of *cis*-[(^{t}BuNPMe)$_2$(NSiMe$_3$)$_2$] (**3**) (1.00 g, 2.45 mmol) in 30 ml of THF, and the reaction mixture was refluxed for 2 days. After drying under vacuum, the residue was washed several times with hexane and dissolved in CH_2Cl_2. Hexane was added until the unreacted gray $FeCl_2$ began to precipitate. After filtration, all volatile components were removed in vacuo to yield a raw product. This purification procedure was repeated several times to finally yield a green solid product (0.58 g, 44.3%). ($C_{16}H_{42}Cl_2N_4P_2Si_2Fe$ calculated: C, 47.03; H, 10.36; N, 13.71; found: C, 47.30; H, 10.62; N, 13.78). MS(EI): m/z (%) 500 (2, M^+–Cl), 408 (20, ligand).

2.3.2. *[(Me$_3$SiN)(^{t}BuNPMe)]$_2$CoCl$_2$ (**7**)*

Solid $CoCl_2$ (0.35 g, 2.7 mmol) and *cis*-[(^{t}BuNPMe)$_2$ (NSiMe$_3$)$_2$] (**3**) (1.0 g, 2.5 mmol) were treated in THF (30 ml) as described above, and separation of the desired product was carried out as reported for [(Me$_3$SiN)(^{t}BuNPMe)]$_2$FeCl$_2$ (**6**). Co complex was isolated as a blue solid (1.0 g, 74%). ($C_{16}H_{42}Cl_2N_4P_2Si_2Co$ calculated: C, 35.86; H, 7.64; N, 10.43; found: C, 35.69; H, 7.86; N, 10.40). MS(EI): m/z (%) 536 (3, M^+), 408 (20, ligand).

2.3.3. *[(Me$_3$SiN)(^{t}BuNPMe)]$_2$NiBr$_2$ (**8**)*

Solid $NiBr_2$ (1.47 g, 6.7 mmol) and *cis*-[(^{t}BuNPMe)$_2$ (NSiMe$_3$)$_2$] (**3**) (1.37 g, 3.4 mmol) were treated in THF (40 ml) as described above, and separation of the desired product was carried out as reported for **6**. Ni complex was isolated as a green solid (1.0 g, 47%). ($C_{16}H_{42}Br_2N_4P_2Si_2Ni$ calculated: C, 30.87; H, 6.86; N, 8.95; found: C, 30.64; H, 6.75; N, 8.93). MS(EI): m/z (%) 627 (1.2, M^+), 468 (5, M^+–2Br), 408 (30, ligand).

2.3.4. *[(2,6-^{i}Pr$_2$C$_6$H$_3$N)(^{t}BuNPMe)]$_2$FeCl$_2$ (**9**)*

Solid $FeCl_2$ (0.40 g, 3.2 mmol) was added to the stirred solution of *cis*-[(^{t}BuNPMe)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$N)$_2$] (**4**) (1.64 g, 2.8 mmol) in 30 ml of THF, and the reaction mixture was stirred at an ambient temperature for 2 days. After drying under vacuum, the residue was washed several times with hexane and dissolved in CH_2Cl_2. Hexane was added until the unreacted gray $FeCl_2$ began to precipitate. After filtration, all volatile components were removed in vacuo to yield a raw product. This purification procedure was repeated several times to finally yield a dark-violet solid product (1.20 g, 60%). ($C_{34}H_{58}Cl_2N_4P_2Fe$ calculated: C, 57.39; H, 8.22; N, 7.87; found: C, 57.87; H, 8.27; N, 7.66). ^{1}H NMR (200 MHz, CD_2Cl_2, 29 °C): $\delta_H = 1.17$ (br. d, 24H, C*H*$_3$ of ^{i}Pr), 1.31 (s, 18H, ^{t}Bu, P_2N_2 cycle), 2.17 (br. m, 6H, MeP), 3.50 (br. s, 4H, C*H* of ^{i}Pr), 6.77 (br. s, 2H, Ar), 6.98 (br. d, 4H, $J = 6.6$ Hz, Ar). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 29 °C): $\delta_C = 21.76$ (s, *C*H$_3$ of MeP), 22.92 (*C*H$_3$, ^{i}Pr), 27.39 (*C*H, ^{i}Pr), 29.59 (t, $J_{PC} = 4.2$ Hz, *C*H$_3$, ^{t}Bu), 118.74 (Ar), 121.66 (Ar), 139.28 (m, Ar), 140.45 (m, Ar). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 31 °C): $\delta_P = -31.88$ (s). MS(EI): m/z (%) 675 (5, M^+–Cl), 641 (36, M^+–2Cl), 584 (80, ligand).

2.3.5. *[(2,6-^{i}Pr$_2$C$_6$H$_3$N)(^{t}BuNPMe)]$_2$CoCl$_2$ (**10**)*

Solid $CoCl_2$ (0.42 g, 3.2 mmol) and *cis*-[(^{t}BuNPMe)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$N)$_2$] (**4**) (1.64 g, 2.8 mmol) were treated in THF (30 ml) as described for [(2,6-^{i}Pr$_2$C$_6$H$_3$N)(^{t}BuNPMe)]$_2$FeCl$_2$ (**9**), and separation of the desired product was carried out as reported for **6**. Co complex was isolated as a green solid (1.57 g, 78.5%). ($C_{34}H_{58}Cl_2N_4P_2Co$ calculated: C, 57.14; H, 8.18; N, 7.84; found: C, 56.82; H, 8.16; N, 7.86.) ^{1}H NMR (200 MHz, CD_2Cl_2, 29 °C): $\delta_H = 1.20$ (d, 24H, C*H*$_3$ of ^{i}Pr), 1.34 (s, 18H, ^{t}Bu, P_2N_2 cycle), 2.19 (m, 6H, MeP), 3.53 (m, 4H, C*H* of ^{i}Pr), 6.79 (m, 2H, Ar), 7.00 (d, 4H, $J = 7.3$ Hz, Ar). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 29 °C): $\delta_C = 21.86$ (s, *C*H$_3$ of MeP), 23.03 (*C*H$_3$, ^{i}Pr), 27.53 (*C*H, ^{i}Pr), 29.71 (t, $J_{PC} = 4.2$ Hz, *C*H$_3$, ^{t}Bu), 118.62 (m, Ar), 121.80 (d, $J = 3.4$ Hz, Ar), 139.258 (m, Ar), 140.64 (m, Ar). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 31 °C): $\delta_P = -31.78$ (s). MS(EI): m/z (%) 679 (2, M^+–Cl), 640 (8, M^+–2Cl), 584 (80, ligand).

