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Synthesis of Asymmetric 2,6-*Bis*(arylimino)pyridines

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The new asymmetric 2,6-*bis*(arylimino)pyridines with halogen and alkyl substituents on different iminoaryl rings can be synthesized in good yields by reacting 2,6-diacetylpyridine with alkyl-substituted anilines under rigorous conditions and successive reactions with halogen substituted anilines under mild conditions.

Key Words: 2,6-*Bis*(arylimino)pyridine, Asymmetric, Successive reaction, Mono(arylimino)pyridine.

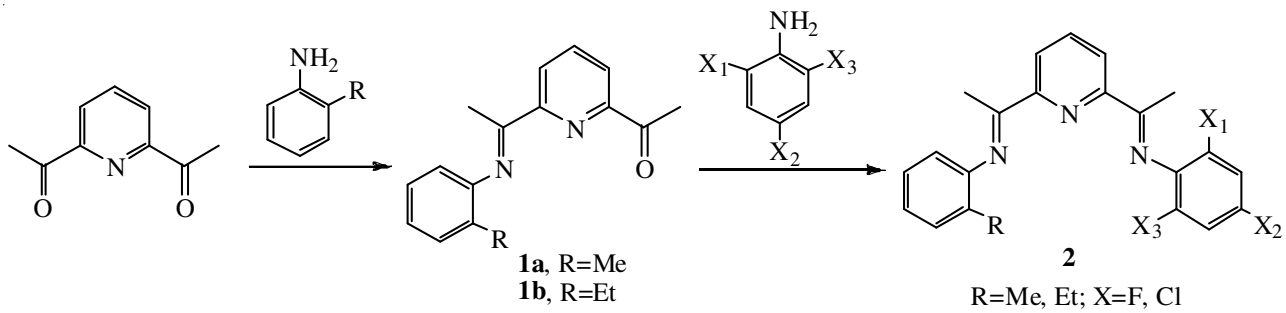
INTRODUCTION

In 1998, Brookhart[1] and Gibson[2] independently reported that alkyl-substituted *bis*(imino) pyridyl iron and cobalt complexes, when activated by methyl aluminoxane, are highly active catalysts for the polymerization or oligomerization of ethylene. Since these initial developments, numerous iron and cobalt complexes bearing different alkyl-substituted *bis*(imino)pyridyl ligands have been reported[3,4]. Recently, Qian *et al.*[5,6] introduced electronic-drawing halogen substituents (F, Cl, Br, I) into imino-aryl ring's *ortho* positions and found that the iron and cobalt complexes with halogen substituents are also active for ethylene polymerization or oligomerization and some catalytic performances can be improved in comparison with alkyl-substituted complexes owing to the electronic effect of halogen atoms[5,6]. It has been shown that the size, nature and regiochemistry of the substituents in the iminoaryl groups are of crucial importance in controlling the polymerization and oligomerization of ethylene[3,7,8].

Asymmetric alkyl-substituted *bis*(imino)pyridyl ligands can also be employed in ethylene polymerization catalysts[9,10]. We tried to tune the catalytic performances by introducing alkyl and halogen substitients into two different iminoaryl groups, which are hardly reported in the literatures. Here we reported a new asymmetric 2,6-*bis*(imino)pyridines and the synthesis methods, which are shown in **Scheme-I**.

EXPERIMENTAL

2,6-Diacetylpyridine was synthesized according to previous works[11]. Substituted anilines were purchased from Acros Organics or Aldrich Chemical Co. and used as received. Silica-alumina catalyst support (grade 135) was purchased from Aldrich Chemical Co. The ^{1}H NMR spectra of ligands were recorded on a Bruker AM-300 MHz spectrometer with tetramethylsilane as an internal standard. IR spectra of the complexes were collected on a Nicolet Nexus 470 FT-IR spectrometer.



Scheme-I: Synthesis of asymmetric 2,6-*bis*(arylimino)pyridines

General procedure for the synthesis of asymmetric 2,6-*bis*(imino)pyridines (2a-j): Ligands **1** were synthesized according to literature[10]. The mixtures of **1**, halogen substituted aniline and toluene in schlenk tube were reacted for 24-48 h at 35 ºC, catalyzed by 4 Å molecule sieze and Si-Al oxide catalyst. After fitrating and removing of solution, the crude product was purified by recrystal in methanol solution to give **2a-j** (**Scheme-I**, Table-1).

