Russian Journal of Organic Chemistry, Vol. 41, No. 9, 2005, pp. 1329–1332. Translated from Zhurnal Organicheskoi Khimii, Vol. 41, No. 9, 2005, pp. 1354–1357.

Dedicated to Full Member of Russian Academy of Sciances N.S. Zefirov on His 70th Anniversary

Design of Schiff Base-Like Postmetallocene Catalytic Systems for Polymerization of Olefins: III.* Synthesis of 1,2-Bis-(arylimino)acenaphthenes Having Cyclic Substituents

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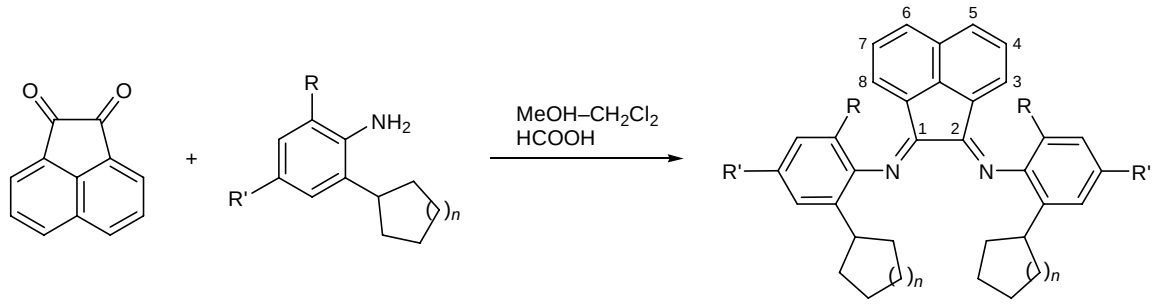
Received May 31, 2005

Abstract—Reactions of substituted cycloalkylanilines with acenaphthenequinone in a mixture of methanol with methylene chloride afforded a number of the corresponding 1,2-bis(cycloalkylarylimino)acenaphthenes. The products may be used as ligands for the synthesis of nickel complexes which are capable of catalyzing olefin polymerization at elevated temperature in the presence of methylaluminoxane.

Johnson *et al*. [2–4] developed catalytic systems for polymerization of ethylene on the basis of diimine nickel and palladium complexes. These systems are highly effective in the temperature range from 4 to 70°C, and they attract attention due to the possibility for controlling properties of the resulting polymer via variation of the polymerization conditions. Moreover, the palladium complexes are capable of catalyzing copolymerization of ethylene with polar monomers. It seemed to be very important to create on the basis of such complexes highly active catalytic systems ensuring formation of olefin polymers with a high molecular weight at a temperature exceeding 70°C.

We previously showed that the temperature range for application of catalysts derived from 1,2-bis(cycloalkylarylimino)acenaphthene nickel complexes can be extended via introduction of cycloalkyl groups into the *ortho* position of the aromatic ring linked to the imino group [5, 6]. The present communication reports on the preparation of the corresponding ligands containing

Scheme 1.



Ia–**Id**, **IIa**–**IId**, **IIIa**–**IIIc**, **IVa**–**IVc** **Va**–**Vd**, **VIa**–**VId**, **VIIa**–**VIIc**, **VIIIa**–**VIIIc**

R = R' = H (**a**), Me (**c**); R = Me, R' = H (**b**); R = cyclo-$C_4H_7(CH_2)_n$, R' = H (**d**);
I, **V**, n = 1; **II**, **VI**, n = 2; **III**, **VII**, n = 4; **IV**, **VIII**, n = 8.

* For communication II, see [1].

1070-4280/05/4109-1329

cyclopentyl, cyclohexyl, cyclooctyl, and cyclododecyl substituents. The synthesis of 1,2-bis(arylimino)acenaphthene ligands is based on the reaction of acenaphthenequinone with anilines. This reaction with alkylanilines as examples was performed in [3, 4]. We extended the known procedure to the preparation of new 1,2-bis(arylimino)acenaphthene structures **V**–**VIII** having cycloalkyl substituents and optimized conditions for their synthesis.

