



Titanium complexes with modifiable pyrazolonato and pyrazolonato-ketimine ligands: Synthesis, characterization and ethylene polymerization behavior

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ABSTRACT

Six titanium complexes bearing pyrazolonato and pyrazolonato-ketimine ligands have been synthesized and characterized. It was found that the ligand structure of the synthesized complexes has a significant effect on the catalytic performance of the complexes. The synthesized complexes were activated with MAO and their activities varied from negligible to high (up to 612 kg_{PE}/(mol_{Ti} h bar)). The pyrazolonato-ketimine complex with a phenyl substituent in the imine part was the most active in the series and it was the only one producing polyethylenes with relatively narrow molecular weight distribution (M_w/M_n from 1.6 to 2.2).

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1. Introduction

Since the successful introduction of chiral Group IV metallocene catalyst to the polymerization of olefins, intensive research in this area has led to exploration of various well-defined transition metal catalyst systems [1–3]. Due to this extensive research of cyclopentadienyl and indenyl bearing complexes, lately non-metallocene complexes have attracted more interest [4–7]. Many successful non-metallocene Group IV complexes bearing, for example, amide [8–12], β -diketimines [13,14], phosphine-imide [15], imine-pyrrolidines [16,17], imido [18,19], alkoxide [20–23] and enamino-ketonato [24,25] ligands have been reported. Some of these catalysts have been shown to exhibit high activities, comparable to those of metallocene catalysts [8,15,16,18]. In addition to Group IV metal complexes, notable achievements have been established among Ni, Pd, Fe and Co complexes with diimine and diimine-pyridine ligands [26–28].

The work done with phenoxy-imine-catalysts (FI-catalysts) and diimine complexes have shown that small changes in the ligand structure around the metal center can lead to profound changes in the performance of the polymerization catalysts [26,29]. By varying the steric and electronic properties of the ligand framework it is not only possible to enhance the activity of the catalyst but also promote synthesis of well-defined polymer structures.

Depending on the catalyst structure hyperbranched polyethylenes, block copolymers, copolymers with polar monomers and polyolefins with narrow PDI through living polymerization are achievable [30–34].

In general ketimine complexes have attracted less attention than their aldimine counterparts. The lack of interest given to ketimine catalysts may partly be explained by the fact that the synthesis of the desired ligand precursors is not always straightforward [35]. However, ketimine type catalysts may have enhanced properties when compared to aldimine analogs. For example Chen et al. synthesized phenoxy-ketimine complexes which proved to be more active in ethylene polymerization than corresponding salicyl aldimine catalysts [36]. Also in contrast to aldimine analogs, the phenoxy-ketimine catalysts have been shown to polymerize ethylene in living manner, even without fluorinated phenyl ring in the imino-moiety [37]. In addition Coates et al. have utilized phenoxy-ketimine complexes in the polymerization of multiblock isotactic polypropylene copolymers [38].

As an augmentation to our previous catalyst development [39,40], we report herein the synthesis of a series of pyrazolonato- and pyrazolonato-ketimine titanium dichloride complexes and their usage as catalyst precursors in ethylene polymerization. Two of these complexes have been previously synthesized (**1-Ti** and **2-Ti**) [41] but to the best of our knowledge no polymerization experiments have been carried out with these compounds. Our interest towards these complexes arose from the fact that their ligand structures offer many sites that can be altered and thus afford possibilities to effect the catalytic performance of these complexes.

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2. Results and discussion

2.1. Synthesis and characterization of Ti-complexes

A general synthetic route for the titanium complexes is presented in Scheme 1. Pyrazolonato ligand precursors **1–2** and corresponding β -diketonato complexes **1-Ti** and **2-Ti** were prepared according to known literature procedures [41,42]. To introduce desirable imine function into the ligand back-bone, new pyrazolonato-ketimine ligand precursors **3–6** were synthesized using an autoclave method we have previously reported [35]. As classical methods of using BuLi or sodium were unsuccessful, titanium complexes **3-Ti–6-Ti** bearing these ligands were synthesized with a straightforward manner by first mixing Et₃N with a ligand precursor and then adding this mixture to a solution of TiCl₄. By this method the desired complexes were obtained with moderate yields (23–29%) as dark red powders.

According to NMR studies the pyrazolone-ketimine ligand precursors **3–6** are in enol-form, indicated by the broad singlet attributed to the OH-group at low field. Crystals of compounds **3** and **5** suitable for X-ray analysis were grown from saturated toluene solutions. The corresponding structures are displayed in Figs. 1 and 2. Selected bond distances and angles for the compounds are listed in Table 1. Interestingly the X-ray analysis revealed that in the solid state these ligand precursors adopt a betaine configuration, which is clearly evident when comparing the significant bond distances. Both compounds have a distance between C1–O1 (1.247(5) and 1.249(2) Å) resembling that of anionic oxygen (~1.25 Å) [43]. As expected for betaine structure also the C6–N7 bond is slightly shorter (1.344(6) and 1.320(8)) than expected for amino configuration (1.353 Å) but still noticeably longer than the ones reported for imino-type structures (1.279 Å) [43]. The X-ray structures of compounds **1** and **2** also exhibit strong hydrogen bond between H(N) and O1 forming a six-member ring [44]. In addition, according to the X-ray structure the aryl-ring attached

