Preparation, Structure, and Ethylene Polymerization Behavior of Bis(imino)pyridyl Chromium(III) Complexes

Miguel A. Esteruelas,*[,†] Ana M. López,[†] Luis Méndez,[‡] Montserrat Oliván,[†] and Enrique Oñate[†]

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain, and Repsol-YPF, Centro de Tecnología, Carretera Extremadura N-V, Km 18, 28930 Móstoles, Madrid, Spain

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The synthesis, characterization, and ethylene polymerization behavior of a family of chromium(III) complexes of formula [2,6-bis(imino)pyridyl]$CrCl_3$ is reported. The X-ray diffraction studies of two of the new compounds show that the geometry around the chromium atom is octahedral, with the three chlorine ligands in a *mer* disposition. The distance between the metal and one of the trans-disposed chlorine atoms is significantly longer than the other two Cr−Cl distances. Treatment of the complexes [2,6-bis(imino)pyridyl]$CrCl_3$ with methylaluminoxane (MAO) leads to very active ethylene polymerization catalysts that afford highly linear polyethylene. The substituents at the ortho position of the N-aryl groups of the 2,6-bis(imino)pyridyl ligands modulate both the catalytic activity and the molecular weights of the resulting polyethylene. The most active catalysts are those with two substituents at the ortho position of the N-aryl groups (activities up to 4×10^7 g (mol of Cr)$^{-1}$ bar^{-1} h^{-1} are achieved). Regarding the size of the substituents, the activity and the molecular weights follow an opposite trend. Systems with two small substituents lead to very active systems, but the molecular weight of the polyethylene is lower than when bulkier substituents are present.

Introduction

The conventional Ziegler−Natta and Phillips catatysts used in the industrial production of polyolefins are heterogeneous systems. The active centers for the first one are usually based on titanium, while the Phillips catalysts employ chromium. The heterogeneous nature of these systems is responsible for certain heterogeneities in the produced polymers, which might be not desirable for some applications.[1]

Kaminsky and Sinn's initial discovery that methylaluminoxane (MAO) affords extremely active catalysts, when combined with titanium and zirconium metallocenes,[2] has led to an explosion of research into the use of metallocene catalysts. Because the active centers of those systems are group 4 metals, they are considered the homogeneous version of the Ziegler−Natta catalysts. Their homogeneous nature allows the production of polymers with narrow molecular weight and comonomer distributions, as well as a better understanding of the factors determining the final properties of the polymers.[3]

Homogeneous models of the Phillips catalysts that parallel the discoveries in group 4 metallocene/MAO systems have been also developed.[4] Thus, cyclopentadienyl−amine,[5] cyclopentadienyl−phosphine,[6] cyclopentadienyl−amido,[7] and a number of pentamethylcyclopentadienyl chromium(III)[8] catalysts have been reported. In addition, non-cyclopentadienyl systems containing 1,1-bis-(2-naphtholato),[9] salicylaldiminato,[10] β-diketiminato,[11]

† Universidad de Zaragoza.
‡ Repsol-YPF.

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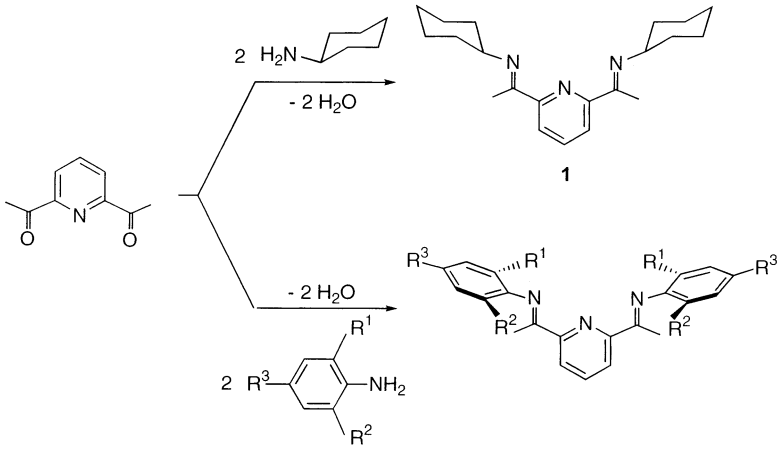
Scheme 1



	R^1	R^2	R^3
2	Et	Et	H
3	CF_3	H	H
4	^{i}Pr	Me	H
5	^{i}Pr	^{i}Pr	H
6	Me	Me	H
7	Me	Me	Me
8	^{t}Bu	H	H
9	OMe	Me	H
10	OMe	H	OMe

imido,[12] and triazacyclohexane[13] ligands are also known. The most active catalysts of those mentioned above are those stabilized by cyclopentadienylamine groups,[5b] which show activities of about 10^6 g (mol of Cr)$^{-1}$ h^{-1} bar^{-1}.

Significant recent developments have also occurred with late-transition-metal systems,[14] in particular, the discovery of exceptionally active catalysts (between 3.7×10^6 and 2.1×10^7 g (mol of Fe)$^{-1}$ h^{-1} bar^{-1}) based on iron and bis(imino)pyridyl ligands, reported independently by the groups of Brookhart[15] and Gibson.[16] Following this discovery, a considerable amount of effort has been dedicated to investigate the nature of the active species[17] and to design new catalysts based on these types of ligands.[18] However, the effort in this field has not led to new polymerization catalysts with activities comparable to those of Brookhart and Gibson's complexes.

In the search for new polymerization catalysts with technological application, we have prepared bis(imino)pyridyl chromium(III) complexes. In this paper, we report the synthesis and full characterization of these compounds, which, in the presence of methylaluminoxane and/or triisobutylaluminum, catalyze the polymerization of ethylene with high and very high activities. We also show the influence of the ligand architecture and the reaction conditions on the polymerization activity and the polymer molecular weight.

Results and Discussion

1. Synthesis and Characterization of the New Compounds. The symmetrical 2,6-bis(imino)pyridyl ligands **1**−**4** (Scheme 1) have been prepared by the catalytic condensation of 2.0 equiv of the corresponding substituted aniline with 1.0 equiv of 2,6-diacetylpyridine in refluxing ethanol and in the presence of acetic acid. The same experimental procedure has been previously used by Gibson and co-workers to obtain the related ligands **5**−**8**.[16b] The 2,6-bis(imino)pyridyl compounds **1**−**4** are isolated as yellow solids in moderate yield (about 50%) after 48 h. Under the same experimental conditions as those mentioned to obtain **5**−**8**, ligands **9** and **10** are formed in very low yield (>5%) even after long reaction periods (up to 5 days) and with molecular sieves to trap the water formed in the reaction. However, we have observed that the use of toluene as solvent, *p*-toluenesulfonic acid as catalyst, and a Dean−Stark apparatus to remove the water formed in the reaction leads to **9** and **10** in high yields (about 80%) after a few hours.

The asymmetrical 2,6-bis(imino)pyridyl ligands **12**−**14** (Scheme 2) have been synthesized by the selective

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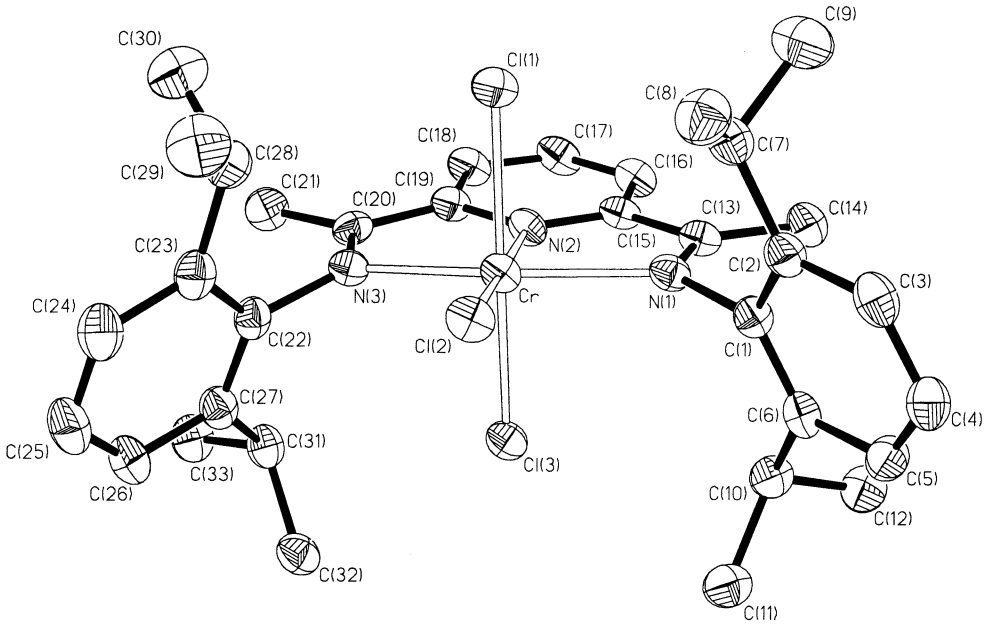
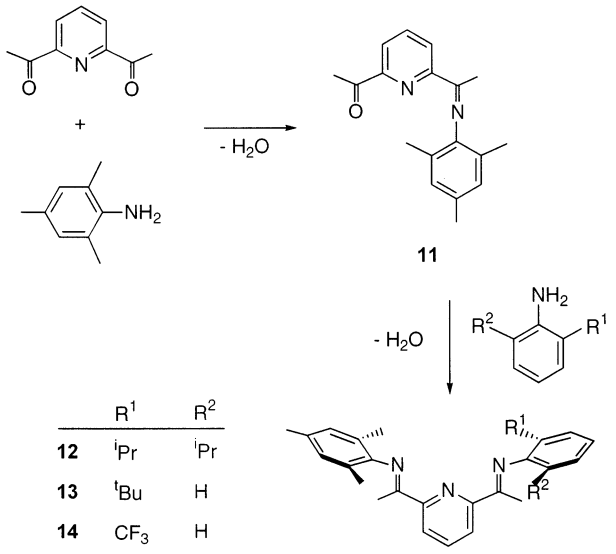


Figure 1. Molecular diagram of the complex {2,6-bis[1-((2,6-diisopropylphenyl)imino)ethyl]pyridine}$CrCl_3$ (**22**). Thermal ellipsoids are shown at 50% probability.

Scheme 2



and consecutive condensations of 1.0 equiv of 2,4,6-trimethylaniline and 1.0 equiv of the corresponding aniline with 1.0 equiv of 2,6-diacetylpyridine. Initially, the treatment of 2,6-diacetylpyridine with 0.85 equiv of 2,4,6-trimethylaniline, under the experimental conditions used to prepare **9** and **10**, leads to **11**. This intermediate, which is isolated as a yellow solid in 38% yield after 45 min, subsequently reacts with 2,6-diisopropylaniline, 2-*tert*-butylaniline, and 2-(trifluoromethyl)-aniline to afford **12**−**14**, which are isolated as yellow solids in 70−80% yield, after 12 h.

