α-Keto-*β*-Diimine Nickel-Catalyzed Olefin Polymerization: Effect of Ortho-Aryl Substituents and Preparation of Stereoblock Copolymers

Anatolij Sokolohorskyj,¹ Ondřej Železník,¹ Ivana Císařová,² Johannes Lenz,³ Albena Lederer,³ Jan Merna ¹

¹Department of Polymers, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic ²Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030, 128 40 Prague 2, Czech Republic

³Leibniz Institute of Polymer Research, Hohe Strasse 6, D-1069 Dresden, Germany and Technische Universität Dresden, Dresden, 01062, Germany

Correspondence to: J. Merna (E-mail: merna@vscht.cz)

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ABSTRACT: A series of α -keto- β -diimine nickel complexes (Ar-N = C(CH₃)-C(O)-C(CH₃)=N-Ar)NiBr₂; Ar = 2,6-R-C₆H₃-, R = Me, Et, *i*Pr, and Ar = 2,4,6-Me₃-C₆H₃-) was prepared. All corresponding ligands are unstable even under an inert atmosphere and in a freezer. Stable copper complex intermediates of ligand synthesis and ethyl substituted nickel complex were isolated and characterized by X-ray. All nickel complexes were used for the polymerization of ethene, propylene, and hex-1-ene to investigate their livingness and the extent of chain-walking. Low-temperature propene polymerization with less bulky ortho-substituents was less isospecific than the one with isopropyl derivative. Propene stereoblock copolymers were

INTRODUCTION The research interest in late transition metal catalysts lies in their low oxophilicity and therefore higher tolerance to polar functional groups.^{1,2} Some of them also undergo "chain-walking" reactions in which the growing center migrates along the growing polymer chain through a series of β -hydride elimination and reinsertion steps. Typical examples of such catalysts are diimine complexes of nickel and palladium.³ Chain-walking enables the formation of various types of polyethylenes ranging from almost linear to hyperbranched ones.^{1,4} On the contrary, higher α -olefins are straightened after their insertion and form more linear polymers.^{5,6} α -Diimine nickel and palladium complexes also belong among of few catalytic systems suitable for living olefin polymerization allowing the preparation of block olefin copolymers including stereoblock copolymers.⁷⁻¹⁴ Soon after the discovery of α -diimine complexes, their six-membered analogs based on β -diimine ligands were introduced.¹⁵ β -Diimine nickel complexes of these basic ligands were

Dedicated to Prof. Jan Roda on the occasion of his 70th birthday.

Materials

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prepared by *i*Pr derivative combining the polymerization at low temperature to prepare isotactic polypropylene (PP) block and at a higher temperature, supporting chain-walking, to obtain amorphous regioirregular PP block. Alternatively, a copolymerization of propene with ethene was used for the preparation of amorphous block. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *00*, 000–000

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approximately 100 times less active than the corresponding α -diimine counterpart and afforded less-branched polyethylene.

Much more active nickel complexes with β -diimine ligand substituted by electron withdrawing group connected to ligand backbone were developed later by Bazan.^{16–20} Activity comparable with that of known α -diimine complexes was achieved with α -keto- β -diimine complex **5d** (Scheme 1). Complexation of organoaluminium cocatalyst to the carbonyl group of ligand, leading to decrease of electron density at nickel metal center, was described as the reason for the high activity. α -Keto- β -diimine nickel complex **5d** was also reported to initiate living polymerization of propene, hex-1ene, and even of ethene, which is the case of only α -diimine palladium complexes⁸ or nickel α -diimine complexes with highly rigid ligands.^{21,22} Trimethylaluminium-free methylaluminoxane (MAO) had to be used to suppress transfer and

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SCHEME 1 Synthesis of α -keto- β -diimine nickel complexes.

termination reactions. Interestingly, achiral α -keto- β -diimine complex **5d** was capable of enantiomorphic site control to yield moderately isotactic polypropylene at low temperatures ([mmmm] = 0.85, $T_{\rm m} = 134$ °C).^{18,20}

Despite the promising catalytic behavior of **5d**, it is the only one α -keto- β -diimine nickel complex published in open literature.^{16,18–20} Derivative combining isopropyl and methyl group in ortho-aryl positions of the ligand was reported in the patent; however, no polymerization data were provided.¹⁷

Herein, we report on a series of three novel α -keto- β -diimine nickel complexes **5a–5c** (Scheme 1) and their catalytic behavior in ethene, propene, and hex-1-ene polymerization. The variation of ortho-aryl substituents was the main focus in the design of the complexes as these positions are crucial for analogous α -diimine catalysts suitable for living polymerizations.^{7,12} Preparation of propene block copolymers using complex **5d** is reported for the first time.

