

Design of Postmetallocene Schiff Base-Like Catalytic Systems for Polymerization of Olefins: XI.* Synthesis of Schiff Bases Containing Cycloalkyl Substituents from 2-Acetyl-6-bromopyridine

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Received December 13, 2007

Abstract—Reactions of substituted cycloalkylanilines with 2-acetyl-6-bromopyridine in methanol gave a number of the corresponding Schiff bases that are promising as ligands for the synthesis of cobalt(II) and iron(II) complexes.

DOI: 10.1134/S1070428009010072

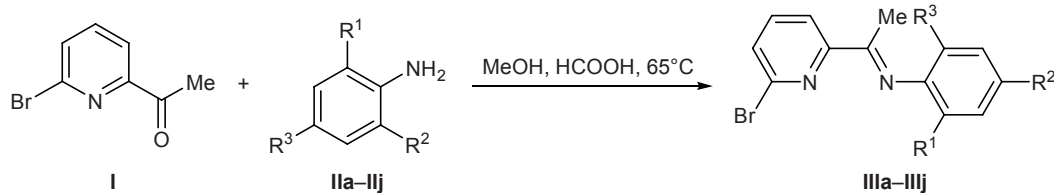
Design of new highly efficient catalytic systems for polymerization of olefins constitutes an important problem, taking into account needs of new polymeric materials. High catalytic activity of iron, copper, nickel, and palladium complexes with bidentate (arylimino)pyridine ligands in olefin polymerization was demonstrated in [2–4]. Therefore, search for new catalysts of this type seems to be promising.

Although complexes derived from bidentate aryliminopyridines are generally capable of promoting only oligomerization of olefins, they can be used for the preparation of branched polyethylene from ethylene via a process known as tandem catalysis which

implies cooperative action of two or more different catalysts in a single reactor to yield a product that is otherwise not accessible by the individual catalysts [4]. Practical application of new catalytic systems for olefin polymerization under existing operational conditions is possible if a catalyst remains highly active at elevated temperature. Unfortunately, most metallocene and postmetallocene catalysts are active only at moderate temperatures [5].

While performing systematic studies in the field of structural modification of metal complexes and their catalytic activity [6, 7], we found that introduction of cycloalkyl substituents into 2,6-bis(arylimino)pyridine

Scheme 1.



R¹ = R² = R³ = H (a); R¹ = R³ = Me, R² = H (b); R¹ = R² = H, R³ = *cyclo*-C₅H₉ (c); R¹ = Me, R² = H, R³ = *cyclo*-C₅H₉ (d); R¹ = R² = Me, R³ = *cyclo*-C₅H₉ (e); R¹ = R³ = *cyclo*-C₅H₉, R² = H (f); R¹ = R² = H, R³ = *cyclo*-C₆H₁₁ (g); R¹ = Me, R² = H, R³ = *cyclo*-C₆H₁₁ (h); R¹ = R² = Me, R³ = *cyclo*-C₆H₁₁ (i); R¹ = R³ = *cyclo*-C₆H₁₁, R² = H (j).

* For communication X, see [1].

iron complexes and 1,2-bis(arylimino)acenaphthene nickel complexes considerably extends the temperature range of their effective application [6]. Furthermore, variation of substituents in these compounds makes it possible to control molecular weight of the resulting polymer so that to convert oligomerization of ethylene into polymerization process [6].

In order to estimate general character of the above relations as applied to bidentate aryliminopyridine nickel, cobalt, and iron halide complexes it was necessary to determine the catalytic activity of such complexes modified by cycloalkyl groups in the polymerization of ethylene at elevated temperature. We believed that promising compounds for modification by cycloalkyl groups may be 6-bromo-2-(1-aryliminoethyl)pyridines. The presence in position 6 of the pyridine ring of a bulky substituent capable of "dynamic" coordination should hamper chain termination through β -H transfer and favor increased activity of the catalyst as a result of reduction of the activation barrier to ethylene insertion due to stabilization of electron-deficient transition state [2, 3].