The 2,6-bis{1-[(2,4,6-trimethylphenyl)imino]benzyl}-pyridine ligand (**17**) has been prepared by starting from 2,6-dicarbonylpyridine dichloride according to Scheme 3. Initially, this compound was transformed into 2,6-dibenzoylpyridine (**15**) by a Friedel−Crafts acylation of benzene with $AlCl_3$ as catalyst. Treatment of **15** with 1.0 equiv of anhydrous nickel dichloride and 2.0 equiv of 2,4,6-trimethylaniline in acetic acid under reflux affords the nickel complex **16**, which is isolated as a brown solid in 89% yield after 4 h. The addition of aminopropyl silica gel to a dichloromethane solution of **16** gives rise to ligand **17**, as a yellow solid in 51% yield. Attempts to obtain **17** by direct condensation of **15** with 2,4,6-trimethylaniline were unsuccessful.

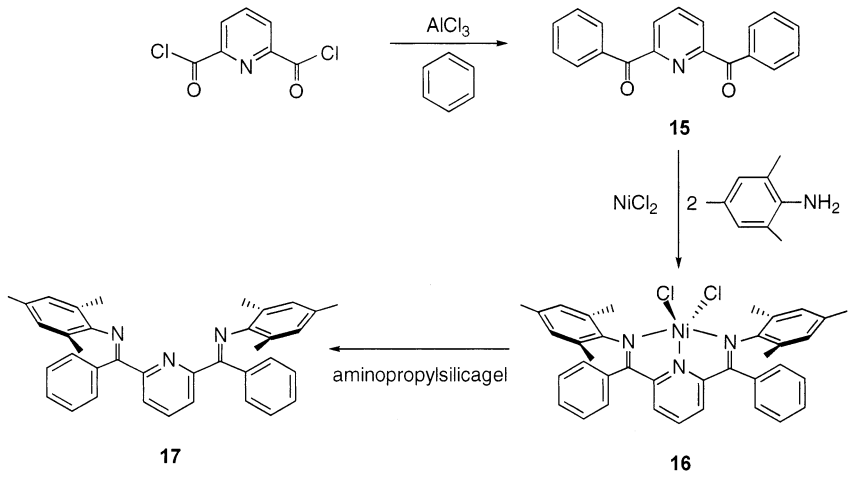
Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 22

Cr−N(1)	2.142(3)	Cr−Cl(1)	2.3415(9)
Cr−N(2)	1.981(3)	Cr−Cl(2)	2.2821(9)
Cr−N(3)	2.142(3)	Cr−Cl(3)	2.2856(9)
N(1)−C(13)	1.308(4)	N(3)−C(20)	1.294(4)
N(1)−Cr−N(2)	77.55(10)	N(1)−Cr−N(3)	153.97(10)
N(2)−Cr−N(3)	77.15(10)	N(1)−Cr−Cl(1)	92.28(7)
N(1)−Cr−Cl(2)	101.00(7)	N(1)−Cr−Cl(3)	87.23(7)
N(2)−Cr−Cl(1)	82.27(8)	N(2)−Cr−Cl(2)	175.35(8)
N(2)−Cr−Cl(3)	89.49(8)	N(3)−Cr−Cl(1)	90.31(7)
N(3)−Cr−Cl(2)	104.69(8)	N(3)−Cr−Cl(3)	86.52(7)
Cl(1)−Cr−Cl(2)	93.40(3)	Cl(1)−Cr−Cl(3)	171.65(4)
Cl(2)−Cr−Cl(3)	94.87(3)		

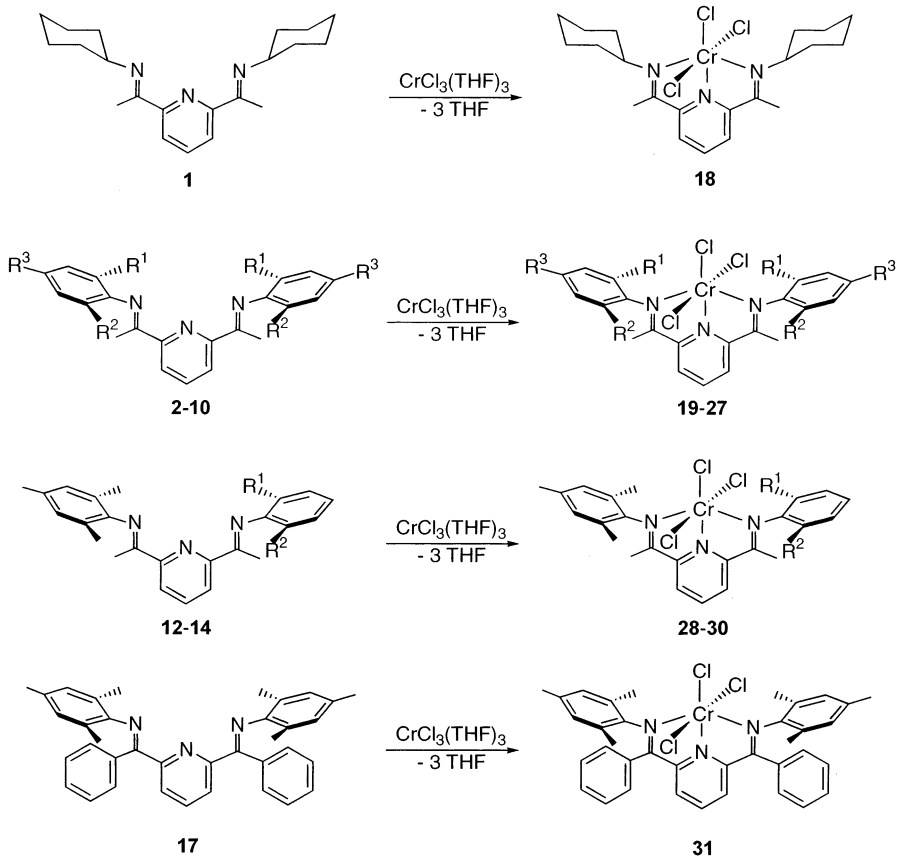
The chromium complexes **18**−**31** (Scheme 4) have been prepared by reaction of $CrCl_3(THF)_3$ with the stoichiometric amount of the corresponding 2,6-bis-(imino)pyridyl ligand in acetone under reflux (compounds **19**, **21**−**25**, **28**, and **29**) or in dichloromethane at room temperature (compounds **18**, **20**, **26**, **27**, **30**, and **31**). They are isolated as green air-stable solids in high yield (60−97%) and were characterized by elemental analysis, FAB mass spectrometry, and IR. Complexes **22** and **31** were further characterized by X-ray crystallography.

Crystals of **22** suitable for X-ray structural determination were grown from a dichloromethane solution layered with pentane. The molecular structure is shown in Figure 1, whereas selected bond lengths and angles are listed in Table 1. The geometry around the chromium atom could be described as a distorted octahedron with the chlorine ligands in a *mer* disposition. The Cl−Cr−Cl and N−Cr−N angles are 93.40(3), 171.65(40), and 94.87(3)° and 77.55(10), 153.97(10), and 77.15(10)°, respectively. The Cr−N(pyridyl) bond distance (Cr−N(2) = 1.981(3) Å) is about 0.16 Å shorter than the Cr−N(imino) bond distances (2.142(3) Å, Cr−N(1) and Cr−

Scheme 3



Scheme 4



	R^1	R^2	R^3
19	Et	Et	H
20	CF_3	H	H
21	^{i}Pr	Me	H
22	^{i}Pr	^{i}Pr	H
23	Me	Me	H
24	Me	Me	Me
25	^{t}Bu	H	H
26	OMe	Me	H
27	OMe	H	OMe

	R^1	R^2
28	^{i}Pr	^{i}Pr
29	^{t}Bu	H
30	CF_3	H

N(3)), with the formal double-bond character of the imino linkages N(1)−C(13) (1.308(4) Å) and N(3)−C(20) (1.294(4) Å) having been retained. The planes of the phenyl rings are oriented essentially orthogonal to the coordination plane of the bis(imino)pyridine unit with angles of 76.67(0.08) and 87.44(0.10)°. Interestingly, the separations between the metal and the mutually trans-disposed chlorine atoms are significantly different. The Cr−Cl(2) bond length (2.2821(9) Å) is statistically identical with the separation between the metal and the chlorine atom disposed trans to the pyridinic nitrogen atom (Cr−Cl(3) = 2.2856(9) Å). However, it is about 0.06 Å shorter than the Cr−Cl(1) distance (2.3415(9) Å).

Crystals of **31** suitable for X-ray structural determination were grown from a dichloromethane solution layered with diethyl ether. The molecular structure of this complex is shown in Figure 2, whereas selected bond lengths and angles are listed in Table 2. The presence of phenyl substituents instead of methyl groups at the C=N carbon atoms of the imino functional groups, as well as the presence of methyl groups instead of isopropyl groups in the N−Ph substituents, does not appear to have any significant influence on the molecular geometry. The most noticeable difference between both structures is the length of the longest Cr−Cl bond (Cr−Cl(1) = 2.326(2) Å), which is shortened about 0.02 Å in **31** with regard to **22**.

2. Ethylene Polymerization. The chromium(III) complexes **18**−**31** were tested for ethylene polymerization under diverse sets of conditions, as shown in Table

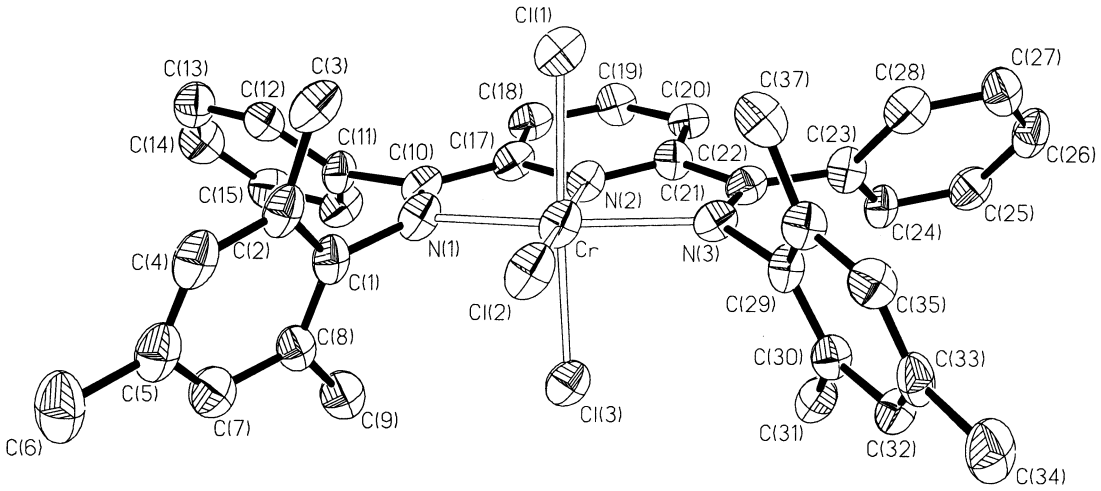


Figure 2. Molecular diagram of the complex {2,6-bis[1-((2,4,6-trimethylphenyl)imino)benzyl]pyridine}$CrCl_3$ (**31**). Thermal ellipsoids are shown at 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 31