EXPERIMENTAL

Materials

All manipulations with air-sensitive compounds were done using standard Schlenk techniques. Nitrogen (SIAD, 99.999%), ethene (Linde, 99.9%), and propene (SIAD, 99.5%) were purified by passing through a column packed with Cu-catalyst and molecular sieves to remove traces of oxygen and water. Dichloromethane (p.a., Penta) was dried over CaH₂ and cryo-distilled under nitrogen. Hex-1-ene (99%, Aldrich) was dried over sodium/potassium alloy and distilled under nitrogen. Methylaluminoxane (MAO) (10 wt % solution in toluene, Aldrich) was used as received. β -Diimine ligands were synthesized and purified according to reported procedures.^{23,24} Complex **5d** was prepared according to literature.¹⁶ Catalysts were dosed as a solid directly to the polymerization vessel or in the form of dichloromethane solutions that were stored at 5 °C. Elemental analyses (C, H, N) were performed on an Elementar Vario EL III Analyzer. ATR-IR spectra were recorded on an FTIR spectrometer Nicolet 6700 using diamond crystal.

Ligand Synthesis

Oxidation of β -diimine ligands was carried out analogously to the procedure reported by Yokota.²⁵ Copper intermediates were obtained as microcrystalline powders and **3a,b** were characterized by powder X-ray diffraction.^{26,27} Decomposition of complexes **3a-d** led to the formation of α -keto- β -diimine ligands in the form of yellow oil or solid.

2,4-Bis(2,6-dimethylphenylimino)pentan-3-one (4a). Cu intermediate 3a (0.12 g, 0.15 mmol) was dissolved in 15 mL chloroform. An aqueous solution of ammonium hydroxide (6%, 40 mL) was added, and the mixture was allowed to stir for 30 min. The organic layer was separated, and the treatment was repeated four times until the aqueous layer stopped turning blue. The organic layer was washed three

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times with water (40 mL) and dried over anhydrous $\rm MgSO_4.$ Evaporation of the solvent afforded $\bf 4a$ as a yellow solid in 79% yield.

¹H NMR (500 MHz, C₆D₆, δ): 6.93 (4H, b, H_m), 6.90 (2H, b, H_p), 1.99 (12H, s, *o*-CH₃), 1.72 (6H, s, α-Me). ³C NMR (500 MHz, C₆D₆, δ): 193.42 (ketone carbon), 168.13 (imine carbon), 128.06, 125.14, 124.21, 123.90 (aromatic carbons), 18.00 (*o*-CH₃), 16.24 (α-Me). IR (ATR, diamond) 1703, (C = 0), 1668 cm⁻¹ (C = N).

2,4-Bis(2,4,6-trimethylphenylimino)pentan-3-one (**4b**). Using the same procedure as for **4a**, **3b** (0.22 g, 0.27 mmol) was decomposed to give **4b** as a yellow solid in 79% yield.

¹H NMR (500 MHz, C₆D₆, *δ*): 6.75 (4H, b, H_m), 2.15 (6H, s, *p*-CH₃), 2.01 (12H, s, *o*-CH₃), 1.75 (6H, s, *α*-Me). 13C NMR (500 MHz, C₆D₆, *δ*): 193.64 (ketone carbon), 168.36 (imine carbon), 145.30, 133.07, 129.13, 128.35, 124.98 (aromatic carbons), 20.78 (*p*-CH₃), 17.97 (*o*-CH₃), 16.25 (*α*-Me). IR (ATR, diamond) 1703, (C = O), 1666 cm⁻¹ (C = N).

2,4-Bis(2,6-diethylphenylimino)pentan-3-one (4c). Using the same procedure as for 4a, 3c (0.24 g, 0.27 mmol) was decomposed to give 4c as a yellow oil in 90% yield.

¹H NMR (500 MHz, C₆D₆, *δ*): 7.04–6.67 (6H, m, H_{Ar}), 2.39 (8H, m, *CH*₂CH₃), 1.75 (6H, s, α-Me), 1.06 (12H, t, CH₂*CH*₃). 13C NMR (500 MHz, C₆D₆, *δ*): 193.45 (ketone carbon), 168.11 (imine carbon), 145.45, 131.20, 126.59, 124.69 (aromatic carbons), 24.77 (*CH*₂CH₃), 16.60 (α-Me), 14.30 (CH₂*CH*₃). IR (ATR, diamond) 1702, (C = 0), 1670 cm⁻¹ (C = N).

Synthesis of Nickel Complexes

Nickel complexes were synthesized analogously to the procedure reported for $5d^{16}$ by the reaction of the corresponding ligand and (1,2-dimethoxyethane)nickel(II) bromide ((DME)-NiBr₂) in CH₂Cl₂.

Complex 5a

4a (0.25 g, 0.78 mmol) and (DME)NiBr₂ (0.22 g, 0.71 mmol) were reacted in CH_2Cl_2 at room temperature for 2.5 h, evaporated, extracted by diethylether, dissolved in CH_2Cl_2 , and filtered. After evaporation, **5a** was obtained as red-brownish powder in 83% yield.

¹H NMR (500 MHz, CDCl₃, δ): 26.7 (s, 12H, *o*-Me), 22.2 (s, 4H, H_m), -16.6 (s, 2H, H_p), -28.8 (s, 6H, α-Me). IR (ATR, diamond) 1700, (C = 0), 1642 cm⁻¹ (C = N). Anal. calcd. for C₂₁H₂₄N₂ONiBr₂: C, 46.80, H, 4.49, N, 5.20; found: C, 46.53, H, 4.83, N, 5.02.

