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Design of Postmetallocene Catalytic Systems of ArylimineType for Olefins Polymerization: XIII.* Synthesis of Tetradentate Bis(2-hydroxy-1-naphthaldimine) Ligands and Their Complexes with Titanium(IV) Dichloride

I. I. Oleinik[a], I. V. Oleinik[a], S. S. Ivanchev[b], and G. A. Tolstikov[a]

[a]*Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090, Russia*
e-mail: oleynik@nioch.nsc.ru
[b]*St. Petersburg Division of Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Russia*

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Abstract— Reactions of 2-hydroxy-1-naphthaldehyde with 1,4-diaminobutane, 1,6-diaminohexane, 4,4'-methylenedianiline and its alkyl- and cycloalkyl-sybstituted derivatives, with 4,4'-sulfonyldianiline, 2,2'- and 4,4'-oxydianiline, 4,4'-(1,4-phenylenebisoxy)dianiline, 4,4'-[propane-2,2-diylbis(1,4-phenylenebisoxy)]dianiline, and *p*-terphenyl-4,4''-diamine afforded a series of the corresponding diimines that at treating with $TiCl_2(OPr\text{-}i)_2$ formed mono- and binuclear complexes of titanium(IV) dichloride with tetradentate ligands $LTiCl_2$ and $L_2(TiCl_2)_2$.

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Desingning new highly effective catalytic systems remains an urgent task for the need in new polymers is still great and the opportunity for the control of their structure and properties depends primarily on the development of catalysts with specific structure [2]. In the preceding paper [1] we substantiated the prospects in the preparation of new catalysts for olefins polymerization through the structure modification of α-diimine, diiminopyridine, and bis(salicylaldimine) complexes consisting in the binding the imine substituents by versatile bridges by using primary alkyl- or aryldiamines in the synthesis of ligands of the modified complexes.

The theoretical basis of this approach to the refining of the structure of the postmetallocene complexes aiming at increasing the catalytic activity and the temperature range of their efficient operation is the concept that to the ligand surrounding the processes are sensitive leading to the decrease in the catalytic activity, to the loss of the "living" character of the polymerization and to the formation of low-molecular polymers at elevated temperature [3] (chain transfer and β-hydride transfer, transfer of the ligand to the aluminum cocatalyst [4], 1,2-"migration" insertion of the alkyl ligand into the C=N bond [5], and "bimolecular deactivation" [6]). It is expectable that since the ligands are of polydentate character the modified catalysts should be more stable against the thermal deactivation for in this event the dissociation becomes stepwise and the reverse process is intramolecular. The latter fact is especially important for the olefin polymerization under homogeneous conditions is carried out at very low catalyst concentration (10^{-4}–10^{-8} mol l^{-1}).

Depending on the bridge structure in the tetradentate bis(phenoxyimine) ligands and on the synthesis conditions in complexing with halides of the IV group transition metals two types of complexes can be obtained, mononuclear $LMCl_2$ or binuclear $L_2(MCl_2)_2$. Our interest in polynuclear complexes [7], in particular, in binuclear phenoxyimine ones [8, 9], is due to the hope that alongside the properties inherent to the mononuclear complexes they would exhibit specific catalytic behavior depending on the bridge character as it has been found in homobinuclear metallocenes. It is presumable that the

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* For Communication XII, see [1].

binuclear complexes apart from the dissociative stability due to the polidentate character of ligands would be more stable against the bimolecular deactivation since the larger steric loading of the molecule should more efficiently prevent the mutual contacts of the active centers.

The use in the polymerization of binuclear complexes opens an opportunity to obtain quite new polymer materials that are not produced in the presence of mononuclear analogs because of the “active centers cooperation” [10] observed only in the olefins polymerization on the binuclear metallocenes and resulting in the formation of high-molecular polymer with a wide molecular-weight distribution, with improved morphology, in the shift of the maximum of catalytic activity to higher temperature, in higher branching in ethylene homopolymerization and in larger fraction of α-olefin in the copolymerization [11].