Cr−N(1)	2.113(3)	Cr−Cl(1)	2.326(2)
Cr−N(2)	1.987(3)	Cr−Cl(2)	2.283(2)
Cr−N(3)	2.108(3)	Cr−Cl(3)	2.296(2)
N(1)−C(10)	1.308(7)	N(3)−C(22)	1.292(8)
N(1)−Cr−N(2)	77.89(8)	N(1)−Cr−N(3)	155.31(13)
N(2)−Cr−N(3)	77.71(10)	N(1)−Cr−Cl(1)	91.10(9)
N(1)−Cr−Cl(2)	103.06(9)	N(1)−Cr−Cl(3)	88.60(10)
N(2)−Cr−Cl(1)	82.77(9)	N(2)−Cr−Cl(2)	177.41(11)
N(2)−Cr−Cl(3)	90.14(9)	N(3)−Cr−Cl(1)	89.54(10)
N(3)−Cr−Cl(2)	101.48(9)	N(3)−Cr−Cl(3)	87.75(9)
Cl(1)−Cr−Cl(2)	94.78(8)	Cl(1)−Cr−Cl(3)	172.81(9)
Cl(2)−Cr−Cl(3)	92.29(8)		

3. In all experiments the chromium complexes were previously dissolved and preactivated in a methylaluminoxane/toluene solution. This treatment acts in two ways: first, it helps to solubilize the poorly soluble complexes and, second, it preforms the actual catalytic species. We have observed that, by doing so, activities are enhanced and there is not an induction polymerization period. These complex/MAO/toluene solutions remain stable for weeks if kept under an inert atmosphere, although it has been observed that in order to reach a high and constant value of activity the solutions must be employed after a period of ca. 30−60 min from their preparation. During this period the complex dissolves and the color of the solution changes from the original green to that of brown tea. This suggests that the formation of the actual catalytic species needs a period of several minutes to be formed at room temperature. To check if a Cr(II) species could be formed during this preactivation period, a similar experiment was performed using [2,6-bis{1-[2,6-(diisopropylphenyl)-imino]ethyl}pyridine]$CrCl_2$ (**32**), the Cr(II) analogue of complex **24**. This catalyst has also shown the need for a preactivation time (even longer than the time needed for **24**) with MAO in order to achieve high and stable catalytic activities, suggesting that activation of Cr(III) does not occur by reduction to Cr(II). Under exactly the same conditions (including the same preactivation time, 60 min), **32** is ca. half as active as **24** (entries 16 and 27).

The substituents of the ligands influence the catalytic behavior of complexes **18**−**31**, with regard to both activity and the molecular weight of the resulting polyethylene. Thus, while complex **18**, which has cyclohexyl groups with no substituents in the 2- and 6-positions attached to the nitrogen atom of the imines, has a low activity (8.30×10^3 g of PE (mol of Cr)$^{-1}$ bar^{-1} h^{-1}, entry 1), those with aromatic groups (**19**−**31**) substituted at least in one of their ortho positions show much higher activities (ranging from 1.25×10^5 to 4.14×10^7 g of PE (mol of Cr)$^{-1}$ bar^{-1} h^{-1}, entries 2−26). The highest activities achieved in the tested set of compounds are obtained for those which bear ligands derived from 2,4,6-trimethylaniline (**24** and **28**−**31**, entries 12−16 and 20−26). It seems that the methyl group in the para position has a beneficial influence on the activity (compare entries 11 and 14). On the other hand, an increase of the bulkiness of the groups in the ortho positions of the anilines renders a less active catalyst (compare entries 6, 8, and 11).

The electronic nature of the aromatic substituents has also a marked influence on the activity. Thus, substitution of one methyl (complex **23**) by a methoxy group (complex **26**) in the ortho position leads to a nonactive species (compare entries 11 and 18). However, the replacement of a *tert*-butyl group (complex **25**) by a trifluoromethyl group at the ortho position (complex **20**) does not seem to affect the catalytic activity (entries 5 and 17).

Changing the substituent on the imine functional group from a methyl to a phenyl has little or no effect on the activity. Thus, complexes **24** (methyl) and **31** (phenyl) render polyethylene with similar productivity.

The molecular weight (M_w) of the polyethylene obtained with catalyst **25** is 257 500. All the other catalysts give polyethylene whose molecular weights (M_w) are between 1630 and 35 900.[19] In most cases, after the reaction is quenched with methanol/HCl, part of the polymer remains dissolved in the heptane used for the assays, and after filtration of the solid fraction and separation of the phases, a waxy fraction is recovered from the heptane layer by evaporation under vacuum. In Table 3 the percentage of waxes obtained in most cases is given. The amount of wax produced is depend-

(19) Usually, a molecular weight distribution smaller than 2 is an indication of the occurrence of some living polymerization processes (ideally $M_w/M_n = 1$). However, the fact that we have not observed any dependence of M_w on the polymerization time rules out this possibility.

Table 3. Results of the Ethylene Polymerization Assays[a]

entry	complex	amt of Cr (μmol)	Al_{MAO}/Cr (pref sol)	coactivator	Al/Cr coactivator	*t* (min)	total wt of polymer (g)	waxes (%)	activity[b]	M_w[c]	M_n	M_w/M_n
1	**18**	3.9	110	MAO	550	60	0.13	*d*	8.30×10^3	*d*	*d*	*d*
2	**19**	1.0	450	MAO	780	30	1.76	24	9.18×10^5	*d*	*d*	*d*
3	**19**	4.6	190	TIBA	810	30	34.69	10	3.80×10^6	2170	1450	1.50
4	**19**	4.6	190	MAO	800	30	15.13	15	1.66×10^6	2690	1450	1.86
5	**20**	5.2	200	TIBA	800	10	1.56	33	4.53×10^5	*d*	*d*	*d*
6	**21**	2.3	190	MAO	820	30	14.82	7.1	3.23×10^6	*d*	*d*	*d*
7	**21**	2.3	190	TIBA	830	30	34.98	4.4	7.66×10^6	5390	2480	2.17
8	**22**	7.5	50	MAO	400	30	12.9	0.9	8.57×10^5	*d*	*d*	*d*
9	**22**	14.1	400	TIBA	400	30	28.6	1.2	1.02×10^6	12900	8150	1.58
10	**22**	7.5	25	TIBAO	400	30	13.6	0	9.06×10^5	35900	27400	1.31
11	**23**	1.9	140	MAO	680	30	45.9	15	1.21×10^7	2130	1380	1.54
12	**24**	1.9	140	MAO	700	3.5	17.7	*d*	4.14×10^7	2100	1600	1.31
13[e]	**24**	1.0	140	MAO	1080	10	5.85	*d*	9.20×10^6	2660	1800	1.48
14	**24**	0.9	140	MAO	1110	30	46.6	*d*	2.51×10^7	1980	1540	1.29
15	**24**	0.9	140	TIBA	1050	30	29.0	*d*	1.52×10^7	1630	1100	1.48
16	**24**	0.5	400	TIBA	810	30	11.4	22	1.24×10^7	*d*	*d*	*d*
17	**25**	3.8	120	MAO	170	60	1.89	*d*	1.25×10^5	257500	4180	61.6
18	**26**	10.3	200	MAO	650	30	traces					
19	**27**	8.4	60	TIBAO	235	30	traces					
20	**28**	3.3	50	TIBAO	830	30	14.85	3.2	2.22×10^6	*d*	*d*	*d*
21	**29**	5.8	990	TIBA	860	30	13.4	34	1.16×10^6	*d*	*d*	*d*
22	**29**	5.8	990	TIBAO	850	30	11.8	41	1.01×10^6	*d*	*d*	*d*
23	**30**	2.2	680	MAO	520	60	40.5	36	4.53×10^6	*d*	*d*	*d*
24	**30**	0.5	680	TIBAO	960	30	12.2	36	1.19×10^7	*d*	*d*	*d*
25	**31**	0.6	730	MAO	1840	30	27.9	21	2.38×10^7	*d*	*d*	*d*
26	**31**	0.6	730	TIBAO	840	30	11.6	34	9.83×10^6	*d*	*d*	*d*
27	**32**	0.5	400	TIBA	805	30	5.02	30	5.44×10^6	*d*	*d*	*d*
28	**32**	4.8	110	MAO	1120	15	81.5	13	1.70×10^7	1740	1130	1.54

[a] Conditions: solvent heptane; temperature 70 °C; ethylene pressure 4 bar. The complexes were dissolved and preactivated in a MAO/toluene solution (ca. 10%); the actual concentration of Al_{MAO} for each solution was estimated from its ^{1}H NMR spectrum. [b] Activity is expressed in units of g of PE (mol of Cr)$^{-1}$ bar^{-1} h^{-1}. [c] Determined by GPC. Refers only to the polymer separated from the wax phase. [d] Not recorded. [e] Temperature 90 °C.

ent on the structure of the catalyst and the nature of the cocatalyst.

The structure of the ligands also influences the molecular weights of the polyethylene. Complexes having bulkier ortho substituents in the phenyl groups give rise to higher molecular weights. This is in agreement with the results observed for the iron and cobalt catalysts with the same types of ligands.[15,16] In this aspect, the molecular weight and molecular weight distribution of the polymer obtained with complex **25** are remarkable. A high molecular weight distribution value has been also observed for the related iron complex.[16b]

The polymers obtained with these chromium complexes are highly linear, and this is reflected in their physical properties: for example, the polymer obtained with **22** (entry 10) has a calculated degree of crystallinity of 80% (T_m = 134 °C, $\Delta H_m = -232$ J g^{-1}).

The copolymerization ability of these complexes has been also tested. Copolymerization with 1-hexene occurs, rendering a branched polyethylene, although the activity results diminished in comparison with those for the production of homopolyethylene. Thus, under the same conditions as those employed in entry 14, but adding 15 mL of 1-hexene (see Experimental Section), complex **24** copolymerizes 1-hexene and ethylene, yielding 34.8 g (activity 1.83×10^7 g (mol of Cr)$^{-1}$ h^{-1} bar^{-1}) of branched polyethylene (M_w = 1470, M_w/M_n = 2.13) having 1.13 butyl branches per 1000 C (T_m = 105 °C, $\Delta H_m = -246$ J g^{-1}).

The effect of the cocatalyst in the productivity and nature of the polymer has been also studied. We have observed that a minimum of MAO is needed for reaching acceptable activities, but then, it can be substituted in part by aluminum alkyls or other aluminoxanes. Figure 3 shows the variation of the activity of complex **19** as a result of the increase of the ratio Al_{MAO}/Cr in the complex/MAO/toluene solution prepared before it is injected in the polymerization reactor. All the polymerization assays were performed under the same conditions, the Al_{TIBA}/Cr (TIBA stands for triisobutylaluminum) ratio being equal to 820. The activity increases slightly when the ratio of MAO increases from 50 to 200, and then it remains stable up to a ratio of 400.

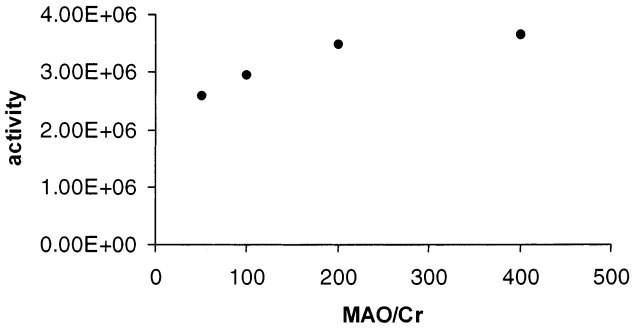


Figure 3. Influence of the Al_{MAO}/Cr ratio of the preformed complex solution on the activity of catalyst **19**. General conditions employed for the assays: 4.3 μmol of Cr, Al_{TIBA}/Cr = 820, 4 bar, 70 °C, 30 min.

