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Novel Unsymmetric α-Diimine Nickel(II) Complexes: Suitable Catalysts for Copolymerization Reactions

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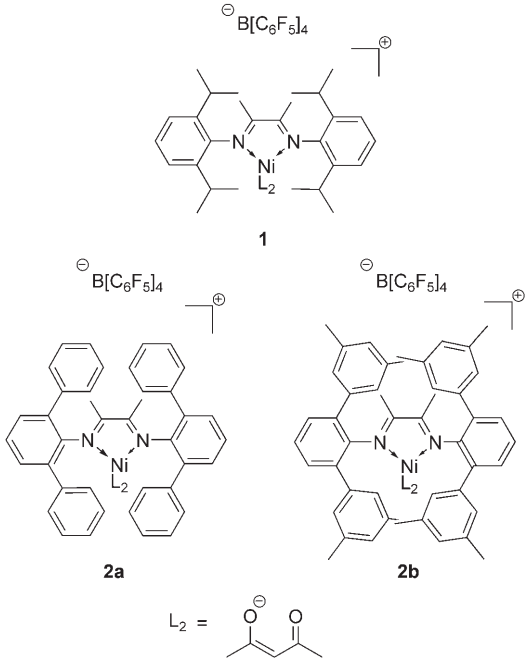
Abstract: We established a strategy to synthesize novel unsymmetric 2,3-diaza-1,4-dithiane ligands. Reaction of $[Ni(acac)_2]$ and trityl tetrakis(pentafluorophenyl)borate in the presence of these ligands afforded the corresponding salt-type complexes. All new compounds were characterized by means of elemental analysis and NMR spectroscopy, and the complexes additionally by mass spectroscopy. NMR spectroscopic experiments on polymers generated by the symmetric ligand/trimethylaluminum catalyst system showed that all products were nearly linear, independent of the polymerization conditions. By contrast, polymers produced by the unsymmetric ligand/trimethylaluminum catalyst system under homopolymerization conditions were branched (15–24‰). Additionally, copolymerization experiments with propylene and 1-hexene afforded copolymers with a branching level of up to 50‰.

Keywords: copolymerization · homogeneous catalysis · N ligands · nickel · polyethylene

Introduction

Today, classical Ziegler–Natta catalyzed copolymerization processes dominate worldwide production of linear low-density polyethylene (LLDPE), affording high-value polyolefins.[1] With the work of Brookhart et al. in the mid-1990s, α-diimine nickel(II) complex precursors such as **1** (Scheme 1) came to academic application in the generation of LLDPE grades exclusively from ethylene.[2]

For mechanistic reasons, predominantly short methyl branches are generated.[3,4] However, the physical properties of these polymeric materials are defined by the fraction of butyl and longer branches present.[5] Recently, we introduced new hydrogen-stable "*ortho*-aryl"-substituted α-diimine nickel(II) complexes such as **2a** and **2b**.[6] Owing to the high steric demand of their particular ligands, these catalysts polymerize ethylene exclusively. Reducing this demand, by abstraction of one phenyl substituent, affords unsymmetric but more open structures, making coordination/insertion of higher 1-olefin monomers accessible.[7] This improves the rheological properties of these polyethylene materials.[5]



Scheme 1. α-Diimine nickel(II) complexes.

Herein we report on a novel and easy synthetic strategy towards unsymmetric α-diimine ligands and their corre-

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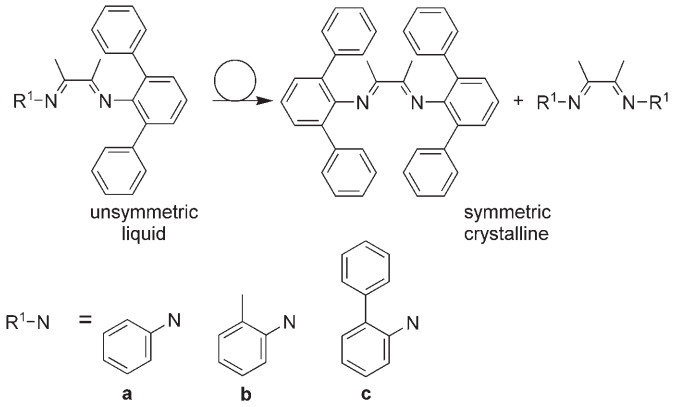
sponding complexes. Copolymerization experiments with propylene and 1-hexene to afford branched LLDPE grades were also performed.

Results and Discussion

Ligand and Complex Synthesis

Some selected unsymmetric α-diimine ligands can be obtained by a simple condensation reaction of α,β-diketones with suitable aniline derivatives such as 2,6-diisopropyl- and 2,6-diphenylaniline, as the corresponding product crystallizes readily in solution.[7] In the first step, the monocondensation product was formed by reaction of equimolar amounts of the diketone and the aniline fragment. Subsequently, the resulting ketimine was reacted with the second aniline derivative in an analogous manner to form crystalline products. However, for other aniline derivatives, for example, **a–c**, liquid products were formed (Scheme 2), which could not be