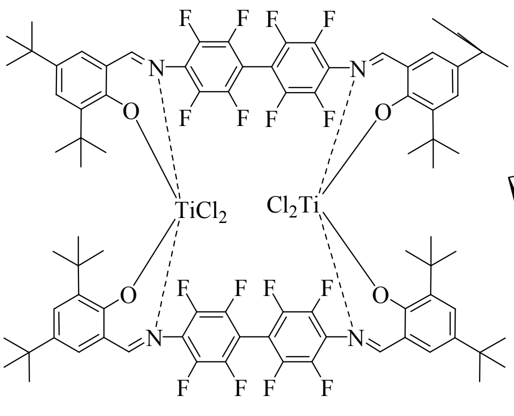
The catalytic activity of complex **A** and its mononuclear analog in ethylene and propylene polymerization was compared in [12]. The activity of the binuclear complex was considerably lower than that of the mononuclear, and the former practically instantly deactivated at 90°C. It was concluded from the characteristics of polymers obtained that the mechanism of the chain propagation and chain transfer in the course of the polymerization was materially identical, and the main process limiting the chain propagation was the bimolecular reaction of the active centers with the growing polymer chain. These data showed the absence of the “active centers cooperation”. Binuclear complex **B** of the monophenoxyimine type is considerably more active that the corresponding mononuclear analog in the ethylene homopolymerization and provides larger amount of 1-hexene units in the copolymerization [13]. These results were ascribed to the effect of “active centers cooperation”. It was shown in [8] that binuclear complexes **C** made it possible to obtain with high efficiency even at 70°C linear polyethylene of high and superhigh molecular weight possessing an elevated melting point.

The examples cited above show that the now existing data on the synthesis and catalytic properties of binuclear complexes with tetradentate phenoxyimine ligands are scanty. In order to describe the structure of these complexes required for the operation of the “active centers cooperation” effect it is necessary to investigate a set of complexes with versatile tetradentate ligands.

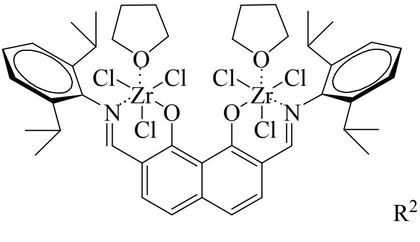
In this work in the frame of the systematic investigation of the influence on the catalytic activity of metallocomplexes of their structural modification [1, 8, 9, 14, 15] we describe the preparation of tetradentate bis(2-hydroxy-1-naphthaldimine) ligands containing various diamine spacers, and their complexes with titanium(IV) dichloride aiming at making them available for testing as catalysts of alkenes polymerization. The 2-hydroxy-1-naphthaldehyde (**I**) was selected as the carbonyl component since in patent [16] complexes with bidentate ligands had been described based on vicinal isomers of hydroxynaphthaldehydes.

The synthesis of tetradentate ligands is underlain by the reaction of the vicinal hydroxyaldehyde with primary diamines formerly performed by an example of substituted salicylaldehydes [8, 9, 12]. We extended this procedure to the preparation of new bis(2-hydroxy-1-naphthaldimine) ligands **III** and optimized the conditions of their synthesis.

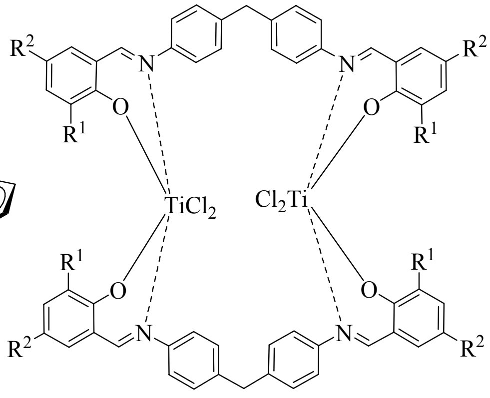
The reaction of hydroxynaphthaldehyde **I** with 1,4-diaminobutane (**IIa**) and 1,6-diaminohexane (**IIb**) in methanol at room temperature required 30 min and no catalyst providing in a quantitative yield the corresponding diimines **IIIa** and **IIIb**. The reaction of diamines **IIc–IIh** proceeded at boiling in methanol in the presence of



