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Design of Postmetallocene Catalytic Systems of Arylimine Type for Olefin Polymerization: XV.* Synthesis of (*N*-Aryl)salicylaldimine Ligands Containing a But-3-enyloxy Group 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 Branch of Russian Academy of Sciences,*
Novosibirsk, 630090 Russia
e-mail: oleynik@nioch.nsc.ru
[b]*St. Petersburg Branch of Boreskov Institute of Catalysis,*
Siberian Branch of Russian Academy of Sciences, Novosibirsk, Russia

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Abstract—A series of (*N*-aryl)salicylaldimines was synthesized by the reaction of salicylaldehydes substituted in the positions *3* and *5* by bulky *tert*-butyl or α-cumyl groups with hydrochlorides of *o*-, *m*-, and *p*-(but-3-enyloxy) aniline in the presence of triethylamine. The obtained compounds formed by the reaction with $TiCl_2(OPr\text{-}i)_2$ complexes of titanium(IV) dichloride L_2TiCl_2.

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The study of kinetic features of ethylene polymerization on (*N*-aryl)salicylaldimine complexes of titanium(IV) dichloride containing an allyloxyphenylimino group activated with methylalumoxane revealed the ability of the catalytic system to produce polyethylenes of superhigh molecular weight possessing an improved morphology of particles [2]. The combination of results obtained allows a conclusion that this feature of the studied catalytic systems is due to the ability of these complexes to immobilize on the polyethylene macromolecules by copolymerization with ethylene.

The existing data on metallocene and bisaryliminopyridine complexes containing an ω-alkenyl group indicate that the activity of the catalytic system is affected by the length of the alkenyl substituent [3]. Apparently in the case of (*N*-aryl)salicylaldimine complexes of titanium(IV) dichloride it is possible to observe a similar dependence. Inasmuch as the published data on the synthesis and properties of such complexes are absent the problem of the control of the complex self-immobilization, of the activity of the obtained heterogeneous catalyst, and of the properties of the formed polyolefin by varying the number of the methylene units in the alkenyl substituent and changing its position in the benzene ring remains unsolved. In order to prove experimentally the mentioned assumption we describe in this report the synthesis of (*N*-aryl)salicylaldimine ligands and complexes of titanium(IV) dichloride containing isomeric *o*-, *m*-, and *p*-(but-3-enyloxy)phenylimino groups. The obtained regularities of the variation in the catalytic activity at the changes in the substituents ensemble in the salicylidene fragment of the ligand show that at certain combination of the substituents optimum values are reached of the catalytic activity and the molecular weight distribution of produced polymers [2, 4]. Evidently the revealed regularities are of a general character, and just these combinations of substituents were used in the synthesis of new salicylaldimine complexes of titanium(IV) dichloride.

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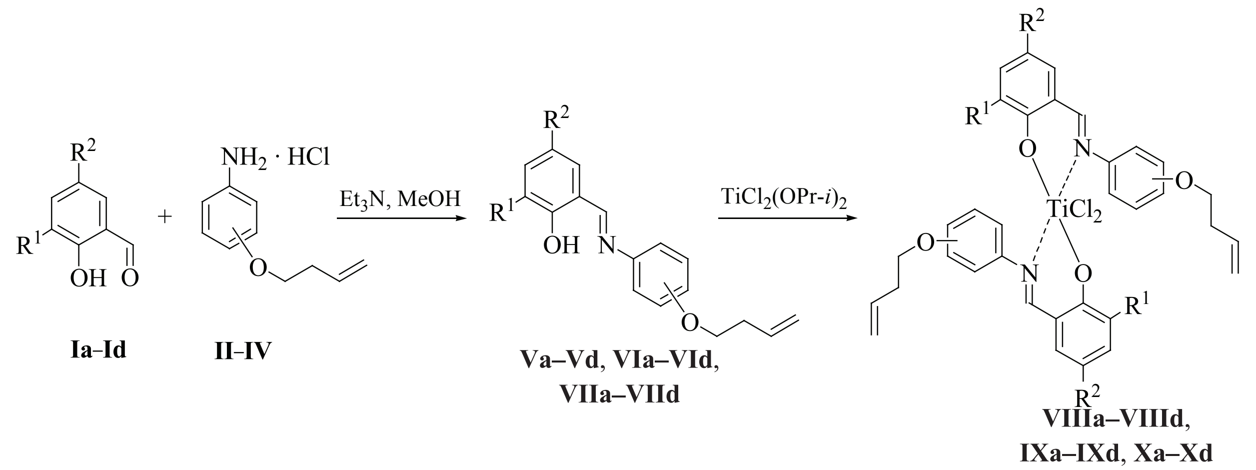
* For Communication XIV, see [1].

The isomeric salicylaldimines **Va–Vd–VIIa–VIId** containing in the arylimine moiety a but-3-enyloxy group were obtained by the reaction of substituted salicylaldehydes **Ia–Id** with but-3-enyloxyanilines generated *in situ* by treating their hydrochlorides **II–IV** with triethylamine at boiling in methanol for 10–15 h. The yields of the corresponding salicylaldimines **Va–Vd–VIIa–VIId** attained 85–96%.



$R^1 = t$-Bu, R^2 = H (**a**); $R^1 = R^2 = t$-Bu (**b**); R^1 = CMe$_2$(Ph), R^2 = H (**c**); $R^1 = R^2$ = CMe$_2$(Ph) (**d**); 2-(but-3-enyloxy) (**II, V, VIII**); 3-(but-3-enyloxy) (**III, VI, IX**); 4-(but-3-enyloxy) (**IV,VII, X**).