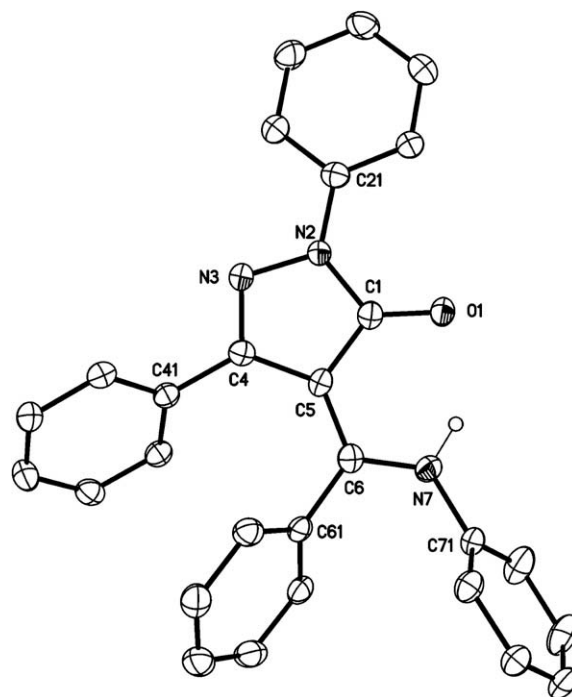


Fig. 1. Molecular structure of the ligand **3**. Displacement parameters are drawn at 50% probability level. Hydrogen atoms (except H(N)) are omitted for clarity.

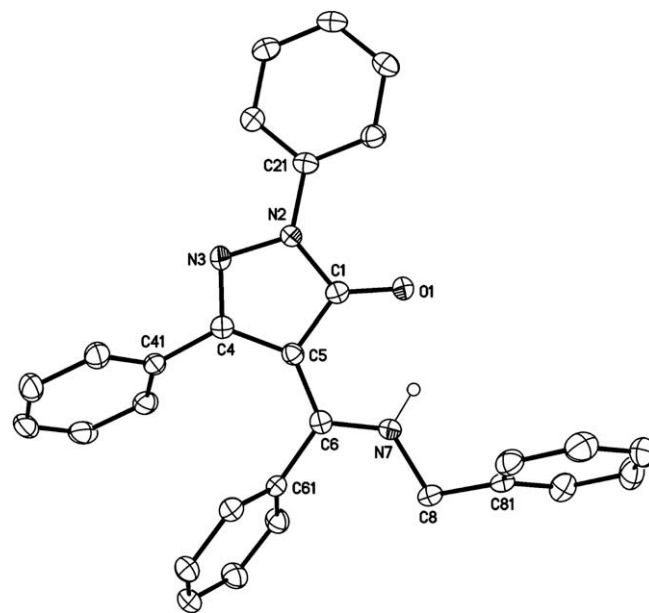
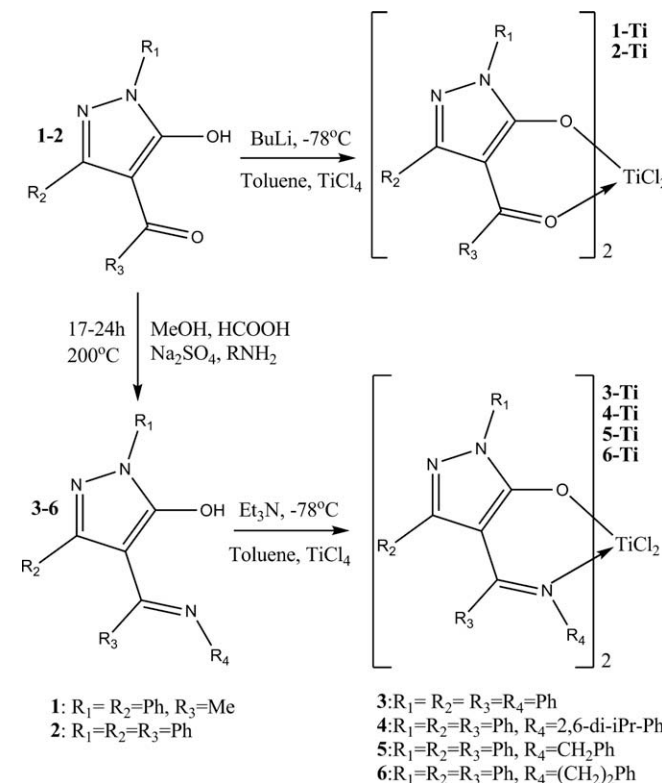


Fig. 2. Molecular structure of the ligand **5**. Displacement parameters are drawn at 50% probability level. Hydrogen atoms (except H(N)) are omitted for clarity.



