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Influence of the *para*-substitution in bis(arylimino)pyridine iron complexes on the catalytic oligomerization and polymerization of ethylene

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Dedicated to Professor Gerhard Erker on the occasion of his 60th birthday.

Abstract

A series of nine bis(arylimino)pyridine iron complexes containing halogen or alkynyl substituents in their ligand frameworks was synthesized and characterized. After activation with methylalumoxane (MAO), these catalysts oligomerize or polymerize ethylene to give highly linear products. The introduction of halogen or alkynyl substituents in the *para*-position of the iminophenyl rings has a great influence on the polymerization activities of the corresponding iron complexes.

Keywords: Bis(arylimino)pyridine iron complexes; Ethylene polymerization; Oligomerization; Polyethylene

1. Introduction

Gibson [1–4] and Brookhart [5–7] independently reported the application of 2,6-bis(arylimino)pyridine iron complexes as effective catalysts for the polymerization and oligomerization of ethylene leading to highly linear products. Especially the substitution pattern of the iminophenyl rings has a great influence on the polymerization activities and the product compositions [1–17]. In the past five years, bis(arylimino)pyridine iron complexes with halogen substituted iminophenyl rings were published by Qian et al. [8,9]. While fluoro, chloro, and bromo substituted bis(arylimino)pyridine compounds and their complexes are known, the analogous iodo substituted compounds were not described in the literature so far. Bromo or iodo substituted compounds are also useful as reactants in palladium catalyzed coupling reactions. Especially Sonogashira coupling reactions [18,19] proved to be widely applicable for the introduction of aliphatic or aromatic substituents employing terminal alkyne derivatives [20–25]. As demonstrated by Ionkin et al. [14], halogen substituents at the iminophenyl rings of bis(arylimino)pyridine compounds can be easily exchanged with aryl groups applying Suzuki coupling reactions. As a more general method, Sonogashira coupling reactions were chosen to combine *para*-bromo and *para*-iodo substituted bis(arylimino)pyridine compounds with ω-alkynyl substituted indene or fluorene derivatives. The corresponding iron complexes were synthesized and used for the catalytic oligomerization and polymerization of ethylene. For Sonogashira reactions, *para*-substitution at the iminophenyl moieties is preferred against *ortho*- and *meta*-substitution due to less steric bulk around the catalytically active iron center and higher symmetry for the finally resulting complexes. The influence of different *para*-substituents on the polymerization behavior was investigated. Attempts to prepare multinuclear iron–zirconium complexes are presented.

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2. Results and discussion

2.1. General remarks

To introduce more complex structures into the bis(arylimino)pyridine ligand framework, Suzuki coupling reactions [14] are in some cases disadvantageous due to the necessity of appropriate arylboronic acids. Other types of coupling reactions, especially Sonogashira reactions, proved to be more useful in this context. As starting materials, bromo or iodo substituted anilines are required. On this way, it is also possible to introduce terminal alkynyl functions into bis(arylimino)pyridine compounds. The combination of halogen substituted bis(arylimino)pyridine compounds and alkynyl substituted fluorenyl or indenyl compounds leads to ligand precursors which should be subsequently reacted with iron(II)chloride and *n*-butyllithium/zirconium tetrachloride to give trinuclear iron–zirconium complexes.

2.2. Synthesis of iodo and alkynyl substituted anilines

The introduction of iodo substituents into the *ortho*- and *para*-positions of aniline [26] or phenol [27] derivatives can be easily performed at room temperature using benzyltrimethylammonium dichloroiodate as an iodinating agent which is available from the addition reaction of benzyltrimethylammonium chloride and iodine monochloride [26].

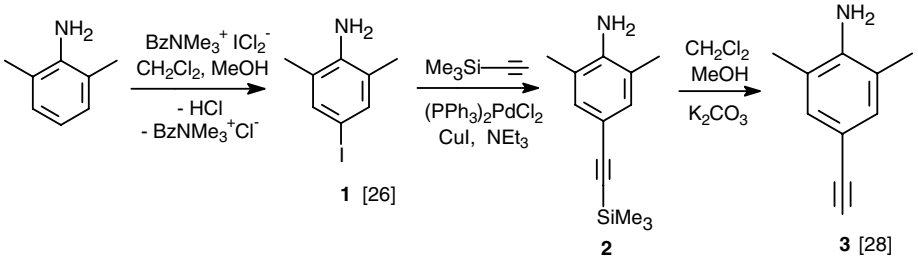
Starting from 2,6-dimethylaniline, 4-iodo-2,6-dimethylaniline (**1**) [26] and 4-ethynyl-2,6-dimethylaniline (**3**) [28] were prepared (see Scheme 1).

The palladium catalyzed reaction of **1** with trimethylsilylacetylene furnished 4-ethynyl-2,6-dimethylaniline (**3**) after removal of the trimethylsilyl protecting group.

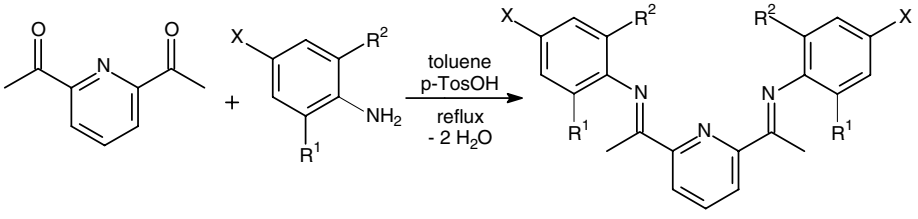
2.3. Preparation of halogen substituted 2,6-bis(arylimino) pyridine compounds

Condensation reactions of 2,6-diacetylpyridine with *para*-bromo or *para*-iodo substituted anilines yielded the 2,6-bis(arylimino)pyridine compounds **4**–**8** (see Scheme 2) [29,30]. For comparison purposes, 2-methylaniline and 2,6-dimethylaniline were also reacted with 2,6-diacetylpyridine to give the well-known corresponding bis(arylimino)pyridine compounds **9** [5] and **10** [6]. The ^{1}H NMR, ^{13}C NMR, and MS data for compounds **1**–**10** are given in Table 1.

Condensation reactions using 3-ethynylaniline, 4-ethynylaniline, or 4-ethynyl-2,6-dimethylaniline (**3**) as aniline compounds did not lead to imino compounds but yielded



Scheme 1. Synthesis of 4-iodo-2,6-dimethylaniline (**1**) and 4-ethynyl-2,6-dimethylaniline (**3**).



compound	R^1	R^2	X	yield [%]
4 [29]	Me	H	Br	28
5 [30]	Me	Me	Br	78
6	H	H	I	53
7	Me	H	I	54
8	Me	Me	I	75
9 [5]	Me	H	H	60
10 [6]	Me	Me	H	68

Scheme 2. Synthesis of 2,6-bis(arylimino)pyridine compounds with *para*-halogen substituted iminophenyl rings.