The structure of imines **Va–Vd, VIa–VId, VIIa–VIId** was established from the combination of analytic and spectral data. The ^{1}H NMR spectra suggest that the Schiff bases we prepared are individual *E*-isomers. The ^{1}H NMR spectra of compounds **Va–Vd, VIa–VId, VIIa–VIId** contain the singlets of the N=CH group in the region 8.45–8.66 ppm. The signals of OH group of the salicylaldimines appear as broadened singlets in the region 13.23–14.41 ppm. The but-*3*-enyloxy group of the Schiff bases **Va–Vd, VIa–VId, VIIa–VIId** gives rise to a characteristic set of signals: The protons of the OCH$_2$ moiety appear as a triplet in the region 3.95–4.11 ppm, the terminal protons appear in the region 4.98–5.24 ppm as two separate doublets of doublets of triplets with the appropriate vicinal spin-spin coupling constants (J_{cis} 10.0–10.4 and J_{trans} 17.0–17.4 Hz), the protons of OCH$_2$C$\underline{H}_2$CH=CH$_2$ group are observed as a multiplet in the region 2.44–2.63 ppm, and the protons of OCH$_2$CH$_2$C$\underline{H}$=CH$_2$ resonated as a doublet of doublets of triplets at 5.80–5.99 ppm.

IR spectra of compounds **Va–Vd, VIa–VId, VIIa–VIId** contain a strong absorption band in the region 1610–1619 cm^{-1} corresponding to the stretching vibrations of the C=N bond of the imine moiety. The mass spectra of the synthesized ligands contain strong peaks of the molecular ions.

The complexes of titanium(IV) dichloride were synthesized in one stage [5] by the reaction of the ligand with TiCl$_2$(OPr-*i*)$_2$. At treating imines **Va–Vd, VIa–VId, VIIa–VIId** with equimolar amount of the TiCl$_2$(OPr-*i*)$_2$ solution in toluene at room temperature complexes of titanium(IV) dichloride **VIIIa–VIIId**, **IXa–IXd**, **Xa–Xd** were obtained in high yields.

The composition of complexes **VIIIa–VIIId**, **IXa–IXd**, **Xa–Xd** is confirmed by combined data of the elemental analysis and the IR spectra from pellets with KBr. In the IR spectra the absorption bands in the region 442–476 (Ti-N), and 541–581cm^{-1} (Ti–O) were observed. At the complex formation the frequency of ν(N=CH) decreased for the complexes with the *ortho*- (**VIIIa–VIIId**) and *para*-location (**Xa–Xd**) of the oxybutenyl substituents by 2–7 cm^{-1}, for the *meta*-isomers **IXa–IXd**, by 15–21 cm^{-1}.

In the ^{1}H NMR spectra of complexes **VIIIa–VIIId**, **IXa–IXd**, **Xa–Xd** alongside the protons of the oxybutenyl fragments, *tert*-butyl and cumyl substituents, and the aromatic protons the characteristic signals are pesent of the protons of HC=N group of the stereoisomeric forms of complexes **VIIIa–VIIId**, **IXa–IXd**, **Xa–Xd** in the region 7.57–8.19 ppm; the singlets of OH group present in the spectra of imines **Va–Vd, VIa–VId, VIIa–VIId** are lacking.

The isomeric (but-3-enyloxy)anilines were synthesized along the protocol including the alkenylation of *o*-, *m*-, and *p*-acetylaminophenols followed by the removal of the acetyl protection analogous to the procedure [6], and for convenient handling and storage the products were converted into hydrochlorides **II–IV**.

EXPERIMENTAL

The analytic and spectral measurements were carried out in the Chemical Service Center for collective use of the Siberian Division, Russian Academy of Sciences.

^{1}H NMR spectra were registered on a spectrometer Bruker AV-400 at operating frequency 400.13 MHz from solutions of compounds in $CDCl_3$. IR spectra were recorded on a spectrophotometer Vector 22 from crystalline samples as pellets with KBr, from oily substances in a pure state. The reaction progress and the purity of compounds obtained were monitored by TLC on Silufol UV-254 plates, eluent chloroform. Elemental analyses were carried out on a CHNS-analyzer Euro EA 3000. The elemental formulas of compounds obtained were calculated from the high resolution mass spectra measured on a spectrometer DFS Thermo Electron Corporation. The melting points were determined in capillaries on an instrument Mettler Toledo FP90 at the heating rate 1 deg/min.

Substituted salicylaldehydes **Ia–Id** and $TiCl_2(OPr\text{-}i)_2$ were prepared by procedures [7, 8].

***o*-, *m*-, and *p*-(But-3-enyloxy)anilines and their hydrochlorides II–IV**. A mixture of 15.1 g (0.1 mol) of an appropriate isomer of acetylaminophenol, 100 ml of acetone, and 13.8 g (0.1 mol) of anhydrous potassium carbonate was stirred for 1 h. To the obtained slurry was added 2 ml of dimethylformamide, ~10–20 mg of potassium iodide, and 20.25 g (0.105 mol) of 4-bromobut-1-ene. The reaction mixture was boiled for 20 h. The precipitate was filtered off, washed with acetone (3 × 20 ml). From the combined filtrates acetone was distilled off, to the residue 75 ml of ethanol and 11 ml (0.11 mol) of conc. hydrochloric acid was added, and the mixture was boiled for 8 h. Ethanol (50 ml) was distilled off on the rotary evaporator, the residue was diluted with 50 ml of water, 20% solution of sodium hydroxide was added to pH 8 , the (but-3-enyloxy)aniline was extracted into methyl *tert*-butyl ether (4 × 30 ml), the extract was dried with $MgSO_4$. The solvent was distilled off, the residue was distilled in a vacuum.