Figure 4 shows the trend in activity, also for complex **19**, when the Al_{TIBA}/Cr ratio is changed keeping constant the Al_{MAO}/Cr ratio (190). The activity shows a maximum around an Al_{TIBA}/Cr ratio of 800.

Three kinds of terminal groups are detected by ^{13}C NMR spectroscopy: vinyl, isopropyl (denoted here as ISOF), and methyl (denoted here as CH3F).[20] The first one denotes β-hydrogen elimination or β-hydrogen transfer to the monomer[21] and the isopropyl end group shows the occurrence of chain transfer to triisobutyl-

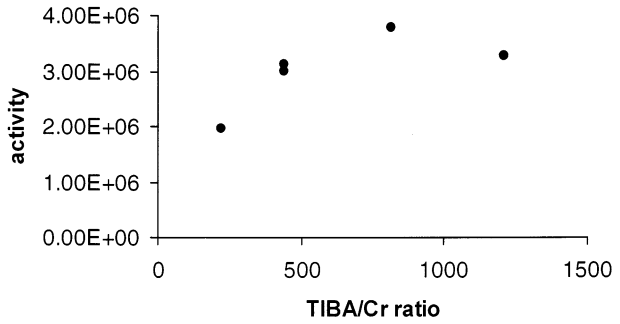


Figure 4. Influence of the Al_{TIBA}/Cr ratio on the activity of complex **19**. General conditions employed for the assays: 4.6 μmol of Cr, $Al_{MAO}/Cr = 190$, 4 bar, 70 °C, 30 min.

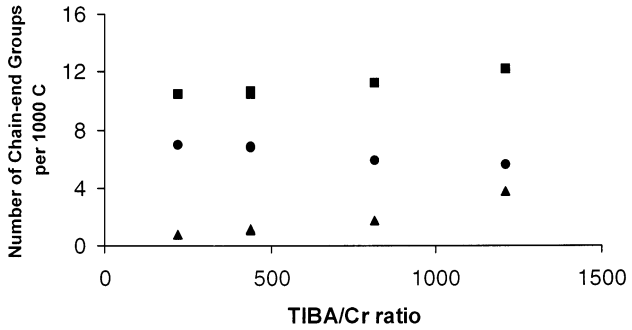


Figure 5. Dependence of the number and nature of the polymer chain-end groups (■, vinyl; ●, CH3F; ▲, ISOF) on the Al_{TIBA}/Cr ratio for ethylene polymerization for complex **19** using the set of conditions shown in Figure 4.

aluminum (TIBA), while the methyl end group can have several origins: from the initial methylation step with MAO, from chain transfer to MAO followed by hydrolysis during the workup of the polymer, and from methyl groups formed after insertion of ethylene into the Cr−H bond formed after β-hydrogen elimination and/or transfer to monomer (Scheme 5). As is shown in Figure 5, when the TIBA/Cr ratio is increased, the number of isopropyl end groups (ISOF) grows. The number of methyl groups (CH3F) increases also parallel to the number of ISOF, while the number of vinyl groups decreases, reflecting an increase in the number of saturated chains.

To reduce the alkylating power of the cocatalyst, TIBA was substituted by tetraisobutylaluminoxane (TIBAO) in some of the assays. Table 4 shows the influence of the substitution of TIBA by TIBAO on the catalytic activity and nature of the chain ends of the polyethylene obtained with complex **22**. This procedure resulted in lower numbers of ISOF and CH3F groups per 1000 C chain ends and comparable, if not higher, activities. In other experiments, the amount of MAO was reduced and it was substituted by TIBAO. In these cases, the termination reaction by alkyl-transfer processes to aluminum is not favored and, consequently, the molecular weights increase (Table 3, entry 10).[22]

(20) Vinyl and CH3F groups assigned according to: Randall, J. C. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1989**, *C29*, 201. The ISOF groups were assigned according to: Sarpal, A. S.; Kapur, G. S.; Chopra, A.; Jain, S. K.; Srivastava, S. P.; Bhatnagar, A. K. *Fuel* **1996**, *75*, 483.

(21) We cannot be certain which mechanism for the formation of vinyl groups is favored: β-hydrogen elimination or transfer to monomer. However, the fact that the molecular weight of the polymer obtained at high pressure (38 bar) with the supported catalyst (see text) is similar to that obtained at lower pressure (4 bar) provides an indication that β-hydrogen elimination could predominate.

Table 4. Effect of the Substitution of TIBA by TIBAO in the Catalytic Activity and Nature of Chain Ends of the Polyethylene Obtained with Complex 22[a]

TIBA/Cr	TIBAO/Cr	amt of PE (g)	activity (g of PE (mol of Cr)$^{-1}$ bar^{-1} h^{-1})	CH3F[b]	ISOF[b]
410	0	14.66	1.07×10^6	5.99	1.91
200	200	15.06	1.09×10^6	5.44	1.64
0	400	16.39	1.18×10^6	2.26	0.40
0	800	18.40	1.33×10^6	2.92	0.63

[a] Conditions: 6.9 μmol of Cr; $Al_{MAO}/Cr = 200$ for the preformed complex solution; temperature 70 °C; ethylene pressure 4 bar; 30 min. [b] Results from ^{13}C NMR spectroscopy, given per 1000 carbon atoms.

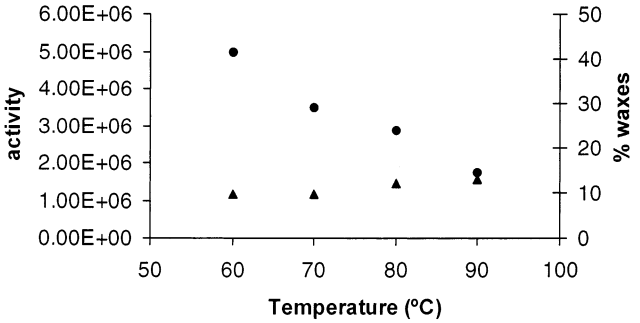


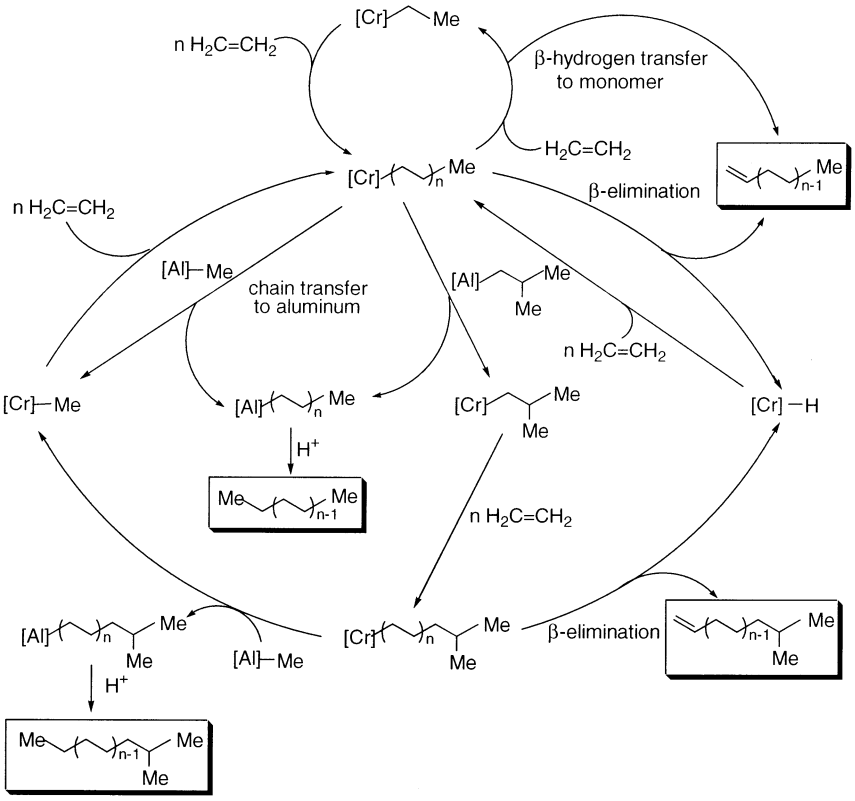
Figure 6. Dependence of the activity (●) and percentage of wax formed (▲) on temperature for complex **19**. General conditions employed for the assays: 4.6 mmol of Cr, $Al_{MAO}/Cr = 190$, $Al_{TIBA}/Cr = 810$, 4 bar, 70 °C, 30 min.

The influence of the temperature on the catalyst behavior has been studied. Figure 6 shows the effect of the temperature on the catalytic performance for complex **19** upon increasing the temperature within the range 60−90 °C. The activity decreases gradually, and there is an increase on the percentage of waxes obtained. This is similar to what is observed with the bis(imino)pyridyl iron and cobalt complexes, where a significant decrease in productivity and molecular weight is reported when the temperature is increased from 35 to 70 °C.[16b] However, according to our results, the stability at high temperatures (over 70 °C) of the chromium complexes seems to be higher than that of the iron and cobalt complexes.

As is known, the application of homogeneous olefin polymerization catalysts in gas-phase or slurry reactions would cause problems such as reactor fouling. This problem could be overcome via heterogeneization of the homogeneous catalysts. Therefore, we have pursued the heterogeneization of our system. An active catalytic system was obtained by prepolymerization of complex **24** with ethylene together with MAO supported on silica (see the Experimental Section). The catalytic system thus obtained was employed for the polymerization of ethylene at a total pressure of 38 bar in isobutane at 80 °C, using TIBA as cocatalyst. The consumption of ethylene was very stable during the assay (60 min), yielding a linear polymer (M_w of 1470, $M_w/M_n = 2.13$) with high productivity (ca. 1300 kg of PE (g of Cr)$^{-1}$ h^{-1}), superior to most Phillips type catalysts.[23]

(22) We have observed (unpublished results) that, by reduction of the trimethylaluminum present in MAO by evaporation, the molecular weights of the polymer are also increased.

Scheme 5. Possible Chain Proprogation and Termination Pathways



Concluding Remarks

A family of air-stable chromium(III) complexes bearing bis(imino)pyridine has been synthesized and characterized. In the presence of methylaluminoxane and/or triisobutylaluminum, these compounds are the most active chromium catalysts reported to date for ethylene polymerization, showing activities up to 4.14×10^7 g of PE (mol of Cr)$^{-1}$ bar^{-1} h^{-1}. The thermal stability of these systems is also remarkable, reaching a maximum of activity at 60−70 °C. Linear polyethylene of molecular weights (M_w) ranging from 35 900 to 1630 are obtained. In the presence of an α-olefin comonomer such as 1-hexene incorporation is observed.