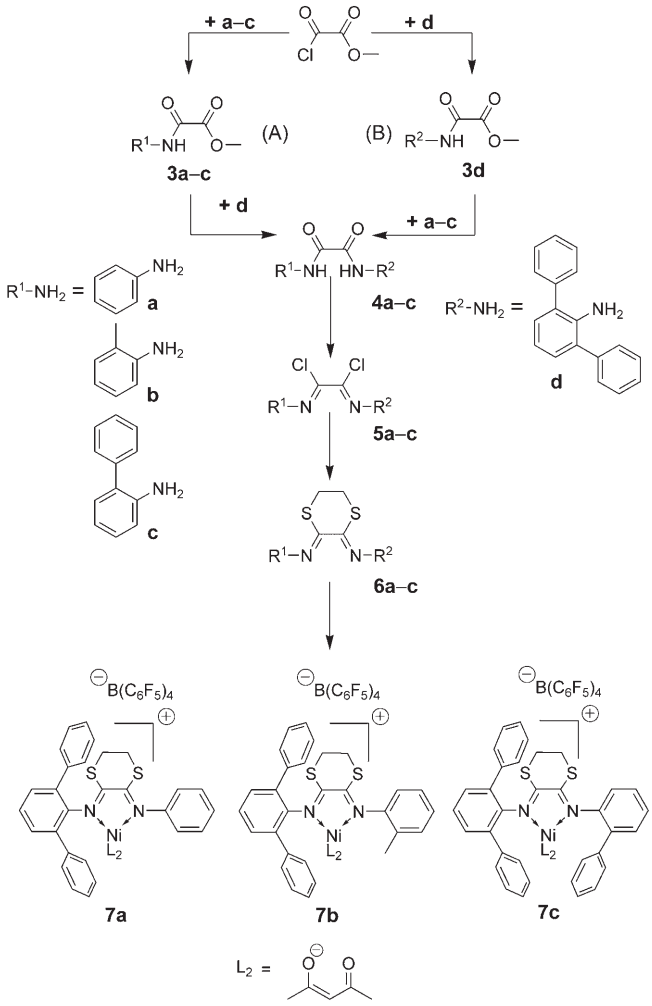


Scheme 2. Transformation pathway from unsymmetric to symmetric α-diimine ligands.

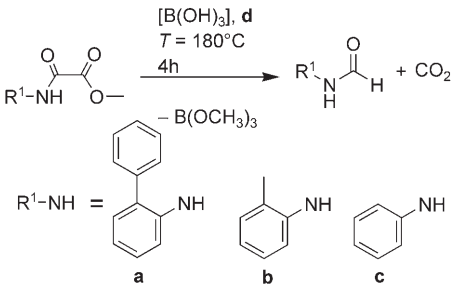
easily purified by crystallization. Unfortunately, such unsymmetric species are unstable and undergo scrambling reactions that form mixtures of the desired ligands and their symmetric counterparts in solution as well as freshly isolated 1,4-diaza-2,3-dimethylbutadienes. Therefore, we designed a four-step synthetic strategy that affords unsymmetric ligands with variable substitution patterns in satisfying yields.

In the first step, the reaction of the anilines **a–d** with methyl chloroglyoxalate at ambient temperature gave the intermediates **3a–d** in quantitative yield (Scheme 3). Whereas **a–c** are commercially available, **d** had to be synthesized by a Suzuki cross-coupling reaction based on 2,6-dibromoaniline and an arylboronic acid. The acid was easily accessible by treatment of the corresponding aryl Grignard compound with trimethylborate.[6]

Compounds **3a–c**, however, did not lead to the formation of **4a–c**. At the required reaction temperature of 180 °C, **3a–c** were quantitatively converted into the corresponding formamides in the presence of boric acid (Scheme 4). We assume that the nucleophilic attack of the amine functionality was hindered due to the steric demand of the aniline **d**.



Scheme 3. Synthetic strategy for unsymmetric α-diimine ligands.



Scheme 4. Decomposition pathway for **3a–c**.

The successful strategy started from **3d**, which readily reacted with the anilines **a–c** to give the desired unsymmetric diamides **4a–c** in up to 60% yield.

The chloroimines **5a–c** were subsequently prepared in quantitative yield by treating **4a–c** with phosphorus pentachloride in thionyl chloride under reflux. The progress of the reaction was monitored by evolution of HCl, which indicated that this straightforward reaction was completed within a time of minutes to one hour. Treatment of **5a–c**

with the dilithium salt of 1,2-ethanedithiol[8] in boiling THF afforded the pure ligands **6a–c** after column chromatography.[9]

The corresponding complexes **7a–c** were obtained by reacting the square-planar diacetylacetonatonickel(II) precursor complex in the presence of **6a–c** with trityl tetrakis(pentafluorophenyl)borate, which abstracts one anionic acetylacetonato ligand.[10] This highly efficient reaction route afforded crystalline, red complexes **7a–c** in up to 95% yield.

Homopolymerization

For complex activation, **2a**, **7b**, and **7c** were treated with trimethylaluminum (TMA) under polymerization conditions in situ. We observed as a general trend at ambient temperature an increase in activity with growing steric demand of the ligand by introducing one (**7c**) or two *ortho*-phenyl (**2a**) substituents on the aniline fragments (Figure 1).[11] This polymerization behavior can be explained by different isomerization rates affording branches in the polymer backbone (see below). Increasing the partial pressure of ethylene from 5 to 10 bar resulted in a significant increase in activity of **7c**/TMA for the ethylene homopolymerization experiment by a factor of 3 ($\approx$450 (kg polymer)(g Ni)$^{-1}$h^{-1}; Figure 1). The polymerization behavior of **2a** under these conditions was published earlier and showed the same trend.[6]

At a constant hydrogen/ethylene feed composition, an increase in molecular weight with growing steric demand of the ligand sphere was expected, owing to a lower associative olefin-exchange rate. Surprisingly, **7c**/TMA generated polymers of notably higher molecular weight ($\approx 4.0\times 10^5$ g mol^{-1}) than **2a**/TMA or **7b**/TMA ($\approx 1.5\times 10^5$ g mol^{-1}). We have no explanation for this effect. However, there are two possible pathways for chain transfer, namely, the associative olefin exchange and termination by hydrogen. The steric constraints of **7c** seemed to provide optimal conditions for polymers of higher molecular weights within this series of catalysts.

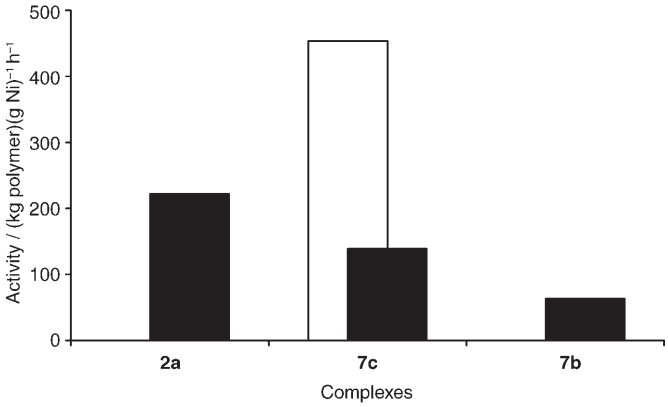


Figure 1. Polymerization activity of **2a**, **7b**, and **7c** at 30 °C and 5 (■) or 10 bar (□) partial ethylene pressure. Polymerization conditions: 2-L Parr autoclave, 800 mL toluene, n(catalyst) = 5 μmol, X (mmol H_2/mol ethylene) = 1.92, X (10 bar) = 0.51.