Scheme 1. Synthetic route for the complexes **1-Ti–6-Ti**.

to the N2 atom is in the same plane as the pyrazolone ring, while the other phenyl rings are out of plane. This indicates that this aryl-ring attached to N2 atom belongs to the same planar conjugated system formed by the betaine moiety (O1, C1, N2, N3, C4, C5, C6, and N7).

In spite of numerous attempts, no crystals suitable for X-ray structure analysis were obtained for complexes **1-Ti–6-Ti**. It can, however, be concluded based on NMR spectra that complexes **1-Ti** and **4-Ti–6-Ti** are C₂ symmetric ones in solution. However, the structure of a compound attributed to a reaction intermediate,

Table 1
Selected bond lengths [Å] for compounds **3**, **5** and **3-Ti***.

Compound 3	
O1–C1	1.247(5)
C1–C5	1.441(6)
C5–C6	1.395(6)
C6–N7	1.344(6)
N7–H7	0.94(5)
Compound 5	
O1–C1	1.2492(15)
C1–C5	1.4410(18)
C5–C6	1.4034(18)
C6–N7	1.3207(17)
N7–C8	1.4648(17)
N7–H7	0.884(12)
Compound 3-Ti*	
O1–C1	1.283(5)
C1–C5	1.429(6)
C5–C6	1.419(7)
C6–N7	1.327(6)
N7–H7	0.871(19)
Ti1–Cl1	2.3604(12)
Ti1–Cl2	2.3184(12)
Ti1–O1	1.941(3)
O1–Ti1–O1A	180.00
O1–Ti1–Cl2	88.53(10)
O1A–Ti1–Cl2	91.47(10)
Cl1–Ti1–Cl1A	180.00

Ti-3*, (Scheme 2) was obtained from a toluene solution and is displayed in Fig. 3. Selected bond distances and angles for this complex are listed in Table 1. **Ti-3*** is a tetragonal bipyramide coordinated complex with the oxygen atoms in axial position to the titanium atom. The X-ray analysis also revealed that **3-Ti*** has a crystallographic C_2 -symmetry. The bond between the titanium center and the oxygen atoms resemble to anionic ones and as such is notably shorter than, for example, the bond between titanium and oxygen in the case of $\text{TiCl}_4 \cdot 2\text{THF}$ (2.105(1) Å compared to 1.941(3) Å in **Ti-3***) [45]. The strong hydrogen bond between N(H) and oxygen atom found in the ligand precursor is preserved but weakened [44]. However, two new hydrogen bonds, one weak and one strong, between N(H) and the Cl-atoms Cl1 and Cl2 are formed [44]. The obtained structure for the reaction intermediate correlates well with the one obtained for related salicylaldiminato titanium complex prepared through similar synthesis route [46].

2.2. Ethylene polymerization

The complexes were activated with MAO and used as catalysts for ethylene polymerization. Results of these experiments are listed in Table 2. In general, after MAO activation all the complexes

except **3-Ti** exhibited low activities in ethylene polymerizations. Catalysts **1-Ti/MAO** and **2-Ti/MAO** with β -diketonato ligands gave unimodal polyethylene as a product, although with broad molecular weight distributions. From the O,N-type complexes, **3-Ti/MAO** behaved as a single-site catalyst producing unimodal polyethylenes with a relatively narrow molecular weight distribution whereas catalyst **4-Ti/MAO** produced unimodal polyethylenes with broad molecular weight distribution. The catalysts **5-Ti/MAO** and **6-Ti/MAO**, with alkyl substituent in the imine-group, produced bimodal polyethylenes with extremely broad molecular weight distributions.

The catalyst **1-Ti/MAO** revealed polymerization activity of 20 kg PE/(mol_{Ti} h bar) at 40 °C carried out polymerization. It seemed to possess low thermal stability and as a result upon increasing polymerization temperature to 80 °C activity was reduced to 2 kg PE/

