

Design of Schiff Base-Like Postmetallocene Catalytic Systems for Polymerization of Olefins: II.¹ Synthesis of 2,6-Bis(aryliminoalkyl)pyridines with Cycloalkyl Substituents

I. I. Oleinik, I. V. Oleinik, I. B. Abdrakhmanov, S. S. Ivanchev, and G. A. Tolstikov

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch,
Russian Academy of Sciences, Novosibirsk, Russia

Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences, Ufa, Bashkortostan, Russia
St. Petersburg Division, Boreskov Institute of Catalysis, Siberian Branch,
Russian Academy of Sciences, St. Petersburg, Russia

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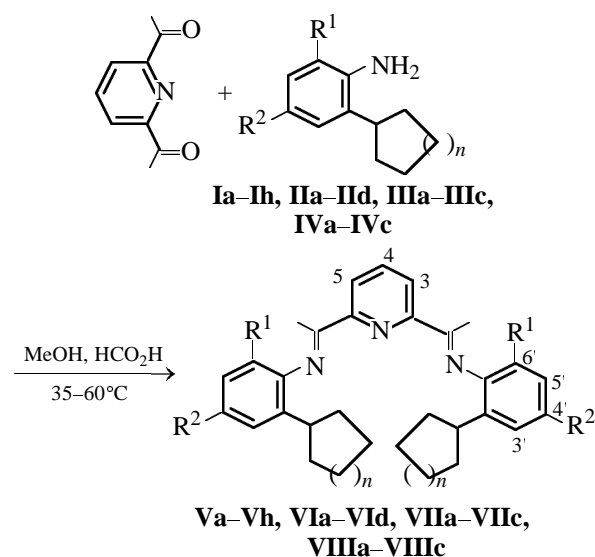
Abstract—Reactions of substituted cycloalkylanilines with 2,6-diacetylpyridine in methanol in the presence of formic acid afforded a wide series of the corresponding bis(cycloalkylaryliminoalkyl)pyridines which can be used as ligands for the preparation of iron and cobalt complexes.

We previously demonstrated the possibility of using halide iron and cobalt complexes with bis(iminoalkyl)pyridine ligands as components of catalytic systems for polymerization of ethylene [2–5]. Interest in such postmetallocene catalytic systems originates from their high activity which is comparable with the activity of metallocene catalysts and their ability to produce unbranched polymer following a mechanism different from that typical of diimine catalytic systems.

We also showed that the temperature range of action of these catalysts can be extended via introduction of cycloalkyl substituents into the ortho position of the aryl ring attached to the imino group [6–8].

The procedure for the synthesis of bis(aryliminoalkyl)pyridine ligands is based on the reaction of 2,6-diacetylpyridine with anilines, which was effected previously using alkyylanilines as examples [3, 4]. In the present work we extended these procedure to anilines containing cycloalkyl substituents with a view to obtain new 2,6-bis(aryliminoalkyl)pyridine structures **V–VIII** and optimized the reaction conditions.

By reactions of 2-cyclopentyl-, 2,6-dicyclopentyl- (**Ia–Ih**), 2-cyclohexyl-, 2,6-dicyclohexyl (**IIa–IIId**), 2-cyclooctyl- (**IIIa–IIIc**), and 2-cyclododecylanilines (**IVa–IVc**) [1] with 2,6-diacetylpyridine on heating in an organic solvent in the presence of molecular sieves



I–VIII, R¹ = R² = H (**a**), Me (**c**); R¹ = Me, R² = H (**b**);
R¹ = *cyclo*-C₄H₇(CH₂)_n, R² = H (**d**); R¹ = Cl, R² = H (**e**);
R¹ = OMe, R² = H (**f**); R¹ = H, R² = OEt (**g**); R¹ = *cyclo*-
C₄H₇(CH₂)_n, R² = OEt (**h**). **I, V**, n = 1; **II, VI**, n = 2; **III**,
VII, n = 4; **IV, VIII**, n = 8.

or a catalytic amount of a mineral or organic acid with simultaneous removal of liberated water by azeotropic distillation we obtained the corresponding 2,6-bis[1-(2-cycloalkylimino)ethyl]pyridines **Va–Vh**, **VIa–VIId**, **VIIa–VIIc**, and **VIIIA–VIIIC**. Methanol turned out to be the best solvent, and formic acid was the best

¹ For communicationh I, see [1].