2.3.6. *[(2,6-^{i}Pr$_2$C$_6$H$_3$N)(^{t}BuNPMe)]$_2$NiBr$_2$ (**11**)*

Solid $NiBr_2$ (0.92 g, 4.2 mmol) was added to the stirred solution of *cis*-[(^{t}BuNPMe)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$N)$_2$] (**4**) (1.64 g, 2.8 mmol) in 30 ml of THF, and the reaction mixture was refluxed for 2 days. Separation of the desired product was carried out as reported for **6**. Ni complex was isolated as a greenish solid (1.65 g, 73.4%). ($C_{34}H_{58}Br_2N_4P_2Ni$ calculated: C, 50.84; H, 7.28; found: C, 51.21; H, 7.58.) ^{1}H NMR (200 MHz, CD_2Cl_2, 29 °C): $\delta_H = 1.16$ (d, 24H, CH_3 of ^{i}Pr), 1.30 (s, 18H, ^{t}Bu, P_2N_2 cycle), 2.16 (m, 6H, MeP), 3.48 (m, 4H, CH of ^{i}Pr), 6.75 (m, 2H, Ar), 6.96 (d, 4H, $J = 7.7$ Hz, Ar). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 31 °C): $\delta_P = -31.65$ (s). MS(EI): m/z (%) 802 (1, M$^+$), 722 (2, M$^+$–Br), 641 (16, M$^+$–2Cl), 584 (80, ligand).

2.3.7. *[(AdN)(^{t}BuNPMe)]$_2$FeCl$_2$ (**12**)*

Solid $FeCl_2$ (0.4 g, 3.2 mmol) and *cis*-[(^{t}BuNPMe)$_2$(AdN)$_2$] (**5**) (1.63 g, 3.1 mmol) were treated in THF (30 ml). Reaction and separation of the desired product were carried out as reported for **6**. Fe complex was isolated as a brown solid (1.20 g, 57.8%). ($C_{30}H_{54}Cl_2N_4P_2Fe$ calculated: C, 54.64; H, 8.25; found: C, 54.61; H, 8.67). MS(EI): m/z (%) 657 (4, M$^+$), 622 (10, M$^+$–Cl), 532 (54, ligand).

2.3.8. *[(AdN)(^{t}BuNPMe)]$_2$CoCl$_2$ (**13**)*

Solid $CoCl_2$ (0.4 g, 3.1 mmol) and *cis*-[(^{t}BuNPMe)$_2$(AdN)$_2$] (**5**) (1.63 g, 3.1 mmol) were treated in THF (30 ml). Reaction and separation of the desired product were carried out as reported for **6**. Co complex was isolated as a blue solid (1.23 g, 60.6%). ($C_{30}H_{54}Cl_2N_4P_2Co$ calculated: C, 54.38; H, 8.21; found: C, 53.81; H, 8.17). MS(EI): m/z (%) 662 (6, M$^+$), 626 (14, M$^+$–Cl), 532 (75, ligand).

2.4. *Polymerization experiments*

A 1-L steel autoclave was charged with 200 ml of toluene and cocatalyst (MAO), thermostated at the temperature required for the experiment, saturated with ethene or propene, and supplemented with the desired amount of precatalyst solution. The monomer pressure (±50 mbar) and temperature (±0.5 °C) were kept constant during each polymerization run. Monomer consumption, polymerization temperature, and pressure were controlled by real-time monitoring. The polymerizations were quenched by opening the system to air, and a set amount (2 ml) of cyclooctane was added as a GC standard to the solution. Probes from the mixture were filtrated through a layer of Al_2O_3 to remove Al-containing species and catalyst decomposition products, then analyzed by GC methods.