The catalytic activity and the molecular weights of the polyethylene depend greatly on the structure and electronic properties of the ligands. The complexes with two substituents in the ortho positions of the parent anilines are more active than those with only one. However, the increase of the steric hindrance of these subtituents produces a decrease in the catalytic activity. Thus, the most active complexes are those bearing two ortho methyl groups. An opposite trend has been observed for the molecular weights of the obtained polyethylene, which increase as the steric requirement of the substituents at the ortho positions increases. The presence of donor groups, such as methoxy, in ortho or para positions of the aryl groups renders nonactive systems.

The molecular weight of the polymer is also influenced by the nature and amount of the employed cocatalyst due to chain-transfer processes to aluminum, as has been demonstrated by NMR analysis of chain end groups. The general trend observed is that the molecular weights increase when the alkylating power of the cocatalyst is reduced.

Experimental Section

General Considerations. All manipulations were carried out under an inert atmosphere, using standard Schlenk techniques. Solvents were refluxed over an appropriate drying agent and distilled prior to use. C, H, and N analyses were measured on a Perkin-Elmer 2400 CHNS/O analyzer. Infrared spectra were recorded on Perkin-Elmer 883 or Spectrum One spectrometers as solids (Nujol mull). ^{1}H, ^{13}C{^{1}H}, and ^{19}F spectra were recorded on a Varian Gemini 2000 or Bruker ARX 300. ^{13}C{^{1}H} NMR (1,2,4-trichlorobenzene, 378 K) polymer analyses were recorded on a Bruker DRX 500 NMR spectrometer. Chemical shifts are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external $CFCl_3$. Coupling constants are given in hertz. Mass spectral analyses were performed with a VG Auto Spec instrument. The ions were produced, FAB$^+$ mode, with the standard Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix. Electron impact MS (operating at 70 eV) was used for the ligands. Molecular weights of the polymers were determined by gel permeation chromatography employing universal calibration in a Waters 150c instrument with differential refractive index (DRI) detector and a Viscotek 150R DV detector and thermal analysis by differential scanning calorimetry employing a Mettler Toledo DSC822E with a scan speed of 10 °C/min. Data given are for the second melt. The chromium content of the prepolymerized catalyst was measured by ion-coupled plasma (ICP) techniques employing an ICP-AES Perkin-Elmer 4300 instrument. Methylaluminoxane (MAO, 10% in toluene), triisobutylaluminum (TIBA, 1 M in heptane), and tetraisobutylaluminoxane (TIBAO, 20% in heptane) were purchased from Witco (now Crompton). 2,6-Bis{1-[2,6-(diisopropylphenyl)imino]ethyl}pyridine (**5**), 2,6-bis{1-[(2,6-dimethylphenyl)imino]ethyl}pyridine (**6**), 2,6-bis-

(23) Typical Phillips catalyst polyethylenes contain 1.5−2.5 ppm of Cr, thus corresponding to productivities in the range of 400−700 kg of PE/g of Cr (see for example: Madueño Casado, M.; Del Amo Fernández, B.; Fernández Sibón, F. J.; Hernández-Vaquero Álvarez, J.; Rodriguez Sinoga, J. (Repsol Química), Eur. Pat. Appl. 1153943, 2001.

{1-[(2,4,6-trimethylphenyl)imino]ethyl}pyridine (**7**), and 2,6-bis{1-[2-(*tert*-butylphenyl)imino]ethyl}pyridine (**8**) were prepared according to published methods.[16b] $CrCl_3(THF)_3$[24] and [2,6-bis-{1-[2,6-(diisopropylphenyl)imino]ethyl}pyridine]$CrCl_2$[25] (**32**) were prepared as previously reported.

Preparation of 2,6-Bis{1-(cyclohexylimino)ethyl}-pyridine (1). Cyclohexylamine (1.4 mL, 12 mmol) was added to a solution of 2,6-diacetylpyridine (500 mg, 3 mmol) in absolute ethanol (10 mL). After the addition of several drops of glacial acetic acid the solution was refluxed for 48 h. When this solution was cooled to room temperature, the product crystallized from ethanol. The pale yellow solid that formed was washed with cold ethanol (4 × 4 mL) and dried in vacuo. Yield: 421.2 mg (42%). MS (EI): *m*/*z* 325.5 (M^+). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.04 (d, 2H, J_{H-H} = 7.8, py H_m), 7.66 (t, 1H, J_{H-H} = 7.8, py H_p), 3.55 (m, 2H, −CH, Cy), 2.39 (s, 6H, N=C*Me*), 1.84−1.24 (m, 20H, $-CH_2-$, Cy). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz, plus APT): δ 164.4 (N=C), 156.9 (py C_o), 136.8 (py C_p), 121.3 (py C_m), 60.3 (NCH), 33.5 ($-CH_2-$), 25.8 ($-CH_2-$), 24.9 ($-CH_2-$), 13.5 (N=C*Me*).

Preparation of 2,6-Bis{1-[2,6-(diethylphenyl)imino]-ethyl}pyridine (2). 2,6-Diethylaniline (1.5 mL, 9.2 mmol) was added to a solution of 2,6-diacetylpyridine (500 mg, 3 mmol) in absolute ethanol (12 mL). After the addition of several drops of glacial acetic acid, the solution was refluxed for 48 h. When this solution was cooled to room temperature, the product crystallized from ethanol. The yellow solid that formed was washed (3 × 5 mL) with cold ethanol, and it was dried in vacuo at 60 °C for 1 day. Yield: 540 mg (48%). MS (EI): *m*/*z* 425 (M^+). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.47 (d, 2H, J_{H-H} = 7.8, py H_m), 7.91 (t, 1H, J_{H-H} = 7.8, py H_p), 7.12−7.00 (m, 6H, Ph), 2.37 (m, 8H, $-CH_2CH_3$), 2.23 (s, 6H, N=C*Me*), 1.13 (m, 12H, $-CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 167.1 (N=C), 155.3 (py C_o), 147.9 (Ar C_{ip}), 137.0 (py C_p), 131.3 (Ar C_o), 126.0 (Ar C_m), 123.4 (Ar C_p), 122.3 (py C_m), 24.5 (CH_2CH_3), 16.7 (N=C*Me*), 13.6 (CH_2CH_3).

Preparation of 2,6-Bis{1-[(2-(trifluoromethyl)phenyl)-imino]ethyl}pyridine (3). 2-(Trifluoromethyl)aniline (1.15 mL, 9.2 mmol) was added to a solution of 2,6-diacetylpyridine (500 mg, 3 mmol) in absolute ethanol (12 mL). After the addition of several drops of glacial acetic acid, the solution was refluxed for 48 h. When this solution was cooled to room temperature, the reaction volume was reduced to afford a pale yellow solid, which was washed with ethanol at 0 °C and dried in vacuo. Yield: 668 mg (48.5%). MS (EI): *m*/*z* 449 (M^+). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.35 (d, 2H, J_{H-H} = 7.8, py H_m), 7.90 (t, 1H, J_{H-H} = 7.8, py H_p), 7.67 (d, 2H, J_{H-H} = 7.8, Ph), 7.51 (d, 2H, J_{H-H} = 7.7, Ph), 7.17 (d, 2H, J_{H-H} = 7.7, Ph), 6.79 (d, 2H, J_{H-H} = 7.8, Ph), 2.35 (s, 6H, N=C*Me*). ^{19}F NMR ($CDCl_3$, 279 MHz): δ −64.3 (CF_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 168.7 (N=C), 155.0 (py C_o), 149.7 (Ar, C_{ip}), 137.3 (py C_p), 132.7 (Ar), 126.5 (q, J_{F-C} = 5 Hz, Ar), 124 (q, J_{F-C} = 273 Hz, CF_3), 123.3 (Ar), 123.1 (py C_m), 119.8 (Ar), 16.7 (N=C*Me*).

Preparation of 2,6-Bis{1-[(2-methyl-6-isopropylphenyl)-imino]ethyl}pyridine (4). 2-Methyl-6-isopropylaniline (1.45 mL, 9.2 mmol) was added to a solution of 2,6-diacetylpyridine (500 mg, 3 mmol) in absolute ethanol (12 mL). After the addition of several drops of glacial acetic acid, the solution was refluxed for 48 h. When this solution was cooled to room temperature, the product crystallized from ethanol. The pale yellow solid that formed was washed with cold ethanol (2 × 6 mL), and it was dried in vacuo at 60 °C for 2 days. Yield: 1.02 g (78%). MS (EI): *m*/*z* 425 (M^+). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.46 (d, 2H, J_{H-H} = 7.9, py H_m), 7.90 (t, 1H, J_{H-H} = 7.9, py H_p), 7.17−6.98 (m, 6H, Ar), 2.81 (spt, 2H, J_{H-H} = 6.8, $CH(CH_3)_2$), 2.24 (s, 6H, N=C*Me*), 2.02 (s, 6H, Me), 1.18 (d, 6H, J_{H-H} = 6.8, $CH(CH_3)_2$), 1.12 (d, 6H, J_{H-H} = 6.8, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz, plus APT): δ 167.3 (N=C), 155.3 (py C_o), 147.7 (Ar C_{ip}), 136.9 (py C_p), 136.4 (Ar C_o), 127.8 (Ar C_p), 125.1 (Ar C_o), 123.4 (Ar C_m), 123.2 (Ar C_m), 122.3 (py C_m), 28.2 ($CH(CH_3)_2$), 23.0 ($CH(CH_3)_2$), 22.7 ($CH(CH_3)_2$), 18.0 (N=C*Me*), 16.7 (*Me*).

Preparation of 2,6-Bis{1-[(2-methyl-6-methoxyphenyl)-imino]ethyl}pyridine (9). 2-Methyl-6-methoxyaniline (841 mg, 6.13 mmol) was added to a solution of 2,6-diacetylpyridine (500 mg, 3 mmol) in toluene (12 mL). After the addition of 0.1 mg of *p*-toluenesulfonic acid, the solution was refluxed for 12 h. During this time the water of the solution was removed using a Dean−Stark apparatus. When this solution was cooled to room temperature, it was concentrated in vacuo to afford a yellow solid, which was washed with methanol and dried in vacuo. Yield: 984 mg (80%). MS (EI): *m*/*z* 401 (M^+). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.49 (d, 2H, J_{H-H} = 7.8, py H_m), 7.88 (t, 1H, J_{H-H} = 7.8, py H_p), 7.00 (t, 2H, J_{H-H} = 7.8, Ar H_p), 6.87 (d, 2H, J_{H-H} = 7.8, Ar H_m), 6.81 (d, 2H, J_{H-H} = 7.8, Ar H_m), 3.77 (s, 6H, OMe), 2.27 (s, 6H, N=C*Me*), 2.10 (s, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 168.9 (N=C), 155.3 (py C_o), 148.0 (Ar C_{ip}), 138.8 (py C_p), 136.8 (Ar), 128.4 (Ar), 123.7 (Ar), 122.6 (Ar), 122.4 (py C_m), 108.9 (Ar), 55.5 (OMe), 17.6 (Me), 16.5 (N=C*Me*).