In the present work we synthesized a series of 6-bromo-2-(1-aryliminoethyl)pyridines with cyclopentyl and cyclohexyl substituents in the aryl fragment as ligands for the above complexes. The ligands were obtained by reaction of 2-acetyl-6-bromopyridine (**I**) with substituted anilines. Analogous reaction with 2,6-diisopropylaniline was reported in [3]. By heating pyridyl ketone **I** with aniline (**IIa**), 2,6-dimethylaniline (**IIb**), and *o*-cycloalkylanilines **IIc–IIj** in methanol in the presence of a catalytic amount of formic acid we obtained 40–93% of the corresponding Schiff bases **IIIa–IIIj** (Scheme 1).

The structure of Schiff bases **IIIa–IIIj** was confirmed by analytical and spectral data. The ^1H NMR spectra of **IIIa–IIIj** contained singlets at δ 2.14–2.30 ppm from the $\text{N}=\text{CCH}_3$ protons; methylene protons in the cycloalkyl substituents resonated as multiplets at δ 1.08–2.02 ppm, and CH protons, at δ 2.19–3.02 ppm; signals from protons in the benzene and pyridine rings appeared in the region δ 6.56–8.31 ppm. In the spectra of Schiff bases **IIIb**, **IIIc**, **IIIe**, **IIIh**, and **IIIi**, singlets from methyl groups attached to the benzene ring were located at δ 1.93–2.14 ppm. Compounds **IIIa–IIIj** displayed in the IR spectra a strong absorption band at 1634–1647 cm^{-1} due to stretching vibrations of the $\text{C}=\text{N}$ bond (cf. [3, 8]). In the mass spectra of **IIIa–IIIj** strong molecular ion peaks were observed.

EXPERIMENTAL

The ^1H NMR spectra were recorded from solutions in carbon tetrachloride on a Bruker AM-400 SY instrument operating at a frequency of 400.13 MHz; the chemical shifts were measured relative to hexamethyldisiloxane as internal reference. The IR spectra were obtained on a Vector 22 spectrometer from samples prepared as KBr pellets or neat substances. The progress of reaction and the purity of products were monitored by TLC on Silufol UV-254 plates using chloroform as eluent. The elemental compositions were calculated from the high-resolution mass spectra which were recorded on a Finnigan MAT-8200 instrument. The melting points were determined by heating samples between glass plates at a rate of 1 deg/min.

2-Acetyl-6-bromopyridine and cycloalkylanilines **IIc–IIj** were synthesized as described in [9, 10].

Schiff bases IIIa–IIIj (general procedure). A mixture of 1 mmol of 2-acetyl-6-bromopyridine (**I**), 1.2 mmol of aniline **IIa–IIj**, 10 ml of methanol, and 5 mg of anhydrous formic acid was heated for 6–12 h until the initial compounds disappeared (according to the TLC data). The solvent was distilled off on a rotary evaporator under reduced pressure (water-jet pump) at a bath temperature of 45°C, and the residue was recrystallized from methanol.

***N*-[1-(6-Bromopyridin-2-yl)ethylidene]aniline (IIIa).** Yield 46%, mp 88.5–89.5°C. IR spectrum: ν 1634 cm^{-1} ($\text{N}=\text{C}$). ^1H NMR spectrum, δ , ppm: 2.30 s (3H, CH_3), 6.78 d (2H, H_{arom} , $J = 8$ Hz), 7.09 t (1H, H_{arom} , $J = 8$ Hz), 7.35 t (2H, H_{arom} , $J = 8$ Hz), 7.53 d (1H, H_{arom} , $J = 8$ Hz), 7.61 t (1H, H_{arom} , $J = 8$ Hz), 8.21 d (1H, H_{arom} , $J = 8$ Hz). Found: $[M]^+$ 274.01100. $\text{C}_{13}\text{H}_{11}\text{N}_2\text{Br}$. Calculated: M 274.01061.