Table 1. Yields, melting points, and analytical data of 2,6-bis[1-(2-R¹-4-R²-6-cycloalkylphenylimino)ethyl]pyridines **V–VIII**

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %			<i>M</i>	
			C	H	N		C	H	N	found	calculated
Va	85	169–170	82.77	7.84	9.37	C ₃₁ H ₃₅ N ₃	82.80	7.85	9.35	449.2817	449.2831
Vb	85	170–172	82.94	8.26	8.84	C ₃₃ H ₃₉ N ₃	82.97	8.23	8.80	477.3128	477.3144
Vc	81	183–185	83.13	8.58	8.30	C ₃₅ H ₄₃ N ₃	83.12	8.57	8.31	505.3459	505.3457
Vd	85	295–297	84.11	8.59	7.25	C ₄₁ H ₅₁ N ₃	84.06	8.77	7.17	585.4075	585.4083
Ve	82	192–195	71.90	6.49	8.15	C ₃₁ H ₃₃ Cl ₂ N ₃ ^a	71.81	6.41	8.10	517.2039	517.2051
Vf	87	163–165	77.68	7.65	8.30	C ₃₃ H ₃₉ N ₃ O ₂	77.66	7.71	8.25	509.3048	509.3042
Vg	98	208–210	78.20	8.05	7.80	C ₃₅ H ₄₃ N ₃ O ₂	78.17	8.06	7.82	537.3352	537.3355
Vh	89	238–240	80.30	8.75	6.20	C ₄₅ H ₅₉ N ₃ O ₂	80.19	8.82	6.24	673.4582	673.4607
VIa	85	193–195	82.85	8.15	8.92	C ₃₃ H ₃₉ N ₃	82.97	8.23	8.80	477.3144	477.3144
VIb	81	215–217	83.15	8.54	8.34	C ₃₅ H ₄₃ N ₃	83.12	8.57	8.31	505.3448	505.3457
VIc	82	234–236	83.27	8.85	7.85	C ₃₇ H ₄₇ N ₃	83.25	8.87	7.87	533.3770	533.3770
VIId	83	223–225	84.30	9.22	6.50	C ₄₅ H ₅₉ N ₃	84.19	9.27	6.54	641.4706	641.4709
VIIa	83	208–210	83.32	8.96	7.80	C ₃₇ H ₄₇ N ₃	83.25	8.87	7.87	533.3770	533.3770
VIIb	85	140–142	83.39	9.11	7.45	C ₃₉ H ₅₁ N ₃	83.37	9.15	7.48	561 ^b	
VIIc	80	128–130	83.50	9.43	7.10	C ₄₁ H ₅₅ N ₃	83.48	9.40	7.12	589 ^b	
VIIIa	84	156–157	83.59	9.85	6.51	C ₄₅ H ₆₃ N ₃	83.67	9.83	6.50	645 ^b	
VIIIb	83	178–180	83.78	10.04	6.18	C ₄₇ H ₆₇ N ₃	83.75	10.02	6.23	673 ^b	
VIIIc	80	168–169	83.50	10.23	6.10	C ₄₉ H ₇₁ N ₃	83.82	10.19	5.98	701 ^b	

^aFound Cl, %: 13.72. Calculated Cl, %: 13.68. ^b We failed to determine the precise molecular weight.

catalyst; these conditions ensured 80–85% yield of the target products.