Table 1
NMR and MS data of compounds **1**–**10** and **19**–**29**

Compound	^{1}H NMR	^{13}C NMR	MS [*m*/*z*]
1	7.23 s (2H, Ar-H), 3.61 s (br, 2H, NH_2), 2.11 s (6H, CH_3)	142.5, 124.2, 79.2 (C_q), 136.4 (Ar-CH), 17.3 (CH_3)	247 $M^{\circ+}$ (100), 120 M − I (28)
2	7.09 s (2H, Ar-H), 3.70 s (br, 2H, NH_2), 2.08 s (6H, CH_3), 0.25 s (9H, $SiMe_3$)	143.6, 121.1, 111.5 (C_q), 132.0 (Ar-CH), 106.6, 90.8 (C_q, C≡C), 17.3 (CH_3), 0.2 ($SiMe_3$)	217 $M^{\circ+}$ (50), 202 M − Me (100)
3	7.09 s (2H, Ar-H), 3.73 s (br, 2H, NH_2), 2.91 s (1H, ≡CH), 2.12 s (6H, CH_3)	143.7, 121.3, 110.5 (C_q), 132.1 (Ar-CH), 109.1 (C_q, C≡C), 74.4 (≡CH), 17.4 (CH_3)	145 $M^{\circ+}$ (100), 130 M − Me (31)
4	8.38 d (2H, Py_{H3}), 7.87 t (1H, Py_{H4}), 7.28–7.36 m (4H, Ar-H), 6.56 d (2H, Ar-H), 2.33 s (6H, CH_3), 2.09 s (6H, CH_3)	167.4, 155.1, 148.9, 129.6, 116.3 (C_q), 136.9, 133.1, 129.3, 122.5, 119.8 (Ar-CH), 17.6, 16.4 (CH_3)	499 $M^{\circ+}$ (60), 484 M − Me (100)
5	8.47 d (2H, Py_{H3}), 7.93 t (1H, Py_{H4}), 7.22 s (4H, Ar-H), 2.25 s (6H, CH_3), 2.02 s (12H, CH_3)	167.8, 154.8, 147.7, 127.7, 115.6 (C_q), 137.0, 130.5, 122.5 (Ar-CH), 17.8, 16.6 (CH_3)	527 $M^{\circ+}$ (58), 512 M − Me (100)
6	8.30 d (2H, Py_{H3}), 7.85 t (1H, Py_{H4}), 7.64–7.68 m (4H, Ar-H), 6.58–6.62 m (4H, Ar-H), 2.38 s (6H, CH_3)	167.8, 155.1, 150.8, 87.2 (C_q), 137.9, 136.9, 122.5, 121.5 (Ar-CH), 16.3 (CH_3)	565 $M^{\circ+}$ (22), 550 M − Me (3), 438 M − I (3)
7	8.36 d (2H, Py_{H3}), 7.87 t (1H, Py_{H4}), 7.23–7.55 m (4H, Ar-H), 6.43 d (2 H, Ar-H), 2.31 s (6 H, CH_3), 2.06 s (6H, CH_3)	167.3, 155.1, 149.6, 129.9, 87.1 (C_q), 139.0, 136.9, 135.3, 122.5, 120.2 (Ar-CH), 17.5, 16.4 (CH_3)	593 $M^{\circ+}$ (22), 578 M − Me (18), 466 M − I (6)
8	8.45 d (2H, Py_{H3}), 7.92 t (1H, Py_{H4}), 7.39 s (4H, Ar-H), 2.28 s (6H, CH_3), 1.97 s (12H, CH_3)	167.8, 154.8, 148.5, 128.0, 86.6 (C_q), 137.4, 136.5, 122.5 (Ar-CH), 17.6, 16.6 (CH_3)	621 $M^{\circ+}$ (74), 605 M − Me (79), 494 M − I (7)
9	8.46 d (2H, Py_{H3}), 7.89 t (1H, Py_{H4}), 7.21–7.28 m (4H, Ar-H), 7.04–7.09 m (2H, Ar-H), 6.72–6.75 m (2H, Ar-H), 2.39 s (6H, CH_3), 2.17 s (6H, CH_3)	166.8, 155.4, 149.9, 127.1 (C_q), 136.8, 130.4, 126.4, 123.6, 122.3, 118.1 (Ar-CH), 17.8, 16.3 (CH_3)	341 $M^{\circ+}$ (47), 326 M − Me (100)
10	8.56 d (2H, Py_{H3}), 7.94 t (1H, Py_{H4}), 6.97–7.15 m (6H, Ar-H), 2.25 s (6H, CH_3), 2.12 s (12H, CH_3)	167.2 155.1, 148.8, 125.4 (C_q), 136.9, 128.0, 123.1, 122.3 (Ar-CH), 18.0, 16.5 (CH_3)	369 $M^{\circ+}$ (37), 354 M − Me (100)
19	7.60–7.63 m (2H), 7.34–7.41 m (2H), 7.07–7.10 m (1H), 6.79–6.82 m (1H), 3.67 s (1H), 0.13 s (9H, $SiMe_3$)	145.5, 144.2 (C_q), 135.8, 129.0, 124.9, 123.8, 122.8, 121.1 (Ar-CH), 46.6 (CH), −2.4 ($SiMe_3$)	188 $M^{\circ+}$ (9), 173 M − Me (3), 115 M − $SiMe_3$ (6), 73 $SiMe_3$ (100)
20	(^{1}H NMR data for the vinylic isomer) 7.70–7.79 m (1H, Ar-H), 7.43–7.48 m (3H, Ar-H), 7.04–7.06 m (1H, Ind-H^2), 3.82–3.88 dt (1H, Ind-H^1), 2.79–2.83 m (1H, CH_2), 2.51–2.60 m (1H, CH_2), 2.28 t (1H, ≡CH), 0.60 s (9H, $SiMe_3$)	(^{13}C NMR data for the vinylic isomer) 147.7, 147.3, 144.9 (C_q), 148.1, 127.3, 124.9, 123.4, 122.4 (Ar-CH), 83.0 (C_q, C≡C), 69.6 (≡CH), 50.4 (CH, Ind-C^1), 21.3 (CH_2), 0.8 ($SiMe_3$)	226 $M^{\circ+}$ (23), 211 M − Me (14), 152 M − H − $SiMe_3$ (33)
21	7.30–7.72 m (7H, Ar-H), 3.82 s (2H, CH_2), 2.43 s (br, 1H, OH), 1.67 s (6H, CH_3)	143.5, 143.1, 141.8, 141.0, 120.7, 65.7 (C_q), 130.5, 128.2, 127.1, 126.9, 125.1, 120.2, 119.7 (Ar-CH), 93.8, 82.8 (C_q, C≡C), 36.7 (CH_2), 31.6 (CH_3)	248 $M^{\circ+}$ (72), 233 M − Me (100)
22	7.35–7.78 m (7H, Ar-H), 3.87 s (2H, CH_2), 3.11 s (1H, ≡CH)	143.6, 143.1, 142.3, 140.9, 120.0 (C_q), 131.0, 128.7, 127.3, 126.9, 125.1, 120.2, 119.7 (Ar-CH), 84.4 (C_q, C≡C), 76.9 (≡CH), 36.7 (CH_2)	190 $M^{\circ+}$ (100), 189 M − H (98)
23	2.65 t (2H, CH_2), 2.36–2.43 m (2H, CH_2), 2.13 s (3H, CH_3), 1.91 t (1H, ≡CH)	206.3 (C_q), 82.8 (C_q, C≡C), 68.7 (≡CH), 42.1, 12.9 (CH_2), 29.8 (CH_3)	96 $M^{\circ+}$ (7), 95 M − H (60), 81 M − H − Me (67)
24/24′	6.53–6.56 m (4H, Cp), 2.79 t (2H, CH_2), 2.43–2.50 m (2H, CH_2), 2.26 s (3H, CH_3), 2.04 t (1H, ≡CH)	150.2, 143.6 (C_q), 131.5, 131.2, 120.8, 120.4 (Cp–CH), 83.1 (C_q, C≡C), 69.7 (≡CH), 35.5, 18.5 (CH_2), 20.9 (CH_3)	144 $M^{\circ+}$ (83), 129 M − Me (100)
25/25′	7.63–7.84 m (3H, Ar-H), 7.36–7.50 m (3H, Ar-H), 7.17–7.20 m (1H, Ar-H), 6.83–7.00 m (1H, Ar-H), 6.57–6.73 m (2H, Cp), 6.22–5.99 m (1H, Cp), 4.19/4.13 s (1H), 3.14 m (2H, Cp), 2.30–2.39 m (2H, CH_2), 2.07–2.10 m (3H, CH_2/≡CH), 0.68 s (3H, CH_3)	153.8/151.6, 144.9/144.6, 144.5, 142.5/142.4, 141.9 (C_q), 135.1, 132.8, 132.3, 131.6, 129.8, 128.1, 127.4, 127.3, 127.3, 127.2, 126.9, 126.4, 126.3, 126.2, 126.1, 126.1, 125.7, 119.8, 119.4, 119.3 (Ar-CH), 85.3/85.1 (C_q, C≡C), 68.6/68.5 (≡CH), 58.2/56.0 (CH), 43.0, 41.1, 41.0, 40.3, 38.7, 14.5/14.4 (CH_2/$C_{q/bridge}$), 17.8/17.3 (CH_3)	310 $M^{\circ+}$ (100), 295 M − Me (21), 165 Fluorenyl (42)
26	8.43 d (1H, Py_{H4}), 7.90 t (2H, $Py_{H3/5}$), 7.29–7.53 m (4H, Ar-H), 6.92–7.19 m (8H, Ar-H), 6.70–6.75 m (2H, Ar-H), 6.07–6.15 m (2H, Ar-H), 3.80 s (4H, CH_2), 2.93–2.98 m (2H, CH), 2.35 s (6H, CH_3), 2.10 s (6H, CH_3), 0.20 ($SiMe_3$)	165.9 (C_q, C=N), 156.1, 150.4, 147.3, 146.9, 140.1, 130.7, 117.6 (C_q), 136.9, 132.8, 130.2, 126.5, 126.2, 125.2, 124.5, 123.5, 121.6, 119.2 (Ar-CH), 88.9, 86.3 (C_q, C≡C), 47.9 (CH), 29.3 (CH_2), 18.6, 16.4 (CH_3), −1.8 ($SiMe_3$)	589 $M^{\circ+}$ (1), 516 M − $SiMe_3$ (8), 412 M − $IndSiMe_3$ (14)

Table 1 (*continued*)