3. Results

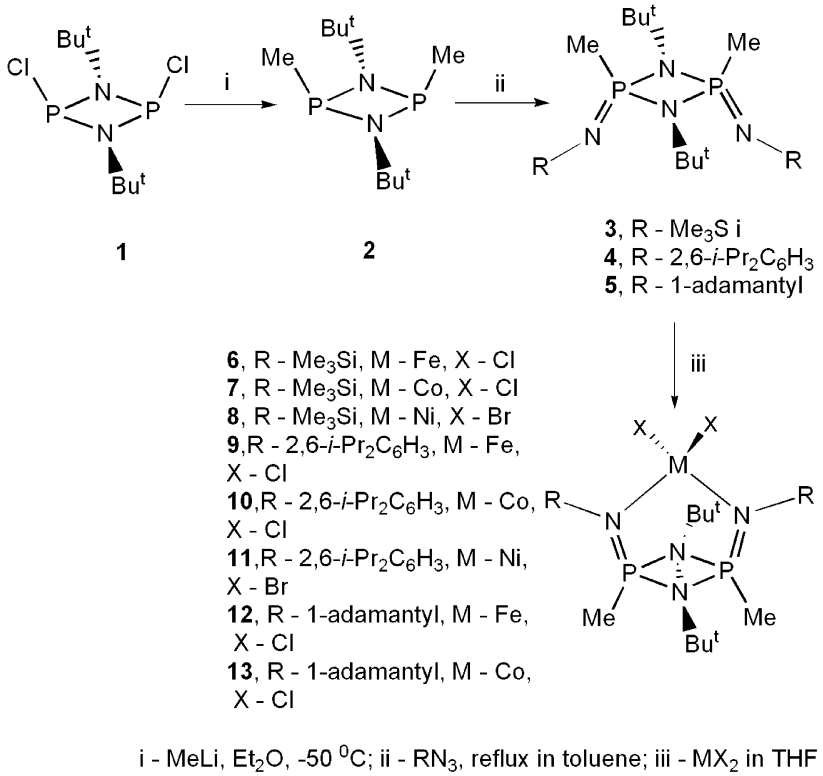
3.1. *Ligand synthesis*

Compounds containing a phosphorus–nitrogen double bond are well known, and one of the most effective synthetic methods for their preparation is the Staudinger reaction [29]. This reaction is the key to the many interesting structures, especially those with inorganic chelating P=N groups [30]. To provide effective metal coordination, the chelating phosphor(V)-imino groups must be in *cis*-orientation. However, all cyclodiphosph(III or V)azanes cannot adopt the thermodynamically stable *cis*-configuration, but undergo *cis–trans* isomerization and appear as inseparable equilibrium mixtures of *cis* and *trans* isomers [17]. Only the *cis*-cyclodiphosph(III or V)azanes with small substituents at the phosphorus (e.g., Me) and ^{t}Bu groups at the nitrogen atoms do not undergo such an isomerization process [31]. One of these stable compounds, *cis*-(ClPN^{t}Bu)$_2$ (**1**), was chosen as a starting material for our study. After methylation of **1** by MeLi, the corresponding *cis*-(MePN^{t}Bu)$_2$ (**2**) was isolated with moderate yield (Scheme 1); the substance was sensitive to the harsh temperatures and partly decomposed during the distillation. In ^{1}H NMR, methyl groups at phosphorus(III) show specific spin–spin coupling with phosphorus ($A_3XX'A'_3$ spin system) [28].

After purification, **2** was introduced into the Staudinger reaction with three different organic azides (Scheme 1). Two of these azides, Me_3SiN_3 and AdN_3 (Ad – 1-adamantyl), were chosen because they were commercially available and relatively stable substances. The preparation of the third azide, 2,6-di-*i*-propylphenylazide (2,6-^{i}Pr$_2$C$_6$H$_3$N$_3$), has been described previously; this substance can be simply obtained from the corresponding aniline [25]. In addition, it was assumed that sterically bulky substituents, such as Me_3Si, 1-adamantyl, and 2,6-di-*i*-propylphenyl, would be beneficial to the catalytic activity of the late transition metal complexes.

After treatment of (^{t}BuNPMe)$_2$ (**2**) with Me_3SiN_3 at 90 °C for 1 day, the ^{31}P NMR spectrum of the raw product revealed a marked upfield shift of the phosphorus signal [from $\delta_P = 173.00$ ppm for (^{t}BuNPMe)$_2$ to $\delta_P = -12.7$ ppm], corroborating the formation of phosphorus(V) species. In addition, a small amount of the *trans* isomer was recognizable from the ^{31}P NMR data ($\delta_P = -2.86$ ppm). Purification of the raw product with hexane extraction gave the desired compound, [(^{t}BuNPMe)$_2$(NSiMe$_3$)$_2$] (**3**), with high yield. The bulk composition and purity of the product were confirmed by ^{1}H NMR and ^{13}C NMR data and by elemental analysis [28]. The Staudinger reaction between (^{t}BuNPMe)$_2$ and AdN_3 or 2,6-^{i}Pr$_2$C$_6$H$_3$N$_3$ gave *cis*-[(^{t}BuNPMe)$_2$(AdN)$_2$] (**4**) and *cis*-[(^{t}BuNPMe)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$N)$_2$] (**5**), respectively (Scheme 1).

The specific spin–spin coupling of MeP protons in ^{1}H NMR spectra was observed for **3**–**5** (see supplemental material). Evidently, such coupling in ^{1}H NMR indicates the presence of a MeP(V)$_2$N$_2$ cycle and can be used as a characteristic fingerprint for these phosphazene systems. The solid-state structure of **3** was revealed by single-crystal X-ray diffraction studies (see supplemental material). However, the crystals obtained for X-ray measurements consisted of **3** in *trans* configuration. This can be explained by contamination of the product by a *trans* isomer (see above), which seems to crystallize better than the *cis* isomer.



Scheme 1.

3.2. Complex synthesis

Treatment of the bis(imino)cyclodiphosph(V)azanes **3**–**5** with anhydrous Fe(II), Co(II) dichlorides, or $NiBr_2$ yielded the metal complexes **6**–**13** (Scheme 1). Ligands **3**–**5** displayed only moderate ability to chelate with the metal precursors, indicated by moderate yields; high temperatures, long reaction times, and an excess of metal halides were needed for the complex preparation. To increase the yields of the complexes with ligands **3** and **5**, the reactions were performed in refluxing THF. Unfortunately, under these conditions, ligand **4** gave only unidentified products; thus, the complexations with **4** were carried out at ambient temperature. Of the metal precursors, $NiBr_2$ revealed the poorest propensity to form complexes, and all attempts to prepare a Ni complex with 1-adamantyl substituted ligand **5** failed.

In general, purification of the complexes was straightforward. THF was evaporated from the reaction mixture, and unreacted ligand was removed by hexane extraction, after which an excess of metal halides was precipitated from the dichlorometane solution of the complex by adding hexane. After filtration, these solvents were removed in vacuum, and target complexes **6–13** were isolated as colored powders. The composition was confirmed by elemental analysis and mass spectroscopy data. As expected, the complexes bearing ligands **3** and **5** appeared to be paramagnetic, and their NMR investigations failed. Surprisingly, for the Fe, Co, and Ni derivatives of *cis*-[(2,6-$Pri_2C_6H_3N$)(ButNPMe)]$_2$, reliable ^{1}H, ^{13}C, and ^{31}P NMR data were recorded. In the ^{31}P NMR spectra, only signals related to the desired complexes were found, and ^{1}H and ^{13}C NMR data revealed C_{2v} symmetry for Fe, Co, and Ni complexes (**9**–**11**) in solution. The same specific spin–spin coupling of phosphorus and PMe protons as in the parent ligand **4** was also observable in ^{1}H NMR spectra of the complexes (see supplemental material).