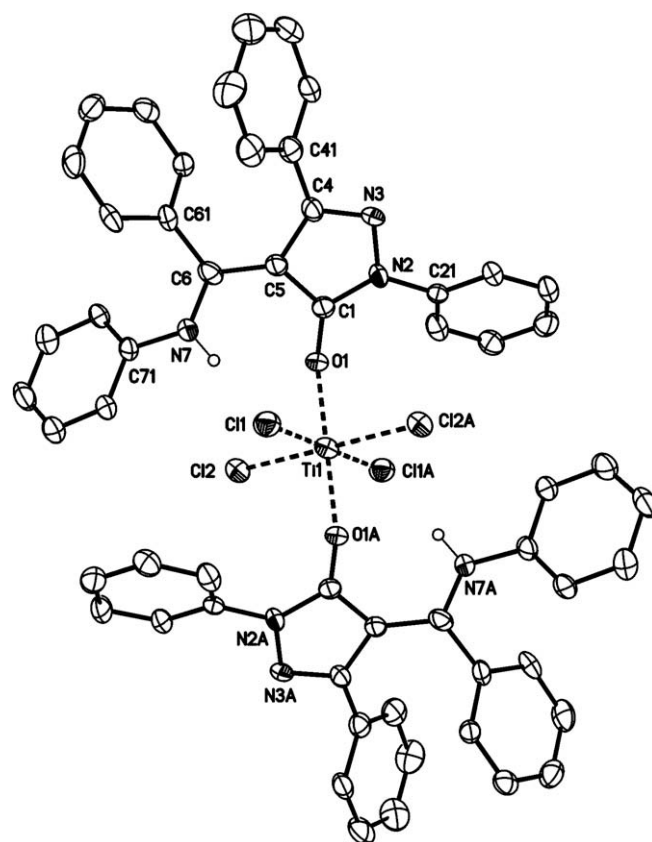
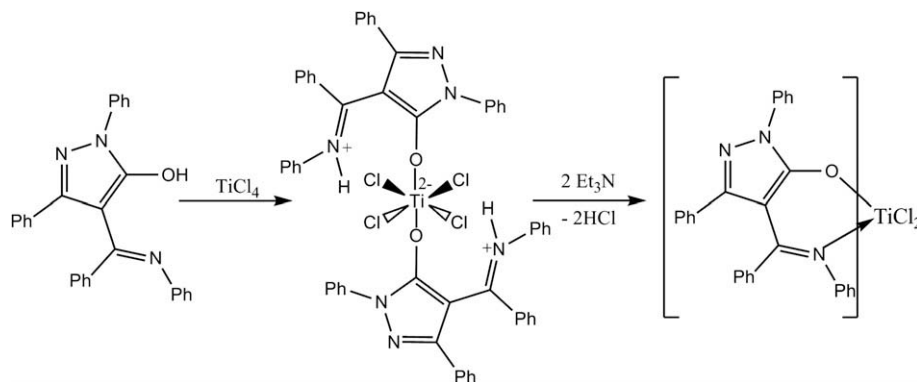


Fig. 3. Molecular structure of the reaction intermediate **3-Ti***. Displacement parameters are drawn at 50% probability level. Hydrogen atoms (except H(N)) are omitted for clarity. The molecule possesses crystallographic C_2 -symmetry.



Scheme 2. Formation of intermediate in the synthesis of complex **3-Ti**.

Table 2
Selected ethylene polymerization results with MAO activated complexes **1-Ti–6-Ti**.

Run	Complex	<i>p</i> (bar) ^a	<i>T</i> _p (°C) ^b	<i>M</i> _w (kg/mol)	<i>M</i> _w / <i>M</i> _n	Activity ^c	<i>T</i> _m (°C) ^d
1	1-Ti	4	40	1020	3.1	17	135
2	1-Ti	4	60	960	4.7	18	135
3	1-Ti	4	80	980	6.6	2	136
4	1-Ti	2	60	820	4.7	5	137
5	1-Ti	6	60	1080	4.9	11	135
6	2-Ti	4	40	600	3.8	2	135
7	2-Ti	4	60	620	5.2	18	135
8	2-Ti	4	80	890	4.8	2	136
9	2-Ti	2	60	950	4.1	5	135
10	2-Ti	6	60	760	5.3	12	137
11	3-Ti	4	40	1620	1.6	342	136
12	3-Ti	4	60	1020	1.6	612	138
13	3-Ti	4	80	690	2.2	564	137
14	3-Ti	2	60	1050	1.9	229	138
15	3-Ti	6	60	1450	1.9	590	137
16	4-Ti	4	40	650	7.1	22	135
17	4-Ti	4	60	630	7.9	25	138
18	4-Ti	4	80	600	3.5	35	137
19	4-Ti	2	60	670	5.2	24	137
20	4-Ti	6	60	610	4.6	32	137
21	5-Ti	4	40	1410/60	Broad ^e	7	136
22	5-Ti	4	60	1200/50	Broad ^e	26	137
23	5-Ti	4	80	1150/50	Broad ^e	5	137
24	5-Ti	2	60	1170/50	Broad ^e	37	136
25	5-Ti	6	60	1030/50	Broad ^e	4	137
26	6-Ti	4	40	490/10	Broad ^e	8	135
27	6-Ti	4	60	470/11	Broad ^e	8	135
28	6-Ti	4	80	440/9	Broad ^e	3	136
29	6-Ti	2	60	490/10	Broad ^e	5	136
30	6-Ti	6	60	480/8	Broad ^e	8	135

^a Monomer pressure.

^b Polymerization temperature.

^c Activity in kg PE/(molTi h bar).

^d Onset melting temperature of polyethylene.

^e Bi-modal molar mass distribution.