***N*-[1-(6-Bromopyridin-2-yl)ethylidene]-2,6-dimethylaniline (IIIb).** Yield 64%, mp 81.5–82.5°C. IR spectrum: ν 1647 cm^{-1} ($\text{N}=\text{C}$). ^1H NMR spectrum, δ , ppm: 2.0 s (6H, CH_3), 2.14 s (3H, CH_3), 6.92 t (1H, H_{arom} , $J = 8$ Hz), 7.04 d (2H, H_{arom} , $J = 8$ Hz), 7.55 d (1H, H_{arom} , $J = 8$ Hz), 7.63 t (1H, H_{arom} , $J = 8$ Hz), 8.31 d (1H, H_{arom} , $J = 8$ Hz). Found: $[M]^+$ 302.04210. $\text{C}_{15}\text{H}_{15}\text{N}_2\text{Br}$. Calculated: M 302.04191.

***N*-[1-(6-Bromopyridin-2-yl)ethylidene]-2-cyclopentylaniline (IIIc).** Yield 78%, mp 67–68°C. IR spectrum: ν 1637 cm^{-1} ($\text{N}=\text{C}$). ^1H NMR spectrum, δ , ppm: 1.48–1.96 m (8H, CH_2), 2.27 s (3H, CH_3), 2.91–3.02 m (1H, CH), 6.56 d (1H, H_{arom} , $J = 8$ Hz), 7.07 t (1H, H_{arom} , $J = 8$ Hz), 7.15 t (1H, H_{arom} , $J = 8$ Hz),

7.30 d (1H, H_{arom} , $J = 8$ Hz), 7.54 d (1H, H_{arom} , $J = 8$ Hz), 7.63 t (1H, H_{arom} , $J = 8$ Hz), 8.25 d (1H, H_{arom} , $J = 8$ Hz). Found: $[M]^+$ 342.07288. $C_{18}H_{19}N_2Br$. Calculated: M 342.07320.

***N*-[1-(6-Bromopyridin-2-yl)ethylidene]-2-cyclopentyl-6-methylaniline (III d)**. Yield 61%, mp 51–52°C. IR spectrum: ν 1642 cm^{-1} (N=C). ^1H NMR spectrum, δ , ppm: 1.44–1.85 m (8H, CH_2), 1.97 s (3H, CH_3), 2.15 s (3H, CH_3), 2.75–2.86 m (1H, CH), 6.98 t (1H, H_{arom} , $J = 8$ Hz), 7.03 d (1H, H_{arom} , $J = 8$ Hz), 7.15 d (1H, H_{arom} , $J = 8$ Hz), 7.55 d (1H, H_{arom} , $J = 8$ Hz), 7.64 d (1H, H_{arom} , $J = 8$ Hz), 8.31 d (1H, H_{arom} , $J = 8$ Hz). Found: $[M]^+$ 356.08880. $C_{19}H_{21}N_2Br$. Calculated: M 356.08885.

***N*-[1-(6-Bromopyridin-2-yl)ethylidene]-2-cyclopentyl-4,6-dimethylaniline (III e)**. Yield 83%, mp 58–59°C. IR spectrum: ν 1643 cm^{-1} (N=C). ^1H NMR spectrum, δ , ppm: 1.42–1.84 m (8H, CH_2), 1.93 s (3H, CH_3), 2.14 s (3H, CH_3), 2.29 s (3H, CH_3), 2.71–2.82 m (1H, CH), 6.85 s (1H, H_{arom}), 6.95 s (1H, H_{arom}), 7.54 d (1H, H_{arom} , $J = 8$ Hz), 7.63 t (1H, H_{arom} , $J = 8$ Hz), 8.30 d (1H, H_{arom} , $J = 8$ Hz). Found: $[M]^+$ 370.10405. $C_{20}H_{23}N_2Br$. Calculated: M 370.10450.

***N*-[1-(6-Bromopyridin-2-yl)ethylidene]-2,6-dicyclopentylaniline (III f)**. Yield 82%, mp 199–200°C. IR spectrum: ν 1639 cm^{-1} (N=C). ^1H NMR spectrum, δ , ppm: 1.43–2.02 m (16H, CH_2), 2.15 s (3H, CH_3), 2.67–2.81 m (2H, CH), 7.05 t (1H, H_{arom} , $J = 7$ Hz), 7.14 d (2H, H_{arom} , $J = 7$ Hz), 7.56 d (1H, H_{arom} , $J = 8$ Hz), 7.65 t (1H, H_{arom} , $J = 8$ Hz), 8.31 d (1H, H_{arom} , $J = 8$ Hz). Found: $[M]^+$ 410.13540. $C_{23}H_{27}N_2Br$. Calculated: M 410.13580.