Compound	^{1}H NMR	^{13}C NMR	MS [*m*/*z*]
27	8.41 d (1H, Py_{H4}), 7.88 t (2H, $Py_{H3/5}$), 7.63–7.75 m (4H, Ar-H), 7.49–7.54 m (2H, Ar-H), 7.19–7.34 m (12H, Ar-H), 6.60–6.63 m (2H, Ar-H), 3.86 s (4H, CH_2), 2.36 s (6H, CH_3), 2.10 s (6H, CH_3)	166.5 (C_q, C=N), 155.8, 145.1, 143.4, 141.1, 134.9, 131.1, 130.6, 122.0, 112.4 (C_q), 136.3, 133.7, 130.5, 130.1, 128.0, 126.9, 126.8, 125.0, 124.4, 120.0, 119.7, 114.6 (Ar-CH), 90.4, 87.8 (C_q, C≡C), 36.7 (CH_2), 17.2, 16.4 (CH_3)	717 $M^{\circ+}$ (2), 702 M − Me (3), 552 M − Flu (8), 165 Flu (100)
28	8.40 d (1H, Py_{H4}), 7.90 t (2H, $Py_{H3/5}$), 7.63–7.76 m (6H, Ar-H), 6.50–7.39 m (22H, Ar-H), 4.19 s (2H, Flu-H[9]), 3.13–3.19 m (4H, Cp–CH_2), 2.35 s (6H, CH_3), 2.17–2.26 m (8H, CH_2), 2.11 s (6H. CH_3), 0.64 s (6H. CH_3)	167.1 (C_q, C=N), 155.2, 151.6, 149.5, 144.9, 144.6, 142.4, 141.9, 127.3, 119.0 (C_q), 136.9, 134.9, 133.7, 132.8, 129.8, 128.0, 127.2, 127.0, 126.8, 126.2, 126.1, 126.0, 122.4, 119.6, 119.2, 118.2 (Ar-CH), 89.5, 80.5 (C_q, C≡C), 58.3, 56.0 (CH), 44.2 (C_q), 43.0, 41.0, 15.2 (CH_2), 17.6, 17.3, 16.4 (CH_3)	957 $M^{\circ+}$ (3), 792 M − Flu (6), 627 M − 2 Flu (5), 165 Flu (100)
29	8.46 d (1H, Py_{H4}), 7.92 t (2H, $Py_{H3/5}$), 7.59–7.75 m (6H, Ar H), 6.48–7.39 m (20H, Ar-H), 4.18 s (2H, Flu_{H9}), 3.11–3.18 m (4H, Cp–CH_2), 2.23 s (6H. CH_3), 2.01 s (6H. CH_3), 2.00–2.35 m (8H, CH_2) 0.62 s (6H. CH_3)	167.4 (C_q, C=N), 154.9, 152.5, 151.6, 144.9, 144.6, 142.4, 141.8, 125.5, 118.4 (C_q), 137.4, 134.9, 132.8, 131.5, 131.1, 128.0, 127.2, 126.8, 126.2, 126.1, 125.9, 124.5, 122.7, 119.6, 119.1 (Ar-CH) 89.1, 80.5 (C_q, C≡C), 58.3, 56.0 (CH), 44.2 (C_q), 43.0, 40.9, 15.3 (CH_2), 17.8, 17.3, 16.6 (CH_3)	985 $M^{\circ+}$ (5), 820 M − Flu (6), 574 M − ($C_{32}H_{29}$) (15), 165 Flu (100)

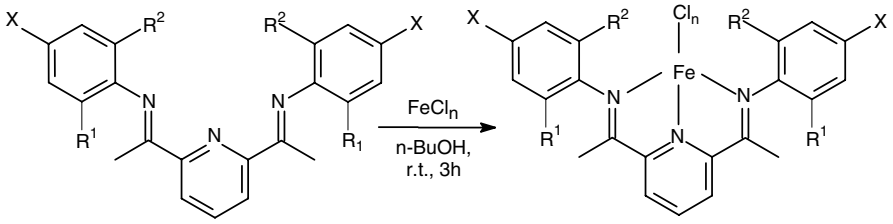
condensation products of the corresponding anilines. While some fluoro, chloro, and bromo substituted bis(arylimino)pyridines are known in the literature [8–10,31,32], compounds **6**–**8** are the first examples containing iodo substituents.

2.4. Synthesis of iron complexes containing halogen substituted 2,6-bis(arylimino)pyridine ligands

The bis(arylimino)pyridine compounds **4**–**10** were reacted with iron(II) chloride or iron(III) chloride to give the corresponding bis(arylimino)pyridine iron complexes **11**–**18** (Scheme 3). Spectral data for complexes **11**–**18** are given in Table 2.

The complexes were characterized by mass spectrometry and elemental analyses. Due to their paramagnetism and their poor solubility, ^{1}H NMR investigations could not be performed for all complexes. Scheme 4 shows the mass spectrum of complex **14**.

The molecular ion appears at $m/z = 719$ with an intensity of 2% relative to the base peak. The loss of one chloro ligand leads to the peak at $m/z = 684$, while the base peak



R^1, R^2 = H, Alkyl
X = Br, I
n = 2, 3

compound	R^1	R^2	X	n	yield [%]
11 [29]	Me	H	Br	2	96
12 [30]	Me	Me	Br	2	92
13	H	H	I	2	37
14	Me	H	I	2	57
15	Me	Me	I	2	78
16	Me	Me	I	3	71
17 [5]	Me	H	H	2	77
18 [6]	Me	Me	H	2	81

Scheme 3. Synthesis of the iron complexes **11**–**18**.

Table 2
MS, elemental analysis, and ^{1}H NMR data of the iron complexes **11**–**18** and **30**–**32**

Complex	MS (*m*/*z*)	^{1}H NMR δ (ppm)	C_{exp} (%)	C_{theor} (%)	H_{exp} (%)	H_{theor} (%)	N_{exp} (%)	N_{theor} (%)
11	625 $M^{\circ+}$ (1), 589 M − H − Cl (4), 499 M − $FeCl_2$ (16), 484 M − $FeCl_2$ − Me (21)	–	44.1	44.1	3.43	3.38	6.69	6.71
12	653 $M^{\circ+}$ (2), 618 M − Cl (3), 527 M − $FeCl_2$ (13), 512 M − $FeCl_2$ − Me (19)	84.62 (2H, $Py_{H3/5}$), 34.17 (1H, Py_{H4}), 16.50 (4H, Ar-H), 12.88 (12H, Ar-CH_3), −20.18 (6H, N=C–CH_3)	45.8	45.9	3.97	3.85	6.41	6.42
13	691 $M^{\circ+}$ (1), 565 M − $FeCl_2$ (4), 438 M − $FeCl_2$ − I (3)	–	36.1	36.5	2.61	2.48	6.03	6.07
14	719 $M^{\circ+}$ (2), 684 M − Cl (7), 649 M − 2Cl (5) 593 M − $FeCl_2$ (100), 578 M − $FeCl_2$ − Me (98)	–	38.9	38.4	3.01	2.94	5.80	5.84
15	747 $M^{\circ+}$ (4), 712 M − Cl (9), 621 M − $FeCl_2$ (61), 606 M − $FeCl_2$ − Me (62)	88.52 (2H, $Py_{H3/5}$), 34.97 (1H, Py_{H4}), 17.00 (4H, Ar-H), 13.43 (12H, Ar-CH_3) −15.44 (6H, N=C–CH_3)	40.7	40.1	3.46	3.37	5.49	5.62
16	783 $M^{\circ+}$ (1), 768 M − Me (4), 621 M − $FeCl_2$ (5), 606 M − $FeCl_2$ − Me (6)	–	39.0	38.3	3.30	3.22	5.43	5.36
17	467 $M^{\circ+}$ (17), 341 M − $FeCl_2$ (46), 326 M − $FeCl_2$ − Me (100)	83.90 (1H, Py_{H4}), 82.58 (2H, $Py_{H3/5}$), 20.15, 7.13, −14.65, −19.04 (each 2H, Ar-H), 17.34 (6H, Ar-CH_3), −23.96 (6H, N=C–CH_3)	58.1	59.0	5.02	4.95	8.78	8.97
18	495 $M^{\circ+}$ (24), 460 M − Cl (15), 444 M − Cl − HMe (26), 369 M − $FeCl_2$ (37), 354 M − $FeCl_2$ − Me (100)	86.19 (2H, $Py_{H3/5}$), 39.60 (1H, Py_{H4}), 16.28 (4H, $Aryl_{H3/5}$), −11.31 (2H, $Aryl_{H4}$), 13.40 (12H, Ar-CH_3), −17.02 (6H, N=C–CH_3)	60.1	60.5	5.33	5.44	8.42	8.47
30	843 $M^{\circ+}$ (1), 678 M − Flu (4), 316 Me–C=N($C_{22}H_{15}$) (21), 165 Flu (100)	–	74.6	75.4	4.79	4.65	4.92	4.98
31	1083 $M^{\circ+}$ (1), 1048 M − Cl (2), 957 M − $FeCl_2$ (2), 165 Flu (100)	–	77.9	78.6	5.76	5.85	3.81	3.87
32	1111 $M^{\circ+}$ (1), 1076 M − Cl (1), 671 M − Me − C=N($C_{23}H_{17}$) (5), 165 Flu (100)	–	77.9	78.8	6.01	6.07	3.66	3.78

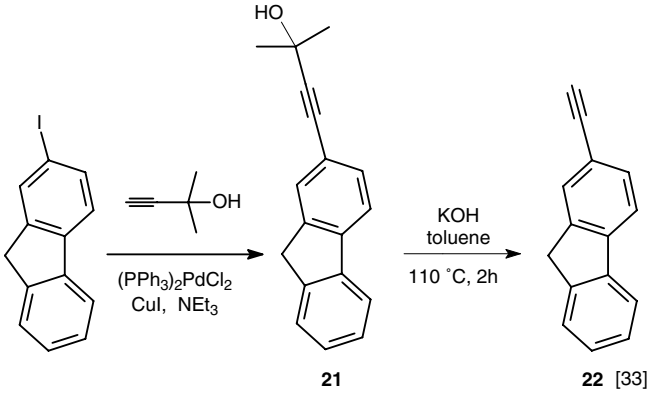
at $m/z = 593$ can be explained with the loss of both chloro ligands and the iron center resulting in the molecular ion of the bis(arylimino)pyridine ligand. Further cleavage of a methyl group from the ligand framework gives the ion with $m/z = 578$.