(mol_{Ti} h bar). Increase in polymerization temperature led also to broader molecular weight distributions. Seemingly the catalyst is not stable at higher temperatures and that partial decomposition of the complex structure may occur at elevated temperatures. Increasing the monomer concentration did not lead to noticeable changes in polymerization behavior with this catalyst. The other O,O-type catalyst system **2-Ti/MAO** behaved similarly with its methyl analog **1-Ti/MAO** in the terms of activity and molecular weight distributions. It exhibited highest activity of 18 kg PE/(mol_{Ti} h bar) at 60 °C followed by activity decrease and broadening of molecular weight distributions values at 80 °C. The molecular weight values of the produced polyethylenes were lower than achieved with corresponding catalyst **1-Ti/MAO** revealing values of 600 000 to 950 000 g/mol.

Catalyst **3-Ti/MAO** with an unsubstituted phenyl group in the imine-part of the complex revealed the highest activities within the studied catalyst precursors. The highest activity of 612 kg PE/(mol_{Ti} h bar) was achieved in 60 °C. The polymerization activity was slightly decreased, to 564 kg PE/(mol_{Ti} h bar), when the temperature was increased to 80 °C. The molecular weight of the formed polyethylene also depended on the polymerization temperature, increased temperature lead to decreased molecular weight values. The changes in molecular weight distribution values with the changes in the polymerization temperature mimic the behavior of a single-site catalyst. Also a slight broadening of MWD can be seen upon temperature increase. Increasing the monomer pressure from 2 bar to 4 bar lead to increased activity while further increase to 6 bar did not enhance the activity of the catalyst anymore.

Using sterically bulky substituents in the imine-moiety is known to enhance the catalytic activity of late transition metal catalysts [47–48]. To investigate if the same concept could be ap-

plied here the steric bulk around the metal center was increased by introducing isopropyl (*iPr*) groups to the 2 and 6 positions of the imino-phenyl ring. This did not, however, improve the catalytic performance but instead lead to significant decrease in polymerization activity. Similar decrease in activity has been observed for some related Group IV metal complexes [49]. No clear effect of monomer pressure was observed with catalyst **4Ti/MAO** and also an increase in polymerization temperature led to only a slight increase in activity. The Mw of the polymers was found to be relatively independent of the polymerization conditions.

The catalyst precursors were further modified by replacing the aromatic group with a benzyl and an ethylphenyl moiety. FI-catalysts with corresponding imino-groups, which we have previously studied [50], displayed interesting properties in ethene polymerizations. The polymer obtained with catalyst **5Ti/MAO**, bearing a benzyl substituent in the imino group, was clearly bimodal and the intensities of molecular weight fractions were found to be dependent on the polymerization temperature. With increasing temperature the higher molecular weight fraction became more dominant and correspondingly the intensity of the lower molecular weight fraction was decreased. The polymerization temperature also had a marked effect on the activity of the catalyst, maximum activity being observed at 60 °C followed by a decrease in higher temperatures. No clear effect of monomer pressure was observed.

Formation of bimodal polymer was observed also when the benzyl group was replaced with an ethylphenyl one. As with the catalyst **5Ti/MAO**, catalyst **6Ti/MAO** produced bimodal polyethylene with the ratios of low- and high-molecular weight parts dependent on the polymerization temperature. Once again the higher molecular weight fraction became dominant when polymerization was performed at elevated temperatures. However, contradictory to behavior of **5Ti/MAO** in the case of **6Ti/MAO** also the monomer pressure had an effect to molecular weight, increase in pressure lead to increase in the intensity of the higher molecular weight part. In general the benzyl substituted catalyst **5Ti/MAO** produced polymers with higher Mw than the ethylphenyl analog **6Ti/MAO**.

The polymerization behavior of **5Ti/MAO** mimics the one reported for the FI-catalyst bearing benzyl substituent [50]. The low activity of the analogous FI-catalyst was explained by the benzyl substituent partially blocking the active polymerization site. The formation of bimodal PEs was also attributed to this phenomenon. However, interestingly **6Ti/MAO** does not show similar behavior as its FI-analog which exhibited high activity in ethene polymerization and produced monomodal PE with narrow MWD. At the moment the reason for the polymerization behavior of these alkyl-substituted pyrazolonato-ketimine catalysts is not clear.

3. Conclusions

Four new (**3-Ti–6-Ti**) and two previously known (**1-Ti** and **2-Ti**) titanium complexes bearing pyrazolonato and pyrazolonato-ketimine ligands have been synthesized and characterized. It was shown that the ligand framework had a significant effect on both the polymerization activity and on the molecular weight distributions of the resulting polymer product. Complexes were activated with MAO and activities of the catalysts in ethylene polymerization varied from 2 to 612 kg mol⁻¹ h⁻¹ bar⁻¹. Moreover the GPC results revealed that the most active catalyst **3-Ti** was the only one that behaved like a single-site catalyst and produced polymer with a narrow molecular weight distribution. The rest of catalysts revealed low polymerization activities despite the dramatic changes in ligand environment from O,O to O,N. The polymeriza-

tion behavior bears a resemblance to related phenyl and alkylphenyl substituted FI-catalysts [49,50]. The remarkable increase in activity can be possibly observed when the ligand environment of complex **3-Ti** is modified by using fluorinated phenyl substituent instead of plain phenyl ring [28,51].