Complex 5b

Using the same procedure as for **5a**, **4b** (0.27 g, 0.78 mmol) were reacted with (DME)NiBr₂ (0.22 g, 0.71 mmol) resulting in red-brownish powder of **5b** in 90% yield.

¹H NMR (500 MHz, CDCl₃, δ): 31.2 (s, 6H, *p*-Me), 26.8 (s, 12H, *o*-Me), 21.9 (s, 4H, H_m), -29.4 (s, 6H, *α*-Me). IR (ATR,

diamond) 1699, (C = 0), 1636 cm⁻¹ (C = N). Anal. calcd. for $C_{23}H_{28}N_2ONiBr_2$: C, 48.72, H, 4.98, N, 4.98. Found: C, 48.54, H, 5.20, N, 4.85.

Complex 5c

Using the same procedure as for **5a**, **4c** (0.30 g, 0.78 mmol) were reacted with (DME)NiBr₂ (0.22 g, 0.71 mmol) resulting in red-brownish powder of **5c** in 54% yield. Recrystallization from CH_2Cl_2 solution layered by hexane gave single monocrystals suitable for X-ray analysis.

¹H NMR (500 MHz, CDCl₃, δ): 27.1 (s, 4H, *CH*₂CH₃), 23.9 (s, 4H, *CH*₂CH₃), 22.0 (s, 4H, H_m), 2.6 (s, 12H, CH₂*CH*₃), 2.0–0.1 (m, 2H), –16.3 (s, 2H, H_p), –27.8 (s, 6H, α -Me). IR (ATR, diamond) 1697 (C = 0), 1646 cm⁻¹ (C = N). Anal. calcd. for C₂₅H₃₂N₂ONiBr₂: C, 50.46, H, 5.42, N, 4.71; found: C, 50.40, H, 5.60, N, 4.62.

Complex 5d

¹H NMR (500 MHz, CDCl₃, δ): 21.4 (s, 4H, H_m), 10.7 (br, 2H, *CH*CH₃), 3.3 (s, 24H, CH*CH*₃), 2.0–0.1 (m, 2H), -15.0 (s, 2H, H_p), -25.5 (s, 6H, α-Me). IR (KBr) 1701, (C = 0), 1632 cm⁻¹ (C = N). Anal. Calcd. for C₂₉H₄₀N₂ONiBr₂: C, 53.49, H, 6.19, N, 4.30; found: C, 53.40, H, 6.20, N, 4.30.

Hex-1-Ene Polymerization

Polymerizations were carried out under dry nitrogen in magnetically stirred 15 mL glass ampoules. The ampoules with toluene, hex-1-ene, and MAO were placed in a bath kept at a desired temperature and tempered for 15 min. The polymerization was initiated by addition of fresh catalyst solution. After the allotted reaction time, the polymerization was terminated by pouring the reaction mixture to a large excess of ethanol acidified with HCl, washed with ethanol, and dried 24 h at 50 °C under vacuum.

Ethene Polymerization

A 100-mL glass reactor with a magnetic stirring bar was evacuated and placed under an ethylene atmosphere. The solvent and MAO were added to nitrogen flux, and reactor was then allowed to stir under desired pressure of ethene for 15 min at the prescribed polymerization temperature. Polymerization was started by the injection of the catalyst solution against nitrogen flux. The pressure of ethylene was kept constant during the reaction. After the allotted polymerization time, the reaction was terminated by pouring the polymerization mixture to a large excess of ethanol acidified with HCl. Polyethylene was separated by filtration, washed with ethanol, and dried under vacuum overnight at 50 °C.

Propene Polymerization

Polymerizations of propene were carried out in toluene in a magnetically stirred jacketed 100-mL glass reactor. The MAO solution was injected against nitrogen flux and evaporated to dryness. The solvent was added against propene flux and reactor was then cooled in dry ice/ethanol bath, and a specified volume of propylene was condensed into the reactor. The reactor was cooled to the appropriate reaction temperature by Julabo F70 cryostat, and the polymerization was



initiated by the injection of the catalyst solution against nitrogen flux. After the desired time, the reaction was terminated by pouring the reaction mixture to a large excess of the ethanol acidified with HCl, and the polymer was washed with ethanol and dried 24 h at 50 $^\circ$ C under vacuum.

Propene Block Copolymers

The first block of a copolymer was prepared in an analogous way to propene homopolymerization. After a desired time for the first block formation, a sample of the reaction mixture for SEC and DSC analysis was taken by a cannula and a second block was synthesized in two different ways. For the second block with regioirregular PP structure, the temperature of the reaction was increased to 0 °C. For the second block with the structure of random ethene/propene copolymer, the reactor was repeatedly (after each 15–30 min) shortly fed with ethene (1.5 bar).