The structure of the products was determined on the basis of their analytical and spectral data (Tables 1, 2). The ¹H NMR spectra of Schiff bases **V–VII** contained singlets from the N=CCH₃ groups in the region δ 2.19–2.39 ppm. Methylene protons in the cycloalkyl groups appeared as multiplets at δ 0.80–2.10 ppm, and the CH protons gave signals at δ 2.28–3.01 ppm. Signals from aromatic protons were located in the region δ 6.48–7.23 ppm. Protons in the pyridine ring gave characteristic signals at δ 7.83–7.98 (t, 4-H) and 8.35–8.48 ppm (d or d.d, 3-H, 5-H). Schiff bases **Vb**, **Vc**, **VIb**, **VIc**, **VIIb**, **VIIc**, **VIIIb**, and **VIIIc** showed in the spectra singlets at δ 1.93–2.19 ppm from the methyl protons at the benzene rings, and the spectra of **Vf** and **Vh** contained signals from the alkoxy groups at δ, ppm: 3.72 s (OCH₃), 1.39 t and 3.24 q (OC₂H₅).

In the IR spectra of **V–VII** we observed a strong absorption band at 1636–1645 cm⁻¹, which corresponds to stretching vibrations of the imine C=N bond. Stretching vibrations of C–H bonds at the pyridine and benzene rings appeared at 3000–3080 cm⁻¹, and C–H bonds of the cycloalkyl fragments and methyl groups (in **Vb**, **Vc**, **VIb**, **VIc**, **VIIb**, **VIIc**, **VIIIb**, and

VIIIc) gave rise to absorption in the region 2835–2960 cm⁻¹.

The mass spectra of **V–VII** contained strong peaks from the molecular ions, and their fragmentation included elimination of a methyl group, leading to a strong [*M* – 15]⁺ ion.

EXPERIMENTAL

The IR spectra were recorded on a Vector-22 spectrometer from samples pelleted with KBr. The ¹H NMR spectra were obtained on a Bruker WP-200SY instrument (200 MHz) from solutions in carbon tetrachloride; hexamethyldisiloxane was used as internal reference. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using chloroform as eluent. The elemental compositions were determined on a Carlo Erba 1106 CHN analyzer, as well as from the high-resolution mass spectra which were run on an MAT-8200 mass spectrometer. The melting points were determined using a heating device; samples were heated at a rate of 1 deg min⁻¹.

Anilines **I–IV** and 2,6-diacetylpyridine were synthesized by the procedures described in [1, 9].

Table 2. IR and ^1H NMR spectra of 2,6-bis[1-(2-R¹-4-R²-6-cycloalkylphenylimino)ethyl]pyridines **V–VIII**