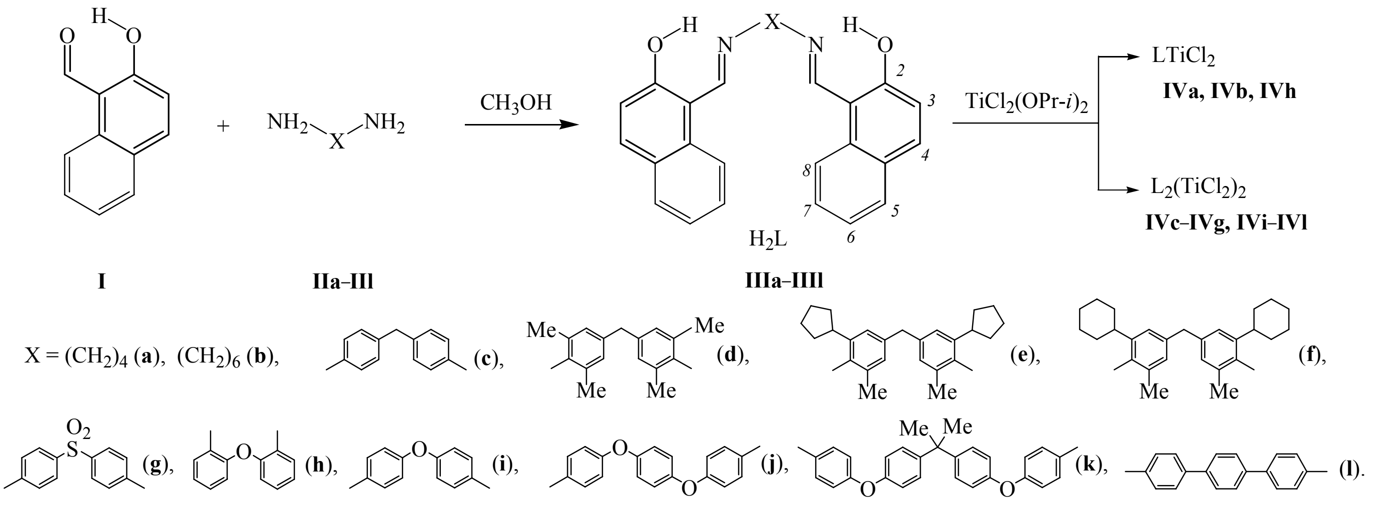
A



B



C



catalytic quantity of formic acid and completed within 0.5–7 h (yields 94–99%). The condensation of hydroxynaphthaldehyde **I** at both amino groups of diamines **IIi–IIl** occurred at boiling the initial compounds in a mixture of methanol and dichloromethane, 1 : 1, in the presence of catalytic quantity of formic acid and afforded diimines **IIIi–IIIl** in 94–98% yield.

The structure of obtained bis(naphthaldimines) **IIIa–IIIl** was established from analytic and spectral data. ^{1}H NMR spectra suggest that the Schiff bases we obtained are individual *E*-isomers. The singlets of groups N=CH in the ^{1}H NMR spectra of bisimines appear in the region 8.51–9.64 ppm. In the spectrum of sulfonyl derivative **IIIg** the signal of the N=CH group is strongly shifted downfield (10.82 ppm). The signals of OH groups of ligands **IIIa–IIIi, IIIk** give rise to broadened singlets in the region 12.50–15.80 ppm (this downfield shift indicates the presence of an intramolecular hydrogen bond between the hydrogen of the OH group and the nitrogen atom of the imine moiety). In the ^{1}H NMR spectra of bisimines **IIIj** and **IIIl** taken in DMSO-d_6 since they were sparingly soluble in $CDCl_3$ the signal of hydroxy group was lacking. The assignment of the proton signals of the naphthalene skeleton was based on the known assignment of signals in the spectrum of 2-hydroxy-1-naphthaldehyde [17]. The spectra of diimines **IIIa** and **IIIb** prepared from diaminoalkanes contain the multiplets of CH_2 groups at 1.42–1.98 ppm and triplets of NCH_2 groups at 3.74 and 3.66 ppm, and in the spectra of diimines **IIIc–IIIf** obtained from methylenedianilines alongside the signals of aromatic protons the singlets belonging to CH_2 groups are observed at 3.82–4.03 ppm. In the IR spectra of bisimines **IIIa** and **IIIb** with methylene spacers the stretching vibrations of the C=N bond from the imine moiety give rise to a strong absorption band at 1636 and 1629 cm^{-1} respectively, whereas in the other Schiff bases the ν(N=CH) frequency is considerably lower (1622–1625 cm^{-1}). In the mass spectra of synthesized ligands a strong peak of the molecular ion was observed.

The phenoxyimine complexes of titanium(IV) dichloride are usually prepared by reaction of the deprotonated form of the ligand with titanium tetrachloride or its adduct with tetrahydrofuran [18]. Although this procedure provides the complexes in good yields it possesses obvious disadvantages for the ligand is deprotonated by the reaction with butyllithium or with alkali metal hydride. We regard as more convenient a newly developed one-stage method of the synthesis of titanium(IV) dichloride complexes [12, 19, 20] underlain by the capability of the alkoxydihalides of IV group elements to deprotonate the ligands. We chose this one-stage method since it lacks the above mentioned drawbacks for the preparation of mono- and binuclear complexes of titanium(IV) dichloride with versatile combination of substituents [8, 9, 15].