Preparation of 2,6-Bis{1-[(2,4-dimethoxyphenyl)imino]-ethyl}pyridine (10). 2,4-Dimethoxyaniline (939 mg, 6.12 mmol, previously purified from the commercial source by sublimation) was added to a solution of 2,6-diacetylpyridine (500 mg, 3 mmol) in toluene (12 mL). After the addition of 0.1 mg of *p*-toluenesulfonic acid, the solution was refluxed for 2 h. During this time the water of the solution was removed using a Dean−Stark apparatus. When this solution was cooled to room temperature, it was concentrated in vacuo to afford a yellow solid, which was washed with methanol and dried in vacuo. Yield: 690 mg (52%). MS (EI): *m*/*z* 433 (M^+). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.36 (d, 2H, J_{H-H} = 7.8, py H_m), 7.83 (t, 1H, J_{H-H} = 7.8, py H_p), 6.73 (d, 2H, J_{H-H} = 8.4, Ar), 6.56 (s, 2H, Ar), 6.52 (d, 2H, J_{H-H} = 8.4, Ar), 3.82 (s, 6H, OMe), 3.78 (s, 6H, OMe), 2.35 (s, 6H, N=C*Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 169.4 (N=C), 157.4, 155.6, 150.1, 136.7, 133.8, 122.4, 120.8, 104.2, 99.6 (py and Ar), 55.5 (OMe), 55.4 (OMe), 16.5 (N=C*Me*).

Preparation of 2-Acetyl-6-[1-(2,4,6-trimethylphenyl-imino)ethyl]pyridine (11). 2,4,6-Trimethylaniline (731 μL, 5.2 mmol) was added to a solution of 2,6-diacetylpyridine (1 g, 6.1 mmol). After the addition of 0.1 mg of *p*-toluenesulfonic acid, the solution was refluxed for 45 min. During this time the water of the solution was removed using a Dean−Stark apparatus. When this solution was cooled to room temperature, it was concentrated in vacuo and methanol added to afford a yellow solid that was washed with methanol and dried in vacuo. Yield: 560 mg (38%). MS (EI): *m*/*z* 280 (M^+). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.56 (d, 1H, J_{H-H} = 7.8, py H_m), 8.12 (d, J_{H-H} = 7.8, 1H, py H_m), 7.93 (t, J_{H-H} = 7.8, 1H, py H_p), 6.89 (s, 2 H, $ArMe_3$), 2.78 (s, 3H, Me), 2.29 (s, 3H, Me), 2.22 (s, 3H, Me), 1.99 (s, 6H, 2 Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 199.9 (C=O), 166.7 (C=N), 155.6, 152.4, 145.9, 137.2, 132.3, 128.5, 125.2, 124.4, 122.5 (py and Ar), 25.6, 20.6, 17.8, 16.2 (Me).

Preparation of 2-{1-[(2,6-Diisopropylphenyl)imino]-ethyl}-6-{1-[(2,4,6-trimethylphenyl)imino]ethyl}pyridine (12). 2,6-Diisopropylaniline (336 μL, 1.78 mmol) was added to a solution of **11** (500 mg, 1.78 mmol) in toluene (10 mL). After the addition of 0.1 mg of *p*-toluenesulfonic acid, the solution was refluxed for 15 h. During this time the water of the solution was removed using a Dean−Stark apparatus. When this solution was cooled to room temperature, it was concentrated in vacuo to afford a yellow solid, which was washed with methanol and dried in vacuo. Yield: 611 mg (78%). MS (EI): *m*/*z* 440 (M^+). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.46 (d, J_{H-H} = 7.8, 1H, py H_m), 8.45 (d, J_{H-H} = 7.8, 1H, py H_m), 7.90 (t, J_{H-H} = 7.8, 1H, py H_p), 7.18−7.06 (m, 3H, Ar^iPr_2),

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6.88 (s, 2 H, $ArMe_3$), 2.75 (spt, $J_{H-H} = 6.9$, 2H, $-CH(CH_3)_2$), 2.28 (s, 3H, Me), 2.25 (s, 3H, Me), 2.22 (s, 3H, Me), 2.00 (s, 6H, $ArMe_2$), 1.14 (d, $J_{H-H} = 6.9$, 12H, $-CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 167.1 (N=C), 167.06 (N=C), 155.4, 155.2, 146.6, 146.4, 136.9, 135.8, 132.3, 128.6, 125.3, 123.6, 123.1, 122.3, 122.2 (py and Ar), 28.2 ($CH(CH_3)_2$), 23.1 ($CH(CH_3)_2$), 22.8 ($CH(CH_3)_2$), 20.6 (Me), 17.7 (Me_2), 16.9 (N=C*Me*), 16.2 (N=C-*Me*).

Preparation of 2-{1-[(2-*tert*-Butylphenyl)imino]ethyl}-6-{1-[(2,4,6-trimethylphenyl)imino]ethyl}pyridine (13). 2-*tert*-Butylaniline (278 μL, 1.78 mmol) was added to a solution of **11** (500 mg, 1.78 mmol) in toluene (10 mL). After the addition of 0.1 mg of *p*-toluenesulfonic acid, the solution was refluxed for 15 h. During this time the water of the solution was removed using a Dean−Stark apparatus. When this solution was cooled to room temperature, it was concentrated in vacuo and methanol added to afford a yellow solid that was washed with methanol and dried in vacuo. Yield: 580 mg (79%). MS (EI): *m*/*z* 413 ($M^+ + 1$). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.46 (d, 1H, $J_{H-H} = 7.8$, py H_m), 8.40 (d, $J_{H-H} = 7.8$, 1H, py H_m), 7.91 (t, $J_{H-H} = 7.8$, 1H, py H_p), 7.43 (d, $J_{H-H} = 7.5$, 1H, Ar^{t}Bu), 7.19 (d, $J_{H-H} = 7.5$, 1H, Ar^{t}Bu), 7.08 (d, $J_{H-H} = 7.5$, 1H, Ar^{t}Bu), 6.90 (s, 2 H, $ArMe_3$), 6.54 (d, $J_{H-H} = 7.5$, 1H, Ar^{t}Bu), 2.40 (s, 3H, Me), 2.29 (s, 3H, Me), 2.23 (s, 3H, Me), 2.01 (s, 6H, $ArMe_2$), 1.36 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 167.4 (N=C), 165.3 (N=C), 155.6, 155.2, 149.6, 146.2, 139.7, 136.8, 132.1, 128.5, 126.4, 126.4, 126.3, 125.3, 123.7, 122.4, 122.0, 119.7 (py and Ar), 35.1 (s, $C(CH_3)_3$), 29.6 (s, $C(CH_3)_3$), 20.7 (Ar*Me*), 17.9 ($ArMe_2$), 16.9 (N=C*Me*), 16.4 (N=C*Me*).

Preparation of 2-{1-[(2-(trifluoromethyl)phenyl)imino]ethyl}-6-{1-[(2,4,6-trimethylphenyl)imino]ethyl}pyridine (14). 2-(Trifluoromethyl)aniline (134 μL, 1.07 mmol) was added to a solution of **11** (300 mg, 1.07 mmol) in toluene (10 mL). After the addition of 0.1 mg of *p*-toluenesulfonic acid, the solution was refluxed for 15 h. During this time, the water of the solution was removed using a Dean−Stark apparatus. When this solution was cooled to room temperature, it was concentrated in vacuo and methanol added to afford a yellow solid, which was washed with methanol and dried in vacuo. Yield: 326 mg (72%). MS (EI): *m*/*z* 423 (M^+). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.47 (dd, $J_{H-H} = 7.8$, $J_{H-H} = 3.8$, 1H, py), 8.37 (d, $J_{H-H} = 7.7$, $J_{H-H} = 3.8$, 1H, py), 7.91 (t, $J_{H-H} = 7.8$, 1H, py), 7.69 (d, $J_{H-H} = 7.5$, 1H, $ArCF_3$), 7.53 (t, $J_{H-H} = 7.7$, 1H, $ArCF_3$), 7.19 (t, $J_{H-H} = 7.7$, 1H, $ArCF_3$), 6.90 (s, 2 H, $ArMe_3$), 6.82 (d, $J_{H-H} = 7.7$, 1H, $ArCF_3$), 2.38 (s, 3H, Me), 2.30 (s, 3H, Me), 2.24 (s, 3H, Me), 2.02 (s, 6H, $ArMe_2$). ^{19}F NMR ($CDCl_3$, 279 MHz): δ −62.5. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 168.7 (N=C), 167.4 (N=C), 167.2, 155.2, 154.9, 149.6, 146.2, 136.9, 132.5, 132.2, 128.4, 126.4 (q, $J_{F-C} = 5$ Hz), 125.2, 123.1, 122.7, 122.5, 122.1, 119.7 (py and Ar), 20.7 (ArMe), 17.8 ($ArMe_2$), 16.8 (N=C*Me*), 16.4 (N=C*Me*).

Preparation of 2,6-Dibenzoylpyridine (15). An orange reddish suspension of 2,6-dicarbonylpyridine dichloride (1 g, 4.9 mmol) and $AlCl_3$ (1.63 g. 12.25 mmol) in benzene (12.5 mL) was heated at reflux for 4 h, giving a red solution. The red solution was cooled to room temperature, and it was stirred for 12 h and then refluxed for 6 h. After the solution was cooled to room temperature, it was poured into distilled water (25 mL) at 0 °C. The organic layer was separated, and the aqueous phase was extracted with diethyl ether (5 mL × 2). The combined organic phases were dried over Na_2SO_4 and evaporated in vacuo. Addition of diethyl ether afforded a white solid, which was washed with cold diethyl ether and dried in vacuo. Yield: 0.95 g (67%). MS (EI): *m*/*z* 288 (M^+). ^1H NMR (acetone-d_6, 300 MHz): δ 8.38−8.28 (m, 3H), 8.12−8.09 (m, 4H), 7.65−7.47 (m, 6H). $^{13}C\{^1H\}$ NMR (acetone-d_6, 75.4 MHz): δ 193.3, 154.7, 139.7, 137.0, 133.7, 131.6, 128.8, 127.5.

Preparation of {2,6-Bis[1-((2,4,6-trimethylphenyl)imino)benzyl]pyridine}$NiCl_2$ (16). An orange suspension of anhydrous $NiCl_2$ (300 mg, 2.31 mmol), 2,6-dibenzoylpyridine (665 mg, 2.31 mmol), and 2,4,6-trimethylaniline (650 μL, 4.63 mmol) in acetic acid (15 mL) was refluxed for 4 h, giving a brown solution. The brown solution was filtered through Celite and concentrated in vacuo to ca. 0.5 mL. Addition of diethyl ether afforded a brown solid, which was washed with diethyl ether (3 × 5 mL) and dried in vacuo. Yield: 1.34 g (89%). Anal. Calcd for $C_{37}H_{35}N_3NiCl_2$: C, 68.23; H, 5.42; N, 6.45. Found: C, 68.19; H, 5.03; N, 6.62. IR (Nujol, cm^{-1}): 1579, 1266, 1025, 703. MS (FAB^+): *m*/*z* 614 ($M^+ - Cl$), 579 ($M^+ - 2Cl$).