Comp. no.	IR spectrum, $\nu(\text{N}=\text{CCH}_3)$, cm^{-1}	^1H NMR spectrum, δ , ppm (J , Hz)
Va	1645	1.40–1.95 m (16H, 8CH ₂), 2.34 s (6H, 2N=CCH ₃), 2.98 m (2H, 2CH), 6.48 d.d (2H, 2H ³ , J_1 8, J_2 2), 6.98–7.12 m (4H, 2H ^{4,5}), 7.21 d.d (2H, 2H ⁶ , J_1 8, J_2 2), 7.85 t (1H, H ⁴ , J 8), 8.39 d (2H, H ^{3,5} , J 8)
Vb	1640	1.50–1.90 m (16H, 8CH ₂), 2.03 s (6H, 2CH ₃), 2.26 s (6H, 2N=CCH ₃), 2.87 m (2H, 2CH), 6.94 d (2H, 2H ³ , J 6), 6.98 t (2H, 2H ⁴ , J 6), 7.12 d (2H, 2H ⁵ , J 6), 7.92 t (1H, H ⁴ , J 7), 8.52 d (2H, H ^{3,5} , J 7)
Vc	1640	1.40–1.90 m (16H, 8CH ₂), 1.93 s (6H, 2CH ₃), 2.19 s (6H, 2CH ₃), 2.27 s (6H, 2N=CCH ₃), 2.76 m (2H, 2CH), 6.75 s (2H, 2H ³), 6.83 s (2H, 2H ⁵), 7.86 t (1H, H ⁴ , J 7), 8.46 d (2H, H ^{3,5} , J 7)
Vd	1640	1.47–2.08 m (32H, 16CH ₂), 2.26 s (6H, 2N=CCH ₃), 2.76 m (4H, 4CH), 6.95–7.10 m (6H, 2H ^{3,4,5}), 7.98 t (1H, H ⁴ , J 8), 8.58 d (2H, H ^{3,5} , J 8)
Ve	1644	1.40–2.10 m (16H, 8CH ₂), 2.29 s (6H, 2N=CCH ₃), 2.90 m (2H, 2CH), 6.93 t (2H, 2H ⁴ , J 7), 7.15 d (2H, 2H ³ , J 7), 7.20 d (2H, 2H ⁵ , J 7), 7.91 t (1H, H ⁴ , J 7), 8.48 d (2H, H ^{3,5} , J 7)
Vf	1645	1.45–1.72 m (16H, 8CH ₂), 2.22 s (6H, 2N=CCH ₃), 2.95 m (2H, 2CH), 3.72 s (2H, 2OCH ₃), 6.67 d (2H, 2H ⁵ , J 7), 6.81 d (2H, 2H ³ , J 7), 6.87 t (2H, 2H ⁴ , J 7), 7.85 t (1H, H ⁴ , J 7), 8.44 d (2H, H ^{3,5} , J 7)
Vg	1641	1.43 t (6H, 2OCH ₂ CH ₃ , J 7), 1.50–1.98 m (16H, 8CH ₂), 2.35 s (6H, 2N=CCH ₃), 3.01 m (2H, 2CH), 3.95 q (4H, 2OCH ₂ CH ₃ , J 7), 6.40 d (2H, 2H ⁶ , J 9), 6.58 d.d (2H, 2H ⁵ , J_1 9, J_2 3), 6.75 d (2H, 2H ³ , J 3), 7.82 t (1H, H ⁴ , J 8), 8.35 d (2H, H ^{3,5} , J 8)
Vh	1636	1.39 t (6H, 2OCH ₂ CH ₃ , J 7), 1.43–1.98 m (32H, 16CH ₂), 2.19 s (6H, 2N=CCH ₃), 2.75 m (4H, 4CH), 3.94 q (4H, 2OCH ₂ CH ₃ , J 7), 6.57 s (4H, 2H ^{3,5}), 7.88 t (1H, H ⁴ , J 8), 8.42 d (2H, H ^{3,5} , J 8)
Vla	1639	1.10–1.80 m (20H, 10CH ₂), 2.36 s (6H, 2N=CCH ₃), 2.55 m (2H, 2CH), 6.50 d.d (2H, 2H ³ , J_1 8, J_2 2), 6.93–7.13 m (4H, 2H ^{4,5}), 7.19 d.d (2H, 2H ⁶ , J_1 8, J_2 2), 7.88 t (1H, H ⁴ , J 8), 8.39 d (2H, H ^{3,5} , J 8)
Vlb	1644	1.05–1.80 m (20H, 10CH ₂), 1.98 s (6H, 2CH ₃), 2.21 s (6H, 2N=CCH ₃), 2.30 m (2H, 2CH), 6.82–7.04 m (6H, 3H ^{3,5}), 7.00 t (2H, 2H ⁴ , J 8), 7.91 t (1H, H ⁴ , J 8), 8.45 d (2H, H ^{3,5} , J 8)