In homopolymer experiments, branches are introduced exclusively by "chain-walking" of the catalytically active species along the polymer backbone.[3] Therefore, increasing the partial pressure of ethylene led to more-linear products, as expected (Table 1, entry 1 and 2, Figure 2). However, the branching concentration can be controlled by ligand archi-

Table 1. Polymerization results[a] of **2a**, **7b**, and **7c**.

Entry	Cat.	t [h]	P [bar]	X	Al/Ni	Alkene (conc. [mol L^{-1}])	Yield [g]	Activity [(kg polymer) g^{-1}h^{-1}]	M_w [$\times 10^{-5}$ g mol^{-1}]	PDI	Overall branching [‰][b]	Distribution[c] Methyl [‰] ([%])	Ethyl [‰] ([%])	Propyl [‰] ([%])	Butyl and longer [‰] ([%])	T_m [°C]
1	**7c**	1.00	5	1.92	1000	–	40.75	139	4.0	2.2	15	13.5 (90)	1.5 (10)	n.a.	n.a.	116.5
2	**7c**	0.17	10	0.51	500	–	44.38	454	8.3	2.5	9	9 (100)	n.a.	n.a.	n.a.	130.9
3	**7c**	1.00	5	1.92	1000	propene (0.6)	34.96	119	3.6	2.1	19	18.1 (94)	0.1 (0.5)	n.a.	1.1 (5.5)	110.5
4	**7c**	0.17	10	0.51	500	propene (0.6)	56.87	570	4.6	2.4	16	16 (100)	n.a.	n.a.	n.a.	115.5
5	**7c**	1.00	5	1.92	1000	1-hexene (0.6)	41.93	143	4.1	2.0	30	27.2 (91)	0.4 (1.5)	n.a.	2.2 (7.5)	102.4
6	**7b**	1.00	5	1.92	1000	–	18.54	63	2.1	2.1	24	21.1 (87)	0.6 (2.5)	0.6 (2.5)	1.9 (8)	104.2
7	**7b**	1.00	5	1.92	1000	propene (0.6)	10.35	35	0.9	1.8	47	41.5 (88)	0.9 (2)	0.5 (1)	4.2 (9)	76.5
8	**7b**	1.00	5	1.92	1000	1-hexene (0.6)	12.79	44	1.2	1.9	40	34.1 (86)	n.a.	n.a.	5.5 (14)	85.6
9	**2a**	0.25	5	1.92	1000	–	16.25	221	1.3	2.6	3	3 (100)	n.a.	n.a.	n.a.	136.2
10	**2a**	0.33	5	1.92	1000	propene (0.6)	24.39	249	2.3	2.3	4	4 (100)	n.a.	n.a.	n.a.	134.1
11	**2a**	0.33	5	1.92	1000	1-hexene (0.6)	24.74	253	1.9	4.2	4	4 (100)	n.a.	n.a.	n.a.	134.3

[a] Polymerization conditions: 2-L Parr autoclave, 800 mL toluene, 30 °C, activator TMA, n (5 bar) = 5 μmol, n (10 bar) = 10 μmol. [b] Degree of branching determined by ^{1}H NMR spectroscopic experiments. [c] Distribution of alkyl side chains determined by integrated ^{13}C NMR spectroscopic experiments. PDI = M_w/M_n, ‰ = per thousand C atoms in the main chain, n.a. = not available.

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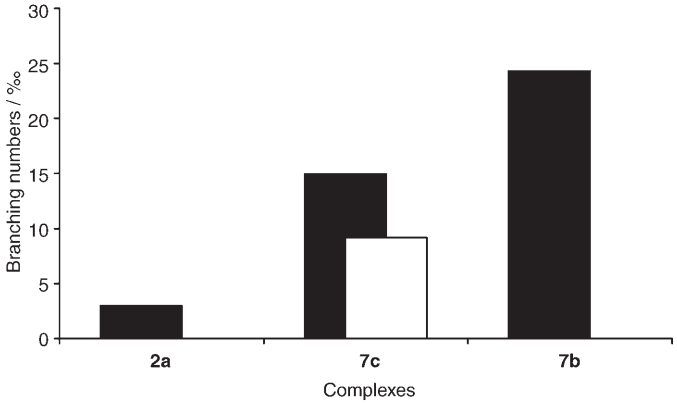

Figure 2. Branching numbers of homopolymers made by **2a**, **7b**, and **7c** at 5 (■) and 10 bar (□).

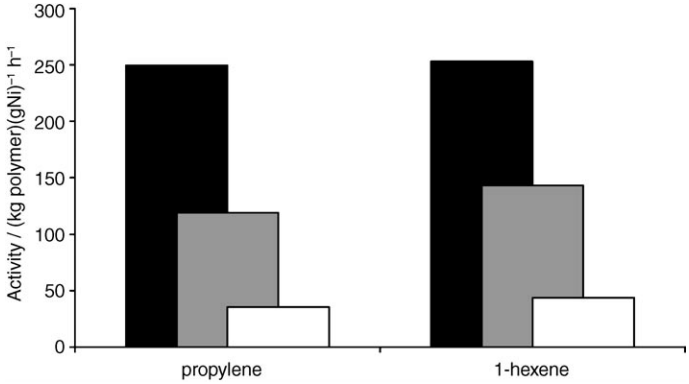

Figure 3. Comparison of polymerization activities of **2a**/TMA (■), **7b**/TMA (□), and **7c**/TMA (■) at 5 bar. Polymerization conditions: 2-L Parr autoclave, 800 mL toluene, weighed comonomer (0.6 mol L^{-1}) added to the reaction matrix by a pressure burette prior to pressurizing the reaction vessel with ethylene/hydrogen. X (5 bar) (mmol H_2/mol ethylene) = 1.92, n (catalyst) = 5 μmol.

tecture: As a general trend, branching numbers at ambient temperature increased with decreasing steric demand of the ligands (Figure 2). Introduction of one phenyl moiety (**7c**) or one methyl substituent in the 2-position (**7b**) changed the branching rate of the particular catalyst. These complexes generated polyethylene grades with 15 alkyl side groups per 1000 carbon atoms of the main chain, that is, 15‰ (**7c**), or 24‰ (**7b**) branching, compared to 3‰ alkyl groups introduced by **2a**, which is substituted at all *ortho* positions.