Polymer Characterization

Molar masses of polyethylenes and polypropylenes were determined by high-temperature PL 220 chromatograph equipped with refractometric and viscometric detector. Separation was performed on two Olexis mixed columns (Polymer Laboratories, 13 μ m) at 150 °C in 1,2,4trichlorobenzene at an elution rate of 1 mL \cdot min⁻¹. Apparent molar masses were calculated using narrow PS standards calibration. Molar masses of poly(hex-1-enes) were determined using Waters Breeze chromatographic system equipped with RI detector operating at 880 nm and multiangle laser light scattering (MALLS) miniDawn TREOS from Wyatt operating at 658 nm. Separations were performed with two columns (Polymer Laboratories Mixed C) at 35 °C in THF at an elution rate of 1 mL \cdot min⁻¹. The dn/dc value $0.078\pm0.002~mL\cdot g^{-1}$ for poly(hex-1-ene) in THF at 35 $^\circ\text{C}$ was used.¹² Molar masses of PP block copolymers were determined using SEC-RI chromatograph against PS calibration (580-1,230,000 g/mol). Separation was performed on one Polymer Laboratories Mixed C at 35 °C in chloroform at an elution rate of 1 mL \cdot min⁻¹.

¹H NMR spectra of ligands and polymers were measured in CDCl₃ at 25 °C on Bruker Avance DRX 500 spectrometer. Number of branches per 1000 total carbon atoms (*N*) was determined according to literature.^{12,20} ¹³C NMR spectra of polypropylenes were measured in C₂D₂Cl₄ at 115 °C using INVGATE pulse sequence, 10-s relaxation delay, and 5000 scans to ensure quantitative spectra. Spectra were assigned as described in literature.²⁰

DSC measurements were performed on a TA Instrument module Q100 at a rate of 10 $^{\circ}C \cdot min^{-1}$ for both heating and cooling. Melting temperatures and enthalpies of fusion were obtained from the second heating run. Enthalpies of the fusion 207 and 297 J \cdot g⁻¹ for hypothetical 100% crystalline isotactic polypropylene and polyethylene, respectively, were used to calculate the degree of their crystallinity.²⁸

X-Ray

Crystallographic data for **5c** was collected on Nonius KappaCCD diffractometer equipped with Bruker APEX-II CCD detector by monochromatized MoK α radiation ($\lambda = 0.71073$ Å) at the temperature of 150(2) K. The structure was solved by direct methods (SHELXS)²⁹ and refined by full matrix least squares based on F^2 (SHELXL97).²⁹ The hydrogen atoms on carbon were calculated into idealized positions and were refined as fixed (riding model) with assigned temperature factors

 $H_{iso}(H) = 1.2 U_{eq}$ (pivot atom) or 1.5 U_{eq} for methyl moiety. One of the methyl moiety is disordered into two positions with occupational factors 0.6:0.4.

To improve the resolution of the complex, PLATON³⁰/ SQUEEZE procedure was used to correct the data for the presence of the disordered solvent. Two potential solvent cavities with the volume of 136 Å³ were found at special positions of inversion. Sixty-nine electrons worth of scattering were located in the void, highest peak corresponds to electron density 5.34 e \cdot Å⁻³.

Crystal data for **5c**: $C_{25}H_{32}Br_2N_2NiO$, $M_r = 595.05$, monoclinic, $P 2_1/n$ (No 14), a = 9.8413 (3) Å, b = 12.2506 (4) Å, c = 22.6665 (8) Å, $\beta = 96.974$ (1)°; Z = 4, $D_x = 1.457$ mg·m⁻³, dark red crystal of dimensions 0.40 × 0.32 × 0.18 mm, the numerical absorption correction was applied ($\mu = 3.68 \text{ mm}^{-1}$) $T_{\text{min}} = 0.34 T_{\text{max}} = 0.55$; 20,957 diffraction collected ($\theta_{\text{max}} = 27.5^{\circ}$), 6228 independent ($R_{\text{int}} = 0.023$) and 5136 observed ($I > 2\sigma(I)$). The refinement converged ($\Delta/$ $\sigma_{\text{max}} = 0.001$) to R = 0.033 for observed reflections and $wR(F^2) = 0.069$, GOF = 1.10 for 297 parameters and all 6228 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{\text{max}} = 0.44$, $\Delta\rho_{\text{min}} = -0.46 \text{ e} \cdot \text{Å}^{-3}$).

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 1522889 Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (e-mail: deposit@ccdc.cam.ac. uk or www: http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Catalysts Synthesis

The synthesis of catalyst was carried out according to the Scheme 1. α -Keto- β -diimine ligand synthesis is based on the procedure developed by Yokota et al.²⁵ and consists of complexation of β -diimine ligands **1a–1d** to copper complexes **2a–2d** which are then oxidized by molecular oxygen to give copper complexes **3a–3d**. These complexes are then decomposed by NH₄OH, yielding the desired α -keto- β -diimine ligands **4a–4d**. Whereas the starting β -diimine ligands and copper complexes **2a–2d** and **3a–3d** are stable on air, the α -keto- β -diimine ligands **4a–4d** are unstable even if they are stored in the dark under an inert atmosphere at -20 °C. Except ligand **4d**, isolatable in a crystalline state, the other ligands, isolated as oils or amorphous solids, has to be



FIGURE 1 ORTEP drawing of 5c. Thermal ellipsoids are set at the 30% probability level. The second position of disordered methyl moiety is omitted for clarity. The selected bond distances (Å) and angles (°): Br1-Ni1 2.3383 (4), Br2-Ni1 2.3521 (4), Ni1-N2 1.991 (2), Ni1-N1 1.995 (2), O1-C2 1.206 (3), N1-C1 1.279 (3), N2-C3 1.278 (3); N2-Ni1-N1 94.15 (8), N2-Ni1-Br1 108.92 (6), N1-Ni1-Br1 112.78 (6), N2-Ni1-Br2 103.29 (6), N1-Ni1-Br2 102.83 (6), Br1-Ni1-Br2 129.075 (18). [Color figure can be viewed at wileyonlinelibrary.com]

complexed to metal in the order of hours to avoid their decomposition. Ligand **4d** can be stored in the fridge for weeks or easily purified by recrystallization from hot hexane.

