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Iron and Cobalt Ethylene Polymerization Catalysts: Variations on the Central Donor

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Three classes of ligands, designed to explore the effect of variations on the central pyridine donor core in bis(imino)pyridine iron and cobalt ethylene polymerization catalysts of the general formula [$LMCl_2$] (M = Fe or Co), have been prepared. The first class comprises six-membered N-heterocycles (pyrimidine and triazine) and the second class five-membered heterocycles (furan and thiophene) as the central donor core. In the third class of ligands, the imine donor arm has been extended by one carbon to give anionic tridentate ligands based on carbazole and neutral analogues based on dibenzofuran and dibenzothiophene. The coordination behavior of these ligands upon reaction with $FeCl_2$ or $CoCl_2$ has been investigated, whereby only in the case of the neutral pyrimidine or the anionic carbazolide unit as the central donor core have stable complexes been obtained. Ethylene polymerization results are compared with the parent bis(imino)pyridine iron and cobalt catalyst systems.

Introduction

The search for well-defined transition-metal-based catalysts for the polymerization of ethylene and α-olefins is an area of intense current interest, both in academic and industrial research laboratories. Compared to relatively ill-defined Ziegler−Natta systems, a key advantage of well-defined or single-site catalysts is the possibility for rational ligand-oriented catalyst design, allowing better control over polymer parameters such as molecular weight, polydispersity, and tacticity.[1] While many of the catalysts developed over the last 40 years are based on early transition metals, recent developments have resulted in highly active late transition metal catalysts.[2−5] Key milestones have been the development of Ni(II) and Pd(II) catalysts containing α-diimine ligands[6] and the bis(imino)pyridine Fe(II) and Co(II) catalysts,[7,8] both of which, upon activation with a cocatalyst such as methyl aluminoxane (MAO), give highly active catalysts for the polymerization of ethylene. Depending on the ligand structure, polyethylene materials ranging from linear α-olefins to high molecular weight polymers can be produced. For the iron and cobalt systems of type I (Figure 1), we have shown in a series of reports that ligand modifications result in changes to the productivity of the catalysts and to the molecular weight of the resultant polyolefins.[9−13] As part of our ongoing studies into structure−activity relationships

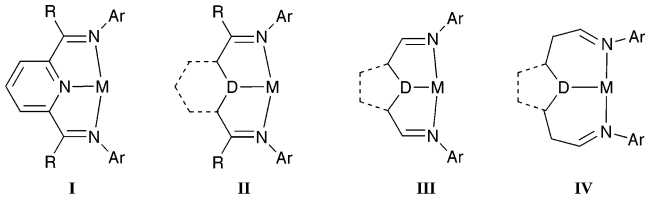

Figure 1. Schematic overview of different ligand types.

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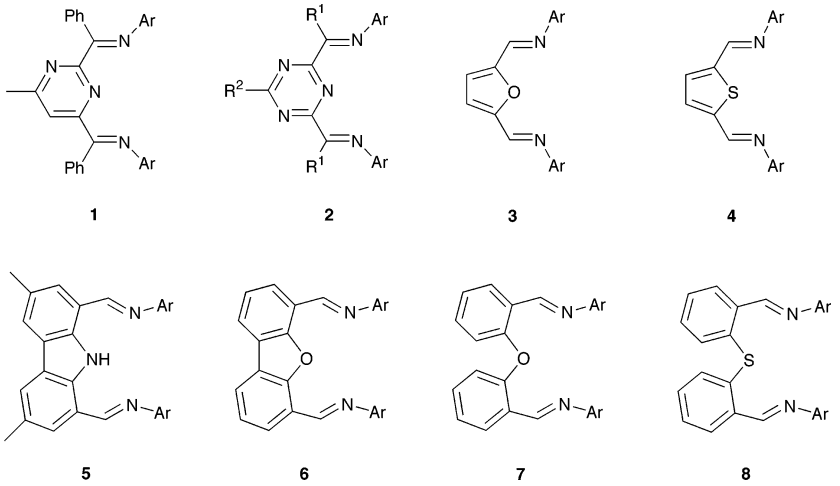

Figure 2. Overview of ligands used in this study.

within this family of polymerization catalysts, we describe here the effect of variations at the central donor core of the ligand.

We have developed synthetic entries into three classes of ligands (II−IV, Figure 1) based on various central donors. These contain the heterocyclic cores pyrimidine, triazine, carbazole, furan, and thiophene, as well as ether and thioether central donors. Type II ligands contain a six-membered heterocyclic core while ligands of type III involve a five-membered heterocyclic donor core. Both are tridentate ligands that form two five-membered chelate rings upon coordination to a metal center. The third group, IV, contains ligands that form two six-membered chelate rings when coordinated to a metal center. The coordination behavior of these ligands with $FeCl_2$ and $CoCl_2$ has been investigated, and the catalytic properties of the complexes for the polymerization of ethylene have been evaluated and compared to those of the parent bis(imino)pyridine complexes of type I.

Results and Discussion

Synthesis of Ligands and Complexes of Type II. A series of ligands of type II (Figure 1) containing the N-heterocycles pyrimidine (**1a**−**d**) and triazine (**2a** and **2b**) were targeted (see Figure 2). A key difference between these ligands and their well-established pyridine analogues is the lower basicities of the pyrimidine and triazine nitrogen donors. For example, the pK_a's of protonated pyrimidine and triazine are 1.1 and 1.0, respectively, whereas protonated pyridine has a pK_a of 5.2. This would be expected to lead to a significant difference in donor strength and electron density at the metal center.[14]

The bis(imino)pyrimidine ligands **1a**−**d** were prepared from 2,4-dibenzoyl-6-methylpyrimidine, which was obtained by a known procedure from freshly prepared benzoylformyl chloride[15] and 6-methyl-2,4-bis(trimethylstannyl)pyrimidine (eq 1, Scheme 1).[16] The condensation of the diketone with various anilines to give the bis(imino)pyrimidine ligands **1a**−**d** proceeded smoothly using $Si(OEt)_4$ as a dehydrating agent in the presence of a catalytic amount of concentrated H_2SO_4.[17] Compounds **1a**−**d** have been analyzed by NMR, IR, and mass spectrometry, and in addition, the molecular structure of ligand **1c** was determined by X-ray crystallography (Figure 3). In all examples known to date, bis(imino)pyridine compounds adopt an *E*,*E* configuration, both in the solid state and in solution.[18−21] By contrast, the bis-

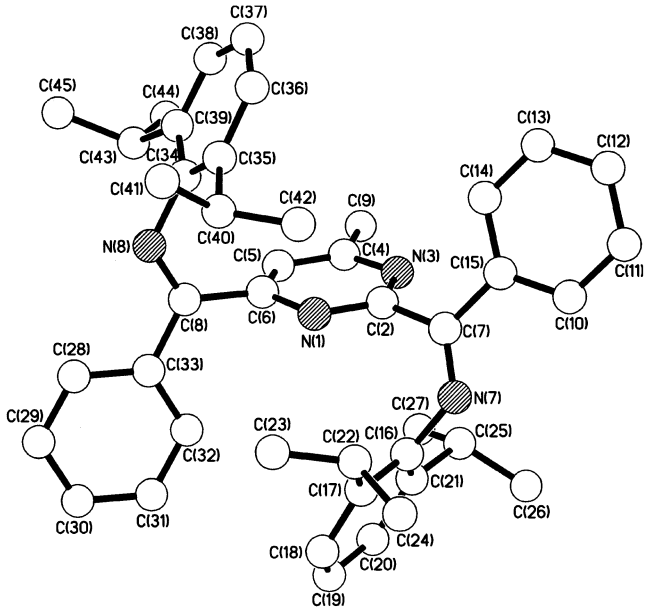

Figure 3. Molecular structure of **1c**.

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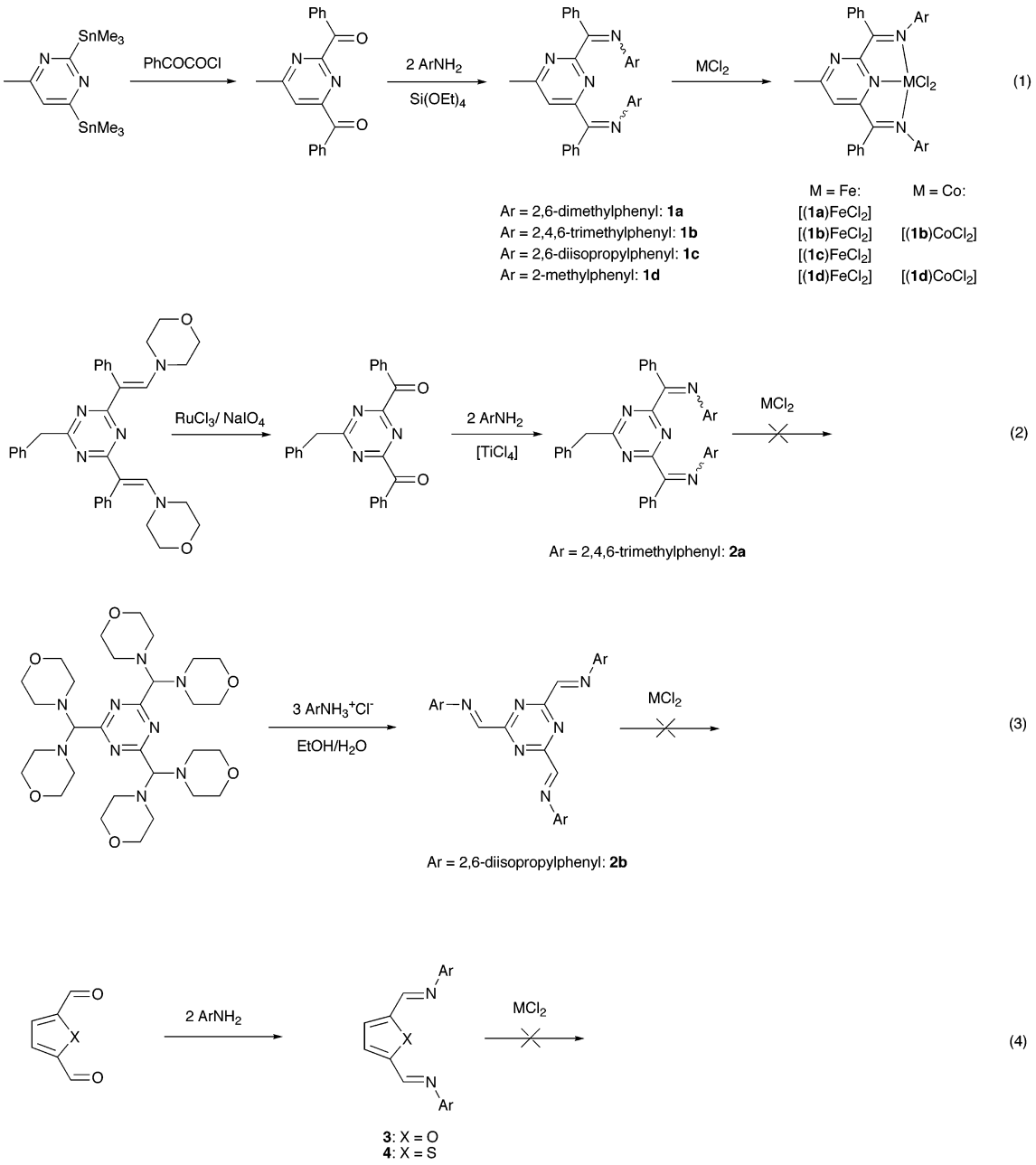
Scheme 1



(imino)pyrimidine derivative **1c** is seen here to exist in the solid state as the *Z*,*Z* isomer, a configuration that is clearly not preorganized for coordination to a metal center in a tridentate fashion. The molecule has pseudo C_2 symmetry about the N(1)···C(4) vector of the pyrimidine ring: indeed, in the crystal structure, there is 65:35 disorder observed for the positions of N(3)/C(5) within this ring. The torsional twists about the C(2)—C(7) and C(6)—C(8) bonds are ca. 61° and 83°, respectively, and those about N(7)—C(16) and N(8)—C(34) are ca. 74° and 89°. The two C═N linkages [C(7)—N(7) 1.287(3) Å, C(8)—N(8) 1.270(3) Å] are similar to those seen in bis(imino)pyridine compounds.[18−20] The only intermolecular packing interaction of note is an edge-to-face stacking of the C(33) and C(34) containing phenyl rings of C_i related pairs of molecules; the centroid···centroid separation is 4.99 Å.

