Russian Journal of General Chemistry, Vol. 74, No. 9, 2004, pp. 1423–1427. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 9, 2004, pp. 1534–1538.

Design of Arylimine Postmetallocene Catalytic Systems for Olefin Polymerization: I. Synthesis of Substituted 2-Cycloalkyl- and 2,6-Dicycloalkylanilines

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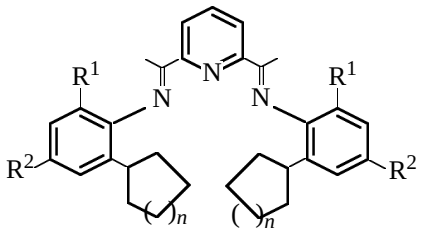
Received September 29, 2003

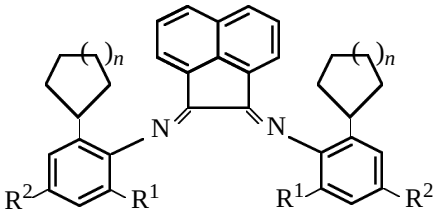
Abstract — A convenient synthetic approach to substituted 2-cycloalkyl- and 2,6-dicycloalkylanilines, involving catalytic hydrogenation on Raney nickel in methanol of readily available *o*-cycloalkenylanilines prepared by reaction of cyclic alkyl halides with anilines.

Over the past decade there has been growing interest in the design of novel postmetallocene catalysts for olefin polymerization [1–3]. The discovery of catalytic polymerization systems on the basis of α-diimine nickel and palladium complexes [4–6], as well as iron and cobalt complexes with tridentate bis(aryliminoalkyl)pyridyl ligands [7–9] has given impetus to structural modification of novel complexes, aimed at enhancing their catalytic activity and temperature range [10–15].

Recently we showed that the structural modification of bis(iminoalkyl)pyridine **A** [11, 13] and diimine **B** ligands [14, 15] by cycloalkyl substitution in the benzene ring *ortho* to the imine nitrogen makes it possible to considerably extend the catalytic activity range to higher temperatures (70–80°C), which is very important for polymerization technology.



A



B

The modified ligands all were derived from substituted anilines containing *ortho*-cycloalkyl substituents. Prior to our work no rational synthetic procedures for such anilines had been reported.

We made use of catalytic hydrogenation of *o*-cycloalkenylanilines readily available by reaction of 3-halocycloalkenes with anilines via Claisen amino rearrangement of the primarily formed *N*-(2-cycloalkenyl)anilines [16, 17].

Aniline and its derivatives **Va**–**Vf** were reacted with 3-chlorocyclopentene (**I**), 3-bromocyclohexene (**II**), 3-bromocycloocta-1,5-diene (**III**), and 3-bromo-

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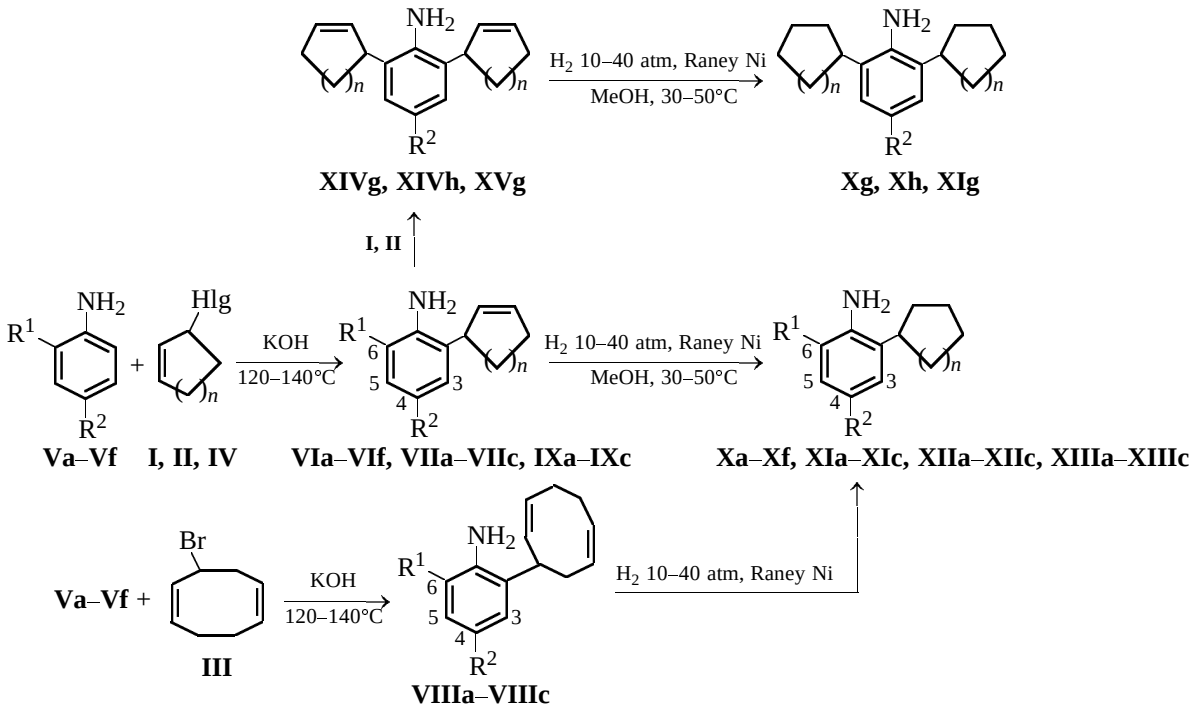