***o*-(But-3-enyloxy)aniline**. Yield 52%, bp 132–134°C (10–12 mm Hg). Oily substance, fast darkening in air. ^{1}H NMR spectrum, δ, ppm: 2.58 m (2H, $OCH_2C\underline{H}_2CH=CH_2$), 3.80 br.s (2H, NH_2), 4.05 t (2H, $OC\underline{H}_2CH_2CH=CH_2$, *J* 6.6 Hz), 5.13 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 10.3, 1.8, 1.1 Hz), 5.20 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 17.2, 1.8, 1.5 Hz), 5.92 d.d.t (1H, $OCH_2CH_2\underline{CH}=CH_2$, *J* 17.2, 10.3, 6.8 Hz), 6.71–6.81 m ($4H_{arom}$). Found $[M]^+$ 163.0996. $C_{10}H_{13}NO$. Calculated *M* 163.0997 (cf. [6]).

***m*-(But-3-enyloxy)aniline**. Yield 75%, bp 133–135°C (5 mm Hg). Oily substance, fast darkening in air. ^{1}H NMR spectrum, δ, ppm: 2.52 m (2H, $OCH_2C\underline{H}_2CH=CH_2$), 3.64 br.s (2H, NH_2), 3.96 t (2H, $OC\underline{H}_2CH_2CH=CH_2$, *J* 6.7 Hz), 5.10 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 10.3, 1.9, 1.1 Hz), 5.16 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 17.4, 1.9, 1.5 Hz), 5.89 d.d.t (1H, $OCH_2CH_2\underline{CH}=CH_2$, *J* 17.4, 10.3, 6.9 Hz), 6.23 t ($1H_{arom}$, *J* 2.2 Hz), 6.26–6.33 m ($2H_{arom}$), 7.04 t ($1H_{arom}$, *J* 8.02 Hz). Found $[M]^+$ 163.0998. $C_{10}H_{13}NO$. Calculated *M* 163.0997.

***p*-(But-3-enyloxy)aniline**. Yield 80%, bp 92–94°C (1 mm Hg). Oily substance, fast darkening in air. ^{1}H NMR spectrum, δ, ppm: 2.49 m (2H, $OCH_2C\underline{H}_2CH=CH_2$), 3.41 br.s (2H, NH_2), 3.93 t (2H, $OC\underline{H}_2CH_2CH=CH_2$, *J* 6.7 Hz), 5.07 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 10.4, 1.8, 1.0 Hz), 5.14 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 17.2, 1.8, 1.5 Hz), 5.89 d.d.t (1H, $OCH_2CH_2\underline{CH}=CH_2$, *J* 17.2, 10.4, 6.9 Hz), 6.62 d ($2H_{arom}$, *J* 8.6 Hz), 6.74 d ($2H_{arom}$, *J* 8.6 Hz). Found $[M]^+$ 163.0995. $C_{10}H_{13}NO$. Calculated *M* 163.0997.

Hydrochlorides **II–IV** were obtained by treating the methanol solutions of isomeric (but-3-enyloxy)anilines with conc. hydrochloric acid taken in 3–5% excess with the subsequent distilling off the solvents in a vacuum of the water-aspirator pump till the constant weight.

(*N*-Aryl)salicylaldimines Va–Vd, VIa–VId, VIIa–VIId. A mixture of 4 mmol of aldehyde **Ia–Id**, 0.798 g (4.4 mmol) of an appropriate (but-3-enyloxy)aniline hydrochloride **II–IV**, 0.444 g (4.4 mmol) of triethylamine, and 10 ml of methanol was boiled for 10–15 h till the disappearance of the initial compounds (TLC monitoring). Methanol was distilled off on a rotary evaporator, the residue was dissolved in 20 ml of $CHCl_3$ and washed with 20 ml of water. The organic layer was dried with $MgSO_4$. Chloroform was distilled off, the residue was subjected to flash-chromatography on silica gel 2–25 μm, eluent $CHCl_3$–hexane, 1 : 2, collecting the first bright yellow fraction. The solvents were distilled off, the residue was triturated with 5 ml of methanol till crystals formed, the precipitate was filtered off, washed with 3 ml of methanol and was kept in a vacuum-desiccator.

2-{[2-(But-3-enyl)oxyphenylimino]methyl}-6-*tert*-butylphenol (Va). Yield 87%. Oily substance. IR spectrum, ν, cm^{-1}: 1613 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.51 s [9H, $C(CH_3)_3$], 2.63 m (2H, $OCH_2C\underline{H}_2CH=CH_2$), 4.11 t (2H, $OC\underline{H}_2CH_2CH=CH_2$, *J* 6.4 Hz), 5.14 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 10.2, 1.8, 1.1 Hz), 5.24 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 17.1, 1.8, 1.5 Hz), 5.99 d.d.t (1H, $OCH_2CH_2\underline{CH}=CH_2$, *J* 17.1, 10.2, 6.8 Hz), 6.85 t (1H$_{arom}$, *J* 7.6 Hz), 6.96–7.03 m (2H$_{arom}$), 7.18–7.27 m (3H$_{arom}$), 7.38 d.d (1H$_{arom}$, *J* 7.6, 1.5 Hz), 8.76 s (1H, CH=N), 14.41 s (1H, OH). Found [*M*]$^+$ 323.1876. $C_{21}H_{25}NO_2$. Calculated *M* 323.1880.