Proton NMR spectra of **1a**−**d** indicate the presence of a mixture of interconverting isomers in solution. A set of crystals of **1c**, taken from the same batch as the single crystal used for X-ray analysis, was dissolved in C_6D_6. The ^{1}H NMR spectrum at 25 °C shows the presence of two isomers in a ratio of 6:1 (Figure S1a). The major species displays two equally intense septets at 3.08 and 3.47 ppm, corresponding to the two inequivalent methine protons of the isopropyl substituents, and a singlet at 1.84 ppm for the 6-CH_3 substituent. The same pattern, two smaller septets at 2.98 and 3.37 ppm and a singlet at 2.01 ppm, is observed for the minor isomer. In addition, very weak signals at 1.80−1.90 ppm are observed, possibly due to other isomers. At 70 °C, these separate sets of signals coalesce to three broad

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resonances (Figure S1b) indicating a fast interconversion between the isomers at higher temperatures. This process is reversible and suggests an *E*/*Z* isomerization via inversion at the imine nitrogen(s).[21,22]

Notwithstanding, the mixture of isomers observed for the free ligands in solution does not prevent the formation of bis(imino)pyrimidine iron(II) and cobalt(II) complexes. Iron complexes [(ligand)$FeCl_2$] of all ligands **1a**−**d** were obtained in good yield by mixing the appropriate bis(imino)pyrimidine ligand with $FeCl_2$ in hot *n*-butanol at 80 °C. For the ligands **1b** and **1d**, the cobalt complexes [(ligand)$CoCl_2$] were prepared via a similar procedure. However, unlike the iron case, no reaction occurred between the bis(imino)pyrimidine derivative **1c**, containing 2,6-diisopropylphenyl substituents, and $CoCl_2$ in *n*-butanol at 80 °C. Since at this temperature there is no significant barrier to *E*/*Z* isomerization, the inability of **1c** to coordinate to cobalt is likely to be a consequence of the increased steric bulk of the isopropyl groups, in combination with an intrinsically weaker metal−ligand interaction compared to iron. All complexes were analyzed by ^{1}H NMR spectroscopy, elemental analysis, mass spectrometry, and magnetic susceptibility measurements.

In order to introduce a different N-heterocyclic central unit, two derivatives **2a** and **2b** containing a triazine core were prepared (Figure 2). The dibenzoyl-triazine precursor for **2a** was prepared by the ruthenium catalyzed oxidation of bis(enamino)triazine with sodium periodate (see Scheme 1, eq 2).[23] Condensation of dibenzoyl-triazine with 2 equiv of 2,4,6-trimethylaniline proceeded smoothly with the use of a catalytic amount of $TiCl_4$. In contrast to the bis(imino)pyrimidine ligands **1a**−**d**, the ^{1}H NMR spectrum of **2a** showed only a single isomer in solution. By analogy to the conformational isomerism seen in the bis(imino)pyrimidine ligands, it is likely that this bis(imino)triazine ligand exists only as the *Z*,*Z* conformer.

Tris(imino)triazine compound **2b** was prepared from the reaction of the morpholino protected triazine with the anilinium salt as depicted in eq 3 (Scheme 1). Also for compound **2b**, only a single isomer was observed by NMR. In this case, because of the smaller hydrogen substituents in this aldimine ligand compared to the phenyl groups in the previous cases, this ligand most likely exists as the *E*,*E*,*E* isomer. Whatever the exact geometry of these ligands, their reactions with either $FeCl_2$ or $CoCl_2$ in *n*-butanol at 80 °C did not yield [(ligand)MCl_2] complexes, and only unreacted ligand and metal chloride were recovered after workup. High isomerization barriers to the conformer suited to coordination, as well as the reduced basicities of these triazine ligands, likely prevent the formation of metal complexes. Increasing the reaction temperature to 120 °C resulted in decomposition of the ligand.

Synthesis of Ligands and Complexes of Type III. Metal complexes containing ligands of type III (Figure 1) with a five-membered N-heterocyclic core, i.e., monoanionic bis(imino)pyrrolide ligands, have been reported previously.[24,25] Iron(II) and cobalt(II) complexes were prepared and characterized, but for both metals, the bis(imino)pyrrolide acted as a bidentate ligand through the pyrrolyl nitrogen and one of the imine arms, most probably due to an insufficient "reach" of the second imine arm. It is only for relatively large metal ions that the bis(imino)pyrrolide ligand has been found to bind in a tridentate fashion.[26] We have explored the possibility of introducing other neutral central donors such as oxygen and sulfur. The bis(imino)furan and bis(imino)thiophene derivatives **3** and **4** (see Figure 2) can be readily prepared from furan-2,5-dicarboxaldehyde[27] or thiophene-2,5-dicarboxaldehyde and 2,6-diispropylaniline (eq 4 in Scheme 1). The ligands were prepared in good yield and fully characterized. However, no reaction between **3** or **4** with $FeCl_2$ was observed in *n*-butanol or THF, at room temperature or at elevated temperatures. Addition of a THF solution of ligand **3** or **4** to a suspension of $CoCl_2$ in THF resulted in the formation of an intensely colored dark green solution, from which in both cases a dark green product was isolated. However, FAB-MS, IR, and ^{1}H NMR spectra showed no indication of the formation of a cobalt complex, and only peaks attributable to the free ligand were observed. Complexes of this type have been previously claimed but were not fully characterized.[28−31]

The poor ligating properties of these two ligands are not surprising. A substantial number of metal complexes with ligands containing bis(imino)furan and bis(imino)thiophene units have been reported, but these units have always been part of a macrocyclic or multidentate ligand and in none of the examples does the oxygen or sulfur atom coordinate to the metal center.[32−34] These observations are consistent with the oxygen and sulfur atoms of the furan and thiophene core of these ligands being rather poor donors. In addition, tridentate ligation of these ligands containing a five-membered central donor core will be disfavored due to insufficient "reach" as already outlined for the bis(imino)pyrrolide system.

Synthesis of Ligands and Complexes of Type IV. It was envisaged that the problems encountered in coordinating

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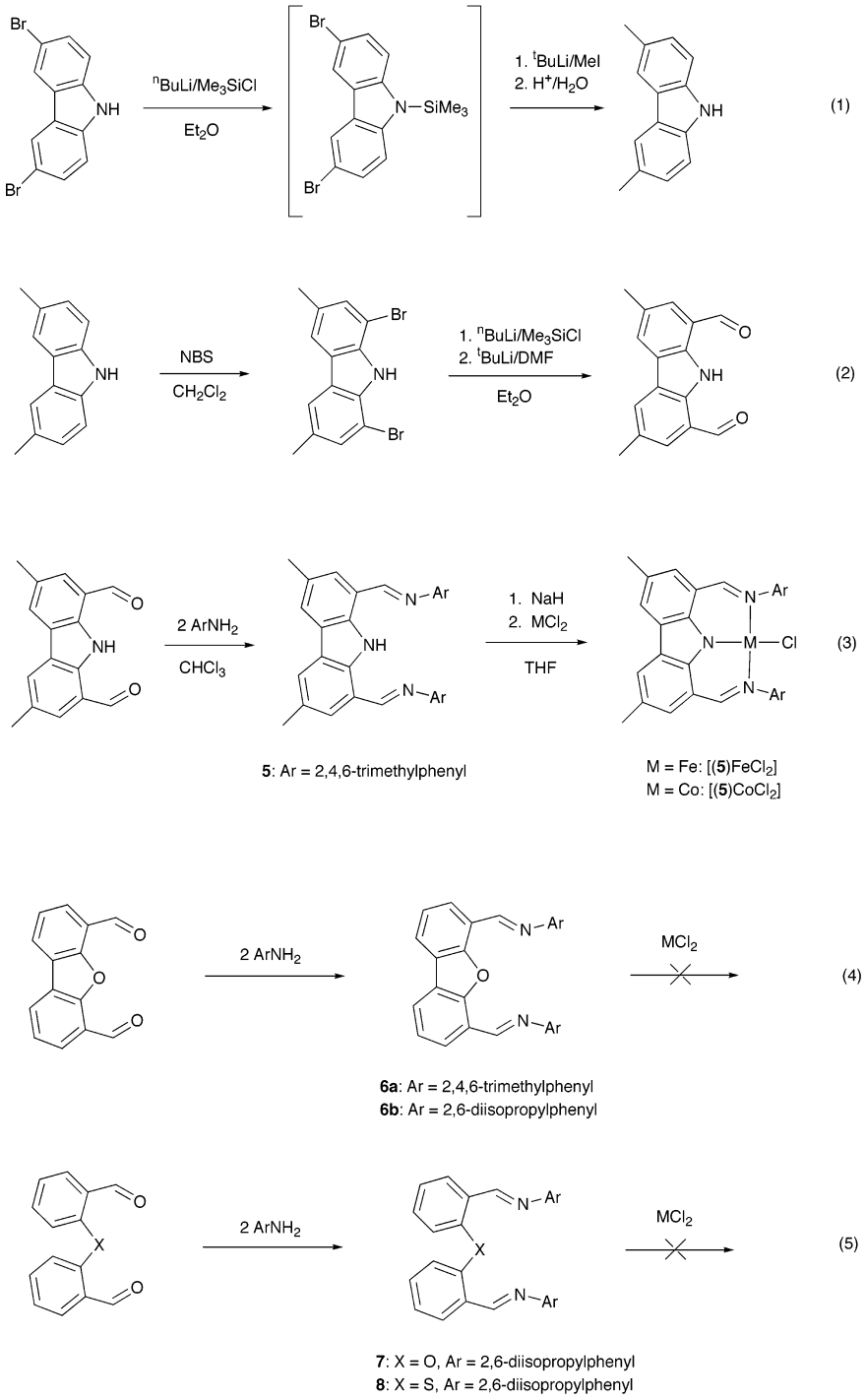
Scheme 2



ligands of type III in a tridentate manner may be overcome by introducing an extra carbon atom linker between the imine moiety and the central heterocyclic core. Thus, a series of complexes with the general framework IV (Figure 1) containing nitrogen, oxygen, and sulfur atoms as the central donor (**5**−**8**, Figure 2) were synthesized. These can form two six-membered chelate rings on coordination to a metal center. In order to introduce a central nitrogen donor, the bis(imino)carbazole **5** was synthesized as depicted in eqs 1−3 (Scheme 2). The starting material for the reaction sequence, 3,6-dibromocarbazole, is commercially available but can also be prepared in quantitative yield by bromination of carbazole with *N*-bromosuccinimide (NBS).[35] Trimethylsilane was chosen as the N−H protective group during the dilithiation of 3,6-dibromocarbazole since it is readily removed during the acidic workup. After quenching the dilithiated intermediate with methyliodide, 3,6-dimethylcarbazole can be obtained in good yield as a white amorphous solid (eq 1). The spectroscopic data and melting point (218−219 °C) correspond well with previously published values.[36,37] 1,8-Dibrominated carbazole can be synthesized by bromination