$R^1 = R^2 = H$ (**a**), Me (**c**); R^1 = Me, R^2 = H (**b**); R^1 = Cl, R^2 = H (**d**); R^1 = OMe, R^2 = H (**e**); R^1 = H, R^2 = OEt (**f**); R^2 = H (**g**); R^2 = OEt (**h**). **I**, Hlg = Cl, *n* = 1; **II**, Hlg = Br, *n* = 2; **IV**, Hlg = Br, *n* = 8. *n* = 1 (**VI, X, XIV**), 2 (**VII, XII, XV**), 4 (**XII**), 8 (**IX, XIII**).

cyclododecene (**IV**) to obtain 2-cycloalkenylanilines **VI**, **VII**, and **IX** and 2-cyclooctadienylanilines **VIII**. 2,6-Dicycloalkenylanilines **XIVg**, **XIVh**, and **XVg** were synthesized by reactions of 2-cycloalkenylanilines **VIa**, **VIf**, and **VIIa** with alkenyl halides **I** and **II**.

We showed that 2-(2-cycloalkenyl)anilines **VIa**–**VIf**, **VIIa**–**VIIc**, and **IXa**–**IXc**, 2-(2,6-dicyclooctadienyl)anilines **VIIIa**–**VIIIf**, and 2,6-di(2-cycloalkenyl)anilines **XIVg**, **XIVh**, and **XVg** are hydrolyzed in mild conditions in the presence of Raney nickel to form 2-cycloalkylanilines and 2,6-dicycloalkylanilines **X**–**XIII** in 95–99% yields. Therewith, the hydrogenation of cyclopentenylaniline **VId** involves no dehalogenation.

Structural assessment of the cycloalkyl- and dicycloalkylanilines was performed on the basis of analytical and spectral data (Tables 1 and 2). The ^{1}H NMR spectra of compounds **X**–**XIII** contain multiplets of the cycloalkyl methylene and methine protons at 1.10–2.09 and 2.35–2.90 ppm, respectively. The amino group of **Xa**–**Xc**, **Xf**–**Xh**, **XIa**–**XIc**, **XIg**, **XIIa**–**XIIc**, and **XIIIa**–**XIIIc** appear as a broadened singlet at 3.19–3.54 ppm. *Ortho* methoxy substitution in 2-cyclopentylaniline **Xa** shifts the amino NH signal downfield by 0.35 ppm (to 3.75 ppm in compound **Xe**), whereas chlorine substitution shifts its signal even stronger (to 4.05 ppm in compound **Xd**). The aromatic protons of the benzene ring absorb at 6.37–7.03 ppm. The spectra of compounds **Xb**, **Xc**–**XIIIb**, and **XIIIc** display methyl singlets at 2.03–2.38 ppm and those of anilines **Xe**, **Xf**, and **Xh**, signals of the alkoxy groups [δ, ppm: 3.75 s (OCH_3; **Xe**), 1.30–1.31 t and 3.82–3.84 q (OC_2H_5, **Xf** and **Xh**).

The IR spectra of compounds **X**–**XIII** contain two strong bands at 3380–3490 cm^{-1}, belonging to stretching vibrations of the amino group. The stretching vibration bands of the benzene CH bonds appear at 3000–3080 cm^{-1} and those of the cycloalkyl CH and CH_2 groups, as well as of the methyl groups, at 2835–2960 cm^{-1}.