4. Experimental

All complex syntheses and polymerization experiments were performed under an argon atmosphere using standard Schlenk techniques. Toluene was dried over sodium flakes and distilled before use. Triethylamine was dried over calcium hydride and distilled before use. TiCl_4 was purchased from Fluka and used as received. Other reagents of high purity grade were purchased from commercial sources and used as received. MAO (30% in toluene) was obtained from Borealis Polymers Ltd.

Polymerization experiments were conducted in 1-L Büchi steel autoclave. Autoclave was charged with 200 mL of dry toluene, cocatalyst (MAO) and heated to desired temperature. Autoclave was saturated with ethylene and polymerization was initiated by addition of precatalyst solution. The monomer pressure, temperature and monomer consumption were controlled by real-time monitoring. Polymerization was quenched with 10% HCl solution in methanol, polymer was precipitated quantitatively by pouring the solution into methanol (400 mL), acidified with a small amount of HCl. Obtained polymer was washed several times with methanol and water followed by drying at 60 °C.

NMR spectra were recorded in CDCl_3 at 25 °C on a Varian Gemini 200 spectrometer operating at 200 MHz (^1H NMR) and 50.286 MHz (^{13}C NMR). Elemental analyses were performed with an EA 1110 CHNS-O CE instrument. EI mass spectra were acquired using a JEOL-SX102 instrument. DSC measurements (melting point) were performed using a Perkin–Elmer DSC-2, calibrated with indium (temperature scanning 10 °C/min). The scan area was from 25 to 232 °C. Molar masses and molar mass distributions of polyethylene samples were determined with a Waters Alliance GPCV 2000 high temperature gel chromatographic device having HMW7, 2*HMWGE, and HMW2 Waters Styrogel columns. Measurements were performed in 1,2,4-trichlorobenzene (TCB) at 160 °C relative to polyethylene standards, and 2,6-di-*tert*-butyl-4-methylphenol was used as a stabilizer. Chromatograms were calibrated using linear polystyrene standards.

The ligand precursors **1–2** and corresponding complexes **1-Ti** and **2-Ti** were synthesized according to known literature procedure [41,42]. The synthesis of precursors **3** and **5–6** we have reported previously [35]. Ligand precursor **4** was synthesized in a similar manner as precursors **3** and **5–6** with the following conditions.

4.1. 4-[(2,6-di-isopropylphenylimino)(phenyl)methyl]-1,3-diphenylpyrazolone-5} (**4**)

1-Phenyl-3-phenyl-4-benzoyl-pyrazolone-5 (1.50 g, 3.61 mmol) was dissolved in 25 ml of MeOH in a test tube. 2,6 Di-isopropylaniline (0.64 g, 3.61 mmol), Na_2SO_4 (2.60 g, 18.05 mmol) and a catalytic amount of formic acid were added to solution. Test tube was placed on steel autoclave and heated to 200 °C, as a result pressure increased to 20 bars. The reaction mixture was vigorously stirred for 16 h. Product was extracted from sodium sulfate with Et_2O and the solvents were removed under reduced pressure. Compound **4** was purified by recrystallization from propanol. Yield 38%.

^1H NMR (CDCl_3 , 200 MHz, 302 K): δ = 0.95 (d, $^3J_{\text{HH}}$ = 6.1 Hz, 6H, CH_3), 1.14 (d, $^3J_{\text{HH}}$ = 6.1 Hz, 6H, CH_3), 3.07 (m, 2H, CH), 6.74–7.23 (m, 14H, H–Ar), 7.38–7.42 (m, 2H, H–Ar), 8.14 (m, 2H, H–Ar), 13.19 (s, 1H, OH).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50.3 MHz, 302 K): δ = 21.57 (CH_3), 25.32 (CH_3), 28.76 (CH, *i*Pr), 98.66 (CH), 119.66 (CH), 123.29 (Ar), 123.29 (Ar), 124.60 (Ar), 127.06 (Ar), 127.29 (Ar), 128.36 (Ar), 128.65 (Ar), 128.73 (Ar), 129.20 (Ar), 129.65 (Ar), 129.95 (Ar), 131.86 (Ar), 133.57 (Ar), 138.97 (Ar), 145.22 (Ar), 151.16 (Ar), 165.66(C=N), 166.33 (C=N).

Anal. Calc. for $\text{C}_{34}\text{H}_{33}\text{N}_3\text{O}$: C, 81.73; H, 6.66; N, 8.41. Found: 81.75; H 6.69; N, 8.39%.

Complexes **1-Ti** and **2-Ti** have been previously published and they were prepared according to known literature procedure [36,37].