2-Cyclopentyl-, 2,6-dicyclopentylanilines **Ia**–**Id**, 2-cyclohexyl-, 2,6-dicyclohexylanilines **IIa**–**IId**, 2-cyclooctylanilines **IIIa**–**IIIc**, and 2-cyclododecylanilines **IVa**–**IVc** were heated with acenaphthenequinone in methanol in the presence of a catalytic amount of formic acid to obtain 1,2-bis(cycloalkylphenylimino)-acenaphthenes **Va**–**Vd**, **VIa**–**VId**, **VIIa**–**VIIc**, and **VIIIa**–**VIIIc**. However, these reactions were not complete even after prolonged heating, and mixtures of the corresponding mono- and diimines were formed. We succeeded in isolating pure compounds **V**–**VIII** in 20–35% yield only by column chromatography, whereas no monoimino derivatives were isolated in the pure state. Analogous results were obtained when the reaction was carried out in acetonitrile in the presence of a catalytic amount of acetic acid or in toluene in the presence of *p*-toluenesulfonic acid with simultaneous removal of water as azeotrope. In the latter case, the reaction was accompanied by tarring. The conversion of acenaphthenequinone into the corresponding diimine was complete in a 2:1 mixture of methanol with methylene chloride in the presence of formic acid; here, the target products **V**–**VIII** were isolated in 84–88% yield (after recrystallization).

The structure of the products was proved by the analytical and spectral data. In the ^{1}H NMR spectra of diimines **V**–**VIII**, signals from CH_2 groups in the cycloalkyl substituents appear as multiplets at δ 1.05–2.15 ppm, and CH protons give rise to signals at δ 2.55–3.11 ppm. Signals from aromatic protons occupy the δ range from 6.79 to 7.38 ppm. The 3-H and 8-H protons of the acenaphthene fragments appear as characteristic doublets at δ 6.44–6.77 ppm, the 5-H and 6-H signals are doublets located in a weaker field, δ 7.76–7.85 ppm, and the 4-H and 7-H signals are triplets at δ 7.30–7.37 ppm. The spectra of diimines **Vb**–**VIIIb** also contain singlets from the methyl protons at δ 2.01–2.12 ppm. Dimethyl-substituted derivatives **Vc**–**VIIIc** show in the spectra signals at δ 1.96–2.02 ppm from the methyl groups in the *ortho* position with respect to the imino group, and more downfield singlets (δ 2.36–2.39 ppm) belong to the *para*-methyl groups.

In the IR spectra of **V**–**VII** we observed a strong absorption band at 1636–1652 cm^{-1} due to stretching vibrations of the C=N bond. The spectral region 2850–2952 cm^{-1} contains absorption bands belonging to stretching vibrations of C–H bonds in the acenaphthene fragment and benzene rings and of CH and CH_2 groups in the cycloalkyl substituents. Diimines **V**–**VIII** characteristically showed a strong molecular ion peak in the mass spectra.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker WP-200 SY instrument (200 MHz) from solutions in carbon tetrachloride containing HMDS as internal reference. The IR spectra were measured on a Vector 22 spectrometer from samples prepared as KBr pellets. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using chloroform as eluent. Flash chromatography was performed on silica gel (5–40 μm) using chloroform as eluent. The elemental analyses were obtained on a Carlo Erba 1106 CHN analyzer. The elemental compositions were also calculated from the high-resolution mass spectra which were recorded on a Finnigan MAT 8200 spectrometer. The melting points were determined by heating a sample placed between glass plates at a rate of 1 deg/min.

Anilines **I**–**IV** and acenaphthenequinone were prepared by the procedures described in [7, 8].

1,2-Bis(cycloalkylphenylimino)acenaphthenes V–VIII (*general procedure***).** A mixture of 0.182 g (1 mmol) of acenaphthenequinone, 2.2 mmol of cycloalkylaniline **I**–**IV**, 10 ml of methanol, 5 ml of dichloromethane, and 5 mg of anhydrous formic acid was heated for 15–20 h under reflux. The solvent was distilled off under reduced pressure at a bath temperature of 45°C, and the residue was subjected to flash chromatography. The first bright yellow fraction was evaporated, and the residue was recrystallized from ethanol.