This decomposition of α -keto- β -dimine ligands is highly accelerated in solution, and only traces of acidity in dichloromethane or chloroform lead to their decomposition to a complex mixture of products in the order of minutes. Thus, α -keto- β -diimine ligands were complexed with (DME)NiBr₂ in dichloromethane immediately after their synthesis, resulting in more stable α -keto- β -diimine nickel(II) bromide complexes 5a-5d. These complexes were isolated in 54-90% yields in the form of red-brownish microcrystalline powders. Although the complexes are paramagnetic, their structure could be characterized by ¹H NMR spectroscopy which gave broad but well-resolved signals of all protons. Further, ligand complexation to nickel was confirmed by shifting of C = NFTIR signals in ligands (1664–1670 cm⁻¹) by \sim 30 cm⁻¹ in the corresponding complexes (1632–1646 cm^{-1}). In the case of 5c, a single crystal suitable for X-ray analysis was obtained by crystallization from dichloromethane solution layered by n-hexane. The solid-state structure of 5c is very similar to structure $5d^{16}$ having a distorted tetrahedral geometry and boat-shaped ligand structure (Fig. 1).

Olefins Homopolymerization Ethene Polymerization

Prepared α -keto- β -diimine complexes **5a–5d** were initially tested in ethene polymerization after activation by 200 equiv. of MAO at 0 °C in toluene (Table 1). Complex **5d**, previously studied by Bazan, catalyzed ethene polymerization leading to polyethylene (PE) with dispersity below 1.10 at -10 °C and 3.5 bar ethene pressure.¹⁸ At our conditions, that is, at 0 °C

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 TABLE 1 Ethene Polymerization Initiated by 5a–5d/MAO in

 Toluene

Run	Cat.	TOF ^a (h ⁻¹)	M ^{,b} (kg·mol ^{−1})	D^{b}	7m [°] (°C)	α ^c (%)	N ^d
1	5a	1,910	219	1.49	119	25	22
2	5b	2,400	301	1.77	123	26	23
3	5c	1,640	302	1.28	96	15	36
4 ^e	5c	3,990	333	1.35	114	21	30
5	5d	2,100	377	1.41	114	24	30

[Ni] = 0.4 mM, Al/Ni = 200, T = 0 °C, toluene 20 mL, p(ethene) = 1.5 bar, $t_{\rm n} = 40$ min.

^a Turnover frequency: mol ethene/(mol_{Ni} \cdot t_p).

^b Molar mass and dispersity determined by SEC in 1,2,4-trichlorobenzene at 150 °C versus PS standards.

 $^{\rm c}$ Melting temperature and crystallinity determined by DSC from the second heating run.

 $^{\rm d}$ Number of branches per 1000 carbon atoms determined by $^{\rm 1}{\rm H}$ NMR. $^{\rm e}$ p(ethene) = 5.5 bar.

and 1.5 bar ethene, PE with slightly broadened molar mass distribution (D = 1.41) was obtained, which could be ascribed to increased extent of the transfer reactions at a higher temperature and eventually also a different batch of MAO cocatalyst. This indicates the limited window of reaction temperatures at which the living ethene polymerization can be achieved with these catalysts. At the same conditions, complexes 5a and 5b bearing methyl substituents in orthoaryl positions yielded PE with broader molar mass distribution, indicating an increased proportion of transfer reactions compared to propagation. This shows the importance of bulkiness of ortho-aryl substituents in preventing the formation of transfer reaction transition state, the structure of which could resemble the one known for relative α -diimine complexes, that is, pentacoordinated bis-olefin hydrido complex¹ (Fig. 2). Larger substituents could destabilize such a transition state by blocking axial positions above and below the ligand-metal plane and suppress the role of transfer. The



FIGURE 2 Suggested structure of transfer reaction transition state.