3.3. Ethene oligomerization

On activation by MAO in toluene, the Ni and Co complexes revealed high catalytic activity in ethene oligomerization, typically in the range of 700–1600 kg/(mol_{cat} h) (Table 1). When the reactions were terminated by addition of acidified methanol to the resulting toluene phase, only a faint precipitation of inorganic material originating from MAO appeared. GC–MS data from samples, filtered through Al_2O_3, revealed the presence of a mixture of olefins (from butenes to C_{18}–C_{20} fractions) (Table 1). The quantities of C_{12}–C_{20} oligomers were calculated directly from the GS data, which were calibrated with cyclooctane. The α value (characteristic for Schulz–Flory oligomer distribution) [32,33] was determined from the molar ratio of C_{16}/C_{14}, and the mol% of lower (C_4–C_{10}) alkenes in the product mixture was calculated by backward extrapolation from C_{12} on the basis of the α value [34].

The central metal atom in MAO-activated bis(imino)cyclodiphosph(V)azanes complexes has a significant influence on the product distribution in ethene oligomerization. After MAO activation, the nickel complexes gave mixtures with a high (up to 94%) proportion of butenes together with hexenes and a recognizable C_{10} fraction ($<1\%$), whereas the cobalt catalysts were prone to produce C4–C20 oligomers with Schulz–Flory

Table 1
Ethylene olygomerization and dimerization results[a]

Entry no.	Catalyst	Product yield (g)	α	Activity[b]	C_4 (wt%)	C_6 (wt%)	C_8[c] (wt%)	C_{10} (wt%)	C_{12} (wt%)	C_{14} (wt%)	C_{16} (wt%)	C_{18} (wt%)
1	**7**	7.75	0.75	1550	14	15	15	14	13	12	10	7
2	**8**	7.95	–	1590	89	10	–	1	–	–	–	–
3	**10**	7.54	0.66	1510	19	19	17	14	11	8	7	5
4	**11**	5.60	–	1120	94	6	–	–	–	–	–	–
5	**13**	3.56	–	720	71	10	–	5	4	5	5	–

[a] Conditions: MAO (Al/M = 1000), 200 ml of toluene, 8 bar of ethylene (under these conditions $[C_2H_4]$ is ∼1 mol/l), reaction temperature 30 °C.
[b] In $kg_{olefins}/(mol_{cat}\ h\ [C_2H_4])$.
[c] Calculated based on α value.

distribution (see the GC data in supplemental material). Quite unexpectedly, the iron complexes displayed very low catalytic activity.

Stability of the cyclodiphosph(V)azane catalysts in the oligomerization reactions also depended on the nature of the central atom. At the start of oligomerization, the Co catalysts were highly active, but they deactivated rapidly, manifesting as a decline in ethene consumption during the reaction. The initial activity of the Ni catalysts was lower than that of the Co catalysts, but activity remained nearly constant during the oligomerization experiments. The Co and Ni catalysts thus seem to provide similar average productivity in ethene oligomerization during the first 30 min (Table 1).

The substitution pattern at the ligand moiety also had an important role in defining the catalytic activity of the complexes. Co catalysts **7** and **10** bearing Me_3Si and bulky 2,6-*i*-$Pr_2C_6H_3$, respectively, exhibited similar catalytic activities, whereas **13** bearing the 1-adamantyl substituted ligand gave 50% lower activity values under similar reaction conditions (Table 1).

The influence of reaction temperature and MAO/M ratio on activity and catalyst selectivity was also investigated for Ni and Co complexes (Tables 2 and 3). The catalysts revealed high sensitivity to the oligomerization temperature (Table 2); experiments conducted at above 50 °C gave only low activities, and oligomerization was terminated above 70 °C. Despite the decrease in catalytic activity with increasing oligomerization temperature, the selectivity of the catalysts remained similar. In ethene dimerization with the Ni catalysts, the proportion of the C_4 fraction increased slightly with increasing temperature, whereas with the Co catalysts, the α value for the Shulz–Flory distribution rose marginally (Table 2), indicating an increase in the amount of C_{12}–C_{16} fractions.

Changes in MAO concentrations did not strongly affect the catalytic activity of the Ni and Co complexes or the selectivity of ethene dimerization by Ni catalysts. However, higher MAO/Co ratios increased the amount of the C_4 fraction, indicating an increased probability of a termination reaction (Table 3).

The Ni catalysts produced a mixture of olefins with a very high quantity of C_4 alkenes (>90%). Detailed NMR studies were performed to determine the ratio between different butene isomers. Dimerization experiments were carried out in deuterated benzene at 30 °C and 8 bar ethene pressure, and filtered samples from the resulting solutions were analyzed by ^1H NMR. These results confirmed the GC data, because the spectra exhibited signals of C_4 olefins, toluene (from MAO solution), and a small amount of C_6 fraction (Fig. 2). Integration of the spectra revealed a butenes-2/butene-1 ratio of 1.6–1.7:1. *trans*-Butene-2 was the dominating butene-2 isomer in the product mixture, with a ratio of 1.4–1.7:1. These observations are in agreement with the values reported for enthalpies of formation for various butenes (Table 6); such thermodynamic control in

Table 2
Influence of the oligomerization temperature on the catalytic behaviour of the complexes

Entry no.	Catalyst	Yield of oligomers (g)	α	T (°C)	Activity[a,b]	C_4[c] (wt%)	C_6[c] (wt%)
1	**7**	8.14	0.72	20	4180*	–	–
2	**7**	7.75	0.75	30	1550	–	–
3	**7**	4.67	0.75	40	1050	–	–
4	**8**	2.86	–	20	1470*	87	13
5	**8**	7.95	–	30	1590	89	10
6	**8**	7.06	–	40	1420	91	9
7	**10**	3.97	0.63	20	2035*	–	–
8	**10**	7.54	0.66	30	1510	–	–
9	**10**	3.11	0.68	40	700	–	–
10	**11**	1.62	–	20	830*	92	8
11	**11**	5.60	–	30	1120	94	6
12	**13**	2.18	–	20	1120*	27	11
13	**13**	3.56	–	30	720	71	10
14	**13**	2.09	–	40	470	51	16

[a] In $kg_{olefins}/(mol_{cat}\ h\ [C_2H_4])$.
[b] Conditions: MAO (Al/M = 1000), 200 ml of toluene, 8 bar of ethylene (*, ethene pressure was 3 bar).
[c] Only for Ni catalysts (for Co complexes, α value is present).