For a detailed discussion, we determined the distribution of alkyl branches of various lengths. Integrated ^{13}C NMR spectroscopic experiments of the polymers showed that branches found in polyethylene grades generated by **2a**/TMA were exclusively methyl groups. By contrast, methyl branches made by **7b**/TMA and **7c**/TMA were in the range of 90%, with 10% (**7c**) and 13% (**7b**) of the side chains composed of longer alkyl groups. For the non-methyl groups here, monophenyl-substituted **7c**/TMA afforded ethyl groups exclusively, compared to the side-chain distribution generated with **7b**/TMA of 2.5% ethyl, 2.5% propyl, and 8% butyl or longer alkyl groups. Increasing the ethylene partial pressure to 10 bar by using **7c**/TMA again yielded 100% methyl branches.

Copolymerization

Copolymerization reactions were performed with ethylene and propylene or 1-hexene as representatives for higher 1-alkenes. Activities as well as the molecular weight showed the same trend observed in the homopolymerization experiments. Activities increased with growing steric demand of the applied ligands (Figure 3). Application of 10 bar ethylene pressure in the presence of propylene led to an activity increase like that observed in the homopolymerization experiments (Table 1, entry 4).

Molecular weight is influenced similarly by hydrogen as well as the steric demand of the applied ligands (see above).[12] In the copolymerization reactions, each particular catalyst produced polymers with a constant molecular weight (M_w) independent of the applied co-momoner and its concentration.

Any attempt to apply symmetric aryl-substituted nickel(II) complexes (e.g., **2a**/TMA) under copolymerization conditions afforded almost linear ethylene homopolymers (4‰ methyl branches); 1-alkene incorporation could not be detected. Most interestingly, the addition of propylene[13] with unsymmetric catalysts produced copolymers with an increased branching level of 19‰ (**7c**) and 47‰ alkyl side chains (**7b**) (Figure 4).

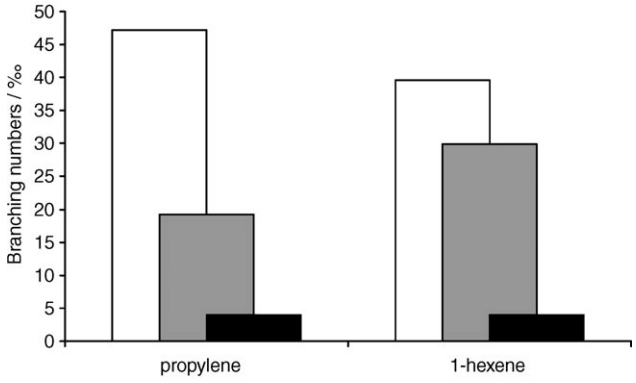

Figure 4. Branching numbers of copolymers made by **2a** (■), **7b** (□), and **7c** (■). Concentration of comonomer = 0.6 mol L^{-1}.

The "gap" in the ligand sphere of **7b** and **7c** creates space for successful coordination/insertion of bulky propylene. Substituting propylene by 1-hexene, we observed again an increase in branching of up to 30‰ (**7c**) and 40‰ (**7b**). This particular ligand substitution allows coordination/insertion of a bulky α olefin as well as polymer-chain isomerization, leading to higher branching numbers. Unsurprisingly, **2a**/TMA afforded no copolymer; the branching level was 4‰ alkyl groups. As methyl groups can be accommodated

to a certain extend in the crystal lattice of the polymer, we tried to increase the fraction of the longer side chains by the copolymerization process.

The distribution under copolymerization conditions shows a more-complex picture. Notably, **2a**/TMA did not incorporate any comonomer under these conditions (see above). Therefore, the quantity and type of alkyl side groups stayed the same. As a general trend for **7b**/TMA and **7c**/TMA, we observed that use of propylene and 1-hexene led to higher amounts of methyl and butyl or longer branches in the resulting polymers, respectively. In ethene/propylene copolymerization experiments, **7c**/TMA generated more methyl branches, increasing the concentration from 13.5 to 18.1‰ on each individual chain (Table 1). Interestingly, in contrast to the homopolymerization experiment, 1.1‰ butyl groups were detected. Thus, propylene incorporation seems to enforce "chain-walking", leading to longer side chains.

In NMR experiments on the copolymers generated by the monomethyl-substituted **7b**/TMA, we observed an increase in methyl branches from 21.1 to 41.2‰ and butyl side chains from 1.9 to 4.2‰. In ethene/1-hexene copolymerization, the trends were the same, with mostly the amount of butyl or longer branches changing. These longer alkyl side groups determine the physical properties, for example, melting behavior. We observed a linear relationship ($R^2 = 0.98$) between melting point and amount of branching that was independent of side-chain distribution (Figure 5).

The almost perfectly linear polyethylene grades melted at

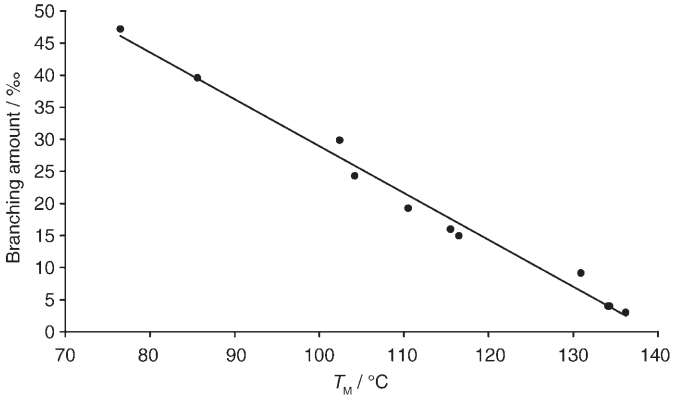

Figure 5. Melting point versus branching number: independence of branching distribution. ● = Branches.

temperatures above 135 °C. With increasing branching numbers, the melting point shifted down to approximately 75 °C. We ascribe this effect to the fraction of long alkyl chains generated by "chain-walking" or under copolymerization conditions, which reduces the melting point substantially.