Vlc	1639	1.15–1.80 m (20H, 10CH ₂), 1.94 s (6H, 2CH ₃), 2.19 s (6H, 2CH ₃), 2.27 s (6H, 2N=CCH ₃), 2.35 m (2H, 2CH), 6.76 s (2H, 2H ³), 6.80 s (2H, 2H ⁵), 7.89 t (1H, H ⁴ , J 8), 8.43 d.d (2H, H ^{3,5} , J_1 8, J_2 3)
Vld	1645	1.05–1.90 m (40H, 20CH ₂), 2.22 s (6H, 2N=CCH ₃), 2.30 m (4H, 4CH), 6.82–7.01 m (6H, 2H ^{3,4,5}), 7.95 t (1H, H ⁴ , J 8), 8.39 d (2H, H ^{3,5} , J 8)
VIIa	1639	1.35–1.80 m (28H, 14CH ₂), 2.36 s (6H, 2N=CCH ₃), 2.88 m (2H, 2CH), 6.49 d (2H, 2H ³ , J 8), 6.90–7.10 m (4H, 2H ^{4,5}), 7.17 d (2H, 2H ⁶ , J 8), 7.90 t (1H, H ⁴ , J 8), 8.39 d (2H, H ^{3,5} , J 8)
VIIb	1641	1.35–1.80 m (28H, 14CH ₂), 1.90 s (6H, 2CH ₃), 2.21 s (6H, 2N=CCH ₃), 2.70 m (2H, 2CH), 6.80–7.05 m (6H, 2H ^{3,4,5}), 7.90 t (1H, H ⁴ , J 8), 8.47 d.d (2H, H ^{3,5} , J_1 8, J_2 3)
VIIc	1640	1.10–1.80 m (28H, 14CH ₂), 1.94 s (6H, 2CH ₃), 2.11 s (6H, 2CH ₃), 2.26 s (6H, 2N=CCH ₃), 2.65 m (2H, 2CH), 6.73 s (2H, 2H ³), 6.78 s (2H, 2H ⁵), 7.89 t (1H, H ⁴ , J 8), 8.42 d.d (2H, H ^{3,5} , J_1 8, J_2 3)
VIIIa	1639	0.80–1.80 m (44H, 22CH ₂), 2.34 s (6H, 2N=CCH ₃), 2.95 m (2H, 2CH), 6.54 d (2H, 2H ³ , J 8), 6.95–7.10 m (4H, 2H ^{4,5}), 7.19 d (2H, 2H ⁶ , J 8), 7.86 t (1H, H ⁴ , J 8), 8.40 d (2H, H ^{3,5} , J 8)
VIIIb	1645	0.70–1.77 m (44H, 22CH ₂), 1.99 s (6H, 2CH ₃), 2.20 s (6H, 2N=CCH ₃), 2.69 m (2H, 2CH), 6.80–7.05 m (6H, 2H ^{3,4,5}), 7.86 t (1H, H ⁴ , J 8), 8.45 d.d (2H, H ^{3,5} , J_1 8, J_2 3)
VIIIc	1642	0.75–1.75 m (44H, 22CH ₂), 1.95 s (6H, 2CH ₃), 2.18 s (6H, 2CH ₃), 2.28 s (6H, 2N=CCH ₃), 2.72 m (2H, 2CH), 6.75 s (2H, 2H ³), 6.80 s (2H, 2H ⁵), 7.84 t (1H, H ⁴ , J 8), 8.43 d.d (2H, H ^{3,5} , J_1 8, J_2 3)

2,6-Bis[1-(2-R¹-4-R²-6-cycloalkylphenylimino)-ethyl]pyridines V–VIII (*general procedure*). A mixture of 0.25 mmol of 2,6-diacetylpyridine, 0.52 mmol of cycloalkylaniline I–IV, 5 mg of anhydrous formic acid, and 10 ml of methanol was heated at 55°C until complete conversion of 2,6-diacetylpyridine (9–15 h). The solvent was distilled off under reduced pressure (water-jet pump) at a bath temperature of 45°C, the residue was dissolved in 15 ml of diethyl ether, and unreacted 2-cycloalkylaniline was extracted into dilute hydrochloric acid (2 × 10 ml). The organic phase was washed with water to pH 7, dried over magnesium sulfate, and evaporated, and the residue was recrystallized from ethanol.

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