***N*-[1-(6-Bromopyridin-2-yl)ethylidene]-2-cyclohexylaniline (III g)**. Yield 90%, mp 101.5–102.5°C. IR spectrum: ν 1635 cm^{-1} (N=C). ^1H NMR spectrum, δ , ppm: 1.13–1.82 m (10H, CH_2), 2.28 s (3H, CH_3), 2.48–2.59 m (1H, CH), 6.57 d (1H, H_{arom} , $J = 7.5$ Hz), 7.08 t (1H, H_{arom} , $J = 7.5$ Hz), 7.15 t (1H, H_{arom} , $J = 7.5$ Hz), 7.27 d (1H, H_{arom} , $J = 7.5$ Hz), 7.54 d (1H, H_{arom} , $J = 8$ Hz), 7.63 t (1H, H_{arom} , $J = 8$ Hz), 8.24 d (1H, H_{arom} , $J = 8$ Hz). Found: $[M]^+$ 356.08880. $C_{19}H_{21}N_2Br$. Calculated: M 356.08885.

***N*-[1-(6-Bromopyridin-2-yl)ethylidene]-2-cyclohexyl-6-methylaniline (III h)**. Yield 67%, mp 82–83°C. IR spectrum: ν 1643 cm^{-1} (N=C). ^1H NMR spectrum, δ , ppm: 1.12–1.95 m (10H, CH_2), 1.97 s (3H, CH_3), 2.14 s (3H, CH_3), 2.27–2.37 m (1H, CH), 6.98 t (1H, H_{arom} , $J = 7.5$ Hz), 7.03 d (1H, H_{arom} , $J = 7.5$ Hz), 7.11 d (1H, H_{arom} , $J = 7.5$ Hz), 7.56 d (1H, H_{arom} , $J =$

8 Hz), 7.64 d (1H, H_{arom} , $J = 8$ Hz), 8.29 d (1H, H_{arom} , $J = 8$ Hz). Found: $[M]^+$ 370.10485. $C_{20}H_{23}N_2Br$. Calculated: M 370.10450.

***N*-[1-(6-Bromopyridin-2-yl)ethylidene]-2-cyclohexyl-4,6-dimethylaniline (III i)**. Yield 40%, oily substance. IR spectrum: ν 1645 cm^{-1} (N=C). ^1H NMR spectrum, δ , ppm: 1.13–1.92 m (10H, CH_2), 1.93 s (3H, CH_3), 2.14 s (3H, CH_3), 2.29 s (3H, CH_3), 2.24–2.34 m (1H, CH), 6.86 s (1H, H_{arom}), 6.92 s (1H, H_{arom}), 7.55 d (1H, H_{arom} , $J = 8$ Hz), 7.64 t (1H, H_{arom} , $J = 8$ Hz), 8.28 d (1H, H_{arom} , $J = 8$ Hz). Found: $[M]^+$ 384.11970. $C_{21}H_{25}N_2Br$. Calculated: M 384.12015.

***N*-[1-(6-Bromopyridin-2-yl)ethylidene]-2,6-dicyclohexylaniline (III j)**. Yield 75%, mp 136–137°C. IR spectrum: ν 1640 cm^{-1} (N=C). ^1H NMR spectrum, δ , ppm: 1.08–1.92 m (20H, CH_2), 2.14 s (3H, CH_3), 2.19–2.29 m (2H, CH), 7.05 t (1H, H_{arom} , $J = 7.5$ Hz), 7.11 d (2H, H_{arom} , $J = 7.5$ Hz), 7.57 d (1H, H_{arom} , $J = 8$ Hz), 7.65 t (1H, H_{arom} , $J = 8$ Hz), 8.28 d (1H, H_{arom} , $J = 8$ Hz). Found: $[M]^+$ 438.16680. $C_{25}H_{31}N_2Br$. Calculated: M 438.16710.

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