Conclusions

As scrambling reactions of classically condensed unsymmetric α-diimine ligands afford their stable symmetric relatives, we developed a new synthetic strategy toward novel unsymmetric α-diimine ligands **6a–c** and their corresponding complexes **7a–c**. On introducing methyl chloroglyoxylate as the starting molecule and different substituted anilines **a–d**, we synthesized by an easy route the new compounds **6a–c**. Subsequently, we obtained the corresponding monocationic α-diimine complexes **7a–c** by treating square-planar diacetylacetonatonickel(II) with trityl borate in the presence of the ligands. This high-yielding and easy synthesis of **7a–c** as well as their unparamagnetic behavior makes them ideal precursors of polymerization catalysts.

Catalyst activity under homopolymerization conditions followed the stepwise increase of steric demand (**7b** < **7c** < **2a**) as propagation is favored compared to chain isomerization. Higher partial ethylene pressure led to a significant increase in activity. The molecular weight of the polymer obtained is influenced by olefin exchange as well as hydrogen effectiveness. Therefore, the ligand architecture of **7c** seems to fit best for affording high-molecular-weight polymers. Application of a comonomer gave activities and molecular weights in the range of the homopolymerization experiments.

As expected, we observed for branching numbers an opposite trend to activity. Symmetric catalyst **2a**/TMA afforded nearly linear products with melting points near 140 °C that were independent of the polymerization conditions applied. The unsymmetric counterparts **7b**/TMA and **7c**/TMA, however, effectively isomerized the polymer chain under homopolymerization conditions according to the steric demand of the ligands. Addition of comonomers generated polyethylene grades with up to 50% branching. The introduced branches were responsible for the significant decrease in melting points to nearly 75 °C.

Experimental Section

For purification, dichloromethane was distilled from CaH_2, *n*-pentane and toluene from sodium, and THF from $LiAlH_4$. Diacetylacetonatonickel(II), biphenyl-2-ylamine, boric acid, *n*-butyllithium (as 1.6 M solution in *n*-hexane), 1,2-dimercaptoethane, phosphorus pentachloride, triethylamine, and thionyl chloride were purchased from Merck, and methyl chloroglyoxylate from Fluka, and used as received. TMA was purchased as 2 M solutions in toluene from Crompton GmbH. Aniline and 2-methylaniline were distilled before application. Ethylene (Linde, grade 3.0), propylene (Linde, grade 2.8), and hydrogen (Linde, grade 5.0) were used as received. 2,6-Diphenylaniline,[6] triphenylcarbenium (trityl) tetrakis(pentafluorophenyl)borate were prepared by literature procedures.[14] All reactions were carried out under an argon atmosphere with standard Schlenk techniques. All synthesized compounds were characterized by ^1H and ^{13}C NMR spectroscopic analysis on a Bruker DRX 400 spectrometer. Chemical shifts (δ) are given in ppm in reference to the ^1H and ^{13}C NMR signals of the deuterated solvents. MALDI-TOF mass spectra were recorded on Bruker Daltonics REFLEX III mass spectrometers in the Section of Mass Spectrometry, University of Ulm. Elemental compositions (C, H, and N) were determined in the Microanalytical Laboratory, University of Ulm.

We performed all polymerization reactions in a 2-L Parr autoclave. Ethylene and hydrogen were continuously fed to the running reaction through calibrated liquid- (Bronkhorst Liquid Flow Sensor L2) or gas-flow meters (Bronkhorst F-201C) at constant pressure. Continuous hydrogen addition was performed by a master–slave control system that allowed a defined amount of H_2 in relation to ethylene consumption

(Bronkhorst E-7000). The system was set up to obtain a constant mole fraction X (n mmol hydrogen/n mol ethylene) that corresponds to 0–75 mL of hydrogen per minute. The polymers were analyzed by NMR spectroscopy in [D_5]bromobenzene at 363 K by using a Bruker AMX-500 spectrometer. The amount and type of branches were determined by ^{1}H and ^{13}C NMR spectroscopy, respectively. Molecular weights and distributions were measured on a Waters HT-GPC instrument (Alliance GPC 2000; 145 °C, 1,2,4-trichlorobenzene) relative to polystyrene standards and universal calibration. Melting points were determined by differential scanning calorimetry (DSC; Perkin–Elmer DCS-7, second heating endotherm).

Synthesis

3d: 2,6-Diphenylaniline (20.0 g, 81.5 mmol) and triethylamine (8.3 g, 81.5 mmol) were dissolved in dry dichloromethane (100 mL) and cooled to 0 °C. Methyl chloroglyoxalate (10 g, 81.5 mmol) diluted in dichloromethane (50 mL) was dropped into this solution. The reaction mixture was then stirred at room temperature for 4 h. The triethylamine hydrochloride was then extracted twice with water (100 mL). After phase separation, the organic phase was dried over sodium sulfate, and the solvent was removed in vacuo. The precipitate was recrystallized from *iso*-propanol to give **3d** (23.8 g, 88 %). ^{1}H NMR (400 MHz, [D_2]tetrachloroethane, 25 °C): δ = 8.32 (s, 1 H, NH), 7.53 (dd, $^3J_{(H,H)}$ = 8.4, 6.8 Hz, 1 H, *p*-amide), 7.46–7.36 (m, 12 H, aromatic), 3.76 ppm (s, OCH_3); ^{13}C NMR (100 MHz, [D_2]tetrachlorethane, 25 °C): δ = 160.4, 154.6, 140.2, 140.0, 130.3, 129.3, 128.7,128.6, 128.5, 127.8, 53.9 ppm; elemental analysis: calcd (%) for $C_{21}H_{17}NO_3$: C 76.12, H 5.17, N 4.23; found: C 75.99, H 5.16, N 4.17.