2.5. Synthesis of alkynyl substituted indene and fluorene compounds

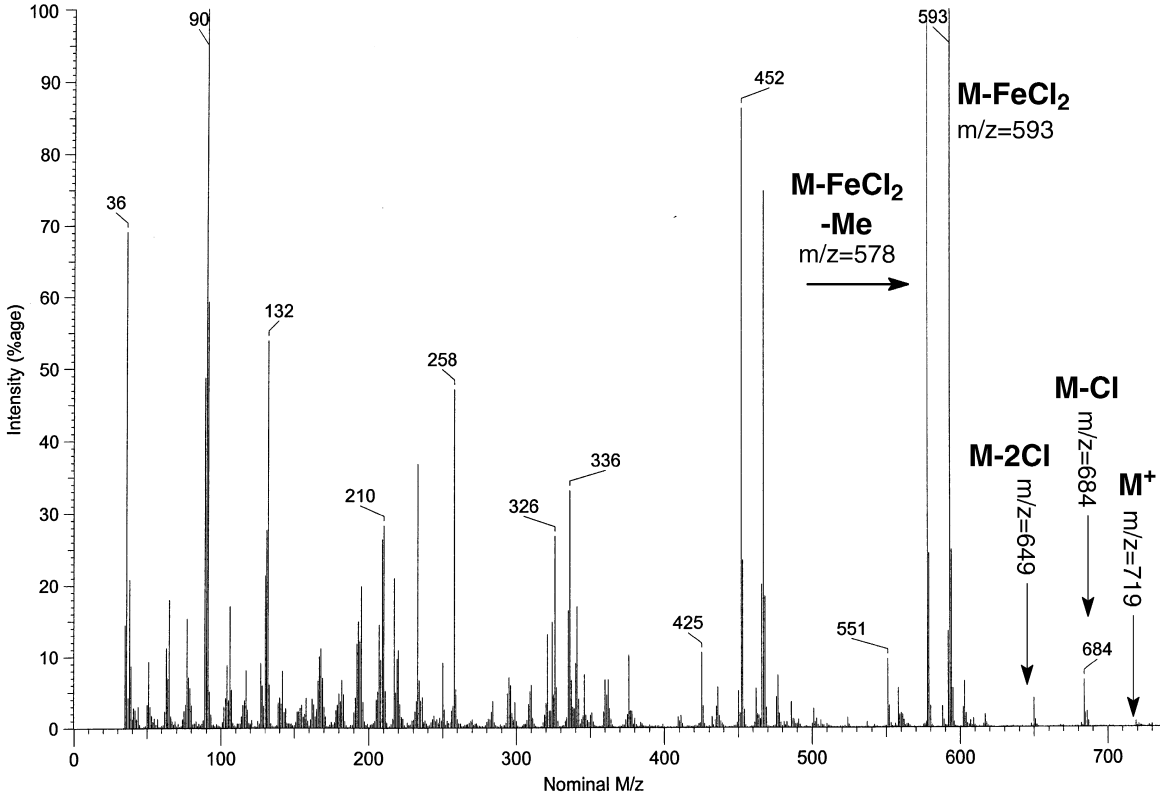
Starting from indene, 1-(trimethylsilyl)indene (**19**) and 1-(2-propynyl)-1-(trimethyl-silyl)indene (**20**) were prepared in high yields (Scheme 5).

2-Iodofluorene was reacted with 2-methylbut-3-yn-2-ol under Sonogashira conditions. Deprotection of the alkynyl function using potassium hydroxide furnished 2-ethynylfluorene (**22**) (Scheme 6) [33].

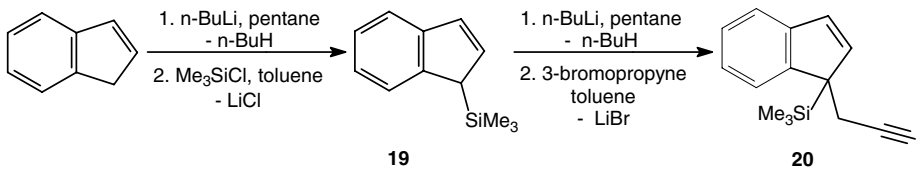
For the synthesis of alkynyl substituted bridged metallocene type ligand precursors, 5-hexyn-2-one (**23**) was prepared according to the literature [34]. Reaction with freshly distilled cyclopentadiene in a mixture of pyrrolidine and methanol yielded 6-(but-3-yn-1-yl)-6-methyl fulvene (**24**) (see Scheme 7). The reaction of fluorenyllithium and fulvene **24** and subsequent hydrolysis gave the C_1 bridged ligand precursor **25** [35]. The ^{1}H NMR, ^{13}C NMR, and MS data for compounds **18**–**25** are given in Table 1.



Scheme 6. Synthesis of 2-ethynyl fluorene (**22**).



Scheme 4. Mass spectrum of complex **14**.

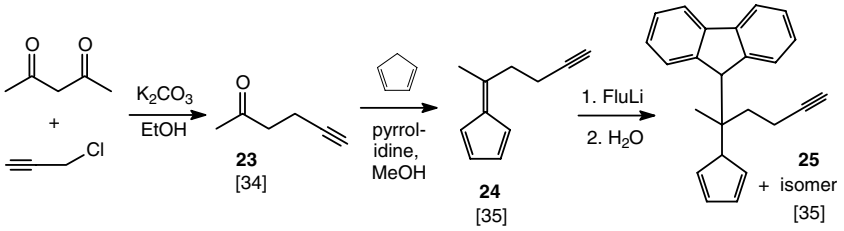


Scheme 5. Preparation of compounds **19** and **20**.

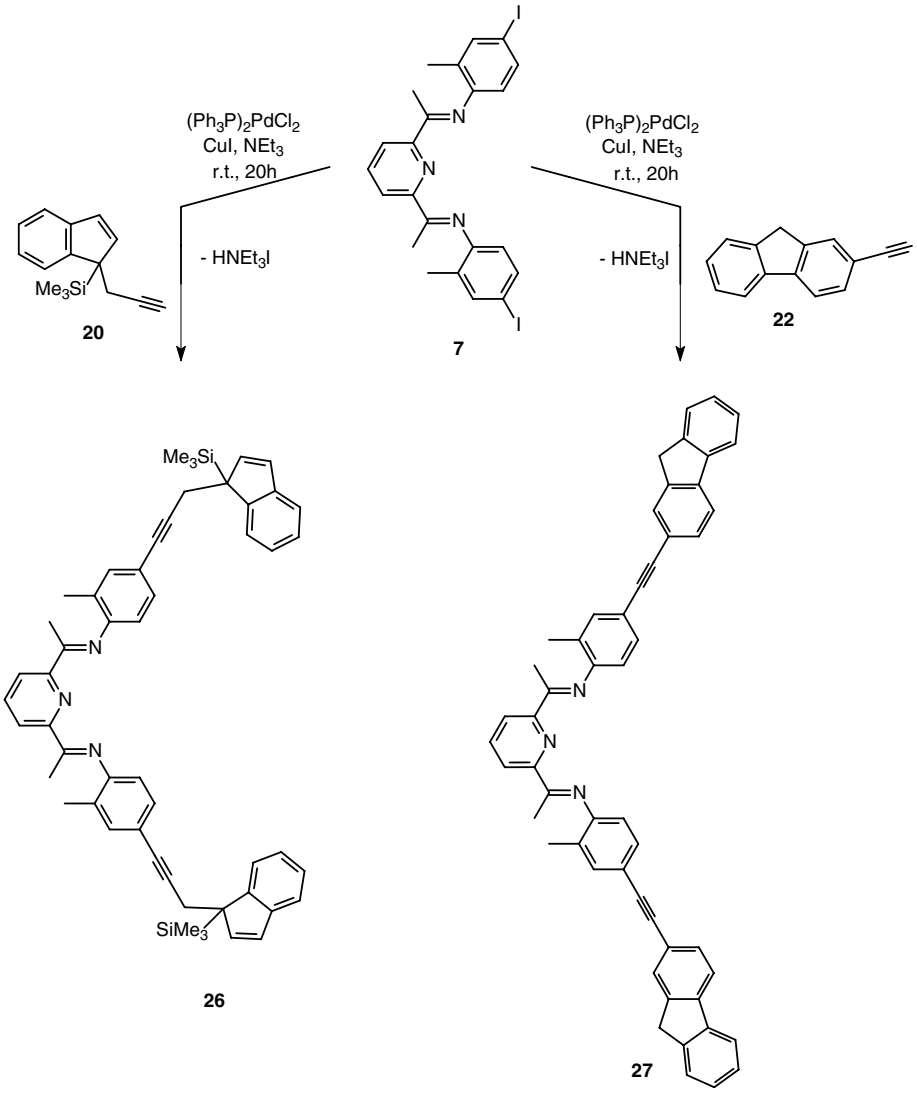
2.6. Sonogashira coupling reactions of halogenated 2,6-bis(arylimino)pyridines with alkynyl substituted indene or fluorene derivatives

The iodo substituted 2,6-bis(arylimino)pyridine compounds **7** and **8** were reacted with bridged or unbridged alkynyl substituted indene or fluorene derivatives using palladium catalyzed Sonogashira coupling. The reactions proceeded smoothly at mild reaction conditions (room temperature, 24 h, see Schemes 8 and 9), and the coupling products were isolated in good yields.