2-{[2-(But-3-enyl)oxyphenylimino]methyl}-4,6-di-*tert*-butylphenol (Vb). Yield 85%. Oily substance. IR spectrum, ν, cm^{-1}: 1617 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.33 s [9H, $C(CH_3)_3$], 1.48 s [9H, $C(CH_3)_3$], 2.59 m (2H, $O\mathbf{CH_2}C\underline{H}_2CH=CH_2$), 4.08 t (2H, $O\mathbf{C\underline{H}_2}CH_2CH=CH_2$, *J* 6.5 Hz), 5.10 d.d.t (1H, $O\mathbf{CH_2}CH_2CH=C\underline{H}_2$, *J* 10.0, 1.8, 1.1 Hz), 5.22 d.d.t (1H, $O\mathbf{CH_2}CH_2CH=C\underline{H}_2$, *J* 17.0, 1.8, 1.5 Hz), 5.95 d.d.t (1H, $O\mathbf{CH_2}CH_2\underline{C}H=CH_2$, *J* 17.0, 10.0, 6.8 Hz), 6.94–7.01 m (2H$_{arom}$), 7.14–7.22 m (3H$_{arom}$), 7.42 d (1H$_{arom}$, *J* 2.4 Hz), 8.72 s (1H, CH=N), 14.11 s (1H, OH). Found [*M*]$^+$ 379.2500. $C_{25}H_{33}NO_2$. Calculated *M* 379.2506.

2-{[2-(But-3-enyl)oxyphenylimino]methyl}-6-(2-phenylpropan-2-yl)phenol (Vc). Yield 91%, mp 66°C. IR spectrum, ν, cm^{-1}: 1610 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.80 s [6H, $C(CH_3)_2$], 2.48 m (2H, $OCH_2C\underline{H}_2CH=CH_2$), 4.00 t (2H, $OC\underline{H}_2CH_2CH=CH_2$, *J* 6.4 Hz), 5.04 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 10.2, 1.8, 0.9 Hz), 5.10 d.d.t (1H, $O\mathbf{CH_2}CH_2CH=C\underline{H}_2$, *J* 17.1, 1.8, 1.5 Hz), 5.85 d.d.t (1H, $O\mathbf{CH_2}CH_2\underline{C}H=CH_2$, *J* 17.1, 10.2, 6.8 Hz), 6.87–6.96 m (3H$_{arom}$), 7.10–7.29 m (8H$_{arom}$), 7.52 d.d (1H$_{arom}$, *J* 7.8, *1*.4 Hz), 8.69 s (1H, CH=N), 13.96 s (1H, OH). Found [*M*]$^+$ 385.2030. $C_{26}H_{27}NO_2$. Calculated *M* 385.2036.

2-{[2-(But-3-enyl)oxyphenylimino]methyl}-4,6-di(2-phenylpropan-2-yl)phenol (Vd). Yield 96%, mp 89°C. IR spectrum, ν, cm^{-1}: 1613 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.73 s [6H, $C(CH_3)_2$], 1.75 s [6H, $C(CH_3)_2$], 2.44 m (2H, $OCH_2C\underline{H}_2CH=CH_2$), 3.95 t (2H, $OC\underline{H}_2CH_2CH=CH_2$, *J* 6.4 Hz), 4.98 d.d.t (1H, $O\mathbf{CH_2}CH_2CH=C\underline{H}_2$, *J* 10.2, 1.9, 1.1 Hz), 5.05 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 17.1, 1.9, 1.5 Hz), 5.80 d.d.t (1H, $OCH_2CH_2C\underline{H}=CH_2$, *J* 17.1, 10.2, 6.9 Hz), 6.87–6.95 m (2H$_{arom}$), 7.11–7.31 m (13H$_{arom}$), 7.39 d (1H$_{arom}$, *J* 2.0 Hz), 8.63 s (1H, CH=N), 13.81 s (1H, OH). Found [*M*]$^+$ 503.2816. $C_{35}H_{37}NO_2$. Calculated *M* 503.2819.

2-{[3-(But-3-enyl)oxyphenylimino]methyl}-6-*tert*-butylphenol (VIa). Yield 88%. Oily substance. IR spectrum, ν, cm^{-1}: 1614 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.50 s [9H, $C(CH_3)_3$], 2.59 m (2H, $O\mathbf{CH_2}C\underline{H}_2CH=CH_2$), 4.08 t (2H, $OC\underline{H}_2CH_2CH=CH_2$, *J* 6.6 Hz), 5.15 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 10.3, 1.8, 1.1 Hz), 5.21 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 17.1, 1.8, 1.5 Hz), 5.94 d.d.t (1H, $OCH_2CH_2\underline{C}H=CH_2$, *J* 17.1, 10.3, 6.9 Hz), 6.84–6.91 m (4H$_{arom}$), 7.25 d.d (1H$_{arom}$, *J* 7.8, 1.0 *Hz*), 7.32 t (1H$_{arom}$, *J* 7.8 Hz), 7.41 d.d (1H$_{arom}$, *J* 7.8, 1.0 *Hz*), 8.63 s (1H, CH=N), 13.86 s (1H, OH). Found [*M*]$^+$ 323.1882. $C_{21}H_{25}NO_2$. Calculated *M* 323.1880.