EXPERIMENTAL

The IR spectra were recorded on a Vector-22 spectrometer in KBr pellets. The ^{1}H NMR spectra were obtained on a Bruker WP-200SY instrument (200 MHz) in CCl_4 solutions, internal reference HMDS. The reaction progress and the purity of the synthesized compounds were controlled by TLC on Silufol UV-254 plates, eluent chloroform. Elemental analysis was performed on a Karlo Erba-1106 CHN analyzer. The brutto formulas were calculated from

Table 1. Yields, boiling points, and elemental analyses of 2-cycloalkylanilines **X**–**XIII**

Comp. no.	Yield, %	bp, °C (0.5 mm Hg)	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
Xa	95	95–96	81.80	9.29	8.72	$C_{11}H_{15}N$	81.94	9.38	8.69
Xb	98	98–100	82.25	9.77	7.98	$C_{12}H_{17}N$	82.23	9.78	7.99
Xc	98	134–136	82.48	10.15	7.41	$C_{13}H_{19}N$	82.48	10.12	7.40
Xd	95	131–133	67.50	7.17	7.21	$C_{11}H_{14}ClN$[a]	67.51	7.21	7.16
Xe	98	123–125	75.28	8.90	7.28	$C_{12}H_{17}NO$	75.35	8.96	7.32
Xf	97	126–128	75.97	9.30	6.83	$C_{13}H_{19}NO$	76.06	9.33	6.82
Xg	95	168–169	83.64	10.20	6.16	$C_{16}H_{23}N$	83.79	10.11	6.11
Xh	97	168–169	78.98	9.80	5.14	$C_{18}H_{27}NO$	79.07	9.96	5.12
XIa	95	81–83	82.31	9.70	8.07	$C_{12}H_{17}N$	82.23	9.78	7.99
XIb	96	100–102	82.51	10.15	7.41	$C_{13}H_{19}N$	82.48	10.12	7.40
XIc	97	133–135	82.73	10.45	6.85	$C_{14}H_{21}N$	82.70	10.41	6.89
XIg	98	165–167	84.06	10.48	5.46	$C_{18}H_{27}N$	83.99	10.57	5.44
XIIa	96	120–121	82.75	10.49	6.95	$C_{14}H_{21}N$	82.70	10.41	6.89
XIIb	98	129–130	82.91	10.64	6.41	$C_{15}H_{23}N$	82.89	10.67	6.44
XIIc	98	145–147	83.10	10.92	6.08	$C_{16}H_{25}N$	83.06	10.89	6.05
XIIIa	97	143–145	83.38	11.23	5.40	$C_{18}H_{29}N$	83.33	11.27	5.40
XIIIb	95	170–172	83.48	11.45	5.15	$C_{19}H_{31}N$	83.45	11.43	5.12
XIIIc	96	180–182	83.59	11.55	4.90	$C_{20}H_{33}N$	83.56	11.57	4.87

[a] Found Cl, %: 18.17. Calculated Cl, %: 18.12.

the high-resolution mass spectra measured on a Finnigan MAT-8200 instrument.

Raney nickel was prepared from a nickel–aluminum alloy (1:1) by the procedure in [18]. Cycloalkenylanilines **VIa**–**VId**, **VIIa**–**VIIc**, and **IXa**, cyclooctadienylanilines **VIIIa**–**VIIIc**, and dicycloalkenylanilines **XIVg** and **XVg** were prepared by the procedures in [16, 17]. Previously unknown **VIe**, **VIf**, **IXb**, **IXc**, and **XIVh** were prepared in a similar way.

2-(2-Cyclopentenyl)-6-methoxyaniline (VIe). Yield 83%, bp 128–130°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.54–2.50 m (4H, $2CH_2$), 3.70 s (3H, OCH_3), 3.73 br.s (2H, NH_2), 4.44 m (1H, CH), 5.72–5.81 m (1H, CH=CH), 5.83–5.90 m (1H, CH=CH), 6.47 d (1H, H^3, *J* 7), 6.54 d (1H, H5, *J* 7), 6.69 t (1H, H^4, *J* 7). Found, %: C 76.22; H 7.84; N 7.42. $C_{12}H_{15}NO$. Calculated, %: C 76.16; H 7.99; N 7.40.

2-(2-Cyclopentenyl)-4-ethoxyaniline (VIf). Yield 85%, bp 118–120°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.28 t (3H, OCH_2CH_3, *J* 7), 1.57–2.50 m (4H, $2CH_2$), 3.25 br.s (2H, NH_2), 3.74 m (1H, CH), 3.80 q (2H, OCH_2CH_3, *J* 7), 5.68–5.76 m (1H, CH=CH), 5.82–5.91 m (1H, CH=CH), 6.36 s (1H, H^3), 6.38–6.47 m (2H, $H^{5,6}$). Found, %: C 76.90; H 8.40; N 6.85. $C_{13}H_{17}NO$. Calculated, %: C 76.81; H 8.43; N 6.89.