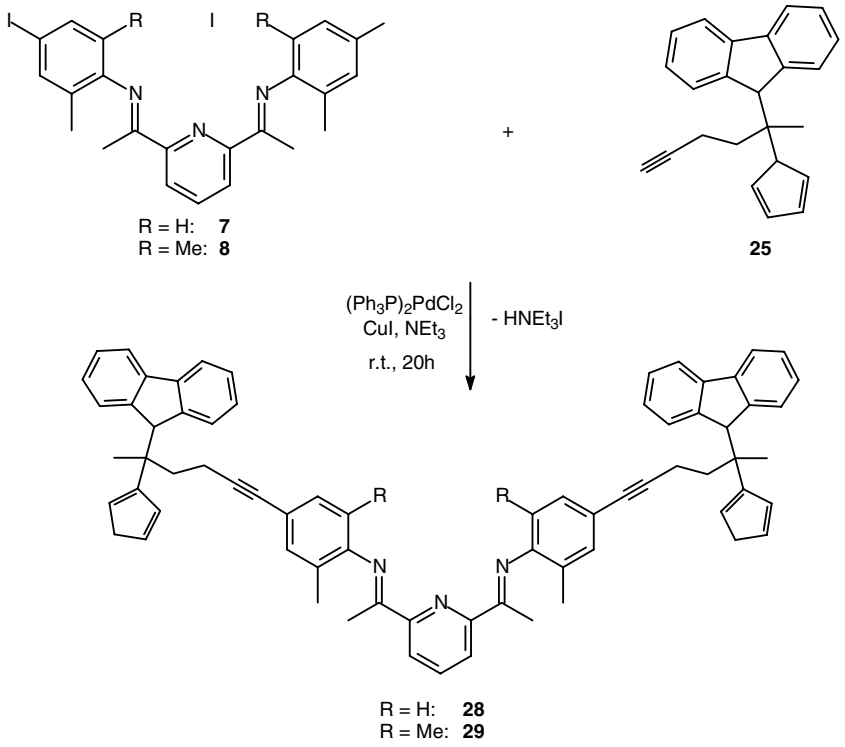
While the fluorenyl substituted compounds **27**–**29** are air stable, the indenyl derivative **26** decomposed on air within a few hours. The bromo substituted bis(arylimino)pyridines **4** and **5** did not react under Sonogashira conditions. Instead of coupling reactions, the loss of the bromo substituents could be observed at prolonged reaction times and elevated temperatures. The ^{1}H NMR, ^{13}C



Scheme 7. Synthesis of the C_1 bridged ligand precursor **25**.



Scheme 8. Sonogashira reactions of compound **7** with unbridged alkynyl substituted indene and fluorene derivatives.



Scheme 9. Synthesis of the alkynyl substituted bis(arylimino)pyridine compounds **28** and **29**.

NMR, and MS data for the ligand precursors **26**–**29** are given in Table 1.

2.7. Preparation of bis(arylimino)pyridine iron complexes from the Sonogashira coupling products 27–29

The fluorenyl substituted 2,6-bis(arylimino)pyridine compounds **27**–**29** were reacted with anhydrous iron(II) chloride affording the corresponding iron complexes **30**–**32** (Schemes 10 and 11) in yields of 55–70%.

In contrast to other bis(arylimino)pyridine iron complexes [17,36], the compounds **30**–**32** are only slightly blue. The spectral data for the complexes **30**–**32** are given in Table 2.

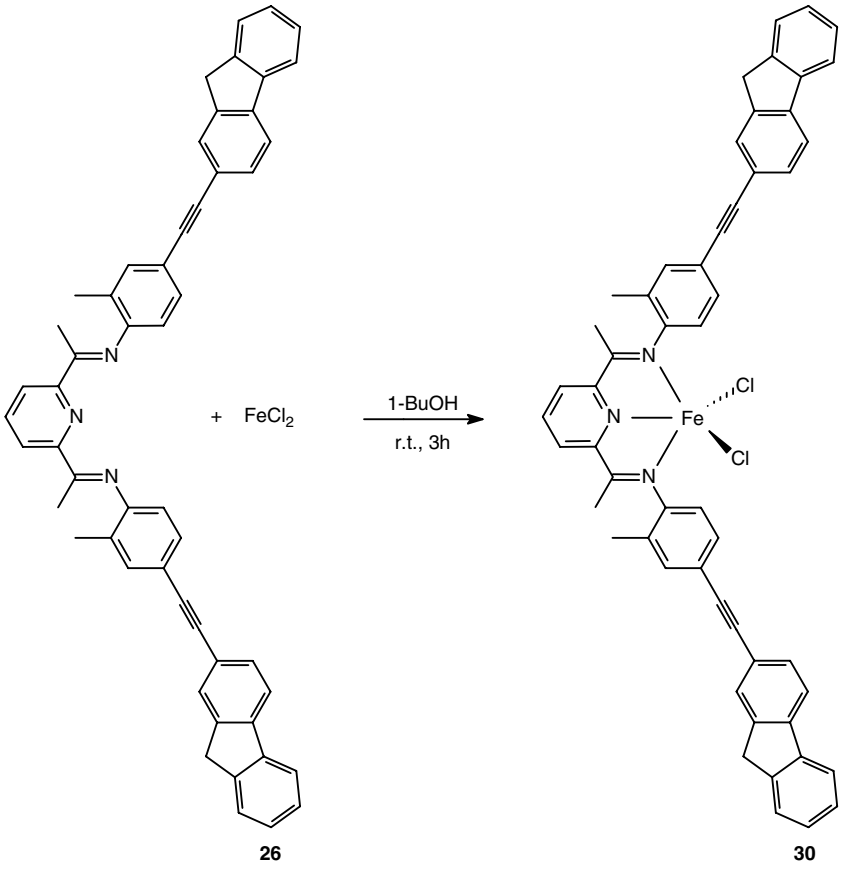
2.8. Attempts to prepare multinuclear complexes from the iron complexes 30–32

The deprotonation of the cyclopentadienyl and fluorenyl moieties of the iron complexes **30**–**32** using *n*-butyllithium and the subsequent reaction with the half-sandwich complex cyclopentadienylzirconium trichloride (in case of complex **30**) or zirconium tetrachloride (for complexes **31** and **32**) did not lead to the desired multinuclear iron–zirconium complexes. However, black solids were isolated which did not show any polymerization activities. The reaction of the bis(arylimino)pyridine ligand precursors **27**–**29** with *n*-butyllithium and cyclopentadienylzirconium trichloride or zirconium tetrachloride also did not yield defined dinuclear zirconium complexes.

A possible explanation for these results could be the nucleophilic attack of *n*-butyllithium on the (imino)pyridine moiety. A couple of reactions of different nucleophiles with bis(arylimino)pyridine compounds have been described in the literature. Deprotonation of the iminomethyl groups [37–39], reduction of the metal centers [40–42], addition of nucleophiles to the imino carbon atoms to give amido complexes [38,43], reductive dimerization at the iminomethyl groups [44,45], alkylation at the pyridine C-2 or C-4 carbon atoms [43,46] and even at the pyridine nitrogen atom [47–49] were observed depending on the applied nucleophilic reagent and the reaction conditions. Since the acidities of the iminomethyl protons and the fluorenyl protons (for free fluorene $pK_a = 22.9$) [50] seem to be similar, both positions may be deprotonated in complexes **30**–**32**. Probably, the competition of these two groups is the reason, why no clean complexation reactions were observed after addition of zirconium tetrachloride or the half-sandwich complex cyclopentadienylzirconium trichloride. Therefore, another synthetic strategy has to be developed on the way to the desired trinuclear iron–zirconium complexes.