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TABLE 2 Propene Polymerization Initiated by 5a-5d/MAO in Toluene

Run	Cat	n _{cat} (µmol)	<i>T</i> (°C)	<i>t</i> _p (h)	TOF ^a (h ⁻¹)	<i>M</i> n ^b (kg·mol ^{−1})	D^{b}	NPM ^c	T _g ^d (°C)	7 [™] d (°C)	α ^d (%)	Ne
6 ^f	5a	10	-10	2	108	35	2.03	0.15	-42	-	-	250
7	5a	20	-30	18	6	108	1.54	0.04	-39	-	-	270
8 ^f	5b	10	-10	2	52	103	1.35	0.04	-45	-	-	233
9	5b	20	-30	18	7	124	1.52	0.04	-40	-	-	254
10 ^f	5c	10	-10	2	38	123	1.40	0.03	-46	-	-	238
11	5c	20	-30	42	13	211	1.18	0.11	-37	-	-	271
12	5c	20	-50	25	7	11	1.69	0.63	-35	68	1	288
13 ^f	5d	10	-10	2	124	188	1.16	0.06	-21	66	2	290
14	5d	40	-10	2	324	179	1.18	0.15	-17	65	3	284
15	5d	10	-30	2	136	34	1.10	0.35	-15	94	8	nd
16	5d	20	-30	18	54	121	1.86	0.34	-20	70	8	295
17	5d	20	-50	8	4	4	1.59	0.14	-20	98	17	308

Al/Ni = 200, m(propene) = 15 g, toluene 40 mL.

^a Turnover frequency: mol propylene/(mol_{Ni} \cdot t_p).

^b Molar mass and dispersity determined by SEC in 1,2,4-trichlorobenzene at 150 °C.

 $^{\rm c}$ Number of polymer molecules per one Ni center NPM = polymer mass/(mol_Ni \cdot $M_{\rm n}).$

increase of ortho-aryl substituents to ethyl groups seems to be sufficient to prevent transfer as PE prepared with **5c** displayed even narrower molar mass distribution than the bulkiest complex **5d** (Table 1, run 3 vs. run 5).

The superior suppression of transfer reactions by ethyl ortho-aryl groups was previously observed also in the case of α -diimine nickel complexes.¹² The increase of ethene pressure with 5c (Table 1, run 3 vs. run 4) leads to the broadening of molar mass distribution which is in accordance with previous observations for complex 5d.¹⁸ Similarly, for α -diimine complexes, the size of substituents influences branching of PE as a consequence of altered extent of chainwalking with respect to propagation.³ More linear PEs are obtained by catalysts 5a and 5b, bearing smaller ortho-aryl substituents than 5c and 5d. The key step of chain-walking, that is, β -H elimination, can only occur in Ni-alkyl complexes. Lower steric hindrance of ligand leads to easier coordination of monomer to Ni center forming an olefin-alkyl complex, thus blocking a vacant position necessary for β -H elimination and decreasing the extent of chain-walking.³ The increase of PE branching, expressed as a number of branches per 1000 total carbon atoms, correlates well with the decrease in their melting temperatures (Table 1).

Propene Polymerization

Our main focus in developing new α -keto- β -diimine complexes was propene polymerization to prepare isotactic polypropylene (PP) in a living manner. We hypothesized that complexes with smaller ortho-aryl substituents could display decreased chain-walking extent and could lead to PPs with higher regioregularity, the first assumption for the possibility of good stereoregularity.

^d Glass transition temperature, melting temperature, and crystallinity determined by DSC from the second heating run.

^e Number of branches per 1000 carbon atoms determined by ¹H NMR.

^f p(propene) = 1.5 bar.

Another important parameter to suppress chain-walking is the reaction temperature which was maintained between -10 and -50 °C (Table 2). Moderate isoselectivity ([mmmm]=0.43 - 0.86) in propene polymerization was previously observed by Bazan for **5d**^{18,20} between -10 and -60 °C, yielding PPs with melting temperature 59–134 °C.

At first, all α -keto- β -diimine complexes **5a–5d** activated by dried MAO were compared in propene polymerization at 1.5 bar at -10 °C (propene does not condense) in toluene (Table 2, runs 6, 8, 10, 13). Turnover frequencies calculated from the amount of PP obtained after 2 h are not in clear correlation with the bulkiness of ligand ortho-aryl substituents **5d** ~ **5a** > **5b** ~ **5c**.

This indicates that ligands steric hindrance is not the only factor influencing the catalyst activity. Similarly in the case of α -diimine ligands, polymerization rate could be increased by the decrease of insertion barrier caused by the destabilization of the ground state of monomer insertion by bulkier ligands.^{11,12,31,32} The narrowest molar mass distribution was obtained for 5d for which living behavior was proved in previous studies.¹⁸ The decrease of ortho-ligand bulkiness increased molar mass dispersity indicating an increase of transfer reactions. While complexes 5b and 5c afforded PP with dispersity bellow 1.40, which could still be considered as a controlled polymerization process, complex 5a produced a polymer with dispersity around 2, characteristic for singlesite catalyst but deviating substantially from the controlled character. Comparison of the molar mass values with theoretical ones allows the quantification of a number of polymer molecules per one nickel center (Table 2, column NPM). In most of the cases, NPM values are very low (albeit calculated using only apparent molar mass values from polystyrene calibration), showing the efficiency of MAO as a cocatalyst is rather low.

To suppress side reactions and achieve a better controllability of propene polymerization, further experiments were performed at -30 to -50 °C. At these conditions, propene was condensed into the reactor to increase its concentration and partially compensate for lowered propagation rate. Catalysts activities are, however, much lower below -30 °C; thus, the polymerization time was prolonged to 8-42 h.