2-(2-Cyclododecenyl)-6-methylaniline (IXb). Yield 81%, bp 152–154°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.18–1.90 m (18H, $9CH_2$), 2.10 s (3H, CH_3), 3.01 m (1H, CH), 3.46 br.s (2H, NH_2), 5.20–5.59 m (2H, 2CH=CH), 6.55 d (1H, H^3, *J* 7), 6.75 t (1H, H4, *J* 7), 6.87 d (1H, H5, *J* 7). Found, %: C 84.17; H 10.65; N 5.10. $C_{19}H_{29}N$. Calculated, %: C 84.07; H 10.77; N 5.16.

2-(Cyclododecenyl)-4,6-dimethylaniline (IXc). Yield 79%, bp 198–200.C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 1.25–1.85 m (18H, $9CH_2$), 2.09 s (3H, CH_3), 2.19 s (3H, CH_3), 2.99 m (1H, CH), 3.27 br.s (2H, NH_2), 5.15–5.57 m (2H, CH=CH), 6.58 s (1H, H^3), 6.65 s (1H, H^5). Found, %: C 84.26; H 10.81; N 4.92. $C_{20}H_{31}N$. Calculated, %: C 84.15; H 10.95; N 4.91.

2,6-Di(2-cyclopentenyl)-4-ethoxyaniline (XIVh). Yield 82%, bp 158–160°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.28 t (3H, OCH_2CH_3, *J* 7), 1.58–2.50 m (8H, $4CH_2$), 3.32 br.s (2H, NH_2), 3.75 m (2H, 2CH), 3.82 q (2H, OCH_2CH_3, *J* 7), 5.65–5.76 m (2H, 2CH=CH), 5.80–5.90 m (2H, 2CH=CH), 6.33 s (2H, $H^{3,5}$). Found, %: C 80.39; H 8.49; N 5.24. $C_{18}H_{23}NO$. Calculated, %: C 80.26; H 8.61; N 5.20.

2-Cycloalkyl- and 2,6-dicycloalkylanilines X–XIII. A solution of 0.1 mol of aniline **VI**–**XI**, **XIV**, or