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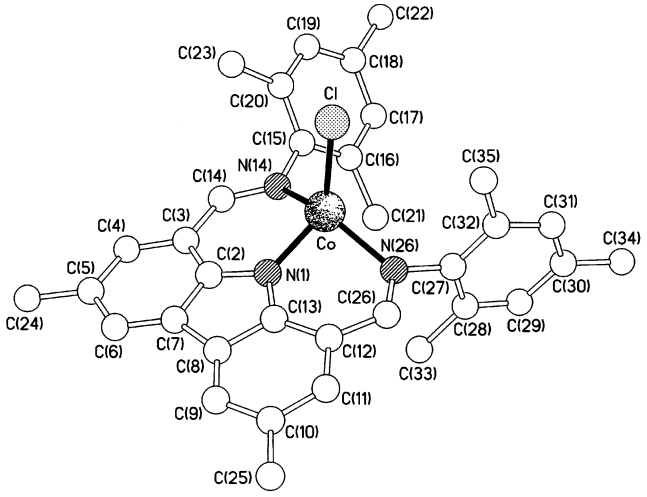

Figure 4. Molecular structure of [(**5**)CoCl]. Selected bond lengths (Å) and angles (deg): Co−Cl 2.226(2), Co−N(1) 1.912(4), Co−N(14) 2.067(4), Co−N(26) 2.073(4), C(14)−N(14) 1.309(6), C(26)−N(26) 1.295(6), N(1)−Co−N(14) 90.7(2), N(1)−Co−N(26) 89.3(2), N(14)−Co−N(26) 140.7(2), N(1)−Co−Cl 124.96(14), N(14)−Co−Cl 100.44(13), N(26)−Co−Cl 111.47(12).

of 3,6-dimethylcarbazole with NBS with exclusion of light in near quantitative yield (eq 2). Formylation of the 1,8-dibromocarbazole can be achieved by quenching the 1,8-dilithiated intermediate with excess anhydrous DMF. The carbazole N−H proton is again protected with a trimethylsilyl group prior to lithiation, and 1,8-diformyl-3,6-dimethylcarbazole is obtained in quantitative yield. Schiff-base condensation of the dialdehyde with 2,4,6-trimethylaniline in chloroform leads to the formation of the bis(imino)carbazole **5** in good yield (eq 3).

Deprotonation of the ligand can be achieved with NaH in THF solution at 65 °C. The resulting sodium salt fluoresces bright green in THF solution, but the fluorescence disappears upon complexation to transition metals; this optical behavior is a useful indicator for successful coordination of the ligand to a transition metal center. After addition of a THF solution of the sodium salt of **5** to $FeCl_2(THF)_{1.5}$ or $CoCl_2$, the green fluorescence disappears completely over 1−2 h. The isolated iron and cobalt complexes [(**5**)FeCl] and [(**5**)CoCl] have been analyzed by FAB-MS, ^{1}H NMR and IR spectroscopy, magnetic moment measurements, and elemental analysis. As expected, these complexes are paramagnetic, with magnetic moments corresponding to high spin configurations. Both complexes show distinct resonances in the ^{1}H NMR spectrum comparable to the ones observed for bis(imino)pyridine iron(II) and cobalt(II) complexes.[9] Crystals suitable for X-ray analysis of cobalt complex [(**5**)CoCl] could be obtained from a concentrated toluene solution. The crystal structure is shown in Figure 4. The geometry around the cobalt center is severely distorted and flattened tetrahedral, the N(1)−Co−Cl and N(14)−Co−C(26) angles, for example, being 124.96(14)° and 140.7(2)°, respectively. Coordination is, as expected, to all three nitrogen centers, the Co−N bond lengths being unexceptional. The Co−N(1) distance is significantly shorter than those to N(14) and N(26) reflecting the constraints of the tridentate ligand, and the formally negatively charged nature of the central donor atom. The 3,6-dimethylcarbazole moiety has a slightly folded geometry, its two phenyl rings being inclined by ca. 6°; the cobalt atom is displaced by 0.35 Å out of the pyrrole ring plane. One of the mesityl rings [that containing C(27)] is oriented essentially orthogonally (ca. 80°) to its associated $CoNC_2$ plane whereas the other is rotated by only ca. 64° out of plane. The two six-membered chelate rings both have folded geometries with out of plane fold angles about N(1)···N(14) and N(1)···N(26) of 18° and 25°, respectively. Centrosymmetrically related pairs of molecules have their carbazole ring systems in a π-stacking relationship, the centroid··· centroid and mean interplanar separations between their pyrrole rings being 3.85 and 3.35 Å, respectively. There are no interactions involving the mesityl rings, the space between their "jaws" being occupied by the included (disordered) solvent toluene molecule.

Oxygen and sulfur donors in the central part of ligand type IV have been investigated in three types of ligands, the dibenzofuran derivative **6** and the diphenyl ether and thioether ligands **7** and **8** (Figure 2). A nitrogen analogue of these latter ligand types, a bis(imino)diphenylamine ligand and its corresponding iron(III) complex, has been reported previously.[38] The bis(imino)dibenzofuran derivative **6** was synthesized from dibenzofuran dicarboxaldehyde[39] and 2 equiv of the appropriate aniline under standard condensation conditions. Addition of the ligand to an $FeCl_2$ solution in ^{n}BuOH at 80 °C did not result in the formation of a complex. Removal of the solvent left the starting materials unreacted. Reactions in other solvents such as THF and dichloromethane were equally unsuccessful. This result was surprising considering the greater flexibility of this ligand compared to the furan derivative **3** and a recent report of the reaction of a similar bis(oxazoline)dibenzofuran ligand with Ni(II), which did result in the formation of a stable Ni(II) complex.[40] In order to allow even more flexibility in the ligand framework, we also synthesized the diphenyl ether and thioether derivatives **7** and **8**. A bis(oxazoline)diphenylthioether ligand similar to **8** was recently reported,[41] but no metal complexes of either **7** or **8** have been reported. All attempts to form metal complexes of **7** and **8** with $FeCl_2$ or $CoCl_2$ were unsuccessful.

Polymerization Results

The catalytic activity of the iron(II) and cobalt(II) complexes of the ligands **1a**−**d** and **5** for the polymerization of ethylene has been evaluated under two sets of conditions. Low-pressure Schlenk line tests were performed using 100 equiv of cocatalyst MAO, and high-pressure tests (4 bar)

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Table 1. Results of Ethylene Polymerization Runs with Iron and Cobalt Precatalysts

run	complex	MAO,[b] equiv	P (bar)	T (°C)	yield (g)	activity (g/mmol·bar·h)	α	M_n	M_w	M_{pk} peak1/peak2	PDI	sat. ends/ 1000C	vinyl ends/ 1000C	sat. ends/ vinyl ends
1[c]	[(**1a**)$FeCl_2$]	100	1	25	23.4	2340		1300	14 000	900	10.3	11.60	8.90	1.30
2	[(**1b**)$FeCl_2$]	100	1	25	21.80	2180		1200	16 000	900	12.9	12.76	10.44	1.22
3[c]	[(**1c**)$FeCl_2$]	100	1	25	4.65	930		3800	130 000	2000/427 000	34.5	6.38	1.45	4.40
4	[(**1d**)$FeCl_2$]	100	1	25	0.13[d] 4.78[e]	491	0.69							
5	[(**1a**)$FeCl_2$]	1000	4	50	7.10	3550		1600	50 000	1000	31.4	5.47	5.35	1.02
6	[(**1b**)$FeCl_2$]	1000	4	50	7.70	3850		1200	39 000	1000	33.1	10.54	7.55	1.40
7	[(**1b**)$FeCl_2$]	1000	4	30	12.40	6200		1400	66 000	900	48.1	9.6	7.2	1.3
8	[(**1b**)$FeCl_2$]	1000	4	15	10.50	5250		1000	80 000	700/89 000	70.5	10.7	9.2	1.2
9	[(**9**)$FeCl_2$]	1000	4	50	19.2	9600		2900	38 000	3300	13.1	6.96	2.97	2.34
10	[(**1c**)$FeCl_2$]	1000	4	50	7.30	490		5400	141 000	2400/126 000	26.5	1.60	1.08	1.48
11	[(**1c**)$FeCl_2$]	1000	4	30	22.20	1480		15000	182 000	153 000	12.5	1.08	0.20	5.40
12[c]	[(**1b**)$CoCl_2$]	100	1	25	3.60	720		9900	26 000	20 000	2.7	1.54	1.20	1.28
13	[(**1b**)$CoCl_2$]	1000	10	50	8.30	1340		12000	30 000	22 000	2.5	1.86	1.50	1.24
14	[(**9**)$CoCl_2$]	100	1	25	11.44	1140		16000	40 000	27 000	2.6	1.1	1.0	1.1
15	[(**1d**)$CoCl_2$]	100	1	25	0.07[d] 2.35[e]	242	0.83							-

[a] General conditions, Schlenk tests at 1 bar: 100 mL of toluene, 100 equiv of MAO, 10 μmol of precatalyst, 1 h run. General conditions, reactor test: isobutane solvent, 0.5 μmol of Fe catalyst or 0.6 μmol of Co catalyst, 1000 equiv of MAO, 1 h run. [b] Cocatalyst. [c] 30 min run. [d] Solid. [e] Liquid.