General procedure for **4a–c**: Compound **3d** (10 g, 30.2 mmol), the corresponding aniline **a–c** (30.2 mmol), and boric acid were heated at 180 °C for 4 h. The mixtures melted at above 150 °C. The eliminated trimethylborate was distilled away. The mixture was allowed to cool to room temperature, and the crude product was dissolved in THF (≈100 mL). The solution was poured into vigorously stirred water, and the brownish product precipitated. The precipitate was recrystallized from methanol/toluene (3:1 *v*/*v*) to give the white product.

4a: Yield: 6.5 g (55 %). ^{1}H NMR (400 MHz, [D_2]tetrachlorethane, 25 °C), δ = 8.98 (s, 1 H, NH), 8.90 (s, 1 H, NH), 7.56–7.30 (m, 17 H, aromatic), 7.18 ppm (t, $^3J_{(H,H)}$ = 7.4 Hz, 1 H, *p*-amide); ^{13}C NMR (100 MHz, [D_2]tetrachlorethane, 25 °C): δ = 158.3, 156.9, 140.2, 139.0, 136.1, 130.2, 129.5, 129.3, 128.7, 128.6, 128.4, 127.7, 125.6, 119.8 ppm; elemental analysis: calcd (%) for $C_{26}H_{20}N_2O_2$: C 79.57, H 5.14, N 7.14; found: C 79.78, H 5.04, N 7.00.

4b: Yield: 5.5 g (45 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.89 (s, 1 H, N), 8.87 (s, 1 H, NH), 7.87 (t, $^3J_{(H,H)}$ = 6.46 Hz, 1 H, *ortho*-amide), 7.53 (dd, $^3J_{(H,H)}$ = 8.46, 6.52 Hz, 1 H, *p*-amide), 7.50–7.30 (m, 12 H, aromatic), 7.27–7.16 (m, 2 H, aromatic), 7.16–7.06 (m, 1 H, aromatic), 2.21 ppm (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.5, 156.8, 140.3, 139.1, 134.2, 130.5, 130.0, 129.7, 128.7, 128.6, 128.4, 128.1, 127.5, 126.7, 125.7, 121.5, 17.3 ppm; elemental analysis: calcd (%) for $C_{27}H_{22}N_2O_2$: C 79.78, H 5.46, N 6.89; found: C 79.75, H 5.44, N 6.78.

4c: Yield: 4.2 g (30 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.06 (s, 1 H, NH), 8.76 (s, 1 H, NH), 8.20 (dd, $^3J_{(H,H)}$ = 8.13 Hz, $^4J_{(H,H)}$ = 0.64 Hz, 1 H, *m*-amide), 7.46 (dd, $^3J_{(H,H)}$ = 8.60, 6.46 Hz, 1 H, *p*-amide), 7.44–7.31 (m, 16 H, aromatic), 7.29 (dd, $^3J_{(H,H)}$ = 7.64 Hz, $^4J_{(H,H)}$ = 1.61 Hz, 1 H, *o*-amide), 7.24–7.19 ppm (m, 3 H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.4, 156.7, 140.4, 139.1, 137.0, 133.0, 132.9, 130.3, 130.0, 129.7, 129.0, 129.0, 128.6, 128.3, 128.2, 128.2, 128.1, 127.5, 125.3, 120.7 ppm; elemental analysis: calcd (%) for $C_{32}H_{24}N_2O_2$: C 82.03, H 5.16, N 5.98; found: C 82.23, H 5.03, N 5.88.

General procedure for **5a–c**: Compounds **4a–c** (12.7 mmol) and phosphorus pentachloride (5.3 g, 25.5 mmol) were heated to 75 °C in thionyl chloride (6.1 g, 51.0 mmol). The reaction started immediately with heating. After gas evolution was complete (after ≈1 h), the reaction mixture was cooled to room temperature. The oily deep-orange product was extracted three times with *n*-pentane (20 mL). The solvent was removed in vacuo, leaving the product as a yellow solid.

5a: Yield: 4.6 g (85 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.60–7.55 (m, 4 H, aromatic), 7.55–7.42 (m, 8 H, aromatic), 7.42–7.36 (m, 3 H, aromatic), 7.28 (tt, $^3J_{(H,H)}$ = 7.49 Hz, $^4J_{(H,H)}$ = 1.17 Hz, 1 H, *p*-imine), 7.01 ppm (dt, $^3J_{(H,H)}$ = 8.58 Hz, $^4J_{(H,H)}$ = 1.10 Hz, 2 H, *o*-imine); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 145.4, 142.6, 139.1, 139.0, 131.8, 129.7, 129.3, 128.9, 128.5, 128.2, 127.4, 126.7, 126.2, 120.6 ppm; elemental analysis: calcd (%) for $C_{26}H_{18}N_2Cl_2$: C 72.73, H 4.23, N 6.52; found: C 72.54, H 4.02, N 6.38.

5b: Yield: 4.6 g (84 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.60–7.30 (m, 13 H, aromatic), 7.17 (d, $^3J_{(H,H)}$ = 7.54 Hz, 2 H, *o*-imine), 6.92 (t, $^3J_{(H,H)}$ = 7.53 Hz, 1 H, *p*-imine), 3.84 ppm (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 140.6, 139.7, 135.6, 133.8, 133.6, 132.1, 132.0, 129.7, 129.3, 128.8, 128.6, 128.5, 128.3, 128.0, 127.2, 118.2, 17.5 ppm; elemental analysis: calcd (%) for $C_{27}H_{20}N_2Cl_2$: C 73.14, H 4.55, N 6.32; found: C 72.95, H 4.45, N 6.19.

5c: Yield: 5.2 g (81 %). ^{1}H NMR (400 MHz, $CDCl_3$,25 °C): δ = 7.48–7.21 (m, 21 H, aromatic), 6.89 ppm (dd, $^3J_{(H,H)}$ = 7.80 Hz, $^4J_{(H,H)}$ = 1.27 Hz, 1 H, *p*-imine); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 143.4, 142.3, 138.8, 138.8, 138.3, 137.8, 132.9, 131.6, 130.3, 129.6, 129.1, 129.0, 128.0, 128.0, 127.6, 127.3, 127.2, 126.5, 126.0, 119.2 ppm; elemental analysis: calcd (%) for $C_{32}H_{22}N_2Cl_2$: C 76.04, H 4.39, N 5.54; found: C 75.90, H 4.50, N 5.45.