Table 3
Influence of MAO concentration on catalytic behaviour of complexes

Entry no.	Catalyst	Yield of oligomers (g)	α	MAO/M	Activity[a,b]	C_4[c] (wt%)	C_6[c] (wt%)
1	**7**	9.13	0.75	500	1830	–	–
2	**7**	7.75	0.75	1000	1550	–	–
3	**8**	5.71	–	500	1140	90	10
4	**8**	7.96	–	1000	1590	89	10
5	**10**	7.16	0.70	500	1430	–	–
6	**10**	7.54	0.66	1000	1510	–	–
7	**11**	5.44	–	500	1090	93	7
8	**11**	5.60	–	1000	1120	94	6

[a] In $kg_{olefins}/(mol_{cat}\ h\ [C_2H_4])$.
[b] Conditions: oligomerization temperature 30 °C, 200 ml of toluene, 8 bar of ethylene.
[c] Only for Ni catalysts (for Co complexes, α value is present).

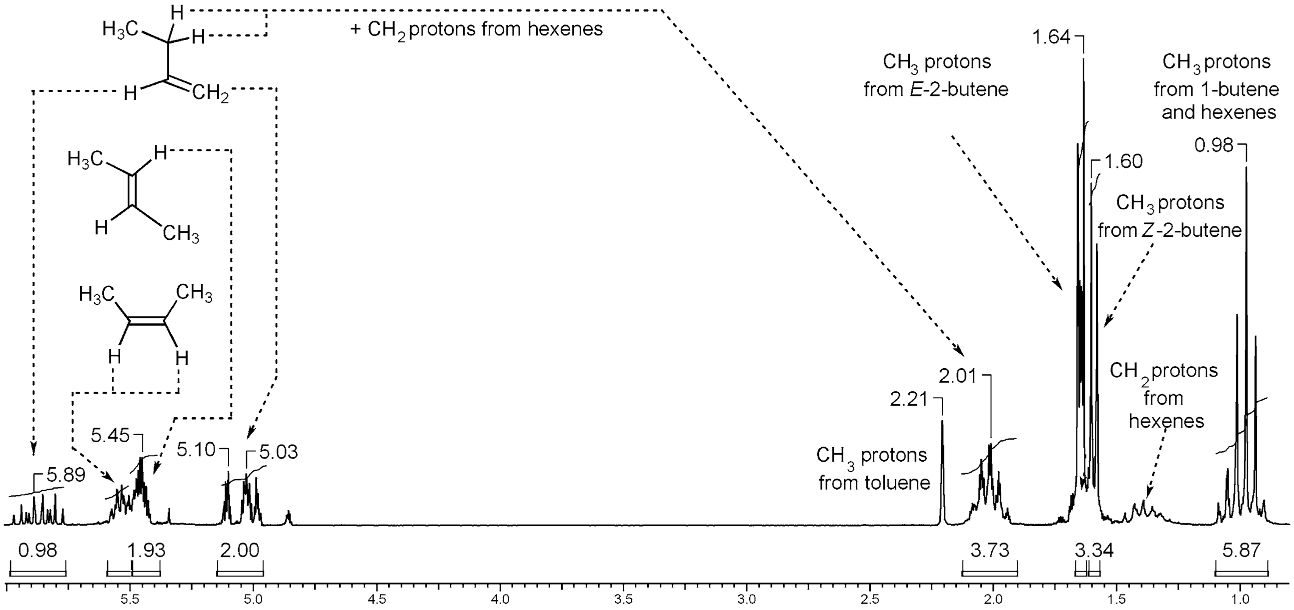


Fig. 2. ^{1}H NMR spectrum of product mixture obtained in ethene dimerization experiments in C_6D_6 where $[(Me_3SiN)(^tBuNPMe)]_2NiBr_2$/MAO (**8**) was used as a catalyst.

Table 4
Propene dimerization results

Entry no.	Catalyst	Mass of the products (g)	T (°C)	MAO/M	Propene pressure (bar)	Activity[a]	Hexene-1 (%)	Hexene-2 and hexene-3 (%)	4-methyl-1-pentene (%)	4-methyl-2-pentene and 2,3-dimethyl-1-butene (%)	C_6 total (wt%)	C_9 (wt%)	C_{12} (wt%)
1	**7**	4.2	20	1000	7	54.2	13	71	7	9	83	13	4
2	**7**	0.4	40	1000	7	15.8	16	65	5	14	71	21	8
3	**8**	11.3	20	1000	7	143.9	5	42	10	43	∼100	<1	<1
4	**8**	3.3	40	1000	7	137.5	8	39	13	40	∼100	<1	<1
5	**10**	2.1	20	1000	7	27.4	20	65	5	10	65	24	11
6	**10**	1.5	40	1000	7	62.5	22	62	5	11	75	14	11
7	**11**	18.0	20	1000	7	229.7	5	53	9	33	∼100	<1	<1
8	**11**	5.8	40	1000	7	240.3	8	41	12	39	∼100	<1	<1
9	**7**	3.2	20	500	7	41.5	15	74	4	7	88	11	1
10	**8**	25.4	20	500	7	323.5	5	43	9	43	∼100	<1	<1
11	**10**	1.4	20	500	7	17.9	4	94	1	1	80	11	9
12	**11**	19.6	20	500	7	250.8	8	32	12	48	∼100	<1	<1
13	**7**	1.6	20	1000	3.5	113.1	22	63	5	10	52	27	21
14	**8**	4.6	20	1000	3.5	328.6	6	35	10	49	∼100	<1	<1
15	**11**	9.3	20	1000	3.5	657.2	6	42	8	44	∼100	<1	<1

[a] $kg_{olefins}/(mol_{cat}\,h\,[C_3H_6])$; at 20 °C and 7 bar, $[C_3H_6] = 15.67$ mol/l; 40 °C and 7 bar, $[C_3H_6] = 4.80$ mol/l; 20 °C and 7 bar, $[C_3H_6] = 2.83$ mol/l.

butene distribution can be the result of a fast and reversible isomerization reaction, catalyzed by Ni–H species (see below).