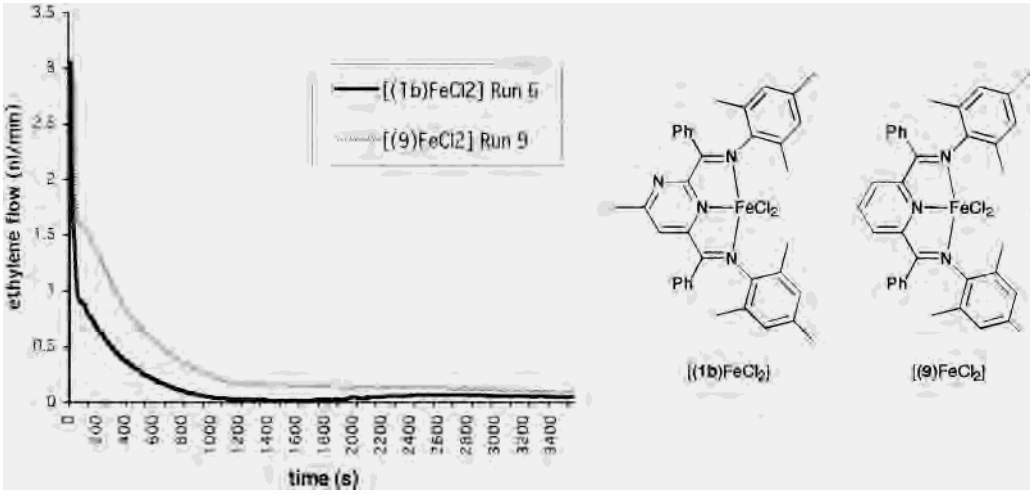

Figure 5. Ethylene uptake versus time for complexes [(**1b**)$FeCl_2$] and [(**9**)$FeCl_2$].

were carried out in a 1 L stainless steel reactor using 1000 equiv MAO. The results are summarized in Table 1.

The first set of experiments (runs 1−4) shows the different behavior of the bis(imino)pyrimidine iron catalysts under Schlenk line conditions. The activities and polymer properties of the 2,6-dimethyl and the 2,4,6-trimethyl derivatives ([(**1a**)-$FeCl_2$] and [(**1b**)$FeCl_2$], respectively) are comparable, whereas the 2,6-diisopropyl derivative [(**1c**)$FeCl_2$] shows a lower activity and yields higher molecular weight polymer, thereby following the same trend as seen for bis(imino)pyridine iron catalysts.[9] This trend is also observed at higher pressure (4 bar) as can be seen from runs 5, 6, and 10. For comparison, we have also prepared [(**9**)$FeCl_2$], the bis(imino)pyridine analogue of precatalyst [(**1b**)$FeCl_2$] (see Figure 5 and run 9). Under the same conditions, the activity of this pyridine derivative is almost three times higher compared to the pyrimidine derivative [(**1b**)$FeCl_2$] (runs 6 and 9). This lower activity is believed to be due to the catalyst decomposing under the conditions employed, as can be seen from the activity profiles for runs 6 and 9 (ethylene uptake over time), shown in Figure 5. The initial rapid ethylene consumption decays much faster in the case of [(**1b**)$FeCl_2$] compared to [(**9**)$FeCl_2$]. A similar trend is seen for the analogous cobalt complexes [(**1b**)$CoCl_2$] and [(**9**)$CoCl_2$] (runs 12 and 14) where the activity of the latter is almost double compared to the pyrimidine derivative. It is also clear from runs 6 versus 7, and 10 versus 11, that reducing the temperature leads to higher activities. We believe that this reduced stability is a result of the weaker donor strength of pyrimidine versus pyridine ligands. Activation of carbazolide complexes [(**5**)FeCl] and [(**5**)CoCl] with MAO did not result in any measurable ethylene polymerization activity under the above Schlenk line conditions. In the case of bis(imino)carbazolide complexes, neutral, rather than cationic, active species would be expected which may lead to a much lower activity. It is also possible that the extra "reach" of the imine donor arms in **5** leads to greater steric hindrance at the potential active site.

The polymer data show that the iron catalysts afford products with a bimodal distribution, the lower molecular weight fraction arising from chain transfer to aluminum. By contrast, the cobalt products show a unimodal product with

a low polydispersity (M_w/M_n). This behavior is similar to that observed for the bis(imino)pyridine analogues.[9] End-group analyses provide further confirmation of the similarities between the pyridine and pyrimidine systems. For example, more saturated end-groups than vinyl end-groups are found in the case of iron due to chain transfer to aluminum, whereas an approximate 1:1 ratio is observed in the case of cobalt, indicating β-H transfer is the sole chain termination pathway.[9] Reducing the steric bulk on the imine aryl substituents as in the 2-methylphenyl derivatives [(**1d**)$FeCl_2$] and [(**1d**)$CoCl_2$] results in the formation of low molecular weight oligomers, consistent with observations made for bis(imino)pyridine oligomerization systems.[10]

In conclusion, we have prepared three types of variation on the central pyridine donor core in bis(imino)pyridine iron and cobalt catalyst systems. The coordination behavior of these new ligands with respect to iron(II) and cobalt(II) has been investigated along with the polymerization behavior of the resulting metal catalysts. In the case of six-membered N-heterocyclic cores, only pyrimidine-based ligands afforded complexes with $FeCl_2$ or $CoCl_2$. Ligands containing triazine or five-membered heterocyclic cores (furan or thiophene) did not react with $FeCl_2$ or $CoCl_2$, which has been attributed to (i) the weaker donor strength of the central donor in these ligands and (ii) in the case of the five-membered heterocycles (furan and thiophene) the larger bite angle. The addition of an extra carbon atom to each chelating arm was investigated with a view to decreasing the bite angle and increasing the overall donor strength of the ligand. However, only in the case of an anionic nitrogen atom (carbazolide) as the central donor were stable Fe(II) and Co(II) complexes obtained, whereas sulfur- and oxygen-based ligands did not yield isolable complexes. Pyrimidine-based complexes afforded active polymerization catalysts upon activation with MAO, although the activity was substantially reduced compared to the pyridine analogues, probably due to reduced catalyst stability under polymerization conditions.

Experimental Section

General. All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glovebox. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Imperial College, Medac Ltd., or SACS at the University of North London. NMR spectra were recorded on a Bruker spectrometer at 250 MHz (^{1}H) and 62.9 MHz (^{13}C) at 293 K; chemical shifts are referenced to the residual protio impurity of the deuterated solvent. Mass spectra were obtained using either fast atom bombardment (FAB), electron impact (EI), or chemical ionization (CI). IR spectra were recorded on a Perkin-Elmer Spectrum GX1 system. In some cases, thin sample films were prepared by evaporating CH_2Cl_2 solutions of the ligands or complexes on NaCl plates. Magnetic susceptibility studies were performed using an Evans balance[42] or the Evans NMR method (solvent, CH_2Cl_2; reference, cyclohexane).[43] Polymer NMR and GPC analyses were performed at BP Chemicals Ltd. ^{1}H NMR analysis was carried out in *p*-xylene-d_{10} at 110 °C and ^{13}C NMR analysis in $C_2D_2Cl_4$/1,2,4-trichlorobenzene at 130 °C using a JEOL GSX270 spectrometer. GPC analyses were carried out on a Waters 150CV (columns supplied by Shodex (807, 806 and 804)) using polyethylene standard reference material NBS1484a.

Compounds 6-methyl-2,4-dichloropyrimidine, trimethyltin chloride, benzoylformyl acid, tetraethyl orthosilicate, 2,5-thiophenedicarboxaldehyde, all anilines, cobalt(II) chloride, and iron(II) chloride were purchased from Aldrich Chemical Co. Benzoylformyl chloride was prepared according to a literature procedure,[15] distilled, and degassed prior to use. 6-Methyl-2,4-bis(trimethylstannyl)pyrimidine and 2,4-dibenzoyl-6-methylpyrimidine were synthesized following an established procedure.[16] 2,4-Bis(1-phenyl-2-morpholinoethen-1-yl)-6-benzyl-1,3,5-triazine,[23] 2,4,6-tris(dimorpholinomethyl)-1,3,5-triazine,[44] 3,6-dibromo-9*H*-carbazole,[35] 2,5-furandicarboxaldehyde,[27] 4,6-dibenzofuran-dicarboxaldehyde,[39] bis(*o*-formylphenyl)ether[45] and $FeCl_2(THF)_{1.5}$[46] were prepared.

2,4-Bis[(2,6-dimethylphenylimino)benzyl]-6-methylpyrimidine (1a). 2,4-Dibenzoyl-6-methylpyrimidine (262 mg, 0.86 mmol) and 2,6-dimethylaniline (230 mg, 1.90 mmol) were combined and treated with one drop of concentrated H_2SO_4. $Si(OEt)_4$ (398 mg, 1.90 mmol) was added and the mixture placed in a flask equipped with a still head. The solution was heated at 140 °C for 4 h. The distillate (EtOH) was then discarded and the residue dissolved in dichloromethane and washed with a saturated solution of $NaHCO_3$, followed by water. The dichloromethane solution was dried ($MgSO_4$), and the volatile components were removed under reduced pressure. The crude product was triturated with cold ethanol and further purified by flash chromatography on silica gel (ethyl acetate/petroleum ether 2:8, $R_f = 0.55$) and by recrystallization from Et_2O to yield yellow prisms (275 mg, 62%). Mp 129 °C. ^{1}H NMR (250 MHz, C_6D_6, rt): δ (ppm) minor isomer 1.95 (s, 6H, *o*-CH_3), 2.03 (s, 3H, CH_3), 2.18 (s, 6H; *o*-CH_3), 6.81−8.05 (m broad, 17H, Ar−*H*); major isomer 1.62 (s, 3H, CH_3), 2.08 (s, 6H, *o*-CH_3), 2.33 (s, 6H, *o*-CH_3), 6.19 (s, 1H, Pyr−*H*), 6.81−8.05 (m broad, 16H, Ar−*H*). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 18.20, 18.35, 18.50, 24.05, 24.23, 162.46, 162.98, 163.37, 163.61, 164.07, 164.18, 167.01, 167.69. IR (KBr): 1635 (ν(C═N)), 1577 cm^{-1}. MS (EI) *m*/*z*: 508 (M^+, 100%), 208 (80%). Anal. Calcd for $C_{35}H_{32}N_4$: C, 82.64; H, 6.34; N, 11.01. Found: C, 82.71; H, 6.40; N, 11.08.

2,4-Bis[(2,4,6-trimethylphenylimino)benzyl]-6-methylpyrimidine (1b). The same procedure as for **1a**, using 2,4,6-trimethylaniline and 2,4-dibenzoyl-6-methylpyrimidine, yielded compound **1b** as yellow needles. Yield: 73%. Mp 200−202 °C. ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) minor isomer 1.87 (s, 6H, *o*-CH_3), 1.91 (s, 6H, *o*-CH_3), 2.19 (s, 3H, *p*-CH_3), 2.20 (s, 3H, *p*-CH_3), 2.58 (s, 3H, CH_3), 6.58−7.78 (m, 15H, Ar−*H*); major isomer 2.01 (s, 6H, *o*-CH_3), 2.03 (s, 6H, *o*-CH_3), 2.22 (s, 6H, *p*-CH_3), 2.30 (s, 3H, CH_3), 6.58−7.78 (m, 15H, Ar−*H*). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 17.59, 18.16, 18.33, 18.51, 18.48, 18.51, 20.37, 20.73, 20.79, 20.83, 24.19, 24.29, 24.53, 24.66, 162.67, 163.54, 163.78, 163.45, 164.45, 164.59, 166.97, 167.62. IR (KBr): 1633 (ν(C═N)), 1577 cm^{-1}. MS (EI) *m*/*z*: 536 (M^+, 100%), 222 (46%). Anal. Calcd for $C_{37}H_{36}N_4$: C, 82.80; H, 6.76; N, 10.44. Found: C, 82.91; H, 6.73; N, 10.45.