1,2-Bis(2-cyclopentylphenylimino)acenaphthene (Va). Yield 88%, mp 166–168°C. IR spectrum, ν, cm^{-1}: 1636, 1661, 2866, 2952. ^{1}H NMR spectrum, δ, ppm: 1.30–1.95 (16H, CH_2), 3.11 m (2H, CH), 6.67d (2H, 3-H, 8-H, J = 8 Hz), 7.16–7.38 m (8H, 3'-H, 4'-H, 5'-H, 6'-H), 7.31 t (2H, 4-H, 7-H, J = 8 Hz), 7.76 d (2H, 5-H, 6-H, J = 8 Hz). Found, %: C 87.10; H 6.91; N 5.90.

M 468.2568. $C_{34}H_{32}N_2$. Calculated, %: C 87.14; H 6.88; N 5.98. *M* 468.2565.

1,2-Bis(6-cyclopentyl-2-methylphenylimino)acenaphthene (Vb). Yield 84%, mp 232–234°C. IR spectrum, ν, cm^{-1}: 1641, 1670, 2866, 2952. ^1H NMR spectrum, δ, ppm: 1.20–1.90 m (16H, CH_2), 2.12 s (6H, 2'-CH_3), 3.06 m (2H, CH), 6.61 d (2H, 3-H, 8-H, *J* = 8 Hz), 7.03–7.21 m (6H, 3'-H, 4'-H, 5'-H), 7.37 t (2H, 4-H, 7-H, *J* = 8 Hz), 7.86 d (2H, 5-H, 6-H, *J* = 8 Hz). Found, %: C 86.96; H 7.35; N 5.49. *M* 496.2888. $C_{36}H_{36}N_2$. Calculated, %: C 87.05; H 7.31; N 5.64. *M* 496.2878.

1,2-Bis(6-cyclopentyl-2,4-dimethylphenylimino)acenaphthene (Vc). Yield 87%, mp 238–240°C. IR spectrum, ν, cm^{-1}: 1646, 1667, 2867, 2954. ^1H NMR spectrum, δ, ppm: 1.30–1.95 (16H, CH_2), 2.02 s (6H, 2'-CH_3), 2.39 s (6H, 4'-CH_3), 2.98 m (2H, CH), 6.67 d (2H, 3-H, 8-H, *J* = 8 Hz), 6.91 s (2H, 5'-H), 7.01 s (2H, 3'-H), 7.37 t (2H, 4-H, 7-H, *J* = 8 Hz), 7.85 d (2H, 5-H, 6-H, *J* = 8 Hz). Found, %: C 87.06; H 7.59; N 5.30. *M* 524.3189. $C_{38}H_{40}N_2$. Calculated, %: C 86.98; H 7.68; N 5.34. *M* 524.3191.

1,2-Bis(2,6-dicyclopentylphenylimino)acenaphthene (Vd). Yield 84%, mp 286–288°C. IR spectrum, ν, cm^{-1}: 1641, 1667, 2866, 2952. ^1H NMR spectrum, δ, ppm: 1.19–2.15 m (32, CH_2), 3.01 m (4H, CH), 6.44 d (2H, 3-H, 8-H, *J* = 8 Hz), 7.10–7.20 m (6H, 3'-H, 4'-H, 5'-H), 7.33 t (2H, 4-H, 7-H, *J* = 8 Hz), 7.84 d (2H, 5-H, 6-H, *J* = 8 Hz). Found, %: C 87.45; H 7.92; N 4.60. *M* 604.3834. $C_{44}H_{48}N_2$. Calculated, %: C 87.37; H 8.00; N 4.63. *M* 604.3817.

1,2-Bis(2-cyclohexylphenylimino)acenaphthene (VIa). Yield 86%, mp 145–146°C. IR spectrum, ν, cm^{-1}: 1634, 1667, 2850, 2923. ^1H NMR spectrum, δ, ppm: 1.10–1.95 (20H, CH_2), 2.72 m (2H, CH), 6.77 d (2H, 3-H, 8-H, *J* = 8 Hz), 7.05-7.28 m (8H, 3'-H, 4'-H, 5'-H, 6'-H), 7.31 t (2H, 4-H, 7-H, *J* = 8 Hz), 7.78 d (2H, 5-H, 6-H, *J* = 8 Hz). Found, %: C 87.03; H 7.36; N 5.70. *M* 496.2881. $C_{36}H_{36}N_2$. Calculated, %: C 87.05; H 7.31; N 5.64. *M* 496.2878.