At treatment of bisimines **IIIa–IIIl** with an equimolar amount of $TiCl_2(OPr\text{-}i)_2$ in toluene solution at room temperature titanium complexes **IVa–IVl** were obtained in high yield. The complexes can be of the mono- or binuclear structure. The choice between the possible structures $LTiCl_2$ and $L_2(TiCl_2)_2$ would be easy from the molecular weight of compounds. Regretfully, we failed to determine the molecular weight of complexes **IV** due to their extremely low solubility. Still, considering the available published data on the structure of the titanium and zirconium dichlorides with tetradentate bis(salicylaldimine) ligands we may assume that ligands **IIIa, IIIb, IIIh** form mononuclear complexes $LTiCl_2$, whereas ligands **IIIc–IIIg, IIIi–IIIl** afford binuclear complexes $L_2(TiCl_2)_2$. As shown in [5, 12, 16, 20, 21] when the imine nitrogen atoms of bisimine ligands are capable due to the mobility and flexibility of the spacer to occupy the contiguous vertexes of an octahedron these ligands form mononuclear complexes $LTiCl_2$, and when the rigidity of the spacer impedes this location of the imine nitrogen atoms the binuclear complexes $L_2(TiCl_2)_2$ are formed. The assumption on difference in the structures of complexes **IVa, IVb, IVh** and those of **IVc–IVg, IVi–IVl** is in agreement with the difference in the structure of titanium dichloride complexes with the ligands obtained from salicylaldehydes with bulky substituents and diamines **IIa–IIl** [1, 8, 9] whose molecular weight has been determined. The molecular weight of analogs of complexes **IVa, IVb, IVh** corresponded to the formula $LTiCl_2$, of analogs of complexes **IVc–IVg, IVi–IVl**, to the structure $L_2(TiCl_2)_2$.

The composition of titanium dichloride complexes **IVa–IVl** is confirmed by elemental analysis and IR spectra. In the IR spectra of complexes **IVa–IVl** absorption bands appear in the region 447–478 (Ti–N) and 542–567cm^{-1} (Ti–O). The complex formation results in significant decrease in the ν(N=CH) frequency in the spectra of complexes **IVa** and **IVb** (by 10–18 cm^{-1}), whereas in the complexes **IVc–IVl** these changes not exceed 1–4 cm^{-1}. Due to low solubility of these complexes and their instability in $CDCl_3$ we failed to register their ^{1}H NMR spectra.

EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Bruker AC-200 at operating frequency 200.13 MHz. IR spectra were recorded on a spectrophotometer Vector 22 from samples pelletized with KBr. The monitoring of reactions progress and checking of the purity of compounds synthesized was carried out by TLC on Silufol UV-254 plates, eluent chloroform. The flash-chromatography [22] was performed with the use of silica gel 5–40 μ, eluent chloroform–hexane, 1 : 1. The empirical formulas of compounds obtained were calculated from the high resolution mass spectra taken of a Finnigan MAT 8200 instrument. The melting points were determined by heating compounds between glass plates at a rate 1 deg/min.

2-Hydroxy-1-naphthaldehyde was obtained by procedure [23], methylenedianilines **IId–IIf**, by method [1], 2,2'- and 4,4'-oxydianilines, by method [24].

Diimines IIIa and IIIb. A mixture of 0.172 g (1 mmol) of 2-hydroxy-1-naphthaldehyde, 0.5 mmol of the corresponding diamine **IIa** or **IIb**, and 10 ml of methanol was stirred at room temperature for 30 min till the disappearance of the initial compounds (TLC monitoring). The separated precipitate was filtered off and washed with 3 ml of methanol.

1,1'-[Tetramethylenebis(iminomethyl)]bis(2-naphthol) (IIIa). Yield 97%, mp 227–229°C. IR spectrum, ν, cm^{-1}: 1636 (N=CH). ^{1}H NMR spectrum ($CDCl_3$+DMSO-d_6), δ, ppm: 1.75–1.98 m (4H, CH_2), 3.74 t (4H, NCH_2, *J* 7.5 Hz), 6.82 d (2H, H^3, *J* 8.5 Hz), 7.19 t (2H, H^6, *J* 8 Hz), 7.40 t (2H, H^6, *J* 8 Hz), 7.58 d (2H, H^5, *J* 8 Hz), 7.66 d (1H, H^4, *J* 8.5 Hz), 7.93 d (1H, H^8, *J* 8 Hz), 8.51 s (2H, CH=N), 13.85 br.s (2H, OH). Found $[M]^+$ 396.18407. $C_{26}H_{24}N_2O_2$. Calculated *M* 396.18377.