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2,4-Bis[(2,6-diisopropylphenylimino)benzyl]-6-methylpyrimidine (1c). The same procedure as for **1a**, using 2,6-diisopropylaniline and 2,4-dibenzoyl-6-methylpyrimidine, gave **1c** as yellow needles. Yield: 82%. ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) minor isomer 0.86 (d, 3H, J = 6.5 Hz, CHMe_2), 0.91 (d, 3H, J = 6.5 Hz, CHMe_2), 2.34 (s, 3H, CH_3), 2.73 (septet, 1H, J = 6.5 Hz, CHMe$_2$), 3.04 (septet, 1H, J = 6.5 Hz, CHMe$_2$), 6.85−7.51 (broad, 13H), 7.69 (s, 1H, Pyr−H), 7.89 (m, 2H, Ar−H); major isomer 0.98 (d, 3H, J = 6.7 Hz, CHMe_2), 1.00 (d, 3H, J = 6.7 Hz, CHMe_2), 1.09 (d, 3H, J = 6.7 Hz, CHMe_2), 1.10 (d, 3H, J = 6.7 Hz, CHMe_2), 2.54 (s, 3H, CH_3 pyr), 2.95 (septet, 1H, J = 6.7 Hz, CHMe$_2$), 3.13 (septet, 1H, J = 6.7 Hz, CHMe$_2$), 6.68 (s, 1H, Pyr−H), 6.85−7.51 (broad m, 16H, Ar−H). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 21.03, 21.29, 21.74, 22.11, 23.37, 23.47, 23.57, 23.87, 24.15, 24.33, 28.28, 28.52, 162.47, 162.54, 162.58, 163.16, 164.25, 164.35, 166.45, 167.67. IR (KBr): 1626 (ν(C═N)), 1578 cm^{-1}. MS (EI) m/z: 620 (100%, M$^+$), 359 (48%), 264 (72%). Anal. Calcd for $C_{43}H_{48}N_4 \cdot H_2O$: C, 80.84; H, 7.89; N, 8.77. Found: C, 80.16; H, 7.82; N, 9.13.

2,4-Bis[(2-methylphenylimino)benzyl]-6-methylpyrimidine (1d). The same procedure as for **1a**, using 2-methylaniline and 2,4-dibenzoyl-6-methylpyrimidine, gave **1d** as yellow needles. Yield: 72%. ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) minor isomer 2.07 (s, 3H, o-CH_3), 2.17 (s, 3H, o-CH_3), 2.33 (s, 3H, CH_3), 6.30−7.80 (m broad, 18 Ar−H), 7.95 (s, 1H, Pyr−H); major isomer 2.21 (s, 3H, o-CH_3), 2.23 (s, 3H, o-CH_3), 2.33 (s, 3H, CH_3), 6.30−7.80 (broad, 18 Ar−H), 6.62 (s, 1H, Pyr−H). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 18.12, 18.26, 24.26, 24.46, 162.54, 163.04, 163.47, 163.70, 163.90, 167.33, 167.64. IR (KBr): 1626 (ν(C═N)), 1576 cm^{-1}. MS (EI) m/z: 480 (67%, M$^+$), 194 (62%), 106 (57%), 91 (100%). Anal. Calcd for $C_{33}H_{28}N_4$: C, 82.47; H, 5.87; N, 11.66. Found: C, 82.40; H, 5.87; N, 11.64.

2,6-Bis[(2,4,6-trimethylphenylimino)benzyl]-pyridine (9). The same procedure as for **1a**, using 2,4,6-trimethylaniline and 2,6-dibenzoylpyridine gave a yellow powder. A sample was purified by flash chromatography on silica gel (ethyl acetate/hexane 1:9, R_f = 0.45) to afford analytically pure material. Yield: 2.3 g (88%). Mp 188−190 °C. ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) 1.98 (s, 12H, CH_3), 2.21 (s, 6H, CH_3), 6.5−7.5 (ArH and pyr$H$). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 18.47, 20.65, 145.64, 146.13, 154.18, 155.19, 155.78, 157.12, 165.21, 165.89, 166.10, 166.58. IR (KBr): 1627 (ν(C═N)) cm^{-1}. Anal. Calcd for $C_{37}H_{35}N_3$: C, 85.18; H, 6.76; N, 8.05. Found: C, 85.26; H, 6.83; N, 7.98.

2,6-Dibenzoyl-4-benzyl-1,3,5-triazine. To a solution of 2,4-Bis-(1-phenyl-2-morpholinoethen-1-yl)-6-benzyl-1,3,5-triazine (2.73 g, 5 mmol) in CCl_4/CH_3CN (20 mL/20 mL) was first added an aqueous solution of sodium periodate (8.94 g, 42 mmol in 30 mL of water) and then 250 mg of $RuCl_3 \cdot (H_2O)_x$ in one portion. The black mixture was vigorously stirred for 1 h at room temperature, diluted with water, transferred to a separating funnel, and extracted twice with dichloromethane. The combined organic phases were dried over magnesium sulfate and filtered, and the solvent was evaporated in vacuo. The crude product was purified by flash chromatography on silica gel using ethyl acetate/petroleum ether 2/8 as eluent to give a yellow crystalline material. Yield: 0.64 g (34%). Mp 118 °C. ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) 4.43 (s, 2H, CH_2), 7.28−7.37 (m, 3H, Ar−H), 7.42−7.51 (m, 6H, Ar−H), 7.61−7.68 (m, 2H, Ar−H), 7.97−8.00 (m, 4H, Ar−H). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 45.54 (CH_2), 127.34, 128.62, 128.75, 129.44, 130.80, 133.51, 134.54, 135.49, 170.51 (NCN), 180.10 (NCCO), 188.99 (CO). IR (KBr): 1679 (ν(C═O)) cm^{-1}. MS (CI) m/z: 397 (MNH_4^+, 100%), 380 (MH$^+$, 53%). Anal. Calcd for $C_{24}H_{17}N_3O_2$: C, 75.98; H, 4.52; N, 11.07. Found: C, 75.86; H, 4.61; N, 11.15.

2,6-Bis[(2,4,6-trimethylphenylimino)benzyl]-4-benzyl-1,3,5-triazine (2a). In a Schlenk tube filled with nitrogen, a solution of titanium tetrachloride (4.0 mL, 4 mmol, 1 M in toluene) was added over 4 h to a mixture of 2,4,6-trimethylaniline (1.66 g, 12.30 mmol) and bis(ketone) **11** in toluene/ether (15 mL/15 mL). Another portion of trimethylaniline (0.5 g, 3.70 mmol) was added after 16 h, followed by a slow addition (4 h) of $TiCl_4$ (2.5 mL, 2.5 mmol, 1 M in toluene). After 48 h, the mixture was diluted with a saturated solution of $NaHCO_3$ (50 mL) and filtered on a Celite layer which was washed copiously with toluene. The organic phase was separated, dried over Na_2SO_4, and evaporated. The purification of the crude product by flash chromatography on silica gel (ethyl acetate/ petroleum ether: 15:85, R_f = 0.40) gave a hygroscopic yellow mousse. Yield 0.27 g (28%.). ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) 1.96 (s, 12H, o-CH_3), 2.22 (s, 6H, p-CH_3), 3.96 (s, 2H, CH_2), 6.58 (s, 4H, Ar−H), 6.93 (m, 2H, Ar−H), 7.22−7.52 (m broad, 13H, Ar−H). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 18.3 (CH_3 ortho), 20.78 (CH_3 para), 45.11 (CH_2), 126.25, 126.77, 127.98, 128.34, 129.01, 131.381, 132.20, 135.10, 136.04, 140.11, 140.93, 145.40, 162.67 (C═N), 171.67 (NCCN), 177.89 (NCN). IR (KBr): 1635 (ν(C═N)), 1523 cm^{-1}. MS EI (m/z): 613 (M$^+$, 100%), 222 (57%). Anal. Calcd for $C_{42}H_{39}N_5$: C, 82.19; H, 6.40; N, 11.41. Found: C, 82.29; H, 6.42; N, 11.50.

2,4,6-Tris[(2,6-diisopropylphenylimino)methyl]-1,3,5-triazine (2b). To a solution of 2,6-diisopropylaniline hydrochloride (2.83 g, 13.2 mmol) in water/ethanol 32 mL/16 mL heated at 60 °C was added in small portions 2,4,6-tris(dimorpholinomethyl)-1,3,5-triazine (1.20 g, 1.88 mmol). The mixture was stirred rapidly for 20 min at this temperature and then cooled to room temperature. Ethanol was removed by rotary evaporation, and the pH of the aqueous phase was adjusted to 13. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated. The crude mixture was purified by column chromatography on deactivated alumina (ethyl acetate/petroleum ether, 5/95) and dried under high vacuum to yield an orange powder. Yield: 0.54 g (45%). Mp 212−213 °C. ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) 1.18 (d, J = 6.8 Hz, 36H, CH(CH_3)$_2$), 2.99 (septet, J = 6.8 Hz, 6H, CH(CH$_3$)$_2$), 7.19 (m, 9H, Ar−H), 8.62 (s, 3H, CHN). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 23.66 (CH_3), 28.01 (CH(CH$_3$)$_2$), 123.2, 125.6, 136.7, 147.7, 160.1 (C═N), 170.1 (NCN). EI mass spectrum (m/z): 642 [(M)$^+$, 100], 187 [(ArN═C)$^+$, 59]. Anal. Calcd for $C_{42}H_{54}N_6$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.53; H, 8.38; N, 12.98. IR (KBr): 1646, 1528 cm^{-1}.

2,5-Bis[(2,6-diisopropylphenylimino)methyl]furan (3). A mixture of furan-2,5-dialdehyde (0.28 g, 2.26 mmol) and 2,6-diisopropylaniline (0.8 g, 2 equiv) were dissolved in 20 mL of dichloromethane. After the addition of a drop of formic acid and two spatulas of $MgSO_4$, the mixture was stirred at room temperature overnight. After filtration, the solvent was evaporated, and the crude product was recrystallized from hot petroleum ether. Yield: 0.78 g (78%). ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) 1.19 (d, 24H, CH_3), 3.01 (sept, 4H,CH(CH$_3$)$_2$), 7.18 (m, 6H, Ar−H), 7.22 (s, 2H, CH−CH), 8.14 (s, 2H, N═CH). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 23.63 (CH_3), 27.90 (CH(CH$_3$)$_2$), 115.54 (C═CH) 123.11, 124.66, 137.63, 148.48 (ArC), 150.77 (C═N), 153.81 (ArC). IR (KBr): 1635 (ν(C═N)) cm^{-1}. MS (EI) m/z: 442 (M$^+$, 100%), 427 ([M − CH$_3$]$^+$, 20%), 254 ([M−ArN═CH]$^+$, 43%)], 188 [(ArN═CH)$^+$, 45]. Anal. Calcd for $C_{30}H_{38}N_2O$: C, 81.40; H, 8.65; N, 6.33. Found: C, 81.34; H, 8.73; N, 6.26%.