4.2. {1,3-diphenyl-4-[phenyl(phenylimino)methyl]-pyrazolone-5}TiCl₂ (**3-Ti**)

3 (2.0 g, 4.81 mmol) was dissolved in 75 ml toluene, cooled down to –78 °C and 5 equivalents (2.44 g, 24.07 mmol) of Et_3N was added to solution. The solution was added to a pre-cooled (–78 °C) solution of TiCl_4 (0.45 g, 2.4 mmol of TiCl_4 in 40 ml of toluene). The resulting mixture was allowed to warm to room temperature and stirred for 48 h. The solution was then filtered through Celite and solvent was removed in vacuo. To remove Et_3N residues, product was kept under vacuum in 40 °C for 20 h. The crude product was recrystallized from saturated toluene solution with yield of 28%.

^1H NMR (CDCl_3 , 200 MHz, 302 K): δ = 6.74–7.40 (m, 36H, Ar), 8.12 (m, 4H, H–Ar).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50.3 MHz, 302 K): δ = 100.10, 119.52, 124.26, 124.70, 125.97, 127.28, 127.31, 127.90, 128.43, 128.68, 128.84, 129.35, 130.04, 130.13, 133.40, 137.42, 138.90, 151.26, 162.72 (C=N), 165.89 (C=N).

Anal. Calc. for $\text{C}_{56}\text{H}_{40}\text{Cl}_2\text{N}_6\text{O}_2\text{Ti}$: C 70.97; H, 4.25; N, 8.87. Found: 71.08; H 4.31; N 8.79%.

MS(EI) *m/z*: 912 (M–Cl) 876 (M–2Cl) 462 (M–2Cl–L) (L = ligand).

4.3. 4-[(2,6-di-isopropylphenylimino)(phenyl)methyl]-1,3-diphenylpyrazolone-5} TiCl₂ (**4-Ti**)

Complex **4-Ti** was prepared by a similar method to that described for **3-Ti** with a yield of 26%.

^1H NMR (CDCl_3 , 200 MHz, 302 K): δ = 0.98 (d, $^3J_{\text{HH}}$ = 6.0 Hz, 12H, CH_3), 1.16 (d, $^3J_{\text{HH}}$ = 6.1 Hz, 12H, CH_3), 3.18 (m, 4H, CH), 6.72–7.27 (m, 28H, H–Ar) 7.38–7.46 (m, 4H, H–Ar) 8.15 (m, 4H, H–Ar).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50.3 MHz, 302 K): δ = 21.63 (CH_3), 25.36 (CH_3), 28.94 (CH, *i*Pr), 98.03 (CH), 119.87 (CH), 123.28 (Ar), 123.30 (Ar), 124.63 (Ar), 127.11 (Ar), 127.28 (Ar), 128.35 (Ar), 128.66 (Ar), 128.73 (Ar), 129.22 (Ar), 129.68 (Ar), 129.98 (Ar), 131.93 (Ar), 133.60 (Ar), 139.01 (Ar), 145.20 (Ar), 151.19 (Ar), 165.74(C=N), 166.45 (C=N).

Anal. Calc. for $\text{C}_{68}\text{H}_{64}\text{Cl}_2\text{N}_6\text{O}_2\text{Ti}$: C, 73.18; H, 5.78; N, 7.53. Found: C, 73.24; H, 5.85; N, 7.49%.

MS(EI) *m/z*: 1116(M), 1081 (M–Cl), 1045 (M–2Cl), 546 (M–2Cl–L), 499 (L) (L = ligand).

4.4. {4-[(benzylimino)(phenyl)methyl]-1,3-diphenylpyrazolone-5}TiCl₂ (**5-Ti**)

Complex **5-Ti** was prepared by a similar method to that described for **3-Ti** with a yield of 23%.

^1H NMR (CDCl_3 , 200 MHz, 302 K): δ = 4.92 (d, $^3J_{\text{HH}}$ = 6.2 Hz, 4H, CH_2), 6.93–7.56 (m, 36 H, H–Ar), 8.13 (d, 4H, $^3J_{\text{HH}}$ = 8.2 Hz, H–Ar).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 50.3 MHz, 302 K): δ = 48.89 (CH_2), 98.08 (CH), 99.95 (CH), 119.67 (Ar), 127.16 (Ar), 127.89 (Ar), 126.87 (Ar), 128.09 (Ar), 128.07 (Ar), 128.49 (Ar), 128.53 (Ar), 128.65 (Ar), 128.98 (Ar), 129.72 (Ar), 131.95 (Ar), 133.21 (Ar), 136.69 (Ar), 139.19 (Ar), 151.23 (Ar), 166.03 (C=N), 166.69 (C=N).

Anal. Calc. for $C_{58}H_{44}Cl_2N_6O_2Ti$: C, 71.39; H, 4.55; N, 8.61. Found: 71.49; H, 4.60; N, 8.57%.

MS(EI) m/z : 940 (M–Cl) 905 (M–2Cl) 476 (M–2Cl–L) 429 (L) (L = ligand).

4.5. {4-[(phenethylimino)(phenyl)methyl]-1,3-diphenyl-pyrazolone-5} $TiCl_2$ (**6-Ti**)

Complex **6-Ti** was prepared by a similar method to that described for **3-Ti** with a yield of 29%.