1,1'-[Hexamethylenebis(iminomethyl)]bis(2-naphthol) (IIIb). Yield 95%, mp 173–174°C (175°C [25]). IR spectrum, ν, cm^{-1}: 1629 (N=CH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.40–1.57 m (4H, CH_2), 1.61–1.82 m (4H, CH_2), 3.66 t (4H, NCH_2, *J* 7.5 Hz), 6.73 d (2H, H^3, *J* 8.5 Hz), 7.14 t (2H, H^6, *J* 8 Hz), 7.38 t (2H, H^7, *J* 8 Hz), 7.56 d (2H, H^5, *J* 8 Hz), 7.65 d (1H, H^4, *J* 8.5 Hz), 8.00 d (1H, H^8, *J* 8 Hz), 9.04 s (2H, CH=N), 14.25 br.s (2H, OH). Found $[M]^+$ 424.21464. $C_{28}H_{28}N_2O_2$. Calculated *M* 424.21506.

Diimines IIIc–IIIh. A mixture of 0.172 g (1 mmol) of 2-hydroxy-1-naphthaldehyde, 0.5 mmol of an appropriate diamine **IIc–IIh**, 10 ml of methanol, and 5 mg of anhydrous formic acid was boiled for 0.5–7 h till the disappearance of the initial compounds (TLC monitoring). On cooling the reaction mixture the separated precipitate was filtered off and washed with 3 ml of methanol.

1,1'-{Methylenebis[(1,4-phenylene)iminomethyl]}bis(2-naphthol) (IIIc). Yield 96%, mp 248–250°C (247–248°C [26]). IR spectrum, ν, cm^{-1}: 1624 (N=CH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.03 s (2H, CH_2), 6.97 d (4H, $H^{3',5'}$, *J* 7.8 Hz), 7.30 d (2H, H^3, *J*8.5 Hz), 7.38 t (2H, H^6, *J* 8 Hz), 7.53 t (2H, H^7, *J* 8 Hz), 7.58 d (2H, H^5, *J* 8 Hz), 7.76 d (2H, H^4, *J* 8.5 Hz), 7.89 d (2H, H^8, *J* 8 Hz), 8.45 d (4H, $H^{2',6'}$, *J* 7.8 Hz), 9.60 s (2H, CH=N), 15.80 br.s (2H, OH). Found $[M]^+$ 506.20023. $C_{35}H_{26}N_2O_2$. Calculated *M* 506.19942.

1,1'-{Methylenebis[(3,5-dimethyl-1,4-phenylene)iminomethyl]}bis(2-naphthol) (IIId). Yield 95%, mp 213–214°C. IR spectrum, ν, cm^{-1}: 1624 (N=CH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.26 s (12H, CH_3), 3.82 s (2H, CH_2), 6.91 s (4H, $H^{3',5'}$), 7.12 d (2H, H^3, J 8.5 Hz), 7.25 t (2H, H^6, J 8 Hz), 7.40 t (2H, H^7, J 8 Hz), 7.68 d (2H, H^5, J 8 Hz), 7.78 d (2H, H^4, J 8.5 Hz), 7.96 d (2H, H^8, J 8 Hz), 9.13 s (2H, CH=N), 14.85 br.s (2H, OH). Found $[M]^+$ 562.26200. $C_{39}H_{34}N_2O_2$. Calculat-ed M 562.26201.

1,1'-{Methylenebis[(3-methyl-5-cyclopentyl-1,4-phenylene)iminomethyl]}bis(2-naphthol) (IIIe). Yield 99%, mp 99–100°C. IR spectrum, ν, cm^{-1}: 1624 (N=CH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.51–2.08 m (16H, CH_2), 2.24 s (6H, Me), 2.99–3.22 m (2H, CH), 3.86 s (2H, CH_2); 6.84 s, 7.00 C (4H, $H^{3',5'}$); 7.12 d (2H, H^3, J 8.5 Hz), 7.23 t (2H, H^6, J 8 Hz), 7.38 t (2H, H^7, J 8 Hz), 7.67 d (2H, H^5, J 8 Hz), 7.77 d (2H, H^4, J 8.5 Hz), 7.96 d (2H, H^8, J 8 Hz), 9.12 s (2H, CH=N), 14.75 br.s (2H, OH). Found $[M]^+$ 562.26200. $C_{39}H_{34}N_2O_2$. Calculated M 562.26201.