TABLE-1
SYNTHESIS OF ASYMMETRIC 2,6-*BIS*(ARYLIMINO)PYRIDINES

Compounds	R	X_1	X_2	X_3	m.p. (ºC)	Yields (%)
2a	Me	Cl	H	H	80-83	53.7
2b	Me	F	H	H	79-81	52.5
2c	Me	H	F	H	84-87	76.4
2d	Me	F	F	H	117-120	62.0
2e	Me	F	H	F	84-87	53.7
2f	Et	Cl	H	H	88-90	72.6
2g	Et	F	H	H	78-81	74.6
2h	Et	H	F	H	126-128	65.7
2i	Et	F	F	H	110-113	72.4
2j	Et	F	H	F	75-77	63.9

2-Chloro-[1-(6-(1-(*o*-tolylimino)ethyl)pyridin-2-yl)-ethylidene]benzenamine (2a): IR (KBr, ν_{max}, cm^{-1}): 3062, 3014, 2969, 2921, 1644, 1575, 1465, 1363, 1316, 1220, 1115, 1066, 817, 779, 736. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41(d, 2H, Py-Hm), 7.90 (t, 1H, Py-Hp), 7.42 (d, 1H, Ph), 7.19-7.28 (m, 3H, Ph), 7.03-7.08 (m, 2H, Ph), 6.85 (d, 1H, Ph), 6.69 (d, 1H, Ph), 2.38 (s, 3H, N=C-CH_3), 2.34 (s, 3H, N=C-CH_3), 2.13 (s, 3H, PhCH_3).

2-Fluoro-[1-(6-(1-(*o*-tolylimino)ethyl)pyridin-2-yl)-ethylidene]benzenamine (2b): IR (KBr, ν_{max}, cm^{-1}): 3065, 3014, 2969, 2922, 1642, 1598, 1571, 1482, 1449, 1363, 1318, 1230, 1108, 1039, 817, 780, 739. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, 2H, Py-Hm), 7.89 (t, 1H, Py-Hp), 7.10-7.25 (m, 5H, ph), 7.04 (t, 1H, Ph), 6.94 (t, 1H, Ph), 6.70 (d, 1H, Ph), 2.42 (s, 3H, N=C-CH_3), 2.34 (s, 3H, N=C-CH_3), 2.13 (s, 3H, PhCH_3).

4-Fluoro-[1-(6-(1-(*o*-tolylimino)ethyl)pyridin-2-yl)-ethylidene]benzenamine (2c): IR (KBr, ν_{max}, cm^{-1}): 3066, 3016, 2960, 2842, 1638, 1603, 1570, 1500, 1448, 1364, 1317, 1232, 1208, 1095, 846, 818, 786, 746. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, 1H, Py-Hm), 8.32 (d, 1H, Py-Hm), 7.88 (t, 1H, Py-Hp), 7.19-7.25 (m, 2H, ph), 7.08 (m, 3H, Ph), 6.81 (m, 2H, Ph), 6.69 (d, 1H, Ph), 2.41 (s, 3H, N=C-CH_3), 2.34 (s, 3H, N=C-CH_3), 2.13 (s, 3H, PhCH_3).

2,4-Difluoro-[1-(6-(1-(*o*-tolylimino)ethyl)pyridin-2-yl)-ethylidene]benzenamine (2d): IR (KBr, ν_{max}, cm^{-1}): 3069, 3011, 2965, 2914, 1642, 1599, 1497, 1427, 1365, 1320, 1280, 1139, 1097, 961, 847, 820, 780, 726. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, 1H, Py-Hm), 8.37 (d, 1H, Py-Hm), 7.90 (t, 1H, Py-Hp), 7.16-7.25 (m, 2H, ph), 7.05 (t, 1H, Ph), 6.92 (m, 3H, Ph), 6.69 (d, 1H, Ph), 2.41 (s, 3H, N=C-CH_3), 2.34 (s, 3H, N=C-CH_3), 2.13 (s, 3H, PhCH_3).

2,6-Difluoro-[1-(6-(1-(*o*-tolylimino)ethyl)pyridin-2-yl)-ethylidene]benzenamine (2e): IR (KBr, ν_{max}, cm^{-1}): 3064, 3014, 2972, 2922, 1644, 1572, 1474, 1364, 1318, 1220, 1113, 1041, 1001, 818, 780, 740. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, 2H, Py-Hm), 7.90 (t, 1H, Py-Hp), 7.17-7.25 (m, 4H, ph), 7.04 (t, 1H, Ph), 6.98 (t, 1H, Ph), 6.69 (d, 1H, Ph), 2.45 (s, 3H, N=C-CH_3), 2.34 (s, 3H, N=C-CH_3), 2.13 (s, 3H, PhCH_3).