Table 2. ^{1}H NMR spectra of 2-cycloalkylanilines **X**–**XIII**

Comp. no.	δ, ppm (*J*, Hz)
Xa	1.50–2.05 m (8H, 4CH_2), 2.90 m (1H, CH), 3.40 br.s (2H, NH_2), 6.44 d.d (1H, H^6, J_1 8, J_2 2), 6.57 t.d (1H, H^5, J_1 8, J_2 2), 6.84 t.d (1H, H^4, J_1 8, J_2 2), 6.95 d.d (1H, H^3, J_1 8, J_2 2)
Xb	1.45–1.97 m (8H, 4CH_2), 2.06 s (3H, CH_3), 2.80 m (1H, CH), 3.39 br.s (2H, NH_2), 6.49 t (1H, H^4, *J* 8), 6.74 d (1H, H^5, *J* 8), 6.84 d (1H, H^3, *J* 8)
Xc	1.45–1.98 m (8H, 4CH_2), 2.03 s (3H, CH_3), 2.15 s (3H, CH_3), 2.85 m (1H, CH), 3.27 br.s (2H, NH_2), 6.57 s (1H, H^3), 6.64 s (1H, H^5)
Xd	1.45–2.09 m (8H, 4CH_2), 2.88 m (1H, CH), 4.05 br.s (2H, NH_2), 6.52 t (1H, H^4, *J* 8), 6.89 d.d (1H, H^3, J_1 8, J_2 2), 7.00 d.d (1H, H^5, J_1 8, J_2 2)
Xe	1.48–2.06 m (8H, 4CH_2), 2.94 m (1H, CH), 3.61 br.s (2H, NH_2), 3.75 c (3H, OCH_3), 6.46–6.64 m (3H, $H^{3,4,5}$)
Xf	1.30 t (3H, OCH_2CH_3, *J* 7), 1.38–1.97 m (8H, 4CH_2), 2.86 m (1H, CH), 3.19 br.s (2H, NH_2), 3.82 q (2H, OCH_2CH_3, *J* 7), 6.56 s (1H, H^3), 6.37 d (2H, $H^{5,6}$, *J* 6)
Xg	1.52–2.08 m (16H, 8CH_2), 2.90 m (2H, 2CH), 3.54 br.s (2H, NH_2), 6.54 t (1H, H^4, *J* 8), 6.83 d (2H, $H^{3,5}$, *J* 8)
Xh	1.31 t (3H, OCH_2CH_3, *J* 7), 1.40–2.05 m (16H, 8CH_2), 2.91 m (2H, 2CH), 3.20 br.s (2H, NH_2), 3.84 q (2H, OCH_2CH_3, *J* 7), 6.42 s (2H, $H^{3,5}$)
XIa	1.10–1.90 m (10H, 5CH_2), 2.35 m (1H, CH), 3.38 br.s (2H, NH_2), 6.47 d.d (1H, H^6, J_1 8, J_2 2), 6.63 t.d (1H, H^5, J_1 8, J_2 2), 6.84 t.d (1H, H^4, J_1 8, J_2 2), 6.92 d.d (1H, H^3, J_1 8, J_2 2)
XIb	1.15–1.95 m (10H, 5CH_2), 2.11 s (3H, CH_3), 2.38 m (1H, CH), 3.35 br.s (2H, NH_2), 6.51 t (1H, H^4, *J* 8), 6.76 d (1H, H^5, *J* 8), 6.83 d (1H, H^3, *J* 8)
XIc	1.10–1.90 m (10H, 5CH_2), 2.04 s (3H, CH_3), 2.14 s (3H, CH_3), 2.52 m (1H, CH), 3.24 br.s (2H, NH_2), 6.41 s (1H, H^3), 6.59 s (1H, H^5)
XIg	1.10–2.00 m (20H, 10CH_2), 2.38 m (2H, 2CH), 3.47 br.s (2H, NH_2), 6.58 t (1H, H^4, *J* 8), 6.80 d (2H, $H^{3,5}$, *J* 8)
XIIa	1.30–1.80 m (14H, 7CH_2), 2.65 m (1H, CH), 3.37 br.s (2H, NH_2), 6.80–7.05 m (4H, $H^{3,4,5,6}$)
XIIb	1.35–1.80 m (14H, 7CH_2), 2.03 s (3H, CH_3), 2.61 m (1H, CH), 3.35 br.s (2H, NH_2), 6.49 t (1H, H^4, *J* 8), 6.71 d (1H, H^5, *J* 8), 6.81 d (1H, H^3, *J* 8)
XIIc	1.45–1.90 m (14H, 7CH_2), 2.03 s (3H, CH_3), 2.14 s (3H, CH_3), 2.61 m (1H, CH), 3.39 br.s (2H, NH_2), 6.55 s (1H, H^3), 6.60 s (1H, H^5)
XIIIa	1.15–1.80 m (22H, 11CH_2), 2.72 m (1H, CH), 3.48 br.s (2H, NH_2), 6.49 d.d (1H, H^6, J_1 8, J_2 2), 6.60 t.d (1H, H^5, J_1 8, J_2 2), 6.84 t.d (1H, H^4, J_1 8, J_2 2), 6.95 d.d (1H, H^3, J_1 8, J_2 2)
XIIIb	1.15–1.85 m (22H, 11CH_2), 2.38 s (3H, CH_3), 2.71 m (1H, CH), 3.35 br.s (2H, NH_2), 6.50 t (1H, H^4, *J* 7), 6.73 d (1H, H^5, *J* 7), 6.82 d (1H, H^3, *J* 7)
XIIIc	1.18–1.82 m (22H, 11CH_2), 2.05 s (3H, CH_3), 2.16 s (3H, CH_3), 2.69 m (1H, CH), 3.48 br.s (2H, NH_2), 6.58 s (1H, H^3), 6.62 s (1H, H^5)

XV in 30 ml of methanol and Raney nickel prepared from 5 g of a nickel–aluminum alloy (1 : 1) were placed into a 100-ml stainless-steel autoclave. The mixture was hydrogenated with hydrogen at 10–40 atm and 30–50°C for 24 h. The catalyst was filtered off, the methanol was removed from the filtrate on a rotary evaporator at a bath temperature of 45°C, and the residue was distilled at 1 mm Hg.

ACKNOWLEDGMENTS

The work was financially supported by the Siberian Branch of the Russian Academy of Sciences (integration project no. 16) and the Ministry of Industry, Science and Technologies of the Russian Federation (State Contract no. 41.015. 1.1.2455).

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