1,1'-{Methylenebis[(3-methyl-5-cyclohexyl-1,4-phenylene)iminomethyl]}bis(2-naphthol) (IIIf). Yield 99%, mp 113–114°C. IR spectrum, ν, cm^{-1}: 1624 (N=CH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.19–1.53 m (12H, CH_2), 1.59–1.98 m (8H, CH_2), 2.26 s (6H, Me), 2.55–2.85 m (2H, CH), 3.86 s (2H, CH_2); 6.84 s, 6.97 s (4H, $H^{3',5'}$); 7.14 d (2H, H^3, J 8.5 Hz), 7.23 t (2H, H^6, J 8 Hz), 7.39 t (2H, H^7, J 8 Hz), 7.68 d (2H, H^5, J 8 Hz), 7.79 d (2H, H^4, J 8.5 Hz), 7.96 d (2H, H^8, J 8 Hz), 9.14 s (2H, CH=N), 14.80 br.s (2H, OH). Found $[M]^+$ 698.38734. $C_{49}H_{50}N_2O_2$. Calculated M 698.38721.

1,1'-{Sulfonylbis[(1,4-phenylene)iminomethyl]}bis(2-naphthol) (IIIg). Yield 94%, mp 267–269°C (265°C [27]). IR spectrum, ν, cm^{-1}: 1624 (N=CH). ^{1}H NMR spectrum ($CDCl_3$ + DMSO-d_6), δ, ppm: 6.59 d (4H, $H^{3',5'}$, J 7.8 Hz), 7.13 d (2H, H^3, J 8.5 Hz), 7.41 t (2H, H^6, J 8 Hz), 7.58 t (2H, H^7, J 8 Hz), 7.80 d (2H, H^5, J 8 Hz), 7.88 d (2H, H^4, J 8.5 Hz), 8.02 d (2H, H^8, J 8 Hz), 8.69 d (4H, $H^{2',6'}$, J 7.8 Hz), 10.82 s (2H, CH=N), 12.50 br.s (2H, OH). Found $[M]^+$ 556.14498. $C_{34}H_{24}N_2O_4S$. Calculated M 556.14567.

1,1'-{Oxybis[(1,2-phenylene)iminomethyl]}-bis(2-naphthol) (IIIh). Yield 95%, mp 222–224°C. IR spectrum, ν, cm^{-1}: 1623 (N=CH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.85–7.31 m (8H_{arom}), 7.35–7.82 m (6H_{arom}), 7.89–8.06 m (4H_{arom}), 8.34 d (2H, H^8, J 8 Hz), 9.32 s (2H, CH=N), 15.35 br.s (2H, OH). Found $[M]^+$ 508.17900. $C_{34}H_{24}N_2O_3$. Calculated M 508.17868.

Diimines IIIi–IIIl. A mixture of 0.172 g (1 mmol) of 2-hydroxy-1-naphthaldehyde, 0.5 mmol of an appropriate diamine **IIi–IIl**, 10 ml of methanola, 10 ml of anhydrous dichloromethane, and 5 mg of anhydrous formic acid was boiled for 0.5–7 h till the disappearance of the initial compounds (TLC monitoring). The solvents were distilled off on a rotary evaporator in a vacuum of a water-jet pump at the bath temperature 45°C, the residue of compounds **IIIi, IIIk, IIIl** was subjected to flash-chromatography. From the first bright yellow fraction the solvent was evaporated, the residue was ground with 5 ml of methanol, the precipitate was filtered off. When isolating diimine **IIIj** the residue after distilling off the solvents was recrystallized from a mixture DMF–methanol, 1:1.

1,1'-{Oxybis[(1,4-phenylene)iminomethyl]}-bis(2-naphthol) (IIIi). Yield 95%, mp 176–177°C. IR spectrum, ν, cm^{-1}: 1622 (N=CH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.05–7.43 m (12H_{arom}), 7.54 t (2H, H^7, J 8 Hz), 7.76 d (2H, H^5, J 8 Hz), 7.86 d (2H, H^4, J 8 Hz), 8.15 d (2H, H^8, J 7.8 Hz), 9.39 s (2H, CH=N), 15.15 br.s (2H, OH). Found $[M]^+$ 508.17799. $C_{34}H_{24}N_2O_3$. Calculated M 508.17868.

1,1'-{(1,4-Phenylenedioxy)bis[(1,4-phenylene)-iminomethyl]}bis(2-naphthol) (IIIj). Yield 94%, mp 245–246°C. IR spectrum, ν, cm^{-1}: 1622 (N=CH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.01–7.19 m (10H_{arom}), 7.36 t (2H, H^6, J 8 Hz), 7.55 t (2H, H^7, J 8 Hz), 7.59–7.70 m (4H_{arom}), 7.80 d (2H, H^5, J 8 Hz), 7.95 d (2H, H^4, J 8.5 Hz), 8.46 d (2H, H^8, J 8 Hz), 9.64 s (2H, CH=N). Found $[M]^+$ 600.20490. $C_{40}H_{28}N_2O_4$. Calculated M 600.20489.