2-{[3-(But-3-enyl)oxyphenylimino]methyl}-4,6-di-*tert*-butylphenol (VIb). Yield 86%, mp 60°C. IR spectrum, ν, cm^{-1}: 1619 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.35 s [9H, $C(CH_3)_3$], 1.49 s [9H, $C(CH_3)_3$], 2.58 m (2H, $OCH_2C\underline{H}_2CH=CH_2$), 4.07 t (2H, $OC\underline{H}_2CH_2CH=CH_2$, *J* 6.6 Hz), 5.13 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 10.2, 1.9, 1.1 Hz), 5.20 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 17.2, 1.9, 1.5 Hz), 5.93 d.d.t (1H, $OCH_2CH_2\underline{CH}=CH_2$, *J* 17.2, 10.2, 6.9 Hz), 6.76–6.87 m (3H$_{arom}$), 7.18 d (1H$_{arom}$, *J* 2.4 Hz), 7.27 t (1H$_{arom}$, *J* 8.0 Hz), 7.42 d (1H$_{arom}$, *J* 2.4 Hz), 8.64 s (1H, CH=N), 13.60 s (1H, OH). Found [*M*]$^+$ 379.2503. $C_{25}H_{33}NO_2$. Calculated *M* 379.2506.

2-{[3-(But-3-enyl)oxyphenylimino]methyl}-6-(2-phenylpropan-2-yl)phenol (VIc). Yield 87%. Oily substance. IR spectrum, ν, cm^{-1}: 1614 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.81 s [6H, $C(CH_3)_2$], 2.56 m (2H, $OCH_2C\underline{H}_2CH=CH_2$), 4.03 t (2H, $OC\underline{H}_2CH_2CH=CH_2$, *J* 6.6 Hz), 5.13 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 10.4, 1.9, 1.0 Hz), 5.20 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 17.0, 1.9, 1.5 Hz), 5.92 d.d.t (1H, $OCH_2CH_2\underline{CH}=CH_2$, *J* 17.0, 10.4, 6.9 Hz), 6.73–6.82 m (3H$_{arom}$), 6.97 t (1H$_{arom}$, *J* 7.8 Hz), 7.15–7.32 m (7H$_{arom}$), 7.57 d.d (1H$_{arom}$, *J* 7.8, *1*.6 Hz), 8.57 s (1H, CH=N), 13.39 s (1H, OH). Found [*M*]$^+$ 385.2035. $C_{26}H_{27}NO_2$. Calculated *M* 385.2036.

2-{[3-(But-3-enyl)oxyphenylimino]methyl}-4,6-di(2-phenylpropan-2-yl)phenol (VId). Yield 93%. Oily substance. IR spectrum, ν, cm^{-1}: 1619 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.71 s [6H, $C(CH_3)_2$], 1.75 s [6H, $C(CH_3)_2$], 2.55 m (2H, $OCH_2C\underline{H}_2CH=CH_2$), 4.01 t (2H, $OC\underline{H}_2CH_2CH=CH_2$, *J* 6.6 Hz), 5.11 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 10.0, 1.9, 1.1 Hz), 5.17 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 17.0, 1.9, 1.5 Hz), 5.90 d.d.t (1H, $OCH_2CH_2\underline{CH}=CH_2$, *J* 17.0, 10.0, 6.9 Hz), 6.70–6.78 m (2H$_{arom}$), 7.13-7.32 m (13H$_{arom}$), 7.42 d (1H$_{arom}$, *J* 2.2 Hz), 8.51 s (1H, CH=N), 13.23 s (1H, OH). Found [*M*]$^+$ 503.2818. $C_{35}H_{37}NO_2$. Calculated *M* 503.2819.

2-{[4-(But-3-enyl)oxyphenylimino]methyl}-6-*tert*-butylphenol (VIIa). Yield 89%, mp 59°C. IR spectrum, ν, cm^{-1}: 1613 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.49 s [9H, $C(CH_3)_3$], 2.59 m (2H, $OCH_2C\underline{H}_2CH=CH_2$), 4.06 t (2H, $OC\underline{H}_2CH_2CH=CH_2$, *J* 6.6 Hz), 5.15 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 10.2, 1.8, 1.1 Hz), 5.21 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 17.2, 1.8, 1.5 Hz), 5.93 d.d.t (1H, $OCH_2CH_2\underline{CH}=CH_2$, *J* 17.2, 10.2, 6.9 Hz), 6.87 t (1H$_{\text{arom}}$, *J* 7.7 Hz), 6.95 d (2H$_{\text{arom}}$, *J* 8.7 Hz), 7.23 d.d (1H$_{\text{arom}}$, *J* 7.7, 1.6 Hz), 7.29 d (2H$_{\text{arom}}$, *J* 8.7 Hz), 7.37 d.d (1H$_{\text{arom}}$, *J* 7.7, 1.6 Hz), 8.62 s (1H, CH=N), 14.04 s (1H, OH). Found [*M*]$^+$ 323.1879. $C_{21}H_{25}NO_2$. Calculated *M* 323.1880.

2-{[4-(But-3-enyl)oxyphenylimino]methyl}-4,6-di-*tert*-butylphenol (VIIb). Yield 91%, mp 63°C. IR spectrum, ν, cm^{-1}: 1616 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.33 s [9H, $C(CH_3)_3$], 1.47 s [9H, $C(CH_3)_3$], 2.56 m (2H, $OCH_2C\underline{H}_2CH=CH_2$), 4.03 t (2H, $OC\underline{H}_2CH_2CH=CH_2$, *J* 6.5 Hz), 5.12 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 10.0, 1.8, 1.1 Hz), 5.20 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 17.0, 1.8, 1.5 Hz), 5.94 d.d.t (1H, $OCH_2CH_2\underline{CH}=CH_2$, *J* 17.0, 10.0, 6.9 Hz), 6.91 d (2H$_{\text{arom}}$, *J* 9.0 Hz), 7.18 d (1H$_{\text{arom}}$, *J* 2.5 Hz), 7.25 d (2H$_{\text{arom}}$, *J* 9.0 Hz), 7.40 d (1H$_{\text{arom}}$, *J* 2.5 Hz), 8.61 s (1H, CH=N), 13.76 s (1H, OH). Found [*M*]$^+$ 379.2508. $C_{25}H_{33}NO_2$. Calculated *M* 379.2506.