Preparation of 2,6-Bis{1-[(2,4,6-trimethylphenyl)imino]benzyl}pyridine (17). A solution of **16** (1 g, 1.53 mmol) in 50 mL of CH_2Cl_2 was stirred over aminopropyl silica gel for 18 h. During this time the color of the solution changed from brown to yellow. The aminopropyl silica gel was filtered and the solution concentrated to ca. 0.5 mL under vacuum. Methanol was added to afford a yellow solid, which was washed with methanol and dried in vacuo. Yield: 408 mg (51%). MS (EI): *m*/*z* 521 (M^+), 506 ($M^+ - Me$), 444 ($M^+ - Ph$), 404 ($M^+ - C_6H_2Me_3$), 388 ($M^+ - NC_6H_2Me_3$). IR (Nujol, cm^{-1}): 1627, 1578, 1562, 1292, 1214, 1173, 1140. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.48−6.60 (m, 16H, Ar), 2.20−1.82 (m, 18H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 165.9 (N=C), 155.2, 149.6, 146.2, 137.9, 136.1, 135.6, 131.7, 130.6, 128.8, 128.0, 125.6, 121.5, 20.7 (Ar*Me*), 18.5 ($ArMe_2$).

Preparation of {2,6-Bis[1-(cyclohexylimino)ethyl]pyridine}$CrCl_3$ (18). A solution of $CrCl_3(THF)_3$ (500 mg, 1.33 mmol) and **1** (435 mg, 1.33 mmol) in dichloromethane (20 mL) was refluxed for 12 h, giving a green solution. During this time a green solution was obtained, which was filtered through Celite. The reaction volume was concentrated, and diethyl ether was added to afford a green solid, which was washed repeatedly with diethyl ether and dried in vacuo. Yield: 549 mg (82%). Anal. Calcd for $C_{21}H_{31}N_3CrCl_3 \cdot 1.5H_2O$: C, 49.37; H, 6.71; N, 8.22. Found: C, 49.24; H, 6.83; N, 7.96. IR (Nujol, cm^{-1}): 1579, 1282, 1200, 891, 805, 350, 290. MS (FAB^+): *m*/*z* 447 ($M^+ - Cl$).

Preparation of {2,6-Bis[1-(2,6-(diethylphenyl)imino)ethyl]pyridine}$CrCl_3$ (19). A solution of $CrCl_3(THF)_3$ (500 mg, 1.33 mmol) and **2** (568 mg, 1.33 mmol) in acetone (15 mL) was refluxed for 6 h, giving a green suspension. The reaction volume was concentrated, and diethyl ether was added to afford a green solid, which was washed repeatedly with diethyl ether and dried in vacuo. Yield: 756 mg (97%). Anal. Calcd for $C_{29}H_{35}N_3CrCl_3$: C, 59.65; H, 6.04; N, 7.19. Found: C, 59.32; H, 6.43; N, 7.38. IR (Nujol, cm^{-1}): 1579, 1263, 1043, 817, 399, 353. MS (FAB^+): *m*/*z* 547 ($M^+ - Cl$).

Preparation of {2,6-Bis[1-((2-(trifluoromethyl)phenyl)imino)ethyl]pyridine}$CrCl_3$ (20). A solution of $CrCl_3(THF)_3$ (500 mg, 1.33 mmol) and **3** (600 mg, 1.33 mmol) in dichloromethane (20 mL) was stirred at room temperature for 5 h. During this time a green solution was obtained, which was filtered through Celite. The reaction volume was concentrated, and diethyl ether was added to afford a green solid, which was washed repeatedly with diethyl ether and dried in vacuo. Yield: 446 mg (52%). Anal. Calcd for $C_{23}H_{17}F_6N_3CrCl_3 \cdot 2H_2O$: C, 42.91; H, 3.29; N, 6.53. Found: C, 43.07; H, 3.07; N, 6.26. IR (Nujol, cm^{-1}): 1604, 1584, 1318, 1175, 1121, 1060, 1038, 767, 363. MS (FAB^+): *m*/*z* 571 ($M^+ - Cl$).

Preparation of {2,6-Bis[1-((2-methyl-6-isopropylphenyl)imino)ethyl]pyridine}$CrCl_3$ (21). A solution of $CrCl_3(THF)_3$ (500 mg, 1.33 mmol) and **4** (568 mg, 1.33 mmol) in acetone (15 mL) was heated to 56 °C overnight, giving a green suspension. The reaction volume was concentrated, and diethyl ether was added to afford a green solid, which was washed repeatedly with diethyl ether (5 × 10 mL) and dried in vacuo. Yield: 670 mg (94%). Anal. Calcd for $C_{29}H_{35}N_3CrCl_3 \cdot 1.5H_2O$: C, 57.01; H, 6.27; N, 6.88. Found: C, 56.75; H, 6.41; N, 6.75. IR (Nujol, cm^{-1}): 1579, 1515, 1273, 1219. 357. MS (FAB^+): *m*/*z* 547 ($M^+ - Cl$).

Preparation of {2,6-Bis[1-((2,6-diisopropylphenyl)imino)ethyl]pyridine}$CrCl_3$ (22). A solution of $CrCl_3(THF)_3$

(500 mg, 1.33 mmol) and **5** (643 mg, 1.33 mmol) in acetone (15 mL) was refluxed for 12 h, giving a green solution. The reaction volume was concentrated, and pentane was added to afford a green solid, which was washed repeatedly with pentane. This solid was recrystallized from CH_2Cl_2/diethyl ether and dried in vacuo. Yield: 769 mg (90%). Anal. Calcd for $C_{33}H_{43}Cl_3CrN_3$: C, 61.92; H, 6.77; N, 6.56. Found: C, 61.96; H, 6.82; N, 5.97. IR (Nujol, cm^{-1}): 1579, 1274, 1215, 937, 802, 778, 399, 371. MS (FAB^+): *m*/*z* 603 ($M^+ - Cl$), 568 ($M^+ - 2\ Cl$).

Preparation of {2,6-Bis[1-((2,6-dimethylphenyl)imino)ethyl]pyridine}$CrCl_3$ (23). A solution of $CrCl_3(THF)_3$ (500 mg, 1.33 mmol) and **6** (493 mg, 1.33 mmol) in acetone (15 mL) was refluxed for 5 h, giving a green suspension. The reaction volume was concentrated, and the green solid was washed repeatedly with acetone (4 × 5 mL) and dried in vacuo. Yield: 521 mg (74%). Anal. Calcd for $C_{25}H_{27}N_3CrCl_3$: C, 56.89; H, 5.16; N, 7.96. Found: C, 56.55; H, 5.46; N, 7.61. IR (Nujol, cm^{-1}): 1575, 1271, 1220, 1106, 1067, 1043, 817, 785, 766, 406, 356. MS (FAB^+): *m*/*z* 491 ($M^+ - Cl$), 456 ($M^+ - 2\ Cl$).

Preparation of {2,6-Bis[1-((2,4,6-trimethylphenyl)imino)ethyl]pyridine}$CrCl_3$ (24). A solution of $CrCl_3(THF)_3$ (500 mg, 1.33 mmol) and **7** (530 mg, 1.33 mmol) in acetone (15 mL) was refluxed overnight, giving a green suspension. The reaction volume was concentrated, and the green solid was washed repeatedly with acetone (4 × 5 mL) and dried in vacuo. Yield: 482 mg (65%). Anal. Calcd for $C_{27}H_{31}N_3CrCl_3$: C, 58.34; H, 5.62; N, 7.56. Found: C, 58.24; H, 5.68; N, 7.17. IR (Nujol, cm^{-1}): 1577, 1269, 1224, 1210, 1100, 1042, 862, 855, 809, 402, 350. MS (FAB^+): *m*/*z* 519 ($M^+ - Cl$), 484 ($M^+ - 2\ Cl$).

Preparation of {2,6-Bis[1-((2-*tert*-butylphenyl)imino)ethyl]pyridine}$CrCl_3$ (25). A solution of $CrCl_3(THF)_3$ (500 mg, 1.33 mmol) and **8** (568 mg, 1.33 mmol) in acetone (10 mL) was refluxed overnight. The resulting green solution was evaporated to ca. 0.5 mL, and diethyl ether was added to afford a green solid that was washed repeatedly with diethyl ether (4 × 5 mL) and dried in vacuo. Yield: 584 mg (75%). Anal. Calcd for $C_{29}H_{35}Cl_3CrN_3$: C, 59.65; H, 6.04; N, 7.20. Found: C, 59.36; H, 6.42; N, 7.35. IR (Nujol, cm^{-1}): 1578, 1286, 1088, 1043, 817, 760, 399, 352. MS (FAB^+): *m*/*z* 547 ($M^+ - Cl$), 512 ($M^+ - 2\ Cl$).

Preparation of {2,6-Bis[1-((2-methyl-6-methoxyphenyl)imino)ethyl]pyridine}$CrCl_3$ (26). A solution of $CrCl_3(THF)_3$ (500 mg, 1.33 mmol) and **9** (536 mg, 1.33 mmol) in dichloromethane (20 mL) was stirred at room temperature for 2 h. During this time a green solution was obtained, which was filtered through Celite. The reaction volume was concentrated, and diethyl ether was added to afford a green solid, which was washed repeatedly with diethyl ether and dried in vacuo. Yield: 665 mg (89%). Anal. Calcd for $C_{25}H_{27}N_3O_2CrCl_3$: C, 53.63; H, 4.86; N, 7.50. Found: C, 53.30; H, 4.79; N, 6.95. IR (Nujol, cm^{-1}): 1646, 1579, 1271, 1082, 775, 528. MS (FAB^+): *m*/*z* 525 ($M^+ - Cl$).

Preparation of {2,6-Bis[1-((2,4-dimethoxyphenyl)imino)ethyl]pyridine}$CrCl_3$ (27). A solution of $CrCl_3(THF)_3$ (500 mg, 1.33 mmol) and **10** (578 mg, 1.33 mmol) in dichloromethane (20 mL) was stirred at room temperature for 2 h. During this time a green suspension was obtained. The reaction volume was concentrated, and diethyl ether was added to afford a green solid, which was washed repeatedly with diethyl ether and dried in vacuo. Yield: 687 mg (87%). Anal. Calcd for $C_{25}H_{27}N_3O_4CrCl_3$: C, 50.73; H, 4.60; N, 7.10. Found: C, 50.48; H, 4.42; N, 6.94. IR (Nujol, cm^{-1}): 1603, 1581, 1504, 1209, 1162, 1025. MS (FAB^+): *m*/*z* 555 ($M^+ - Cl$).

Preparation of {2-[1-((2,6-Diisopropylphenyl)imino)ethyl]-6-[1-((2,4,6-trimethylphenyl)imino)ethyl]pyridine}$CrCl_3$ (28). A solution of $CrCl_3(THF)_3$ (500 mg, 1.33 mmol) and **12** (587 mg, 1.33 mmol) in acetone (20 mL) was refluxed for 2 h, giving a green solution. The reaction volume was concentrated to ca. 1 mL, and diethyl ether was added to afford a green solid, which was washed repeatedly with diethyl ether and dried in vacuo. Yield: 686 mg (86%). Anal. Calcd for $C_{30}H_{37}N_3CrCl_3 \cdot 1.5H_2O$: C, 60.25; H, 6.24; N, 7.03. Found: C, 59.84; H, 6.13; N, 6.67. IR (Nujol, cm^{-1}): 1665, 1574, 1270, 1218, 1042, 801, 399, 357. MS (FAB^+): *m*/*z* 561 ($M^+ - Cl$).