2-Chloro-[1-(6-(1-(2-ethylphenylimino)ethyl)pyridin-2-yl)ethylidene]benzenamine (2f): IR (KBr, ν_{max}, cm^{-1}): 3068, 3015, 2970, 2926, 1638, 1570, 1470, 1365, 1320, 1225, 1114, 1007, 820, 790, 750. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, 2H, Py-Hm), 7.82 (t, 1H, Py-Hp), 7.07-7.22 (m, 4H, ph), 7.01 (m, 2H, Ph), 6.78 (m, 1H, Ph), 6.60 (d, 1H, Ph), 2.44 (q, 2H, Ph-CH_2-), 2.30 (s, 3H, N=C-CH_3), 2.28 (s, 3H, N=C-CH_3), 1.08 (t, 3H, Ph-C-CH_3).

2-Fluoro-[1-(6-(1-(2-ethylphenylimino)ethyl)pyridin-2-yl)ethylidene]benzenamine (2g): IR (KBr, ν_{max}, cm^{-1}): 3063, 3017, 2969, 2872, 1639, 1571, 1481, 1449, 1364, 1305, 1219, 1115, 822, 781, 742. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, 2H, Py-Hm), 7.83 (t, 1H, Py-Hp), 7.08-7.20 (m, 6H, Ph), 7.02 (t, 1H, Ph), 6.60 (d, 1H, Ph), 2.44 (q, 2H, Ph-CH_2-), 2.30 (s, 3H, N=C-CH_3), 2.28 (s, 3H, N=C-CH_3), 1.08 (t, 3H, Ph-C-CH_3).

4-Fluoro-[1-(6-(1-(2-ethylphenylimino)ethyl)pyridin-2-yl)ethylidene]benzenamine (2h): IR (KBr, ν_{max}, cm^{-1}): 3068, 2968, 2925, 2870, 1633, 1597, 1570, 1500, 1448, 1363, 1318, 1235, 1208, 1095, 846, 819, 762. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, 2H, Py-Hm), 7.81 (t, 1H, Py-Hp), 7.10-7.20 (m, 4H, ph), 7.01 (t, 2H, Ph), 6.74 (t, 2H, Ph), 2.44 (q, 2H, Ph-CH_2-), 2.34 (s, 3H, N=C-CH_3), 2.28 (s, 3H, N=C-CH_3), 1.08 (t, 3H, Ph-C-CH_3).

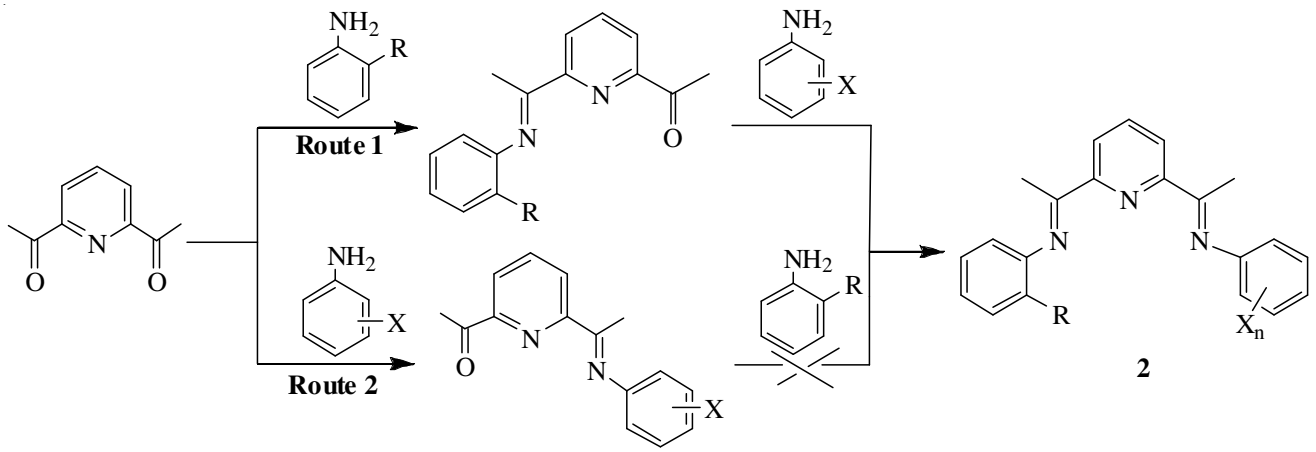
2,4-Difluoro-[1-(6-(1-(2-ethylphenylimino)ethyl)-pyridin-2-yl)ethylidene]benzenamine (2i): IR (KBr, ν_{max}, cm^{-1}): 3070, 2965, 2920, 2870, 1641, 1573, 1496, 1449, 1365, 1279, 1242, 1197, 1138, 1098, 961, 848, 820, 778, 739. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, 2H, Py-Hm), 7.82 (t, 1H, Py-Hp), 7.08-7.20 (m, 2H, ph), 7.01 (t, 1H, Ph), 6.84 (m, 3H, Ph), 6.60 (d, 1H, Ph), 2.44 (q, 2H, Ph-CH_2-), 2.34 (s, 3H, N=C-CH_3), 2.28 (s, 3H, N=C-CH_3), 1.08 (t, 3H, Ph-C-CH_3).