The decrease in molar mass dispersity with the decrease in reaction temperature to -30 °C was observed for complexes 5a, 5c, and 5d (Table 2, run 7) while it led to broadening of molar mass distribution for complex 5b. For complex 5c, dispersity 1.18 (run 11) was achieved demonstrating the wellcontrolled character of propene polymerization. Interestingly, the most active complex 5d, which yielded PP with very narrow molar mass distribution after 2 h, produced a polymer with rather broad molar mass distribution after prolongation of the reaction time to 18 h (run 15 vs. run 16). Similarly, further decrease in temperature -50 °C led to PPs with substantially increased dispersity and only low molar mass (Table 2, runs 12 and 17). The increase in polymer molar mass dispersity at decreased temperature could indicate that the reaction mixture is less homogeneous due to the limited access of monomer to polymer coil. In the case of 5c and 5d that both afford partially crystalline PPs, this inhomogeneity could also result from the separation of formed polymer from the reaction mixture. The regular increase of dispersity with the decrease in reaction temperature was previously also observed for 5d.20

Our highest interest lied in the ability of new α -keto- β diimine complexes to catalyze isospecific propene polymerization. Whereas the reference complex 5d produced isotactic PP capable of crystallization already at -10 °C, the less bulky complex 5c produced amorphous polymer up to -30 °C and only slightly crystalline PP was formed by 5c at -50 °C. The least bulky complexes **5a** and **5b** formed only amorphous PPs at -30 °C with very low polymerization activities. Prepared PPs were characterized by ¹H NMR spectroscopy and selected samples also by ¹³C NMR spectroscopy (Fig. 3) to determine their branching and deduce the information about the extent of chain-walking. In the case of α diimine complexes, smaller ortho-aryl substituents lead to the decrease of chain-walking^{1,3} as a consequence of improved access of monomer to the growing center and the transformation of alkyl-metal complexes (the species which can undergo chain-walking) to alkyl-olefin-metal complex. In contrast to our expectations that α -keto- β -diimine complexes could behave similarly as their α -diimine analogs, the decrease of ortho substituents bulkiness led to the increase of chain-walking in propene polymerization. This is indicated by the decrease in a number of branches in prepared PPs with the decrease of ligand bulkiness. Thus, the most regular PP was formed by the bulkiest complex 5d, followed by 5c and **5a,b**.



FIGURE 3 ¹H NMR (upper) and ¹³C NMR (lower) spectra (500 MHz, 115 °C, 1,1,2,2-C₂D₂Cl₄) of polypropylenes obtained by catalysts **5a** (run 7) and **5d** (run 16) at -30 °C.

This shows that the mechanism of chain-walking during higher α -olefin polymerization may be different for α -keto- β diimine complexes than for α -diimine derivatives. This might be connected with the different geometry of α -keto- β -diimine complexes having six-membered ligand-metal ring compared to five-membered ligand-metal ring in α -diimine complexes. The decrease in reaction temperature caused the decrease of chain-walking for all catalysts as indicated by an increase of branching. The reaction temperature thus seems to be the only tool which allows the preparation of regular PPs. Comparison of ¹³C NMR spectra of PPs prepared by 5a and 5d (Fig. 3) shows much more regular structure of PP prepared by bulkier complex 5d. Due to regioselectivity and isospecificity of 5d, the most abundant methyl signal of PP (run 16) corresponds to mmmm pentad (44%). In contrast, PP prepared by 5a (run 7) shows plenty of signals connected with 1,3-insertions of propene leading to oligoethylene sequences and only very low proportion of mmmm pentads (\sim 5%).

TABLE 3 Hex-1-ene (C6) and 4-Methylpent-1-ene (4MP1) Polymerization Initiated by **5c**/MAO in Toluene

Run	Monomer	<i>Т</i> (°С)	t _p (h)	Conv.ª	<i>M</i> n ^b (kg·mol ^{−1})	D^{b}	Nc
18	C6	25	2	29	179	1.31	95
19	C6	-10	18	13	77	1.12	133
20	4MP1	25	2	0	-	-	-
21	4MP1	-10	18	0	-	-	-

Monomer/Ni = 1000, [Ni] = 1 mM, Al/Ni = 200, total volume 10 mL.

^a Monomer conversion calculated from the mass of polymer obtained. ^b Molar mass and dispersity determined by SEC-MALLS in THF against PS standards.

^c Number of branches per 1000 carbon atoms determined by ¹H NMR.

Higher α-Olefin Polymerization

5d was also reported to initiate controlled polymerization of hex-1-ene beside that of ethene and propene.¹⁸ Therefore, we attempted hex-1-ene and 4-methylpent-1-ene polymerization with the most promising new catalyst 5c, which displayed both controlled and isospecific polymerization of propene (Table 3). Hex-1-ene polymerization initiated by 5c/MAO yielded poly(hex-1-ene) with relatively narrow molar mass distribution both at -10 and 25 °C, suggesting a controlled polymerization. Chainwalking led to a significant polymer rearrangement (>40% of 1,6-insertions) at 25 °C as displayed by 95 br./1000 C compared to poly(hex-1-ene) which would be obtained by regular 1,2insertions (167 br./1000 C). As in the case of propene, the chainwalking extent decreased with the decrease in temperature giving a poly(hex-1-ene) with 20% of 1,6-inserted hexene units. Polymerization of 4-methylpent-1-ene initiated by 5c/MAO did not produce any polymer neither at -10 °C nor at 25 °C, which could be ascribed to the high steric bulk of the monomer.