2-{[4-(But-3-enyl)oxyphenylimino]methyl}-6-(2-phenylpropan-2-yl)phenol (VIIc). Yield 89%, mp 75°C. IR spectrum, ν, cm^{-1}: 1613 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.79 s [6H, $C(CH_3)_2$], 2.56 m (2H, $OCH_2C\underline{H}_2CH=CH_2$), 4.02 t (2H, $OC\underline{H}_2CH_2CH=CH_2$, *J* 6.6 Hz), 5.13 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 10.2, 1.8, 1.0 Hz), 5.19 d.d.t (1H, $OCH_2CH_2\underline{CH}=CH_2$, *J* 17.2, 1.8, 1.5 Hz). 5.91 d.d.t (1H, $OCH_2CH_2\underline{CH}=CH_2$, *J* 17.2, 10.2, 6.9 Hz), 6.87 d (2H$_{\text{arom}}$, *J* 8.9 Hz), 6.94 t (1H$_{\text{arom}}$, *J* 7.8 Hz), 7.15–7.19 m (3H$_{\text{arom}}$), 7.26–7.30 m (5H$_{\text{arom}}$), 7.54 d.d (1H$_{\text{arom}}$, *J* 7.8, 1.5 Hz), 8.55 s (1H, CH=N), 13.54 s (1H, OH). Found [*M*]$^+$ 385.2032. $C_{26}H_{27}NO_2$. Calculated *M* 385.2036.

2-{[4-(But-3-enyl)oxyphenylimino]methyl}-4,6-di-(2-phenylpropan-2-yl)phenol (VIId). Yield 89%, mp 110°C. IR spectrum, ν, cm^{-1}: 1617 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.72 s [6H, $C(CH_3)_2$], 1.76 s [6H, $C(CH_3)_2$], 2.56 m (2H, $OCH_2C\underline{H}_2CH=CH_2$), 4.02 t (2H, $OC\underline{H}_2CH_2CH=CH_2$, *J* 6.7 Hz), 5.13 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 10.0, 1.8, 1.1 Hz), 5.20 d.d.t (1H, $OCH_2CH_2CH=C\underline{H}_2$, *J* 17.0, 1.8, 1.5 Hz), 5.91 d.d.t (1H, $OCH_2CH_2\underline{CH}=CH_2$, *J* 17.0, 10.0, 6.9 Hz), 6.87 d (2H$_{\text{arom}}$, *J* 8.9 Hz), 7.12-7.32 m (13H$_{\text{arom}}$), 7.41 d (1H$_{\text{arom}}$, *J* 2.3 Hz*),* 8.50 s (1H, CH=N), 13.40 s (1H, OH). Found [*M*]$^+$ 503.2810. $C_{35}H_{37}NO_2$. Calculated *M* 503.2819.

Complexes VIIIa–VIIId, IXa–IXd, Xa–Xd. A mixture of 2 mmol of (*N*-aryl)salicylaldimine **Va–Vd, VIa–VId, VIIa–VIId,** 10 ml of anhydrous dichloromethane**,** and 2.39 g of toluene solution containing 0.237 g (1 mmol) of $TiCl_2(OPr\text{-}i)_2$ was stirred at room temperature under an argon atmosphere for 24 h. The solvent was distilled off from the formed dark-red solution in a vacuum of the water-aspirator pump. The residue was washed with hexane (2 × 2 ml) on the filter and was dried in a vacuum of an oil pump at 100°C for 1 h. The corresponding complexes were obtained as red-brown powders.

Bis(2-{[2-(but-3-enyl)oxyphenylimino]methyl}-6-*tert*-butylphenoxy)titanium(IV) dichloride (VIIIa). Yield 91%. IR spectrum, ν, cm^{-1}: 1609 (C=N), 570 (Ti–O), 462 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.43–1.62 m [18H, $C(CH_3)_3$], 2.59–2.68 m (4H, $OCH_2C\underline{H}_2CH=CH_2$), 4.09–4.12 m (4H, $OC\underline{H}_2CH_2CH=CH_2$), 4.96–5.25 m (4H, $OCH_2CH_2CH=C\underline{H}_2$), 5.89–6.03 m (2H, $OCH_2CH_2C\underline{H}=CH_2$), 6.55–7.42 m (14H$_{\text{arom}}$), 7.70–7.82 m (2H, CH=N). Found, %: C 65.98; H 6.55; Cl 9.05; N 3.67. $C_{42}H_{48}Cl_2N_2O_4Ti$. Calculated, %: C 66.06; H 6.34; Cl 9.29; N 3.67.

Bis(2-{[2-(but-3-enyl)oxyphenylimino]methyl}-4,6-di-*tert*-butylphenoxy)titanium(IV) dichloride (VIIIb). Yield 89%. IR spectrum, ν, cm^{-1}: 1612 (C=N), 581 (Ti–O), 473 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.34–1.63 m [36H, $C(CH_3)_3$], 2.58–2.69 m (4H, $OCH_2C\underline{H}_2CH=CH_2$), 4.07–4.13 m (4H, $OC\underline{H}_2CH_2CH=CH_2$), 4.94–5.31 m (4H, $OCH_2CH_2CH=C\underline{H}_2$), 5.86–6.04 m (2H, $OCH_2CH_2C\underline{H}=CH_2$), 6.62-7.52 m (12H$_{\text{arom}}$), 7.60–7.78 m (2H, CH=N). Found, %: C 68.29; H 7.44; Cl 8.03; N 3.22. $C_{50}H_{64}Cl_2N_2O_4Ti$. Calculated, %: C 68.57; H 7.37; Cl 8.10; N 3.20.