1H NMR ($CDCl_3$, 200 MHz, 302 K): δ = 2.91 (t, $^3J_{HH}$ = 7.4 Hz) 4H, CH_2), 3.47 (t, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 6.80–7.57 (m, 36, H–Ar), 8.14 (d, $^3J_{HH}$ = 8.8 Hz, 4H, H–Ar).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 50.3 MHz, 302 K): δ = 37.25 (CH_2), 47.02 (CH_2), 98.76 (CH), 120.28 (CH), 124.56 (Ar), 126.87 (Ar), 127.05 (Ar), 127.22 (Ar), 127.90 (Ar), 128.36 (Ar), 128.48 (Ar), 128.69 (Ar), 128.98 (Ar), 129.83 (Ar), 129.94 (Ar), 134.12 (Ar), 137.45 (Ar), 139.23 (Ar), 151.28 (Ar), 165.94 (C=N), 167.13 (C=N).

Anal. Calc. for $C_{60}H_{48}Cl_2N_6O_2Ti$: C, 71.79; H, 4.82; N, 8.37; Found: C, 71.83; H, 4.84; N, 8.34%.

MS(EI) m/z : 1004 (M), 968 (M–Cl), 933 (M–2Cl), 490 (M–2Cl–L) (L = ligand).

4.6. Crystal structure studies

The single-crystal X-ray diffraction study of **3**, **5**, and **3-Ti*** were carried out on a Bruker–Nonius Kappa-CCD diffractometer at 123(2) K using Mo $K\alpha$ -radiation (λ = 0.71073 Å). Direct Methods (SHELXS-97) were used for structure solution and full-matrix least-squares refinement on F^2 (SHELXL-97). [52] H atoms were localized by difference Fourier synthesis and refined using a riding model (H(N) free). The crystals of **3** are non-merohedral twins with 2 domains.

4.6.1. Compound **3**

Yellow crystals, $C_{28}H_{21}N_3O$, M = 415.48, crystal size $0.48 \times 0.16 \times 0.08$ mm, triclinic, space group $P\bar{1}$ (No.2), a = 9.0149(6) Å, b = 11.6245(8) Å, c = 12.2481(12) Å, α = 107.866(6)°, β = 101.893(6)°, γ = 107.889(5)°, V = 1096.80(16) Å³, Z = 2, ρ (calc) = 1.258 Mg m⁻³, $F(0\ 0\ 0)$ = 436, μ = 0.078 mm⁻¹, 3864 reflexes ($2\theta_{max}$ = 50°), 3864 unique [R_{int} = 0.000], 293 parameters, R_1 ($I > 2\sigma$) = 0.080, wR_2 (all data) = 0.227, Goodness-of-fit = 1.05, largest diff. peak and hole 0.377 and -0.364 e Å⁻³.

4.6.2. Compound **5**

Yellow crystals, $C_{29}H_{23}N_3O$, M = 429.50, crystal size $0.30 \times 0.25 \times 0.20$ mm, triclinic, space group $P\bar{1}$ (No. 2), a = 10.041(1) Å, b = 10.150(1) Å, c = 11.596(1) Å, α = 94.32(1)°, β = 95.32(1)°, γ = 98.47(1)°, V = 1159.13(19) Å³, Z = 2, ρ (calc) = 1.231 Mg m⁻³, $F(0\ 0\ 0)$ = 452, μ = 0.076 mm⁻¹, 21881 reflexes ($2\theta_{max}$ = 50°), 4043 unique [R_{int} = 0.029], 301 parameters, 1 restraint, R_1 ($I > 2\sigma$) = 0.035, wR_2 (all data) = 0.081, Goodness-of-fit = 1.05, largest diff. peak and hole 0.180 and -0.195 e Å⁻³.

4.6.3. Compound **3-Ti***

Red crystals, $C_{56}H_{42}Cl_4N_6O_2Ti$, M = 1020.66, crystal size $0.20 \times 0.10 \times 0.05$ mm, triclinic, space group $P\bar{1}$ (No. 2), a = 10.650(1) Å, b = 10.943(1) Å, c = 11.967(1) Å, α = 111.24(1)°, β = 106.13(1)°, γ = 97.49(1)°, V = 1206.5(2) Å³, Z = 1, ρ (calc) = 1.405 Mg m⁻³, $F(0\ 0\ 0)$ = 526, μ = 0.450 mm⁻¹, 10150 reflexes ($2\theta_{max}$ = 50°), 4231 unique [R_{int} = 0.087], 316 parameters, 1 restraint, R_1 ($I > 2\sigma$) = 0.066, wR_2 (all data) = 0.165, Goodness-of-fit = 1.01, largest diff. peak and hole 0.361 and -0.453 e Å⁻³.

5. Supplementary material

CCDC 738034, 738035 and 738036 contain the Supplementary crystallographic data for compounds **3**, **5** and **3-Ti***. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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