2,5-Bis[(2,6-diisopropylphenylimino)methyl]thiophene (4). A mixture of thiophene dialdehyde (0.25 g; 1.78 mmol) and 2,6-diisopropylaniline was dissolved in 20 mL of dichloromethane. After the addition of a drop of formic acid and two spatulas of $MgSO_4$, the mixture was stirred at room temperature overnight. After filtration, the solvent was evaporated, and the crude product was recrystallized from hot petroleum ether. Yield: 0.63 g (77%). ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) 1.22 (d, 24H, CH_3), 3.03 (sept, 4H,CH(CH_3)$_2$), 7.17 (m, 6H, Ar—H), 7.50 (s, 2H, CH—CH), 8.32 (s, 2H, N═CH). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 23.51 (*C*H$_3$), 28.05 (*C*H(CH$_3$)$_2$), 123.04, 124.51, 131.42, 137.71, 145.94, 148.42, 154.83 (Ar*C*). IR (KBr): 1623 (ν(C═N)) cm^{-1}. MS (EI) *m*/*z*: 458 (M$^+$, 100%), 443 ([M − CH$_3$]$^+$, 20%). Anal. Calcd for $C_{30}H_{38}N_2S$: C, 78.55; H, 8.35; N, 6.11. Found: C, 78.48; H, 8.31; N, 6.04%.

3,6-Dimethyl-9*H*-carbazole. 3,6-Dibromo-9*H*-carbazole (5.3 g, 16.3 mmol) was dissolved in 200 mL of diethyl ether, and 7.0 mL (17.5 mmol) of *n*-BuLi (2.5 M in hexane) was added dropwise at 0 °C. After stirring for 1 h at this temperature, 2.2 mL (17.3 mmol) of trimethylsilyl chloride was added, and the reaction mixture was allowed to warm to room temperature. The suspension briefly became a clear solution followed by the formation of a white precipitate. After stirring at rt for 1 h, the suspension was cooled to −78 °C, and 45 mL (67.5 mmol) of *t*-BuLi (1.5 M in pentane) was added. The thick, white suspension was then stirred at 0 °C for 3 h after which it was cooled to −78 °C. At this temperature, 5.0 mL (82 mmol) of methyliodide was added, and the reaction mixture was allowed to warm to rt overnight. The reaction mixture was hydrolyzed by the addition of 50 mL of 1 M aqueous HCl. The layers were separated, and the organic phase was washed with 2 × 50 mL of 1 M aqueous HCl solution and 50 mL of H_2O, dried over $MgSO_4$, and filtered, and all volatiles were removed on a rotary evaporator. The crude product was recrystallized from hot hexane/ethanol to afford an off-white, amorphous solid. Yield: 3.0 g (94%). Mp 218−219 °C. R_f (SiO_2, hexane/EtOAc 10:1) 0.19. ^{1}H NMR (250 MHz, C_6D_6, rt): δ (ppm) 2.44 (s, 6H, CH_3), 6.46 (br, 1H, NH), 7.00 (d, 2H, ^3J(HH) = 8.2 Hz, Ar—H), 7.21 (d, 2H, ^3J(HH) = 8.2 Hz, Ar—H), 7.81 (s, 2H, Ar—H). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ 21.4 (*C*H$_3$), 110.2 (Ar—*C*), 120.2 (Ar—*C*), 123.38 (Ar—*C*), 127.0 (Ar—*C*), 128.5 (Ar—*C*), 138.0 (Ar—*C*). MS (EI) *m*/*z*: 195 (M$^+$, 100%). The spectroscopic data are consistent with previously published values for 3,6-dimethyl-9*H*-carbazole, obtained via different synthetic routes.[36,37]

1,8-Dibromo-3,6-dimethyl-9*H*-carbazole. 3,6-Dimethyl-9*H*-carbazole (4.78 g, 24.5 mmol) was dissolved in 400 mL of dichloromethane. After addition of 50g of silica gel, the reaction flask was immersed in an ice bath. *N*-Bromosuccinimide, 8.68 g (49.0 mmol), dissolved in 400 mL of dichloromethane, was added over a period of 2 h at 0 °C under the exclusion of light. After the addition was completed, the reaction mixture was stirred at rt for another 30 min. The solution was filtered, and the filtrate was washed with 3 × 50 mL of 1 M aqueous NaOH and 1 × 50 mL of 3 M aqueous NaCl solutions, dried over $MgSO_4$, and filtered. The solvent was removed on a rotary evaporator to afford an off-white solid. Yield: 8.25 g (95%). Mp 142−143 °C. R_f (SiO_2, hexane/EtOAc 10:1) 0.53. ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) 2.48 (s, 6H, CH_3), 7.41 (s, 2H, Ar—H), 7.71 (s, 2H, Ar—H), 8.10 (br, 1H, NH). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 21.2 (*C*H$_3$), 103.9 (Ar—*C*), 119.7 (Ar—*C*), 124.7 (Ar—*C*), 129.7 (Ar—*C*), 130.8 (Ar—*C*), 136.9 (Ar—*C*). MS (EI) *m*/*z*: 353 (M$^+$), 272 ([M − Br]$^+$). Anal. Calcd for $C_{14}H_{11}Br_2N$: C, 47.63; H, 3.14; N, 3.97. Found: C, 47.83; H, 3.23; N, 3.67%.

1,8-Diformyl-3,6-dimethyl-9*H*-carbazole. *n*-BuLi [3.0 mL (7.5 mmol), 2.5 M in hexane] was added to a solution of 2.48 g (7.0 mmol) of 1,8-dibromo-3,6-dimethyl-9*H*-carbazole in 100 mL of diethyl ether at 0 °C. After stirring for 1 h, 0.98 mL (7.7 mmol) of trimethylsilyl chloride was added, and the reaction mixture was allowed to warm to ambient temperature. The suspension briefly became a clear solution followed by the formation of a white precipitate. After stirring for 1 h at rt, the suspension was cooled to −78 °C, and 20 mL (30 mmol) of *t*-BuLi (1.5 M in pentane) was added. After completed addition, the reaction mixture was stirred at 0 °C for 3 h. At −78 °C, 3.8 mL (38.7 mmol) of anhydrous dimethylformamide was added, and the reaction mixture was allowed to warm to room temperature overnight. Hydrolysis was performed at 0 °C by the addition of 50 mL of 1 M aqueous HCl. The organic phase was washed with 2 × 50 mL of 1 M aqueous NaOH and 2 × 50 mL of 3 M aqueous NaCl solutions, dried over $MgSO_4$, and filtered, and the solvent was removed on a rotary evaporator to afford the product as a yellow solid. Yield: 1.73 g (98%). Mp 241−242 °C. R_f (SiO_2, hexane/EtOAc 5:1) 0.13. ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) 2.60 (s, 6H, CH_3), 7.68 (s, 2H, Ar—H), 8.11 (s, 2H, Ar—H), 10.17 (s, 2H, O═CH), 11.44 (br, 1H, NH). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 21.2 (*C*H$_3$), 120.1 (Ar—*C*), 123.4 (Ar—*C*), 127.1 (Ar—*C*), 129.3 (Ar—*C*), 132.8 (Ar—*C*), 136.9 (Ar—*C*), 192.7 (O═*C*H). IR (thin film): 3449 (m, ν(N—H)), 3013 (w), 2956 (w), 2916 (w), 2838 (w), 2800 (w), 2737 (w), 1675 (s, ν(C═O)), 1622 (m), 1593 (s) 1487 (m), 1316 (m), 1218 (m), 1156 (w), 1114 (m), 1071 (m), 997 (w), 967 (m), 860 (m), 825 (w), 779 (w), 719 (m), 685 (w), 617 (m) cm^{-1}. MS (EI) *m*/*z*: 251 (M$^+$), 222 ([M − CH═O]$^+$). Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.51; H, 5.12; N, 5.40%.

1,8-Bis[(2,4,6-trimethylphenylimino)methyl]-3,6-dimethyl-9*H*-carbazole (5). 1,8-Diformyl-3,6-dimethyl-9*H*-carbazole [470 mg (1.87 mmol)] and 530 μL (3.77 mmol) of 2,4,6-trimethylaniline were dissolved in 100 mL of chloroform. After addition of 5 drops of glacial acetic acid and 4 Å molecular sieves, the reaction mixture was refluxed for 3 days and then filtered hot. All volatiles were removed on a rotary evaporator to afford a yellow solid. The crude product was purified by crystallization from hot ethanol/hexane. Yield: 640 mg (70%). Mp 226−227 °C. ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) 2.09 (s, 12H, *o*-CH_3), 2.25 (s, 6H, *p*-CH_3), 2.58 (s, 6H, CH_3), 6.82 (s, 4H, Ph—H_m), 7.39 (s, 2H, Ar—H), 8.03 (s, 2H, Ar—H), 8.41 (s, 2H, N═CH), 12.27 (br, 1H, NH). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 18.3 (*o*-*C*H$_3$), 20.7 (*p*-*C*H$_3$), 21.3 (*C*H$_3$), 119.2 (Ar—*C*), 123.4 (Ar—*C*), 123.4 (Ar—*C*), 127.6 (Ar—*C*), 128.2 (Ar—*C*), 128.7 (Ar—*C*), 130.8 (Ar—*C*), 132.8 (Ar—*C*), 136.5 (Ar—*C*), 149.1 (Ar—*C*), 163.5 (N═*C*H). IR (thin film): 3385 (m, ν(N—H)), 3006 (w), 2970 (w), 2946 (m), 2916 (m), 2860 (w), 1638 (m), 1612 (s), 1589 (s), 1480 (s), 1444 (m), 1380 (w), 1316 (s), 1221 (s), 1203 (s), 1108 (w), 1080 (w), 978 (m), 855 (s), 739 (w), 674 (w), 661 (w) cm^{-1}. EI mass spectrum *m*/*z*: 485 (M$^+$), 470 ([M − CH$_3$]$^+$). Anal. Calcd for $C_{34}H_{35}N_3$: C, 84.08; H, 7.26; N, 8.65. Found: C, 84.16; H, 7.17; N, 8.77%.