2,6-Difluoro-[1-(6-(1-(2-ethylphenylimino)ethyl)-pyridin-2-yl)ethylidene]benzenamine (2j): IR (KBr, ν_{max}, cm^{-1}): 3063, 3017, 2966, 2927, 2872, 1640, 1571, 1478, 1450, 1365, 1318, 1219, 1117, 999, 823, 780, 743. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, 2H, Py-Hm), 7.83 (t, 1H, Py-Hp), 7.08-7.20 (m, 5H, ph), 7.02 (t, 1H, Ph), 6.60 (d, 1H, Ph), 2.45 (q, 2H, Ph-CH_2-), 2.30 (s, 3H, N=C-CH_3), 2.28 (s, 3H, N=C-CH_3), 1.08 (t, 3H, Ph-C-CH_3).

RESULTS AND DISCUSSION

Most symmetric alkyl-substituted 2,6-*bis*(arylimino)-pyridyl ligands are commonly prepared by condensing 2,6-*bis*(acetyl)pyridine with 2 equiv. of the required aniline in the presence of an acid catalyst (*e.g.*, formic acid, acetic acid, *p*-toluene sulfonic acid). However, in most cases the halogen substituted 2,6-*bis*(imino)pyridines cannot be prepared in the same manner as reported alkyl substituted ones. Qian *et al.*[5,6,12] found a new methods to prepare halogen substituted 2,6-*bis*(imino)pyridines with silica-alumina catalyst support as an efficient catalyst under extremely mild reaction conditions.

Unsymmetrical alkyl-substituted 2,6-*bis*(arylimino)-pyridines can be prepared by the successive condensation



Scheme-II: Two possible synthetic routes of 2,6-*bis*(arylimino)pyridines

reactions of 2,6-diacetylpyridine with two different anilines. For example, Esteruelas *et al*.[10] prepared a family of unsymmetrical *bis*(arylimino)pyridines by, first, treating 2,6-diacetylpyridine with 2,4,6-trimethylaniline and, second, addition of the second aniline.

The new asymmetric 2,6-*bis*(imino)pyridines (**2**) can also be synthesized by the successive condensation reactions of 2,6-diacetylpyridine with a alkyl-substituted aniline and a halogen-substituted aniline. Two synthesis routes can be adopted in theory, shown in **Scheme-II**.

Halogen-substituted anilines are much more expensive than alkyl-substituted anilines, so the **route 1** is more economical in theory. Furthermore, in **route 1**, 2,6-diacetylpyridine can react with alkyl-substituted aniline to obtain mono(arylimino)pyridine firstly under the conditions of high temperature or refluxing in toluene or propanol and mono(imino)pyridine can react further with halogen-aniline to produce asymmetric 2,6-*bis*(imino)pyridines catalyzed by silica-alumina catalyst support under mild reaction conditions. In route **2**, the first step can be realized with silica-alumina catalyst support as catalyst under mild reaction conditions, but the second step can not be accomplished due to instable halogen-substituted mono(arylimino)pyridine under rigorous experiment conditions. So the asymmetric 2,6-*bis*(imino)-pyridines with halogen and alkyl substituents on different iminoaryl rings can be synthesized in good yields by 2,6-diacetylpyridine reacting firstly with alkyl-substituted anilines under rigorous conditions and successive reactions with halogen substituted anilines under mild conditions.

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