2.9. Results of the catalytic oligomerization and polymerization of ethylene

The iron complexes **11**–**18** and **30**–**32** were used as catalyst precursors for the homogeneous polymerization and oligomerization of ethylene. The complexes were activated with methylalumoxane (MAO) applying a ratio Fe:Al =



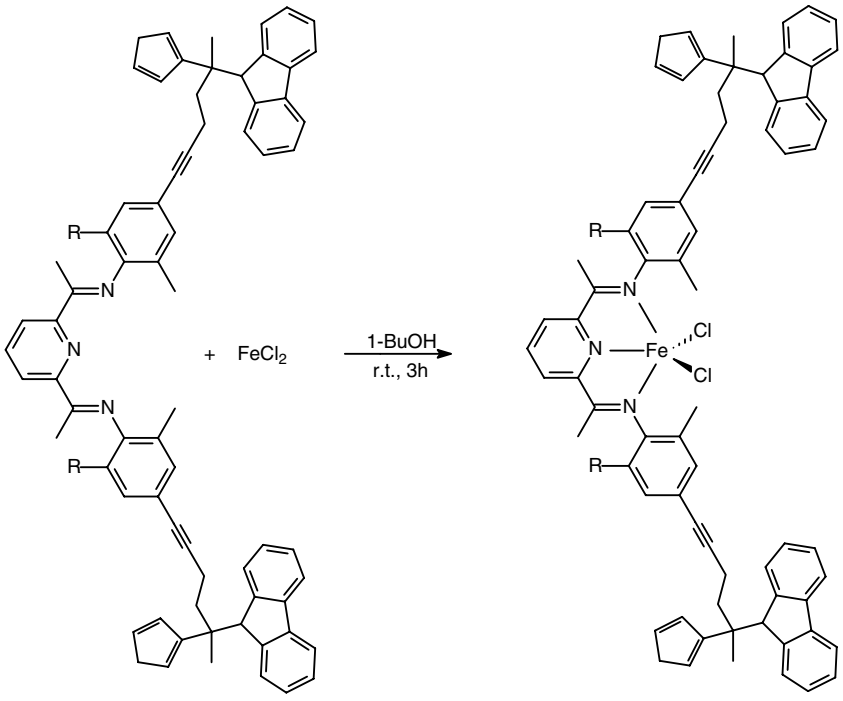
Scheme 10. Synthesis of complex **30**.

1:2500. The polymerization runs were routinely performed at a temperature of 60 °C over one hour employing an ethylene pressure of 10 bar. As a solvent *n*-pentane was used. The polymerization results are given in Table 3. The liquid fractions (noted as ''oligomer share'' in Table 3) contained α-olefins (chain length C_6–C_{40}) with purities higher than 95%. These oligomer mixtures were characterized by gas chromatography while the polymers were characterized using GPC.

The complexes **11**, **14**, **17**, and **30** produced exclusively oligomers. Surprisingly, also complex **13** which does not contain substituents at the *ortho*-positions to the imino nitrogen atoms was an active ethylene oligomerization catalyst albeit its activity was distinctly lower compared with complexes **11**, **14**, **17**, and **30**. The activity of complex **13** could be explained with the size of the iodo substituents at the *para*-positions of the iminophenyl rings, since analogous bis(arylimino)pyridine compounds with smaller substituents (H, Me, F) at the same positions usually afford inactive ionic complexes of the type $[ML_2]^{2+}[MCl_4]^{2-}$ when reacted with iron(II) chloride [51].

Due to steric reasons, 2,6-bis(arylimino)pyridine compounds containing halogen substituents at the *para*-positions of the iminophenyl rings seemed to be most suitable for Sonogashira coupling reactions with alkynyl substituted indenyl or fluorenyl derivatives. For investigation of the influence of different *para*-substituents on both the polymerization activity and the resulting product compositions, the well-known *para*-unsubstituted bis(arylimino)-pyridine iron complexes **17** and **18** were chosen as references. While complex **17** produces α-olefins with high activity [5], complex **18** polymerizes ethylene to high molecular weight polyethylenes [6]. With 2,4-dialkyl substituted bis(arylimino)pyridine iron complexes [36,52], lower oligomerization activities were achieved compared with complex **17**. Also, some iron(II) complexes with 2-methyl-4-halogen substituted ligand frameworks were described in the literature [9,53] which, in contrast, exhibited higher oligomerization activities compared with the reference complex **17**. As therefore expected, the iron complexes **11** and **14** showed higher oligomerization activities compared with the 4-unsubstituted complex **17** (Scheme 12).

The extremely high polymerization activities of 4-halogen-2-methyl substituted complexes can be explained with the electronic influence of the electronegative halogen substituents in the *para*-positions of the iminophenyl rings, since the electron donating *ortho*-methyl groups remained unvaried. The complex containing fluorine substituents [9] showed the highest activity among the 4-halogen-2-methyl substituted complexes. Due to the high electronegativity of fluoro substituents, the electron density at the cationic iron center is significantly reduced.

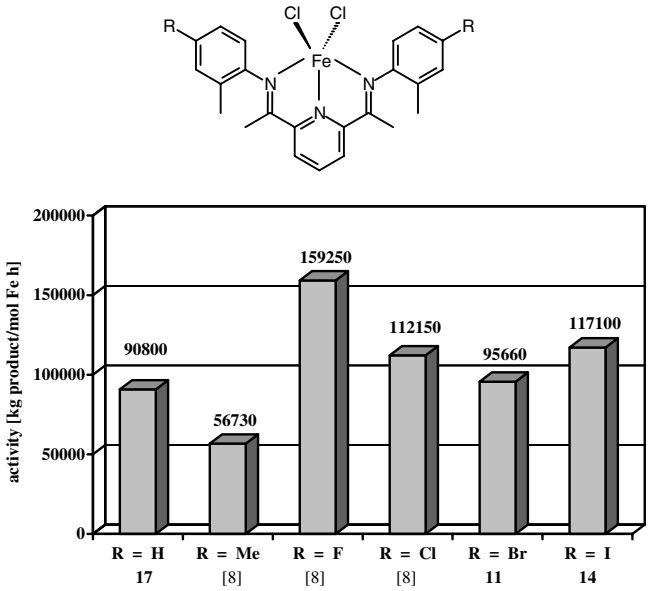


Scheme 11. Synthesis of the iron complexes **31** and **32**.

Table 3
Ethylene polymerization results for the iron complexes **11**–**18** and **30**–**32** (solvent: 250 ml *n*-pentane, activator: MAO, Fe:Al = 1:2500, 10 bar ethylene, 60 °C, 1h)

Complex	Activity (kg/mol Fe h)	M_n (g/mol)	M_w (g/mol)	PD	Oligomer share (wt.%)
11	95660	–	–	–	100
12	41100	19400	92940	4.80	–
13	2490	–	–	–	94.4
14	117100	–	–	–	100
15	146650	22700	102400	4.51	–
16	224170	27160	122500	4.51	–
17	90800	–	–	–	100
18	27900	6670	90950	13.6	–
30	24590	–	–	–	100
31	74275	14050	198900	14.2	–
32	89820	16200	158000	9.70	–

Therefore, its Lewis acidic character increases and the coordination of an ethylene molecule is facilitated. Complexes with chloro or bromo substituents at the *para*-positions gave lower activities, while the introduction of iodo substituents again increased the activity. Possibly due to the sterically more demanding iodo substituents, complex **14** showed a higher polymerization activity than the corresponding bromo substituted complex **11**. The same effect could be observed comparing the polymerization catalysts **12**, **15**, and **18** (see Table 3). Again, the *para*-unsubstituted reference complex **18** showed the lowest polymerization activity among these three complexes, while the activity increases from bromo (complex **12**) to iodo substitution (complex **15**). The iron(III) complex **16** with a tremendous polymerization activity of 224170 [kg PE/mol Fe h] was found to be even more active than its analogous iron(II) complex **15**. This result can be explained with a stronger Lewis acidic character of the iron(III) center compared with an iron(II) center and, therefore, an increased affinity to coordinate an electron rich ethylene molecule. The combination of substituents with contrary electronic properties at the iminophenyl rings seems to favor high polymerization activities, since iron complexes with 2,4-dialkyl, 2,4-dihalogen, 2,6-dialkyl, or 2,6-dihalogen substituted ligand frameworks are reported to exhibit lower activities than catalysts with 2-alkyl-4-halogen or 2,6-dialkyl-4-halogen substituted iminophenyl rings [8,9,36,52,53].



Scheme 12. Activities of 4-halogen-2-methyl substituted 2,6-bis(arylimino)pyridine iron complexes. All complexes produce 100% oligomers.