Preparation of {2-[1-((2-*tert*-Butylphenyl)imino)ethyl]-6-[1-((2,4,6-trimethylphenyl)imino)ethyl]pyridine}$CrCl_3$ (29). A solution of $CrCl_3(THF)_3$ (500 mg, 1.33 mmol) and **13** (549 mg, 1.33 mmol) in acetone (20 mL) was refluxed for 2 h 30 min, giving a green solution. The reaction volume was concentrated to ca. 1 mL, and diethyl ether was added to afford a green solid, which was washed repeatedly with diethyl ether (2 × 10 mL) and dried in vacuo. Yield: 715 mg (94%). Anal. Calcd for $C_{28}H_{33}N_3CrCl_3 \cdot 1.5H_2O$: C, 59.00; H, 5.84; N, 7.37. Found: C, 58.56; H, 6.12; N, 7.31. IR (Nujol, cm^{-1}): 1698, 1664, 1574, 1286, 1086, 855, 815, 757. MS (FAB^+): *m*/*z* 535 ($M^+ - Cl$).

Preparation of {2-[1-((2-(Trifluoromethyl)phenyl)imino)ethyl]-6-[1-((2,4,6-trimethylphenyl)imino)ethyl]pyridine}$CrCl_3$ (30). A solution of $CrCl_3(THF)_3$ (250 mg, 0.67 mmol) and **14** (282 mg, 0.67 mmol) in dichloromethane (10 mL) was stirred at room temperature for 6 h, giving a green suspension. The reaction volume was concentrated to ca. 1 mL, and pentane was added to afford a green solid, which was washed repeatedly with pentane and dried in vacuo. Yield: 307 mg (79%). Anal. Calcd for $C_{25}H_{24}Cl_3F_3CrCl_3$: C, 51.61; H, 4.16; N, 7.22. Found: C, 52.04; H, 4.38; N, 6.91. IR (Nujol, cm^{-1}): 1578, 1319, 1270, 1175, 1122, 1060, 1037, 357. MS (FAB^+): *m*/*z* 546 ($M^+ - Cl$), 520 ($M^+ - 2\ Cl$), 485 ($M^+ - 3\ Cl$).

Preparation of {2,6-Bis[1-((2,4,6-trimethylphenyl)imino)benzyl]pyridine}$CrCl_3$ (31). A solution of $CrCl_3(THF)_3$ (200 mg, 0.53 mmol) and **17** (278 mg, 0.53 mmol) in dichloromethane (20 mL) was stirred at room temperature for 18 h. During this time a green suspension was obtained. The reaction volume was concentrated, and pentane was added to afford a green solid, which was washed repeatedly with pentane and dried in vacuo. Yield: 327 mg (90%). Anal. Calcd for $C_{37}H_{35}N_3CrCl_3$: C, 65.35; H, 5.19; N, 6.18. Found: C, 64.92; H, 5.14; N, 5.72. IR (Nujol, cm^{-1}): 1578, 1557, 1283, 1044, 855, 407. MS (FAB^+): *m*/*z* 643 ($M^+ - Cl$).

Polymerization Assays. Preparation of Catalyst Solutions. The weighed amount of chromium complex is charged into a Schlenk tube. Air is eliminated from the Schlenk tube by successive vacuum/nitrogen (SEO, N2 B50, further purified over molecular sieves and alumina beds) steps. Then the desired volume of MAO/toluene solution (10%) is added. The solution is then stirred at 500 rpm for the time set.

Polymerization Assays at 4 bar. General Procedure. A 1.3 L glass autoclave reactor vessel is employed. Air and polar impurities are eliminated from the reactor previous to every polymerization experiment by washing at 70 °C with heptane (650 mL) and TIBA (5 mL, 1 M in heptane) under nitrogen (SEO, N2 B50, further purified over molecular sieves and alumina beds) for 30 min with stirring. After washing, the reactor is charged with 600 mL of heptane, degassed, and saturated with ethylene to a pressure of 4 bar at the set temperature. Then, first, the required volume of the cocatalyst solution and, second and immediately, the catalyst solution are added. Polymerizations are effected at constant pressure, the consumption of ethylene being monitored by means of a Tylan Model FM 380 mass flowmeter. The temperature is measured by means of a PT-100 probe immersed in the reaction solvent. Regulation of the temperature is provided by a combination of heating and cooling systems operating simultaneously by passing two fluids through two external jackets at the walls of the reactor vessel. The heating is effected with oil from a circulating oil bath (Haake N3). Refrigeration is obtained from cold tap water controlled by an electrovalve connected to a Toho TM-104 controller. Ethylene (SEO, N35) is further purified by passing it through activated molecular sieves (13 X, 4 Å) and activated alumina beds previous to its introduction in the polymerization reactor. Stirring is carried out at 1200 rpm. After the time set for the

experiment, the contents of the reactor are discharged and a methanol/HCl solution is added. Filtration, washing, and drying of the resulting solid (70 °C/10 mmHg for ca. 20 h) gives the nonsoluble fraction of the resulting polymer. To collect the soluble waxes, the filtrates are decanted and the upper layer evaporated under vacuum.

Copolymerization Assay of Ethylene and 1-Hexene with Complex 24. The temperature was set at 70 °C. A 15 mL portion of 1-hexene was added to the polymerization medium. MAO in toluene was then added (0.8 mL) to the vessel before 0.1 mL (0.0009 mmol) of a solution of **24** in MAO/toluene was added as well. Ethylene was continuously supplied in order to keep a constant pressure. The consumption of ethylene was maintained for 30 min. During this period the temperature reached a maximum of 74 °C for a couple of minutes, being controlled by the refrigeration system at ca. 70 °C most of the time. Afterward, the polymerization mixture was added to a methanol/HCl solution. Filtration, washing, and drying of the resulting solid (70 °C/10 mmHg for ca. 20 h) gave 34.84 g (activity 1.83×10^7 g of PE (mol of Cr)$^{-1}$ bar^{-1} h^{-1}) of a white powder (branched polyethylene according to the ^{13}C NMR spectrum with 1.13 Bu branches, 12.57 vinyl groups, and 13.24 end methyl groups per 1000 C). GPC: $M_w = 2290$, $M_w/M_n = 1.59$. DSC: $T_{max} = 105$ °C, $\Delta H_m = -246$ J g^{-1}.

Preparation of the Prepolymerized Catalyst. In a Schlenk tube, 0.5 g of silica-MAO TA02794/HL/PQ (provided by Witco, now Crompton), 10 mL of dry toluene, and 25 mg of **24** were mixed together under nitrogen. To this mixture was also added 5.0 mL of MAO/toluene (10%). The Schlenk tube was then immersed in an ice bath, and the contents were stirred with a Teflon magnetic bar at 800 rpm. Ethylene was passed through the Schlenk tube at atmospheric pressure for 4.15 h. The ice bath was then removed, the solvent evaporated in vacuo, and the solid dried. The total weight of solids was 2.06 g. From ICP measurement the content of Cr was determined to be 0.11(5) wt % and that of Al 14.6 wt %.

Ethylene Polymerization with Prepolymerized Catalyst. In a 2 L stainless steel autoclave heated to reach an internal temperature of 80 °C charged with isobutane (1 L) and TIBA (1.0 M, 0.9 mL), ethylene was added up to a total internal pressure of ca. 35 bar. Then, 100 mg of the prepolymerized catalyst prepared above were added by dragging it with an ethylene current, and the internal pressure in the reactor increased up to ca. 38 bar. Polymerization started immediately. Ethylene was added continuously in order to keep a constant internal pressure. The consumption of the gas feed was very stable all through the 60 min of duration of the assay. Afterward, the reactor was vented and cooled to room temperature. The solids were discharged and washed thoroughly with acidified methanol. The total weight of polymer obtained after drying in vacuo for 20 h was 150.53 g (1309 kg of PE (g of Cr)$^{-1}$ h^{-1}). The polyethylene obtained was linear, according to the ^{13}C NMR spectrum, with 17.7 vinyl groups and 16.7 end methyl groups per 1000 C. GPC: $M_w = 1470$, $M_w/M_n = 2.13$.

X-ray Analysis of 22 and 31. Two irregular green crystals of size 0.40 × 0.16 × 0.06 mm (**22**) and 0.26 × 0.06 × 0.02 mm (**31**) were mounted on a Bruker Smart APEX CCD diffractometer at 100.0(2) K equipped with a normal-focus, 2.4 kW sealed-tube source (molybdenum radiation, $\lambda = 0.710\ 73$ Å) operating at 50 kV and 40 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 30 s, covering 0.3° in ω. The cell parameters were determined and refined by a least-squares fit of 4325 (**22**) or 2704 (**31**) collected reflections. The first 100 frames were collected at the end of the data collection to monitor crystal decay. Absorption correction was performed with the SADABS program (this is based on the method of Blessing[26]). Lorentz and polarization corrections were also performed. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares using the Bruker SHELXTL program package[27] minimizing $w(F_o^2 - F_c^2)^2$. Both compounds crystallize with solvent molecules: dichloromethane (**22**) or dichloromethane/diethyl ether (**31**). The non-hydrogen atoms were anisotropically refined, and the disordered solvent molecules (**31**) were refined with restrained geometry. The hydrogen atoms were observed or calculated and refined riding on their bonded carbon atoms. Weighted R factors (R_w) and goodness of fit (S) are based on F^2; conventional R factors are based on F.

Table 5. Crystal Data and Data Collection and Refinement Details for 22 and 31

	22	**31**
	Crystal Data	
formula	$C_{33}H_{43}Cl_3CrN_3 \cdot CH_2Cl_2$	$C_{37}H_{35}Cl_3CrN_3 \cdot CH_2Cl_2 \cdot {}^1/_2OC_4H_{10}$
mol wt	724.98	802.02
color and habit	green, irregular block	green, irregular block
symmetry, space group	monoclinic, $P2_1/c$	monoclinic, $C2/c$
a, Å	13.4267(15)	24.126(11)
b, Å	16.5582(19)	21.521(10)
c, Å	16.5357(19)	16.378(7)
β, deg	101.922(2)	96.119(12)
V, Å^3	3597.0(7)	8455(6)
Z	4	8
D(calcd), g cm^{-3}	1.339	1.260
	Data Collection and Refinement	
diffractometer	Bruker Smart APEX	
λ(Mo Kα), Å	0.710 73	
monochromator	graphite oriented	
scan type	ω scans	
μ, mm^{-1}	0.717	0.618
2θ range, deg	3−56	3−46
temp, K	100	100
no. of data collected	38329	26387
no. of unique data	8564 ($R_{int} = 0.0874$)	5887 ($R_{int} = 0.1640$)
no. of params/restraints	398/0	474/60
R1[a] ($F^2 > 2\sigma(F^2)$)	0.0442	0.0605
wR2[b] (all data)	0.1032	0.1546
S[c] (all data)	0.790	0.839

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] GOF $= S = \{\sum[(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

Crystal data and details of the data collection and refinement are given in Table 5.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray studies, and bond distances and angles for **22** and **31**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020561U

(26) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

(27) SHELXTL, version 6.1; Bruker Analytical X-ray Systems, Madison, WI.