General procedure for **6a–c**: 1,2-Dimercaptoethane (400 mg, 4.25 mmol) was diluted with THF (20 mL), cooled to −78 °C, and then deprotonated with *n*BuLi (6.9 mL, 4.3 mmol, 1.6 M). The reaction mixture was then stirred at room temperature for another 2 h. Then **5a–c** (2.00 mmol) dissolved in THF (20 mL) was dropped slowly (30 min) into the solution, and the reaction mixture was heated under reflux for another 2 h. The crude product was allowed to cool to ambient temperature. The solvent was removed in vacuo, and the orange product was purified by column chromatography over neutral aluminum oxide 90 (Merck) with an eluent of *n*-hexane/ethyl acetate (4:1 *v*/*v*). The product eluted as the last compound from the column.

6a: Yield: 262 mg (30 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.56–7.37 (m, 12 H, aromatic), 7.14 (t, $^3J_{(H,H)}$ = 7.53 Hz, 1 H, *p*-imine), 6.89 (d, $^3J_{(H,H)}$ = 7.57 Hz, 2 H, *o*-imine), 2.93–2.75 ppm (m, 4 H, ethyl bridge); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 156.0, 155.2, 140.7, 139.5, 132.1, 129.8, 129.7, 128.9, 128.8, 128.3, 127.8, 127.0, 125.3, 120.2, 31.4, 29.8 ppm; elemental analysis: calcd (%) for $C_{28}H_{22}N_2S_2$: C 74.63, H 4.92, N 6.22; found: C 74.53, H 4.81, N 6.20.

6b: Yield: 346 mg (37 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.61–7.55 (m, 4 H, *o*-aryl), 7.45–7.26 (m, 9 H, aromatic), 7.22–7.11 (m, 1 H, *o*-imine), 7.14 (t, $^3J_{(H,H)}$ = 7.40 Hz, 1 H, *m*-imine), 7.04 (t, $^3J_{(H,H)}$ = 7.30 Hz, 1 H, *p*-imine), 6.72 (d, $^3J_{(H,H)}$ = 7.65 Hz, 1 H, *o*-CH_3 *m*-imine), 3.10–2.40 (m, 4 H, ethyl bridge), 2.06 ppm (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 155.5, 154.9, 147.8, 144.9, 139.5, 132.0, 130.5, 129.7, 129.6, 128.1, 127.8, 126.9, 126.0, 125.2, 124.9, 118.7, 31.2, 29.7, 17.5 ppm; elemental analysis: calcd (%) for $C_{29}H_{24}N_2S_2$: C 74.96, H 5.21, N 6.03; found: C 74.95, H 5.13, N 6.09.

6c: Yield: 314 mg (30 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.90–7.70 (m, 21 H, aromatic), 6.91 (d, $^3J_{(H,H)}$ = 7.70 Hz, 1 H, *o*-imine), 2,35 ppm (ddd, $^2J_{(H,H)}$ = 10.67 Hz, $^3J_{(H,H)}$ = 7.57, 3.57 Hz, 4 H, ethyl bridge); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 156.0, 155.7, 151.4, 147.2, 144.6, 139.3, 139.2, 132.0, 130.7, 130.2, 129.7, 129.6, 129.4, 128.0, 127.7, 126.8, 126.6, 125.2, 124.9, 119.8, 30.6, 30.1 ppm; elemental analysis: calcd (%) for $C_{34}H_{26}N_2S_2$: C 77.53, H 4.98, N 5.32; found: C 77.60, H 4.96, N 5.39.

General procedure for **2a**, **7a–c**: *N*,*N*′-butane-2,3-diylidenebis(1,1′:3′,1″-terphenyl-2′-amine)[6] or **6a–c** (0.6 mmol) and [Ni(acac)$_2$] (154 mg, 0.6 mmol; acac = acetylacetonato) were placed in a dried flask equipped with a rubber septum. Dichloromethane (25 mL) was added, and the solution was stirred vigorously until all solid particles dissolved to give a green to brown solution. Trityl tetrakis(pentafluorophenyl)borate (553 mg, 0.6 mmol) in dichloromethane (10 mL) was added slowly (≈5 min) with a syringe. The resultant dark-red solution was stirred overnight. The solution was concentrated to 10 mL and left to stand for another 4 h. The solution was then taken up with a syringe and subjected to chromatography through an alumina flash column (6–10 cm) with dichloromethane (40 mL) as eluent. The volume was decreased again to approximately 10 mL, and *n*-pentane (50 mL) was added slowly with vigorous stirring to precipitate a dark-red oil. The slightly colored supernatant was decanted, and the oil was extracted with dichloromethane

(15 mL). The procedure was repeated twice and the pure oil dried in vacuo to yield a dark-red glassy powder.[15]

7a: Yield: 734 mg (95%). ^{1}H NMR (400 MHz, [D$_2$]tetrachlorethane, 25°C): δ=7.71–7.56 (m, 12H, aromatic), 7.25 (t, $^3J_{(H,H)}$=7.60 Hz, 1H, *p*-imine), 7.10 (d, $^3J_{(H,H)}$=7.57 Hz, 2H, *o*-imine), 5.49 (s, 1H, CH), 2.95–2.76 (m, 4H, ethyl bridge), 1.46 ppm (s, 6H, CH$_3$); ^{13}C NMR (100 MHz, [D$_2$]tetrachlorethane, 25°C): δ=187.7, 165.6, 165.1, 147.5 (br d, $^1J_{(C,F)}$=233.6 Hz), 141.3, 140.3, 137.3 (br d, $^1J_{(C,F)}$=243.8 Hz), 136.3 (br d, $^1J_{(C,F)}$=239.2 Hz), 131.8, 130.6, 129.9, 129.4, 128.8, 128.2, 128.1, 127.2, 126.5, 124.2 (br q, C–B), 120.0, 101.1, 31.4, 29.8, 24.1 ppm; MS (MALDI-TOF): *m*/*z* (%)=606.9 (100) [M–borate]$^+$; elemental analysis: calcd (%) for $C_{57}H_{29}BF_{20}N_2NiO_2S_2$: C 53.15, H 2.25, N 2.18; found: C53.17, H 2.27, N 2.17.