Table 4
Influence of the size of *para*-substituents in iron complexes with 2-methyl-4-halogen or 2-methyl-4-alkynyl substituted bis(arylimino)pyridine ligands on the product character

Complex	*para*-Substituent	Oligomer share [wt.%]
17	H	100
11	Br	100
14	I	100
30	2-Fluorenylethynyl	100
31	5-(9-Flu)-5-(1-Cp)-hex-1-yn-yl	0

The 2-methyl-4-alkynyl substituted complex **30** containing an ethynylfluorenyl group produced exclusively oligomers yielding a very similar product composition compared to the "iodo precursor" **14**. If the two-dimensional ethynylfluorenyl groups were replaced by three-dimensional substituents, the resulting complex **31** produced exclusively polymer (see Table 4). Complex **30** exhibits a dramatically lower oligomerization activity compared with complexes **11** and **14** containing 2-methyl-4-halogen substituted bis(arylimino)pyridine ligands. The expanded conjugated π-electron system of the ligand framework including both ethynylfluorenyl moieties possibly stabilizes the cationic iron center by transferring some electron density to the cationic metal center.

In contrast to complex **30**, the conjugated π-electron systems in complexes **31** and **32** only include the internal alkynyl groups but not the cyclopentadienyl and fluorenyl groups so the transfer of π-electron density from these groups to the metal center is prevented. The polymerization activities of complexes **31** and **32** are distinctly higher compared with the activities of complex **30** and reference complex **18** (see Table 3). As indicated for the complexes with iodo substituted bis(arylimino)pyridine ligands, not only the electronegativity of the *para*-substituents at the iminophenyl rings is decisive for high polymerization activities, but also their bulkiness. Bulky groups at the *para*-positions also exert influence on the molecular weights of the polymerization products. Although only one of the *ortho*-positions of the bis(arylimino)pyridine ligand in complex **31** is substituted, the steric bulk caused by the cyclopentadienyl and fluorenyl units seems to be high enough to decrease the rate of β-H elimination significantly. The average molecular weights M_n and M_w produced with **31**/MAO are 14050 and 198900 g/mol. These values are very similar to those obtained for the polyethylene produced with **32**/MAO ($M_n = 16200$ g/mol, $M_w = 158000$ g/mol). Therefore, substitution at both *ortho*-positions to the imino groups is not obligatory for polymer producing bis(arylimino)pyridine iron catalysts, if the *para*-positions are substituted with sterically demanding groups.

3. Conclusion

Seven new bis(arylimino)pyridine iron complexes containing halogen or alkynyl substituents in their ligand frameworks were synthesized and characterized. After activation with methylalumoxane (MAO), these catalysts oligomerize or polymerize ethylene to give highly linear products. The influence of substituents in the *para*-positions of the iminophenyl groups on the ethylene polymerization activities and the product compositions was investigated. Both the size and the electronegativity of the substituents play an important role. In case of rather small halogen substituents (F, Cl, Br), the electronegativity is the decisive factor leading to the highest activity for the fluoro substituted complex and decreased activities for the corresponding chloro and bromo substituted complexes. If iodo substituents were introduced in the *para*-positions, again a higher polymerization activity was observed along with an increased content of higher molecular weight olefins in the resulting product compositions. When sterically demanding alkynyl substituted cyclopentadienyl-fluorenyl-moieties were introduced applying Sonogashira coupling reactions, the resulting complexes produced exclusively polymers. Attempts to prepare multinuclear iron–zirconium complexes from the fluorenyl or cyclopentadienyl-fluorenyl substituted mononuclear iron complexes failed, possibly due to side reactions at the imino groups.

4. Experimental

4.1. General considerations

All experimental work was routinely carried out using Schlenk technique. Dried and purified argon was used as inert gas. Solvents were purified by distillation from appropriate drying agents. Methylalumoxane (30% in toluene) was purchased from Crompton (Bergkamen) and Albemarle (Baton Rouge, USA/Louvain–La Neuve, Belgium). Ethylene (3.0) and argon (4.8/5.0) were supplied by Rießner Company (Lichtenfels). All other starting materials

were commercially available and were used without further purification.

NMR spectra were recorded at 25 °C on a Bruker ARX 250 spectrometer. The chemical shifts in the ^{1}H NMR spectra are referred to the residual proton signal of the solvent ($\delta = 7.24$ ppm for $CDCl_3$, $\delta = 5.32$ ppm for $CDCl_2$) and in ^{13}C NMR spectra to the solvent signal ($\delta = 77.0$ ppm for $CDCl_3$, $\delta = 53.5$ ppm for $CDCl_2$). Mass spectra were routinely recorded at the Zentrale Analytik of the University of Bayreuth with a VARIAN MAT CH-7 instrument (direct inlet, EI, $E = 70$ eV) and a VARIAN MAT 8500 spectrometer. GC/MS spectra were recorded with a HP 5890 gas chromatograph in combination with a HP 5971A mass detector. At the Zentrale Analytik of the University of Bayreuth, GC/MS spectra were routinely recorded with a HP5890 gas chromatograph in combination with a MAT 95 mass detector. For the analysis of organic compounds, especially oligomer mixtures, a PERKIN ELMER Auto System gas chromatograph was used. GPC measurements were routinely performed by SABIC Company (Riyadh, Saudi Arabia). Some of the elemental analyses were performed by the Mikroanalytisches Labor Pascher at Remagen. The residual analyses were performed with a VarioEl III CHN instrument.

Compounds **1**–**3** and **23**–**25** were prepared according to the mentioned literature.

*4.2. Synthesis of the 2,6-bis(arylimino)pyridine compounds **4**–**10***

To a solution of 0.82 g (5 mmol) 2,6-diacetylpyridine in 150 ml of toluene were added 12.5 mmol (2.5 equiv) of a substituted aniline and a few milligrams of *para*-toluenesulfonic acid. The reaction mixture was heated under reflux for 8–24 h applying a Dean–Stark-trap. After cooling to room temperature, an amount of 200 ml of a saturated sodium hydrogencarbonate solution was added, the organic phase was separated, filtered over sodium sulfate and silica. The solvent was removed and 10 ml ethanol were added. The imino compounds precipitated when stored at −20 °C for some days (yields: 50–80%).

*4.3. Synthesis of 1-trimethylsilylindene (**19**) and 1-(2-propinyl)-1-trimethylsilylindene (**20**)*

Indenyllithium (50 mmol) or 1-(trimethylsilyl)indenyllithium (50 mmol) were suspended in 200 ml of toluene. The alkylation reagent (50 mmol) was added, and the reaction mixture was stirred at room temperature over night. Filtration over sodium sulfate and removal of the solvent in vacuo yielded the substituted indene derivatives **19** and **20** as bright yellow viscous oils (90–95%).

*4.4. Synthesis of 2-ethynylfluorene (**22**)*

2-Iodofluorene (6 mmol) was dissolved in 30 ml of triethylamine. Bis(triphenylphosphino)palladium dichloride (83 mg, 0,12 mmol), copper(I) iodide (45 mg, 0,24 mmol), and 2-methylbut-3-yne-2-ol (1 ml, 7 mmol) were added, and the reaction mixture was stirred for 20 h at room temperature. After removal of the solvent, water (50 ml) and *n*-pentane (50 ml) were added. The organic phase was separated, and the aqueous phase was extracted with *n*-pentane. The combined organic phases were dried over sodium sulfate. Removal of the solvent in vacuo and recrystallization from *n*-pentane furnished 4-(2-fluorenyl)-2-methylbut-3-yn-2-ol (**21**) as colorless crystals in 85% yield.

4-(2-Fluorenyl)-2-methylbut-3-yn-2-ol (5 mmol) (**21**) was dissolved in 100 ml of a mixture of methanol and methylene chloride (4:1). Anhydrous potassium carbonate (7.5 mmol) was added. After 2 h of stirring at room temperature, the mixture was filtered over sodium sulfate, and the solvent was removed in vacuo. The raw product was purified by column chromatography (ethyl acetate/*n*-pentane = 3:7). Yield: 80%.

*4.5. General procedure for the Sonogashira coupling reactions of halogenated bis(aryl-imino)pyridines with the ω-alkynyl functionalized indene and fluorene derivatives **26**–**29***

In 15 ml of triethylamine, an amount of 0.35 mmol of the iodo substituted 2,6-bis(arylimino)pyridine compound **7** or **8**, 0.70 mmol of an alkynyl substituted indene or fluorene derivative, bis(triphenylphosphino)palladium dichloride (7 μmol) and copper(I) iodide (14 μmol) were dissolved. The mixture was stirred for 20 h at room temperature. After removal of the solvent, water (50 ml) and *n*-pentane (50 ml) were added. The organic phase was separated, and the aqueous phase was extracted several times with *n*-pentane. The combined organic phases were dried over sodium sulfate. Removal of the solvent in vacuo, purification by column chromatography, and recrystallization from *n*-pentane furnished the coupling products as yellowish or brownish powders (yields: 55–60%).

*4.6. General synthesis of the 2,6-bis(arylimino)pyridine iron(II) and iron(III) complexes **11**–**18** and **30**–**32***

An amount of 1.0 mmol of the 2,6-bis(arylimino)pyridine compound was dissolved in 20 ml 1-butanol and reacted with 1.0 mmol of anhydrous iron(II) chloride or iron(III) chloride resulting in an immediate color change. The mixture was stirred for 3 h at room temperature, whereby the complexes precipitated. *n*-Pentane (10 ml) was added for complete precipitation. The iron complexes were filtered over a glass frit, washed three times with 15 ml *n*-pentane and were dried in vacuo. Yields: 37–96%.