3.4. Propene dimerization

Propene oligomerization properties of the Ni and Co catalysts were evaluated by applying standard reaction conditions: 20 °C and 7 bar propene pressure. Under these conditions, the Co catalysts showed low catalytic activity [70–100 $kg/(mol_{cat}\,h)$], whereas the Ni catalysts were highly active [up to 3600 $kg/(mol_{cat}\,h)$] (Table 4). The resulting toluene solutions were analyzed by GC–MS methods as described above. The samples produced by Co complexes included dissolved propene and C_6 fraction with admixtures of C_9 and C_{12} olefines, whereas the Ni catalysts produced mainly C_6 alkenes with traces of higher olefins (see the GC data in supplemental material).

NMR and GC methods were used to analyze the proportions of the hexene isomers in the C_6 fraction in detail. Considering all possible combinations for propene dimerization, nine different hexenes (12 with *cis*/*trans* isomers) can be expected (Scheme 3). The propene dimerization reaction with Ni catalyst **10** was carried out in deuterobenzene, after which the reaction solution was refluxed for a long time to remove propene, which is very soluble in toluene and benzene. ^{1}H and ^{13}C NMR spectra of Al_2O_3-filtrated samples were measured and compared with ^{1}H and ^{13}C NMR spectra of pure alkenes available from the Aldrich NMR Library. Based on this comparison, six different hexenes were identified: hexene-1, hexenes-2, hexenes-3, 4-methyl-1-pentene, 4-methyl-2-pentene, and 2,3-dimethyl-1-butene. To verify these results, ^{1}H and ^{13}C NMR spectra of pure hexenes (purchased from Aldrich) and their mixtures with appropriate compositions were recorded and used for analysis of propene dimerization products.

In the original GC chromatograms, five signals corresponding to C_6 olefins were detected. To ensure reliable data on product composition in the reaction mixture, these results were compared with the GC data obtained for pure alkenes and their combinations. With the applied GC method, the *cis*/*trans* isomers were noted to have almost the same retention times, excluding *cis*- and *trans*-2-hexenes. This information was then used to calculate the quantities of different hexenes in the products (Table 4). Summarizing the results, 1-hexene content in the mixtures remained <20% for the Ni and Co catalysts. The Co catalysts produced hexene-2 and hexene-3 as the main products, whereas the Ni catalysts produced mixtures of olefins with two main fractions: hexene-2/hexene-3 (the result of 1,2–2,1 propene insertions) and 4-methyl-2-pentene/2,3-dimethyl-1-butene (the result of 1,2–1,2 propene insertions, Scheme 3) (Table 4).

The influence of oligomerization conditions on catalysis (dimerization activity and content of the resulting olefin mixtures) was studied with the Ni complexes. The catalysts were found to be sensitive to reaction temperature and excessive MAO, and the best activities were achieved at low polymerization temperatures and MAO concentrations and high propene pressure (Table 4). In all experiments, the content of hexene-1 and 4-methyl-1-pentene in products remained constant, whereas the hexene-2/hexene-3 fraction decreased slightly with increasing temperature and propene pressure (Table 4). Only C_6 olefins with very small traces of higher fractions were recognized in GC–MS experiments.

3.5. *Ethene and propene codimerization*

As described above, bis(imino)cyclodiphosph(V)azane Ni complexes catalyze selective ethene or propene dimerization reactions. The mixtures of olefins obtained with these catalysts had high proportions (up to 90–100%) of butenes or hexenes. Based on these results, possible codimerization of ethene and propene was expected. The codimerization experiments were carried out in toluene at 30 °C. The set amounts of propene were introduced into the autoclave, which was then filled with ethene up to 4 bar total pressure. The resulting olefin mixtures were investigated by GC methods.

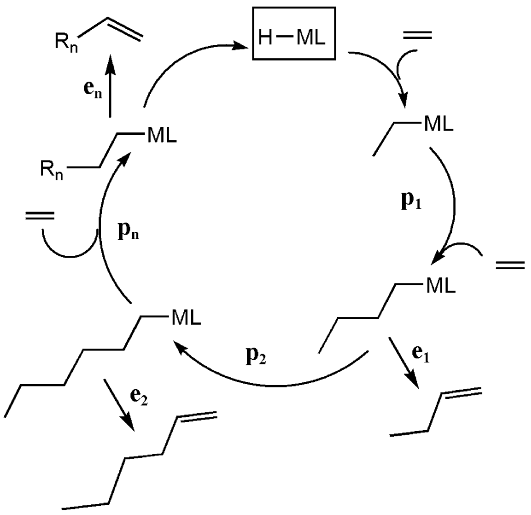
Appearance of a new fraction between C_4 and C_6 olefins was detected (see the GC data in supplemental material). The content of the C_5 olefins in the resulting mixtures depended on the initial ratio of the monomers (Table 5). Propene was observed in all mixtures.

4. Discussion

Table 5
Propene ethene codimerization results

Entry no.	Catalyst	Ethene consumption (l)	Ethene pressure (bar)	Propene pressure (bar)	Activity[a]	C_6/C_5 ratio (mol)	C_6/C_5 ratio (wt)
1	**8**	2.43	3	1	640	1.2	1.4
2	**8**	1.98	2	2	520	1.0	1.2
3	**8**	1.46	1	3	390	0.75	0.9
4	**11**	2.87	3	1	760	0.35	0.4
5	**11**	1.99	2	2	525	0.4	0.5
6	**11**	1.23	1	3	325	0.7	0.8

[a] Calculated from ethene consumption.



p - chain propagation (olefin insertion),
e - chain termination (β-hydrogen elimination)

Scheme 2.

In this study, the bis(imino)cyclodiphosph(V)azane complexes of the late transition metals were synthesized and characterized. In the olefin oligomerization experiments, these complexes exhibited behavior similar to that of known late transition metal catalysts (e.g., those used in SHOP). The complex species containing M–H bonds are widely considered to be the catalytic sites for the oligomerization reaction. They are thought to be formed via β-H elimination from the intermediate metal alkyl complexes (Scheme 2) [35,36].

To draw a full analogy with the accepted mechanism (Scheme 2), Co and Ni hydride species are proposed to be active intermediates in Co and Ni bis(imino)cyclodiphosph(V)azane-catalyzed olefin oligomerization processes. Complex activation by MAO can lead to methyl-substituted cationic species, which can be transformed into cationic Co and Ni hydride species after one or two ethene insertions followed by elimination.