7b: Yield: 733 mg (94%). ^{1}H NMR (400 MHz, [D$_2$]tetrachlorethane, 25°C): δ=7.66–7.60 (m, 4H, *o*-aryl), 7.46–7.31 (m, 9H, aromatic), 7.28–7.23 (m, 1H, *o*-imine), 7.09 (t, $^3J_{(H,H)}$=7.50 Hz, 1H, *m*-imine), 7.06 (t, $^3J_{(H,H)}$=7.45 Hz, 1H, *p*-imine), 6.83 (d, $^3J_{(H,H)}$=7.55 Hz, 1H, *o*-CH$_3$, *m*-imine), 5.45 (s, 1H, CH), 3.15–2.55 (m, 4H, ethyl bridge), 2.34 (s, 3H, CH$_3$), 1.48 ppm (s, 6H, CH$_3$); ^{13}C NMR (100 MHz, [D$_2$]tetrachlorethane, 25°C): δ=186.9, 166.7, 166.1, 147.9, 147.1 (br d, $^1J_{(C,F)}$=234.8 Hz), 145.2, 138.6, 137.0 (br d, $^1J_{(C,F)}$=240.9 Hz), 136.3 (br d, $^1J_{(C,F)}$=239.6 Hz), 131.9, 130.6, 129.4, 129.0, 128.8, 127.6, 126.4, 123.8 (br q, C–B), 126.0, 125.2, 124.8, 118.0, 102.2, 30.9, 29.7, 24.2, 18.1 ppm; MS (MALDI-TOF): *m*/*z* (%)=621.3 (100) [M–borate]$^+$; elemental analysis: calcd (%) for $C_{58}H_{31}BF_{20}N_2NiO_2S_2$: C 53.50, H 2.38, N 2.15; found: C 53.52, H 2.40, N 2.15.

7c: Yield: 776 mg (95%). ^{1}H NMR (400 MHz, [D$_2$]tetrachlorethane, 25°C): δ=7.93–7.74 (m, 21H, aromatic), 6.91 (d, $^3J_{(H,H)}$=7.70 Hz, 1H, *o*-imine), 5.51 (s, 1H, CH), 2.45–2.21 (m, 4H, ethyl bridge), 1.55 ppm (s, 6H, CH$_3$); ^{13}C NMR (100 MHz, [D$_2$]tetrachlorethane, 25°C): δ=187.5, 166.0, 165.7, 151.4, 147.8, 147.7 (br d, $^1J_{(C,F)}$=232.8 Hz), 143.8, 140.8, 139.5, 136.7 (br d, $^1J_{(C,F)}$=241.4 Hz), 136.3 (br d, $^1J_{(C,F)}$=238.7 Hz), 131.4, 130.5, 130.4, 129.6, 129.7, 128.8, 128.3, 126.8, 124.5 (br q, C–B), 126.3, 125.9, 125.4, 124.6, 119.6, 30.4, 29.9, 24.2 ppm; MS (MALDI-TOF): *m*/*z* (%)=683.4 (100) [M–borate]$^+$; elemental analysis: calcd (%) for $C_{63}H_{33}BF_{20}N_2NiO_2S_2$: C 55.47, H 2.42, N 2.05; found: C 55.49, H 2.44, N 2.05.

2a: Yield: 827 mg (95%). ^{1}H NMR (400 MHz, [D$_2$]tetrachlorethane, 25°C): δ=7.55–7.45 (m, 12H, aromatic), 7.35–7.18 (m, 14H, aromatic), 5.34 (s, 1H, CH), 1.60 (s, 6H, CH$_3$), 1.44 ppm (s, 6H, CH$_3$); ^{13}C NMR (100 MHz, [D$_2$]tetrachlorethane, 25°C): δ=186.5, 176.2, 148.2 (br d, $^1J_{(C,F)}$=240.0 Hz), 138.7, 138.2 (br d, $^1J_{(C,F)}$=248.1 Hz), 136.6, 136.3, 136.3 (br d, $^1J_{(C,F)}$=250.3 Hz), 130.9, 129.4, 129.3, 128.8, 128.6, 124.0 (br q, C–B), 101.9, 24.4, 20.4 ppm; MS (MALDI-TOF): *m*/*z* (%)=697.4 (100) [M–borate]$^+$; elemental analysis: calcd (%) for $C_{69}H_{39}BF_{20}N_2NiO_2$: C 60.13, H 2.83, N 2.03; found: C 60.16, H 2.85, N 2.03.

General polymerization procedure: The pressure reactor was evacuated at 125°C prior to use, and **7a–c** (10 μmol) were dissolved in dichloromethane (4 mL). For polymerization, toluene was (800 mL) injected by an HPLC pump into the reaction vessel, followed by the red solution of the complex by a syringe. The argon atmosphere was then exchanged with an ethylene/hydrogen mixture, and the pressure was set to 5 or 10 bar. For copolymerization experiments, the weighed comonomer was injected into the vessel prior to the ethylene/hydrogen mixture. The internal temperature was set to 30°C. Polymerization was started by the injection of the TMA activator, diluted in toluene (15 mL), into the vessel through a pressure burette. The experiments were run under steady-state conditions at 30°C and 5 or 10 bar ethylene pressure. After complete reaction, the reactor was decompressed. The solid product and the reaction matrix were transferred into acidified methanol (2 L) and stirred for a further hour. After filtration, the polymer was dried overnight under room conditions and finally at 80°C and reduced pressure (10 Torr).

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[11] **7a**/TMA showed only low activity under these conditions. Therefore, we abstain from a detailed discussion.

[12] The particular PDIs lie in the range of single-site catalysts.

[13] **7a–c**/TMA-catalyzed propylene homopolymerization experiments were not successful in both toluene as reaction matrix and liquid propylene.

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[15] All attempts to grow single crystals of **7a–c** suitable for X-ray diffraction analysis were unsuccessful so far.

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