1,2-Bis(6-cyclohexyl-2-methylphenylimino)acenaphthene (VIb). Yield 84%, mp 203–205°C. IR spectrum, ν, cm^{-1}: 1638, 1674, 2850, 2924. ^1H NMR spectrum, δ, ppm: 1.05–1.90 m (20H, CH_2), 2.04 s (6H, 2'-CH_3), 2.63 m (2H, CH), 6.60 d (2H, 3-H, 8-H, *J* = 8 Hz), 7.01–7.26 m (6H, 3'-H, 4'-H, 5'-H), 7.37 t (2H, 4-H, 7-H, *J* = 8 Hz), 7.86 d (2H, 5-H, 6-H, *J* = 8 Hz). Found, %: C 87.04; H 7.60; N 5.34. *M* 524.3191. $C_{38}H_{40}N_2$. Calculated, %: C 86.98; H 7.68; N 5.34. *M* 524.3191.

1,2-Bis(6-cyclohexyl-2,4-dimethylphenylimino)acenaphthene (VIc). Yield 85%, mp 223–225°C. IR spectrum, ν, cm^{-1}: 1641, 1665, 2851, 2925. ^1H NMR spectrum, δ, ppm: 1.03–2.10 m (20H, CH_2), 1.99 s (6H, 2'-CH_3), 2.38 s (6H, 4'-CH_3), 2.55 m (2H, CH), 6.66 d (2H, 3-H, 8-H, *J* = 8 Hz), 6.87 s (2H, 5'-H), 6.94 s (2H, 3'-H), 7.33 t (2H, 4-H, 7-H, *J* = 8 Hz), 7.79 d (2H, 5-H, 6-H, *J* = 8 Hz). Found, %: C 86.79; H 8.03; N 5.12. *M* 552.3505. $C_{40}H_{44}N_2$. Calculated, %: C 86.91; H 8.02; N 5.07. *M* 552.3504.

1,2-Bis(2,6-dicyclohexylphenylimino)acenaphthene (VId). Yield 87%, mp 314–316°C. IR spectrum, ν, cm^{-1}: 1645, 1664, 2866, 2952. ^1H NMR spectrum, δ, ppm: 1.05–1.95 m (40H, CH_2), 2.74 m (4H, CH), 6.77 d (2H, 3-H, 8-H, *J* = 8 Hz), 7.01–7.26 m (6H, 3'-H, 4'-H, 5'-H), 7.31 t (2H, 4-H, 7-H, *J* = 8 Hz), 7.79 d (2H, 5-H, 6-H, *J* = 8 Hz). Found, %: C 87.27; H 8.48; N 4.26. *M* 660.4414. $C_{48}H_{56}N_2$. Calculated, %: C 87.22; H 8.54; N 4.24. *M* 660.4443.

1,2-Bis(2-cyclooctylphenylimino)acenaphthene (VIIa). Yield 85%, mp 140–142°C. IR spectrum, ν, cm^{-1}: 1652, 1669, 2849, 2919. ^1H NMR spectrum, δ, ppm: 1.15–1.85 m (28H, CH_2), 3.05 m (2H, CH), 6.72 d (2H, 3-H, 8-H, *J* = 8 Hz), 6.95–7.19 m (8H, 3'-H, 4'-H, 5'-H, 6'-H), 7.31 t (2H, 4-H, 7-H, *J* = 8 Hz), 7.79 d (2H, 5-H, 6-H, *J* = 8 Hz). Found, %: C 86.78; H 8.08; N 5.00. *M* 552.3500. $C_{40}H_{44}N_2$. Calculated, %: C 86.91; H 8.02; N 5.07. *M* 552.3504.

1,2-Bis(2-cyclooctyl-6-methylphenylimino)acenaphthene (VIIb). Yield 86%, mp 203–204°C. IR spectrum, ν, cm^{-1}: 1645, 1668, 2848, 2919. ^1H NMR spectrum, δ, ppm: 1.05–1.87 m (28H, CH_2), 2.01 s (6H, 2'-CH_3), 2.95 m (2H, CH), 6.62 d (2H, 3-H, 8-H, *J* = 8 Hz), 6.98–7.21 m (6H, 3'-H, 4'-H, 5'-H), 7.30 t (2H, 4-H, 7-H, *J* = 8 Hz), 7.81 d (2H, 5-H, 6-H, *J* = 8 Hz). Found, %: C 86.85; H 8.29; N 4.86. *M* 580.3907. $C_{42}H_{48}N_2$. Calculated, %: C 86.85; H 8.33; N 4.82. *M* 580.3817.