The nature of the central metal in catalyst species plays a significant role in defining the catalytic behavior of the complex, particularly the composition of the resulting olefin mixture. In ethene oligomerization, the bis(imino)cyclodiphosph(V)azane Co complexes produced olefins with the Schulz–Flory distribution from C_4 to C_{20}, but mixtures of alkenes with high (up to 95%) ethene dimerization products were obtained with Ni catalysts. Dimerization can be considered a particular case of oligomerization in which the termination reaction (β-hydrogen transfer to the metal) is much faster than olefin insertion into a metal–alkyl bond (Scheme 2) [37]. Ni alkyl species apparently revealed much higher instability toward β-H elimination than the analogous Co intermediates, which caused the selectivity of Ni catalysts in ethene dimerization.

In propene oligomerization, both the Ni and Co complexes produced mixtures of alkenes with high proportions (up to 100%) of dimerization products (C_6 olefins). The selective propene dimerization by Co catalysts compared with their behavior in ethene oligomerization indicates that the β-H transfer to cobalt and ethene insertion into the Co–alkyl bond occur more rapidly than the propene insertion. This means that in the case of the Co catalysts, ethene insertion is a clearly more favored process than propene insertion.

The species containing the metal–hydrogen bonds, which are responsible for alkene oligomerization, are generally considered to also catalyze the isomerization of the produced olefin oligomers through a reversible addition/elimination to the C–C bond [35,36]. In ethene and propene oligomerizations with bis(imino)cyclodiphosph(V)azane Co and Ni catalysts, this results in the formation of 1- and 2-butenes and hexenes with different double-bond positions.

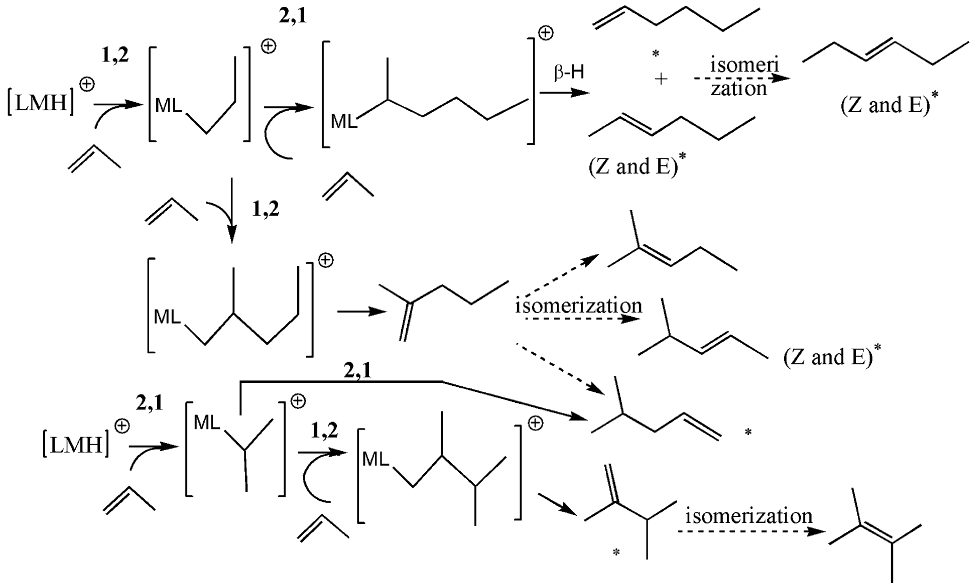
The higher content of linear 2- and 3-hexenes compared with 1-hexene in propene dimerization products (Table 4) can be explained by a fast and reversible isomerization of hexene-1, leading to the thermodynamically more preferable hexene-2 and hexene-3 (Table 6).

According to Scheme 3, hexene-1 can be formed as a result of 1,2 propene insertion into the M–H bond, followed by a 2,1 insertion. With Co catalysts, this dimerization route is favored, as revealed by the ratio of linear/branched hexenes in the product mixtures (Table 4). In contrast, the probabilities for a 1,2 propene insertion followed by a 1,2 or a 2,1 insertion are almost equal in propene dimerization catalyzed by Ni complexes (Table 4). They produced mixtures of olefins with two main fractions: hexene-2/hexene-3 (result of 1,2–2,1 propene insertions) and 4-methyl-2-pentene/2,3-dimethyl-1-butene (result of 1,2–1,2 propene insertions, Scheme 3). In this case, the hexene isomerization process also plays a major role in forming the thermodynamically preferred hexene-2, hexene-3, and 4-methyl-2-pentene. 2,3-Dimethyl-1-butene can be the result of a 1,2 propene insertion into the *iso*-propyl Ni species formed by a Markovnikoff addition of Ni–H particles to the propene (2,1 propene insertion into Ni–H bond) (Scheme 3).

Table 6
Thermodynamic data for butenes and hexenes

Entry no.	Compounds	ΔH_f°(g) at 298 K (kJ/mol)
1	1-Butene	−0.63
2	*cis*-2-Butene	−7.70
3	*trans*-2-Butene	−10.80
4	1-Hexene	−42.09
5	*cis*-2-Hexene	−52.77
6	*trans*-2-Hexene	−54.32
7	*cis*-3-Hexene	−48.04
8	*trans*-3-Hexene	−54.87
9	4-Methyl-1-pentene	−51.64
10	*cis*-4-Methyl-2-pentene	−57.89
11	*trans*-4-Methyl-2-pentene	−61.91
12	2,3-Dimethyl-1-butene	−66.77

The ethene–propene codimerization experiments with Ni catalysts revealed no significant difference in the activation energies of the ethene and propene insertions into the Ni–alkyl bond (propagation step, Scheme 2), because the content of the resulting olefin mixtures is regulated by the initial ratios of the comonomers. Such catalytic behavior was observed for both Ni complexes investigated (Table 6). In addition, Ni compound **11**, bearing di-*i*-propylphenyl groups, produced the olefin mixtures with higher content of pentenes relative to the C_6 fraction than



M - Co, Ni, L - phosph(V)azane ligand, * alkenes found in products mixture,
1,2 or **2,1** - way of propene insertion

Scheme 3.