1,1'-{(Propane-2,2-diyl)bis[(1,4-phenylene)-oxy(1,4-phenylene)iminomethyl]}bis(2-naphthol) (IIIk). Yield 95%, mp 152–154°C. IR spectrum, ν, cm^{-1}: 1623 (N=CH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.70 C (6H, Me), 6.98–7.41 m (20H_{arom}), 7.55 t (2H, H^7, J 8 Hz), 7.75 d (2H, H^5, J 8 Hz), 7.83 d (2H, H^4, J 8 Hz), 8.13 d (2H, H^8, J 8 Hz), 9.37 s (2H, CH=N), 15.05 br.s (2H, OH). Found $[M]^+$ 718.28256. $C_{49}H_{38}N_2O_4$. Calculated M 718.28314.

1,1'-[(4,4''-*p*-Terphenylene)bis(iminomethyl)]-bis(2-naphthol) (IIIl). Yield 98%, mp 344–345°C (345–347°C [26]). IR spectrum, ν, cm^{-1}: 1625 (N=CH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.98 d (4H_{arom}, J 8 Hz), 7.09–7.41 m (16H_{arom}), 7.55 t (2H, H^7, J 8 Hz), 7.75 d (2H, H^5, J 8 Hz), 7.83 d (2H, H^4, J 8 Hz), 8.13 d (2H, H^8, J 7.8 Hz), 9.70 s (2H, CH=N). Found $[M]^+$ 568.21450. $C_{40}H_{28}N_2O_2$. Calculated M 568.21506.

Titanium(IV) dichloride complexes IVa–IVl. A mixture of 1 mmol of ligand **IIIa–IIIl**, 40 ml of anhydrous dichloromethane, and 1 mmol of $TiCl_2(OPr\text{-}i)_2$

as a solution (0.350 mmol/g) in anhydrous toluene was stirred under an argon atmosphere for 24 h. The solvents were distilled off in a vacuum of a water-jet pump, the residue was maintained in a vacuum of an oil; pump for 1 h at 100°C.

[1,1'-Tetramethylenebis(iminomethyl)bis(2-naphthyloxy)]titanium(IV) dichloride (IVa). Dark orange powder. Yield 97%. IR spectrum, ν, cm^{-1}: 1618 (C=N), 542 (Ti–O), 447 (Ti–N). Found, %: C 60.49; H 4.43; Cl 13.65; N 5.58. $C_{26}H_{22}Cl_2N_2O_4Ti$. Calculated, %: C 60.84; H 4.32; Cl 13.82; N 5.46.

[1,1'-Hexamethylenebis(iminomethyl)bis(2-naphthyloxy)]titanium(IV) dichloride (IVb). Brown powder. Yield 99%. IR spectrum, ν, cm^{-1}: 1619 (C=N), 550 (Ti–O), 460 (Ti–N). Found, %: C 61.90; H 4.95; Cl 13.16; N 5.27. $C_{28}H_{26}Cl_2N_2O_4Ti$. Calculated, %: C 62.13; H 4.84; Cl 13.10; N 5.18.

Bis{1,1'-methylenebis[(1,4-phenylene)-iminomethyl]bis(2-naphthyloxy)}bis[titanium(IV) dichloride] (IVc). Red-brown powder. Yield 94%. IR spectrum, ν, cm^{-1}: 1623 (C=N), 550 (Ti–O), 478 (Ti–N). Found, %: C 67.09; H 4.01; Cl 11.46; N 4.46. $C_{70}H_{48}Cl_4N_4O_4Ti_2$. Calculated, %: C 67.44; H 3.88; Cl 11.37; N 4.49.

Bis{1,1'-methylenebis[(3,5-dimethyl-1,4-phenylene)iminomethyl]bis(2-naphthyloxy)}-bis[titanium(IV) dichloride] (IVd). Dark brown powder. Yield 99%. IR spectrum, ν, cm^{-1}: 1621 (C=N), 556 (Ti–O), 470 (Ti–N). Found, %: C 68.78; H 4.89; Cl 10.15; N 4.25. $C_{78}H_{64}Cl_4N_4O_4Ti_2$. Calculated, %: C 68.94; H 4.75; Cl 10.44; N 4.12.