Preparation of Stereoblock Copolymers

Catalyst **5d** was used for the homopolymerization of ethene, propene, and hex-1-ene only.¹⁸ Due to its rare ability of living and simultaneously isospecific polymerization, we decided to



FIGURE 4 SEC-RI traces of first polypropylene block (dash) and *i*PP-block-(ethene-*co*-propene) copolymer (solid), run 25.

test **5d** for the preparation of stereoblock polymers based on isotactic polypropylene (*i*PP) block connected to the rubbery block. *i*PP block was prepared by **5d**/MAO at -10 to -50 °C followed by the growth of rubbery block by two different strategies. The first strategy, adopted by Coates for α -diimine catalysts,^{10,11} takes the advantage of α -keto- β -diimine Ni complexes to undergo intensive chain-walking above -10 °C to form amorphous regioirregular polypropylene (*rir*PP) block (Table 4, runs 22–23). Thus, the only change in reaction temperature can switch between the formation of semicrystalline and an amorphous polymer. In our case, two block copolymers *i*PP-block-*rir*PP were prepared by first polymerizing propene at -30 °C for 1 h (Table 4, run 22) or at -50 °C for 16 h (run 23) followed by 30 min propene polymerization at 0 °C.

The good control of polymerization is demonstrated by the increase of molar mass after each reaction step while

TABLE 4 Preparation of Stereoblock Copolymers by 5d/MAO in Toluene

Run	Block	Mon. ^a	<i>T</i> (°C)	<i>t</i> _p (h)	<i>m</i> _p (g)	<i>Т</i> _g ^b (°С)	<i>Т</i> _m ^ь (°С)	$M_{\rm n}^{\rm c}$ (kg·mol ⁻¹)	D^{c}
22	1 st	C3	-30	1	-	-	98	27	1.18
	$1^{st} + 2^{nd}$	C3	0	1.5	0.795	-19 (-51)	73	100	1.18
23	1 st	C3	-50	16	-	-19	109	nd	nd
	1^{st} $+2^{nd}$	C3	0	16.5	0.130	-17	54 (90–120)	nd	nd
24	1 st	C3	-10	1	-	-14	65	95	1.21
	$1^{st} + 2^{nd}$	C3 + C2	-10	2	0.961	-24	67	155	1.35
25 ^d	1 st	C3	-10	1	-	-18	64	74	1.19
	$1^{st} + 2^{nd}$	C3 + C2	-10	2	1.245	-17 (-46)	64 (98)	215	1.25
26	1 st	C3	-30	2	-	-15	94	34	1.10
	$1^{st} + 2^{nd}$	C3 + C2	-30	2.5	0.172	-18	92 (115)	41	1.15

[Ni] = 0.5 mM, Al/Ni = 200, toluene 20 mL.

^a Monomers: C₃, propene (7.5 g); C₂, ethene (1.5 bar).

^b Determined by DSC.

 $^\circ$ Molar mass and dispersity determined by SEC in CHCl_3 at 35 $^\circ C$ versus PS standards.

^d 50 mL toluene. nd = not determined.

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FIGURE 5 DSC plot of first polypropylene block (dash) and PPblock-(ethene-*co*-propene) copolymer (solid), run 25.

preserving very narrow molar mass distribution. The block structure in the final copolymer (run 22) is reflected by melting temperature connected to *i*PP block and glass transition temperature of regular polypropylene block (-19 °C) and *rir*PP block (-51 °C).

The second strategy relies on the formation of the rubbery block by classical propene/ethene copolymerization, leading to iPP-block-(ethene-co-propene) type of copolymers (Table 4, runs 24–26). *i*PP block was prepared at -10 °C for 1 h (runs 25 and 26) or at -30 °C for 2 h (run 24) followed by feeding of ethene into the reactor in 15- to 30-min intervals. The increase of molar mass and retention of narrow molar mass distribution was observed in all cases, confirming the controlled character of the copolymerization (Fig. 4). Block structure of copolymers was indicated by the preservation of melting temperature of iPP block in the copolymer and the decrease in $T_{\rm g}$ corresponding to the rubbery block (runs 24 and 25). Due to higher ethene reactivity compared to propene, ethene-rich copolymers were formed in some cases, which also displayed their melting temperature (runs 25 and 26, Fig. 5).

CONCLUSIONS

Three new α -keto- β -diimine complexes **5a–c** were prepared and compared for ethene, propene, and hex-1-ene polymerization with complex **5d**. The suppression of chain-walking in propene polymerization is more efficient with more bulky complexes. Only complexes **5c** and **5d** were able to form isotactic or isotactically enriched polypropylene. For the first time, complex **5d** was used to prepare stereoblock copolymers containing *i*PP block and a rubbery block (*rir*PP or ethene-*co*-propene).

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