Me_3Si-substituted Ni catalyst **8**. In the presence of the bulky aryl substituents near the metal center of catalyst **11**, coordination of ethene versus a larger propene molecule can be sterically preferable for codimerization. As a result of this steric control, the probability of formation of ethene–ethene and ethene–propene dimers is enhanced.

5. Conclusion

In this study, highly active ethene and propene oligomerization and dimerization catalysts based on bis(imino)cyclodiphosph(V)azane Co and Ni complexes are described. The catalytic activity of these complexes is sensitive to high oligomerization temperature and monomer concentration. In contrast to Co catalysts, which produce olefins with a Schulz–Flory distribution, Ni complexes can selectively dimerize ethene. This may be due to the increased instability of Ni–alkyl intermediates toward β-H elimination. Both Co and Ni complexes catalyzed propene dimerization. A 1,2 insertion of propene followed by a 2,1 insertion into a M–H bond is the main reaction pathway in propene dimerization by Co catalysts. In Ni complexes, the probabilities of 1,2–1,2 and 1,2–2,1 propene insertions are almost equal, reflecting the composition of the resulting hexene mixtures.

Acknowledgments

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Supplementary material

Supplementary material includes the NMR data of obtained ligands and complexes, structural data for *trans*-$[(^tBuNPMe)_2(NSiMe_3)_2]$, *trans*-(**3**) (CCDC-283071) in cif format, and GC chromatograms of the ethene dimerization and oligomerization and ethene–propene codimerization.

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References

[1] D. Vogt, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1, VCH, Weinheim, New York, Basel, Cambridge, Tokyo, 1996, p. 245.
[2] D. Vogt, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1, VCH, Weinheim, New York, Basel, Cambridge, Tokyo, 1996, pp. 246–248.
[3] W. Keim, in: M. Graziani (Ed.), Fundamental Research in Homogeneous Catalysis, vol. 4, Plenum, New York, 1984, p. 131.
[4] E.F. Lutz, J. Chem. Educ. 63 (1986) 202.
[5] W. Keim, New J. Chem. 11 (1987) 531.
[6] D. Vogt, in: B. Cornils, W.A. Herrmann (Eds.), Aqueous-Phase Organometallic Catalysis, VCH, Weinheim, 1998, p. 547.
[7] M. Wang, H. Zhu, K. Jin, D. Dai, L. Sun, J. Catal. 220 (2003) 392.
[8] S. Bogärt, T. Chenal, A. Mortreux, G. Nowogorcki, W.C. Lehmann, J.-F. Carpentier, Organometallics 20 (2001) 199.
[9] K.-D. Hungenrg, J. Kerth, F. Langhauser, H.-J. Müller, P. Müller, Angew. Makromol. Chem. 227 (1995) 159.
[10] C.M. Killian, L.K. Johnson, M. Brookhart, Organometallics 16 (1997) 2005.
[11] B.L. Small, M.J. Carney, D.M. Holman, C.E. O'Rourke, J.A. Halfen, Macromolecules 37 (2004) 4375.
[12] B.L. Small, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 7143.
[13] K.P. Tellmann, V.G. Cibson, A.J.P. White, D.J. Williams, Organometallics 24 (2005) 280.
[14] F. Speiser, P. Braunstein, Organometallics 23 (2004) 2633.
[15] F. Speiser, P. Braunstein, Organometallics 23 (2004) 2625.
[16] J. Heinicke, M. Köhler, N. Peulecke, W. Keim, J. Catal. 225 (2004) 16.
[17] L. Stahl, Coord. Chem. Rev. 210 (2000) 203.
[18] G.G. Briand, T. Chivers, M. Krahn, Coord. Chem. Rev. 233–234 (2002) 237.
[19] L.P. Grocholl, L. Stahl, R.J. Staples, Chem. Commun. (1997) 1465.
[20] K.V. Axenov, V.V. Kotov, M. Klinga, M. Leskelä, T. Repo, Eur. J. Inorg. Chem. (2004) 4702.
[21] K.V. Axenov, M. Klinga, M. Leskelä, T. Repo, Organometallics 24 (2005) 1336.
[22] T. Chivers, M. Krahn, G. Schatt, Inorg. Chem. 41 (2002) 4348.
[23] G.R. Lief, C.J. Carrow, L. Stahl, R.J. Staples, Chem. Commun. (2001) 1562.
[24] T. Chivers, C. Fedorchuk, M. Krahn, M. Parvez, G. Schatt, Inorg. Chem. 40 (2001) 1936.
[25] S. Al-Benna, M.J. Sarsfield, M. Thornton-Pett, D.L. Ormsby, P.J. Maddox, P. Bres, M. Bochmann, J. Chem. Soc., Dalton Trans. (2000) 4247.
[26] M. Bochmann, M.J. Sarsfield, US Patent WO 2000047592.
[27] T.G. Hill, R.C. Haltiwanger, M.L. Thompson, S.A. Katz, A.D. Norman, Inorg. Chem. 33 (1994) 1770.
[28] The synthesis of $[(^tBuNPMe)_2(NSiMe_3)_2]$ was reported by O.J. Scherer, G. Schnabl, Chem. Ber. 109 (1976) 2996.
[29] R.A. Shaw, Phosphorus and Sulfur 4 (1978) 101.
[30] W.Q. Tian, Y.A. Wang, J. Org. Chem. 69 (2004) 4299.
[31] I. Silaghi-Dumitrescu, I. Haiduc, Phosphorus and Sulfur 91 (1994) 21.
[32] P.J. Flory, J. Chem. Am. Soc. 62 (1940) 1561.
[33] G.V. Schulz, Z. Phys. Chem. B 30 (1935) 379.
[34] This method was used in Ref. [13] to calculate the olefin mixture composition
[35] J. Scupiňska, Chem. Rev. 91 (1991) 613.
[36] S.M. Pillai, M. Ravindranathan, S. Sivaram, Chem. Rev. 86 (1986) 353.
[37] D. Vogt, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1, VCH, Weinheim, New York, Basel, Cambridge, Tokyo, 1996, p. 260.