4.7. Polymerization of ethylene in the 1 l Büchi autoclave

An amount of 0.2–2 mg of the desired iron complex was suspended in 5 ml of toluene. Methylalumoxane (30% in toluene, Fe:Al = 1:2500) was added resulting in an immedi-

ate color change. The mixture was added to a 1 l Schlenk flask filled with 250 ml *n*-pentane. This mixture was transferred to a 1 l Büchi laboratory autoclave under inert atmosphere and thermostated at 60 °C. An ethylene pressure of 10 bar was applied for 1 h. The polymer was filtered off using a glass frit, washed with diluted hydrochloric acid, water, and acetone, and finally dried in vacuo.

To the oligomer solutions diluted hydrochloric acid was added. The organic phase was separated and dried over sodium sulfate. *n*-Pentane was distilled using a Vigreux column. The resulting oligomer mixtures were characterized using gas chromatography.

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References

[1] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 849.
[2] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, J. Am. Chem. Soc. 121 (1999) 8728.
[3] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem., Int. Ed. 37 (1999) 428.
[4] G.J.P. Britovsek, G.K.B. Clentsmith, V.C. Gibson, D.M.L. Goodgame, S.J. McTavish, Q.A. Pankhurst, Catal. Commun. 3 (2002) 207.
[5] B.L. Small, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 7143.
[6] B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 120 (1998) 4049.
[7] B.L. Small, M. Brookhart, Macromolecules 12 (1999) 2120.
[8] Y. Chen, C. Qian, J. Sun, Organometallics 22 (2003) 1231.
[9] Y. Chen, R. Chen, C. Qian, X. Dong, J. Sun, Organometallics 22 (2003) 4312.
[10] Z. Zhang, S. Chen, X. Zhang, H. Li, Y. Ke, Y. Lu, Y. Hu, J. Mol. Catal. A: Chem. 230 (2005) 1.
[11] F. Pelascini, F. Peruch, P.J. Lutz, M. Wesolek, J. Kress, Eur. Polym. Sci. 41 (2005) 1288.
[12] K. Lappalainen, K. Yliheikkilä, A.S. Abu-Surrah, M. Polamo, M. Leskelä, T. Repo, Z. Anorg. Allg. Chem. 631 (2005) 763.
[13] A.S. Ionkin, W.J. Marshall, D.J. Adelman, A.L. Shoe, R.E. Spence, T. Xie, J. Polym. Sci. A: Polym. Chem. 44 (2006) 2615.
[14] A.S. Ionkin, W.J. Marshall, D.J. Adelman, B. Bobik Fones, B.M. Fish, M.F. Schiffhauer, Organometallics 25 (2006) 2978.
[15] V.C. Gibson, N.J. Long, P.J. Oxford, A.J.P. White, D.J. Williams, Organometallics 25 (2006) 1932.
[16] Y.V. Kissin, C. Qian, G. Xie, Y. Chen, J. Polym. Sci. A: Chem. 44 (2006) 6159.
[17] F.A.R. Kaul, G.T. Puchta, G.D. Frey, E. Herdtweck, W.A. Herrmann, Organometallics 26 (2007) 988.
[18] K. Sonogashira, Y. Tohda, N. Hagihara, Tetrahedron Lett. 16 (1975) 4467.
[19] K. Sonogashira, in: E. Negishi, A. Meijere (Eds.), Handbook of Organopalladium Chemistry for Organic Synthesis, Wiley, VCH, New York, 2002, and references cited therein.
[20] I. Paterson, R.D.M. Davies, R. Marquez, Angew. Chem., Int. Ed. 40 (2001) 603.
[21] N.D.P. Cosford, L. Tehrani, J. Roppe, E. Schweiger, N.D. Smith, J. Anderson, L. Bristow, J. Brodkin, X. Jiang, I. McDonald, S. Rao, M. Washburn, M.A. Varney, J. Med. Chem. 46 (2003) 204.
[22] O. Mongin, L. Porres, L. Moreaux, J. Merta, M. Blanchard-Desce, Org. Lett. 4 (2002) 719.
[23] R.W. Wagner, J. Seth, S.I. Yang, D. Kim, D.F. Bocian, D. Holten, J.S. Lindsey, J. Org. Chem. 63 (1998) 5042.
[24] S. Höger, S. Rosselli, A.-D. Ramminger, V. Enkelmann, Org. Lett. 4 (2002) 4269.
[25] K. Onitsuka, M. Fujimoto, N. Ohshiro, S. Takahashi, Angew. Chem., Int. Ed. 38 (1999) 689.
[26] S. Kajigaeshi, T. Kakinami, H. Yamasaki, S. Fujisaki, T. Okamoto, Bull. Chem. Soc. Jpn. 61 (1988) 600.
[27] S. Kajigaeshi, T. Kakinami, H. Yamasaki, S. Fujisaki, M. Kondo, T. Okamoto, Chem. Lett. (1987) 2109.
[28] K.-S. Jeong, Y.L. Cho, S.-Y. Chang, T.-Y. Park, J.U. Song, J. Org. Chem. 64 (1999) 9459.
[29] R. Schmidt, M.B. Welch, R.D. Knudsen, S. Gottfried, H.G. Alt, J. Mol. Catal. A: Chem. 222 (2004) 9.
[30] R. Schmidt, U. Hammon, M. B. Welch, H. G. Alt, B. E. Hauger, R. D. Knudsen, US 6458905, 2002.
[31] I.S. Paulino, U. Schuchardt, J. Mol. Catal. A: Chem. 211 (2004) 55.
[32] Z. Zhang, J. Zou, N. Cui, Y. Ke, Y. Hu, J. Mol. Catal. A: Chem. 219 (2004) 249.
[33] G.T. Crisp, Y.-L. Jiang, Synth. Commun. 28 (1998) 2571.
[34] J. Flahaut, P. Miginiac, Helv. Chim. Acta 61 (1978) 2275.
[35] M.B. Welch, H.G. Alt, B. Peifer, US 5631203, 1997.
[36] G.J.P. Britovsek, S. Mastroianni, G.A. Solan, S.P.D. Baugh, C. Redshaw, V.C. Gibson, A.J.P. White, D.J. Williams, M.R.J. Elsegood, Chem. Eur. J. (2000) 2221.
[37] D. Enright, S. Gambarotta, G.P.A. Yap, P.H.M. Budzelaar, Angew. Chem., Int. Ed. 41 (2002) 3873.
[38] J. Scott, S. Gambarotta, I. Khorobkov, P.H.M. Budzelaar, J. Am. Chem. Soc. 127 (2005) 13019.
[39] M.W. Bouwkamp, E. Lobkovsky, P.J. Chirik, Inorg. Chem. 45 (2006) 2.
[40] D. Reardon, G. Aharonian, S. Gambarotta, G.P.A. Yap, Organometallics 21 (2002) 5.
[41] J. Scott, S. Gambarotta, I. Khorobkov, P.H.M. Budzelaar, Organometallics 24 (2005) 6298.
[42] M.W. Bouwkamp, S.C. Bart, E.J. Hawrelak, R.J. Trovitch, E. Lobkovsky, P.J. Chirik, Chem. Commun. (2005) 3406.
[43] Q. Knijnenburg, J.M.M. Smits, P.H.M. Budzelaar, Organometallics 25 (2006) 1036.
[44] H. Sugiyama, G. Aharonian, S. Gambarotta, G.P.A. Yap, P.H.M. Budzelaar, J. Am. Chem. Soc. 124 (2002) 12268.
[45] Q. Knijnenburg, J.M.M. Smits, P.H.M. Budzelaar, Compt. Rend. Chim. 7 (2004) 865.
[46] J. Campora, C.M. Perez, A. Rodriguez-Delgado, A.M. Naz, P. Palma, E. Alvarez, Organometallics 26 (2007) 1104.
[47] I. Khorobkov, S. Gambarotta, G.P.A. Yap, P.H.M. Budzelaar, Organometallics 21 (2002) 3088.
[48] G.K.B. Clentsmith, V.C. Gibson, P.B. Hitchcock, B.S. Kimberley, C.W. Rees, Chem. Commun. (2002) 1498.
[49] I.J. Blackmore, V.C. Gibson, P.B. Hitchcock, C.W. Rees, D.J. Williams, A.J.P. White, J. Am. Chem. Soc. 127 (2005) 6012.
[50] I.F. Tupitsyn, N.N. Zatsepina, Russ. J. Gen. Chem. 72 (2002) 405.
[51] A.S. Abu-Surrah, K. Lappalainen, U. Piironen, P. Lehmus, T. Repo, M. Leskelä, J. Organomet. Chem. 648 (2002) 55.
[52] R. Schmidt, M.B. Welch, S.J. Palackal, H.G. Alt, J. Mol. Catal. A: Chem. 179 (2002) 155.
[53] R. Schmidt, M.B. Welch, R.D. Knudsen, S. Gottfried, H.G. Alt, J. Mol. Catal. A: Chem. 222 (2004) 17.