1,2-Bis(6-cyclooctyl-2,4-dimethylphenylimino)acenaphthene (VIIc). Yield 85%, mp 219–220°C. IR spectrum, ν, cm^{-1}: 1639, 1664, 2851, 2919. ^1H NMR spectrum, δ, ppm: 1.02–1.81 m (28H, CH_2), 1.96 s (6H, 2'-CH_3), 2.37 s (6H, 4'-CH_3), 2.94 m (2H, CH), 6.68 d (2H, 3'-H, 8-H, *J* = 8 Hz), 6.83 s (2H, 5'-H), 6.92 s (2H, 3'-H), 7.35 t (2H, 4-H, 7-H, *J* = 8 Hz), 7.81 d (2H, 5'-H, 6-H, *J* = 8 Hz). Found, %: C 86.80; H 8.51; N 4.65. *M* 608.3885. $C_{44}H_{52}N_2$. Calculated, %: C 86.79; H 8.51; N 4.65. *M* 608.3879.

1,2-Bis(2-cyclododecylphenylimino)acenaphthene (VIIIa). Yield 84%, mp 282–283°C. IR spec-

trum, ν, cm^{-1}: 1644, 1667, 2846, 2930. ^1H NMR spectrum, δ, ppm: 1.10–1.90 m (44H, CH_2), 2.96 m (2H, CH), 6.68 d (2H, 3-H, 8-H, *J* = 8 Hz), 6.96–7.22 m (8H, 3'-H, 4'-H, 5'-H, 6'-H), 7.30 t (2H, 4-H, 7-H, *J* = 8 Hz), 7.80 d (2H, 5-H, 6-H, *J* = 8 Hz). Found, %: C 86.72; H 9.07; N 4.25. *M* 664.4820. $C_{48}H_{60}N_2$. Calculated, %: C 86.69; H 9.09; N 4.21. *M* 664.4756.

1,2-Bis(6-cyclododecyl-2-methylphenylimino)-acenaphthene (VIIIb). Yield 85%, mp 238–239°C. IR spectrum, ν, cm^{-1}: 1642, 1667, 2860, 2929. ^1H NMR spectrum, δ, ppm: 1.15–1.98 m (44H, CH_2), 2.12 s (6H, 2'-CH_3), 2.88 m (2H, CH), 6.62 d (2H, 3-H, 8-H, *J* = 8 Hz), 7.00–7.25 m (6H, 3'-H, 4'-H, 5'-H), 7.31 t (2H, 4-H, 7-H, *J* = 8 Hz), 7.81 d (2H, 5-H, 6-H, *J* = 8 Hz). Found, %: C 86.70; H 9.33; N 3.96. *M* 692.5053. $C_{50}H_{64}N_2$. Calculated, %: C 86.65; H 9.31; N 4.04. *M* 692.5069.

1,2-Bis(6-cyclododecyl-2,4-dimethylphenyl-imino)acenaphthene (VIIIc). Yield 85%, mp 256–258°C. IR spectrum, ν, cm^{-1}: 1640, 1665, 2851, 2925. ^1H NMR spectrum, δ, ppm: 1.07–1.95 m (44H, CH_2), 1.98 s (6H, 2'-CH_3), 2.36 s (6H, 4'-CH_3), 2.82 m (2H, CH), 6.67 d (2H, 3-H, 8-H, *J* = 8 Hz), 6.79 s (2H, 5'-H), 6.89 s (2H, 3'-H), 7.33 t (2H, 4-H, 7-H, *J* = 8 Hz), 7.81 d (2H, 5-H, 6-H, *J* = 8 Hz). Mass spectrum, *m*/*z*: 720 $[M]^+$. Found, %: C 86.69; H 9.56; N 3.81. $C_{52}H_{68}N_2$. Calculated, %: C 86.61; H 9.50; N 3.88.

This study was performed under financial support by the Siberian Division, Russian Academy of Sciences (Integration project no. 150) and by the Ministry of Industry, Science, and Technology of the Russian Federation (State contract no. 41.015.1.1.2455).

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