Bis[2-{[2-(but-3-enyl)oxyphenylimino]methyl}-6-(2-phenylpropan-2-yl)phenoxy]titanium(IV) dichloride (VIIIc). Yield 86%. IR spectrum, ν, cm^{-1}: 1608 (C=N), 566 (Ti-O), 444 (Ti-N). ^{1}H NMR spectrum, δ, ppm: 1.53–1.89 m [12H, $C(CH_3)_2$], 2.48–2.66 m (4H, $OCH_2C\underline{H}_2CH=CH_2$), 3.89–4.13 m (4H, $OC\underline{H}_2CH_2CH=CH_2$), 4.89–5.16 m (4H, $OCH_2CH_2CH=C\underline{H}_2$), 5.62–6.01 m (2H, $OCH_2CH_2C\underline{H}=CH_2$), 6.39–7.53 m (24H$_{\text{arom}}$), 7.68–7.81 m (2H, CH=N). Found, %: C 70.42; H 5.99; Cl 7.76; N 3.11. $C_{52}H_{52}Cl_2N_2O_4Ti$. Calculated, %: C 70.35; H 5.90; Cl 7.99; N 3.16.

Bis[2-{[2-(but-3-enyl)oxyphenylimino]methyl}-4,6-di-(2-phenylpropan-2-yl)phenoxy]titanium(IV) dichloride (VIIId). Yield 85%. IR spectrum, ν, cm^{-1}: 1608 (C=N), 558 (Ti–O), 471 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.55–1.82 m [24H, $C(CH_3)_2$], 2.42–2.67 m (4H, $OCH_2C\underline{H}_2CH{=}CH_2$), 3.95–4.15 m (4H, $OC\underline{H}_2CH_2CH{=}CH_2$), 4.94–5.15 m (4H, $OCH_2CH_2CH{=}C\underline{H}_2$), 5.77–6.11 m (2H, $OCH_2CH_2C\underline{H}{=}CH_2$), 6.69–7.48 m (32$H_{arom}$), 7.63–7.78 m (2H, CH=N). Found, %: C 75.33; H 6.43; Cl 6.21 N 2.57. $C_{70}H_{72}Cl_2N_2O_4Ti$. Calculated, %: C 74.79; H 6.46; Cl 6.31; N 2.49.

Bis(2-{[3-(but-3-enyl)oxyphenylimino]methyl}-6-*tert*-butylphenoxy)titanium(IV) dichloride (IXa). Yield 93%. IR spectrum, ν, cm^{-1}: 1599 (C=N), 573 (Ti–O), 459 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.33–1.62 m [18H, $C(CH_3)_3$], 2.42–2.54 m (4H, $OCH_2C\underline{H}_2CH{=}CH_2$), 3.62–4.00 m (4H, $OC\underline{H}_2CH_2CH{=}CH_2$), 5.08–5.21 m (4H, $OCH_2CH_2CH{=}C\underline{H}_2$), 5.76–5.97 m (2H, $OCH_2CH_2C\underline{H}{=}CH_2$), 6.57–7.64 m (14$H_{arom}$), 7.97–8.12 m (2H, CH=N). Found, %: C 65.81; H 6.38; Cl 9.36; N 3.49. $C_{42}H_{48}Cl_2N_2O_4Ti$. Calculated, %: C 66.06; H 6.34; Cl 9.29; N 3.67.

Bis (2-{[3-(but-3-enyl)oxyphenylimino]methyl}-4,6-di-*tert*-butylphenoxy)titanium(IV) dichloride (IXb). Yield 88%. IR spectrum, ν, cm^{-1}: 1599 (C=N), 573 (Ti–O), 476 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.33–1.48 m [36H, $C(CH_3)_3$], 2.47–2.60 m (4H, $OCH_2C\underline{H}_2CH{=}CH_2$), 3.96–4.09 m (4H, $OC\underline{H}_2CH_2CH{=}CH_2$), 5.07–5.22 m (4H, $OCH_2CH_2CH{=}C\underline{H}_2$), 5.81–5.98 m (2H, $OCH_2CH_2C\underline{H}{=}CH_2$), 6.83–7.46 m (12$H_{arom}$), 7.60–7.71 m (2H, CH=N). Found, %: C 68.76; H 7.47; Cl 7.96; N 3.08. $C_{50}H_{64}Cl_2N_2O_4Ti$. Calculated, %: C 68.57; H 7.37; Cl 8.10; N 3.20.

Bis[2-{[3-(but-3-enyl)oxyphenylimino]methyl}-6-(2-phenylpropan-2-yl)phenoxy]titanium(IV) dichloride (IXc). Yield 93%. IR spectrum, ν, cm^{-1}: 1598 (C=N), 541 (Ti–O), 468 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.66–1.81 m [12H, $C(CH_3)_2$], 2.47–2.59 m (4H, $OCH_2C\underline{H}_2CH{=}CH_2$), 3.88–4.07 m (4H, $OC\underline{H}_2CH_2CH{=}CH_2$), 5.09–5.21 m (4H, $OCH_2CH_2CH{=}C\underline{H}_2$), 5.83–5.95 m (2H, $OCH_2CH_2C\underline{H}{=}CH_2$), 6.64–7.58 m (24$H_{arom}$), 7.70–7.73 m (2H, CH=N). Found, %: C 70.53; H 6.02; Cl 7.73; N 3.06. $C_{52}H_{52}Cl_2N_2O_4Ti$. Calculated, %: C 70.35; H 5.90; Cl 7.99; N 3.16.