4,6-Bis[(2,4,6-trimethylphenylimino)methyl]dibenzofuran (6a). 4,6-Dibenzofuran-dicarbaldehyde (448 mg, 2 mmol) and 2,4,6-trimethylaniline (0.57 mL, 4 mmol) were dissolved in 10 mL of ethanol, to which was added 1 drop of glacial acetic acid and 4 Å molecular sieves. The mixture was refluxed overnight. The yellow precipitate was filtered, washed with cold ethanol, and dried in vacuo. Yield: 0.83 g (90%). ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) 8.87 (s, 2H, CH═N), 8.32 (d, 2H, J = 7.7 Hz, ArH), 8.12 (d, 2H, J = 7.7 Hz, ArH), 7.52 (t, 2H, J = 7.7 Hz, ArH), 6.90 (s, 4H, ArH_m), 2.29 (s, 6H, ArMe_p), 2.16 (s, 12H, ArMe_o). ^{13}C NMR

(63 MHz, $CDCl_3$, rt): δ (ppm) 156.92 (*C*H═N), 155.74, 148.93, 133.21, 128.77, 126.99, 124.94, 124.59, 123.53, 123.42, 120.94 (Ar*C*), 20.73 (*p*-*C*H$_3$), 18.27 (*o*-*C*H$_3$). MS (EI) *m*/*z*: 459 ([M]$^+$, 40%).

4,6-Bis[(2,6-diisopropylphenylimino)methyl]dibenzofuran (6b). 4,6-Dibenzofuran-dicarbaldehyde (448 mg, 2 mmol) and 2,6-diisopropylaniline (0.75 mL, 4 mmol) were dissolved in a mixture of 5 mL of ethanol and 5 mL of 2-propanol, to which was added 1 drop of glacial acetic acid and 4 Å molecular sieves. The mixture was refluxed overnight. The yellow precipitate was filtered, washed with cold ethanol, and dried in vacuo. Yield: 0.94 g (87%). ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) 8.82 (s, 2H, C*H*═N), 8.32 (d, 2H, J = 7.7 Hz, Ar*H*), 8.15 (d, 2H, J = 7.7 Hz, Ar*H*), 7.54 (t, 2H, J = 7.7 Hz, Ar*H*), 7.26−7.06 (m, 6H, Ar*H*), 2.99 (sept, 4H, J = 6.8 Hz, C*H*Me$_2$), 1.15 (d, 24H, J = 6.8 Hz, C*H*$_3$). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 156.10 (*C*H═N), 149.50, 137.47, 125.02, 124.31, 123.62, 123.49, 123.00, 120.82 (Ar*C*), 27.94 (*C*H(CH$_3$)$_2$), 23.46 (CH(*C*H$_3$)$_2$). MS (EI) *m*/*z*: 543 ([M]$^+$, 50%).

Bis[*o*-((2,6-diisopropylphenylimino)methyl)phenyl]ether (7). Standard condensation of bis(*o*-formylphenyl)ether with 2 equiv of 2,6-diisopropylaniline in ethanol afforded the product in 95% yield. ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) 8.60 (s, 2H, C*H*═N), 8.31 (dd, 2H, J = 1.6, 7.7 Hz, Ar*H*), 7.46 (m, 2H, Ar*H*), 7.29 (m, 2H, Ar*H*), 7.14−7.07 (m, 6H, Ar*H*), 6.87 (d, 2H, J = 7.4 Hz, Ar*H*), 2.88 (sept, 4H, J = 6.8 Hz, C*H*Me$_2$), 1.06 (d, 24H, J = 6.8 Hz, C*H*$_3$). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 157.29 (*C*H═N), 157.08, 149.44, 137.52, 132.79, 127.97, 127.19, 124.35, 124.15, 122.95, 118.71 (Ar*C*), 27.89 (*C*H(CH$_3$)$_2$), 23.36 (*C*H$_3$). MS (EI) *m*/*z*: 544 (M$^+$, 65%), 368 ([M − ArN]$^+$, 100%). Anal. Calcd for $C_{38}H_{44}N_2O$: C, 83.78; H, 8.14; N, 5.14. Found: C, 83.79; H, 8.05; N, 5.12%.

Bis(*o*-formylphenyl)thioether. Bis(*o*-formylphenyl)thioether was prepared according to the same procedure as described for bis(*o*-formylphenyl)ether.[45] Yield: 91%. ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) 10.36 (s, 2H, C*H*═O), 7.96 (m, 2H, Ar*H*), 7.47 (m, 4H, Ar*H*), 7.17 (m, 2H, Ar*H*). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 191.52 (*C*H═O), 138.60, 135.03, 134.68, 132.58, 131.81, 127.89 (Ar*C*). MS (EI) *m*/*z*: 242 (M$^+$, 30%), 213 ([M − CHO]$^+$, 100%). Anal. Calcd for $C_{14}H_{10}O_2S$: C, 69.40; H, 4.16. Found: C, 69.33; H, 4.28%.

Bis[*o*-((2,6-diisopropylphenylimino)methyl)phenyl]thioether (8). Condensation of bis(*o*-formylphenyl)thioether with 2 equiv of 2,6-diisiopropylaniline in ethanol afforded the product in 95% yield. ^{1}H NMR (250 MHz, $CDCl_3$, rt): δ (ppm) 8.71 (s, 2H, C*H*═N), 8.23 (m, 2H, Ar*H*), 7.43 (m, 4H, Ar*H*), 7.22 (m, 2H, Ar*H*), 7.15−7.10 (m, 6H, Ar*H*), 2.92 (sept, 4H, J = 6.8 Hz, CHMe$_2$), 1.11 (d, 24H, J = 6.8 Hz, C*H*$_3$). ^{13}C NMR (63 MHz, $CDCl_3$, rt): δ (ppm) 160.33 (*C*H═N), 149.01, 137.55, 136.70, 135.93, 132.36, 131.84, 129.05, 127.89, 124.25, 122.99 (Ar*C*), 27.94 (*C*H(CH$_3$)$_2$), 23.47 (*C*H$_3$). MS (EI) *m*/*z*: 560 (M$^+$, 100%), 384 ([M − ArN$^+$, 25%). Anal. Calcd for $C_{38}H_{44}N_2S$: C, 81.38; H, 7.91; N, 4.99. Found: C, 81.28; H, 7.86; N, 4.89%.

2,4-Bis[(2,6-dimethylphenylimino)benzyl]-6-methylpyrimidine Iron(II) Dichloride, [(1a)FeCl$_2$]. A suspension of **1a** (80 mg, 0.15 mmol) in *n*-butanol was added dropwise at 80 °C to a solution of $FeCl_2$ (20 mg, 0.15 mmol) in *n*-butanol (10 mL) to yield a dark green solution. After being stirred at 80 °C for 30 min, the reaction volume was concentrated, and diethyl ether (10 mL) was added to precipitate the product as a green powder, which was subsequently washed with diethyl ether (2 × 10 mL), filtered, and dried to afford 65 mg (62%) of [(**1a**)$FeCl_2$]. Mp 238 °C dec. ^{1}H NMR (250 MHz, CD_2Cl_2, rt, all peaks appear as broad singlets): δ (ppm) −26.2 (CH$_3$ pyr), −10.8, −9.4, 6.5, 7.2, 7.8, 8.0, 8.2, 9.9 (Ar−H), 10.8 (Ar−H), 14.2, 15.6, 75.8 (Pyr−H). IR (KBr): 1616 (ν(C═N)), 1578 cm^{-1}. FAB mass spectrum (*m*/*z*): 634 (M$^+$, 45%), 599 ([M − Cl]$^+$, 100%). Anal. Calcd for $C_{35}H_{32}N_4FeCl_2$: C, 66.16; H, 5.43; N, 8.81. Found: C, 65.85; H, 5.26; N, 8.73. μ_{eff} (Evans NMR method) = 4.9 μ_B.

2,4-Bis[(2,4,6-trimethylphenylimino)benzyl]-6-methylpyrimidine Iron(II) Dichloride, [(1b)FeCl$_2$]. The described procedure using **1b** and $FeCl_2$ gave [(**1b**)$FeCl_2$] as a green powder in 69% yield. ^{1}H NMR (250 MHz, CD_2Cl_2, rt, all peaks appear as broad singlets): δ (ppm) −28.1 (CH$_3$ pyr), 6.5, 7.4, 7.9, 8.1, 10.1 (Ar−*H*), 11.5 (Ar−H), 13.9, 15.2, 20.3, 21.2, 75.5 (Pyr−*H*). IR (KBr): 1635, 1624, 1616 (ν(C═N)), 1578 cm^{-1}. FAB mass spectrum (*m*/*z*): 662 [(M)$^+$, 46], 627 [(M − Cl)$^+$, 100]. Anal. Calcd for $C_{37}H_{36}N_4FeCl_2$: C, 66.98; H, 5.47; N, 8.44. Found: C, 66.63; H, 5.27; N, 8.32. μ_{eff} (Evans NMR method) = 4.4 μ_B.

2,4-Bis[(2,6-diisopropylphenylimino)benzyl]-6-methylpyrimidine Iron(II) Dichloride, [(1c)FeCl$_2$]. The described procedure using **1c** and $FeCl_2$ gave [(**1c**)$FeCl_2$] as a green powder in 59% yield. Mp 176 °C dec. ^{1}H NMR (250 MHz, CD_2Cl_2, rt, all peaks appear as broad singlets): δ (ppm) −42.5 (CH$_3$ pyr), −10.4 (Ar−*H*), −9.8 (Ar−*H*), −9.4, −8.9, −8.6, 0.0, 0.2, 1.1, 2.1, 2.2, 2.6, 3.5, 4.7, 6.0, 6.7, 7.2, 7.6, 8.3, 9.3, 9.5, 9.8, 9.9, 12.5, 12.9, 15.1, 82.9 (Pyr−*H*). IR (KBr): 1635, 1623, 1617 (ν(C═N)), 1577 cm^{-1}. MS (FAB) *m*/*z*: 746 (M$^+$, 25%), 711 ([M − Cl]$^+$, 40%), 621 ([M − $FeCl_2$]$^+$, 100). Anal. Calcd for $C_{43}H_{48}N_4FeCl_2$: C, 69.08; H, 6.47; N, 7.49. Found: C, 69.15; H, 5.77; N, 7.25. μ_{eff} (Evans NMR method) = 4.4 μ_B.

2,4-Bis[(2-methylphenylimino)benzyl]-6-methylpyrimidine Iron(II) Dichloride, [(1d)FeCl$_2$]. The described procedure using **1d** and $FeCl_2$ gave [(**1d**)$FeCl_2$] as a green powder in 71% yield. Mp 133 °C dec. The solubility of complex [(**1d**)$FeCl_2$] in dichloromethane was insufficient for NMR analysis. IR (KBr): 1581 (ν(C═N)) cm^{-1}. MS (FAB) *m*/*z*: 606 (M$^+$, 24%), 571 ([M − Cl]$^+$, 84%). Anal. Calcd for $C_{33}H_{28}N_4FeCl_2$: C, 65.26; H, 4.65; N, 9.22. Found: C, 65.15; H, 4.55; N, 9.09. μ_{eff} (Evans balance) = 4.8 μ_B.