Bis{1,1'-methylenebis[(3-methyl-5-cyclopentyl-1,4-phenylene)iminomethyl]bis(2-naphthyloxy)}-bis[titanium(IV) dichloride] (IVe). Dark brown powder. Yield 95%. IR spectrum, ν, cm^{-1}: 1620 (C=N), 555 (Ti–O), 465 (Ti–N). Found, %: C 71.67; H 5.79; Cl 8.86; N 3.78. $C_{94}H_{88}Cl_4N_4O_4Ti_2$. Calculated, %: C 71.67; H 5.63; Cl 9.00; N 3.56.

Bis{1,1'-methylenebis[(3-methyl-5-cyclohexyl-1,4-phenylene)iminomethyl]bis(2-naphthyloxy)}bis-[titanium(IV) dichloride] (IVf). Dark brown powder. Yield 92%. IR spectrum, ν, cm^{-1}: 1621 (C=N), 559 (Ti–O), 469 (Ti–N). Found, %: C 71.98; H 5.98; Cl 8.49; N 3.59. $C_{98}H_{96}Cl_4N_4O_4Ti_2$. Calculated, %: C 72.15; H 5.93; Cl 8.69; N 3.43.

Bis{1,1'-sulfonylbis[(1,4-phenylene)iminomethyl]bis(2-naphthyl-oxy)}bis[titanium(IV) dichloride] (IVg). Red-brown powder. Yield 99%. IR spectrum, ν, cm^{-1}: 1622 (C=N), 560 (Ti–O), 460 (Ti–N). Found, %: C 60.38; H 3.41; Cl 10.29; N 4.28. $C_{68}H_{44}Cl_4N_4O_8S_2Ti_2$. Calculated, %: C 60.64; H 3.29; Cl 10.53; N 4.16.

{1,1'-Oxybis[(1,2-phenylene)iminomethyl]bis-(2-naphthyloxy)}titanium(IV) dichloride (IVh). Dark brown powder. Yield 92%. IR spectrum, ν, cm^{-1}: 1620 (C=N), 559 (Ti–O), 464 (Ti–N). Found, %: C 65.40; H 3.60; Cl 11.18; N 4.47. $C_{34}H_{22}Cl_2N_2O_3Ti$. Calculated, %: C 65.30; H 3.55; Cl 11.34; N 4.48.

Bis{1,1'-oxybis[(1,4-phenylene)iminomethyl]-bis(2-naphthyloxy)}bis[titanium(IV) dichloride] (IVi). Brown powder. Yield 99%. IR spectrum, ν, cm^{-1}: 1621 (C=N), 550 (Ti–O), 460 (Ti–N). Found, %: C 65.18; H 3.68; Cl 11.15; N 4.64. $C_{68}H_{44}Cl_4N_4O_6Ti_2$. Calculated, %: C 65.30; H 3.55; Cl 11.34; N 4.48.

Bis{1,1'-(1,4-phenylenedioxy)bis[(1,4-phenylene)-iminomethyl]bis(2-naphthyloxy)}bis-[titanium(IV) dichloride] (IVj). Dark brown powder. Yield 98%. IR spectrum, ν, cm^{-1}: 1621 (C=N), 550 (Ti–O), 461 (Ti–N). Found, %: C 66.78; H 3.84; Cl 9.70; N 4.02. $C_{80}H_{52}Cl_4N_4O_8Ti_2$. Calculated, %: C 66.97; H 3.65; Cl 9.88; N 3.90.

Bis{1,1'-(propane-2,2-diyl)bis[(1,4-phenylene)-oxy(1,4-phenylene)iminomethyl]bis(2-naphthyloxy)}bis[titanium(IV) dichloride] (IVk). Orange-brown powder. Yield 99%. IR spectrum, ν, cm^{-1}: 1622 (C=N), 567 (Ti–O), 460 (Ti–N). Found, %: C 70.46; H 4.51; Cl 8.62; N 3.49. $C_{98}H_{72}Cl_4N_4O_8Ti_2$. Calculated, %: C 70.43; H 4.34; Cl 8.49; N 3.35.

Bis{[1,1'-(4,4''-*p*-terphenylene)bis(iminomethyl)]-bis(2-naphthyloxy)}bis-[titanium(IV) dichloride] (IVl). Dark brown powder. Yield 99%. IR spectrum, , cm^{-1}: 1624 (C=N), 551 (Ti–O), 470 (Ti–N). Found, %: C 69.78; H 3.97; Cl 10.15; N 4.23. $C_{80}H_{52}Cl_4N_4O_4Ti_2$. Calculated, %: C 70.09; H 3.82; Cl 10.34; N 4.09.

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