Bis[2-{[3-(but-3-enyl)oxyphenylimino]methyl}-4,6-di-(2-phenylpropan-2-yl)phenoxy]titanium(IV) dichloride (IXd). Yield 91%. IR spectrum, ν, cm^{-1}: 1598 (C=N), 554 (Ti–O), 470 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.66-1.76 m [24H, $C(CH_3)_2$], 2.50–2.57 m (4H, $OCH_2C\underline{H}_2CH{=}CH_2$), 3.95–4.04 m (4H, $OC\underline{H}_2CH_2CH{=}CH_2$), 5.09–5.20 m (4H, $OCH_2CH_2CH{=}C\underline{H}_2$), 5.79–5.93 m (2H, $OCH_2CH_2C\underline{H}{=}CH_2$), 6.72–7.44 m (32$H_{arom}$), 7.57–7.75 m (2H, CH=N). Found, %: C 75.01; H 6.61; Cl 6.21; N 2.46. $C_{70}H_{72}Cl_2N_2O_4Ti$. Calculated, %: C 74.79; H 6.46; Cl 6.31; N 2.49.

Bis(2-{[4-(but-3-enyl)oxyphenylimino]methyl}-6-*tert*-butylphenoxy)titanium(IV) dichloride (Xa). Yield 90%. IR spectrum, ν, cm^{-1}: 1608 (C=N), 560 (Ti–O), 450 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.40–1.61 m [18H, $C(CH_3)_3$], 2.41–2.60 m (4H, $OCH_2C\underline{H}_2CH{=}CH_2$), 3.84–4.07 m (4H, $OC\underline{H}_2CH_2CH{=}CH_2$), 5.01–5.22 m (4H, $OCH_2CH_2CH{=}C\underline{H}_2$), 5.79–5.98 m (2H, $OCH_2CH_2C\underline{H}{=}CH_2$), 6.54–7.45 m (14$H_{arom}$), 7.94–8.18 m (2H, CH=N). Found, %: C 66.37; H 6.48; Cl 9.34; N 3.77. $C_{42}H_{48}Cl_2N_2O_4Ti$. Calculated, %: C 66.06; H 6.34; Cl 9.29; N 3.67.

Bis(2-{[4-(but-3-enyl)oxyphenylimino]methyl}-4,6-di-*tert*-butylphenoxy)titanium(IV) dichloride (Xb). Yield 95%. IR spectrum, ν, cm^{-1}: 1609 (C=N), 572 (Ti–O), 473 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.27–1.63 m [36H, $C(CH_3)_3$], 2.41–2.60 m (4H, $OCH_2C\underline{H}_2CH{=}CH_2$), 3.81–4.07 m (4H, $OC\underline{H}_2CH_2CH{=}CH_2$), 5.09–5.23 m (4H, $OCH_2CH_2CH{=}C\underline{H}_2$), 5.78–5.98 m (2H, $OCH_2CH_2C\underline{H}{=}CH_2$), 6.52–7.80 m (12$H_{arom}$), 7.94–8.19 m (2H, CH=N). Found, %: C 68.45; H 7.54; Cl 7.91; N 3.11. $C_{50}H_{64}Cl_2N_2O_4Ti$. Calculated, %: C 68.57; H 7.37; Cl 8.10; N 3.20.

Bis[2-{[4-(but-3-enyl)oxyphenylimino]methyl}-6-(2-phenylpropan-2-yl)phenoxy]titanium(IV) dichloride (Xc). Yield 94%. IR spectrum, ν, cm^{-1}: 1609 (C=N), 558 (Ti–O), 442 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.75–1.79 m [12H, $C(CH_3)_2$], 2.51–2.59 m (4H, $OCH_2C\underline{H}_2CH{=}CH_2$), 3.94–4.03 m (4H, $OC\underline{H}_2CH_2CH{=}CH_2$), 5.11–5.22 m (4H, $OCH_2CH_2CH{=}C\underline{H}_2$), 5.83–5.97 m (2H, $OCH_2CH_2C\underline{H}{=}CH_2$), 6.79–7.56 m (24$H_{arom}$), 7.70–7.75 m (2H, CH=N). Found, %: C 70.36; H 5.86; Cl 7.89; N 3.11. $C_{52}H_{52}Cl_2N_2O_4Ti$. Calculated, %: C 70.35; H 5.90; Cl 7.99; N 3.16.

Bis[2-{[4-(but-3-enyl)oxyphenylimino]methyl}-4,6-di-(2-phenylpropan-2-yl)phenoxy]titanium(IV) dichloride (Xd). Yield 87%. IR spectrum, ν, cm^{-1}: 1609 (C=N), 558 (Ti–O), 466 (Ti–N). ^{1}H NMR spectrum, δ, ppm: 1.68–1.78 m [24H, $C(CH_3)_2$], 2.48–2.59 m (4H, $OCH_2C\underline{H}_2CH{=}CH_2$), 3.97–4.05 m (4H, $OC\underline{H}_2CH_2CH{=}CH_2$), 5.13–5.22 m (4H, $OCH_2CH_2CH{=}C\underline{H}_2$), 5.87–5.98 m (2H, $OCH_2CH_2C\underline{H}{=}CH_2$), 6.90–7.45 m (32$H_{arom}$), 7.60–7.72 m (2H, CH=N). Found, %: C 74.73; H 6.57; Cl 6.21; N 2.49. $C_{70}H_{72}Cl_2N_2O_4Ti$. Calculated, %: C 74.79; H 6.46; Cl 6.31; N 2.49.

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