2,4-Bis[(2,4,6-dimethylphenylimino)benzyl]-6-methylpyrimidine Cobalt(II) Dichloride, [(1b)CoCl$_2$]. The described procedure using **1b** and $CoCl_2$ gave [(**1b**)$CoCl_2$] as a brown powder in 73% yield. Mp > 300 °C. ^{1}H NMR (250 MHz, CD_2Cl_2, rt, all peaks appear as broad singlets): δ (ppm) −28.0 (Ar−*H*), −25.9 (Ar−*H*), −1.5, −1.0, 2.1, 2.7, 3.5, 4.7, 12.8, 14.1, 27.0 (CH$_3$ pyr), 98.4 (Pyr−*H*). IR (KBr): 1583 (ν(C═N)) cm^{-1}. MS (FAB) *m*/*z*: 630 ([M − Cl]$^+$, 100%). Anal. Calcd for $C_{37}H_{36}N_4CoCl_2$: C, 66.68; H, 5.44; N, 8.41. Found: C, 66.44; H, 5.60; N, 8.56. μ_{eff} (Evans NMR method) = 4.5 μ_B.

2,4-Bis[(2-methylphenylimino)benzyl]-6-methylpyrimidine Cobalt(II) Dichloride, [(1d)CoCl$_2$]. The described procedure using **1d** and $CoCl_2$ gave [(**1d**)$CoCl_2$] as a brown powder in 80% yield. Mp 175 °C dec. ^{1}H NMR (250 MHz, CD_2Cl_2, rt, all peaks appear as broad singlets): δ (ppm) −21.8, −21.1, −17.7, −17.4, −14.4, −12.1, −10.7, −10.2, −8.2, −5.1, −4.1, −2.9, −2.5, −1.6, −0.7, 0.0, 0.4, 0.7, 0.9, 1.1, 1.6, 2.5, 2.9, 42.2 (3H, CH$_3$), 85.3 (1H, Pyr−*H*). IR (KBr): 1609 (ν(C═N)), 1578 cm^{-1}. MS (FAB) *m*/z: 574 ([M − Cl]$^+$, 100%). Anal. Calcd for $C_{33}H_{28}N_4CoCl_2$: C, 64.93; H, 4.62; N, 9.18. Found: C, 64.79; H, 4.59; N, 8.98. μ_{eff} (Evans NMR method) = 4.1 μ_B.

2,6-Bis[(2,4,6-trimethylphenylimino)benzyl]-pyridine Iron(II) Dichloride, [(9)FeCl$_2$]. The described procedure using 2,6-bis-[(2,4,6-trimethylphenylimino)phenyl]pyridine and $FeCl_2$ gave [(**9**)$FeCl_2$] as a green powder in 71% yield. Mp > 300 °C. ^{1}H NMR (250 MHz, CD_2Cl_2, rt, all peaks appear as broad singlets): δ (ppm) 1.6, 7.4, 7.7 (4H, Ar−*H*), 11.9 (10H, Ar−*H*), 14.8, 22.8 (12H, o-CH$_3$), 63.0 (1H, Pyr−H_p), 78.1 (2H, Pyr−H_m). IR (KBr): 1653,

1635, 1576 (ν(C═N)) cm^{-1}. MS (FAB) *m*/*z*: 648 ([M]$^+$, 50%), 613 ([M − Cl]$^+$, 100%). Anal. Calcd for $C_{37}H_{35}N_3FeCl_2$: C, 68.53; H, 5.44; N, 6.48. Found: C, 68.63; H, 5.54; N, 6.59. μ_{eff} (Evans NMR method) = 4.7 μ_B.

2,6-Bis[(2,4,6-trimethylphenylimino)benzyl]-pyridine Cobalt-(II) Dichloride, [(9)CoCl$_2$]. The described procedure using 2,6-bis[(2,4,6-trimethylphenylimino)phenyl]pyridine and $CoCl_2$ gave [(**9**)$CoCl_2$] as a brown powder in 80% yield. Mp > 300 °C. ^{1}H NMR (250 MHz, CD_2Cl_2, rt, all peaks appear as broad singlets): δ (ppm) −26.1 (10H, Ar−*H*), −0.7 (4H, Ar−*H*), 3.5, 6.0 (6H, CH_3), 16.5 (12H, CH_3), 37.8 (1H, Pyr−H_p), 103.1 (2H, Pyr−H_m). IR (KBr): 1609 (ν(C═N)), 1578 cm^{-1}. MS (FAB) *m*/*z*: 615 ([M − Cl]$^+$, 100%), 580 ([M − 2Cl]$^+$, 20%). Anal. Calcd for $C_{37}H_{35}N_3CoCl_2$: C, 68.21; H, 5.41; N, 6.45. Found: C, 66.96; H, 5.62; N, 6.24. μ_{eff} (Evans NMR method) = 4.3 μ_B.

1,8-Bis[(2,4,6-trimethylphenylimino)methyl]-3,6-dimethylcarbazolide Iron(II) Chloride, [(5)FeCl]. Sodium hydride (465 mg, 19.3 mmol) and 940 mg (1.94 mmol) of 1,8-bis(2,4,6-trimethylphenylimino)-3,6-dimethyl-9*H*-carbazole (**5**) were placed in a Schlenk flask, and 60 mL of THF was added. The reaction mixture was stirred at 65 °C for 16 h. After cooling to ambient temperature, the deep orange solution was removed by filtration, added to a suspension of 456 mg (1.94 mmol) of $FeCl_2(THF)_{1.5}$ in 40 mL THF, and stirred at rt for 16 h. The solvent was then removed in vacuo, and the residue was extracted with dichloromethane. This solution was concentrated to 5 mL, and the product was precipitated by the addition of pentane (50 mL). After washing with diethyl ether (3 × 30 mL) and drying in vacuo, the product was obtained as an orange-red, microcrystalline solid. Yield: 934 mg (84%). ^{1}H NMR (250 MHz, CD_2Cl_2, rt, all peaks appear as broad singlets): δ (ppm) −33.6 (12H, *o*-CH_3), 8.6 (4H, Ph−H_m), 11.9 (2H, Ar−*H*), 18.8 (6H, CH_3 or *p*-CH_3), 33.3 (6H, CH_3 or *p*-CH_3), 59.3 (2H, Ar−*H*). IR (KBr): 3010 (w), 2948 (w), 2918 (w), 2860 (w), 1631 (w, ν-(C═N)), 1610 (w), 1576 (s), 1470 (m), 1373 (m), 1343 (w), 1306 (w), 1281 (w), 1242 (w), 1206 (s), 1196 (s), 1138 (m), 991 (w), 853 (m), 764 (w), 735 (w), 674 (w), 659 (w) cm^{-1}. MS (FAB) *m*/*z*: 575 (M$^+$), 540 ([M − Cl]$^+$). Anal. Calcd for $C_{34}H_{34}ClFeN_3 \cdot 1.4CH_2Cl_2$: C, 61.19; H, 5.34; N, 6.05. Found: C, 61.46; H, 5.18; N, 5.67%. μ_{eff} (Evans NMR method) = 5.2 μ_B.

1,8-Bis[(2,4,6-trimethylphenylimino)methyl]-3,6-dimethylcarbazolide Cobalt(II) Chloride [(5)CoCl]. The described procedure using **5**, NaH, and $CoCl_2$ gave [(**5**)$CoCl_2$] as a deep red powder in 81% yield. Crystals suitable for X-ray analysis were grown by slow cooling of a hot, concentrated solution in toluene to ambient temperature. ^{1}H NMR (250 MHz, CD_2Cl_2, rt, all peaks appear as broad singlets): δ (ppm) −15.6 (12H, *o*-CH_3), 11.0 (4H, Ph−H_m), 18.6 (6H, *p*-CH_3), 22.2 (2H, Ar−*H*), 42.5 (6H, CH_3), 48.9 (2H, Ar−*H*). IR (KBr): 3005 (w), 2948 (w), 2915 (w), 2857 (w), 1627 (w, ν(C═N)), 1603 (m), 1573 (m), 1544 (s), 1477 (m), 1446 (m), 1364 (m), 1313 (m), 1242 (m), 1208 (s), 1197 (s), 1141 (s), 984 (m), 857 (m), 768 (w), 731 (m), 674 (w) cm^{-1}. MS (FAB) *m*/*z*: 578 (M$^+$), 543 ([M − Cl]$^+$). Anal. Calcd for $C_{34}H_{34}ClCoN_3 \cdot C_7H_8$: C, 73.37; H, 6.31; N, 6.26. Found: C, 73.35; H, 6.40; N, 6.22%. μ_{eff} (Evans NMR method) = 4.4 μ_B.

Table 2. Crystallographic Data for Compounds **1c** and [(**5**)CoCl][a]

	1c	[(**5**)CoCl]
chemical formula	$C_{43}H_{48}N_4$	$C_{34}H_{34}N_3ClCo$
solvent		C_7H_8
fw	620.9	671.2
space group	*I*2/*a* (No. 15)	*Pbca* (No. 61)
a (Å)	21.109(2)	11.629(2)
b (Å)	8.849(2)	15.875(2)
c (Å)	41.185(6)	37.944(4)
β (deg)	102.09(2)	
V (Å^3)	7522(2)	7005(1)
Z	8	8
ρ_{calcd} (g cm^{-3})	1.096	1.273
μ (mm^{-1})	0.06	0.60
R1[b]	0.054	0.066
wR2[c]	0.129	0.148

[a] Details in common: Bruker P4 diffractometer, graphite monochromated Mo Kα radiation (λ = 0.71073 Å), *T* = 20 °C, refinement based on F^2. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

X-Ray Crystallography. Table 2 provides a summary of the crystallographic data for compounds **1c** and [(**5**)CoCl]. CCDC 207084 and 207085.

General Polymerization Procedures. (a) High-Pressure Reactor Tests. A 1 L stainless steel reactor was baked out under a nitrogen flow for at least 1 h at >85 °C and subsequently cooled to the temperature of polymerization. Isobutane (0.5 L) and MAO (10 wt% in toluene) were introduced into the reactor and stirred at reaction temperature for at least 1 h. Ethylene was introduced by overpressure, and the difference between the total pressure and the initial pressure (isobutane and nitrogen: ca. 10 bar) is the pressure quoted in Table 1. The catalyst solution in toluene was then injected under nitrogen. The reactor pressure was maintained constantly throughout the polymerization run by computer controlled addition of ethylene. The polymerization time was 60 min. Runs were terminated by venting off all volatiles, and the reactor contents were isolated, washed with aqueous HCl and methanol, and dried in a vacuum oven at 50 °C.

(b) Schlenk-Flask Ethylene Polymerization Tests. The precatalyst was dissolved in toluene (100 mL), and MAO (10 wt % in toluene) was added via syringe. The Schlenk flask was placed in a water bath and purged with ethylene, and the contents magnetically stirred and maintained under ethylene (1 bar) for the duration of the polymerization (60 min). The polymerization was terminated by the addition of aqueous hydrogen chloride. The solid PE was recovered by filtration, washed with methanol (50 mL), and dried (vacuum oven at 50 °C).

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Supporting Information Available: Additional figures and X-ray Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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